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Molecular Catalysts for Energy Conversion

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Molecular Catalysts for Energy Conversion

With 286 Figures

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Preface

Over the past decade the topic of energy and environment has been acknowledged among many people as a critical issue to be solved in 21st century since the Kyoto Protocol came into effect in 1997. Its political recognition was put forward especially at Heiligendamm in 2007, when the effect of carbon dioxide emission and its hazard in global climate were discussed and shared universally as common knowledge. Controlling the global warming in the economical framework of massive development worldwide through this new century is a very challenging problem not only among political, economical, or social circles but also among technological or scientific communities. As long as the humans depend on the combustion of fossil for energy resources, the waste heat exhaustion and CO₂ emission are inevitable.

In order to establish a new era of energy saving and environment benign society, which is supported by technologies and with social consensus, it is important to seek for a framework where new clean energy system is incorporated as infrastructure for industry and human activities. Such a society strongly needs innovative technologies of least CO₂ emission and efficient energy conversion and utilization from remaining fossil energies on the Earth. Energy recycling system utilizing natural renewable energies and their conversion to hydrogen may be the most desirable option of future clean energy society. Thus the society should strive to change its energy basis, from fossil-consuming energy to clean and recycling energy.

In the future “clean energy society,” a closed hydrogen cycle consisting of hydrogen generation, storage, transmission, and usage that are driven by a solar energy as the energy source is to be established. For such purpose, water photoelectrolysis, photosynthesis from CO₂ to bioenergy, electrochemical solar cells, and fuel cells should be the most important combinations of technologies. In this sense, a dream of humans toward sustainable energy society should be realized with hydrogen-mediated energy conversion systems.

Technological background for such dream is being enforced by a wide spectrum of researches in above-mentioned fields. Fuel cells and artificial photosynthesis are the most developing fields in the last few decades. One of the key

technologies for such developments should be the electrocatalysts for electrochemical energy conversion. The efficiency and utilization of energy conversion highly depend on the electrocatalysts that determine the reaction route, energy barrier through the rate-controlling process, and frequency factor. The history of electrocatalysts dates back to the beginning of 20th century, when electrode kinetics started to be investigated with the language of the “current and overpotential.” For an energy conversion system, Sir William R. Grove first proposed a model of fuel cell in 1839 using hydrogen and oxygen gases with platinum electrocatalysts. Today many researchers aim to invent and investigate new electrocatalysts for variety of electrochemical reactions, and such trend will continue to look for the most efficient and cost-competitive catalyst materials.

A new possibility of electrocatalysts is proposed in this context, which would assist in developing vast field of electrocatalysts. The organic complex catalysts for energy conversion, which are emerging technologies in the last several decades, are the main topic of the book focusing on energy and environment technologies. Such molecular catalysts have wide variety of applications in the field of fuel cell technology, electrochemical solar cells, artificial photosyntheses, and so on. Since these molecular catalysts have many potential advantages over inorganic or metal-alloy catalysts due to their cost performance, capability of manipulating structures through molecular design and synthesis, variety of immobilization processes on the catalyst substrate, etc., a firm strategy for their design and application is awaited to cope with the expeditious solution of the latest energy and environment issues.

This book aims to provide a scientific and technological basis for the design and application of molecular catalysts for energy conversion and environment protection, and to establish a method of efficient processing, manufacturing, and development. This book is expected to be beneficial for those people who are studying, researching, or developing molecular catalysts as the electrocatalysts or photocatalysts in energy conversion systems.

Chapter 1 introduces the historical overview and the underlying designing concepts of molecular catalysts with the scope of new developing field. Chapters 2 through 3 give fundamental aspects of the elementary reactions associated with the electrocatalytic processes and measuring techniques of molecular catalysts. From Chaps. 4 to 7, developing fields of molecular catalysts in fuel-cell energy conversion systems are discussed with variety of examples in the anode and the cathode of the reacting gas systems. Chapters 8 through 10 give another new field of molecular catalysts, and electrochemical solar cells and photosynthesis technology are presented with examples of dye-sensitizers for photochemical reactions, nano-materials for photoelectrodes and charge-transport media. Chapters 11 and 12 discuss new applications of molecular catalysts in environmental cleaning and in sensor technology. Chapters 13–15 provide fundamental knowledge for the catalyst researches, which are indispensable tools for understanding elementary molecular processes in the electrocatalytic and photocatalytic processes. Finally Chap. 16 gives the summary

and future prospects of molecular catalysts in the energy conversion technology in various possible fields of applications.

This book is contributed by many of the renowned authors in the related field of researches, and chapters are arranged through intent discussions and interplay of authors and editors. It is carefully planned so that all the chapters keep good balances and therefore provide the readers with adequate state-of-the-art technologies and knowledge concerning the newly emerging field of molecular catalysts for energy conversion. Lastly we would like to express our hearty acknowledgments to all the contributors and to the staff of Springer Verlag for their willing interest and generous assistance, without which this book would not have been published in success.

Tsukuba
Mito
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Tatsuhiro Okada
Masao Kaneko

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List of Abbreviations

ADP	Adenosine-diphosphate (Sect. 2.5.1)
AFM	Atomic force microscopy (Sect. 1.2.2.1)
AM 1.5 G	Air mass 1.5 global-tilt (Sect. 9.1)
AOP	Advanced oxidation process (Sect. 11.2.1)
APCE	Absorbed photon-to-current conversion efficiency (Sect. 9.2.3)
ATP	Adenosine-triphosphate (Sect. 1.1, Sect. 2.5.1)
ATR	Attenuated total reflection (Sect. 9.2.1)
ATR-FTIR	Attenuated total reflectance Fourier transform infra-red spectroscopy (Sect. 4.4.1)
BET	Brunauer-Emmett-Teller (Sect. 5.3.2, Sect. 7.2.2)
BOD	Biological oxygen demand (Sect. 11.3.1)
BPCC	Biophotochemical cell (Sect. 8.4)
BSSE	Basis set superposition error (Sect. 15.2)
CB	Carbon black (Sect. 7.1, Sect. 14.1)
CCD	Coupled devise (Sect. 12.3.5)
CcO	Cytochrome <i>c</i> oxidase (Sect.5.1)
CCSD(T)	Coupled-cluster calculations with single and double substitutions with inclusion of noniterative triple excitations (Sect. 15.5)
CNT	Carbon nanotube (Sect. 7.1)
COD	Chemical oxygen demand (Sect. 11.3.1)
CT	Charge transport (Sect. 2.1)
CV	Cyclic voltammetry (Sect. 3.2.5, Sect. 14.1)
CW	Continuous wave (Sect. 12.5.3)
DFT	Density Functional Theory (Sect. 1.2.1.1, Sect. 13.2.4, Sect. 15.3)
DHE	Dynamic hydrogen electrode (Sect. 3.2.1)
DMFC	Direct methanol fuel cell (Sect. 1.2.2.2, Sect. 3.2.3, Sect. 4.3, Sect. 7.1, Sect. 13.1, Sect. 14.1)
DP	Proticity (proton motive force) (Sect. 2.5.1)

DSC	Dye-sensitized solar cell (Sect. 10.1)
DSSC	Dye-sensitized solar cell (Sect. 3.3.5, Sect. 8.1, Sect. 9.1)
DTA	Differential thermal analysis (Sect. 4.3.3)
EDX	Energy-dispersive X-ray analysis (Sect. 4.5.3)
EIS	Electrochemical impedance spectroscopy (Sect. 3.3.1)
EX	Explicit finite difference method (Sect. 13.4.2.2)
EXAFS	Extended X-ray absorption fine structure (Sect. 15.7, Sect. 4.3.3, Sect. 5.3.2)
FDM	Finite difference method (Sect. 13.4.2)
FE SEM	Field emission scanning electron microscope (Sect. 4.3.3)
FF	Fill factor (Sect. 3.3.4, Sect. 8.3)
FWHM	Full width half maximum (Sect. 14.3.1.2)
GDE	Gas diffusion electrodes (Sect. 7.2.1)
GDL	Gas diffusion layer (Sect. 3.2.4)
GGA	Generalized gradient approximation (Sect. 15.5)
HER	Hydrogen evolution reaction (Sect. 1.2.2.1)
HF	Hartree-Fock (Sect. 15.3)
HOMO	Highest occupied molecular orbital (Sect. 1.2.1.2, Sect. 5.3.2, Sect. 9.1, Sect. 15.7)
HOPG	Highly oriented pyrolytic graphite (Sect. 7.3)
HOR	Hydrogen oxidation reaction (Sect. 1.2.2.1, Sect. 15.7)
HREELS	High-resolution electron energy loss spectroscopy (Sect. 14.3.2.1)
IEC	Ion exchange capacity (Sect. 2.5.2)
IMI	Intermittent microwave irradiation (Sect. 7.2.3)
IPCC	Intergovernmental Panel on Climate Change (Sect. 16.1)
IPCE	Incident photon-to-current conversion efficiency (Sect. 8.3, Sect. 9.2.3)
IR	Infrared spectroscopy (Sect. 14.1)
IRAS	Infrared reflection absorption spectroscopy (Sect. 14.1)
ISC	Intersystem crossing (Sect. 11.2.2)
ISO	International Standard Organization (Sect. 16.3.3)
ITO	Indium tin oxide (Sect. 2.2.2, Sect. 8.3, Sect. 13.2.2)
LCA	Lifecycle assessment (Sect. 16.3.3)
LEED	Low energy electron diffraction (Sect. 14.1)
LHE	Light-harvesting efficiency (Sect. 9.2.3)
LSD	Local spin density (Sect. 15.5)
LSV	Linear scanning voltammogram (Sect. 3.2.5)
LUMO	Lowest unoccupied molecular orbital (Sect. 9.1, Sect. 1.2.1.2, Sect. 15.7)
MB	Methylene blue (Sect. 11.2.2)
MEA	Membrane electrode assembly (Sect. 3.2.4, Sect. 5.1, Sect. 6.3, Sect. 7.1, Sect. 14.2.1)
MLCT	Metal-to-ligand charge transfer (Sect. 9.2.1)
MNc	Metal naphthalocyanines (Sect. 11.2.2)
MO	Molecular orbital (Sect. 2.4.3)

MOR	Methanol oxidation reaction (Sect. 4.3, Sect. 15.7)
MP	Metal porphyrin (Sect. 11.2.2)
MP2	Second-order Møller-Plesset perturbation calculations (Sect. 15.3)
MPc	Metal phthalocyanine (Sect. 11.2.2)
MV2+	Methylviologen (Sect. 2.2.2)
MWCNT	Multi-walled carbon nanotubes (Sect. 7.2.1)
Nd-YAG	Neodymium-Yttrium-Aluminum-Garnet (Sect. 12.4.3)
NE	Net energy (Sect. 16.3.2)
Nf	Nafion (Sect. 2.2.2)
NHE	Normal hydrogen electrode (Sect. 1.2.1, Sect. 3.2.1, Sect. 9.1, Sect. 11.2.1, Sect. 14.3.2.1)
NOW	Non-contact optical waveguide spectroscopy (Sect. 13.2.2)
ORR	Oxygen reduction reaction (Sect. 1.2.1, Sect. 2.4.3, Sect. 3.2.2, Sect. 6.1, Sect. 7.2.1, Sect. 15.7, Sect. 16.5)
OEC	Oxygen evolving center (Sect. 16.5)
PAH	Polycyclic aromatic hydrocarbons (Sect. 12.2.3)
PEFC	Polymer electrolyte fuel cell (Sect. 4.3, Sect. 6.1, Sect. 7.1, Sect. 14.1)
PEM	Polymer electrolyte membrane/proton-exchange membrane (Sect. 2.5.1)
PPy	Polypyrrole (Sect. 5.3.2)
PS	Photoelectron spectroscopy (Sect. 14.3.2.1)
PSCA	Potential-step chronoamperometry (Sect. 3.3.3)
PSCAS	Potential Step chronoampero spectrometry (Sect. 2.2.2)
PTFE	Polytetrafluoroethylene (Sect. 14.2.1)
Q	Quencher (Sect. 2.3.2)
RB	Rose bengal (Sect. 11.2.2)
RDE	Rotating disk electrode (Sect. 3.2.2)
RHE	Reversible hydrogen electrode (Sect. 3.2.1, Sect. 4.4.2, Sect. 7.2.3)
RRDE	Rotating ring-disk electrode (Sect. 3.2.2)
SAED	Selected area electron diffraction (Sect. 14.2.1)
SCE	Saturated calomel electrode (Sect. 4.3.2, Sect. 5.3.2, Sect. 7.2.3, Sect. 9.2.1)
SCV	Spectroscopic voltammogram (Sect. 2.2.2)
SEIRAS	Surface enhanced infrared spectroscopy (Sect. 4.3.1, Sect. 13.3)
SEIRAS	Surface enhanced infrared reflection absorption spectroscopy (Sect. 14.3.2.2)
SHE	Standard hydrogen electrode (Sect. 3.2.1, Sect. 8.4)
SOWG	Slab optical waveguide (Sect. 13.1)
SPR	Surface plasmon resonance (Sect. 13.2.2)
STM	Scanning tunneling microscope (Sect. 1.2.2.1, Sect. 7.3)
TCO	Transparent conducting oxide (Sect. 9.1, Sect. 10.4)
TSC	Thermally stimulated current (Sect. 10.2)

XXIV List of Abbreviations

TEM	Transmission electron microscope (Sect. 4.3.3, Sect. 7.2.1, Sect. 14.1)
TG	Thermo-gravimetry (Sect. 4.3.3)
TOF-SIMS	Time-of-flight secondary ion mass spectroscopy (Sect. 6.4.4)
TPD	Temperature-programmed desorption (Sect. 7.3, Sect. 14.3.2.1)
T-T	Triplet-triplet (Sect. 12.5)
UHV	Ultra-high vacuum (Sect. 14.1)
UNEP	United Nations Environment Programme (Sect. 16.1)
UPD	Underpotential deposition (Sect. 4.4.1)
UV/Vis	Ultraviolet/visible (Sect. 13.3.1)
VUV	Vacuum ultraviolet process (Sect. 11.2.1)
WC	Tungsten carbide (Sect. 1.2.2.1, Sect. 6.4.2)
XANES	X-ray absorption near-edge structure (Sect. 4.3.3, Sect. 5.3.2)
XAS	X-ray absorption spectroscopy (Sect. 15.7)
XPS	X-ray photoelectron spectroscopy (Sect. 4.3.3, Sect. 7.3, Sect. 15.7)
XRD	X-ray diffraction (Sect. 4.3.3, Sect. 5.3.2, Sect. 6.4.2)

Historical Overview and Fundamental Aspects of Molecular Catalysts for Energy Conversion

T. Okada, T. Abe, and M. Kaneko

Abstract In this chapter we focus on the historical background of the electrocatalysts especially of molecular catalysts that are considered as key technology for energy conversion systems. The energy conversion is a basic process with which humans can utilize natural energy by converting into useful forms of energy such as heat, electricity, or other secondary energies. The most important process to be established in this century will be the usage of renewable energy, which has least impact on the global environment. The central technologies for this process will be solar cells, photosynthesis, and fuel cells. Hydrogen energy society would be the most probable choice interconnecting these technologies, and toward this goal the establishment of efficient catalysts is indispensable. The designing of molecular catalysts is an important issue for solving the energy conversion yields and efficiency. Through biomimetic approaches many good candidates of catalysts for energy conversion have been studied. Porphyrins from cytochrome analogs have been studied since late 1960s as oxygen reduction center or oxygen carrier with variety of modifications. Also reduction of H^+ is part of an artificial photosynthesis, and many supra-molecular and hybrid complexes are studied since 1970s. The chapter starts with the history and design concepts of oxygen reduction catalysts and fuel oxidation catalysts in fuel cells, to cope with the control of multi-electron transfer reactions. The state-of-the-art molecular catalysts are characterized as metal–nitrogen ligand complex or metal–nitrogen–oxygen conjugates on carbon support. Photochemical reduction of H^+ is reviewed which is coupled to water oxidation, where historically metallophthalocyanines or polypyridyl complexes are studied intensively since mid-1980s. Charge separation antenna chlorophylls are models of dye-sensitizers for photoreductive H_2 evolution, and these are incorporated in Graetzel cell for electrochemical solar cells. Design and application of molecular catalysts for these cells are reviewed.

1.1 Introduction: Why Molecular Catalysts? A New Era of Biomimetic Approach Toward Efficient Energy Conversion Systems

The principle of fuel cell was discovered as early as in 1839 by Sir William Grove [1]. He demonstrated the H_2 – O_2 fuel cell with Pt electrodes contacting H_2 and O_2 gas reservoirs separated by H_2SO_4 aqueous solution, which was

the first event that humans acquired electric energy generation with a feed of fuels. It is interesting to note that in the same year A. E. Becquerel discovered the principle of photoelectric effect when illuminating one of a pair of silver/silver halide electrodes in dilute acid [2]. Although Sir Grove's discovery was a big historical milestone, the technology needed 120 years further to find its major application when Gemini space flights implemented the mission with fuel cell power sources in 1960s. Also solar cells using silicon p-n junction were first established just in the mid-1950s. These facts symbolically show that the technology relies much on the development of material science for its true commercialization. For energy conversion systems, the efficiency seriously counts before they become of use.

The life on the earth flourished after the plant cells acquired the inherent energy conversion systems of solar energy 2,700 million years ago. Photosynthesis occurs in chloroplast of plant cells, and photon energy is converted to phosphorylation of H^+ -ATPase and production of carbohydrate with more than 30% yield [3]. How the plants acquired such a high conversion efficiency is a very intriguing topic, but this leads us to an encouraging strategy that we mimic such sophisticated organs so that we finally obtain a system of high energy conversion using biomimetic materials.

After the Stone Age, the humans first invented tools for their lives mostly from minerals especially from metals. Alchemists in the medieval era extracted metal elements and synthesized materials from minerals. Today inorganic chemists and metallurgists use materials made from variety of elements in the periodic table. Although the number of inorganic materials is enormous, the community of organic chemists produces much more organic compounds almost unlimitedly. In the future of an advanced stage of biomimetic chemistry, humans will be able to synthesize such natural products as they like. It is therefore expected that we can achieve a high efficiency of energy conversion by adapting materials with biological concepts. This chapter intends to give an idea of how we produce new and useful catalysts for energy conversion in various fields, e.g., fuel cells, artificial photosynthesis, etc.

1.2 Molecular Catalysts for Fuel Cell Reactions

Fuel cells that operate at temperatures lower than 100°C and 100–500°C are categorized as “low-temperature fuel cells” and “medium-temperature fuel cells,” respectively, and these include alkaline fuel cells, phosphoric acid fuel cells, polymer electrolyte fuel cells, and direct liquid-feed fuel cells [4, 5]. The common feature is that designing high performance electrocatalysts is crucial in order to achieve high-energy conversion in the gas (or liquid fuel) reactions that are occurring on an electron conducting solid phase.

Most of the elements on periodic table were surveyed as electrocatalyst as early as 1950s and for metal alloys by 1960s [4, 6]. The applications of these

elements were for chloralkali electrolysis, water electrolysis, H_2O_2 production, and fuel cells. Investigations on fuel cell catalysts reached a commercial level when Davytan invented Ni- and Ag-supported active carbon electrodes for KOH alkaline fuel cells in 1950s. Sintered porous Ni electrodes by Bacon (1952) and Doppelskelett-Katalysator (DSK) electrodes made of Raney Ni or Pd by Justi (1954) were applied for alkaline fuel cells [4, 7]. Especially fuel cell catalysts were highlighted by many electrochemists during 1960s when NASA launched space mission projects. A big problem was “the sluggish character of O_2 reduction,” as pointed out by U. R. Evans [8]. This limitation is due to the low reactivity of O_2 that has electronically triplet ground state.

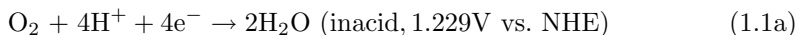
Slow kinetics require high-efficiency electrocatalysts. Materials usable for fuel cell catalysts are located near the center of the periodic table (around VIII_a group metals), and especially those usable in acid media are only Pt or Pt-based alloys [4], which are less available than other components of fuel cells. It is inferred then if we rely on merely metal or alloy catalysts, we have very few possibilities to find innovative materials.

Organic metal complexes such as porphyrins and phthalocyanines attracted much attention as alternatives to precious metal catalysts since 1960s [9–11]. These are the basic components in hemes of oxygen transport or cytochrome C of respiratory chains [3, 12]. The peripheral ligand structures of pyrrole-N rings give the metal center an important function to adsorb O_2 and transfer electrons to reduce it to H_2O . These molecules have a wide variety of molecular designing, and would be a potential candidate to tailor efficient electrocatalysts for fuel cell electrodes.

Historically nonmetallic catalysts have been studied for O_2 reduction for almost 40 years, but recently some fuel oxidation catalysts for H_2 , CH_3OH , and HCOOH oxidation are also attracting interests as reported in the literature [13–15]. The fuel oxidation catalysts made from organic metal complexes are rather rare because Pt is the most active and practical material used in commercialized fuel cells since the NASA space era. Major concepts for designing organic metal complexes are to facilitate adsorption and dehydrogenation reactions of fuel molecules on the catalyst surface, and secondly to increase the tolerance against a by-product CO. In the following, fuel cell catalysts for oxygen reduction reaction and fuel oxidation reaction are reviewed and their designing strategy are discussed for structure optimization of organic metal complexes, based on postulated reaction mechanisms.

1.2.1 Oxygen Reduction Catalysts

The scheme for oxygen reduction reaction (ORR) in acid medium is depicted in Fig. 1.1 [16, 17]. The main process is four-electron reduction of O_2 together with 4H^+ :



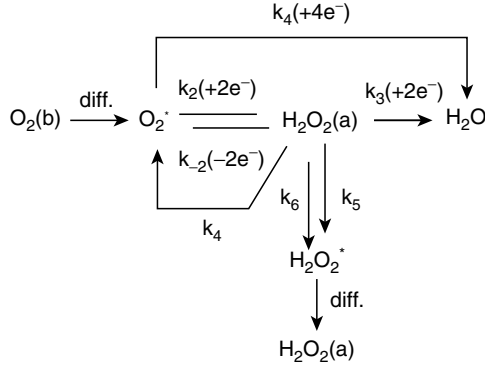
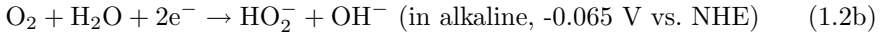
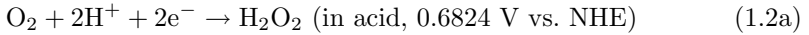


Fig. 1.1. Oxygen reduction scheme in acid electrolyte. *: in the vicinity of catalyst surface, (a): adsorbed on catalyst surface, (b) in bulk solution ([16], copyright Elsevier)

where NHE stands for normal hydrogen electrode as a reference potential. Another and undesirable path is two-electron reduction of O_2 :



for which O–O bond breaking does not occur and peroxide is produced. The most active electrocatalyst for O_2 reduction is found to be Pt and relatives like Pd and Ni, called VIII_a metals in the periodic table [4]. The goal of electrochemists is to postulate the precise mechanism of ORR on metal catalysts, and then to find a strategy to increase the catalyst activity. Computer simulation results developed in the last decade will be a powerful tool for this purpose.

Strategy of Electrocatalysts for Oxygen Reduction Reaction

Anderson et al. conducted an ab initio calculation of O_2 reduction [18]. The rate-determining step is assumed to lie on the first electron transfer to O_2 with H^+ ,



followed by several charge transfer steps with H^+ .

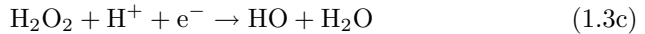
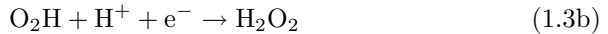


Figure 1.2 shows calculated energies along the reaction sequence (1.3a) to (1.3d). Similar calculations are reported for O_2 attached to Pt atoms, and it is shown that activation energies of the steps (1.3a) and (1.3c) are significantly

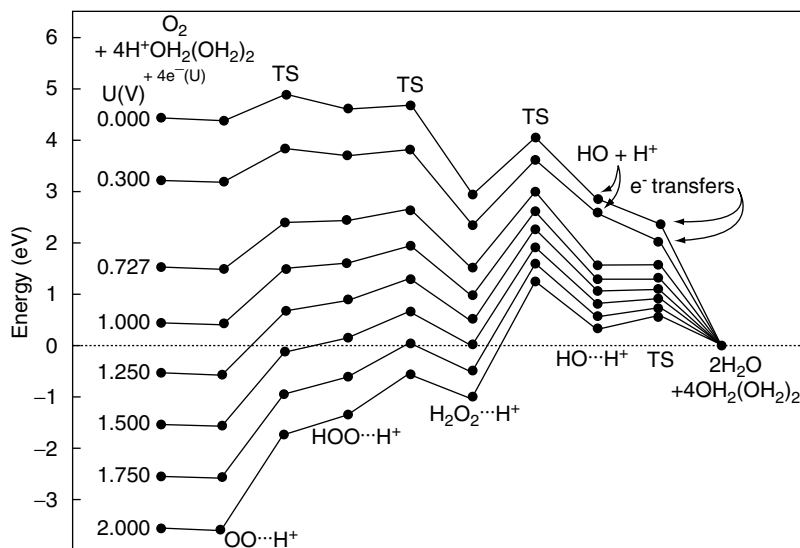


Fig. 1.2. Energies as functions of electrode potential for the O_2 reduction sequence. Transition state (TS) and hydrogen bonded precursor ($\text{O}\cdots\text{H}^+$) points are shown ([18], copyright the American Chemical Society)

decreased while that of the step (1.3d) is increased [19]. Since the highest barrier of the activation energy resides in the step (1.3c), H_2O_2 accumulates during the reaction scheme. The activation of stretching of $\text{HO}\cdots\text{OH}$ bond is an important process, for which the catalyst surface needs to provide its reaction field to facilitate the bond breaking. In this respect Zinola et al. reports on interesting results about the adsorption state of O_2 on $\text{Pt}(111)$ surface [20]. According to the calculation based on the extended Hückel molecular orbital method, the most stable configuration is bridge side-on contacting two adjacent Pt atoms. Due to the large population of π^* orbitals by d -electrons from Pt, $\text{O}\cdots\text{O}$ bond is weakened [21]. A criteria for a good catalyst for ORR is that the metal supplies sufficient back donation from its d -band to π^* orbital of O_2 . This is for the O_2 in the gas phase, and in the liquid phase the situation will be toward a stable adsorption of O_2 , but this trend would come to reality especially at negative polarization of the Pt electrode.

Nørskov et al. performed density functional theory (DFT) energy calculation of ORR along the reaction coordinate on various metal catalysts, for both dissociative ($1/2\text{O}_2 + * \rightarrow \text{O}^*$, where $*$ denotes adsorption site on the catalyst surface) and associative ($\text{O}_2 + * \rightarrow \text{O}_2^*$) mechanisms of O_2 [22]. They defined the maximal activity by using the activation barrier of the rate-limiting step among sequences of elementary steps, and plotted the activity of ORR as a function of the oxygen-binding energy. As shown in Fig. 1.3, a volcano-type curve was obtained and Pt and Pd were found to show a peak activity among transition metals. On the left side of volcano, H^+ transfer to adsorbed O is

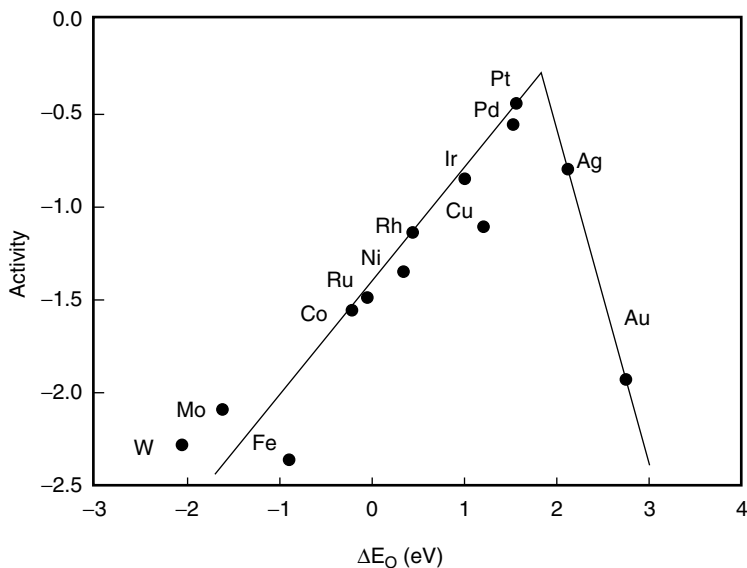
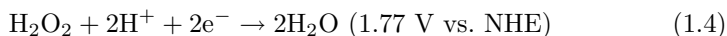


Fig. 1.3. Activity of ORR plotted as a function of the oxygen binding energy. ([22], copyright the American Chemical Society)

rate determining, and on the right side, H^+ and e^- addition to adsorbed O_2 is rate determining. Designing the metal catalyst that shows medium range of M–O binding energy would be preferable for high ORR activity.

Volcano-type curves are also discussed based on d-band vacancies (number of unpaired d electrons [23]) and % d character of transition metals (the extent of participation of d -orbitals in the metallic bond [24]), which are related to the adsorbed oxygen intermediate on the metal surface [17]. Figure 1.4 shows log current density plotted against d-band vacancies [25]. Oxygen adsorption that is neither too weak nor too strong looks like a prerequisite for the catalyst surface, which is the pathway of ORR.

In experiments, the mechanism of ORR was discussed with polarization curves in both acid and alkaline media. On dropping mercury electrode, Heyrovsky observed two waves corresponding to (1.2a) for the first step and



for the second step [4]. The following ORR rate–potential relations were verified

$$v = k_c [O_2] \exp \left\{ \frac{-(1-\alpha)FE}{RT} \right\} \quad (\alpha = 0.5, \text{ acid}) \quad (1.5a)$$

$$v = k_c \frac{[O_2][H_2O]}{[OH^-]} \exp \left\{ \frac{-(2-\alpha)FE}{RT} \right\} \quad (\alpha = 0.5, \text{ alkaline}) \quad (1.5b)$$

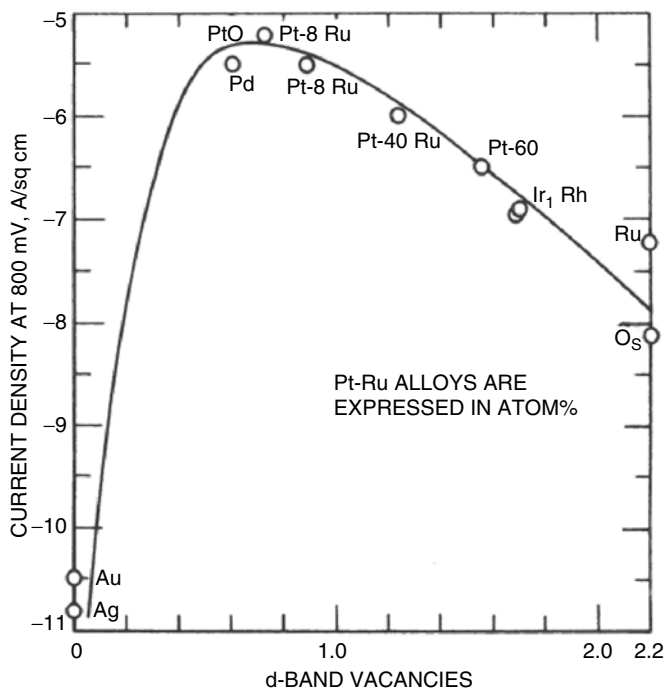


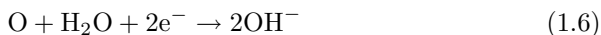
Fig. 1.4. ORR current density in 85% orthophosphoric acid at -460 mV RHE at 25°C , plotted against d -orbital vacancy of the metal ([25], copyright Taylor & Francis)

by Bagotskiy and Yabloova at Hg electrode, and Krasilshchikov at Ag electrode [26]. Bennion derived these rate equations based on the assumption that the first charge transfer (1.3a) is rate-determining in the case of the acid media, and the second step



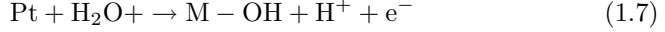
is rate-determining in the case of the alkaline media [27].

Evans proposed the “pseudo-splitting” model of ORR in alkaline media [28]. When O_2 adsorbs on oxide surface of transition metals, it makes bridge adsorption on the metal or oxide, but not necessarily split into atomic O. Then the surrounding OH groups give the hydrogen to the adsorbed O_2 like in the Grotthuss hopping, so that in effect bare O atoms are formed at the next site. This bare O site moves to the kink-site on the surface where it gets hydrogen from a water molecule:



If this is the case, the desirable catalyst is to provide active centers for O_2 (or split O) that gets hydrogen from neighboring water molecules.

In acid solutions, ORR on noble metals is sensitive to the adsorbed oxygen coverage and formation of surface oxides. ORR activity on oxide-free Pt was higher than that on oxidized Pt electrodes [4]. The reaction mechanism on Pt has been argued, based on the observed results: (1) observed Tafel slope was $2.3RT/F$, and (2) reaction order at constant potential for O_2 was 1 and for H^+ was $3/2$ [29]. Assume that Frumkin isotherm holds for reversible Pt–OH formation from H_2O ,



$$\frac{\theta_{OH}}{1 - \theta_{OH}} = \frac{[H_2O]}{[H^+]} \exp \left\{ \frac{-\Delta G_{OH} - r\theta_{OH} + FE}{RT} \right\} \quad (1.8)$$

which takes into account the repulsive interactions between adsorbed OH [30]. The rate equation for the rate-determining step (1.3a) where vacant site reacts with O_2 and H^+ is written as follows [29].

$$v = k[O_2][H^+](1 - \theta_{OH}) \exp \left\{ \frac{-(1 - \beta)\Delta G_r - \beta(\Delta G_p + r\theta_{OH}) - \beta FE}{RT} \right\} \quad (1.9)$$

where ΔG_r and ΔG_p are the free energies of adsorption of O_2 and O_2H , respectively. We get from (1.8) in the medium range of θ_{OH} ($\theta_{OH}/(1 - \theta_{OH}) \approx 1$), the Temkin type isotherm:

$$\frac{r\theta_{OH}}{RT} = -\ln H^+ + \frac{FE}{RT} - \frac{\Delta G_{OH}}{RT} \quad (1.10)$$

Substitution of (1.10) into (1.9) yields

$$v = k[O_2][H^+]^{1+\beta} \exp \left\{ \frac{-(1 - \beta)\Delta G_r + \beta(\Delta G_{OH} - \Delta G_p) - 2\beta FE}{RT} \right\} \quad (1.11)$$

which for $\beta = 0.5$ accords with the experimental results (1) and (2). This result means that the presence of OH on Pt more or less hinders the start of ORR. When $\theta_{OH} \rightarrow 0$, (1.9) gives the Tafel slope $2.3 \times 2RT/F$, which is also observed at large overpotential range. Whether O_2 reduction proceeds via direct four-electron path or via two-stage path with H_2O_2 as an intermediate is a matter of debate among electrochemists. Although H_2O yield of ORR is more than 98% on Pt, H_2O_2 production is shown to occur in the case of anion specific adsorption or of atomic H adsorption at <0.3 V vs. NHE.

Watanabe et al. give a strategy for designing Pt alloy catalysts that provide high ORR activity on the basis of d-band modification by the second element [31]. Figure 1.5 illustrates the O_2 bonding mode and the change of electronic structure of Pt induced by the second element. The best composition of the alloy corresponds to the condition where high probabilities of both the donation from π orbital of O_2 to d_{z^2} orbital of M and the back donation from partially filled d_{xz} and d_{yz} orbital of M to antibonding π^* orbital of O_2

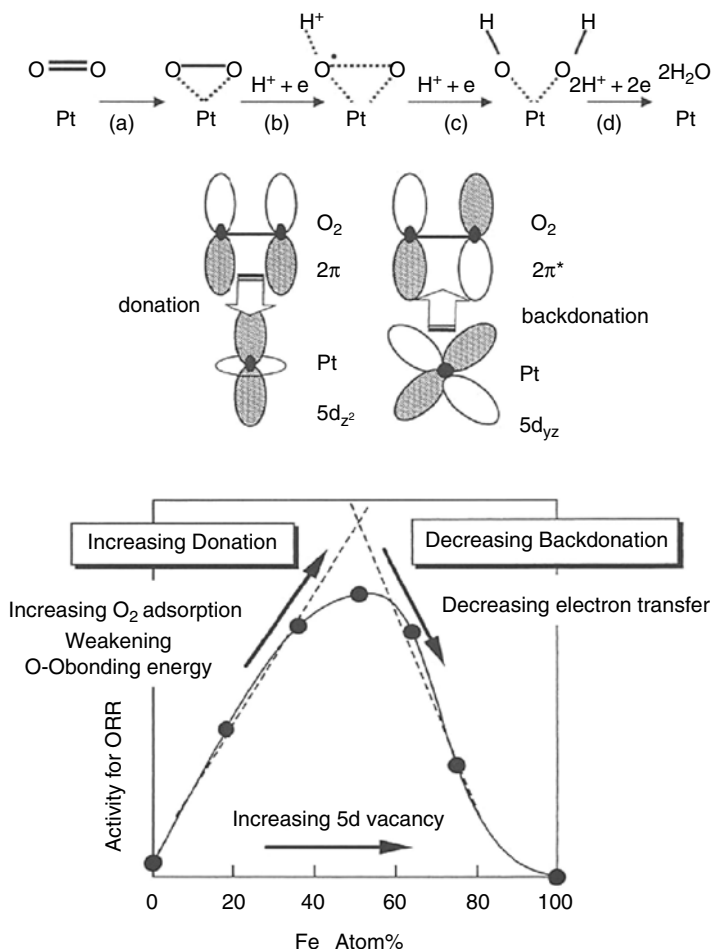


Fig. 1.5. Proposed mechanism of the enhancement of ORR by alloying Pt with Fe-group metals ([31], copyright The Electrochemical Society)

are satisfied. In addition to the electronic structure of the metal, the importance of the geometric factor such as the interatomic distance of metals was pointed out by Jalan et al. [32]. In ORR involving lateral adsorption of O_2 on the catalyst surface, the interatomic distance would affect the adsorption and O–O bond rupture, and then the catalytic activity.

In conclusion, best ORR catalysts will be achieved by aiming at materials that have (1) medium range of M–O bonding energy, (2) large population of π^* orbital of O_2 by d -electron back donation from M so that O–O bond weakens, (3) smallest oxide formation even at potentials 1.0 V NHE, (4) high rate of H^+ addition from neighboring H_2O on the catalyst surface, and (5) anticorrosive nature in acid media. Bockris et al. mentioned as indirect methods the use

of redox mediators to change the path of ORR, for example HNO_3/NO that shows faster reduction and oxidation rates than O_2 [4].

Oxygen Reduction Reaction on Macrocycles

The spin structure of O_2 (triplet) restricts the reactivity of O_2 with molecules having singlet ground states, but this spin restriction is overcome when O_2 coordinates to metal centers of macrocycles [10]. In ORR, O_2 interacts and receives electrons from the metal center. In the course of the reaction, two intermediate states should be experienced, (1) the metal center is reduced to lower valence state, (2) oxygen molecule adsorbs on the central metal ion to interact electronically with the macrocyclic molecule. (3) Further to make sure the four-electron reduction of O_2 to H_2O , cleavage of O–O bond should occur through the reaction scheme.

Typical examples of metal macrocycles are metalloporphyrins and metallophthalocyanines (Fig. 1.6). The use of macrocycles to ORR catalysts was first reported by Jasinski in mid-1960s [9], and was applied as a fuel cell cathode [33]. These macrocyclic complexes can bind a dioxygen molecule to the metal center in the N4 moiety, and transfer electrons via conjugated aromatic rings surrounding the active center. Prior to this electron transfer, the central metal ion should be reduced from M(III) to M(II) state. Randin proposed the concept of redox catalysis where the redox potential of the central metal plays an important role [34]. According to Lever et al. the central metals should have accessible d -orbitals located at the level between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the macrocycles [10]. Metals that meet the above two conditions are mostly transition metals with partially filled d -electron orbitals (group VI_a to VIII).

The role of a macrocyclic molecule surrounding the metal center can be considered in two ways:

1. Macrocycles modify the electronic structure of metal and relocate its redox potential so that O_2 can accept electrons from half-filled metal d -orbitals.
2. Macrocycles are mediators that connect the electronic levels of O_2 and the metal if those are too far apart, and ease the transition of electrons.

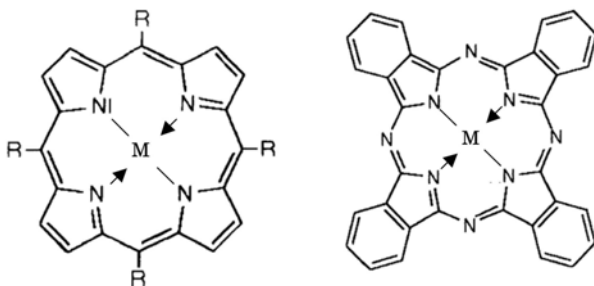


Fig. 1.6. Porphyrin and phthalocyanine complex structures. M = transition metal

As regards the former mechanism, macrocycles shift the redox potential of the metal to negative directions, and drive from M(III) to M(II) state. This would facilitate the electron transfer from M to O₂ [34]. Concerning the latter mechanism, Hoffmann et al. suggested that the energy of the π^* HOMO of O₂ should lie close to the level of d-band energy of M, in order to form the most favorable intermediates that bind the ligand O₂ with extra-planar configuration [35].

About the catalytic activity of a metal chelate in relation to its redox potential, two kinds of correlations are reported. In the case (1) stated above, the linear correlations are expected as discussed by Randin [34] and Zagal et al [36]. In the case (2), the volcano shaped curve would be expected because the energy of *d*-orbitals in macrocycles decreases linearly on going from Mn to Ni on the periodic table as calculated by Taube [37], where the energy level of O₂ HOMO should lie. Linear and volcano-type plots examined experimentally are illustrated in Fig. 1.7 [36] and Fig. 1.8 [38]. There are other factors such as the change of rate-determining steps or the difference of mechanisms of four-electron or two-electron O₂ reduction. In Fig. 1.7, Fe or Mn phthalocyanines reveal M(III)/M(II) redox potentials that are close to the potential of ORR and promote four-electron mechanism, while on Co phthalocyanines ORR takes place at a potential very far from that of M(III)/M(II) couple and proceeds with two-electron mechanism. Therefore the explanation of the ORR activity and the redox potential relations needs careful study.

Two types of interactions can be assumed for the central *metal*-dioxygen complex. One is the side-on structure (Griffiths model) and the other is the end-on structure (Pauling model), the former may be further categorized into

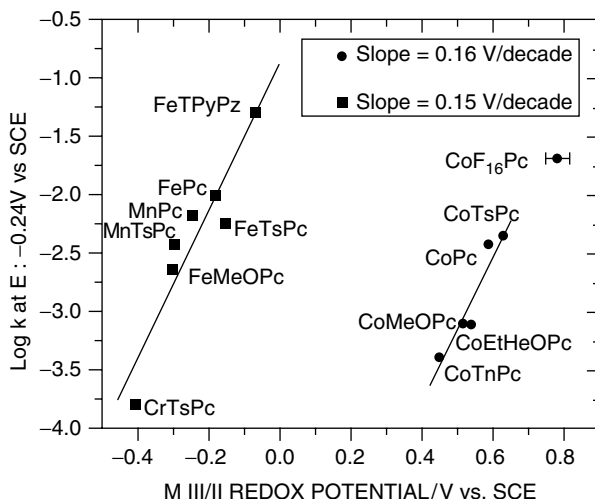


Fig. 1.7. ORR activity of various metallophthalocyanines in 0.1 M NaOH plotted against the first oxidation potential ([36], copyright Pergamon Press)

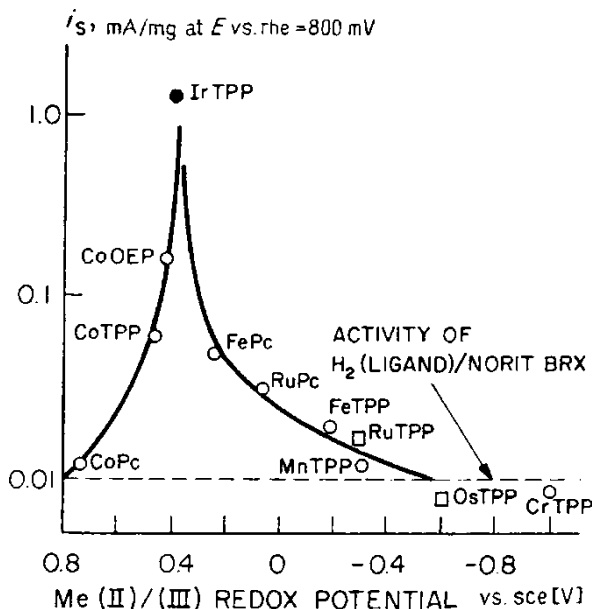


Fig. 1.8. ORR activity of various metallophthalocyanines in 4 M H_2SO_4 plotted against the redox potential ([38], copyright Verlag Chemie GmbH)

1:1 and 2:1 coordination according to the number of sites per O_2 molecule (Fig. 1.9 [39]). Upon coordination of the O_2 molecule to a metal center, $2p$ electrons of O_2 interact with d -orbitals of the metal through (1) a σ -type bond by donation from bonding orbital of O_2 to acceptor orbital d_{z^2} of the metal and (2) a π -backbond interaction between the $d\pi$ (d_{xy}, d_{yz}) orbital of the metal and the partially occupied π^* antibonding orbital of O_2 .

Collman et al. synthesized dicobalt cofacial porphyrin dimers in which two porphyrin rings were constrained in parallel by two amide bridges of varying length, and found that four-atom bridges produced good four-electron reduction of O_2 [40]. Yeager discussed the four-electron reduction efficiency and the coordination of O_2 on metal complexes [39,41], based on the data of Collman et al. and of Liu et al. [42]. A *cis*-configuration of O_2 between two metal centers separated by about 0.4 nm was the most efficient structure for O_2 reduction. The assumed mechanism was that a *cis*- μ -peroxo intermediate formed between Co(II) – Co(II) of two porphyrin rings favors H^+ access and O–O bond rupture. However, Mn and Fe phthalocyanine monomers also showed direct reduction of O_2 to H_2O [31]. This was attributed to the catalytic ability of phthalocyanines for chemically decomposing H_2O_2 to H_2O . The second reasoning was the mode of interaction of O_2 with the metal centers. For iron phthalocyanines, side-on configuration was preferred and O–O bond cleaving was promoted by back donation of d -electrons from the metal center. Fast exchange of $\text{M(III)}/\text{M(II)}$ couple was also a prerequisite for four-electron reduction of O_2 .

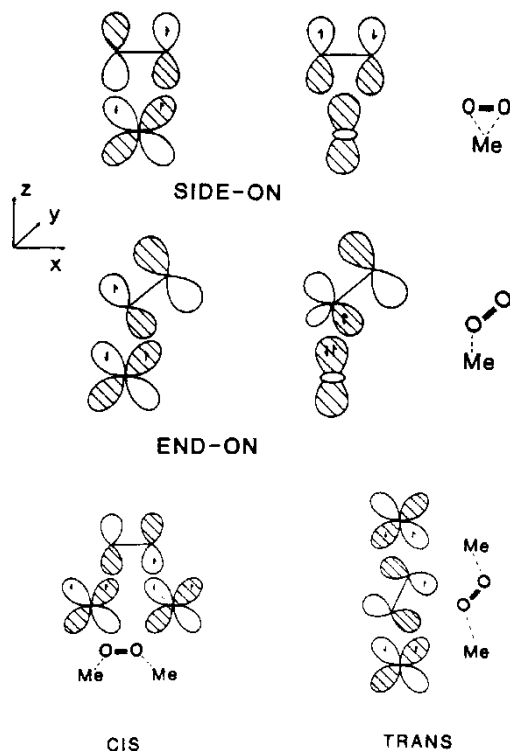


Fig. 1.9. Various types of interactions of O_2 with transition metal species ([39], copyright Elsevier)

1.2.2 Fuel Oxidation Catalysts

As fuels hydrocarbon (methanol, formic acid, ethanol, dimethylether, etc.) can be the candidate besides H_2 , but environmental and hazardous concerns to humans in addition to energetic considerations limit the fuels to only a few [43]. In this section H_2 , methanol, and formic acid oxidation, and the topic of CO poisoning will be discussed especially with future possibility of macrocyclic or metal complex catalysts.

Hydrogen Oxidation Catalysts and CO Poisoning

Reaction of H_2 on metal electrodes has been the most frequently studied subject among electrochemists. The cathodic reduction of H^+ to H_2 , the hydrogen evolution reaction (HER) has many basic and common features to other electrochemical systems, and many reviews and publications have been historically done so far [44–46]. Important results were obtained in 1957 when Conway and Bockris found a linear relationship between the exchange current density $\log i_0$ of HER and the work function of metal electrodes [47]. A volcano

curve correlation between $\log i_0$ and the heat of adsorption of H on metals was reported in 1958 by Parsons and Gerischer, based on the transition state theory [46]. Kita et al. reported a periodic change of $\log i_0$ when plotted against the atomic number of metals, with a peak around Pt [6]. They investigated the correlations between $\log i_0$ and various physical parameters of metals, and concluded that the most important factors to be the work function and heat of adsorption of hydrogen. They categorized metals into “d-metals” (transition and Ib metals in the periodic table) and “sp-metals” (metals after IIb) for which the HER reaction intermediates are the adsorbed hydrogen atom H(a) and the adsorbed hydrogen molecule ion H_2^+ (a), respectively.

Comparing to HER, the anodic reaction of H_2 to H^+ (hydrogen oxidation reaction, HOR), although acknowledged as the important reaction in fuel cells, gathered rather smaller number of reviews until the last decade. This is due to the experimental restrictions for H_2 reactions, where gaseous reactants should be supplied under controlled manner rather than the reactants in the electrolyte. In 1990s the number of literatures surged especially in the design of CO-tolerant metal or alloy catalysts for fuel cell applications. The HOR mechanism in acid media is based on the slow Tafel step followed by fast Volmer step [46]:



At least two types of H_{ad} are acknowledged, on-top H and hollow-site UPD H on the Pt crystal surfaces.

Most of the literatures discuss the CO or anion adsorption to characterize the HOR on Pt electrodes. The tailor-made surface approach of the catalyst is the recent trend of researches, which looks for the good design of CO-tolerant anode catalysts after studying the facets of single crystals or sub-monolayer of second elements. Techniques developed before 1990s, for example, scanning tunneling microscope (STM), atomic force microscopy (AFM), and in situ spectroelectrochemical methods greatly assisted in observing structural sensitivity of the reacting catalyst surfaces under polarization measurements. According to the recent results, kinetics of HOR and of CO oxidation on Pt is strongly influenced by the crystal facets, anion adsorption, and oxidation of Pt surfaces [46]. In sulfuric acid solutions, Pt(111) surface shows the least reactive and the highest activation energy among single crystal surfaces, considering its high surface atomic density (1.53×10^{15} atoms cm^{-2}) that results in the high energy of interaction with anions.

The first nonprecious metal catalysts for HOR were tungsten carbide (WC), WS_2 , and MoS_2 [48]. The remarkable point was no CO poisoning, but the fuel cell performance was not satisfactory. HOR catalysts based on organic metal complexes are so far rather few. Crystal structure of heterodimeric hydrogenase enzymes is recently published [49], and its model with a nickel–ruthenium dinuclear aqua complex forming a bridging hydrido ligand,

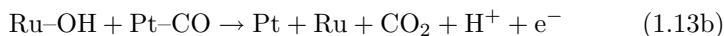
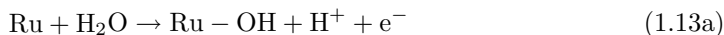
Ni(μ -H)Ru is reported to oxidize H_2 into H^+ in aqueous solutions at 20°C [50]. Based on biomimetic approach using DFT calculations of nitrogenase active sites, Nørskov et al. proposed MoS_2 as potential electrocatalyst for HER [51]. Further developments in search for practical HOR catalysts are expected in the near future.

Hydrocarbon Oxidation Catalysts

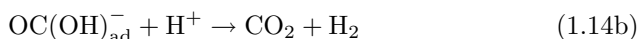
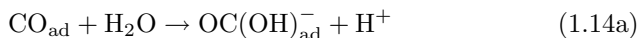
Direct methanol fuel cell (DMFC) is acknowledged as a “dream fuel cell” among electrochemists because this fuel cell enables a simplified system without the need for fuel reformers and other parasitic systems, a high power density that exceeds lithium ion batteries and easy storage or recharging of fuels [52]. Especially as power sources for small-scale devices such as mobile phones, laptops, and personal digital assistance (PDA), DMFC has many advantages over existing energy sources, and the projected performance can easily satisfy the future cost target. In the last decade, study of DMFCs increased both for the system and for component materials [53]. Since one of the major problems with DMFC is low activity of methanol oxidation reaction, the catalyst research attracts many electrochemists as ever-increasing topics [54, 55].

For methanol oxidation, Pt–Ru alloy has been the most studied catalyst for more than 40 years, but alternatives have been pursued in many possibilities. Those examples were platinum based alloys (Pt–Sn, Pt–Mo, Pt–Ni, Pt–Fe) [56, 57], platinum finely dispersed on oxide supports like TiO_2 , MoO_2 , WO_3 , etc [58–62]. New base catalysts were proposed, e.g., mixture of nickel-tungsten alloy and WC prepared from nickel tungstate [63]. New types of catalysts were also proposed, e.g., rare earth cuprates [64], or organic metal complexes as a cocatalyst with platinum [13, 65–68]. In the study of the electrochemical CO oxidation on carbon-supported and heat-treated metal porphyrins, van Baar et al. found Rh, Ir, and Co chelates as good electrocatalysts, and proposed a mechanism similar to the water gas shift reaction [69]. Bett et al. reported the enhancement of methanol oxidation on Pt cocatalyzed with Sn and Ru macrocycles, and discussed the activity in relation to their redox potentials [13].

As the mechanism of methanol oxidation on Pt, dual paths, i.e., CO path, and non-CO path are considered as possible routes [70]. Non-CO path (direct path) assumes formate species (HCOO_{ad}) as an intermediate, and this changes into CO_2 as a reaction product [71]. CO path (indirect path) makes a poison that strongly adsorbs on the catalyst surface. To cope with this problem, several concepts for CO-tolerant catalysts for methanol oxidation are proposed so far. For example, as possible mechanisms in Pt–Ru alloy, two points are noticed to consider a role of Ru element. One is the bifunctional mechanism, and Ru provides a site of oxygen-containing species, and oxidizes CO that adsorbs on Pt site [72, 73].



Due to the presence of OH on Ru derived from H₂O, CO can be oxidized at a lower potential (0.4 V vs. NHE) than on pure Pt (0.6 V vs. NHE). The second idea is called the ligand mechanism, in which Ru weakens CO bonding on Pt by inducing *d*-electron deficiency in the electronic structure of Pt, thus catalyzing the oxidation of CO at potentials much lower than that observed for Pt [74]. Whether or not these mechanisms also apply for the catalysis involving macrocycles is still a matter of debate, but it is interesting to refer to the basic idea of van Baar et al. who worked on metal macrocycles for CO oxidation and ascribed the mechanism similar to that of the water gas shift reaction [69].



On metal macrocycles CO_{ad} is polarized as $-\text{C}^{\delta+}=\text{O}^{\delta-}$, and this induces a nucleophilic attack of H₂O from the surrounding, resulting in hydroxycarbonyl species $-\text{CO}(\text{OH})^-$, from which H is pulled off and CO₂ emerges. A support for this mechanism is that CO can be oxidized to CO₂ even in a full coverage of CO, because H₂O can be supplied from the surroundings (Rideal–Eley mechanism). This is in contrast to the case of bifunctional mechanism, where a site for OH_{ad} is required to oxidize CO_{ad}, both of which are adsorbed species coming from the atmosphere (Langmuir–Hinshelwood mechanism).

Formic acid oxidation is acquiring attention in recent years because of the increasing needs of developing small-scale fuel cells for portable devices [75]. Although formic acid has lower specific energy of 1,630 Wh kg⁻¹, as compared with methanol (6,073 Wh kg⁻¹), the former has the advantage that theoretical cell voltage 1.40 V exceeds that of methanol (1.21 V) and the fuel crossover through the polymer electrolyte is low, which is a major problem for methanol [43]. This is because anionic species dissociated from formic acid is rejected from entering in the polymer electrolyte membranes. As in the case of DMFC, formic acid oxidation shows large overpotential, and the fuel catalyst is a crucial topic for the commercialization of fuel cell [76].

The best catalyst studied so far are Pt–Pd alloy and Pd nanoparticles [75, 77]. Recent research proposes new materials such as Pt with submonolayer-deposited Pb (PtPb_{UPD}) [78], Bi-modified Pt [79], intermetallic phases of Pt–Bi, Pt–In and Pt–Pb [80]. Use of macrocyclic compound tetrasulfophthalocyanine as a cocatalyst for Pt is a new challenge as a formic acid oxidation promoter [15]. Although the mechanism of formic acid oxidation is not yet clarified as that of methanol, CO and formate are observed on Pt surface, and similar mechanisms are considered as for methanol oxidation reaction that involve the active intermediate and the poisoning intermediate [81–84].

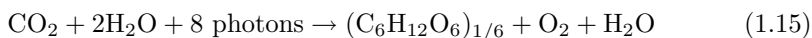
Bemirci, based on the theoretical work by Nørskov et al. [85], interpreted the behaviors of alloy catalysts [86]. Two concepts are introduced:

1. One is the shift of d-band centers of surface atoms by overlayers calculated by DFT, which through the chemisorption energy of reacting molecules determines the reactivity of the alloy.
2. The second is the segregation energy that determines the configuration of alloy elements on the catalyst surface.

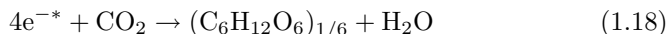
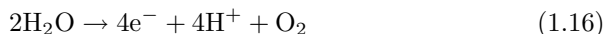
The geometric effect is ignored. According to the criteria, good alloys like Pt–Ru can be selected by seeking the negative shift (weak adsorption) of d-band centers for metals suffering from poisoning by CO-like species (Pt), and positive shift (strong adsorption) for elements that provide OH species (Ru). Also segregation affects the surface atomic composition, and the metal that provides multiple sites for the reactant should segregate while the other element offering OH should anti-segregate. On the other hand, for HCOOH oxidation, the second element should reduce the number of CO adsorption sites on Pt by geometric hindrance (third-body effect). Thus Pt should anti-segregate and d-band center shifts up while those of the second element remains constant, which applies well for Pt–Au and Pt–Pd alloys.

1.3 Molecular Catalysts for Artificial Photosynthetic Reaction

Photosynthesis is the most important energy conversion system on our earth. It supports almost all the biological energies by converting solar energy into chemical energy by utilizing an extremely sophisticated and complicated molecule based system. The photosynthetic system will be shown in Chap. 8; the important point of photosynthesis is represented by the (1.15) where carbon dioxide and water is reacted by utilizing solar visible light photons to produce a main product, carbohydrate, shown by $C_6H_{12}O_6$.



This reaction is represented by the following three major processes (1.16), (1.17), and (1.18), where water is an electron donor providing electrons to the whole system (see also Chap. 8). The electrons obtained from water at the Mn protein complex (1.16) are excited by solar photons at the chlorophyll reaction center (two steps) to form high energy electron (e^{-*}) (1.17), and the e^{-*} reduces CO_2 to carbohydrate (1.18) via reduction of NADP to NADPH.



This process is represented by Fig. 8.1 shown later where the electron from water is driven by two steps (at the Photosystems II and I, abbreviated to PSII and I) at the reaction center chlorophyll to higher energy, and finally reduces

CO₂ to produce carbohydrate. Molecular metal complexes and metal clusters play an important role in photoinduced electron transfer and catalysis.

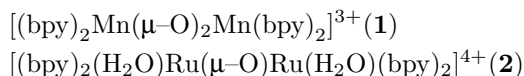
In Sects. 1.3.1, 1.3.2, and 1.3.3, the important water oxidation catalysts, reduction catalysts, and photoinduced chemical reactions for devices will be described.

1.3.1 Water Oxidation Catalyst

Catalytic water oxidation (dark reaction) is the first and important reaction of the electron flow in the photosynthesis represented by Fig. 8.1 (see Chap. 8) where water is used as a source of electrons provided to the whole system. Since water oxidation is so important for the biological activities, its catalyst and reaction mechanism have been reported in many books and reviews [87–93].

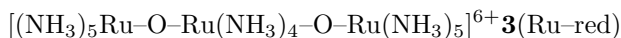
In the photosynthesis a Mn-protein complex works as a catalyst for the difficult four-electron oxidation of two molecules of water to form one O₂ molecule (1.16). It is inferred that at least four Mn ions are involved in the active center, but its structure is not yet completely elucidated.

Molecular metal-containing catalysts for water oxidation have been attracting attention a great deal as models for the photosynthetic catalyst. Many structural models have been synthesized [93]. Among them, tetrakis(2, 2'-bipyridine)(di-μ-oxo)di-Mn complex (**1**) and tetrakis(2, 2'-bipyridine)(μ-oxo) di-Ru complex (**2**, Meyer's complex) are typical examples that showed some activity for water oxidation, but the activity was not high enough for water oxidation.



Water oxidation catalysis has been studied both by chemical method (Fig. 1.10a) using Ce(IV) as oxidant and electrocatalytic method (Fig. 1.10b) using polymer-coated electrode [91–93].

It has been found that ammine-ligand-based Ru complexes, trinuclear, dinuclear, and mononuclear ones, show high activity as catalysts for water oxidation [91–93]. Because the catalyst – trinuclear Ru–ammine complex called Ru–red (**3**) – is very active, it can even evolve observable O₂ bubbles in the presence of a strong oxidant such as Ce(IV) ion in water.



1.3.2 Reduction Catalyst

When aiming to establish a real photosynthesis model, the CO₂ reduction must be considered as the reaction part for the gain of fuels. As shown in previous literature [94], in a thermodynamic sense, the multi-electron reductions of CO₂ particularly into CH₄ as well as CH₃OH are more favored than

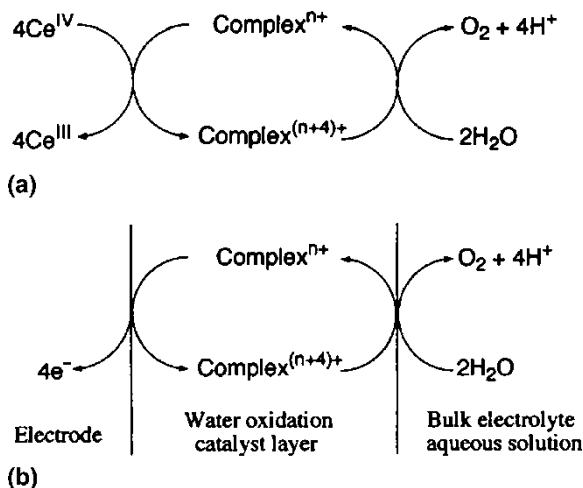


Fig. 1.10. Chemical water oxidation catalyst represented by complex^{n+} (a) and electrochemical water oxidation catalyst (b)

the H^+ reduction into H_2 . However, CO_2 activation is essentially difficult due to its stable structure (considering the bond moment of $\text{C}-\text{O}(\text{CO}_2, 2.3 \text{ D})$ [95], C is positively charged, while O is negatively charged; CO_2 is expected to act as an electron acceptor rather than an electron donor due to its high ionization potential [96], which means that the C atom in CO_2 is the activation point). Therefore, all CO_2 reductions have poor feasibility in a kinetic sense, suggesting that a highly efficient and active catalyst site must be fabricated via catalysis chemistry. The potential for various kinds of metal complex to act as catalysts for CO_2 reduction has been studied via photochemistry and electrochemistry; however, there has been no example of a photoinduced CO_2 reduction along with the electron donation originating from water oxidation, although the chemical activation of CO_2 is now the focus of continuous attention.

It is possible to replace CO_2 fixation by the H^+ reduction into H_2 in order to establish a water photolysis system. It has been known that Pt and its colloidal particles are the most active catalysts for the reductions of H^+ as well as O_2 [17, 97–99]; however, Pt is a rare and precious material. According to statistical data [100], $\sim 1.0 \times 10^5 \text{ kg}$ of Pt corresponding to 45% of overall demands (in 2003) is used as catalyst, making it highly desirable to design and develop a new catalyst alternative to Pt, especially using molecular catalysts.

In the present section, typical examples of molecule-based catalysts for CO_2 and H^+ reductions will be shown.

CO₂ Reduction Catalyst

Metallophthalocyanines

The catalyses of metallophthalocyanine (denoted as MPc for the 1:1 complex) and its derivatives for CO₂ reduction have been extensively studied [e.g., 101, 102]. It has also been acknowledged that a metal-free phthalocyanine is incapable of CO₂ reduction [103], suggesting that interaction between a metal ion and CO₂ is essential for the catalytic reduction; in addition, a metallodiphthalocyanine with a sandwich-structure (i.e., the 1:2 complex of MPc₂) was also applied to the CO₂ reduction [104], but the MPc₂ exhibited poor catalysis due to little opportunity for the CO₂ coordination to metal ion.

Among the MPcs of monophthalocyanine, CoPc is the most typical and active electrocatalyst, which often results in CO formation [101, 102, 105–109]; however, in the water phase, the H⁺ reduction into H₂ takes place competitively (selectivity (CO/H₂ ratio), $\sim 1.5 : 1$ [105]). Therefore, the development of a much more kinetically efficient catalyst site in CO₂ reduction process than in H⁺ reduction has been the focus of attention in order to accomplish selective CO₂ reduction in an aqueous media as well as fabricate a real reduction site towards an artificial photosynthetic model. The use of a polymer matrix as a catalyst supporter was effective for an active and selective CO₂ reduction [106, 107]. The catalyst membrane composed of CoPc and poly(4-vinylpyridine) (PVP) performed active and selective CO₂ reduction in comparison with a neat CoPc coating (selectivity (CO/H₂ ratio), $\sim 4 : 1$) [107]. This was ascribed to the coordinative and weakly basic properties of PVP; namely, the coordination of PVP to CoPc can cause an increase in electron density on the Co ion, which facilitates the intermediate formation; furthermore, the weakly basic property of PVP can favorably function as a H⁺ source for the dehydration process in producing CO from CO₂.

The CoPc derivatives substituted with the butoxy group (CoPc(BuO)₈) [108] or the cyano group (CoPc(CN)₈) [109] can also exhibit active catalysis for CO₂ reduction (*cf.* activity: CoPc(BuO)₈ > CoPc > CoPc(CN)₈). Those show typical characteristics for redox catalysis affected by the electronic property of the complex employed. When substituting CoPc for the electron-donating group, the electron density of the CoPc(BuO)₈ becomes high in comparison with the others, affecting the redox potential in the form of CoPc(BuO)₈ (negative) < CoPc < CoPc(CN)₈ (positive). Therefore, in a highly basic CoPc(BuO)₈ system, an electrophilic addition reaction of CO₂ onto CoPc(BuO)₈ (CO₂-adduct formation) is expected to take place favorably, which efficiently induces reduction catalysis.

The electronic property of the CoPcs can also be the key factor affecting their catalysis mechanisms. Catalysis by CoPc for CO₂ reduction has been considered to take place through the two-electron reduced species. However, it appeared that the electrocatalytic CO₂ reduction by CoPc takes place at a more negative potential than the second reduction of Co(II)Pc, which may

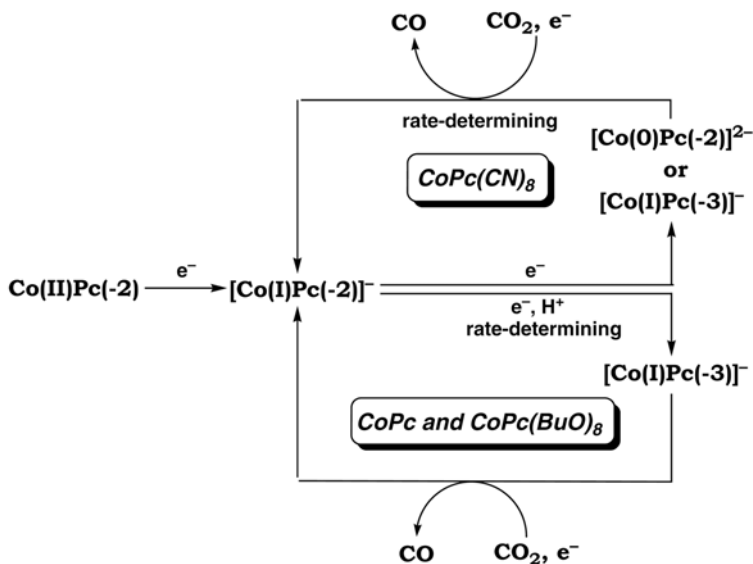


Fig. 1.11. Proposed mechanisms of electrocatalytic CO₂ reduction by the CoPc and its derivatives ([109], copyright Wiley)

indicate the involvement of a further reduced species of CoPc with the CO₂ reduction. In order to elucidate the catalysis mechanism, an in situ potential-step chronoamperospectroscopy (PSCAS) was conducted in a pyridine solution containing the CoPcs. Based on the PSCAS results, the mechanisms of CO₂ reduction by the CoPcs were proposed (Fig. 1.11) [107–109].

Polypyridyl Metal Complexes

Tanaka et al. have studied and clarified the catalysis of polypyridyl ruthenium complexes involving carbonyl ligand in organic solution (Fig. 1.12) [110–113]. In those catalyses, the complex (e.g., $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ (bpy = 2,2'-bipyridine)) usually underwent reductive cleavage of the Ru–CO bond to form CO under electrochemical conditions, whereupon the reduced species ($[\text{Ru}(\text{bpy})_2(\text{CO})]^0$) reacted with CO₂ to recover the original complex. When employing the specific conditions (such as a low temperature [111], an introduction of a ligand (such as naphthylpyridine) leading to a stabilization of the Ru–CO in complex [112, 113], etc.), the reductive cleavage of the Ru–CO can be suppressed, resulting in higher reduction products such as HCHO [111], CH₃OH [111], and CH₃COCH₃ (in the presence of the alkylation reagent (CH₃I)) [113].

A number of molecule-based catalysts, including MPc, are water-insoluble, and those catalyses in the water phase have usually been investigated within a heterogeneous system. For example, the preparation

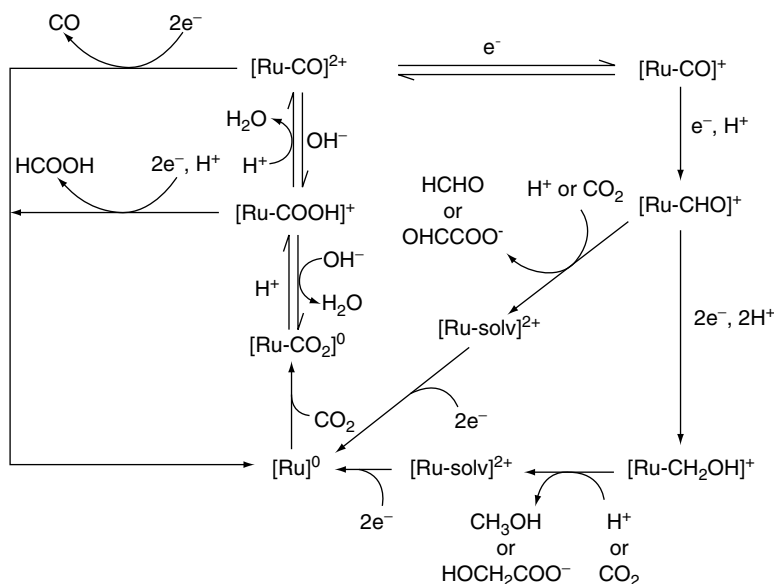


Fig. 1.12. Formation pathways of HC(O)H, CH₃OH, H(O)CCOOH, and HOCH₂COOH by polypyridyl ruthenium complexes involving carbonyl ligands ([111], copyright the American Chemical Society)

of a modified electrode was particularly effective in elucidating the molecular catalysis of the water-insoluble complex in the water phase. By embedding such a complex into a water-insoluble polymer and confining it to an electrode surface, the heterogeneous catalyst system of a molecular aggregate can be formed, which may also show unique and/or active catalysis that cannot be achieved using a homogeneous solution or a neat catalyst [114]. Employing a polypyridyl noble metal complex of carbonyl ligand (e.g., $[Ru(bpy)_2(CO)_2]^{2+}$ [115], $[Ru(L)(CO)_2(CH_3CN)]_2^{2+}$ (L = pyrrole-substituted bpy) [116], $[Re(bpy)(CO)_3Cl]^{2+}$ [117], etc.) as a catalyst in a polymer matrix, metal-metal bonding occurred due to the molecular aggregation of the complex, which leads to an efficient and selective CO₂ reduction in the water phase.

Polypyridyl-type transition metal complexes have also been studied for their potential catalytic activity for CO₂ reduction [118–121]. $[Co(terpy)_2]^{2+}$ (terpy = 2,2' : 6',2''-terpyridine) embedded in a Nafion membrane exhibited catalysis for a selective formate formation (selectivity (HCOOH/H₂ ratio), ~4 : 1) [118], for which bimolecular catalysis by $[Co(terpy)_2]^+$ (one-electron reduced species) is proposed. Such a cooperative catalysis is also a typical characteristic of molecular aggregates of which catalyst molecules are closely arranged within a polymer matrix. 4-Vinylterpyridine (4-v-tpy) complexes of Cr, Ni, Co, Fe, Ru, and Os have been prepared and assessed for CO₂ reduction

[121]. By confining the complex onto an electrode through the electropolymerization of the vinyl group, these molecular aggregates resulted in the sole formation of formaldehyde via a four-electron transfer although the complex can induce only the formate formation in a homogeneous solution. The complexes of the first row transition metals were more active than those of the second or third rows, owing to the lower stability of the latter complexes.

Reduction Catalyst for H₂ Production

Colloidal Pt has been recognized as one of the most popular and active catalysts for H₂ formation [97–99]. In addition to the polychloroplatinates of PtCl₄²⁻ and PtCl₆²⁻, *cis*-Pt(NH₃)₃Cl₂ (*cis*-platin) [122, 123] as well as the polypyridyl Pt complex ions (i.e., [Pt(bpy)₂]²⁺ [124] and [Pt(terpy)Cl]⁺ [125]) can also act as starting materials for zero-valent Pt capable of H⁺ reduction catalysis. Catalysis by Pt colloid is remarkably dependent on particle size. As for this, protection of metal particles using water-soluble polymers or polymeric micelles was effective for inhibiting coagulation [126–129]. Bimetallic nanoclusters of core/shell structure (Au/Pt, Au/Pd, Au/Rh, Pt/Ru (cf. where the molar ratio of both elements is 1:1), etc.) have also been prepared from the corresponding high-valent metal ions [130–134].

Hydrogenase has been known as a biological catalyst capable of both H⁺ reduction and H₂ oxidation [135–137], similar to a Pt catalyst. It has been recognized that these reactions proceed at the binuclear active sites of iron only ([Fe]H₂ase (Fig. 1.13) [138]) or both nickel and iron ions ([FeNi]H₂ase (Fig. 1.13) [138]) coordinating CN⁻ and CO ligands within a sulfur-rich environment [49, 139, 140]. Although it is of difficulty to apply the hydrogenase enzyme to an artificial photosynthetic system involving O₂ evolution since the enzyme is unstable against O₂, the model compounds of hydrogenase have been passively developed and elucidated via electrochemistry [138, 141–143], in order to gain insights into the relationship between structure and function, as well as the catalysis mechanism.

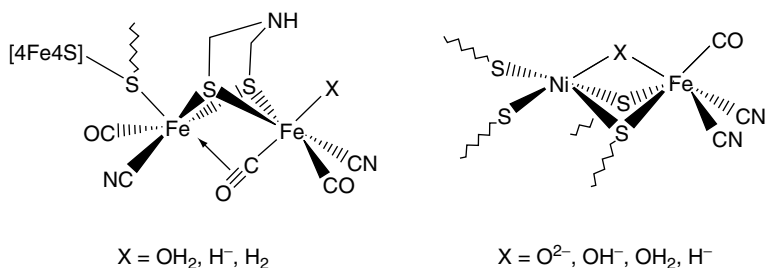


Fig. 1.13. Chemical structures of the active sites of [Fe]-only (left) and [NiFe] (right) hydrogenases (X are putative ligands) ([138], copyright the American Chemical Society)

The catalytic reactions for the consumption and production of H_2 take place through metal-bound dihydrogen and hydrides, respectively [144]. In addition, many of the functions of the hydrogenase enzymes (E) seem to have proceeded through a heterolytic process, according to the following equation ($\text{H}_2 + \text{E} \rightarrow \text{EH}^- + \text{H}^+$) [145]. The finding of dihydrogen complex by means of synthetic chemistry has attracted attention as a means to gain insights into hydrogen reactivity [146]. Since H_2 oxidation and H^+ reduction represents an equilibrium reaction, the discovery was expected to signal a breakthrough in efforts to fabricate an efficient molecular catalyst to reduce H^+ . Collman et al. have found metalloporphyrin hydrides and dihydrogen complexes capable of functions ($\text{H}_2/\text{D}_2\text{O}$ exchange, dihydrogen activation, nicotinamide reduction) identical to hydrogenase enzymes [147]. In order to design a H^+ reduction catalyst, they also studied hydride transfer and dihydrogen elimination by $\text{K}[\text{Ru}^{\text{II}}(\text{OEP})(\text{THF})(\text{H})]$ (OEP = octaethylporphyrin) [148]. The anionic $\text{Ru}(\text{II})$ hydride did not cause the reductive elimination of H_2 but the hydride transfer to H^+ into H_2 took place, while H_2 evolution was oxidatively induced from the $\text{Ru}(\text{III})$ hydride through a bimolecular process via heterolytic H_2 complex formation (Fig. 1.14). The distinct reactivity between the hydride complexes was dependent on the metal-hydride bond strength with the oxidation states.

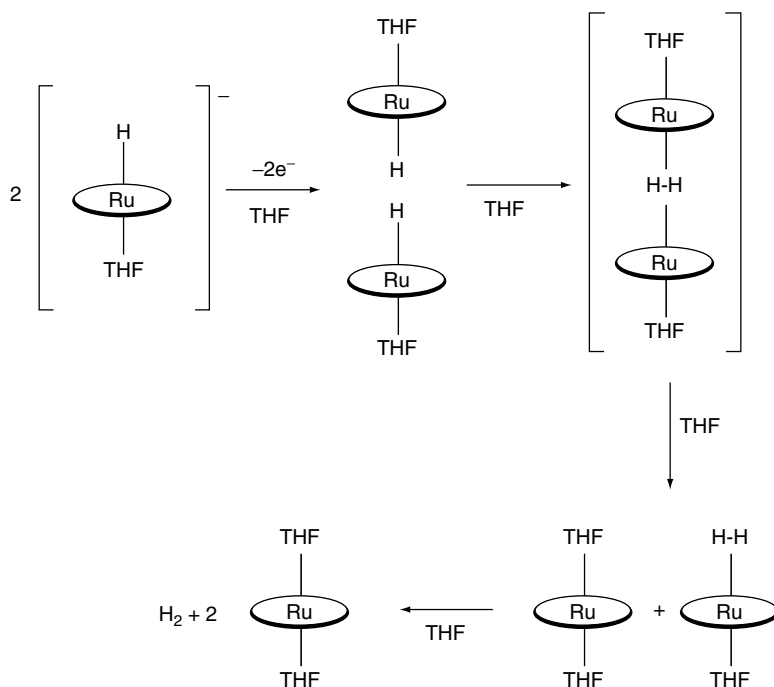


Fig. 1.14. Proposed mechanism for bimolecular dihydrogen elimination from ruthenium porphyrin hydrides ([148], copyright the American Chemical Society)

Savéant et al. have exhibited molecular catalysis by MTPP ($M = \text{Fe}$, or Rh ; TPP = tetraphenylporphyrin) in an aprotic solution containing proton sources [149, 150]. Although hydride complex was expected to enable the H^+ reduction catalysis in each case to form H_2 , the activity was not sufficiently high ($\sim 20 \text{ h}^{-1}$). We have also demonstrated an electrocatalytic H^+ reduction by the molecular aggregates of MTPP ($M = \text{Mn}$, Fe , or Co) incorporated into a Nafion membrane (denoted as $\text{Nf}[\text{MTPP}]$) [151, 152], where the intermediate for bimolecular catalysis by MTPP in the polymer matrix is inferred to be π -proton complex on the phenyl group ($\text{MTPP} \cdots \text{H}^+ \cdots \text{H}^+ \cdots \text{MTPP}$) rather than metal-hydride.

$[\text{Co}(\text{terpy})_2]^{2+}$ dispersed in a Nafion membrane also showed a bimolecular catalysis for H^+ reduction [153], similar to the case for CO_2 reduction (*vide supra*); however, it emerged that electrocatalysis varies with the pH conditions employed. Under acidic pH conditions ($\text{pH} < \sim 4$), the electrocatalytic H^+ reduction was induced by $[\text{Co}(\text{terpy})_2]^+$ ($\text{Co}(\text{I})$), while under weakly acidic $\sim$ neutral pH conditions ($\text{pH} > \sim 4$), the H^+ reduction took place after forming $[\text{Co}(\text{terpy})_2]^{+}$ ($\text{Co}(0)$). The pH-dependent electrocatalysis was attributable to the weak basicity of the electrogenerated $\text{Co}(\text{I})$, where $\text{Co}(\text{I})$ can coordinate H^+ under low pH conditions ($\text{pH} < \sim 4$), resulting in an intermediate ($\text{Co}(\text{I})\text{-H}$). However, since the reduction potential of $\text{Co}(\text{II})$ into $\text{Co}(\text{I})$ is pH-independent above $\text{pH} \sim 4$, the H^+ reduction took place via $\text{Co}(0)\text{-H}$.

It has also been shown that high molecular weight polynuclear iron complexes with the repeating unit $(\text{Fe}_4^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3)$ for Prussian Blue [154], and $\text{KFe}^{\text{III}}[\text{Ru}^{\text{II}}(\text{CN})_6]$ for Ruthenium Purple [155]) can efficiently catalyze the electrochemical H^+ reduction to produce H_2 as a molecular catalyst particularly in those reduced states.

1.3.3 Photodevices for Photoinduced Chemical Reaction in the Water Phase

Considerable efforts have been made to create an active and efficient photocatalysis system ever since Honda and Fujishima reported the photoelectrochemical water splitting by UV-responsive TiO_2 electrode [156]. Considering the theoretical conversion efficiency of solar energy, it is desirable to create a photoenergy conversion system responsive to visible light across the entire solar spectral region. The dye-sensitized photovoltaic cell (called the Grätzel cell), which consists of a Ru complex-adsorbed TiO_2 electrode and a Pt counter in an organic solution containing I_3^-/I^- couple, is the most typical instance leading to an efficient photoenergy conversion under visible-light irradiation [157]. Although such a sensitization to TiO_2 by dye has also been applied to water photolysis (Fig. 1.15), only a photoinduced H_2 formation takes place [158]; namely, there has been no example of the H_2 formation along with the multi-electron transfer oxidation of water into O_2 by the oxidized species of dye (*vide supra*). Visible-light-responsive inorganic semiconductors, such as CdS , might also be candidates for potential photocatalysts [159], but

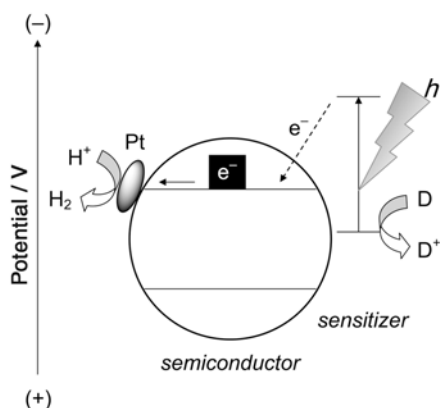
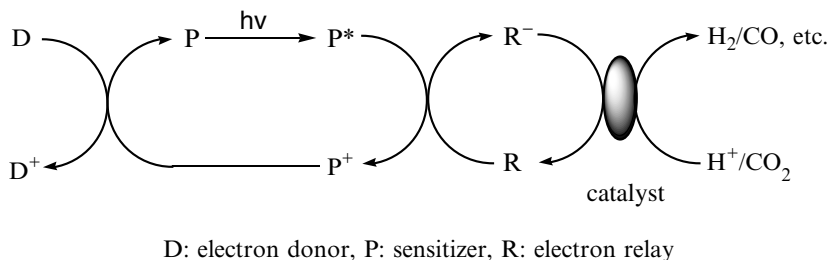


Fig. 1.15. Reaction scheme for photoinduced dihydrogen formation by means of sensitization to TiO_2 by dye molecule

they cannot be used due to their self-oxidation under irradiation. Currently, in order to enable the efficient uptake of visible-light energy into output, photocatalyst fabrications are extensively conducted by means of band engineering such as (i) donor-level formation by the doping of foreign elements [160], (ii) new stable valence band formation in a more negative position [161], and (iii) a controllable band formation by preparing a solid solution [162], etc. Recently, although a few potential photocatalysts have emerged which are capable of achieving the overall water splitting under visible-light irradiation [e.g., 163, 164], they would still be insufficient for those practical uses in terms of efficiency. Moreover, there remains almost no example of a photocatalyst that visible-light energy of $>600\text{ nm}$ in the wavelength is available for the photoinduced reaction of water [165]. Considering the historical aspects of photocatalysis study with inorganic compounds, it is now vital to design and develop a novel and efficient photocatalytic compound by opening up new aspects of molecular catalysis. In the present section, typical examples of molecule-based photodevices concerned with photo/chemical conversion will be shown.

Conventional Photochemical Reaction Systems

The photochemical reactions involving CO_2/H^+ reduction have been studied according to Scheme 1.1 [166–169]; however, no real model of photosynthesis has yet been established (i.e., H_2O cannot serve as the electron donor for the reductions of CO_2 and H^+). This is because the charge recombination between the oxidized species of a photosensitizer (P^+) and the reduced species of an electron relay (R^-) takes place quickly. In that scheme, the molecular catalysts (such as polypyridyl ruthenium complexes ($[\text{Ru}(\text{bpy})_2\text{COH}]^+$ [166], $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ [167], etc.), and metal-cyclams [168], etc.) resulted in the



Scheme 1.1. Scheme of the photochemical CO₂ and H⁺ reduction

reduction products (CO and/or HCOOH) through two-electron transfer, while higher hydrocarbons (CH₄, C₂H₄, and C₂H₆) were exceptionally formed only when using Ru or Os colloids as a catalyst [169]. As for H⁺ reduction, the above-mentioned metal catalysts (e.g., Pt) were typically applied to the photoinduced H₂ formation system.

According to Scheme 1.1, visible-light decomposition of aqueous ammonia (NH₃) into N₂ was successfully achieved, where O₂ can act as an electron acceptor [170, 171]. There has long been a serious problem of our society releasing excessive NH₃ especially from livestock waste, which far exceeds the amount that can be decomposed into safe N₂ by the natural N₂ cycle. This novel photocatalytic reaction is expected to represent a breakthrough in efforts to establish a future artificial solar N₂ cycle system.

Recently, a few examples of a supramolecule of a photosensitizer covalently linked to a catalyst molecule have been shown to result in reduction products (in the presence of a sacrificial donor) [172, 173]. Re polypyridine complexes have also been known to function as UV-responsive photocatalysts for CO₂ reduction [174, 175]. A supramolecule of the Ru–Re heteronuclear complex (Fig. 1.16) caused a CO formation at the Re moiety along with a visible-light absorption by the Ru moiety [172]. Photoinduced H₂ formation was also found to occur at the Pt moiety within the Ru–Pt supramolecular complex (Fig. 1.16) [173].

New Aspects of Molecule-Based Photodevices

Photoelectrochemistry is one of the most promising methods of investigating and establishing a photoenergy conversion system [176]. Molecule-based photoelectrodes have been fabricated by means of self-assembled monolayers (SAMs) [177, 178] and Langmuir–Blodgett (LB) films [179]. Although such systems can successfully achieve photoinduced charge separation through unidirectional electron transfer, the resulting photocurrent has often been identified as having a magnitude of only a few $\mu\text{A cm}^{-2}$. This low output is attributable to the monolayered structure, which is only capable of modest light absorption by photoexcitation center. It has also been impossible for SAM and LB films to be coupled with the electron donation from water (or OH[−]) although

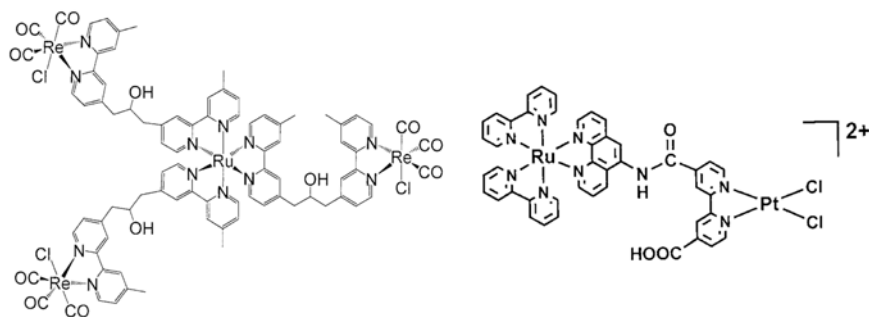


Fig. 1.16. Chemical structures of supramolecules capable of photoinduced reduction ([172] and [173], copyright the American Chemical Society)

the oxidation of two water molecules (or two OH^- ions) into O_2 is the most important process because of its fundamental and first step for yielding H_2 in a water photolysis system. In other words, those imply that multilayered photoexcitation molecules need to be loaded onto an electrode in order to fabricate an efficient photoresponsive device.

The p/n organic bilayers, which have consisted of p- and n-type organic conducting materials, have been applied to dry-type photodevices such as solar cells, field-effect transistors, and in electroluminescence applications [180]. Recently, we have also revealed a novel and advanced function of the p/n organic bilayer as a photoelectrode working in the water phase (Fig. 1.17). Namely, an organic solid | water interface in a p/n organic bilayer was found to be capable of photoinduced oxidation/reduction along with photoconduction of the carriers (i.e., holes/electrons) generated in the interior [181–187], where wide visible-light energy of the wavelength $< 750 \text{ nm}$ is available for the photoinduced reaction at the above-mentioned interface. The details were described elsewhere [188]. In particular, it is noted that an organic bilayer of 3, 4, 9, 10-perylenetetracarboxyl-bisbenzimidazole (PTCBI, n-type semiconductor) and cobalt phthalocyanine (CoPc, p-type semiconductor) enables O_2 evolution at the interface of CoPc/water through hole conduction by the CoPc layer, which consequently leads to stable and efficient photoelectrochemical water splitting [185]. However, studies on the application of organic bilayers to photodevices in water are currently at a nascent stage. A large variety of photoelectrode devices could be fabricated by varying the combinations of both electron and hole conductors, meaning it would also become increasingly important to investigate and accumulate fundamental knowledge concerning a solid | water interface that has potential characteristics. The utilization of such a p/n organic bilayer as the photoelectrode could also reveal a new aspect of photoelectrochemical research and technology, particularly in areas in which few examples of inorganic semiconducting materials have been reported.

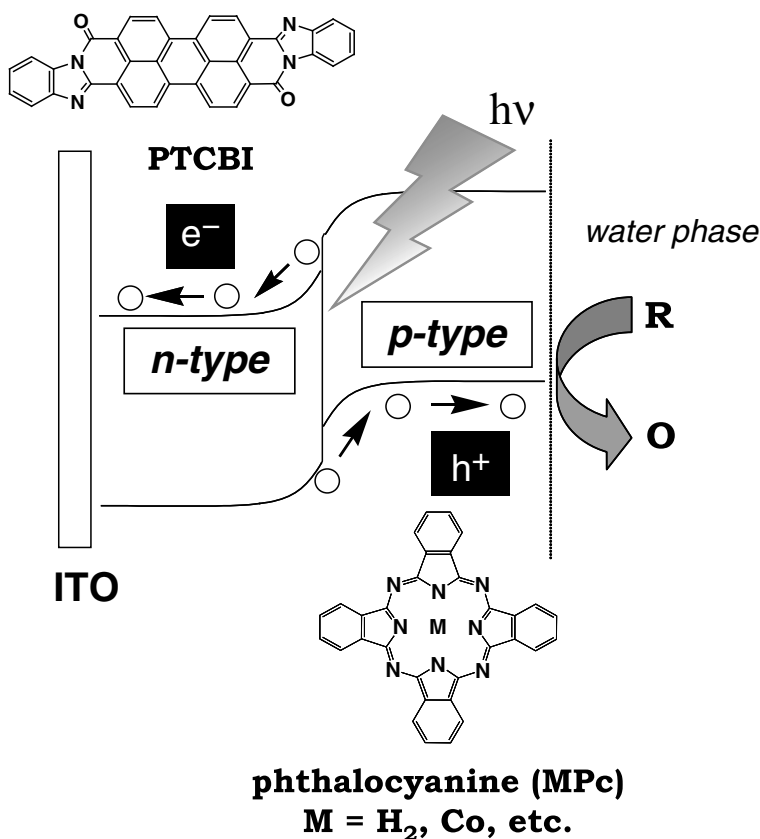


Fig. 1.17. Chemical structures of perylene derivative (PTCBI) and phthalocyanine (MPc), and a schematic illustration of the photoanodic reaction at the MPc/water interface

1.4 Summary

The tremendous consumption of fossil fuels emitting carbon dioxide (CO_2) is considered to be a serious factor responsible for the so-called greenhouse effect. The Nobel Peace Prize committee in 2007 showed a concern that this is not only a matter of global environment but also a matter of all nations coexisting in peace. It is important to recognize that global warming is closely related to energy resources, and further, that the main energy resource, oil, could be exhausted by the middle of this century. Therefore, there is an urgent need to create renewable energy resources free of environmental pollution.

Photosynthesis in nature consists of water oxidation, two photoexcitation steps, and the reduction of carbon dioxide (CO_2) into carbohydrates (see (1.15)), where the chemical energies are gained from CO_2 and H_2O under solar irradiation; while in the backward reaction, living things spontaneously release

energy through consuming chemical energy to sustain life (*i.e.*, combustion reaction). That is, (1.15) of the photosynthetic reaction and the combustion reaction shows a good example of renewable energy system. Similar to this, any new energy resources should be compatible with the energy cycle on the earth.

Molecular hydrogen (H_2) is now attracting a great deal of attention as clean energy, with which the following reactions represent one of the most promising and feasible future energy systems (1.19).



The forward and backward electron transfer reactions in (1.19) correspond to water splitting (Δ = thermal, electric, or solar energy) and fuel cell (denoted as FC) reactions (Δ = electric energy), respectively. Although (1.19) is a very simple reaction, the multi-electron transfer must take place efficiently to accomplish the reaction, where noble metals conventionally play essential roles as catalysts for the kinetically limiting redox reactions.

There are considerable expectations of the FC system as an ideal source of energy that does not exhaust the greenhouse gases, which is currently practically in use as social energy. However, unless employing a pathway without emitting greenhouse gases in H_2 production, the FC technology is of little value. Therefore, water photolysis is likely to be the most promising procedure for supplying the H_2 energy to the FC system, in which (1.19) can represent an ultimate renewable energy system. However, both the H_2 production and the FC system remain cost-ineffective.

To establish the ultimate renewable energy system, one of the key requirements is to create highly active, efficient, and stable catalysts as an alternative to noble metal catalysts. The energy recycle systems consisting of renewable energy like artificial photosynthesis (water oxidation and CO_2/H^+ reduction) and fuel cell (H_2 oxidation and O_2 reduction) reactions await many challenges, especially for designing new molecular catalysts toward the goal of renewable energy society.

References

1. W.R. Grove, *Phil. Mag.* **14**, 127 (1839)
2. R. Williams, *J. Chem. Phys.* **32**, 1505 (1960)
3. L.J. Kleinsmith, V.M. Kish, *Principles of Cell Biology* (Harper & Row, New York 1988)
4. J.O.M. Bockris, S. Srinivasan, *Fuel Cells: Their Electrochemistry* (McGraw-Hill, New York 1969)
5. K. Kordesch, G. Simader, *Fuel Cells and Their Applications* (VCH, Weinheim 1996)
6. H. Kita, T. Kurisu, *J. Res. Inst. Catal., Hokkaido Univ.* **21**, 200 (1973)
7. A.J. Appleby, F.R. Foulkes, *Fuel Cell Handbook* (Van Nostrand Reinhold, New York 1989)

8. U.R. Evans, *Nature* **218**, 602 (1968)
9. R. Jasinski, *Nature* **201**, 1212 (1964)
10. J.H. Zagal, *Coordination Chem. Rev.* **119**, 89 (1992)
11. T. Abe, M. Kaneko, *Prog. Polym. Sci.* **28**, 1441 (2003)
12. L. Stryer, *Biochemistry* (W. H. Freeman, San Francisco, CA 1975)
13. J.S. Bett, H.R. Kunz, A.J. Aldykiewicz Jr., J.M. Fenton, W.F. Bailey, D.V. McGrath, *Electrochem. Acta* **43**, 3645 (1998)
14. R. Venkataraman, H.R. Kunz, J.M. Fenton, *J. Electrochem. Soc.* **151**, A703 (2004)
15. X. Zhou, W. Xing, C. Liu, T. Lu, *Electrochem. Commn.* **9**, 1469 (2007)
16. H.S. Wroblowa, Y.C. Pan, G. Razumsney, *J. Electroanal. Chem.* **69**, 195 (1976)
17. K. Kinoshita, *Electrochemical Oxygen Technology*, Chap. 2 (Wiley, New York, 1992)
18. A.B. Anderson, T.V. Albu, *J. Am. Chem. Soc.* **121**, 11855 (1999)
19. A.B. Anderson, T.V. Albu, *J. Electrochem. Soc.* **147**, 4229 (2000)
20. C.F. Zinola, A.J. Arviá, G.L. Estiú, E.A. Castro, *J. Phys. Chem.* **98**, 7566 (1994)
21. E. Leiva, C. Sánchez, in *Handbook of Fuel Cells – Fundamentals, Technology and Applications*, Vol. 2, Chap. 11, ed. by W. Vielstich, H.A. Gasteiger, A. Lamm (Wiley, Chichester, 2003)
22. J.K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J.R. Kitchin, T. Bligaad, H. Jónsson, *J. Phys. Chem. B* **108**, 17886 (2004)
23. M.L. Rao, A. Danjanovic, J.O.M. Bockris, *J. Phys. Chem.* **67**, 2508 (1963)
24. L. Pauling, *Proc. Roy. Soc. Lond.* **A196**, 343 (1949)
25. A.J. Appleby, *Catal. Rev.* **4**, 221 (1970)
26. K.J. Vetter, *Electrochemical Kinetics* (Academic, New York, 1967)
27. M. Eisenberg, in *Physical Chemistry An Advanced Treatise*, Vol. IXB, Chap. 9, ed. by H. Eyring, D. Henderson, W. Jost (Academic, New York, 1970)
28. U.R. Evans, *Electrochim. Acta* **14**, 197 (1969)
29. A.J. Appleby, in *Modern Aspects of Electrochemistry*, Vol. 9, Chap. 5, ed. by B.E. Conway, J.O.M. Bockris (Plenum, New York, 1974)
30. E. Gileadi, *Electrode Kinetics*, Chap. 19 (Wiley-VCH, New York, 1993)
31. T. Toda, H. Igarashi, H. Uchida, M. Watanabe, *J. Electrochem. Soc.* **146**, 3750. (1999)
32. V. Jalan, E.J. Taylor, *J. Electrochem. Soc.* **130**, 2299 (1983)
33. R. Jasinski, *J. Electrochem. Soc.* **112**: 526 (1965)
34. J.P. Randin, *Electrochim. Acta* **19**, 83 (1974)
35. R. Hoffmann, M.M.L. Chen, D.L. Thorn, **16**: 503 (1977)
36. J.H. Zagal, M. Gulppi, M. Isaacs, G. Cárdenas-Jirón, M.J. Aguirre, *Electrochim. Acta* **44**, 1349 (1998)
37. R. Taube, *Pure Appl. Chem.* **38**, 427 (1974)
38. J.A.R. van Veen, J.F. van Baar, C.J. Kroese, J.G.F. Coolegem, N. de Wit, H.A. Colijn, *Ber. Bunsenges. Phys. Chem.* **85**, 693 (1981)
39. E. Yeager, *J. Mol. Cat.* **38**, 5 (1986)
40. J.P. Collman, P. Denisevich, Y. Konai, M. Marrocco, C. Koval, F.C. Anson, *J. Am. Chem. Soc.* **102**, 6027 (1980)
41. E. Yeager, *Electrochim. Acta* **29**, 1527 (1984)
42. H.Y. Liu, M.J. Weaver, C.B. Wang, C.K. Chang, *J. Electroanal. Chem.* **145**, 439 (1983)
43. U.B. Demirci, *J. Power Sources* **169**, 239 (2007)

44. J. Horiuti, in *Physical Chemistry An Advanced Treatise*, Vol. IXB, Chap. 6, ed. by H. Eyring, D. Henderson, W. Jost (Academic, New York, 1970)
45. O.A. Petrii, G.A. Tsirlina, *Electrochim. Acta* **39**, 1739 (1994)
46. N.M. Marković, in *Handbook of Fuel Cells – Fundamentals, Technology and Applications*, Vol. 2, Chap. 26, ed. by W. Vielstich, H.A. Gasteiger, A. Lamm (Wiley, Chichester, 2003)
47. B.E. Conway, J.O.M. Bockris, *J. Chem. Phys.* **26**, 532 (1957)
48. H. Böhm, *J. Power Sources* **1**, 177 (1976)
49. A. Volbeda, M.H. Charon, C. Piras, E.C. Hatchikian, M. Frey, J.C. Fontecilia-Camps, *Nature* **373**, 580 (1995)
50. S. Ogo, R. Kabe, K. Uehara, B. Kure, T. Nishimura, S.C. Menton, R. Harada, S. Fukuzumi, Y. Higuchi, T. Ohhara, T. Tamada, R. Kuroki, *Science* **316**, 585 (2007)
51. B. Hinnemann, P.G. Moses, J. Bonde, K.P. Jørgensen, J.H. Nielsen, S. Horch, I. Chorkendorff, J.K. Nørskov, *J. Am. Chem. Soc.* **127**, 5308 (2005)
52. C. Lamy, J.M. Léger, S. Srinivasan, in *Modern Aspects of Electrochemistry*, Vol. 34, Chap. 3, ed. by J.O.M. Bockris, B.E. Conway, R.E. White (Kluwer/Plenum, New York, 2001)
53. S. Wasmus, A. Küver, *J. Electroanal. Chem.* **461**, 14 (1999)
54. A. Hamnett, *Catal. Today* **38**, 445 (1997)
55. T. Iwasita, in *Handbook of Fuel Cells – Fundamentals, Technology and Applications*, Vol. 2, Chap. 41, ed. by W. Vielstich, H.A. Gasteiger, A. Lamm (Wiley, Chichester, 2003)
56. M.M. Janssen, J. Moolhuysen, *Electrochim. Acta* **21**, 861, 869 (1976)
57. T. Iwasita, *Electrochim. Acta* **47**, 3663 (2002)
58. L.W. Niedrach, H.I. Zelig, *J. Electrochem. Soc.* **116**, 152 (1969)
59. P.J. Kulesza, L.R. Faulkner, *J. Electroanal. Chem.* **259**, 81 (1989)
60. P.K. Shen, A.C.C. Tseung, *J. Electrochem. Soc.* **141**, 3028 (1994)
61. Y. Wang, E.R. Fachini, G. Cruz, Y. Zhu, Y. Ishikawa, J.A. Colucci, C.R. Cabrera, *J. Electrochem. Soc.* **148**, C222 (2001)
62. R.Z. Khaliullin, A.T. Bell, *J. Phys. Chem. B* **106**, 7832 (2002)
63. G.T. Burnstein, C.J. Barnett, A.R.J. Kucernak, K.R. Williams, *Electrochem. Soc. Lett.* **143**, L139 (1996)
64. V. Raghuvier, K.R. Thampi, N. Xanthopoulos, H.J. Mathieu, B. Viswanathan, *Solid State Ionics* **140**, 263 (2001)
65. Goetz M, Wendt H, Workshop Electrocatalysis in Indirect and Direct Methanol PEM Fuel Cells (Portoroz, Slovenia, 1999), pp. 87–90
66. T. Okada, Y. Suzuki, T. Hirose, T. Ozawa, *Chem. Comm.* **2001**, 2492 (2001)
67. T. Okada, Y. Suzuki, T. Hirose, T. Ozawa, *Electrochim. Acta* **49**, 385 (2004)
68. T. Okada, N. Arimura, C. Ono, M. Yuasa, *Electrochim. Acta* **51**, 1130 (2005)
69. J.F. van Baar, J.A.R. van Veen, J.M. van der Eijk, T.h.J. Peters, N. de Wit, *Electrochim. Acta* **27**, 1315 (1982)
70. E. Herrero, W. Chrzanowski, A. Wieckowski, *J. Phys. Chem.* **99**, 10423 (1995)
71. Y.X. Chen, A. Miki, S. Ye, H. Sakai, M. Osawa, *J. Am. Chem. Soc.* **125**, 3680 (2003)
72. M. Watanabe, S. Motoo, *J. Electroanal. Chem.* **60**, 267 (1975)
73. T. Yajima, H. Uchida, M. Watanabe, *J. Phys. Chem.* **108**, 2654 (2004)
74. T. Frelink, W. Visscher, J.A.R. van Veen, *Surf. Sci.* **335**, 353 (1995)
75. Y. Zhu, Z. Khan, R.I. Masel, *J. Power Sources* **139**, 15 (2005)

76. P. Waszczuk, A. Crown, S. Mitrovski, A. Wieckowski, in *Handbook of Fuel Cells – Fundamentals, Technology and Applications*, Vol. 2, Chap. 43, ed. by W. Vielstich, H.A. Gasteiger, A. Lamm (Wiley, Chichester, 2003)
77. C. Rice, S. Ha, R.I. Masel, A. Wieckowski, *J. Power Sources* **115**, 229 (2003)
78. S. Uhm, S.T. Chung, J. Lee, *Electrochem. Comm.* **9**, 2027 (2007)
79. S. Kang, J. Lee, J.K. Lee, S.Y. Chung, Y. Tak, *J. Phys. Chem.* **110**, 7270 (2006)
80. E. Casado-Rivera, D.J. Volpe, L. Alden, C. Lind, C. Downie, T. Vázquez-Alvarez, A.C.D. Angelo, F.J. DiSalvo, H.D. Abruña, *J. Am. Chem. Soc.* **126**, 4043 (2004)
81. R. Parsons, T. VanderNoot, *J. Electroanal. Chem.* **257**: 9 (1988)
82. X.H. Xia, T. Iwasita, *J. Electrochem. Soc.* **140**, 2559 (1993)
83. J.D. Lović, A.V. Tripković, S.L.J. Gojković, K.D.J. Popović, D.V. Tripković, P. Olszewski, A. Kowal, *J. Electroanal. Chem.* **581**, 294 (2005)
84. G. Samjeské, A. Miki, S. Ye, M. Osawa, *J. Phys. Chem.* **110**, 16559 (2006)
85. A. Ruban, B. Hammer, P. Stoltze, H.L. Skriver, J.K. Nørskov, *J. Mol. Catal. A* **115**, 421 (1997)
86. U.B. Demirci, *J. Power Sources* **173**, 11 (2007)
87. D.O. Hall, K.K. Rao, *Photosynthesis*, 6th edn (Cambridge University Press, Cambridge, 1999)
88. W. Ruetinger, G.C. Dismukes, *Chem. Rev.* **97**, 1 (1997)
89. R. Manchanda, G.W. Brudvig, *Coord. Chem. Rev.* **144**, 1 (1995)
90. V.L. Pecoraro, M.J. Baldwin, A. Gelasco, *Chem. Rev.* **94**, 807 (1994)
91. D. Wöhrle, M. Kaneko, Macromolecular metal complexes in biological systems, in *Metal Complexes and Metals in Macromolecule*, Chap. 2, ed. by D. Wöhrle, A.D. Pomogailo (Wiley-VCH, New York, 2003), pp. 25–63
92. M. Kaneko, D. Wöhrle, Photocatalytic properties, in *Metal Complexes and Metals in Macromolecule*, Chap. 13, ed. by D. Wöhrle, A.D. Pomogailo (Wiley-VCH, New York, 2003), pp. 573–600
93. M. Yagi, M. Kaneko, *Chem. Rev.* **101**, 21 (2001)
94. I. Taniguchi, Electrochemical and photochemical reduction of Carbon dioxide, in *Modern Aspects of Electrochemistry*, ed. by J.O.M. Bockris, B.E. Conway, R.E. White (Springer, Berlin, 1989), pp. 327–400
95. E. Tiemann, J. Demaison, *Landolt-Börnstein Tables, New Series, II/6* (Springer, Berlin, 1983)
96. M.H. Halmann, *Chemical Fixation of Carbon Dioxide* (CRC Press, Boca Raton, FL, 1993)
97. J.M. Lehn, J.P. Sauvage, *Nouv. J. Chem.* **1**, 449 (1977)
98. J. Kiwi, M. Grätzel, *J. Am. Chem. Soc.* **101**, 7214 (1979)
99. N. Toshima, M. Kuriyama, Y. Yamada, H. Hirai, *Chem. Lett.* 793 (1981)
100. S. Shimizu, *J. Adv. Sci.* **16**, i.1 (2005)
101. S. Meshitsuka, M. Ichikawa, K. Tamaru, *J. Chem. Soc. Chem. Commun.* 158 (1974)
102. N. Furuya, K. Matsui, *J. Electroanal. Chem.* **271**, 181 (1989)
103. M. Isaacs, F. Armijo, G. Ramírez, E. Trollund, S.R. Biaggio, J. Costamagna, M.J. Aguirre, *J. Mol. Catal. A:Chem.* **229**, 249 (2005)
104. T.V. Magdesieva, K.P. Buttin, T. Yamamoto, D.A. Tryk, A. Fujishima, *J. Electrochem. Soc.* **150**, E608 (2003)
105. C.M. Lieber, N.S. Lewis, *J. Am. Chem. Soc.* **106**, 5033 (1984)

106. T. Yoshida, K. Kamato, M. Tsukamoto, T. Iida, D. Schlettwein, D. Wöhrle, K. Kaneko, *J. Electroanal. Chem.* **385**, 209 (1995)
107. T. Abe, T. Yoshida, S. Tokita, F. Taguchi, H. Imaya, M. Kaneko, *J. Electroanal. Chem.* **412**, 125 (1996)
108. T. Abe, F. Taguchi, T. Yoshida, S. Tokita, G. Schnurpfeil, D. Wöhrle, M. Kaneko, *J. Mol. Catal. A: Chem.* **112**, 55 (1996)
109. T. Abe, H. Imaya, T. Yoshida, S. Tokita, D. Schlettwein, D. Wöhrle, M. Kaneko, *J. Porphyrins Phthalocyanines* **1**, 315 (1997)
110. H. Ishida, K. Tanaka, T. Tanaka, *J. Chem. Soc. Chem. Commun.* 131 (1987)
111. H. Nagao, T. Mizukawa, K. Tanaka, *Inorg. Chem.* **33**, 3415 (1994)
112. H. Nakajima, K. Tanaka, *Chem. Lett.* 891 (1995)
113. T. Mizukawa, K. Tsuge, H. Nakajima, K. Tanaka, *Angew. Chem. Int. Ed.* **38**, 362 (1999)
114. Y. Kurimura, M. Kaneko, Metal-Polymer Complex, in *Polymeric Materials Encyclopedia*, ed. by J.C. Salamone (CRC Press, Boca Raton, FL, 1996), pp 4149–4155
115. M.N. Collomb-Dunand-Sauthier, A. Deronzier, R. Ziessel, *Inorg. Chem.* **33**, 2961 (1994)
116. S. Chardon-Noblat, A. Pellissier, G. Cripps, A. Deronzier, *J. Electroanal. Chem.* **597**, 28 (2006)
117. J. Hawecker, J.M. Lehn, R. Ziessel, *J. Chem. Soc. Chem. Commun.* 328 (1984)
118. T. Yoshida, T. Iida, T. Shirasagi, R.J. Lin, M. Kaneko, *J. Electroanal. Chem.* **344**, 355 (1993)
119. K.M. Lam, K.Y. Wong, S.M. Yang, C.M. Che, *J. Chem. Soc. Dalton Trans.* 1103 (1995)
120. J.A. Ramos Sende, C.R. Arana, L. Hernández, K.T. Potts, K.M. Keshevarz, H.D. Abruña, *Inorg. Chem.* **34**, 3339 (1995)
121. G. Chiericato Jr., C.R. Arana, C. Casado, I. Cuadrado, H.D. Abruña, *Inorg. Chim. Acta* **300–302**, 32 (2000)
122. F. Mebsout, J.M. Kauffmann, G.J. Patriarche, *J. Pharm. Biomed. Anal.* **6**, 441 (1988)
123. M. Fleischmann, G. Sundholm, *J. Electroanal. Chem.* **30**, App. 4 (1971)
124. T. Abe, K. Takahashi, Y. Shiraishi, N. Toshima, M. Kaneko, *Macromol. Chem. Phys.* **201**, 102 (2000)
125. T. Abe, K. Hirano, Y. Shiraishi, N. Toshima, M. Kaneko, *Eur. Polym. J.* **37**, 753 (2001)
126. P. Keller, A. Moradpour, *J. Am. Chem. Soc.* **102**, 7193 (1980)
127. E. Amouyal, D. Grand, A. Moradpour, P. Keller, *Nouv. J. Chem.* **6**, 241 (1982)
128. R. Rafaeloff, Y. Haruvy, G. Binenboym, G. Baruch, L.A. Rajbenbach, *J. Mol. Catal.* **22**, 219 (1983)
129. N. Toshima, T. Takahashi, H. Hirai, *Chem. Lett.* 1031 (1987)
130. A. Harriman, *J. Chem. Soc. Chem. Commun.* 24 (1990)
131. N. Toshima, M. Harada, T. Yonezawa, K. Kushihashi, K. Asakura, *J. Phys. Chem.* **95**, 7448 (1991)
132. T. Yonezawa, N. Toshima, *J. Mol. Catal.* **83**, 167 (1993)
133. N. Toshima, K. Hirakawa, *Polym. J.* **31**, 1127 (1999)
134. N. Toshima, *Pure Appl. Chem.* **72**, 317 (2000)
135. A.W. Addison, W.R. Cullen, D. Dolphin, B.R. James, *Biological Aspects of Inorganic Chemistry* (Wiley, New York, 1977)

136. H.G. Schlegel, K. Schneider, *Hydrogenase: Their Catalytic Activity, Structure and Function* (Erich Goltze KG, Göttingen, 1978)
137. S. Aono, I. Okura, A. Yamada, J. Phys. Chem. **89**, 1593 (1985)
138. M. Razavet, V. Artero, M. Fontecave, Inorg. Chem. **44**, 4786 (2005)
139. J.W. Peters, W.N. Lanzilotta, B.J. Lemon, L.C. Seefeldt, Science **282**, 1853 (1998)
140. A.K. Jones, E. Silvery, S.P.J. Albracht, F.A. Armstrong, Chem. Commun. 866 (2002)
141. C. Greco, G. Zampella, L. Bertini, M. Bruschi, P. Fantucci, L. De Gioia, Inorg. Chem. **46**, 108 (2007)
142. L. Duan, M. Wang, P. Li, Y. Na, N. Wang, L. Sun, Dalton Trans. 1277 (2007)
143. D. Chong, I.P. Georgakaki, R. Mejia-Rodriguez, J. Sanabria-Chinchilla, M.P. Soriaga, M.Y. Darensbourg, Dalton Trans. 4158 (2003)
144. R.H. Crabtree, Inorg. Chim. Acta **125**, L7 (1986)
145. A.I. Krasna, D. Rittenberg, J. Am. Chem. Soc. **76**, 3015 (1954)
146. G.J. Kubas, Acc. Chem. Res. **21**, 120 (1988)
147. J.P. Collman, P.S. Wangenknütt, R.T. Hembre, N.S. Lewis, J. Am. Chem. Soc. **112**, 1294 (1990)
148. J.P. Collman, P.S. Wangenknütt, N.S. Lewis, J. Am. Chem. Soc. **114**, 5665 (1992)
149. I. Bhugun, D. Lexa, J.M. Savéant, J. Am. Chem. Soc. **118**, 3982 (1996)
150. V. Grass, D. Lexa, J.M. Savéant, J. Am. Chem. Soc. **119**, 7526 (1997)
151. T. Abe, F. Taguchi, H. Imaya, F. Zhao, J. Zhang, M. Kaneko, Polym. Adv. Technol. **9**, 559 (1998)
152. F. Taguchi, T. Abe, M. Kaneko, J. Mol. Catal. A: Chem. **140**, 41 (1999)
153. T. Abe, M. Kaneko, J. Mol. Catal. A: Chem. **169**, 177 (2001)
154. T. Abe, F. Taguchi, S. Tokita, M. Kaneko, J. Mol. Catal. A: Chem. **126**, L89 (1997)
155. T. Abe, G. Toda, A. Tajiri, M. Kaneko, J. Electroanal. Chem. **510**, 35 (2001)
156. A. Fujishima, K. Honda, Nature **238**, 37 (1972)
157. B. O'Regan, M. Grätzel, Nature **353**, 737 (1991)
158. E. Bae, W. Choi, J. Phys. Chem. B **110**, 14792 (2006)
159. M. Grätzel, *Energy Resources Through Photochemistry and Catalysis* (Academic, London, 1983)
160. S.M. Ji, P.H. Borse, H.G. Kim, D.W. Hwang, J.S. Jang, S.W. Bae, J.S. Lee, Phys. Chem. Chem. Phys. **7**, 1315 (2005)
161. Y. Shimodaira, H. Kato, H. Kobayashi, A. Kudo, Bull. Chem. Soc. Jpn. **80**, 885 (2007)
162. W. Yao, J. Ye, J. Phys. Chem. B **110**, 11188 (2006)
163. Z. Zou, J. Ye, K. Sayama, H. Arakawa, Nature **414**, 625 (2001)
164. K. Maeda, K. Teramura, H. Masuda, T. Takata, N. Saito, Y. Inoue, K. Domen, J. Phys. Chem. B **110**, 13107 (2006)
165. I. Tsuji, H. Kato, A. Kudo, Chem. Mater. **18**, 1969 (2006)
166. J. Hawecker, J.M. Lehn, R. Ziessel, J. Chem. Soc. Chem. Commun. **56**, (1985)
167. H. Ishida, T. Terada, K. Tanaka, T. Tanaka, Inorg. Chem. **29**, 905 (1990)
168. C.A. Craig, L.O. Spreer, J.W. Otvos, M. Calvin, J. Phys. Chem. **94**, 7957 (1990)
169. I. Willner, R. Maidan, D. Mandler, H. Dürr, G. Dörr, K. Zengerle, J. Am. Chem. Soc. **109**, 6080 (1987)

170. M. Kaneko, N. Katakura, C. Harada, Y. Takei, M. Hoshino, *Chem. Commun.* 3436 (2005)
171. J. Nemoto, C. Harada, Y. Takei, N. Katakura, M. Kaneko, *Photochem. Photobiol. Sci.* **6**, 77 (2007)
172. B. Gholamkhass, H. Mametsuka, K. Koike, T. Tanabe, M. Furue, O. Ishitani, *Inorg. Chem.* **44**, 2326 (2005)
173. H. Ozawa, M. Haga, K. Sakai, *J. Am. Chem. Soc.* **128**, 4926 (2006)
174. G. Ruiz, E. Wolcan, A.L. Capparelli, M.R. Féliz, *J. Photochem. Photobiol. A: Chem.* **89**, 61 (1995)
175. H. Hori, F.P.A. Johnson, K. Koike, K. Takeuchi, T. Ibusuki, O. Ishitani, *J. Chem. Soc. Dalton Trans.* 1019 (1997)
176. M. Kaneko, I. Okura, *Photocatalysis* (Kohdansha–Springer, Tokyo, 2002)
177. H. Imahori, K. Mitamura, Y. Shibano, T. Umeyama, Y. Matano, K. Yoshida, S. Isoda, Y. Araki, O. Ito, *J. Phys. Chem. B* **110**, 11399 (2006)
178. H. Ma, M.S. Kang, Q.M. Xu, K.S. Kim, and A.K.Y. Jen, *Chem. Mater.* **17**, 2896 (2005)
179. S. Yang, L. Fan, S. Yang, *J. Phys. Chem. B* **108**, 4394 (2004)
180. W. Brütting, *Physics of Organic Semiconductor* (Wiley-VCH, Weinheim, 2005)
181. T. Abe, K. Nagai, M. Kaneko, T. Okubo, K. Sekimoto, A. Tajiri, T. Norimatsu, *ChemPhysChem* **5**, 716 (2004)
182. T. Abe, K. Nagai, Sekimoto, A. Tajiri, T. Norimatsu, *J. Electroanal. Chem.* **583**, 327 (2005)
183. T. Abe, K. Nagai, Sekimoto, A. Tajiri, T. Norimatsu, *Electrochem. Commun.* **7**, 1129 (2005)
184. T. Abe, K. Nagai, T. Ogiwara, S. Ogasawara, M. Kaneko, A. Tajiri, T. Norimatsu, *J. Electroanal. Chem.* **587**, 127 (2006)
185. T. Abe, K. Nagai, S. Kabutomori, M. Kaneko, A. Tajiri, T. Norimatsu, *Angew. Chem. Int. Ed.* **45**, 2778 (2006)
186. T. Abe, K. Nagai, T. Matsukawa, A. Tajiri, T. Norimatsu, *J. Solid State Electrochem.* **11**, 303 (2007)
187. T. Abe, K. Nagai, H. Ichinohe, T. Shibata, A. Tajiri, T. Norimatsu, *J. Electroanal. Chem.* **599**, 65 (2007)
188. T. Abe, K. Nagai, *Org. Electron.* **8**, 262 (2007)

Charge Transport in Molecular Catalysis in a Heterogeneous Phase

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Abstract This chapter focuses on the fundamental aspects in controlling charge transport (CT) processes through molecules in energy conversion systems. The central reactions involved in the energy conversion are the charge separation and charge transfer processes along the reaction coordinates from reactant molecules, assisted by the catalyst active sites. In some cases the polymer medium plays an important role in the charge transport processes that are the models of molecular aggregates in biomimetic systems. The mechanism of charge transport in heterogeneous phase is discussed in detail since this makes often the rate-limiting process in the whole system, and its design is especially important to establish a high energy conversion efficiency. Charge transfer reactions at the electrode surface is outlined where the metal complex is involved as a catalyst of the redox reaction. The metal complex furnished with the functional groups and the metal active center is tailored through the optimum design of the charge transfer complexes. Finally the proton transport in a heterogeneous phase that mediates the redox and chemical reactions is introduced and its mechanism is briefly discussed.

2.1 Introduction

Molecule-based nano-devices are attracting a great deal of attention. They are important for catalysis especially in relevance to energy conversion, solar cells, fuel cells, and artificial photosynthetic devices that are expected to provide a renewable energy resource [1–4]. Chemical-energy-conversion devices such as fuel cells and artificial photosynthetic devices require molecular catalysts especially for multielectron redox reactions such as water oxidation, dioxygen reduction, proton reduction, hydrogen oxidation, carbon dioxide reduction, etc. [5, 6]. The development of molecular catalysts that show high activity and stability is a key research in order to create nano-devices in this field. Polymeric solid materials find promising applications as matrixes for functional molecules in these nano-devices. The development of polymeric matrixes to establish rapid charge and molecular transport is desired in relevance to molecular catalysis. In both the above materials rapid charge and

molecular transport in heterogeneous materials is required for the devices to work efficiently.

The present chapter reviews fundamental aspects in charge transport (CT) in a heterogeneous phase such as solid polymeric materials. After the introduction section (Sect. 2.1), mechanistic features of CT in polymer films and related polymeric materials confining functional redox molecules are described in Sect. 2.2, focusing especially on recent progresses in the present authors' groups. In Sect. 2.3, our attention is particularly focused on molecular CT under photoexcited state of light-absorbing molecules. CT in a fuel cell system is described in Sects. 2.4 and 2.5, where the electron transfer in the molecule is first discussed because this determines the rate of redox reactions. Typical reaction formula and elementary theory of electron transfer at the electrode–electrolyte interface under the electric field are also briefly reviewed. The dioxygen-reduction reaction is mentioned mechanistically because this is acknowledged as the major rate-limiting process in fuel cell reactions. Especially those on metal macrocycles is a matter of importance due to recent demands of noble metal-free catalysts for fuel cell developments. Finally H^+ transport in a polymer electrolyte is discussed in Sect. 2.5, which is an important physicochemical process connecting H_2 oxidation at the fuel electrode (the anode) and O_2 reduction at the air electrode (the cathode).

2.2 Charge Transport (CT) by Molecules in a Heterogeneous Phase

2.2.1 General Overview

One of the important functions of a molecule is charge transport (CT) that is achieved mainly by redox reactions in its ground as well as photoexcited states. On incorporating molecules in a heterogeneous phase, the matrix is provided with a function of transporting charges under dark or under light irradiation, which can lead to electronic and photonic devices. In the present section, charge transport in a heterogeneous phase with incorporated redox molecules in their ground state are described, and that under photoexcited state is treated in Sect. 2.3. Both the ground and excited states electron transfer is important to obtain a complete understanding of electron transport event. So far, CT processes in ground and photoexcited states have been studied separately by the scientists in each field of electrochemistry and photochemistry, respectively. They have never been discussed together. An overview and fundamental problems on each topics will at first be given, and then the following part concentrates on the review of the results by the present authors. CT takes place by different mechanisms, i.e., physical diffusion of redox molecules, charge hopping between redox molecules, and the combined process of diffusion and charge hopping. For charge hopping the distance between the molecules which the charge can hop is especially important.

2.2.2 Mechanism of Charge Transport

In order to investigate charge transfer in a ground state, electrochemical technique is usually used. In this case a modified electrode coated with a heterogeneous material membrane such as a synthetic polymer containing redox molecules is utilized (Fig. 2.1). Charges are transported via redox reactions of the molecules in the matrix. This process is regarded as a kind of charge propagation. The electrochemical method provides information on integrated charge transport in the heterogeneous phase in addition to elucidating one single step of the charge transfer between molecules [4, 6, 7].

Charge propagation is understood as a diffusion of charges in a matrix, so that it is represented by an apparent diffusion coefficient ($D_{\text{app}} \text{ cm}^2 \text{ s}^{-1}$). Such charge diffusion was expressed by a Dahms–Ruff equation which combines terms of physical diffusion (a kind of physical replacement) of the redox center molecules (D_{phys}) and charge hopping between them (D_e) (Fig. 2.2) [(2.1) and (2.2)] [8, 9], where k_{ex} is the rate constant of charge exchange between two molecules, δ is the charge hopping distance, and c is the concentration of redox molecule in the polymer matrix.

$$D_{\text{app}} = D_{\text{phys}} + D_e \quad (2.1)$$

$$D_e = k_{\text{ex}} \delta^2 c \quad (2.2)$$

It is concluded that, if the D_{app} value is independent of the concentration, the charge transfer is contributed only by physical diffusion of the redox center, and if it is dependent on the concentration, the process is composed of both diffusion and charge hopping. Many papers reported dependence of D_{app} upon c which leads to determination of the charge transport mechanism.

Andrieux and Saveant proposed, as shown in (2.3), for a system where only charge hopping takes place [10].

$$D_{\text{app}} = (1/6)k_{\text{ex}}\delta^2 c \quad (2.3)$$

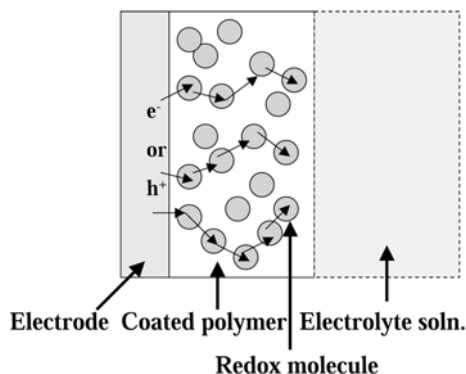


Fig. 2.1. Charge transport by redox molecules confined in an electrode-coated polymer membrane

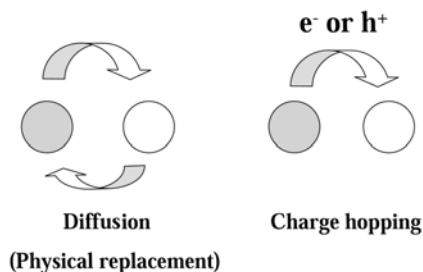


Fig. 2.2. Charge transport mechanism by redox molecules diffusion (physical replacement) or charge hopping

It is now important that charge hopping takes place by a percolation mechanism if bounded motion of the confined charge-transporting molecules does not take place at all, where bounded motion is a kind of local oscillation of the confined redox molecules at the confined position. The charge transport by conducting carbon particles in an insulating matrix is the typical example for the percolation process although this example is not a molecular process. Such percolation process can be analyzed by a Monte Carlo simulation.

Monte Carlo simulation was carried out by Blaich and Saveant based on a percolation process, and D_{app} was obtained as (2.4) considering charge hopping and bounded motion of the redox center [11]. In this model charge transport by molecular diffusion is not taken into account.

$$D_{\text{app}} = (1/6)k_{\text{ex}}(\delta^2 + 3\lambda^2)c \quad (2.4)$$

In addition to these mechanistic studies many papers have been published by other groups.

Alternatively and more simply than the above treatments, CT mechanism by redox centers can be investigated by measuring the dependence of the initial charge transport rate (V_{ct}) or D_{app} on the concentration of redox centers (c , represented by $\text{M} = \text{mol dm}^{-3}$) in a matrix when there exists sufficient bounded motion of the redox molecules so that percolation process can be neglected. If charge propagation takes place by a diffusion mechanism (physical replacement), V_{ct} should be proportional to c . If it takes place by a charge hopping mechanism with sufficient bounded motion, V_{ct} should be proportional to c^2 . However, it should be noted here that charge hopping is to be treated by a percolation theory as also mentioned later if bounded motion does not exist. These processes are represented by the following equations [12].

Diffusion of Redox Molecules (Physical Replacement):

$$V_{\text{ct}} = k_1 c \quad (2.5)$$

Charge Hopping between Redox Molecules with Sufficient Bounded Motion:

$$V_{ct} = k_2 c^2 \quad (2.6)$$

Combination of Diffusion and Hopping:

$$V_{ct} = k_1 c + k_2 c^2 \quad (2.7)$$

The mechanism can be determined by these relations or by plotting the value V_{ct}/c (or D_{app}) against c (2.8, 2.9, and 2.10) as shown in Fig. 2.3. Instead of the V_{ct} values, D_{app} can also be used for determining the mechanism the same as the above treatment.

$$V_{ct}/c = k_1 \quad (2.8)$$

$$V_{ct}/c = k_2 c \quad (2.9)$$

$$V_{ct}/c = k_1 + k_2 c \quad (2.10)$$

Besides the charge transport rate, the fraction of the redox molecule which accepts charge(s) (R_{ct}) is another important factor to represent the characteristics of the charge transport. In a diffusion mechanism R_{ct} is usually independent of c and reaches a high value of more than 0.8–0.9 after saturation, or sometimes it decreases when c is too high due to hindrance of molecular diffusion. The R_{ct} value after saturation of the charge propagation against c is shown in the Fig. 2.4. In a hopping mechanism R_{ct} is strongly dependent on c and with sufficient bounded motion (*vide supra*), R_{ct} can increase with the increase of c . However, without or with insufficient bounded motion, R_{ct} can increase only when c is high enough (percolation threshold) since charge hopping is possible only when a nearest neighboring molecule is located within a charge hopping distance.

When a matrix such as a polymer membrane was used to incorporate redox molecules, charging current flows giving overestimate of the charges oxidizing or reducing the redox molecules. It is therefore recommended to measure the real redox state change of the molecules by adopting in situ visible

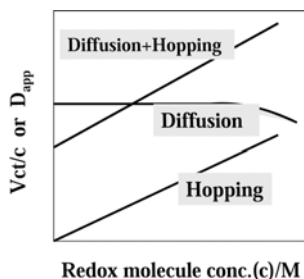


Fig. 2.3. Determination of charge transport mechanism

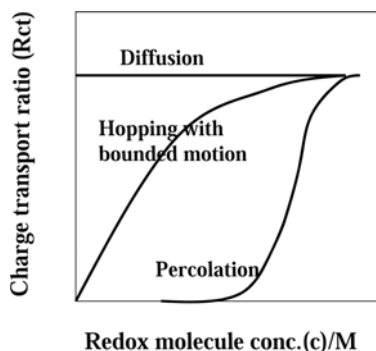


Fig. 2.4. Charge transport ratio depending on mechanism

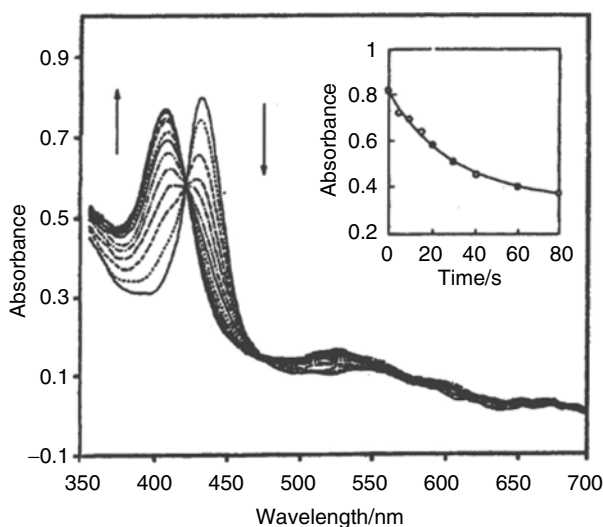


Fig. 2.5. Visible absorption spectral change of 0.1 M $[\text{Co(III)TPP}(-2)]^+$ incorporated into a Nafion membrane soaked in a 0.1 M NaClO_4 aq. soln. at pH 1.2 under potential step from 0.6 to -0.55 V (vs. Ag–AgCl). Inset: decrease in absorbance at 430 nm with time ([13], copyright John Wiley & Sons, Ltd.)

absorption spectral change measurement following potential step in an electrochemical measurement; this was called spectrocyclic voltammetry (SCV) or potential-step chronoamperospectrometry (PSCAS) [4,6]. One example is the CT by tetraphenylporphyrin Co(III) complex ($[\text{Co(III)TPP}(-2)]^+$) confined in a Nafion membrane coated on an indium tin oxide (ITO; transparent indium tin oxide-coated glass electrode). Visible absorption spectral change on potential step from 0.6 to -0.55 V (vs. Ag–AgCl) is shown in Fig. 2.5 exhibiting clear reduction of the complex with time [13]. The inset shows the absorbance decrease at 430 nm vs. reaction time.

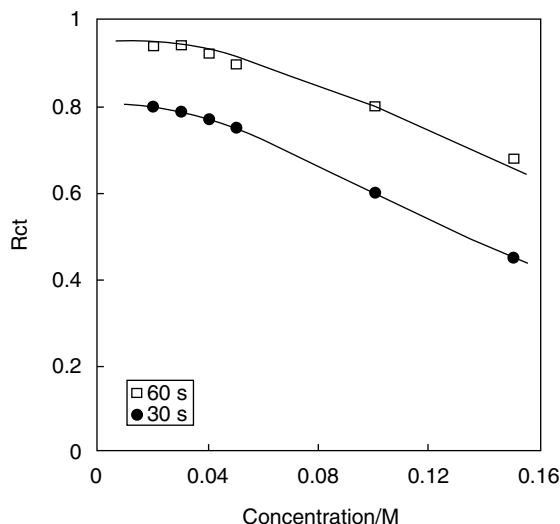


Fig. 2.6. CT ratio R_{ct} vs. concentration after potential step for reduction of $[\text{Co(III)TPP}(-2)]^+$ incorporated into a Nafion membrane exhibiting a typical diffusion CT mechanism ([13], copyright John Wiley & Sons Ltd.)

R_{ct} values are plotted against c as shown in Fig. 2.6 exhibiting a typical diffusion mechanism for which R_{ct} decreases distinctly with the concentration increase due to hindrance for molecular diffusion at higher concentrations.

The typical results on charge transport mechanism depending on the kind of redox molecules and matrix are shown in Table 2.1. The redox centers used are methyl viologen (MV^{2+}), polymer pendant MV^{2+} (Poly- MV^{2+}), tris(2,2'-bipyridine)ruthenium(II) complex ($\text{Ru}(\text{bpy})_3^{2+}$), polymer pendant $\text{Ru}(\text{bpy})_3^{2+}$ (Poly- $\text{Ru}(\text{bpy})_3^{2+}$), Co(II)TPP , Zn(II)TPP , tetrakis(2,2'-bipyridine)- μ -oxo-diruthenium(II,III) ($[(\text{bpy})_2\text{RuORu}(\text{bpy})_2]^{3+}$), and $[(\text{NH}_3)_5\text{Ru}-\text{O}-\text{Ru}(\text{NH}_3)_4-\text{O}-\text{Ru}(\text{NH}_3)_5]^{6+}$ (Ru-red, trinuclear Ru-amine complex). The matrix (electrode-coated polymer membrane) is mostly Nafion (Nf), a sulfonated perfluoroalkyl polyanion (1).

A Nafion membrane comprises hydrophilic columns composed of anionic sulfonate groups, hydrophobic columns composed of main chains, and inter-layer regions between hydrophilic and hydrophobic columns. Cationic substrate can be adsorbed well from an aqueous solution, and the adsorbed material is usually located mainly in the hydrophilic columns or interlayer regions, so that a real local concentration of the adsorbed material should be calculated by adopting a localization factor (α) which shows the degree of localization. The α value was estimated as 5.1 for a Nafion film cast from its alcoholic solution, and 40 for a commercially available film [12]. In many cases the thickness of a membrane was taken as $1\text{ }\mu\text{m}$, concentration of redox center molecules (c) $0.01\text{--}1\text{ M}$ (M = molar concentration, mol dm^{-3}), and the coverage of the redox molecule $10^{-9} - 10^{-7}\text{ mol cm}^{-2}$.

Table 2.1. Summary of charge transport with typical examples

Mechanism	Rate	Bounded motion	Examples (redox center/polymer)	Dapp/cm ² s ⁻¹
Physical diffusion	$V_{ct} = k_1 c$	Easy	$MV^{2+} \rightarrow MV^{+}/Nf$	11
			$Ru(bpy)_3^{3+} \rightarrow Ru(bpy)_3^{2+}/Nf$	0.85
			$[Co^{III}TPP(-2)]^{+} \rightarrow Co^{II}TPP(-2)/Nf$	4.4
			$[Co^{II}TPP(-2)]^{+} \rightarrow Co^{III}TPP(-2)/Nf$	0.73
			$Ru(bpy)_3^{2+} \rightarrow Ru(bpy)_3^{3+}/Nf$	0.24
Charge hopping	$V_{ct} = k_2 c^2$	Easy Difficult (but possible) Very difficult Percolation	$[Co^{II}TPP(-2)]^{+} \rightarrow [Co^{III}TPP(-1)]^{2+}/Nf$	0.03
			$[Zn^{II}TPP(-2)] \rightarrow [Zn^{II}TPP(-1)]^{+}/P-2VP$	0.13
			$[(bpy)_2RuORu(bpy)_2]^{3+} \rightarrow [(bpy)_2RuORu(bpy)]_2^{4+}/Nf$	
			$Poly-MV^{2+} \rightarrow Poly-MV^{+}$	
			$Poly-Ru(bpy)_3^{2+} \rightarrow Poly-Pu(bpy)_3^{3+}$	
Diffusion + hopping	$V_{ct} = k_1 c + k_2 c^2$		$Ru-red \rightarrow Ru-brown(Oxidation)/Nf$	

Nf = Nafion, P-2VP = Poly(2-vinylpyridine), Poly- = Polystyrene

The results of the Table 2.1 lead to important general behavior concerning CT mechanism as follows.

1. **Charge transport mechanism:** The mechanism is determined by the interaction of the matrix with the redox species after accepting charges. When this interaction is weak and the product can diffuse in the matrix, charge is transported by a diffusion mechanism, but when the interaction is strong and the product cannot diffuse, charge is transported by a hopping mechanism. The mechanism can therefore be different for transport of either positive or negative charges even for a same redox center/matrix system. Typical example for this is the $\text{Ru}(\text{bpy})_3^{2+}$ /Nafion system.
2. R_{ct} (fraction of redox molecule-accepting charges): For a diffusion mechanism, R_{ct} value after saturation of charge transport is independent on the redox center concentration (c), and usually high reaching 0.8–1. For a hopping mechanism, R_{ct} is strongly dependent on c and can increase only at high concentrations.
3. D_{app} : For a diffusion mechanism apparent diffusion coefficient of the charge (D_{app}) is independent of c , or often decreases with c , and usually shows a relatively high value of the order of 10^{-8} – $10^{-10} \text{ cm}^2 \text{ s}^{-1}$. For a hopping mechanism D_{app} is dependent on c , usually shows a low value of the order of less than $10^{-11} \text{ cm}^2 \text{ s}^{-1}$, and can increase only at high concentrations.
4. **Diffusion of large molecules:** Large and hydrophobic molecules such as metal tetraphenylporphyrins and metal phthalocyanines incorporated by a mixture casting method are located mainly in the hydrophilic columns or interlayer regions of Nafion, and can diffuse there exhibiting fairly high D_{app} .
5. **Redox molecules covalently attached to polymers:** CT takes place only by a hopping mechanism even when the corresponding monomeric molecule transports charges by a diffusion mechanism.
6. **Percolation mechanism:** When it is difficult for both diffusion and bounded motion to occur, the charges are transported by a percolation process. According to the percolation theory, probability of charge propagation (percolation) (P) against redox center concentration is expressed by a sigmoidal curve. R_{ct} was calculated for a static percolation process by a Monte Carlo simulation. When the concentration (represented by occupied probability p of redox center) is low, charge propagation does not take place because the distance between molecules is too large for the charge to hop (Fig. 2.7). When the concentration increases, the charge starts to propagate, and R_{ct} increases steeply at a threshold concentration c_{th} .

No example is yet found for which charge is transported at first by diffusion of redox molecules and then by charge hopping between them.

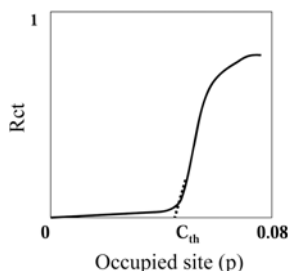


Fig. 2.7. R_{ct} vs. redox molecule concentration (represented by occupied site p in the simulation) in a percolation process

2.3 Charge Transfer by Molecules Under Photoexcited State in a Heterogeneous Phase

2.3.1 Overview

Electron transport between molecules is the most essential process in biological systems. Electron transfer in biological substances such as enzymes is very rapid, so that it is in many cases investigated by utilizing electron transfer in a photoexcited state with a laser flash photolysis technique. By this method one single reaction of an electron transfer from a molecule to another or from a functional group to another can be measured. For this purpose a specific position of an enzyme is modified with a redox center molecule such as metal complex, and electron transfer is studied with a laser flash photolysis.

In earlier times, the central metal ion of the iron heme in *cytochrome c* or myoglobin was substituted by Zn, Ru ion was coordinated to a surface imidazole of a histidine residue, and then the electron transfer from the photoexcited Zn porphyrin to the Ru moiety was investigated [14,15]. The relation between the rate constant for the electron transfer k_{et} and the spatial distance between the redox centers (R) was represented by the known (2.11) showing that the electron transfer takes place via a spatially nearest pathway.

$$-\ln k_{et} = R \quad (2.11)$$

According to the Marcus theory [16] the rate of nonadiabatic electron transfer with weak exergonicity shows a bell-shape behavior with respect to the free energy difference ($-\Delta G$) between electron donor and acceptor giving a maximum rate when ΔG equals reorganization energy of the medium. Extensive studies have been published especially on intramolecular electron transfer in this regard. However, it is not the aim of the present section to review these works. Intermolecular electron transfer between a photoexcited redox molecule and a ground state one in a heterogeneous phase will be discussed in this section.

Electron (or charge) transfer reaction of a photoexcited molecule is investigated by the following methods:

1. Measurement of a steady state ultraviolet and visible (UV–Vis.) absorption spectrum when the back electron transfer is slow, and when the equilibrium under irradiation shifts to the product side. Such reaction is called a photoredox system. There have been not many examples of this type. When the back electron transfer is rapid, the presence of some sacrificial donor or acceptor is effective to shift the reaction to the product side and therefore to monitor the reaction.
2. Monitoring a transient absorption spectrum with a laser flash photolysis method especially when the rates of electron transfer and the back reaction (recombination) are rapid.
3. Measurement of emission intensity or emission decay (lifetime) when the photoexcited state emits light (luminescence, either fluorescence or phosphorescence), and the emission is quenched by electron transfer.

2.3.2 Mechanism of Charge Transfer at Photoexcited State in a Heterogeneous Phase

Emission intensity and decay of a photoexcited probe gives important information on the mechanism of the electron transfer, mobility of the probe, and nature of the microenvironment around the probe. Since electron transfer from or to an excited state of a probe quenches the emission, quenching reflects the electron transfer. The mechanism of electron-transfer quenching can in general be divided into two extreme cases (Fig. 2.8).

One is a dynamic quenching for which donor and acceptor molecules diffuse freely, collide, and react. The other is a static quenching for which the molecules do not diffuse, and when a quencher (Q) molecule exists in a quenching sphere around the probe, it quenches the emission (electron transfer takes place).

Such quenching is analyzed by plotting relative emission intensity (I_0/I , where I_0 is the emission intensity without Q , and I is that with Q) against Q concentration according to the Stern-Volmer equation (2.12)[17, 18] (called

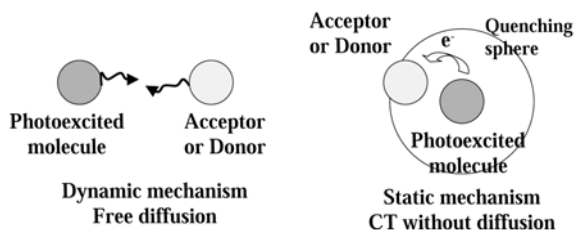


Fig. 2.8. Electron-transfer mechanism in a photoexcited state

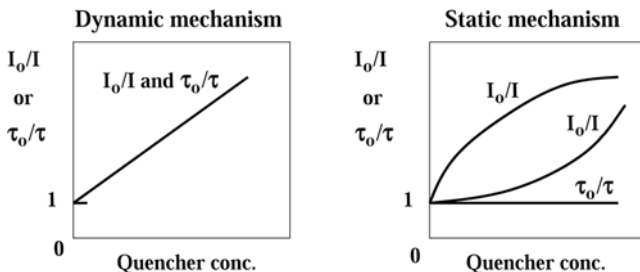


Fig. 2.9. Stern-Volmer plots for typical dynamic and static-electron-transfer mechanisms

Stern-Volmer plots [17]), where $[Q]$ is the Q concentration and k_{sv} is the Stern-Volmer constant.

$$I_0/I = 1 + k_{sv}[Q] \quad (2.12)$$

The Stern-Volmer plots based on the lifetime of the excited state (τ , reciprocal of the first-order decay constant of the excited state) is also an important parameter to determine the electron-transfer mechanism. For a complete dynamic quenching case, both the I_0/I and τ_0/τ plots are linear and fall on a same line (Fig. 2.9).

For a complete static quenching case, the I_0/I plots are upwardly curved according to the Perrin equation [19] represented by (2.13) under higher concentration conditions as shown in Fig. 2.9. For this static quenching the plots τ_0/τ do not have a slope, i.e., the excited state involving quencher(s) in its quenching sphere does not emit at all, but the excited state involving no quencher in its quenching sphere emits the same as the system without quencher.

$$I_0/I = \exp(K_1[Q]) \quad (2.13)$$

Since $K_1 = VN_A$ (V is the quenching sphere volume and N_A is Avogadro's number), quenching distance can be determined from the slope of $\ln(I_0/I)$ versus $[Q]$ plots for a static quenching case. In other static quenching cases the I_0/I plots are downwardly curved (see Fig. 2.9).

For a heterogeneous phase there exist two major problems as follows:

1. The microenvironment of the excited state is not homogeneous but different, depending on the location of the probe, which affects emission decay and quenching of the excited state. This is reflected in a multi-exponential decay of the excited state.
2. The (electron transfer) quenching mechanism can consist of both dynamic and static ones, which makes the I_0/I plots complicated. The equations to analyze electron-transfer quenching were derived based on the following standpoints [20, 21].
 - (a) The number of different sites; 1-site or 2-sites.
 - (b) Dynamic or static quenching as well as their combination.

- (c) The incorporation equilibrium of Q into the quenching sphere around a probe; one-step equilibrium or multistep one.
- (d) The rate of static quenching; either very fast so that emission is negligible, or the emission should be considered since it is competitive with the quenching.
- (e) For multistep equilibria between Q and probe; the static quenching rate is proportional to the number of Q in the quenching sphere, or independent of the number of Q .

Based on these factors 11 models and corresponding equations have been proposed for 1-site model, and 2 models for 2-site model as reported [20].

For a complete static quenching case (2.14) was derived considering the size of the probe by assuming that the probes are distributed randomly in a matrix [20],

$$I/I_0 = \exp [-4\pi (R_0^3 - s^3) N_A 10^{-24} [Q]/3] \quad (2.14)$$

where R_0 is the electron-transfer distance (nm, center-to-center of donor and acceptor), s is the contact distance between donor and acceptor (nm), $[Q]$ is the Q concentration (mol dm^{-3}) in the matrix.

In a polysiloxane film containing dispersed $\text{Ru}(\text{bpy})_3^{2+}$ and MV^{2+} , electron-transfer quenching of the photoexcited Ru complex by MV^{2+} was investigated [21]. The Stern-Volmer plots for the relative emission quantum yield (equals to I_0/I) and relative lifetime of the excited state (τ_0/τ) were plotted against MV^{2+} concentration. A flat (no slope) τ_0/τ plots showed evidently that the electron-transfer quenching takes place by a static mechanism. By applying the (2.14) ($s = 0.82 \text{ nm}$), the electron-transfer distance R_0 was obtained as 1.4 nm (Fig. 2.10) that is a similar value as the ground state electron-transfer distance obtained by an electrochemical method, and is also a reasonable value considering the electron-transfer distance in biological systems often reported to be around 1.3 nm .

In biological systems proteins mediate electron transfer. This mediation takes place either through bonds of the protein, or through space for which aromatic amino acid residues are considered to mediate the electron transfer in the space. Aromatic amino acid residue model, 3-methylindole as a model of

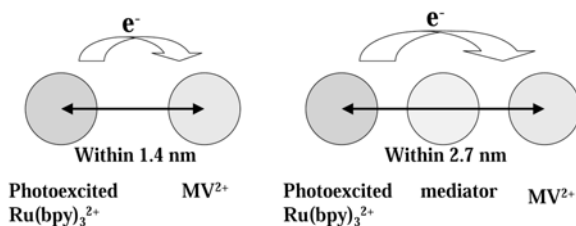


Fig. 2.10. Static electron transfer from photoexcited $\text{Ru}(\text{bpy})_3^{2+}$ to MV^{2+} in a polysiloxane film in the absence and the presence of mediator (3-methylindole), a tryptophan model

tryptophan residue, was codispersed in the above $\text{Ru}(\text{bpy})_3^{2+}/\text{MV}^{2+}$ system. In the presence of the mediator model the electron transfer was enhanced very much [20]. An equation taking into account mediated electron transfer was derived, and applied to the results giving mediated electron-transfer distance of 2.7 nm, about twice as that without the mediator. Tryptophan itself or a model of tyrosine (*p*-Cresol) was not effective for the mediation.

Electron-transfer quenching of excited $\text{Ru}(\text{bpy})_3^{2+}$ by MV^{2+} incorporated in a poly(ethylene oxide) film took place both by static and dynamic mechanisms different from the above polysiloxane film, and the electron-transfer distance was 1.7 nm [22].

These and other results showed that electron transfer in a heterogeneous phase takes place usually by a static mechanism, but a dynamic mechanism can also be involved when diffusion or bounded motion of the redox molecules in the polymer matrix is possible. Electron-transfer distance in a photoexcited state studied by a photochemical method is in principle comparable to that in a ground state investigated by electrochemical methods.

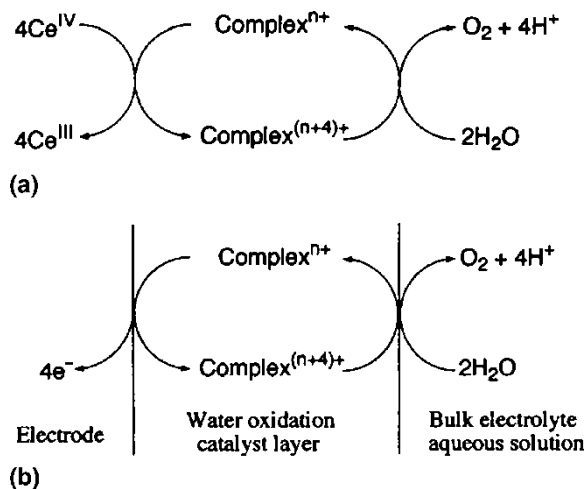
2.4 Charge Transfer and Electrochemical Reactions in Metal Complexes

2.4.1 Charge Transfer in Metal Complexes

Redox reactions occurring between two metal complexes (or a complex and an electrode) can be categorized into two mechanisms in view of the configuration of ligands surrounding the central metal ions [23]. One is outer-sphere reaction and the other is inner-sphere reaction. Outer sphere reaction is defined as the case where electron transfer occurs in the metal complex, without exchange reactions of ligands, or at least no chemical bonds are broken or formed between the metal and ligands. On the other hand, in the inner-sphere reaction, reacting metal complexes transfer ligand(s) or go through an activation state connected with bridged ligands between two complexes (or a complex and an electrode). In the latter mechanism breaking and forming of bonds between ligands and metal centers of reacting complexes occur in combination with the electron transfer.

Whether the outer-sphere reaction or the inner-sphere reaction occurs is determined by relative speed of the molecular arrangement of ligands and that of electron transfer. The outer-sphere mechanism would occur preferentially when (1) the redox reaction rate is much faster than the ligand exchange reaction, and (2) the bonding distance between the metal center and the ligand does not change much with the valence change of the central metal. If the ligand-metal structure needs to change by strong interactions and causes a high energy of rearrangement, the possibility of charge transfer becomes small. Marcus theory incorporates the reorganization energy as a principal contribution to the transition state of reacting species in the rate equations

Table 2.2. Calculated values of $|\Delta|$ for bridges consisting of pyrrole ligands of M_1 and M_2 ($=Fe$) and different inserted molecules ([26], copyright Royal Society of Chemistry)



[16, 24, 25]. The electron transfer at the electrode with the complex or redox reactants is discussed in Sect. 2.4.2.

The electron conduction inside molecules becomes a central problem when one considers electron transfer between separate redox sites. S. Larsson studied the electron transfer between metal centers in proteins and concluded that connecting bridges (saturated or aromatic rings) with orbital energies close to the metal orbitals give rise to high transfer capabilities, the transfer range extending more than 1.5 nm [26]. Also conjugated double bonds or π -bonds in the moiety facilitate non-localized electron transfer as compared with σ -transfer in the same bridges. The probability for electron transfer is proportional to the square of energy gap parameter Δ , which is expressed as a function of the transfer capability between adjacent atomic orbitals of the bridge compounds. Table 2.2 presents the calculated value of Δ , for which electron transfer becomes probable for $\Delta > 10^3$ a.u. A conjugated π system transfer electrons well, but saturated aliphatic or peptide chain also serves in so far as they fill the gap between the ligands [26]. The rate of long-range (>0.5 nm) electron transfer, in organic and metal complexes, proteins, and intermolecular electron transfer, falls off exponentially with distance R [27].

$$k_{ET} = k_0 \exp[-\beta(R - R_0)] \quad (2.15)$$

It is noted that the charge transfer complexes are mostly furnished with conjugated systems like aromatic rings, pyrrole rings, pyridyl rings, or other heterocyclic ring chelates surrounding the metal center with specific d-band energy levels modified by the chelates [28]. N4 ligand structures around the active metal centers are characteristic features of porphyrins and phthalocyanines, which are the basic components in biological systems such as hemes of

oxygen transport or cytochromes of respiratory chains [29]. The central metal ion can be considered as the reaction site that accepts electrons from the peripheral N-containing ligand moieties. It is discussed in Sect. 1.2 (Chap. 1) that N4 ligands connect the electronic levels of the reactants and the central metal if those are too far apart, and ease the transition of electrons.

The reaction formulas often show a common feature if the reaction proceeds through single rate-determining step. In an enzymatic reaction, the substrate that reacts with the enzyme often interacts with the central metal, forms a complex, and then this complex turns into a product regenerating the original enzyme [29]. The enzyme works as a catalyst.



Here S is substrate, SE is the substrate–enzyme complex and P is product. With increasing the substrate concentration $[S]$, the reaction rate v levels off and approaches a saturated value V because the process is rate-limited by the amount of SE . Michaelis–Menten formula gives [29]

$$v = V \frac{[S]}{[S] + K_m} \quad (2.17a)$$

where K_m is Michaelis constant:

$$K_m = \frac{[S][E]}{[SE]} = \frac{k_{-1} + k_{+2}}{k_{+1}} \quad (2.17b)$$

with k_{+1} , k_{-1} and k_{+2} being forward and reverse rate constants of reaction (2.16a), respectively, and that of reaction (2.16b).

Suppose that the catalyst E is adsorbed on the surface of a support. The substrate S comes from the atmosphere (or liquid phase), and forms a complex in the same ways as the enzymatic reaction. Assuming the Langmuir-type adsorption of E on the surface, the reaction rate is described by the following equation,

$$v = k[S] \frac{K[E]}{1 + K[E]} \quad (2.18a)$$

$$K = \frac{\theta_E}{(1 - \theta_E)[E]} = \exp\left(\frac{-\Delta G_E^0}{RT}\right) \quad (2.18b)$$

which is similar to (2.17a), but here the surface population of E determines the rate. K is the adsorption equilibrium constant, θ_E the coverage of E , ΔG_E^0 the standard free energy of adsorption and k is the net rate constant.

When the electron transfer between the substrate and the electrode is involved in the reaction, the net rate is determined by the exponential function of the electric potential. Butler–Volmer equation gives the rate of charge transfer at the electrode surface as a function of the electrode potential [30]:

$$v = k_{\text{ox}}[R] \exp\left(\frac{\alpha F(E - E_0)}{RT}\right) - k_{\text{red}}[O] \exp\left(-\frac{(1 - \alpha)F(E - E_0)}{RT}\right) \quad (2.19)$$

where k_{ox} and k_{red} are the rate constants, $[R]$ and $[O]$ are the concentrations of species in reduced and oxidized forms, respectively, E and E_0 are the electrode potential and its equilibrium value and F , R , and T have usual meanings. If the preceding reaction involves adsorbed intermediates, combination of (2.18a) and (2.19) makes the rate equations complex, but the analysis of rate equations gives a clue to the reaction route and mechanism (see Sect. 2.4.3).

2.4.2 Charge Transfer at Electrode Surfaces

Electron transfer between a metal electrode and reactant species is one of the most fundamental processes in electro-catalyst reactions.



Theoretical foundations were made by Gurney [31], Randles [32], Marcus [16,24], and by Gerischer [33] for the adiabatic electrode processes. Later Dogonadze and Levich developed the quantum-mechanical theory of both adiabatic and nonadiabatic electron transfer reactions [34]. In adiabatic processes, the nuclear motion of the atoms is supposed to be independent of the motion of electrons because of the large mass differences (Born-Oppenheimer approximation). Then the electronic energies (wave functions) are described as a function of nuclear configuration at each time an electronic transition occurs without the change of nuclear conformation (Frank-Condon principle). This means that the electron transfer occurs at iso-energetic levels between donor and acceptor atoms [25,35].

The probability P of radiationless electron transfer between reacting species and the electrode metal is given by the integral of neutralization frequency over electronic energy ε , applying the Frank-Condon principle (the nuclear configuration of species is fixed during the electron transfer) [36]:

$$P = \frac{kT}{h} \int_{-\infty}^{\infty} v(\varepsilon) N(\varepsilon) \tau(\varepsilon) \kappa(\varepsilon) f(\varepsilon) \rho(\varepsilon) d\varepsilon \quad (2.21)$$

where $v(\varepsilon)$ is frequency factor, $N(\varepsilon)$ the population of reactants having energies in the range ε and $\varepsilon + d\varepsilon$, $\tau(\varepsilon)$ nuclear transmission coefficient, $\kappa(\varepsilon)$ electronic transmission coefficient, $\rho(\varepsilon)$ the electronic density in the metal, and $f(\varepsilon)$ the Fermi-Dirac distribution term, with the Fermi energy ε_F corresponding to half-filled electron energy [25].

$$f(\varepsilon) = \frac{1}{1 + \exp \{(\varepsilon - \varepsilon_F)/kT\}} \quad (2.22)$$

In the transition state theory, the electron transfer occurs at the point where two parabolic curves of reactants and products meet on the frame of Gibbs free energy surface along reaction coordinates (Fig. 2.11). Based on both energy conservation and the Frank-Condon principle through the potential

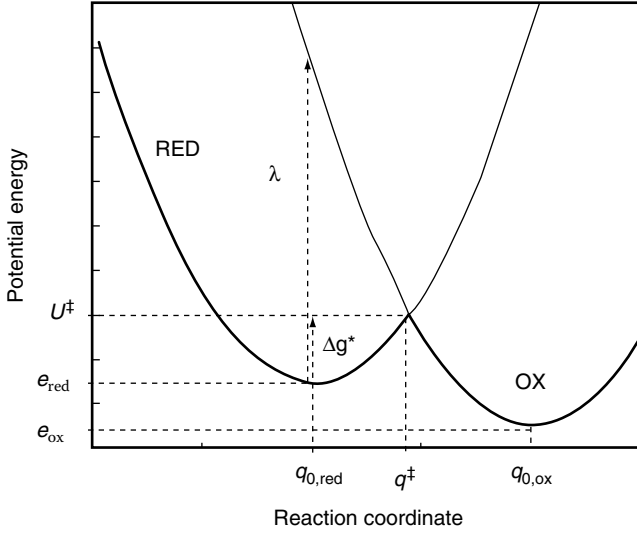


Fig. 2.11. Potential energy surface along reaction coordinates for the reaction (2.20)

energy curves in the reaction coordinate q , the rate constant for the forward (anodic) reaction is given by a transition at the intersect of two curves:

$$k_f = \nu \exp\left(-\frac{\Delta g^*}{kT}\right) \quad (2.23)$$

where ν is the vibrational frequency along q , and Δg^* is the Gibbs energy difference between the transition state and the reactant system. R. A. Marcus derived a formula for redox electrode reactions using classical electrostatic models [23,25]. The potential energy surface is approximated by the harmonic oscillator model:

$$U_{\text{red}} = e_{\text{red}} + \frac{1}{2}m\omega^2 (q - q_{0,\text{red}})^2 \quad (2.24a)$$

$$U_{\text{ox}} = e_{\text{ox}} + \frac{1}{2}m\omega^2 (q - q_{0,\text{ox}})^2 \quad (2.24b)$$

At the intercept of two curves, the coordinate gives $q = q^{\ddagger}$ and $U = U^{\ddagger}$, and

$$U^{\ddagger} = e_{\text{red}} + \frac{1}{2}m\omega^2 (q^{\ddagger} - q_{0,\text{red}})^2 = e_{\text{ox}} + \frac{1}{2}m\omega^2 (q^{\ddagger} - q_{0,\text{ox}})^2 \quad (2.25)$$

From this $q^{\ddagger}$ is obtained as

$$q^{\ddagger} = \frac{1}{2} (q_{0,\text{ox}} + q_{0,\text{red}}) + \frac{e_{\text{ox}} - e_{\text{red}}}{m\omega^2 (q_{0,\text{ox}} - q_{0,\text{red}})} \quad (2.26)$$

Then the activation energy Δg^* for the oxidation reaction is obtained as follows:

$$\Delta g^* = U^{\ddagger} - e_{\text{red}} = \frac{(\lambda + \varepsilon - \varepsilon_F - e\eta)^2}{4\lambda} \quad (2.27a)$$

where $\varepsilon - \varepsilon_F - e\eta = e_{\text{ox}} - e_{\text{red}}$ and

$$\lambda \equiv \frac{1}{2}m\omega^2 (q_{0,\text{ox}} - q_{0,\text{red}})^2 \quad (2.27b)$$

Here ε is the energy states in the electrode metal and η is the overpotential of the electrode.

Substitution of (2.23) for $N(\varepsilon)$ in (2.21) and combination of (2.27) gives the formula of the current-overpotential relations:

$$j = A[R] \int \rho(\varepsilon) \{1 - f(\varepsilon)\} \exp \left\{ -\frac{(\lambda + \varepsilon - \varepsilon_F - e\eta)^2}{4\lambda kT} \right\} d\varepsilon \\ - A[O] \int \rho(\varepsilon) f(\varepsilon) \exp \left\{ -\frac{(\lambda - \varepsilon + \varepsilon_F + e\eta)^2}{4\lambda kT} \right\} d\varepsilon \quad (2.28)$$

After simplifying the equation by replacing the Fermi–Dirac distribution with step function and taking the average of $\rho(\varepsilon)$, as ρ^* , one gets

$$j = 2A\rho^* \sqrt{\lambda kT} \left\{ [R] \operatorname{erfc} \left(\frac{\lambda - e\eta}{2\sqrt{\lambda kT}} \right) - [O] \operatorname{erfc} \left(\frac{\lambda + e\eta}{2\sqrt{\lambda kT}} \right) \right\} \quad (2.29)$$

which shows the limiting currents at high overpotentials. If (2.27) is simplified by taking the energy at the Fermi level $\varepsilon = \varepsilon_F$, it is obtained

$$j = \frac{1}{2} A[R] \rho(\varepsilon_F) \exp \left\{ -\frac{(\lambda - e\eta)^2}{4\lambda kT} \right\} - \frac{1}{2} A[O] \rho(\varepsilon_F) \exp \left\{ -\frac{(\lambda + e\eta)^2}{4\lambda kT} \right\} \\ = k_0[R] \exp \left\{ \frac{\alpha_+(-\lambda + e\eta)}{kT} \right\} - k_0[O] \exp \left\{ -\frac{\alpha_-(\lambda + e\eta)}{kT} \right\} \quad (2.30a)$$

$$\alpha_+ = \frac{kT}{e} \frac{\partial \ln i_+}{\partial \eta} = \frac{1}{2} - \frac{e\eta}{2\lambda} \quad (2.30b)$$

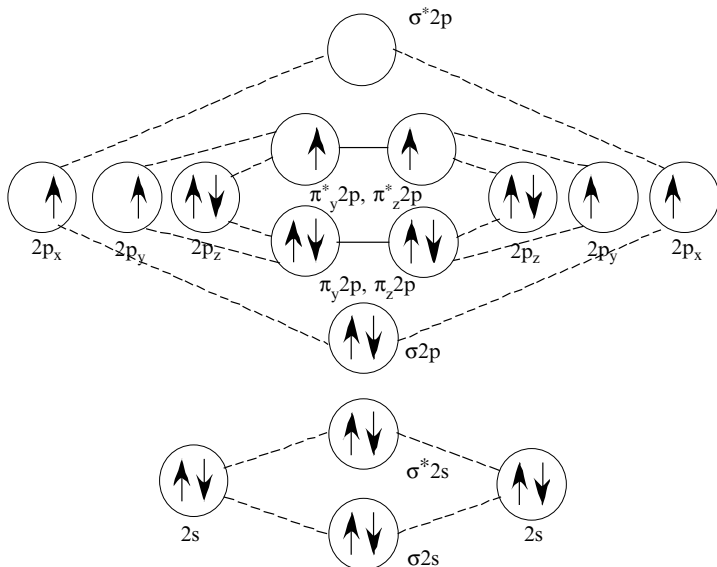
$$\alpha_- = \frac{kT}{e} \frac{\partial \ln i_-}{\partial \eta} = \frac{1}{2} + \frac{e\eta}{2\lambda} \quad (2.30c)$$

which takes the same form as in (2.19) with $\alpha_+ + \alpha_- = 1$ [25].

When solvent molecules surround the reacting species, their motion greatly affects the progress of reactions along the reaction coordinate. Increasing the interaction of solvent molecules with the reacting species, the electrode process changes from the outer sphere to inner sphere reactions. The kinetics changes from simple electron transfer to adiabatic processes involving bond-breaking at the electrode. N. S. Hush gives comprehensive overview of this process and presents modification of vibrational contribution in the reorganization energy λ [37].

2.4.3 Oxygen Reduction Reaction at Metal Macrocycles

The oxygen atom has the electronic structure of $(1s)^2(2s)^2(2p)^4$. Upon forming O_2 molecule the overlap of 2p atomic orbitals gives rise to the molecular orbital (MO) consisting of a σ_g bond and two π bonds, i.e. [38].

Atomic orbital of O Molecular orbital of O₂ Atomic orbital of O**Fig. 2.12.** Molecular orbital of O₂ in the ground state ([38], copyright Clarendon Press)

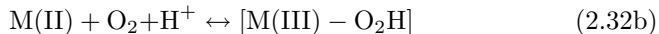
$$\text{O}[1s^2 2s^2 2p^4] + \text{O}[1s^2 2s^2 2p^4] \rightarrow \text{O}_2[KK(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p)^2(\pi 2p)^4(\pi^* 2p)^2] \quad (2.31)$$

Here KK denotes filled K shell of O₂ molecule [$KK = (\sigma 1s)^2(\sigma^* 1s)^2$] and $*$ denotes antibonding molecular orbital. Filling electrons from the lower level of MO, two unpaired electrons locate in a doubly degenerated π^* antibonding molecular orbital ($\pi_y^* 2p$ and $\pi_z^* 2p$), forming a triplet ground state (Fig. 2.12). The excess of bonding over nonbonding electrons is four, as seen in the electronic configuration (2.31). The bond order is two with four bonding orbitals and two antibonding orbitals. This explains the high stability of O₂ molecules. When O₂ is reduced on the catalyst surface, the electrons added occupy antibonding orbitals π^* decreasing the bond order and increasing the O–O bond distance [39]. Thus filling in the π^* orbital by increasing the back donation from the d-band metal interacting with O₂ or by shifting the electrode potential to negative directions increases the chance of oxygen reduction reaction.

Macrocycles such as porphyrins and phthalocyanines are biomimetic materials located in the center of heme or cytochrome C, enabling oxygen transport or charge transfer during respiratory reactions [29]. Their ability to adsorb O₂ on the metal center is an important function together with charge transfer through N ligands in the pyrrole structure.

Oxygen reduction reaction (ORR) on macrocycles is thought to occur via outer-sphere reaction mechanism. As for the reaction mechanism, van Veen

et al. proposed the following schemes [40]:



The number of active sites is potential dependent, and the Nernst equation for the step (2.32a) gives

$$E = E_0 + \frac{RT}{F} \ln \frac{\text{M(III)}}{\text{M(II)}} \quad (2.33)$$

whereas (2.32b) gives, together with (2.33),

$$[\text{M(III)} - \text{O}_2\text{H}] = K_0[\text{O}_2][\text{H}^+][\text{M(III)}] \exp \left\{ -\frac{F(E - E_0)}{RT} \right\} \quad (2.34)$$

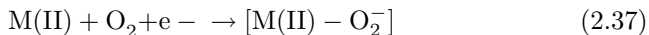
Using (2.19) for the step (2.32c) where only the reduction reaction is taken into account,

$$v = k_0 K_0 [\text{O}_2][\text{H}^+][\text{M(III)}] \exp \left\{ -\frac{(2 - \alpha)F(E - E_0)}{RT} \right\} \quad (2.35)$$

Assuming $\alpha = 0.5$, the Tafel slope (slope of the curve of E vs. $\log v$) as obtained experimentally for iron phthalocyanines, $-2RT/3F$ (-40 mV at 25°C), is explained [40]. If M(II) forms in consumption of M(III) , i.e., $[\text{M(II)}] + [\text{M(III)}] = \text{constant}$, then another equation results in [cf. (2.18a)]:

$$v = k_0 [\text{O}_2] \frac{\exp \left\{ -\frac{(2 - \alpha)F(E - E_0)}{RT} \right\}}{1 + \exp \left\{ -\frac{F(E - E_0)}{RT} \right\}} \quad (2.36)$$

At large overpotentials, the number of M(II) sites becomes potential-independent, and the first one electron-transfer step becomes rate-controlling.



In this case the reaction rate is

$$v = k_0 [\text{O}_2] \exp \left\{ -\frac{(1 - \alpha)F(E - E_0)}{RT} \right\} \quad (2.38)$$

with the Tafel slope of $-2RT/F$ (-120 mV at 25°C). This is the case where ORR occurs at potential much more negative than the $\text{M(III)}/\text{M(II)}$ couple, and H_2O_2 is the main product of the reaction. Zagal et al. discussed the

ORR mechanism on metallophthalocyanines, and suggested that the redox potential, pK_a of the couples

$$pK_a = \log \left(\frac{[M(III)OH^-][H^+]}{[M(III)][H_2O]} \right) \quad (2.39)$$

and pH of the electrolytes determine the Tafel slopes [41]. In acid media, they assumed that the reaction (2.32b) is rate-determining at low polarization resulting in the Tafel slope of $-RT/F$ (-60 mV at 25°C), while the reaction (2.32a) is rate-determining at high polarization with the Tafel slope of $-2RT/F$ (-120 mV at 25°C). Table 2.3 presents some reported results of Tafel slopes measured for O_2 reduction at transition metal macrocycles.

Table 2.3. Reported Tafel slopes in ORR on macrocycles

Macrocycles	Condition	Tafel slope/mV decade ⁻¹	Major product	Ref.
CoTAA	0.5 M H ₂ SO ₄ , 25°C	-60	H ₂ O	[42]
Fe polyphthalocyanine	6 M KOH, 25°C	-85	—	[43]
CoTSP	0.05 M H ₂ SO ₄ , 20°C	-135	H ₂ O ₂	[44]
	0.1 M NaOH, 20°C	-120	H ₂ O ₂	
CoTSP	0.05 M H ₂ SO ₄ , 25°C	-155	H ₂ O ₂	
	M NaOH, 25°C	-120	H ₂ O ₂	[41]
FeTSP	0.05 M H ₂ SO ₄ , 25°C	-65	H ₂ O ₂	
	0.1 M NaOH, 25°C	-30 to -35	H ₂ O ₂	
CoTPP	0.5 M HClO ₄ + 0.5	-120	H ₂ O ₂	[45]
CoTPP + 4Ru(NH ₃) ₅ ²⁺	M NH ₄ PF ₆	-90	H ₂ O	
Pyrolyzed CoTMPP	0.3 M HClO ₄ , RT	-52 to -61	H ₂ O	
Pyrolyzed CoPc		-70 to -149	H ₂ O	[46]
Pyrolyzed CoCy		-110 to -141	H ₂ O ₂	
Poly(CoTAPP)	0.5 M H ₂ SO ₄ , 20°C	-58 (low η)	H ₂ O ₂	[47]
Poly(CoTAPc)		-116 (high η)	H ₂ O ₂	
Pyrolyzed	0.5 M H ₂ SO ₄ , 20°C	-60 (low η)	H ₂ O ₂	
CoTMeOPP		-120 (high η)		[48]
	1 M KOH, 20°C	-40 (low η)	H ₂ O	
		-120 (high η)		
FePc	0.5 M H ₂ SO ₄ , 20°C	-65	H ₂ O	
		-121	H ₂ O	[49]
Heat-treated FePc		-63		

CoTAA: cobalt dibenzotetraazaannulene, Co(Fe)TSP: cobalt (iron) tetrasulfonate phthalocyanine, CoTPP: cobalt tetrapyridylporphyrin, CoTMPP: cobalt tetramethoxyphenylporphyrin, CoPc: cobalt phthalocyanine, CoCy: cobalt cyclam, CoTAPP: cobalt tetra(*o*-aminophenyl)porphyrin, CoTAPc: cobalt 4, 4', 4'', 4'''-tetraaminophthalocyanine, CoTMeOPP: cobalt 5,10,15,20-tetra(methoxyphenyl)porphyrin, FePc: iron phthalocyanine

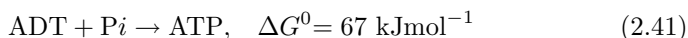
2.5 Proton Transport in Polymer Electrolytes

2.5.1 Proton Transfer Reactions

For photosynthesis and adenosine-triphosphate (ATP) production at plant cells, P. Mitchell proposed a mechanism in which the H^+ motive force across the chloroplast membrane is utilized as the energy required for the oxidative phosphorylation of adenosine-diphosphate (ADP) [50]. During the charge separation by the light energy, the proticity (proton-motive force) ΔP produces electric potential $\Delta\psi$ and H^+ driving force ΔpH that is accumulated across the membrane (active transport of H^+) [51]:

$$\Delta P = \Delta\psi - \frac{2.3RT}{F}\Delta pH \quad (2.40)$$

i.e., energy liberated during the electron transport by redox reactions is stored as ΔpH . ATP is synthesized as a dark reaction, at the consumption of the electrochemical potential difference of H^+ across the membrane (Fig. 2.13a).



where Pi represents inorganic orthophosphate. The coupling of electron and proton transports plays an important role in ATP synthesis [29, 52]. Førlund et al. point out that the energy conversion efficiency from redox reaction to ATP synthesis is as high as 0.96, and the process takes place in close to equilibrium conditions [53].

This is in close resemblance to fuel cell systems, where the chemical reactions are converted into the electric potential,

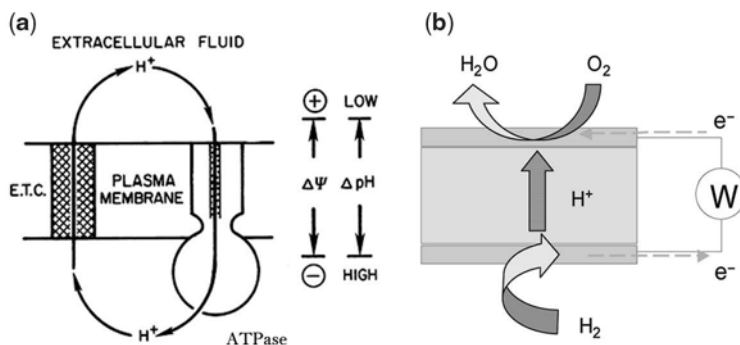
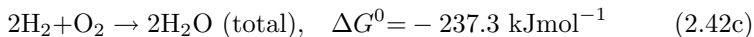
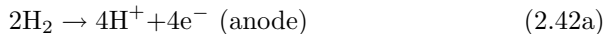


Fig. 2.13. (a) Chemiosmotic proton translocation model for ATP synthesis in which electron transport chain and proton conduction pathway are coupled ([51], copyright Plenum Press). (b) Energy conversion in fuel cells in which chemical energy of fuel oxidation is converted to electricity by a coupled transport of electron in the outer circuit and proton in the polymer electrolyte membrane

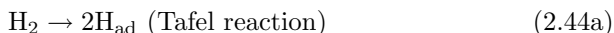


$$E_{\text{rev}}^0 = -\Delta G^0 / 4F = 1.23 \text{ V} \quad (2.43)$$

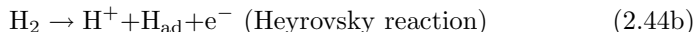
which drives the H^+ transport across the membrane (Fig. 2.13b). In the case of the chloroplast membrane, H^+ is transported through the proton channel formed across the membrane, and this is coupled to the ATP production. In fuel cell membranes (polymer electrolyte membrane or proton exchange membrane, PEM), H^+ is driven by the potential difference across the membrane that separates the H_2 and the O_2 gas electrodes. Since H^+ mediates the reactions at the anode and the cathode as in (2.42a) and (2.42b), its conduction sometimes limits the overall fuel cell current.

Although the transmembrane potential in normal biological systems is of the order far less than 100 mV, mitochondria or chloroplast membranes show 200 mV for ΔP . This large potential would not be a result of Nernstian diffusion potential but significantly by a surface charge potential [51]. According to the chemiosmotic hypothesis by P. Mitchell, the electron transport proteins and the proton ATPase complex, which are incorporated in a bilayer structure of a cell membrane, are coupled so that electrogenic pumping of H^+ creates a high ΔP as in (2.40). This high ΔP drives the synthesis of ATP as H^+ flows down along a proton conduction pathway in the ATPase [51]. Whether or not H^+ migrates faster in the membrane than in aqueous solution, and how so in sub-molecular level, is a central question not answered yet.

Proton transfer at the catalyst surface is an important topic in relation to energy conversion systems such as fuel cell catalysts, photoexcited water splitting, and electrochemical solar cells. H^+ ion discharge at the metal electrodes occurs in two steps:



or



followed by



The subject was reviewed for hydrogen evolution reactions [54,55] and for hydrogen oxidation reactions [56], also briefly in Chap. 1.

2.5.2 Proton Transport in Polymer Electrolytes

A number of investigations are reported about the structure and H^+ conduction mechanism in PEM, made of perfluorosulfonated ionomers [57,58]. Since this is a phase-separated membrane with inverse micelle microstructures, H^+ is preferentially conducted through the water-containing ionic channels of about 4 nm domains connected by 1 nm channels [59]. Figure 2.14 depicts diffusion

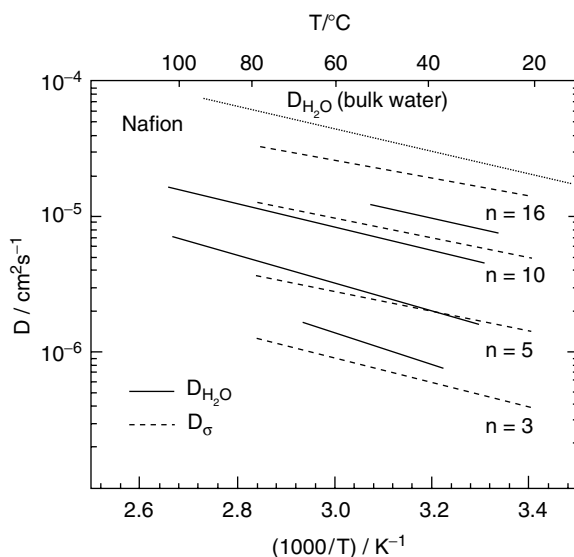


Fig. 2.14. Proton conductivity diffusion coefficient (mobility) and water self-diffusion coefficient of Nafion 117 (EW = 1100 g/equiv), as a function of temperature and the degree of hydration ($n = [\text{H}_2\text{O}]/[-\text{SO}_3\text{H}]$) ([57], copyright the American Chemical Society)

coefficients for H^+ transport and for water molecules in Nafion 117 membranes [57]. At high water content, H^+ transfers by Grotthuss mechanism (an interchange between H_3O^+ and H_2O for H^+ movement) through the bulk-like water in the ionic channel, and its diffusion is faster than H_2O . With decreasing water content, H^+ transport is suppressed and becomes of vehicular mechanism. This fact indicates a strong interaction of $-\text{SO}_3^-$ and H_2O .

The state of water inside of PEM strongly affects H^+ conduction, indicating a coupled transport of H^+ and H_2O . This is confirmed by measuring the water drag coefficient $t_{\text{H}_2\text{O}}$ (number of H_2O carried with H^+) [60]. Table 2.4 summarizes the transport parameters measured in perfluorosulfonated ionomer membranes. The ion-exchange capacity (IEC), i.e., density of sulfonic acid groups has a strong influence on the transport parameters. When the ion-exchange capacity increases, H^+ conductivity and water content increases. In comparison to this, the ratio of nonfreezing water, which is defined as the water not frozen even when the membrane is cooled down below -20°C , and is assumed as the water strongly interacting with H^+ and $-\text{SO}_3^-$ sites, does not increase much. The result implies that channel volume and unbound water are critical factors for H^+ conduction, together with $t_{\text{H}_2\text{O}}$ [60,61]. Design of a high H^+ conducting PEM is to be accomplished by tailoring main chain and side chain units and by partial cross-linking, thus controlling the ionic channel structures [60]. However, in order to achieve higher performance membranes,

Table 2.4. Characteristic properties of perfluorinated ionomer membranes in fully hydrated state

Membrane	PFSI A	PFSI B1	PFSI B2
IEC ^a /meq g ⁻¹	0.91	0.91	1.1
Thickness (wet state)/ μm	220	205	150
Water content ^b / $n\text{H}_2\text{O}$ ($n\text{SO}_3^-$) ⁻¹	20.8	19.1	23.6
Nonfreezing water ^c / $n\text{H}_2\text{O}$ ($n\text{SO}_3^-$) ⁻¹	12.5–13.1	11.4–11.9	14.7–15.3
Ratio of nonfreezing water	0.61	0.61	0.63
H ⁺ conductivity ^d $\kappa/\text{S cm}^{-1}$	0.15	0.14	0.19
Activation energy of H ⁺ conduction $E_a(\text{H}^+)/\text{kJ mol}^{-1}$	8.7	8.9	7.6
H ₂ O diffusion coefficient ^e $D_{\text{H}_2\text{O}}/\text{m}^2 \text{s}^{-1}$	7.1×10^{-10}	5.7×10^{-10}	8.6×10^{-10}
Activation energy of H ₂ O transport $E_a(\text{H}_2\text{O})/\text{kJ mol}^{-1}$	20.0	19.6	18.8
Water transference coefficient ^f $t_{\text{H}_2\text{O}}$	3.11	2.96	3.21

^aMole of SO_3^- per gram of dry membrane^bNumber of moles of H_2O per mole of SO_3^- ^cNumber of moles of H_2O per mole of SO_3^- that does not freeze down to -20°C (determined from DSC curves [61])^dDetermined by AC impedance method at 25°C [60]^eDetermined by PG-NMR method at 30°C [61]^fNumber of moles of H_2O dragged per mole of H^+ (determined by streaming potential method at 25°C [60])

for example high temperature H^+ conducting polymer electrolytes where no H_2O may participate, some biomimetic concepts should be applied to give a solution. A model would be the H^+ -conducting pathway in the cell membrane, in which a special structure for H^+ hopping conduction should play a role.

2.6 Summary

Charge transport (CT) by or between redox molecules in a heterogeneous phase have been described. Depending on the materials and systems, various methodologies and theories have been adopted to analyze CT processes. CT is classified mainly into two categories, one is charge propagation in a matrix that is of importance in electronic and energy conversion devices, and the other is a single-step charge transfer between molecules important in biological and its mimetic systems as well as in fundamental redox chemistries.

The former charge propagation is a successive multistep charge transport in a matrix essential for the system to function as a practical device. Such charge propagation is often investigated by electrochemical methods. A single-step charge (often electron) transfer between two molecules is a key process in biological activities and also in chemical reactions. This electron-transfer event is often studied by a laser flash photolysis or by utilizing other photoexcited state phenomena since the process is often very rapid, but electrochemical measurements are of course a powerful tool for this purpose. A successive electron transfer between different redox molecules resulting in multi-gear cycles plays a key role in biological activities. Well-designed and sophisticated multi-gear charge transfer cycles utilizing functional molecules would definitely promise us innovative energy-conversion devices capable of resolving the big issue of global warming threatening our civilization now.

Controlling the charge transfer in macrocycles and other metal complexes is the major task in order to improve the rate of energy conversion in fuel cell reactions. This should be achieved by designing ligands that mediate an efficient electron transfer between metal centers and reactants that show intrinsically different energy levels. The reaction mechanism and rate-determining step should change depending on the ligand structure, which can be evaluated by redox potentials of the complexes or Tafel slopes in the polarization curves. Proton transport is also an important topic in relation to biological membranes and fuel cell electrolytes. Elucidation of detailed mechanism and its application in membrane designing would give broad range of possibilities in accomplishing materials based on a biomimetic concept.

References

1. C. Nicolini, *Biophysics of Electron Transfer and Molecular Bioelectronics* (Plenum, New York, 1998)
2. M. Graetzel, K. Kalyanasundaram, *Curr. Sci.* **66**, 706 (1994)
3. G.J. Meyer, *Molecular Level Artificial Photosynthetic Materials Progress in Inorganic Chemistry* (Wiley-Interscience, New York, 1997)
4. M. Yagi, M. Kaneko, *Adv. Polym. Sci.* **199**, 143 (2006)
5. M. Yagi, M. Kaneko, *Chem. Rev.* **101**, 21 (2001)
6. T. Abe, M. Kaneko, *Prog. Polym. Sci.* **28**, 1441 (2003)
7. M. Kaneko, in *Metal Complexes and Metals in Macromolecules* chap. 14, ed. by D. Woehrle, A.D. Pomogailo (Wiley-VCH, Weinheim, 2006)
8. H.J. Dahms, *J. Phys. Chem.* **72**, 362 (1968)
9. I. Ruff, J. Friedlich, *J. Phys. Chem.* **75**, 3297 (1971)
10. C.P. Andrieux, J.M. Saveant, *J. Electroanal. Chem.* **11**, 377 (1980)
11. D.N. Blauch, J.M. Saveant, *J. Am. Chem. Soc.* **114**, 3323 (1992)
12. J. Zhang, F. Zhao, M. Kaneko, *J. Porphyrins Phthalocyanines* **3**, 1 (1999)
13. F. Zhao, J. Zhang, T. Abe, M. Kaneko, *J. Porphyrins Phthalocyanines* **3**, 238 (1999)
14. M.J. Therien, M. Selman, H.B. Gray, *J. Am. Chem. Soc.* **112**, 2420 (1990)

15. D.N. Beratan, J.N. Onuchic, J.N. Betts, B.E. Bowler, H.B. Gray, *J. Am. Chem. Soc.* **112**, 7915 (1990)
16. R.A. Marcus, *J. Chem. Phys.* **24**, 966 (1955); **43**, 679 (1956)
17. O. Stern, M. Volmer, *Phys. Z.* **20**, 183 (1919)
18. N.J. Turro, *Modern Molecular Photochemistry* (Benjamin/Cummings, Menlo Park, 1978)
19. J. Perrin, *Comp. Rend. Acad. Sci. Paris* **184**, 1097 (1924); **178**, 1978 (1927)
20. K. Nagai, N. Takamiya, M. Kaneko, *Macromol. Chem. Phys.* **197**, 2983 (1996)
21. K. Nagai, N. Tsukamoto, N. Takamiya, M. Kaneko, *J. Phys. Chem.* **99**, 6648 (1995)
22. T. Abe, T. Ohshima, K. Nagai, S. Ishikawa, M. Kaneko, *React. Funct. Polym.* **37**, 133 (1998)
23. E. Leiva, S. Sánchez, in *Handbook of Fuel Cells – Fundamentals, Technology and Applications* vol. 2, chap. 12, ed. by W. Vielstich, H.A. Gasteiger, A. Lamm (Wiley, Chichester, 2003)
24. R.A. Marcus, *J. Electroanal. Chem.* **483**, 2 (2000)
25. J. Koryta, J. Dvořák, L. Kavan, *Principles of Electrochemistry* chap. 5 (Wiley, Chichester, 1987)
26. S. Larsson, *J. Chem. Soc. Faraday Trans.* **2**, 1375 (1983)
27. P.F. Barbara, T.J. Meyer, M.A. Ratner, *J. Phys. Chem.* **100**, 13148 (1996)
28. S. Roth, in *Hopping Transport in Solids*, chap. 11, ed. by M. Pollak, B. Shklovskii (Elsevier, Amsterdam, 1991)
29. L. Stryer, *Biochemistry* (W. H. Freeman, San Francisco, 1975)
30. A.J. Bard, L.R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, chap. 3 (Wiley, New York, 1980)
31. R.W. Gurney, *Proc. Roy. Soc.* **A134**, 137 (1931)
32. J.E.B. Randles, *Trans. Faraday Soc.* **48**, 828 (1952)
33. H. Gerischer, *Z. Phys. Chem. NF* **26**, 223, 325 (1960)
34. V.G. Levich, in *Physical Chemistry: An Advanced Treatise*, vol. IXB, chap. 12, ed. by H. Eyring, D. Henderson, W. Jost (Academic Press, New York, 1970)
35. J. Goodisman, *Electrochemistry: Theoretical Foundations* (Wiley, New York, 1987)
36. A.J. Appleby, in *Modern Aspects of Electrochemistry*, vol. 9, chap. 5 ed. by B.E. Conway, M. Bockris JO' (Plenum, New York, 1974)
37. N.S. Hush, *J. Electroanal. Chem.* **460**, 5 (1999)
38. C.A. Coulson, *Valence*, chap. 4 (Clarendon Press, Oxford, 1961)
39. J.H. Zagal, *Coord. Chem. Rev.* **119**, 89 (1992)
40. J.A.R. van Veen, J.F. van Baar, C.J. Kroese, J.G.F. Coolegem, N. de Wit, H.A. Colijn, *Ber. Bunsenges. Phys. Chem.* **85**, 693 (1981)
41. J. Zagal, P. Bindra, E. Yeager, *J. Electrochem. Soc.* **127**, 1506 (1980)
42. F. Beck, *J. Appl. Electrochem.* **7**, 239 (1977)
43. A.J. Appleby, M. Savy, *Electrochim. Acta* **22**, 1315 (1977)
44. J. Zagal, R.K. Sen, E. Yeager, *J. Electroanal. Chem.* **83**, 207 (1977)
45. C. Shi, F.C. Anson, *Electrochim. Acta* **39**, 1613 (1994)
46. E. Claude, T. Addou, J.M. Latour, P. Aldebert, *J. Appl. Electrochem.* **28**, 57 (1997)
47. O.E. Mouahid, C. Coutanceau, E.M. Belgsir, P. Crouigneau, J.M. Léger, C. Lamy, *J. Electroanal. Chem.* **426**, 117 (1997)
48. M.R. Tarasevich, K.A. Radyushkina, G.V. Zhutavaeva, *Russian J. Electrochem.* **40**, 1174 (2004)

49. S. Baranton, C. Coutanceau, E. Garnier, J.M. Léger, J. Electroanal. Chem. **590**, 100 (2006)
50. P. Mitchell, Nature **191**, 144 (1961)
51. R. Pethig, in *Modern Bioelectrochemistry*, chap.7, ed. by F. Gutmann, H. Keyzer (Plenum Press, New York, 1986)
52. S. Ohki, in *Comprehensive Treatise of Electrochemistry*, vol. 10, chap. 1, ed. by S. Srinivasan, YuA. Chizmadzhev, M. Bockris JO', B.E. Conway, E. Yeager (Plenum Press, New York, 1985)
53. K.S. Førland, T. Førland, S. Kielstrup-Ratkje, *Irreversible Thermodynamics*, chap. 10 (Wiley, Chichester, 1988)
54. H. Kita, T. Kurisu, J. Res. Inst. Catalysis, Hokkaido Univ. **21**, 200 (1973)
55. J. Horiuti, in *Physical Chemistry An Advanced Treatise*, vol. IXB, chap. 6, ed. by H. Eyring, D. Henderson, W. Jost (Academic Press, New York, 1970)
56. M.W. Breiter, in *Handbook of Fuel Cells – Fundamentals, Technology and Applications*, vol. 2, chap. 25, ed by W. Vielstich, H.A. Gasteiger, A. Lamm (Wiley, Chichester, 2003)
57. K.D. Kreuer, S.J. Paddison, E. Spohr, M. Schuster, Chem. Rev. **104**, 4637 (2004)
58. K.A. Mauritz, R.B. Moore, Chem. Rev. **104**, 4535 (2004)
59. *T.D. Gierke, W.Y. Hsu, (1982) In: Eisenberg A, Yeager HL (eds) Perfluorinated Ionomer Membranes. ACS Symposium Series 180, Am. Chem. Soc., Washington DC, chap. 13
60. T. Okada, M. Saito, K. Hayamizu, in *Electroanalytical Chemistry Research Developments*, ed by P.N. Jiang chap. 2 (Nova Science, New York, 2007)
61. M. Saito, K. Hayamizu, T. Okada, J. Phys. Chem. B **109**, 3112 (2005)

Electrochemical Methods for Catalyst Evaluation in Fuel Cells and Solar Cells

T. Okada and M. Kaneko

Abstract In this chapter, electrochemical methods for the catalyst research for fuel cells, charge transport in electrode reaction, and heterogeneous charge transport are presented and discussed with some examples of data measurements and analyses. In fuel cell research and development, the most utilized tools for the oxygen reduction reaction (cathode reaction) are the rotating disk and rotating ring-disk electrodes in a three-compartment electrochemical cell. Cyclic voltammograms and linear-sweep voltammetry are often used for the mechanism discussion. For further experiments the half-cell (model fuel cell), a single fuel cell or fuel cell stack experiments are carried out in order to see the catalyst performances in a gas-phase condition. The advantages or disadvantages of these methods are discussed. The evaluation methods for the anode catalysts are also presented. In artificial photosynthesis and photoelectrochemical processes the measurement techniques involve heterogeneous charge transport analysis by in situ spectroelectrochemical methods and impedance spectroscopy. In solar cells the electrochemical impedance spectroscopy combined with photoelectrochemical cells provide powerful tools for kinetic analyses.

3.1 Introduction

Electrochemical measuring techniques are important tools for the evaluation and mechanism elucidation of the catalyst reactions and underlying charge transport processes. Since the commercial systems such as solar cells and fuel cells are very complicated ones, simplified electrochemical methods for lab-scale testing are very useful and reliable for efficiently pursuing the research and development of such energy conversion systems.

In electrochemical measurements, current (reaction rate) and potential (driving force) of electrodes are directly controlled or monitored in time series so that it is easy to study reaction kinetics at a given condition [1]. Steady-state voltammograms, potential sweep methods with or without hydrodynamic control in the electrolyte, are widely used methods for investigation and screening of fuel cell catalysts. Especially rotating ring-disk electrodes and cyclic voltammograms are important tools, which are discussed in Sect. 3.2.

Scale-up investigations from elementary electrochemical systems to practical fuel cell testing systems are described.

Charge transport mediated by metal complexes in heterogeneous media and reactions at electrode | electrolyte interface are important topics in solar cells and artificial photosynthesis. Charge transport parameters, conductivity, and capacitance measurements by transient techniques and AC impedance spectroscopy are discussed in Sect. 3.3. Simple electrochemical methods appear inadequate for a quantitative measurement of reactants and products, and spectroscopic monitoring techniques prove as important tools for this purpose. Such techniques will be briefly mentioned here.

3.2 Electrochemical Measuring System for Catalyst Research in Fuel Cells

Fuel cell, a device for direct conversion of chemical energy into electrical energy, potentially produces very high efficiency (more than 80% as compared to 30% for internal combustion engines) [2]. In commercial systems, however, the efficiency drops to 40–60% due to limitations by slow reaction and diffusion rates of reactants. Efficient catalysts are indispensable for realizing high performance fuel cell systems. In order to facilitate the innovative catalyst research, this section shows methods of direct and useful electrochemical testing of catalyst materials.

3.2.1 Reference Electrode

The first step of catalyst testing in fuel cell electrodes will be practiced by measuring the current–potential relations that are performed using electrochemical equipments and test cells. The potential of electrodes E determines the driving force of the reaction, which is related to the Gibbs free energy of reaction by the following formula.

$$E = -\Delta G/nF \quad (3.1)$$

Thus the definition of E is important for electrochemical researches. Since there is no absolute standard for the “potential zero,” a conventional standard of zero potential is defined in which “an inert electric conductor (platinum) immersed in a solution of H^+ activity 1 and contacting with H_2 gas of activity 1 takes $E = 0$ at every temperature” [3].

In accordance with this definition, standard hydrogen electrode (SHE), or normal hydrogen electrode (NHE), is used as a reference electrode from which all the potentials of catalyst electrodes are measured. In some cases non-polarizable electrodes, which keep constant potentials determined by thermodynamic equilibrium reactions at electrode | electrolyte interface are used for convenience in place of SHE (reversible electrode of the second kind [3,4]).

Table 3.1. Standard electrode potentials

Electrode	Temperature/°C	Electrode potential/V
Pt H ₂ (<i>a</i> = 1) H ⁺ (<i>a</i> = 1)	At all temperature	0
Ag AgCl sat. KCl	25	0.1970
Hg Hg ₂ Cl ₂ sat. KCl	25	0.2412
Hg Hg ₂ Cl ₂ 1M KCl	25	0.2801
Hg Hg ₂ SO ₄ sat. K ₂ SO ₄	25	0.6400
Hg HgO 0.1 M NaOH	25	0.9260

Table 3.1 presents some of the popular reference electrodes used for this purpose [3–5]. The choice of such reference electrodes is determined depending on experimental conditions, e.g., solution pH, ease of installation into the electrochemical systems. The advantage of using such alternative reference electrodes is compactness, fast response, and stable potentials of known E values in reference to SHE.

Because leakage of electrolytes from reference electrodes is very crucial for pure electrochemical systems containing catalyst electrodes that are very sensitive to impurity materials such as chloride ions, reference electrodes using H₂ gas are recommended for fuel cell researches. Reversible hydrogen electrode (RHE) is often used in electrochemical and fuel cell testing, the potential of which is defined as that of “Pt electrode immersed in the same solution and contacting with H₂ gas of activity 1 at every temperature.” The potential of RHE in reference to SHE is expressed as follows.

$$\text{RHE} = \text{SHE} - \frac{RT}{F} \text{pH} \quad (3.2)$$

Figure 3.1 shows some examples of RHE. For small-scale systems where the space of reference electrodes is limited, miniature-type RHE are used [6]. Some gas-tight types are designed so that they need no H₂ gas lines. Dynamic hydrogen electrode (DHE) is fabricated to utilize the hydrogen-evolving cathode as the Pt|H₂, H⁺ electrode by applying electricity from outer source through an auxiliary electrode [7]. In order to attain stable Pt|H₂, H⁺ potential, the current should be chosen so that the potential becomes as close as that of RHE.

3.2.2 Rotating Ring-Disk Electrode

In screening new materials as electrocatalysts for fuel cells, it is important that the best candidates are selected from huge number of samples synthesized and prepared starting from the widest spectra of concepts. The largeness of initial sample group will be a key of success in discovering the best innovative catalysts. For efficient researches, simple, easy, and less time-consuming measuring techniques are needed to evaluate large number of samples.

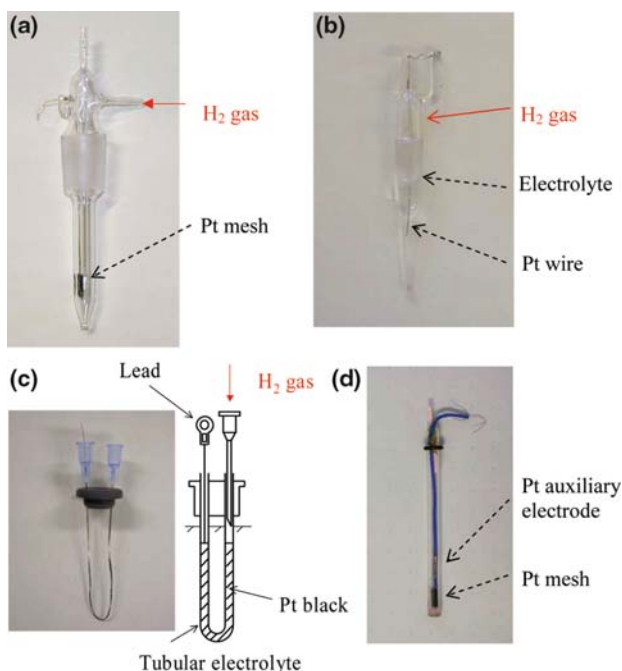


Fig. 3.1. Examples of RHE as reference electrodes for electrochemical measurements of electrocatalysts in the solution. (a) Conventional glass RHE with H_2 gas flowing through the solution in contact with Pt, (b) glass RHE with H_2 gas stored in the upper part of the sealed glass by electrolysis after the solution is filled in the vessel, (c) microtubular RHE where the gas is separated from the solution by polymer electrolyte tube, (d) glass DHE where two Pt gauze electrodes are installed and one part works as Pt/ H_2 electrode

For that reason, majority of electrochemists and catalyst researchers use rotating disk electrode (RDE) or rotating ring-disk electrode (RRDE) to start the experiments with only a few milligrams of test samples [1, 8]. The apparatus is shown in Fig. 3.2. The catalyst sample is loaded on a disk part of the RRDE (RDE) electrode, and the electrode is immersed downward in acid (or alkaline) electrolyte solution in a 3-electrode electrochemical glass cell. Depending on the measuring system, the solution is deaerated with N_2 gas or bubbled with O_2 (or H_2) gas, or methanol (or other type of fuel) is dissolved in the solution. The amount of catalyst loading on the disk electrode is crucial for high utilization of catalysts, and Schmidt et al. recommend ultra-low loading (about $30 \mu\text{g}(\text{Pt}) \text{ cm}^{-2}$ catalyst per apparent area of the surface) from catalyst dispersion in pure water and then covering with thin Nafion film from diluted solution as a binder [9]. Watanabe et al. report that the mass transport through Nafion film comes into effect for large film thickness, and recommend less than $0.2 \mu\text{m}$ thickness in order to minimize the need of mass transport correction in the kinetic current measurements [10].

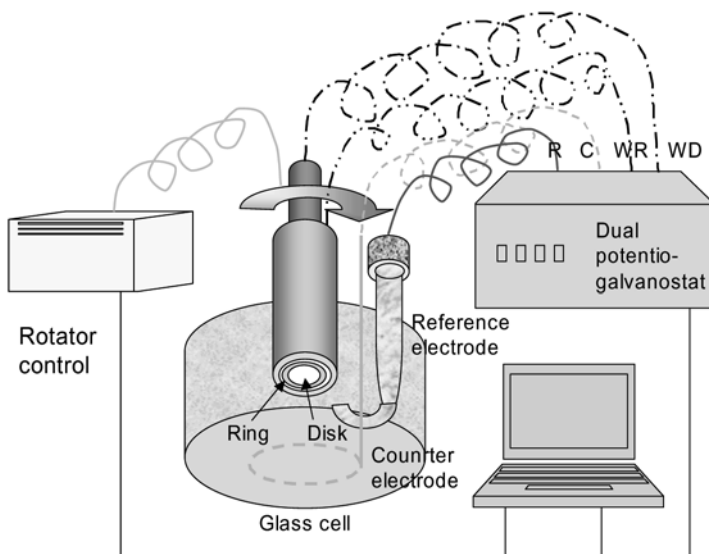


Fig. 3.2. Sketch of a rotating ring-disk electrode apparatus

A steady hydrodynamic condition is realized by revolving the electrode at fixed rotation rates. The solution at the vicinity of the electrode makes a whirlpool motion, lifted upward, and then spread to radial direction at the spinning electrode surface. This motion forms a hydrodynamic boundary layer of electrolyte solution, the thickness of which is expressed as follows [1,8],

$$y_h = 3.6 \left(\frac{\nu}{\omega} \right)^{1/2} \quad (3.3)$$

using the kinematic viscosity $\nu(\text{cm}^2 \text{s}^{-1})$ of the solution and rotation speed ω (rad s^{-1}) of the electrode ($\omega = 2\pi f$, f in revolution per second). y_h is estimated to be 500–220 μm , depending on the rotation rate of 500–2,500 rpm (rotation per minute). When a substance O diffuses normal to the electrode and reacts at the surface, a concentration profile grows in this hydrodynamic boundary layer [1]. Using the steady-state convective-diffusion equation, the diffusion layer is defined with thickness δ_O . This gives

$$\delta_O = 1.61 D_O^{1/3} \omega^{-1/2} \nu^{1/6} \quad (3.4)$$

where D_O is diffusion coefficient of species O . $\delta_O \approx 0.5(D_O/\nu)^{1/3} y_h$ and is about 5% of the hydrodynamic boundary layer [1,8]. When the current is limited by diffusion of O and its concentration at the electrode surface is 0, the Levich equation for the limiting current results in [1,8].

$$i_l = 0.620 n F A D_O^{2/3} \omega^{1/2} \nu^{-1/6} [O]_b \quad (3.5)$$

where n is number of electrons transferred and A is electrode surface area (cm^2). i_l is proportional to the bulk concentration $[O]_b$ and $\omega^{1/2}$.

In many cases the current is limited not only by the diffusion of O but also by the slow charge transfer process at the electrode surface. The current first rises linearly with $\omega^{1/2}$, but then levels off and reaches the limiting kinetic current i_k .

$$i_k = nFAk_f(E)[O]_b \quad (3.6)$$

In this case the current is more generally expressed by the following equation (Koutecky–Levich equation; see Appendix A).

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_{l,c}} = \frac{1}{i_k} + \frac{1}{0.620nFAD_O^{2/3}\omega^{1/2}\nu^{-1/6}[O]_b} \quad (3.7)$$

Note that this is in close resemblance to Michaelis–Menten formula (2.17). Plot of inverse of current against inverse of $\omega^{1/2}$ gives a straight line with the intercept $1/i_k$ and the slope $0.620nFAD_O^{2/3}\nu^{-1/6}[O]_b$ (Koutecky–Levich plot). This plot is mostly used in the study of oxygen reduction reaction (ORR), and at a given electrode potential the charge transfer rate and n are evaluated from the RDE measurement. The example of such plots is shown in Fig. 3.3 [11].

Rotating ring-disk electrode (RRDE) has additional ring electrode surrounding the disk electrode. The reaction product produced at the disk is swept away from the spinning disk by centrifugal force, reaches and reacts at the ring under fixed potential. With fixed geometry of the disk and the

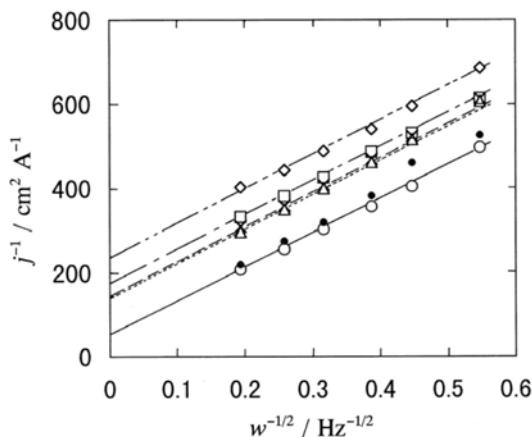


Fig. 3.3. Koutecky–Levich plots for ORR at 0.2 V vs. SCE on bare and the Nafion[®]-film-covered platinum in various solutions saturated with O_2 gas. The intercept (i_k^{-1}) shows that i_k decreases on changing from bare platinum (*circle*) to Nafion[®]-film-covered platinum in 0.05 M H_2SO_4 (*cross*). For Nafion[®]-film-covered platinum in 0.05 M H_2SO_4 + 0.0005 M $NiSO_4$, i_k decays with time 2 h (*triangle*), 22.5 (*square*), and 95 h (*diamond*) ([11], copyright Royal Society of Chemistry)

ring, the ratio of the disk current i_D and the ring current i_R , takes a constant value of collection efficiency $N = |i_R/i_D|$ [12]. Using this unique value the yield of H_2O formation from O_2 and the number of electrons n transferred to O_2 in oxygen reduction reaction (ORR) are obtained by RRDE measurement (Appendix B).

$$\%H_2O = 100 \frac{i_D - i_R/N}{i_D + i_R/N} \quad (3.8)$$

$$n = 2 \left(1 + \frac{\%H_2O}{100} \right) = \frac{4i_D}{i_D + i_R/N} \quad (3.9)$$

Thus RRDE is a very useful tool for the kinetic study of ORR.

A more sophisticated plot was proposed by Wroblowa et al. for the analysis of the reaction pathway of ORR [13]. They obtained diagnostic criteria for a mechanistic study of ORR on a rotating ring-disk electrode. The disk-to-ring current ratio $i_D N/i_R$ vs. $\omega^{-1/2}$ plot gives a criterion about the O_2 reduction path, and when the intercept J of the plot is equal to 1, the direct 4-electron reduction from O_2 to H_2O does not proceed and only H_2O_2 path occurs (Fig.3.4). Especially when the slope is 0, H_2O_2 is not further reduced to H_2O . When J is larger than 1, two cases exist: (1) no 4-electron reduction occurs but H_2O_2 is reduced further to H_2O (2 + 2-electron reduction), or (2) both 4-electron reduction and 2 + 2-electron reduction occur.

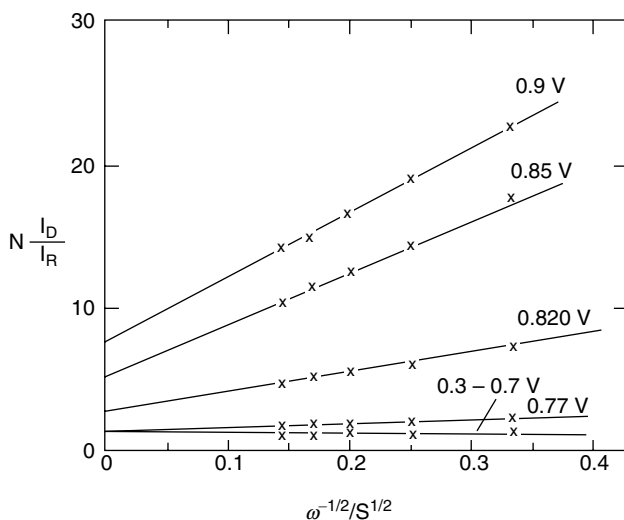


Fig. 3.4. $i_D N/i_R$ vs. $\omega^{-1/2}$ plots of Au disk in alkaline solution ([13], copyright Elsevier)

3.2.3 Gas Electrodes of Half-Cell Configuration

Although RRDE and other electrochemical methods in the liquid phase are convenient and fast for screening, tests with gas electrodes are more recommended to assess the catalysts performance in more real and practical fuel cell conditions. Several types of half-cells are designed for this purpose. One primitive approach is to use the fuel cell itself and change the feeding gas conditions. The gas compartment in study is fixed while the other compartment is arranged to become the RHE reference electrode and at the same time the counter electrode by flowing H_2 gas. This half-cell mode gives easy conversion between a single cell and a half-cell mode in the same apparatus, just by switching the gas stream [14]. Figure 3.5 illustrates the example of this half-cell mode, where the cathode of small-scale microtubular direct methanol fuel cell (DMFC) [15] is changed to H_2 electrode and the anode performance is studied.

A counter electrode may be in the liquid electrolyte that contacts the other side of the gas-flowing electrode across the polymer electrolyte membrane [16]. The gas-flowing electrode is a model of one side of the fuel cell electrodes. Figure 3.6 illustrates such a half-cell, where the gas stream contacts the working electrode while counter and reference electrodes are immersed in liquid electrolyte that is thermostated by a heater and a controller.

For the purpose of devising a rapid half-cell technique that could mimic the complete fuel cell, a simple half-cell based on RDE was reported by TamizhMani et al [17]. The catalysts blended with Nafion solution were loaded

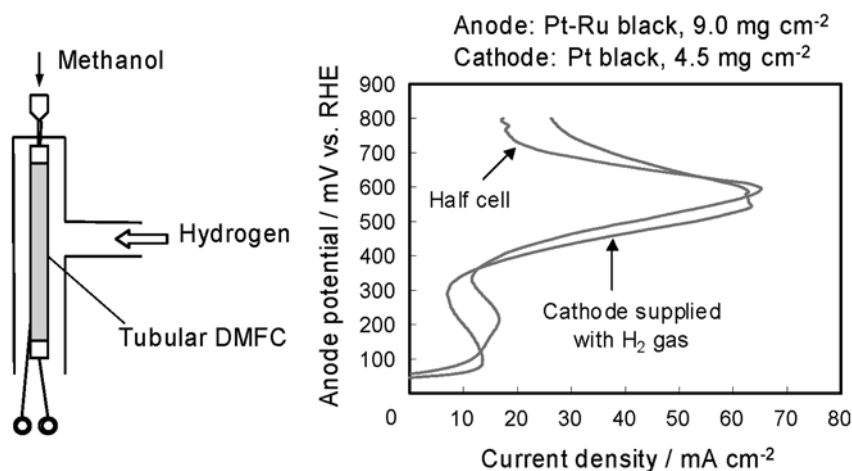


Fig. 3.5. Polarization curves obtained by switching the cathode air surrounding the microtube to H_2 gas, thus enabling a half-cell measurements of the methanol electrode (anode). The figure also illustrates the other type of half-cell, where tubular DMFC is immersed in 0.5 M H_2SO_4 , and anode polarization is measured by 3-electrode system

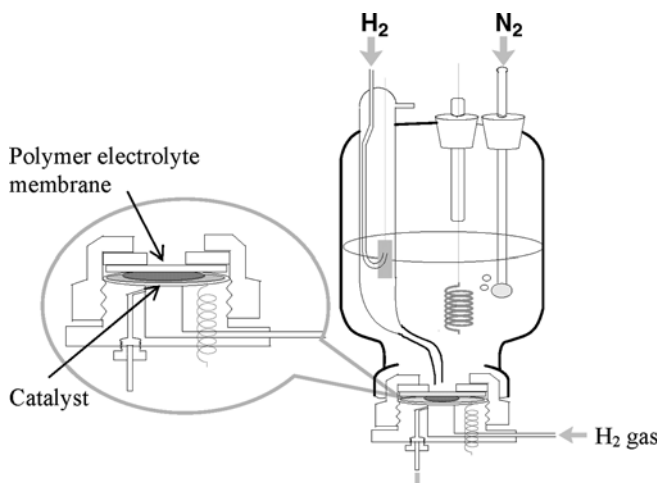


Fig. 3.6. A half-cell for the gas reactions on catalyst layer prepared in contact with polymer electrolyte membrane

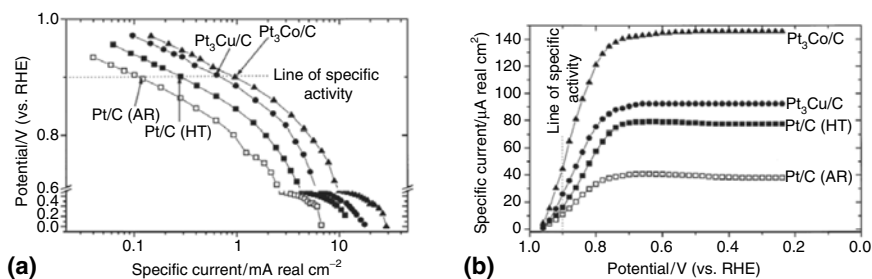


Fig. 3.7. Comparison of (a) H_2/O_2 single fuel cell and (b) RDE (O_2 saturated HF) performances of Pt/C and Pt-alloy/C ([17], copyright Elsevier)

on glassy carbon RDE, with loading $0.165 \text{ mg(Pt)} \text{ cm}^{-2}$. ORR polarization curves were measured in oxygen saturated H_2SO_4 or HF at a disk rotation speed of 1,500 rpm and a potential scan rate of 10 mV s^{-1} . Figure 3.7 shows comparison of RDE and single fuel cell test results where the kinetic current at various catalyst samples was investigated. In H_2SO_4 the polarization curves overlapped in the kinetic region due to the anion adsorption on Pt that interferes with oxygen adsorption, but in non-adsorbing HF the characteristic kinetic currents were discriminated, which correlated with the performances in fuel cells.

A partially immersed rotating vertical electrode was used as a model of gas diffusion electrode [18]. Figure 3.8 shows a sketch of the apparatus where the electrochemical cell was filled with liquid electrolyte in the lower part and the gas was flown in the upper part. The catalyst was loaded on the vertical electrode in contact with the gas and the electrolyte in the upper and

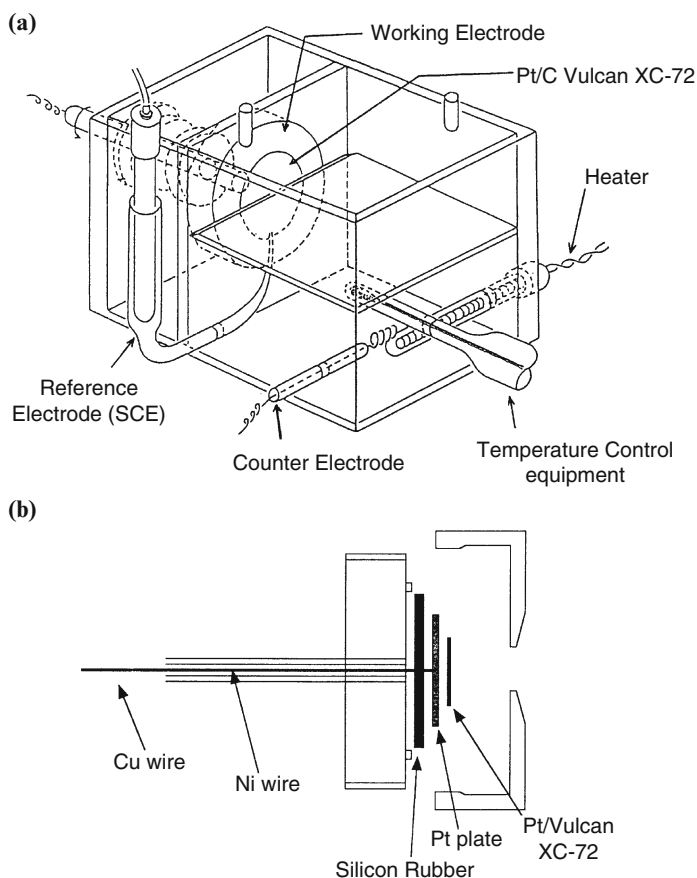


Fig. 3.8. Sketch of partially immersed rotating vertical electrode apparatus (a) and cross-sectional view of the specimen holder (b) ([18], copyright The Electrochemical Society of Japan)

lower part, respectively. Figure 3.9 compares the polarization performances of various catalysts measured in RDE, model half-cell, and fuel cell.

3.2.4 Fuel Cell Test Station

After best candidates of catalysts are screened by rapid and simple electrochemical techniques, they should ultimately be tested in a real fuel cell condition. Figure 3.10 illustrates such a fuel cell testing apparatus. The system consists of three parts: (1) gas supply (humidification) lines into the cell, and gas outlet (water condenser) lines out of the cell; (2) single (or stack) fuel cell; and (3) electrochemical measuring apparatus. A single fuel cell is made of a membrane electrode assembly (MEA) that is a composite of two (anode and

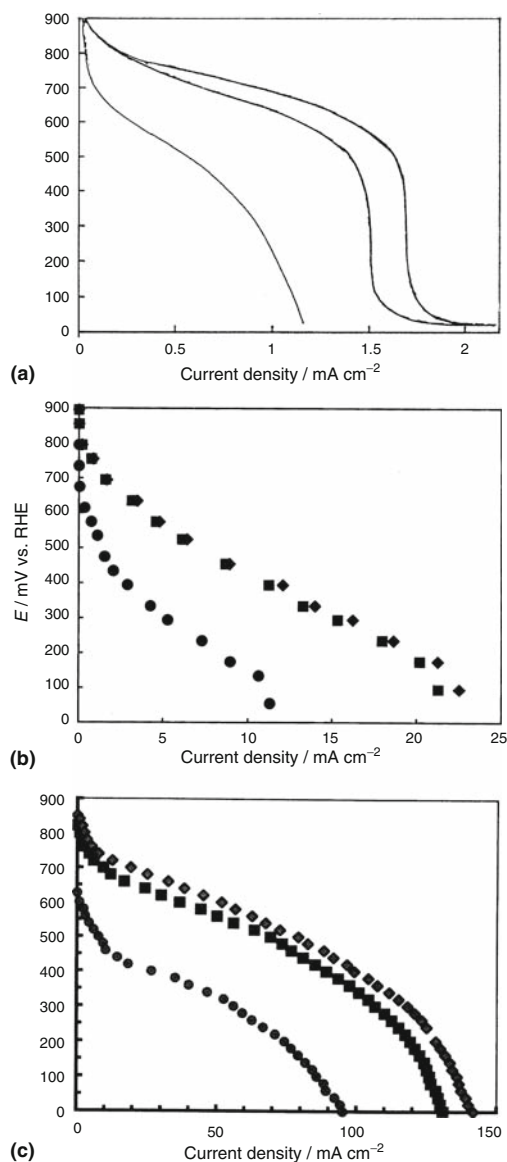


Fig. 3.9. Comparison of polarization curves for the composite catalysts Pt-(CoTCPP + CoTMPyP)/C (100/0, 60/40 and 0/100 from top to bottom) obtained by (a) rotating disk electrode (300 rpm) in 0.05 M H_2SO_4 at 25 °C at 10 mV s^{-1} , (b) partially immersed rotating vertical electrode (3.56 rpm) in 0.05 M H_2SO_4 at 30 °C at 0.8 mV s^{-1} and (c) single fuel cell H_2/O_2 at 70 °C. Catalysts were prepared from $\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$ and CoTCPP + CoTMPyP with mixing ratio 100/0, 60/40 and 0/100, supported on graphite powder (20 wt%) and heat-treated in Ar at 600 °C for 2 h. TCPP: tetrakis(4-carboxyphenyl)porphyrin, TMPyP: tetrakis(1-methyl-4-pyridyl)porphyrin ([18], copyright The Electrochemical Society of Japan)

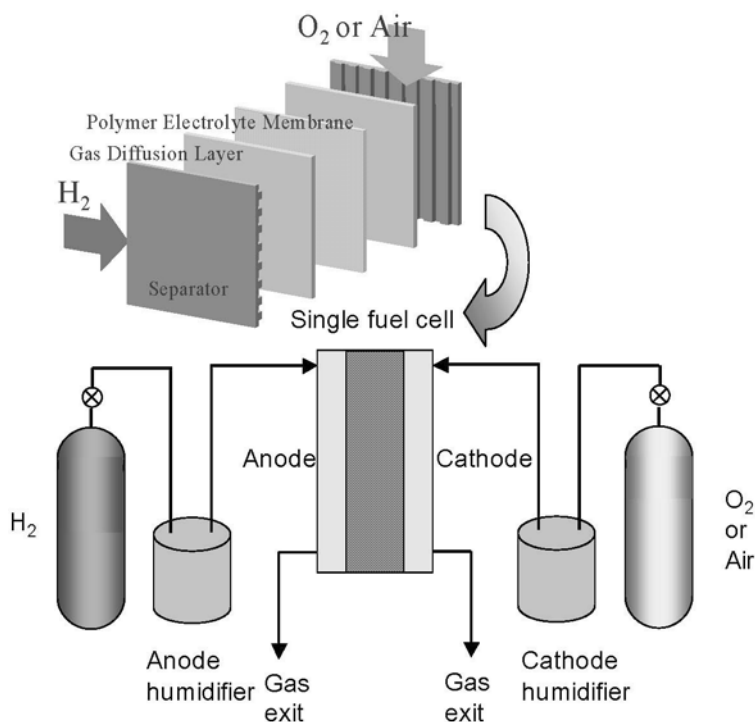


Fig. 3.10. Single fuel cell system

cathode) catalyst layers (catalyst powder pasted on porous carbon paper or cloth) hot-pressed on both sides of the polymer electrolyte membrane. This MEA is sandwiched between a pair of carbon blocks, in the inside of which gas-flow channels are arranged to distribute the anode and cathode gases. The end plates fix the whole cell, allowing the electric current flow through the cell.

MEA fabrication including membrane cleaning, gas diffusion layer (GDL) preparation from carbon paper, catalyst loading, and hot pressing are presented in publications [19–22]. Typically, catalyst powder is mixed with 5% Nafion[®] solution and ethanol in 3:50:3 ratio and the mixture is vigorously stirred until viscous ink is obtained. This ink is pasted uniformly on a wet-proofed carbon paper (e.g. TORAY TGP-H-090), which is prepared by immersing in PTFE solution (polyFlon[®]) followed by drying in air at 350 °C for 30 min (3.5 mg (PTFE) cm⁻²). The Nafion[®] 115 polymer electrolyte membrane is cleansed by successive immersion in 3% H_2O_2 solution at 80 °C, deionized hot water, hot 1 M H_2SO_4 , and deionized hot water, each for 1 h. Two sets of catalyst loaded carbon paper (anode and cathode) are hot-pressed on both sides of the pretreated membrane at 100 kg cm⁻², 135 °C for 3 min [23].

Electrochemical measurements are conducted after MEA is conditioned by flowing anode and cathode gases. Anode (H_2) and cathode (air or O_2) gas-flow rates are set so that H_2 and O_2 stoichiometry becomes 1.5–2 and 2.5–4, respectively. Gasses are humidified to 60–70 °C dew points. Polarization curves are obtained with Ohmic drop compensation by, for example, current interrupter method. In some cases liquid fuels such as methanol or formic acid are used in place of H_2 for direct liquid feed fuel cells. In these cases liquid fuels are injected to the anode by a peristaltic pump.

Since more practical testing conditions are preferable for the catalyst researches that should aim at the ultimate application stages, the reliability of various testing methods will follow the order: the fuel cell mode, the half-cell mode, and the electrochemical measuring cell. Unfortunately, cost and time required for sample preparation and measurement may also be in this order. These points should be taken into consideration every time a research planning is made.

3.2.5 Electrochemical Methods for Electrocatalysts

Catalyst-supported electrodes are evaluated using electrochemical techniques in a 3-electrode glass cell or in a half-cell or a fuel cell. Along with ordinary steady-state measurements like polarization curves, standard and most widely used methods are cyclic voltammograms (CVs) and linear-scanning voltammograms (LSVs). These are the dynamic analyses of the chemical, diffusional, and valence changes of reactants and catalyst surfaces, and are useful in determining kinetic factors involved in the catalytic reactions. Other specific methods are flow-through methods [8], AC impedance methods [24, 25], and microelectrode methods [26] for which the readers may refer to monographs of electrochemical methods.

LSV offers important parameters concerning the number of electrons in the reaction, transfer coefficients, diffusion coefficients of reactants, etc. The current is monitored during the anodic or cathodic linear sweep of the electrode potential (i.e., the electrode potential is controlled such as $E(t) = E_i - vt$ where v (V s^{-1}) is potential scan rate), and the peak position (potential) and intensity of the current are evaluated [1, 5]. There are two extreme cases, (1) very fast reaction kinetics is assumed $\text{O} \leftrightarrow \text{R}$, (2) the reaction proceeds only one way $\text{O} \rightarrow \text{R}$ (irreversible charge transfer).

For the case (1), the electrode potential shows reversible (Nernstian) response to the reaction species (concentration $[\text{O}]$ (M) and $[\text{R}]$ (M), for the oxidant and reductant, respectively) at the electrode surface:

$$E = \frac{RT}{nF} \ln \frac{[\text{O}]}{[\text{R}]} \quad (3.10)$$

The peak potential E_p (V) and peak current i_p (A) are expressed as follows, for the reduction reaction of O to R with planar diffusion to the electrode surface [1, 5].

$$E_p = E_{p/2} - 2.2 \frac{RT}{nF} = \frac{56.5}{n} \text{ mV (at } 25^\circ\text{C)} \quad (3.11a)$$

$$\begin{aligned} i_p &= 43.1 n^{3/2} A \left(\frac{F}{RT} \right)^{1/2} [O]_b D_O^{1/2} v^{1/2} \\ &= 269 n^{3/2} A [O]_b D_O^{1/2} v^{1/2} \text{ (at } 25^\circ\text{C)} \end{aligned} \quad (3.11b)$$

where A (cm^2) is the electrode area and D_O ($\text{cm}^2 \text{ s}^{-1}$) is diffusion coefficient of O . From the separation of peak and half-peak potentials $E_p - E_{p/2}$, the number of electrons n , and from peak current dependence on $v^{1/2}[O]_b$, D_O is estimated if n is known or vice versa.

For the case (2), the peak potential E_p and peak current i_p are expressed as follows [1, 4].

$$E_p = E^{0'} - \frac{RT}{\alpha n_\alpha F} \left[0.780 + \ln \left(\frac{D_O^{1/2}}{k^0} \right) + \ln \left(\frac{\alpha n_\alpha F v}{RT} \right)^{1/2} \right] \quad (3.12a)$$

$$E_p = E_{p/2} - 1.86 \frac{RT}{\alpha n_\alpha F} = \frac{47.7}{\alpha n_\alpha} \text{ mV (at } 25^\circ\text{C)} \quad (3.12b)$$

$$\begin{aligned} i_p &= 47.8 n A \left(\frac{\alpha n_\alpha F}{RT} \right)^{1/2} [O]_b D_O^{1/2} v^{1/2} \\ &= 299 n A (\alpha n_\alpha)^{1/2} [O]_b D_O^{1/2} v^{1/2} \text{ (at } 25^\circ\text{C)} \end{aligned} \quad (3.12c)$$

where $E^{0'}$ is formal potential, α and n_α are transfer coefficients, and the number of electrons involved in the rate-determining charge transfer reaction and k^0 (cm s^{-1}) is standard heterogeneous rate constant. An analysis of O_2 reduction at Nafion[®] film-covered Pt electrode is carried out as shown in Fig. 3.11, where parameters αn_α and $[O]_b D_O^{1/2}$ are obtained from E_p vs. $\log v$ and i_p vs. $v^{1/2}$ plots [11].

Figure 3.12 shows a set of LSV data on Pt(111) in 0.1 M NaOH with various concentrations of methanol [27]. The peak potential first shows v dependence and then tends to level off with v . The scan rate dependence of the current is first $v^{1/2}$ form but then becomes linear form. Here CH_3OH oxidation in alkaline media appears as a mixed control of mass transfer and irreversible methanol adsorption on Pt.

CV measurements are performed with the continuous potential cycling. The potential sweep is switched at time $t = \lambda$, then it carries on to the reverse direction, and this sweep is repeated in the fixed potential range. In the case of (1), the mass transfer controlled reversible reaction, the relations concerning the anodic and the cathodic peaks give [5]

$$E_{pa} - E_{pc} = 2.303 \frac{RT}{nF} = \frac{59}{n} \text{ mV (at } 25^\circ\text{C)} \quad (3.13a)$$

$$E^{0'} = (E_{pa} - E_{pc})/2 \quad (3.13b)$$

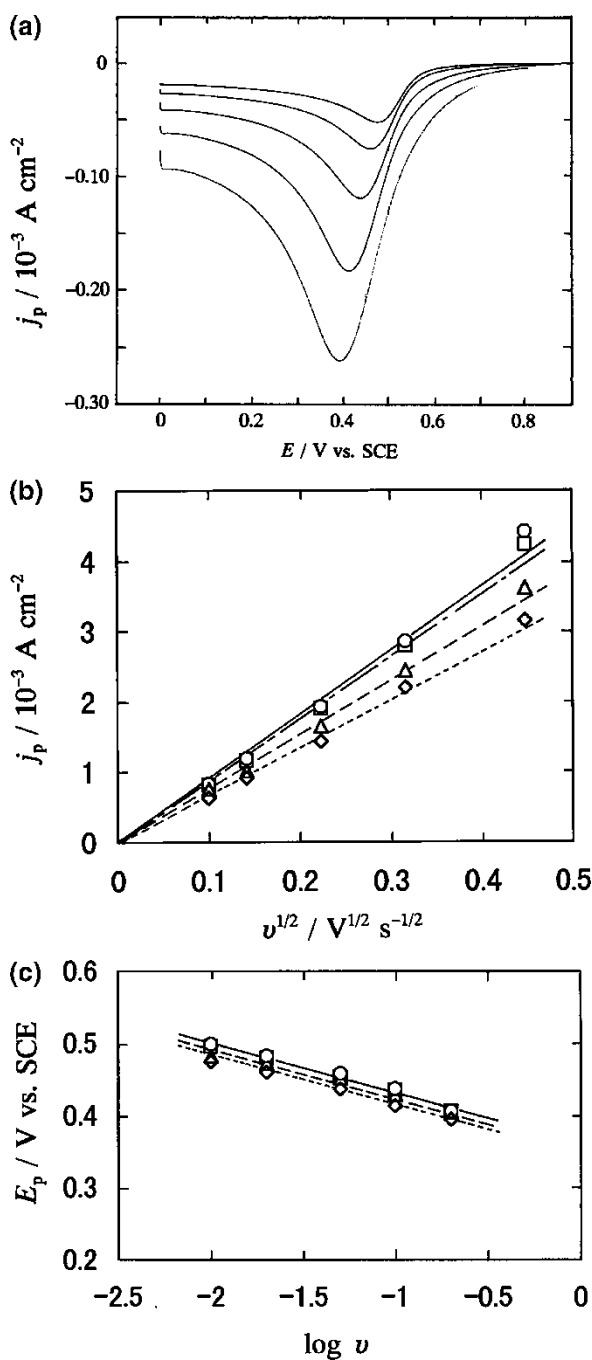


Fig. 3.11. E_p vs. $\log v$ and i_p vs. $v^{1/2}$ plots for the Nafion[®]-coated Pt RDE ([11], copyright Royal Society of Chemistry)

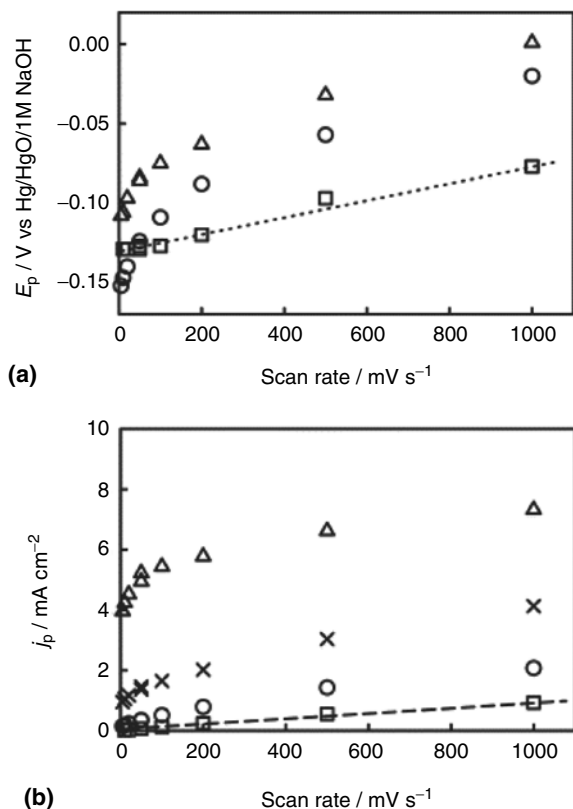


Fig. 3.12. Scan rate dependence of the peak potential (a) and peak current (b) measured for Pt(111) in 0.1 M NaOH with CH₃OH. CH₃OH concentration: 0 M (*square*), 0.005 M (*circle*), 0.025 M (*triangle*) and 0.1 M (*cross*) ([27], copyright Elsevier)

with symmetric shape in the CV curves in the forward and reverse directions ($i_{pa}/i_{pc} = 1$, if the baseline is properly corrected [5]). Equation (3.13a) is used for a diagnostic test of the Nernstian response (reaction reversibility), if the number of electrons involved n is known.

For other cases, CVs show very complicated behavior, but it should be mentioned that for the study of surface processes on catalysts where mass transfer controlled steps are not of direct interest, CV shows rather characteristic feature and the analysis provides a valuable routine tool. One example is the process of monolayer adsorption on the electrode surface. In the case of mass transfer controlled CV, the current–potential curve first goes through a peak and then reaches a nonzero current value before reversing the potential scan. In contrast to this, for the electrochemisorption process the current goes down to the zero level after the peak value. Also dependence of the peak current on the potential scan rate v is very different: in the mass transfer-controlled CV, the peak current is proportional to $v^{1/2}$, but in the

adsorption process, it is proportional to v . For the reversible Langmuir-type adsorption case, the peak potential gives v independent value [5]

$$E_{\text{pa}} = E_{\text{pc}} = E^{0'} \quad (3.14a)$$

$$i_{\text{pa}} = i_{\text{pc}} \propto v \quad (3.14b)$$

When the electrochemisorption process becomes irreversible, i_{pa} shifts positively from i_{pc} depending on the scan rate.

Hydrogen and oxygen monolayers on Pt and other noble metal electrodes are typical examples of monolayer adsorption/desorption processes. Figure 3.13 shows CV on polycrystalline Pt in H_2SO_4 , which clearly presents the relation (3.14a) and (3.14b) for hydrogen adsorption/desorption peaks while oxide formation/reduction peaks do not show a reversible feature [28]. From the area of hydrogen desorption peak or adsorption peak (C cm^{-2}) that are independent of v , true area of Pt can be calculated by using the value $210 \mu\text{C cm}^{-2}$ (Pt) [29].

A useful application of CV is practiced for the CO oxidation peak on Pt, when the catalyst surface is covered with CO as poisoning species for many of small organic molecule (SOM) oxidation reactions. Figure 3.14 depicts a

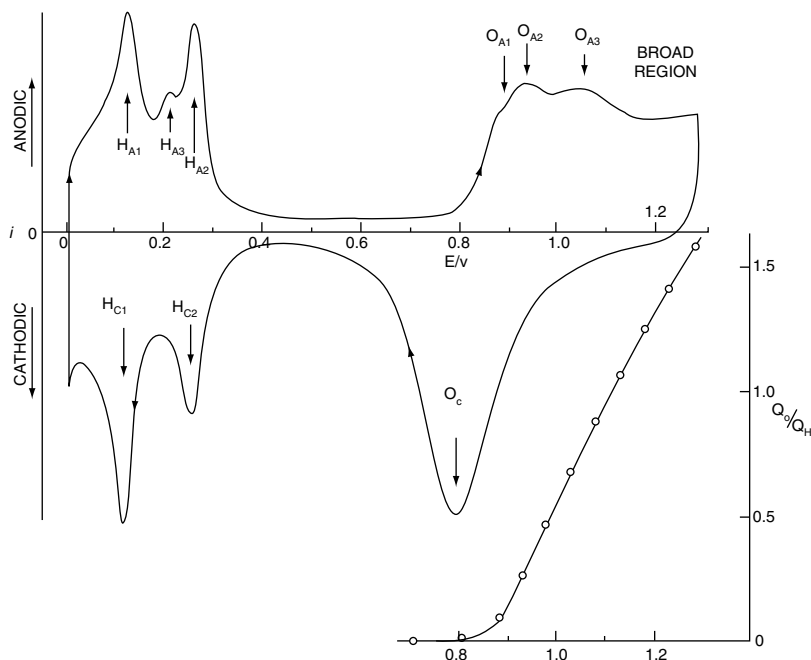


Fig. 3.13. Hydrogen adsorption/desorption peaks on Pt in 0.5 M H_2SO_4 obtained by CV at a scan rate of 100 mV s^{-1} . Also shown is the Pt oxide formation peaks and integrated charge as a function of potential ([28], copyright Elsevier)

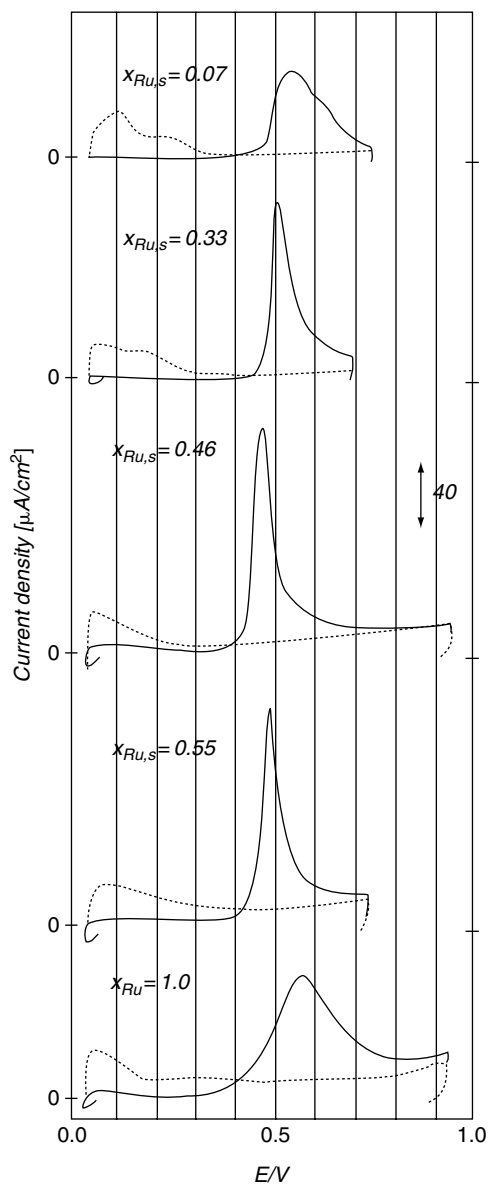


Fig. 3.14. CO stripping voltammetry of sputter-cleaned Pt–Ru alloys of various surface ratios in 0.5 M H_2SO_4 at a scan rate of 20 mV s^{-1} . The first (*solid line*) and the second (*dash-dotted line*) positive-going sweeps are depicted ([30], copyright the American Chemical Society)

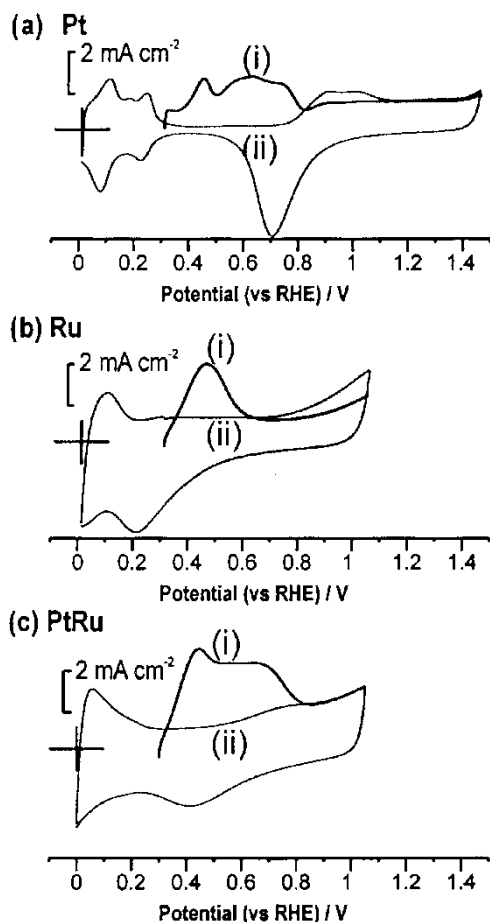


Fig. 3.15. Linear sweep stripping voltammograms of UPD Cu from the surface of Pt, Ru and Pt–Ru alloy measured in $0.1\text{ M H}_2\text{SO}_4 + 2 \times 10^{-3}\text{ M CuSO}_4$ at 10 mV s^{-1} , while Cu was adsorbed at 0.3 V for 60 s . Background scans were performed in $0.1\text{ M H}_2\text{SO}_4$ ([31], copyright the American Chemical Society)

comparison of CO stripping voltammetry on Pt–Ru alloys of various surface ratios [30]. From the peak shift, the best catalytic activity for CO oxidation is obtained with 46% Ru composition. Kucernak et al. developed a new method to probe Pt and Ru active surface areas in Pt–Ru alloys by using underpotential deposition (UPD) of Cu [31]. Figure 3.15 shows linear-sweep stripping voltammograms for Cu with which the area of metallic Ru is determined since stripping of UPD Cu occurs at 0.38 V from Ru sites and at 0.6 V from Pt sites.

For molecular catalysts such as porphyrins and phthalocyanines, characteristic CVs are often used to get knowledge about the redox potentials of metal centers surrounded by complex chelate structures. Figure 3.16 is an

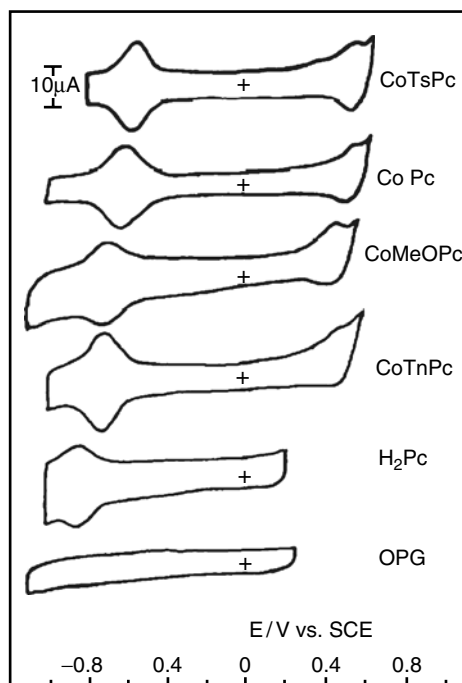


Fig. 3.16. CVs measured for various cobalt phthalocyanines adsorbed on ordinary pyrolytic graphite (OPG) in 0.1 M NaOH at 200 mV s^{-1} at 22°C , showing redox potentials of M(II)/M(III) couples ([32], copyright Elsevier)

example of such CVs measured on various metallophthalocyanines in 0.1 M NaOH [32]. Correlations of potentials of M(III)/M(II) redox couples and the activity of ORR are discussed in Chap. 1.

3.3 Electrochemical Measuring System for Heterogeneous Charge Transport and Solar Cells

3.3.1 Testing Method of Charge Transport in Heterogeneous Systems

Charges can be transported by redox reactions of molecules incorporated in a membrane. Such charge transport is investigated by utilizing electrode-coated membrane incorporating redox molecules. About the mechanism of charge transport, either diffusion or charge hopping, or combination of both, refer Chap. 2. Since charge transport can be regarded as a kind of charge diffusion, the rate of charge transport is represented by an apparent diffusion coefficient

of the charges (D_{app}) [33]. This D_{app} is obtained by the slope of a conventional Cottrell's plots (3.15) by chronoamperometry or chronospectrometry,

$$i = nFcD_{\text{app}}^{1/2}/(\pi t)^{1/2} \quad (3.15)$$

where i is the current density, n is the number of charges involved in the reaction, F is Faraday's constant, c is the redox center concentration, and t is the reaction time.

The rate of charge transport is usually measured by the amount of charge passed (coulomb number) as shown by the above equation. However, it happens sometimes that such coulomb number does not show the true change of the redox molecules because of some charging current of the polymer film. Observation of the true change of the redox molecule by spectroscopy can give more exact charge propagation rate rather than the measurement of the coulomb number. An in situ spectrocyclic voltammetry (SCV) or potential-step chronoamperospectrometry (PSCAS) [34, 35], which combines conventional voltammetry with visible absorption spectroscopy was adopted to study the mechanism [33].

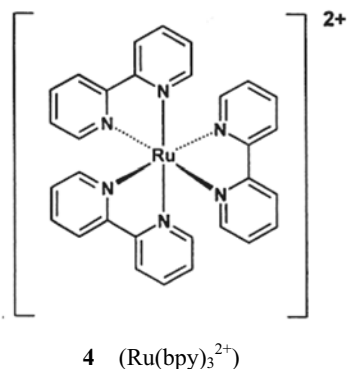
For this purpose a diode array UV-Vis absorption spectrophotometer is a good instrument by which a UV-Vis spectrum can be measured in a short timescale of 1 s–1 ms. A conventional quartz cell with the size of $1 \times 1 \times 4.5$ cm (height) is equipped with an indium tin oxide (ITO) transparent conductive glass working electrode coated with a polymer membrane incorporating redox compounds, a Pt counter, and a Ag|AgCl reference electrodes so that the monitoring light of the spectrophotometer is irradiated on the ITO working electrode in order to in situ measure the spectral change of the redox compound during the potential sweep applied by a conventional electrochemical instrument. In order to measure the spectral change of an solution, a thin layer cell can be used that comprises of an ITO working, Pt mesh or transparent Pt-coated ITO counter electrodes sandwiching a thin layer solution by utilizing a thin spacer of less than 0.5 mm thickness. This thin layer cell is put into a conventional quartz cell containing a redox electrolyte solution, and sucks the solution by a kind of osmosis; a reference electrode can be put into the solution outside of the thin layer cell.

Charge transport, conductivity, capacitance, and electrode reaction such as charge transfer in electrode|polymer systems can be evaluated by using alternating current impedance spectroscopy. For the alternating current impedance spectroscopic (ACIS) measurement, two sets of Pt foil electrodes (e.g., 1×1 cm size) with a separation of 2–5 mm is put into a redox electrolyte solution or into a gel/redox electrolyte solution while it is still warm and liquid state before cooling down to form a solid. Most typically a 10 mV amplitude sine wave is applied to the electrodes in the frequency range from 100 mHz to 20 kHz with a frequency analyzer.

About the details of ionic conductivity measured by electrochemical impedance spectroscopy (EIS), the readers may refer to Sect. 3.3.3 and to the literature [36].

3.3.2 Evaluation of Charge Transport by Redox Molecules Incorporated in a Heterogeneous Phase

A typical example of charge hopping mechanism is tris(2,2'-bipyridine) ruthenium(II) complex (**4**, $\text{Ru}(\text{bpy})_3^{2+}$) incorporated into a Nafion membrane on its oxidation from 2^+ to 3^+ .



The visible absorption spectral change of the $\text{Ru}(\text{bpy})_3^{2+}$ /Nafion (Fig. 3.17) after potential steps from 0 to 1.3 V vs. SCE showed the decrease of the 2^+ complex (453 nm) with a concomitant increase of the absorption by the 3^+ complex (around 420 nm), whose rate was second order with respect to the concentration. The apparent second-order rate constant for the charge

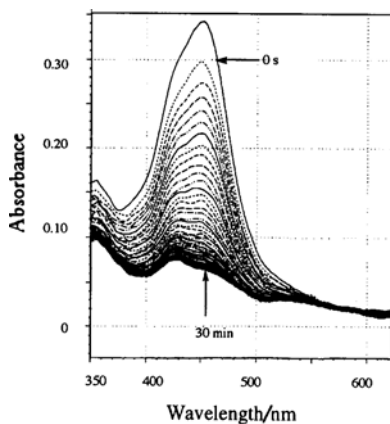


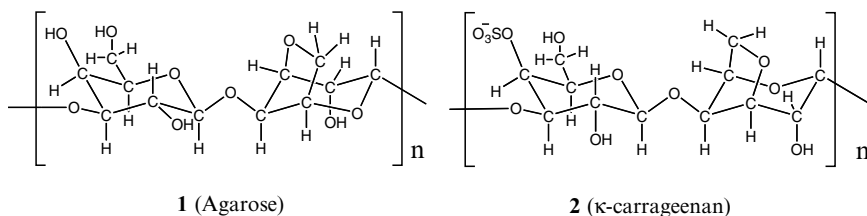
Fig. 3.17. Visible absorption spectral change of $\text{Ru}(\text{bpy})_3^{2+}$ (0.3 M) in Nafion coated on an ITO electrode soaked in a 0.1 M NaClO_4 aqueous solution at pH 1.2 after potential step from 0 to 1.3 V (vs. SCE) as measured by a potential step chronospectrometry ([35], copyright Elsevier)

hopping was obtained as $k_2 = 1.1 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$. The D_{app} value was obtained to be $2 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ from (3.15) by modifying the equation to use the real change of the Ru complex instead of using the i value.

3.3.3 AC Impedance Spectroscopy to Evaluate Charge Transport, Conductivity, Double-Layer Capacitance, and Electrode Reaction

In this section evaluation of the above parameters is described by taking electrochemical processes in a solid-state polysaccharide gels as an example. It has been well known that hydrophilic polymers form a hydrogel that contains a large excess water inside. However, diffusion of molecules and ions in these gels has scarcely been studied due to the lack of suitable methodology. The present author has found that a tight and elastic polysaccharide solid containing excess water can be used as a solid medium for electrochemical measurements in the same way as liquid water, and that diffusion of molecules and ions takes place in this solid in the same way as in a liquid [37–39]. This allows the solid to be used not only as a medium for electrochemistry, but also as a solid reactor for various chemical reactions.

The typical polysaccharides mentioned in the present section are agarose (1) and κ -carrageenan (2). It has well been known that polysaccharides form a tight and elastic solid containing excess water [40].



Cyclic voltammograms of 5 mM $\text{Fe}(\text{CN})_6^{3-}$ in a 2 wt% agarose solid, in a 2 wt% κ -carrageenan solid, and in an aqueous solution containing 0.5 M KCl are shown in Fig. 3.18. The voltammograms in the agarose and κ -carrageenan solids show very similar features as in liquid water including the redox potential, and peak currents, but with a slightly larger peak separation for the solid systems. The solid was so tight and stable that CV could be measured without any outer cell or vessel.

Impedance spectra of a 5 mM $\text{Fe}(\text{CN})_6^{3-}$ were measured in 2 wt% agarose and κ -carrageenan solids, and in an aqueous solution containing 0.5 M KCl at the rest potentials (Fig. 3.19) [38].

All the spectra (Fig. 3.19a) show linear relations characteristic for a diffusion-controlled process in the bulk phase at low frequencies (<30 Hz). However, at high frequencies (Fig. 3.19b) semicircles are clearly seen in the

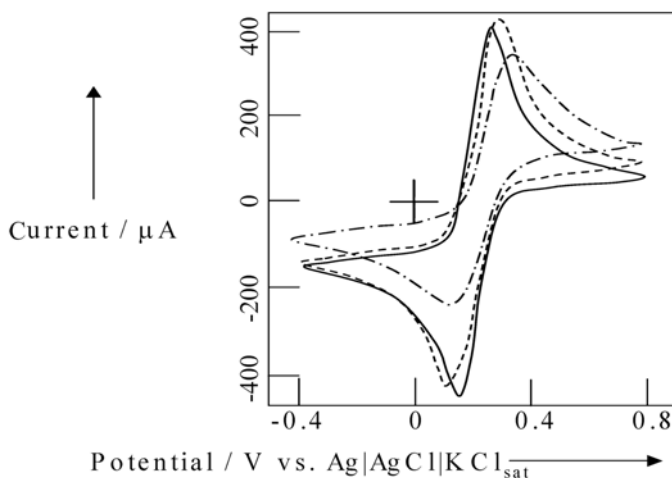


Fig. 3.18. Cyclic voltammograms of 5 mM $\text{Fe}(\text{CN})_6^{3-}$ in 2 wt% agarose (*dash-dotted line*) [3]; 2 wt% κ -carrageenan (*dashed line*) and aqueous solution (*solid line*) containing 0.5 M KCl in the range from -0.4 to 0.8 V (vs. $\text{Ag}|\text{AgCl}|\text{KCl}_{\text{sat}}$). Working electrode is ITO, and counter electrode Pt. scan rate, 20 mV s^{-1} ([38], copyright Elsevier)

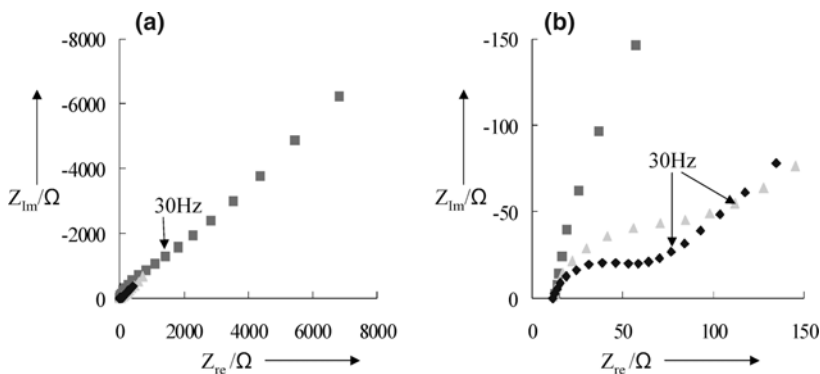


Fig. 3.19. Impedance spectra of 5 mM $\text{Fe}(\text{CN})_6^{3-}$ in 2 wt% agarose (*squares*), 2 wt% κ -carrageenan (*triangles*), and aqueous solution (*diamonds*)-containing 0.5 M KCl at the rest potentials: Frequency range is from 20 kHz to 100 mHz (25 data points per spectrum) ([38], copyright Elsevier)

κ -carrageenan solid and in an aqueous solution, while the impedance spectrum in the agarose solid is slightly different showing a larger semicircle. These semicircles at high frequencies are determined both by the capacitance (C_{dl}) in the double layer and charge transfer resistance (R_{ct}) at the electrode|solution interface. The estimated equivalent circuit for the impedance spectra of Fig. 3.19 is shown in Fig. 3.20 based on the Randles circuit. The solution

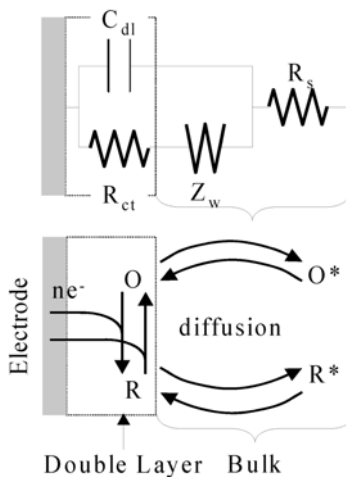


Fig. 3.20. Electrochemical redox system along with its equivalent circuit

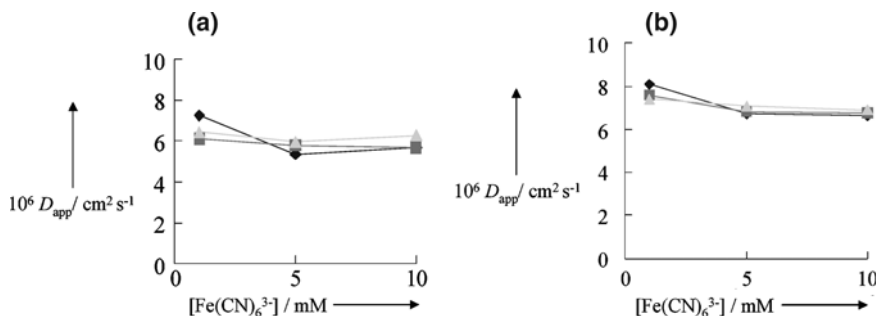


Fig. 3.21. (a) Concentration dependence for the diffusion coefficient (D_{app}) of $\text{Fe}(\text{CN})_6^{3-}$ in 2 wt% agarose (*squares*), 2 wt% κ -carrageenan (*triangles*), and aqueous solution (*diamonds*) containing 0.5 M KCl at the rest potential. (b) D_{app} based on Cottrell's equation ([38], copyright Elsevier)

resistance (R_s) was determined from the equivalent circuit, and then D_{app} of the $\text{Fe}(\text{CN})_6^{3-}$ was calculated.

The concentration dependence of D_{app} of $\text{Fe}(\text{CN})_6^{3-}$ determined by the electrochemical impedance spectroscopy (EIS) is shown in Fig. 3.21a. D_{app} was estimated also by a potential-step chronoamperometry (PSCA) method under a potential step from -0.2 (vs. $\text{Ag}|\text{AgCl}|\text{KCl}_{\text{sat}}$) to $+0.5$ V and is shown in Fig. 3.21b. It is remarkable that the diffusion of the $\text{Fe}(\text{CN})_6^{3-}$ takes place in the solid to the same extent as in an aqueous solution. The D_{app} values from both measurements were almost the same, and almost independent of the $\text{Fe}(\text{CN})_6^{3-}$ concentration. The D_{app} obtained by EIS was slightly lower than that by PSCA; since in the PSCA measurement direct current is used in the potential step, a concentration gradient generated in the double layer

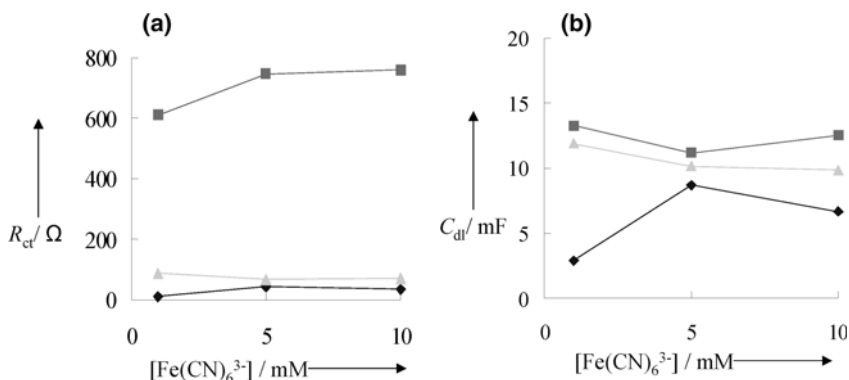


Fig. 3.22. Concentration dependence of (a) the charge transfer resistance (R_{ct}) and (b) the double-layer capacitance (C_{dl}) of Fe(CN)_6^{3-} in 2 wt% agarose (squares), 2 wt% κ -carrageenan (triangles) and aqueous solution (diamonds) containing 0.5 M KCl at the rest potential ([38], copyright Elsevier)

would cause slightly higher D_{app} value. The D_{app} of Ru(bpy)_3^{2+} in the 2 wt% κ -carrageenan solid ($4.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) was about 70% of the D_{app} in the 2 wt% agarose solid ($6.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$). This result indicates that the diffusion of Ru(bpy)_3^{2+} in the κ -carrageenan solid is suppressed slightly by the anionic groups of the κ -carrageenan [38].

The contact angle of water on the present solid surface was almost zero showing that the surface is super-hydrophilic. The concentration dependence of the charge transfer resistance (R_{ct}) at the electrode|solid interface is shown in Fig. 3.22a.

It is remarkable that the R_{ct} in the 2 wt% κ -carrageenan solid was almost the same as that in the aqueous solution, although the R_{ct} in the 2 wt% agarose solid was much larger than that in the aqueous solution. In spite of the high hydrophilicity of the solid surface, there could be some contact problem between the electrode and the agarose solid. As for the κ -carrageenan, the sulfonate anionic groups would improve the contact between the electrode and the solid.

The dependence of the double-layer capacitance (C_{dl}) on the Fe(CN)_6^{3-} concentration is shown in Fig. 3.22b. In the aqueous solution, C_{dl} tends to increase with the Fe(CN)_6^{3-} concentration, but for the solid system C_{dl} values are only weakly dependent on the Fe(CN)_6^{3-} concentration. At 5 mM Fe(CN)_6^{3-} concentration, C_{dl} values of the solids are similar to that in the aqueous solution.

The polysaccharide concentration dependence of D_{app} in the agarose and κ -carrageenan solids containing 10 mM Fe(CN)_6^{3-} is shown in Fig. 3.23.

The D_{app} in an aqueous solution containing 10 mM Fe(CN)_6^{3-} is also shown (on the y -axis) in Fig. 3.23. The D_{app} values in the κ -carrageenan solid are even higher than that in the aqueous solution. It can clearly be seen

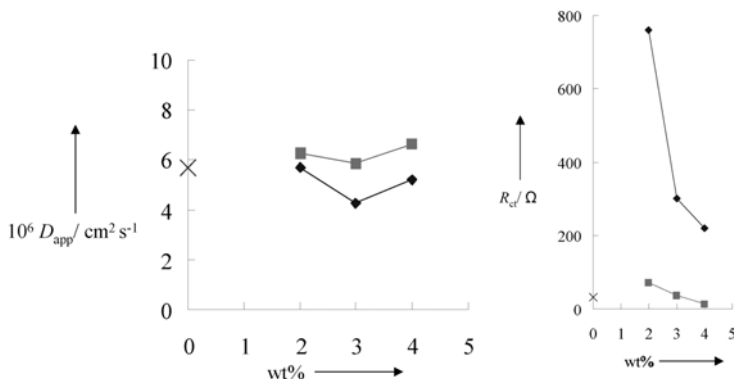


Fig. 3.23. Polysaccharide concentration dependence of R_{ct} for 10 mM $\text{Fe}(\text{CN})_6^{3-}$ in 2, 3, 4 wt% agarose (*diamonds*) and 2, 3, 4 wt% κ -carrageenan (*squares*) and aqueous solution (*crosses*) containing 0.5 M KCl at the rest potential ([38], copyright Elsevier)

that the polysaccharide concentration does not greatly affect the molecular diffusion in the solid. Figure 3.23 shows the plots of charge transfer resistance (R_{ct}) vs. polysaccharide concentration for the 10 mM $\text{Fe}(\text{CN})_6^{3-}$ in the agarose and κ -carrageenan solids. The plot on the vertical line in Fig. 3.23 shows the R_{ct} (32.6 Ω) in the aqueous solution containing 10 mM $\text{Fe}(\text{CN})_6^{3-}$. The R_{ct} in the κ -carrageenan solid is of the same order of magnitude as in an aqueous solution and even lower in the 4 wt% κ -carrageenan. In Fig. 3.22 it was shown that κ -carrageenan anionic groups improve the charge transfer between the electrode and the redox compound in the solid. A high concentration of the $-\text{SO}_3^-$ groups would facilitate charge transfer between the electrode and the redox compound. It is surprising that the R_{ct} decreased with increasing polysaccharide concentration in the solids. The reason is not clear yet, but one reason might be a technical problem; since a higher polysaccharide concentration causes a higher viscosity of the polysaccharide solution when it is warm, the insertion of the electrodes into this solution could give a better and more stable contact between the electrodes and the medium. It was shown that the ionic conductivity also increases with the polysaccharide concentration. This fact and the results of Fig. 3.23 for the R_{ct} indicate that the increase of the polysaccharide concentration does not increase the resistance for molecular/ionic diffusion probably because the increase of the polysaccharide concentration induces the growth of the chain aggregation rather than increasing the cross-linked structures that can be a resistance for molecular/ionic diffusion.

3.3.4 I–V Characteristics of Solar Cells

The instrument to measure a photocurrent (I) vs. photovoltage characteristics (I – V characteristics) of a solar cell is commercially available. However, a conventional electrochemical measurement instrument can also be used for

Table 3.2. Results of output characteristics for (a) all-plastic PEN/ITO/TiO₂(SP-210)/N3 cell and (b) FTO/TiO₂(P-25)/N3 cell using 1.0 wt% κ -carrageenan solid containing AN/ME (1:1) solution with LiI/Pr₄Ni/I₂ (0.1 M/0.5 M/0.05 M) and TBP (0.5 M), irradiated by a solar simulator (AM1.5, 100 mW cm⁻²) ([41], copyright Elsevier)

Electrode	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	η (%)
PEN/ITO(a)	2.68	0.80	0.72	1.54
FTO(b)	8.67	0.75	0.65	4.23
Ratios of a/b	0.31	1.07	1.11	0.36

this purpose by connecting both the counter and reference electrode terminals of the instrument to the counter electrode of the solar cell. As shown in the following figures, four parameters are important to evaluate characteristics of a solar cell; a short-circuit photocurrent (J_{sc}) that is the current density (mA cm⁻²) under short-circuit conditions (i.e., the voltage is zero), an open-circuit photovoltage (V_{oc}) when the circuit is open (i.e., the current is zero), a fill factor (FF) that is the fraction of the real maximum output power (W_{real}) of the cell divided by an ideal output ($= J_{sc} \times V_{oc}$) (i.e., $FF = W_{real} / J_{sc} \times V_{oc}$), and an energy conversion efficiency of a solar cell (η) that is the percentage of the output power ($J_{sc} \times V_{oc} \times FF$) divided by incident irradiation power (e.g., mW cm⁻²). The W_{real} can be calculated by estimating the maximum area surrounded by the I - V curve, I and V axes. The photocurrent is expressed usually by a photocurrent density per unit area (e.g., in mA cm⁻²); in this case photocurrent is expressed by J /mA cm⁻² instead of using I . In order to compare the performance (especially η) of different solar cells, the irradiation conditions should be normalized. An average solar light irradiation of 100 mW cm⁻² light intensity at airmass 1.5 (AM 1.5) is used corresponding to a simulated solar light intensity passing a 1.5 airmass for which an airmass 1 means the thickness of atmospheric air layer when the sun is incident vertically on the earth from the top. Such simulated solar irradiation is obtained by a solar simulator that uses a xenon lamp in combination with a filter.

The I - V characteristics of both the conventional (FTO/TiO₂(P-25)) and plastic (PEN/ITO/TiO₂(SP-210)) dye-sensitized solar cells (DSSC) are shown in Fig. 3.24 (about DSSC and PEN see Sect. 3.3.5), and the results are summarized in Table 3.2 [41]. The important parameters here are open circuit photovoltage (V_{oc}), short circuit photocurrent density (J_{sc}), and fill factor (FF) that is the parameter to show the ratio of the real maximum output power per ideal output power ($= V_{oc} \times J_{sc}$).

3.3.5 Impedance Spectroscopy to Evaluate Multistep Charge Transport of a Dye-Sensitized Solar Cell

In many actual devices charge transport is a multistep process. This is especially true for a photochemical device such as solar cell and luminescent

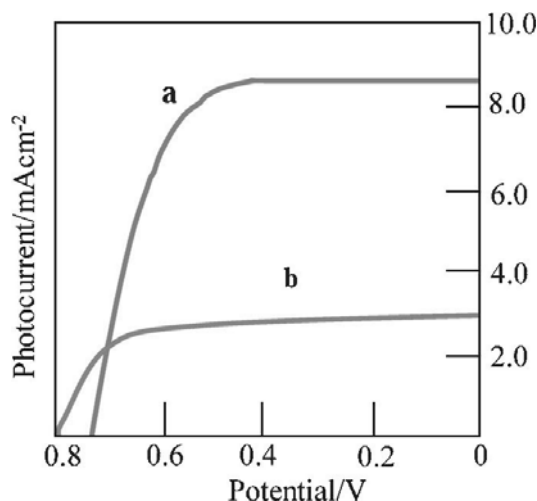


Fig. 3.24. $I-V$ characteristics of (a) conventional FTO/TiO₂(P-25)/N3 and (b) all plastic cell PEN/ITO/TiO₂(SP-210)/N3 using 1.0 wt% κ -carrageenan solid containing excess AN/ME(1:1) with Pr₄Ni/I₃(1:1), irradiated by a solar simulator (AM1.5, 100m Wcm⁻²) ([41], copyright Elsevier)

devices. A typical example is the dye-sensitized solar cell (DSSC) that is attracting a great deal of attention as a near future solar cell. The details of the DSSC are described in Chaps. 8–10; it involves at least eight-step charge transport processes. Such multistep charge transport can be investigated by an alternating current impedance spectroscopy; see also Chap. 8. In this section, investigation of a DSSC by an electrochemical impedance spectroscopy (EIS) is described by taking an all-plastic DSSC cell as an example.

A plastic DSSC is attracting attention because it has thin, lightweight, and flexible properties due to using plastic substrates. On the other hand, the plastic DSSC has a low efficiency compared with the DSSC using a glass-conductive substrate. It is of importance to compare the difference by analyzing the mechanism, especially charge transport problem, to clarify the reason. EIS is a good method to elucidate the charge transport behavior.

A conventional TiO₂ film with P-25 (FTO/TiO₂ (P-25)) was prepared as a reference cell by using a fluorine-doped indium tin oxide-coated conductive glass (FTO), and for a plastic cell an indium tin oxide-coated polyethylene naphthalate (PEN/ITO) film (125- μ m thick, transmittance of 80%, surface resistance of 10 Ω cm⁻²) was used as transparent conductive plastic electrode both for anode (using SP-210 low temperature TiO₂ paste) and cathode substrates. A platinized PEN/ITO was used as a cathode. A 1:1 (volume) mixture of acetonitrile (AN) and 2-methoxyethanol (ME) was used

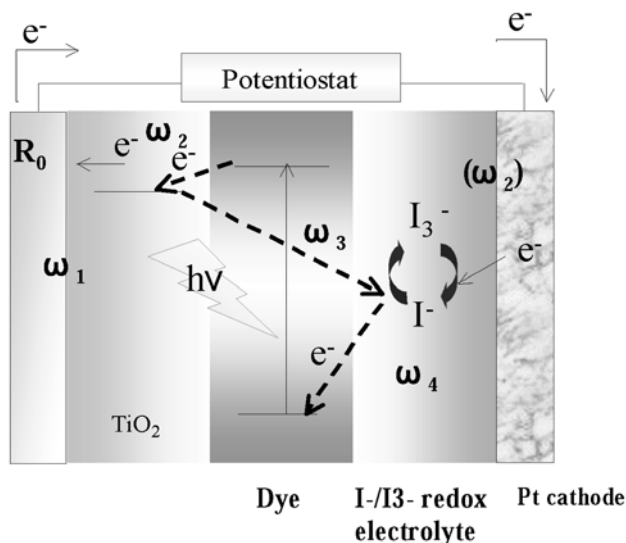


Fig. 3.25. Charge transport processes of a dye-sensitized solar cell (DSSC): refer also the text

as a medium. For the redox electrolyte, a mixture of 0.5 M $(\text{Pr})_4\text{NI}$ and 0.05 M I_2 was used with 0.1 M LiI and 0.5 M 4-tertiary butyl-pyridine (TBP) added to the mixture. As a dye *cis*-bis(isothiocyanato)bis(2, 2'-bipyridyl-4, 4'-dicarboxylato)-ruthenium(II), $\text{Ru}(\text{dcbpy})_2(\text{NCS})_2$ (called N3) was used by adsorbing into the nanoporous TiO_2 thin film. For a plastic cell 1.0 wt% κ -carrageenan gel was used to incorporate the I_3^-/I^- redox electrolyte solution.

In order to investigate the different performance, it is of importance to study the charge transport in the cell during irradiation as shown in Fig. 3.25 where the resistances are assigned as follows [41]:

1. R_o , ohmic resistance of the cell, especially the resistance of the base conduction layer of the TiO_2 anode
2. ω_1 , Resistance at the $\text{TiO}_2|\text{conducting layer interface}$
3. ω_2 , Resistance between TiO_2 particles (and at the interface of $\text{Pt}|\text{electrolyte solution}$)
4. ω_3 , Resistance at the $\text{TiO}_2|\text{electrolyte solution and TiO}_2|\text{dye interfaces}$
5. ω_4 , Resistance for diffusion of I^-/I_3^- redox electrolytes

To investigate the reason for the higher performance of the conventional FTO/ TiO_2 (P-25) cell and the plastic PEN/ITO/ TiO_2 (SP-210) cell, impedance spectra were measured and shown in Fig. 3.26.

The analysis results are shown in Table 3.3. It is clear that all the resistance R_o (resistance at the electrode surface), ω_1 , ω_3 , and ω_4 are higher for the plastic cell, which is the main problem of the plastic cell.

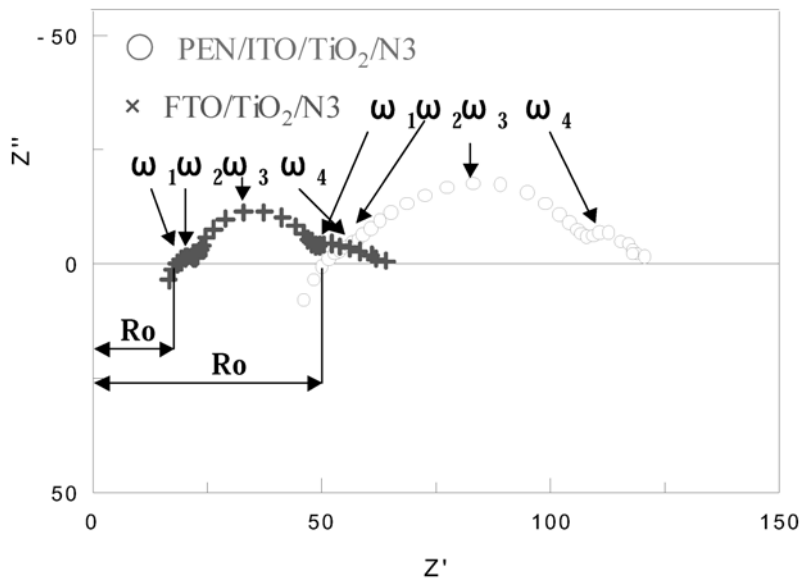


Fig. 3.26. Impedance spectra of (a) conventional FTO/TiO₂(P-25)/N3 and (b) all plastic cell PEN/ITO/TiO₂(SP-210)/N3 using 1.0 wt% κ -carrageenan solid containing excess AN/ME(1:1) with Pr₄NI/I₃(1:1), irradiated by a solar simulator (AM1.5, 100mWcm⁻²) ([41], copyright Elsevier)

Table 3.3. Impedance analysis results of a conventional FTO/TiO₂(P-25)/N3 and all-plastic cell PEN/ITO/TiO₂(SP-210)/N3 using 1.0 wt% κ -carrageenan solid containing excess AN/ME(1:1) with Pr₄NI/I₃(1:1), irradiated by a solar simulator (AM1.5, 100 mW cm⁻²) ([41], copyright Elsevier)

Working electrode	R_0	ω_1	ω_3	ω_4
FTO/TiO ₂ /N3	18.6	15.4	25.2	19.3
PEN/ITO/TiO ₂ /N3	52.6	32.8	61.9	30.8

3.4 Summary

Electrochemical measurements provide fundamental understandings of energy conversion systems such as reaction efficiency, energy density, reaction mechanism etc. Especially charge transport steps mediated by redox complexes are studied with this method, giving parameters like diffusion coefficients and many reaction parameters in heterogeneous reactions.

In electrocatalyst researches, RDE and RRDE are powerful tools for evaluating the oxygen reduction efficiency of the fuel cell catalyst. CV and LSV offer knowledge of rate-determining step, redox potentials and set of parameters of diffusion/charge transfer steps that are important steps for energy conversion in heterogeneous systems. In simple diagnosis, CV tells us that for

rate-determining chemisorption process the anodic and cathodic curves are symmetric at the current zero line and show no shift in the peak potentials in both directions. The peak current is proportional to the scan rate. For mass-transfer controlled process this is not the case, and peak potentials are separated and the peak current is proportional to the square root of scan rate.

There are several modes of fuel cell testing, and because the gas reactant is involved the most realistic testing is conducted by subscale fuel cells. However, expensive cost and time make it difficult to always do so. Testing methods with simulated fuel cell conditions should be developed that can handle not only catalyst screening but also evaluation of kinetic parameters and mechanism elucidation.

In heterogeneous systems where redox molecules or ions play an important role in transporting charges, it is of special importance to investigate charge propagation in the heterogeneous phase as well as charge transfer at electrode surface. Especially in a solar cell comprising heterogeneous molecules such as a dye-sensitized solar cell (DSSC), investigation of a multistep charge transport provides important clue to enhance the cell performance. Such charge transport can be studied by an alternating current impedance spectroscopy (ACIS). The analysis method of a solar cell performance was given, and the analysis of a multistep charge transport by ACIS was explained by taking a DSSC.

Appendix A

Consider the electrode reaction:



The current of the above reaction is expressed by the Butler–Volmer equation, if the forward and backward rates are proportional to the concentration of O and R, respectively:

$$i = i_0 A \left\{ \frac{[R]_s}{[R]_b} \exp\left(\frac{\alpha n F \eta}{RT}\right) - \frac{[O]_s}{[O]_b} \exp\left(-\frac{(1-\alpha)n F \eta}{RT}\right) \right\} \quad (3.17)$$

where i_0 is the exchange current density; $[R]_s$, $[R]_b$ and $[O]_s$, $[O]_b$ are the surface and bulk concentration of the reductant and oxidant species, respectively; α is transfer coefficient; and η is overpotential. At $\eta = 0$, the forward and backward reaction rates take the equal value and opposite signs, and the magnitude is i_0 .

Suppose that $\eta < 0$ and the cathodic reaction rate is much larger than that of anodic rate. Equation (3.17) becomes

$$i = -k[O]_s \quad (3.18a)$$

$$k \equiv -i_0 \frac{A}{[O]_b} \exp\left(-\frac{(1-\alpha)n F \eta}{RT}\right) \quad (3.18b)$$

When the mass transport of O is very fast so that $[O]_s = [O]_b$, i takes the charge transfer reaction rate.

$$i_k = -k[O]_b \quad (3.19)$$

When on the other hand, the mass transport is much slower than that of charge transfer, and takes the limiting value, then $[O]_s$ decreases to 0. In (3.18), this corresponds to the case $-\eta \gg 1$. Assuming Fick's diffusion equation with the thickness of diffusion layer δ and diffusion coefficient D_O in the solution,

$$i_l = -nFAD_O \frac{[O]_b - [O]_s}{\delta} \quad (3.20)$$

and for the limiting case of $[O]_s = 0$,

$$i_l = -nFAD_O \frac{[O]_b}{\delta} \quad (3.21)$$

Combination of (3.18), (3.20), and (3.21) gives a general formula:

$$\frac{i}{i_0} = - \left(1 - \frac{i}{i_l} \right) \exp \left(- \frac{(1 - \alpha)nF\eta}{RT} \right) \quad (3.22)$$

Suppose that the reaction is under mixed control of diffusion and charge transfer processes. The current density i_m in this case is expressed in two ways, one is (3.18) and the other is (3.20).

$$i_m = -k[O]_s = -nFAD_O \frac{[O]_b - [O]_s}{\delta} \quad (3.23)$$

Substitution of (3.19) and (3.21) gives

$$\frac{i_m}{i_k} = \frac{[O]_s}{[O]_b} \quad (3.24a)$$

$$\frac{i_m}{i_l} = 1 - \frac{[O]_s}{[O]_b} \quad (3.24b)$$

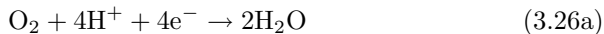
and

$$\frac{1}{i_m} = \frac{1}{i_k} + \frac{1}{i_l} \quad (3.25)$$

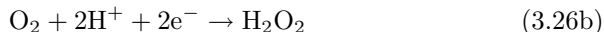
Using (3.5) and (3.21), the diffusion layer thickness δ is expressed by (3.4). Substitution of (3.4) for δ into (3.21) gives Levich equation (3.5), and into (3.25) gives the Koutecky–Levich equation (3.7).

Appendix B

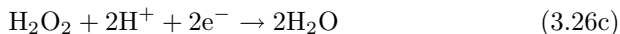
In ORR, O_2 molecule is reduced at the disk electrode in two pathways. One is the 4-electron reduction in which O_2 is reduced to H_2O :



The other is the 2-electron pathway in which O_2 is reduced to H_2O_2 :



which may be further reduced to H_2O through the following reaction:



Suppose that the fraction of O_2 that takes the route (3.26a) is a ($0 < a < 1$). This means the fraction $1 - a$ of O_2 goes to (3.26b). Also the fraction of H_2O_2 that takes the route (3.26c) is b ($0 < b < 1$). The disk current i_{D} consists of the current $i_{\text{D},1}$ for the reaction (3.26a), $i_{\text{D},2}$ for the reaction (3.26b) and $i_{\text{D},3}$ for the reaction (3.26c):

$$i_{\text{D}} = i_{\text{D},1} + i_{\text{D},2} + i_{\text{D},3} \quad (3.27)$$

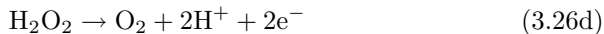
for which the following proportionality holds:

$$i_{\text{D},1} = 4pa \quad (3.28a)$$

$$i_{\text{D},2} = 2p(1 - a) \quad (3.28b)$$

$$i_{\text{D},3} = 2p(1 - a)b \quad (3.28c)$$

On the right-hand side of (3.28), numbers correspond to those of electrons involved. The amount of H_2O_2 is expressed as the fraction of O_2 that goes to the route (3.26b) but does not go to the route (3.26c), *i.e.*, it is proportional to $(1 - a)(1 - b)$. When this H_2O_2 reaches the ring electrode, the current i_{R} is observed for the reaction, if the ring potential is set to oxidize H_2O_2 :



Assuming the collection efficiency of the ring-disk electrode to be N , the following relation yields:

$$i_{\text{R}}/N = 2p(1 - a)(1 - b) = (1 - b)i_{\text{D},2} \quad (3.29)$$

Combination of (3.29) with (3.28b) and (3.28c) gives

$$i_{\text{D},2} - i_{\text{D},3} = i_{\text{R}}/N \quad (3.30)$$

% H_2O is by definition expressed as follows:

$$\frac{\% \text{H}_2\text{O}}{100} = \frac{a + (1 - a)b}{a + (1 - a)(b + 1 - b)} \quad (3.31)$$

which after substitution of (3.27), (3.28a), and (3.30) yields (3.8). Also the number of electrons is

$$n = \frac{4a + 4(1 - a)b + 2(1 - a)(1 - b)}{a + (1 - a)(b + 1 - b)} = 2 \left(1 + \frac{\% \text{H}_2\text{O}}{100} \right) \quad (3.32)$$

which gives (3.9).

References

1. A.J. Bard, L.R. Faulkner, *Electrochemical Methods: Fundamentals and Applications* (Wiley, New York, 1980)
2. K. Kordesch, G. Simader, *Fuel Cells and Their Applications* (VCH, Weinheim, 1996)
3. Hampel CA (ed.), *The Encyclopedia of Electrochemistry* (Robert E. Krieger, New York, 1972)
4. J. Koryta, J. Dvořák, J. Kavan, *Principles of Electrochemistry*, chap. 3 (Wiley, Chichester, 1987)
5. M. Noel, K.I. Vasu, *Cyclic Voltammetry and the Frontiers of Electrochemistry* (Aspect, London, 1990)
6. M. Kunitatsu, H. Qiao, T. Okada, *J. Electrochem. Soc.* **152**, E161 (2005)
7. J. Giner, *J. Electrochem. Soc.* **111**, 376 (1964)
8. Z. Galus, in *Physical Methods of Chemistry*, vol. II, chap. 3, ed. by B.W. Rossiter, J.F. Hamilton (Wiley, New York, 1986)
9. T.J. Schmidt, H.A. Gasteiger, G.D. Stäb, P.M. Urban, D.M. Kolb, R.J. Behm, *J. Electrochem. Soc.* **145**, 2354 (1998)
10. M. Watanabe, H. Igarashi, K. Yoshioka, *Electrochim. Acta* **40**, 329 (1995)
11. T. Okada, Y. Ayato, J. Dale, M. Yuasa, I. Sekine, O.A. Asbjørnsen, *Phys. Chem. Chem. Phys.* **2**, 3255 (2000)
12. W.J. Albery, M.L. Hitchman, *Ring-Disk Electrodes* (Clarendon Press, Oxford, 1971)
13. H.S. Wroblowa, Y.C. Pan, *J. Electroanal. Chem.* **69**, 195 (1976)
14. R. Venkataraman, H.R. Kunz, J.M. Fenton, *J. Electrochem. Soc.* **151**, A710 (2004)
15. M. Kunitatsu, T. Okada, *Electrochem. Solid-State Lett.* **7**, A389 (2004)
16. H. Yano, C. Ono, H. Shiroishi, T. Okada, *Chem. Comm.* **2005**, 1212 (2005)
17. G. Tamizhmani, J.P. Dodelet, D. Guay, L. Dignard-Bailly, *J. Electroanal. Chem.* **444**, 121 (1998)
18. T. Okada, T. Higashino, M. Yuasa, I. Sekine, *Electrochemistry* **69**, 758 (2001)
19. E.A. Ticianelli, C.R. Derouin, S. Srinivasan, *J. Electroanal. Chem.* **251**, 275 (1988)
20. M.S. Wilson, S. Gottesfeld, *J. Appl. Electrochem.* **22**, 1 (1992)
21. F.N. Büchi, G.G. Scherer, *J. Electroanal. Chem.* **404**, 37 (1996)
22. S. Escibano, P. Aldebert, M. Pineri, *Electrochim Acta* **43**, 2195 (1998)
23. H. Yano, C. Ono, H. Shiroishi, M. Saito, Y. Uchimoto, T. Okada, *Chem. Mater.* **18**, 4505 (2006)
24. E.R. Brown, J.R. Sandifer, in *Physical Methods of Chemistry*, vol. II, chap. 4, ed. by B.W. Rossiter, J.F. Hamilton (Wiley, New York, 1986)
25. D.D. Macdonald, *Transient Techniques in Electrochemistry* (Plenum, New York, 1977)
26. S.R. Taylor, A.C. Hillier, M. Seo (eds.) (2000) *Localized In-situ Methods for Investigating Electrochemical Interfaces*. Proceedings Volume 99-28, The Electrochemical Society, Inc.
27. C. Nishihara, T. Okada, *J. Electroanal. Chem.* **577**, 355 (2005)
28. H. Angelstein-Kozłowska, B.E. Conway, W.B.A. Sharp, *J. Electroanal. Chem.* **43**, 9 (1973)
29. T. Biegler, D.A.J. Rand, R. Woods, *J. Electroanal. Chem.* **29**, 269 (1971)

30. H.A. Gasteiger, N. Markovć, P.N. Ross, E.J. Cairns, *J. Phys. Chem.* **98**, 617 (1994)
31. C.L. Green, A. Kucernak, *J. Phys. Chem. B* **106**, 1036 (2002)
32. J. Zagal, M. Páez, A.A. Tanaka, J.R. dos Santos Jr, C.A. Linkous, *J. Electroanal. Chem.* **339**, 13 (1992)
33. M. Kaneko, *Prog. Polym. Sci.* **26**, 1101 (2001)
34. J. Zhang, F. Zhao, M. Kaneko, *J. Porphyrins Phthalocyanines* **3**, 1 (1999)
35. M. Yagi, K. Nagai, T. Onikubo, M. Kaneko, *J. Electroanal. Chem.* **383**, 61 (1995)
36. H. Ueno, Y. Endo, Y. Kaburagi, M. Kaneko, *J. Electroanal. Chem.* **570**, 95 (2004)
37. M. Kaneko, N. Mochizuki, K. Suzuki, H. Shiroishi, K. Ishikawa, *Chem. Lett.* **31**, 530 (2002)
38. H. Ueno, M. Kaneko, *J. Electroanal. Chem.* **568**, 87 (2004)
39. N. Mochizuki, H. Ueno, M. Kaneko, *Electrochim. Acta.* **49**, 4143 (2004)
40. S. Arnott, A. Fulmer, W.E. Scott, *J. Mol. Biol.* **90**, 269 (1974)
41. J. Nemoto, M. Sakata, T. Hoshi, H. Ueno, M. Kaneko, *J. Electroanal. Chem.* **599**, 23 (2007)

Molecular Catalysts for Fuel Cell Anodes

T. Okada

Abstract Only a few examples of molecular catalysts have so far been reported for the anode (fuel oxidation reaction) of fuel cells, because platinum is considered as the only and most active and stable catalyst for the oxidation of hydrogen or other fuels in fuel cells. However, it is widely acknowledged that the drawback of platinum is its cost competitiveness and serious poisoning by CO. Pt–Ru alloy is considered as the solution to this problem, but uprisng cost of Ru is hindering its true commercialization. Another problem is the dissolution of Ru at much less noble potentials than Pt. In this chapter, new class of materials that can subsidize Pt or alloy catalysts with high CO tolerance are introduced and their possibilities are discussed for future applications to the anode catalysts. Composite catalysts are proposed that are made of platinum precursor and organic complexes containing nitrogen ligands and transition metal centers, supported on carbon powder and heat-treated at moderate temperatures. The performance of novel catalysts is studied for methanol oxidation, formic acid oxidation, and H₂ oxidation reactions, all of which are important anode reactions in fuel cells. Structural analyses of the catalysts are presented by X-ray diffraction, X-ray photoelectron spectroscopy, X-ray absorption spectroscopy, transmission and scanning electron microscopy, and thermal analyses. Possible mechanisms of CO tolerance of these new catalysts are discussed.

4.1 Introduction

Fuel cells are promising systems as the clean power-generation device because of their high efficiency of energy conversion with minimum pollutant exhaust [1,2]. The system converts the chemical energy of fuel oxidation directly into electricity, and unlike the internal combustion engine, there is no limitation of Carnot cycle that considerably lowers the power efficiency [3,4]. In a typical hydrogen–oxygen fuel cell,



the reaction product contains no pollutant or particulates, and can be called an ideal “clean energy source.”

Generally, fuels are not limited to hydrogen. In the latest era of information technology, portable devices such as cell phones, laptop computers, and personal digital assistants (PDAs) are extensively distributing, and for such small apparatus high-power-density batteries are strongly demanded. Direct liquid-feed fuel cells are attracting attention as the new-generation mobile energy sources, because of projected power density higher than that of lithium secondary batteries [5]. In the latter system formic acid, methanol, ethanol, etc., become the candidate fuels. Here CO_2 is emitted as the reaction product and the system is not strictly clean, but considering its efficiency the CO_2 emission is much smaller than for other systems of electric energy storage.

Alkaline fuel cells, phosphoric acid fuel cells, polymer electrolyte fuel cells, and direct liquid feed fuel cells are categorized as “low (and medium) temperature fuel cells” because they are operated at less than 500°C [4]. In a typical fuel cell system, hydrogen or oxygen gases are oxidized or reduced in separate gas chambers on reaction zones called anode or cathode catalyst layers, respectively. The catalyst for such low-temperature fuel cells is a key technology in order to guarantee its smooth reaction and high power efficiency. Except for the alkaline fuel cells, platinum or related noble metals are mostly used as catalysts because chemical (i.e., anticorrosion) stability and longevity become the major specification for durable operation, in addition to their high catalytic ability [6]. Especially for the anode, the catalyst researches have so far mostly been centered on platinum or platinum alloys.

When carbon-containing substances are involved as fuels, the monopoly of platinum catalysts is not always the case. For terrestrial (especially stationary) applications fuels are in many cases supplied from the natural gas or the city gas, and H_2 is obtained from CH_4 through the reformer reaction. In this case the anode gas typically contains about 40–75% H_2 , 15–25% CO_2 , a few percent N_2 , and small amount of residual CH_4 (1%) and CO (10–100 ppm) [6]. CO is a poisoning species on platinum, and strongly inhibits hydrogen oxidation reaction when CO level is above 10 ppm [6]. In direct liquid-feed fuel cells, carbon monoxide (CO) that forms as the by-product of the fuel oxidation reaction poisons platinum catalysts [7]. In order to avoid CO poisoning, the amount of platinum must be increased which in turn reflects severely on the cost.

Platinum-based alloy electrocatalysts have been recognized as the most promising candidate for CO -tolerant anode catalysts [8–10], and Pt-Ru [11–13], Pt-Sn [14–16], Pt-Pd [17–19] or ternary alloys [7, 20, 21] have been investigated for more than four decades. Depending on the reaction involved, the optimum alloy catalyst and its composition differ from one system to another. For example, for simple organic molecules like HCOOH , CH_3OH and $\text{C}_2\text{H}_5\text{OH}$, Pt-Ru , and Pt-Sn have been most widely investigated [10]. In all cases the platinum is the main reaction site, and the second element is a cocatalyst (modifier or promoter) that mitigates the poisoning effect of CO on Pt [22, 23]. Total non-precious anode catalysts are not yet developed, although

new base catalysts are proposed, e.g., mixture of nickel–tungsten alloy and WC that was prepared from nickel tungstate by H_2 reduction with CH_3 in a furnace [24].

There is another possibility that novel second nonmetal component would be considered as options to cocatalysts, before total non-precious catalysts are realized. The examples are Pt finely dispersed on metal oxides such as WO_3 , MoO_2 , and TiO_2 [25–27]. In this case the oxides work as substrate to modify the electronic state of Pt at the periphery of Pt–oxide interface. The same concept applies when organic compounds serve as the cocatalyst, in which CO poisoning on Pt is mitigated by oxygenated species adsorbed on organic compounds. For designing such catalyst and cocatalyst systems, the mechanism of fuel oxidation reactions needs to be discussed, which will be made in following sections.

4.2 Concept of Composite Electrocatalysts in Fuel Cells

Electrochemical oxidation reactions of small organic molecules (formic acid and alcohols) are multi-electron processes, and need high overpotential. The rate-determining step is considered to be in the dehydrogenation process, which is the fragmentation of the alkyl moiety of fuel molecules adsorbed on the catalyst surface [28]. Another mechanism is that OH association to the adsorbed intermediate species becomes the rate-determining step [20, 29]. For formic acid and methanol oxidation, a by-product CO forms and seriously poisons the Pt surface. Pt–Ru and other alloys as the CO-tolerant catalysts had been surveyed early in 1960s [11–13].

The mechanism of CO tolerance assumed for the alloy catalysts is considered in two ways [9, 10, 23, 28]:

1. Bifunctional effect: The second element adsorbs oxygen-containing species (normally derived from H_2O), and this species oxidize CO on Pt surface [30].
2. Electronic (or ligand) effect: The second element modifies the electronic state of Pt so that *d*-electron deficiency increases, which reduces the back donation of electron from Pt to CO, and weakens CO–Pt bonding [22, 31].

The role of Ru as the second element that is added to the Pt catalyst is to take part in either of the above two processes, then eliminate CO poisoning and promote the fuel-oxidation reactions.

Learning from the above mechanisms, a new concept for the new CO-tolerant catalysts is proposed using organic metal complexes. The scheme is depicted in Fig. 4.1, where CO adsorbed on Pt surface is eliminated or liberated by the action from the nascent site on organic metal complexes. This idea could be rationalized by the pioneering work of selective CO oxidation on metalloporphyrins, which was reported by van Baar et al. in 1982 [32, 33]. According to these authors mononuclear Ir-porphyrins supported on carbon and

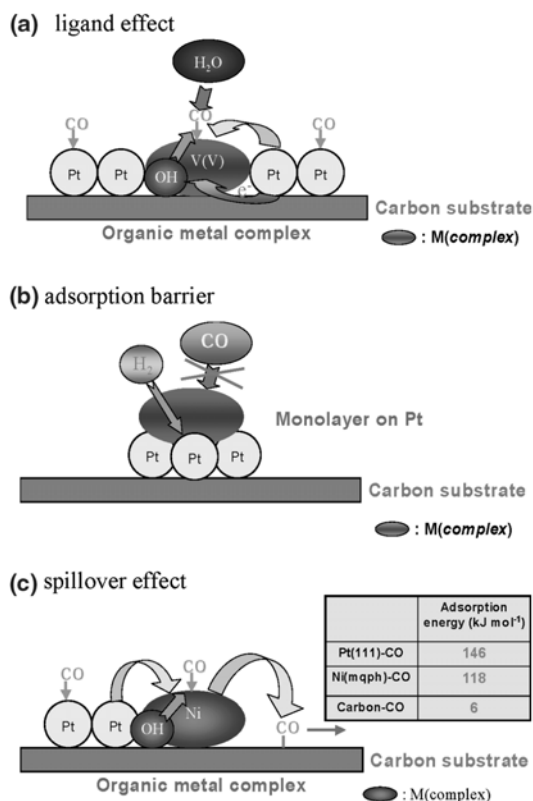


Fig. 4.1. Scheme of new CO-tolerant electrocatalysts based on organic metal complexes

heat-treated (700°C) in an inert atmosphere show substantial CO oxidation activity at low overpotential. They ascribed this to the mechanism similar to the water gas shift reaction [33]. A few steps are assumed to be involved: (1) CO adsorption on metal center, (2) nucleophilic attack of water, and (3) decarboxilation.

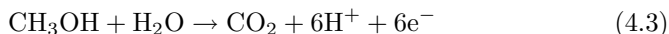


Thereby a higher oxidation state of the metal results in a reduced back donation and therefore an increased positive charge on CO, which facilitates the nucleophilic attack by H₂O. This mechanism appears attractive for designing CO-tolerant catalysts if certain energy level of *d*-electron-deficient metal centers is tailored by combination of transition metals with specific organic complexes.

The second conceptual basis originates from the successful work carried out for oxygen reduction reaction catalysts. A composite catalyst based on Pt and Co(*mqph*) (cobalt *N, N'*-mono-8-quinolyl-*o*-phenylenediamine), supported on carbon and heat-treated in an inert atmosphere showed promising performances compared with pure Pt, even if the amount of Pt was reduced by 70% [34]. Because Co(*mqph*) exhibited only 2-electron reduction of O₂, it was inferred that H₂O₂ generated on Co(*mqph*) was further reduced on neighboring Pt sites thus resulting in 4-electron reduction to H₂O, based on the cooperation between two elements. In this case O₂ first adsorbs on the metal centers and oxygenated species is likely to form as the intermediate. In CO poisoning on Pt, this species is expected to oxidize CO, if both species meet at the active center.

4.3 Methanol Oxidation Reaction

In electrochemical methanol oxidation reaction, the 6-electron oxidation process occurs on the catalyst surface:



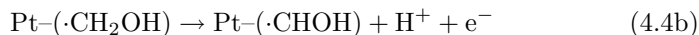
Slow kinetics and CO poisoning on Pt-based catalysts are major problems of direct methanol fuel cells (DMFCs), and this causes larger amount of Pt in DMFC than in polymer electrolyte fuel cell (PEFC) using H₂ and air. CO-tolerant Pt–Ru alloy catalysts are known to be the best solution to date, but searches for alternatives are a growing topic. This section discusses novel CO-tolerant electrocatalysts for methanol oxidation reaction (MOR), based on organic metal complexes as cocatalysts to Pt, which were produced by heat-treatment method [35–37].

4.3.1 Mechanism of Methanol Oxidation Reaction

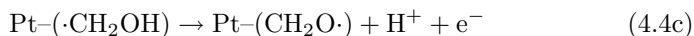
Many investigations have been done on MOR mechanisms on Pt electrocatalyst, because this metal is known to be the only active electrocatalyst for oxidation of small organic molecules [10, 28, 38]. Methanol molecule adsorbed on the Pt surface first dissociates on the alkyl side, where H⁺ is liberated with e[−] [38, 39].



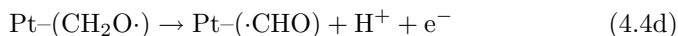
where $\cdot$ denotes the adsorption site on Pt. On the second step there are two possibilities, one is dehydrogenation at the alkyl side,



the other is at the OH side



The third step produces formyl-like species



which further forms CO adsorbed on Pt surface



This CO hinders further adsorption of the reaction intermediate, and ultimately poisons the catalyst surface. CO adsorption and desorption are strongly dependent on the potential and surface condition of the metal [40]. Leiva and Sánchez summarized theoretical calculation works of methanol oxidation on Pt, and concluded CO as the “energetic sink” [38]. Oxidation of CO to CO₂ needs adsorbed oxygenated species ·OH in order to accomplish the reaction [30].

Osawa et al. using surface-enhanced infrared spectroscopy (SEIRAS) reported that there is another route for oxidation of Pt-(CH₃OH), and identified formate species [H-C(O·)₂]⁻ as the reactive intermediate, which directly forms from CH₃OH together with ·OH and then yields CO₂ [41]. Thus methanol is considered to oxidize through dual pathways, CO path and non-CO path [42].

Lamy et al. proposed the following properties needed for the electrocatalysts of MOR [39]:

1. Capable of dissociating the adsorbed methanol molecule
2. Sufficient concentration of adsorbed oxygenated species at its surface
3. Easy removal of poisoning species CO

Tailoring multimetallic electrocatalysts is necessary, e.g., Pt, Ru, and Sn each bearing one of the above properties. However, designing the composition of alloys with active sites of elements close to each other on the catalyst surface is a difficult task. The stability of multimetallic alloy against dissolution is another problem for practical sense.

4.3.2 New Electrocatalysts for Methanol Oxidation Reaction

As alternatives of Pt–Ru alloy for MOR electrocatalysts, several kinds of materials are proposed including platinum based alloy catalysts [15,43], platinum finely dispersed on oxide supports like TiO₂, MoO₂, WO₃ etc. [25–27,44,45].

Entirely new conceptual catalysts are proposed, e.g., rare earth cuprates [46], or organic metal complexes as a cocatalyst with platinum [35–37,47,48]. In 1998 Bett et al. reported the enhancement of MOR for Pt cocatalyzed with Sn phthalocyanines and Ru tetramethylcyclam for the first time, and discussed the activity in relation to their redox potentials, where lowering the redox potential increased MOR activity [47]. Macrocycles were adsorbed from pyridine solution to the surface of Pt/Vulcan XC-72. Also Goetz et al. reported binary catalysts consisting of Pt and nickel phthalocyaninetetrasulfonic acid [48]. Unfortunately the structure dependence of the metal complex was

critical, and the performance reported to date was not sufficient. Methanol oxidation on a polymerized nickel porphyrin complex was reported in basic media [49], but the function of the complex was 3-D Ni(II)/Ni(III) redox centers.

Screening tests are conducted to see the validity of simple organic compounds as cocatalyst to Pt in order to elucidate the effects of ligand structures on the MOR activity. Nitrogen and oxygen ligand containing organic metal complexes, *N, N'*-bis(salicylidene)ethylenediamine (*salen*), *N, N'*-bis(salicylidene)phenylenediamine (*salophen*), *N, N'*-mono-8-quinolyl-*o*-phenylenediamine (*mqph*), and *N, N'*-bis(anthranilidene)ethylenediamine (*anthen*), coordinated to V, Mn, Fe, Co, Ni, Cu, Mo, Pd, and Sn are synthesized and tested (Fig. 4.2) [37]. Major differences are the number of N ligands, i.e. 2N + 2O for *salen* and *salophen*, 3N for *mqph*, and 4N for *anthen*. Mixture of platinum precursor $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2 \cdot x\text{H}_2\text{O}$ and each of the organic metal complexes are supported on graphite powder (1–2 μm) and heat-treated at 600°C in Ar gas. This heat treatment is important to finish the catalysts with high catalytic performance and robustness in long-term use. The catalyst powder (abbreviated as Pt-M(*complex*)/C) is put on a glassy carbon disk electrode, and electrochemical measurements are performed for MOR activity.

Figure 4.3a depicts the polarization curves in deaerated 1 M CH_3OH + 0.05 M H_2SO_4 measured with Pt-Co(*mqph*)/C of various mixing ratios, heat-treated at 600°C [36]. A good synergetic effect is observed for the mixing ratio 60:40, 50:50, and 40:60 of Pt and Co(*mqph*), resulting in more than tens of times larger current than pure Pt. The potential at 1 mA cm^{-2} is over 500 mV, 320 mV, and 170 mV vs. SCE (saturated calomel electrode) for Pt/C, 50/50 Pt-Co(*mqph*)/C, and Pt-Ru/C, respectively. It is important that the organic metal complex is supported on carbon substrate, because organic molecules may decompose completely if not adsorbed on the carbon substrate.

When $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ is used in place of Co(*mqph*), Pt surface is strongly poisoned by CO, and the activity does not go over that of pure Pt, as seen in Fig. 4.3b. Two kinds of cobalt porphyrin complexes, cobalt tetraphenylporphyrin [Co(*TPP*)] and cobalt tetrakis(methoxyphenyl)porphyrin Co(*TMPP*)] heat-treated at 600°C are tested as well. Pt-Co(*TMPP*)/C shows higher activity than Pt-Co(*TPP*)/C, probably because of smaller decomposition during the heat treatment. The ligand structure is changed for *salophen*, *salen*, *anthen*, and *mqph*, fixing the central metal to Co. Polarization curves of 50:50 mixed catalysts Pt-Co(*complex*)/C as shown in Fig. 4.4 reveals a strong ligand dependence on the MOR catalytic activity, and *mqph* appears as the best ligand coordinated to Co.

Table 4.1 summarizes the MOR performances of the mixed catalysts of 50:50 Pt-M(*complex*)/C, with various combinations of central metals and ligand structures. In general, VIII_b transition metals reveal best as central metals. In view of the overpotential, the best candidates of mixed catalysts are found to be Pt-VO(*salen*)/C, Pt-Fe(*salen*)/C, Pt-Ni(*mqph*)/C, and Pt-Pd(*mqph*)/C [37]. Although the overpotential is larger than 20%

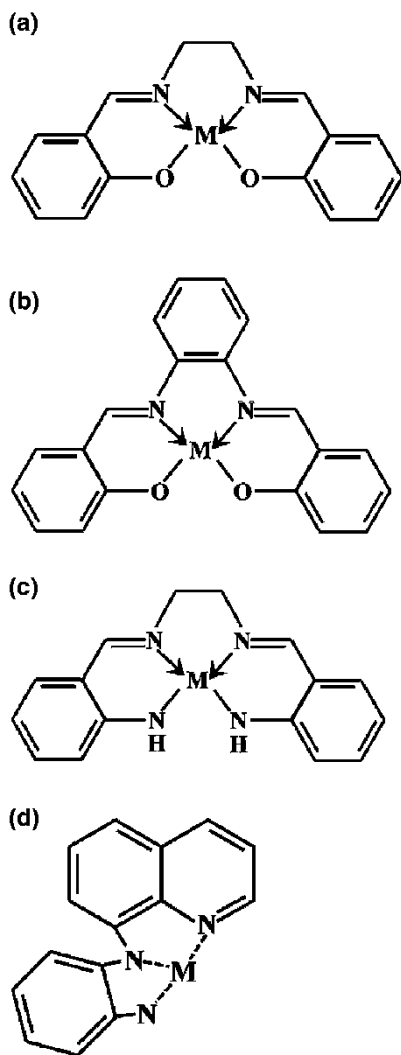


Fig. 4.2. Chemical structure of organic metal complexes tested. (a) *Salen*, (b) *salophen*, (c) *anthen*, (d) *mqph*. Coordination by acetate ligands is omitted ([37], copyright Elsevier)

Pt–Ru/C by about 120 to 140 mV, these catalysts show higher current density than Pt–Ru/C. Seeing the CO oxidation mechanism by van Baar et al. [33], the *d*-electron deficiency and the low redox potential of the metal would be important factors, because these factors relate to the CO binding and its nucleophilic attack by H₂O, which should mitigate the CO poisoning on Pt.

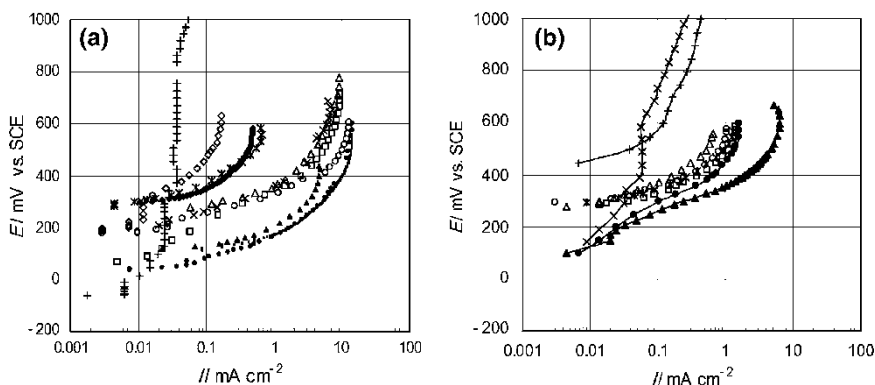


Fig. 4.3. (a) Polarization curves of MOR on Pt-Co(*mqph*)/C in 1 M CH₃OH + 0.05 M H₂SO₄ at 25°C, in deaerated condition with N₂ gas. Mixing ratio of Pt(NH₃)₄Cl₂·xH₂O and Co(*mqph*): 100:0 (*), 80:20 (×), 60:40 (Δ), 50:50 (○), 40:60 (□), 20:80 (◇), 0:100 (+). Also data of 10% Pt/C (◆), 10% Pt-Ru/C (·, ▲), and 20% Pt-Ru/C (■) are overlaid. (b) Polarization curves of MOR on Pt-Co(NH₃)₆/C, Pt-Co(*TPP*)/C, and Pt-Co(*TMPP*)/C. Mixing ratio of Pt(NH₃)₄Cl₂·xH₂O and Pt-Co(NH₃)₆: 100:0 (*), 60:40 (Δ), 50:50 (○), 40:60 (□). Mixing ratio of Pt(NH₃)₄Cl₂·xH₂O and Pt-Co(*TPP*): 50:50 (·), 0:100 (+). Mixing ratio of Pt(NH₃)₄Cl₂·xH₂O and Pt-Co(*TMPP*): 50:50 (▲), 0:100 (×) ([36], copyright Elsevier)

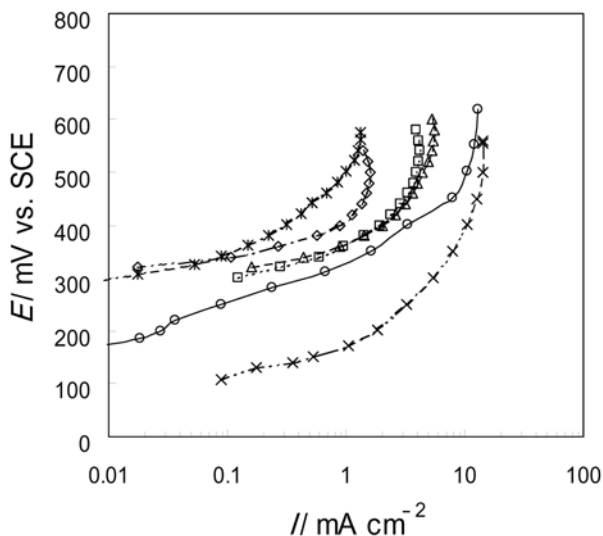


Fig. 4.4. Polarization curves of MOR on mixed catalysts with 50:50 mixing ratio, Pt-Co(*salophen*)/C (◇), Pt-Co(*salen*)/C (□), Pt-Co(*anthen*)/C (Δ), and Pt-Co(*mqph*)/C (○), supported on graphite powder and heat-treated at 600°C. As a comparison, polarization curves on 12% Pt/C (*) and 20% Pt-Ru/C (ElectroChem, (×)) are also shown. Solution: 1 M CH₃OH + 0.05 M H₂SO₄ at 25°C, in deaerated condition with N₂ gas ([37], copyright Elsevier)

Table 4.1. Performances of mixed catalysts Pt-M(*complex*)/C, supported on graphite powder and heat-treated at 600°C, together with those of 12% Pt/C and 20% Pt-Ru/C ([37], copyright Elsevier)

Catalysts	$I_{\max}/mA$ cm^{-2}	E_{ini}/mV vs. SCE	E ($I = 1mAcm^{-2}$) $/mV$ vs. SCE
Pt-V(<i>mqph</i>)/C	13.4	190	310
Pt-VO(<i>salen</i>)/C	12.4	150	310
Pt-Mn(<i>mqph</i>)/C	15.6	220	294
Pt-Fe(<i>mqph</i>)/C	14.7	170	320
Pt-Fe(<i>salen</i>)/C	18.4	100	310
Pt-Co(<i>mqph</i>)/C	12.8	184	320
Pt-Co(<i>anthen</i>)/C	5.3	260	360
Pt-Co(<i>salen</i>)/C	4.1	260	360
Pt-Co(<i>salophen</i>)/C	1.6	310	410
Pt-Ni(<i>mqph</i>)/C	25.0	170	305
Pt-Ni(<i>salen</i>)/C	2.7	300	390
Pt-Cu(<i>mqph</i>)/C	16.3	240	349
Pt-Mo(<i>mqph</i>)/C	9.5	200	358
Pt-Pd(<i>mqph</i>)/C	34.9	50	294
Pt-Sn(<i>mqph</i>)/C	5.4	120	281
Pt-Co(<i>TPP</i>)/C	1.6	147	459
Pt-Co(<i>TMPP</i>)/C	6.4	143	358
12% Pt/C	0.66	299	>500
20% Pt-Ru/C	14.3	80	170

$I_{\max}$: maximum current density, E_{ini} : initiation potential, $E(I = 1mA cm^{-2})$: potential at the current density $I = 1mA cm^{-2}$.

4.3.3 Structure of Composite Catalysts

Whether the organic metal complexes on carbon substrate are destroyed or remain intact is a matter of interest that relates to the role of composite catalysts in MOR.

Figures 4.5a-d show thermogravimetry (TG) and differential thermal analysis (DTA) curves for $Pt(NH_3)_4Cl_2 \cdot xH_2O$ and Co(*complex*) mixture with 50:50 mixing ratios on carbon [37]. For Pt-Co(*salophen*)/C clear decomposition occurs in two steps accompanied by two DTA peaks, first at 200–210°C and second at 250–300°C, with 15% decrease. Here decomposition of precursors proceeds to metallic Pt and Co, probably in the alloy state. On the other hand, for Pt-Co(*salen*)/C, Pt-Co(*anthen*)/C, and Pt-Co(*mqph*)/C, the decomposition seems not complete and TG curves are smooth. The mass change is about 10%, and Co complexes do not completely decompose. The interaction energy between aromatic moiety of complexes and graphite surface probably mitigates the thermal decomposition of molecules. Van Veen

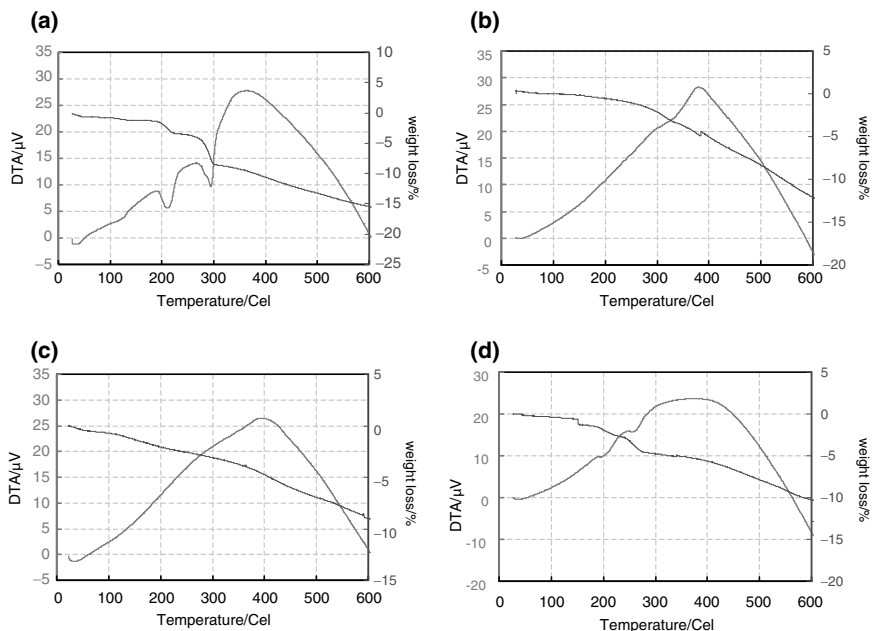


Fig. 4.5. Thermogravimetry (TG) and differential thermal analysis (DTA) curves of mixed catalysts with 50:50 mixing ratios, (a) Pt–Co(*salophen*)/C, (b) Pt–Co(*salen*)/C, (c) Pt–Co(*anthen*)/C, and (d) Pt–Co(*mqph*)/C, supported on graphite powder. Heating rate: $5^{\circ}\text{C min}^{-1}$ in Ar atmosphere ([37], copyright Elsevier)

et al. indicate the “thermal modification” of metal chelates when they are supported and heat-treated on carbon [50].

Morphology of the Pt–Co(*mqph*)/C catalyst heat-treated at various temperatures observed by field emission scanning electron microscope (FE SEM) is shown in Fig. 4.6, with mixing ratio as a parameter. Increasing the temperature resulted in the increase in the size of Pt particles. For pure Co(*mqph*)/C, no metallic deposition was observed at 400°C , but above 600°C decomposition occurred and metallic particles appeared as distinct grains. At intermediate mixing ratios, characteristic structure appeared that was supposedly attributable to the mixture of Pt or Pt alloy particles and partially decomposed Co(*mqph*). The results indicate that at 600°C the mixed catalyst is finely dispersed and stabilized on the carbon substrate. In the case of Pt–Co(NH_3)₆/C, the resulting state appears to be almost the mixture of metallic particles on the graphite substrate.

X-ray diffraction (XRD) patterns of mixed catalysts are compared in Fig. 4.7 for four kinds of Pt–Co(*complex*)/C with 50:50 mixing ratios, heat-treated at 600°C [37]. For Pt–Co(*salophen*)/C, strong Pt peaks indicates metallic particles of Pt, together with Co and CoPt₃ peaks of intermetallic

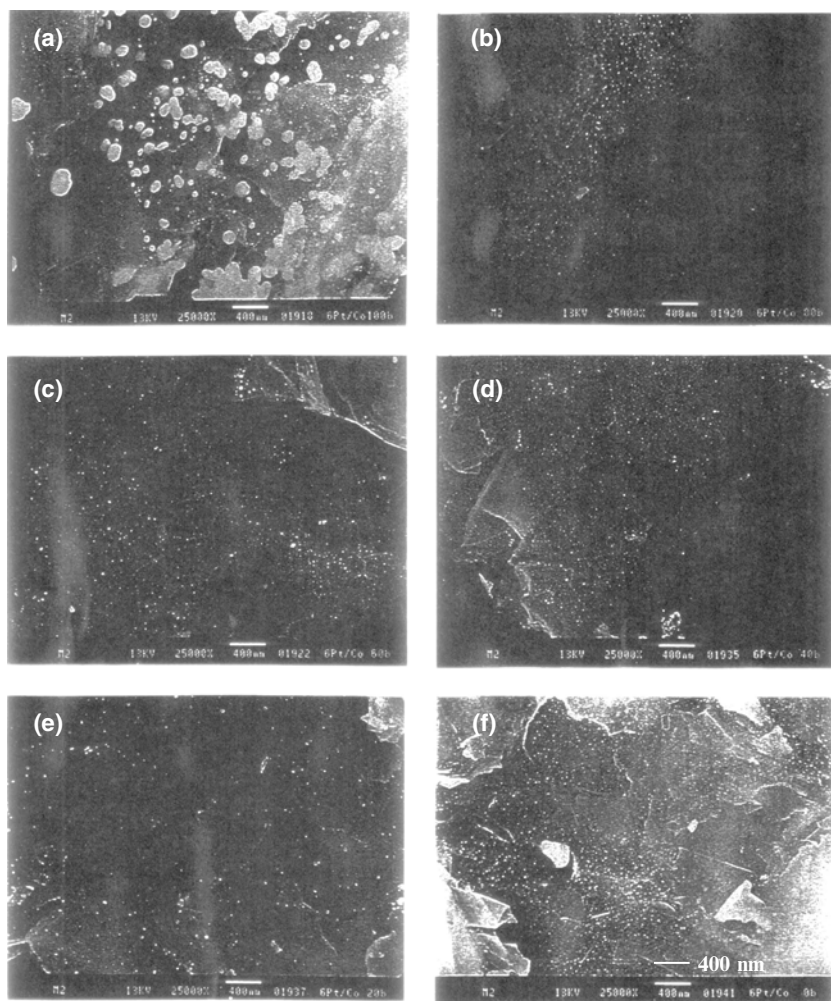


Fig. 4.6. FE SEM pictures of Pt–Co(*mqph*)/C heat-treated at 600°C. Mixing ratio of $\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot x\text{H}_2\text{O}$ and $\text{Co}(\text{mqph})$: 100:0 (a), 80:20 (b), 60:40 (c), 40:60 (d), 20:80 (e), 0:100 (f) ([36], copyright Elsevier)

compounds between Pt precursor and Co complex. Sharp decomposition in TG and DTA curves shown in Fig. 4.5a also indicate the formation of inter-metallic compounds. This is similar to the case of Pt–Co(NH_3)₆/C. The lowest catalytic ability may be ascribed to the complete decomposition of precursors during the heat-treatment. In the case of Pt–Co(*salen*)/C, Pt peaks shifted positively, indicating the formation of solid-solution between Pt and Co. Pt–Co(*anthen*)/C and Pt–Co(*mqph*)/C gave similar XRD patterns, and peaks are

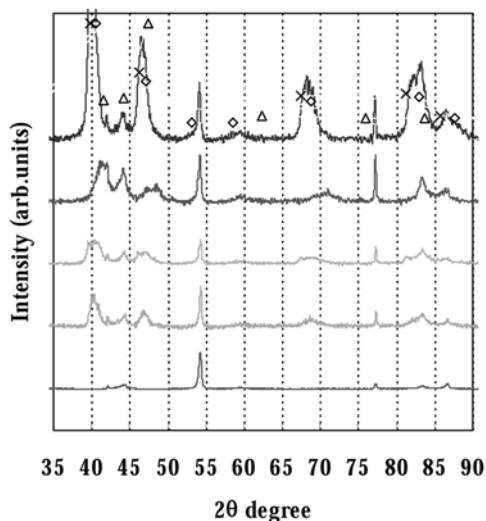


Fig. 4.7. X-ray diffraction patterns of mixed catalysts, Pt-Co(*complex*)/C, with 50:50 mixing ratio, supported on graphite powder and heat-treated at 600°C. From top to bottoms curves, Pt-Co(*salophen*)/C, Pt-Co(*salen*)/C, Pt-Co(*anthen*)/C, Pt-Co(*mqph*)/C, and graphite powder. Peak assignments: (×) Pt (39.8°, 46.2°, 67.5°, 81.3°, 85.7°); (Δ) Co (41.6°, 44.3°, 47.4°, 62.3°, 75.9°, 83.7°); (◇) CoPt₃ (40.5°, 47.1°, 53.1°, 58.6°, 68.8°, 83.0°, 87.6°) ([37], copyright Elsevier)

mainly those of Pt. Gradual decomposition of mixed catalysts as seen in the thermal analysis indicates that Co complexes are not completely destroyed.

Figure 4.8 illustrates X-ray photoelectron spectroscopy (XPS) spectra of Pt 4f_{7/2}, Co 2p_{3/2}, and N 1s for three kinds of 50/50 Pt-Co(*complex*)/C, before and after the heat treatment at 600°C [37]. Heat treatment causes a shift of the Pt 4f_{7/2} peak in negative direction towards 71.2 eV (metallic Pt), indicating the change of valence from Pt(II) to Pt(0). On the other hand, Co 2p_{3/2} peak is more positive than 778.2 eV of metallic Co, and the peak does not shift much for Co complex after the heat treatment as compared to that of non-heat-treated state except for Pt-Co(*salophen*)/C, where a shoulder appears at 778.2 eV. For N 1s peaks, peak splitting at 401 eV observed for Pt-Co(*salophen*)/C shows demetallated N, while for Pt-Co(*salen*)/C and Pt-Co(*anthen*)/C major peaks around 399 eV are identified as N of metal nitride, indicating a coordination between Co and N.

These results are supported by X-ray absorption spectroscopy measured for the Pt-Co(*complex*)/C catalysts. Figure 4.9 shows Co K-edge X-ray absorption near-edge structure (XANES) spectra of Co ion for the mixed catalysts measured before and after the heat treatment [51]. All the Co K-edge XANES spectra are located between the spectra for Co(0) and Co(III). For the Co(*anthen*) and Co(*salen*), the XANES spectra shifted to lower energy

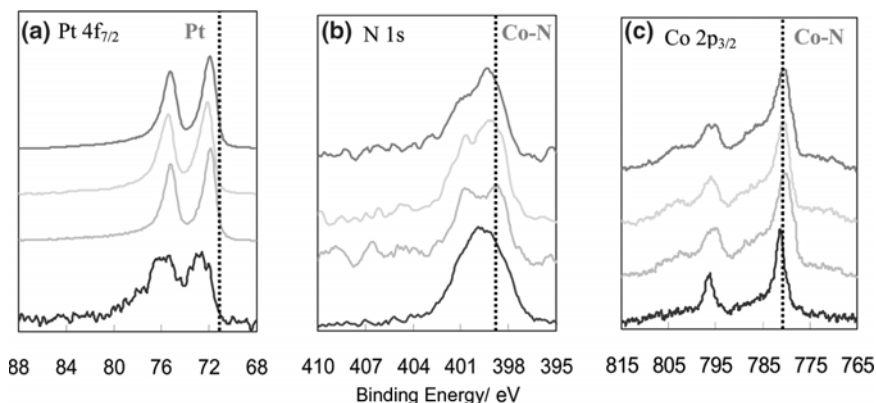


Fig. 4.8. X-ray photoelectron spectroscopy of mixed catalysts Pt-Co(*complex*)/C, with 50:50 mixing ratios, heat-treated at 600°C. (a) Pt 4f_{7/2}, (b) N 1s, (c) Co 2p_{3/2}. From top to bottoms curves, Pt-Co(*anthen*)/C, Pt-Co(*salen*)/C, Pt-Co(*salophen*)/C after the heat treatment and Pt-Co(*salophen*)/C before the heat treatment. If Co complex is de-metallated, peaks should appear at 778 eV (metallic Co) and 400.5 eV (non-coordinated N) ([37], copyright Elsevier)

after the heat treatment, as compared to the Co(*mqph*). For Co(*anthen*) and Co(*salen*) the partial decomposition to form Co occurred more than for Co(*mqph*). However, the major trend is that the metal coordination structures in the Co(*complex*) more or less remained on the graphite powder even after the heat treatment.

Also shown in Fig. 4.9 are the Co K-edge extended X-ray absorption fine structure (EXAFS) spectra for the Pt-Co(*complex*)/C composite catalysts before and after the heat treatment. The first peak at around 1.4 Å due to the Co-N interaction slightly shifts to a larger distance through the heat treatment. For the Co(*anthen*) and Co(*salen*), the peaks became smaller and a novel peak at 2.2 Å appeared that corresponds to Co metal, indicating a partial demetallation of the complexes. The Co-N₃ coordination structure of Co(*mqph*) remains after the heat treatment, as compared to coordination structures in Co(*anthen*) and Co(*salen*) [51]. Van Veen et al. [52] also prepared several Co-N₄ catalysts on carbon black (Vulcan XC-72R) in a similar way and examined their catalytic activities for the electrochemical reduction of oxygen. They confirmed by EXAFS that the Co-N₄ moieties exist on the carbon black after the heat-treatment at 700°C, although some metallic cobalt also appeared.

The trends of above results agree with TG-DTA, transmission electron microscope (TEM) morphologies, and XRD patterns. While the precursor Pt(NH₃)₄Cl₂·xH₂O is completely decomposed by the heat-treatment up to 400°C, M(*mqph*), M(*anthen*), and M(*salen*) in the mixed state show mild decompositions. The metal-ligand coordination structures play a certain role in MOR on the Pt catalysts.

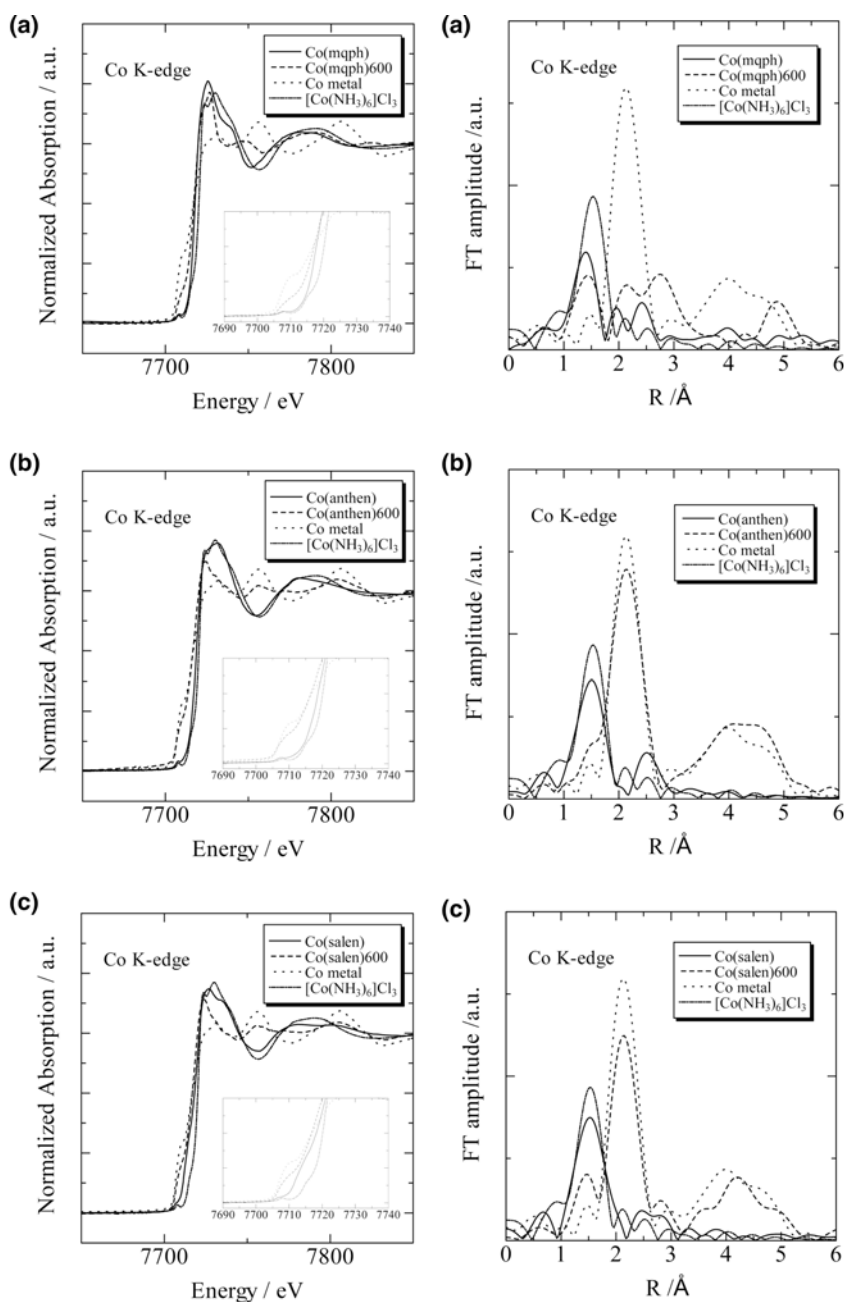


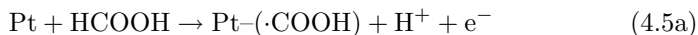
Fig. 4.9. Co K-edge XANES spectra (left figure) and Co K-edge EXAFS spectra (right figure) of (a) Pt-Co(*mqph*)/C, (b) Pt-Co(*anthen*)/C, and (c) Pt-Co(*salen*)/C (mixing ratio: 50:50) ([51], copyright Elsevier)

4.4 Formic Acid Oxidation Reaction

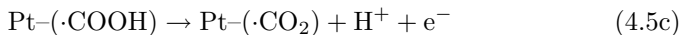
Because formic acid shows higher specific-energy density and also higher open-circuit potential as well as lower crossover rate through the polymer electrolyte membrane as compared to methanol, direct formic acid fuel cell is an attractive option for mobile fuel cell applications [53]. The problem is that no specific catalyst exists for formic acid oxidation. In recent researches, good catalysts have been reported such as Pd and Pd alloy nanoparticles or combination of Pt and porphyrin complexes supported on carbon. Since the oxidation product CO_2 is made within the HCOOH molecule, simple kinetics is expected, but in reality the mechanism is not fully clarified.

4.4.1 Mechanism of Formic Acid Oxidation

HCOOH oxidation on Pt occurs through $\cdot\text{COOH}$ intermediate [23]:



This intermediate adsorbs strongly on Pt, and decomposition reaction yields either the adsorbed poison $\cdot\text{CO}$ or oxidation to CO_2 . Parsons et al. proposed a parallel path mechanism in which HCOOH oxidizes through either poison intermediate ($\cdot\text{CO}$) or active intermediate [54].



Adsorbed CO on Pt surface strongly hinders free site from further reaction [55, 56]. As the active intermediate, Clavilier et al. suggested $\cdot\text{COOH}$ using electrochemically modulated infrared reflectance (EMIR) spectroscopy [56]. Recently Behm et al. [57] and Osawa et al. [58] reported with in situ attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectroscopy experiment that the active intermediate involves formate species $[\text{H}-\text{C}(\text{O})_2]^-$.

It is known that HCOOH oxidation is a structure-sensitive process, and depending on the facet Pt shows low poisoning and low activity behavior on Pt(111) and hysteresis behavior on Pt(100) in which the electrode once deactivated recovers activity after the poison is eliminated at a high potential [59]. This structural sensitivity leads to the idea of “ensemble effect” [59], and since $\cdot\text{CO}$ formation needs more Pt sites than direct oxidation through active intermediate, a “surface modifier” can selectively enhance direct HCOOH oxidation by reducing the adsorption sites for CO by geometrical hindrance (third-body effect) [60].

Enhancement of catalytic activity for HCOOH by underpotential deposited (UPD) Pb on Pt was recently reported by Lee et al [61]. UPD Bi modification of Pt was also effective for HCOOH oxidation [62]. These enhancement effects are ascribed to the reduced poisoning formation on modified Pt surface due to electronic or third-body effect of the modifier metals.

The ordered intermetallic phases that were prepared by mixing stoichiometric amount of Pt and other metals then heating under vacuum and quenching, exhibited good catalysis for HCOOH and other organic molecule oxidation [63].

Masel et al. reported that Pd-deposited Pt was unusually active for formic acid oxidation [53]. However CO stripping showed that CO once adsorbed was not quickly oxidized. They mentioned that oxidation of HCOOH on Pt/Pd was not inhibited by CO because unlike Pt–Ru, the reaction occurs via a direct electrooxidation mechanism (4.5c) [64]. This feature encouraged them to use Pd alloy nanoparticle catalysts for direct formic acid fuel cells.

We learn from above results that since HCOOH is a small molecule that needs small number of reaction site and only two electrons, modification of the catalyst surface that hinders the adsorption sites for CO is expected to enhance the HCOOH oxidation reaction.

4.4.2 Formic Acid Oxidation on Composite Catalysts

The idea of composite catalysts based on platinum and organic complexes for HCOOH oxidation reaction has been practiced recently by Xing et al. [65]. They observed a promoting effect of Pt catalyst by iron tetrasulfophthalocyanine (FeTSPc) in electrochemical and fuel cell experiments. Figure 4.10 shows cyclic voltammograms and polarization curves of Pt and modified Pt electrodes with FeTSPc. By addition of FeTSPc the peak oxidation current of active intermediate at 0.40 V vs. Ag/AgCl increased more than eight times as compared with that of Pt. They ascribed this enhancement to the mechanism where formation of poisoning intermediate was suppressed by adsorption of FeTSPc.

Following the investigations on CH₃OH oxidation reaction, Ni(*mqqh*) was used together with Pt to prepare a composite catalyst. Figure 4.11 illustrates polarization curves of HCOOH oxidation on Pt/C, Pt–Ru/C, and Pt–Ni(*mqqh*)/C in acidic environment. The heat-treatment temperature strongly affected the HCOOH oxidation current, and optimum temperature appeared at 350°C. From C–V curves shown in Fig. 4.12, it is inferred that the first peak appearing at 0.6 V vs. RHE (reversible hydrogen electrode) on Pt–Ni(*mqqh*)/C increases much more than on Pt/C or Pt–Ru/C. This fact indicates that Pt–Ni(*mqqh*)/C is a promising candidate as HCOOH oxidation catalyst.

In Fig. 4.13, the current density at 0.5 V vs. RHE is plotted for various catalysts at different temperatures. The activation energies obtained from Arrhenius plots are 20.4 kJ mol^{−1} for Pt, 19.0 kJ mol^{−1} for Pt–Ru, and 15.4 kJ mol^{−1} for Pt–Ni(*mqqh*), showing a smaller energy barrier for the active intermediate path with Pt–Ni(*mqqh*) than with others. Peak potentials on CO stripping experiments carried out with CO + H₂ gas bubbling in 0.5 M H₂SO₄ are 0.79 V, 0.59–0.6 V, and 0.58–0.6 V for Pt, Pt–Ru, and Pt–Ni(*mqqh*), respectively. Remarkably, CO peak is diminished much more on Pt–Ni(*mqqh*) than on Pt or Pt–Ru, indicating that CO formation is suppressed on Pt surface when Ni(*mqqh*) existed.

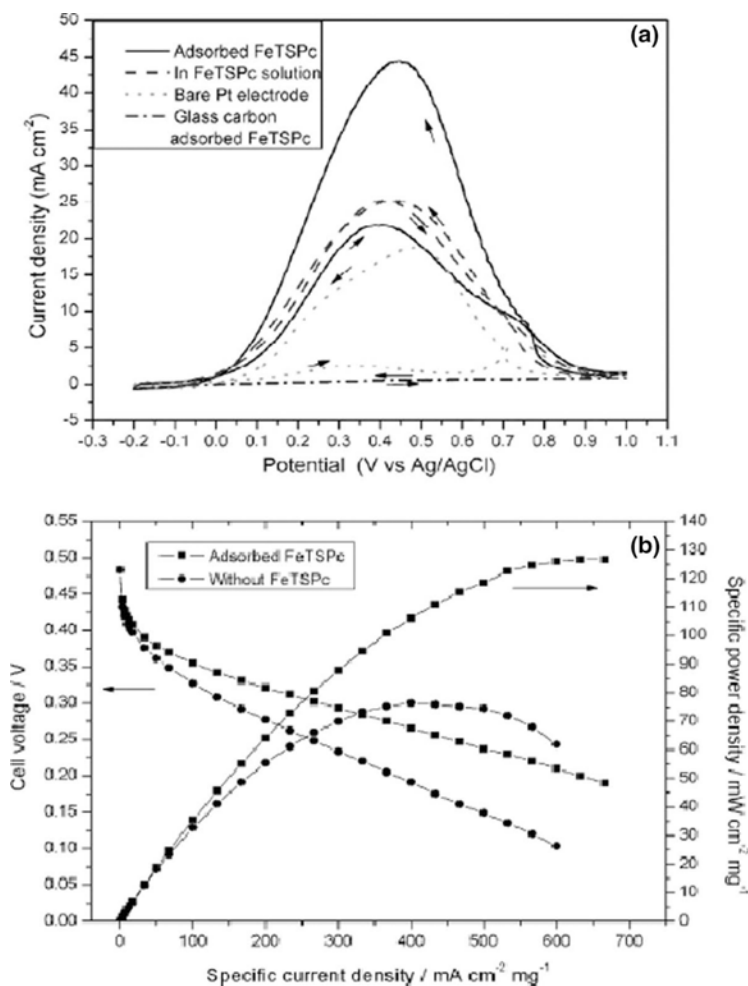


Fig. 4.10. (a) The cyclic voltammograms in 1.0 M HCOOH + 0.5 M H₂SO₄ at scanning rate 100 mV s⁻¹ at 25°C. (— · — · —) glassy carbon electrode-adsorbed FeTSPc, (....) bare Pt electrode, (—) Pt electrode-adsorbed FeTSPc, and (- - -) Pt electrode in 0.1 mg mL⁻¹ FeTSPc solution. (b) Polarization curves of the direct formic acid fuel cell at 60°C, before and after the anode electrode adsorbs FeTSPc: (- - - -) without adsorbing FeTSPc, (-■-■-) after the anode electrode adsorbing FeTSPc. Anode: Pt loading 0.5 mg cm⁻² fed with 6M HCOOH; cathode: Pt loading 1.5 mg cm⁻² fed with O₂. Specific current density equals to current density/Pt loading ([65], copyright Elsevier)

Fuel cell testing was conducted at 60°C using a single cell with 6 M HCOOH aqueous solution as the anode fuel at the flow rate of 1 mL min⁻¹, and O₂ gas as oxidant at the flow rate of 100 mL min⁻¹ at the cathode. Catalyst loadings were 0.3 mg(Pt) cm⁻² for the anode and 1.0 mg(Pt) cm⁻² for the cathode.

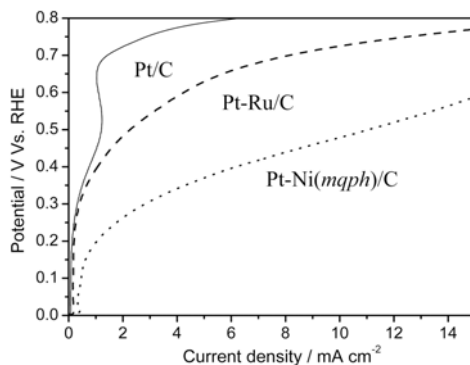


Fig. 4.11. Polarization curves of HCOOH oxidation on Pt/C, Pt-Ru/C, and Pt-Ni(*mqph*)/C (heat-treated at 350°C) in 1 M HCOOH + 0.5 M H₂SO₄ at 25°C

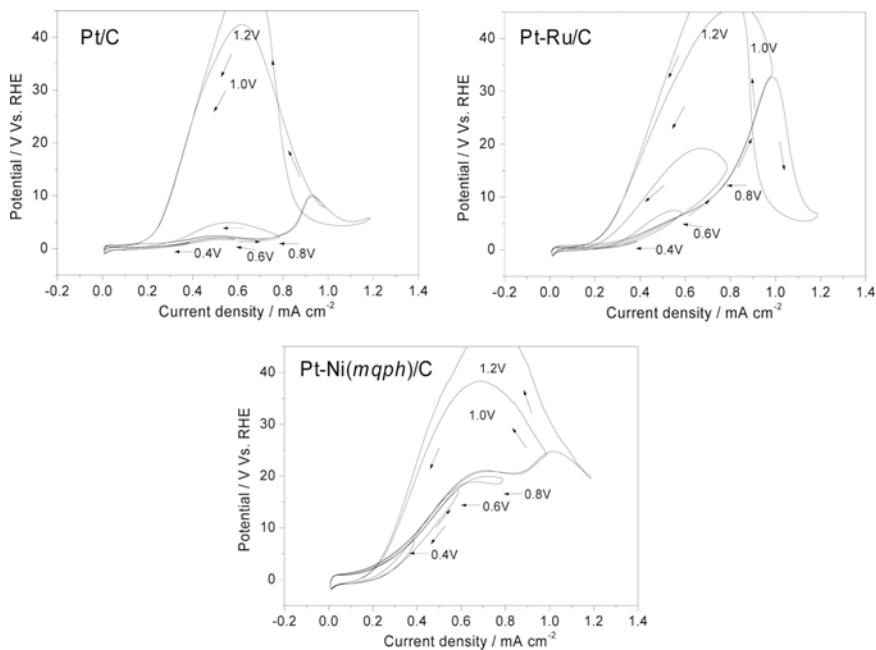


Fig. 4.12. Cyclic voltammograms of HCOOH oxidation on Pt/C, Pt-Ru/C and Pt-Ni(*mqph*)/C (heat-treated at 350°C) in 1 M HCOOH + 0.5 M H₂SO₄ measured at 25°C at a scan rate of 50 mV s⁻¹. The vertex potentials are indicated in the figure

Figure 4.14 compares the performances of cells using Pt/C, Pt-Ru/C, and Pt-Ni(*mqph*)/C as anode catalysts. Open-circuit voltage of the fuel cells was 0.68 V, 0.71 V, and 0.79 V for Pt/C, Pt-Ru/C, and Pt-Ni(*mqph*)/C catalysts, respectively. The peak power density divided by the amount of Pt per cm² at the anode was 85 mW cm⁻² mg⁻¹, 108 mW cm⁻² mg⁻¹, and

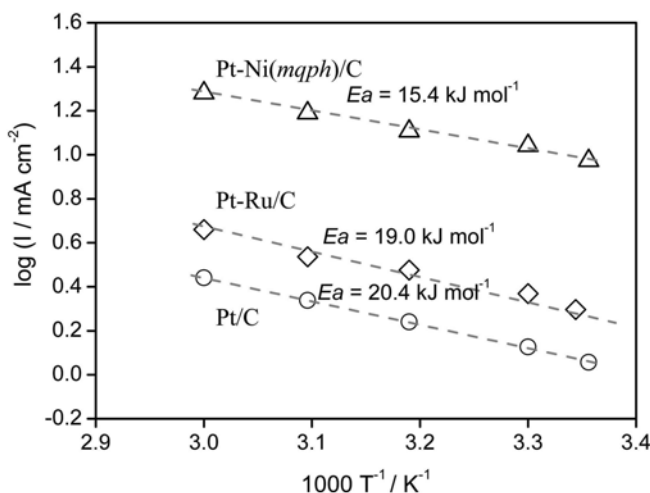


Fig. 4.13. Arrhenius plots of HCOOH oxidation current density on Pt/C, Pt-Ru/C, and Pt-Ni(*mqph*)/C (heat-treated at 350°C) in 1 M HCOOH + 0.5 M H₂SO₄ measured at various temperatures

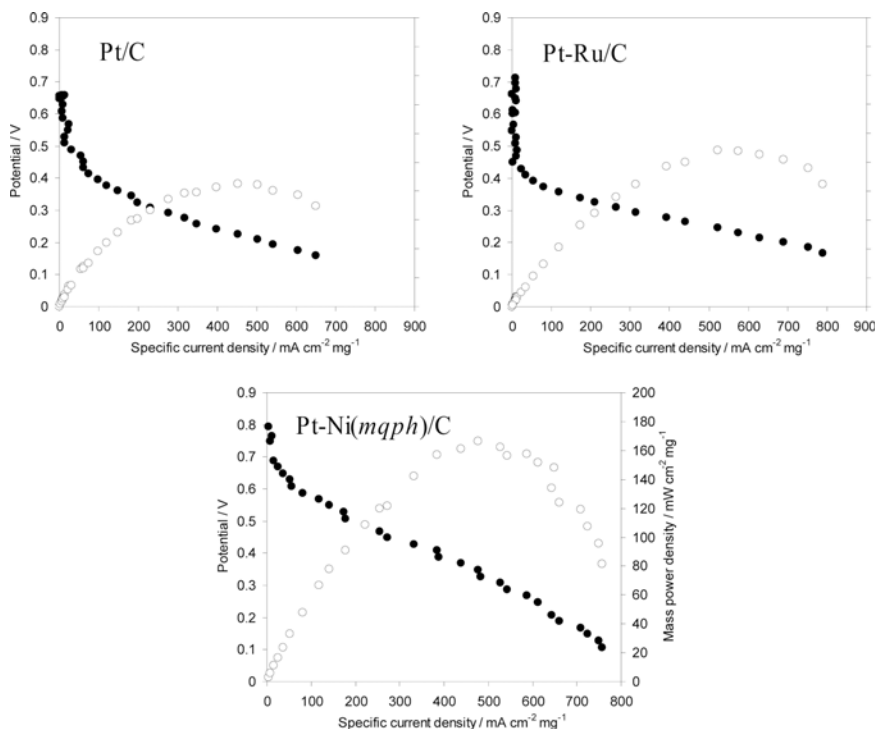


Fig. 4.14. Polarization curves of the direct formic acid fuel cell at 60°C. Anode: Pt loading 0.3 mg cm⁻², fed with 6 M HCOOH; cathode: Pt loading 1.0 mg cm⁻², fed with O₂. Specific current density equals to current density/Pt loading

166 mW cm⁻² mg⁻¹, respectively. These values rank as one of the best results reported so far, and show that Pt-Ni(*mqph*)/C composite catalyst can be expected for use in direct formic acid fuel cell applications.

4.5 CO-Tolerant Electrocatalysts for Hydrogen Oxidation Reaction

In fuel cells using reformat gas, even small amount (10 ppm) of CO degrades seriously the platinum catalysts for hydrogen oxidation reaction (HOR). Pt-Ru alloy is the only and most studied material as CO-tolerant anode catalyst, but there are still some problems for commercialization. Although many alternatives have been proposed as CO-tolerant electrocatalysts, very few are reported successful compared with Pt-Ru for practical uses as regards the initial performance and longevity.

CO-tolerant anode catalysts using molecular catalysts are challenging topic, and several works have been directed so far to find alternatives for Pt-Ru. The potential range for H₂ oxidation is much lower than those for methanol or formic acid, and this demands a new design concept. Carbon-supported transition-metal porphyrin catalysts [33], macrocycles on Pt or Pt-Ru catalysts [47], have been studied in view of their possibilities as CO oxidation catalysts. Successful results were first reported by Venkataraman et al. in 2004, where enhancement of CO tolerance of Pt cocatalyzed by metal-macrocycles was tested using a single fuel cell [66]. Ruthenium tetramethylethylcyclam (RuTMC) or molybdenum tetrakis(methoxyphenyl) porphyrin (MoTMPP) was adsorbed or precipitated from methanol on high surface area carbon black. Pt was deposited on the carbon black containing pre-adsorbed complex. Table 4.2 shows their results, indicating a direct correlation between redox potential of the complex and the anodic polarization in H₂ with 104 ppm CO. They also found that sulfur-containing Pt catalysts exhibited inhibition of CO adsorption and that activity of CO oxidation started at potentials as low as 0.2 V NHE [67]. The sulfided Pt showed much better CO tolerance than Pt.

In this section a novel system of CO-tolerant H₂ oxidation catalysts is investigated extending the cases of methanol and formic-acid oxidation catalysts. It is expected that their performance and longevity will be greatly enhanced by heat-treating the mixed precursors of Pt and organic metal complexes on carbon in an inert atmosphere [68–71]. The mechanism of CO tolerance, whether redox potential of the complex plays a role or not, is also an important subject to discuss.

4.5.1 Electrochemical and Fuel Cell Testing

Platinum precursor Pt(NH₃)₄Cl₂ · *x*H₂O and organic metal complexes are supported with 50:50 mass percent ratio on the carbon black (Vulcan XC-72R),

Table 4.2. Anode polarization and CO stripping potentials for complexes with different redox potentials^a ([66], copyright The Electrochemical Society)

Complex	Redox potential/V	Electroactive species (%)	Anode polarization at $i = 400 \text{ mA cm}^{-2} \text{ V}$	CO stripping peak potential/V
Pt	—	—	0.499	0.589
Pt–Ru	—	—	0.178	0.360
RuTMC14 ^b	0.189	5.56	0.363	0.526
RuTMC15	0.133	5.47	0.356	0.475
RuTMC16	0.123	7.14	0.35	0.472
Ru(NH ₃) ₆ Cl ₃	−0.013	32.75	0.3	0.445
MoTMPP ^c	−0.020	21.41	0.278	0.4
FeTMPP	0.235	15.37	0.457	0.578
CoPc ^d	0.042	4.02	0.429	0.561

^aSurface coverage of complexes: ca. two monolayers.^bRuthenium tetramethylcyclam, 14 member ligand.^cTMPP: tetrakis(methoxyphenyl)porphyrin^dCobalt phthalocyanines

and heat-treated for 2 h in Ar atmosphere, to obtain composite catalysts. The catalyst-supported carbon powder was mixed with 5 wt% Nafion solution (Aldrich) to get an ink of the mixture, which was then pasted on the wet-proofed carbon paper disk. The amount of Pt in the mixed catalyst was $5.4 \times 10^{-1} \text{ mg(Pt) cm}^{-2}$, for the apparent electrode area of the disk. The test specimens were made as a half-MEA that was prepared by hot-pressing the catalyst-loaded carbon paper disk to one side of Nafion 115 membrane. The catalysts are tested for the HOR electrochemical performances using a half-cell consisting of a Teflon holder with H₂ gas inlet and outlet containing CO [68]. The platinum plate and the reversible hydrogen electrode (RHE) in deaerated 1 M HClO₄ served as the counter and the reference electrodes, respectively.

Results are summarized in Table 4.3, where the retention of the current in H₂ + 100 ppm CO are shown in reference to pure H₂ condition, together with the mass activities of HOR in pure H₂. Both the central metal and the ligand structures of Pt–M(*complex*)/C affected strongly the CO tolerance.

Among catalysts tested, Pt–VO(*salen*)/C and Pt–Ni(*mqqh*)/C proved very promising performances as CO-tolerant anode catalysts for reformat fuel cells. Figure 4.15 compares their performances with those of the commercial 20% Pt/C (ElectroChem, MA) and 20% Pt–10% Ru/C (Johnson Matthey, Inc. Co) of the same Pt amount. In comparison to Pt/C and Pt–Ru/C, the composite catalysts appear to reveal higher tolerance in this test condition.

Figure 4.16a presents the effect of the heat treatment temperature on the catalytic activity of Pt–VO(*salen*)/C [69], shown as normalized HOR currents at 100 mV RHE in a half-cell, and mass activities of HOR current (current per

Table 4.3. Ligand and central metal dependencies of the current at 0.1 V RHE in H₂ gas containing 100 ppm CO for Pt-M(*complex*)/C composite catalysts ([71], copyright *Journal of New Materials and Electrochemical Systems*)

Catalysts ^a	Mass activity/ $\text{\AA mg(Pt)}^{-1}$	Current ratio/% ^b
	H ₂	100 ppm CO/H ₂
20% Pt-VO(<i>salen</i>)/C	4.7 ₇	42 ₇
20% Pt-Ni(<i>mqph</i>)/C	4.1 ₃	36 ₈
20% Pt-Cu(<i>fsaaep</i>)/C	1.5 ₃	21 ₂
20% Pt-Ru(<i>mqph</i>)/C	2.0 ₇	12 ₇
20% Pt-VO(<i>dqpr</i>)/C	1.7 ₉	10 ₆
20% Pt-Mn(<i>mqph</i>)/C	1.1 ₉	9.6
20% Pt-VO(<i>anthen</i>)/C	3.7 ₁	8.4
20% Pt-VO(<i>fsaaep</i>)/C	1.8 ₉	4.7
20% Pt-VO(<i>mqph</i>)/C	1.9 ₃	0.1

^aCatalysts were heat-treated at 400°C in Ar.

^bHydrogen oxidation currents at 0.1 V vs. RHE derived from the polarization curves normalized by those measured in pure H₂.

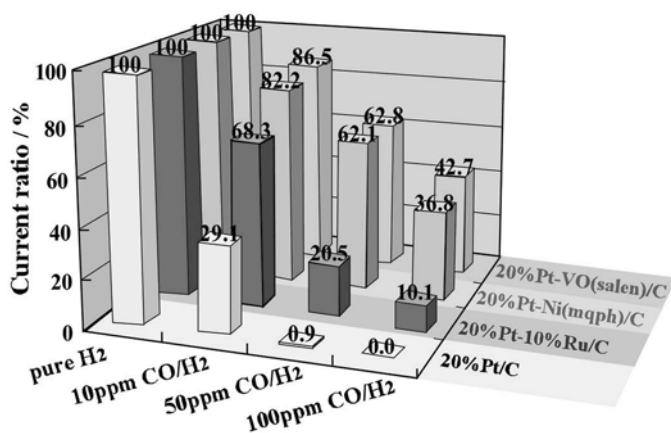


Fig. 4.15. Comparison of Pt-VO(*salen*)/C and Pt-Ni(*mqph*)/C heat-treated at 400°C, with Pt/C and Pt-Ru/C for the H₂ oxidation currents containing various amounts of CO. The mass activities in H₂ are 4.8 $\text{\AA mg(Pt)}^{-1}$, 4.1 $\text{\AA mg(Pt)}^{-1}$, 4.1 $\text{\AA mg(Pt)}^{-1}$ and 7.6 $\text{\AA mg(Pt)}^{-1}$, for Pt-VO(*salen*)/C and Pt-Ni(*mqph*)/C, Pt-Ru/C and Pt/C, respectively ([71], copyright *Journal of New Materials and Electrochemical Systems*)

unit mass of Pt). The optimum heat treatment temperature appears around 400°C. In Fig. 4.16b for similar plots for Pt-Ni(*mqph*)/C, the highest mass activity appears also around 400°C [70].

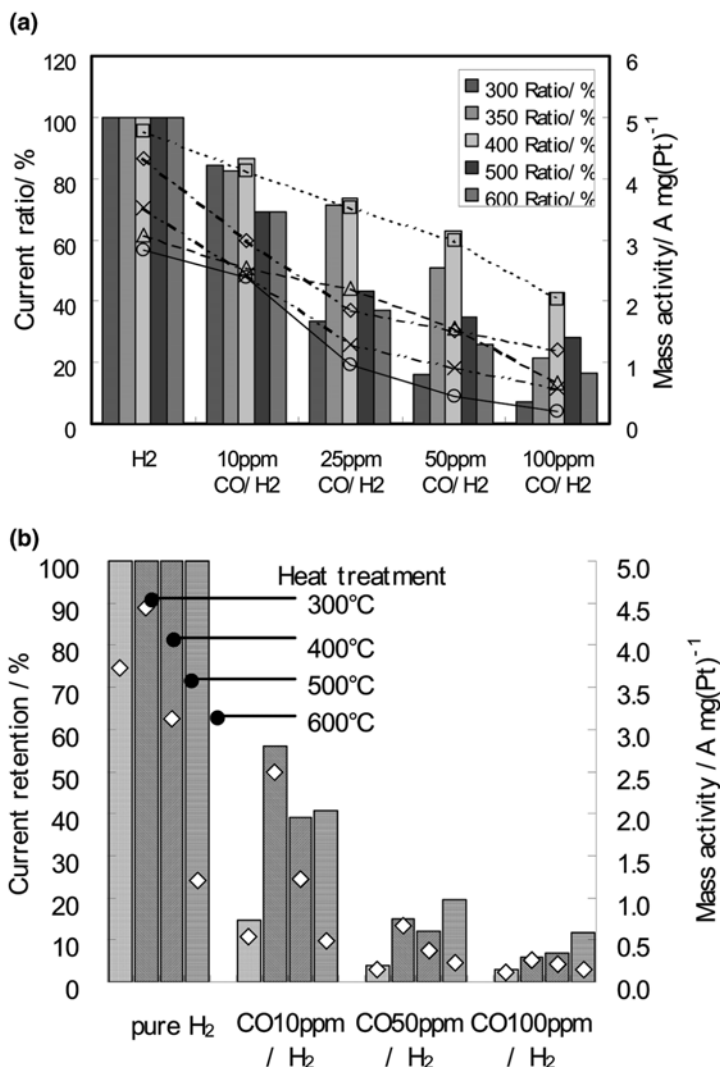


Fig. 4.16. Effect of heat treatment temperature of 20% Pt-M(*complex*)/C on the H_2 oxidation current containing various amounts of CO. (a) Pt-VO(*salen*)/C ([71], copyright *Journal of New Materials for Electrochemical Systems*), (b) Pt-Ni(*mqph*)/C ([70], copyright *The Electrochemical Society of Japan*). H_2 oxidation current containing CO, in current ratio as compared to H_2 (bars), and the HOR mass activity against Pt (symbols)

The catalyst performance was tested in a single fuel cell mode at 70°C . Membrane electrode assemblies (MEAs) having active areas of 4 cm^2 were prepared for a fuel cell by hot-pressing the anode and the cathode catalyst-loaded carbon paper ($2 \times 2\text{ cm}^2$) to each side of the Nafion 115 membrane. Anode

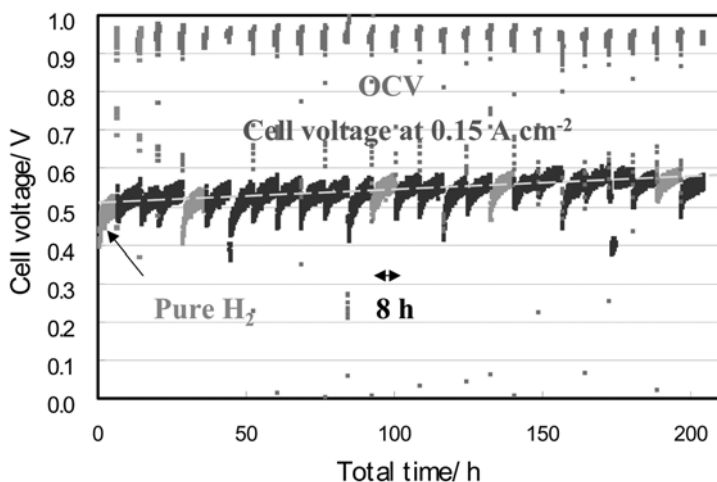


Fig. 4.17. Cell voltage and open circuit voltage of a single cell using Pt-Ni(*mqph*)/C anode catalyst operated at 0.15 A cm^{-2} with $\text{H}_2 + 10 \text{ ppm CO/air}$ at 70°C ([70], copyright *The Electrochemical Society of Japan*)

and the cathode gases were H_2 (CO)/air, each humidified at 60°C . Results of polarization curves for Pt-VO(*salen*)/C and Pt-Ni(*mqph*)/C as anode catalysts are summarized in Table 4.4, where peak power density (W cm^{-2}) and the cell voltage (V) at fixed current are compared. As long as the reformate gas containing 10–50 ppm CO is used, the new composite catalysts performed quite good, which is in agreement with the results of half-cell experiments.

4.5.2 Durability Testing

So far very few reports have been published on the longevity of molecular catalysts, which is an important issue for practical applications. The composite catalysts were tested in a single fuel cell mode at 70°C [70]. Figure 4.17 shows the time course of the cell voltage, where a constant current 0.15 A cm^{-2} was applied with $\text{H}_2 + 10 \text{ ppm CO}$ as the anode gas and air as the cathode gas during a daily start-stop mode operation. There is observed no appreciable decays of the voltages for this operation time. It is expected that the composite catalyst endures the CO-containing fuel operation for a long time.

Only little changes were observed in the polarization curves before and after 204 h operation, for the case of H_2 with 10 ppm CO. For the cases of 50 ppm and 100 ppm CO, the polarization curves declined after the longevity tests [71]. The fact that higher content of CO causes more serious degradation infers the occurrence of metal dissolution in the degradation mechanism.

Table 4.4. Test results of single fuel cell performances with various kinds of anode catalysts measured at 70°C. In each column, the first figure shows peak power density (W cm^{-2}) with retention in reference to pure H_2 in the parenthesis, and the second and the third figures show cell voltage (V) at 0.25 Å cm^{-2} and 0.3 Å cm^{-2} , respectively, obtained from the polarization curve. Anode gas: H_2 with various amounts of CO, cathode gas: air ([71], copyright *Journal of New Materials for Electrochemical Systems*)

Catalyst	Gas			
	H_2	$\text{H}_2 + 10 \text{ ppm CO}$	$\text{H}_2 + 50 \text{ ppm CO}$	$\text{H}_2 + 100 \text{ ppm CO}$
Pt/C(E-TEK) 0.41 mg Pt cm^{-2}	0.21 (100%) 0.52, 0.51	0.063 (30%) 0.02, ~0	0.029 (14%) ~0, ~0	0.018 (8.6%) ~0, ~0
Pt/C(ElectroChem) 0.30 mg Pt cm^{-2}	0.28 (100%) 0.57, 0.54	0.092 (34%) 0.32, 0.24	0.031 (11%) <0.05, ~0	0.020 (7.2%) ~0, ~0
Pt-Ru/C(JM) 0.30 mg Pt cm^{-2}	0.24 (100%) 0.59, 0.58	0.14 (58%) 0.48, 0.38	0.31 (54%) 0.36, 0.33	0.15 (63%) 0.40, 0.38
Pt-VO(<i>salen</i>)/C 0.29 mg Pt cm^{-2}	0.19 (100%) 0.52, 0.50	0.18 (93%) 0.48, 0.46	0.13 (69%) 0.45, 0.46	0.070 (36%) 0.23, 0.13
Pt-Ni(<i>mqqh</i>)/C 0.29 mg Pt cm^{-2}	0.22 (100%) 0.51, 0.48	0.20 (90%) 0.51, 0.48	0.12 (53%) 0.43, 0.38	0.080 (37%) 0.32, 0.22

4.5.3 Structural Characterization

Figures 4.18a–c present transmission electron microscopy (TEM) images of Pt–VO(*salen*)/C heat-treated at 300°C, 400°C, and 600°C, respectively. The particle size grows with increasing heat-treatment temperature. At 400°C the catalysts revealed the highest electrochemical performance, and the particle size observed by TEM is about 1–2 nm, showing good dispersion of metal particles on the carbon support. At 600°C the particle agglomerates to the size of 3–5 nm. The compositions of elements in the particle and on the carbon support as observed by energy-dispersive X-ray (EDX) analysis furnished in scanning TEM reveals that the amount of vanadium, both on the carbon and on the metal particle, decreases as the heat-treatment temperature increases. At 400°C, the vanadium complex surrounds the platinum nanoparticles on the carbon support and protects them from agglomeration.

Figure 4.19 shows XPS spectra of Pt–Ni(*mqqh*)/C, in which Pt 4f and Ni 2p peaks display characteristic changes depending on the heat-treatment temperature. At around 300°C, platinum precursor decomposes to Pt particles on the carbon surface. Between 300°C and 600°C, Ni(*mqqh*) is partially decomposed and makes a mixture with metallic Pt, but the initial complex structure is retained. Above 600°C, the metal complex starts to decompose to form nickel metal clusters or alloys with Pt.

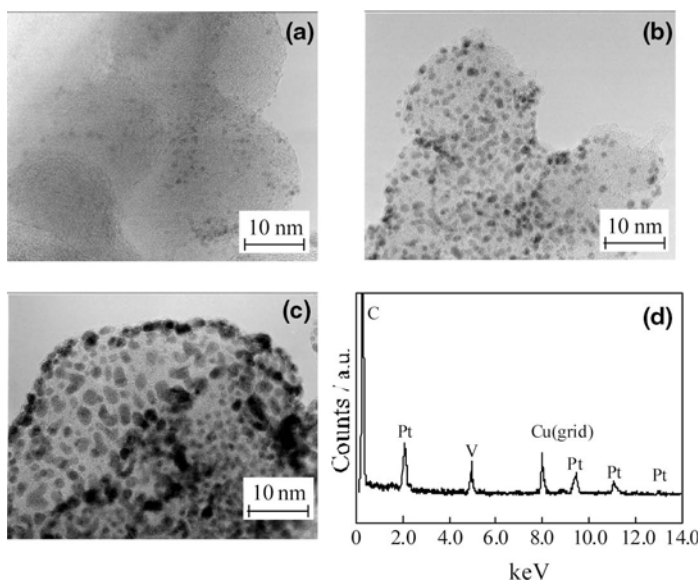


Fig. 4.18. Transmission electron micrograph images of the 20% Pt–VO(*salen*)/C powder heat-treated at (a) 300°C, (b) 400°C, and (c) 600°C in argon atmosphere. (d) Typical EDX spectra of metallic particles on Vulcan carbon support heat-treated at 400°C ([69], copyright the American Chemical Society)

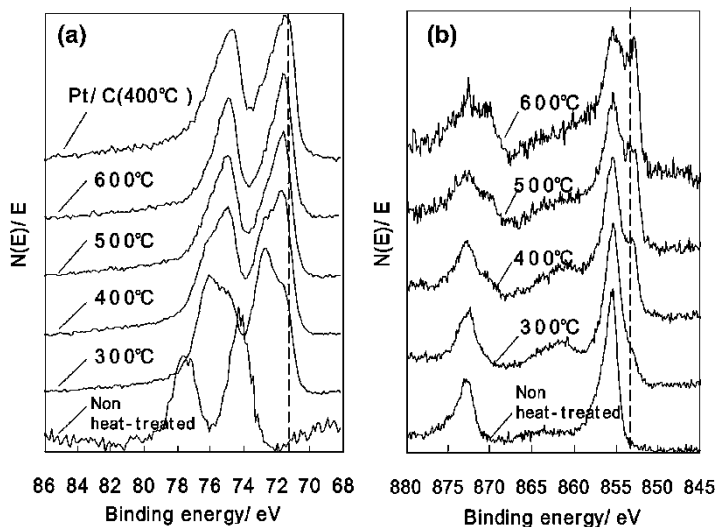


Fig. 4.19. XPS spectra of Pt–Ni(*mqph*)/C heat-treated at various temperatures. (a) Pt 4f and (b) Ni 2p. In (a), spectrum of Pt/C heat-treated at 400°C is overlaid at the top. Vertical bars indicate Pt 4f_{7/2} and Ni 2p_{3/2}, respectively ([71], copyright *Journal of New Materials for Electrochemical Systems*)

XPS spectra of the Pt–VO(*salen*)/C catalysts measured in the energy regions of Pt 4f and V 2p are summarized in Table 4.5, for binding energies and relative intensities. Before the heat treatment, the Pt 4f region displays the binding energy of Pt(II), corresponding to a chlorinated precursor species. After the heat treatment, platinum changes from Pt(II) in the metal precursor to the reduced state Pt(0), with larger amount for increasing heat-treatment temperature. For vanadium, two peaks observed for the non-heat-treated specimen in the 2p_{1/2} and 2p_{3/2} region can be assigned to V(IV) and V(V) states. The oxidation of vanadium, i.e., V(IV) (516.4 eV) to V(V) (517.3 eV) occurs in parallel with the reduction of platinum valence state. The relative intensity of V(V)/V(IV) in the catalysts increases with increasing heat-treatment temperature, i.e., from 0.4 (non-heat treatment) to 6.4 (heat-treated at 600°C). These results show that the change of valence state of vanadium in Pt–VO(*salen*)/C catalysts reflects the oxidation state of platinum.

It is assumed that the catalytic activity of Pt–VO(*salen*)/C links to the higher valence states of vanadium. When CO molecule coordinates to the central metal of chelate in a higher oxidation state, CO is activated resulting in a reduced back donation from the metal, which in turn induces a nucleophilic attack by H₂O (Fig. 4.1a) [33]. Invisible on TEM but observed by EDX are vanadium-covered Pt surface [69], which implies the possibility of the barrier layer of VO(*salen*) for CO penetration (Fig. 4.1b), thus inhibits CO poisoning. Surnev et al. investigate on the CO adsorption sites on vanadium

Table 4.5. Results of XPS spectra of the Pt–VO(*salen*)/C composite catalysts in the energy regions of Pt 4f and V 2p ([69] copyright the American Chemical Society)

<i>Pt</i> –VO(<i>salen</i>)/C	Doublet	Binding energy (eV)		Relative intensity/%	Doublet	Binding energy (eV)		Relative intensity/%
		Pt4f _{5/2}	Pt4f _{7/2}			V2p _{1/2}	V2p _{3/2}	
Non-heat treatment	I	77.2	73.9	100	I	523.5	516.2	70.8
						525.1	517.7	
Heat-treatment temperature ^a	300°C				I			V ⁴⁺
	400°C				I			V ⁴⁺
	500°C				I			V ⁴⁺
	600°C				I			V ⁴⁺

^aHeat-treated at 300, 400, 500, and 600°C for 2 h in flowing argon

oxide-Pd(111) model surface, which show a decrease of CO coverage with increase in vanadium oxide coverage [72]. The third mechanism is that the organic complexes may provide CO spillover sites near the platinum particle (Fig. 4.1c), and increase the mobility of CO so that free active sites are available for HOR on Pt.

The vanadium K-edge and platinum L-edge spectra in Pt-VO(*salen*)/C after the heat treatment are analyzed by the X-ray absorption spectroscopy. X-ray absorption near-edge structure (XANES) spectra give detailed information on the local structure and oxidation states of the central vanadium atoms. Figure 4.20a shows the K-edge XANES spectra of vanadium before and after the heat treatment at 400°C. The absorption position from K-edge locates in the order of Pt-VO(*salen*)/C (non-heat treatment) < Pt-VO(*salen*)/C (heat-treated at 400°C) < V₂O₅. The heat treatment at 400°C causes the oxidation state shifted from V(IV) to V(V), which is in agreement with the results of XPS analysis.

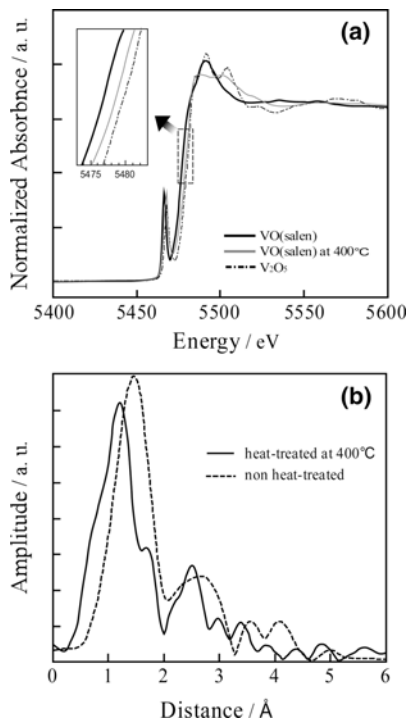


Fig. 4.20. (a) Vanadium K-edge XANES and (b) Fourier transform of normalized *k*³-weighted EXAFS spectra of the Pt-VO(*salen*)/C powder before and after the heat treatment at 400°C. V₂O₅ is used as the reference sample ([69], copyright the American Chemical Society)

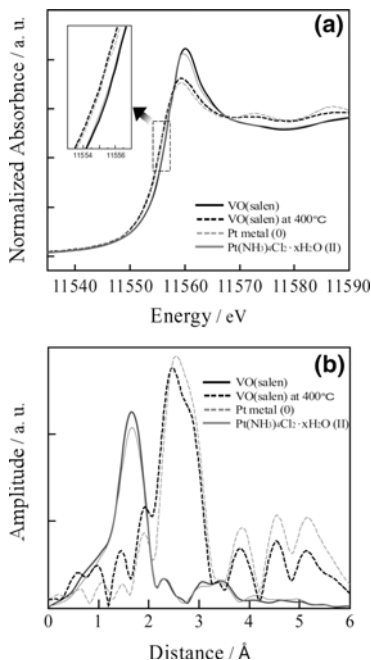


Fig. 4.21. (a) Platinum L-edge XANES and (b) Fourier transform of normalized k^3 -weighted EXAFS spectra of the Pt-VO(*salen*)/C powder before and after the heat treatment at 400°C. Pt metal and Pt(NH₃)₃Cl₂ · xH₂O are used as the reference samples ([69], copyright the American Chemical Society)

Figure 4.20b illustrates Fourier transforms of normalized k^3 weighted extended X-ray absorption fine structure (EXAFS) spectra of vanadium, before and after the heat treatment at 400°C. In this figure, two peaks are observed around 1.5 Å and 2.8 Å for non-heat-treated catalysts, and around 1.2 Å and 2.5 Å for the heat-treated catalysts, respectively. The first and the second peaks are assigned to V=O and V-N bonds, respectively. These results confirm the existence of coordination states between V and N after the heat treatment, the distances V=O and V-N in the Pt-VO(*salen*)/C being slightly decreased.

Characterization of platinum species in Pt-VO(*salen*)/C is conducted by XANES. Figure 4.21a shows the Pt L₃-edge XANES spectra of the non-heat-treated catalyst and the heat-treated catalyst at 400°C. As shown in the inset for the absorption edge, the absorption positions coincide between non-heat-treated Pt-VO(*salen*)/C and Pt(NH₃)₄Cl₂ · xH₂O, and between heat-treated Pt-VO(*salen*)/C and Pt metal, supporting the change of valence states as observed by XPS.

Fourier transforms of normalized k^3 -weighted EXAFS spectra are shown in Fig. 4.21b. The nearest neighbor distance depends on the valence state of

Pt, which is around 1.6 Å for the non-heat-treated sample and 2.7 Å for the heat-treated sample, attributable to Pt(II) and Pt(0) oxidation states, respectively.

4.6 Summary

Pt-M(*complex*)/C composite catalysts exhibit very high catalytic ability as oxidation catalysts of small organic molecules (methanol and formic acid), and the activity is strongly dependent on the structure of ligands and metal centers. Especially Pt-VO(*salen*)/C and Pt-Ni(*mqqh*)/C heat-treated at 400–600°C reveal very high performance compared with Pt/C and Pt-Ru/C alloy catalysts. The merit of heat-treatment exists not only in improved catalytic performance but also in longevity. XRD and TEM indicate the partial alloy formation during the heat treatment at 600°C, but the feature is very different for different ligand structures. The thermal analysis and XPS show that decomposition of mixed catalysts is rather moderate during the heat-treatment, and the initial molecular structure appears to remain on the carbon substrate. The sites derived from the organic metal complex moiety exerts some function on the Pt sites so that the latter would be able to oxidize organic molecules, mitigating CO poisoning as compared to Pt alone.

Pt-M(*complex*)/C composite catalysts are also effective for HOR in the reformat gas environment. Fuel cell running test reveals promising results in the longevity of the composite catalysts. It is suggested that the valence state of the central metal in the Pt-M(*complex*)/C catalysts plays a crucial role in the catalytic ability. XPS and X-ray absorption spectroscopy indicate the change of valence states of central metals *M* through the heat treatment, and also the existence of bonding states between *M* and *N* after the heat treatment. The carbon-black supporting material plays an important role to account for such stability of complexes.

Since the organic complex components are leasily designed with variety of structural possibilities, such molecular catalysts are expected to become promising candidates for future applications as the anode catalysts in fuel cells.

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References

1. T.F. Fuller, *Electrochem. Soc. Interface* **6** Fall, 26 (1997)
2. M. Wang, *J. Power Sources* **112**, 307 (2002)
3. A.J. Appleby, F.R. Foulkes, *Fuel Cell Handbook*, Chap. 2 (Van Nostrand Reinhold, New York, 1989)
4. K. Kordesch, G. Simader, *Fuel Cells and Their Applications*, Chap. 2 VCH, (Weinheim, 1996)
5. C.K. Dyer, *J. Power Sources* **106**, 31 (2002)
6. T.R. Ralph, M.P. Hogarth, *Platinum Metals Rev.* **46**, 117 (2002)
7. M.P. Hogarth, T.R. Ralph, *Platinum Metals Rev.* **46**, 146 (2002)
8. J.O.M. Bockris, S. Srinivasan, *Fuel Cells: Their Electrochemistry*, Chap. 7 (McGraw-Hill, New York, 1969)
9. M. Watanabe, in *Handbook of Fuel Cells – Fundamentals, Technology and Applications*, Vol. 2, Chap. 28, ed. by W. Vielstich, H.A. Gasteiger, A. Lamm (Wiley, Chichester, 2003)
10. T. Iwasita, in *Handbook of Fuel Cells – Fundamentals, Technology and Applications*, Vol. 2, Chap. 41, ed. by W. Vielstich, H.A. Gasteiger, A. Lamm (Wiley, Chichester, 2003)
11. J.O'M. Bockris, H. Wroblowa, **7**, 428 (1964)
12. O.A. Petry, B.I. Podlovchenko, A.N. Frumkin, H. Lal, *J. Electroanal. Chem.* **10**, 253 (1965)
13. L.W. Niedrach, D.W. McKee, J. Paynter, I.F. Danzig, *Electrochem. Technol.* **5**, 318 (1967)
14. K.J. Cathro, *J. Electrochem. Soc.* **116**, 1608 (1969)
15. M.M.P. Janssen, J. Moolhuysen, *Electrochim. Acta* **21**, 861–869 (1976)
16. M.M.P. Janssen, J. Moolhuysen, *J. Catal.* **46**, 289 (1977)
17. A. Capon, R. Parsons, *J. Electroanal. Chem.* **65**, 285 (1975)
18. M.J. Llorca, J.M. Feliu, A. Aldaz, J. Clavilier, *J. Electroanal. Chem.* **376**, 151 (1994)
19. C. Rice, S. Ha, R.I. Masel, A. Wieckowski, *J. Power Sources* **115**, 229 (2003)
20. A. Aramata, M. Masuda, *J. Electrochem. Soc.* **138**, 1949 (1991)
21. W.T. Napporn, H. Laborde, J.M. Léger, C. Lamy, *J. Electroanal. Chem.* **404**, 153 (1996)
22. T. Frelink, W. Visscher, J.A.R. van Veen, *Surf. Sci.* **335**, 353 (1995)
23. C. Sánchez, E. Leiva, in *Handbook of Fuel Cells – Fundamentals, Technology and Applications*, Vol. 2, Chap. 5, ed. by W. Vielstich, H.A. Gasteiger, A. Lamm (Wiley, Chichester, 2003)
24. G.T. Burstein, C.J. Barnett, A.R.J. Kucernak, K.R. Williams, *Electrochem. Soc. Lett.* **143**, A139 (1996)
25. L.W. Niedrach, H.I. Zelig, *J. Electrochem. Soc.* **116**, 152 (1969)
26. P.J. Kulesza, L.R. Faulkner, *J. Electroanal. Chem.* **259**, 81 (1989)
27. P.K. Shen, A.C.C. Tseung, *J. Electrochem. Soc.* **141**, 3082 (1994)
28. P. Waszczuk, A. Crown, S. Mitrovski, A. Wieckowski, in *Handbook of Fuel Cells – Fundamentals, Technology and Applications*, Vol. 2, Chap. 43, ed. by W. Vielstich, H.A. Gasteiger, A. Lamm (Wiley, Chichester, 2003)
29. A. Aramata, M. Masuda, T. Kadera, *J. Electrochem. Soc.* **136**, 3288 (1989)
30. M. Watanabe, S. Motoo, *J. Electroanal. Chem.* **60**, 267 (1975)
31. J. McBreen, S. Mukerjee, *J. Electrochem. Soc.* **142**, 3399 (1995)

32. J.F. van Baar, J.A.R. van Veen, N. de Wit, *Electrochim. Acta* **27**, 57 (1982)
33. J.F. van Baar, J.A.R. van Veen, J.M. van der Eijk, T.H.J. Peters, N. de Wit *Electrochim. Acta* **27**, 1315 (1982)
34. T. Okada, M. Yoshida, T. Hirose, K. Kasuga, T. Yu, M. Yuasa, I. Sekine, *Electrochim. Acta* **45**, 4419 (2000)
35. T. Okada, Y. Suzuki, T. Hirose, T. Toda, T. Ozawa, *Chem. Commun.* **2001**, 2492 (2001)
36. T. Okada, Y. Suzuki, T. Hirose, T. Ozawa, *Electrochim. Acta* **49**, 385 (2004)
37. T. Okada, N. Arimura, C. Ono, M. Yuasa, *Electrochim. Acta* **51**, 1130 (2005)
38. E. Leiva, C. Sánchez, in *Handbook of Fuel Cells – Fundamentals, Technology and Applications*, Vol. 2, Chap. 11, ed. by W. Vielstich, H.A. Gasteiger, A. Lamm (Wiley, Chichester, 2003)
39. C. Lamy, J.M. Léger, S. Srinivasan, in *Modern Aspects of Electrochemistry*, Vol. 34, Chap. 3, ed. by J.O.M. Bockris, B.E. Conway, R.E. White (Kluwer, New York, 2001)
40. P. Waszczuk, A. Wieckowski, P. Zelenay, S. Gottesfeld, C. Coutanceau, J.M. Léger, C. Lamy, *J. Electroanal. Chem.* **511**, 55 (2001)
41. Y.X. Chen, A. Miki, S. Ye, H. Sakai, M. Osawa, *J. Am. Chem. Soc.* **125**, 3680 (2003)
42. E. Herrero, W. Chrzanowski, A. Wieckowski, *J. Phys. Chem.* **99**, 10423 (1995)
43. T. Iwasita, *Electrochim. Acta* **47**, 3663 (2002)
44. Y. Wang, E.R. Fachini, G. Cruz, Y. Zhu, Y. Ishikawa, J.A. Colucci, C.R. Cabrera, *J. Electrochem. Soc.* **148**, C222 (2001)
45. R.Z. Khaliullin, A.T. Bell, *J. Phys. Chem. B* **106**, 7832 (2002)
46. V. Raghuveer, K.R. Thampi, N. Xanthopoulos, H.J. Mathiue, B. Viswanathan, *Solid State Ionics* **140**, 263 (2001)
47. J.S. Bett, H.R. Kuntz, J.M. Fenton, W.F. Bailey, D.V. McGrath *Electrochim. Acta* **43**, 3645 (1998)
48. M. Goetz, H. Wendt, in *Proceedings of the Workshop on Electrocatalysis in Indirect and Direct Methanol PEM Fuel Cells* (Portoroz, Slovenia, 1999) pp. 87–90
49. A. Ciszewski, G. Milczarek, *J. Electroanal. Chem.* **426**, 125 (1997)
50. J.A.R. van Veen, J.F. van Baar, C.J. Kroese, *J. Chem. Soc. Faraday Trans. 1* **77**, 2827 (1981)
51. M. Saito, H. Shiroishi, C. Ono, S. Tsuzuki, T. Okada, Y. Uchimoto, *J. Mol. Catal. A: Chemical* **248**, 99 (2006)
52. A.L. Bouwkamp-Wijnoltz, W. Wisscher, J.A.R. van Veen, S.C. Tang, *Electrochim. Acta* **45**, 379 (1999)
53. C. Rice, S. Ha, R.I. Masel, A. Wieckowski, *J. Power Sources* **115**, 229 (2003).
54. A. Capon, R. Parsons, *Electroanal. Chem. Interfacial Electrochem.* **44**, 1 (1973)
55. K. Kunimatsu, *J. Electroanal. Chem.* **213**, 149 (1986)
56. S.G. Sun, J. Clavilier, A. Bewick, *J. Electroanal. Chem.* **240**, 147 (1988)
57. Y.X. Chen, M. Heinen, Z. Jusys, R.J. Behm, *Angew. Chem. Int. Ed.* **45**, 981 (2006)
58. G. Samjeské, A. Miki, S. Ye, M. Osawa, *J. Phys. Chem. B* **110**, 16559 (2006)
59. J.M. Feliu, E. Herrero, In *Handbook of Fuel Cells – Fundamentals, Technology and Applications*, Vol. 2, Chap. 42, ed. by W. Vielstich, H.A. Gasteiger, A. Lamm (Wiley, Chichester, 2003)
60. U.B. Demirci, *J. Power Sources* **173**, 11 (2007)
61. S. Uhm, S.T. Chung, J. Lee, *Electrochem. Commun.* **9**, 2027 (2007)

- 62. S. Kang, J. Lee, J.K. Lee, S.Y. Chung, Y. Tak, *J. Phys. Chem. B* **110**, 7270 (2006)
- 63. E. Casado-Rivera, D.J. Volpe, L. Alden, C. Lind, C. Downie, T. Vázquez-Alvarez, A.C.D. Angelo, F.J. DiSalvo, H.D. Abruña, *J. Am. Chem. Soc.* **126**, 4043 (2004)
- 64. R. Larsen, R.I. Masel, *Electrochem. Solid State Lett.* **7**, A148 (2004)
- 65. X. Zhou, W. Xing, C. Liu, T. Lu, *Electrochem. Commn.* **9**, 1469 (2007)
- 66. R. Venkataraman, H.R. Kunz, J.M. Fenton, *J. Electrochem. Soc.* **151**, A703 (2004)
- 67. R. Venkataraman, H.R. Kunz, J.M. Fenton, *J. Electrochem. Soc.* **151**, A710 (2004)
- 68. H. Yano, C. Ono, H. Shiroishi, T. Okada, *Chem. Commun.* **2005**, 1212 (2005)
- 69. H. Yano, C. Ono, H. Shiroishi, M. Saito, Y. Uchimoto, T. Okada, *Chem. Mater.* **18**, 4505 (2005)
- 70. T. Okada, J. Qiao, T. Kahara, C. Ono, *Electrochemistry* **75**, 169 (2007)
- 71. T. Okada, H. Yano, C. Ono, *J. New Mater. Electrochem. Sys.* **10**, 129 (2007)
- 72. S. Surnev, M. Sock, G. Kresse, J.N. Andersen, M.G. Ramsey, F.P. Netzer, *J. Phys. Chem. B* **107**, 4777 (2003)

Macrocycles for Fuel Cell Cathodes

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Abstract The direct four-electron reduction of O_2 to H_2O is an important issue in developing efficient cathode catalysts for fuel cells. Cobaltporphyrins have been demonstrated to serve as catalysts for the four-electron reduction of O_2 , especially in the forms of dicobalt cofacial porphyrins and multinuclear cobaltporphyrins. Simple cobaltporphyrins with spontaneous face-to-face aggregation properties are also expected as efficient catalysts. For practical application as fuel cell cathode catalysts, it is necessary to use cobaltporphyrins dispersed on carbon particles with high surface area. Here, the recent developments on porphyrin-based catalysts and attempts to prepare face-to-face aggregates of cobaltporphyrins adsorbed dispersively on carbon black are summarized. The catalyst has been prepared by using a homogenizer in mixing cobaltporphyrin and carbon black, which gives rise to electroreduction of O_2 at a remarkably positive potential and shows a high selectivity for the direct four-electron reduction process.

5.1 Introduction

In the fuel cell, the platinum catalyst supported by carbon particles, such as carbon black, is used for the catalyst of the cathode which is reducing oxygen as an oxidizing agent. In order to obtain electric energy from the hydrogen fuel supplied to the anode side efficiently, oxygen needs to be reduced with four electrons to water [1]. The theoretical electromotive force of 1.23 V for the fuel cell corresponds to the potential where O_2 is reduced by a one-step four-electron reduction ($O_2 + 4e^- + 4H^+ = 2H_2O$). It is equivalent to the potential where the maximum oxidization power of oxygen is derived. Actual electromotive force declines to 0.7–1.0 V, because of the changes in the reduction mechanism in addition to the presence of activation polarization or concentration polarization. That is, when the reduction of oxygen generates hydrogen peroxide ($O_2 + 2e^- + 2H^+ = H_2O_2$) and then hydrogen peroxide is reduced to water ($H_2O_2 + 2e^- + 2H^+ = 2H_2O$) by the two-step mechanism, the overall reaction is identical to that of a one-step mechanism but the theoretical electromotive force declines to the potential of the first two-electron reduction.

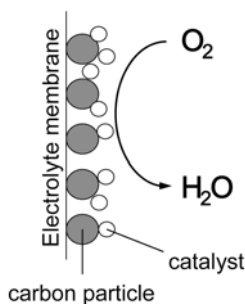


Fig. 5.1. Catalysis of reduction of O_2 to H_2O at fuel cell cathodes

In order to suppress such a two-step mechanism as much as possible, it is necessary to raise the selectivity of the one-step four-electron reduction using a suitable cathode catalyst (Fig. 5.1).

On the other hand, cytochrome *c* oxidase (CcO), which is the oxidation enzyme of a respiratory system in an aerobic organism, exists in the mitochondrial membrane and catalyzes the four-electron reduction of O_2 , taken in by breathing, into H_2O . Since it has two or more hemes and copper atoms per molecule as a prosthetic group, it is thought that these cooperative effects are participating in the enzymatic functions. However, the mechanism still has many points to be solved. In order to reproduce the catalytic function of CcO by an artificial system, various heme derivatives have been synthesized. Interestingly, four-electron reduction of O_2 is difficult with the heme derivative of a single core, and becomes feasible using a molecular assembly system or a polynuclear complex [2]. Investigation of the structure of an active site reveals that high activity is derived when O_2 bridges two metal ions to form a μ -peroxo dinuclear complex.

Such a metal complex may lead to reduction of the amount of the platinum used expensively as a substitute of a platinum-based catalyst for the cathode catalyst of the fuel cell. Especially the metal complexes that has macrocyclic ligands, such as porphyrins and phthalocyanines, have been widely investigated including basic studies on the dynamics of O_2 coordination and the structure of the intermediates, which was prompted by the finding that cobalt cofacial porphyrins (Fig. 5.2) show high catalytic activity for the four-electron reduction of O_2 [3]. In order to be actually able to use as a fuel cell catalyst, it is necessary to solve many subjects, such as preparation of highly dispersed adsorption of the metal complexes onto the carbon support as a catalyst carrier, and improvement in durability. However, the metal complex catalysts are advantageous over the platinum-based catalysts in terms of the flexibility of a molecular design. Therefore, they are one of the promising candidate as a cathode catalyst with the possibility of showing high catalytic activity.

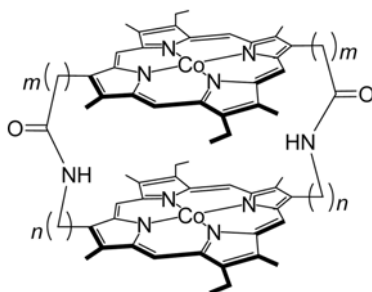


Fig. 5.2. Cobalt cofacial diporphyrin complexes designed for O_2 reduction catalysts

In this chapter, the cathode side of the membrane electrode assembly (MEA) in fuel cells is focused, and the latest progress of the metal complex cathode catalyst aiming at development of the platinum-free catalyst is described.

5.2 Molecular Design of Macrocycles for Fuel Cell Cathodes

Since platinum is expensive and rare, various alloy systems including a cobalt palladium alloy are studied as the substitute of the Pt/C cathode catalyst. In these metal catalysts, only the surface of metal particles is working as the catalytically active site, and the bulk phase does not participate in activity. On the other hand, one metal atom can serve as the active site in the case of a metal complex catalyst, leading to the effective use of a little amount of metal atoms. The overpotential at the cathode side is influenced by the activation overpotential of the catalyst, resistance of the catalyst layer, and the amount of O_2 supply. In the case of a metal complex catalyst, the redox potential of the complex also decides the potential where O_2 is reduced, in addition to these factors.

The performance of a cathode catalyst is evaluated by actually producing MEA and measuring the current-voltage characteristics. However, since a large quantity of the catalyst is required for production of MEA, easy screening using the modified electrode instead is performed. For example, one can expect a high activity of a catalyst when the peak potential for the oxygen reduction wave obtained with a cyclic voltammetry experiment is close to the standard potential for the four-electron reduction of oxygen. When the activity of many metal complex catalysts is systematically measured by such a method, it is clear that a molecular assembly system and the polynuclear complexes show higher catalytic activity than a mononuclear complex. For example, cobalt tetraphenylporphyrin is a two-electron reduction catalyst of oxygen. If the phenyl groups of the *meso* positions are replaced with pyridine-4-yl group and the ruthenium or osmium ammine complexes are coordinated, the degree

of selectivity of the four-electron reduction of oxygen is increased [4]. On the other hand, studies on the structure of an active site of the catalyst reveals that four-electron reduction of O_2 becomes feasible when the oxygen forms a μ -peroxo complex by bridging two metal centers. It is clear from a series of researches using cobalt diporphyrins that $O=O$ bond order decreases by the μ -peroxo complex formation and that the O_2 reduction current increases notably with the decrease in steric repulsion. Simple and highly convenient methods to prepare the μ -peroxo complexes using μ -(di)oxo complexes have been proposed [5].

5.3 Diporphyrin Cobalt Complexes and Related Catalysts

5.3.1 Diporphyrin Cobalt Complexes

Mononuclear complex of cobalt porphyrin (CoP) is known to function as a two-electron reduction catalyst of O_2 [6]. On the other hand, the cofacial diporphyrin complexes (Fig. 5.3a), capable of forming μ -peroxo complexes ($P\text{Co}-O-O-\text{CoP}$) by sandwiching O_2 with the two metal atoms, show higher selectivity for the four-electron reduction of O_2 due to the decrease in the $O=O$ bond order upon the formation of the μ -peroxo bridge to allow the cleavage of O_2 [3, 7]. When a rigid pillar such as anthracene (Fig. 5.4a) or biphenylene unit (Fig. 5.4b) is introduced at a one side of the two porphyrin

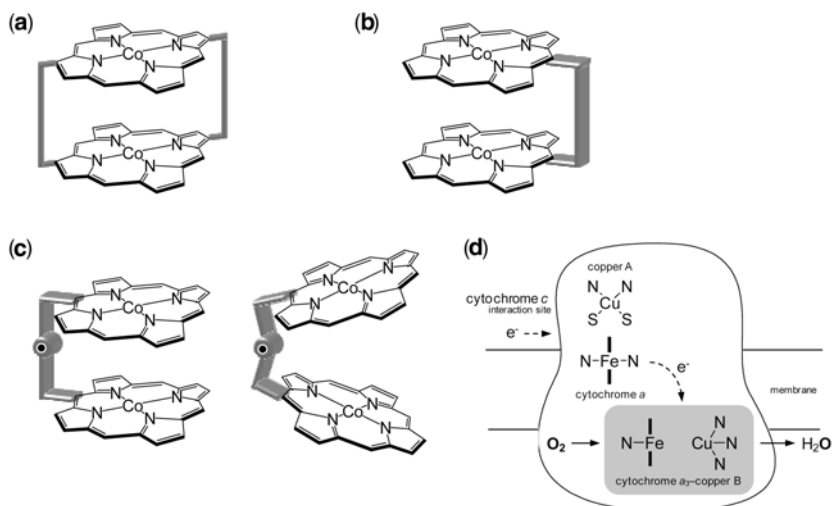


Fig. 5.3. Diporphyrin-type cobalt complexes examined as electrocatalyst for oxygen reduction

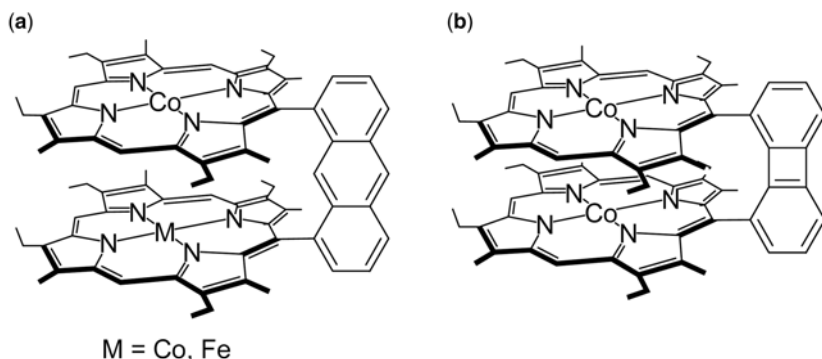


Fig. 5.4. Diporphyrin-type metal complexes pillared by rigid groups to bind the porphyrin rings

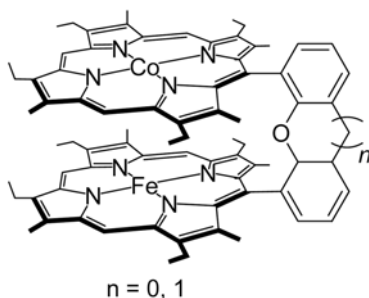


Fig. 5.5. Flexible diporphyrin cobalt-iron complex designed for facile accommodation of oxygen

rings to bind them (Fig. 5.3b), the steric repulsion upon the coordination of O_2 is eased, and the current for the reduction of O_2 (i.e. turnover speed of the catalyst) becomes remarkably large [8,9].

In relation to this, diporphyrin complexes, which have a flexible linkage between the two porphyrin rings like a hinge and thus two porphyrin rings can open and close according to the accommodation of O_2 (Fig. 5.5) [10–12], are found to catalyze the four-electron reduction of O_2 characterized by fast kinetics (Fig. 5.3c) [13]. Using ferryl intermediates generated by the photo excitation of μ -peroxo iron complexes [14–16], application of the similar reactions has spread to highly selective catalytic oxidation of sulfide molecules for synthetic applications [17].

On the other hand, the dinuclear complex (Fig. 5.6) designed as a model of the structure of the active site of CcO (Fig. 5.3d) is shown clearly to function as a four-electron reduction catalyst of O_2 under physiological conditions [18]. However, in actual CcO, it is known that there is a substantial distance between hem a_3 and Cu_B . That is, O_2 coordinated to hem a_3 is unlikely to

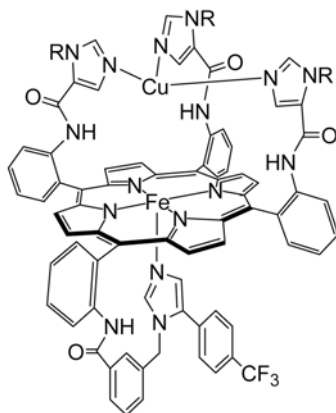


Fig. 5.6. Iron porphyrin designed as the proposed model of the active site of CcO in Fig. 5.3d

reach the Cu_B site, and the role of Cu_B is still unknown. Thus, to regard the O₂-bridged dinuclear structure in Fig. 5.6 as the model of the active site of CcO is still an open issue to be solved.

5.3.2 Polypyrrole Cobalt Complexes

Metal complexes with macrocyclic ligands such as porphyrins and phthalocyanines that contain four nitrogen donors (i.e. metal-N₄ chelates) adsorbed on carbon are expected to be alternates to the conventional carbon-supported platinum catalyst in fuel cells. The source of nitrogen atoms does not necessarily have to be macrocyclic ligands. Yeager et al. found activity with a heat-treated mixture of transition metal salts, such as cobalt and iron, and nitrogenous polymers such as polyacrylonitrile adsorbed on charcoal [19]. Dodelet and coworkers have employed NH₃ and CH₃CN as the precursors of nitrogen atoms and found that, for iron-based catalysts, the nitrogen atoms on the carbon support must be of a pyridine type [20–22]. It has been reported that heat treatment of carbon supports in NH₃/H₂/argon atmosphere is effective to enrich their surfaces with nitrogen atoms and to provide the pyridine-type coordination site [23]. Activities of the resulting catalysts after adsorbing iron ions are comparable to those of conventional iron complexes with pyridine-type ligands adsorbed on carbon supports [24–26]. For cobalt-based catalysts, on the other hand, a pyrrole-type nitrogen atom is preferred [27], and its development has awaited a convenient method to provide a tetrapyrrole-type coordination site on carbon such as those of porphyrins and phthalocyanines.

It has been reported that a carbon nanoparticle modified with a cobalt-adsorbed polypyrrole (PPy) film is a good electrocatalyst for the reduction of O₂ [28, 29]. Extended X-ray absorption fine-structure (EXAFS) spectroscopy

and X-ray diffraction (XRD) experiments have revealed that the cobalt ion is coordinated by four nitrogens as the donor atoms, and that the Co–N₄ structure is successfully maintained after heat treatment under an inert atmosphere up to ca. 700°C without deposition of metallic cobalt [28].

To accommodate cobalt ions at a coordination site within the PPy layer by a heterogeneous process, the PPy layer has been produced at the surface of a high surface-area carbon nanoparticle by a fluid-bed electrolysis. Carbon black with a large Brunauer–Emmett–Teller (BET) surface area has been employed for the carbon materials, because it is a common support used for platinum-based catalysts. Obtaining a PPy coating on carbon black involve electropolymerization of pyrrole at the surface of the carbon black, which has been accomplished by suspending carbon black into an electrolyte solution of pyrrole and electrolyzing the suspension at a platinum wire as a working electrode with vigorous stirring. Carbon black, upon continuous contact with the platinum electrode, serves as the working electrode during the electrolysis. The resulting PPy/CB particle has been suspended into a solution of cobalt acetate in CH₃OH, which has been then refluxed for a sufficiently long time to allow accommodation of cobalt ions at the suitable site (Fig. 5.7).

The pristine CoPPy/CB catalyst shows moderate electrocatalytic activity for the reduction of O₂. To prepare a CoPPy/CB-modified disk electrode for evaluation of the catalytic activity, an alcoholic suspension of CoPPy/CB containing Nafion has been used as a mother liquor for dip-coating. In the cyclic voltammograms obtained with the electrode modified with CoPPy/CB under O₂, the catalytic current for the reduction of O₂ appears near 0.23 V vs. SCE, while the Co(III/II) couple appears at a more positive potential in the absence of O₂ near 0.3 V. The Co(III/II) potential is, however, much more negative than the Co^{3+/2+} potential in aqueous solutions ($E^f = 1.68$ V vs. SCE) [30], which suggests that the cobalt ion is coordinated by donor atoms in PPy, rather than merely adsorbed on the PPy/CB surface.

Added support for coordination of PPy to the cobalt ion has been furnished by EXAFS spectroscopy [28]. The Fourier-transformed EXAFS function yields an atomic distance of $R_{\text{Co-N}} = 2.07$ Å which is comparable to the typical coordinate bond lengths in cobalt complexes such as cobalt porphyrins

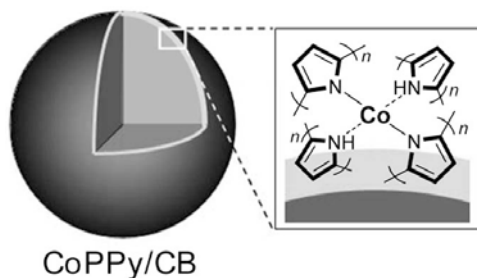


Fig. 5.7. Proposed structure of the active site of the CoPPy/CB catalyst

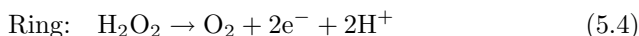
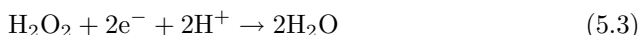
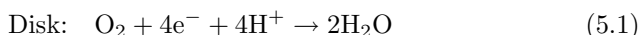
and phthalocyanines. The EXAFS function gives a first-shell cobalt–nitrogen coordination number of 4, which is suggestive of the Co–N₄ structure.

A significant feature of the CoPPy/CB catalyst is a positive shift in the O₂ reduction potential accomplished by heat treatment at elevated temperatures. After heat treatment of the catalyst at 700°C under vacuum, the catalytic current for the reduction of O₂ appears near 0.38 V vs. SCE. Heat treatment of the catalyst not only shifts the half-wave potential to a significantly positive side but also nearly doubles the peak current, while the reduction of O₂ occurs in a single step for both pristine and heat-treated catalysts. No current response is obtained at the electrode under argon, which confirms that these currents are due to the reduction of O₂. Koutecký–Levich plots obtained from the diffusion-limited currents on rotated disk electrodes have revealed that the heat-treated catalyst reduces O₂ with four electrons ($n_{\text{app}} = 3.7$), while a two-electron reduction is predominant for the pristine catalyst ($n_{\text{app}} = 2.8$). One could speculate that such a difference in the reactivity comes from the presence of two parallel reactions, one involving the bridging of O₂ to two proximate cobalt centers and giving rise to the four-electron reduction of O₂ according to $\text{O}_2 + 4\text{e}^- + 4\text{H}^+ = 2\text{H}_2\text{O}$, and the other involving a single cobalt center and yielding the two-electron reduction of O₂ according to $\text{O}_2 + 2\text{e}^- + 2\text{H}^+ = \text{H}_2\text{O}_2$. The typical platform to promote the four-electron reduction of O₂ is the covalently linked cofacial metalloporphyrins (Fig. 5.3), allowing for both ends of O₂ molecules to interact with the cobalt centers in the transition state. The improved catalytic activity upon heat treatment has been ascribed to the shortening of the cobalt–cobalt distance, allowing for O₂ molecules to bridge the two proximate cobalt centers.

A maximum in the electrocatalytic activity has been obtained for the CoPPy/CB catalyst near 700°C with a subsequent decrease. X-ray diffraction experiments have revealed that, at temperatures near 1,000°C, metallic cobalt aggregates are formed and consequently the catalytic activity decreases. XPS measurements have shown that nitrogen atoms are no longer detected after heat treatment near 1,000°C.

The typical experimental procedure to evaluate the activity of the metal macrocycle catalysts are summarized as follows. The potential of the disk electrode (E_{D}) is swept with rotating the electrode at 100 rpm in perchloric acid saturated with O₂, using the CoPPy/CB modified electrode. The obtained current–potential curves are shown in Fig. 5.8.

Here, the potential of the platinum ring (E_{R}) is maintained at the value at which H₂O₂ is oxidized. The amount of H₂O₂ in the system can be derived from the value of i_{R} .



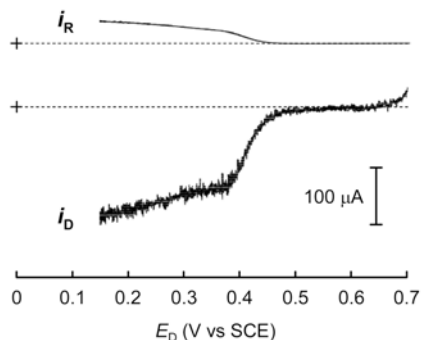


Fig. 5.8. Current-potential curves for the reduction of O_2 at the disk electrode surface, modified by a Nafion film containing the CoPPy/CB catalyst (after heat treatment at 600°C under an inert atmosphere) [28]. The electrolyte solution was an aqueous $HClO_4$ (1 M) saturated with 1 atm O_2 . The disk potential (E_D) was swept at a speed of 5 mV/s. The ring potential (E_R) was set at 1.2 V. Electrode rotation rate was 100 rpm. The reference electrode was SCE

The collection efficiency is 0.119, and is quite smaller than the value of $N = 0.37$ peculiar to the electrode. The current based on the four electron reduction of O_2 according to (5.1) is 2.11 times the current originating in the two-electron reduction according to (5.2). Moreover, N_K^{-1} is independent of the electrode rotation rate ω . Therefore, the reaction according to (5.3) is virtually not taking place or is very slow. The value of i_R/N corresponds to the current based on (5.2). The number of electrons transferred in average is determined, using the ratio of this current to i_D (N_K/N), to be $n_{av} = 4 - 2N_K/N = 3.4$. The four-electron reduction of O_2 is quite more dominant than the two-electron reduction, and it proceeds in the one-step reaction without producing H_2O_2 that leads to the degradation of the electrolyte, which is an important property as a fuel cell cathode catalyst.

The Co/PPy/C catalyst has been synthesized by a multiple modification method for the purpose of modifying Co- N_4 structure in a higher density [31]. The Co/PPy/C catalyst has been prepared by electropolymerization of pyrrole onto the surface of carbon particles which is dispersed in the electrolyte solution containing the pyrrole, followed by complexation using cobalt acetates. This modification procedure is then repeated for several times to increase the density of the active site at the surface of the carbon particles.

The carbon nanoparticles prepared by the multiple modification method is suspended into Nafion solution, and pseudo MEA is fabricated by casting the catalyst onto an edge-plane pyrolytic graphite electrode. The catalyst has been found to reduce O_2 with four electrons ($n_{app} = 3.3$) at a remarkably positive potential ($E_p = 0.31$ V vs. SCE). The activity of the catalyst is further improved after heat treatment ($E_p = 0.42$ V vs. SCE, $n_{app} = 3.8$).

This type of catalyst has been developed to various analogues containing a variety of metal ions [32].

Zelenay et al. have reported that a cobalt complex supported on carbon particles, prepared by impregnating an aqueous solution of cobalt nitrate into a composite of polypyrrole and carbon black (Vulcan XC 72), is useful as a cathode catalyst of a polymer electrolyte fuel cell [33]. This catalyst has been coupled with a PtRu anode catalyst, and an MEA has been fabricated for a test cell. The output of 0.15 W cm^{-2} has been obtained for 100 h or more by using H_2 as the fuel. Emphasis is placed on the fact that the heat treatment, well used in the research of an electrode catalyst using a metal complex, is not employed. Instead, pretreatment has been carried out under constant supply of H_2 and O_2 in 80°C by holding the MEA with an applied voltage of 0.40 V for a long time. During the pretreatment, activity improves gradually over 30 h. It has been established by the observation of a XANES and a XAFS spectrum that the active site, in which the Co(II) center is coordinated to the nitrogen atom of the pyrrole ring, is formed efficiently. The point that the irreversible structural changes in the process of continuously operating as an electrode catalyst has led to the formation of effective O_2 reduction site is very interesting.

Conductive polymer ligand-coated carbon particles have also been prepared by a fluid-bed electrolysis of 2-(3-pyridyl)thiophene using carbon particles as the working electrode [34]. The resulting particle has been suspended into a solution of cobalt acetate in DMF. The surface of the carbon particles has been successfully modified with the highly dispersed cobalt complex. The modified carbon particles have been then suspended into an alcoholic solution of Nafion, and a pseudo MEA has been prepared on an electrode by casting the solution. The electrocatalytic reduction of O_2 has been examined using the modified electrode. When the catalyst is prepared using a carbon black with a large surface area and pyrrole is added as a complementary ligand, the catalytic potential for the reduction of O_2 appears at $E_p = 0.37 \text{ V}$ vs. SCE. The catalyst reduces O_2 with four electrons ($n_{\text{app}} = 3.1$). The improved activity of the catalyst has revealed that nitrogen atoms of the pyridine-type ligand contribute to accumulate cobalt ions at the surface of the catalyst. The catalytic activity improves remarkably after the heat treatment of the catalyst under argon. The catalyst has thus revealed the possibility to be used as the cathode catalyst for platinum-free fuel cells.

Polyaniline has also been shown to be an effective ligand to accumulate cobalt ions, giving rise to the O_2 reduction site [35]. A mixture of aniline and pyrrole has been electropolymerized in the presence of suspended carbon black in an electrolyte solution. The resulting particles have been suspended again in methanol containing cobalt acetate, which is then refluxed for a sufficiently long time to complex with cobalt ions. The resulting catalyst reduces O_2 with four electrons ($n_{\text{app}} = 3.4$) at a positive potential ($E_p = 0.28 \text{ V}$ vs. SCE). The catalytic activity of the catalyst improves by the heat treatment under an inert gas atmosphere ($E_p = 0.40 \text{ V}$ vs. SCE, $n_{\text{app}} = 3.9$).

5.3.3 Cobalt Thienylporphyrins

A long π conjugated system in which the thienyl groups are connected at 2,5-positions, prepared from a porphyrin complex as a monomer bearing at least one 3-thienyl group linked at the *meso* position of the porphyrin ring with remaining *meso* positions substituted with alkyl groups, has been found to be a novel electrocatalyst for the reduction of O_2 , characterized by the presence of an O_2 bridging site and the moderate electric conductivity [36,37] (Fig. 5.9).

As the similar molecule of the polymer obtained by electrolytic polymerization of the porphyrin complex (Fig. 5.10), a π conjugated model has been constructed from a molecule in which 2-thienyl group is bound to the 5-position of the thiophene ring (Fig. 5.11) as a repeating unit, using a periodic boundary conditions. The band structure have revealed that the resulting structure is characterized by a band gap equivalent to that of polythiophene ($E_g = \text{ca. } 2\text{ eV}$) and a structure with a distance of adjacent porphyrin rings suitable for accommodation of O_2 as a bridging ligand for the formation of the μ -peroxo complex. The resulting coordination site can be regarded as a structure in which the cofacial multiple porphyrin complexes are bound to the main chain of a conducting polymer as a pendant group.

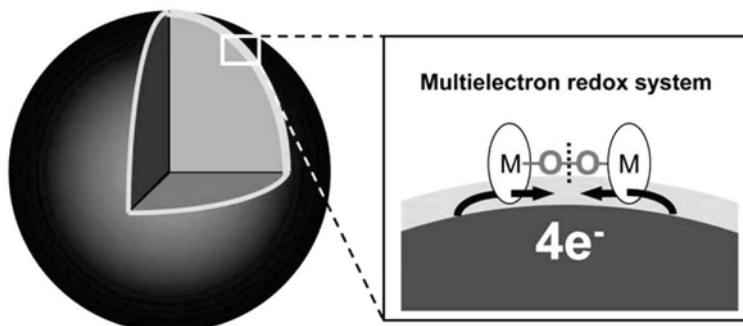


Fig. 5.9. Metal complex/carbon catalyst for fuel cell cathodes designed for high selectivity for the four-electron reduction of O_2 and low-resistance overpotentials

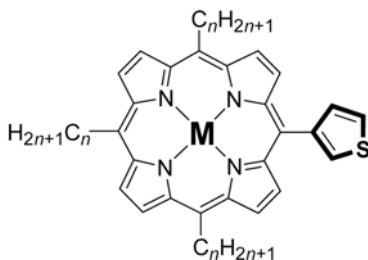


Fig. 5.10. 5-(3-thienyl)-10,15,20-trialkyl-21H,23H-porphine

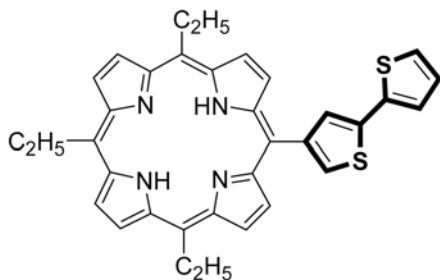


Fig. 5.11. Structure of a monomer unit used for the calculated polymer model

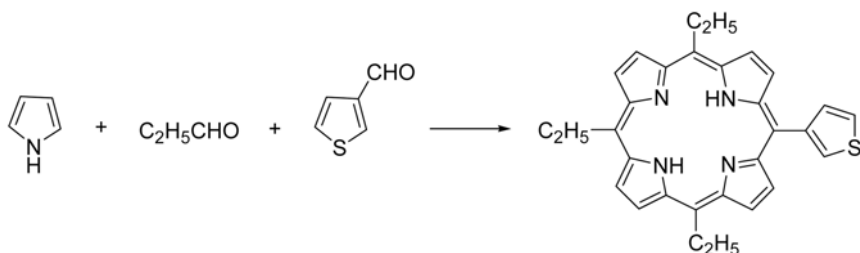


Fig. 5.12. Synthesis of 5-(3-thienyl)-10,15,20-triethyl- 21*H*,23*H*-porphine

The corresponding polymer has successfully been synthesized as follows. Considering the steric repulsive effect around the oxygen coordination site, ethyl groups have been employed as the alkyl group in Fig. 5.10 ($n = 2$). The porphyrin monomer bearing a 3-thienyl group at one of the *meso* positions and three ethyl groups at the remaining *meso* positions, 5-(3-thienyl)-10,15,20-triethyl-21*H*,23*H*-porphine ($H_2(ttep)$) has been synthesized by the condensation of propionaldehyde and 3-thiophenecarbaldehyde (Fig. 5.12).

Synthetic difficulty of porphyrin rings using aliphatic aldehydes and aromatic aldehydes is that aliphatic aldehydes are generally volatile and their reactivity with a pyrrole ring remarkably differs from aromatic aldehydes. That is, under conditions for the usual porphyrin ring formation at elevated temperatures, control of an aldehyde ratio is highly difficult because of the volatility of one of the aldehyde. Therefore, it becomes very easy to generate the side products and acyclic oligomers into which two or more thiophene rings are introduced. In order to solve such a problem, the solution of pyrrole in propionic acid has been preheated to temperatures suitable for the ring-closing reaction, and the mixture of aldehydes with a predetermined ration has been slowly added to the solution to increase the yield of the desired product. After extraction of the product with hexane, purification with silica gel column chromatography have yielded purple needle crystals. The target cobalt complex $[Co(ttep)]$ has been prepared by dissolving the ligand in dimethylformamide and refluxing in the presence of a fourfold excess amount of cobalt acetate. The obtained complex is polymerizable due to the presence of thienyl

groups at the *meso* position and sufficient stability based on the effect of alkyl groups to prevent decomposition of the porphyrin ring.

Oxidative polymerization of $H_2(ttep)$ using $FeCl_3$ as an oxidizer gives the corresponding polymer in a high yield. Due to the steric effect of the bulky porphyrin ring bound to the β -position of the thiophene ring, a high regularity with an HT-HT content of more than 95% has been accomplished although the polymerization is carried out at room temperature. Also, a high conductivity has been confirmed after I_2 doping ($\sigma_{RT} \approx 4 \times 10^{-1} S/cm$). Since the obtained polymer has the HOMO level higher than the unsubstituted polythiophene due to the localization of HOMO on the porphyrin ring, it has been obtained in a highly doped state. Moreover, in order to maintain the balance of solubility suitable for polymerization and the steric repulsion of the porphyrin rings, the ethyl group is highly effective as the alkyl group.

The structural regularity of the polymer originates from the controlled bond formation between the thiophene rings, which is regulated by the porphyrin ring. Trimer models (HT-HT, HH-TH, and HH-TT triads) have been calculated to predict the heat of formation, which have shown that the HH-TH triad is significantly unstable. In the polymerization of β -substituted thiophene, the β -substituents are aligned on the basis of the regioregularity of the thiophene rings. The Soret absorption band of porphyrin ring shows a red shift, accompanied by the polymerization. From these results, it has been confirmed that the porphyrin rings are arranged cofacially, giving rise to the structure suitable for accommodation of O_2 to produce the bridged peroxo bond.

Electropolymerization of $[Co(ttep)]$ has been carried out, and the polymeric thin film has been prepared on the surface of a carbon electrode. To the CH_2Cl_2 solution of $[Co(ttep)]$ containing tetra(*n*-butyl)ammonium perchlorate as a supporting electrolyte is immersed a glassy carbon disk electrode as the working electrode, a platinum wire as an auxiliary electrode, and an Ag/AgCl as a reference electrode. When the potential of the working electrode is repeatedly scanned in the range of 0–2.0 V, the smooth polymer film of $[Co(ttep)]_n$ is generated on the electrode surface. This electrode is then transferred into the water containing the perchloric acid with a concentration of 1.0 M. Cyclic voltammetry recorded using the auxiliary electrode (the platinum wire) and the reference Ag/AgCl electrode under conditions saturated with O_2 have revealed a reduction wave due to the catalytic reduction of O_2 at a peak potential of $E_p = 0.38 V$, which have revealed that the polymeric film is effective as the O_2 reduction catalyst.

As a next step, a convenient method to prepare the electropolymerized film of $[Co(ttep)]_n$ on a carbon particle has been examined, using the electrolysis in the presence of the carbon particles as the working electrode which is distributed in the electrolyte solution. The catalyst obtained by such a method is abbreviated as $[Co(ttep)]_n/C$ (Fig. 5.13).

In order to support the polymer complex $[Co(ttep)]_n$ on a carbon particle by electrolytic polymerization, a carbon particle with a large surface area

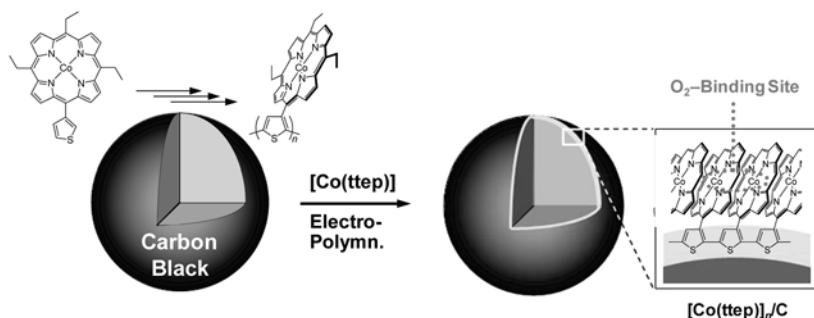


Fig. 5.13. Preparation of a $[\text{Co}(\text{ttep})]_n/\text{C}$ catalyst using a fluid-bed electrolytic polymerization method

(carbon black with a BET surface area of ca. $800 \text{ m}^2/\text{g}$) is dispersed in the solution of $[\text{Co}(\text{ttep})]$, and a supporting electrolyte is added in the suspension. Then, a reference electrode, a working electrode, and the auxiliary electrode (both platinum wires) are installed, and fixed potential is applied to the working electrode, with constant vigorous stirring of the electrolysis solution. By the electrolytic method, it has been established that the dispersed particles act as the working electrode when they contacted a platinum wire to produce the electropolymerized film efficiently on the carbon particles (Fig. 5.13). Electrolytic polymerization proceeds also on the platinum wire inserted as the working electrode. However, since the polymerized film is electroconductive, it works as an electrode to contact particles continuously during the course of the polymerization. The obtained $[\text{Co}(\text{ttep})]_n/\text{C}$ catalyst has been dispersed in an alcohol solution of Nafion. The modified electrode has been prepared by casting the suspension on the edge-plane pyrolytic graphite electrode. The catalyst activity in oxygen reduction has been investigated using the modified electrode. In a perchloric acid with a concentration of 1.0 M, cyclic voltammetry has been carried out using the platinum wire as the auxiliary electrode and the Ag/AgCl reference electrode under oxygen-saturated conditions, which have revealed a reduction wave at $E_p = 0.48 \text{ V}$ vs. SCE due to the electroreduction of O_2 . This value is remarkably more negative than that obtained for the $[\text{Co}(\text{ttep})]_n$ catalyst produced on the surface of the glassy carbon electrode. Higher activity has been accomplished by using the carbon particles as the support of the catalyst. Moreover, diffusion-limited current obtained with a rotating disk electrode (i_L) has been analyzed by using the Koutecky–Levich plots (i_L^{-1} vs. $\omega^{-1/2}$). The high selectivity for the four-electron reaction ($n_{\text{app}} = 3.8$) has been accomplished, revealing that the catalytically active center and the electron transfer path are provided by the polymeric structure characterized by high regioregularity of the main chain. Furthermore, when the catalyst is heat-treated under inert atmosphere, the catalytic activity improves to $E_p = 0.51 \text{ V}$. In this case, the rotating disk electrode reduces O_2 at $E_{1/2}(\text{O}_2) = 0.57 \text{ V}$ vs. SCE ($= 0.81 \text{ V}$ vs. NHE). These results suggest that O_2 reduction proceeds at potentials more positive than that for the two-electron

reduction. Catalyst activity changes also with the conditions of electrolytic polymerization heat treatment. Further improvement in the catalytic activity is anticipated by optimizing these conditions to produce a homogeneous thin film of $[\text{Co}(\text{ttep})]_n$ on a carbon particle, thereby reducing the resistance overpotential for the reduction of O_2 .

The performance of a complex catalyst should be evaluated by using MEA to obtain the I - V curve, but to use half-wave potentials of the O_2 reduction obtained at a rotating disk electrode ($E_{1/2}(\text{O}_2)$) is also a simple method for convenient comparison of the activity. The theoretical electromotive force of a fuel cell is determined by the potential at which O_2 receives electrons, so the performance of many complex catalysts can be conveniently measured for evaluation by such a method. By using $E_{1/2}(\text{O}_2)$ at low electrode rotation rates and thus at low currents, the potentials for the reduction of O_2 catalyzed by various metal complexes have been systematically compared under the conditions of small resistance overpotentials. It has been revealed that most of the conventional metal complex catalysts reported so far are operating as a two-electron reduction catalyst. Only a few metal complex catalyst works as a one-step four-electron reduction catalyst. Investigation on the durability is not sufficient at the present. The complex mainly mentioned in this section, the heat-treated $[\text{Co}(\text{ttep})]_n/\text{C}$ catalyst, shows the highest activity ($E_{1/2}(\text{O}_2) = 0.57 \text{ V vs. SCE}$ ($= 0.81 \text{ V vs. NHE}$)) among the metal complex catalysts, and has a capability of reducing O_2 at potentials where the four-electron reaction selectively takes place.

5.4 Porphyrin Assemblies Based on Intermolecular Interaction

The diporphyrins described in the Section 5.3.1 require the synthetic process with the multiple steps. On the other hand, there have also been reported cofacial dimers suitable for accommodation of O_2 by the bridging bond formation formed spontaneously (Fig. 5.14). The porphyrin complexes bearing four ionic substituents introduced at the *meso* positions have been found to form ion pairs with the similar complexes bearing the opposite charges (Fig. 5.15), which provide the typical models of Fig. 5.14a [38–41]. The ionic pair which has a composition of 1:1 is prepared by such a simple method, which has been confirmed by using the job plots obtained from the absorption spectra of the solution containing both the complexes with different compositions. Interestingly, the dimeric structure is supposed to be maintained even after adsorption to the surface of an electrode.

Dimeric porphyrins bearing a direct metal–metal bond (Fig. 5.16) have also been reported as the simply contained cofacial dimer (Fig. 5.14b) [42, 43]. Interestingly, mononuclear iridium porphyrins adsorbed on the surface of an electrode have been found to form rearranged cofacial dimers upon oxidation ($2[\text{HIrP}] \rightleftharpoons [\text{PIr-IrP}] + 2\text{H}^+ + 2\text{e}^- : E^{\text{f}} = \text{ca. } 0.37 \text{ V vs. NHE}$). Interestingly,

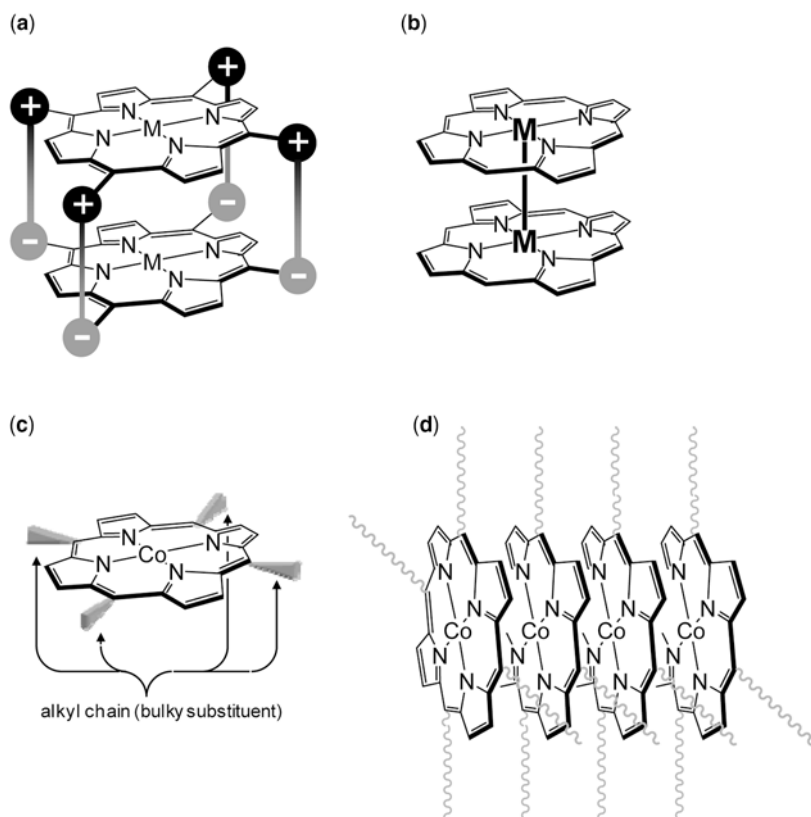


Fig. 5.14. Porphyrin assemblies as electrocatalysts for four-electron reduction of oxygen

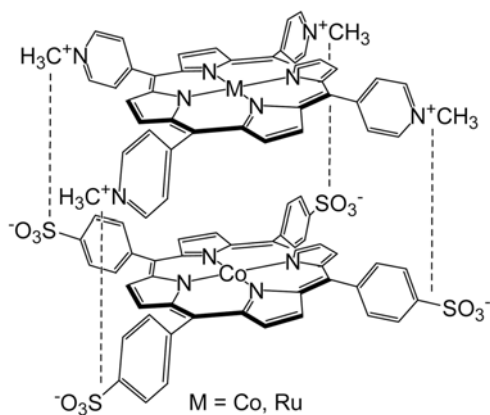


Fig. 5.15. Ion pair-type diporphyrin metal complexes

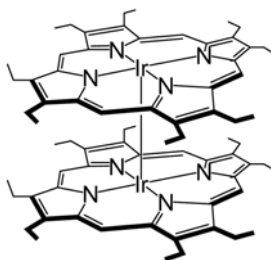


Fig. 5.16. Iridium diporphyrin bearing an Ir–Ir bond

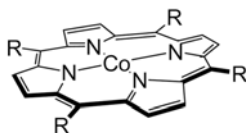


Fig. 5.17. Meso-tetraalkylporphyrin cobalt complexes used as the electrocatalyst for oxygen reduction by adsorption onto carbon black

only the dimer has been found to work as a four-electron reduction catalyst of O_2 . Therefore, as the overpotential for the reduction of O_2 becomes sufficiently large and reaches the reduction potential to form the mononuclear complex (0.37 V), it has been confirmed that the catalytic reduction current of O_2 is halved rapidly. That is, the structure of the catalytically active site changes with the electrode potential reversibly, and hence one can use the same electrode surface both for the four-electron reduction of O_2 and the two-electron reduction of O_2 , based on the electrode potential.

Similar structures in which porphyrin complexes are regularly arranged and adsorbed on an electrode with a specific intermolecular distance have been found for cobalt mononuclear porphyrins (Fig. 5.17) adsorbed on the surface of an edge-plane pyrolytic graphite electrode [44–46]. *Meso*-substituted cobalt porphyrins adsorbed on carbon black have been prepared as the catalysts for the electroreduction of O_2 . The catalyst, which has been prepared by using a homogenizer in mixing cobalt tetraethylporphyrin and carbon black, gives rise to the electroreduction of O_2 at a remarkably positive potential ($E_p = 0.45$ V vs. SCE) and shows a high selectivity for the four-electron reduction ($n = 3.8$). Electrochemical study and EXAFS analysis have revealed that the adsorbed face-to-face dimeric aggregates of cobalt porphyrin molecules are highly efficient catalysts for electroreduction of O_2 .

The degree of the steric repulsion between the almost planar porphyrin molecules is determined by the alkyl substituents bound to the *meso* position. Therefore, in order to maintain the distance between the central cobalt atoms suitable for the accommodation of O_2 , it has been established that the structure of the alkyl chains is an important factor (Fig. 5.14c) [47–50].

A regular arrangement structure of a porphyrin ring has been found in many organized molecular assemblies and supramolecular systems (Fig. 5.14d) [51–53]. The reverse micelles of cobalt porphyrins bearing long alkylamidophenyl substituents at the *meso* positions in alcohols by spontaneous self-organization are the typical examples that have been applied to the catalyst for the electroreduction of O_2 (Fig. 5.20) [54].

It has been reported that cobalt(II) *meso*-tetrakis(4-hexadecylamidophenyl) porphyrin (CoTAPP) self-assembles in ethanol/1-propanol 2/1 (v/v) to form a rod-like micelle with nanoscale dimensions. Static light scattering (SLS) and spectroscopic experiments reveal that the nanorod is a face-to-face aggregate having a hydrophobic corona around a polar core and is thus characterized as a reverse micelle.

A curious feature is the electrocatalysis of O_2 reduction by the CoTAPP aggregate adsorbed at the surface of a graphite electrode immersed in an aqueous electrolyte solution. To determine the effect of the cofacial orientation on the catalytic activity, one can take advantage of the insolubility of CoTAPP in H_2O and the very slow rate of aggregation in alcohols. Thus, a pristine alcoholic solution of CoTAPP is presumed to contain the monomeric complex alone, while the rod-like aggregate formed after ultrasonic irradiation should survive during the electrode preparation and electrochemical measurements. Indeed, when these solutions are used as the mother liquors to prepare the modified electrode by dip-coating, a quite different electrochemical response has been obtained. In Fig. 5.18, curves a and b represent cyclic voltammograms

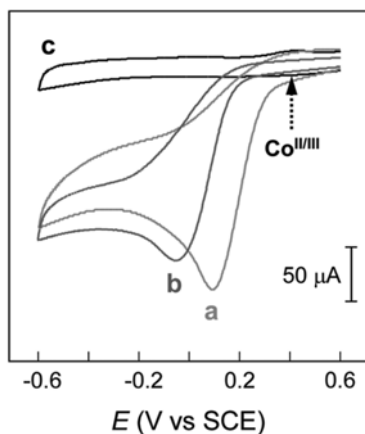


Fig. 5.18. Cyclic voltammogram for the reduction of O_2 at edge-plane pyrolytic graphite electrodes (0.28 cm^2) coated with $1.6 \times 10^{-10}\text{ mol cm}^{-2}$ of CoTAPP. The supporting electrolyte, 1 M $HClO_4$, was saturated with O_2 (curves a and b) or argon (curve c). CoTAPP was deposited on the electrode surface by transferring a pristine solution of CoTAPP in ethanol/1-propanol 2/1 (v/v) to record curve b, or a micellar solution of CoTAPP prepared by ultrasonic irradiation of the pristine solution for 6 h to record curves a and c. The electrodes were covered with 8 μL of 0.5 wt% Nafion in 2-propanol and air dried. Scan rate = 0.1 V s^{-1}

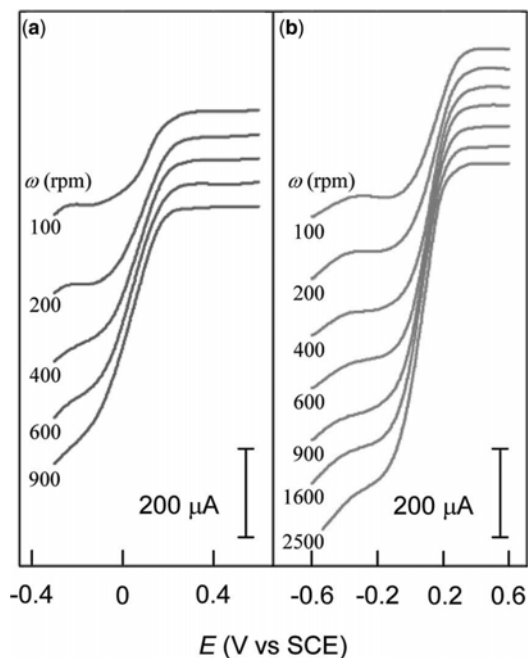


Fig. 5.19. (a) Reduction of O_2 with the electrode used to record curve b in Fig. 5.18 operated as a rotating disk electrode under O_2 . Electrode rotation rates were 100, 200, 400, 600, and 900 rpm. (b) Reduction of O_2 with the electrode used to record curve a in Fig. 5.18. Electrode rotation rates were 100, 200, 400, 600, 900, 1,600, and 2,500 rpm

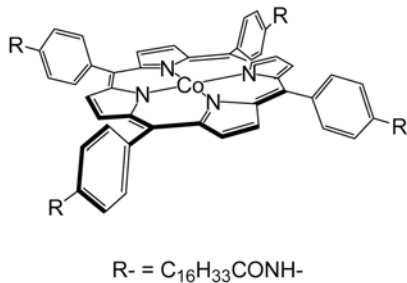


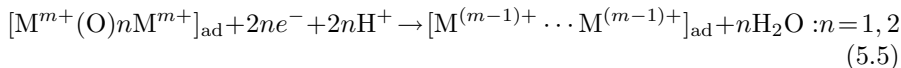
Fig. 5.20. Cobaltporphyrin that forms nanorod-type reversed micelles in alcohols

for the reduction of O_2 at the modified electrode coated with the aggregate and the monomeric complex, respectively. A positive shift in the O_2 reduction potential has been accomplished by the aggregation of CoTAPP, while the Co(III/II) couple is almost unaffected by the aggregation and appears at an even more positive potential (0.41 V) in the absence of O_2 (curve c).

Figure 5.19 shows current–potential curves for the reduction of O_2 at a rotating disk electrode coated with the aggregate and the monomeric complex.

While the reduction occurs in a single step for both electrodes, the plateau current at the slowest rotation rate is nearly doubled by the conversion of the coating from the monomeric complex to the aggregate. Koutecky–Levich plots have revealed that the aggregate reduces O_2 with four electrons ($n_{\text{app}} = 3.7$), while a two-electron reduction is predominant for the monomeric complex ($n_{\text{app}} = 2.0$). Such a difference in the reactivity stems from the presence of two parallel reactions, one involving the binding of O_2 to two proximate cobalt centers in the aggregate and giving rise to the four-electron reduction of O_2 to H_2O , and the other involving a single cobalt center and yielding the two-electron reduction of O_2 to H_2O_2 . Covalently linked cofacial metalloporphyrins have been the typical platform to explore such a cooperative effect of metal centers in promoting the four-electron reduction of O_2 . The cobalt–cobalt distance in the CoTAPP aggregate is in the range of those for the covalently bound cofacial porphyrins, allowing for both ends of O_2 molecules to interact with the cobalt centers in the transition state.

On the other hand, μ -(di)oxo porphyrin complexes adsorbed on the glassy carbon electrodes containing manganese [55,56] and iron [57–62] as the central metal atoms and similar complexes containing vanadium [63–66,74] produce a type of complex on the electrode ($[\text{M}^{(m-1)+} \dots \text{M}^{(m-1)+}]_{\text{ad}}$) by the electrolytic reduction under strongly acidic conditions (5) that are capable of O_2 accommodation to form the μ -peroxo-bridged structure, based on the analysis of the reaction mechanism using in situ electrochemical Raman spectroscopy [75,76]. For this reason, four-electron reduction of O_2 occurs highly selectively at the electrode that acts as the electron reservoir, to produce H_2O as the reduced product of O_2 quantitatively.



5.5 Multinuclear Complexes as Electron Reservoirs

If electrons are delivered toward a central metal core from many sites of the complex periphery, it is considered that many electrons can be taken out from the central metal core at once so that the number of electrons available for the reduction of O_2 may be multiple. Such a concept of multiple electron transfer process has been materialized by construction of a four-electron reduction system of O_2 (Fig. 5.21). For example, when the ammine complex of ruthenium or osmium are coordinated to the pyridyl groups at the *meso* position of a cobalt porphyrin, these peripheral complexes serve as the electron reservoir to donate electrons into the central core, resulting in the increase in the selectivity for the four-electron reduction of O_2 (Fig. 5.22) [77–80]. It has been established that the supply of the electron to the catalytically active site is based on the back electron transfer from the ruthenium or osmium centers to the ligand at the *meso* position of the porphyrin ring [81]. The effect of two or

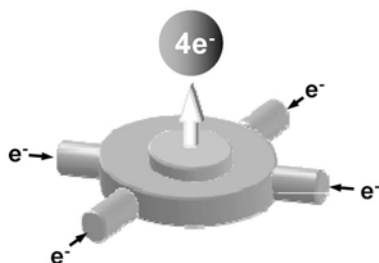


Fig. 5.21. Porphyrin complexes bearing four peripheral electron reservoirs

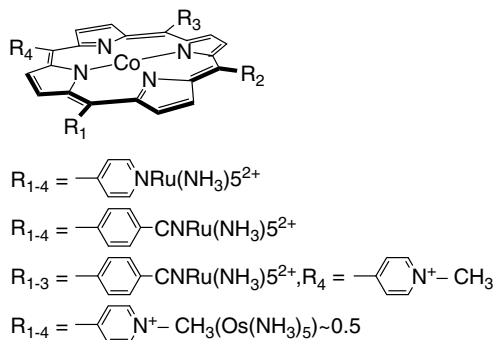


Fig. 5.22. Porphyrin cobalt complexes tetrametalated at the periphery

less ammine complexes per central cobalt is insufficient, and three or more peripheral complexes are necessary for the four-electron reduction mechanism. Four-electron transfer within the short time in which O_2 molecule is coordinated is considered to be the requirements of the four-electron reduction, which is accomplished by the presence of the multiple peripheral complexes.

5.6 Summary

The direct four-electron reduction of O_2 to H_2O is an important issue in developing efficient cathode catalysts for fuel cells. Cobaltporphyrins have been demonstrated to serve as catalysts for the four-electron reduction of O_2 , especially in the forms of dicobalt cofacial porphyrins and multinuclear cobaltporphyrins. Simple cobaltporphyrins with spontaneous face-to-face aggregation properties are also expected as efficient catalysts. For practical application as fuel cell cathode catalysts, it is necessary to use cobaltporphyrins dispersed on carbon particles with high surface area. In this chapter the recent developments on porphyrin-based catalysts and attempts to prepare face-to-face aggregates of cobaltporphyrins adsorbed or electrochemically polymerized dispersively on carbon black are summarized. The catalyst gave rise to electrore-

duction of O₂ at a remarkably positive potential and showed a high selectivity for the direct four-electron reduction process.

References

1. K. Kinoshita, *Electrochemical Oxygen Technology* (Wiley, New York, 1992)
2. J.P. Collman, R. Boulatov, C.J. Sunderland, L. Fu, *Chem. Rev.* **104**, 561 (2004)
3. J.P. Collman, P. Denisevich, Y. Konai, M. Marrocco, C. Koval, F.C. Anson, *J. Am. Chem. Soc.* **102**, 6027 (1980)
4. C. Shi, F.C. Anson, *J. Am. Chem. Soc.* **113**, 9564 (1991)
5. E. Tsuchida, K. Oyaizu, *Coord. Chem. Rev.* **237**, 213 (2003)
6. R.R. Durand Jr., F.C. Anson, *J. Electroanal. Chem.* **134**, 273 (1982)
7. R.R. Durand Jr., C.S. Bencosme, J.P. Collman, F.C. Anson, *J. Am. Chem. Soc.* **105**, 2710 (1983)
8. C.K. Chang, H.Y. Liu, I. Abdalmuhdi, *J. Am. Chem. Soc.* **106**, 2725 (1984)
9. C.-L. Ni, I. Abdalmuhdi, C.K. Chang, F.C. Anson, *J. Phys. Chem.* **91**, 1158 (1987)
10. C.J. Chang, Y. Deng, A.F. Heyduk, C.K. Chang, D.G. Nocera, *Inorg. Chem.* **39**, 959 (2000)
11. C.J. Chang, Y. Deng, S.-M. Peng, G.-H. Lee, C.-Y. Yeh, D.G. Nocera, *Inorg. Chem.* **41**, 3008 (2002)
12. L.L. Chng, C.J. Chang, D.G. Nocera, *J. Org. Chem.* **68**, 4075 (2003)
13. C.J. Chang, Y. Deng, C. Shi, C.K. Chang, F.C. Anson, D.G. Nocera, *Chem. Commun.* **2000**, 1355 (2000)
14. Z.-H. Loh, S.E. Miller, C.J. Chang, S.D. Carpenter, D.G. Nocera, *J. Phys. Chem. A* **106**, 11700 (2002)
15. C.J. Chang, E.A. Baker, B.J. Pistorio, Y. Deng, Z.-H. Loh, S.E. Miller, S.D. Carpenter, D.G. Nocera, *Inorg. Chem.* **41**, 3102 (2002)
16. J.M. Hodgkiss, C.J. Chang, B.J. Pistorio, D.G. Nocera, *Inorg. Chem.* **42**, 8270 (2003)
17. B.J. Pistorio, C.J. Chang, D.G. Nocera, *J. Am. Chem. Soc.* **124**, 7884 (2002)
18. R. Boulatov, J.P. Collman, I.M. Shiryayeva, C.J. Sunderland, *J. Am. Chem. Soc.* **124**, 11923 (2002)
19. S. Gupta, D. Tryk, L. Bae, W. Aldred, E. Yeager, *J. Appl. Electrochem.* **19**, 19 (1989)
20. H. Wang, R. Côté, G. Faubert, D. Guay, J.P. Dodelet, *J. Phys. Chem. B* **103**, 2042 (1999)
21. M. Lefèvre, J.P. Dodelet, P. Bertrand, *J. Phys. Chem. B* **106**, 8705 (1999)
22. M. Lefèvre, J.P. Dodelet, *Electrochim. Acta* **48**, 2749 (2003)
23. F. Jaouen, S. Marcotte, J.P. Dodelet, G. Lindbergh, *J. Phys. Chem. B* **107**, 1376 (2003)
24. J. Jiang, A. Kucernak, *Electrochim. Acta* **47**, 1967 (2002)
25. M. Bron, J. Radnik, M. Fieber-Erdmann, P. Bogdanoff, S. Fiechter, *J. Electroanal. Chem.* **535**, 113 (2002)
26. M. Bron, S. Fiechter, M. Hilgendorff, P. Bogdanoff, *J. Appl. Electrochem* **32**, 211 (2002)
27. A.L. Bouwkamp-Wijnoltz, W. Visscher, J.A.R. van Veen, S.C. Tang, *Electrochim. Acta* **45**, 379 (1999)

28. M. Yuasa, A. Yamaguchi, H. Itsuki, K. Tanaka, M. Yamamoto, K. Oyaizu, *Chem. Mater.* **17**, 4278 (2005)
29. W. Seeliger, A. Hamnett, *Electrochim. Acta* **37**, 763 (1992)
30. A.J. Bard, J. Jordan, R. Parsons (eds.), *Standard Potentials in Aqueous Solutions*. (Marcel Dekker, New York, 1985)
31. M. Yuasa, K. Oyaizu, H. Murata, K. Tanaka, M. Yamamoto, *Kobunshi Ronbunshu* **63**, 601 (2006)
32. M. Yuasa, K. Oyaizu, H. Murata, K. Tanaka, M. Yamamoto, S. Sasaki, *Electrochemistry* **75**, 800 (2007)
33. R. Bashyam, P. Zelenay, *Nature* **443**, 63 (2006)
34. K. Oyaizu, A. Yamaguchi, Y. Iai, K. Tanaka, M. Yuasa, *Kobunshi Ronbunshu* **63**, 189 (2006)
35. H. Murata, Y. Iai, T. Otake, K. Oyaizu, K. Kozawa, M. Yuasa, *Electrochemistry* **75**, 964 (2007)
36. K. Oyaizu, M. Hoshino, M. Ishikawa, T. Imai, M. Yuasa, *J. Polym. Sci., A* **44**, 5403 (2006)
37. M. Yuasa, K. Oyaizu, A. Yamaguchi, T. Imai, M. Kitao *Kobunshi Ronbunshu* **63**, 182 (2006)
38. M. Yuasa, K. Imura, I. Sekine, *Mater. Technol.* **18**, 171 (2000)
39. K. Yamamoto, S. Nakazawa, A. Matsufuji, T. Taguchi, *J. Chem. Soc., Dalton Trans.* **2001**, 251 (2001)
40. T. Imaoka, S. Nakazawa, K. Yamamoto, *Chem. Lett.* **2001**, 412 (2001)
41. T. Imaoka, K. Yamamoto, *Phys. Chem. Chem. Phys.* **3**, 4462 (2001)
42. J.P. Collman, K. Kim, *J. Am. Chem. Soc.* **108**, 7847 (1986)
43. J.P. Collman, L.L. Chng, D.A. Tyvoll, *Inorg. Chem.* **34**, 1311 (1995)
44. C. Shi, B. Steiger, M. Yuasa, F.C. Anson, *Inorg. Chem.* **36**, 4294 (1997)
45. M. Yuasa, R. Nishihara, C. Shi, F.C. Anson, *Polym. Adv. Technol.* **12**, 266 (2001)
46. M. Yuasa, K. Oyaizu, M. Kitao, K. Fujita, *Kobunshi Ronbunshu* **63**, 607 (2006)
47. K. Oyaizu, Y. Fujito, T. Sato, M. Kitao, A. Yamaguchi, M. Yuasa, *Polym. Prepr. Jpn.* **53**, 2260 (2004)
48. M. Kitao, A. Yamaguchi, K. Oyaizu, M. Yuasa, *Polym. Prepr. Jpn.* **53**, 4063 (2004)
49. M. Yuasa, K. Oyaizu, H. Itsuki, K. Ikkanda, K. Tanaka, A. Yamaguchi, *Polym. Prepr. Jpn.* **53**, 2261 (2004)
50. M. Yuasa, K. Oyaizu, A. Yamaguchi, *Polym. Prepr. Jpn.* **53**, 4760 (2004)
51. H. Uno, A. Masumoto, N. Ono, *J. Am. Chem. Soc.* **6**, 12082 (2003)
52. M. Shirakawa, S. Kawano, N. Fujita, K. Sada, S. Shinkai, *J. Org. Chem.* **68**, 5037 (2003)
53. K. Kano, K. Fukuda, H. Wakami, R. Nishiyabu, R.F. Pasternack, *J. Am. Chem. Soc.* **122**, 7494 (2000)
54. M. Yuasa, K. Oyaizu, A. Yamaguchi, M. Kuwakado, *J. Am. Chem. Soc.* **126**, 11128 (2004)
55. K. Oyaizu, A. Haryono, H. Yonemaru, E. Tsuchida, *J. Chem. Soc., Faraday Trans.* **94**, 3393 (1998)
56. K. Oyaizu, T. Nakagawa, E. Tsuchida, *Inorg. Chim. Acta* **305**, 184 (2000)
57. K. Oyaizu K, A. Haryono, J. Natori, H. Shinoda, E. Tsuchida, *Bull. Chem. Soc. Jpn.* **73**, 1153 (2000)
58. K. Oyaizu, A. Haryono, J. Natori, E. Tsuchida, *J. Chem. Soc. Faraday Trans.* **94** 3737 (1998)

59. A. Haryono, K. Oyaizu, K. Yamamoto, J. Natori, E. Tsuchida, *Chem. Lett.* **3**, 233 (1998)
60. K. Oyaizu, A. Haryono, Y. Nishimura, K. Yamamoto, E. Tsuchida, *Bull. Chem. Soc. Jpn.* **72**, 1781 (1998)
61. K. Oyaizu, E.L. Dewi, E. Tsuchida, *Inorg. Chim. Acta* **321**, 205 (2001)
62. K. Oyaizu, E. Tsuchida, *Inorg. Chim. Acta* **355**, 414 (2003)
63. K. Oyaizu, E. Tsuchida, *J. Am. Chem. Soc.* **120**, 237 (1998)
64. K. Oyaizu, E.L. Dewi, E. Tsuchida, *J. Electroanal. Chem.* **498**, 136 (2001)
65. E.L. Dewi, K. Oyaizu, E. Tsuchida, *Inorg. Chim. Acta* **342**, 316 (2003)
66. E. Tsuchida, K. Yamamoto, K. Oyaizu, N. Iwasaki, F.C. Anson, *Inorg. Chem.* **33**, 1056 (1996)
67. K. Oyaizu, K. Yamamoto, K. Yoneda, E. Tsuchida, *Inorg. Chem.* **35**, 6634 (1996)
68. K. Yamamoto, K. Oyaizu, E. Tsuchida, (1996) *J. Am. Chem. Soc.* **118**, 12665 (1996)
69. E. Tsuchida, K. Yamamoto, K. Oyaizu, *J. Electroanal. Chem.* **438**, 167 (1997)
70. E. Tsuchida, K. Oyaizu, E.L. Dewi, T. Imai, F.C. Anson, *Inorg. Chem.* **38**, 3704 (1999)
71. K. Oyaizu, E.L. Dewi, E. Tsuchida, *Inorg. Chem.* **42**, 1070 (2003)
72. K. Oyaizu, E. Tsuchida, *J. Am. Chem. Soc.* **125**, 5630 (2003)
73. K. Oyaizu, E. Tsuchida, *Inorg. Chim. Acta* **353**, 332 (2003)
74. E.L. Dewi, K. Oyaizu, H. Nishide, E. Tsuchida, *J. Power Sources* **130**, 286 (2004)
75. E. Tsuchida, K. Yamamoto, K. Oyaizu, Multi-electron transfer process of a Vanadium dinuclear complex for molecular conversions, in *Metal Containing Polymeric Materials* ed. by C.U. Pittman, C.E. Carraher, B.M. Culberston, M. Zeldin, J.E. Sheets (Plenum, New York, 1996), pp. 139–149
76. E. Tsuchida, K. Yamamoto, K. Oyaizu, Multi-electron transfer and catalytic mechanisms in oxidative polymerization, in *Bioinorganic Catalysis*, 2nd edition, revised and expanded, ed. by J. Reedijk, E. Bouwman (Marcel Dekker, New York, 1999) pp. 535–562
77. C. Shi, F.C. Anson, *Inorg. Chem.* **31**, 5078 (1992)
78. H.-Z. Yu, J.S. Baskin, B. Steiger, F.C. Anson, A.H. Zewail, *J. Am. Chem. Soc.* **121**, 484 (1999)
79. B. Steiger, F.C. Anson, *Inorg. Chem.* **33**, 5767 (1994)
80. C. Shi, F.C. Anson, *Inorg. Chem.* **35**, 7928 (1996)
81. F.C. Anson, C. Shi, B. Steiger, *Acc. Chem. Res.* **30**, 437 (1997)

Platinum-Free Catalysts for Fuel Cell Cathode

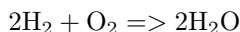
N. Koshino and H. Higashimura

Abstract In this chapter, we will review platinum-free catalysts for fuel cell cathodes; metal particles, metal oxides/carbides/nitrides/chalcogenides, carbon materials, and metal complexes, in terms of their practical feasibility for fuel cell. We will focus on metal complexes and their heat-treated materials, which could be promising catalysts for fuel cell cathodes. We will see that the catalyst performance depends largely on metal centers, ligand structures, and heat-treatment temperatures. In addition, we will introduce newly developed catalysts designed from dinuclear metal complexes.

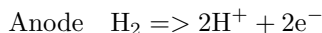
6.1 Introduction

Accompanied with increasing concerns to environmental issues in recent years, a lot of attentions have been focused on fuel cells. There are several types of fuel cells such as polymer electrolyte fuel cell (PEFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MOFC), solid oxide fuel cell (SOFC), and so on [1,2]. Each fuel cell has characteristic features in operating temperatures, electrolytes, catalysts, etc. Among these fuel cells, PEFC using proton-exchange membrane as electrolyte and hydrogen as fuel has some advantages of low operating temperature, which facilitates daily start-up and shutdown, and high power density. Therefore, PEFC has been intensively studied toward practical application for vehicles and small power generators.

PEFC generates electricity using the following chemical reaction when hydrogen is used as the fuel.



At the anode, H_2 generates H^+ ions and electrons, and at the cathode O_2 reacts with H^+ ions and electrons to produce H_2O . Both the reactions are caused by electrode catalysts, in which platinum (Pt) is generally used.



Although the reaction potential is theoretically 1.23 V, the cell voltage actually becomes somewhat smaller [2]. One of the main reasons for the voltage drop is due to the sluggishness of oxygen reduction reaction (ORR) at the cathode, which is much slower than hydrogen oxidation reaction at the anode.

Thus, the cathode catalyst plays one of the most important roles in showing the performance of PEFC. In this chapter, platinum-free catalysts for cathode are discussed.

6.2 Drawbacks of Using Pt as Catalysts in PEFC

Platinum, one of the precious metals, is very rare and expensive. It is recently said that the number of vehicles in the world is about 760 million in 2005 [3] and that the amount of Pt used for the PEFC catalysts per vehicle is estimated approximately 100 g under the current technology [4]. Calculated from these values, 76,000 t of Pt will be required to replace all the vehicles with PEFC vehicles. On the other hand, the amount of Pt on the earth is estimated to be about 50,000 t [5], which is below the required amount of Pt. The utilization of Pt catalyst in PEFC was estimated to be in the range of 20–30% [6–8]. Although there are several attempts to increase the Pt utilization, it is not certain to solve this issue. Moreover, Pt is widely used for other application such as catalyst for automobiles (mostly used in mufflers), jewelry, and so on (Fig. 6.1) [8]. Hence, the resource amount of Pt would be short in the future, even though the attempts to reduce the amount of Pt for the PEFC catalysts are now in progress [9–11].

As shown in the recent fluctuation of Pt price (Fig. 6.2) [12], the price has become more than double in 8 years and may go on rising because of the increased utilization of PEFC. If the catalyst amount is 100 g per vehicle and the cost is ¥5,000/g, it will cost ¥500,000 only for Pt per vehicle, leading to one of the biggest problem for spreading PEFC vehicle.

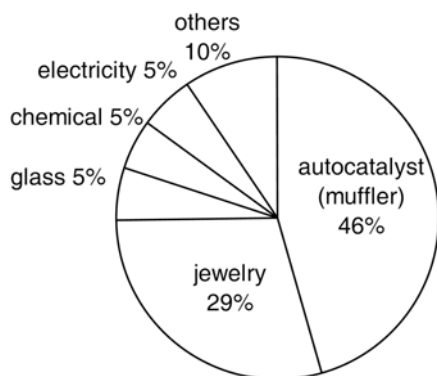


Fig. 6.1. Demand ratio of Pt in 2005

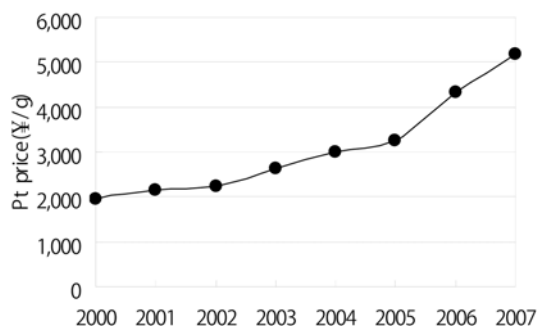


Fig. 6.2. Price fluctuation of Pt in 2000–2007

Considering these drawbacks of Pt for PEFC catalysts, it is required to develop Pt-free catalysts, which are desired to be based on non-precious metals.

6.3 Mechanistic Aspects of Oxygen Reduction by Cathode Catalyst

The reduction of O_2 catalyzed by Pt at the cathode is much slower than the oxidation of H_2 by Pt catalyst at the anode. Actually, the exchange current density of ORR at the cathode is in the range of 10^{-7} – 10^{-9} $A\ cm^{-2}$ [13, 14], and on the other hand, that of the hydrogen oxidation reaction at the anode is ca. 10^{-3} $A\ cm^{-2}$ [15]. It is reported that the Pt loading on the cathode of membrane-electrode assembly (MEA) is difficult to reduce, although the Pt amount on the anode may be reduced to one-tenth when pure H_2 is used [16, 17].

The sluggishness of ORR is attributed to the strength of the O–O bond of O_2 , which has dissociation energy of $498\ kJ\ mol^{-1}$ [18]. H_2O_2 , which is two-electron-reduced species of O_2 , can be observed as a side reaction in four-electron reduction of O_2 leading to H_2O . The reduction of H_2O_2 takes place relatively smoothly, which reflects that the dissociation energy of the O–O bond in H_2O_2 is $211\ kJ\ mol^{-1}$ [18]. Figure 6.3 shows the reaction scheme of ORR on Pt surface [19, 20].

First, O_2 is adsorbed on Pt surface (i), which is expressed as $O_{2,ad}$ in Fig. 6.3. The reduction of $O_{2,ad}$ by four-electron transfer directly produces H_2O (ii), but that by two-electron transfer generates adsorbed hydrogen peroxide, $H_2O_{2,ad}$ (iii). $H_2O_{2,ad}$ is two-electron-reduced to produce H_2O (iii), while $O_{2,ad}$ can be regenerated from $H_2O_{2,ad}$ (iv). However, once H_2O_2 is desorbed (vi), H_2O_2 can generate hydroxyl radical, which would result in the degradation of polymer electrolyte in PEFC [21, 22]. Therefore, it is desired for the cathode catalyst to achieve four-electron reduction to H_2O completely.

At the first step (i) in Fig. 6.3, the configuration of O_2 adsorbed on Pt surface has a large effect on whether four-electron reduction to H_2O (ii) or

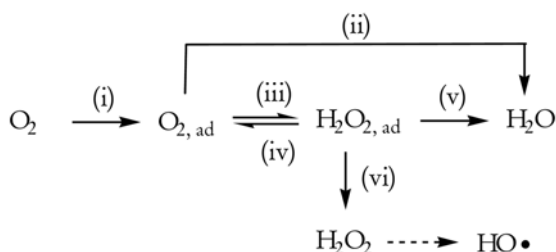


Fig. 6.3. Reaction scheme of oxygen reduction on Pt surface

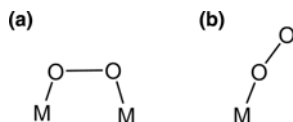


Fig. 6.4. Two configurations of O_2 adsorption on Pt surface: Yeager (a) and Pauling (b) models

two-electron reduction to H_2O_2 (iii) follows. Two models are often discussed in ORR: Yeager model (a) and Pauling model (b) (Fig. 6.4) [23]. The two-site configuration (a), which is a 1,2-peroxo-dimetal complex formed by the reaction O_2 with two metals, would produce H_2O via four-electron transfer. On the other hand, the one-site configuration (b), which is an end-on superoxo-metal complex generated by the reaction O_2 with one metal, would generate H_2O_2 via two-electron transfer.

For the cathode catalyst of PEFC, not only the activity of ORR but also the selectivity for four-electron transfer is important.

6.4 Platinum-Free Catalysts for Fuel Cell Cathode

As mentioned above, Pt is so far considered the best cathode catalyst of ORR, but Pt is an expensive metal of low abundance. Since the amount of Pt for the cathode catalyst is difficult to reduce drastically, it has been recently very important to develop Pt-free catalysts for PEFC [24–28]. An overview of Pt-free catalysts including (i) metal particles, (ii) metal oxides, carbide, nitrides, and chalcogenides, (iii) carbon materials, and (iv) metal complex-based catalysts, is described here from the following perspective.

Requirements for cathode catalysts of PEFC

- High activity for ORR
- Efficient four-electron-transfer
- Durability for long periods
- Cost performance
- Abundance of natural resources

6.4.1 Metal Particles

It is known that nanoparticles of transition metals such as Co, Ni, Pd, Ag, and Au are active for ORR [29–33]. However, Co, Ni, and Ag nanoparticles gradually dissolve in acidic media. Although Pd and Au nanoparticles are fairly stable in acidic media, these are also precious metals with such high prices as ¥1200/g (Pd) and ¥2600/g (Au)[12].

An Italian company, ACTA, developed non-precious metal catalyst which is called HypermecTM [34, 35]. The precursor is based on transition metal-supported polymer composites, and the catalysts are obtained after calcination (Fig. 6.5). HypermecTM consists of subnanometer metal clusters (Fe, Co, Ni) supported on carbon black (e.g., Vulcan). It was shown that HypermecTM has ORR activity and stability in alkaline media; however, the applicability of HypermecTM to acidic-type PEFC seems to be not shown [35].

Yamanaka found Cu/carbon black cathode catalyst [36], in which it was proposed that the active sites were proposed to be not Cu particles but quinone/hydroquinone groups on the carbon black and Cu²⁺ ion provided the adsorption sites of O₂ (Fig. 6.6). The carbon modification by phosphoric acid was speculated to enhance the diffusion of H⁺ over the carbon surface.

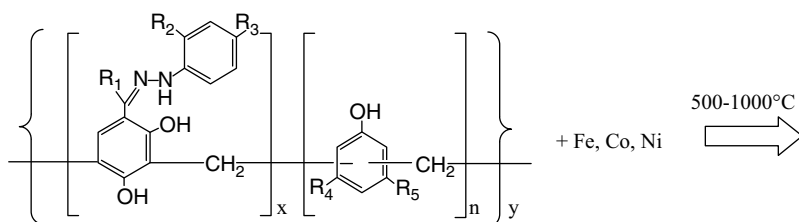


Fig. 6.5. Manufacturing process of HypermecTM [34]

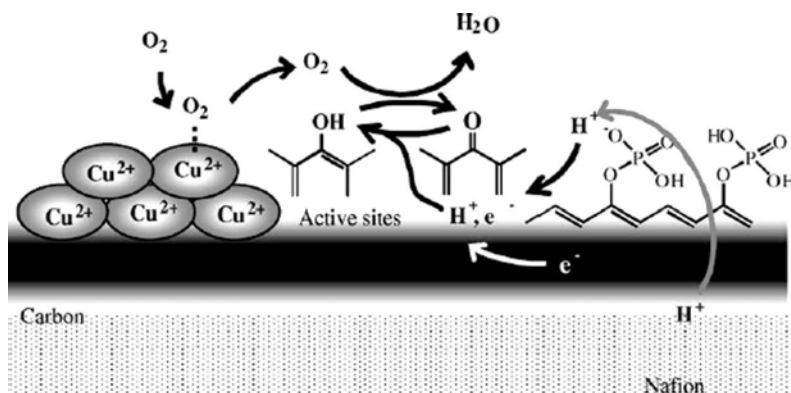


Fig. 6.6. The speculated scheme of Cu/carbon black cathode for ORR ([36], copyright Elsevier)

For the cathode catalysts based on metal particles, the application to acidic PEFC seems to be difficult because of the low stability in acidic media, although the application to alkali-type fuel cell may be possible.

6.4.2 Metal Oxides, Carbides, Nitrides, and Chalcogenides

Although some studies on metal-oxide catalysts for ORR have been reported, most of them suffer from dissolution in acidic media and low catalytic activity of ORR. Ota and his coworkers have proposed that 4- and 5-group metal oxides have potentiality for fuel cell cathode catalysts, because those metal oxides have high chemical stability [37,38]. They prepared nitrogen-doped metal oxides (ZrO_xN_y and TaO_xN_y) and found that those materials were fairly stable in acidic media. From the leaching test of ZrO_xN_y in $0.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ at 30°C (Fig 6.7), the dissolution of Zr was negligible after the initial stage [37]. The catalytic activity of ZrO_xN_y for ORR significantly depends on the heat-treatment temperature. Figure 6.8 shows the voltage–current curves of ZrO_xN_y catalyst deposited at various substrate temperatures ($50\text{--}800^\circ\text{C}$) [37]. The ORR current density on ZrO_xN_y deposited at 800°C was about 30 times greater than that at 50°C . The catalytic activity for the ORR increased with the increasing crystallinity analyzed by X-ray diffraction spectroscopy (XRD) and with decreasing ionization potential.

Cr, Mo, and W in 6-group metals can form metal carbides. Since tungsten carbide (WC) is considered to show Pt-like properties [39,40], WC catalysts for ORR have been studied. But most of the catalysts are used in alkaline media, and the application to acidic media seems to be limited [41,42]. Ota et al. found that the stability of WC catalysts increased by addition of Ta [43,44]. Cr-based catalysts were also prepared by heat-treatment of chromium carbide (CrC) under NH_3 -containing atmosphere [45]. From X-ray diffraction (XRD)

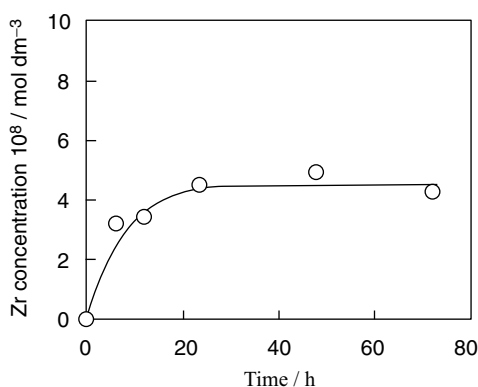


Fig. 6.7. Zr concentration dissolved from ZrO_xN_y in $0.1 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$ at 30°C as a function of time ([37], copyright The Electrochemical Society)

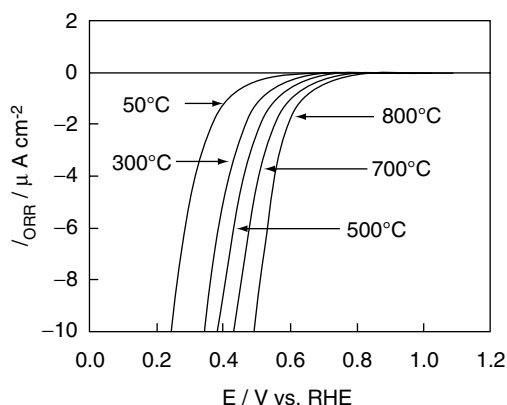


Fig. 6.8. Potential–current curves in ORR for ZrO_xN_y catalysts deposited at various substrate temperatures ([37], copyright The Electrochemical Society)

study, chromium nitride (CrN) and/or chromium carbonitride (CrCN) would be catalytic species. From the fact that Mo_2N and W_2N supported on carbon black functioned as effective catalysts in PEFC [46,47], doping of nitrogen has good influence on the catalysts for Mo and W as well. No obvious degradation for the W_2N catalyst was observed under fuel cell conditions within 80 h [47].

Ruthenium compounds are well known to catalyze various oxidation reactions, and the Ru compounds have been studied as Pt-free catalysts for ORR [48]. Among these compounds, ruthenium chalcogenides would be one of the most attractive catalysts from the viewpoints of catalytic activity and selectivity. It was reported that the ORR activity of Ru-chalcogenides roughly followed the order of $\text{Ru} < \text{RuS} < \text{RuTe} < \text{RuSe}$ as shown in Fig. 6.9 [49]. For the selectivity of RuSe catalyst, the amount of H_2O_2 generated via two-electron reduction of O_2 depended on the content of Se [48,50]. The catalyst containing 14 mol% of Se forms less than 7% H_2O_2 , while the Se-free Ru cluster generated over 20% H_2O_2 during ORR. Figure 6.10 shows PEFC performance curves with Ru-based electrocatalysts. The electrochemical performances for RuSe and Fe-doped RuSe (RuFeSe) catalysts were approximately 35% and 45% compared with that for Pt catalyst [51]. But the ORR activity of RuSe catalysts decreased in repeated CV scan timescale [52,53]. Popov and his coworkers developed nitrogen-doped Ru-based catalysts prepared from RuCl_3 and propylene diamine, followed by heat-treatment at 600–900°C [54]. The resulting nanosized RuN_x catalysts exhibited comparable catalytic activity to Pt catalyst and generated less than 2% H_2O_2 during ORR. Thus, Ru-based catalysts seem possible for Pt alternatives, however the resource amount of Ru is more limited than that of Pt.

In general, it seems that the problem for the metal-oxide-based catalysts at the cathode is the low activity and that for the metal nitride-based one is the low durability. Both the weak points can be improved by incorporating

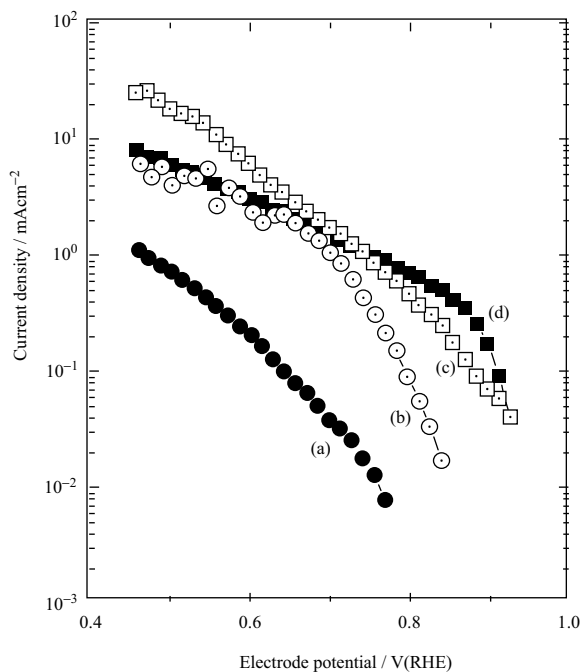


Fig. 6.9. Potential–current characteristics for ORR on Ru_xX_y catalysts in 0.5 M H_2SO_4 : (a) Ru_xS_y , (b) Ru_xTe_y , (c) $\text{Mo}_x\text{Ru}_y\text{Se}_y$, and (d) Ru_xSe_y . ([49], copyright Elsevier)

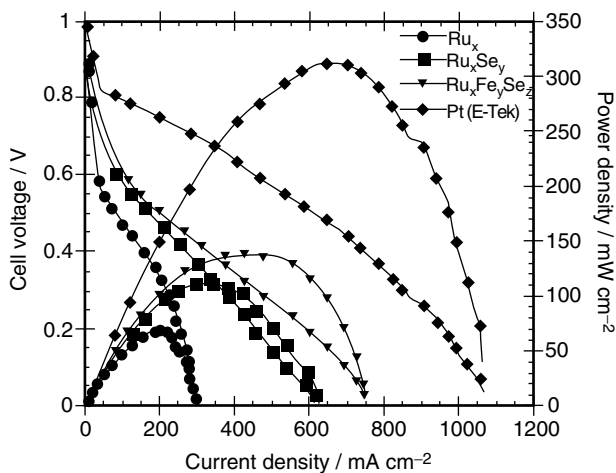


Fig. 6.10. PEFC performance curves with Ru-based cathode catalysts at 80°C ([51], copyright Elsevier)

nitrogen atoms. The ruthenium chalcogenide-based catalysts show good catalytic property, however Ru is one of precious metals.

6.4.3 Carbon Materials

Carbon materials, which are generally used for supporting catalysts in PEFC, have been investigated as cathode catalyst. Ozaki reported carbon-based catalysts prepared by carbonization of poly(furfuryl alcohol) in the presence of transition metal complexes, melamine, and BF_3 [55–58]. The ORR activities of the resulting “carbon alloys” were higher than that of the original carbon: 1.7–4.8 times for N-doped carbons, 3.6 times for the B-doped carbon, and 7.1–22 times for BN-doped carbons [58] (Fig. 6.11).

Another type of nitrogen-doped carbon (CN_x) catalyst was developed by Ozkan [59–61]. The catalysts were prepared by pyrolysis of acetonitrile with metal acetate (Fe, Co, Ni) over alumina, silica, and magnesia supports. The most active catalysts were Fe-derived catalysts, seeming to show about one-tenth activity toward Pt catalyst (Fig. 6.12), and the selectivity of four-electron transfer was 3.8–3.95 [61]. It was proposed that ORR activity of these carbon catalysts were related to pyridine- and pyrrole-like nitrogen atoms located on graphene edge [55–61]. Several types of nitrogen atoms are illustrated in Fig. 6.13 with the corresponding binding energies [62].

For the use of carbon materials themselves as cathode catalysts, the ORR activity has been increased by the dope of nitrogen atoms into graphene structure. But the catalytic activity of carbon material catalyst seems still lower than that of Pt catalyst, and the long-term durability test would be required.

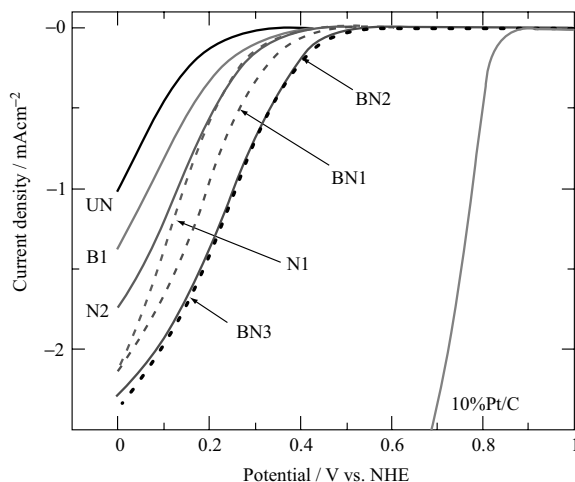


Fig. 6.11. Hydrodynamic voltammograms of the carbon-based catalysts for ORR (0.5 M H_2SO_4) ([58], copyright Elsevier)

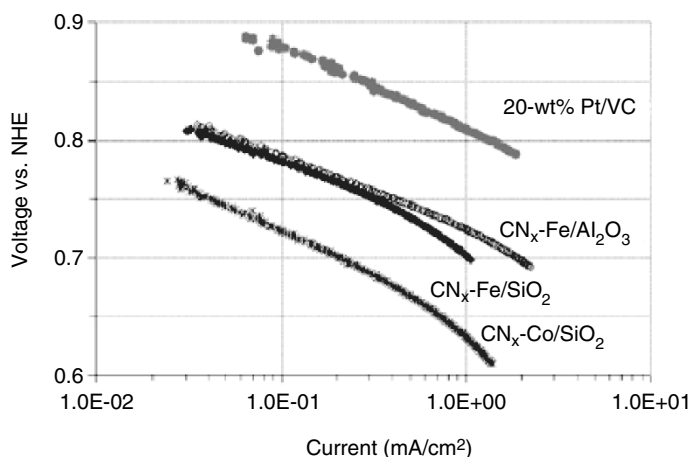


Fig. 6.12. Tafel plots of CN_x catalysts and commercial 20 wt% Pt/C ($0.5 \text{ M H}_2\text{SO}_4$) ([61], copyright Elsevier)

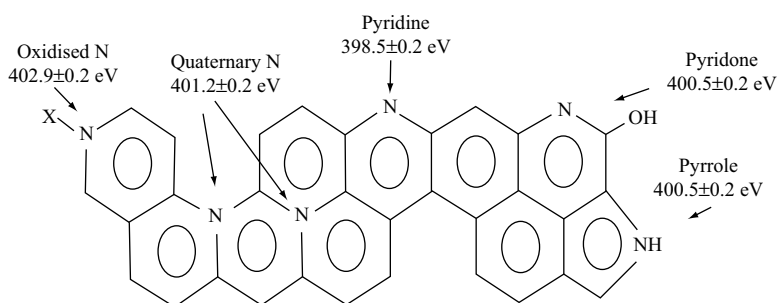


Fig. 6.13. The nitrogen-doped structures at the carbon surface and the corresponding binding energy for N1s electrons ([62], copyright Elsevier)

6.4.4 Metal Complex-Based Catalysts

Reactions of transition metal complexes with O_2 are well known [63], and the metal complexes with macrocyclic N_4 -type ligands such as porphyrins and phthalocyanines have been studied for application to cathode catalysts [26, 64, 65]. Bagotzky et al. found out that ORR activity and stability of M-N_4 -type complexes supported on carbon black were improved by heat-treatment [66]. Although the chemical structure after the heat-treatment was not clear, some experimental data supported the existence of M-N_4 moiety. It is proposed that the metal complex parts still connect to carbon surface even after pyrolysis (Fig. 6.14) [67].

The ORR activity of the heat-treated M-N_4 -type catalysts has been evaluated mostly using the first transition elements, in which Co and Fe seem

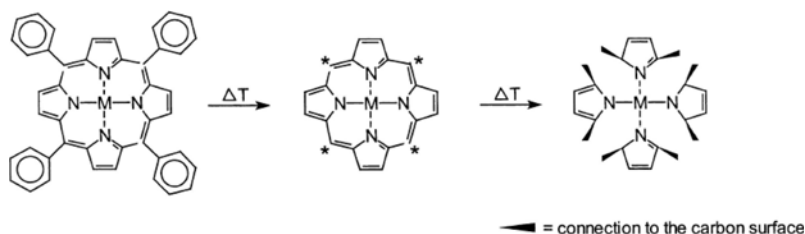


Fig. 6.14. Proposed scheme in the heat-treatment of metal porphyrine with carbon black ([67], copyright The American Chemical Society)

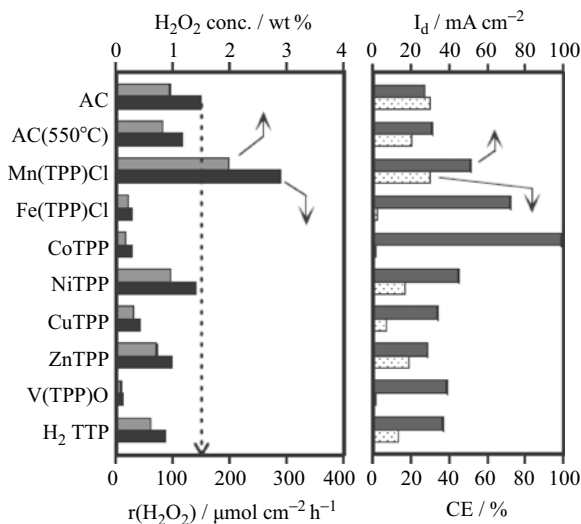


Fig. 6.15. Catalytic activities and selectivities of metal porphyrins heat-treated at 550°C on active carbon (AC) at 25°C (CE = current efficiency for H₂O₂ formation) ([72], copyright The Chemical Society of Japan)

to be suitable for metal centers [64, 68–71]. Yamanaka examined the activity and selectivity for ORR by heat-treated metal porphyrin catalysts under fuel cell conditions [72]. As shown in Fig 6.15, heat-treated Co- and Fe-porphyrin catalysts produced less H₂O₂ with higher current densities. Although the selectivity of heat-treated Co- and Fe-N₄ catalysts was comparatively high, small amount of H₂O₂ was still generated during ORR. Schulenburg proposed, from the catalytic stability of heat-treated Fe-N₄, that H₂O₂ caused the degradation of active sites [73].

Dodelet and coworkers developed ORR catalysts from metal acetates and perylenetetracarboxylic dianhydride, which were heat-treated with NH₃ [74–76]. The Fe-based catalyst was the most effective for ORR [75]. Existence of two active sites, FeN₂/C and FeN₄/C, was proposed from time-of-flight secondary ion mass spectroscopy (TOF-SIMS) analyses, suggesting that the

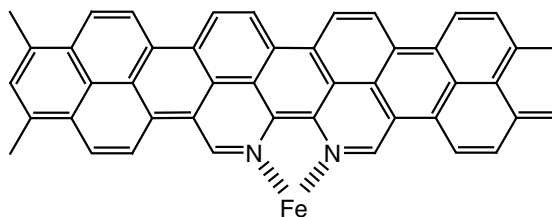


Fig. 6.16. Postulated structure of the FeN₂/C site ([77], copyright The American Chemical Society)

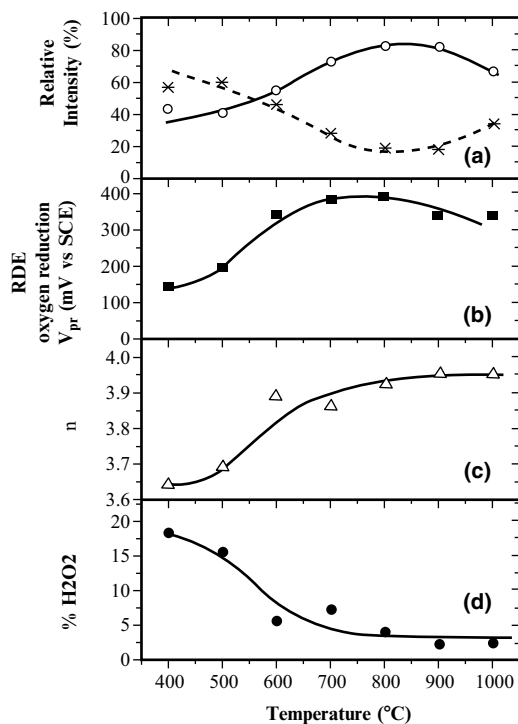


Fig. 6.17. (a) The relative ratios of FeN₂/C (open circles) and FeN₄/C (stars), and their relation with (b) the catalytic activity, (c) the electron transfer number (*n*), and (d) the selectivity for H₂O₂ ([78], copyright Elsevier)

former site was more active than the latter [77]. It was also described that four-electron reduction of O₂ mainly took place on the FeN₂/C site (Fig. 6.16), while on FeN₄/C site two-electron reduction was dominant (Fig. 6.17) [78]. The carbon components and surface conditions have large influences on four-electron reduction efficiency [71, 79].

Recently, Los Alamos National Laboratory has developed a new class of ORR catalyst (Co-PPY-C), which was prepared from cobalt salt, polypyrrole, and carbon black [80]. The Co moieties were captured in polypyrrole matrix

with strong Co-pyrrole interactions (Fig. 6.18). The ORR activity of non-heat-treated Co-PPY-C catalyst was better than the heat-treated one at 800°C, hence traditional heat-treatment was not necessary for this catalyst [81]. The most striking property of the catalyst was that no apparent degradation was observed for 100 h (Fig. 6.19). They described that Co-PPY-C was the first example to show both a promising activity and stability as a non-precious cathode catalyst.

Maruyama and Abe found the cathode catalysts prepared by carbonization of iron enzymes, e.g. catalase and hemoglobin [82–84]. The heat-treatment temperature had a large influence on specific surface area of the catalysts, and the catalytic activity increased with an increase in the specific surface

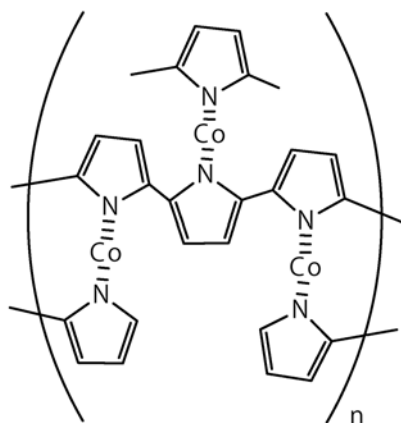


Fig. 6.18. Schematic representation of Co-PPY-C [80]

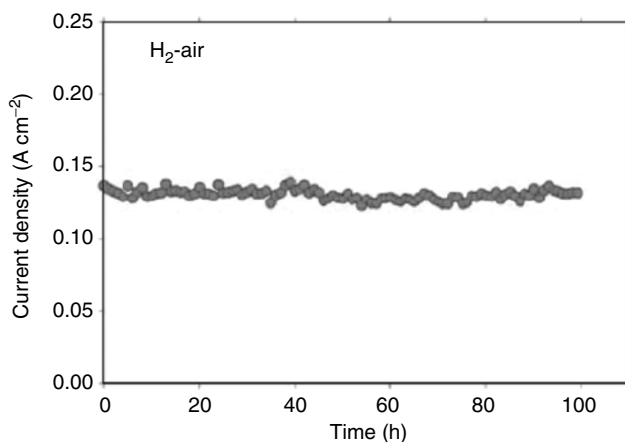


Fig. 6.19. Long-term performance of an H₂-air fuel cell with Co-PPY-C composite cathode ([80], copyright Nature Publishing Group)

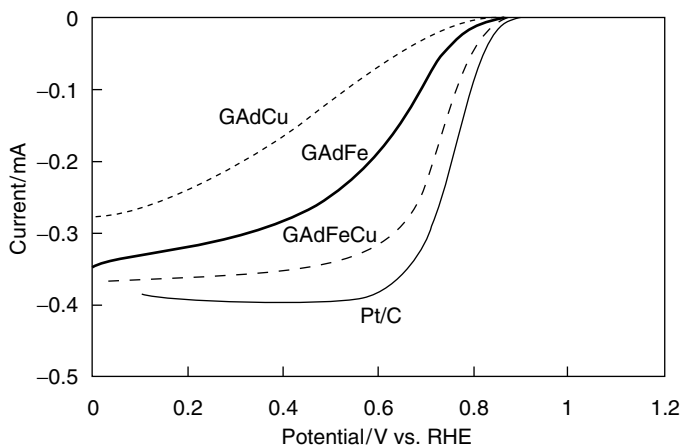


Fig. 6.20. Relationships between electrode potential and oxygen reduction current of glucose/adenine (GAd)-based catalysts: GAdFe (solid line), GAdCu (dotted line), GAdFeCu (dashed line), and Pt/C (thin line) in O_2 -saturated 0.1 M $HClO_4$ at 25°C ([86], copyright The Royal Society of Chemistry)

area. The fuel cell performance gradually decreased within 50 h at 80°C; however, the reason of the degradation has not been clarified.

The same group has recently developed another type of cathode catalyst, which is prepared by carbonation of glucose with metal acetates (Fe, Co, and Cu) (Fig. 6.20) [85, 86]. The stability of glucose-based catalysts increased by co-carbonization with nitrogen-containing substrates such as glycine and adenine, and the remarkable loss of PEFC performance was not observed during 100 h continuous operation. They proposed that addition of nitrogen sources enhanced the formation of graphene-layered structure on the surface of the carbonized materials. It was also reported that the combination of Fe and Cu was better than the Fe-only or Cu-only component [86].

Sawai and Uda studied the ORR by Prussian-blue-based catalysts, although the conditions were not acidic but neutral (pH 7.6) [87]. The onset potential of Cu–Fe mixed catalyst was higher than Pt catalyst, and the average number of electron transfer of Cu–Fe catalyst was 3.95 (Fig. 6.21).

There are a lot of metal-complex-based catalysts as Pt-free cathode catalysts. For most of such catalysts, the heat-treatments are effective to increase the ORR activity. The catalysts resulting from Co, Fe, and Cu complexes are likely to provide active centers suitable for ORR. It has been generally considered that the stability in acidic conditions is one of the most difficult problems for the metal complex-based catalysts; however the finding that the Co-PPY-C catalyst shows the durability in PEFC to some extent may open the possibility of the metal complex catalysts.

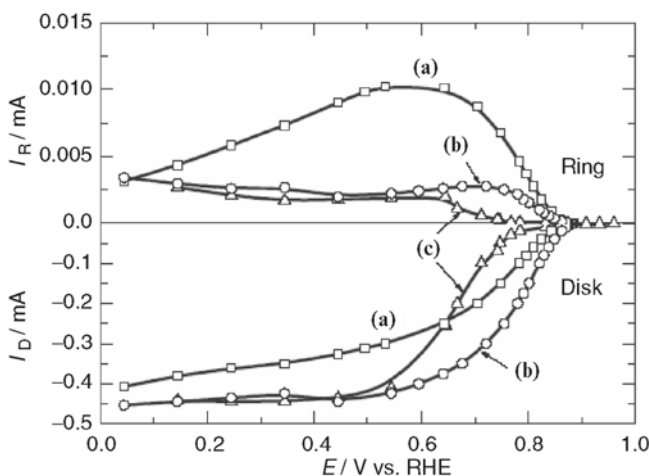


Fig. 6.21. Rotating ring-disk electrode voltammograms for ORR with (a) HT-Co[Fe]PB/C, (b) HT-Cu[Fe]PB/C, and (c) Pt/C in 1 M potassium phosphate buffer solution (pH 7.6) saturated with oxygen ([87], copyright The Chemical Society of Japan)

6.4.5 Catalysts Designed from Dinuclear Metal Complexes

Aerobic organisms also gain energy from ORR catalyzed by enzymes. In human beings, cytochrome *c* oxidases catalyze four-electron reduction of O_2 , which active centers consist of Cu/Fe dinuclear complexes [88, 89]. As mentioned above, two-site configuration is favorable to four-electron reduction of O_2 . When O_2 interacts with two metal atoms, two bridge configurations as 1,2-peroxo complexes (Fig. 6.22) can be taken into account from theoretical studies [64].

The trans-bridge interaction is often observed in the reactions of metal porphyrins and metal phthalocyanines with O_2 in homogeneous systems [90, 91]. Face-to-face porphyrins and corrols are capable to take trans-bridge configurations [92–96]. The four-electron reduction of O_2 was achieved using “cofacial” dicobalt complex with porphyrin dimers on graphite [93] (Fig. 6.23). The selectivity of ORR depends on the distances between two metal centers, and around 4.5 Å seems to be suitable for selective four-electron reduction of O_2 [96]. Yuasa and Oyaizu developed a new cathode material obtained from polythiophene with porphyrins as side chains and carbon particle (Fig. 6.24) [97, 98]. They proposed that each porphyrin was arranged in a proper distance on carbon particle, hence high selectivity for four-electron reduction of O_2 was achieved (>3.8). It was also reported that the ORR activity was improved by heat-treatment.

The *cis*-bridge interaction is proposed by Yeager [99], and as described above, it is likely to occur on noble metals such as Pt, leading to four-

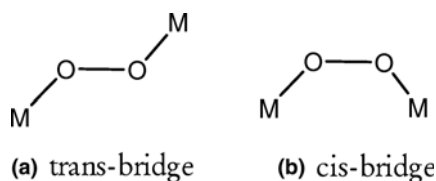


Fig. 6.22. Two bridge configurations of O_2 interaction with two metal atoms

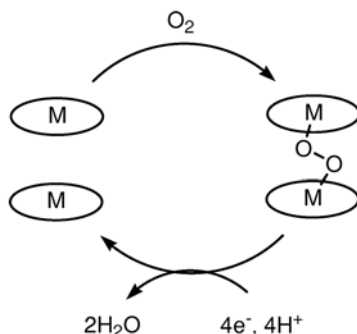


Fig. 6.23. Catalytic cycle for a face-to-face-type metal complex

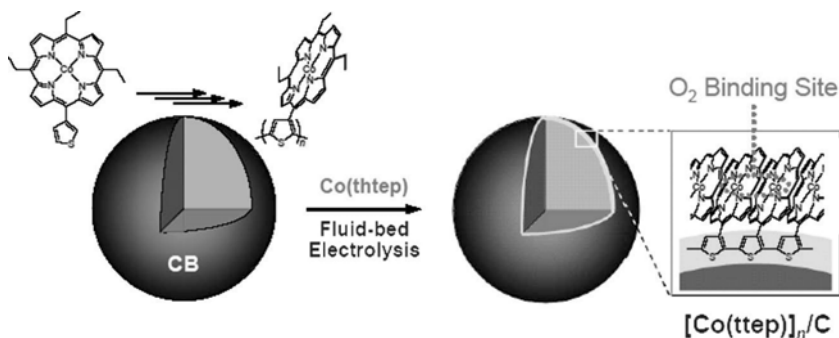


Fig. 6.24. Preparative procedure of the *trans*-bridge type catalyst [98]

electron reduction of O_2 . However, it seems that the idea of applying the *cis*-bridge interaction for ORR catalysts has not been reported. The authors, who were interested in dinuclear metal catalysts [100,101], and Okada [102,103] have designed “adjacent” dinuclear catalysts, which could form *cis*-bridge interaction with O_2 like Pt [104]. In order to examine the hypothesis, two dinuclear cobalt complexes (shown in Fig. 6.25) were prepared, followed by heat-treatment with carbon to produce the catalysts. The catalytic activity of ORR depended largely on the heat-treatment temperatures, and the ORR activity of the cathode catalyst based on Co_2L^2 complex reached a maximum at $450^\circ C$ (Fig. 6.26).

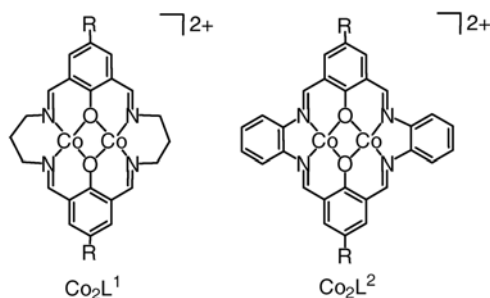


Fig. 6.25. Chemical structures of adjacent dinuclear complexes

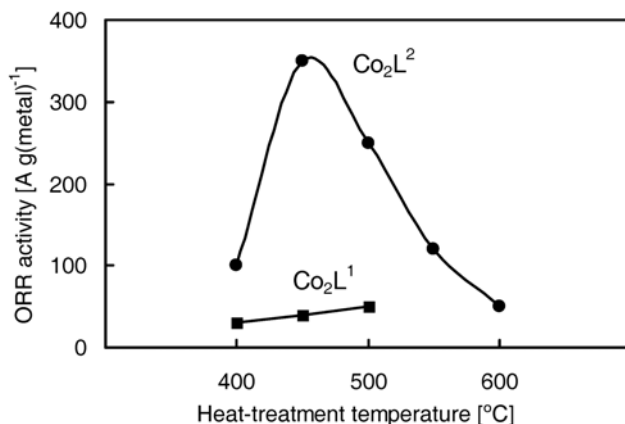


Fig. 6.26. Dependence of ORR activity on heat-treatment temperature of the adjacent dinuclear complexes

It was found that the Co_2L^2 catalyst was five times more active than the Co_2L^1 catalyst, showing high activity in comparison with Pt catalyst (Table 6.1). Thus, “adjacent” dinuclear catalysts have been found to work as cathode catalysts, although the selectivity of four-electron reduction of O_2 to H_2O is not enough high yet. The further study to improve the activity, selectivity, and durability is now under progress.

The catalysts based on dinuclear metal complexes are designed from two bridge configurations of O_2 with two metals: *trans*-bridge type and *cis*-bridge type. The former has aligned metal complex units and the latter possesses adjacent dinuclear complex moieties. Both catalysts show good activity for ORR activity by heat-treatment, but further studies on durability would be especially needed.

Table 6.1. The activity and selectivity for ORR by the Co_2L^1 and Co_2L^2 catalysts^a

Complex	Heat-treatment temperature	ORR activity ^c ($\text{A g}(\text{metal})^{-1}$)	%H ₂ O ^d (%)
Co_2L^1	Non	0.65	59
	500°C ^b	60	90
Co_2L^2	Non	40.8	64
	450°C ^b	350	80
Pt ^e	—	220	>98

^aThe cathode catalysts were prepared by dispersion of the adjacent dinuclear complexes on carbon black (Ketjen Black). The electrochemical measurement in 0.05 M H_2SO_4 was performed using rotating ring-disk electrode (RRDE) apparatus.

^bThe catalyst-dispersed carbon black was heat-treated for 2 h under nitrogen atmosphere using a tube furnace.

^cThe ORR activity is expressed as mass activity: (disk current)/(metal amount on the electrode).

^d%H₂O: Selectivity of O₂ reduction to H₂O calculated by the equation 1 in [105].

^e20wt. % Pt on carbon (ElectroChem Inc.).

6.5 Summary

The Pt-free cathode catalyst will become essential for spreading use of acidic PEFC, because the present Pt catalyst has the drawbacks of resource amount and cost. Many attempts for the catalyst have been reported such as metal particles; metal oxides, carbides, nitrides, and chalcogenides; carbon materials; and metal complex-based catalysts. At the present, no catalysts obtained from abundant and inexpensive materials, which show the comparable activity, selectivity, and durability of ORR to Pt catalyst, have been developed. However, the studies on the Pt-free cathode catalyst are steadily progressing, so the catalyst used practically for acidic PEFC will be developed in the near future. Recently, alkaline fuel cell using anion-exchange membranes has been also interesting because some Pt-free catalysts can be used [106, 107], which may be another candidate of fuel cell system.

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References

1. W. Vielstich, H. Gasteiger, A. Lamm (eds.), *Handbook of Fuel Cells Fundamentals Technology and Applications*, vol. 1 (Wiley, Chichester, 2003)
2. J. Larminie, A. Dicks, *Fuel Cell Systems Explained* (Wiley, Chichester, 2003)
3. 2007–2008 World Motor Vehicle Market Report, Overseas Automobile Council
4. H.A. Gasteiger, S.S. Kocha, B. Sompalli, F.T. Wagner, *Appl. Catal. B Environ* **56**, 9 (2005)
5. <http://www.nims.go.jp/jpn/news/press/pdf/press178.pdf>
6. Platinum 2006, Johnson Matthey translated to Japanese by Tanaka Kikinzoku Kogyo
7. US DOE Hydrogen Program FY 2004 Progress Report, http://hydrogen.energy.gov/pdfs/progress04/ivb2_uribe.pdf
8. C. Wang, M. Waje, X. Wang, J.M. Tang, R.C. Haddon, Y. Yan, *Nano Lett.* **4**, 345 (2004)
9. D. Thompsett, in *Pt alloys as oxygen reduction catalysts*, ed. by W. Vielstich, H. Gasteiger, A. Lamm, *Handbook of Fuel Cells Fundamentals Technology and Applications*, vol. 3, Chap. 37 (Wiley, Chichester, 2003), pp. 467–480
10. T. Tada, in *Handbook of Fuel Cells Fundamentals Technology and Applications*, ed. by W. Vielstich, H. Gasteiger, A. Lamm, vol. 3, Chap. 38 (Wiley, Chichester, 2003), pp. 481–488
11. E. Antolini, J.R.C. Salgado, E.R. Gonzalez, *J. Power Sources* **160**, 957 (2006)
12. E. Antolini, *Appl. Catal. B Environ* **74**, 337 (2007)
13. Data taken from the Web site of Tanaka Kikinzoku Kogyo: <http://www.tanaka.co.jp>
14. S. Mukerjee, S. Srinivasan, A.J. Appleby, *Electrochimica Acta* **38**, 1661 (1993)
15. A. Parthasarathy, B. Dave, S. Srinivasan, A.J. Appleby, C.R. Martin, *J. Electrochem. Soc.* **139**, 2530 (1992)
16. N.M. Marković, B.N. Grgur, P.N. Ross, *J. Phys. Chem. B* **101**, 5405 (1997)
17. H.A. Gasteiger, J.E. Panels, S.G. Yan, *J. Power Sources* **127**, 162 (2004)
18. D.R. Lide (ed.), *CRC Handbook of Chemistry and Physics*, 87th edn. (CRC, West Palm Beach, FL, 2006)
19. J. Parkash, D.A. Tryk, E.B. Yeager, *J. Electrochem. Soc.* **146**, 4145 (1999)
20. P.N. Ross, in *Oxygen reduction reaction on smooth single crystal electrodes*, ed. by W. Vielstich, H. Gasteiger, A. Lamm, *Handbook of Fuel Cells Fundamentals Technology and Applications*, vol. 2, Chap. 31 (Wiley, Chichester, 2003) pp. 465–480
21. T. Kinumoto, M. Inaba, Y. Nakayama, K. Ogata, R. Umebayashi, A. Tasaka, Y. Iriyama, Z. Ogumi, *J. Power Sources* **158**, 1222 (2006)
22. D. Liu, S. Case, *J. Power Sources* **162**, 521 (2006)
23. W.E. Mustain, J. Parkash, *J. Electrochem. Soc.* **154**, A668 (2007)
24. B. Wang, *J. Power Sources* **152**, 1 (2005)
25. L. Zhang, J. Zhang, D.P. Wilkinson, H. Wang, *J. Power Sources* **156**, 171 (2006)
26. J.H. Zagal, F. Bedioui, J.P. Dodelet, *N₄-Macrocyclic Metal Complexes* (Springer, New York, 2006)
27. H. Tributsch, *Electrochimica Acta* **52**, 2302 (2007)
28. R. Borup, J. Meyers, B. Pivovar, Y.S. Kim, R. Mukundan, N. Garland, D. Myers, M. Wilson, F. Garzon, D. Wood, P. Zelenay, K. More, K. Stroh, T. Zawodzinski, J. Boncella, J.E. McGrath, M. Inaba, K. Miyatake, M. Hori, K. Ota, Z. Ogumi, S. Miyata, A. Nishikata, Z. Siroma, Y. Uchimoto, K. Yasuda, K. Kimijima, N. Iwashita, *Chem. Rev.* **107**, 3904 (2007)

29. M.A. Garcia-Contreras, S.M. Fernandez-Valverde, J.R. Vargas-Garcia, *J. Alloys Compds.* **434**, 522 (2007)
30. M. Shao, P. Liu, J. Zhang, R. Adzic, *J. Phys. Chem. B* **111**, 6772 (2007)
31. H.K. Lee, J.P. Shim, M.J. Shim, S.W. Kim, J.S. Lee, *Mater. Chem. Phys.* **45**, 238 (1996)
32. F. Gao, M.S. El-Deab, T. Okajima, T. Ohsaka, *J. Electrochem. Soc.* **152**, A1226 (2005)
33. V. Raghuvier, A. Manthiram, A.J. Bard, *J. Phys. Chem. B* **109**, 22909 (2005)
34. P. Bert, C. Bianchini, World Patent WO2004-036674 (2004)
35. X. Ren, Fuel cell seminar 2006, Honolulu (2006), [http://www.fuelcellseminar.com/pdf/2006/Wednesday/3B/Ren_Xiaoming.0900_3B.296\(rv4\).pdf](http://www.fuelcellseminar.com/pdf/2006/Wednesday/3B/Ren_Xiaoming.0900_3B.296(rv4).pdf)
36. Y. Nabae, I. Yamanaka, K. Otsuka, *Appl. Catal. A Gen.* **280**, 149 (2005)
37. S. Doi, A. Ishihara, S. Mitsushima, N. Kamiya, K. Ota, *J. Electrochem. Soc.* **154**, B362 (2007)
38. A. Ishihara, K. Lee, S. Doi, S. Mitsushima, N. Kamiya, M. Hara, K. Domen, K. Fukuda, K. Ota, *Electrochem. Solid-State Lett.* **8**, A201 (2005)
39. L.H. Bennett, J.R. Cuthill, A.J. McAlister, N.E. Erickson, R.E. Watson, *Science* **184**, 563 (1974)
40. R.J. Colton, J.W. Rabalais *Chem. Phys. Lett.* **34**, 337 (1975)
41. F. Mazza, *J. Electrochem. Soc.* **110**, 847 (1963)
42. H. Meng, P.K. Shen, *Electrochem. Commun.* **8**, 588 (2006)
43. K. Lee, A. Ishihara, S. Mitsushima, N. Kamiya, K. Ota, *Electrochimica Acta* **49**, 3479 (2004)
44. K. Ota, A. Ishihara, S. Mitsushima, K. Lee, Y. Suzuki, N. Horibe, T. Nakagawa, N. Kamiya, *J. New Mater. Electrochem. Syst.* **8**, 25 (2005)
45. J.H. Kim, A. Ishihara, S. Mitsushima, N. Kamiya, K. Ota, *Chem. Lett.* **36**, 514 (2007)
46. H. Zhong, H. Zhang, G. Liu, Y. Liang, J. Hu, B. Baolian Yi, *Electrochem. Commun.* **8**, 707 (2006)
47. H. Zhong, H. Zhang, Y. Liang, J. Zhang, M. Wang, W. Xiaoli, *J. Power Sources* **164**, 572 (2007)
48. J.W. Lee, B.N. Popov, *J. Solid State Electrochem.* **11**, 1355 (2007)
49. N. Alonso-Vante, I.V. Malakhov, S.G. Nikitenko, E.R. Savinova, D.I. Kochubey, *Electrochimica Acta* **47**, 3807 (2002)
50. M. Bron, P. Bogdanoff, S. Fiechter, I. Dorbandt, M. Hilgendorff, H. Schulenburg, H. Tributsch, *J. Electroanal. Chem.* **500**, 510 (2001)
51. R.G. González-Huerta, J.A. Chávez-Carvayar, O. Solorza-Feria, *J. Power Sources* **153**, 11 (2006)
52. D. Cao, A. Wieckowski, J. Inukai, N. Alonso-Vante, *J. Electrochem. Soc.* **153**, A869 (2006)
53. A. Lewera, J. Inukai, W.P. Zhoua, D. Cao, H.T. Duonga, N. Alonso-Vante, A. Wieckowski, *Electrochimica Acta* **52**, 5759 (2007)
54. L. Liu, H. Kim, J.W. Lee, B.N. Popova, *J. Electrochem. Soc.* **154**, A123 (2007)
55. J. Ozaki, *Tanso* **218**, 178 (2005)
56. J. Ozaki, S. Tanifuji, N. Kimura, A. Furuichi, A. Oya, *Carbon* **44**, 1324 (2006)
57. J. Ozaki, T. Anahara, N. Kimura, A. Oya, *Carbon* **44**, 3348 (2006)
58. J. Ozaki, N. Kimura, T. Anahara, A. Oya, *Carbon* **45**, 1847 (2007)
59. P.H. Matter, U.S. Ozkan, *Catal. Lett.* **109**, 115 (2006)
60. P.H. Matter, L. Zhang, U.S. Ozkan, *J. Catal.* **239**, 83 (2006)

61. P.H. Matter, E. Wang, M. Arias, E.J. Biddinger, U.S. Ozkan, *J. Mol. Catal. A Chem.* **264**, 73 (2007)
62. E. Raymundo-Pinero, D. Cazorla-Amoros, A. Linares-Solano, J. Find, U. Wild, R. Schlögl, *Carbon* **40**, 597 (2002)
63. T. Abe, M. Kaneko, *Prog. Polym. Sci.* **28**, 1441 (2003)
64. J.H. Zagal, *Coord. Chem. Rev.* **119**, 89 (1992)
65. J.A. Rob van Veen, J.F. van Baar, K.J. Kroese, *J. Chem. Soc. Faraday Trans. 1* **77**, 2827 (1981)
66. V.S. Bagotzky, M.R. Tarasevich, K.A. Radyushkina, O.A. Levina, S.I. Andrusyova, *J. Power Sources* **2**, 233 (1978)
67. A.L. Bouwkamp-Wijnoltz, W. Visscher, J.A.R. van Veen, A.M. Boellaard, E. van der Kraan, S.C. Tang, *J. Phys. Chem. B* **106**, 12993 (2002)
68. G. Lalonde, G. Faubert, R.D. Côte, D. Guay, J.P. Dodelet, L.T. Weng, P. Bertrand, *J. Power Sources* **61**, 227 (1996)
69. A. Biloul, P. Gouérec, M. Savy, G. Scarbeck, S. Besse, J. Riga, *J. Appl. Electrochem.* **26**, 1139 (1996)
70. Z.F. Ma, X.Y. Xie, X.X. Ma, D.Y. Zhang, Q. Ren, N. Heß-Mohr, V.M. Schmidt, *Electrochem. Commun.* **8**, 389 (2006)
71. C. Médard, M. Lefèvre, J.P. Dodelet, F. Jaouen, G. Lindbergh, *Electrochimica Acta* **51**, 3202 (2006)
72. I. Yamanaka, T. Onizawa, H. Suzuki, N. Hanaizumi, K. Otsuka, *Chem. Lett.* **35**, 1330 (2006)
73. H. Schulenburg, S. Stankov, V. Schünemann, J. Radnik, I. Dorbandt, S. Fiechter, P. Bogdanoff, H. Tributsch, *J. Phys. Chem. B* **107**, 9034 (2002)
74. G. Faubert, R. Côte, J.P. Dodelet, M. Lefèvre, P. Bertrand, *Electrochimica Acta* **44**, 2589 (1999)
75. P. He, M. Lefèvre, G. Faubert, J.P. Dodelet, *J. New Mater. Electrochem. Syst.* **2**, 243 (1999)
76. M. Lefèvre, J.P. Dodelet, P. Bertrand, *J. Phys. Chem. B* **104**, 11238 (2000)
77. M. Lefèvre, J.P. Dodelet, P. Bertrand, *J. Phys. Chem. B* **106**, 8705 (2002)
78. M. Lefèvre, J.P. Dodelet, *Electrochimica Acta* **48**, 2749 (2003)
79. F. Jaouen, F. Charreteur, J.P. Dodelet, *J. Electrochem. Soc.* **153**, A689 (2006)
80. R. Bashyam, P. Zelenay, *Nature* **443**, 63 (2006)
81. P. Zelenay, R. Bashyam, E. Brosha, F. Garzon, S. Conradson, C. Johnston, R. Mukundan, J.U.S. Ramsey, DOE, Hydrogen Annual Progress Report, 2006, http://www.hydrogen.energy.gov/pdfs/progress06/v.c.7_zelenay.pdf.
82. J. Maruyama, I. Abe, *Chem. Mater.* **17**, 4660 (2005)
83. J. Maruyama, I. Abe, *Chem. Mater.* **18**, 1303 (2006)
84. J. Maruyama, J. Okamura, K. Miyazaki, I. Abe, *J. Phys. Chem. C* **111**, 6597 (2006)
85. J. Maruyama, *J. Electrochem. Soc.* **154**, B297 (2007)
86. J. Maruyama, *Chem. Commun.* **27**, 2879 (2007)
87. K. Sawai, D. Uda, *Chem. Lett.* **35**, 1166 (2006)
88. J.P. Collman, N.K. Devaraj, R.A. Decréau, Y. Yang, Y.L. Yan, W. Ebina, T.A. Eberspacher, C.E.D. Chidsey, *Science* **315**, 1565 (2007)
89. J.P. Collman, R. Boulatov, C.J. Sunderland, L. Fu, *Chem. Rev.* **104**, 561 (2004)
90. T.D. Smith, J.R. Pilbrow, *Coord. Chem. Rev.* **13**, 173 (1974)
91. E.W. Abel, J.M. Pratt, R. Whelan, *J. Chem. Soc. D: Chem. Commun.* 449 (1971)

92. R.R. Durand, C.S. Bencosme, J.P. Collman, F.C. Anson, *J. Am. Chem. Soc.* **105**, 2710 (1983)
93. C.J. Chang, Z.H. Loh, C. Shi, F.C. Anson, D.G. Nocera, *J. Am. Chem. Soc.* **126**, 10013 (2004)
94. K.M. Kadish, L. Frémond, Z. Ou, J. Shao, C. Shi, F.C. Anson, F. Burdet, C.P. Gros, J.M. Barbe, R. Guilard, *J. Am. Chem. Soc.* **127**, 5625 (2005)
95. J. Rosenthal, D.G. Nocera, *Acc. Chem. Res.* **40**, 543 (2007)
96. S. Fukuzumi, K. Okamoto, C.P. Gros, R. Guilard, *J. Am. Chem. Soc.* **126**, 10441 (2004)
97. K. Oyaizu, M. Yuasa, *Kemikaru Enjiniyaringu (Chemical Engineering)* **52**, 175 (2007)
98. K. Oyaizu, NEDO Accomplishment Report No. 100007986 (2006)
99. E. Yeager, *J. Electrochem. Soc.* **128**, 160C (1981)
100. H. Higashimura, K. Fujisawa, Y. Moro-oka, M. Kubota, A. Shiga, A. Terahara, H. Uyama, S. Kobayashi, *J. Am. Chem. Soc.* **120**, 8529 (1998)
101. N. Koshino, J.H. Espenson, *Inorg. Chem.* **42**, 5735 (2003)
102. T. Okada, S. Gotou, T. Hirose, I. Sekine, *J. Inorg. Organometal. Polym.* **9**, 199 (1999)
103. T. Okada, M. Yoshida, T. Hirose, K. Kasuga, T. Yu, M. Yuasa, I. Sekine, *Electrochimica Acta* **45**, 4419 (2000)
104. T. Okada, N. Koshino, T. Matsunaga, H. Higashimura, M. Iwata, K. Suenobu, JP Patent (Application Number 2007-61014)
105. T. Okada, K. Katou, T. Hirose, M. Yuasa, I. Sekine, *J. Electrochem. Soc.* **146**, 2562 (1999)
106. K. Matsuoka, Y. Iriyama, T. Abe, M. Matsuoka, Z. Ogumi, *J. Power Sources* **150**, 27 (2007)
107. K. Asazawa, K. Yamada, H. Tanaka, A. Oka, M. Taniguchi, T. Kobayashi, *Angew. Chem. Int. Ed.* **46**, 8024 (2007)

Novel Support Materials for Fuel Cell Catalysts

J. Nakamura

Abstract The novel electrocatalysts particularly using carbon nanotubes (CNT) are reviewed, which showed higher catalytic performance compared to commercial carbon supports in $\text{H}_2\text{-O}_2$ fuel cell as well as direct methanol fuel cell. The difference in the catalytic properties probably originated from the interface nature between catalyst particles and the CNT surface.

7.1 Introduction

The catalytic material used in the present polymer electrolyte fuel cell (PEFC) technology includes platinum, but is expensive and insufficient to commercialize. The efficient Pt-loading is thus an important technique for the development of PEFC. One of the possibilities is the application of carbon nanotubes (CNTs) as a support of Pt catalysts. The carbon black (CB) shown in Fig. 7.1 has been generally used as the Pt supports, where the problem of Pt/CB is that the Pt particles are trapped in deep cracks of CB, which are the crystal boundaries of the small carbon particles consisting of CB. Such particles cannot work as catalysts of electrodes because the effective formation of the triple-phase boundary (gas, electrode, and electrolyte) is essential for PEFC. The CNTs supports do not have such cracks so that most Pt particles are used as effective catalysts as shown in Fig. 7.2a. Another prospect is that the network constructed by CNTs is considered to be micropores or gas lines resulting in the high performance of membrane electrode assembly (MEA). As can be seen in Fig. 7.2b, the surface of CNT is composed of graphite basal plane so that the electric conductivity is very high and the durability against oxidation of carbon is very good. As for the reduction in Pt usage, it has been reported that Pt electrode catalysts supported on CNT shows excellent performance of $\text{H}_2\text{-O}_2$ fuel cell [1–7] and direct methanol fuel cell (DMFC) [8–15]. Furthermore, Ru-Pt/CNT catalysts show higher tolerance for CO poisoning compared to RuPt/carbon black (CB) catalysts [16–18]. The reports concerning support effect of carbon electrode have suggested that catalytic activities

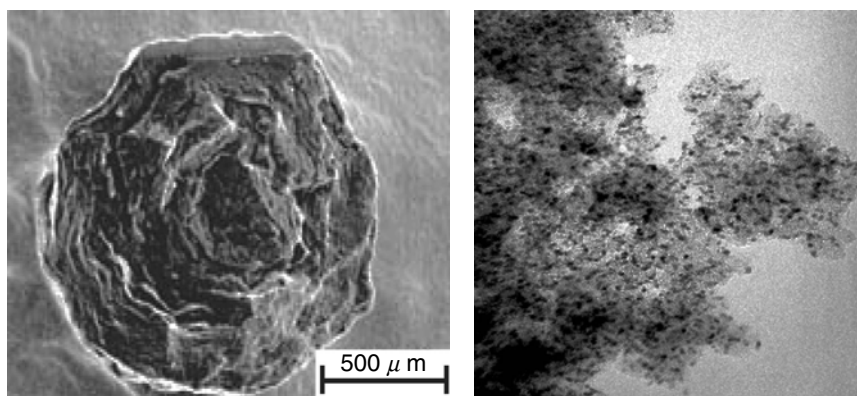


Fig. 7.1. TEM image of carbon black

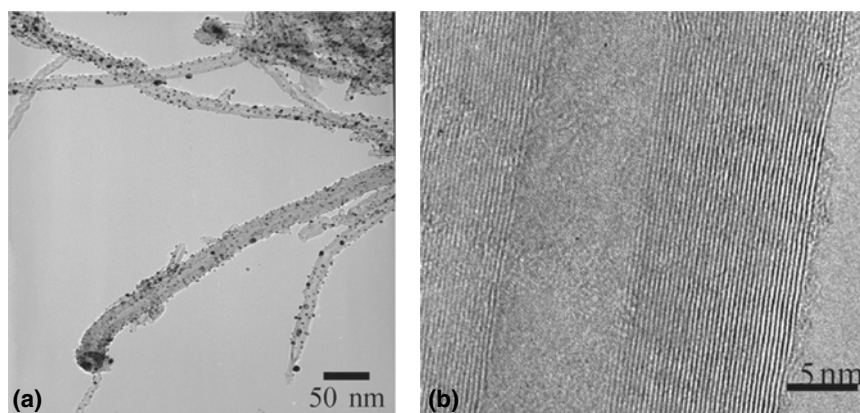


Fig. 7.2. (a) Pt catalysts supported by carbon nanotube, (b) Cross section of carbon nanotube

or electronic structures of catalyst nanoparticles are very different depending on the interface character between catalysts and carbon surface [19]. The preparation methods of CNT-supported electrocatalysts have been reviewed by Lee et al. [20].

In this chapter, the effects of carbon electrodes upon catalytic properties, particularly catalyst supports using carbon nanotubes are reviewed. The difference in the catalytic properties originated from the interface nature so that the surface science studies of metal particles deposited on carbon surface are included.

7.2 Performance of Electrocatalysts Using Carbon Nanotubes

7.2.1 H₂–O₂ Fuel Cell

The performance of the MEA using CNT should be evaluated in terms of physical properties and electrocatalytic activity. The former includes electric conductivity and diffusion of proton. The latter means the specific catalytic activity, dispersion of catalysts, or electroactive surface area. In the low current density region, the voltage drop in the potential–current curve, generally known as activation polarization, reflects the sluggish kinetics intrinsic to oxidation reactions and reduction reactions at the anode and cathode surfaces. The voltage drop in the middle to high current density range, or Ohmic polarization, arises from limitations in proton transport through the electrolyte membrane from anode to cathode and/or limitations in electron flow in the electrode materials. Here shown are literatures reporting higher catalytic activity of CNT-supported catalysts judging from the low current density region.

The first examples are the CNT supported electro-catalysts for oxygen reduction reaction (ORR) in PEFC. Li et al. [4] have constructed a membrane electrode assembly (MEA) of PEFC with an oriented CNT film as the cathode. Figure 7.3 shows higher performance of the single-cell of the MEA than those

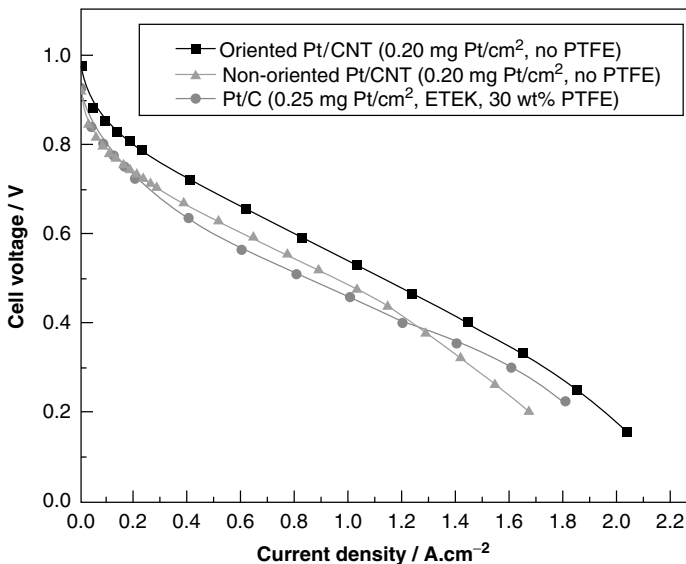


Fig. 7.3. *I*–*V* curves of PEFCs with the oriented Pt/CNT film, the non-oriented Pt/CNT film, Pt/C with 30 wt% PTFE as the cathode catalyst layers, 0.2 mg of Pt/cm² (Pt/C, 20 wt%, E-TEK) in the anode, and Nafion 112 as the membrane. Test conditions: cell and O₂ humidification at 343 K; H₂ humidification at 358 K, H₂ and O₂ pressure and flow rate at 0.2 MPa and 0.2 L/min, respectively [4]

using non-oriented Pt/CNT and Pt/C(with 30 wt% PTFE). Higher performance in the activation-controlled region (low current density) was attributed to the enhanced specific activity of Pt due to the unique interaction of Pt and CNT. Shaijumon et al. [5] have used composites of Pt/MWCNT (multi-walled carbon nanotube) and commercial Pt-loaded carbon black (Pt/C, E-TEK) as electrocatalysts for ORR in PEFC. Cathode catalyst with 50% Pt/MWCNT and 50% Pt/C showed best performance, which was explained by better dispersion and good accessibility of MWCNT support and Pt electrocatalysts for ORR in PEFC. Villers et al. [6] have prepared MEA of MWCNTs grown over the fibers of a commercial porous carbon paper. The tubes were then covered with Pt nanoparticles in order to test these gas diffusion electrodes (GDEs) for ORR in H_2SO_4 solution and in $\text{H}_2\text{-O}_2$ fuel cells. Pt/MWCNT electrodes largely outperform the commercial electrode for ORR in GDE experiments using H_2SO_4 at pH 1. On the other hand, when the same electrodes are used as the cathode in a $\text{H}_2\text{-O}_2$ fuel cell, they perform only slightly better than the commercial electrodes in the potential range going from -0.9 to -0.7 and have a lower performance at lower voltages.

Figure 7.4a shows the I - V curves for the Pt/CNT and the Pt/CB electrodes [3]. The amounts of Pt are 12 and 29 wt% for Pt/CNT and the Pt/CB electrodes, respectively. It was clearly shown that the voltages of the Pt/CNT

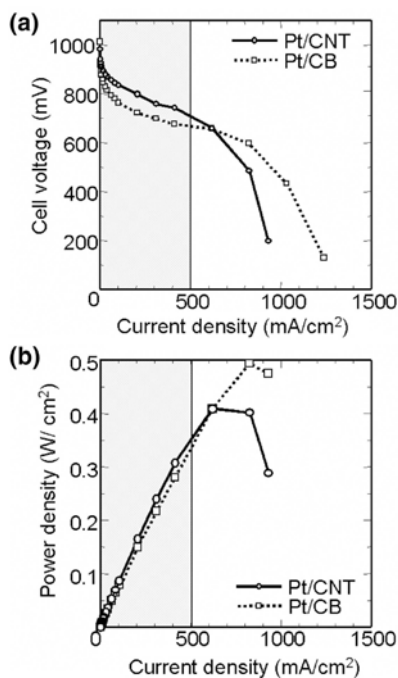


Fig. 7.4. Performance of the 12 wt% Pt/CNT and the 29 wt% Pt/CB electrodes. (a) I - V curves. (b) Power density-current density curves [3]

electrodes overwhelmed that of the Pt/CB electrodes at 0–400 mA/cm² by 10%. The power densities of the Pt/CNT and the Pt/CB electrodes are shown in Fig. 7.4b. The maximum power density of the Pt/CNT was 0.41 W/cm² recorded at 600 mA/cm². The voltage drop above 400 mA/cm² was ascribed to the proton diffusion through thick membrane because of the low surface area of CNT (70 m²/g) compared to the carbon black. The MWCNTs (multi-walled CNTs) with 20–50 nm diameters were used as carbon supports. The MWCNTs were dispersed well in ethanol after treatment with mixed acid, and Pt nanoparticles were attached on all the MWCNTs. The Pt particles were deposited with the size of 2–4 nm mainly on the CNT surfaces. This is considered to contribute to more efficient Pt usage than the Pt/CB electrodes with forming more triple-phase boundaries. The high conductivity of CNTs might be also important for the high performance with low Pt load.

Non-Pt fuel cell catalysts will decrease the demand for Pt by PEFCs, enabling more Pt to be available for use in other essential products, and make fuel cells more popular. Mo₂C has been reported to possess similar electronic and chemical characters to those of Pt. The application to PEFC catalysts has been investigated by Matsumoto et al. [7]. When carbon nanotubes (CNTs) rather than CB were used as the support for Mo₂C anode catalyst, the performance of H₂–O₂ fuel cell was improved, especially below 600 mA/cm². Figure 7.5 shows the *I*–*V* curves of the fuel cells with Mo₂C/CNT, Mo₂C/CB, and Pt/CB anode catalysts. Mo₂C/CNT showed much higher voltages than Mo₂C/CB. The advantage of CNT used as an electrode material is thus clearly shown here. Currently, the highest loading of Mo₂C on CNT is 16 wt%. It is expected that higher loading of Mo₂C leads to more generation of electric power. It should be noted that the performance of Mo₂C/CNT was recorded even after one week operation. Figure 7.5b shows transmission electron microscope (TEM) images of the Mo₂C/CNTs, where the Mo₂C particles, mainly 2–20 nm in size, were attached to the CNT surfaces.

In general, CO will adsorb very strongly on the Pt surface in the fuel cell anode, blocking the active sites and causing serious degradation in the electrode performance. It is thus necessary to develop CO-tolerant catalyst materials, which can endure CO poisoning at low overpotentials. CO-tolerant electro-catalysts have been prepared by combinations of Pt with less noble elements, such as ruthenium, tin, molybdenum, and other transition metals. Pt–Ru supported on carbon (Pt–Ru/C) has emerged as one of the most promising electrocatalysts for applications as a CO-tolerant anode material in PEFC. However, the cell voltage with 100 ppm CO compared to pure hydrogen obtained with Pt–Ru/C anode is still too far from that acceptable for practical applications. We have found that Pt–Ru/CNT reveals very high CO tolerance under 100 ppm CO. The effect of supporting carbon materials on the electrode performance was studied using defective and defect-free carbon nanotubes (CNTs), fishbone-type CNTs, and carbon black [18]. The defective CNTs were prepared by oxidation to examine

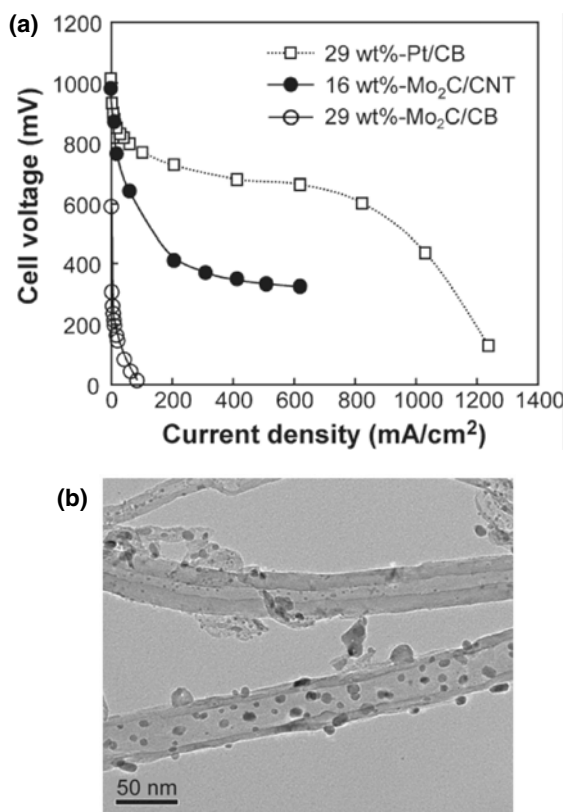


Fig. 7.5. (a) Performance of fuel cells using anodes of Mo₂C/CNT, Mo₂C/CB with Pt/CB cathodes. The results of Pt/CNT (cathode and anode) and Pt/CB (cathode and anode) are also included here. (b) TEM image of Mo₂C nanoparticles on CNTs [7]

the effect of carbon surface. The surface of fishbone-type CNT is composed of edges of graphene sheets, whose electronic conductivity is quite low. Table 7.1 summarizes the hydrogen oxidation currents of Pt-Ru and Pt catalysts using different carbon supports in H₂ gas and in H₂ with various concentrations of CO at the same Pt amount. In order to confirm the carbon support effect, the preparation of the catalysts and subsequent current measurements were repeated two or three times. The mass activities in H₂ gas were 1.8 Å mg (Pt)⁻¹, 1.5 Å mg (Pt)⁻¹, 0.9 Å mg (Pt)⁻¹, 2.1 Å mg (Pt)⁻¹, 1 Å mg (Pt)⁻¹, and 1 Å mg (Pt)⁻¹ for Pt-Ru/defect-free CNTs, Pt-Ru/defective CNTs, Pt-Ru/fishbone-type CNTs, Pt-Ru/VulcanXC-72C, Pt/defect-free CNTs, and Pt/defective CNTs, respectively. In pure H₂, the catalytic activities of all the Pt-Ru catalysts were not much different regardless of carbon materials. It was remarkable that the catalytic activity of Pt-Ru/defect-free

Table 7.1. HOR mass activity of Pt–Ru and Pt catalysts at 50 mV RHE measured in 1 M HClO₄ at 343 K after the polarization for 1 h 2[18]

Catalyst	Support	$\text{\AA mg(Pt)}^{-1}$			
		H ₂	10 ppm CO/H ₂	50 ppm CO/H ₂	100 ppm CO/H ₂
Pt–Ru	Defect-free CNTs	1.5	1.2	1.1	0.9
		1.8	1.6	1.4	1.0
		2.1	1.8	1.7	1.5
	Defective CNTs	0.7	0.5	0.3	0.14
		1.5	1.2	0.73	0.54
		1.6	1.1	0.7	0.4
	Fishbone-type CNTs	0.7	0.46	0.25	0.16
		0.92	0.67	0.53	0.32
		1.2	1.1	0.87	0.17
	VulcanXC-72C	0.73	0.4	0.12	0.09
		2.1	1.2	1.0	0.57
Pt	Defect-free CNTs	1.1	0.5	0.06	0.03
	Defective CNTs	1.0	0.24	0.014	0.004

CNTs was maintained under 100 ppm level CO with good reproducibility, in contrast to the fact that the catalytic activity of Pt–Ru/defective CNTs, Pt–Ru/fishbone-type CNTs, and Pt–Ru/VulcanXC-72C decreased with increasing CO concentration.

Electro-oxidation of CO using Pt/CNTs has been studied by Li et al. [17] with CO-stripping voltammogram and chronoamperometry measurements. In the electro-oxidation of CO, all the Pt/CNT samples showed lower on-set as well as peak potentials than the conventional Pt/XC-72 electro-catalyst, indicating that the Pt/CNT samples were more resistant to CO poisoning and could be superior anode electro-catalyst for PEFC. They thought that larger amount of oxygen-containing functional groups, higher percentage of mesopores, and higher graphitic crystallinity of the pretreated CNTs were crucial for the performance enhancement, e.g., by strengthening the interaction between Pt nanoparticles and the CNT support and enhancing the mass diffusion in the electro-chemical reaction.

7.2.2 DMFC

The next examples are the CNT-supported electrocatalysts in direct methanol fuel cell (DMFC). Li et al. [10] have prepared Pt/MWCNT catalysts by two methods, (A) HCHO reduction and (B) ethylene glycol reduction. The average particle size of Pt/MWCNT(B) is 2.6 nm, which is smaller than that of Pt/MWCNT(A), 3.4 nm. The CNTs used in these experiments were produced from high-purity graphite by arc-discharge evaporation method. The

Brunauer-Emmett-Teller (BET) surface area of the CNT samples was about $42 \text{ m}^2/\text{g}$. Cathodic polarizations obtained in direct methanol fuel cells (DMFCs) are shown in Fig. 7.6. Identical anode catalysts based on a 30 wt%

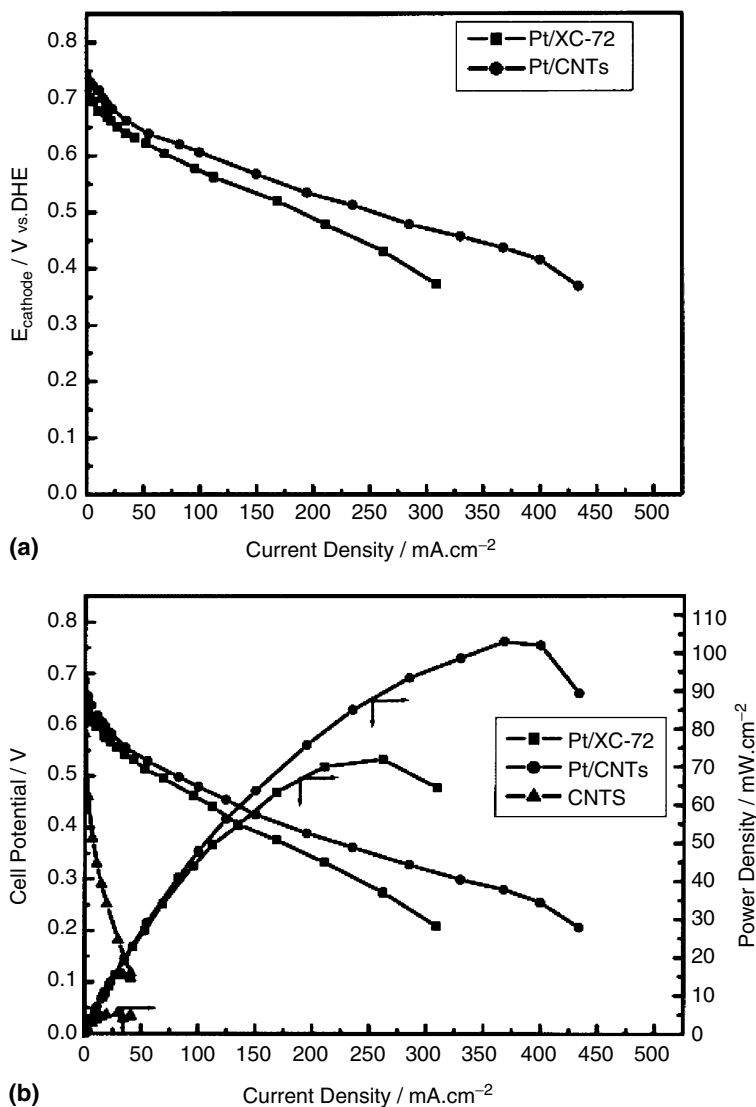


Fig. 7.6. (a) Comparison of the cathode polarization curve for the oxygen reduction reaction at 90 °C in the DMFC at Pt/XC-72 or Pt/CNTs cathode catalysts. (b) Comparison of polarization data for the DMFC in the presence of Pt/XC-72, Pt/CNTs or CNTs cathode catalysts at 90 °C. 1.0 M CH_3OH , 0.2 MPa O_2 feed. Anode, Pt-Ru/C (20 wt. % Pt, 10 wt. % Ru, JM; catalyst loading 2.0 mg Pt-Ru/ cm^2); membrane, Nafion-115 (DuPont) [10]

Pt-Ru/C catalysts were used in all the experiments. The same Pt metal loading of these Pt-based catalysts for cathodes is employed (1.0 mg Pt/cm^2). At a cathodic potential of 700 mV [vs. RHE (reversible hydrogen electrode) in the activation-controlled region], the current density of DMFC was 5.7 mA/mg Pt for Pt/MWNTs(A), 14.7 mA/mg Pt for Pt/MWNTs(B), and only 2.5 mA/mg Pt for Pt/XC-72, which means that the MWCNT-supported platinum catalysts (A and B samples) show higher ORR mass activity in the activation-controlled region. Thus, the mass activity of Pt/CNTs is approximately six times higher than that of the Pt/XC-72 sample. A further enhancement in cell performance in the high current density region was observed by using a Pt/CNTs cathode, as compared to the cathode with XC-72. This may be due to a faster oxygen–water transport through the active cathode layer could be achieved. The maximum power density of a single cell with our Pt/CNTs sample was 103 mW/cm^2 , while that with the Pt/XC-72 sample was only about 70 mW/cm^2 .

As for methanol electrooxidation, Chen et al. [14] have reported that the microwave synthesized Pt/CNTs catalysts exhibited higher catalytic activity for methanol electrooxidation at room temperature than a commercial Pt/C catalyst. Figure 7.7 shows the cyclic voltammograms of the methanol electrooxidation over the microwave synthesized Pt/CNTs catalyst and the E-TEK Pt/C catalyst, respectively, in the electrolyte of 2 M $\text{CH}_3\text{OH}/1 \text{ M H}_2\text{SO}_4$ at room temperature. The voltammetric features are in good agreement with most published works. The current peak at about 0.70 V versus SCE (saturated calomel electrode (SCE) in the forward scan is attributed to methanol electrooxidation on the catalysts. It is clearly shown that this peak is significantly higher in the microwave-synthesized

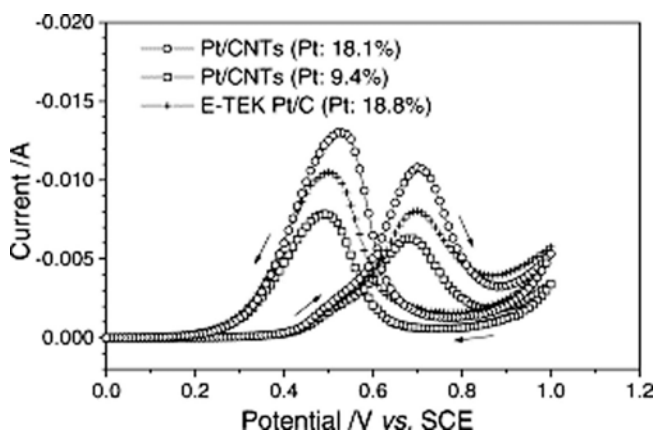


Fig. 7.7. Cyclic voltammograms of methanol electrooxidation over the microwave synthesized Pt/CNTs and E-TEK Pt/C catalysts in $2 \text{ mol L}^{-1} \text{ CH}_3\text{OH}/1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ at a scan rate of 20 mV s^{-1} at room temperature [14]

Pt/CNTs catalyst than in the E-TEK Pt/C catalyst at the same Pt loading. Similar results have been reported by Mu et al. [12], in which Pt/CNT composite materials show higher electrocatalytic activity and better tolerance to poisoning species in MOR than the commercial E-TEK catalyst. Tian et al. [13] have synthesized Pt electrocatalysts supported on MWCNT with different average diameters, 10 nm, 30 nm, and 50 nm, by the rapid intermittent microwave irradiation (IMI) technique for polymer electrolyte and direct methanol fuel cells. The electrochemical measurement indicates that Pt/MWCNT nanocomposites synthesized by the IMI method display a significantly higher electrochemically active area and higher catalytic activity for the methanol oxidation reaction in comparison to a commercial Pt/C catalyst. In addition, Pt supported on MWCNTs with the average diameter of 10 nm has the highest electrocatalytic activity for MOR. Prabhuram et al. [15] have reported that the Pt–Ru/MWCNT synthesized by a simple sodium borohydride reduction exhibited a higher methanol oxidation current than did the Pt–Ru/MWCNT-synthesized more complex methods by showing the cyclic voltammetry and chronoamperometry results. They showed that in the DMFC performance test the Pt–Ru/MWCNT nanocatalyst used at the anode of the fuel cell yielded higher performance than did the commercial E-TEK Pt–Ru/C catalyst.

7.3 Why Is Carbon Nanotube So Effective as Support Material?

In order to clarify the reason for the advantage of CNT, we have studied model systems of metal catalysts/highly oriented pyrolytic graphite (HOPG) [21]. Since the CNT used in our studies is thick with diameter of 40–100 nm, the surface of CNT can be regarded as the basal plane of graphite. In ultrahigh vacuum chambers, metal particles of Pd or Pt are vapor-deposited on the HOPG surface by heating Pd or Pt filaments. Figures 7.8a, b show scanning tunneling microscope (STM) images of Pt particles on the HOPG surface. It is clearly shown that Pt particles with diameter of 1–6 nm are distributed on the surface. It tends that Pt particles are densely localized at the step edges. As shown in Fig. 7.8b, the shape of Pt particles is flat with one or two atomic heights. The height of Pt particles are plotted as a function of the diameter in Fig. 7.9. Here, data of Pd are also included in this figure. The shape of Pt particles is quite different from that of Pd particles. STM observation shows that Pt particles are attached like two dimension islands on HOPG instead of spherical particles, suggesting the interaction is strong at the interface between Pt and the flat graphite surface.

It should be noted that the shape of Pt particles was also relatively flat on CNT, but spherical on CB. Figure 7.10 shows transmission electron microscope (TEM) images of Pt/CNT, in which Pt particles are not spherical, but in a elongated shape. This suggests that electronic structures of Pt

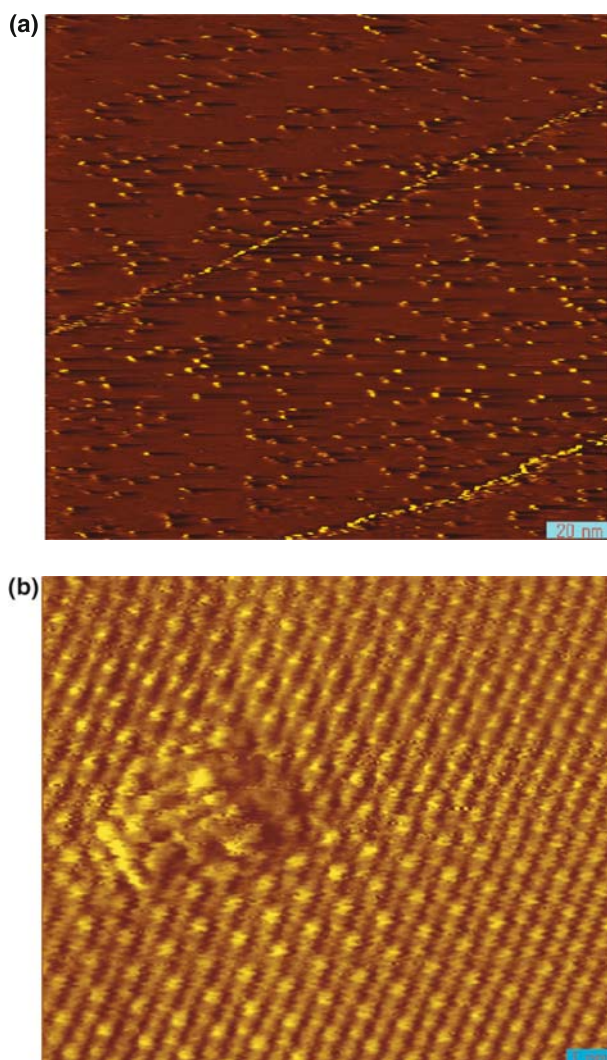


Fig. 7.8. (a) STM image of Pt/HOPG 172 nm^2 (b) STM atomic image of Pt/HOPG 7 nm^2

should be different between CNT support and CB support. In fact, X-ray photoelectron spectroscopy (XPS) measurements show that Pt 4f core level is shifted to higher energy with decreasing the size of Pt particles on HOPG. This is currently ascribed to charge transfer from Pt to carbon by hybridization of wave functions between the small Pt particles and the graphite surface. The reduction of the particle size leads to a decrease in adsorption energy of hydrogen on Pt, which is shown by temperature programmed desorption (TPD)

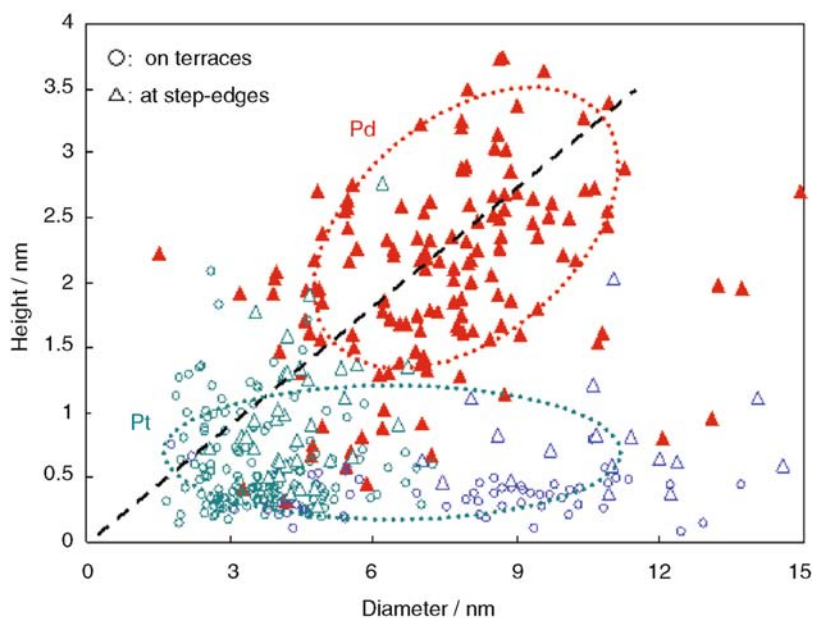


Fig. 7.9. The height of Pt and Pd particles on HOPG as a function of diameter

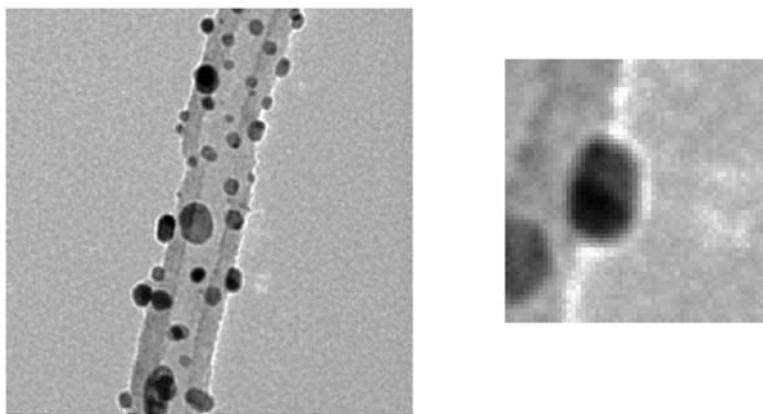


Fig. 7.10. TEM image of Pt/CNT

of H_2 as well as H_2 – D_2 exchange reaction at high pressures. The decrease in the adsorption energy can be explained by lowering d-band center induced by electron transfer from Pt to carbon upon reduction of particles size. That is, support effect of carbon, which explains the results of real catalysts of CNT supported catalysts.

References

1. Z. Liu, X. Lin, J.Y. Lee, W. Zhang, M. Han, L.M. Gan, *Langmuir* **18**, 4054 (2002)
2. T. Matsumoto, T. Komatsu, T. Arai, T. Yamazaki, M. Kijima, H. Shimizu, Y. Takasawa, J. Nakamura, *Chem. Commun.* 840–841 (2004)
3. T. Matsumoto, T. Komatsu, T. Arai, T. Yamazaki, M. Kijima, H. Shimizu, Y. Takasawa, J. Nakamura, *Catal. Today* **90**, 277 (2004)
4. W. Li, X. Wang, Z. Chen, M. Waje, Y. Yan, *Langmuir* **21**, 9386 (2005)
5. M.M. Shaijumon, S. Ramaprabhu, N. Rajalakshmi, *Appl. Phys. Lett.* **88**, 253105 (2006)
6. D. Villers, S.H. Sun, A.M. Serventi, J.P. Dodelet, *J. Phys. Chem. B* **110**, 25916 (2006)
7. T. Matsumoto, Y. Nagashima, T. Yamazaki, J. Nakamura, *Electrochem. Solid-State Lett.* **9**, A160 (2006)
8. C.A. Bessel, K. Laubernds, N.M. Rodriguez, R.T.K. Baker, *J. Phys. Chem. B* **105**, 1115 (2001)
9. E.S. Steigerwalt, G.A. Deluga, C.M. Lukehart, *J. Phys. Chem.* **106**, 760 (2002)
10. W. Li, C. Liang, J. Qiu, W. Zhou, H. Han, Z. Wei, G. Sun, Q. Xin, *Carbon* **40**, 787 (2002)
11. W. Li, C. Liang, W. Zhou, J. Qiu, Z. Zou, G. Sun, Q. Xin, *J. Phys. Chem. B* **107**, 6292 (2003)
12. Y. Mu, H. Liang, J. Hu, L. Jiang, L. Wan, *J. Phys. Chem. B* **109**, 22212 (2005)
13. Z.Q. Tian, S.P. Jiang, Y.M. Liang, P.K. Shen, *J. Phys. Chem. B* **110**, 5343 (2006)
14. W. Chen, J. Zhao, J.Y. Lee, Z. Liu, *Mater. Chem. Phys.* **91**, 124 (2005)
15. J. Prabhuram, T.S. Zhao, Z.X. Liang, R. Chen, *Electrochim. Acta* **52**, 2649 (2007)
16. Y. Liang, H. Zhang, B. Yi, Z. Zhang, Z. Tan, *Carbon* **43**, 3144 (2005)
17. L. Li, G. Wang, B. Xu, *Carbon* **44**, 2973 (2006)
18. E. Yoo, T. Okada, T. Kizuka, J. Nakamura, *Electrochemistry* **2**, 146 (2007)
19. C.A. Bessel, K. Laubernds, N.M. Rodriguez, R.T. Baker, *J. Phys. Chem.* **105**, 1115 (2001)
20. K. Lee, J. Zhang, H. Wang, D.P. Wilkinson, *J. Appl. Electrochem.* **36**, 507 (2006)
21. T. Kondo, K. Izumi, K. Watahiki, Y. Iwasaki, J. Nakamura, to be published

Molecular Catalysts for Electrochemical Solar Cells and Artificial Photosynthesis

M. Kaneko

Abstract Molecular catalysts for electrochemical solar cells and an artificial photosynthesis were described. The fundamental principle of molecule-based solar cells was at first explained in comparison to conventional semiconductor-based solar cells, concluding that both the principles are not very different although the materials for both the solar cells are entirely different. As a typical example for the molecule-based solar cell a dye-sensitized solar cell called Graetzel's cell was introduced by explaining important points of its function mechanism in relevance to functional molecules used in the cell. As a candidate for future energy conversion device, an artificial photosynthesis was proposed, and a scientific approach towards this goal was indicated to use water oxidation molecular catalyst for utilizing water as a final electron source.

8.1 Introduction

Global warming by greenhouse-effect gas such as CO_2 is becoming more and more a serious problem on our Earth. In order to solve this problem, development of renewable energy resource is an urgent issue all over the world. In order to suppress the CO_2 emission coming from burning of fossil fuels, solar cells and artificial photosynthesis are attracting a great deal of attention. An artificial photosynthesis that can produce energy-rich compound like H_2 from solar energy and water is an important research topic, but we would need much more time to introduce such sustainable energy resource in our civilization. On the other hand, solar cells based on semiconductor p-n junction such as amorphous or polycrystalline silicone solar cells are already used in our society, but because of their high cost it is not easy yet to replace the fossil fuels by solar cells. In order to develop much higher cost-performance solar cell, a new concept cell should be developed. A molecule-based device is one of the candidates for such new principle.

A dye-sensitized solar cell composed of a nanoporous TiO_2 thin film photoanode and a platinum cathode in combination with an I_3^-/I^- redox electrolytes solution is attracting attention as a next generation solar cell based

on sensitization by dye molecules [1,2]. Tremendous researches have been conducted on this so-called dye-sensitized solar cell (DSSC). In many countries companies have been planning its commercialization, and in Australia commercial products have appeared in the market. In the organic molecule-based DSSC the most important merit is their fabrication with a much lower cost than those made by inorganic semiconductors, which promises their widespread in the world. In the present chapter such molecule-based solar cells are focused as a future candidate capable of substituting fossil fuels.

An artificial photosynthesis that can produce energy-rich compounds such as H_2 from solar energy and water is one candidate for future sustainable energy resource. However, real achievement of an artificial photosynthesis still needs more time of research and development, so that in this chapter a guiding principle for solar energy conversion using functional molecules will be introduced.

8.2 Overview on Principles of Molecule-Based Solar Cells

Solar cells are usually fabricated by using junctions of semiconductors such as p-n or Schottky junction of inorganic semiconductors. This can be achieved by utilizing photophysical processes of semiconductors. However, photoenergy conversion into electrical energy can in principle also be achieved by utilizing photochemical processes of molecules as shown in the Table 8.1.

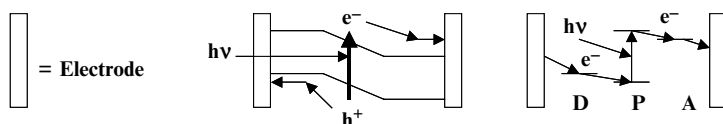
In both the photophysical and photochemical processes fundamental processes are nearly the same, i.e., they comprise (1) photoexcitation and formation of electron/hole pair or exciton, (2) charge separation into electrons and holes (carrier formation), (3) diffusion or transport of electrons and/or holes, and (4) accumulation of charges at electrodes (anode for electrons and cathode for holes) generating photocurrent at the outer circuit (Table 8.1).

A fundamental and typical photochemical device is represented by the photochemical system in the Table 8.1 where photoexcitation center (P) (usually a dye sensitizer) is combined with electron donor (D) and/or electron acceptor (A) to achieve photoinduced charge separation. Many variations are possible for the photochemical system such as a photochemical system where electron-donating polymer and electron-accepting polymer are mixed to form a thin film capable of converting photon energy into electrical power.

A photochemical system comprising a dye-sensitized solar cell is also one variation of the photochemical system where A is substituted by electron-accepting semiconductor such as TiO_2 or ZnO . Although the fundamental process of the photochemical system is similar to the photophysical one, the problems involved are entirely different from the photophysical one since intermolecular interaction is important in the order of nanometer size as follows.

Table 8.1. Principle of solar cell for photophysical cell and photochemical cell

Fundamental process	Photophysical system	Photochemical system based on molecules
Photoexcitation and e^-/h^+ couple formation	Electron transition from valence band (VB) to conduction band (CB) in semiconductor	Electron transition from photoexcited dye (P^*) to electron acceptor (A) or from electron donor (D)
Charge separation	Carrier (e^- and h^+) transport by electric field at junction (p-n, Schottky, etc.) in semiconductor	Electron transfer from donor or to acceptor
Diffusion of separated charges	Diffusion of e^- and h^+ in semiconductor	Diffusion of reduced A and/or oxidized D or charge-hopping between A or D molecule
Typical example	p-n junction semiconductor solar cell	Dye-sensitized solar cell (DSSC)
Representative sketch	See below	See below



8.2.1 Photon Absorption

When assuming that sensitizers with a $1\text{ nm} \times 1\text{ nm}$ size and molar absorption coefficient of $10^4\text{ M}^{-1}\text{ cm}^{-1}$ are densely spread as a monolayer on an irradiated surface, its absorbance is only 1.7×10^{-3} , meaning that only a small portion of the irradiated photon can be absorbed and utilized. It is therefore important to increase effective surface area against the incident light in order to utilize the photon effectively. The dye-sensitized solar cell (DSSC) [1] got success to achieve high roughness factor reaching 10^3 of the irradiated surface. In the above example, roughness factor of 590 achieves the absorbance 1 capable of absorbing 90% of the incident light at the absorption maximum.

8.2.2 Suppression of Charge Recombination to Achieve Effective Charge Separation

In a molecule-based device suppression of charge recombination is especially of importance. Design of a device based on dynamics of forward and backward charge transfer is particularly required to suppress charge recombination. A solid-state device is often designed where photoexcited state electron transfer is much faster than that in a homogeneous solution where diffusion-limited

second-order rate constant are only of the $10^{10} \text{ M}^{-1}\text{s}^{-1}$ order in a maximum case. However, for a solid-state device back electron transfer (recombination) is also fast. In order to suppress this kind of rapid charge recombination in a solid state, a sophisticated device design is needed such as adopting second electron acceptor or utilizing solid/liquid interface at which the separated negative and positive charges can be located in each different phase. A typical example is seen in the DSSC mentioned later in Sect. 8.3.

8.2.3 Diffusion of Separated Charges

The diffusion of separated charges towards electrode would take place by the charge-carrier concentration gradient on the electrode surface according to the Fick's first law (8.1), where F is the Faraday constant ($96,500 \text{ C (mol electron)}^{-1}$), D diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$), c carrier concentration ($\text{M} = \text{mol dm}^{-3}$) based on the device solid-layer volume, and dc/dx concentration gradient of the charges.

$$\text{Charge flux } J = -FD(dc/dx) \quad (8.1)$$

For instance, in a rough estimation, when a $10\text{-}\mu\text{m}$ thick layer generates $10 \text{ mM}/10\text{-}\mu\text{m}$ carrier concentration gradient, a D value of $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ is needed to produce photocurrent density of 10 mA cm^{-2} . Based on such estimation, utilization of a device comprising redox molecules confined in a solid or polymer layer is not appropriate to generate this much photocurrent since the charge diffusion by molecules is at the highest only $D = 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ order, two orders of magnitude lower than the above D value. The TiO_2 electron-accepting layer of the DSSC is important also from this point of view since the D value of electron diffusion in the TiO_2 is estimated to be $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ order, which suffices to generate photocurrent of the 10 mA cm^{-2} order.

8.2.4 Electrode Reaction

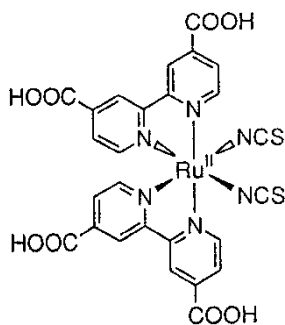
When charges are transported in a molecule-based layer to inject the charges into the electrode, the charge injection rate can be determined by charge diffusion above the electrode since the charge injection is usually not rate-determining step in an electrochemistry. When assuming that the diffusion layer thickness in the molecule-based layer in contact with the electrode is $1\text{-}\mu\text{m}$, and that the charge concentration gradient is $10 \text{ mM}/1\text{-}\mu\text{m}$, even 100 mA cm^{-2} photocurrent could be possible if D value of the charges is $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ order.

8.3 Dye-Sensitized Solar Cell (DSSC)

As mentioned in Sect. 8.1, a dye-sensitized solar cell (DSSC) is attracting a great deal of attention as a new concept solar cell utilizing molecule-based

sensitization by a dye [1]. Commercial solar cells are made of semiconductor junctions, mostly p-n junction, that combines p- and n-semiconductors. Although high cost-performance solar cells made of amorphous semiconductors have been developed after the oil crisis in 1973, the cost of the solar cells is still too high to be widely spread in the society, so that development of inexpensive solar cells is an important research subject to utilize it as a renewable energy resource for our civilization. Photochemical solar cells utilizing photocatalytic processes have been attracting attention to develop high cost-performance cells, but up to 1991 it was difficult to construct cells with high conversion efficiency. A new type photochemical solar cell called Graetzel's cell that utilizes a dye-sensitized TiO_2 film is now attracting a great attention for the future high cost-performance solar cell [1].

After the first report on UV light water photolysis with n- TiO_2 photoanode [3], sensitization of this large bandgap ($E_g = 3.2\text{ eV}$) semiconductor to utilize visible light has been an important research subject, and dye-sensitization of TiO_2 photoanode by Ru polypyridine complexes was tried in the 1980s. Adsorption of tris(4, 4'-dicarboxy-2,2'-bipyridine)ruthenium(II) ($\text{Ru}(\text{dcbpy})_3^{2+}$) onto a TiO_2 photoanode-generated photocurrent by a monochromatic 460 nm visible light (intensity 0.22 mW cm^{-2}) with short-circuit photocurrent (J_{sc}) $36\text{ }\mu\text{A cm}^{-2}$ and conversion efficiency 44% [4]. In relevance to dye-sensitized systems, photocurrent has been the order of tens $\mu\text{A cm}^{-2}$. After following this work, dye sensitization of a nanoporous TiO_2 film soaked in an organic medium containing iodine/iodide redox electrolytes successfully generated open-circuit photovoltage (V_{oc}) 0.68 V, J_{sc} 11.2 mA cm^{-2} , fill factor (FF) 0.68, and conversion efficiency 7.1% under AM 2 irradiation conditions (100 mW cm^{-2}) [1], which evoked great attention to produce high cost-performance solar cell with efficiency of about 10% [2] comparable to the efficiency of an amorphous silicone photovoltaic cell. A typical dye used is $\text{Ru}(\text{dcbpy})_2(\text{SCN})_2$ (**1**) where dcbpy is 4,4'-dicarboxyl-4,4'-bipyridine (called N3 dye). DSSC is described also in Chaps. 9 and 10, so that in this chapter only the primary important points of the DSSC are summarized at first, and then solidification of the redox electrolyte solution by using polysaccharides gel will be introduced.



1: N3 dye

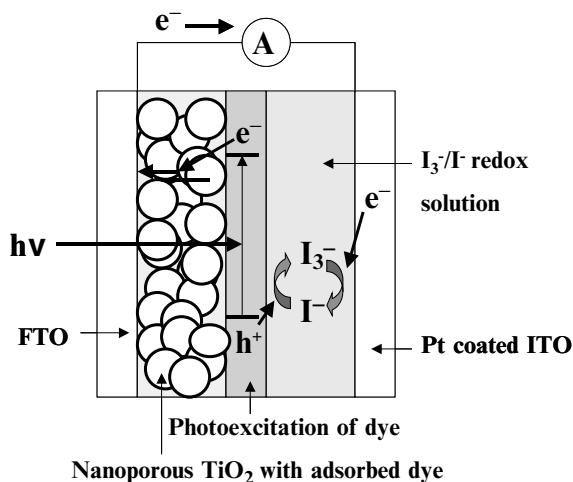


Fig. 8.1. Structure and mechanism of a dye-sensitized solar cell (DSSC)

The primary reaction of this dye-sensitized solar cell (DSSC) is electron injection from the photoexcited state of the adsorbed dye into the conduction band of TiO_2 , which takes place very rapidly in a femtosecond (fs) order. The concept of this cell is depicted in Fig. 8.1.

This cell functions in photoregenerating I_3^-/I^- redox couple, so that it is a kind of photoregenerative solar cell. The characteristics of this cell is summarized as follows [1, 5, 6]:

1. The light-to-electricity conversion efficiency reached nearly 11% under air mass (AM) 1.5 and 100 mW cm^{-2} solar simulator irradiation, which corresponds to that of an amorphous silicone solar cell. The incident photon-to-current conversion efficiency (IPCE) at the absorption peak wavelength reaches over 80% meaning that the conversion efficiency per incident photon reaches nearly 100% when considering the negative effect of the scattering and reflection of the incident light by the cell. The absorption edge of the dye (800 nm) is not sufficient to utilize efficiently the solar light. The development of a dye with absorption at higher wavelength could lead to higher conversion efficiency.
2. The roughness factor of the nanometer size (20–30 nm) TiO_2 film is almost 1,000 when the TiO_2 film thickness is $10 \mu\text{m}$, which is the important reason for the high efficiency.
3. The above-mentioned Ru complex dye (**1**) is chemically attached at the $-\text{OH}$ group on the TiO_2 surface, which realizes rapid electron injection (in the decades of fs order) from the photoexcited dye to the conduction band of the semiconductor. In such a case where the interaction of the dye and the acceptor (TiO_2) is very strong and that the density of the electron-accepting level is high, Marcus theory that is applied to a conventional

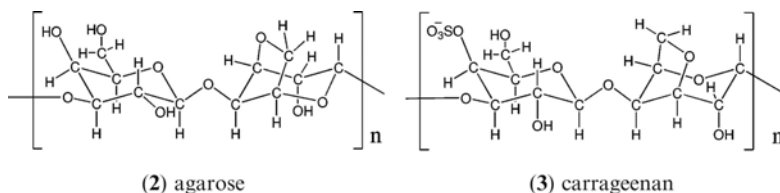
electron transfer between molecules is not applicable, and the electron transfer is considered to take place without vibrational relaxation.

4. The injected electron is suggested to be transported by diffusion with random walk among trap levels in the TiO_2 . The diffusion coefficient of the electrons is high with $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ order.
5. Electron transfer from I^- to the oxidized dye takes place in 100 ns, which is faster than the charge recombination between the injected electron and the oxidized dye (μs to ms) by three orders of magnitude. This slow back electron transfer in comparison to the forward electron transport is also an important factor of the high efficiency of the present DSSC.
6. Diffusion of the redox electrolytes in the solution is 10^{-6} to $10^{-5} \text{ cm}^2 \text{ s}^{-1}$. Specific charge transport via the interaction of the iodide/iodine might also be possible. Other redox electrolytes are not effective.
7. As for the counter electrode Pt is the best. Some catalytic reaction on the Pt surface to enable rapid reduction of iodine to iodide must be involved.
8. The solvent is limited only to organic liquid such as acetonitrile, propionecarbonate, etc. Water decreases drastically the performance of the cell. Water is considered to prohibit the bonding of the dye onto the TiO_2 .
9. Attempts have been conducted to solidify the liquid by use of polymer gels or p-semiconductors, and high efficiency more than 7% is also reported.
10. Continuous operation of the cell more than 10,000 h has been achieved, and DSSC has already been commercialized in Australia. Many chemical industries are developing this type solar cell for a possible future commercialization.

As for the item 9, a precursor mixture composed of polycarbonate (medium), oligomer, redox electrolyte, and radical initiator was injected into a sandwich cell, and heated at $80\text{--}100^\circ\text{C}$ to solidify the electrolyte solution, which attained 7.3% conversion efficiency with the solid cell [7].

One of the problems of the DSSC to be solved for practical use is that it uses organic liquid. To overcome this problem solidification of the organic redox electrolyte solution by molten salts and gelator [8] or by polymer film [9] has been achieved. Another approach is to use water [10,11], but the efficiency and stability of the cell in an aqueous phase have been low.

We have reported that polysaccharides such as agarose (2) and κ -carrageenan (3) can form a tight and elastic solid containing excess water, and that electrochemical and photochemical reactions can take place in the solid the same as in pure water [12]. The hardness of the solid is, for instance, almost the same as a brick cheese and one third of a conventional rubber eraser for a 2 wt% κ -carrageenan solid involving excess water.



We have expected that such an interesting solid containing a large excess liquid could offer a solid-state medium for the photosensitized cell. We have succeeded in substituting the water in the solid with organic liquid, and found that this solid involving organic solvent and I^-/I_3^- redox electrolyte works well as a medium for the TiO_2 cell with a well-known N3 dye sensitizer. The following is a typical method to fabricate a DSSC using polysaccharide to fabricate a solid type cell [13, 14]:

A colloidal aqueous solution of TiO_2 fine powders (P-25) was spin-coated on an Indium tin oxide (ITO)-coated conductive glass substrate electrode ($1.0\text{ cm} \times 2.0\text{ cm}$) and heated at 100°C for 30 min. This procedure was repeated several times and then finally the TiO_2 -coated ITO was heated at 450°C for 30 min to prepare a nanoporous TiO_2 thin film of $10\text{-}\mu\text{m}$ thickness. This ITO/ TiO_2 film was soaked in a $1.5 \times 10^{-4}\text{ M}$ ethanol solution of **1** (N3) to adsorb the complex dye onto the TiO_2 . A 2 wt% κ -carrageenan was dissolved in water by applying very carefully a high frequency wave (2.45 GHz). Before solidifying the solution was poured onto the TiO_2 /N3 film and solidified by cooling down to room temperature. $(C_3H_7)_4NI$ and I_2 (10:1) were dissolved in a mixture of acetonitrile and 3-methyl-2-oxazolidinone (1:1) so that their concentrations become 0.3 M and 0.03 M, respectively, and the water in the carrageenan solid on the TiO_2 /N3 film was substituted by the mixture solution by pouring the mixture onto the TiO_2 /N3/carrageenan solid film. As for the counter electrode, a 5 mM H_2PtCl_6 ethanol solution was spin-coated on an ITO electrode plate, and then the coated ITO was heated at 450°C for 1 h to prepare a transparent Pt-coated ITO. The ITO/ TiO_2 /N3/solid (involving organic liquid with $(C_3H_7)_4NI$ and I_2) working and the ITO/Pt counter electrodes were put together to fabricate a dye-sensitized cell. The effective area of the TiO_2 was $0.4\text{ cm} \times 0.5\text{ cm}$ (0.20 cm^2). This cell was irradiated from the TiO_2 side with a 98 mW cm^{-2} visible light from a 500 W xenon lamp using a Toshiba L-42 and IRA-25S cutoff filters. It was confirmed by spectral distribution analysis that the conversion efficiency (η') obtained in the present irradiation conditions can be corrected to the conversion efficiency (η) under solar simulator (AM1.5 and 100 mW cm^{-2}) irradiation conditions by $\eta = \eta' \times 0.9$.

The typical $J-V$ characteristics of the above cell are shown in Fig. 8.2 [13] where J is the photocurrent density in mA cm^{-2} , and V is the photovoltage.

In the Fig. 8.2 short-circuit photocurrent (J_{sc}) of 16.25 mA cm^{-2} , open-circuit photovoltage (V_{oc}) of 0.72 V, fill factor (FF) of 0.61, and light-to-electricity conversion efficiency (η') of 7.23% are obtained, and the η' value corresponds to $\eta = 6.5\%$ under solar simulator at AM1.5 and 100 mW cm^{-2} much better than the corresponding conventional liquid-type cell fabricated under the same conditions giving a corrected η value of 4.9%.

The charge transport process in a DSSC involves multisteps as shown in Fig. 8.3. In order to analyze such multistep charge transport, an alternating current impedance spectroscopy was applied to both the solid and liquid type cells to analyze the cell performance (refer also Chap. 3). The impedance spectra are shown in Fig. 8.4, and the results are summarized in Table 8.2.

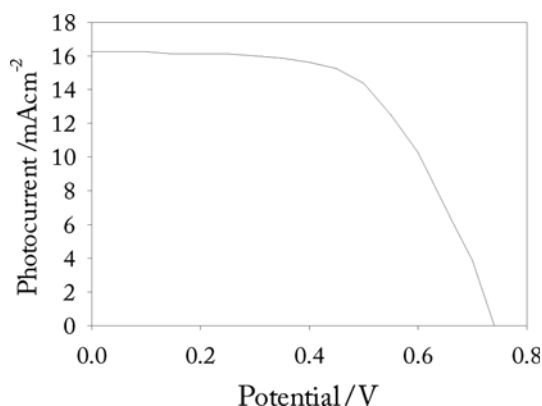


Fig. 8.2. *I-V* curve of the solid-state dye-sensitized solar cell, $\text{TiO}_2/\text{N3}/\text{Carrageenan}$ solid involving aconitrile/3-methyl-2-oxazolidinone (1/1) and $(\text{C}_3\text{H}_7)_4\text{NI}/\text{I}_2(0.3\text{ M}/0.03\text{ M})/\text{Pt}$, under 500 W xenon lamp irradiation at 98 mW cm^{-2} ([13], copyright Chemical Society, Japan)

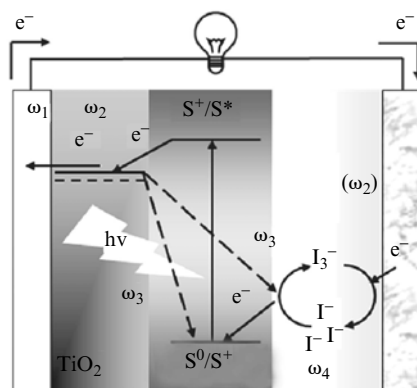


Fig. 8.3. Charge transport processes of a dye-sensitized solar cell (S=sensitizer dye)

The resistance (ω) of each step of the charge transport processes, represented by the semicircle diameter of the impedance spectrum, has been assigned as follows [15]:

1. ω_1 ; at the interface of $\text{TiO}_2/\text{conducting layer}$
2. ω_2 ; between TiO_2 particles (and at the interface of $\text{Pt}/\text{electrolyte solution}$)
3. ω_3 ; at the interface of $\text{TiO}_2/\text{electrolyte solution}$ and TiO_2/dye
4. ω_4 ; diffusion of I_3^-/I^- redox electrolytes

The impedance spectra of both the liquid and solid type cells exhibited similar features showing that the charge transport processes of both the cells proceed similarly. The ω_1 values were so small that they could not be decided exactly. The absence of the semicircle due to ω_2 for both the cells might indicate most

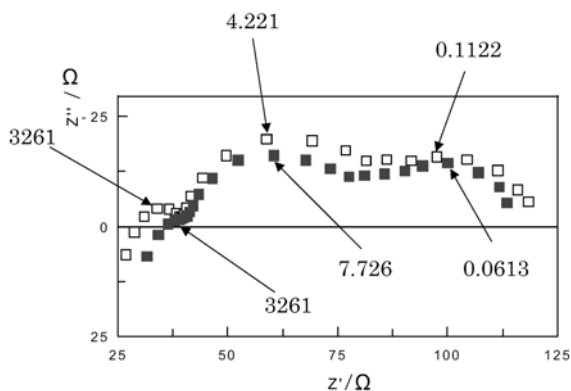


Fig. 8.4. Impedance spectra of 1 wt % κ -carrageenan solid (■) and liquid (□) type cells with AN/ME (1:1) containing LiI/Pr₄NI/I₂ (0.1 M/0.5 M/0.05 M) and TBP (0.5 M) measured from 20 kHz to 10 mHz. The numbers represent Hz ([14], copyright Elsevier)

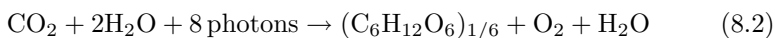
Table 8.2. Results of impedance analysis for the 1 wt % κ -carrageenan solid and liquid type cells with AN/ME (1:1) containing LiI/Pr₄NI/I₂ (0.1 M/0.5 M/0.05 M) and TBP (0.5 M). ITO base electrode was used instead of FTO ([14], copyright Elsevier)

Electrolyte	Medium/wt%	$J_{sc}/\text{mA cm}^{-2}$	V_{oc}/V	FF	$\eta/\%$	ω_3	ω_4
Liquid		8.49	0.73	0.54	3.35	41.0	40.3
κ -carrageenan	1.0	8.29	0.75	0.53	3.28	39.9	37.0

probably that the resistance between the TiO₂ particles (and at the interface of Pt/electrolyte solution) is negligible. Small differences were observed in ω_3 and ω_4 (Table 8.2), and the solid-type cell exhibited even smaller resistance than the liquid-type one. It could be concluded from these analyses that both the liquid- and solid-type cells exhibit essentially similar efficiencies at every photoelectrochemical process.

8.4 Artificial Photosynthesis

The important point of photosynthesis was described in Chap. 1. The photosynthesis is a kind of photocatalytic reduction of carbon dioxide with water driven by solar visible light energy to produce carbohydrate as a main product. This process is represented by Fig. 8.5 where the electron from water is driven by two steps (at the Photosystems II and I, abbreviated to PSII and I) at the reaction center chlorophyll to higher energy, and finally reduces CO₂ to produce carbohydrate (8.2).



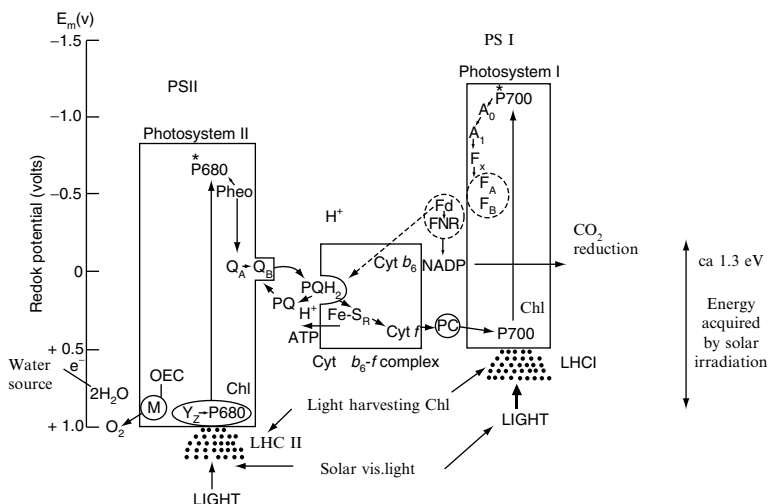


Fig. 8.5. Photosynthesis: Electron flow from water $\rightarrow$ OEC (oxygen-evolving center) $\rightarrow$ P680 (reaction center chlorophyll, Chl) $\rightarrow$ Pheo (pheophytin, Chl without Mg) $\rightarrow$ Quinones (Q_A, Q_B) $\rightarrow$ Cytochrome b_6-f complex $\rightarrow$ PC (plastocyanin) $\rightarrow$ P700 (reaction center Chl) $\rightarrow$ A_0, A_1 (acceptors) $\rightarrow$ F_A, F_B (iron-sulfur center) $\rightarrow$ F_d (ferredoxin) $\rightarrow$ FNR (F_d -NADP reductase) $\rightarrow$ NADP (nicotinamide adenine dinucleotide phosphate, reduced to NADPH) $\rightarrow$ CO_2 (Hall & Rao, Photosynthesis, copyright Cambridge University Press)

Between the water oxidation and the CO_2 reduction catalyses many electron transfer steps is involved; for the details refer the Fig. 8.5. The efficiency of the electron flow is almost 100% with negligible back electron transfer (charge recombination), which is realized by dynamics of the electron transfer where the forward electron transfer rate is much higher than the backward one by almost two to three orders of magnitude.

The photosynthetic product is regarded to store high-energy electrons. We take the products as foods and the high-energy electrons in the foods are accepted by O_2 (produced by the photosynthesis) by respiration, thereby liberating free energy for biological activities to reproduce water and CO_2 . Combustion of fossil fuels (oxidation by O_2) also liberates energy and reproduce water and CO_2 . Thus the energy cycle on the earth is represented by circulation of electrons coming from water and driven by solar photon energy, which is supported by the photosynthesis.

Taking the photosynthesis as a model for photochemical solar energy conversion, an artificial photosynthetic system was proposed (Fig. 8.6) to create fuels from solar energy and water by utilizing photocatalytic reactions [16]. This scheme considers minimum requirements to achieve photochemical energy conversion. Only one photoexcitation center (P) was designed for the first stage scheme. Dark catalyses of water oxidation (C_2) and proton (or CO_2) reduction (C_1) are designed, which should be coupled electrically with

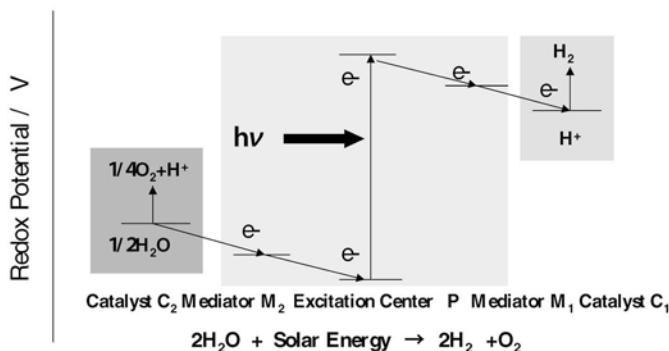


Fig. 8.6. Artificial photosynthetic system [16]

the photoexcitation center via mediators (M_2 and M_1). In order to decompose water by this system, the energy gap between the ground and the photoexcited states of P should be less than 3 eV (wavelength larger than 400 nm), the redox potential of C_2 should at least be more positive than 0.82 V (vs. standard hydrogen electrode (SHE), at pH7), and that of C_1 more negative than -0.41 V (vs. SHE, pH 7). Other than these energy level requirements, it is of importance to suppress back electron transfer by (1) kinetic design of the electron transfer reactions, and (2) adoption of heterogeneous phase to achieve unidirectional electron transfer. For this purpose, not only the reaction under irradiation but also dark reactions such as water oxidation and proton reduction are important. As for the photoexcitation center, either dye sensitizers (often metal complex), small bandgap semiconductors or dye-sensitized large bandgap semiconductors are candidates.

To realize this model system, it is essential to establish each unit and then to combine the units by utilizing molecular aggregates or various assemblies. Some results towards this goal will be described in the following Sect. 8.5 about dark catalyses.

The present author proposed a biophotochemical cell (BPCC) by which electrical power is generated using a highly porous TiO₂ film anode and an O₂-reducing cathode directly with biomass or its wastes used as electron donor during simultaneous solar decomposition and cleaning (Fig. 8.7) [17–19].

This system is extended to an interesting system [20] in which water is used instead of biomass, i.e., water/O₂ is used as a regenerative redox couple to create electrical power using only solar energy and water as shown in Fig. 8.8 with a porous semiconductor-coated sensitizer photoanode in the presence of a molecular water oxidation catalyst (refer Sect. 8.5.6) as designed from the artificial molecular photosynthetic system shown in the Fig. 8.6.

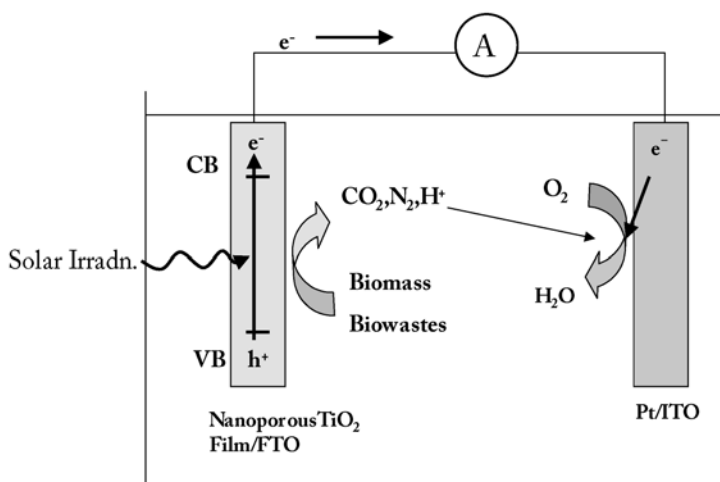


Fig. 8.7. Biophotochemical cell with a highly porous TiO_2 photoanode and a Pt-coated cathode for simultaneous solar decomposition of biomass or biowastes and electrical power generation [20]. Under anaerobic conditions H_2 is produced by H^+ reduction

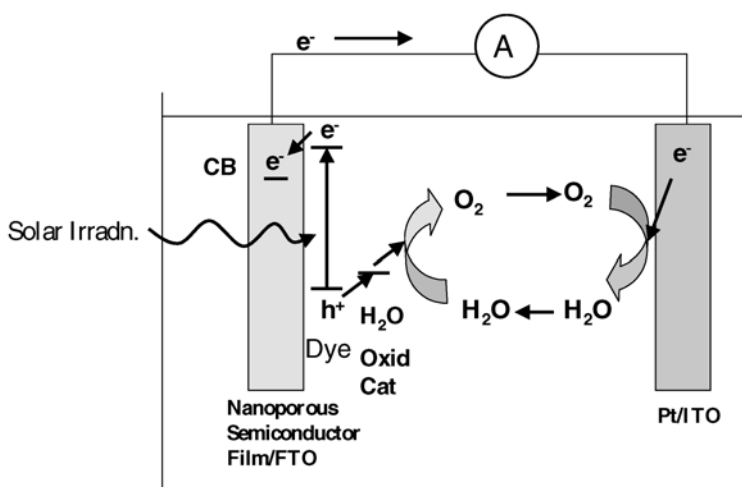


Fig. 8.8. Aquophotochemical cell with a highly porous semiconductor photoanode coated with a sensitizer in combination with water oxidation catalyst and a Pt-coated cathode for solar electrical power generation from water [20]

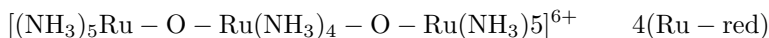
8.5 Dark Catalysis for Artificial Photosynthesis

In this section dark catalyses (water oxidation and proton reduction) are described. Please refer Sect. 2.3 about photoexcited state charge transfer that is of importance in an artificial photosynthetic system. See Sect. 1.3.2.1 for the CO_2 reduction catalysis.

8.5.1 Dark Catalysis for Water Oxidation

The schemes to investigate water oxidation catalyst, chemical water oxidation, and electrocatalytic one have been shown in the Sect. 1.3.1. Many studies have been conducted on Mn complexes since photosynthesis uses a Mn protein complex to oxidize water-evolving O₂ at the oxygen-evolving center (OEC), but most of the model Mn complexes showed almost no or only a low catalytic activity for water oxidation [21]. Tetrakis(2,2' -bipyridine)(di- μ -oxo)di-Mn complex (**2**) is a typical example of a Mn complex (as for the structure refer Sect. 1.3.1). However, in an aqueous solution it did not show any catalytic activity, but in a heterogeneous phase (in an adsorbed clay or insoluble part in water present in excess over its solubility), it showed water oxidation activity [22]. Tetrakis(2,2' -bipyridine)(μ -oxo)di-Ru complex (**3**, Meyer's complex) is another typical example that showed activity for water oxidation, but the activity is not very high and the complex was rather unstable.

The trinuclear Ru-ammine complex called Ru-red (**4**) has been found to be a very active catalyst; it can evolve observable dioxygen bubbles in the presence of strong oxidant such as Ce(IV) ion [21–24].



It has been established that other ammine-ligand-based Ru complexes including mononuclear (e.g., $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$) and dinuclear ones are all active catalysts for water oxidation both in a homogeneous aqueous solution and in a heterogeneous phase such as in a polymer membrane and clay. Important results on these Ru–ammine-based complex catalysts are as follows:

1. Trinuclear (Ru-red) and dinuclear complexes are capable of four-electron oxidation of water by one molecule. Mononuclear complexes are capable of either four-electron or two-electron oxidation of water, two catalyst molecules being required for the latter case.
2. Bimolecular decomposition of the catalyst takes place at its high oxidation state forming N₂ by oxidation of the ammine ligands in competition of water oxidation. Such bimolecular decomposition is prohibited remarkably by isolating the catalysts with each other in a polymer matrix (e.g., Nafion). The catalytic activity itself remains similar in a heterogeneous polymer phase as in a homogenous aqueous solution.
3. On assuming a random distribution of the catalyst in a polymer matrix, the bimolecular decomposition distance was estimated; it was almost contact distance between the molecules [21].
4. When two catalyst molecules are needed for the four-electron water oxidation, the catalytic activity shows an optimum catalyst concentration in a polymer matrix since bimolecular decomposition still takes place, and co-operative distance between catalysts can be determined by also assuming a random distribution.

5. For the electrocatalytic water oxidation using a polymer (Nafion)-coated electrode dispersing catalysts in the polymer membrane, charge transport from the electrode to the catalyst taking place by charge-hopping is important. This charge transport by hopping is facilitated by high concentration of the catalyst in the polymer matrix, which is a contradictory requirement for the bimolecular decomposition, so that optimum and delicate concentration conditions exist for the electrocatalytic system. The charge hopping distance (r_o) and bimolecular decomposition distance (r_d) can also be determined by assuming a random distribution.
6. Amino acid residue models such as a tyrosine residue model (p-cresol) lengthen remarkably the charge-hopping distance, which can solve the problem in the electrocatalysis mentioned in the above item (5) and enhance remarkably the catalytic activity.

Some details of the above items are explained below.

When Ru-red was used as a catalyst in the presence of a large excess of Ce(IV) oxidant, the rate of O_2 evolution was first order with respect to the catalyst concentration showing that Ru-red is capable of four-electron oxidation of water. During the catalysis N_2 was formed as a decomposition product, whose formation rate was second order with respect to the catalyst concentration showing that the decomposition is bimolecular. The decomposition distance in a polymer (Nafion) matrix was estimated by assuming a random distribution of the catalyst molecule in the matrix. As for the details refer the review [21].

8.5.2 Dark Catalysis for Proton Reduction

Proton reduction is an important catalysis in water photolysis. Pt and PtO_2 have been the most well-known and active catalyst for proton reduction to produce dihydrogen. However, these colloidal or powder catalysts are not suited to construct a conversion system based on molecules. It is therefore desirable to use molecular catalyst for constructing an artificial photosynthetic system.

It was reported that cobalt-tetraphenylporphyrin complex (CoTPP) coated on an electrode catalyzes electrocatalytic proton reduction [25], but the activity was not very high. It has been found that metal porphyrins (such as metal tetraphenylporphyrin, MTPP) and metal phtahlocyanines (MPc) when incorporated into a polymer membrane coated on an electrode exhibit high activity in electrocatalytic proton reduction to produce H_2 [26, 27]. It was shown that these polymer-metal complex catalysts are much more active than a conventional platinum-based electrode.

8.6 Conclusion and Future Scopes

The photosynthesis supports almost all the energy of biological activities. Such photosynthesis is a highly sophisticated and complicated molecular system compiling in an extremely exact fashion highly functional molecules by use

of many protein molecules. This photosynthetic system provides us with a good model to achieve efficient solar energy conversion. The successful dye-sensitized solar cell (DSSC) is one of the examples to convert solar visible light energy into electrical energy by using a molecule-based design. This DSSC has a potential to substitute conventional semiconductor-based solar cells because of its high cost-performance; of course toward this direction much more efforts should be invested to increase its conversion efficiency from the present 11% level hopefully to 15% and also to increase its stability and long-term durability.

An artificial photosynthesis has been attracting a great deal of attention from the middle of 1970s, for instance to photolyze water into H_2 and O_2 under solar irradiation. However, differently from the above DSSC, this task is much more difficult to achieve so that the research is still on a very fundamental level. Through the present author's experience it should be said that we need much more effort and breakthrough idea for achieving real solar-to-chemical energy conversion. Since this research direction is of importance for our future civilization, we should invest much more fund and effort towards this goal.

References

1. O'Regan GM *Nature* **353**, 737 (1991)
2. M. Wei, Y. Konishi, H. Zhou, M. Yanagida, H. Sugihara, H. Arakawa, J. Mater. Chem. **16**, 1287 (2006)
3. A. Fujishima, A. Honda, *Nature* **238**, 37 (1972)
4. J. Desilvestro, M. Graetzel, L. Kavan, J. Moser, J. Am. Chem. Soc. **107**, 2988 (1985)
5. M. Kaneko, I. Okura (eds.) *Photocatalysis – Science and Technology* (Kodansha, Tokyo, 2002)
6. Proceedings of the 12th International Conference, Photochemical Conversion and Storage of Solar Energy. Oldenbourg Wissenschaftsverlag, Muenchen (2000)
7. S. Hayase, in *Recent Advances in Research and Development for Dye-Sensitized Solar Cells*, ed. by H. Arakawa (CMC, Tokyo 2001), p. 270
8. W. Kubo, T. Kitamura, K. Hanabusa, Y. Wada, S. Yanagida, Chem. Commun. **2002**, 374 (2002)
9. S. Mikoshiba, H. Sumino, M. Yonetsu, S. Hayase, Abst. of 13th International Conference on Photochemical Conversion and Storage of Solar Energy (W6-70), (Snowmass, 2000)
10. Q. Dai, J. Rabani, Chem. Commun. **2001**, 2142 (2001)
11. M. Kaneko, T. Nomura, C. Sasaki, Macromol. Chem. Rapid Commun. **24**, 444 (2003)
12. M. Kaneko, N. Mochizuki, K. Suzuki, H. Shiroishi, Chem. Lett. **2002**, 530 (2002)
13. M. Kaneko, T. Hoshi, Chem. Lett. **32**, 872 (2003)
14. M. Kaneko, T. Hoshi, Y. Kaburagi, H. Ueno, J. Electroanal. Chem. **572**, 21 (2004)
15. T. Hoshikawa, R. Kikuchi, K. Sasaki, K. Eguchi, Electrochemistry, **70**, 675 (2002)

16. M. Kaneko, 11th Symposium on Unsolved Problems of Polymer Chemistry. The Society of Polymer Science, (Tokyo, 1976) p. 21
17. M. Kaneko, J. Nemoto, H. Ueno, N. Gokan, K. Ohnuki, M. Horikawa, R. Saito, T. Shibata, *Electrochem. Commun.* **8**, 336 (2006)
18. M. Kaneko, H. Ueno, K. Ohnuki, M. Horikawa, R. Saito, T. Shibata, J. Nemoto, *Biosensors Bioelectronics* **23**, 140 (2007)
19. J. Nemoto, M. Horikawa, K. Ohnuki, T. Shibata, H. Ueno, K.M. Hoshino, J. *Appl. Electrochem.* **37**, 1039 (2007)
20. M. Kaneko, (2006) PCT Pat. Appl.: PCT/JP2006/305185 (March 9th)
21. M. Yagi, M. Kaneko, *Chem. Rev.* **101**, 21 (2001)
22. R. Ramaraj, A. Kira, M. Kaneko, *Angew. Chem. Int. Ed.* **25**, 1009 (1986)
23. R. Ramaraj, A. Kira, M. Kaneko, *J. Chem. Soc. Faraday Trans. 1* **83**, 1539 (1987)
24. R. Ramaraj, M. Kaneko, *Adv. Polym. Sci* **123**, 215 (1995)
25. M.R. Kellett, T.G. Spiro, *Inorg. Chem.* **24**, 2373–2378 (1958)
26. T. Abe, H. Imaya, S. Tokita, D. Woehrle, M. Kaneko, *J. Porphyrins Phthalocyanines* **1**, 215 (1997)
27. F. Taguchi, T. Abe, M. Kaneko, *J. Mol. Cat. A Chem.* **140**, 41 (1999)

Molecular Design of Sensitizers for Dye-Sensitized Solar Cells

K. Hara

Abstract In this chapter, we focus on the detailed molecular design of sensitizers, such as metal complexes, porphyrins, and metal-free organic dyes, for dye-sensitized solar cells (DSSCs), which is one of promising unconventional solar cells. Over the last decade, interest in DSSCs has increased because these unconventional solar cells exhibit high solar-energy-to-electricity conversion efficiencies of up to 11% and have the potential for low-cost production. The main components of a DSSC are a nanocrystalline oxide semiconductor electrode, a sensitizer, an electrolyte containing redox ions, and a counter electrode. The sensitizer determines the photoresponse range of the solar cell and mediates the primary steps of photon absorption and the subsequent electron-transfer process. The relationship between the solar-cell performance of DSSCs and the properties of sensitizer in terms of the structures, photophysical, photoelectrochemical, and electrochemical properties are discussed.

9.1 Introduction

Over the last decade, interest in dye-sensitized solar cells (DSSCs), a promising molecular photovoltaic technology, has increased because these unconventional solar cells exhibit high performance and have the potential for low-cost production [1–9]. The fundamental principles of DSSCs have been studied extensively, and DSSCs have been developed for commercial applications. Recently, high solar-energy-to-electricity conversion efficiencies, up to 11% under air mass 1.5 global-tilt (AM 1.5 G) irradiation, have been obtained with small cells [9,10]. In addition, large-area module systems of DSSCs have been developed for commercial applications [11–13]. The main components of a DSSC are a nanocrystalline oxide semiconductor electrode, a sensitizer, an electrolyte containing redox ions, and a counter electrode. The sensitizer determines the photoresponse range of the solar cell and mediates the primary steps of photon absorption and the subsequent electron-transfer process.

Figure 9.1 shows a schematic of a DSSC and presents the mechanism of electric power generation in the DSSC. First, a sensitizer molecule adsorbed

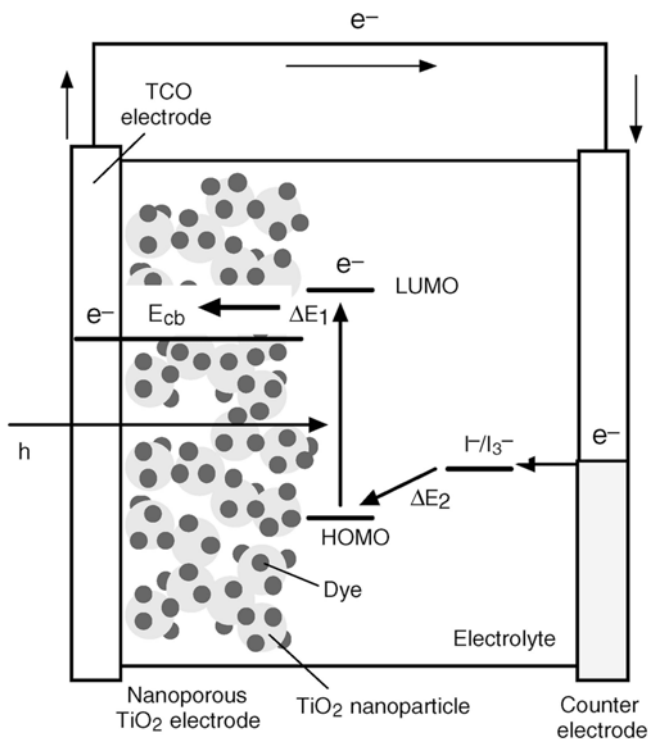


Fig. 9.1. Schematic of a DSSC presenting the mechanism of electric power generation

on the surface of a nanocrystalline TiO_2 electrode absorbs the incident photon flux and is excited from the ground state to the excited state. One type of photoexcitation causes transfer of an electron from the highest occupied molecular orbital (HOMO) of the sensitizer to the lowest unoccupied molecular orbital (LUMO). Subsequent injection of the excited electron into the conduction band of the TiO_2 electrode results in oxidation of the sensitizer molecule. The injected electron diffuses through the TiO_2 electrode toward the transparent conducting oxide (TCO)-coated electrode and eventually reaches the counter electrode through the external load and wiring. The oxidized sensitizer is reduced by the I^- ions in the electrolyte, regenerating the ground state of sensitizer, and I^- ions are oxidized to I_3^- ions. The I_3^- ions diffuse toward the counter electrode and are then reduced to I^- ions. Overall, electric power is generated without permanent chemical transformation.

The solar-energy-to-electricity conversion efficiency, η (%), of solar cells, including DSSCs, can be estimated from the following equation:

$$\eta(\%) = \frac{J_{\text{sc}} \times V_{\text{oc}} \times \text{FF}}{I_0} \times 100 \quad (9.1)$$

where I_0 is the photon flux (ca. 100 mW cm^{-2} for AM 1.5 G), J_{sc} is the short-circuit current density under irradiation, V_{oc} is the open-circuit voltage, and FF is the fill factor, which is determined by the shunt and series resistances of the solar cell. Basically, the V_{oc} value is determined by the energy gap between the Fermi level of the TiO_2 electrode, which is located near the conduction band-edge level (E_{cb}), and the redox potential of the I^-/I_3^- in the electrolyte. The E_{cb} value of the TiO_2 electrode and the redox potential of I^-/I_3^- are estimated to be -0.5 V and 0.4 V vs. normal hydrogen electrode (NHE), respectively [4]. Thus, for a DSSC with a TiO_2 electrode and an I^-/I_3^- redox mediator, the maximum V_{oc} is expected to be approximately 0.9 V , although the E_{cb} of the TiO_2 electrode and the redox potential of I^-/I_3^- depends strongly on the type and concentration of electrolyte components, resulting in the actual V_{oc} values.

The J_{sc} value is directly determined by the properties of the sensitizers. For example, the energy gap between the HOMO and LUMO of the sensitizer (which corresponds to the band gap, E_{g} , for inorganic semiconductor materials) directly determines the photoresponse range of the DSSC. Absorption over a wide range of wavelengths, extending into the near-IR region due to a small HOMO–LUMO energy gap, is necessary for harvesting a large fraction of the solar spectrum, producing a large J_{sc} , and thus highly efficient solar-cell performance. In addition, the energy levels of the HOMO and LUMO must match the iodine redox potential and the E_{cb} of the TiO_2 electrode, respectively. For electron injection, the LUMO must be sufficiently more negative than E_{cb} ; the energy gap between the two levels, ΔE_1 , is the driving force for electron injection. The HOMO must be sufficiently more positive than the redox potential of I^-/I_3^- to accept electrons effectively; the difference between these two levels is given by ΔE_2 . Generally, ΔE_1 and ΔE_2 must be larger than approximately 0.2 eV for the respective electron-transfer reactions to take place with optimal efficiency.

Thus, the molecular structure of the sensitizer must be strategically and carefully designed so that its properties are optimal for DSSC performance. In this chapter, we discuss the detailed molecular design of sensitizers, such as metal complexes, porphyrins, and metal-free organic dyes, in terms of the structures and properties needed for highly efficient solar-cell performance.

9.2 Metal-Complex Sensitizers

9.2.1 Molecular Structures of Ru-Complex Sensitizers

Generally, Ru-bipyridyl complexes are suitable photosensitizers because their excited states have long lifetimes and because oxidized Ru(III) is chemically stable. Ru-bipyridyl complexes have been studied intensively as sensitizers for homogeneous photocatalytic reactions and dye-sensitization systems. In the late 1970s, a Ru-bipyridyl complex bearing carboxyl groups

to anchor the complex to the semiconductor surface was synthesized, and single-crystal TiO_2 photoelectrodes sensitized by the complex were studied [14]. In subsequent years, researchers designed new complexes by modifying the original structure to improve solar-cell performance (Figs. 9.2a–c) [15–45]. For example, Grätzel and coworkers developed *cis*-dithiocyanato

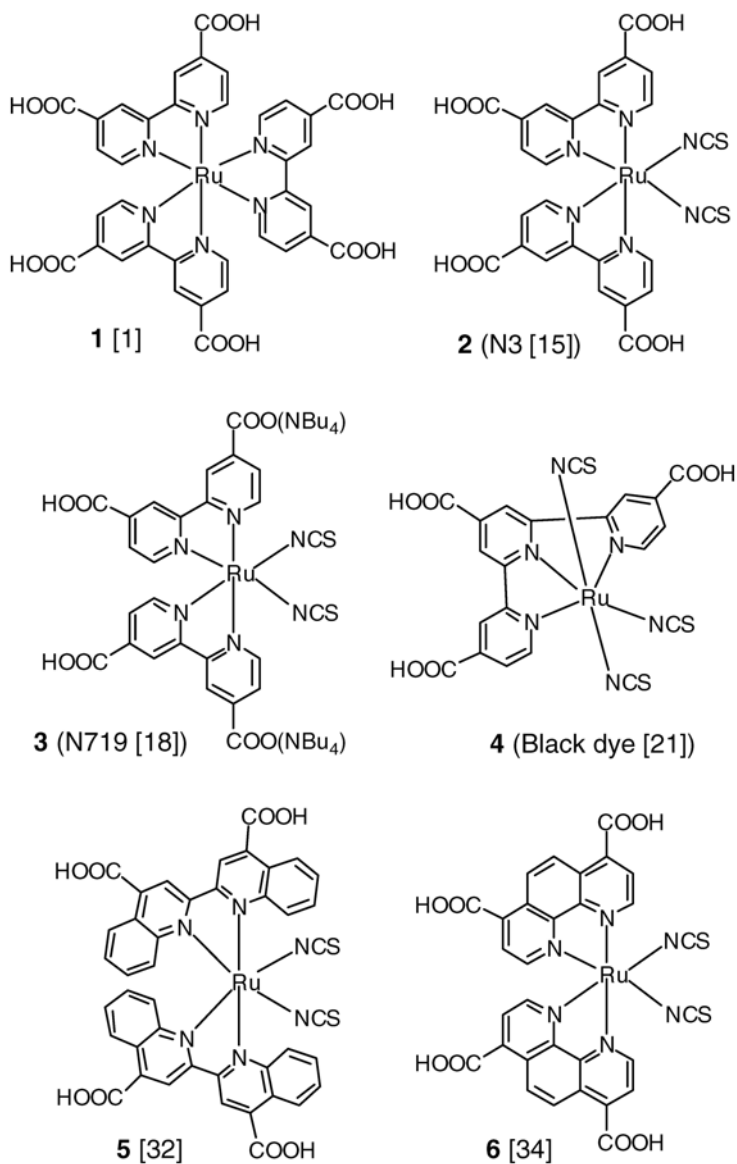


Fig. 9.2a. Molecular structures of Ru-complex sensitizers for DSSCs

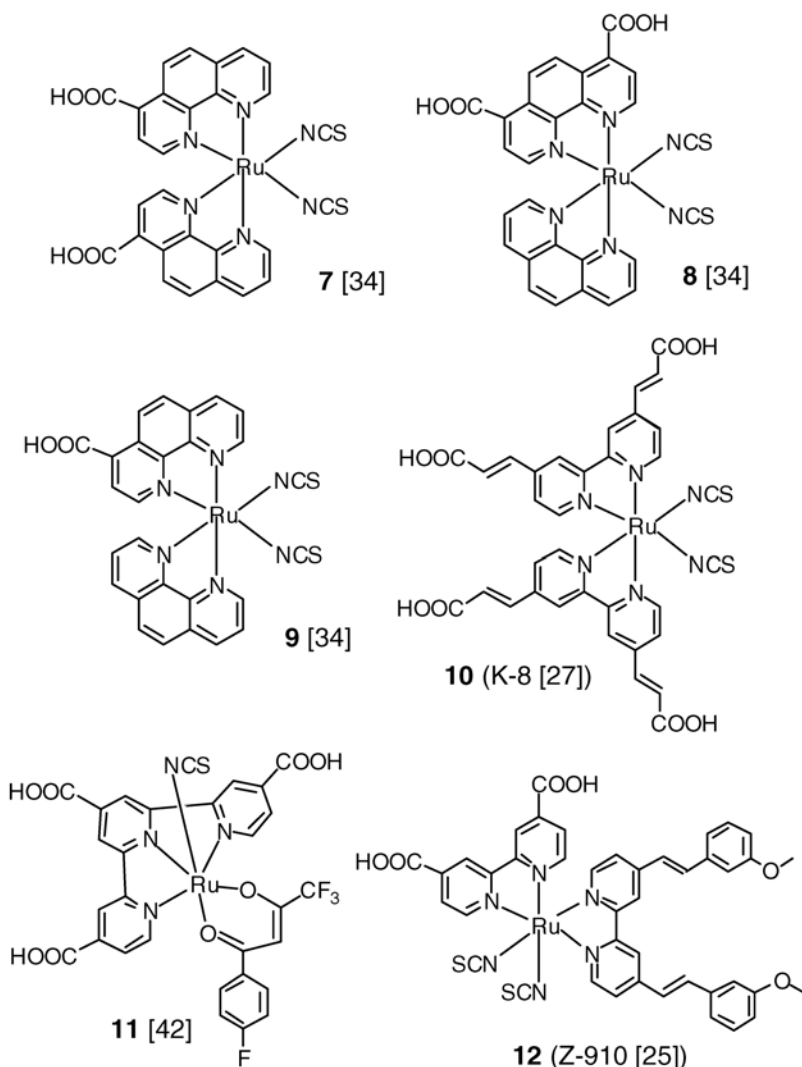


Fig. 9.2b. Molecular structures of Ru-complex sensitizers for DSSCs

bis(4, 4'-dicarboxy-2, 2'-bipyridine)ruthenium(II), N3 dye (**2**) [15, 17, 18], and trithiocyanato 4, 4'4''-tricarboxy-2, 2' : 6', 2''-terpyridine ruthenium(II), black dye (**4**) [21], which are efficient sensitizers for DSSCs.

Figure 9.3 shows the UV-visible (UV-Vis) absorption spectra of several Ru complexes (**2**, **4-6**) in alcoholic solution. The strong absorption at 300–400 nm is due to the $\pi-\pi^*$ absorption band of the bipyridine ligand. The absorption peaks (λ_{max}) due to the metal-to-ligand charge transfer (MLCT) transition are observed in the visible region from 400 to 650 nm. Complex **2** absorbs over

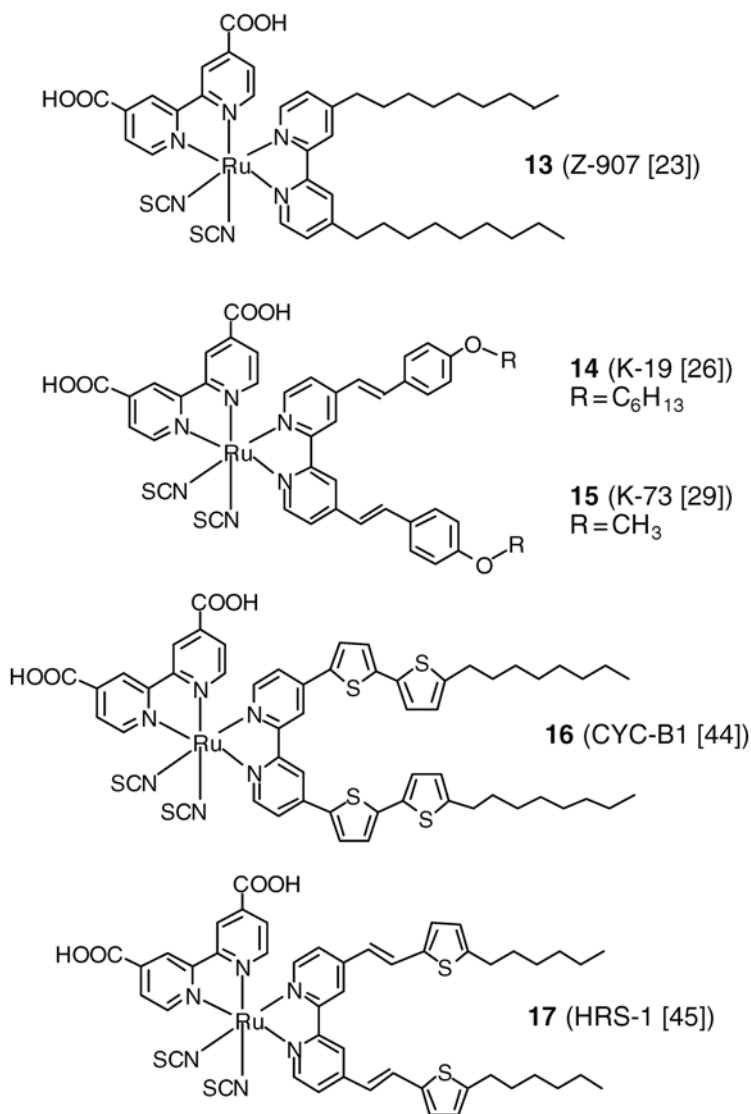


Fig. 9.2c. Molecular structures of Ru-complex sensitizers for DSSCs

a wide range of the visible region from 400 to near 800 nm and **4** absorbs in the near-IR region up to 900 nm due to the MLCT transition. Thus, these Ru complexes absorb in a broad range (from the UV to the near-IR), which should permit the harvesting of a large fraction of the solar spectrum. The molar absorption coefficients, ϵ , at $\lambda_{\max}$ for these Ru complexes range from 7,000 to 18,000 M⁻¹ cm⁻¹.

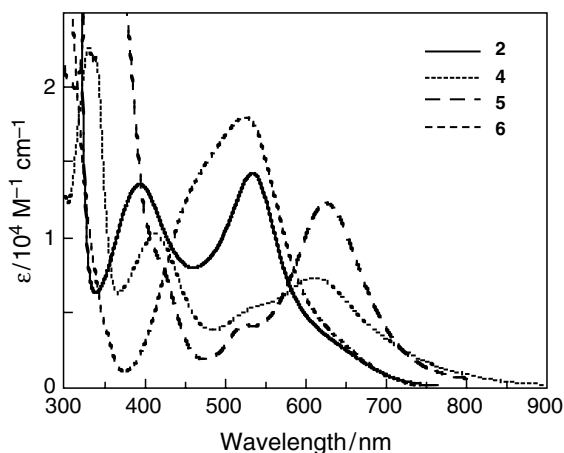


Fig. 9.3. UV-visible absorption spectra of Ru-complex sensitizers

The oxidation potential (E_{ox}) of **2**, which corresponds to the HOMO level is 0.85 V vs. saturated calomel electrode (SCE) [15], and the LUMO level estimated from the E_{ox} and the 0–0 transition energy (1.75 eV) is –0.90 V vs. SCE [15]. These energy levels are energetically suitable for electron-transfer processes in DSSC systems.

These Ru complexes have carboxyl groups that anchor the molecules to the TiO_2 surface, and this anchoring results in a large electronic interaction between the ligands and the conduction band of TiO_2 . FT-IR analysis indicates the Ru complexes are adsorbed on the TiO_2 surface by means of carboxylate bidentate coordination [16, 20, 34, 46–48]. In the attenuated total reflection (ATR) FT-IR absorption spectra of **4** adsorbed on a TiO_2 film [48] (Fig. 9.4), the absorption peak at 2100 cm^{-1} is attributed to the $\text{N}=\text{C}$ stretching absorption band of the NCS ligand. The absorption band at $1,600\text{ cm}^{-1}$ is due to asymmetric $\text{O}-\text{C}-\text{O}$ stretching in the carboxylate ($-\text{COO}^-$) group. The absorption peaks due to the ring-stretching mode of the terpyridyl ligand are observed at $1,536$, $1,468$, and $1,419\text{ cm}^{-1}$ [21, 47, 48]. A weak absorption band at $1,723\text{ cm}^{-1}$ due to $\text{C}=\text{O}$ stretching of the protonated carboxyl group has also been observed [47]. These spectral features indicate that two carboxylate groups of the terpyridyl ligand are attached to the TiO_2 surface.

The coverage of the TiO_2 surface with a Ru complex such as **2** approaches 100%, as calculated from the surface area of TiO_2 and the amount of adsorbed dye. X-ray diffraction analysis of the crystal structure of **2** anchored to the TiO_2 surface indicates that anchoring of the complex to the TiO_2 anatase surface via two carboxyl groups of both bipyridine ligands is the most favorable geometry thermodynamically [49].

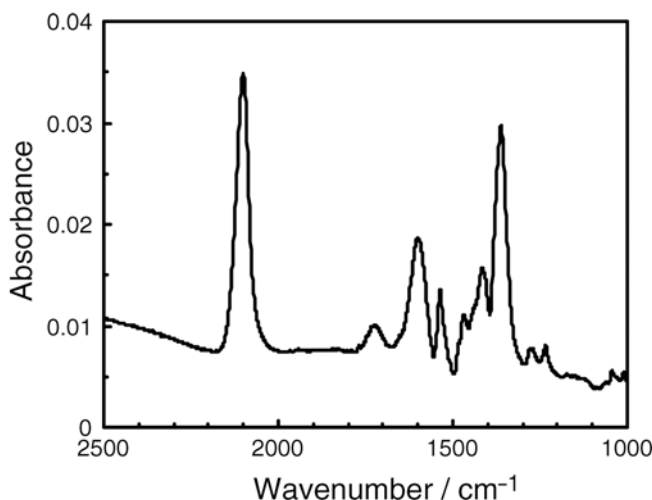


Fig. 9.4. An ATR-FT-IR absorption spectrum of Ru complex **4** adsorbed on a TiO₂ film

9.2.2 Electron-Transfer Processes

Electron-transfer processes in a DSSC based on Ru complex **2** are schematically shown in Fig. 9.5. Photoexcitation of a Ru-complex sensitizer results in an intramolecular MLCT transition. The HOMO and LUMO are derived from the *d*-orbital of Ru metal and the π^* orbital of the bipyridyl ligand, respectively [7]. The NCS ligands, which are strongly electron donating, shift the HOMO level negatively (thus red-shifting the absorption of the complex) and also accept electrons from iodide ions. After the photoexcitation, the excited electrons located in the bipyridyl ligands are efficiently injected into the conduction band of the TiO₂ electrode through the carboxyl groups anchored to the TiO₂ surface.

Transient absorption spectroscopy using laser systems is used to study the electron-transfer processes in DSSCs, such as electron injection from Ru-complex sensitizers into the conduction band of semiconductor electrodes [50–56]. The rate of electron transfer from the sensitizer to the semiconductor largely depends on the configuration of the adsorbed sensitizer material on the semiconductor surface and the energy gap between the LUMO of the sensitizer and the E_{cb} of the semiconductor (Fig. 9.1). For example, the rate constant for electron injection, k_{inj} , is given by Fermi's golden rule expression:

$$k_{\text{inj}} = \left(\frac{4\pi^2}{h} \right) |V|^2 \rho(E) \quad (9.2)$$

where V is the electronic coupling between the sensitizer and the semiconductor, $\rho(E)$ is the density of states of the conduction band, and h is the

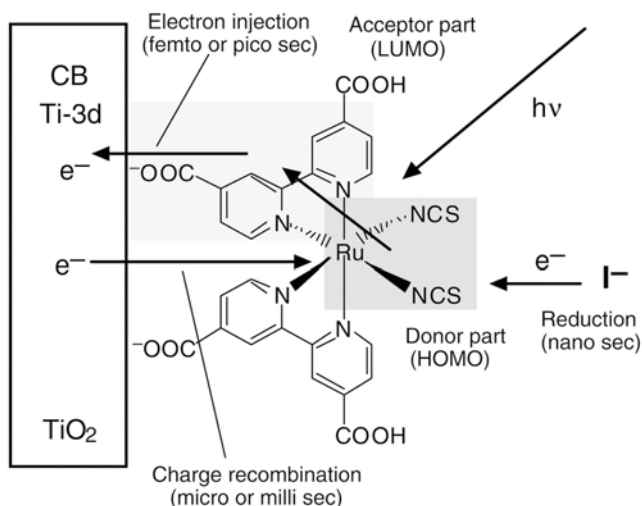


Fig. 9.5. Electron-transfer processes in a DSSC based on Ru complex **2**

Planck constant. The value of V is attributed to overlap between the wavefunction of the excited states of the sensitizer and the conduction band, and it depends largely on the distance between the adsorbed sensitizer material and the semiconductor surface. The strong adsorption of Ru-complex sensitizers on the semiconductor surface, via the carboxyl groups, results in a large V between the π^* orbital of the excited state of the sensitizer and the conduction band of TiO_2 , which consists of the unoccupied $3d$ orbital of Ti^{4+} . In addition, the conduction band of the semiconductor has a continuous and relatively large density of states. Thus, electron injection from the sensitizer to the semiconductor occurs at a higher rate than does relaxation from the excited state to the ground state. For example, electron injection from **2** into TiO_2 occurs on the order of femtoseconds, as measured by transient absorption spectroscopy [50–56]. This ultrafast rate of electron injection contributes to high solar-energy-to-electricity conversion efficiencies.

The rate constant for electron injection also strongly depends on the semiconductor materials employed. The electron injection rate with **2** in a ZnO system is slower than in a TiO_2 system [54, 57]. The different rate constant may be caused by the difference in the electronic coupling between the π^* orbital of the dye and the accepting orbitals in ZnO and TiO_2 and/or by the difference in the density of states of the two semiconductor materials. The states near the E_{cb} of ZnO consist of the $4s$ orbitals of Zn^{2+} , whereas those of TiO_2 consist of the $3d$ orbitals of Ti^{4+} ; and this difference results in an expected difference in their electronic coupling with the π^* orbital of the dye.

For effective charge separation, charge recombination between injected electrons and the oxidized dye (dye cations) must be much slower than electron injection and electron transfer from I^- into the oxidized dye (i.e., regenera-

tion of the dye). Charge recombination between injected electrons on TiO_2 and cations of **2** occurs on the order of microseconds to milliseconds [50,58–61] (the actual time depends strongly on the potential of the electrode), whereas electron injection is ultrafast (Fig. 9.5). This difference leads to effective charge separation and thus to high solar-cell performance. Electron injection involves electron transfer from the bipyridyl ligand to TiO_2 , whereas charge recombination involves electron transfer from TiO_2 to Ru^{3+} . Thus, the slow charge recombination is apparently due to the large separation between the TiO_2 and the Ru^{3+} imposed by the bipyridyl ligands.

Electron transfer from I^- to the oxidized sensitizer, corresponding to regeneration of the sensitizer ground state, is also required for effective charge separation. The kinetics of this reaction has also been investigated by transient absorption spectroscopy [59,61]. The electron-transfer rate from I^- to cations of **2** is estimated to be 100 ns [59], which is much faster than the rate for charge recombination between injected electrons and dye cations. Thus, fast regeneration of the oxidized sensitizer also contributes to efficient charge separation in this system (Fig. 9.5).

9.2.3 Performance of DSSCs Based on Ru Complexes

The photocurrent action spectrum for a DSSC based on Ru complex **4** is shown in Fig. 9.6. The incident photon-to-current conversion efficiency (IPCE, %), which corresponds to the external quantum efficiency, is given by

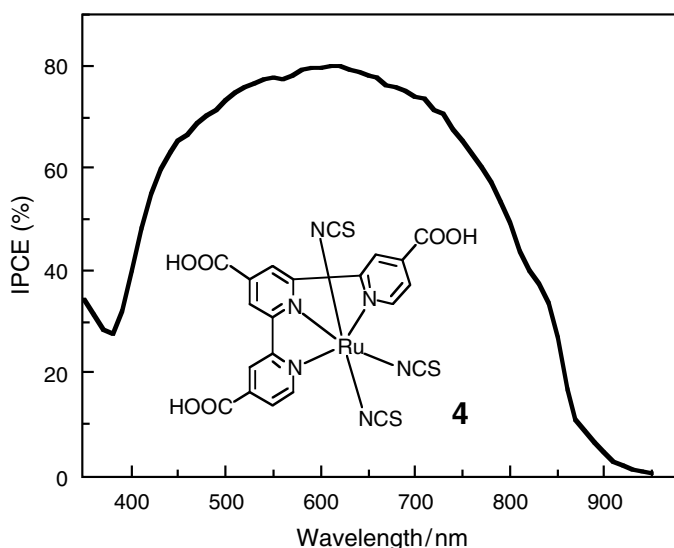


Fig. 9.6. An IPCE spectrum for a DSSC based on Ru complex **4**

$$\text{IPCE}(\%) = \frac{1240(\text{eV} \cdot \text{nm}) \times J_{\text{ph}}}{\lambda \times \Phi} \times 100 \quad (9.3)$$

where $J_{\text{ph}}(\text{mA cm}^{-2})$ is the short-circuit photocurrent density obtained under monochromatic irradiation, and λ (nm) and $\Phi(\text{mW cm}^{-2})$ are the wavelength and the intensity, respectively, of the monochromatic light. The IPCE is also given by

$$\text{IPCE} = \text{LHE} \times \phi_{\text{inj}} \times \eta_c \quad (9.4)$$

$$\text{LHE} = 1 - T = 1 - 10^{-A} \quad (9.5)$$

where LHE is the light-harvesting efficiency of the dye-sensitized TiO_2 electrode, ϕ_{inj} is the quantum yield of electron injection from the dye to TiO_2 , η_c is the efficiency of collection of the injected electrons at the back contact, T is transmittance, and A is absorbance. For a nanocrystalline and nanoporous TiO_2 electrode (e.g., $10 \mu\text{m}$ thickness), which can adsorb a large amount of dye, LHE is almost equal to unity. Therefore, the IPCE value is predominantly determined by ϕ_{inj} and η_c .

Photons with a wide range of wavelengths (350–950 nm) can be converted to current with the DSSC based on **4** (Fig. 9.6). IPCE values higher than 70% are observed from 480 to 730 nm, with a maximum value of 80% at 613 nm. When the reflection and absorption losses in the TCO substrate are considered, the net photon-to-current conversion efficiency in this range exceeds 90%, which indicates a highly efficient DSSC with high ϕ_{inj} and η_c values.

The photovoltaic performances of DSSCs based on Ru-complex sensitizers are presented in Table 9.1. High η values ($>10\%$) have been attained with DSSCs based on Ru complexes. The best photovoltaic performance, $\eta = 11\%$, was obtained with DSSCs based on **3** ($J_{\text{sc}} = 17.73 \text{ mA cm}^{-2}$, $V_{\text{oc}} = 0.846 \text{ V}$, $\text{FF} = 0.75$) [9] and **4** ($J_{\text{sc}} = 20.9 \text{ mA cm}^{-2}$, $V_{\text{oc}} = 0.736 \text{ V}$, $\text{FF} = 0.722$) [10].

We have studied the effect of the number and position of carboxyl groups anchored to the TiO_2 surface on the performance of DSSCs. We synthesized Ru-phenanthroline complexes **7**, **8**, and **9**, which have one or two carboxyl groups (Fig. 9.2b) [34, 35]. No remarkable differences in the absorption properties and the HOMO and LUMO levels of the three complexes were observed. Action spectra showing the absorbed photon-to-current conversion efficiency (APCE) as a function of wavelength for DSSCs based on **7**, **8**, and **9** are shown in Fig. 9.7. The APCE values were determined from the IPCE and LHE values:

$$\text{APCE} = \text{IPCE}/\text{LHE} \quad (9.6)$$

The figure clearly indicates that the APCE values for the DSSC based on **9** (one carboxyl group) are lower than the values for DSSCs based on **7** and **8** (two carboxyl groups) [34], which suggests that solar-cell performance depends strongly on the anchoring geometry of the Ru-phenanthroline complexes on the TiO_2 surface. The electron injection yield from **9** to TiO_2 is much lower than the yields from **7** and **8**, as indicated by transient absorption

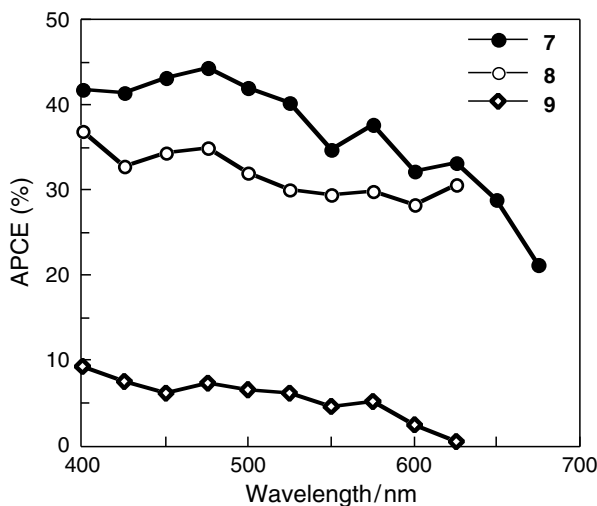
Table 9.1. Performance of DSSCs based on Ru-complex sensitizers

Dye	$\lambda_{\max}/\text{nm}^{\text{a}}$	$\varepsilon/\text{M}^{-1}\text{cm}^{-1}$	$J_{\text{sc}}/\text{mA cm}^{-2}$	V_{oc}/V	FF	$\eta(\%)$	Reference
2	535	14,000	18.2	0.72	0.73	10.0	[15]
2	535	14,000	19	0.60	0.65	7.4	[20]
3	535	14,000	17	0.73	0.68	8.4	[20]
3	535	14,000	17.73	0.846	0.75	11.18	[9]
4	602	7,500	20.53	0.72	0.704	10.4	[21]
4	602	7,500	20.9	0.736	0.722	11.1	[10]
6	525	18,000	12.5	0.74	0.71	6.6	[34]
10	555	18,000	18	0.64	0.75	8.64	[27]
11	586	7,000	19.10	0.661	0.722	9.12	[42]
12	543	16,850	17.2	0.777	0.764	10.2	[25]
13	543	12,200	15.2	0.764	0.676	7.8	[23]
14 ^b	543	18,200	14.61	0.711	0.671	7.0 ^b	[26]
15	545	18,000	17.22	0.748	0.694	9.5	[29]
16	400	46,400	23.92	0.65	0.55	8.54	[44]
17	542	18,700	20	0.68	0.69	9.5	[45]

Irradiated light: 100 mW cm^{-2} , electrode: nanocrystalline TiO_2 electrode, electrolyte: iodine redox in organic solvents.

^aThe values were measured in solution (solvent is different).

^bIonic liquid electrolyte was used.

**Fig. 9.7.** APCE spectra for DSSCs based on Ru complexes **7**, **8**, and **9**

spectroscopy [35]. Therefore, two anchoring carboxyl groups are necessary for effective electron injection from Ru-complex sensitizers to the TiO_2 electrode with a large electronic coupling between the dye and the conduction band of

TiO₂. Decreases in solar-cell performance as the number of carboxyl groups decreases has also been observed for DSSCs based on other Ru-trisbipyridyl complexes [41]. Note, however, that organic dyes, which have only one anchoring carboxyl group, are also efficient sensitizers for DSSCs, as will be discussed later. This clearly indicates that the number of carboxyl groups, which are necessary for an anchoring geometry favorable for effective electron injection, depends on the molecular structure of the sensitizer.

9.2.4 Other Metal-Complex Sensitizers for DSSCs

In addition to Ru complexes, other metal complexes have also been synthesized, and their performance in DSSCs has been investigated. These include Fe complexes [62,63], Pt complexes [64], and Os complexes [65–69] (Fig. 9.8). A DSSC based on a square-planar Pt complex (**19**) shows an efficiency of 3% ($J_{sc} = 7.00 \text{ mA cm}^{-2}$, $V_{oc} = 0.60 \text{ V}$, FF = 0.77) under simulated AM 1.5 G solar irradiation [64]. A DSSC based on Os complex **21** gives a wide photore-sponse range (400–1100 nm) with a maximum IPCE of 65%, corresponding to $J_{sc} = 18.5 \text{ mA cm}^{-2}$ under AM 1.5 G irradiation [69]. However, solar-cell

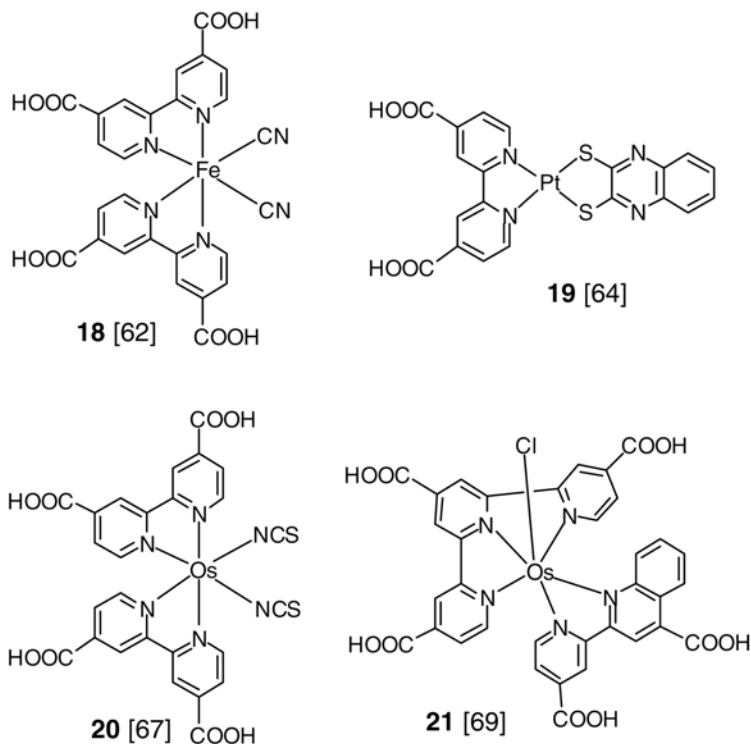


Fig. 9.8. Molecular structures of Fe, Pt, and Os-complex sensitizers

performance exceeding that of the Ru-complex sensitizers has not been attained. This is believed to be because the energy levels of the HOMO and the LUMO of Ru complexes are best matched to the iodine redox potential and the conduction band level of the TiO_2 electrode, respectively.

9.3 Porphyrins and Phthalocyanines

Porphyrin [70–79], phthalocyanine [80–82], and naphthalocyanine [83] derivatives have also been employed as sensitizers in DSSCs (Fig. 9.9). A DSSC with a nanocrystalline TiO_2 electrode sensitized by Cu chlorophyllin **22** shows an

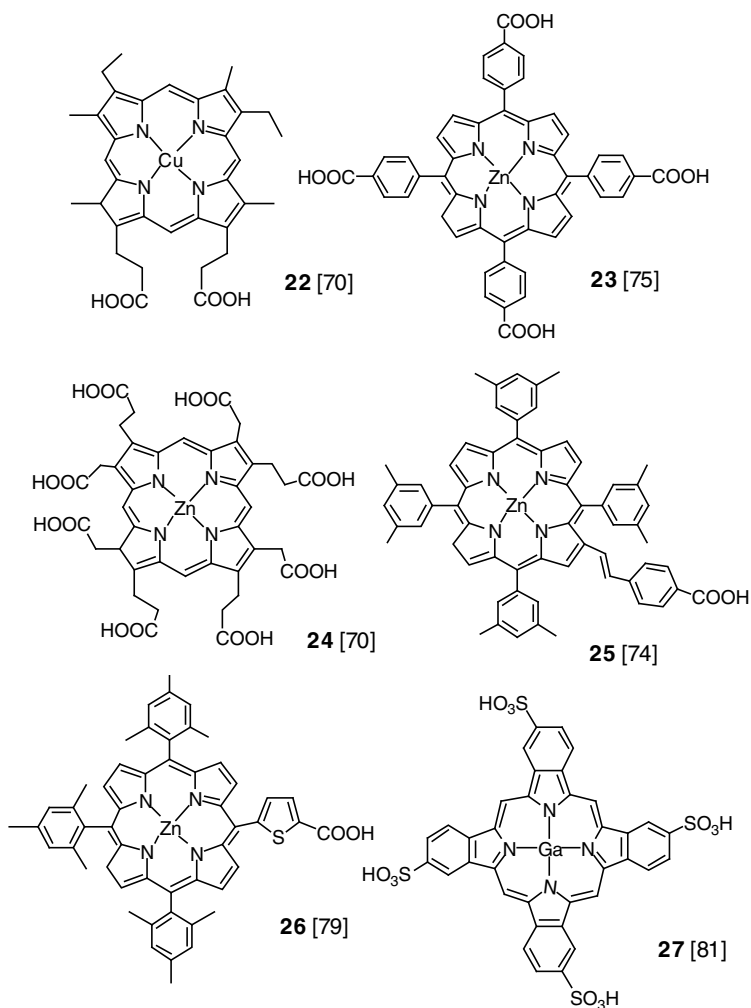


Fig. 9.9. Molecular structures of porphyrin and phthalocyanine sensitizers

efficiency of 2.6% ($J_{sc} = 9.4 \text{ mA cm}^{-2}$, $V_{oc} = 0.52 \text{ V}$) under 100 mW cm^{-2} irradiation [70]. Nazeeruddin et al. reported a DSSC based on Zn-porphyrin **25** that shows an efficiency of 4.8% ($J_{sc} = 9.7 \text{ mA cm}^{-2}$, $V_{oc} = 0.66 \text{ V}$, $FF = 0.75$) under AM 1.5 G irradiation [74]. Ultrafast electron transfer ($<100 \text{ fs}$ to $\sim 10 \text{ ps}$) from a Zn-porphyrin sensitizer to TiO_2 was observed by transient absorption spectroscopy [58].

Co-adsorbates, such as cholic acid (CA) derivatives, improve the photovoltaic performance of solar cells based on porphyrins and phthalocyanines [70], although the amount of the dye adsorbed on the TiO_2 surface is decreased by the presence of the co-adsorbate. The co-adsorbate is directly added to the dye solution during the dye-adsorption process, and the dye and co-adsorbate molecules are adsorbed simultaneously onto the TiO_2 surface. For example, Kay and Grätzel reported that the use CA derivatives in DSSCs based on porphyrin sensitizers improves both the J_{sc} value and the V_{oc} of the solar cells [70]. In addition, He et al. reported that **3 α** , **7 α** -dihydroxy-**5 β** -cholic acid improves the IPCE of DSSCs based on Zn-phthalocyanine sensitizers [82]. Strong intermolecular interactions between porphyrin and phthalocyanine molecules lead to dye aggregation, which in turn leads to quenching processes by means of energy-transfer or charge-transfer reactions between the aggregated molecules and/or between aggregated molecules and monomers. Thus, the co-adsorbates would improve solar-cell performance by suppressing dye aggregation on the surface. In addition, co-adsorbates are believed to improve the V_{oc} by suppressing recombination between the injected electrons and I_3^- ions [70]. Co-adsorbates also improve the photovoltaic performance of DSSCs based on other Ru-complex sensitizers, such as **4** [21, 47, 48] and **6** [34].

9.4 Organic Dyes

9.4.1 Molecular Structures of Organic-Dye Sensitizers for DSSCs

Metal-free organic dyes can also be utilized as sensitizers in DSSCs. In early studies of dye-sensitized photoelectrochemical electrodes, 9-phenylxanthene dyes, such as rose bengal and rhodamine B, were used as sensitizers for ZnO electrodes [84, 85]. Organic dyes have several advantages: a wide variety of structures can be obtained, structural modification is easy, and organic dyes have high molar absorption coefficients relative to those of Ru-complex sensitizers, owing to intramolecular π - π^* transitions. In addition, dyes do not contain noble metals, such as Ru, Pt, and Os, which might limit the use of metal-containing sensitizers in large-scale commercial applications. The photovoltaic performance of DSSCs based on organic-dye sensitizers has been improved [86–139]. Recently, high efficiencies ($>8\%$) under AM 1.5 G irradiation have been obtained with DSSCs based on organic dyes [104, 105, 124, 139].

The molecular structures of some organic-dye sensitizers are shown in Figs. 9.10a–c. 9-Phenylxanthene, perylene, cyanine, merocyanine, aniline, and

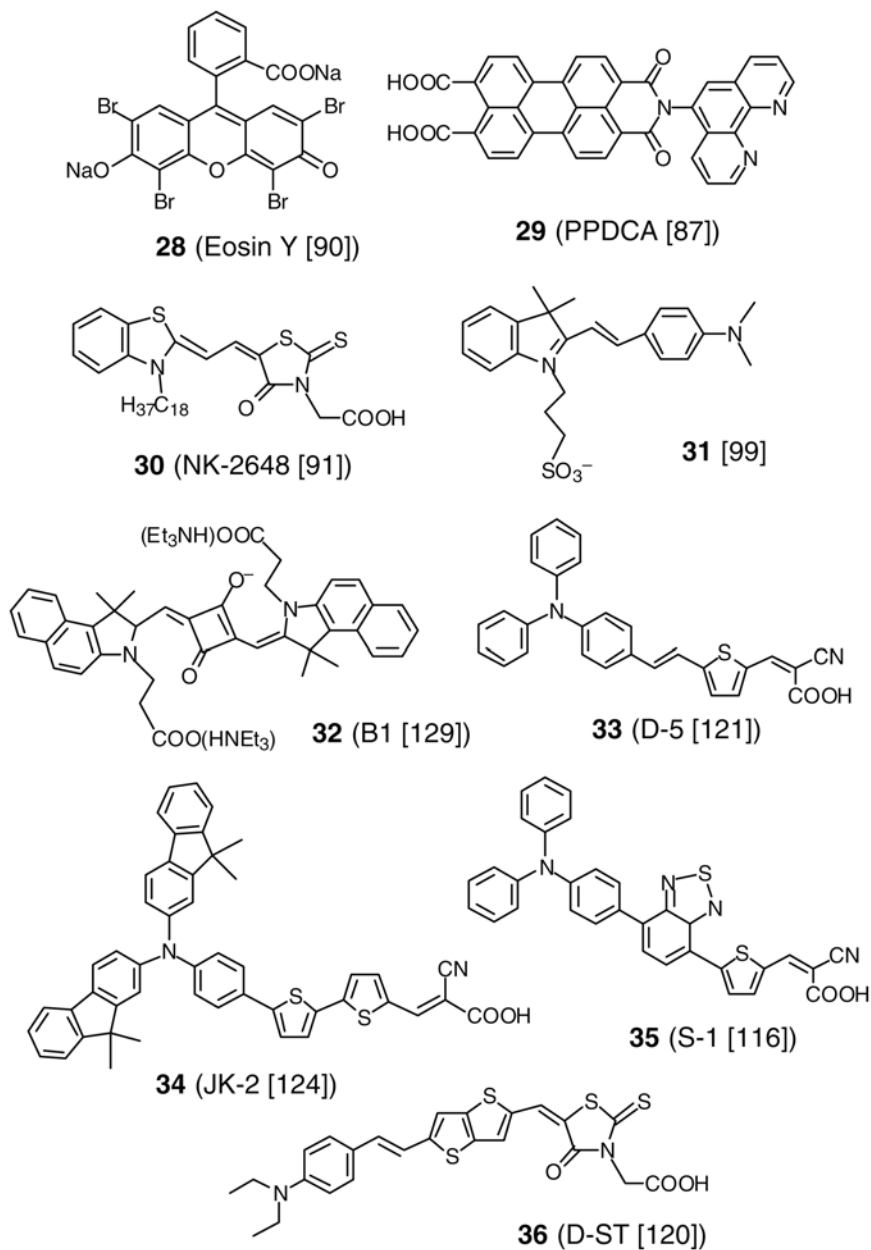


Fig. 9.10a. Molecular structures of organic-dye sensitizers for DSSCs

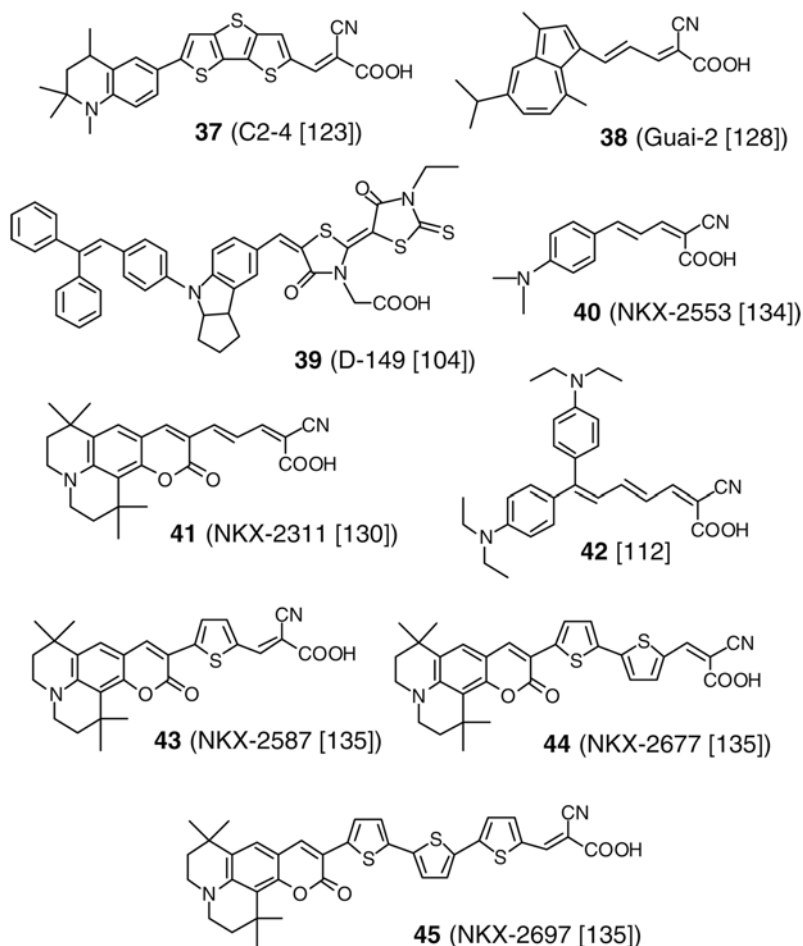


Fig. 9.10b. Molecular structures of organic-dye sensitizers for DSSCs

coumarin dyes have been used as efficient sensitizers. These molecules consist of a donor moiety (e.g., an aniline, a coumarin, or a benzothiazol unit) and an acceptor moiety (e.g., carboxylic acid, an acrylic acid, or a rhodanine ring) connected by a π -conjugated structure, such as a carbon–carbon double bond backbone or an oligothiophene moiety. This donor–acceptor structure gives a strong absorption with a large absorption coefficient in the visible region due to the intramolecular π – π^* transition. In addition, organic-dye sensitizers, like metal-complex sensitizers, have an anchoring group such as a carboxyl group and a sulfonic group to adsorb to the TiO_2 surface.

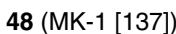


Fig. 9.10c. Molecular structures of organic-dye sensitizers for DSSCs

Figure. 9.11 shows the absorption spectra of organic-dye sensitizers NKX-2553 (**40**), NKX-2677 (**44**), and NKX-2883 (**46**) in *t*-BuOH–acetonitrile (50:50 vol %) solution. Strong absorption peaks due to the π – π^* transition are observed in the visible region from 450 to 550 nm. The ϵ values at $\lambda_{\max}$ for these dyes range from 41,200 to 97,400 M^{−1} cm^{−1}, and these values are larger than those for Ru-complex sensitizers. The strong absorption in the visible region is desirable for harvesting the solar spectrum. The electron distribution in the HOMO and LUMO of NKX-2311 (**41**) clearly indicates that an intramolecular charge transfer from the donor moiety (coumarin unit) to the acceptor moiety (acrylic acid substituent) occurs upon photoexcitation of the dye (Fig. 9.12). Similar intramolecular charge transfers upon photoexcitation have been predicted for other organic dyes by means of theoretical calculations

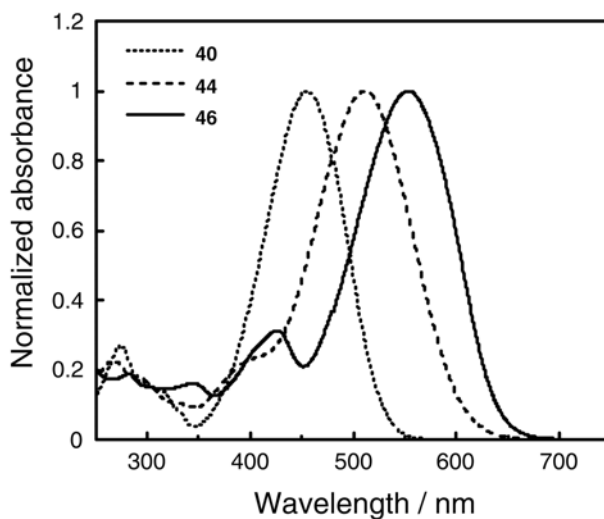


Fig. 9.11. UV-visible absorption spectra of organic-dye sensitizers

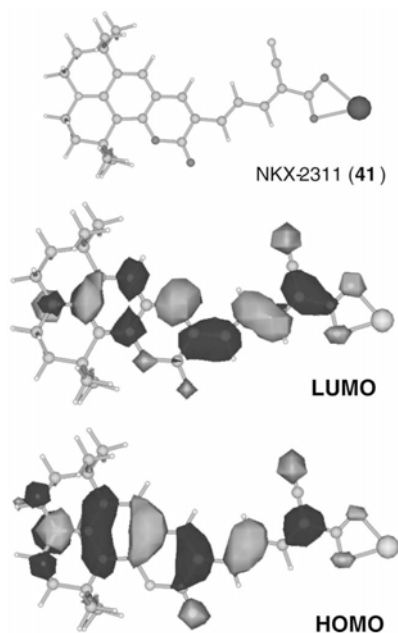


Fig. 9.12. Electron distribution in the HOMO and LUMO of NKX-2311 (41)

[123, 124, 134, 135, 140]. After the intramolecular charge transfer, the excited electron can be injected into the conduction band of the TiO_2 electrode via the anchoring carboxyl group.

Organic-dye molecules are believed to adsorb on nanocrystalline TiO_2 electrodes in a monolayer. For example, the amounts of dye adsorbed on a TiO_2 electrode ($10\text{ }\mu\text{m}$ thick) are $1.6 \times 10^{-7}\text{ mol cm}^{-2}$ for **43** and $2.0 \times 10^{-7}\text{ mol cm}^{-2}$ for **44** [135], and these amounts are larger than the amounts for other dyes: e.g., $1.3 \times 10^{-7}\text{ mol cm}^{-2}$ for **2** [15]. These results suggest that strong interactions between the organic-dye molecules due to the π - π stacking interaction result in highly ordered adsorption of the dyes on the TiO_2 surface. Organic dyes are also adsorbed on the TiO_2 surface via carboxylate bidentate coordination, as indicated by ATR-FT-IR absorption analysis [131, 134, 135]. Carboxylate coordination causes a strong electronic interaction between the π^* orbital of the excited state of the dye and the conduction band of TiO_2 , which results in effective electron injection from the dye into the TiO_2 .

9.4.2 Performance of DSSCs Based on Organic Dyes

The IPCE spectra for DSSCs composed of a nanocrystalline TiO_2 electrode, organic-dye sensitizers **44** and **46**, and an iodine redox (I^-/I_3^-) electrolyte are shown in Fig.9.13, along with the irradiance of the solar spectrum (under AM 1.5 G conditions). Photons with a wide range of wavelengths (350–800 nm) can be converted to current with the DSSCs based on these organic dyes. IPCE values higher than 70% were observed at 420–660 nm, where the irradiance of the solar spectrum is relatively strong; the maximum values were 77% at 498 nm for the DSSC based on **44** and 81% at 490 nm for the DSSC based on **46**.

The photovoltaic performances of DSSCs based on organic-dye sensitizers are listed in Table 9.2. A DSSC based on D149 dye (**39**) produced a high η (up to 9.0%) under AM 1.5 G irradiation (100 mW cm^{-2}) [104, 105]. Kim et al.

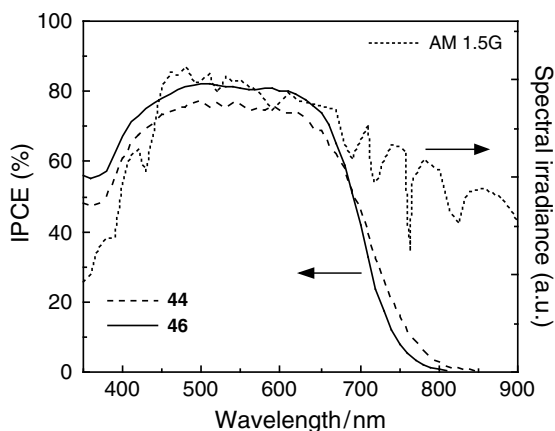


Fig. 9.13. IPCE spectra for DSSCs based on NKX-2677 (**44**) and NKX-2883 (**46**), and the spectral irradiance of standard AM 1.5 G

Table 9.2. Performance of DSSCs based on organic-dye sensitizers

Dye	$\lambda_{\text{max}}/\text{nm}^{\text{a}}$	$\varepsilon/\text{M}^{-1}\text{cm}^{-1}$	$J_{\text{sc}}/\text{mA cm}^{-2}$	V_{oc}/V	FF	$\eta(\%)$	Reference
30	517	91,000	11.4	0.60	0.65	4.5	[91]
31	551	77,900	16.5	0.42	0.63	4.7	[99]
32	679	180,000	8.6	0.591	0.73	3.7	[129]
33	476	37,600	11.9	0.66	0.68	5.1	[121]
34	452	39,000	14.0	0.753	0.77	8.0	[124]
35	491	27,500	10.44	0.546	0.66	3.77	[116]
36	488	50,100	15.23	0.56	0.73	6.23	[120]
37	444	32,950	8.84	0.522	0.63	2.92	[123]
39	526	68,700	18.5	0.693	0.624	8.0	[104]
39	526	68,700	19.96	0.653	0.694	9.0	[105]
38	453	58,000	7.88	0.468	0.588	2.9	[128]
40	454	41,200	10.4	0.71	0.74	5.5	[134]
42	470	41,500	16.4	0.61	0.66	6.6	[112]
41	504	51,900	14.0	0.60	0.71	6.0	[130]
44	511	64,300	13.5	0.71	0.77	7.4	[135]
47	525	70,000	15.9	0.69	0.75	8.2	[139]
49	473	35,800	14.0	0.74	0.74	7.7	[137]

Irradiated light: 75–00 mW cm⁻², electrode: nanocrystalline TiO₂ electrode, electrolyte: iodine redox in organic solvents

^aThe values were measured in solution (solvent is different).

designed some new organic dyes and reported an efficiency of 8.0% ($J_{\text{sc}} = 14.0 \text{ mA cm}^{-2}$, $V_{\text{oc}} = 0.753 \text{ V}$, $\text{FF} = 0.77$) with a DSSC based on JK-2 dye (**34**) [124]. We also obtained an η value of 7.4% ($J_{\text{sc}} = 13.5 \text{ mA cm}^{-2}$, $V_{\text{oc}} = 0.71 \text{ V}$, $\text{FF} = 0.77$ with a DSSC based on coumarin dye **44** under simulated AM 1.5 G irradiation (100 mW cm⁻²) with an aperture mask and without an antireflection (AR) film [135]. The η value was further improved to 8.2% with a DSSC based on **47**, which has expanded π -conjugation relative to that of **44**; the expanded conjugation improved the photoresponse range of the dye [139]. This η value is close to the value of 8.9% ($J_{\text{sc}} = 16.5 \text{ mA cm}^{-2}$, $V_{\text{oc}} = 0.75 \text{ V}$, $\text{FF} = 0.72$) obtained with a DSSC based on Ru complex **3** under similar conditions. In addition, a high J_{sc} value (18.8 mA cm⁻²; with a mask and without an AR film) was obtained with a DSSC based on **46** [138]. These results indicate that organic dyes can perform nearly as well as Ru complexes in DSSCs.

9.4.3 Electron Transfer from Organic Dyes to TiO₂

Figure 9.14 shows transient absorption monitored at 4,000 nm for a TiO₂ film with adsorbed **44** after excitation at 540 nm, and an energy diagram for a DSSC based on **44** is shown in Fig. 9.15. The increase in absorption after the photoexcitation of **44** (Fig. 9.14) is attributed to injection of electrons into

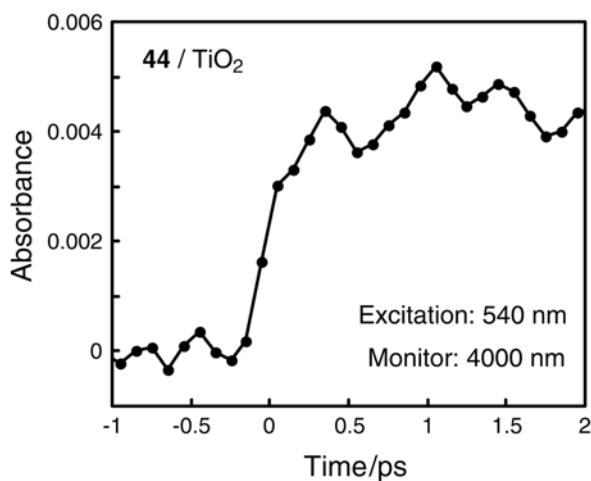


Fig. 9.14. Transient absorption monitored at 4,000 nm for a TiO_2 film with adsorbed **44** after excitation at 540 nm

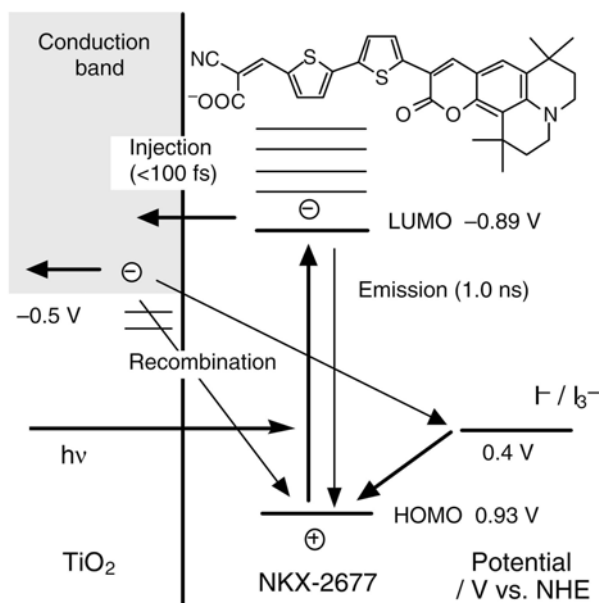


Fig. 9.15. Schematic energy diagram of a DSSC based on **44**

the conduction band of TiO_2 . The increase clearly indicates that electron injection from the dye into the conduction band of TiO_2 occurs rapidly (within <100 fs). This injection rate is much faster than the emission lifetime (1.0 ns), which corresponds to a deactivation of the excited electron (Fig. 9.15) [135].

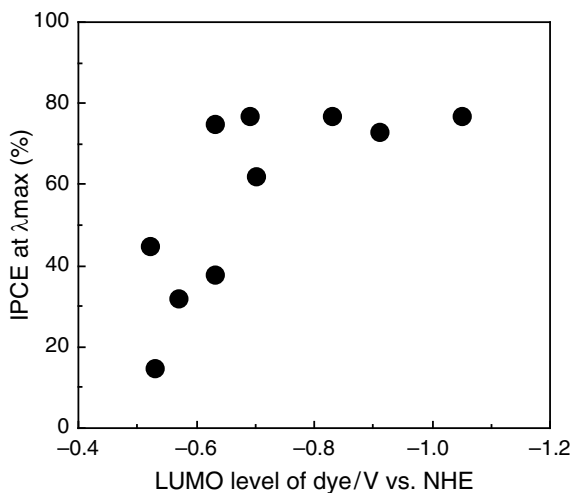


Fig. 9.16. A plot of the IPCE values at $\lambda_{\max}$ for DSSCs based on coumarin dyes as a function of the LUMO level of the dyes

Therefore, a high electron-injection yield (nearly unity) from the dye to TiO_2 was achieved in the system. Ultrafast electron injection from organic dye **42** into the conduction band of TiO_2 (within <100 fs) was also observed by transient absorption spectroscopy [112]. These results indicate that ultrafast and highly efficient electron injection from organic dyes to TiO_2 can be achieved.

A high electron-injection yield from the dye to the TiO_2 electrode strongly depends on the relationship between the conduction band edge of the TiO_2 electrode and the LUMO level of the dye (Fig. 9.15). A plot of the IPCE values at $\lambda_{\max}$ for DSSCs based on coumarin dyes as a function of the LUMO level of the dyes [131] (Fig. 9.16) indicates that DSSCs based on coumarin dyes with LUMO levels more negative than ca. -0.7 V vs. NHE show high IPCEs, whereas dyes with LUMO levels more positive than -0.7 V do not exhibit high IPCEs. Electron injection from such dyes to TiO_2 is suppressed as the energy gap between the conduction band edge level of TiO_2 and the LUMO level of the dye decreases. Consideration of the conduction band-edge of TiO_2 , ca. -0.5 V vs. NHE [4], suggests that an energy gap of ca. 0.2 eV between the LUMO of the dye and the conduction band edge of TiO_2 is a necessary driving force for effective electron injection and thus high IPCEs, as mentioned in introduction. In fact, in DSSCs based on a nanocrystalline ZnO electrode, transient absorption spectroscopy has revealed that the electron-injection yield from dyes to ZnO depends markedly on the LUMO levels of the dye sensitizer used [56, 141].

9.4.4 Electron Diffusion Length

Although high efficiencies have been achieved with DSSCs based on organic-dye sensitizers, the performance of these DSSCs has not yet exceeded that of DSSCs based on Ru complexes (11%). We believe that the lower performance of DSSCs based on organic dyes is probably due to the lower V_{oc} values generated in DSSCs based on organic dyes. To obtain a high V_{oc} , a higher concentration of an additive in the electrolyte (such as 4-*tert*-butylpyridine (TBP), which suppresses charge recombination between the electrons and I_3^- ions and shifts the E_{cb} of TiO_2 electrode negatively) is required for DSSCs based on a coumarin dye than is required for DSSCs based on Ru complexes [133, 135]. This result suggests that charge recombination occurs more easily in DSSCs based on a coumarin dye than in DSSCs based on Ru complexes. To clarify the differences between the behaviors of DSSCs based on Ru complexes and those based on organic dyes, we must investigate the electron-transport kinetics in DSSCs based on organic dyes.

Many researchers have focused on electron transport in nanocrystalline TiO_2 electrodes to understand the behavior of DSSCs [142–150]. In DSSCs, electron transport is important for high solar-cell performance because this process competes with charge recombination between electrons and dye cations and between electrons and redox ions (I_3^-), which are the loss processes in the system. For the photogenerated electrons to be collected, electron transport in the nanocrystalline TiO_2 electrode must predominate over both charge-recombination processes. The electron-transport kinetics in nanocrystalline TiO_2 electrodes is defined by electron diffusion length (L) as the following equation:

$$L = \sqrt{D \cdot \tau} \quad (9.7)$$

where D is the electron diffusion coefficient, and τ is the electron lifetime. We investigated electron-transport kinetics in terms of D and τ in DSSCs based on coumarin dyes by intensity-modulated photocurrent spectroscopy (IMPS) and intensity-modulated photovoltage spectroscopy (IMVS), respectively [151]. We found that the τ values for DSSCs with coumarin dyes **43**, **44**, and **45** were much shorter than the value for the DSSC based on Ru complex **3**, which suggests that charge recombination between conduction-band electrons in the TiO_2 and I_3^- ions in the electrolyte occurs more easily in solar cells based on coumarin dyes (Fig. 9.17) [151]. In contrast, no large differences between the D values for DSSCs based on coumarin dyes and **3** were observed [151]. These results indicate that the L value is affected more markedly by the change in the τ value when the dye is changed. The details of the mechanism underlying the different τ values for **3** and coumarin dyes are unclear at present. The difference may be due to the different molecular sizes and structures of **3** and coumarin dyes. On the basis of results obtained to date, we can conclude that the lower V_{oc} values for DSSCs based on organic dyes relative to those based on Ru complexes are due to the shorter τ values, which result in shorter L values.

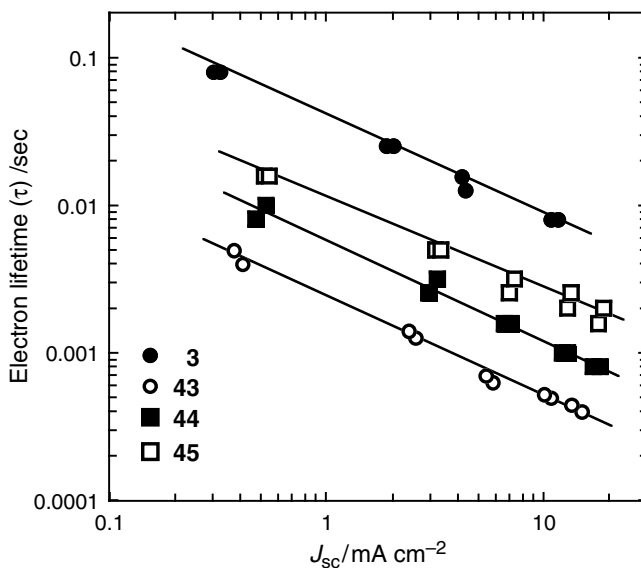


Fig. 9.17. Electron lifetimes (τ) obtained with DSSCs based on Ru complex **3** and coumarin dyes **43**, **44**, and **45**

Further strategic molecular design of organic dyes is required to achieve higher η values. A new approach toward improving the performance of DSSCs based on organic dyes involves engineering of the interface between the organic dyes and the TiO_2 surface, which can be controlled by the structural modification of the dye molecule to reduce charge recombination between the electrons and I_3^- ions. With this goal in mind, we designed and synthesized carbazole dyes **48–50** (Fig. 9.10c) [137]. The most important feature of these new dyes (MK-1, **48** and MK-2, **49**) is the presence of *n*-hexyl substituents on the oligothiophene backbone. We expected that the long alkyl chains would prevent the approach of I_3^- ions to TiO_2 surface and thus increase the τ value.

The electron lifetimes for DSSCs based on MK dyes are shown in Fig. 9.18. It is remarkable that the τ values for the DSSCs based on **48** and **49**, which bear alkyl chains, were longer than the values for the DSSCs based on coumarin dyes **43** and **45**, which have thiophenes without alkyl chains (Fig. 9.18) [137]. In addition, the τ value for the DSSC based on MK-3 (**50**), which does not bear alkyl chains, was much shorter than the values for the DSSCs based on **48** and **49** [137]. These results clearly indicate that alkyl chains effectively increase the electron lifetimes, perhaps, as previously suggested, by preventing the the I_3^- ions from approaching the TiO_2 surface due to a steric effect, a hydrophobic effect, or both, thereby decreasing the I_3^- concentration near the TiO_2 surface. As a result, we attained a high η and a relatively high V_{oc} ($\eta = 7.7\%$, $J_{sc} = 14.0 \text{ mA cm}^{-2}$, $V_{oc} = 0.74 \text{ V}$, $\text{FF} = 0.74$) with a DSSC based on **49**, owing to the increased electron lifetime [137].

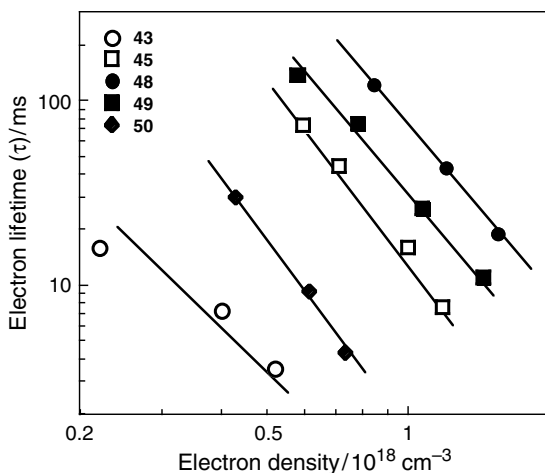


Fig. 9.18. Electron lifetimes for DSSCs based on MK dyes 48, 49, and 50

Our success with these alkyl-functionalized dyes strongly suggests that the photovoltaic performance of DSSCs based on organic-dye sensitizers can be improved further.

9.5 Stability

9.5.1 Photochemical and Thermal Stability of Sensitizers

The commercialization of DSSCs will require long-term stability of the dye molecules and of individual solar cells or large-area modules. The photostability and thermal stability of Ru complexes have been investigated in detail [15, 152–156]. For example, the thiocyanate (NCS) ligand of **2** is oxidized to a cyano group ($-\text{CN}$) under photoirradiation in methanol solution, as indicated by UV–Vis absorption and NMR spectroscopy [15, 152]. Substitution of the NCS ligand of **3** by solvents (acetonitrile and 3-methoxypropionitrile) and TBP has been observed at elevated temperatures ($80\text{--}110^\circ\text{C}$) [156]. Decarboxylation of **2** occurs at temperatures higher than 290°C under N_2 and higher than 250°C in air [154]. When the dye is adsorbed onto the TiO_2 surface, the decarboxylation occurs at temperatures above 320°C in air.

High dye stability can be obtained in a DSSC system by including I^- ions as the electron donor to dye cations. Degradation of the NCS ligand to a CN ligand due to an intramolecular electron transfer producing Ru^{2+} from Ru^{3+} occurs within $0.1\text{--}1\text{ s}$ [152], whereas the rate for reduction of Ru^{3+} to Ru^{2+} due to electron transfer from I^- ions to the dye cations is on the order of nanoseconds [50]. This comparison indicates that one molecule of **2** can contribute to the photon-to-current conversion process with a turnover number of at least $10^7\text{--}10^8$ without degradation [152]. Taking this into consideration, **2** is considered to be sufficiently stable in the redox electrolyte under irradiation.

We investigated the thermal stability of coumarin dyes **41** and **44**. In thermogravimetric analysis of the dyes, an 8% drop in mass was observed for **44** at around 278°C under an O₂ atmosphere [135], and a similar mass drop was observed for **41** at around 230°C under a N₂ atmosphere [130]. FT-IR absorption spectroscopy clearly indicated that these mass drops are due to decomposition of the dye by decarboxylation [130]. From these results, we conclude that the thermal stability of organic dyes such as **44** is as good as that of **2**.

9.5.2 Long-Term Stability of Solar-Cell Performance

The long-term stability of small DSSCs and large-area modules is currently being investigated for commercial applications [11, 13, 25, 29, 152, 157, 158]. DSSCs based on Ru complexes such as **2** and **3** have good long-term stability under continuous irradiation. For example, Grätzel and coworkers achieved 7,000 h of cell stability under 1,000 W m⁻² with a UV cutoff filter [152]. They concluded that the good long-term stability of the DSSC is due to effective photoinduced electron transfer from the Ru-complex sensitizer into the conduction band of the semiconductor, and from the iodine redox mediator to the sensitizer. The turnover number of one sensitizer molecule, which is defined by the number of electrons produced by one sensitizer molecule, reaches 500 million. Furthermore, Kern et al. reported a long-term stability of more than 10,000 h with a cell in the absence of UV light at 17°C at 2.5 sun [157].

We investigated the long-term stability of a DSSC based on coumarin dye **46** under continuous AM 1.5 G irradiation through a UV (<420 nm) cut-off filter (100 mW cm⁻², 50–55°C) under open-circuit conditions. No signs of dye degradation and no decrease in solar-cell performance were observed over a period of 1,000 h (Fig. 9.19) [138]. This result suggests that coumarin dyes

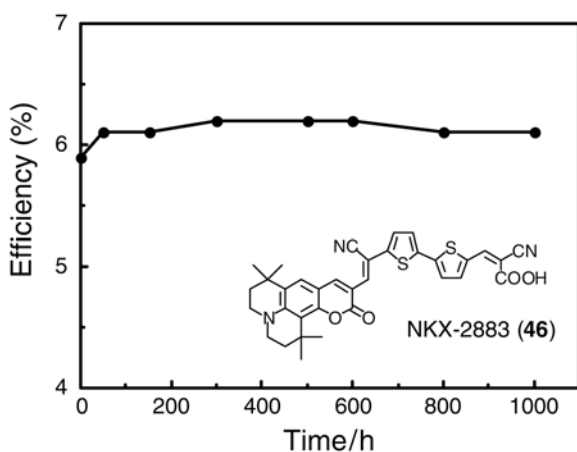


Fig. 9.19. Long-term stability of performance for a DSSC based on NKX-2883 (**46**)

are also relatively stable under irradiation in solar cells, where redox ions are present and electron-transfer processes occur effectively. Taken together, these results strongly indicate that DSSCs show sufficient long-term stability during irradiation, although the stability of cell performance under UV irradiation and at high temperature and humidity must be investigated in further detail.

9.6 Summary and Perspectives

The best solar-energy-to-electricity conversion efficiency (11% with small cells) has been attained with DSSCs based on Ru-complex sensitizers **3** and **4** [9, 10]. Organic-dye sensitizers, such as merocyanine dyes, coumarin dyes, and carbazole dyes, also show high performance as sensitizers for DSSCs.

For commercial applications, cell efficiencies higher than 11% (e.g., 15%) and module efficiencies higher than 10% are sure to be desired. To attain 15% cell efficiency, both J_{sc} and V_{oc} must be further improved. Expanding the absorption of the sensitizers to the near-IR region is necessary for improved J_{sc} . The absorption threshold of **4** is close to 900 nm, and this value is expected to be the optimal threshold for single-junction solar cells, whose E_g is ca. 1.4 eV. A high J_{sc} value (20.9 mA cm^{-2}) was achieved with a DSSC based on **4** (with an aperture mask and an AR film) [10]. Development of new sensitizers that can absorb in the near-IR region with relatively large absorption coefficients is also desired. Improvement of the IPCE of DSSCs sensitized by **4** (or new sensitizers) in the 800–900 nm range (Fig. 9.6), would increase the J_{sc} from 20.9 mA cm^{-2} to about 25 mA cm^{-2} . Improvement of V_{oc} from 0.75 V to the optimal value of ca. 0.9 V is also important for achievement of higher efficiencies. The fact that V_{oc} values have not yet reached the optimal value is mainly attributed to charge recombination between injected electrons and redox ions (I_3^-). Molecular design of the sensitizers to suppress charge recombination would improve the V_{oc} . In addition, long-term stabilities of dye molecules and solar-cell performance under more rigorous conditions (e.g., high temperature at near 80°C, high humidity, and UV exposure) will be required for outdoor applications.

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References

1. N. Vlachopoulos, P. Liska, J. Augustynski, M. Grätzel, *J. Am. Chem. Soc.* **110**, 1216 (1988)
2. B. O'Regan, M. Grätzel, *Nature* **353**, 737 (1991)
3. G. Smestad, C. Bignozzi, R. Argazzi, *Sol. Energy Mater. Sol. Cells* **32**, 259 (1994)
4. A. Hagfeldt, M. Grätzel, *Chem. Rev.* **95**, 49 (1995)
5. A. Kay, M. Grätzel, *Sol. Energy Mater. Sol. Cells* **44**, 99 (1996)
6. K. Kalyanasundaram, M. Grätzel, *Coord. Chem. Rev.* **177**, 347 (1998)
7. A. Hagfeldt, M. Grätzel, *Acc. Chem. Res.* **33**, 269 (2000)
8. M. Grätzel, *J. Photochem. Photobiol. C Photochem. Rev.* **4**, 145 (2003)
9. M.K. Nazeeruddin, F. De Angelis, S. Fantacci, A. Selloni, G. Viscardi, P. Liska, S. Ito, B. Takeru, M. Grätzel, *J. Am. Chem. Soc.* **127**, 16835 (2005)
10. Y. Chiba, A. Islam, Y. Watanabe, R. Komiya, N. Koide, L. Han, *Jpn. J. Appl. Phys.* **45**, L638 (2006)
11. P.M. Sommeling, M. Späth, H.J.P. Smit, N.J. Bakker, J.M. Kroon, *J. Photochem. Photobiol. A Chem.* **164**, 137 (2004)
12. K. Okada, H. Matsui, T. Kawashima, T. Ezure, N. Tanabe, *J. Photochem. Photobiol. A Chem.* **164**, 193 (2004)
13. T. Toyoda, T. Sano, J. Nakajima, S. Doi, S. Fukumoto, A. Ito, T. Tohyama, M. Yoshida, T. Kanagawa, T. Motohiro, T. Shiga, K. Higuchi, H. Tanaka, Y. Takeda, T. Fukano, N. Katoh, A. Takeichi, K. Takechi, M. Shiozawa, *J. Photochem. Photobiol. A Chem.* **164**, 203 (2004)
14. S. Anderson, E.C. Constable, M.P. Dare-Edwards, J.B. Goodenough, A. Hamnett, K.R. Seddon, R.D. Wright, *Nature* **280**, 571 (1979)
15. M.K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos, M. Grätzel, *J. Am. Chem. Soc.* **115**, 6382 (1993)
16. R. Argazzi, C.A. Bignozzi, T.A. Heimer, F.N. Castellano, G.J. Meyer, *Inorg. Chem.* **33**, 5741 (1994)
17. M.K. Nazeeruddin, E. Müller, R. Humphry-Baker, N. Vlachopoulos, M. Grätzel, *J. Chem. Soc. Dalton Trans.* **23**, 4571 (1997)
18. M.K. Nazeeruddin, S.M. Zakeeruddin, R. Humphry-Baker, M. Jirousek, P. Liska, N. Vlachopoulos, V. Shklover, C.H. Fischer, M. Grätzel, *Inorg. Chem.* **38**, 6298 (1999)
19. T. Renouard, R.A. Fallahpour, M.K. Nazeeruddin, R. Humphry-Baker, S.I. Gorelsky, A.B.P. Lever, M. Grätzel, *Inorg. Chem.* **41**, 367 (2002)
20. M.K. Nazeeruddin, R. Humphry-Baker, P. Liska, M. Grätzel, *J. Phys. Chem. B* **107**, 8981 (2003)
21. M.K. Nazeeruddin, P. Péchy, T. Renouard, S.M. Zakeeruddin, R. Humphry-Baker, P. Comte, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G.B. Deacon, C.A. Bignozzi, M. Grätzel, *J. Am. Chem. Soc.* **123**, 1613 (2001)
22. P. Wang, S.M. Zakeeruddin, I. Exnar, M. Grätzel, *Chem. Commun.* 2972 (2002)
23. P. Wang, S.M. Zakeeruddin, P. Comte, R. Charvet, R. Humphry-Baker, M. Grätzel, *J. Phys. Chem. B* **107**, 14336 (2003)
24. N. Hirata, J.J. Lagref, E.J. Palomares, J.R. Durrant, M.K. Nazeeruddin, M. Grätzel, D. Di Censo, *Chem. Eur. J.* **10**, 595 (2004)
25. P. Wang, S.M. Zakeeruddin, J.E. Moser, R. Humphry-Baker, P. Comte, V. Aranyos, A. Hagfeldt, M.K. Nazeeruddin, M. Grätzel, *Adv. Mater.* **16**, 1806 (2004)

26. P. Wang, C. Klein, R. Humphry-Baker, S.M. Zakeeruddin, M. Grätzel, *J. Am. Chem. Soc.* **127**, 808 (2005)
27. C. Klein, M.K. Nazeeruddin, P. Liska, D. Di Censo, N. Hirata, E. Palomares, J.R. Durrant, M. Grätzel, *Inorg. Chem.* **44**, 178 (2005)
28. D. Kuang, C. Klein, H.J. Snaith, J.E. Moser, R. Humphry-Baker, P. Comte, S.M. Zakeeruddin, M. Grätzel, *Nano Lett.* **6**, 769 (2006)
29. D. Kuang, S. Ito, B. Wenger, C. Klein, J.E. Moser, R. Humphry-Baker, S.M. Zakeeruddin, M. Grätzel, *J. Am. Chem. Soc.* **128**, 4146 (2006)
30. O. Schwarz, D. van Loyen, S. Joskusch, N.J. Turro, H. Dürr, *J. Photochem. Photobiol. A Chem.* **132**, 91 (2000)
31. V. Aranyos, H. Grennberg, S. Tingry, S.E. Lindquist, A. Hagfeldt, *Sol. Energy Mater. Sol. Cells* **64**, 97 (2000)
32. A. Islam, K. Hara, L.P. Singh, R. Katoh, M. Yanagida, S. Murata, Y. Takahashi, H. Sugihara, H. Arakawa, *Chem. Lett.* 490 (2000)
33. Y. Takahashi, H. Arakawa, H. Sugihara, K. Hara, A. Islam, R. Katoh, Y. Tachibana, M. Yanagida, *Inorg. Chem. Acta* **310**, 169 (2000)
34. K. Hara, H. Sugihara, Y. Tachibana, A. Islam, M. Yanagida, K. Sayama, H. Arakawa, G. Fujihashi, T. Horiguchi, T. Kinoshita, *Langmuir* **17**, 5992 (2001)
35. K. Hara, H. Horiuchi, R. Katoh, L.P. Singh, K. Sugihara Sayama, S. Murata, M. Tachiya, H. Arakawa, *J. Phys. Chem. B* **106**, 374 (2002)
36. A. Islam, H. Sugihara, M. Yanagida, K. Hara, G. Fujihashi, Y. Tachibana, R. Katoh, S. Murata, H. Arakawa, *New J. Chem.* **26**, 966 (2002)
37. M. Yanagida, T. Yamaguchi, M. Kurashige, K. Hara, R. Katoh, H. Sugihara, H. Arakawa, *Inorg. Chem.* **42**, 7921 (2003)
38. R. Argazzi, N.Y.M. Iha, H. Zabri, F. Odobel, C.A. Bignozzi, *Coord. Chem. Rev.* **248**, 1299 (2004)
39. M.K. Nazeeruddin, S.M. Zakeeruddin, J.J. Lagref, P. Liska, P. Comte, C. Barolo, G. Viscardi, K. Schenk, M. Grätzel, *Coord. Chem. Rev.* **248**, 1317 (2004)
40. A.S. Polo, M.K. Itokazu, N.Y.M. Iha, *Coord. Chem. Rev.* **248**, 1343 (2004)
41. K. Kilsa, E.I. Mayo, B.S. Brunshawig, H.B. Gray, N.S. Lewis, J.R. Winkler, *J. Phys. Chem. B* **108**, 15640 (2004)
42. A. Islam, F.A. Chowdhury, Y. Chiba, R. Komiya, N. Fuke, N. Ikeda, K. Nozaki, L. Han, *Chem. Mater.* **18**, 5178 (2006)
43. S.R. Jang, R. Vittal, J. Lee, N. Jeong, K.J. Kim, *Chem. Commun.* 103 (2006)
44. C.Y. Chen, S.J. Wu, C.G. Wu, J.G. Chen, K.C. Ho, *Angew. Chem. Int. Ed.* **45**, 5822 (2006)
45. K.J. Jiang, N. Masaki, J.B. Xia, S. Noda, S. Yanagida, *Chem. Commun.* 2460 (2006)
46. K.S. Finnie, J.R. Bartlett, J.L. Woolfrey, *Langmuir* **14**, 2744 (1998)
47. C. Bauer, G. Boschloo, E. Mukhtar, A. Hagfeldt, *J. Phys. Chem. B* **106**, 12693 (2002)
48. K. Hara, T. Nishikawa, M. Kurashige, H. Kawauchi, T. Kashima, K. Sayama, K. Aika, H. Arakawa, *Sol. Energy Mater. Sol. Cell* **85**, 21 (2005)
49. V. Shklover, Y.E. Ovchinnikov, L.S. Braginsky, S.M. Zakeeruddin, M. Grätzel, *Chem. Mater.* **10**, 2533 (1998)
50. Y. Tachibana, J.E. Moser, M. Grätzel, D.R. Klug, J.R. Durrant, *J. Phys. Chem.* **100**, 20056 (1996)

51. T. Hannappel, B. Burfeindt, W. Storck, F. Willig, *J. Phys. Chem. B* **101**, 6799 (1997)
52. R.J. Ellingson, J.B. Asbury, S. Ferrere, H.N. Ghosh, J.R. Sprague, T. Lian, A.J. Nozik, *J. Phys. Chem. B* **102**, 6455 (1998)
53. S. Iwai, K. Hara, S. Murata, R. Katoh, H. Sugihara, H. Arakawa, *J. Chem. Phys.* **113**, 3366 (2000)
54. J.B. Asbury, E. Hao, Y. Wang, H.N. Ghosh, T. Lian, *J. Phys. Chem. B* **105**, 4545 (2001)
55. G. Benkő, J. Kallioinen, J.E.I. Korppi-Tommola, A.P. Yartsev, V. Sundström, *J. Am. Chem. Soc.* **124**, 489 (2002)
56. R. Katoh, A. Furube, A.V. Barzykin, H. Arakawa, M. Tachiya, *Coord. Chem. Rev.* **248**, 1195 (2004)
57. J.B. Asbury, Y.Q. Wang, T. Lian, *J. Phys. Chem. B* **103**, 6643 (1999)
58. Y. Tachibana, S.A. Haque, I.P. Mercer, J.R. Durrant, D.R. Klug, *J. Phys. Chem. B* **104**, 1198 (2000)
59. S.A. Haque, Y. Tachibana, D.R. Klug, J.R. Durrant, *J. Phys. Chem. B* **102**, 1745 (1998)
60. S. Nasr, S. Hotchandani, P.V. Kamat, *J. Phys. Chem. B* **102**, 4944 (1998)
61. S.A. Haque, Y. Tachibana, R.L. Willis, J.E. Moser, M. Grätzel, D.R. Klug, J.R. Durrant, *J. Phys. Chem. B* **104**, 538 (2000)
62. S. Ferrere, B.A. Gregg, *J. Am. Chem. Soc.* **120**, 843 (1998)
63. M. Yang, G.J. Meyer *Inorg. Chem.* **39**, 3738 (2000)
64. A. Islam, H. Sugihara, K. Hara, L.P. Singh, R. Katoh, M. Yanagida, Y. Takahashi, S. Murata, H. Arakawa, G. Fujihashi, *Inorg. Chem.* **40**, 5371 (2001)
65. M. Alebbi, C.A. Bignozzi, T.A. Heimer, G.M. Hasselmann, G.J. Meyer, *J. Phys. Chem. B* **102**, 7577 (1998)
66. G. Sauvé, M.E. Cass, S.J. Doig, I. Lauermann, K. Pomykal, N.S. Lewis, *J. Phys. Chem. B* **104**, 3488 (2000)
67. D. Kuciauskas, M.S. Freund, H.B. Gray, J.R. Winkler, N.S. Lewis, *J. Phys. Chem. B* **105**, 392 (2001)
68. D. Kuciauskas, J. Monat, R. Villahermosa, H.B. Gray, N.S. Lewis, J.K. McCusker, *J. Phys. Chem. B* **106**, 9347 (2002)
69. S. Altobello, R. Argazzi, S. Caramori, C. Contado, S. Da Fré, P. Rubino, C. Choné, G. Larramona, C.A. Bignozzi, *J. Am. Chem. Soc.* **127**, 15342 (2005)
70. A. Kay, M. Grätzel, *J. Phys. Chem.* **97**, 6272 (1993)
71. S. Cherian, C.C. Wamser, *J. Phys. Chem. B* **104**, 3624 (2000)
72. T. Ma, K. Inoue, K. Yao, H. Noma, T. Shuji, E. Abe, J. Yu, X. Wang, B. Zhang, *J. Electroanal. Chem.* **537**, 31 (2002)
73. F. Odobel, E. Blart, M. Lagrée, M. Villieras, H. Boujtita, N.E. Murr, S. Caramori, C.A. Bignozzi, *J. Mater. Chem.* **13**, 502 (2003)
74. M.K. Nazeeruddin, R. Humphry-Baker, D.L. Officer, W.M. Campbell, A.K. Burrell, M. Grätzel, *Langmuir* **20**, 6514 (2004)
75. W.M. Campbell, A.K. Burrell, D.L. Officer, K.W. Jolley, *Coord. Chem. Rev.* **248**, 1363 (2004)
76. R. Mosurkal, J.A. He, K. Yang, L.A. Samuelson, J. Kumar, *J. Photochem. Photobiol. A Chem.* **168**, 191 (2004)
77. L. Schmidt-Mende, W.M. Campbell, Q. Wang, K.W. Jolley, D.L. Officer, M.K. Nazeeruddin, M. Grätzel, *Chem. Phys. Chem.* **6**, 1253 (2005)

78. H. Imahori, S. Hayashi, T. Umeyama, S. Eu, A. Oguro, S. Kang, Y. Matano, T. Shishido, S. Ngamsinlapasathian, S. Yoshikawa, *Langmuir* **22**, 11405 (2006)
79. S. Eu, S. Hayashi, T. Umeyama, A. Oguro, M. Kawasaki, N. Kadota, Y. Matano, H. Imahori, *J. Phys. Chem. C* **111**, 3528 (2007)
80. M.K. Nazeeruddin, R. Humphry-Baker, M. Grätzel, B.A. Murrer, *Chem. Commun.* 719 (1998)
81. H. Deng, Y. Zhou, H. Mao, Z. Lu, *Synth. Met.* **92**, 269 (1998)
82. J. He, G. Benkő, F. Korodi, T. Polivka, R. Lomoth, B. Akermarck, L. Sun, A. Hagfeldt, V. Sundström, *J. Am. Chem. Soc.* **124**, 4922 (2002)
83. X. Li, N.J. Long, J.N. Clifford, C.J. Campbell, J.R. Durrant, *New J. Chem.* **26**, 1076 (2002)
84. H. Gerischer, H. Tributsch, *Ber. Bunsen. Phys. Chem.* **72**, 437 (1968)
85. M. Matsumura, Y. Nomura, H. Tsubomura, *Bull. Chem. Soc. Jpn.* **50**, 2533 (1977)
86. B. O'Regan, D.T. Schwartz, *J. Appl. Phys.* **80**, 4749 (1996)
87. S. Ferrere, A. Zaban, B.A. Gregg, *J. Phys. Chem.* **101**, 4490 (1997)
88. S. Ferrere, B.A. Gregg, *New J. Chem.* **26**, 1155 (2002)
89. T.N. Rao, L. Bahadur, *J. Electrochem. Soc.* **144**, 179 (1997)
90. K. Sayama, M. Sugino, H. Sugihara, Y. Abe, H. Arakawa, *Chem. Lett.* 753 (1998)
91. K. Sayama, S. Tsukagoshi, K. Hara, Y. Ohga, A. Shinpou, Y. Abe, S. Suga, H. Arakawa, *J. Phys. Chem. B* **106**, 1363 (2002)
92. K. Sayama, S. Tsukagoshi, T. Mori, K. Hara, Y. Ohga, A. Shinpou, Y. Abe, S. Suga, H. Arakawa, *Sol. Energy Mater. Sol. Cells* **80**, 47 (2003)
93. A.C. Khazraji, S. Hotchandani, S. Das, P.V. Kamat, *J. Phys. Chem. B* **103**, 4693 (1999)
94. F.G. Gao, A.J. Bard, L.D. Kispert, *J. Photochem. Photobiol. A Chem.* **130**, 49 (2000)
95. H. Tian, P.H. Liu, W. Zhu, E. Gao, D.J. Wu, S. Cai, *J. Mater. Chem.* **10**, 2708 (2000)
96. T. Yoshida, K. Terada, D. Schlettwein, T. Oekermann, T. Sugiura, H. Minoura, *Adv. Mater.* **12**, 1214 (2000)
97. T. Yoshida, M. Iwaya, H. Ando, T. Oekermann, K. Nonomura, D. Schlettwein, D. Wöhrle, H. Minoura, *Chem. Commun.* 400 (2004)
98. Z.S. Wang, F.Y. Li, C.H. Huang, *Chem. Commun.* 2063 (2000)
99. Z.S. Wang, C.H. Li, F.Y. Huang, *J. Phys. Chem. B* **105**, 9210 (2001)
100. K. Hara, T. Horiguchi, T. Kinoshita, K. Sayama, H. Sugihara, H. Arakawa, *Sol. Energy Mater. Sol. Cells* **64**, 115 (2000)
101. A. Ehret, L. Stuhl, M.T. Spitler, *J. Phys. Chem. B* **105**, 9960 (2001)
102. Q.H. Yao, L. Shan, F.Y. Li, D.D. Yin, C.H. Huang, *New J. Chem.* **27**, 1277 (2003)
103. T. Horiuchi, H. Miura, S. Uchida, *Chem. Commun.* 3036 (2003)
104. T. Horiuchi, H. Miura, K. Sumioka, S. Uchida, *J. Am. Chem. Soc.* **126**, 12218 (2004)
105. S. Ito, S.M. Zakeeruddin, R. Humphry-Baker, P. Liska, R. Charvet, P. Comte, M.K. Nazeeruddin, P. Pechy, M. Takata, H. Miura, S. Uchida, M. Grätzel, *Adv. Mater.* **17**, 1202 (2005)
106. M. Matsui, K. Nagasaka, S. Tokunaga, K. Funabiki, T. Yoshida, H. Minoura, *Dyes Pigm.* **58**, 219 (2003)

107. M. Matsui, Y. Hashimoto, K. Funabiki, J.Y. Jin, T. Yoshida, H. Minoura, *Synth. Met.* **148**, 147 (2005)
108. K. Funabiki, N. Sugiyama, H. Iida, J.Y. Jin, T. Yoshida, Y. Kato, H. Minoura, M. Matsui, *J. Fluorine Chem.* **127**, 257 (2006)
109. M. Matsui, H. Mase, J.Y. Jin, K. Funabiki, T. Yoshida, H. Minoura, *Dyes Pigm.* **70**, 48 (2006)
110. A. Otsuka, K. Funabiki, N. Sugiyama, T. Yoshida, H. Minoura, M. Matsui, *Chem. Lett.* **35**, 666 (2006)
111. T. Dentani, K. Funabiki, J.Y. Jin, T. Yoshida, H. Minoura, M. Matsui, *Dyes Pigm.* **72**, 303 (2007)
112. S. Kitamura, M. Ikeda, K. Shigaki, T. Inoue, N.A. Anderson, X. Ai, T. Lian, S. Yanagida, *Chem. Mater.* **16**, 1806 (2004)
113. H. Otaka, M. Kira, K. Yano, S. Ito, H. Mitekura, T. Kawata, F. Matsui, *J. Photochem. Photobiol. A Chem.* **164**, 67 (2004)
114. R. Mosurkal, J.A. He, K. Yang, L.A. Samuelson, J. Kumar, *J. Photochem. Photobiol. A Chem.* **168**, 191 (2004)
115. K.R. Justin Thomas, J.T. Lin, Y.C. Hsu, K.C. Ho, *Chem. Commun.* 4098 (2005)
116. M. Velusamy, K.R. Justin Thomas, J.T. Lin, Y.C. Hsu, K.C. Ho, *Org. Lett.* **7**, 1899 (2005)
117. S. Tan, J. Zhai, H. Fang, T. Jiu, J. Ge, Y. Li, L. Jiang, D. Zhu, *Chem. Eur. J.* **11**, 6272 (2005)
118. C. Li, W. Wang, X. Wang, B. Zhang, Y. Cao, *Chem. Lett.* **34**, 554 (2005)
119. Y. Chen, C. Li, Z. Zeng, W. Wang, X. Wang, B. Zhang, *Chem. Lett.* **34**, 762 (2005)
120. S.L. Li, K.J. Jiang, K.F. Shao, L.M. Yang, *Chem. Commun.* 2792 (2006)
121. D.P. Hagberg, T. Edvinsson, T. Marinado, G. Boschloo, A. Hagfeldt, L. Sun, *Chem. Commun.* 2245 (2006)
122. P. Qin, X. Yang, R. Chen, L. Sun, T. Marinado, T. Edvinsson, G. Boschloo, A. Hagfeldt, *J. Phys. Chem. C* **111**, 1853 (2007)
123. R. Chen, X. Yang, H. Tian, X. Wang, A. Hagfeldt, L. Sun, *Chem. Mater.* **19**, 1007 (2007)
124. S. Kim, J.K. Lee, S.O. Kang, J. Ko, J.H. Yum, S. Fantacci, F. De Angelis, D. Di Censo, M.K. Nazeeruddin, M. Grätzel, *J. Am. Chem. Soc.* **128**, 16701 (2006)
125. D. Kim, J.K. Lee, S.O. Kang, J. Ko, *Tetrahedron* **63**, 1913 (2007)
126. H. Choi, J.K. Lee, K. Song, S.O. Kang, J. Ko, *Tetrahedron* **63**, 3115 (2007)
127. S. Kim, H. Choi, D. Kim, K. Song, S.O. Kang, J. Ko, *Tetrahedron* **63**, 9206 (2007)
128. X.H. Zhang, C. Li, W.B. Wang, X.X. Cheng, X.S. Wang, B.W. Zhang, *J. Mater. Chem.* **17**, 642 (2007)
129. A. Burke, L. Schmidt-Mende, S. Ito, M. Grätzel, *Chem. Commun.* 234 (2007)
130. K. Hara, Y. Tachibana, Y. Ohga, A. Shinpo, S. Suga, K. Sayama, H. Sugihara, H. Arakawa, *Sol. Energy Mater. Sol. Cells* **77**, 89 (2003)
131. K. Hara, T. Sato, R. Katoh, A. Furube, Y. Ohga, A. Shinpo, S. Suga, K. Sayama, H. Sugihara, H. Arakawa, *J. Phys. Chem. B* **107**, 597 (2003)
132. K. Hara, M. Kurashige, Y. Dan-oh, C. Kasada, A. Shinpo, S. Suga, K. Sayama, H. Arakawa, *New J. Chem.* **27**, 783 (2003)
133. K. Hara, Y. Dan-oh, C. Kasada, Y. Ohga, A. Shinpo, S. Suga, K. Sayama, H. Arakawa, *Langmuir* **20**, 4205 (2004)

134. K. Hara, T. Sato, R. Katoh, A. Furube, T. Yoshihara, M. Murai, M. Kurashige, S. Ito, A. Shinpo, S. Suga, H. Arakawa, *Adv. Funct. Mater.* **15**, 246 (2005)
135. K. Hara, Z.S. Wang, T. Sato, A. Furube, R. Katoh, H. Sugihara, Y. Dan-oh, C. Kasada, A. Shinpo, S. Suga, *J. Phys. Chem. B* **109**, 15476 (2005)
136. Z.S. Wang, K. Hara, Y. Dan-oh, C. Kasada, A. Shinpo, S. Suga, H. Arakawa, H. Sugihara, *J. Phys. Chem. B* **109**, 3907 (2005)
137. N. Koumura, Z.S. Wang, S. Mori, M. Miyashita, E. Suzuki, K. Hara, *J. Am. Chem. Soc.* **128**, 14256 (2006)
138. Z.S. Wang, Y. Cui, K. Hara, Y. Dan-oh, C. Kasada, A. Shinpo, *Adv. Mater.* **19**, 1138 (2007)
139. Z.S. Wang, Y. Cui, Y. Dan-oh, C. Kasada, A. Shinpo, K. Hara, *J. Phys. Chem. C* **111**, 7224 (2007)
140. Y. Kurashige, T. Nakajima, S. Kurashige, K. Hirao, *J. Phys. Chem. A* **111**, 5544 (2007)
141. R. Katoh, A. Furube, K. Hara, S. Murata, H. Sugihara, H. Arakawa, M. Tachiya, *J. Phys. Chem. B* **106**, 12957 (2002)
142. F. Cao, G. Oskam, G.J. Meyer, P.C. Searson, *J. Phys. Chem.* **100**, 17021 (1996)
143. G. Schlichthörl, S.Y. Huang, J. Sprague, A.J. Frank, *J. Phys. Chem. B* **101**, 8141 (1997)
144. L. Dloczik, O. Ieperuma, I. Lauermaann, L.M. Peter, E.A. Ponomarev, G. Redmond, N.J. Shaw, I. Uhlendorf, *J. Phys. Chem. B* **101**, 10281 (1997)
145. L.M. Peter, K.G.U. Wijayantha, *Electrochem. Commun.* **1**, 576 (1999)
146. S. Nakade, M. Matsuda, S. Kambe, Y. Saito, T. Kitamura, T. Sakata, Y. Wada, H. Mori, S. Yanagida, *J. Phys. Chem. B* **106**, 10004 (2002)
147. S. Nakade, T. Kanzaki, W. Kubo, T. Kitamura, Y. Wada, S. Yanagida, *J. Phys. Chem. B* **109**, 3480 (2005)
148. J. Bisquert, V.S. Vikhrenko, *J. Phys. Chem. B* **108**, 2313 (2004)
149. T. Oekermann, Y. Yoshida, H. Minoura, K.G.U. Wijayantha, L.M. Peter, *J. Phys. Chem. B* **108**, 8364 (2004)
150. J. Nelson, R.E. Chandler, *Coord. Chem. Rev.* **248**, 1181 (2004)
151. K. Hara, K. Miyamoto, Y. Abe, M. Yanagida, *J. Phys. Chem. B* **109**, 23776 (2005)
152. O. Kohle, M. Grätzel, A.F. Meyer, T.B. Meyer, *Adv. Mater.* **9**, 904 (1997)
153. B. Durham, J.V. Casper, J.K. Nagle, T.J. Meyer, *J. Am. Chem. Soc.* **104**, 4803 (1982)
154. M. Amirasr, M.K. Nazeeruddin, M. Grätzel, *Thermochim. Acta* **348**, 105 (2000)
155. R. Grünwald, H. Tributsch, *J. Phys. Chem. B* **101**, 2564 (1997)
156. H.T. Nguyen, H.M. Ta, T. Lund, *Sol. Energy Mater. Sol. Cells* **91**, 1934 (2007)
157. R. Kern, N. van der Burg, G. Chmiel, J. Ferber, G. Hasenhindl, A. Hinsch, R. Kinderman, J. Kroon, A. Meyer, T. Meyer, R. Niepmann, J. van Roosmalen, C. Schill, P. Sommeling, M. Späth, I. Uhlendorf, *Opto-Electronics Rev.* **8**, 284 (2000)
158. H. Pettersson, T. Gruszecki, *Sol. Energy Mater. Sol. Cells* **70**, 203 (2001)

Fabrication of Charge Carrier Paths for High Efficiency Cells

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Abstract Directions to high efficiency dye-sensitized solar cells (DSC) are discussed. In order to increase efficiencies for DSCs, effective light harvesting and efficient charge collection from charge separation interfaces are required. In this report, we discuss hybrid cells consisting of two-dye-stained TiO_2 layers in order to harvest light with wide range of wavelength. The hybrid structure was prepared by staining TiO_2 layers under a pressurized CO_2 condition. In addition, surface passivation of dye molecules under pressurized CO_2 atmosphere is discussed. The surface passivation increased electron diffusion coefficients and made the electron lifetime longer, resulting in increases in short-circuit current (J_{sc}) and open-circuit voltage (J_{sc}). Ion-path was introduced into quasi-solidified media by use of surface-modified straight nanopores of porous alumina. The fabrication of charge carrier paths such as electron-paths and ion-paths increased photovoltaic properties for DSCs.

10.1 Introduction

Photoconversion efficiencies for dye-sensitized solar cells (DSC) have been reported to reach 10–11% [1] which is almost the same as that of amorphous Si type solar cells. The next target of the efficiency has been set to be 15%. In order to increase the efficiency, we focused on improving light harvesting and charge collections. Figure 10.1 shows a working principle of DSCs. Electrons of dye molecules are excited by light exposure, followed by injected into TiO_2 layers. These electrons diffuse in TiO_2 layers by hopping electron traps. On the counter electrode, iodine receives these electrons from the counter electrode by the aid of Pt catalysts attached on the electrode to form iodide. The iodide diffuses in an electrolyte solution and collides with the oxidized Ru(III) dye molecule and gives electrons to the Ru dye. Decrease in photovoltaic properties is brought about by back electron transfers from electrons in TiO_2 layers to iodine or oxidized Ru(III) dye molecules. The interface of the TiO_2 /dye/electrolyte is a charge-separation area. In order to increase the efficiency, how to collect charges from the charge-separation area is crucial.

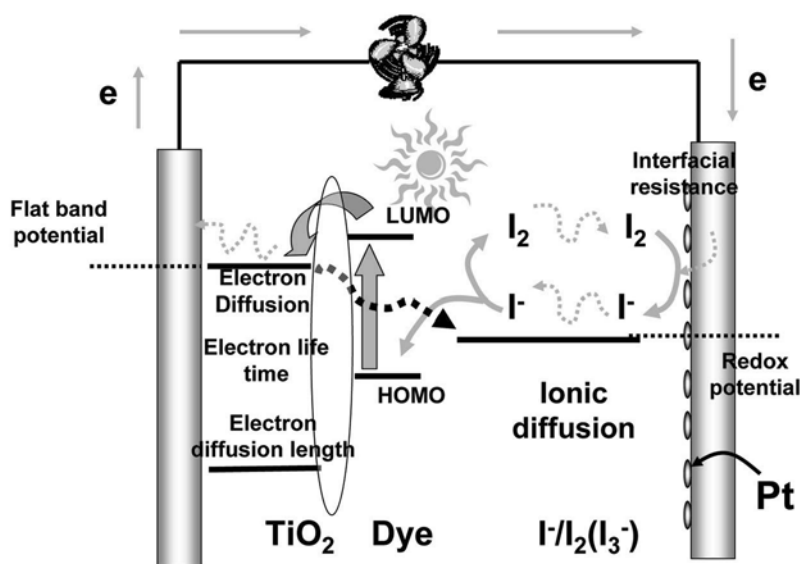


Fig. 10.1. Working principle of DSCs

In this chapter, we focus on the fabrication of charge path (electron-paths and ion-paths) which is brought about by surface modifications of nano- TiO_2 surfaces as well as light harvesting. Figure 10.1 also shows parameters which determine photovoltaic properties. To know the relationship between these parameters and photovoltaic properties are very important.

10.2 Fabrication of Electron-Paths

Efficient light harvesting is one of the most crucial items to prepare high efficiency DSCs. In order to extend absorption of dyes to near-IR region, various Ru dyes [2–5] and organic dyes [6–9] have been reported for dye-sensitized solar cells (DSC). Among them, (*cis*-di(thiocyanato)-*N,N'*-bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II)) (N_3 dye) and $(\text{C}_4\text{H}_9)_4\text{N}_3(\text{Ru}(\text{Htcterpy}))(\text{NCS})_3$ (tcterpy=4,4',4''-tricarboxy-2,2',2''-terpyridine) (black dye) are the representative dyes. The latter has visible absorption extending into near-IR region up to 900 nm and 10.4% efficiency has been reported [10, 11]. Dye molecules are adsorbed on porous TiO_2 layers by dipping the substrate into a dilute dye solution. However, staining the surface of the highly porous TiO_2 layers was not easy because dye molecules are difficult to diffuse into these nanopores. It has been reported that the diffusion rate of molecules in supercritical CO_2 fluid is 10^{-7} – $10^{-8} \text{ m}^2/\text{s}$ which is 10 times higher than that in liquid phase [12]. This prompted us to stain the nanoporous TiO_2 surface in supercritical CO_2 fluid [13]. In this chapter, we use a word “pressurized CO_2 ”

instead of “supercritical CO_2 ” because it was difficult to determine exactly whether or not the reaction always proceeded under supercritical CO_2 conditions. Bando and her coworkers used supercritical CO_2 to stain organic dyes (Eosin Y) on porous TiO_2 layers. They have reported improved photovoltaic performances. However, the photocurrent was low (3.5 mA/cm^2) [14].

Figure 10.2 shows the relationship between the dipping time and the amount of dyes adsorbed on a porous TiO_2 layer when the substrate was dipped into a black-dye solution [13]. The dye-uptake on TiO_2 layer increased gradually and it took 100 h for the curve to level off. On the other hand, the dye uptake on a TiO_2 layer swiftly occurred in the pressurized CO_2 atmosphere and completed within 2 h. Figure 10.3 shows the photovoltaic properties for DSCs prepared by a dipping process and a CO_2 process. Open-circuit voltage

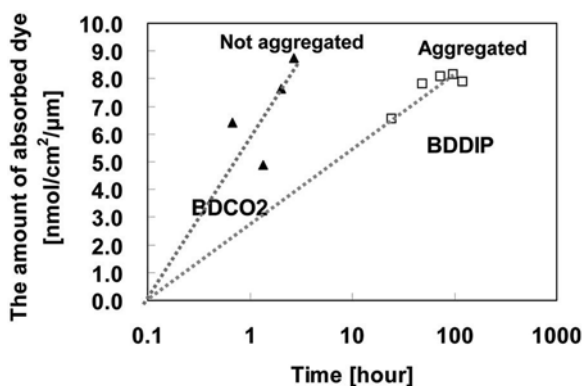


Fig. 10.2. Relationship between the amount of dye uptake and adsorption time

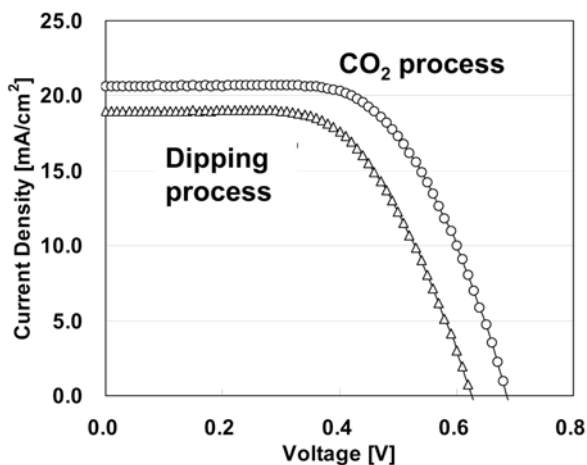


Fig. 10.3. Photovoltaic properties for cells prepared by CO_2 and dipping processes

(V_{oc}) and short-circuit voltage (J_{sc}) for the cell prepared by the CO_2 process were higher than those prepared by a dipping process. In order to clarify the reason, electron lifetime and electron diffusion coefficient in the porous TiO_2 layer were measured. These results were summarized in Figs. 10.4 and 10.5. The electron diffusion coefficient for the cell prepared by the CO_2 process was higher and the electron lifetime was longer. It has been reported that TiO_2 surfaces have various electron surface states which disturb electron diffusions [15–18]. In addition, it has been reported that the surface trap becomes a center for the charge recombination [15–18]. We have already reported that the surface states of TiO_2 layers can be evaluated by measuring thermally stimulated current (TSC) which is associated with trap distributions [19]. After

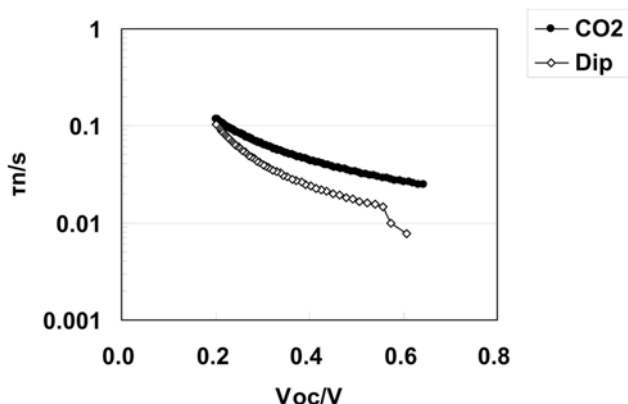


Fig. 10.4. Electron lifetime for cells prepared by pressurized CO_2 process and dipping process

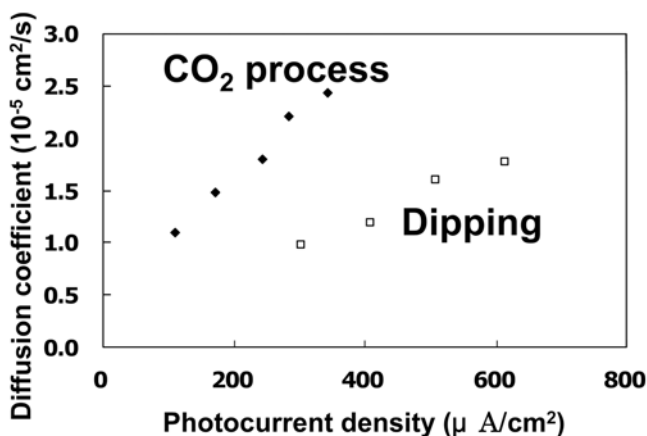


Fig. 10.5. Electron coefficient for cells prepared by pressurized CO_2 process and dipping process

the TiO_2 surface was covered with dye molecules, the TSC for the TiO_2 layer decreased, supporting strongly the explanation that the surface state of the TiO_2 was passivated by the adsorption of the dye molecule [19]. The increase in V_{oc} and J_{sc} of the cell prepared by the CO_2 process can be explained by the better coverage of TiO_2 surface with black-dye molecules, because the black dye diffuses into tiny pores in the pressurized CO_2 condition. Black dye passivates effectively the surface states of TiO_2 prepared under the pressurized CO_2 condition, which aids to make electron diffusion paths in TiO_2 layers.

10.3 Suppression of Black-Dye Aggregation in a Pressurized CO_2 Atmosphere

Another interesting phenomenon on DSCs prepared by the pressurized CO_2 process is the fact that black-dye aggregation was suppressed. Black dye is commonly adsorbed with co-adsorbents such as deoxycholic acid (DCA) in order to suppress black-dye aggregation [11, 14, 17]. It has been reported that dye aggregation decreases photovoltaic performances and dye-aggregation inhibitors improve the photovoltaic performances for the cell [10]. When a TiO_2 substrate was dipped in the black-dye solution, the absorption peak of stained TiO_2 electrode blue shifted gradually and peaks of 520–530 nm increased. Considering the fact that the blue shift was not observed in the presence of an aggregation inhibitor (deoxycholic acid), it is reasonable to explain that the shift is associated with the black-dye aggregation. Even when the dye was adsorbed on a porous TiO_2 electrode in the pressurized CO_2 condition for 2 h, the blue shift was not observed, suggesting that the dye aggregation was also suppressed under the pressurized CO_2 condition. The black-dye concentration dissolved in a pressurized CO_2 liquid was 0.87×10^{-4} M at 10 MPa and 0.53×10^{-4} M at 15 MPa respectively, which was extremely lower than that used for the dipping condition (3×10^{-4} M).

It was found that the reaction rate between black-dye molecules and TiOHs on TiO_2 layers was much faster in a pressurized CO_2 condition than that in a dipping condition by measuring visible spectra (615 nm) of a stained TiO_2 plate. Absorption of black dye on the TiO_2 plate occurred swiftly and the amount was saturated within 10 min under the pressurized CO_2 condition. However, the black-dye uptake occurred gradually during 60 min in the dipping condition. It has been reported that TiOHs of the TiO_2 surface react with CO_2 molecules under the pressurized CO_2 condition to form Ti-O-CO-O linkages and the linkage disappears again to form Ti-OH and CO_2 at atmospheric pressure [21]. It is reasonable to explain that the reaction between Ti-O-CO-O- and HOCO-dye molecules occurs swiftly than that between Ti-OH and HOCO-dye because of the increased negativity of the Ti atom, namely, TiO_2 surface is activated under the pressurized CO_2 condition.

Considering these experimental results, the higher photovoltaic performance of DSCs prepared under a pressurized CO_2 condition is explained as

follows. In the pressurized CO_2 fluid, black dye is highly diluted and the dye aggregation is retarded. In spite of the diluted dye concentration, the black-dye uptake occurs swiftly, because the dye reacts with Ti-O-CO-O on TiO_2 surface swiftly. Because of the higher diffusion rate of the dye molecules under the pressurized CO_2 condition, dye molecules diffuse swiftly to the inner part of the pores of the TiO_2 layers. The dye coverage on the TiO_2 layer completes swiftly, which retards additional dye adsorption causing aggregation. When the dye concentration is low in the dipping process, it would take long time to obtain the good coverage by black-dye molecules, which would cause in turn dye aggregation.

10.4 Two-Layer TiO_2 Structure for Efficient Light Harvesting

In order to increase photo-conversion efficiency for DSCs, sunlight with wide range of wavelength has to be harvested by dye molecules. DSCs stained by mixed dye solution have been already reported [22]. The cell we are aiming at is shown in Fig. 10.6. The cell consists of a two-dye layer (A and B) and a three-dimensional porous Ti or W electrode. It is very difficult to prepare the two-layer structure by dipping the porous TiO_2 substrate merely in dye solutions. We found that a pressurized CO_2 process makes it possible. To begin with, TiO_2 substrate was stained with dye A in the pressurized CO_2 condition. At this moment, the half-top of the substrate was stained by the dye A. Then, the substrate was stained by dye B which covers the rest of the unstained TiO_2 layer. We compared two type of DSC, namely, a two-dye layer

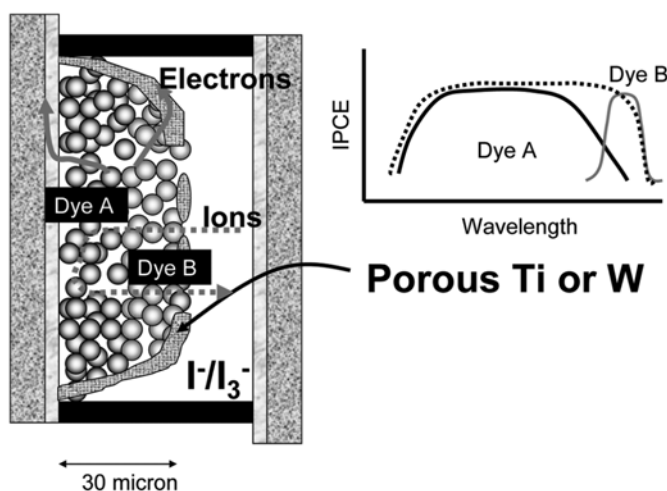


Fig. 10.6. Three-dimensional TiO_2 electrode consisting of two-dye layer and three-dimensional porous Ti or W electrode

structure (two-layer type) and a mixed dye structure (cocktail type). When black dye was mixed with dyes with absorption edge having more than 700 nm (cocktail type), the efficiency decreased, probably, because of the unfavorable dye aggregations or energy transfers. However, the decrease in efficiency was not observed for two-layer type cells. This shows that the two-layer type cell has high potential for harvesting wide range of light by using IR dyes and visible dyes. For example, a two-layer structure consisting of black dye and NK3705 (Hayashibara Co. Ltd.) was J_{sc} : 21.8 mA/cm², V_{oc} : 0.70 V, which was higher than that of a cell stained with black dye only (J_{sc} : 20.4 mA/cm², V_{oc} : 0.70 V) and that of a cell stained with NK3705 dye only (J_{sc} : 4.2 mA/cm², V_{oc} : 0.62 V). An interesting point is that the V_{oc} (0.70 V) of the cell consisting of the two-layer structure was not decreased in spite of the low V_{oc} (0.62 V) of the cell stained by NK3705 dye only. The details are reported elsewhere [23, 24].

When a cell thickness exceeds 30 μ m, it is expected that electron collections from the top of the TiO₂ layer to the bottom transparent conductive oxide layers (TCO layer) become difficult. In order to collect the insufficient electron, we prepared three-dimensional electrode shown in Fig. 10.6. The problem was the thickness of Ti or W electrode because more than 150 nm thickness of Ti or W films were needed in order to obtain surface resistivity less than 10 ohm/square. Thick sputtered Ti or W electrodes covered the whole of the porous TiO₂ electrode and prevented the smooth diffusion of I₃⁻/I⁻. We solved the diffusion problem by using porous Ti or W three-dimensional electrodes. The preparation of thick and porous Ti electrode was not easy. The difficulty was overcome by burying various tetrapod-type ZnO nano-materials in the Ti layer, followed by washing away the ZnO nano-materials [24]. J_{sc} for DSC consisting of TCO and W electrode was 17.5 mA/cm², which was higher than 16 mA/cm² for DSC consisting of only TCO.

10.5 TCO-Less All-Metal Electrode-Type DSC

Transparent conductive oxide-layer-less DSCs (TCO-less DSC) have been studied [25, 26] because TCO glass is one of the most expensive staffs. Figure 10.7 shows a TCO-less DSC structure consisting of all-metal electrodes we have reported [24]. Figure 10.7 also shows I - V curve and the efficiency was 7.43% which was almost the same as that for a DSC consisting of TCO glass. The results show that electrons are really collected from the three-dimensional porous electrode shown in Fig. 10.6. In addition, the porous Ti electrode opened a way to fabricating high-efficiency TCO-less DSC.

10.6 Ion-Path in Quasi-Solid Medium

Solidification of electrolytes is one of crucial research items for DSCs [27–31]. Solidification prevents ionic diffusions and decreases photovoltaic performances for DSCs. The decrease in the photovoltaic performances

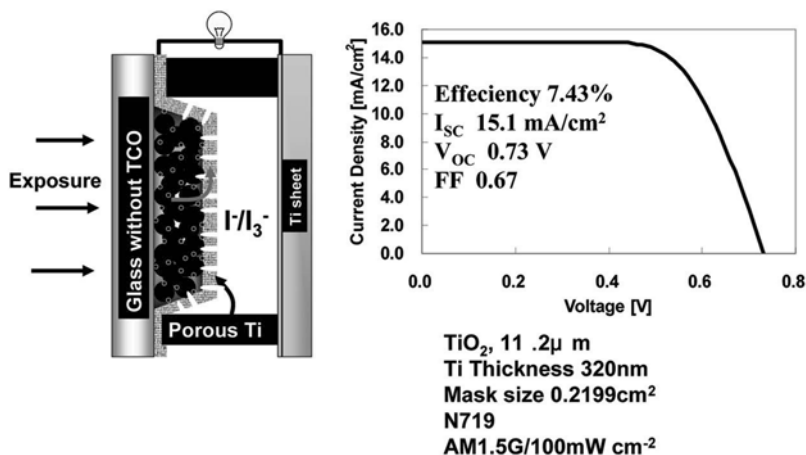


Fig. 10.7. Photovoltaic properties for TCO-less-DSC (all metal electrode)

becomes serious when the content of electro-inactive solidification materials increases and cells are close to all solid-type DSCs. We solved the problem by fabricating ion-paths in the solidified electrolytes [32, 33], where, I^-/I_3^- species are concentrated and are carried by Grötthuss mechanism. Figure 10.8 shows the DSC structure we proposed (b). A high-charge carrier concentration area is needed between TiO_2 layer and counter electrode (Fig. 10.8B-2). On the contrary, charge carrier concentration has to be low in nanopores of TiO_2 layer (Fig. 10.8B-1); otherwise, back electron transfer (dark current) increases (Fig. 10.8a).

In order to realize Fig. 10.8b structure, we used nanoparticles or nanoporous Al_2O_3 film as electrochemically inactive supporter. Appearance of the former is hard clay and the clay can be pasted on the TiO_2 layer to form the solid B-2 [29]. Figure 10.9 shows DSC structure consisting of porous alumina films. In order to concentrate the redox species in Al_2O_3 , the surface of these alumina nanopore walls was chemically modified with imidazolium iodide moiety consisting of long alkyl groups (C12 in Fig. 10.9). The fact that I_2 is concentrated in alumina pore wall was observed by using adsorption experiments using Raman and UV-VIS absorption spectroscopy. Figure 10.9 shows photovoltaic properties for the quasi-solid DSCs consisting of the surface-modified Al_2O_3 films. J_{sc} increased after the solidification. These are very interesting results because photovoltaic properties usually decrease after quasi-solidification.

The cell consists of a porous alumina surface modified with PEDOT-PSS (conductive polymer) are shown in Fig. 10.10. Charge carriers in the film are electron and the carrier concentration is higher in the porous alumina film. On the contrary, charges are carried ionically by iodine/iodide redox species in the TiO_2 nanopores. The cell efficiency after solidification was almost the same as

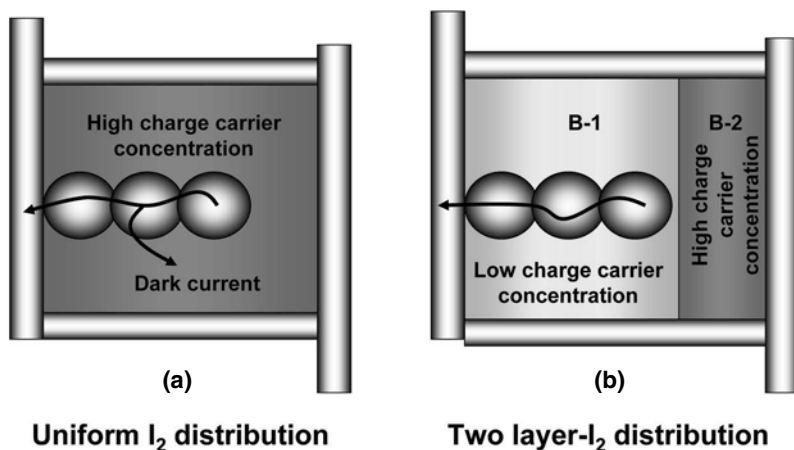
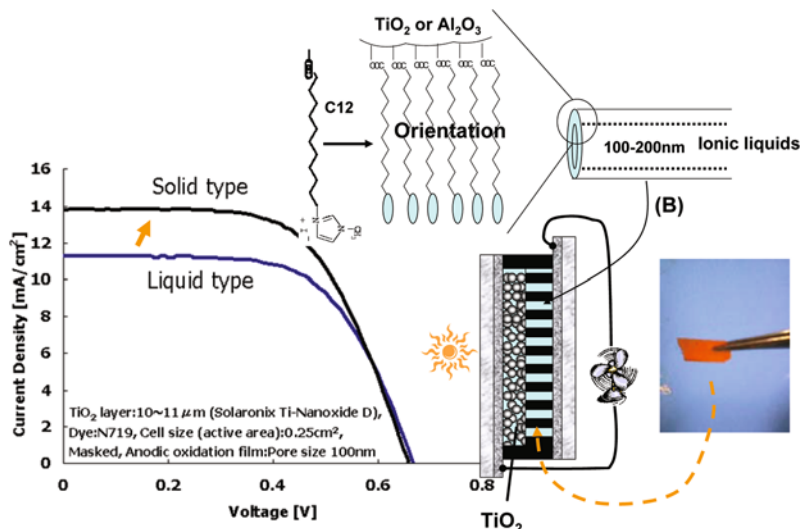


Fig. 10.8. Concept for high-efficiency quasi-solid-DSC consisting of two carrier concentration regions



that before solidification. If pores in TiO_2 were fully filled with PEDOT-PSS and iodine/iodide redox species were not added, back electron transfer from the TiO_2 layer to the PEDOT-PSS occurs very swiftly and the photovoltaic property decreased. The hybrid cell consisting of ionic and electronic-charge carrier layers proved again the generality of the effectiveness of the cell structure shown in Fig. 10.8.

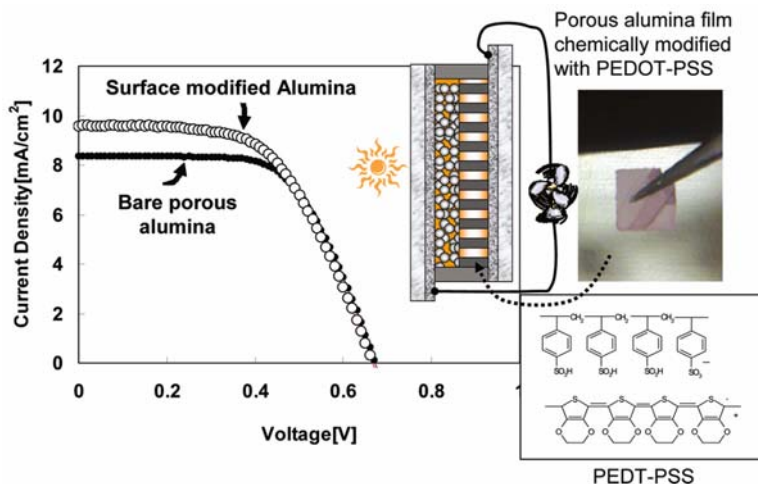


Fig. 10.10. Photovoltaic properties for quasi-solid-DSC consisting of surface modified Al_2O_3 films with PEDOT-PSS

10.7 Summary

Directions to high-efficiency DSCs were proposed from the viewpoint of charge collection and light harvesting. In order to harvest light with wide range of wavelength, DSCs with two-layer TiO_2 layers were prepared for the first time. The cell was prepared by a pressurized CO_2 process, where TiO_2 surface was activated and the adsorption of dye molecules occurred swiftly from the top of the TiO_2 layers. It was proved that the cell with two-layer TiO_2 layers had higher efficiency than each cell stained by single dye. Electron-paths in TiO_2 layers were prepared by staining a TiO_2 layer under a pressurized CO_2 condition, where surface states on the TiO_2 surface was passivated better than that prepared in a dipping condition and dye aggregation was suppressed. Ion-paths in quasi-solidified media were fabricated by surface modification of nanoparticles or porous alumina on which iodine and iodide were concentrated. Hybrid charge carrier media consisting of conductive polymers (PEDOT-PSS) and iodide/iodine redox species was proved to exhibit high efficiencies after quasi-solidification. A two-layer media consisting of high-charge carrier area and low-charge carrier area, in which the former has high conductivity in the bulk area and the latter suppress the back electron transfer reaction, was proposed as high-efficiency quasi-solid state DSCs.

References

1. B. O'Regan, M. Grätzel, *Nature* **353**, 737 (1991)
2. M.K. Nazeerudin, A. Kay, I.I. Rodicio, R. Humphry-Baker, E. Muller, P. Liska, N. Vlachopoulos, M. Grätzel, *J. Am. Chem. Soc.* **115**, 6382 (1993)

3. T. Renouard, R.A. Fallahpour, M.K. Nazeeruddin, R. Humphry-Baker, S.I. Gorelsky, A.B.P. Lever, M. Grätzel, *Inorg. Chem.* **41**, 367 (2002)
4. R. Amadelli, R. Argazzi, C.A. Bignozzi, F. Scandola, *J. Am. Chem. Soc.* **112**, 7099 (1990)
5. Z.S. Wang, C.H. Huang, B.W. Zhang, Y.Y. Hou, P.H. Xie, H.J. Qian, K. Ibrahim, *New J. Chem.* **24**, 567 (2000)
6. Z.S. Wang, F.Y. Li, C.H. Huang, L. Wang, M. Wei, L.P. Jim, N.Q. Li, (2000) *J. Phys. Chem. B* 104: 9676.
7. Z.S. Wang, K. Hara, Y. Dan-oh, C. Kasada, A. Shinpo, S. Suga, H. Arakawa, H. Sugihara, *J. Phys. Chem. B* **109**, 3907 (2005)
8. K. Hara, M. Kurashige, Y. Dan-oh, C. Kasada, A. Shinpo, S. Suga, K. Sayama, H. Arakawa, *New J. Chem.* **27**, 783 (2003)
9. Y.G. Kim, J. Walker, L.A. Samuelson, J. Kumar, *Nano Lett.* **3**, 523 (2003)
10. M.K. Nazeeruddin, P. Pechy, T. Renouard, S.M. Zakeeruddin, R. Humphry-Baker, P. Comte, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G.B. Deacon, C.A. Bignozzi, M. Grätzel, *J. Am. Chem. Soc.* **123**, 1613 (2001)
11. Z.S. Wang, T. Yamaguchi, H. Sugihara, H. Arakawa, *Langmuir* **21**, 4272 (2005)
12. P.G. Jessop, T. Ikariya, R. Noyori, *Nature* **368**, 231 (1994)
13. Y. Ogomi, S. Sakaguchi, T. Kado, M. Kono, Y. Yamaguchi, S. Hayase, *J. Electrochem. Soc.* **153**(12), A2294 (2006)
14. K.K. Bando, Y. Mitsuzuka, M. Sugino, H. Sugihara, K. Sayama, H. Arakawa, *Chem. Lett.* 853 (1999)
15. S. Nakade, Y. Saito, W. Kubo, T. Kanzaki, T. Kitamura, Y. Wada, S. Yanagida, *Electrochem. Commun.* **5**, 804 (2003)
16. S. Sakaguchi, H. Ueki, T. Kato, T. Kado, R. Shiratuchi, W. Takashima, K. Kaneto, S. Hayase, *J. Photochem. Photobio. A. Chem.* **164**, 117 (2004)
17. T. Yoshida, T. Oekermann, K. Okabe, D. Schlettwein, K. Funabiki, H. Minoura, *Electrochem.* **70**, 470 (2002)
18. F. Fabregat-Santiago, J. García-Cañadas, E. Palomares, J.N. Clifford, S.A. Haque, J.R. Durrant, G. Garcia-Belmonte, J. Bisquert, *J. Appl. Phys.* **96**, 6903 (2004)
19. Y. Noma, T. Kado, D. Ogata, Y. Hara, S. Hayase, *Jpn. J. Appl. Phys.* **47**, 505 (2008)
20. L.M. Peter, K.G.U. Wijayatha, *Electrochim. Acta* **45**, 4543 (2000)
21. W. Gu, C.P. Tripp, *Langmuir* **22**, 5748 (2006)
22. H. Otaka, M. Kira, K. Yano, S. Ito, H. Mitekura, T. Kawatam, F. Matsui, *J. Photochem. Photobio. A: Chem.* **164**, 67 (2004)
23. Y. Ogomi, S. Sakaguchi, S. Hayase, *Proceeding of SPIE* (San Diego, 2007).
24. Y. Kashiwa, Y. Yoshida, S. Hayase, *Appl. Phys. Lett.* **92**, 033308 (2008)
25. J.M. Kroonl et al., *Prog. Photovolt: Res. Appl.* **13**, 333 (2005)
26. N. Fuke, A. Fukui, Y. Chiba, R. Komiya, R. Yamanaka, L. Han, *Jpn. J. Appl. Phys.* **46**, L420 (2007)
27. K. Tennakone, G.K.R. Senadeera, V.P.S. Perera, I.R.M. Kottegoda, L.A.A. De Silra, *Chem. Mater.* **11**, 2474 (1999)
28. P. Wang, S.M. Zakeeruddin, J. Moser, M.K. Nazeeruddin, T. Sekiguchi, M. Gratzel, *Nat. Mater.* **2**, 402 (2003)
29. W. Kubo, K. Murakoshi, T. Kitamura, S. Yoshida, M. Haruki, K. Hanabusa, H. Shirai, Y. Wada, S. Yanagida, *J. Phys. Chem. B* **105**, 12809 (2001)
30. P. Wang, S.M. Zakeeruddin, I. Exnar, M. Grätzel, *Chem. Commun.* **2002**, 2972 (2002)

31. P. Wang, S.M. Zakkeruddin, P. Comte, I. Exnar, M. Grätzel, *J. Am. Chem. Soc.* **125**, 1166 (2003)
32. T. Kato, T. Kado, S. Tanaka, A. Okazaki, S. Hayase, *J. Electrochem. Soc.* **153**, A626 (2006)
33. T. Kato, S. Hayase, *J. Electrochem. Soc.* **154**, B112 (2007)

Environmental Cleaning by Molecular Photocatalysts

D. Wöhrle, M. Kaneko, K. Nagai, O. Suvorova, and R. Gerdes

Abstract Visible light absorbing organic photosensitizers and photocatalysts active in photodegradation of pollutants were described in this chapter. An important reactive is singlet oxygen obtained by energy transfer from the photoexcited sensitizer to triplet oxygen (*photosensitized oxidative degradation*). The other possibility when the photosensitizer is on the surface of inorganic semiconductors like TiO_2 is formation of superoxide radicals (*photocatalytic oxidative degradations*). The degree of degradation depending on the reactivity of the pollutants was discussed against these reactive species. It was shown that visible light photons have sufficient energy which can be transformed into highly reactive species of oxygen for degradation of pollutants. Technical applications were shown. In general the use of solar visible light is relatively open field for oxidative degradation of pollutants. In the Sect. 11.2 oxidative methods for photodegradation of pollutants were described. At first a short overview on UV processes for water cleaning was given in the Sect. 11.2.1. More details of photodegradation of pollutants with oxygen by the visible light were described in the Sect. 11.2.2.

Visible light decomposition of ammonia to dinitrogen in the presence of a photosensitizer based on electron relay (photo-induced electron transfer) was shown in the Sect. 11.3. The photodecomposition of aqueous ammonia with visible light into N_2 was achieved by a photocatalytic system consisting of a sensitizer, an electron mediator, and an electron acceptor (O_2) as an artificial nitrogen cycle.

Finally, in the Sect. 11.4 the use of thin films of visible light absorbing organic semiconductors for the photodecomposition of pollutants was described. Thin films of an organic *p*-conductor and an organic *n*-conductor on Nafion were active by irradiation with visible light in the photocatalytic oxidation of amines.

11.1 Introduction

Visible light absorbing organic photosensitizers or photocatalysts are in several investigated cases surprisingly active in the photodegradation of pollutants. One important reactive species after excitation of a photosensitizer either monomolecular in solution or polymer bound is singlet oxygen obtained by energy transfer from the excited photosensitizer to triplet oxygen

(*photosensitized oxidative degradation*). The other possibility when the photosensitizer is on the surface of inorganic semiconductors like TiO_2 is after excitation of the photosensitizer mainly the formation of superoxide radicals (*photocatalytic oxidative degradations*). The degree of degradation depends, of course, on the reactivity of the pollutants against these reactive species. It is important to point out that photons of visible light have enough energy which can be transformed into highly reactive species of oxygen for degradation of pollutants. Only in few cases up to now technical applications were envisaged (see [40]). Especially the use of visible light of solar radiation is a relatively open field for oxidative degradation of pollutants. Therefore more systematic fundamental research must be carried out. In Sect. 11.2 oxidative methods for photodegradation of pollutants are described. At first, a short overview on different methods of UV processes for water cleaning is given in Sect. 11.2.1. Then in more detail photodegradation of pollutants with oxygen in the visible region of light is described in Sect. 11.2.2.

Further, visible light decomposition of ammonia to dinitrogen in the presence of a photosensitizer is discussed (Sect. 11.3). This is based on an electron relay (photo-induced electron transfer): The photodecomposition of aqueous ammonia with visible light into N_2 by a photocatalytic system consisting of a sensitizer, an electron mediator, and an electron acceptor (O_2). It will be pointed out that by this system the biomass waste problem by using visible light in relevance to treatment of nitrogen compounds as well as ammonia pollutant problem in our daily life could be solved (artificial nitrogen cycle).

Finally, in Sect. 11.4 the use of thin films of visible light absorbing organic semiconductors for the photodecomposition of pollutants is envisaged. Thin films of an organic *p*-conductor and an organic *n*-conductor on Nafion are active by irradiation with visible light in the photocatalytic oxidation of amines.

11.2 Oxidative Methods for the Photodegradation of Pollutants in Wastewater

11.2.1 Comparison of Different Methods of UV Processes for Water Cleaning

Water is one component essential for our life, and therefore not only of special interest for scientists and engineers but also but also for economists and many others. Water in the purest form does not exist in the environment and has anomalous solvent properties. In the environment it is contaminated with gases from air, inorganic compounds, and trace elements necessary to use as drinking water. Contaminated drinking water and wastewater contain toxic elements, compounds, and/or microorganisms (bacteria, virus, fungi) in a concentration which is dangerous for human life or the environment (animals, plants, microfauna/flora). Contamination of water results from development of industry and high level of population in some areas contributing

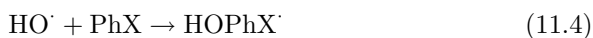
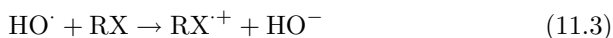
to our standard of life. Chemical production leads to million of tons of unwanted by-products. Because water is essential for our live, efficient methods must be developed to reduce or eliminate toxic pollutants. This is a challenging goal not only for microbiology, because we hope that microorganisms will do the job, but also several compounds are persistent in the environment because they are resistant against microorganisms or oxidations under natural aerobic conditions. In general, two main strategies must be applied: (i) chemical treatment of polluted drinking, surface, and groundwater; and (ii) chemical treatment of wastewater containing biocidal and nonbiodegradable compounds. Used waters of normal anthropogenic origin can be treated in biological treatment stations. Chemical treatment of wastewater must be applied where the capacity of biological treatment stations cannot be adapted due to the growth of regional population and consumption of water. More recent developments in the domain of chemical water treatment have led to oxidative and photooxidative procedures for organic compounds.

Nature is an immense photoreactor with the sun as intensive source of electromagnetic radiation. In this photoreactor, water is the liquid and air the gaseous medium. Consequently, artificial photo-induced and photo-initiated processes in these media were investigated scientifically to remove pollutants from water and air. Based on the results photochemical technologies were developed in the recent decades and are widely employed. In this subsection an overview on some of the reactions in water in the presence of some auxiliary oxidants will be given. This is necessary to point out that new methods are also necessary which use in the presence of oxygen the energy of visible light for excitation. The improved oxidative degradation procedures for organic compounds applying catalytic and photochemical methods are generally referred to advanced oxidation processes (AOP). It has a strong impact on the design and construction of new light sources, photochemical reactors, and the preparation of new photocatalysts. Due to the importance of water cleaning from pollutants immense literature is available, and only some hints for books and reviews are given [1–4].

Common wet oxidation processes are chlorination (disadvantages: toxic chlorine; formation of toxic, carcinogenic, and mutagen compounds possible), ozonization (disadvantages: toxic ozone; high energy consumption for production of ozone; possible toxic side-products and germ carriers), Fenton process – $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ [5] – (disadvantages: acidic pH; high amount of Fe salts), etc.

AOP processes for oxidation of organic pollutants use a combination of UV light and oxidants (H_2O_2 , O_3 , etc.). The degradation is initiated in most cases by generation and subsequent reaction of hydroxyl radicals $\text{HO}\cdot$. After fluorine with an oxidation potential of 3.03 vs. NHE (standard hydrogen electrode), hydroxyl radicals with an oxidation potential of 2.80 V vs. NHE is the most powerful oxidizing agent (for comparison: ozone 2.07, hydrogen peroxide 1.78, permanganate 1.68, and chlorine 1.36 V vs. NHE). The efficiency of oxidative degradation processes are based on the reactivity of radical intermediates, the energy needed to homolyse a given chemical bond and also on

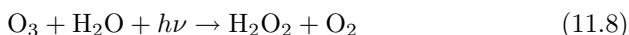
the concentration of dissolved oxygen. Hydroxyl radicals remove at first an hydrogen atom by H-abstraction (11.1). The generated organic radicals form by addition of molecular oxygen peroxy radicals (11.2) which initiate chain reactions of oxidative degradations finally to carbon dioxide, water and inorganic salts. Besides H-abstraction also electron transfer of RX to HO $\cdot$ are possible as another way of oxidative degradation (11.3). Further electrophilic additions can occur (11.4).



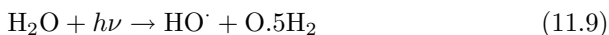
H₂O₂/UV Process: By photolysis of H₂O₂ two hydroxyl radicals per quantum of radiation absorbed are obtained (11.5).



O₃/UV Process: Aqueous solutions saturated with ozone are irradiated with UV light of $\lambda = 254\text{ nm}$. Rates of oxidative degradation are much higher than those when either UV light or ozone is used separately. A two-step process has been proposed involving the light-induced homolysis of ozone and subsequent production of hydroxyl radicals (11.6 and 11.7). It was also observed that photolysis of ozone leads to hydrogen peroxide (11.8) which can further react (11.5). A more promising method is the combination of O₃ and H₂O₂ with UV irradiation.



Vacuum ultraviolet (VUV) Process: This process works with UV light of $\lambda < 190\text{ nm}$ (Xe excimer lamps) where air (oxygen) and water absorb. Excitation in the VUV spectral domain in most cases leads to the homolysis of chemical bonds. VUV photolysis of water is a means of highly efficient generation of hydroxyl radicals (11.9) attacking then the dissolved or dispersed substrate. Also, for example, chlorinated and fluorinated hydrocarbons are readily attacked, and the formed radicals initiate further oxidative degradations.



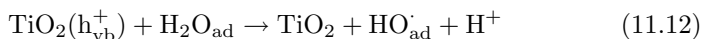
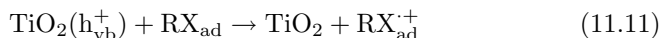
Practically any organic contaminant that is reactive with a hydroxyl radical can potentially be treated. A wide variety of organic and explosive contaminants are susceptible to destruction by UV oxidation, including petroleum hydrocarbons, chlorinated hydrocarbons used as industrial solvents and

cleaners, and ordnance compounds such as TNT, RDX, and HMX. In many cases, chlorinated hydrocarbons that are resistant to biodegradation may be effectively treated by UV/oxidation. Typically, easily oxidizable organic compounds are those with double bonds (e.g., TCE, PCE, vinyl chloride) as well as simple aromatic compounds (e.g., toluene, benzene, xylene, and phenol), and they are rapidly destroyed in UV oxidation processes.

Limitations of the different UV/oxidation processes are:

- The aqueous stream being treated must provide a good transmission of UV light (high turbidity causes interference). Turbidity does not affect direct chemical oxidation of the contaminant by H_2O_2 or O_3 .
- Free radical scavengers can inhibit the contaminant destruction efficiency. Excessive dosages of chemical oxidizers may act as a scavenger.
- The aqueous stream to be treated by UV oxidation should be relatively free of heavy metal ions (less than 10 mg/L) and insoluble oil or grease to minimize the potential for fouling of the quartz sleeves.
- When UV/O_3 is used on volatile organics, the contaminants may be volatilized (e.g., “stripped”) rather than destroyed. They would then have to be removed from the off-gas by activated carbon adsorption or catalytic oxidation.
- Costs may be higher than competing technologies because of energy requirements.
- Pretreatment of the aqueous stream may be required to minimize ongoing cleaning and maintenance of UV reactor and quartz sleeves.

TiO₂/UV Process: During the recent decades the application of semiconductor photocatalysis for degradation of organic pollutants was largely developed [4, 6]. The main degradation products of chlorinated aromatic oxidations mediated by TiO_2/UV are CO_2 , HCl , and H_2O . TiO_2 is activated in different domains of UV light, compatible also with sunlight activation. Excited TiO_2 exhibit a strong oxidation potential of an electron-depleted valence band (h_{vb}^+ : valence band hole; e_{cb}^- : conduction band electron) 11.10. Then two oxidations can mainly occur: (i) electron transfer from an adsorbed substrate RX results in the formation of a radical cation 11.11, and (ii) by electron transfer from adsorbed water yields hydroxyl radicals 11.12.



The main drawbacks of the TiO_2/UV process are the relatively low quantum yield of ~ 0.05 , limited irradiation zone in a scattering and absorbing heterogeneous medium (recently methods for immobilization of TiO_2 were developed [7, 8]), and recovery of TiO_2 particles. Even that solar radiation on earth in the UV is only $\sim 1.5\%$ ($\sim 45\%$ visible region, ~ 53.5 IR region) the TiO_2/UV process was applied with potential use of solar radiation.

In summary, the conclusion can be made that for a given case of water treatment the most efficient procedure or combination of procedures has to be determined taking into account the pollutant nature, the absorption spectrum, the concentration and reactivity, as well as inhibitory effects of pollutant mixtures and the presence of radical trapping agents as most important parameters. Possible technical solutions may then be found in modular installations which can be adapted and/or combined in accordance with the fundamental rules of photochemical technology and substrate reactivity.

It is now pointed out that it is necessary to develop further methods. Especially the use of visible light including solar radiation ($\sim 45\%$ in the visible region) is a prospective energy-saving alternative. The use of visible light for photooxidative degradation will be treated in the following subsections.

11.2.2 Photodegradation of Pollutants with Oxygen in the Visible Region of Light

Visible light-driven photooxidations are seen under the viewpoint of environmentally friendly or “green” chemistry, taking into account three points of unlimited natural resources: (a) *oxygen (from air)*, (b) *water as solvent*, (c) *use of visible light (also solar radiation)*. A photosensitizer absorbing in the visible region of light and fulfilling some additional presuppositions. Therefore suitable photosensitizers are treated first. Then the reactive oxygen species formed under irradiation in the presence of the photosensitizer will be introduced. Afterwards the degradation of different pollutants will be discussed.

Structure and Photophysical Properties of Photosensitizers Absorbing in the Visible Region of Light

One possibility for photodegradation of pollutants is that the photosensitizer are water soluble which means it should be either negatively or positively charged. Advantageous are heterogeneous photosensitizers because they can easily be separated from the aqueous medium and reused again. Classical commercially available photosensitizers are methylene blue (MB) and rose bengal (RB) [9]. Metal phthalocyanines (MPc) and metal porphyrins (MP; as *ms*-tetraaryl derivatives) bearing, for example, sulfonic acid or quarternized N-groups belong to the more advanced photosensitizers (Fig. 11.1). MPcs ($R = -SO_3H$) with $M = Zn(II), Al(III)OH, Ga(III)(OH)$ are prepared by cyclotetramerization of 4-sulphophthalic acid in the presence of urea and metal salts [10–12] whereas MPcs ($R = -SO_3H$) with $M = Si(IV)(OH)_2, Ge(IV)(OH)_2$ were obtained by the sulfonation of the unsubstituted MPc ($R = H$) [13]. Other negatively, positively, or zwitterionically charged phthalocyanines are described in [10]. Charged tetraarylporphyrins are in general commercially available. For heterogeneous systems in principle coordinative, covalent, or ionic binding at organic polymers or the surface of inorganic carriers is possible. One example is the ionic binding of MPcs ($R = -SO_3H$) at a positively charged

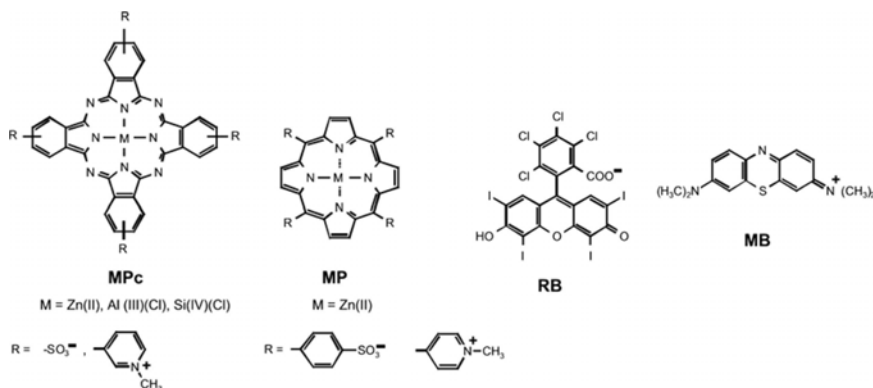


Fig. 11.1. Structures of metal phthalocyanines (MPc), metal ms-tetraarylporphyrins (MP), rose bengal (RB), and methylene blue (MB)

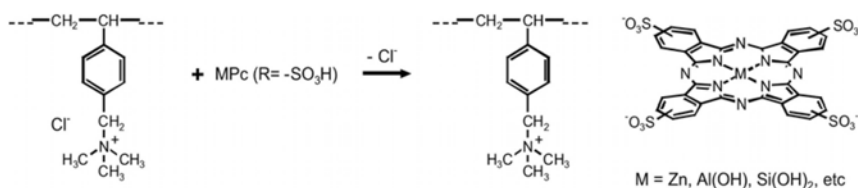


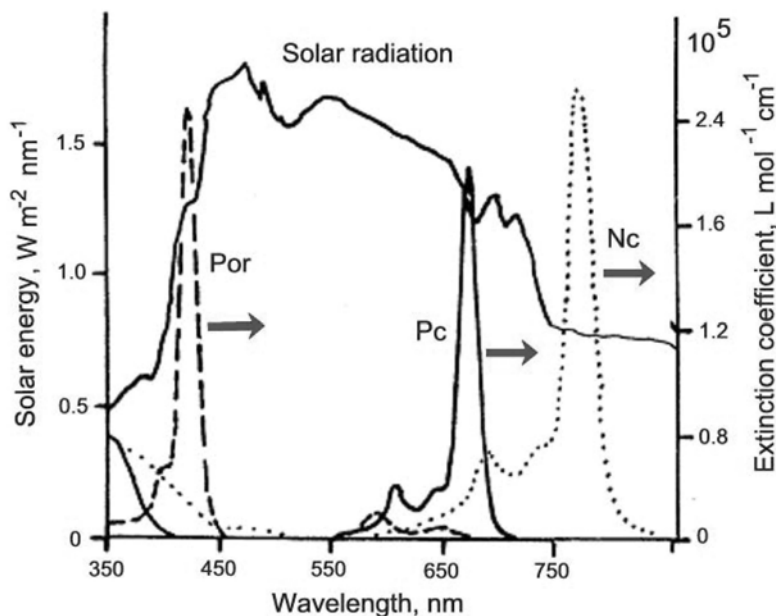
Fig. 11.2. Ionic binding of sulfonated MPcs at an ion exchanger

commercial ion exchanger (Fig. 11.2) [13]. An organic anion exchanger like Amberlite IRA 400 was suspended in an aqueous solution containing sulfonated phthalocyanines with different metal ions. Loadings with metal complexes of $4\text{--}10\text{ }\mu\text{mol g}^{-1}$ were obtained. Other examples for reported ionic binding are at linear soluble poly(vinylbenzyltriethylammonium chloride) or ionenes [14]. For a heterogeneous photocatalytic system the photosensitizer is adsorbed on the surface of an inorganic semiconductor like TiO_2 .

The photophysical properties of the visible light absorbing systems are given in Table 11.1. The first important one is absorption in the visible region of light ($\lambda = 390\text{--}760\text{ nm}$). Figure 11.3 shows exemplarily the absorption spectra (values see Table 11.1) of MPc, MP, and metal naphthalocyanines (MNC) that contains naphthalene rings at the tetraazaporphyrin macrocycle instead of benzene rings in MPc. The most intensive absorptions exhibit high absorption coefficients $\varepsilon > 10^5\text{ L mol}^{-1}\text{ cm}^{-1}$ which means that in the absorbing light region a high amount of energy of the photons is transferred to the excited state of the photocatalysts. The metal ion in the core of the ligand of the MPc or MP is the decisive key if a photoreaction can successfully be carried out under irradiation with visible light in the presence of oxygen [15]. In the case of metal ions with open *d* electron configuration, such as Co(II), Fe(II), Mn(II), the reaction of a substrate with oxygen runs catalytically. Metal-centered binding of the substrate occurs which leads after a subsequent

Table 11.1. Photophysical properties of some monomolecular dissolved photosensitizers

Compound	λ (nm)	Φ_F^a	τ_S^b (ns)	Φ_{ISC}^a	τ_T^b (μ s)	Φ_Δ^c
ZnPc	672	0.30	3.8	0.65	800	0.55
ZnP	418	0.04	2.7	0.88	1,200	0.85
Si(R) ₂ Nc	786			0.30	330	0.30
RB	549	0.11	0.08	0.61	30	0.75
MB	614	0.04	0.4	0.52	450	0.49

^aQuantum yield of fluorescence or ISC of $S_1 \rightarrow T_1$.^bSinglet or triplet life times.^cQuantum yield of singlet oxygen formation.**Fig. 11.3.** UV-Vis spectra of monomolecular dissolved Zn(II) complexes of ms-tetraphenylporphyrin (ZnP), phthalocyanine (ZnPc), and naphthalocyanine (ZnNc) with their extinctions (right side); and solar radiation on earth (AM1) with intensity (left side)

binding/interaction with oxygen to the oxidized substrate. For photosensitized oxidations the MPc and MP contain metal ions with closed p or d electron configuration, such as Mg(II), Al(III), Si(IV), Zn(II). Now, after absorption of visible light the excited metal complex transfers by weak interaction energy to oxygen (type II-reactions, energy transfer). The “free” energy-rich oxygen (singlet oxygen) is then responsible for the oxidation leading to a different oxidized substrate.

After absorption of light by the photosensitizer the excited singlet state is reached first which has a short lifetime in the ns region [16–19] (Table 11.1). In the case of ZnPc a reasonable fluorescence Φ_F of 0.3 is evident. Therefore ZnPc can be used as fluorescence detector. The application of positively charged ZnPcs as fluorescence contrast agent for the cancer B16 pigmented melanoma was described which is better than the commercially applied ALA [20]. With exception of the naphthalocyanine all other photocatalysts transfer with ISC quantum yields of >0.5 the energy to the excited triplet state which has long life times in the ms till μ s range. This energy can be used to generate by energy transfer singlet oxygen.

An important point is the photooxidative stability of the photosensitizer during irradiation under oxygen. For phthalocyanines the mechanism of photooxidation was studied in detail by the authors [21, 22]. For example, in the case of MPcs the energy-rich singlet oxygen reacts as shown by HOMO–LUMO energy calculations with the carbon atoms of the iminoisoin-dolenine units and finally phthalimide results as reaction product. The degradation of MPcs during photooxidations was determined by the decrease of the Q-band at $\lambda \sim 680$ nm in the visual spectrum. The tendency for the decomposition for some charged, water-soluble photosensitizers are in the order MPc ($M = \text{Si(IV)(OH)}_2$, $R = -\text{SO}_3\text{H}$) $<$ MPc($M = \text{Al(III)OH}$, $R = -\text{SO}_3\text{H}$) $<$ MPc($M = \text{Zn(II)}$, $R = -\text{SO}_3\text{H}$) $<$ RB $<$ MB [23]. Other metal phthalocyanines exhibit stabilities between the mentioned metal complexes. Especially the Si complex of Pc on an anion exchanger (Fig. 11.2) is very stable and not decomposing under irradiation. For MPcs the stability is influenced by the kind of substituent [24]. Electron-withdrawing substituents enhance the photooxidative stability whereas electron-donating ones reduce it. Comparing the three macrocyclic metal complexes it was found that MNcs are much less stable compared to MPc and MP [21, 22] which means that MNcs can be not employed as photosensitizer in photooxidation reactions.

Another important point to discuss is aggregation of charged photosensitizer in water. After UV–Vis spectra in aqueous solution, for example, MPcs ($R = -\text{SO}_3\text{H}$) with $M = \text{Zn(II)}$ are strongly aggregating (monomeric MPc at $\lambda \sim 675$ nm, aggregated MPc at $\lambda \sim 640$ nm) whereas MPcs ($R = -\text{SO}_3\text{H}$) with $M = \text{Si(IV)(OH)}_2$ and Ge(IV)(OH)_2 are due to the shielding effect of the substituents at the Si and Ge monomeric dissolved in water. In the aggregated state dissipation of the energy of the excited state occurs. Monomerization is a fundamental prerequisite for the photochemical activity [10, 14, 23]. The aggregated MPcs can be monomerized by adding an oppositely charged detergent as cetyltrimethylammonium chloride (CTAC) to negatively charged MPcs. Also water-soluble, sterically hindered bulk ZnPc is more monomeric, and therefore it is more photoactive [25]. Another possibility for good monomerization is the ionic binding at ion exchangers such as Amberlite (Fig. 11.2).

Reactive Species of Oxygen

The question now is what kind of molecular oxygen is active in visible light-driven photooxidations? In Sect. 11.2.1 it was pointed out that in reactions under UV light under different conditions hydroxyl radicals $\text{HO}^\cdot$ are formed, for example, by homolysis of H_2O or H_2O_2 as the most dominant species for the degradation of pollutants. Then mainly radical reactions occur.

The situation with visible light-absorbing photocatalysts in the presence of oxygen is partly different. One reactive species for monomolecular distributed photocatalysts is *singlet oxygen* ($^1\text{O}_2$). If the photosensitizer is adsorbed on the surface of the semiconductor TiO_2 *superoxide radical* ($\text{HO}_2^\cdot$) are formed as reactive species which can react also to *hydroxyl radicals* ($\text{HO}^\cdot$).

The photooxidations under formation of *singlet oxygen* as one possibility include the following elementary steps 11.13–11.15; for an energy diagram see Fig. 11.4 [10, 18, 19, 26]. Excitation in the absorption region of the photosensitizer yields the excited singlet state ($^1\text{PS}^*$) and then by intersystem crossing (ISC) the excited triplet state ($^3\text{PS}^*$; 11.13; Fig. 11.4) (for photophysical parameters of the photosensitizer see Table 11.1). Then the spin allowed triplet–singlet energy transfer from $^3\text{PS}^*$ to triplet oxygen ($^3\text{O}_2$, $^3\Sigma_g^-$) results in singlet oxygen ($^1\text{O}_2$, $^1\Delta_g$; 11.14) followed by the oxidation of a substrate (Sub; 11.15; type II photooxidation). Such processes are named *photosensitized oxidative degradations*.

Thermodynamically the energy transfer from $^3\text{PS}^*$ to $^3\text{O}_2$ is possible for metal porphyrins (MP) and metal phthalocyanines (MPc) whereas with metal naphthalocyanines (MNc) a thermal equilibrium exists: $E(^1\text{O}_2 - ^3\text{O}_2) = 94.2$,

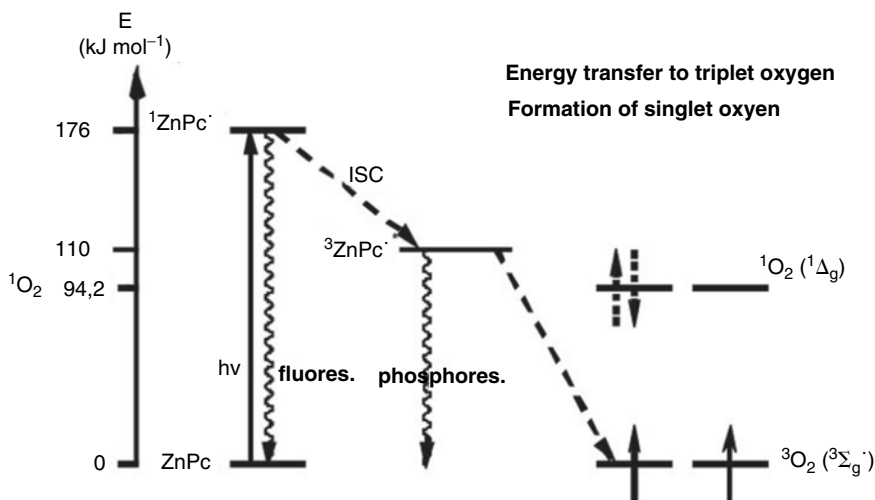
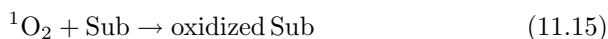
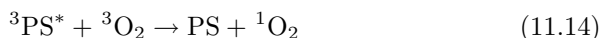


Fig. 11.4. Schematic energy diagram for the formation of singlet oxygen after excitation of Zn(II) phthalocyanine (ZnPc)

$E_T(\text{Por}) = 153$, $E_T(\text{Pc}) = 110$, $E_T(\text{Nc}) = 90 \text{ kJ mol}^{-1}$ (Fig. 11.4). The singlet oxygen quantum yields, Φ_Δ , were determined either by a photochemical method using 1,2-diphenylisobenzofuran as chemical quencher or photophysically by the luminescence method [10, 26]. It is seen in Table 11.1 that – with exception of MNcs – values for Φ_Δ of 0.5–0.9 were determined. Nearly all triplet energy is transferred to oxygen. Also further experiments prove qualitatively the presence of singlet oxygen in photooxidations. Due to a longer lifetime of singlet oxygen in D_2O the reaction rate increases in this solvent whereas addition of a physical quencher of singlet oxygen such as sodium azide reduces the reaction rate [9, 10, 14, 23]. It is generally accepted that singlet oxygen is the main reactive species. Singlet oxygen has a rich but specific chemistry (en-reactions, cycloadditions, H-abstraction, insertion reactions) [18, 19, 27–29] but this means that not every substrate can be oxidized. For degradation of pollutants it may be necessary that the singlet oxygen-driven degradations must perhaps followed by other methods like microbiological treatment.



Other reactive species of oxygen cannot be ruled out. Photoinduced electron transfer reactions can lead to the superoxide radical anion O_2^- (with H^+ it is the superoxide radical HO_2 or its anion O_2^-) which further can react to H_2O_2 (type III photooxidation). These intermediates are also able to oxidize a substrate with electron donor abilities as it was shown for the photooxidation of a mercaptane [14].

The second possibility is the excitation of the photosensitizer adsorbed on the surface of anatase TiO_2 which leads to *superoxide radicals* [30–32]. By irradiation with visible light the excitation of the semiconductor is excluded because TiO_2 is not absorbing in the visible region of light, and therefore the formation of electron/hole pairs did not occur. Now the surface adsorbed photosensitizer absorbs visible light and injects an electron into the conduction band of TiO_2 (11.16 and 11.17; Fig. 11.5). These electrons serve as reacting sites to activate oxygen under formation of superoxide radical (11.18). Indeed, formation of these radicals has been evidenced by using a luminescent probe (luminol) [31]. Thermodynamically it is favourable that electrons in the conduction band of TiO_2 not only can reduce oxygen but also H_2O_2 (obtained from HO_2) which results in $\text{HO}^\cdot$ (11.19 and 11.20). The reaction of the radical cation PS^+ obtained after excitation of the photocatalysts is so far not clarified. Principally it is possible that a donor, for example the pollutant, is oxidized by PS^+ giving again the PS. These processes with photosensitizers on inorganic semiconductors are named *photocatalytic oxidative degradations*.

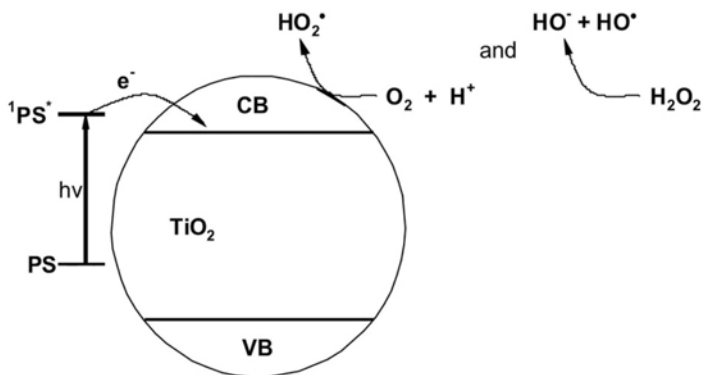
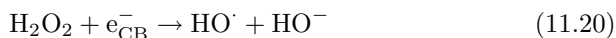
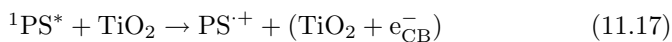


Fig. 11.5. Schematic diagram for the formation of superoxide radical after excitation of a photocatalyst on TiO_2



Measurements for the Determination of the Activity of Photodegradation

Most simple but very important is to measure the oxygen consumption over time volumetrically in a thermostated equipment. The authors use a 100-mL vessel with stirrer connected with a Marhan apparatus (Normag) and a Dosimat (Metrohm) thermostated at 25°C and connected with a computer (Fig. 11.6) [10, 13–15, 23]. From the initial rate of the oxygen consumption over time the turnover frequency (moles $\text{O}_2 \text{ min}^{-1}/\text{mol Pc}$) is calculated to compare the activities. By heating the temperature dependence allows to determine activation energies. For photooxidations irradiation is carried out with a simple quartz-halogen lamp of a slide projector at, for example, 180 mW cm^{-2} . Cutoff filters were taken to get visible light. For irradiation under solar radiation a parabolic reflector concentrating the solar light was used by the authors (Fig. 11.7) [33]. A simple satellite receiver bowl was covered with an aluminium foil. Light was concentrated on the thermostated reactor and the oxygen consumption was measured. Solar light of an intensity of $\sim 55 \text{ mW cm}^{-2}$ was concentrated then to $\sim 1,000 \text{ mW cm}^{-2}$.

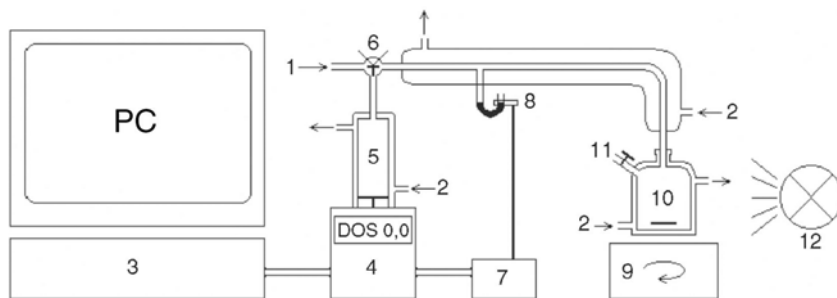


Fig. 11.6. Laboratory equipment for the measurement of the oxygen consumption over time. 1: Gas inlet for the Dosimat. 2: Thermostated water. 3: Computer. 4, 5: Dosimat. 7, 8: Hg light barrier. 9: Stirrer. 10: 100-mL reaction vessel. 11: Introduction for catalyst solution. 12: Quartz-halogen lamp (light intensity at the reaction vessel $\sim 180 \text{ mW cm}^{-2}$)

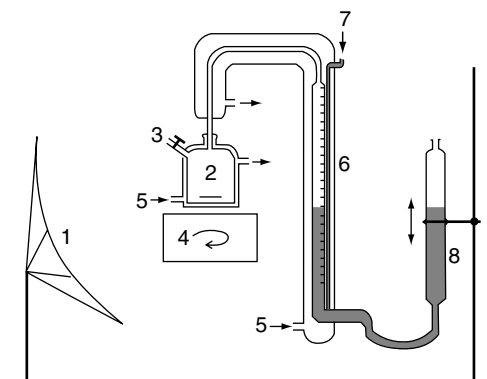


Fig. 11.7. Solar reaction with 100-mL reaction vessel and satellite receiver bowl covered with aluminium foil (light intensity at the reactor $\sim 1,000 \text{ mW cm}^{-2}$). 1. Receiver bowl. 2. 100-mL reaction vessel. 3. Introduction for catalyst solution. 4. Stirrer. 5. Thermostated water. 6, 7. Graduated glass tube. 8: Hg reservoir)

The conversion of the employed product and formation of intermediates or the product can be also followed by taking out a sample. Then by gas chromatography, HPLC, mass spectra, UV-Vis spectra, etc., a detailed analysis can be made. proSys GmbH (Bremen) together with the authors developed a loop reactor ($\sim 250 \text{ cm}$ high and $\sim 0.5 \text{ m}$ in diameter) which is employed for wastewater cleaning under irradiation with quartz-halogen lamps or solar light.

Photooxidative Degradation of Pollutants

At first sensitized photooxidations are compared shortly with catalytic oxidations using phthalocyanines as photosensitizers or catalysts, respectively [15]. In Fig. 11.8 reaction equations for photosensitized and catalytic oxidations of

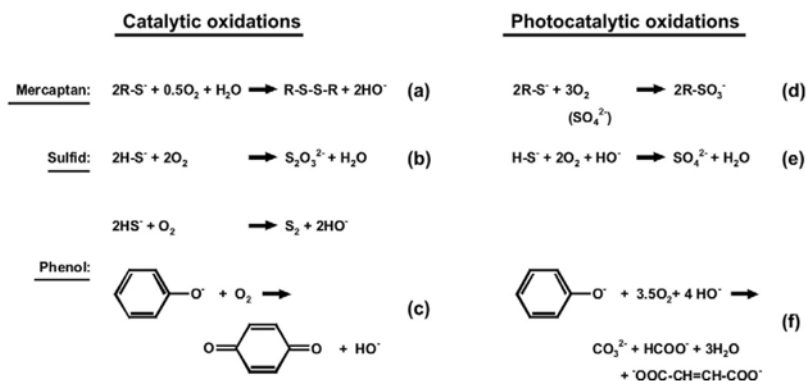


Fig. 11.8. Equations for catalytic oxidations and photooxidations of mercaptans, sulfide, and phenol

mercaptans, sulfide and phenol are shown. The catalytic oxidations with MPc ($M = Co(II)$, $Fe(II)$, $V(IV)O$) result in disulfides, thiosulfate or sulfur and quinone (reactions a, b, c). More efficient are photosensitized oxidations via singlet oxygen with MPc ($M = Zn(II)$, $Al(III)OH$ or $Si(IV)(OH)_2$) to sulfonic acids, sulfate and carbonate (also other products) (reactions d, e, f). Mainly the following phthalocyanines were employed as photosensitizers in an aqueous alkaline solution with an excess of the substrates to be oxidized [15]. Low molecular weight MPcs dissolved in water [10, 13, 14, 23, 25, 33, 34], impregnated or bound on SiO_2 or TiO_2 [10, 32, 35, 36], encapsulated in zeolite NaX [36], ionically bound at charged polymers [13, 37]; oligomeric MPc dissolved in water [38, 39]. Based on the high activity and stability of this polymer-bound photosensitizer a patent application was made [40], and greater plants are under investigation by the proSys company in Bremen. Beside phthalocyanines a hint to some reports using porphyrins in photooxidations is given [41–44]. It should be pointed out that the phototoxicity of porphyrins and Zn and Al phthalocyanines in the photodynamic therapy of cancer is also based on the visible light activation of oxygen [45–47]. Naphthalocyanines were successfully applied as photosensitizers in the photodynamic therapy of cancer [46, 48–50]. Further MPcs show excellent photodynamic activity against pathogenic microorganisms [51, 52].

Sulfur-Containing Compounds

Especially known for the catalytic activity of MPcs is the catalytic oxidation of sulfur compounds in the petroleum industry employing $Co(II)$ or $V(IV)O$ phthalocyanines as catalysts for removal of sulfide and mercaptans from gasoline fractions [15, 53–56]. Sulfide, sulfite, thiosulfate, and mercaptans are by-products of industrial processes and pollutants of waste and natural water. At low concentrations the toxic properties of aqueous solutions can be eliminated by bacterial oxidation [57]. But sulfide concentrations above $70\text{--}200\text{ mg L}^{-1}$

inhibit bacterial metabolism. Wastewater from the oil industry may contain sulfide up to 25 g L^{-1} . The complete oxidation of sulfur-containing compounds to nontoxic ones before discharging them into waterways is the necessary solution of this environmental pollution problem [58]. Well known is that sulfide and other sulfur compounds are removed by strong oxidants (H_2O_2 , NaOCl) which have the disadvantage using often an excess of oxidants and that the oxidants can destroy also the microflora and microfauna. Photooxidations are more effective.

Figure 11.9 shows that sulfide is catalytically oxidized also by MPc ($\text{M} = \text{Zn(II)}$, $\text{R} = -\text{SO}_3\text{H}$) after the O_2 consumption up to around thio-sulfate (Fig. 11.8, reaction b). The catalytic oxidation using water-soluble CoPcs stop at sulfur and thiosulfate involving a small amount of sulfate [59]. Switching on the light efficient singlet oxygen-driven photooxidation up to sulfate occurs (Fig. 11.8, reaction e) [14]. Also other oxidation compounds of sulfur such as sulfite or thiosulfate can be employed and are photooxidized up to sulfate (Fig. 11.10) [14, 34]. This means that an excellent wastewater cleaning from sulfide with visible light using photosensitizers is possible. The reactions are carried out in the presence of a detergent like cetyltrimethylammonium chloride (CTAC) under weak alkaline conditions to monomerize the MPcs.

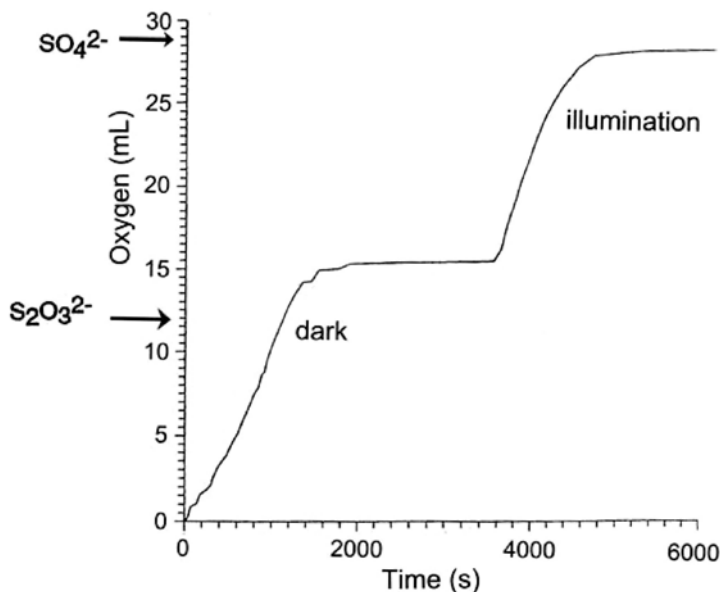


Fig. 11.9. Oxidation and photooxidation (light intensity 180 mW cm^{-2}) of hydrogen sulfide (0.7 mmol) in aqueous solution in the presence of MPc ($\text{M} = \text{Zn(II)}$, $\text{R} = -\text{SO}_3\text{H}$) ($0.5 \mu\text{mol}$) and CTAC (0.1 mol L^{-1}) at pH 9

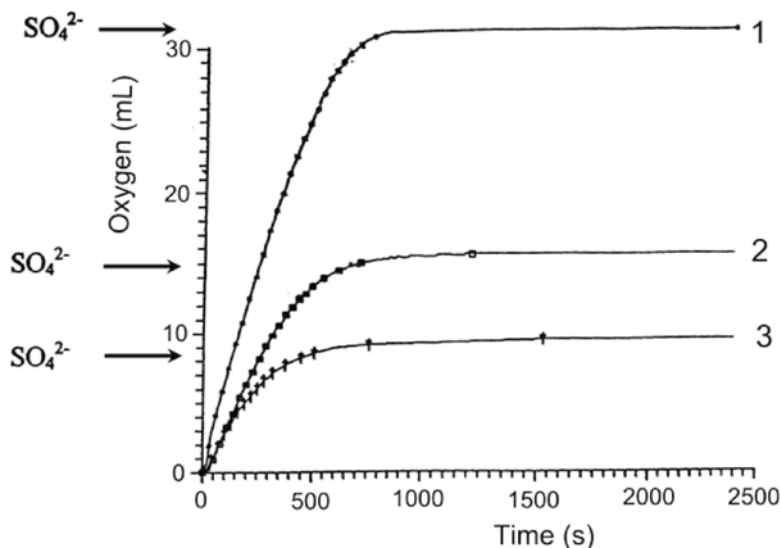


Fig. 11.10. Photooxidation (light intensity 180 mW cm^{-2}) of 0.71 mmol hydrogen sulfide (plot 1), 0.75 mmol sulfite (plot 3), and 0.375 mmol thiosulfate (plot 2) in aqueous solution in the presence of MPc ($M = \text{Zn(II)}$, $R = -\text{SO}_3\text{H}$) ($0.5 \mu\text{mol}$) and CTAC (0.1 mol L^{-1}) at pH 9

Surprisingly, the photosensitized activity of oligomeric MPcs ($M = \text{Zn(II)}$) being substituted by carboxylic acid groups for water solubility is higher than that of the analogous low molecular weight MPcs [38]. The activities of low molecular weight and oligomeric metal complexes increase further by addition of a detergent. It is pointed out that the higher activity of the oligomers is connected with increased formation of singlet oxygen by intercomponent transfer in polynuclear phthalocyanine complexes. Figure 11.11 shows that the activity for the photooxidation of sulfide increases in the presence of detergents CTAC or Triton [14]. Also addition of linear water-soluble polymers like PVBTAC (linear polystyrene substituted in the four positions with $-\text{N}^+(\text{CH}_3)_3$ and ionenes can result in better monomerization and therefore better activities [14]. The catalytic and photocatalytic oxidations at high pH values of S_x^- and S^{2-} by positively charged water-soluble porphyrins MP ($M = \text{Co(II)}$, $R = N\text{-methyl-4-pyridyl}$) occur in two steps. At first the catalytic oxidations results in thiosulfate which in a second step under irradiation also gives sulfate [43, 44]. MP with $M = \text{Co(II)}$ exhibits a higher photosensitized activity compared to the corresponding Fe(II) and Mn(II) complexes.

2-Mercaptoethanol as example of a thiol is photooxidized to the corresponding sulfonic acid (Fig. 11.8, reaction d) with MPc ($M = \text{Zn(II)}$, $R = -\text{SO}_3\text{H}$) in the presence of CTAC whereas in the dark no oxidation occurs (Fig. 11.12, plots 4 and 3, respectively) [10]. MPc ($M = \text{Co(II)}$, $R = -\text{SO}_3\text{H}$)

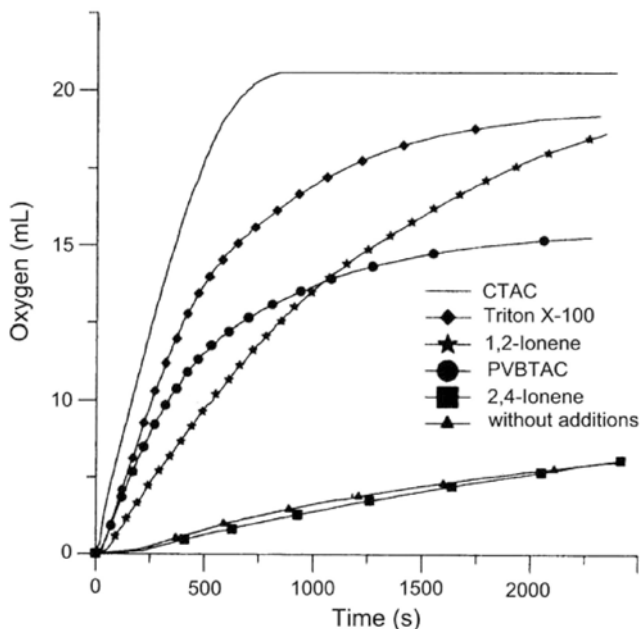


Fig. 11.11. Photooxidation (light intensity 180 mW cm^{-2}) of 0.71 mmol sodium sulfide in aqueous solution in the presence of $0.5 \mu\text{mol}$ MPc ($M = \text{Zn(II)}$, $R = -\text{SO}_3\text{H}$) at pH 9 in the presence of different detergents or polymers. 32 mL O_2 consumption corresponds to reaction e in Fig. 11.8

shows only a catalytic and no photoeffect (Fig. 11.12, plot 1) under formation of the disulfide (Fig. 11.8; reaction a). The catalytic effect is reduced after addition of CTAC to get the monomeric state of the metal complex (Fig. 11.12, plot 2). For ZnPcs on carriers the photoactivity is lower compared to the homogeneous phase [10] but increases by addition of tetrabutylammonium chloride (TBAC) [33]. The photocatalytic oxidation of 2-mercaptoethanol decreases: MPc ($R = -\text{H}$) in zeolite NaX $>$ MPc($R = -\text{COOH}$) in the layered hydrotalcite $>$ MPc($R = -\text{H}$) on SiO_2 [36].

Phenols

Also toxic phenols and chlorinated phenols are among the basic soluble pollutants of industrial and communal wastewater. Especially polychlorinated aromatics are persistent in the environment because of their resistance to oxidation under aerobic conditions leading to accumulation in the biosphere [60,61]. For destruction of phenols and halogenated aromatics different methods like incineration, $\text{H}_2\text{O}_2/\text{UV}$, TiO_2/UV [5, 62], UV in ionic liquids [63], etc. are used. Another method is based on iron tetrasulfophthalocyanine as catalyst in the presence of H_2O_2 as oxidant [5].

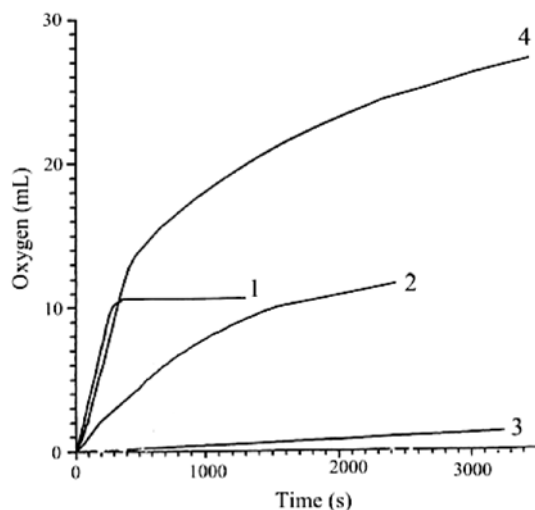


Fig. 11.12. Oxidation and photooxidation (light intensity 180 mW cm^{-2}) of 2-mercaptoethanol using sulfonated phthalocyanines ($0.5 \mu\text{mol}$) at pH 13. Plot 1: 1.4 mmol thiolate and MPc ($M = \text{Co(II)}$, $R = -\text{SO}_3\text{H}$) both in the dark and under irradiation, plot 2 under addition of 0.1 mol L^{-1} CTAC. Plot 3: 0.7 mmol thiolate and MPc ($M = \text{Zn(II)}$, $R = -\text{SO}_3\text{H}$) and 0.1 mol L^{-1} CTAC in the dark; plot 4 under irradiation. 9 mL or 26 mL O_2 consumption correspond to reactions a or d in Fig. 11.8, respectively

The literature about singlet oxygen-mediated photodegradation of aquatic phenolic pollutants up to 1993 was reviewed [64]. With nonhumic and humic materials as photosensitizers a degradation of different phenols to products of quinone structure, and in some cases polymeric products were observed. Photooxidation of 2,4,6-trimethylphenol with rose bengal under irradiation at $\lambda > 520 \text{ nm}$ results only in the formation of a hydroperoxycyclohexadienone as reactive product [65]. With solid neodymium diphthalocyanine as photocatalyst 4-chlorocatechol was observed as main photooxidation product of 4-chlorophenol [66]. The photosensitizers rose bengal and ruthenium trisbipyridyl dication were bound at linear water-soluble copolymers of poly(vinylbenzyl chloride) [67, 68]. The polymer-bound RB shows high activity in the formation of singlet oxygen. But photooxidation of phenol yielded only *p*-benzoquinone as main product. Rose bengal is under formation of singlet oxygen also active in the photooxidation of 2-chlorophenol [69]. By HPLC pyrocatechol, 2-chloro-benzoquinone, 2-chlorohydroquinone, and maleic acid were found as degradation products. The rate of 2-chlorophenol decay increases as pH of the reaction solution rises from 5 to 10.3 (pK of 2-chlorophenol is 8.53) (Fig. 11.13). Therefore the photodegradation has to be carried out in a weak alkaline solution.

The photooxidation of phenol using MPcs ($M = \text{Zn(II)}$, Al(III)OH , Ga(III)OH , Si(IV)(OH)_2 , Ge(IV)(OH)_2 ; $R = -\text{SO}_3\text{H}$) was investigated in

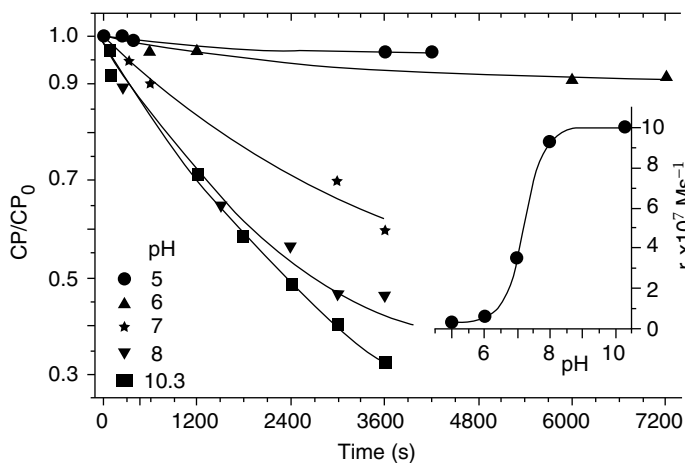


Fig. 11.13. Decrease of the relative 2-chlorophenol concentration for various pH values of the reaction solution

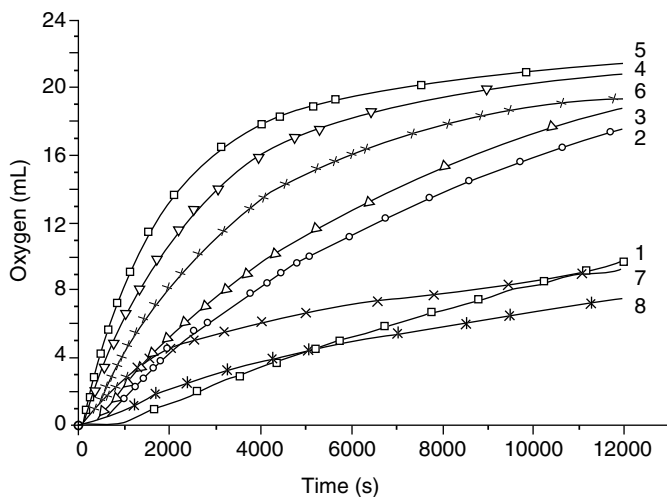


Fig. 11.14. Photooxidation (light intensity 180 mW cm^{-2}) of phenol (0.36 mmol) in aqueous alkaline solution at pH 10 in the presence of MPcs ($R = -\text{SO}_3\text{H}$) ($0.25 \mu\text{mol}$). Plot 1 M = Zn(II), plot 2 M = Al(III)OH, plot 3 M = Ga(III)OH, plot 4 M = Si(IV)(OH)₂, plot 5 M = Ge(IV)(OH)₂, plot 6 RB, plot 7 MB, plot 8 Ru. 31 mL O₂ consumption corresponds to reaction f in Fig. 11.8

detail [13, 15, 23, 33]. As photooxidation products carbonate, maleic/fumaric acids according to reaction f in Fig. 11.8 were determined. For the oxygen consumption measurements an alkaline aqueous solution containing 0.36 mmol phenol was used. A reaction according to reaction f consumes 30.7 mL O_2 which was found for active photosensitizers. Figures 11.14 and 11.15 compare

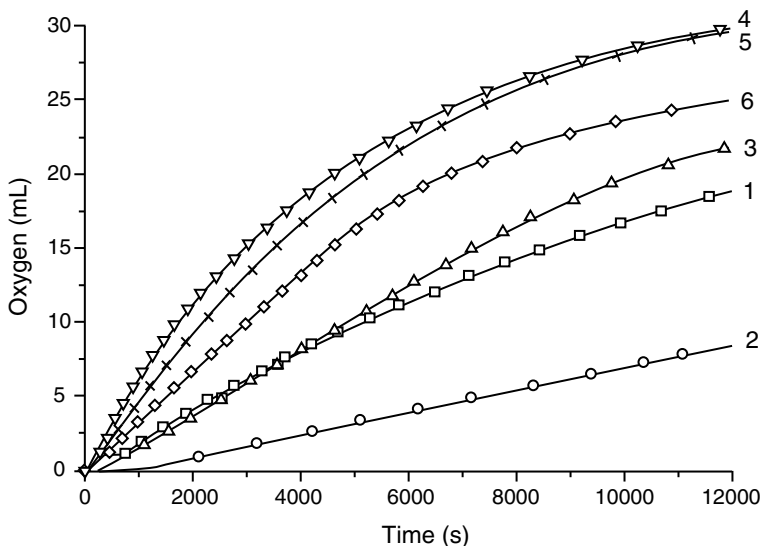


Fig. 11.15. Same as in Fig. 11.14 now in the presence of 2.5 g Amberlite IRA 400 containing $10\mu\text{mol}$ of a photosensitizer (compounds of plots 1–6 the same as in Fig. 11.14)

now the activities of either low molecular weight complexes or the complexes bound ionically on an ion exchanger (Fig. 11.2) at pH 10. The reactions with low molecular weight photosensitizers were carried out without the detergent CTAC. It is seen that in every case MPcs ($\text{M} = \text{Si(IV)(OH)}_2$ or Ge(IV)(OH)_2 ; $\text{R} = -\text{SO}_3\text{H}$) either low molecular weight or on the ion exchanger are most active whereas experiments with the Zn(II) complex show low activities (Figs. 11.14, 11.15, plots 1, 4, and 5) [13]. Due to the axial substituents at the Si(IV) and Ge(IV) these metal complexes are in every case monomeric, and they are surprisingly also more stable against photodecomposition. Reverse situations are evident for the zinc(II) complex. Good activities were also measured for the classical photosensitizer rose bengal (RB) whereas methylene blue (MB) is not useful due to its rapid photodecomposition. Also the ruthenium trisbipyridyl dication (Ru) is not very active. Several times reuse of the Si(IV) complex on Amberlite shows the excellent photostability of this photosensitizer (Fig. 11.16) which is one prerequisite for a practical application. As mentioned for the photooxidation of sulfide, carboxylated oligomeric MPcs ($\text{M} = \text{Zn(II)}$, $\text{R} = -\text{COOH}$) are more active in the photooxidation of phenol than analogous low molecular weight complexes [39].

The reactions of chlorinated phenols with sulfonated phthalocyanines are exemplarily shown for the photooxidation of the toxic 2-chlorophenol in Fig. 11.17 [33]. For irradiation under laboratory conditions the light intensity is 180 mW cm^{-2} (Fig. 11.6) and under solar radiation $\sim 1,000\text{ mW cm}^{-2}$ (Fig. 11.7). Under irradiation the phenol derivative is efficiently photooxidized

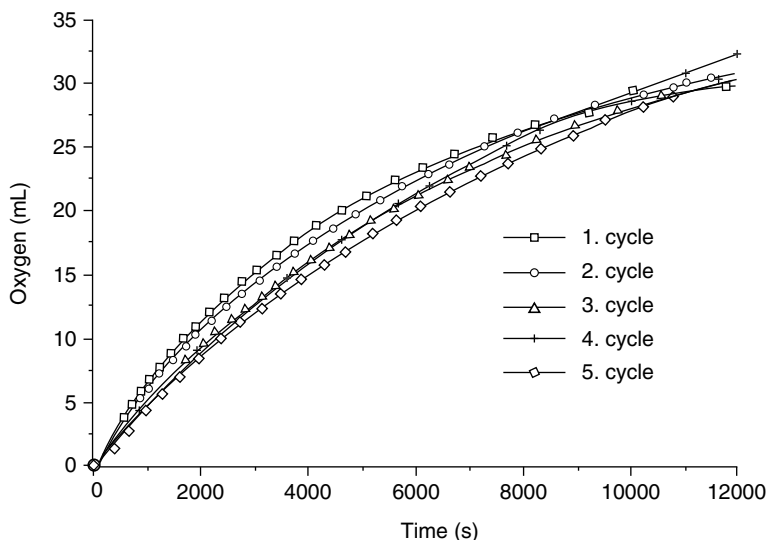


Fig. 11.16. Photooxidation (light intensity 180 mW cm^{-2}) of phenol (0.36 mmol) in aqueous alkaline solution at pH 10 in the presence of $10 \mu\text{mol}$ MPc ($\text{M} = \text{Si(IV)(OH)}_2$, $\text{R} = -\text{SO}_3\text{H}$) on 2.5 g Amberlite IRA 400 (Fig. 11.2) employed five times

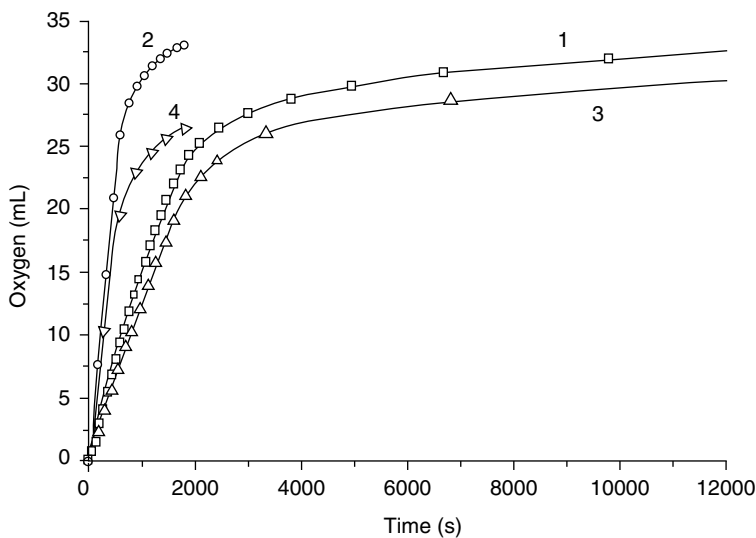


Fig. 11.17. Photooxidation of 0.35 mmol 2-chlorophenol (0.36 mmol) in aqueous alkaline solution at pH 10. (i) Containing $0.25 \mu\text{mol}$ MPc ($\text{M} = \text{Al(III)(OH)}$, $\text{R} = -\text{SO}_3\text{H}$) irradiation by a slide projector (plot 1) or by solar radiation (plot 2). (ii) Containing $0.25 \mu\text{mol}$ MPc ($\text{M} = \text{Zn(II)}$, $\text{R} = -\text{SO}_3\text{H}$) and 0.1 mol L^{-1} CTAC irradiation with a slide projector (plot 3) or by solar radiation (plot 4)

Table 11.2. Photodegradation of phenol-containing wastewater (salt content 40 mg/L) from pharmaceutical industry in the presence of MPc (M = Si(OH)₂, R = -SO₃H) on an ion exchanger (Fig. 11.2)

	Before treatment	After treatment	Degradation
Phenol index	2,863 mg/L	43 mg/L	98.5%
COD value ^a	136 mg/L	54 mg/L	60.6%
pH value	13.13	11.54	

^aCOD: Chemical oxygen demand determined by K₂Cr₂O₇/H₂SO₄ method.

(products are for example CO₂ and Cl⁻) using a quartz-halogen lamp (Fig. 11.17, plots 1 and 3). Due to the higher light intensity of concentrated solar light, the photooxidations under solar light are more efficient (Fig. 11.17, plots 2 and 4). Also PdPc (R = -SO₃H) is active in the photodegradation of chlorophenols [70].

Also the metal-free phthalocyanine on TiO₂ exhibits good photocatalytic in the photooxidation at pH 9.2 [32]. A final oxygen consumption after 10 h by irradiation with a halogen lamp of 38 mW/cm² of around 3.5 mol O₂/mol phenol and a formation of around 1 mol CO₂/mol phenol was determined which corresponds to reaction f in Fig. 11.8. No photocatalytic oxidation of phenol was observed by irradiation at $\lambda > 450$ nm. In contrast, ZnPc (R = -SO₃H) on TiO₂ showed only a low activity in the photooxidation of phenol (only around 0.6 mol O₂/mol phenol after 3.3 h irradiation) [71]. With methylene blue, rhodamine B, etc. as photocatalysts on TiO₂ degradations of phenol and chlorophenol between 60% and 70% were determined after 5 h irradiation at pH 5 [72, 73].

Industrial phenol containing wastewater was irradiated with a artificial fluorescent lamp in the presence of Si(OH)₂Pc (R = -SO₃H) on an ion exchanger (Fig. 11.2) as heterogeneous photosensitizer (in collaboration with proSys company, Bremen [74]). It can be seen from Table 11.2 that an efficient degradation of phenol was obtained. Therefore this stable heterogeneous photosensitizer is suitable for wastewater cleaning in an industrial scale.

Different Pollutants

Most pesticides are resistant to chemical and/or photochemical degradation under typical environmental conditions [75]. Advanced oxidation processes (AOP) are at present considered to have considerable potential for photodegradation of pesticides under UV conditions. Reaction pathways and mechanisms of photodegradation under conditions of AOPs were recently reviewed [76]. Recently also the photocatalytic oxidative degradations in the visible region of light were described.

The photodegradation of the herbicides atrazine and ametryn with visible light in neutral aqueous solution using metal-free sulfonated tetraryl-porphyrins as photosensitizers was recently described [77]. Degradations to dealkylated s-triazines of 30% for atrazine and 63% for ametryn were found. A mechanism via the superoxide radical anion was proposed. The herbicide terbutylazine was treated with rose bengal on TiO_2 by irradiation with visible light in aqueous solution at pH 5.6 [30]. A rapid degradation of RB was observed and the sensitizer must be added repeatedly several times. The organophosphorous insecticide dichlorovos can be photodegraded into Cl^- , H_2O , CO_2 , and other compounds in an aqueous solution containing semiconductor powders of TiO_2 or ZnO with riboflavine or other photosensitizers [78]. It should be mentioned that a medium-pressure mercury lamp with λ_{max} of 365 nm was employed. Using riboflavine on TiO_2 after 3.5 h a degradation of dichlorovos of around 70% was observed. Addition of H_2O_2 enhanced the liberation of Cl^- to 89% compared to 62% for the photoreaction without H_2O_2 (20). Also photoreactions under solar radiation were carried out. The photodegradation of atrazine with thionine and eosin Y on TiO_2 by irradiation with a xenon lamp is mentioned [31]. After 5 h around 60% photodegradation was determined, and CO_2 was detected. In summary, it is necessary to study the photodegradation of pesticides in more detail and to compare photosensitized and photocatalytic degradations of various pesticides.

With sensitizers on TiO_2 a photocatalytic degradation not only of phenols but also of chlorinated hydrocarbons such as 1,2-dichloroethane or trichloroethylene is possible [72,73]. At first photosensitizers (methylene blue, rhodamine B, etc.) are adsorbed from an aqueous solution on TiO_2 . Then a suspension of TiO_2 -dye in water of pH 5 was irradiated in the presence of a pollutant with a xenon lamp. After 5 h around 70% degradation of the chlorinated hydrocarbons was achieved. Figure 11.18 shows the degradation of 1,2-dichloroethane and the evolution of CO_2 over time. Photodegradation of CCl_4 in the visible region of light was observed in an aqueous solution of a nonionic surfactant containing Fe^{3+} as visible light sensitizer [79]. Also

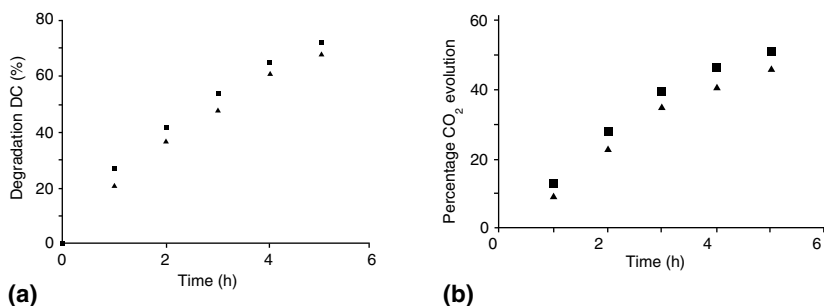


Fig. 11.18. Visible light-induced decomposition of 1,2-dichloroethane by sensitizer-modified TiO_2 ; ▲ methylene blue, ■ rhodamine. a: degradation. b: evolution of CO_2

Table 11.3. Photodegradation of polycyclic aromatic hydrocarbons-containing wastewater (salt content 40 mg/L) from industry in the presence of MPc (M = Si(OH)₂, R = -SO₃H) on an ion exchanger (Fig. 11.2)

	Before treatment	After treatment	Degradation
Amount PAK	640 µg/L	14 µg/L	97.8%
COD value ^a	83 mg/L	<15 mg/L	>81.2%
pH value	7.25	7.05	

^aCOD: Chemical oxygen demand determined by K₂Cr₂O₇/H₂SO₄ method.

photosensitized oxidative degradation of hydrocarbons is possible. Polycyclic aromatic hydrocarbons (PAKs) containing wastewater was irradiated with a artificial fluorescent lamp in the presence of Si(OH)₂Pc (R = -SO₃H) on an ion exchanger (Fig. 11.2) as heterogeneous photocatalyst (in collaboration with proSys company, Bremen [74]). Table 11.3 shows efficient degradation of PAKs. Therefore this stable heterogeneous photosensitizer is suitable not only for the degradation phenol containing wastewater as discussed before (Table 11.2).

Finally some photooxidative degradations of some other compounds are mentioned.

- Some tryptophan-containing dipeptides were studied in water solution at pH 7 using rose bengal as photosensitizer. Different oxidation products were obtained by attack of singlet oxygen. But no mineralization was observed [80]. In addition, the rose bengal-sensitized photooxidation of 2-dimethylamino-5,6-dimethylpyrimidin was reported [81].
- Products of the riboflavin-sensitized photooxidation of the sympathomimetic drug isoproterenol were identified by HPLC [82]. It is proposed that superoxide radical anions are generating *N*-isopropylaminochrome as main product.
- A derivative of Co(II) ms-tetraphenylporphyrin was used for the photooxidation of aromatic aldehydes [83]. In this case reversible binding of oxygen and its reduction to O₂⁻ occurs. Co(II) in the porphyrin is oxidized to Co(III). Oxidation products of the aldehydes were not identified.
- Zn(II)Pc-bearing dendrimer substituents were investigated for the singlet oxygen-induced oxidation of 1,3-diphenylisobenzofuran [84]. The oxidation rate decreased with increasing number of dendrimer generation. Also the photoactivity of a Zn(II) porphyrin derivative intercalated in titanium sodium phosphate was studied [85].
- The photodegradation of rhodamine B, salicylic acid and orange II was examined in the presence of FePc (R = -SO₃H) and H₂O₂ under visible light irradiation [86,87]. The FePc derivative has a good catalytic character in this system. The light-activated reaction process involves the formation of reactive hydroxyl radicals.

11.3 Visible Light Decomposition of Ammonia to Nitrogen with $\text{Ru}(\text{bpy})_3^{2+}$ as Sensitizer

11.3.1 Nitrogen Pollutants and Their Photodecomposition

Because of the increasing amount of livestock waste, a number of studies have been carried out to establish the effective waste-treatment system for protection of local and global environment from water pollution. In particular, a methane fermentation system has been extensively developed to diminish the chemical and biological oxygen demand (COD and BOD) from the cattle-waste slurry. In recent years, emission of NO_3^- from the livestock waste has been recognized as a serious pollutant of ground and surface water. Nitrate ions are the products from enzymatic oxidation of ammonia (NH_3) that originates from urea in the livestock waste by the enzymatic reaction of urease emitted from microorganisms. Removal and collection of NH_3 from the cattle-waste slurry before methane fermentation can contribute to prevent a high-level nitrate pollution of surface and groundwater.

In an earlier study, TiO_2 was found to photoelectrochemically decompose water under UV light irradiation [88], and since then many organic and inorganic compounds have been decomposed by this photocatalyst [89–91]. The photodecomposition of ammonia in neutral water has been reported by using TiO_2 -supported Pt or Pd catalyst, and nitrogen (and nitrogen oxides) was obtained [92]. TiO_2/Pt decomposed aqueous ammonia into nitrogen, while pure TiO_2 decomposed NH_3 into nitrite and nitrate [93]. Some reports are found on photodecomposition of ammonia with TiO_2 in a gas phase [94, 95]. UV light decomposition of ammonia by platinized TiO_2 was achieved to produce N_2 [96]. However, visible light conversion of ammonia into nitrogen has not been reported both in liquid and gas phases. The present authors have found that an aqueous solution of ammonia can photochemically be converted into nitrogen and hydrogen by UV irradiation nearly with a stoichiometric 1:3 ratio (volume) by using platinized titanium dioxide (TiO_2) suspension [97]. For the sensitization of TiO_2 or other large band gap semiconductors in order to use visible light that is abundant in the solar irradiation, many attempts have been conducted [91], but the wavelength capable to be utilized and the catalytic activity have not been satisfactory enough. To create a new visible light photocatalyst based on molecules instead of semiconductors, it was attempted to construct a photocatalytic system using a dye sensitizer, and has got success in photodecomposing aqueous ammonia with visible light into N_2 by a photocatalyst composed of a sensitizer (tris(2,2'-bipyridine)-ruthenium(II), $\text{Ru}(\text{bpy})_3^{2+}$), an electron mediator (methylviologen, MV^{2+}), and an electron acceptor (O_2); the results are described in Sect. 11.3.

11.3.2 Photochemical Electron Relay with Ammonia

A 5-ml aqueous solution of $\text{Ru}(\text{bpy})_3^{2+}$, $\text{K}_2\text{S}_2\text{O}_8$, and NH_3 was prepared. The solution was irradiated with visible light under argon atmosphere by a

halogen lamp. During the irradiation gas bubbles were clearly observed, and after 1 h irradiation, 220 μl N_2 was formed by the decomposition of NH_3 . H_2 was not formed in this system since electron-accepting $\text{K}_2\text{S}_2\text{O}_8$ was used in this mixture. It was confirmed by each blank experiment that both the Ru complex and $\text{K}_2\text{S}_2\text{O}_8$ as well as visible light irradiation were needed for the N_2 formation from NH_3 .

The irradiation of the aqueous solution of NH_3 and $\text{Ru}(\text{bpy})_3^{2+}$ by visible light in the presence of $\text{K}_2\text{S}_2\text{O}_8$ induced the formation of $\text{Ru}(\text{bpy})_3^{2+}$ by oxidation of the photoexcited Ru complex by $\text{K}_2\text{S}_2\text{O}_8$. This photochemical reaction was monitored in situ under irradiation by visible absorption spectral change of the aqueous solution of NH_3 , $\text{Ru}(\text{bpy})_3^{2+}$, and $\text{K}_2\text{S}_2\text{O}_8$ using a diode array UV–Vis spectrophotometer according to our design [98], as shown in Fig. 11.19 where the absorption peak at the 452 nm due to the $\text{Ru}(\text{bpy})_3^{2+}$ disappeared during the irradiation with the simultaneous increase of the peak at 420 nm due to the formation of $\text{Ru}(\text{bpy})_3^{3+}$.

By a separate experiment it was confirmed that NH_3 does not quench the photoexcited $\text{Ru}(\text{bpy})_3^{2+}$ at all. The following oxidation of ammonia by the photochemically formed 3^+ Ru complex would be not rapid since under the steady state during irradiation, the 3^+ Ru complex was the predominant species. It was also confirmed by a separate experiment that NH_3 is decomposed into N_2 by $\text{Ru}(\text{bpy})_3^{3+}$. It is therefore concluded that the reaction occurs by the photochemical oxidation of the Ru(II) complex to Ru(III) by $\text{K}_2\text{S}_2\text{O}_8$, leading the following degradative oxidation of NH_3 by the Ru(III) complex to yield N_2 (Scheme 11.1).

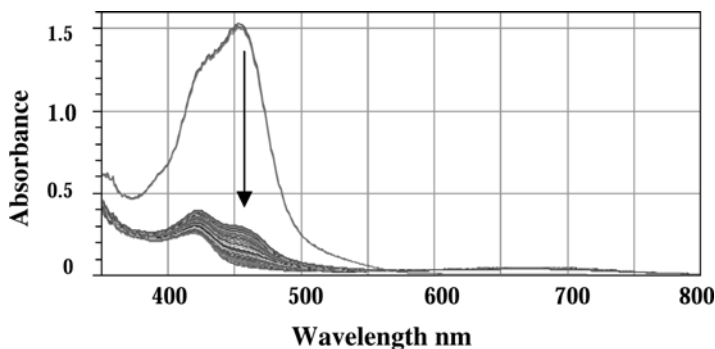
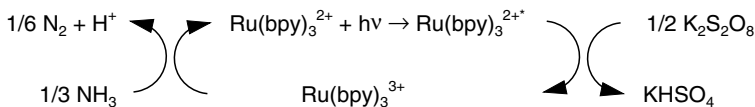


Fig. 11.19. In situ visible absorption spectral change of the aqueous solution, 1 mM NH_3 /0.1 mM $\text{Ru}(\text{Bpy})_3^{2+}$ /10 mM $\text{K}_2\text{S}_2\text{O}_8$ at pH 5.3, under visible light irradiation from a 500 W xenon lamp through a UV cutoff filter (L-42) and IR cutoff filter (IRA-25S) with the light intensity of 101 mW cm^{-2} . The spectrum was measured with a 5 s interval, total photoreaction time being 600 s after starting irradiation ([99], copyright Royal Soc. Chem.)



Scheme 11.1

In order to develop a visible light-driven photocatalyst based on molecules instead of UV light-driven semiconductors, electron mediator was used in combination with O_2 electron acceptor with a sensitizer (here Ru(bpy)_3^{2+}). It is interesting that methylviologen, a well-known mediator for proton reduction towards H_2 evolution [89,91], can work as an electron acceptor to produce N_2 as follows. At first the photochemical reaction of an aqueous mixture of NH_3 (3 M, ca. 5%), Ru(bpy)_3^{3+} (0.1 mM), and methylviologen (MV^{2+}) (10 mM) (at $\text{pH} = 12.3$) was investigated by an in situ visible absorption spectroscopy [98] during photoirradiation. The in situ visible absorption spectrum under irradiation of the above mixture is shown in Fig. 11.20.

The formation of viologen cation radical (MV^+) having absorption maxima at 395 and 603 nm was clearly observed. However, N_2 formation was not observed under this condition because of the facts that (1) NH_3 did not quench the photoexcited Ru(bpy)_3^{2+} , and (2) the electron transfer from the photoexcited Ru(bpy)_3^{2+} to MV^{2+} has well been established [89,91]. Therefore, it can be concluded that in the above system methylviologen works as an acceptor from the photoexcited Ru complex in place of $\text{K}_2\text{S}_2\text{O}_8$ to accumulate viologen cation radical. Ammonia works as electron donor to the formed

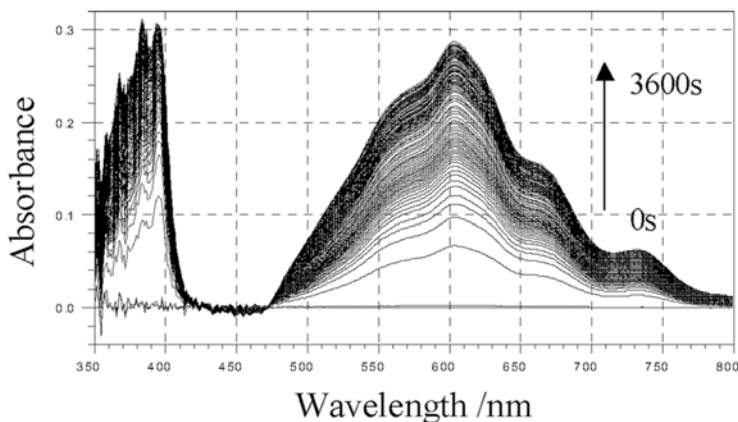
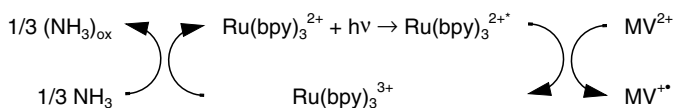


Fig. 11.20. In situ visible absorption spectral change of the aqueous solution, 3M NH_3 /0.1 mM Ru(bpy)_3^{2+} /10 mM MV^{2+} ($\text{pH} 12.3$) under irradiation from a 500 W xenon lamp through UV cutoff filter (L-42) and IR cutoff filter (IRA-25S) at the light intensity of 101 mW cm^{-2} . Measured by taking the absorption of the solution before irradiation as a base line of the spectra ([99], copyright Royal Soc. Chem.)

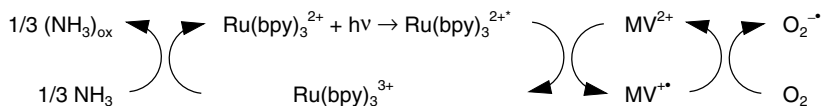
$\text{Ru}(\text{bpy})_3^{3+}$ in addition to the accumulation of some oxidized product of ammonia $((\text{NH}_3)_{\text{ox}})$ (Scheme 11.2) [99]. As for the candidate of $(\text{NH}_3)_{\text{ox}}$ hydrazine or NH_3^+ might be possible. However, the mixture of hydrazine, $\text{Ru}(\text{bpy})_3^{2+}$ and MV^{2+} produced MV^+ very rapidly and N_2 also was formed both under dark and illumination, so that hydrazine would not be possible as for the $(\text{NH}_3)_{\text{ox}}$. By stopping photoirradiation of the mixture shown in Scheme 11.2, about 10% decrease of the absorbance by MV^+ was observed showing that all the components in the mixture are most probably in a dynamic equilibrium state under irradiation. The structure of $(\text{NH}_3)_{\text{ox}}$ is the subject to be investigated in future. In the reaction of Scheme 11.2 the presence of Pt catalyst in the solution did not induce H_2 formation since the pH of the solution was basic due to the NH_3 . However, Scheme 11.2 shows that NH_3 was photochemically decomposed into an oxidized product $((\text{NH}_3)_{\text{ox}})$ by accumulating MV^+ , the latter of which is capable of reducing protons to H_2 by decreasing the pH to neutral or to acidic conditions.



Scheme 11.2

11.3.3 Photochemical Decomposition of Ammonia to Dinitrogen by a Photosensitized Electron Relay

It is important that the presence of O_2 in this system induced N_2 evolution (Scheme 11.3) as a result of MV^+ oxidation to MV^{2+} [99]. The turnover number of MV^{2+} was calculated to be 9 per 9 h supporting the molecular photocatalytic reaction of Scheme 11.3 in relevance to the turnover of MV^{2+} by O_2 .



Scheme 11.3

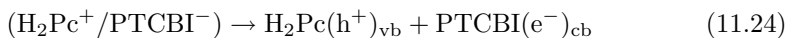
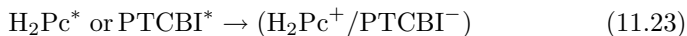
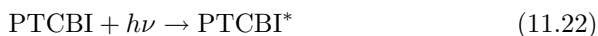
The system shown in Scheme 11.3 could solve the biomass waste problem by using visible light in relevance to treatment of nitrogen compounds as well as ammonia pollutant problem in our daily life, and would lead to a solar (visible light) artificial nitrogen cycle.

This kind of photoinduced electron relay system would in principle be possible also by using solid-state materials as revealed by our earlier work reporting the photoinduced solid-state electron relay from EDTA via the photoexcited $\text{Ru}(\text{bpy})_3^{2+}$ to MV^{2+} in a cellulose matrix [100]. Such a visible light photocatalyst system composed of molecules has the same function as semiconductor photocatalysts, which could promise a large varieties of design and applications not only for livestock waste treatment but also for other photo-cleaning of the environment in the near future.

11.4 Visible Light Responsive Organic Semiconductors as Photocatalysts

11.4.1 Photoelectrochemical Character of Organic Semiconductors in Water Phase

As described before, TiO_2 is responsive only for UV light. To utilize visible light, various organic semiconductors have been investigated as photocatalyst. One example is organic bilayers composed of a perylene derivatives (3,4,9,10-perylenetetracarboxyl-bisbenzimidazole, PTCBI) and metal-free phthalocyanine (H_2Pc). They are known as typical photovoltaic materials for visible light in dry systems as illustrated in 11.21–11.24 [101, 102]. Charge separation behavior and electron-hole migration processes were applied not only for dry electrode system but also for nonelectrode systems such as tuning of high-power-laser ablation [103]. The efficiency of the photovoltaic effect increased by inserting an insulating i-layer between the p- and n-layers [104], and by introduction of the bulk heterojunction concept [105].



The combination of layers of CoPc/PTCBI acted as a photoanode on ITO for the catalytic oxidation of OH^- in water [106]. The valence band of CoPc is 0.30 V more positive than the oxidation potential of O_2/OH^- , and the hole of CoPc has a potential to oxidize OH^- into O_2 . In the case of $\text{H}_2\text{Pc}/\text{PTCBI}$ the valence band of H_2Pc is similar to CoPc , but oxidation of OH^- did not occur even under positive applied potential. However, in the presence of IrO_2 as a cocatalyst, the hole of H_2Pc oxidized OH^- into O_2 .

Based on the action spectrum of the photocurrent it was proved that absorption by the PTCBI by irradiation with visible light ($\lambda < 750 \text{ nm}$) can efficiently induce the generation of a photoanodic current at the interface of CoPc/water (or IrO_2) coupled with the hole-conducting character of CoPc

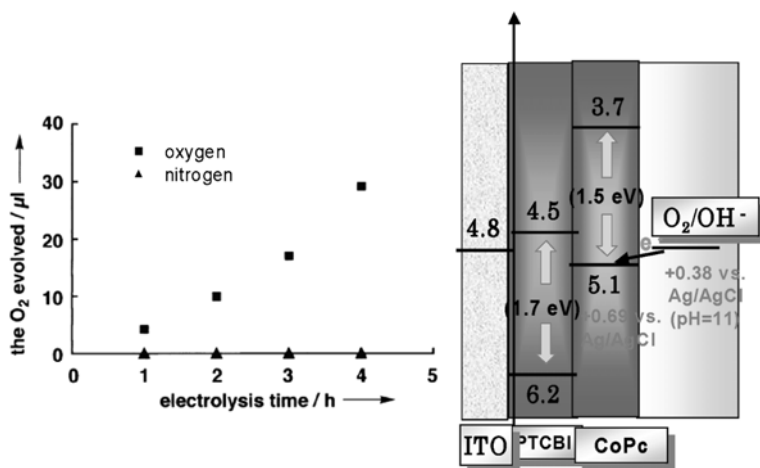


Fig. 11.21. Time course of amount of oxygen evolved at ITO/PTCBI/CoPc in an aqueous NaOH solution of pH = 11. Applied potential of +0.4 V vs. Ag/AgCl, and film thickness of 160 nm (PTCBI)/50 nm (CoPc). Optical image of a gelled capsule (left), and its radius depending on the angle by image analysis. The right side shows the potential diagram of the bilayer and O_2/OH^-

(or H_2Pc). These are the first examples of water splitting using organic semiconductor assisted by visible light, which also means stability of the bilayer in the water phase and under oxidative conditions (Fig. 11.21).

11.4.2 Photoelectrochemical Oxidations by Irradiation with Visible Light

The oxidation of organic molecules also takes place on the surface of H_2Pc by combination with PTCBI and other n-type semiconductors [107, 108]. The oxidation is possible in an aqueous electrolyte, implying stability of the H_2Pc /PTCBI combination, whereas stability against humidity is a problem in the field of organic solar cell systems. In the case of the reverse combination of H_2Pc /PTCBI on ITO, the photoelectrode worked in a water phase with coexisting redox molecules ($\text{Fe}^{\text{III}}(\text{CN})_6^{3-}$ as electron acceptor) [109]. However, the action spectrum for the photocathodic current indicated that under a broad visible light irradiation ($\lambda = 400 \sim 750 \text{ nm}$) only the PTCBI can induce the photocurrent generation. This was supported in the case of the photoanodic combination that the PTCBI exciton can solely contribute to carrier generation through charge separation at the H_2Pc /PTCBI interface. The photocathodic combination showed novel photocathodic characteristics at the organic solid/water interface coupled with electron conduction through the n-type semiconductor.

11.4.3 Photochemical Decomposition of Amines Using Visible Light and Organic Semiconductors

Based on the photoelectrochemistry of $\text{H}_2\text{Pc}/\text{PTCBI}$ we have designed decomposition of organic amines by the photocatalyst adsorbed layer on Nafion as shown in Fig. 11.22 [110]. An initial concentration of trimethylamine (TMA) of $9.6 \times 10^{-7} \text{ mol}$ ($1.8 \times 10^{-6} \text{ mol/L}$) was used. Due to the adsorption by Nafion the concentration of TMA decreased to 15% within 10 min. The decrease of TMA was enhanced with a thicker layer of PTCBI, and this phenomenon was similar to the photoanodic current of the $\text{H}_2\text{Pc}/\text{PTCBI}$ bilayer system for the 2-mercaptoethanol oxidation. The incident wavelength dependence of the TMA decrease is also similar to the photoanodic character where the action spectrum is similar to the absorption spectra of PTCBI. These results suggested that photocatalytic oxidation takes place based on the p-n bilayer process where the oxidation is due to the holes in H_2Pc , and the electron transfer at $\text{H}_2\text{Pc}/\text{TMA}$ controls the whole processes.

To investigate the stability of the photocatalyst, we repeated the TMA addition. In the case of Nafion monolayer and PTCBI/ H_2Pc /Nafion trilayer in the dark, the decrease rate became lower by repeating the addition of TMA, whereas in the PTCBI/ H_2Pc /Nafion trilayer under illumination, the repeating decrease of TMA concentration was clearly observed for more than 20 times over 2 days. As for the decomposition products, carbon dioxide was detected almost quantitatively. These results imply the possibility of the application of organic semiconductors absorbing in the visible light region for practical use especially by utilizing adsorbed layers.

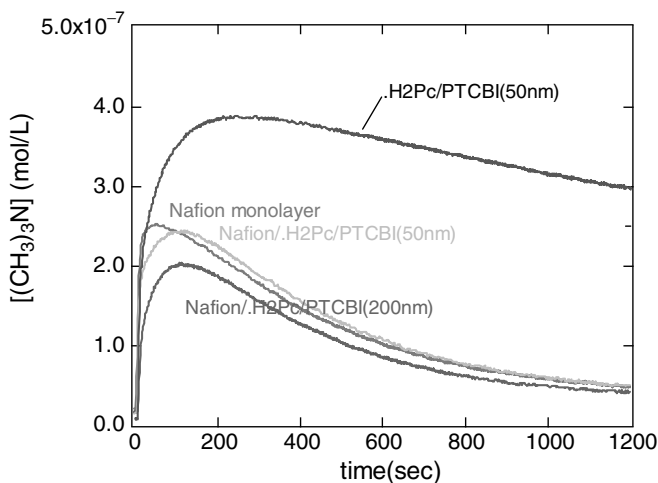


Fig. 11.22. Decreases of the concentration of trimethylamine in the presence of (a) Nafion/ H_2Pc /PTCBI (50 nm), (b) Nafion/ H_2Pc /PTCBI (200 nm), (c) Nafion (50 μm), (d) H_2Pc /PTCBI (200 nm)/glass

References

1. T. Oppenländer (ed.), *Photochemical Purification of Water and Air: Advanced Oxidation Processes* (Wiley-VCH, Weinheim, 2002)
2. J.R. Pfaffin, E.N. Ziegler, *Encyclopedia of Environmental Science and Technology* vol. 1 & 2 (Gordon and Breach, Amsterdam, 2005)
3. A. Parsons (ed.), *Advanced Oxidation Processes for Water and Wastewater Treatment* (IWA, London, 2004)
4. O. Legrini, E. Oliveros, A.M. Braun, *Chem. Rev.* **93**, 671 (1993)
5. B. Meunier, A. Sorokin, *Acc. Chem. Res.* **30**, 470 (1997)
6. M.R. Hoffmann, S.C. Martin, W. Choi, D.W. Bahnemann, *Chem. Rev.* **95**, 69 (1995)
7. A. Mills, S. Hodgen, S.K. Lee, *Res. Chem. Intermed.* **31**, 295 (2005)
8. S. Gelover, P. Mondragon, A. Jimenez, *J. Photochem. Photobiol. A: Chem.* **165**, 241 (2004)
9. M.C. DeRosa, *Coord. Chem. Rev.* **351**, 233 (2002)
10. G. Schneider, D. Wöhrle, W. Spiller, J. Stark, E. Schulz-Ekloff, *Photochem. Photobiol.* **60**, 333 (1994)
11. H. Ali, R. Langlois, J.R. Wagner, *Photochem. Photobiol.* **47**, 713 (1988)
12. J.H. Weber, D.H. Busch, *Inorg. Chem.* **4**, 469 (1965)
13. R. Gerdes, O. Bartels, G. Schneider, D. Wöhrle, G. Schulz-Ekloff, *Polym. Adv. Technol.* **12**, 1 (2001)
14. W. Spiller, D. Wöhrle, G. Schulz-Ekloff, W.T. Ford, G. Schneider, J. Stark, *J. Photochem. Photobiol. A: Chem.* **95**, 161 (1996)
15. D. Wöhrle, O. Suvorova, G. Gerdes, O. Bartels, L. Lapok, N. Baziakina, S. Makarov, A. Slodek, *J. Porphyrins Phthalocyanines* **8**, 1020 (2004)
16. J.R. Darwent, P. Douglas, A. Harriman, G. Porter, M.C. Richoux, *Coord. Chem. Rev.* **44**, 83 (1982)
17. T. Nyokong, *Coord. Chem. Rev.* **251**, 1707 (2007)
18. A.M. Braun, M.T. Maurette, E. Oliveros, *Photochemical Technology* (Wiley, Chichester, 1991)
19. D. Wöhrle, M.W. Tausch, W.D. Stohrer, *Photochemie.* (Wiley-VCH, Weinheim, 1998)
20. V. Mantareva, D. Petrova, L. Avramov, I. Angelov, E. Borosova, M. Peeva, D. Wöhrle, *J. Porphyrins Phthalocyanines* **9**, 47 (2005)
21. A.K. Sobbi, D. Wöhrle, D. Schlettwein, *J. Chem. Soc. Perkin Trans.* **2**, 481 (1993)
22. G. Schnurpfeil, A.K. Sobbi, W. Spiller, D. Kliesch, H. Wöhrle, *J. Porphyrins Phthalocyanines* **1**, 159 (1997)
23. R. Gerdes, D. Wöhrle, W. Spiller, G. Schneider, G. Schnurpfeil, *J. Photochem. Photobiol. A: Chem.* **111**, 65 (1997)
24. H. Shinohara, O. Tsaryova, G. Schnurpfeil, D. Wöhrle, *J. Photochem. Photobiol. A: Chem.* **184**, 50 (2006)
25. V. Iliev, V. Alexiev, L. Bilyarska, *J. Mol. Catal. A: Chem.* **137**, 15 (1999)
26. W. Spiller, H. Kliesch, D. Wöhrle, S. Hackbarth, B. Roeder, G. Schnurpfeil, *J. Porphyrins Phthalocyanines* **2**, 145 (1998)
27. M. Prein, W. Adam, *Angew. Chem.* **108**, 519 (1996)
28. E.A. Lissi, M.V. Encinas, P. Lemp, M.A. Rubio, *Chem. Rev.* **93**, 699 (1993)
29. A.A. Gormann, *Adv. Photochem.* **17**, 217 (1992)

30. H. Ross, J. Bendig, S. Hecht, *Solar Energ. Mater. Solar Cells* **33**, 475 (1994)
31. D. Chatterjee, A. Mahata, J. Photochem. Photobiol. A: Chem. **165**, 19 (2004)
32. V. Iliev, J. Photochem. Photobiol. A Chem. **151**, 195 (2002)
33. R. Gerdes, O. Bartels, G. Schneider, D. Wöhrle, G. Schulz-Ekloff, *Intern. J. Photoenergy* **1**, 41 (1999)
34. V. Iliev, A. Ileva, *J. Mol. Cat. A Chem.* **103**, 147 (1993)
35. D. Wöhrle, O. Suvorova, N. Trombach, E.A. Schupack, R. Gerdes, N.M. Semenov, O. Bartels, A.A. Zakurazhnov, G. Schnurpfeil, A. Wendt, *J. Porphyrins Phthalocyanines* **5**, 381 (2001)
36. V. Iliev, A. Ileva, L. Bulyarska, *J. Mol. Catal. A Chem.* **126**, 99 (1997)
37. D. Jiang, G. Pan, B. Zao, *Appl. Catal. A General* **201**, 169 (2000)
38. V. Iliev, *J. Photochem. Photobiol. A Chem.* **149**, 23 (2002)
39. V. Iliev, A. Mihaylova, L. Bilyarska, *J. Mol. Cat. A Chem.* **184**, 121 (2002)
40. G. Schneider, D. Wöhrle, R. Gerdes, *European patent* 2004, 1,204,475
41. A.K. Griesbeck, A. Bartoschek, *Chem. Commun.*, 1594 (2002)
42. L. Meites, P. Zumann (eds.) *Handbook of Organic Electrochemistry* (CRC Press, Cleveland, 1977)
43. S.M. Chen, *J. Mol. Cat. A Chem* **138**, 1 (1999)
44. S.M. Chen, S.W. Chiu, *J. Mol. Catal. A Chem.* **166**, 243 (2001)
45. I. Rosenthal, E. Ben-Hur, in *Phthalocyanines: Properties and Applications*, ed. by C.C. Leznoff, A.B.P. Lever (VCH, New York, 1989)
46. A. Weitemeyer, H. Kliesch, U. Michelsen, A. Hirth, D. Wöhrle, in *Photodynamic Tumor Therapy: 2nd and 3rd Generation Photosensitizers*, ed. by J.G. Moser (Harwood, London, 1998) p. 87
47. B.W. Henderson, T. Dougherty, *J. Photochem. Photobiol.* **55**, 145 (1992)
48. S. Müller, V. Mantareva, N. Stoichkova, H. Kliesch, A. Sobbi, D. Wöhrle, M.J. Shopova, *Photochem. Photobiol. B Biol.* **35**, 167 (1996)
49. M. Shopova, D. Wöhrle, V. Mantareva, S. Müller, *J. Biomed. Opt.* **4**, 276 (1999)
50. M. Shopova, M. Peeva, N. Stoichkova, G. Jori, D. Wöhrle, G. Petrov, *J. Porphyrins Phthalocyanines* **9**, 798 (2001)
51. G. Jori, *Environ. Toxicol. Oncol.* **25**, 505 (2006)
52. V. Mantareva, V. Kussovski, I. Angelov, E. Borosova, L. Avramov, G. Schnurpfeil, D. Wöhrle, *Bioorg. Med. Chem.* **15**, 4829 (2007)
53. B. Basu, S. Satapathy, A.K. Bhatnagar, *Catal. Rev. Sci. Eng.* **35**, 571 (1993)
54. A.K. Sharipov, S.V. Kortunenko, *Petroleum Chem.* **37**, 558 (1997)
55. R.A. Meyers, *Handbook of Petroleum Refining Processes* (McGraw-Hill, New York, 1986)
56. A.P. Hong, S.D. Boyce, M.R. Hoffmann, *Environ. Sci. Technol.* **23**, 533 (1989)
57. S. Dannenberg, M. Kroder, W. Dilling, H. Cypionka, *Arch. Microbiol.* **158**, 93 (1992)
58. M. Chandra, A. Grinshpun, K.F. O'Driscoll, G.L. Rempel, *J. Mol. Catal.* **26**, 267 (1984)
59. H. Fischer, G. Schulz-Ekloff, D. Wöhrle, *Chem. Eng. Technol.* **20**, 462–624 (1997)
60. M. Alexander, *Science* **211**, 132 (1981)
61. G. Gottschalk, H.J. Knackmuss, *Angew. Chem. Int. Ed. Engl.* **32**, 1398 (1993)
62. P.R. Gogate, A.B. Pandit, *Adv. Environ. Res.* **8**, 553 (2004)
63. Q. Yang, *J. Photochem. Photobiol. A Chem.* **165**, 229 (2004)

64. N.A. Garcia, J. Photochem. Photobiol. B Biol. **22**, 185 (1994)
65. P.G. Tratnyek, J. Hoigne, J. Photochem. Photobiol. A Chem. **84**, 153 (1994)
66. N. Nensala, T. Nyokong, J. Mol. Catal. A Chem. **164**, 69 (2000)
67. M. Nowakowska, M. Kepczynski, K. Szczubialka, Pure Appl. Chem. **73**, 491 (2001)
68. M. Suzuki, Y. Ohta, M. Kimura, K. Hanabusa, H. Shirai, D. Wöhrle, Chem. Commun 213 (2000)
69. J.S. Miller, Water Res. **39**, 412 (2005)
70. M. Hu, Y. Xu, Z. Xion, Chem. Lett. **33**, 1092 (2004)
71. R. Gerdes, *Doctoral Thesis* Universität Bremen (2000)
72. D. Chatterjee, A. Mahata, Appl. Catal. B: Environ. **33**, 119 (2001)
73. D. Chatterjee, A. Mahata, J. Photochem. Photobiol. A Chem. **153**, 199 (2002)
74. R. Gerdes, D. Wöhrle, Unpublished results (2007)
75. Grover R, Cessna AJ (eds) *Environmental Chemistry and Herbicides* (CRC Press, Boca Raton, 1991)
76. H.D. Burrows, M. Canle, J.A. Santaballa, S. Steenken, J. Photochem. Photobiol. B: Biol. **76**, 71 (2002)
77. S.L.H. Rebelo, A. Melo, R. Coimbra, M.E. Azenha, M.M. Pereira, H.D. Burrows, Environ. Chem. Lett. **5**, 29 (2007)
78. S.A. Naman, Z.A.A. Khammas, F.M. Hussein, J. Photochem. Photobiol. A: Chem. **153**, 229 (2002)
79. Y. Cho, H. Park, W. Choi, J. Photochem. Photobiol. A: Chem. **165**, 43 (2004)
80. A. Posadaz, A. Biasutti, C. Casale, J. Sanz, F. Amat-Guerri, N.A. Garcia, Photochem. Photobiol. **80**, 132 (2004)
81. S.R. Dixon, C.H.J. Wells, Pest. Sci. **14**, 444 (2006)
82. W.A. Massad, J.M. Mariou, N.A. Garcia, Pharmazie **61**, 1019 (2006)
83. H. Chen, T. An, Y. Fang, K. Zhu, J. Mol. Catal. A: Chem. **147**, 165 (1999)
84. K. Kasuga, T. Akita, N. Matsuura, M. Handa, T. Sugimori, Chem. Lett. 966 (2002)
85. K. Kasuga, K. Ohmori, H. Tanaka, M. Handa, T. Sugimori, Inorg. Chem. Commun. **9**, 1019 (2006)
86. X. Tao, W. Ma, T. Zhang, J. Zhao, Angew. Chem. **113**, 3103 (2001)
87. X. Tao, W. Ma, T. Zhang, J. Zhao, Chem. Eur. J. **8**, 1321 (2002)
88. A. Fujishima, K. Honda, Nature **238**, 37 (1972)
89. A. Fujishima, K. Hashimoto, T. Watanabe, *TiO₂ Photocatalysis: Fundamental and Applications* (BKC, Tokyo, 1999)
90. K. Kalyanasundaram, M. Graetzel (eds.), *Photosensitization and Photocatalysis Using Inorganic and Organometallic Compounds* (Kluwer, Dordrecht, 1993)
91. M. Kaneko, I. Okura, (eds.), *Photocatalysis: Science and Technology* (Kodansha/Springer, Tokyo/Berlin 2002)
92. J. Taguchi, T. Okuhara, Appl. Cat. A: Gen. **89**, 194 (2000)
93. W. Choi, J. Lee, S. Kim, S. Hwang, M.C. Lee, T.K. Lee, J. Ind. Eng. Chem. **9**, 96 (2003)
94. M. Nazir, J. Takasaki, H. Kumazawa, Chem. Eng. Commun. **190**, 322 (2003)
95. H.D. Jang, S.K. Kim, S.J. Kim, J. Nanoparticle Res. **3**, 141 (2001)
96. J. Lee, H. Park, W. Choi, Environ. Sci. Technol. **36**, 5462 (2002)
97. M. Kaneko, N. Gokan, N. Katakura, Y. Takei, M. Hoshino, Chem. Commun., 1625 (2005)
98. M. Kaneko, K. Suzuki, Y. Kaburagi, J. Photochem. Photobiol. A:Chem. **169**, 71 (2005)

99. M. Kaneko, N. Katakura, C. Harada, Y. Takei, M. Hoshino, *Chem. Commun.*, 3436 (2005)
100. M. Kaneko, J. Motoyoshi, A. Yamada, *Nature* **285**, 468 (1980)
101. C.W. Tang, *Appl. Phys. Lett.* **48**, 183 (1986)
102. D. Wöhrle, L. Kreienhoop, G. Schnurpfeil, J. Elbe, B. Tennigkeit, S. Hiller, D. Schlettwein, *J. Mater. Chem.* **5**, 1819 (1995)
103. K. Nagai et al., *Appl. Surf. Sci.* **197**, 808 (2002)
104. M. Hiramoto et al., *Appl. Phys. Lett.* **58**, 1062 (1991)
105. P. Peumans, S. Uchida, S.R. Forrest, *Nature (London)* **425**, 158 (2003)
106. T. Abe, K. Nagai et al., *Angew. Chem. Int. Ed.* **45**, 2778 (2006)
107. T. Abe, K. Nagai et al., *Chem. Phys. Chem.* **5**, 716 (2004)
108. T. Abe, K. Nagai et al., *J. Electroanal. Chem.* **587**, 127 (2006)
109. T. Abe, K. Nagai, *J. Electroanal. Chem.* **583**, 327 (2005)
110. K. Nagai, T. Abe, JP patent

Optical Oxygen Sensor

N. Asakura and I. Okura

Abstract Photoexcited triplet state of porphyrins and phthalocyanines is efficiently quenched by molecular oxygen and the quenching reaction is based on the first-order kinetics on the oxygen concentration. Therefore, phosphorescence measurement and lifetime measurement of the photoexcited triplet state are applied for optical oxygen sensing techniques. In the case of phosphorescence measurement platinum or palladium porphyrins, which emit only phosphorescence under room temperature and normal pressure, are suitable sensor molecules and are useful for visual oxygen sensor. The triplet lifetime measurement is independent of both the porphyrin concentration and the excitation light intensity, thus the measurement can adapt to a variety of application. Optical oxygen sensor based on phosphorescence measurement and the lifetime measurement is applied for solid surface measurement and an investigation of the oxygen concentration inside a living cell. When porphyrin is painted on solid surface, an oxygen concentration on the surface alters depending on air pressure change and phosphorescence intensity response to the change, because an oxygen concentration increases with increase in oxygen partial pressure. Phosphorescence intensity of the painted surface becomes larger at low pressure, and likewise the intensity becomes smaller at high pressure. The flow image of a flying airplane or a running car seems to be clarified by optical oxygen sensing in a wind tunnel experiment. Oxygen sensitivity and responsibility was investigated on the surface of solid oxygen sensor devices, which are porphyrin encapsulated polymer and porphyrin immobilized aluminum oxide plate. Optical oxygen sensor is also applied for an investigation and a making image of an oxygen concentration inside a living cell and development of phosphorescence lifetime measurement system combined with microscope. It is known that porphyrins accumulate inside a cell when a living cell is soaked in porphyrin solution. Therefore, the oxygen concentration inside the cell was investigated by phosphorescence lifetime of the accumulated porphyrins. Lifetime measurement is a powerful tool for the experiment, because the accumulated porphyrins are localized and are not spread over whole cell homogeneously. Pulsed Nd-YAG laser was used as an excitation light and CCD detector was set in microscope. Phosphorescence from the accumulated Pt-porphyrin inside a cell was detected through an objective lens, so that an emitting image of whole cell was directly obtained and the oxygen concentration distribution was determined from phosphorescence lifetimes at the point of CCD pixels.

12.1 Introduction

Photoexcited triplet state of porphyrins is efficiently quenched by molecular oxygen and the quenching reaction is based on the first-order kinetics on the oxygen concentration. Therefore, phosphorescence measurement and lifetime measurement of the photoexcited triplet state are applied for optical oxygen sensing techniques. In the case of phosphorescence measurement platinum and palladium porphyrins emitting phosphorescence under room temperature and normal pressure are suitable sensor molecules and are useful for visual oxygen sensor.

In this chapter, optical oxygen sensor based on phosphorescence measurement and the lifetime measurement is applied for solid surface measurement and an investigation of the oxygen concentration inside a living cell.

The aim of the optical oxygen sensor on solid surface is an investigation into air resistance for airframe design of a rocket, an airplane, and a car. When porphyrin is painted on solid surface, an oxygen concentration on the surface alters depending on air pressure change and phosphorescence intensity changes according to the air pressure, because an oxygen concentration increases with oxygen partial pressure. Phosphorescence intensity of the painted surface becomes larger at low pressure, and likewise the intensity becomes smaller at high pressure. The air resistance of a flying airplane or a running car seems to be clarified by optical oxygen sensing in a wind tunnel experiment.

Optical oxygen sensor is also applied for an investigation and a making image of an oxygen concentration inside a living cell. It is known that porphyrins accumulate inside a living cell when the cell is soaked in porphyrin solution. Therefore, the oxygen concentration inside the cell is investigated by phosphorescence lifetime of the accumulated porphyrins. Lifetime measurement is a powerful tool for the experiment, because the accumulated porphyrins are localized and are not spread over whole living cell homogeneously. A novel application of optical oxygen sensor and development of measurement system combined with microscope is described.

12.2 Theoretical Aspect of Optical Oxygen Sensor of Porphyrins

12.2.1 Advantage of Optical Oxygen Sensing

Several methods for oxygen detection have been reported and some based on titration [1], amperometric [2], chemiluminescence [3], or thermoluminescence [4]. Winkler titration has been employed for the measurement of oxygen for many years and is considered, to some extent, to be the standard method [1]. However, the time-consuming and cumbersome nature of the titration has hindered its application to process monitoring. The Clark electrodes provided a breakthrough technique for the measurement of oxygen and have become the

conventional method. The Clark electrode is stable against many conditions and quite reliable. The electrode, however, has problems for some measurements, such as small scale analyzing, measurement of low oxygen concentration, and high speed analyzing. One of the defeats is oxygen consumption since oxygen is reduced on the cathode. Therefore, misleading data are easily generated on small amount of analyte. Thus, the movement of oxygen through the membrane in the electrode is the diffusion-limited passage, and the diffusion resistance causes measurement error, such as fouling of the membrane or a change in flow conditions in the testing fluid [5,6].

Thus, there is an intense interest in novel and superior oxygen sensing technique. Optical oxygen sensing is one of the solutions to the problems of oxygen sensors. Optical oxygen sensor is a chemical sensor and porphyrin compounds or ruthenium complexes are mainly used for a sensing molecule. The photoexcited triplet state of porphyrin (or ruthenium complex) is easily quenched by oxygen, and oxygen concentration can be detected by monitoring the photoexcited triplet state, such as phosphorescence intensity, luminescence intensity [7,8], and lifetime [9]. Optical oxygen sensors do not consume oxygen and are free from electrical interferences. Moreover, optical oxygen sensing became a useful sensor for various applications.

12.2.2 Principle of Optical Oxygen Sensor

Figure 12.1 shows simple energy diagram of porphyrin compounds. Three energy levels are the ground state (S_0), the photoexcited singlet state (S_1), and the photoexcited triplet state (T), respectively. When the light whose wavelength corresponds to the energy gap between S_0 and S_1 is irradiated to porphyrin, an electron at S_0 is pumped up to S_1 , and the porphyrin energy level increases the photoexcited singlet state. The photoexcited singlet state flows down two pathways. One is to return to the ground state consuming the excess electronic energy in the form of heat to the surrounding medium or

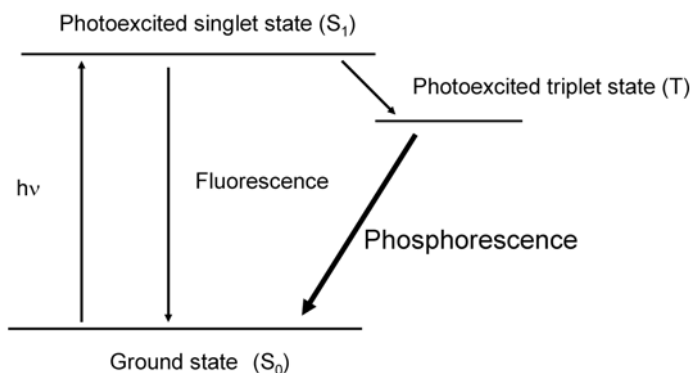


Fig. 12.1. Energy diagram of porphyrins

by emission of a photon known as fluorescence. Decay time of fluorescence is usually short, 10^{-9} to 10^{-7} s. The other is to transfer down to the photoexcited triplet state. When the electron transfer to the photoexcited triplet state occurs, electron spin changes and spin pair between the ground state and the photoexcited triplet state becomes forbidden transition.

The photoexcited triplet state flows to the ground state consuming the energy in the form of heat or a photon known as phosphorescence. In the case of phosphorescence, the electron at the triplet state falls down to the ground state with change of electron spin, so that phosphorescence lifetime is longer than fluorescence, being about 10^{-5} to 10 s [10, 11].

The photoexcited triplet state is capable of reaction with other molecules, such as reduction, oxidation, and energy transfer. Porphyrins in the photoexcited triplet state particularly facilitate a reaction with oxygen. Energy level of the photoexcited triplet state of porphyrins is nearby the redox potential of oxygen and the LUMO of oxygen, thus oxygen becomes superoxide anion radical (O_2^-) by electron donation from porphyrin or becomes singlet oxygen ($^1\text{O}_2$) by energy transfer from porphyrin. As these reactions are first-order kinetics of oxygen concentration, the photoexcited triplet state or phosphorescence depends on the amount of oxygen. The relation between the photoexcited triplet state and oxygen concentration based on first-order kinetics reaction is described as follows:

In the absence of oxygen, the photoexcited triplet state returns to the ground state undergoing some relaxations such as internal conversion and thermal radiation. Each rate constant represents $k_1, k_2, \dots$

$$\frac{d[\text{T}]}{dt} = -(k_1 + k_2 + \dots) [\text{T}] \quad (12.1)$$

$$\ln[\text{T}] = -\sum k_n t + \text{Const.} \quad (12.2)$$

$$\frac{1}{\sum k_n} = \tau_0 \quad (12.3)$$

where $[\text{T}]$ is the concentration of the photoexcited triplet state and τ_0 (s) is the lifetime of the photoexcited triplet state.

In the case of oxygen reacting with the photoexcited triplet state, the rate is represented as follows:

$$\frac{d[\text{T}]}{dt} = -\left(\sum k_n + k_{\text{et}}[\text{O}_2]\right) [\text{T}] \quad (12.4)$$

$$\tau = \frac{1}{\sum k_n + k_{\text{et}}[\text{O}_2]} \quad (12.5)$$

where k_{et} is the rate constant in the reaction with oxygen, $[\text{O}_2]$ is oxygen concentration, τ (s) is lifetime of the photoexcited triplet state in the presence of oxygen. The relation between lifetime and oxygen concentration is

$$\tau_0/\tau = 1 + \tau_0 k_{\text{et}}[\text{O}_2] \quad (12.6)$$

$\tau_0 k_{\text{et}} (= K_{\text{sv}})$, Stern–Volmer constant, in the equation, Stern–Volmer equation, evaluate the oxygen sensitivity of optical oxygen sensors [12].

The Stern–Volmer equation shows that lifetime of the photoexcited triplet state corresponds to oxygen concentration. Therefore, phosphorescence lifetime measurement is one of the useful methods for optical oxygen sensing. Phosphorescence intensity substitutes for phosphorescence lifetime as far as porphyrin molecules do not interact strongly with each other at the ground state. Under this condition,

$$I_0/I = \tau_0/\tau (= 1 + K_{\text{sv}}[\text{O}_2]) \quad (12.7)$$

where I_0 and I are phosphorescence intensity in the absence and the presence of oxygen, respectively.

12.2.3 Brief History of Optical Oxygen Sensors

Kautsky discovered that the phosphorescence [13] and the fluorescence [14] of surface-adsorbed dyes such as tryptaflavin, benzoflavin, safranin, chlorophyll, and porphyrins were sensitively quenched by molecular oxygen, which, in its electronic ground state, was a triplet molecule. This led to the design of the first optical sensor for oxygen. Depending on the measurement of either phosphorescence or fluorescence, extremely low sensitivities (typical detection limit in phosphorimetry 0.067 Pa oxygen) are achieved [15]. Zakharov and Grishaeva [16] have utilized this effect to devise an optical sensor for low oxygen levels as they occur in wastewater. Detection limits are reported to be as low as 0.5 mg oxygen per liter. The fast growing interest in optical sensors has led to a variety of other sensor types in the past. Bergman [17] and others [18–22] have used polycyclic aromatic hydrocarbons (PAHs) which are found to be efficiently quenched by oxygen in the 0–40 kPa range. The PAHs are either dissolved in a polymer [19–22], soaked into porous glass [17], or covalently immobilized on glass support [18]. Peterson et al., by combining Kautsky's adsorption technique with the sensitivity of the PAHs, developed a fiber-optic sensor for oxygen based on the oxygen-sensitive fluorescence of Amberlite-adsorbed perylene dibutyrate [23].

Changes in luminescence intensity can therefore be used to monitor oxygen [24]. It is also shown that the fluorescent dye pyrene butyric acid (PBA) might be used to determine oxygen in biological microenvironments. Subsequently, PBA is used by several workers for oxygen measurement in tissue [25, 26]. PBA is also used in a gaseous oxygen sensor [20], with a thin layer of the dye (10 μm thick) trapped behind a 6- μm thick gas-permeable Teflon membrane. For in vivo oxygen concentration measurement, a catheter tip sensor that can be used in tissue or introduced into blood vessels has been developed [5]. The fluorescence dye (perylene dibutyrate) used in this system is held behind a 25- μm thick porous polypropylene gas-permeable membrane. The oxygen concentration is calculated using an equation derived from the Stern–Volmer relationship, including a correction for the non-linearity of the response.

Recently, phosphorescence quenching-based sensors have increasingly become the focus of attention as they have several advantages over fluorescence-based ones. The longer excited state lifetimes of phosphorescent indicators give rise to high quenching efficiency by oxygen. In addition, the long excitation and emission wavelengths are more compatible with the available optical monitoring technology. Historically, the first optical sensors for oxygen described in the literature are based on room-temperature phosphorescence quenching of immobilized dyes, though these dyes tended to be photolabile [27]. Indeed, this tends to be a general problem associated with excited triplet state molecules and is one of the major drawbacks associated with their use. As molecules in the triplet state have long lifetimes, they should in principle form the basis of an extremely sensitive oxygen sensor. However, until recently, there have been few molecules that exhibit a strong phosphorescence yield at room temperature. Recently, several probes that are suitable for room-temperature phosphorescence applications have been presented. More recent room-temperature phosphorescence quenching-based sensors have utilized metal chelates such as tetrakis(pyrophosphito)dipalladate (II) [28] and 8-hydroxy-7-iodo-5-quinolinesulfuric acid (ferron) chelates [29], the organic dyes, camphorquinone [30] and erythrosin B [31] and metalloporphyrins [32]. In the following sections optical oxygen sensors using metalloporphyrins are described.

12.3 Optical Oxygen Sensor by Phosphorescence Intensity

12.3.1 Phosphorescent Compounds

In this section, optical oxygen sensor based on the phosphorescence intensities is described. Platinum porphyrins, palladium porphyrins, and ruthenium complexes are useful phosphorescent molecules because they emit relatively strong phosphorescence under room temperature and normal pressure and because the phosphorescence is in visible light region. These properties are very suitable for application of optical oxygen sensor. Figure 12.2 shows some structures of platinum porphyrins, palladium porphyrins, and ruthenium complexes.

12.3.2 Immobilization of Phosphorescent Molecules for Optical Oxygen Sensor and Measurement System

Phosphorescent molecules should be immobilized on polymer or base to make an optical oxygen sensor. Both high gas-permeability and solvent-impermeability are desirable for the polymer or base. Silicone rubber, glass, polystyrene, aluminum oxide, etc. relatively meet to the demands. Structures of some suitable polymers are shown in Fig. 12.3. Phosphorescent molecules

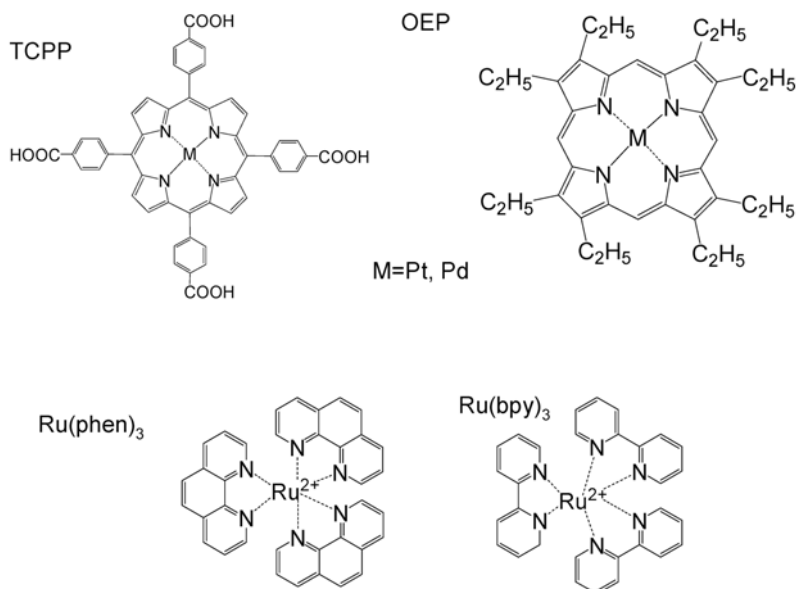


Fig. 12.2. Structures of phosphorescent compounds

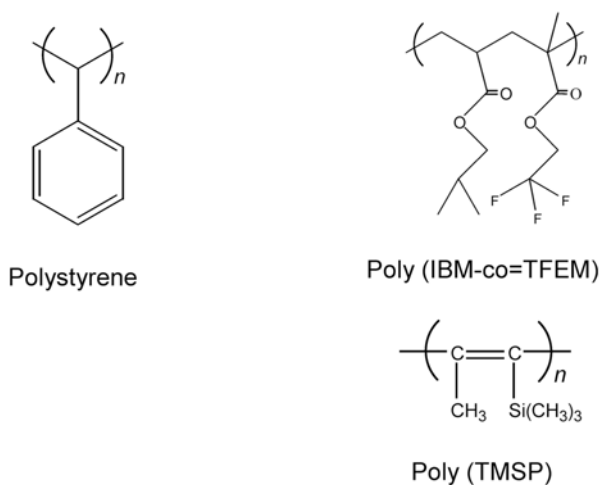


Fig. 12.3. Structures of polymer used to optical oxygen sensor film

and polymer are formed into film and applied for phosphorescence intensity measurements. The size of the film is normally 1×2 cm and attached to measurement system. In the case of optical fiber probe measurement system, the film is cut into small pieces which fit on the probe tip.

Figure 12.4 shows a measurement system of phosphorescence intensity. The system consists of excitation light unit, emission detector unit, and mixed gas

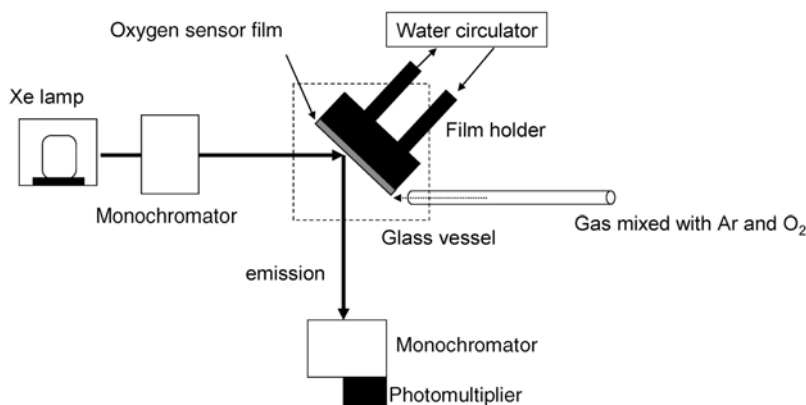


Fig. 12.4. Typical measurement system of phosphorescence intensity

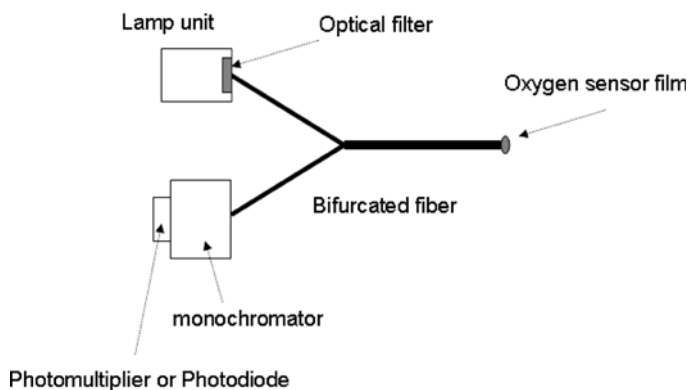


Fig. 12.5. Phosphorescence intensity measurement system by optical fiber probe

flow unit. The excitation light unit selects single wavelength from Xe lamp by monochromator and the emission detector unit detects phosphorescence intensity at single wavelength by monochromator and photomultiplier. These two units are a typical system which can measure emission spectrum. In the mixed gas flow unit, sensor film set on a holder in a glass vessel. Mixed gas flows in the glass vessel and the percentage of oxygen to argon is well defined by gas flow meter.

Measurement of phosphorescence intensity by optical fiber probe is also developed as shown in Fig. 12.5. Purpose of this system is miniaturizing of phosphorescence intensity measurement. Excitation light is guided to one optical fiber of bifurcated optical fiber and the other fiber terminus set in monochromator to detect phosphorescence. Sensor film is attached at the tip in which two fibers bunch together. This system is only demands thin sensor film because oxygen concentration on the film surface is detected by emission

at the reverse surface of the film. Sensitivity of oxygen concentration is not so high in this system, but the fiber probe system has conveniences that can be applied for many situations.

12.3.3 Optical Oxygen Sensor with Platinum Octaethylporphyrin Polystyrene Film (PtOEP-PS Film)

Platinum octaethylporphyrin (PtOEP) as a sensor molecule is widely used for this type of sensor. Polystyrene is one of the suitable matrixes for optical oxygen sensor, because polystyrene has high transparency, good gas-permeability, and solvent-impermeability.

The phosphorescence spectra under various oxygen concentrations are corrected by measurement system like Fig. 12.3 and Fig. 12.6 showing selected three spectra under 0% oxygen, 25% oxygen, and 100% oxygen. Excitation light wavelength is 535 nm. The maximum intensity of phosphorescence spectrum under 0% oxygen is 646 nm and the other two spectra have the same peak wavelength and the same shape. The shape of spectrum is almost the same as the spectrum of PtOEP in solvent, indicating no specific interactions between PtOEP molecules and polystyrene. Phosphorescence intensity at 646 nm decreases with oxygen concentration increase, showing that phosphorescence is quenched by oxygen. These results show that the photoexcited triplet state of PtOEP is quenched by oxygen as mentioned in Sect. 12.2.

Figure 12.7 shows the relation between phosphorescence intensity at 646 nm and oxygen concentration. Phosphorescence intensity remarkably decreases at low oxygen concentration. This curve is analyzed according to Stern–Volmer equation (refer (12.6)) and Stern–Volmer plot shows in Fig. 12.8.

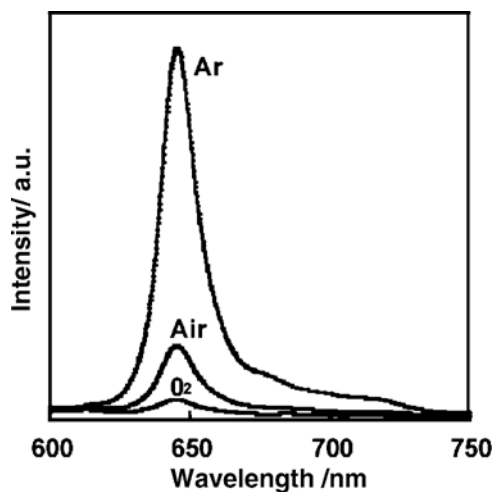


Fig. 12.6. Phosphorescence spectra of PtOEP-PS film. One hundred percent oxygen, air, and 100% argon from bottom to up

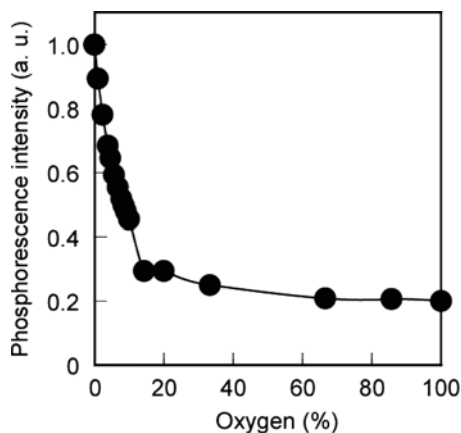


Fig. 12.7. Relation between oxygen concentration and phosphorescence intensity of PtOEP-PS film

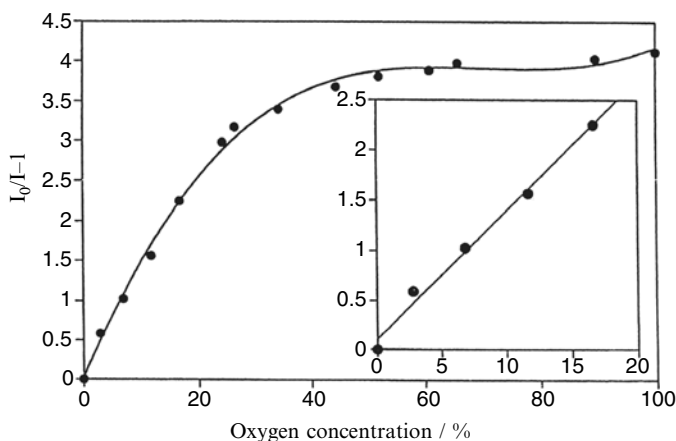


Fig. 12.8. The Stern–Volmer plot of PtOEP-PS film. Inset is an enlargement below 20% oxygen

The Stern–Volmer plots well fit to linear relationship at least for oxygen concentrations up to about 20%. Usually, the results of plateau region at higher oxygen concentrations have been explained by some different theories. One hypothesis is that the photoexcited PtOEP forms complex with oxygen under high oxygen concentration, and the photoexcited state returns to ground state with release of thermal energy, not phosphorescence. Thus, the photoexcited triplet state is lost without phosphorescence radiation at high oxygen concentration.

The other hypothesis is a difference in oxygen concentration inside PS film. PS film is a large extent of thickness compared with porphyrin molecules, and the surface is different from inside in oxygen concentration. Therefore, the

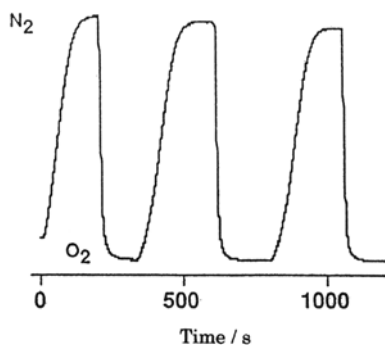


Fig. 12.9. Response test of PtOEP-PS film to gas change from 100% oxygen into 100% nitrogen

phosphorescence is not quenched thoroughly at high oxygen concentration. In another words, inside of PS film still emits phosphorescence at higher oxygen concentration.

Figure 12.9 shows response of PtOEP-PS film to oxygen. The PtOEP-PS film is in 100% oxygen up to 0 s, and then the gas is suddenly changed into 100% nitrogen at the time of 0 s. Phosphorescence intensity is raising just after gas change, and after 100 s the intensity comes up to the maximum intensity under 100% nitrogen. When the gas is changed 100% nitrogen into 100% oxygen, the phosphorescence intensity becomes quickly low in tens of second. This experiment indicates that PS film has slow response to gas, and diffusion inside PS film is not so faster than expected. To develop high-speed optical sensor, some polymers and supports are required.

12.3.4 Optical Oxygen Sensor with PtOEP and Supports

Ceramic materials such as glass have been widely used as supports for optical sensors owing to their superior properties over organic polymers [33–40]. The glass materials and inorganic ceramics prepared by the sol–gel process are transparent, making them highly suitable for quantitative spectrophotometric tests [41,42]. The glasses are also chemically inert, photostable and thermally stable, compared with polymer matrixes, making them highly suitable for applications in harsh environments, and the preparation of the doped glasses is technically simple. Thus, the trapping procedure is straightforward and non-specific compared with the covalent binding of a reagent to a solid support. The reagents are generally non-leachable, thus offering clear advantages over reagent adsorption techniques. Finally, glass materials of various shapes, as well as thin films, are easily prepared. This section describes the fabrication of porphyrin-doped sol–gel glasses and the optical-oxygen sensing properties of these materials [43].

Other sensor characteristics such as photostability and storage stability are also described. Recently, a novel doping method has been introduced using the sol-gel polymerization process. The dopant (in this case, PtOEP) is incorporated in the sol-gel glass at the early stages (or even before initiation) of the polymerization step. Thus, when the dry xerogel is formed the dopants remain physically encapsulated within the glass matrix but maintain their ability to interact with diffusing species. An optical oxygen sensor using PtOEP-doped silica gel glasses is described below.

Absorption maxima of the PtOEP-doped silica glass show a red shift, compared with the initial acetone solution (absorption maxima = 536, 502, and 380 nm in glass; 533, 500, and 377 nm in acetone solution). This red shift can be explained by the lower polarity of the silica matrix, which consists of siloxane (Si-O-Si) and silanol (Si-OH) groups [34, 44, 45]. Phosphorescence spectra of the PtOEP-doped silica glass under de-oxygenated, ambient, and oxygenated conditions are shown in Fig. 12.10, indicating effective quenching of the phosphorescence intensity by oxygen. The emission spectrum of the silica matrix shows no red (or blue) shift and no differences in peak shape, compared with that of the acetone solution (646 nm in both instances). The emission maxima intensities increase strongly on going from the oxygenated to the ambient and de-oxygenated conditions and well fit to the Stern-Volmer equation. Hence, the sol-gel process can provide a good matrix with no interactions between PtOEP and silica during the optical sensing of oxygen.

The silica matrix shows high response to oxygen concentration change compared with polymer matrix such as polystyrene. Response time of the silica matrix sensor to oxygen and nitrogen was measured. Figure 12.11 shows phosphorescence intensity change when 100% nitrogen gas is switched to 100% oxygen (a), and when 100% oxygen is switched to 100% nitrogen (b). The response time from nitrogen to oxygen is within 5 s, and from oxygen to nitrogen

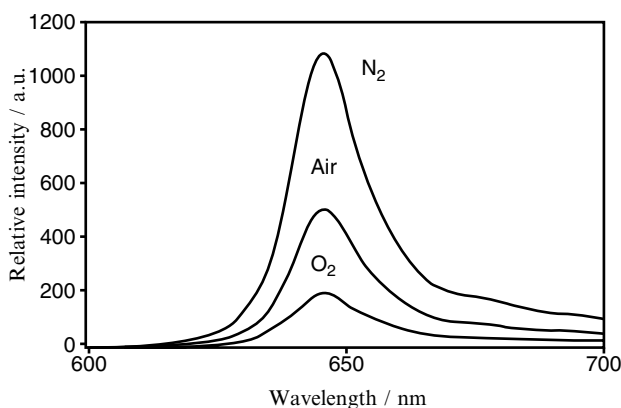


Fig. 12.10. Phosphorescence spectra of PtOEP immobilized silica. One hundred percent oxygen, air, and 100% argon from bottom to up

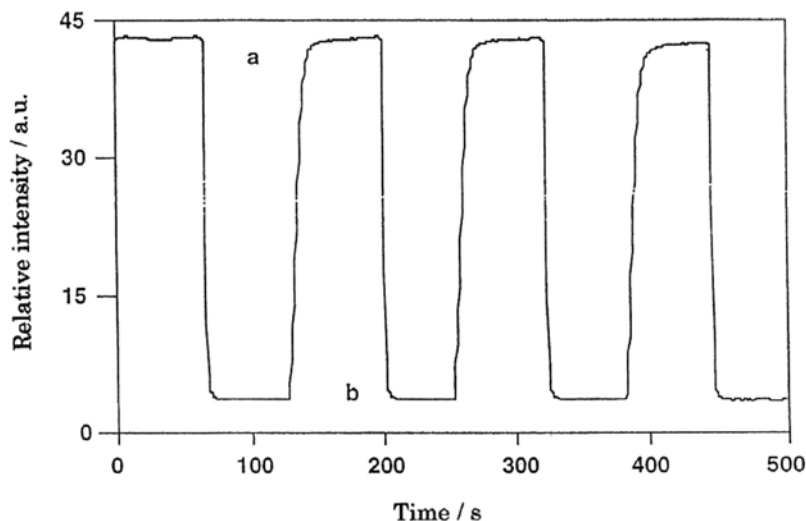


Fig. 12.11. Response test of PtOEP-PS immobilized silica to gas change from 100% oxygen into 100% nitrogen

is 10 s. Response time of the silica matrix sensor is very short compared with polymer matrix-derived optical sensors, and the results correspond to former reports by McEvoy et al. [46]. The fast response obviously comes from the microporous texture of the sol-gel matrix.

12.3.5 Application of Optical Oxygen Sensor for Air Pressure Measurements

Optical oxygen sensing on the surface of sensor film is applied for air pressure measurements. To sum up the relation between oxygen concentration and air pressure briefly, oxygen concentration on the surface becomes higher when air pressure is high. Otherwise oxygen concentration on the surface becomes lower when air pressure is low. Therefore, air resistance in which the surface of object such as a ball, a car, and an airplane is undergoing can be measured by optical oxygen sensor.

In conventional measurement of air resistance, an electrical pressure sensor is used. Optical oxygen sensor has a lot of advantages in comparison of the electrical pressure sensor. Figure 12.12 is a good example for a comparison between optical sensor and electrical sensor, and shows that optical oxygen sensor is superior to the conventional pressure sensor. Two pictures in Fig. 12.9 are the result of wind tunnel test for a rocket model (diameter: 11 cm). The left picture is in the case of optical oxygen sensor, and the right one is an electrical pressure sensor. The rate of wind is 1121 km/h (Mach 0.9) at room temperature. The result measured by the optical oxygen sensor, PtOEP, is

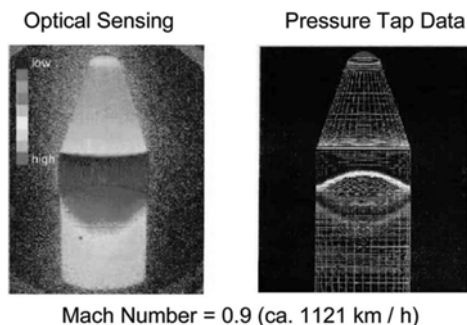


Fig. 12.12. Air resistance image pictures of a rocket model under 1121 km/h. The left picture is the result of optical oxygen sensing. Blue shows low air resistance, and red shows high air resistance. The right picture is obtained is an electrical pressure sensing

painted on the whole surface of the rocket model and the phosphorescence from the surface is recorded by charge coupled devise (CCD) camera. The recorded data are represented by colors from red to blue, and red shows high pressure (high oxygen concentration) and blue shows low pressure, referring to the color bar in the picture. This picture shows that air resistance in which the rocket undergoes is clarified precisely. Optical oxygen sensor easily makes it possible to imaging of air resistance, because every PtOEP molecule painted on the surface detects oxygen concentration. Actually, the rocket model emits phosphorescence, so that we can see distribution of air resistance at the same moment. A real time and visual monitoring is a great advantage of optical oxygen sensor.

The right picture is the result measured by electrical sensor. A lot of the electrical sensors embed in the rocket model and wind tunnel test is done. The picture is calculated distribution of air resistance. In this case, a number of pressure data are the same as that of the sensor, thus data at every point are gathered and analyzed. Pressure data of the area between sensors are not obtained but are interpolated by computing simulation. This experiment requires a lot of cost and long time but unfortunately correct distribution is not obtained.

Optical oxygen sensor gives us the correct data immediately, so this technology is applied for air flame design of a car, a bullet train, and airplane. Figure 12.13a and b shows air resistance measurements on a car body model and at door mirror model. Air resistance imaging is measured, when a car is running at 40, 100, and 137 km/h. The distribution of pressure is represented by colors from red to blue, and red shows high pressure (high oxygen concentration) and blue shows low pressure, referring to the color bar in the right side.

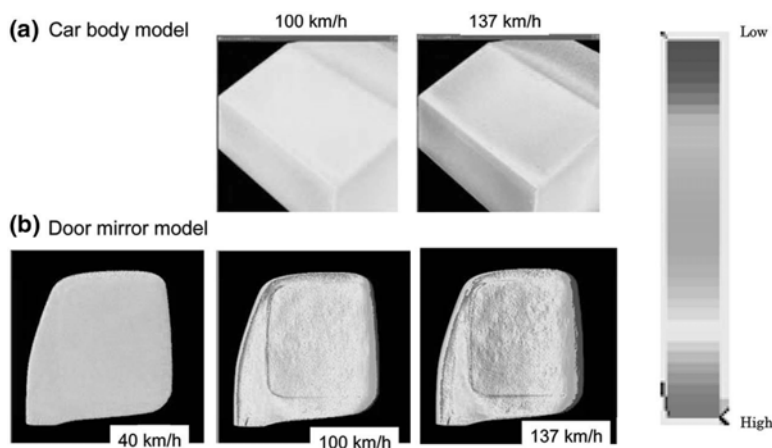


Fig. 12.13. Air resistance image pictures of (a) car body model and (b) door mirror model. Wind tunnel test was done under 40, 100, and 137 km/h. Relative magnitude of air resistance is respect to color bar at the right side in figure

12.4 Optical Oxygen Sensor by Phosphorescence Lifetime Measurements

Phosphorescence lifetime and oxygen concentration are related with the first-order kinetics, the Stern–Volmer equation (refer (12.6)). In this section, optical oxygen sensor by phosphorescence lifetime measurement is described. phosphorescence lifetime measurement requires special equipment in the measurement system, but is suitable for precisely measurement of oxygen concentration.

12.4.1 Advantages of Phosphorescence Lifetime Measurement

Advantage of optical oxygen sensor by phosphorescence lifetime measurement is independent of phosphorescence intensity. Phosphorescence intensity depends on both the number of porphyrin molecules and excitation light intensity. If the thickness of sensor film is different in the area of the film, thick part emits strongly and thin part emits weakly. Correction of the uneven thickness factor is hard work with little success, and to make a flat film is also difficult. In application to air pressure measurements described in Sect. 12.2.5, irradiation of excitation light is a troublesome problem. Homogeneous irradiation of excitation light to the whole surface of PtOEP-painted object requires fine adjust of light intensity and angle which the light should be poured. Lifetime, however, is calculated from the change of the time dependence phosphorescence intensity, so that neither concentration of porphyrin nor excitation light

intensity affects the lifetime. Therefore, optical oxygen sensor by phosphorescence lifetime measurement is suitable for precise measurement of oxygen concentration.

12.4.2 Phosphorescence Lifetime Measurement

Phosphorescence lifetime is measured by flash photolysis. Excitation light should be pulse laser or flash lamp, and the time range of pulse should be lower than one microsecond because phosphorescence lifetime is regularly more than microsecond. Photocurrent detector, such as photomultiplier and CCD camera, is desired to equip time resolution and to synchronize with excitation light. Single photon counting is the most popular technique to measure emission lifetime.

One of the measurement systems is shown in Fig. 12.14. Excitation pulse laser is a dye laser excited by N_2 -laser (337 nm). Phosphorescence through a

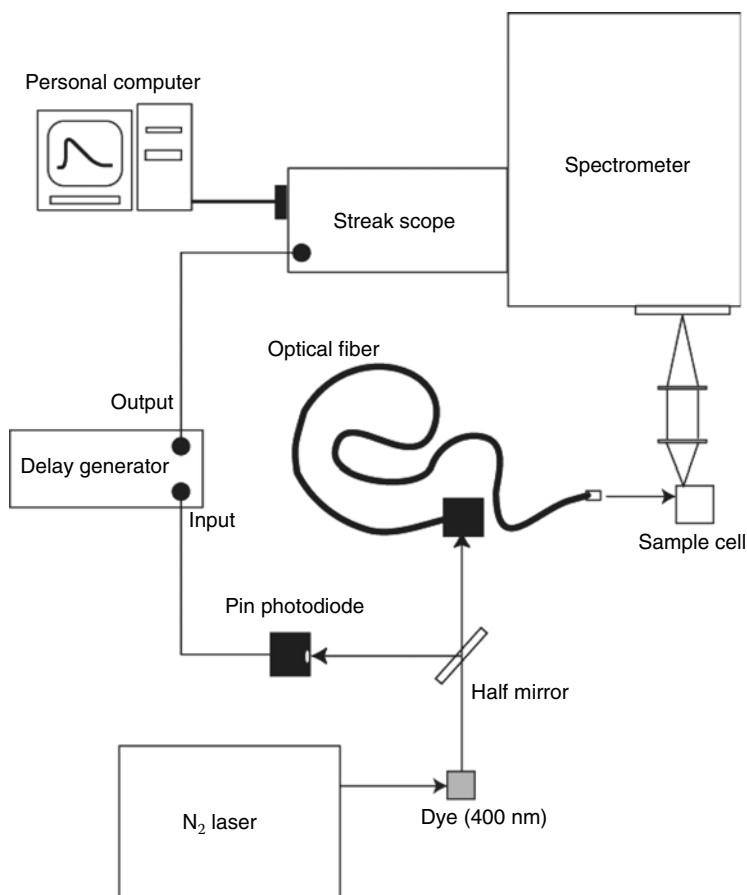


Fig. 12.14. Typical measurement system of phosphorescence lifetime

spectrometer is recorded by streak scope, which works as time resolved CCD. In this system, time resolved phosphorescence spectra are obtained during one pulse laser irradiation. Pathway of the pulse is bifurcated by a halfmirror, and one is to guide for sample and the other is to a pin photodiode by which the electric signal is input into a delay generator. A delay generator adjusts a timing to start streak scope scan. Lifetime at single wavelength is analyzed by first-order kinetics. Phosphorescence is detected just after irradiating laser pulse, and then the phosphorescence decay is observed. The decay curve fits the first-order kinetics and lifetime is determined (see (12.1)—(12.3)). Likewise, lifetime in the presence of oxygen is determined, and relationship between lifetime and oxygen concentration obeys the Stern–Volmer equation (see (12.4)—(12.6)).

There is another method of lifetime measurement. Correlation spectroscopy is known as the other popular lifetime measurement, but the technique is not suitable for optical oxygen sensing based on phosphorescence measurement. Correlation spectroscopy does not require a pulse laser or a flash lamp as excitation light, and excitation light intensity is modulated as sine curve. The problem about excitation light intensity described above (Sect. 12.4.1) is not solved yet.

Some examples of optical oxygen sensor based on phosphorescence lifetime are given with oxygen sensitivity of Pt-tetrakis(4-carboxyphenyl)porphyrin (PtTCPP) and Pd(II)-tetrakis(4-carboxyphenyl)porphyrin (PdTCPP). Structures of PtTCPP and PdTCPP are shown in Fig. 12.12. Phosphorescence lifetime of PtTCPP and PdTCPP are listed in Table 12.1. The data shows lifetimes at oxygen concentration 0%, 5%, 10%, and 15%. Lifetime becomes shorter with increase in oxygen concentration, showing that oxygen quenches the photoexcited triplet state of PtTCPP and PdTCPP. Figure 12.15 shows the Stern–Volmer plot of the data in Table 12.1.

12.4.3 Distribution of Oxygen Concentration Inside Single Living Cell by Phosphorescence Lifetime Measurement

As mentioned above, the lifetime is a constant value and is not affected by the concentration of phosphorescence molecules and/or light intensity. These

Table 12.1. Phosphorescence lifetime of PtTCPP and PdTCPP

	PtTCPP	PdTCPP
O ₂	Lifetime/ μ s	Lifetime/ μ s
0%	31.1	238
5%	2.8	4.6
10%	1.4	2.3
15%	1.0	ND

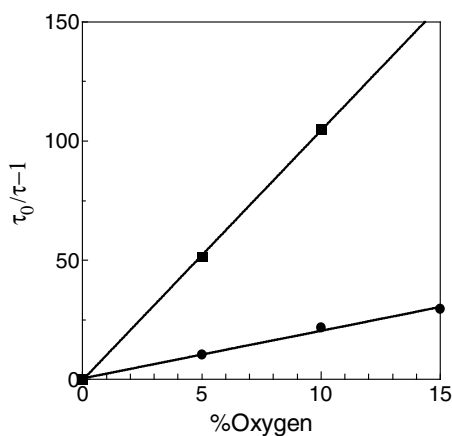


Fig. 12.15. The Stern–Volmer plot of PtTCCP and PdTCCP. Closed squares are PtTCCP and closed circles are PdTCCP

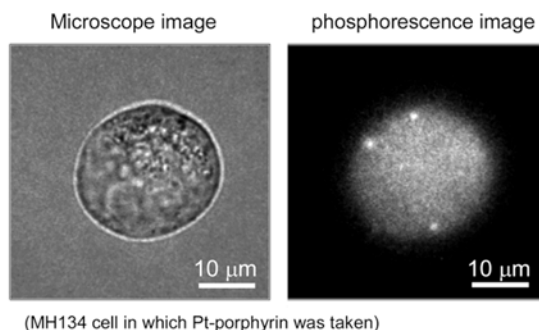


Fig. 12.16. Pictures of MH134 cell after PtTCCP uptake. The left picture is microscope image, and the right picture is phosphorescence image

properties are suitable for oxygen concentration imaging under complicated conditions. Here, novel application of the optical oxygen sensor for oxygen concentration imaging inside living cell is described.

Oxygen concentration imaging can clarify the distribution of oxygen inside a living cell, but it is difficult to clear which part inside cell is high or low oxygen concentration. For example, which is high oxygen concentration around nuclear or at cytosol? How about mitochondria? There is intense interest in experiments which reveal how oxygen concentration inside a cell is. The possibility of oxygen concentration imaging has been explored by optical oxygen sensing technique.

Optical oxygen sensor based on phosphorescence intensity applied to making the oxygen concentration imaging inside a cell. The results are shown in Fig. 12.16. The left picture is MH134 cell recorded by microscope. The

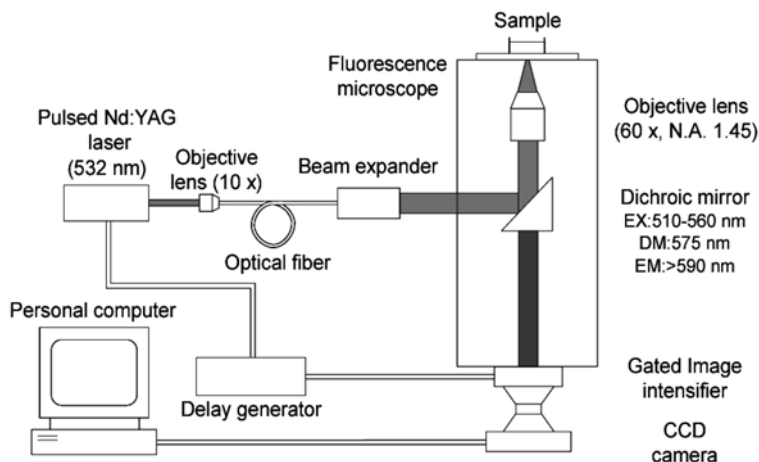


Fig. 12.17. Phosphorescence lifetime imaging system combining laser flash photolysis and microscope

right picture is phosphorescence intensity imaging of MH134 cell in which Pt-TCPP is taken. The phosphorescence image has bright areas and dim areas inside the cell. The concentration of PtTCPP is high at the bright areas and oxygen concentration is unknown. The distribution of PtTCPP inside a cell is not homogeneous, and conditions of uptake of PtTCPP strongly affect the distribution. Thus, to make homogeneous distribution of PtTCPP in a cell is hardly possible. In the case of oxygen concentration imaging inside a cell, optical oxygen sensor based on phosphorescence lifetime is the most powerful tool.

Figure 12.17 shows the lifetime imaging system combining laser flash photolysis and microscope [47]. This system consists of a microscope, a pulse laser, and a CCD detector. Pulse laser for excitation is a pulsed Nd-YAG (neodymium-yttrium-aluminum-garnet) laser. The excitation light is guided to beam expander through an optical fiber, and irradiated to a sample set on the stage of a microscope. The phosphorescence from the sample is recorded by CCD camera equipped with imaging intensifier. The CCD camera is synchronized with a pulse oscillation, which is controlled by a delay generator.

This system records phosphorescence image at the moment in which a delay generator determines. Thus, lifetime is calculated from some phosphorescence images at different delay times. Recorded phosphorescence images are shown in Fig. 12.18. MH134 cells (2×10^5 cell per well) were seeded in 3.5-cm tissue culture dishes in Eagle MEM containing 1.0×10^{-5} M PtTCPP and incubated in the dark at 37°C for 2 h. Cells were then harvested and were centrifuged to remove the cellular components and PtTCPP. The cells were subcultured in 3.5-cm glass-based dishes and applied for the measurement. Phosphorescence intensity represented a red-color image. Bright

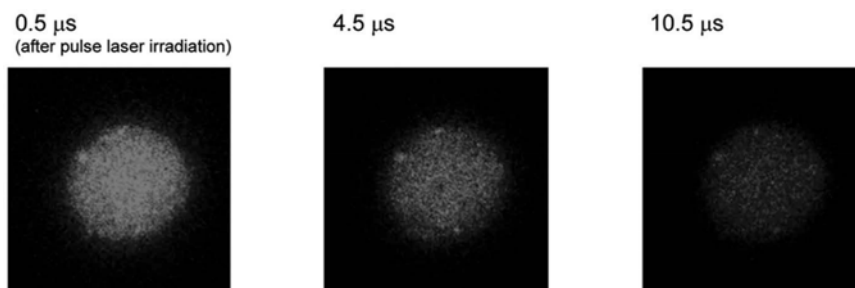


Fig. 12.18. Time dependence of phosphorescence image in MH134 cell. From left to right, 0.5 and 4.5, and 10.5 μs after PtTCCP excitation. Phosphorescence intensity is represented by red color contrast

phosphorescence is emitted from cell at 0.5 μs after excitation pulse irradiation. Phosphorescence intensity became lower at 4.5 μs and then phosphorescence hardly observed at 10.5 μs . The decrease in phosphorescence intensity is fitted to single exponential decay and the lifetime is calculated. In the experiment, 17 sheets of phosphorescence image were recorded every 2 μs starting from 0.5 μs after excitation pulse irradiation. Phosphorescent intensity at typical one pixel in the image data was picked out and was plotted to intensity vs. time as shown in Fig. 12.19a. Figure 12.19b shows semi-logarithmic plots of the phosphorescence decay. The result of calculation shows that lifetime at the point is 18.2 μs .

This analysis is applied for all pixels in the image data and oxygen concentration image is shown in Fig. 12.20. The color of the image indicates the phosphorescence lifetime of the PtTCCP. The region colored in blue means low concentration of oxygen and the red region means high concentration of oxygen.

Membrane is relatively blue and cytoplasm is mainly red in Fig. 12.20. Oxygen concentrations of typical points of membrane and cytoplasm are 20 and 16 μs , respectively. This means oxygen concentration in the cytoplasm is lower than that in the membrane. This may be caused by diffusion of oxygen from the outside to the inside of the cell and oxygen is consumed inside a cell especially mitochondria located in the cytoplasm so that oxygen concentration in the cytoplasm may be lower than that in the membrane.

12.5 Optical Oxygen Sensor T–T Absorption

In this section, two optical oxygen sensors based on triplet–triplet absorption (T–T absorption) are described. One is the photoexcited triplet lifetime measurements, and the other is T–T stationary quenching which is novel optical oxygen sensing. T–T absorption is electron transition from the lowest energy level in the photoexcited triplet state to the second or the higher energy level in the triplet state.

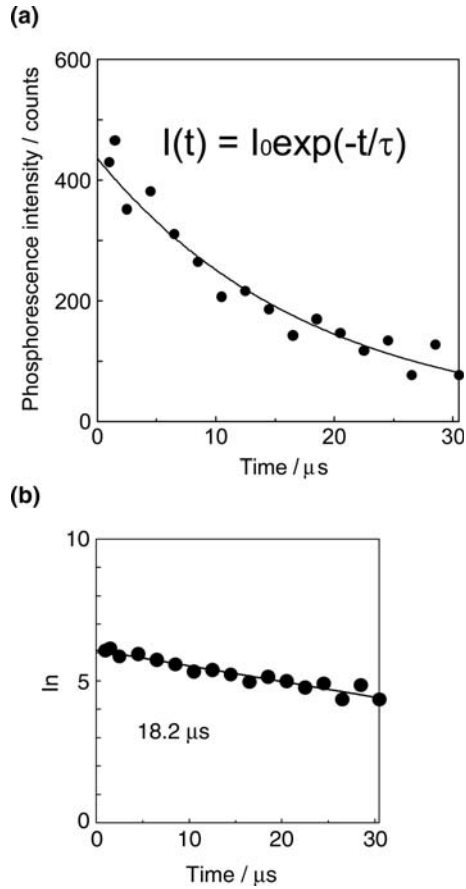


Fig. 12.19. (a) Phosphorescence intensity as a function of time at the specific single pixel of Fig. 12.18. (b) Logarithm plot of (a)

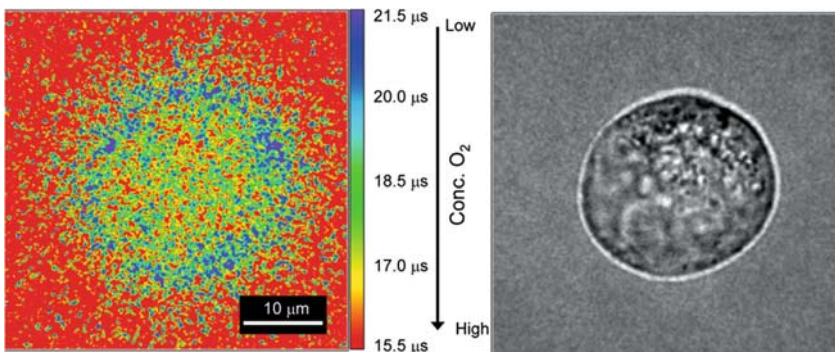


Fig. 12.20. Oxygen distribution in MH134 cell (the left) and microscope image (the right). Oxygen concentration is respect to color bar in the right side of the oxygen distribution picture

12.5.1 Advantage of Optical Oxygen Sensor Based on T–T Absorption

As mentioned above, very few compounds emit phosphorescence under room temperature and normal pressure, such as platinum porphyrins, palladium porphyrins, and ruthenium complexes, and so on. These phosphorescent compounds are of importance in visualizing oxygen concentration. The application of optical oxygen sensor does not become wider in using only these compounds. Moreover, few supports such as polystyrene and silica are utilized for making optical oxygen sensor film.

T–T absorption is not a special property and can be measured in many compounds. Especially most porphyrin compounds and its derivatives have relatively strong T–T absorption, and the photoexcited triplet lifetime is easily measured. A variety of porphyrins and metallo-porphyrins are applied for optical oxygen sensor. Figure 12.21 shows some selected compounds, being suitable for T–T absorption measurement.

12.5.2 Optical Oxygen Sensor Based on the Photoexcited Triplet Lifetime Measurement

Outline of optical oxygen sensor based on the photoexcited triplet lifetime measurement. Energy diagram and T–T absorption are illustrated in Fig. 12.22. Three energy levels are the ground state (S_0), the photoexcited singlet state (S_1), and the lowest energy level of the photoexcited triplet state (T_1), respectively. The photoexcited triplet state (T_1) is generated via the photoexcited singlet state (S_1), after absorption occurs. At this moment the photoexcited triplet state (T_1) can absorb the light of which corresponds to T_1 – T_n energy. T_n is the second or the higher energy level

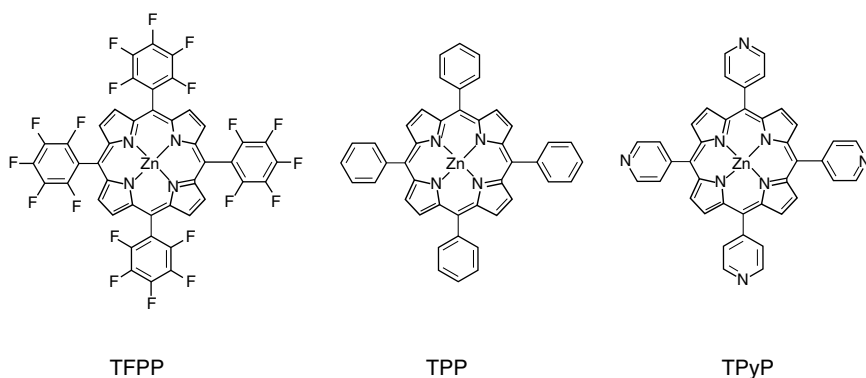


Fig. 12.21. Structures of zinc porphyrins. TFPP is zinc 5,10,15,20-tetrakis-(pentafluorophenyl)-porphyrin, TPP is zinc 5,10,15,20-tetrakis-phenyl-porphyrin, and TPyP is zinc 5,10,15,20-tetrakis-pyridyl-porphyrin

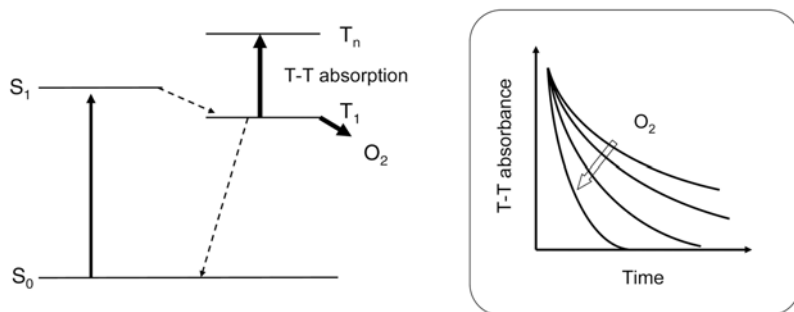


Fig. 12.22. Schematic drawing of T-T absorption with energy diagram. S_0 is the ground state, S_1 is photoexcited singlet state, T_1 is photoexcited triplet state, T_n is the second or the higher photoexcited triplet state

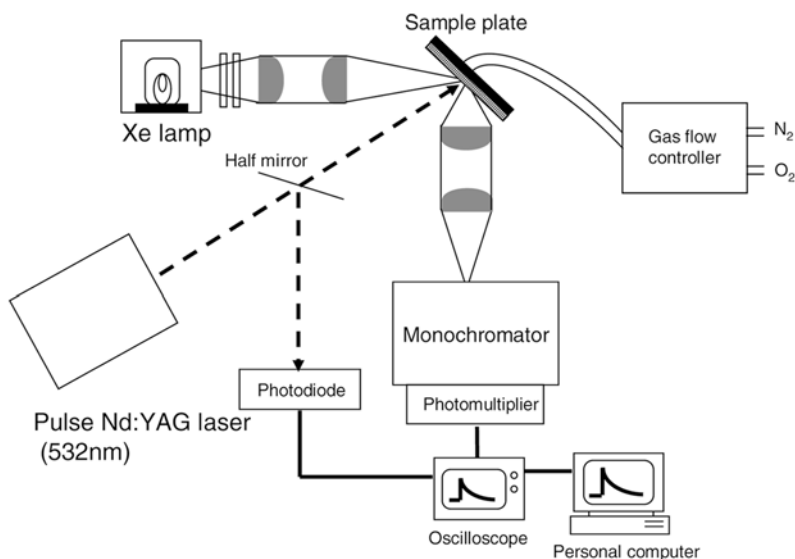


Fig. 12.23. Triplet lifetime measurement system

in the photoexcited triplet state. This is transient absorption according to the first-order kinetics shown in the right side of Fig. 12.22. In the presence of oxygen T-T absorption decay becomes faster. This principle is the same as phosphorescence lifetime (see Sect. 12.4). Since porphyrins have relatively strong T-T absorption in the area of 400–500 nm, T-T absorption is good indicator to detect the photoexcited triplet state.

Figure 12.23 shows a typical measurement system. The system consists of excitation pulse laser, Xe lamp for monitoring T-T absorption, a detector unit synchronized with oscillation of the pulse laser, and mixed gas flow unit.

A pulsed Nd-YAG laser is regularly used as the excitation pulse laser, because second harmonic generation of Nd-YAG laser (532 nm) is suitable for excitation of porphyrin and 10 ns of pulse width is short enough to detect the photoexcited triplet state. T-T monitor light of Xe lamp is irradiated to sensor film attached on mirror, and single wavelength, for example 470 nm, is selected out of the reflected light through monochromator. Intensity of the selected single wavelength is measured by photomultiplier. In the mixed gas flow unit, sensor film set on a holder in a glass vessel. Mixed gas flows in the glass vessel and the percentage of oxygen to argon is well defined by gas flow meter.

ZnTFPP-PS Film

Zinc porphyrins are no phosphorescent compound, but are one of the useful compounds for optical oxygen sensor based on the photoexcited triplet lifetime because the lifetime of zinc porphyrins is long compared with other metal porphyrins. Structure of zinc 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (ZnTFPP) is shown in Fig. 12.21. ZnTFPP-PS film is set in the measurement system described in Sect. 12.4.2.1. Figure 12.24 shows time dependence T-T absorption decays at 470 nm in the absence of oxygen and in 50% oxygen. The lifetime at 0% oxygen is 22.8 ms and at 50% oxygen is 6.4 μ s, indicating that the photoexcited triplet state is quenched by oxygen.

The lifetime ZnTFPP-PS film at various oxygen concentrations was analyzed by Stern-Volmer equation as shown in Fig. 12.25. These data well fit to the Stern-Volmer equation in every oxygen concentration, though phosphorescence lifetime measurement of PtOEP-PS film only fit to the Stern-Volmer equation in the area of low oxygen concentration (Fig. 12.8). This result shows that lifetime measurement is suitable for precise investigation of oxygen concentration.

ZnTFPP-PS Immobilized on Al₂O₃

Porous aluminum oxide (Al₂O₃) was prepared by anodic oxidizing of aluminum. In the case of Al₂O₃, sensitivity to oxygen is higher than polymer. Figure 12.26 shows illustration of the surface of Al₂O₃. Al₂O₃ is prepared by electrolysis of aluminum. Two aluminum plates set on acidic solution such as HNO₃ or H₂SO₄ solution and voltage of 3 V is applied between the two aluminum plates. Oxidation of aluminum occurs on anode aluminum and Al₂O₃ layer is formed on the surface of the anode aluminum. The Al₂O₃ layer has a lot of micro pores, honeycomb structure, on which porphyrin molecules attach. Figure 12.27 shows time dependence T-T absorption decays at 470 nm in the absence of oxygen and in 0.5% oxygen. These decays show single exponential decay and the lifetime at 0% oxygen is 100 μ s and at 0.5% oxygen is 2.6 μ s, indicating that the photoexcited triplet state is quenched by oxygen. The lifetime at various oxygen concentrations was analyzed by the Stern-Volmer equation as shown in Fig. 12.28.

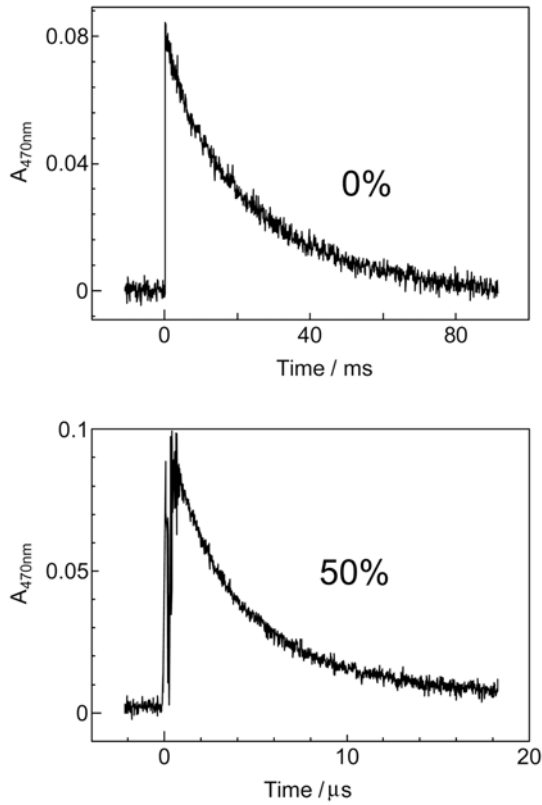


Fig. 12.24. Time dependence of T-T absorption decays of ZnTFPP-PS film. The top is under 0% oxygen, and the bottom is 50% oxygen

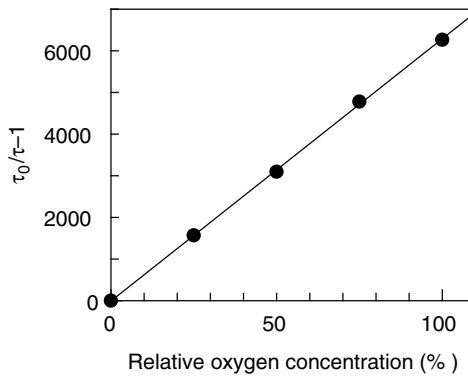


Fig. 12.25. The Stern-Volmer plot of ZnTFPP-PS film

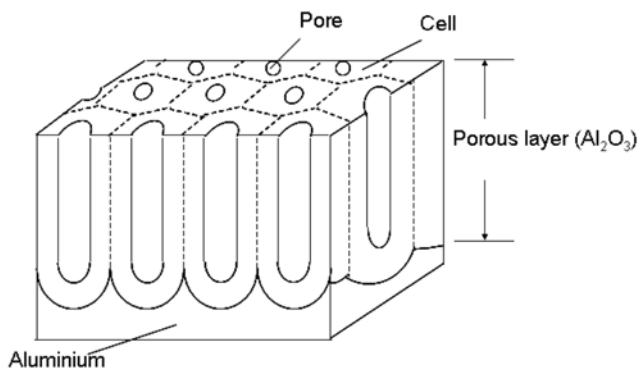


Fig. 12.26. Imaging illustration of aluminum oxide

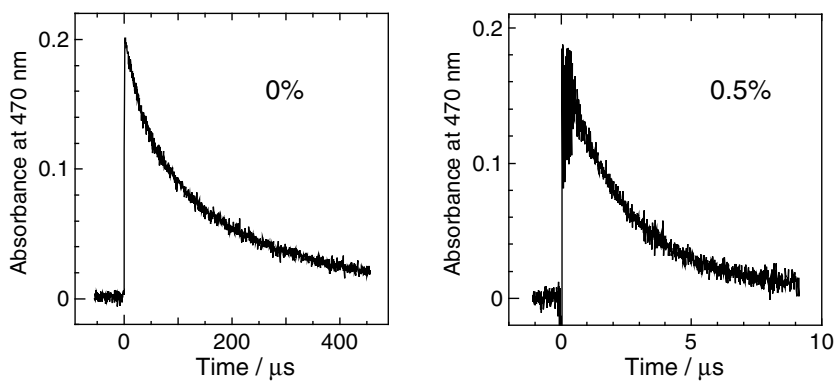


Fig. 12.27. Time dependence of T-T absorption decays of ZnTFPP immobilized Al_2O_3 . The left is under 0% oxygen, and the right is 0.5% oxygen

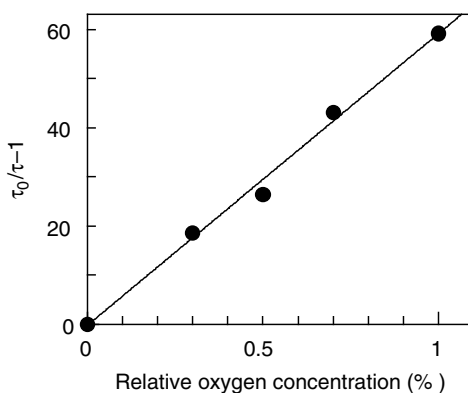


Fig. 12.28. The Stern-Volmer plot of ZnTFPP immobilized Al_2O_3

12.5.3 Optical Oxygen Sensor Based on Stationary T–T Absorption (Stationary Quenching)

Stationary quenching is based on T–T absorption during continuous S_0 – S_1 excitation [48]. The schematic drawing of stationary quenching is shown in Fig. 12.29. As shown in Fig. 12.29a, S_0 is excited to S_1 , S_1 is down to T_1 or S_0 , and then T_1 is back to S_0 . This cycle continuously occurs when S_0 – S_1 is continuously excited by steady state light irradiation. Thus, the concentration of S_0 , S_1 , and T_1 is constant according to the photochemical properties of the porphyrin such as fluorescence quantum yield and molar coefficient of absorption. As shown in Fig. 12.29b T–T absorption is added to this cycle when another light having just energy to T–T transition is irradiated. In the presence of oxygen, $[T_1]$ becomes low because the oxygen quenches the photoexcited triplet state as mention above (Sect. 12.1.1). Therefore, T–T absorption should become small, depending on the decrease of $[T_1]$ (Fig. 12.29c and d). The change of $[T_1]$ is monitored by stationary T–T absorption, and the oxygen concentration estimated.

Stationary quenching is different from lifetime measurement though T–T absorption monitoring. Lifetime measurement monitors T–T absorption change during the relaxation from the photoexcited triplet state to the ground state. Pulse laser is used for the flash excitation. Stationary quenching measurement, however, monitors T–T absorption of the photoexcited state which is continuously generated by CW (continuous wave) laser. Figure 12.30 shows the measurement system of stationary quenching. This system is similar to lifetime measurement system (Fig. 12.23). The excitation laser is a CW laser, not pulse laser. T–T absorbance of the photoexcited state is monitored by Xe

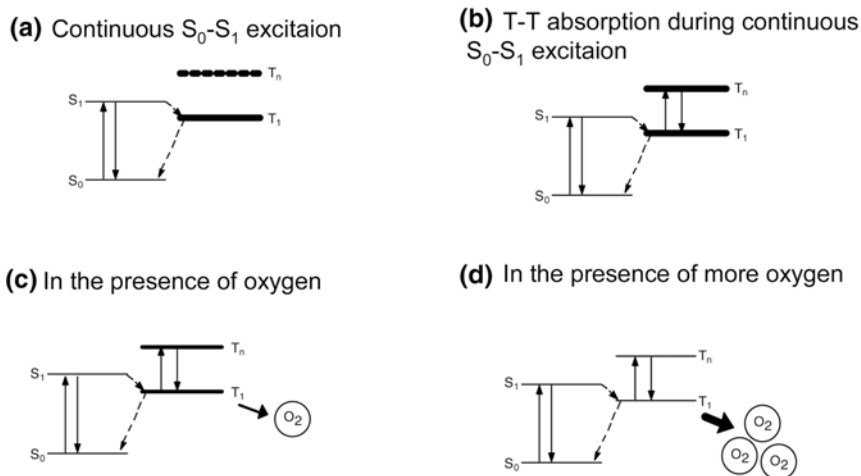


Fig. 12.29. Schematic drawing of stationary quenching

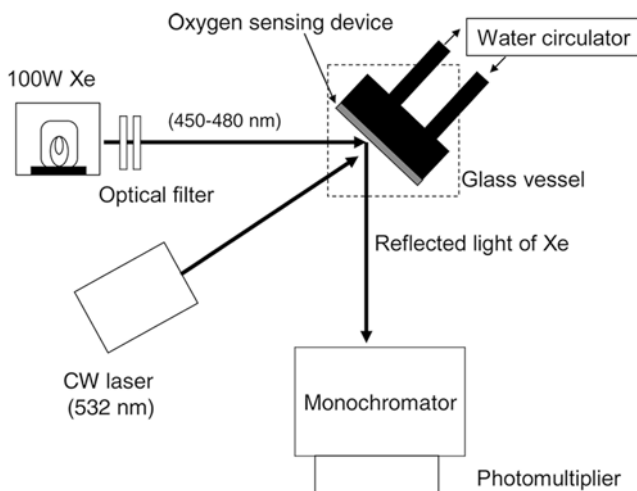


Fig. 12.30. Measurement system of stationary quenching

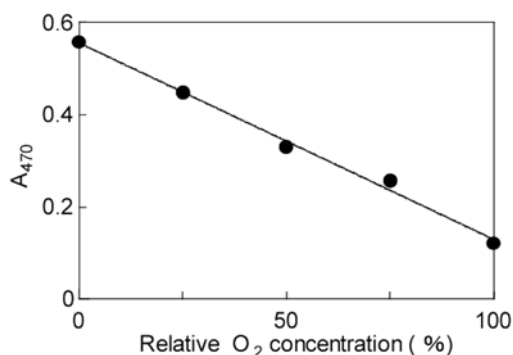


Fig. 12.31. Stationary T-T absorption of ZnTFPP-PS film as a function of oxygen concentration

lamp and photomultiplier. The wavelength around 470 nm is selected from the Xe lamp by optical filter, and the light is irradiated. The light through the sample film (reflected light shown in Fig. 12.30) is gathered and detected photomultiplier via monochromator.

Figure 12.31 shows that T-T absorption intensity of ZnTFPP-PS film as a function of O_2 concentration. S_0 - S_1 excitation light is CW laser (532 nm), and T-T absorption between 450 and 480 nm is monitored. This result shows that linear relationship between T-T absorption intensity and oxygen concentration is obtained by stationary quenching measurement.

12.6 Summary

In this chapter optical oxygen sensor with porphyrin compounds was described. Measurements of phosphorescence intensity, phosphorescence lifetime, and T-T absorption are fundamental techniques of optical oxygen sensing. Optical oxygen sensors are a powerful and useful tool because the oxygen concentration is visually measured.

Remarkable example in experiment of optical oxygen sensors is air resistance imaging. Application for air resistance imaging is one of the successful experiments, and the methodology will contribute to air flame design of a car, a train, and an airplane.

Optical oxygen sensor is also applied for an investigation into an oxygen concentration inside a living cell. This is a novel application of optical oxygen sensors and oxygen concentration imaging (distribution of oxygen concentration inside cell) is clarified.

References

1. D.A. Skoog, D.M. West, F.J. Holler, *Fundamentals of Analytical Chemistry*, 5th edn. (Saunders, Philadelphia, 1988), p. 344
2. L.C. Clark, U.S. Patent 2,913,386, 1959.
3. T.M. Freeman, W.R. Seitz, *Anal. Chem.* **53**, 98 (1981)
4. H.D. Hendricks, U.S. Patent 3,709,663, 1973.
5. X.M. Li, H.Y. Wong, in *Transient D.O. Measurement Using a Computerized Membrane Electrode*, ed. by S. Aiba. Horizons of Biochemical Engineering (University of Tokyo Press, Tokyo, 1987), p. 213
6. X.M. Li, H.Y. Wong HY, U.S. Patent 4,921,582, 1990
7. G.J. Mohr, O.S. Wolfbeis, *Anal. Chim. Acta* **316**, 239 (1995)
8. A.V. Vaughan, M.G. Baron, R. Narayanaswamy, *Anal. Comm.* **33**, 393 (1996)
9. H.N. McMurray, P. Douglas, C. Busa, M.S. Garley, *J. Photochem. Photobiol. A: Chem.* **80**, 283 (1994)
10. G.N. Lewis, M. Kasha, *J. Am. Chem. Soc.* **66**, 2100 (1944)
11. P.F. Lott, R.J. Hurtubise, *J. Chem. Edu.* **51**, A315 (1974)
12. S. Fischkoff, J.M. Vanderkooi, *J. Gen. Physiol.* **65**, 663 (1975)
13. H. Kautsky, A. Hirsch, *Z. Anorg. Allg. Chem.* **222**, 126 (1935)
14. H. Kautsky, G.O. Mler, *Z. Naturforsch.* **2A**, 167 (1947)
15. H. Kautsky, A. Hirsch, F. Davidsher, *Ber. Dtsch. Chem. Ges.* **65**, 1762 (1932)
16. I.A. Zakharov, T.I. Grishaeva, *Zhur. Prikl. Spektrosk.* **36**, 980 (1982); *Engl. Ed.* p. 697
17. I. Bergmann, *Nature* **218**, 396 (1968)
18. O.S. Wolfbeis, H. Offenbacher, H. Kroneis, H. Marsoner, *Mikrochim Acta* **I**, 153 (1984)
19. H.W. Kroneis, H.J. Marsoner, *Sens. Actuators* **4**, 587 (1983)
20. D. Lber, N. Opitz, *Sens. Actuators* **4**, 641 (1983)
21. M.E. Cox, D. Dunn, *Appl. Optics* **24**, 2114 (1985)
22. O.S. Wolfbeis, H.E. Posch, H. Kroneis, *Anal. Chem.* **57**, 2556 (1985)

23. J.I. Peterson, R.V. Fitzgerald, D.K. Buckhold, *Anal. Chem.* **56**, 62 (1984)
24. J.L. Gehrich, D.W. Lbers, N. Opitz, D.R. Hansmann, W.W. Miller, J.K. Tusa, M. Yafuso, *IEEE Trans. Biomed. Eng. BME* **33**, 117 (1986)
25. I.S. Longmuir, J.A. Knopp, *J. Appl. Physiol.* **41**, 598 (1976)
26. M.H. Mitnick, F.F. Jis, *J. Appl. Physiol.* **41**, 593 (1976)
27. M. Kautsky, *Trans. Faraday Soc.* **35**, 216 (1939)
28. X.M. Li, K.Y. Wong, *Anal. Chim. Acta* **262**, 27 (1992)
29. Y.M. Liu, R. Pereiro-Garcia, M.J. Valencia-Gonzalez, M.E. Diaz-Garcia, A. Sanz-Medel, *Anal. Chem.* **66**, 836 (1994)
30. J.M. Charlesworth, *Sens. Actuators B* **22**, 1 (1994)
31. N. Velasco-Garcia, R. Pereiro-Garcia, M. Diaz-Garcia, *Spectrochim. Acta* **51A**, 895 (1995)
32. D.M. Papkowsky, G.V. Ponomarev, W. Trettnak, P. O'Leary, *Anal. Chem.* **67**, 4112 (1995)
33. J. Samuel, A. Strinkovsk, S. Shalom, K. Lieberman, M. Ottolenghi, D. Avnir, A. Lewis, *Mater. Lett.* **21**, 431 (1994)
34. D. Avinir, D. Levy, R. Reisfeld, *J. Phys. Chem.* **88**, 5956 (1984)
35. R. Zusman, C. Rottman, M. Ottolenghi, D. Avnir, *J. Non-Cryst. Solids* **122**, 107 (1990)
36. G.E. Badini, K.T.V. Grattan, A.C.C. Tseung, *Analyst* **120**, 1025 (1995)
37. I. Kuselman, O. Lev, *Talanta* **40** 749 (1993)
38. L. Yang, S.S. Saavedra, *Anal. Chem.* **67**, 1307 (1995)
39. K.T.V. Grattan, G.E. Badini, A.W. Palmer, A.C.C. Tseung, *Sens. Actuators A* **483**, 25 (1991)
40. U. Narang, P.N. Prasad, F.V. Bright, K. Ramanathan, N.D. Kumar, B.D. Malhotra, M.N. Kamalasanan, S. Chandra, *Anal. Chem.* **66**, 3139 (1994)
41. C.J. Brinker, D.E. Clark, D.R. Ulrich (eds.) *Better Ceramics Through Chemistry II*, vol. 73 (Elsevier, New York, 1986), *MRS Symposium*
42. C.J. Brinker, G.W. Scherer, *The Physics and Chemistry of Sol-Gel Processing* (Academic Press, New York, 1990)
43. S.-K. Lee, I. Okura, *Analyst* **122**, 81 (1997)
44. Z. Grauer, D. Avinir, S. Yariv, *Can. J. Chem.* **62**, 1889 (1984)
45. D. Avinir, V.R. Kaufman, R. Reisfeld, *J. Non-Cryst. Solids* **74**, 395 (1985)
46. A.K. McEvoy, C.M. McDonagh, B.D. MacCraith, *Analyst* **121**, 785 (1996)
47. T. Saito, N. Asakura, T. Kamachi, I. Okura, *J. Porphyrins Phthalocyanines* **11**(3), 160 (2007)
48. N. Asakura, K. Mochizuki, T. Kamachi, I. Okura, *Measurement Sci. Technol.* **17**(6), 1237 (2006)

Adsorption and Electrode Processes

H. Shiroishi

Abstract In order to understand a whole electrode processes, it is important to analyze not only the adsorbed molecules on a substrate but also a series of dynamic processes like diffusion, convection, and self-exchange reaction of reacting species. Several types of adsorption isotherms (e.g. Langmuir-, Fraundlich-, Temkin type, etc.) are introduced and applied for elementary processes in direct methanol fuel cells (DMFCs). The mechanism of selective oxygen reduction on platinum by the adsorption of 2,2'-bipyridine is studied by Monte Carlo simulation. Using a slab optical waveguide (SOWG), the properties of functional materials at a solid and liquid interface are elucidated. A digital simulation method based on finite differential methods is applied to electrochemical measurements, i.e., static and dynamic voltammograms and potential-step method, which proves to be a powerful tool for the investigation of electrode processes.

13.1 Introduction

A series of electrode processes begin at the interface of an electrode, and the influence propagates toward the bulk of an electrolyte. In a Grätzel cell, photoenergy conversion begins from photoexcited dye molecules adsorbed on titanium dioxide, and the electrons injected to the titanium dioxides circulate via I_3^-/I^- redox couple in the bulk of an electrolyte, suggesting that it is important for the development of energy conversion devices not only to understand the molecular properties adsorbed onto a substrate but also to analyze a series of diffusion, convection, and self-exchange reaction of redox couples.

This chapter begins with the explanation of adsorption isotherms (e.g. Langmuir-, Fraundlich-, and Temkin types). Next, the author introduces an interesting application of adsorption for direct methanol fuel cells (DMFCs): selective oxygen reduction on platinum was achieved by the adsorption of 2,2'-bipyridine. This mechanism has been revealed by a Monte Carlo simulation.

A slab optical waveguide (SOWG) spectroscopy will be shown in the next paragraph. The properties of a functional material at a solid and liquid

interface are not always similar to those in bulk electrolytes. The SOWG spectroscopy has specific advantages for the investigation of the interface: high sensitivity due to multiple internal reflection and high interfacial selectivity owing to evanescent waves.

The method of digital simulation for electrochemical measurements will be explained in the third paragraph. The basics of finite differential methods will be explained at first as followed by the application to electrochemical measurements: static and dynamic voltammograms and a potential-step method. The charge transfer of redox molecules fixed to the polymer matrix will be introduced in the last paragraph based on a percolation theory.

13.2 Adsorption Isotherms and Kinetics

There are two kinds of adsorption mechanism – physisorption and chemisorption. In physisorption, molecules are adsorbed on a solid surface by van der Waals force, whereas in chemisorption, chemical bond(s) are formed between molecules and a solid surface. The enthalpy of chemisorption (ca. 200 kJ/mol) is one order of magnitude as large as that of physisorption (ca. 20 kJ/mol). In chemisorption, the formation of chemical bond(s) causes a change in the electronic states of the molecule to promote catalysis on a solid surface. The process of adsorption is actually pivotal to electron transfer reactions on the electrode. In this section, after basic isotherms used in the solution systems are introduced, the application of the adsorption to selective oxygen reduction on platinum will be shown.

13.2.1 Langmuir Isotherms

Langmuir equation is derived from some quite reasonable assumptions as follows [1]:

- (1) A molecule is adsorbed on specific sites of a solid surface.
- (2) The adsorption energy of a molecule is independent of the existence of molecule(s) in the neighbor site(s).

The adsorption and the desorption reactions on a solid surface in the solution are expressed as



where A is an adsorbate molecule, S a specific site of a solid surface, k_d a dissociation rate constant, and k_a an association rate constant.

The adsorption rate of the adsorbate (v_a) is represented as

$$v_a = k_a C(\Gamma_e - \Gamma_t) \quad (13.2)$$

where C is the concentration of the molecule, Γ_t the surface concentration of the adsorbate at time t , and Γ_e the equilibrium surface concentration.

The desorption rate of the adsorbate (v_d) is expressed by the following equation:

$$v_d = k_d \Gamma_t \quad (13.3)$$

The time derivative of the surface concentration is expressed by subtracting (13.3) from (13.2) as

$$\frac{d\Gamma_t}{dt} = k_a C (\Gamma_e - \Gamma_t) - k_d \Gamma_t \quad (13.4)$$

We obtain the following equation by the integration of (13.4) as:

$$\Gamma_t = \frac{k_a C \Gamma_e}{k_a C + k_d} \{1 - \exp\{-(k_a C + k_d)t\}\} \quad (13.5)$$

When $k_a C \gg k_d$, (13.5) is simplified as

$$\Gamma_t = \Gamma_e \{1 - \exp(-t/\tau)\} \quad (13.6)$$

where $\tau = 1/(k_a C + k_d)$. Then,

$$\exp\left\{-\frac{t}{\tau}\right\} = \frac{\Gamma_e - \Gamma_t}{\Gamma_e} \quad (13.7)$$

It can be converted into the following equation by taking logarithm of (13.7):

$$-\frac{t}{\tau} = \ln \left| \frac{\Gamma_e - \Gamma_t}{\Gamma_e} \right| \quad (13.8)$$

According to (13.8), we can estimate k_a and k_d values by measuring time-dependent surface concentration.

At the equilibrium condition, equating v_a and v_d gives

$$k_a C (\Gamma_e - \Gamma_t) = k_d \Gamma_t \quad (13.9)$$

and dividing by Γ_t converts (13.9) to the following equation:

$$k_a C (1 - \theta) = k_d \theta \quad (13.10)$$

where $\theta = \Gamma_t/\Gamma_e$, then Langmuir equation is derived as follows:

$$\theta = \frac{KC}{1 + KC} \quad (13.11)$$

where $K = k_a/k_d$.

13.2.2 Freundlich Isotherm

It is more difficult the theoretical treatment of the adsorption at the solid/liquid interface than that at the solid/gas interface. In general, a single-layered adsorbate tends to be formed at the solid/liquid interface, since solvent molecules often disturb the interaction between adsorbates. Freundlich proposed an empirical isotherm expressed as the following equation in which the weight of a solute adsorbed onto an adsorptive medium increases linearly with the n^{-1} th power of the concentration in the solution [1]:

$$y = kc^{1/n} \quad (13.12)$$

where y is the weight of a solute adsorbed onto 1 g of the adsorptive medium, c is the concentration of a solute. Taking the logarithm of (13.12) yields

$$\log y = \log k + (1/n) \log c \quad (13.13)$$

Freundlich isotherm is applicable to an adsorption system where we can observe a linear relationship between $\log y$ and $\log c$, and the isotherm can be often applied to the adsorption of gas.

13.2.3 Temkin Isotherm

Temkin suggested that the deviation from Langmuir isotherm was due to the heterogeneities of the surface such as the edges of crystal growth planes, screw dislocations, and kink sites [2]. In his model, the surface was regarded as the assemblage of small pieces of equal size and the standard free energy of the adsorption decreased with increasing surface coverage θ as follows:

$$\Delta \overline{G}_\theta^0 = \Delta G_0^0 - fRT\theta \quad (13.14)$$

where $\Delta \overline{G}_\theta^0$ and ΔG_0^0 are the standard free energy of the adsorption at coverage θ and on the free surface ($\theta = 0$). The coverage (θ) for Temkin-type isotherm is expressed by the following equation based on the assumption:

$$\theta = \frac{1}{f} \ln \frac{1 + a_0 P}{1 + a_0 P \exp(-f)} \quad (13.15)$$

where P is an effective pressure in Pa, a_0 related to the standard free energy of adsorption at initial micro-adsorption (ΔG_0^0) and expressed as follows:

$$a_0 = \exp(-\Delta G_0^0/RT) \quad (13.16)$$

f is defined as the rate of change in the apparent standard free energy of adsorption with coverage:

$$f = \frac{1}{RT} \frac{d\Delta \overline{G}_\theta^0}{d\theta} \quad (13.17)$$

where $\Delta \overline{G}_\theta^0$ is the standard free energy of adsorption at coverage θ .

The concentration-dependent relationship is obtained from (13.15) by replacing P with the concentration of the adsorbate, C as follows:

$$\theta = \frac{1}{f} \ln \frac{1 + a_0 C}{1 + a_0 C \exp(-f)} \quad (13.18)$$

Temkin-type isotherm reproduced the adsorption behavior of methanol [3], organic compounds [4] and CO [5] on platinum. The heterogeneity of the platinum and its alloy surface was supposed to operate in their mechanism.

Figure 13.1A shows the cyclic voltammograms of a platinum electrode in 0.05 M H_2SO_4 after immersing into each solution of cobalt bis(dicarbollide) (H^+B^-) and chloro-protected bis(dicarbollide) (H^+BCl^-) for 10 min at 0.515 V (vs. RHE) to examine the adsorption of these compounds to the

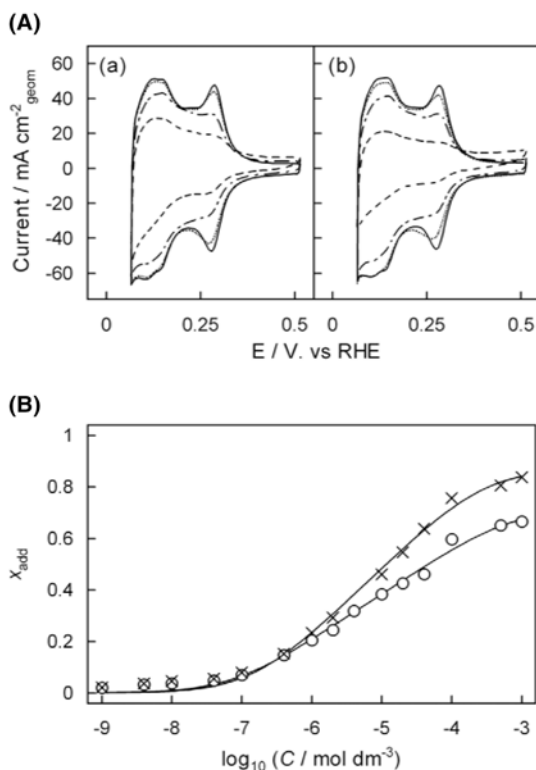


Fig. 13.1. (A) Cyclic voltammograms between 0.515 and 0.065 V of (a) H^+BCl^- and (b) H^+B^- at various concentrations in 0.05 M H_2SO_4 under N_2 . —, 0 mM; ···, 10 nM; ---, 1 μM; - - -, 0.1 mM. Scan rate is 20 mV s⁻¹. (B) Temkin isotherm of H^+BCl^- (○) and H^+B^- (×). Coverage was calculated based on the charges of hydrogen adsorption/desorption region in CVs. The solid lines are calculated based on (13.18') with parameters shown in Table 13.1 (reproduced from Shiroishi et al. (2006) [6] by permission of Elsevier Science)

Table 13.1. Parameters obtained by Temkin-type isotherm analysis [6]

	H^+B^-	H^+BCl^-
f	7.48	9.07
$10^{-6}a_0$	6.58	13.27
$x_{\max}$	0.87	0.71

electrode surface [6]. The coverage of surface area on the platinum can be estimated from the decrease of the hydrogen adsorption/desorption peaks in cyclic voltammograms.

The coverage is represented as

$$\theta = x_{\text{add}}/x_{\text{max}} \quad (13.19)$$

where x_{add} and x_{max} are the fraction covered by the adsorbate at a given and saturated concentrations, respectively, so that (13.18) transforms to

$$x_{\text{add}} = \frac{x_{\text{max}}}{f} \ln \frac{1 + a_0 C}{1 + a_0 C \exp(-f)} \quad (13.18')$$

The physical parameters in (13.18') can be estimated by fitting experimental result using the non-linear least square method summarized in Table 13.1. Temkin isotherm with the calculated curves is shown in Fig. 13.1B.

13.2.4 Application for Selective Reaction on Metal Surface by Adsorbate

In this section, I show an example that the selective reaction was achieved with adsorbates on a metal surface [7]. Direct methanol fuel cells (DMFCs) presently suffer from the high overvoltage of methanol oxidation reaction and methanol crossover through an electrolyte membrane. Many studies have been performed to overcome the issue. Selective oxygen reduction on platinum in the presence of methanol was achieved by using some additives with a pyridyl structure [8]. Fortunately the migration of these additives from the cathode to the anode was negligibly small so that no interference to the anode catalyst layer was anticipated when they were used at the cathode side of fuel cells. This approach might be one of the effective solutions to reduce the negative potential shift of the cathode due to the methanol crossover effect of DMFC.

Figure 13.2 shows the polarization curves of oxygen reduction in the absence and presence of methanol in 0.1 M HClO_4 using an RRDE measurement. Also compared are the polarization curves in the same condition but with a 2,2'-bipyridine (abbreviated as 2,2'-bpy) additive. In the absence of methanol, the onset potential where oxygen reduction current rose was improved by 0.026 V compared to that without bpy, as was observed in sulfuric acid [8]. This is because 2,2'-bpy molecules adsorbed on platinum interfere with the

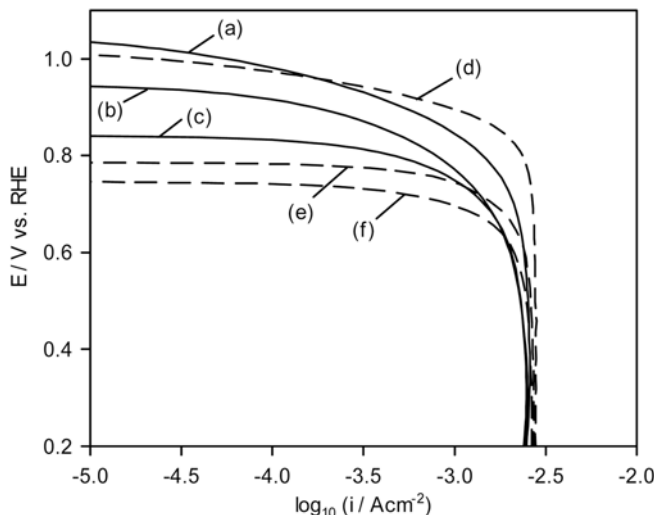


Fig. 13.2. Polarization curves for oxygen reduction in 0.1 M CH_3OH –0.1 M HClO_4 . Scan rate is 5 mV s^{-1} . Rotating speed of the disk electrode is 300 rpm. (a) 0 M MeOH –0.1 mM bpy ; (b) 0.1 M MeOH –0.1 mM bpy ; (c) 1 M MeOH –0.1 mM bpy ; (d) 0 M MeOH –0 M bpy ; (e) 0.1 M MeOH –0 M bpy ; (f) 1 M MeOH –0 M bpy (reproduced from Shiroishi et al. (2005) [7] by permission of American Chemical Society)

formation of platinum oxide species. Without 2,2'-bpy, the overpotential of oxygen reduction increased ca. 0.2 V in the presence of 0.1 M methanol, but with 2,2'-bpy this was improved to 0.06 V.

We call “Free site” as a Pt site that is not occupied by 2,2'-bpy, and define x_{free} as the fraction of “Free site” through discussion:

$$x_{\text{free}} = 1 - x_{\text{bpy}} \quad (13.20)$$

We normalized methanol oxidation currents that were measured in the absence of oxygen gas, by x_{free} , to estimate the methanol oxidation activity per “Free site”. Figure 13.3 depicts the plots for dependence of normalized methanol oxidation current on the fraction of 2,2'-bpy sites. If methanol oxidation activity per one Pt site does not change, current normalized by “Free sites” would be independent on fraction of 2,2'-bpy sites because methanol oxidation is not a diffusion controlled reaction on platinum. However, the normalized current decreased with increasing fraction of 2,2'-bpy sites indicating that methanol oxidation activity per “Free site” decreased with increasing fraction of 2,2'-bpy sites.

Methanol oxidation was extensively investigated in the last four decades [3, 9–12]. The first process of methanol oxidation is the adsorption from the bulk solution onto platinum, which is followed by successive dehydrogenation of methanol to form linear and bridged CO [13]:

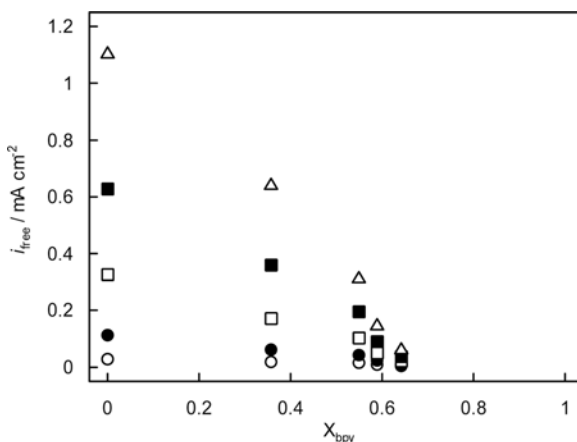
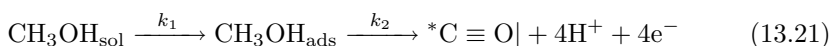


Fig. 13.3. Relationship between methanol oxidation current normalized by “Free site” and the fraction of platinum sites on which 2,2'-bpy molecules were adsorbed at various applied potential. $\circ$, 0.60 V; $\bullet$, 0.65 V; $\square$, 0.70 V; $\blacksquare$, 0.75 V; $\triangle$, 0.80 V (reproduced from Shiroishi et al. (2005) [7] by permission of American Chemical Society)



where $*C \equiv O|$ expresses methanol dehydrogenation fragments bonded to Pt surface. It is widely accepted that methanol adsorption requires more than two platinum sites. Several researchers postulated that three platinum sites were needed to adsorb methanol [3, 13, 14], whereas Parsons and Vander-Noot suggested that four platinum sites are required to adsorb methanol [11]. Gasteiger et al. described that they adopted 3 site methanol model in their statistical calculation by which they estimated the optimum ratio between platinum and ruthenium for methanol oxidation because there were found no significant differences among the number of methanol adsorption sites in their calculation [13]. The number of platinum sites required for methanol adsorption is still open for discussion, thus we performed Monte Carlo simulation of methanol adsorption using a two-dimensional square lattice model for Pt (100) and a hexagonal lattice model for Pt (111) assuming that one methanol occupied two to four sites (Fig. 13.4). We made the following simple assumptions:

1. Adsorbed species neither change nor diffuse on the surface of platinum, which is close to the assumption called “molecular adsorption frozen in disorder” as was adopted in the simulation of methanol adsorption on Pt/Ru alloys [14].
2. 2,2'-bpy molecules on the surface are randomly dispersed and there are no interaction between them because the interaction between 2,2'-bpy molecules on platinum is weak due to its conformation.

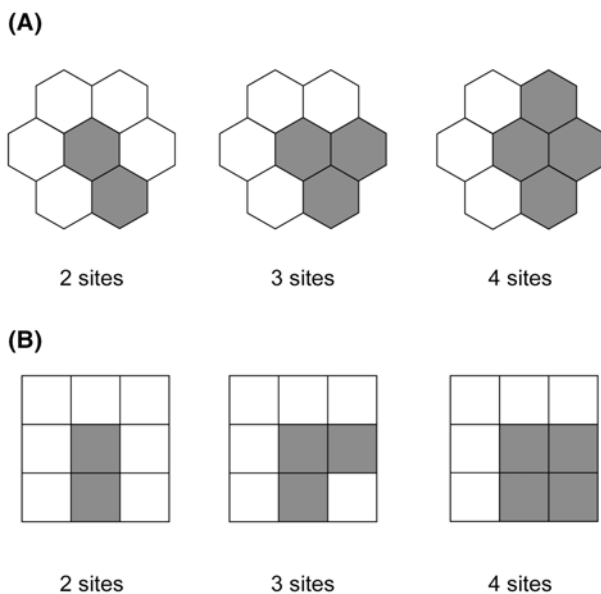


Fig. 13.4. Methanol adsorption models used in the simulation for (A) two-dimensional hexagonal lattice and (B) two-dimensional square lattice site models (reproduced from Shiroishi et al. (2005) [7] by permission of American Chemical Society)

3. Methanol molecules are not adsorbed on the sites where a 2,2'-bpy molecule is already adsorbed, and no interaction between methanol and 2,2'-bpy is considered.

Procedures used for the simulation of the adsorption process are as follows, both in the square lattice and the hexagonal lattice whose sizes are 1000×1000 with periodic boundary condition:

1. Trials of a specific number of 2,2'-bpy additions are performed in the lattice. A specific angle is chosen randomly from the all-available angles to put a 2,2'-bpy molecule at a randomly selected site. If no available angle exists at the site, nothing occurs.
2. Twofold methanol adsorption was performed until the lattice was saturated with methanol. After available angles are sought at a randomly selected site, a methanol molecule is put at a randomly chosen angle in the similar manner as above. If there is no available angle to put, nothing occurs.
3. Similarly, threefold and fourfold methanol adsorptions were performed respectively after methanol molecules were removed from the lattice.
4. Methanol molecules were erased from the lattice, and above steps 1 to 3 were repeated until the lattice was filled with 2,2'-bpy molecules.

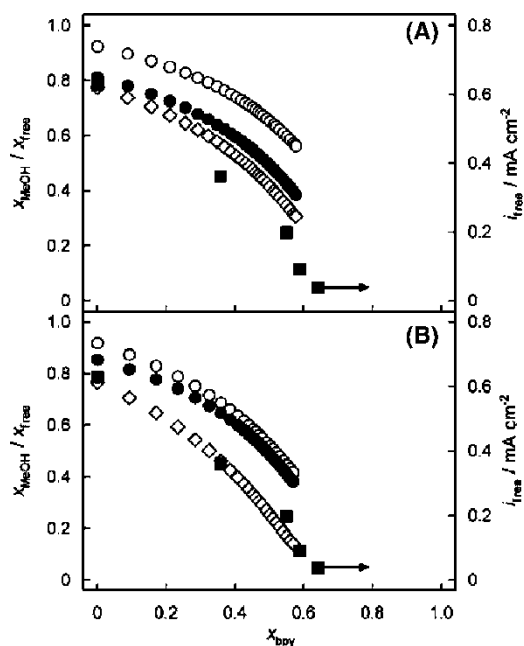


Fig. 13.5. Dependence of the fraction of methanol adsorption sites normalized by the fraction of “Free sites” (left axis) on the fraction of the platinum sites on which bpy molecules were adsorbed with (A) two-dimensional hexagonal lattice and (B) two-dimensional square lattice site models. $\circ$, 2 site model; $\bullet$, 3 site model; $\diamond$, 4 site model. Relationships between experimental methanol oxidation current normalized by “Free sites” and the fraction of platinum sites on which 2,2'-bpy molecules were adsorbed at 0.75 V are also superposed (right axis) (reproduced from Shiroishi et al. (2005) [7] by permission of American Chemical Society)

Figure 13.5 shows the dependence of the fraction of methanol adsorption sites normalized by the fraction of “Free sites” on the fraction of the 2,2'-bpy adsorption sites to estimate the number of methanol molecules per Pt free site. The values are comparable with the normalized current at any potentials shown in Fig. 13.3, although in strict sense kinetic Monte Carlo simulations are required to compare the values with the normalized current. Simulation with 4 site methanol model nicely reproduces the tendency that the normalized current approaches 0 along with the fraction of 2,2'-bpy sites both in square lattice and hexagonal lattice models.

Extensive studies on oxygen reduction have also been performed during four decades, and well reviewed in literatures [15,16]. The mechanism of oxygen reduction on platinum is being revealed by DFT studies in recent years [17]. According to their studies, oxygen reduction occurs on platinum through two overall processes. One is the two-electron reduction to peroxide, which takes place at a single platinum site with an end-on oxygen molecule. The

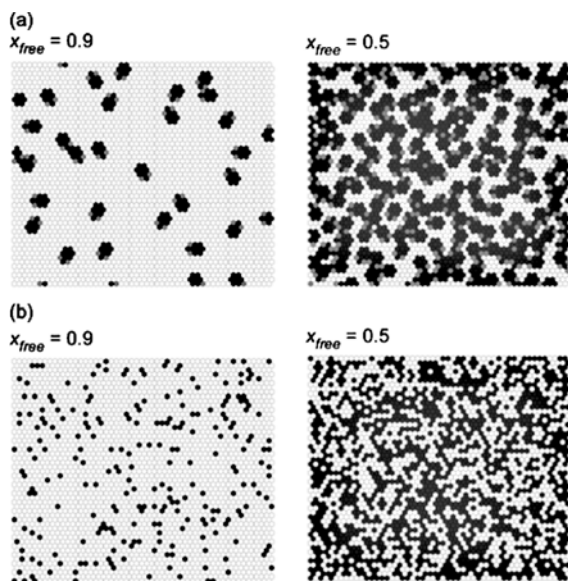


Fig. 13.6. Snapshots of adsorption simulation displayed only by 50×50 area for two-dimensional hexagonal lattice model: (a) 2,2'-bpy model and (b) single site adsorbate model (reproduced from Shiroishi et al. (2005) [7] by permission of American Chemical Society)

other is four-electron reduction to water at a dual site with a di- σ bonded oxygen [18]. It can be assumed that oxygen molecules are promptly reduced on platinum not to interfere with the adsorption of “next” oxygen molecules below 0.9 V, thus four-electron oxygen reduction can occur with at least two free nearest neighbor sites unlike methanol oxidation.

It is revealed that the geometrical selectivity by a single site model is higher than that by the multi-site 2,2'-bpy model, since occupied sites are concentrated in the multi-site model (Fig. 13.6). However, the ratio increases with the increase in x_{bpy} , and it reaches ca. 2 at $x_{\text{bpy}}=0.6$, but this is not enough to explain the observed selectivity toward oxygen reduction against methanol oxidation as seen in Fig. 13.2. This is because the turnover number per one site of oxygen reduction is higher than that of methanol oxidation, and the concentration of oxygen is much lower than that of methanol.

13.3 Slab Optical Waveguide Spectroscopy

An interface is a common boundary surface between two different phases, whose properties are different from that of single phases. Characteristics of interfaces have been utilized for developing catalytic reactors, sensors, and energy conversion devices. It is important to elucidate the properties of these

interfaces for improving these devices. Current efforts are focused on developing analytical devices and methods at molecular level in particular. Surface enhanced infrared spectroscopy (SEIRAS) is one of these analytical methods. Increasing attention has been paid to slab optical waveguide (SOWG) techniques by which we can investigate the interfaces in UV/Vis region sensitively and selectively. SOWG techniques and its applications will be introduced in this section.

13.3.1 Principle

A slab optical waveguide (SOWG) spectroscopy in the UV/Vis region was developed by Kato et al. [19] in 1994. The photons in the UV/Vis region propagate in the optical waveguide with a thickness ranging from sub-mm to micro-meter corresponding to the core of an optical fiber by total internal reflection. An observed material (or a solution) was placed on an SOWG substrate in a typical configuration as shown in Fig. 13.7. The minimum incident angle depends on the observed materials. According to Snell's law, the critical angle is expressed as follows:

$$\sin \theta_c = \frac{n_1}{n_2} \quad (13.22)$$

where n_1 and n_2 are the refractive indexes of the observed material and the SOWG substrate, respectively. For example, when the dilute aqueous solution ($n_1 = 1.33$) is measured with SOWG substrates made of dense flint glass ($n_2 = 1.81$) and quartz ($n_2 = 1.47$), the critical angles are 47.3° and 64.8° , respectively. Sapphire and polymethyl methacrylate (PMMA) can be used as the substrates of SOWG.

Evanescent waves are produced at the external side (the observed material(s) or solution) of the SOWG substrate when sinusoid waves are internally

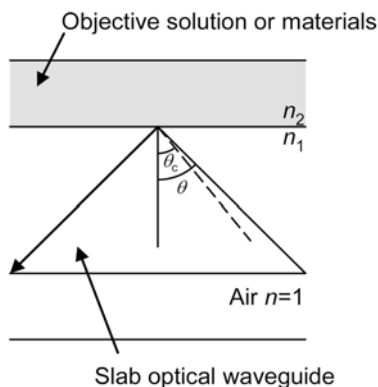


Fig. 13.7. Scheme of total internal reflection in slab optical waveguide

reflected off at an angle greater than the critical angle. The intensity of evanescent waves decreases exponentially with increasing distance from the surface of the SOWG substrate as follows:

$$E = E_0 \exp(-x/d_p) \quad (13.23)$$

where E and E_0 are the intensity of evanescent waves at x and 0 of the distance, respectively, and the distance at which the intensity of the evanescent waves weakens to $1/e$ (d_p) is represented as

$$d_p = \frac{\lambda}{2\pi \sqrt{n_1^2 \sin^2 \theta - n_2^2}} \quad (13.24)$$

where λ (nm) is the wavelength of the incident light. Figure 13.8 depicts the relationship between d_p and the incident angle when the dilute aqueous solution ($n_1 = 1.33$) is used. Since maximum distance reached by evanescent waves is $3d_p$, the SOWG spectroscopy enables selective measurement only existing within the penetration depth of evanescent waves; the interface. When observed material(s) absorb the evanescent waves, the light intensity detected by spectrophotometer decreased drastically in the SOWG because of amplifying signals by multiple reflections and absorptions.

There are several methods to lead photons into the SOWG. A coupling prism [19] has a good coupling efficiency. We can now use commercially available substrates whose both edges are cut and polished at 60° , which are easy handling. The setting to the apparatus is simplified by using these substrates so that good repeatability is obtained in the experiments.

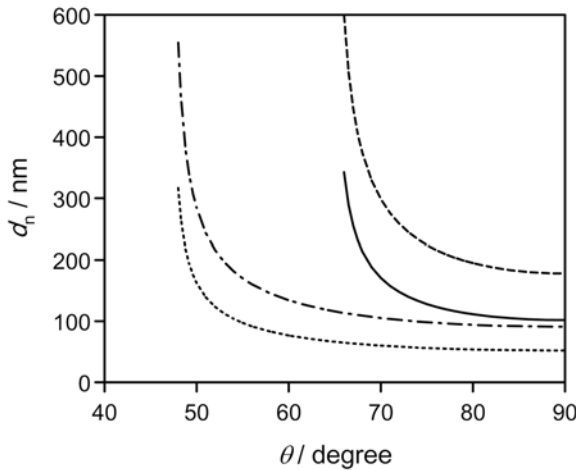


Fig. 13.8. Dependence of d_n on incident angles calculated by (13.4) at $n_2 = 1.33$. —, quartz SOWG at 400 nm, ---, quartz SOWG at 700 nm, ..., dense flint glass SOWG at 400 nm, -.-, dense flint glass SOWG at 700 nm

The sensitivity of the SOWG spectroscopy depends on the number of reflection, the penetration depth of evanescent waves, and the degree of hydrophilicity of the interface.

The SOWG spectroscopy has advantages over conventional spectroscopic techniques for selective measurement at the interface: (1) The penetration depth of evanescent waves is so short that we can analyze the molecules within ca. 1 μm from the interface selectively and nondestructively. (2) The orientation of the adsorbed molecules can be analyzed by the polarized incident light [20]. (3) The spectroscopy is suitable for real-time measurement of spectral changes caused by the electrochemical fluctuation and/or external factors. (4) A required amount of a sample is smaller than that in the conventional spectroscopic techniques. These advantages enabled us to analyze the molecules adsorbed onto the interface.

13.3.2 Application of Slab Optical Waveguide Spectroscopy

There are two available SOWG spectroscopic techniques to study molecules existing on the electrode interface: the direct SOWG spectroscopy [21–26] and noncontact optical waveguide spectroscopy (NOW) [27, 28].

In the direct SOWG spectroscopy, a working electrode is made by evaporating transparent conductive materials such as indium tin oxide (ITO) onto the SOWG substrate (ITO-SOWG). Both counter and reference electrodes are arranged onto the ITO-SOWG electrode (Fig. 13.9). In the method, the observed materials can be analyzed near the interface where evanescent waves are intense. It should be noted that the transparent wavelength region of the electrode must contain the adsorption band(s) of observed molecules and when a working electrode is made of evaporating noble metal(s), the absorption of noble metal and surface plasmon resonance (SPR) are observed on the absorption of the observed molecule(s) cumulatively.

Recent studies have been performed for the electron transfer reactions of dyes (e.g. methylene blue [23]) and cytochrome *c* [24]. Ayato and co-workers

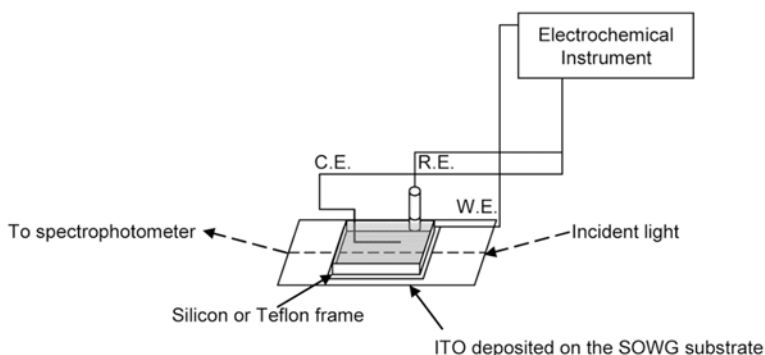


Fig. 13.9. Schematic diagram of the direct OWG spectroscopy

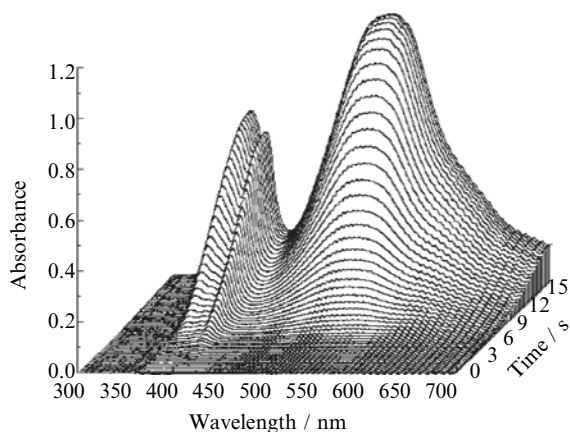


Fig. 13.10. Time-resolved SOWG spectra synchronized with cyclic voltammetric measurements in 0.3 M KBr solution containing 0.1 mM HV. Sweep rate: 20 mV s^{-1} (reproduced from Ayato et al. (2005) [25] by permission of Elsevier Science)

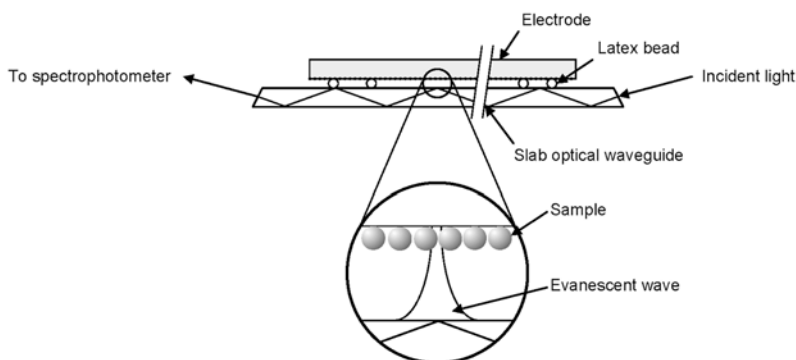


Fig. 13.11. Scheme of noncontact slab optical waveguide spectroscopy

studied the redox reaction of heptyl viologen on ITO by direct SOWG spectroscopy [25,26]. Figure 13.10 depicts SOWG absorption spectra synchronizing with cyclic voltammetric measurements for the negative-going scan. In their research, it is elucidated that an absorption band from 450 to 650 nm is consisted of at least three kinds of the electronic states, and the adsorption states of heptyl viologen cation radical were varied with time, the electronic potential, and the concentration of heptyl viologen.

Ohno et al. [27] developed noncontact slab optical waveguide spectroscopy (NOW), in which a working electrode is placed on the SOWG within a distance reached by the evanescent waves using a spacer to measure the behavior of molecules on the electrode (Fig. 13.11). Only electrolyte without samples is

injected into the space between the electrode and the SOWG substrate. An advantage of the method is free from the restriction of the electrode, while the sensitivity of the method is less than that of the direct SOWG spectroscopy. We can use a polymer membrane [28] and latex beads with a diameter of 120 nm dispersed in the buffer solution [29] as spacers to control the distance between the electrode and the SOWG substrate.

13.4 Methods of Digital Simulation for Electrochemical Measurements

The species generated by the electrochemical reaction on the electrode propagate toward the bulk solution. The phenomenon can be represented as partial differential equation(s). It becomes difficult to solve the equation(s) analytically, when several chemical reaction or specific conditions are included in the equation.

On the other hand, the processing capabilities of a personal computer increased by one order of magnitude in the last decade. Today a personal computer is capable of doing many jobs which could be processed only by a workstation before. Theoretical calculation using a personal computer is widely applied to the analysis of experimental data, e.g. chemical equilibrium, the rate of reaction, and molecular orbital calculations. We can not only solve the equation(s) numerically but also fit experimental results using a non-linear least square method to estimate physical parameters.

In this section, I will introduce the method of the numerical simulations for electrochemical measurements. The partial differential equations are built up from the electrode interface both hydrostatic and hydrodynamic conditions, and explain how to solve these equations numerically. The difference between a planar electrode and a matrix-coated electrode will also be discussed in this section.

13.4.1 Formulation of Electrochemical System

Figure 13.12 shows the region related to the electrochemical process, which consists of three layers. Electrochemical reactions between an electrode and material(s) occur at the electrical double layer whose thickness is ca. 10^{-7} cm. The diffusion layer about 0.01–0.25 cm thick locates at the outside of the electrical double layer. The concentrations of redox species in the outside of the diffusion layer called the convection layer are regarded as same as those in the bulk solution.

Hydrostatic Condition

At first, the equations for the oxidation of a redox molecule at a planar electrode are formed under hydrostatic condition in this section. Figure 13.13

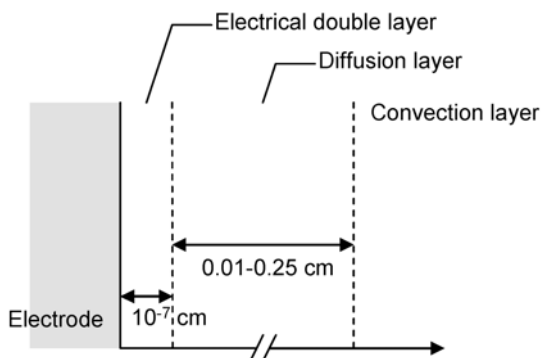


Fig. 13.12. Scheme of the structure near the electrode

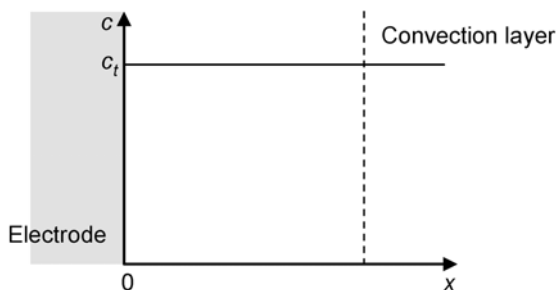


Fig. 13.13. Scheme of the electrode for the numerical calculation

shows the scheme of the neighborhood of the electrode under hydrostatic condition, where the distance from the electrode and the concentration of the redox species are taken as x - and y -axes, respectively. The concentrations of the redox species are defined as the functions of time and position. According to the law of mass conservation, the total concentration of the redox species $c_t(x, t)$ are expressed as

$$c_t(x, t) = c_{\text{ox}}(x, t) + c_{\text{red}}(x, t) \quad (13.25)$$

where $c_{\text{ox}}(x, t)$ and $c_{\text{red}}(x, t)$ (mol cm^{-3}) are the concentrations of the oxidized and reduced molecules, respectively.

The following equations are needed for the electrochemical simulation: (i) the concentration of the oxidant at the electrode interface, (ii) mass transport in the diffusion layer, and (iii) the boundary condition at the interface between diffusion and convection layers.

- (i) The concentration of the oxidant at the electrode interface

When the concentration of the redox species obeys a Nernstian equation, the concentration of the oxidant on the electrode is represented as

$$c_{\text{ox}}(0, t) = c_t(x, t) \left/ \left[1 + \exp \left\{ -\frac{nF}{RT} (E - E^0) \right\} \right] \right. \quad (13.26)$$

where E is the applied potential on the electrode, E^0 the redox potential of the molecule, n the number of electrons, F (C mol^{-1}) the Faraday constant. Equation (13.26) can be used as a boundary condition on the electrode ($x = 0$).

When a charge injection from the electrode to the molecule is the rate-determining step, we must formulate the molar flux at the electrode taking the reaction rates into account.

A redox reaction between the electrode and the redox molecule is shown by the following equation:



where k_1 (cm s^{-1}) and k_2 (cm s^{-1}) are the rate constants for the reduction and the oxidation of the redox molecules by the electrode, respectively. These constants can be expressed as functions of electrode potential [30]:

$$k_1 = \frac{i'_0}{nF} \exp \left[-\frac{\alpha nF(E - E^0)}{RT} \right] \quad (13.28)$$

$$k_2 = \frac{i'_0}{nF} \exp \left[\frac{(1 - \alpha)nF(E - E^0)}{RT} \right] \quad (13.29)$$

where i'_0 ($\text{Amol}^{-1} \text{cm}$) is the exchange current density at 1 mol cm^{-3} , n the charge number of the electrode reaction, α the transfer coefficient, E^0 (V) the redox potential of the molecule, and $E(V)$ the applied potential.

A molar flux from the electrode at time t is represented as

$$N(0, t) = k_2 c_{\text{red}}(0, t) - k_1 c_{\text{ox}}(0, t) \quad (13.30)$$

Total material balance in the micro-volume ($A\Delta x$) in contact with the electrode is represented as

$$AN(0, t) - A\Delta x \frac{\partial c_{\text{ox}}(0, t)}{\partial t} = SN(\Delta x, t) \quad (13.31)$$

where A (cm^2) is the area of the electrode, $N(x, t)$ ($\text{mol cm}^{-2} \text{s}^{-1}$) the molar flux of charge (or the oxidized molecules).

When the oxidized molecules are consumed by a catalytic reaction, (13.31) is replaced by the following equation:

$$AN(0, t) - \left\{ A\Delta x \frac{\partial c_{\text{ox}}(0, t)}{\partial t} + A\Delta x R_A(0, t) \right\} = AN(\Delta x, t) \quad (13.31')$$

where $R_A(x, t)$ ($\text{mol cm}^{-3} \text{s}^{-1}$) is the rate of the catalytic reaction.

$N(\Delta x, t)$ is expressed by Fick's law as

$$N(\Delta x, t) = -D \frac{\partial C(\Delta x, t)}{\partial x} \quad (13.32)$$

where D ($\text{cm}^2 \text{s}^{-1}$) is the diffusion coefficient of the redox molecule.

(ii) Diffusion of charge in the diffusion layer

Since the convection flux is negligible in the diffusion layer, a diffusion equation is expressed as [31]

$$\frac{\partial c(x, t)}{\partial t} = D \frac{\partial^2 c(x, t)}{\partial x^2} \quad (13.33)$$

where $c(x, t)$ is the concentration of the oxidized or reduced molecules.

A conventional diffusion equation including a catalytic reaction in the diffusion layer is represented as

$$\frac{\partial c_{\text{ox}}(x, t)}{\partial t} + R_A(x, t) = D \frac{\partial^2 c_{\text{ox}}(x, t)}{\partial x^2} \quad (13.33')$$

(iii) Analytical solution of partial differential equation

The boundary conditions are needed to solve the partial differential equation(s) analytically. When potential-step chronoamperometry is applied to the system, the boundary conditions can be expressed as

$$c_{\text{red}}(x, 0) = c_{\text{bulk}} \quad (13.34)$$

$$\lim_{x \rightarrow \infty} c_{\text{red}}(x, t) = c_{\text{red, bulk}} \quad (13.35)$$

$$c_{\text{red}}(0, t) = 0 \quad (13.36)$$

where $c_{\text{red, bulk}}$ is the concentration of the reduced molecule in the bulk solution.

The equation of the concentration profile is obtained by solving (13.33) with the boundary conditions as follows:

$$c_{\text{red}}(x, t) = c_{\text{bulk}} \text{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \quad (13.37)$$

Since the flux at the electrode is proportional to the diffusion coefficient and the slope of the concentration, the current, i (A), is represented as

$$\frac{i}{nFA} = D \left(\frac{\partial c_{\text{red}}}{\partial x} \right)_{x=0} \quad (13.38)$$

The Cottrell equation which describes the change in current with respect to time is derived from (13.37) and (13.38):

$$i(t) = \frac{nFAD^{1/2}c_{\text{red, bulk}}}{\pi^{1/2}t^{1/2}} \quad (13.39)$$

The cumulative charge $Q(t)$ is expressed as the integral form of (13.39):

$$Q(t) = \frac{2nFAD^{1/2}c_{\text{red,bulk}}}{\pi^{1/2}}t^{1/2} \quad (13.40)$$

If the diffusion layer expands with time infinitely, which means that the concentration gradient becomes gentle infinitely, the current and the accumulated charge are proportional to $t^{-1/2}$ and $t^{1/2}$, respectively. However, the diffusion layer has a finite thickness because of the convection caused by the temperature distribution in the solution.

The interface between the diffusion and the convection layers, the concentrations of the redox species are regarded as same as those in the bulk solution so that the following boundary condition is substituted for (13.35) to simulate the actual electrochemical system:

$$C_{\text{red}}(l, t) = C_{\text{bulk}}(t) \quad (13.41)$$

where l (cm) is the thickness of the diffusion layer which depends on the shape of the electrochemical cell, temperature, the direction of the electrode, and the kind of the electrolyte. Figure 13.14 shows the concentration profiles for a virtual oxygen reduction calculated by using the diffusion coefficient and the concentration of oxygen at 298 K in 0.05 M H_2SO_4 . When the thickness of the diffusion layer is 200 μm , the concentration change reaches to the interface between the diffusion and the convection layers within 2 s, and the concentration gradient becomes constant in the diffusion layer almost 10 s. Whereas, in the case that the concentration profile calculates by (13.37) derived based on the same boundary conditions as those of (13.39) and (13.40),

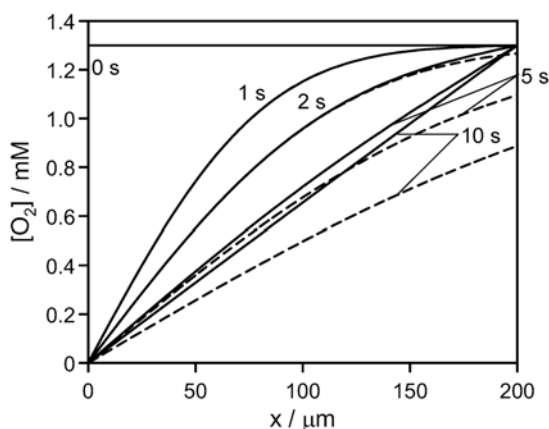


Fig. 13.14. Time dependence of the concentration distribution of an oxygen ($D = 2.00 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$, $C = 1.30 \times 10^{-6} \text{ mol cm}^{-3}$, $n = 4$) at a virtual potential-step measurement from 1.23 to 0.3 V. —, $l = 0.200 \text{ mm}$. ---, calculated by (13.13)

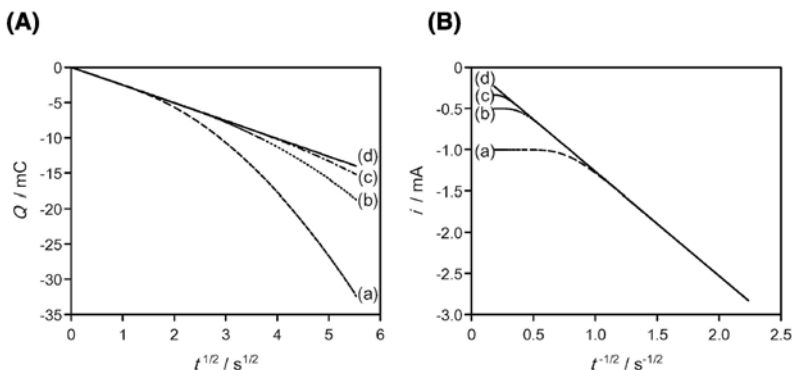


Fig. 13.15. (A) Anson plots and (B) Cottrell plots for virtual oxygen reduction. The simulated parameters are same as Fig. 13.14. (a) $l = 0.1$ mm, (b) $l = 0.2$ mm, (c) $l = 0.3$ mm, (d) the lines calculated by (13.40) (in (A)) and (13.39) (in (B))

the concentration gradient decreases with time infinitely due to the expansion of the diffusion layer. Hence the actual current and cumulative charge are larger than those obtained by (13.39) and (13.40), respectively. Figure 13.15 shows (A) Cottrell plot and (B) Anson plot (Q vs. $t^{1/2}$ plot) for the virtual oxygen reduction at various thicknesses of the diffusion layer. The current–time curves at $l = 0.1$ mm and $l = 0.2$ mm coincided with those calculated by (13.39) only within 1 and 2 s, respectively. This is because the boundary condition expressed by (13.35) disagrees with the boundary condition in the electrochemical system as mentioned above. The cumulative charge–time curve at $l = 0.1$ mm and $l = 0.2$ mm is consistent with those calculated by (13.40) within ca. 3 and 8 s, respectively.

Each electrochemical system has the specific thickness of the diffusion layer which depends on the condition of the electrochemical measurement as described above. A potential-step measurement for the reduction and/or the oxidation of a material with a known diffusion coefficient is useful for the determination of the diffusion layer thickness. The concentration gradient is regarded as constant under steady state condition shown in Fig. 13.16, thus the diffusion layer thickness is represented using a steady state current (i_s) as

$$l = nFADc_{\text{red,bulk}}i_s^{-1} \quad (13.42)$$

Another method for estimating diffusion layer thickness is to fit simulated curves to the experimental $Q-t$ or $I-t$ curve using the non-linear least square method. Figure 13.17 shows the Anson plot for the oxygen reduction using a Pt disk electrode and a curve fitting by the method. The thickness of the diffusion layer was estimated as 0.24 mm in the electrochemical system. This method also allows us to estimate another parameter such as the diffusion coefficient, the concentration, and the geometrical electrode area.

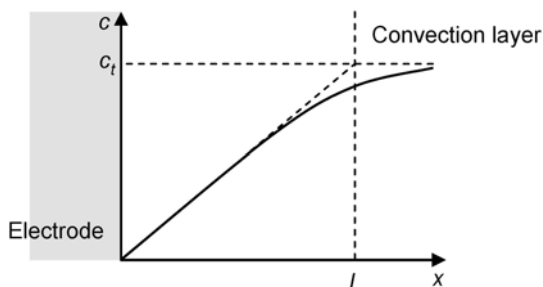


Fig. 13.16. Scheme of the concentration profile at steady state

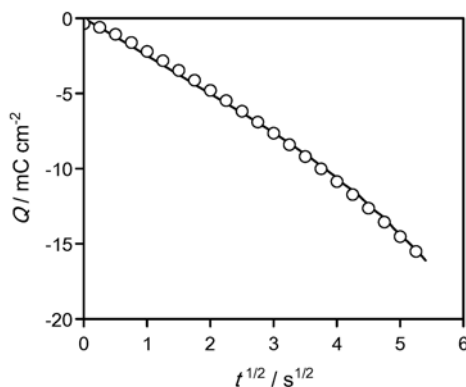


Fig. 13.17. Anson plot for oxygen reduction with a Pt disk electrode in 0.05 M H_2SO_4 . The curve is best fitted one obtained by non-linear least square method

Hydrodynamic Condition

The current obtained from the working electrode is governed by the slowest processes of the three: (i) the diffusion of the reactant to the electrode surface, (ii) the charge transfer rate at the electrode, and (iii) the diffusion of the product to the bulk electrolyte. The rotating disk electrode method is one of the hydrodynamic measurement methods, by which we can dominate (i) and (iii) of the electrochemical processes to estimate the charge transfer rate at the electrode indirectly. In this section, the partial differential equation for the rotating disk electrode will be explained concisely.

Figure 13.18 shows the concentration profile of the virtual oxygen molecules reduced with the disk electrode at the various rotating speeds. The concentration gradient increases with increasing rotating speed.

The equation of general flux J is expressed as [3]

$$J = -D\nabla c - \frac{zF}{RT}Dc\nabla\phi + c\mathbf{v} \quad (13.43)$$

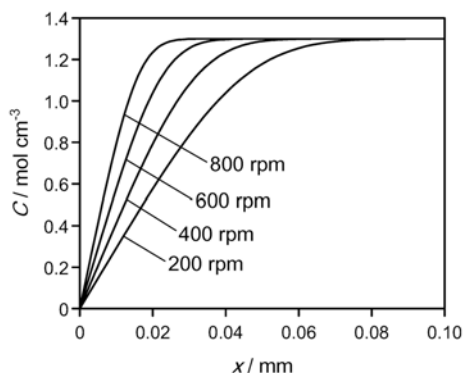


Fig. 13.18. Concentration profiles for virtual oxygen reduction at various rotating speeds

where $\mathbf{v}$ is the velocity vector for the motion of the solution. The terms on the right-hand side are the contribution of diffusion, migration, and convection. The second term can be negligible with an excess of supporting electrolyte. The partial differential equation for one-dimensional diffusion and convection is represented as follows:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} \quad (13.44)$$

The velocity of x -axis v_x is expressed as follows:

$$v_x = -0.51\omega^{3/2}\nu^{-1/2}y^2 \quad (13.45)$$

where ω (rad s^{-1}) and ν ($\text{cm}^2 \text{s}^{-1}$) are the angular velocity and kinetic viscosity, respectively.

13.4.2 Finite Differential Methods

In electrochemical measurements, the boundary conditions such as the concentration of materials at the electrode vary from second to second, so that it is impossible to obtain the analytical solution except under simple and specific conditions. In this section, I will introduce the solutions of the above partial differential equations by numerical methods. Partial differential equation(s) are solved numerically by using discretized functional values, which are called finite difference methods (FDM) [32]. In the finite difference methods, the partial differential equation(s) are calculated after being converted into simple algebraic equations or simultaneous linear equations. After Richardson et al. [33] firstly reported an FDM in 1910 [33], various numerical solution methods have been developed such as implicit-type FDMs and the finite element methods.

FDMs are classified into two types by the kind of algebraic equations obtained by the approximation of the partial differential equation(s): the explicit type and the implicit type. The implicit type FDMs are sub-classified as iterative type and non-iterative type solutions by which the algebraic equations are solved once and for all.

In this section, after I introduce an explicit finite difference method concisely which is a simple and very easy for programming, the Crank–Nicolson method which is one of the implicit-type FDMs with a good stability and convergence will be introduced briefly. More details of the FDMs are written in the literature [32].

Approximate Method in the FDMs

The concept of the approximate method in the FDMs is shown in Fig. 13.19. The continuous function $u(x)$ is discretized by h . The slope of tangent at A can be approximated by using the chord AB as

$$\left. \frac{du(x)}{dx} \right|_A \cong \frac{u(x+h) - u(x)}{h} \quad (13.46)$$

We can also approximate the slopes of tangent at A by the chord AC or BC as follows:

$$\left. \frac{du(x)}{dx} \right|_A \cong \frac{u(x) - u(x-h)}{h} \quad (13.47)$$

$$\left. \frac{du(x)}{dx} \right|_A \cong \frac{u(x+h) - u(x-h)}{2h} \quad (13.48)$$

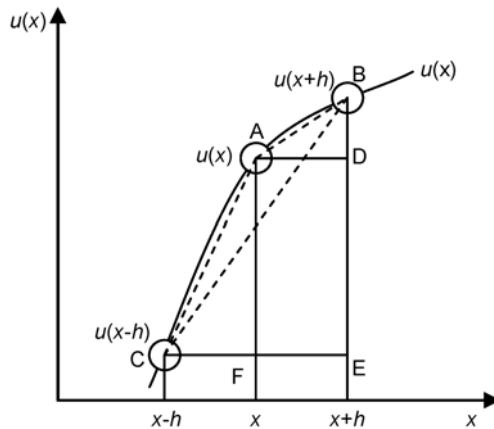


Fig. 13.19. Slope of $u(x)$ at point A

Equations (13.46), (13.47), and (13.48) are called as forward difference formula, backward difference formula, and central difference formula, respectively. The approximating difference equation of the second derivative is represented as follows:

$$\begin{aligned}\frac{d^2u(x)}{dx^2} &\cong \frac{u'(x + \frac{h}{2}) - u'(x - \frac{h}{2})}{h} \\ &= \frac{1}{h} \left\{ \frac{u(x+h) - u(x)}{h} - \frac{u(x) - u(x-h)}{h} \right\} \\ &= \frac{u(x-h) - 2u(x) + u(x+h)}{h^2}\end{aligned}\quad (13.49)$$

For a simple notation, $u(x, t)$ is generally written as follows:

$$u(x, t) = u(ih, jk) = u_{i,j} \quad (13.50)$$

where $x = ih$ and $t = jk$. On the basis of the notation, (13.49) is represented as

$$u''(x) \cong \frac{u_{i-1} - 2u_i + u_{i+1}}{h^2} \quad (13.49')$$

Explicit Finite Difference Method

A most simple solution method is an explicit finite difference method (EX method) in the numerical solutions. Equation (13.33) is discretized using (13.46) and (13.49):

$$\frac{c_{i,j+1} - c_{i,j}}{k} = D \frac{c_{i-1,j} - 2c_{i,j} + c_{i+1,j}}{h^2} \quad (13.51)$$

This can be written as

$$c_{i,j+1} = Dr c_{i-1,j} + (1 - 2Dr) c_{i,j} + Dr c_{i+1,j} \quad (13.52)$$

where $r = k/h^2$. In the EX method, the concentration at $(j+1)$ th time level can be estimated with the concentration at three points of j th time level, as is clearly understandable from (13.52). However, we must use the EX method under $Dr \leq 0.5$ for numerical stability and convergence. Although the EX method is a simple and powerful tool, we have to check the numerical results carefully as follows:

- (i) Check the program carefully. Run the program under the condition where analytical solution can be obtained, and compare the results with that based on analytical solution.
- (ii) Make sure that the results coincide with those with less grid spacing.
- (iii) Confirm that the boundary conditions are satisfied in the resulting calculations.

Crank–Nicolson Method

When using the explicit-type FDM, we must satisfy the condition as mentioned above: whenever $Dr \leq 0.5$, so that it takes a lot of time to calculate the concentration profiles, although the method is a simple algorithm. The restriction can be overcome by implicit-type FDMs such as Crank–Nicolson method which are always numerically stable regardless of the Dr value. However, two procedures are added before computation compared to those in the explicit-type FDM: (i) the transformation of the equation and (ii) the solution of the simultaneous linear equations.

In the Crank–Nicolson method, the difference equation(s) are expressed by the average of finite differential approximations at the j th and $(j - 1)$ th time level. The difference equation of (13.33'') is expressed as the following equation by the Crank–Nicolson method:

$$\frac{c_{i,j} - c_{i,j-1}}{k} = \frac{D}{2} \left(\frac{c_{i-1,j} - 2c_{i,j} + c_{i+1,j}}{h^2} + \frac{c_{i-1,j-1} - 2c_{i,j-1} + c_{i+1,j-1}}{h^2} \right) \quad (13.53)$$

This can be written as

$$-Drc_{i-1,j} + (2 + 2Dr)c_{i,j} - Drc_{i+1,j} = Drc_{i-1,j-1} + (2 - 2Dr)c_{i,j-1} + Drc_{i+1,j-1} \quad (13.54)$$

The number of the simultaneous linear equations is the same as that of the grid points, and the equations are expressed by using a matrix as follows:

$$\begin{bmatrix} 1 & & & & & \\ a & b & & & & \\ & a & b & & & \\ & & \cdots & & & \\ & & & a & b & a \\ & & & & a & b & a \\ & & & & & & 1 \end{bmatrix} \begin{bmatrix} c_{0,j} \\ c_{1,j} \\ c_{2,j} \\ \vdots \\ c_{l-2,j} \\ c_{l-1,j} \\ c_{l,j} \end{bmatrix} = \begin{bmatrix} e \\ f_1 \\ f_2 \\ \vdots \\ f_{l-2} \\ f_{l-1} \\ g \end{bmatrix} \quad (13.55)$$

where $a = -Dr$, $b = 2 + 2Dr$, e is the concentration of the oxidant at $t = j$, f_i is the term on the right-hand side of (13.54), and $g = c_{\text{bulk}}$. We can calculate the concentration profiles from 0 s to a necessary time by solving the matrix using the Gaussian elimination method.

13.5 Digital Simulation for Polymer-Coated Electrodes

Electrochemical investigation into polymer-coated electrodes with a dispersed redox center has been undergone for last three decades [34–55]. These electrodes have wide application such as chemical sensors [56], electrocatalysis [57], and energy conversion devices [58].

Needless to say, a polymer layer coated on an electrode has a finite thickness. This causes a discrepancy in electrochemical results between the finite condition and the infinite condition from which equations in the solution system are derived. Another difference between these two systems is that the diffusion of molecules in a polymer layer is much slower than that in a solution. The contribution of the charge hopping mechanism to the whole charge propagation in a polymer-coated electrode would become greater than that in a solution system. In this section, the digital simulations for the polymer-coated electrodes will be introduced [59–61].

13.5.1 Hydrostatic Condition

Figure 13.20 shows the scheme of a polymer-coated electrode in which functional molecules were dispersed. When the exchange of the redox molecules is neglected at the interface between the polymer layer and the electrolyte solutions, the following equation is substituted for (13.41) as the boundary condition:

$$\frac{\partial C(l, t)}{\partial x} = 0 \quad (13.56)$$

In the case that we use the above boundary condition in (13.55), (13.56) can be written as

$$g = C_{l-1, j-1} \quad (13.57)$$

The above boundary condition is applied to the polymer-coated electrode systems such as the tris(2,2'-bipyridine)ruthenium(II) ion ($[\text{Ru}(\text{bpy})_3]^{2+}$) incorporated into a Nafion film by a mixed cast method or an ion exchange method. In these systems, $[\text{Ru}(\text{bpy})_3]^{2+}$ diffuses only in the Nafion layer due to the electrostatic interaction between $[\text{Ru}(\text{bpy})_3]^{2+/3+}$ and the sulfonic acid

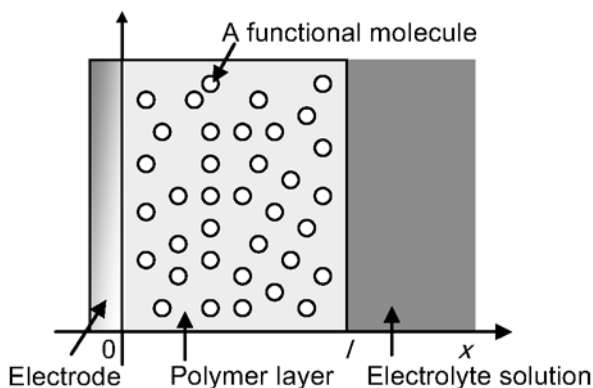


Fig. 13.20. Scheme of a polymer-coated electrode with dispersed functional molecules

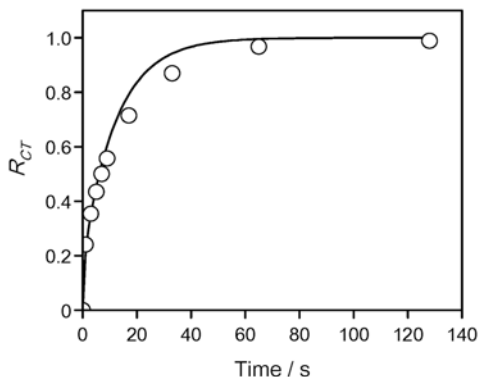


Fig. 13.21. Time dependence of R_{CT} estimated by absorption spectral change at potential-step measurement from 0.6 V (vs. Ag|AgCl) to 1.4 V using ITO/Nafion[Ru(bpy) $_3^{2+}$] electrode in 0.1 mol dm $^{-3}$ KNO $_3$ (pH 1). The solid line was a simulated curve ($D = 3.2 \times 10^{-10}$ cm ^{2} s $^{-1}$, $l = 1 \times 10^{-4}$ cm, $C_T = 4.2 \times 10^{-4}$ mol cm $^{-3}$) (reproduced from Shiroishi et al. (2001) [60] by permission of Society of Computer Chemistry, Japan)

groups in Nafion. Spectroelectrochemical measurements can be performed in such systems by using the ITO electrode. Figure 13.21 shows the time dependence of the fraction of the functional molecules that accepted charges (R_{CT}) estimated by absorption spectral change at a potential-step measurement using an ITO|Nafion[Ru(bpy) $_3^{2+}$] electrode.

The equation of the time-dependent R_{CT} value under the infinite condition is represented by (13.58) [31]:

$$R_{CT} = \frac{2D^{1/2}}{\pi^{1/2}} \frac{t^{1/2}}{l} \quad (13.58)$$

The diffusion coefficient was estimated as 3.23×10 cm ^{2} s $^{-1}$ using the slope of the R_{CT} vs. $t^{1/2}$ plot based on (13.58) $R_{CT} \approx 0.5$ where the R_{CT} value under the finite condition coincides with that calculated by (13.58). The simulated curve under the finite boundary condition coincided with the experimentally obtained values in all time as shown in Fig. 13.21.

The electrochemical and spectral results can be also simulated in the case that oxidized (or reduced) species consumed by a catalytic reaction by using (13.33') substituted for (13.33). The first-order catalytic reaction employed to (13.33') gives

$$\frac{\partial c(x, t)}{\partial t} + kc(x, t) = D \frac{\partial^2 c(x, t)}{\partial x^2} \quad (13.33'')$$

where k (s $^{-1}$) is the rate constant of catalytic reaction. Figure 13.22A shows a series of cyclic voltammograms at various k values. The anodic current beyond the redox potential increased with the k value. Time dependences of

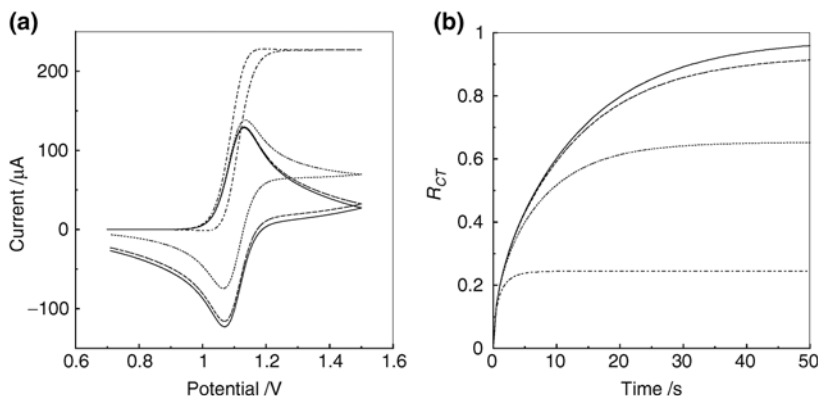


Fig. 13.22. Virtual electrochemical measurements of a material ($D = 3 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$, $E = 1.1 \text{ V}$ vs. a standard electrode) at various k values using ES-1. -, $k = 0 \text{ s}^{-1}$; ---, $5 \times 10^{-3} \text{ s}^{-1}$; ..., $5 \times 10^{-2} \text{ s}^{-1}$; -.-, $5 \times 10^{-1} \text{ s}^{-1}$. (a) Cyclic voltammogram from 0.7 to 1.5 V at 20 mV s^{-1} . (b) Time dependence of R_{CT} at an applied potential from 0.7 to 1.5 V (reproduced from Shiroishi et al. (2001) [60] by permission of Society of Computer Chemistry, Japan)

R_{CT} under the finite condition at various k values in virtual potential-step measurements are shown in Fig. 13.22B. The increase of k value reduced the time to reach the plateaus, and also lowered the plateau values.

We can simulate not only the electrochemical results (e.g. current and concentration profiles) but also quantitative spectral changes in these systems. However, when the interaction between polymer matrix and the redox species is too strong to diffuse the redox species in the polymer matrix, the singular charge propagation phenomenon occurs as shown in Sect. 13.6.

13.5.2 Hydrodynamic Condition

I give an outline of the digital simulation of the rotating disk electrode measurement using a Pt covered with a Nafion film for the typical example of hydrodynamic condition in the section. Figure 13.23 shows the scheme of the Pt disk electrode covered with the polymer layer whose thickness is $l_0 \text{ cm}$.

The mass balances under the reversible and the irreversible conditions at the electrode surface are expressed by (13.26) and (13.31''), respectively. The mass balance of the oxidized molecules in a micro-volume ($1 \text{ cm} \times 1 \text{ cm} \times \Delta x \text{ cm}$) at the polymer side of the interface between phase 0 and phase 1 is expressed as

$$N_{l_0 - \Delta x} - \Delta x \frac{\partial C_{P0}(l_0 - \Delta x, t)}{\partial t} = N_{l_0} \quad (13.59)$$

where $N_{l_0 - \Delta x}$ and N_{l_0} are molar fluxes at $x = l_0 - \Delta x$ and at $x = l_0$, respectively, and are represented as

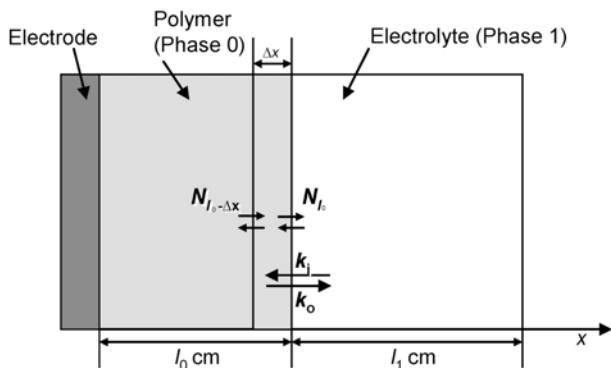


Fig. 13.23. Schematic diagram of the polymer-coated electrode

$$N_{l_0 - \Delta x} = -D_0 \frac{\partial C_{P0}(l_0 - \Delta x, t)}{\partial x} \quad (13.60)$$

$$N_{l_0} = k_o C_{P0}(l_0 - \Delta x, t) - k_i C_{P1}(l_0, t) \quad (13.61)$$

where $k_i(\text{s}^{-1})$ and $k_o(\text{s}^{-1})$ are the rate constants of the inflow and outflow at the interface between the polymer layer and the electrolyte solution. Applying (13.60) and (13.61) to (13.59) yields

$$-D_0 \frac{\partial C_{P0}(l_0 - \Delta x, t)}{\partial x} - \Delta x \frac{\partial C_{P0}(l_0 - \Delta x, t)}{\partial t} = k_o C_{P0}(l_0 - \Delta x, t) - k_i C_{P1}(l_0, t) \quad (13.62)$$

Since the convection is negligible near the interface, the mass balance at the solution side of the interface is represented as follows:

$$k_o C_{P0}(l_0 - \Delta x, t) - k_i C_{P1}(l_0, t) - \Delta x \frac{\partial C_{P1}(l_0, t)}{\partial t} = -D_1 \frac{\partial C_{P1}(l_0 + \Delta x, t)}{\partial x} \quad (13.63)$$

Mass transfer in the phase 0 and phase 1 is expressed as (13.33) and (13.44), respectively. These equations can be solved by the calculus of the finite difference methods as shown above.

13.6 Classical Monte Carlo Simulation for Charge Propagation in Redox Polymer

Charge transport in a polymer membrane involving dispersed redox centers is divided into two mechanisms. One is physical diffusion of the redox center, and the other is charge hopping which takes place by charge exchange between

the redox centers. When the redox center was attached to a polymer chain covalently or by strong electrostatic force, the charge transport usually takes place by a charge hopping mechanism.

The apparent diffusion coefficient can be obtained by measuring time dependence of current using an electrochemical potential-step method. Observation of charged fraction of molecules (R_{CT}) by UV/Vis absorption spectral change gives a more direct information about charge transport [62]. When charge transfer takes place by a charge hopping mechanism, a redox center molecule can transfer charge to another one existing within charge hopping distance (r_0). It can be regarded that a kind of intermolecular connections is formed among these molecules when charge hopping takes place. A process controlled by such connection is similar to a contact process [63] and a forest fire process [64] which can be explained by a percolation physics.

It is of interest and importance to analyze and visualize charge propagation in a polymer membrane in order to construct devices. In this section, charge propagation taking place only by a charge hopping in a polymer membrane was analyzed and visualized with a Monte Carlo simulation [65]. A relationship between charge hopping distance and critical percolation concentration is derived by measuring the fraction of oxidized (or reduced) center molecules and applied to the actual polymer systems confining Ru complex redox centers.

13.6.1 Visualization of Charge Propagation

Figure 13.24 shows the concept of the Monte Carlo simulation. A uniform sphere sites model was employed for the simulation. The left of the display is taken as the electrode side and the right as the membrane/solution interface.

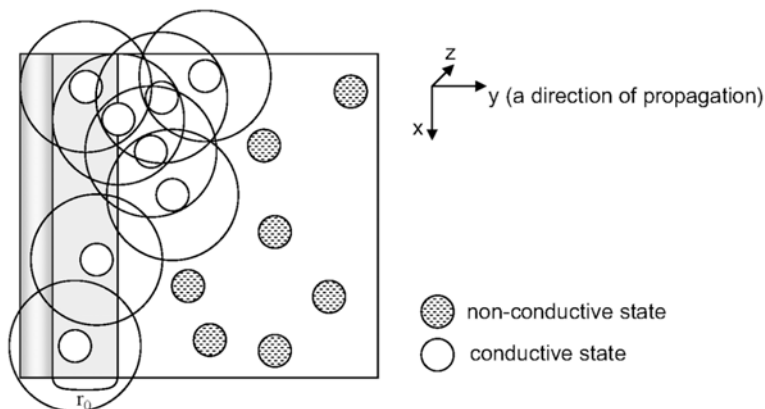


Fig. 13.24. Scheme of charge hopping simulation in polymer membrane using Monte Carlo method. The left side is electrode side (reproduced from Shiroishi et al. (2001) [65] by permission of John Wiley & Sons, Ltd.)

Redox center molecule was regarded as a site dispersed in the polymer membrane. The redox molecular size (s), charge hopping distance (r_0 , distance between molecular centers), and the position of sites are real numbers in this model. The site dispersion subroutine was programmed to exclude overlapping with another site. Charges propagate from electrode to polymer/solution interface (toward y -axis). A site can transfer a charge to another one existing within r_0 , which is regarded as a kind of connection formation. The connection among sites was checked from the electrode surface to the sites that do not have another connecting site within r_0 . The scale of the present simulation is 50×50 and the XY plane was displayed.

Figure 13.25 shows visualized charge propagation from the electrode (left side) through a polymer membrane. It should be noted that below the critical percolation probability charges do not propagate over the whole membrane, but are localized only near the electrode. The charge can reach the polymer/solution interface only when the concentration is above the percolation threshold ($p = 0.0566$) leaving minor fraction of uncharged sites in the polymer membrane.

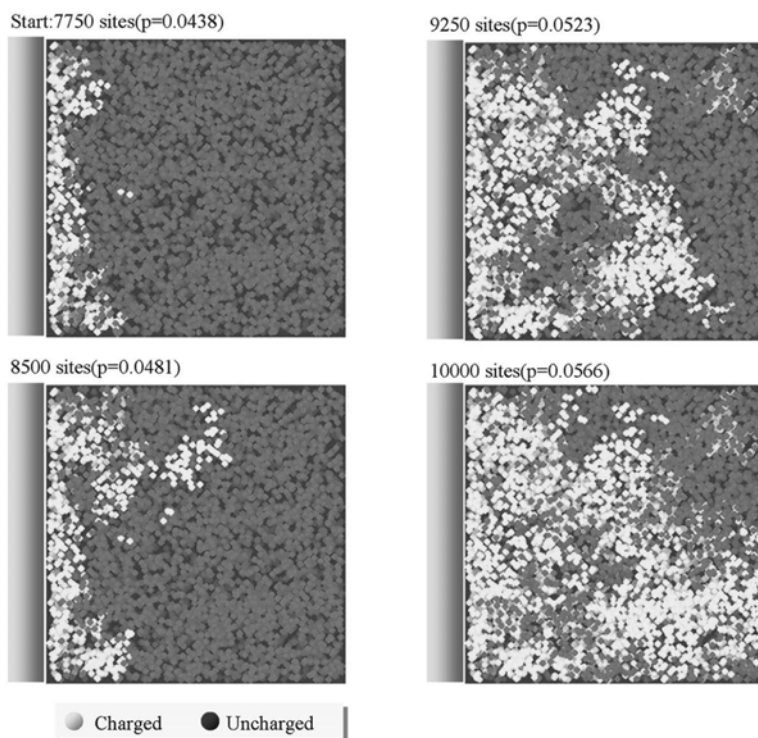


Fig. 13.25. Charge propagation in polymer membrane with increasing sites using a uniform sphere sites model. The diameter of sites(s) is 1 and the charge hopping distance (r_0) is 2. White sites were charged, and gray sites not charged (reproduced from Shiroishi et al. (2001) [65] by permission of John Wiley & Sons, Ltd.)

13.6.2 Determination of a Charge Hopping Distance

Assuming that the unit length of the simulation is 1 nm, occupation probability (p) can be converted into concentration (c) by the following equation:

$$c = \frac{3pD}{4 \times 10^{-24}\pi(s/2)^3 N_A} \quad (13.64)$$

where c (mol dm^{-3}) is concentration of the redox molecule, D is the fraction of the space filled with spheres at the closest packed conditions ($D = 0.74$), s is the diameter of sites, and N_A is Avogadro's number.

Figure 13.26 shows the dependence of R_{CT} on concentration calculated by (13.64) with various charge hopping distances. The critical percolation concentration (c_p) determined by the inflection point of the R_{CT} vs. concentration plot decreases with the increase of the charge hopping distance (r_0).

In a uniform sphere sites model, the critical percolation probability is derived from the following equation [66]:

$$\frac{r_0}{r_s} = P \quad (13.65)$$

where $P = 0.705 \pm 0.004$, and r_s is defined by the following equation and called as an average distance between sites:

$$\frac{4\pi(r_s/2)^3}{3} = \frac{1}{n'} \quad (13.66)$$

where n' is the number of sites in a unit volume at a percolation threshold. The relationship between n' and concentration was expressed by the following equation when the unit length of simulation is taken as 1 nm:

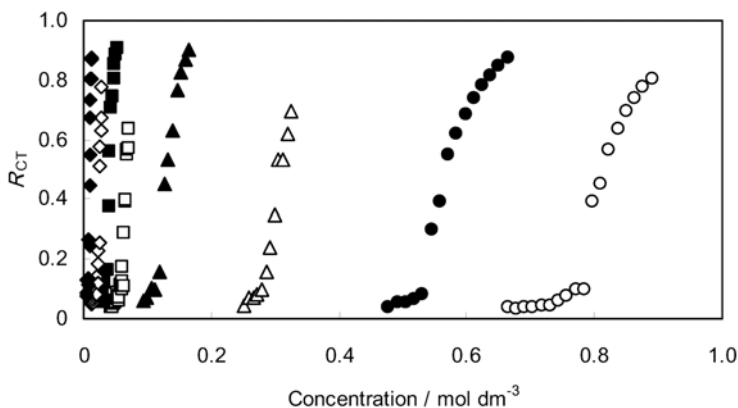


Fig. 13.26. Dependence of R_{CT} on concentration using a uniform sphere sites model at $s = 1.0$, $r_0 = 1.15$; ●, $r_0 = 1.25$; △, $r_0 = 1.5$; ▲, $r_0 = 2$; □, $r_0 = 2.5$; ■, $r_0 = 3$; ◇, $r_0 = 3.5$; ◆, $r_0 = 4$ (reproduced from Shiroishi et al. (2001) [65] by permission of John Wiley & Sons, Ltd.)

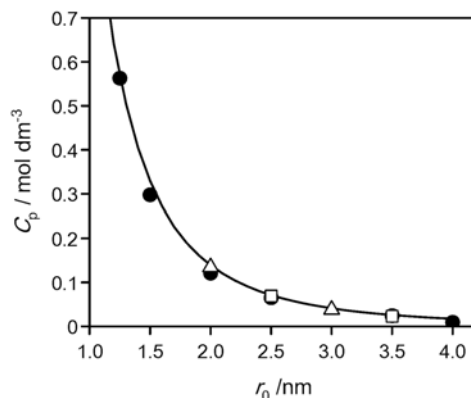


Fig. 13.27. Dependence of c_p on r_0 using uniformed sphere sites model at $\bullet$, $s = 1$; Δ , $s = 1.5$; $\square$, $s = 2$. The line was calculated by (13.6) (reproduced from Shiroishi et al. (2001) [65] by permission of John Wiley & Sons, Ltd.)

$$n' = N_A c_p \times 10^{-24} \quad (13.67)$$

Equation (13.68) is derived from (13.65), (13.66), and (13.67)

$$c_p = \frac{6P^3}{10^{-24}r_0^3\pi N_A} \quad (13.68)$$

The plots of critical percolation concentration (c_p) vs. charge hopping distance (r_0) are shown in Fig.13.27. The c_p values were obtained by the inflection points of the plot of R_{CT} vs. concentration (Fig.13.26) calculated by the Monte Carlo simulation. The curve calculated by (13.68) agrees well with the results regardless of the site size.

Figure 13.28 shows the experimental plots between R_{CT} and concentration in a polymer membrane after reaching steady states by a potential-step method. The experimental data of R_{CT} vs. c for polymer-pendant methylviologen system (PMV) [67] is also shown in Fig.13.28 as a reference. Percolation threshold could be determined from the inflection point of these plots suggesting that the diffusion of redox center is very slow. Thus, charge propagation taking place by a charge hopping mechanism in a polymer membrane can be simulated with the present model. In the calculation localization of the complex in the film was taken into account as follows. A Nafion film consists of the hydrophobic and hydrophilic regions. The cationic complex is adsorbed only in the hydrophilic regions. We applied this model to the Nafion system simply by considering the effect of localization. The degree of localization (α) is 5.1 [51]. The charge hopping distance for Nafion[Ru-O-Ru] and Nafion[Ru(Pvbpy)(bpy) $_2^{2+}$] is calculated to 1.20 and 1.00 nm, respectively. Equation (13.68) is of importance and useful for designing various devices.

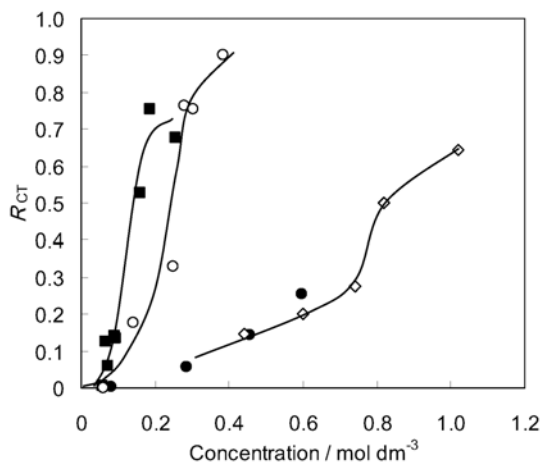


Fig. 13.28. The dependence of R_{CT} values on the concentration in the various systems of PSCAS measurement after reaching steady states. ◇, PMV; ●, Ru[P(St-Vbpy)](bpy)₂²⁺; ○, Ru(PVbpy)(bpy)₂²⁺; ■, Ru-O-Ru (reproduced from Shiroishi et al. (2001) [65] by permission of John Wiley & Sons, Ltd.)

References

1. D.D. Duong, Fundamentals of pure component adsorption equilibria, in D.D. Duong (ed.), *Adsorption Analysis: Equilibria and Kinetics* (Imperial College Press, London, 1998), pp. 11–48
2. E. Gileadi, B.E. Conway The behavior of intermediates in electrochemical catalysis, in *Modern Aspects of Electrochemistry*, vol. 3, ed. by J.O.M. Bockris, B.E. Conway (Butterworth, London, 1964), pp. 343–442
3. V.S. Bagotzky, Y.B. Vassiliev, *Electrochim. Acta* **12**, 1323 (1967)
4. S. Mukerjee, R.C. Urian, S.J. Lee, E.A. Ticianelli, J. McBreen, *J. Electrochem. Soc.* **151**, A1094 (2004)
5. K.T. Jeng, J.O.M. Bockris, *J. Electroanal. Chem.* **330**, 541 (1992)
6. H. Shiroishi, Y. Ayato, J. Rais, K. Kunimatsu, M. Osawa, T. Okada, *Electrochim. Acta* **51**, 1225 (2006)
7. H. Shiroishi, Y. Ayato, T. Okada, K. Kunimatsu, *Langmuir* **21**, 3037 (2005)
8. H. Shiroishi, Y. Ayato, K. Kunimatsu, T. Okada, *Chem. Lett.* **33**, 792 (2004)
9. T. Iwashita, *Electrochim. Acta* **47**, 3663 (2002)
10. S. Wasmus, A. Kuver, *J. Electroanal. Chem.* **461**, 14 (1999)
11. R. Parsons, T. VanderNoot, *J. Electroanal. Chem.* **257**, 9 (1988)
12. K. Kunimatsu, H. Kita, *J. Electroanal. Chem.* **218**, 155 (1987)
13. H.A. Gasteiger, N.M. Markovi, E.J. Cairns, *J. Phys. Chem.* **97**, 12020 (1993)
14. M. Christov, K. Sundmacher, *Surf. Sci.* **547**, 1 (2003)
15. P.N. Ross Jr., Oxygen reduction reaction on smooth single crystal electrodes, in *Handbook of Fuel Cells – Fundamentals, Technology and Applications*, vol. 2, ed. by W. Vielstich, H.A. Gasteiger, A. Lamm (Wiley, New York, 2003), pp. 465–480
16. A.J. Appleby, *J. Electroanal. Chem.* **357**, 117 (1993)
17. R.A. Sidik, A.B. Anderson, *J. Electroanal. Chem.* **528**, 69 (2002)

18. R.R. Adzic, J.X. Wang, *J. Phys. Chem. B* **102**, 8988 (1998)
19. K. Kato, A. Takatsu, N. Matsuda, R. Azumi, M. Matsumoto, *Chem. Lett.* **24**, 437 (1995)
20. K. Fujita, K. Taniguchi, H. Ohno, *Talanta* **65**, 1066 (2005)
21. N. Matsuda, A. Takatsu, K. Kato, *Chem. Lett.* **25**, 105 (1996)
22. J.T. Bradshaw, S.B. Mendes, N.R. Armstrong, S.S. Saavedra, *Anal. Chem.* **75**, 1080 (2003)
23. N. Matsuda, J.H. Santos, A. Takatsu, K. Kato, *Thin Solid Film* **445**, 313 (2003)
24. N. Matsuda, J.H. Santos, A. Takatsu, K. Kato, *Thin Solid Film* **438–439**, 403 (2003)
25. Y. Ayato, A. Takatsu, K. Kato, J.H. Santos, T. Yoshida, N. Matsuda, *J. Electroanal. Chem.* **578**, 137 (2005)
26. Y. Ayato, A. Takatsu, K. Kato, N. Matsuda, *J. Electroanal. Chem.* **595**, 87 (2006)
27. H. Ohno, K. Fukuda, F. Kurusu, *Chem. Lett.* **29**, 76 (2000)
28. K. Fujita, H. Ohno, *Polym. Adv. Technol.* **14**, 486 (2003)
29. K. Fujita, C. Suzuki, H. Ohno, *Electrochem. Commun.* **5**, 47 (2003)
30. A. Fujishima, M. Aizawa, T. Inoue, *Denkikagakusouteihou* (Gihoudou Syuppan, Tokyo, 1984), pp. 139–143
31. A.J. Bard, L.R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2nd edn. (John Wiley & Sons, New York, 2001).
32. G.D. Smith, *Numerical Solution of Partial Differential Equations: Finite Difference Methods*, 3rd edn. (Oxford University Press, Kings Lynn, 1985)
33. L.F. Richardson, *Philos Trans Roy Soc London Ser A* **210**, 307–357 (1910)
34. N. Oyama, F.C. Anson, *J. Am. Chem. Soc.* **101**, 3450 (1979)
35. I. Rubinstein, A.J. Bard, *J. Am. Chem. Soc.* **102**, 6642 (1980)
36. I. Rubinstein, A.J. Bard, *J. Am. Chem. Soc.* **103**, 5007 (1981)
37. T.P. Henning, H.S. White, A.J. Bard, *J. Am. Chem. Soc.* **103**, 3937 (1981)
38. H.S. White, J. Leddy, A.J. Bard, *J. Am. Chem. Soc.* **104**, 4811 (1982)
39. C.R. Martin, I. Rubinstein, A.J. Bard, *J. Am. Chem. Soc.* **104**, 4817 (1982)
40. J.S. Facci, R.H. Schmehl, R.W. Murray, *J. Am. Chem. Soc.* **104**, 4959 (1982)
41. D.A. Buttry, F.C. Anson, *J. Am. Chem. Soc.* **105**, 685 (1983)
42. D.A. Buttry, J.M. Saveant, F.C. Anson, *J. Phys. Chem.* **88**, 3086 (1984)
43. Y.M. Tsou, F.C. Anson, *J. Phys. Chem.* **89**, 3818 (1985)
44. N. Oyama, T. Ohsaka, M. Kaneko, H. Yamamoto, *J. Phys. Chem.* **90**, 3850 (1986)
45. R.W. Murray, B.A. White, *J. Am. Chem. Soc.* **109**, 2576 (1987)
46. R.W. Murray, E.F. Dalton, *J. Phys. Chem.* **95**, 6383 (1991)
47. A.M. Hodges, O. Johansen, J.W. Loder, A.W.H. Mau, J. Rabani, W.H.F. Sasse, *J. Phys. Chem.* **95**, 5966 (1991)
48. F.C. Anson, D.N. Blauch, J.M. Saveant, C.F. Shu, *J. Am. Chem. Soc.* **113**, 1922 (1991)
49. C.S. Sosnoff, M. Sullivan, R.W. Murray, *J. Phys. Chem.* **98**, 13643 (1994)
50. K. Aoki, R. Rajagopalan, A. Heller, *J. Phys. Chem.* **99**, 5102 (1995)
51. M. Yagi, K. Nagai, A. Kira, M. Kaneko, *J. Electroanal. Chem.* **394**, 169 (1995)
52. J.W. Long, C.S. Velazquez, R.W. Murray, *J. Phys. Chem.* **100**, 5492 (1996)
53. M. Yagi, T. Mitsumoto, M. Kaneko, *J. Electroanal. Chem.* **448**, 131 (1998)
54. J. Zhang, M. Yagi, M. Kaneko, *J. Electroanal. Chem.* **445**, 109 (1998)
55. J. Zhang, F. Zhao, M. Kaneko, *Electrochim. Acta* **44**, 3367 (1999)

56. G.E. Benedetto, P.G. Zambonin, F. Palmisano, *Biosens Bioelectron* **11**, 1001 (1996)
57. M. Yagi, K. Kinoshita, M. Kaneko, *J. Phys. Chem.* **100**, 11098 (1996)
58. M. Kaneko, Photoelectric conversion by polymeric and organic materials, in *Organic Conductive Molecules and Polymers*, vol. 4, ed. by N.S. Nalwa (John Wiley & Sons, New York, 1997), pp. 669.
59. H. Shiroishi, S. Tokita, M. Kaneko, *J. Comput. Chem. Jpn.* **1**, 65 (2002)
60. H. Shiroishi, T. Nomura, K. Ishikawa, S. Tokita, M. Kaneko, *J. Chem. Software* **7**, 145 (2001)
61. H. Shiroishi, T. Shoji, T. Nomura, S. Tokita, M. Kaneko, *J. Chem. Software* **8**, 41 (2002)
62. S.A. Trammel, T.J. Meyer, *J. Phys. Chem.* **103**, 104 (1999)
63. T. Ohtsuki, T. Keyes, *Phys. Rev. A* **33**, 1223–1232 (1986)
64. G. MacKay, N. Jan, *J. Phys. A* **17**, L757 (1984)
65. H. Shiroishi, K. Ishikawa, K. Hirano, M. Kaneko, *Polym. Adv. Technol.* **12**, 237 (2001)
66. G.E. Pike, C.H. Seager, *Phys. Rev. B* **10**, 1421 (1974)
67. J. Zhang, T. Abe, M. Kaneko, *J. Electroanal. Chem.* **438**, 133 (1997)

Spectroscopic Studies of Molecular Processes on Electrocatalysts

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Abstract Catalyst preparation procedures for Pt catalysts with high performance for polymer electrolyte fuel cells (PEFCs) were presented: electroless plating and direct hydrogen reduction methods. Model catalyst electrodes with different mesoscopic structures were studied using in situ infrared reflection absorption spectroscopy (IRAS) to determine structural properties of these electrodes and potential effect of the mesoscopic structure on the reactivity of the fuel cell catalyst. Special attention was paid to the mechanisms for oxidation of methanol on these model electrodes and on actual fuel cell catalysts. The mechanism for methanol oxidation on a Pt surface is not complicated; under less positive electrode potential conditions, methanol decomposes to produce CO and atomic hydrogens on the Pt surface, whereas methanol changes into formate under more positive electrode potential conditions in the presence of OH species. Both intermediates are catalyst poison and desorb as CO₂ from the catalyst surface upon further oxidation.

14.1 Introduction

Polymer electrolyte fuel cells (PEFCs) are attracting a large amount of attention due to their potential as a clean and mobile power source for applications such as fuel-cell vehicles and cogeneration systems for domestic electricity and heating [1–4]. At present, significant barriers remain with regard to cell cost and power output [5,6]. A number of studies have focused on the preparation of fine nanometer size Pt particles that are highly dispersed on carbon black. Details regarding Pt particle size, particle form, crystal surface index plane dependencies, and dispersion degree dependencies remain controversial, despite extensive investigative approaches, including transmission electron microscopy (TEM), infrared spectroscopy (IR), and cyclic voltammetry (CV) [7–15]. At present, the most conventional preparation method for fuel cell catalysts is sintering. Typically, carbon black (XC-72 CB) is impregnated with a solution containing a platinum salt or platinum complex, the catalyst is heated at high temperature under high vacuum, and then reduced using hydrogen.

Despite such complicated preparation methods, there has been no decisive improvement in cell power output.

Although catalyst preparation using the electroless plating method has various potential advantages, the application of electroless plating has not been studied sufficiently for fuel cell Pt catalysts [7, 15–17]. Electroless plating is a method for depositing metal ions in a plating solution with a reducing agent. This method has some advantages: metals can be plated on substrates simply by dipping them in solution; it is not necessary to optimize current and voltage distributions, because electricity is not used; metals of uniform thickness can be plated on substrates with complex forms if they have touched the solution; and metals can be plated on nonconductors. The simplicity with which platinum can be plated simply by dipping carbon in plating solution is very important from the perspective of cost performance. Moreover, not only electroless reduction of platinum catalysts, but also surface modification of polymer electrolytes on the catalysts, can be carried out successively in the same batch.

On the other hand, very fine Pt particles of less than 2 nm in diameter have been successfully produced by a direct $\text{Pt}^{2+}(\text{Pt}^{4+})$ reduction process through hydrogen gas bubbling [18]. Hydrated cations ($\text{Pt}^{2+}(\text{H}_2\text{O})_n$ or $\text{Pt}^{4+}(\text{H}_2\text{O})_n$) can collide with H_2 gas in pure water, and stepwise reduction proceeds through collision. Since this method is extremely simple and useful for cost performance, these catalysts were characterized from a standpoint of practical application. It was found that Pt catalysts prepared by both electroless plating and direct reduction of $\text{Pt}^{2+}(\text{Pt}^{4+})$ solvated cations through H_2 gas in pure water show excellent performance with high fuel cell output efficiencies, and, further, that the particle size distribution of Pt particles in the electrocatalysts is an important key factor for output power [19].

Methanol oxidation is of interest from both a fundamental and a practical perspective. Numerous studies in the literature have shown that the establishment of a mechanism for methanol oxidation has yet to be solved. Even though a number of studies on the adsorption of methanol on flat single crystal Pt(111) have been reported, the specific paths for methanol decomposition, the adsorption geometry of methanol and its derivatives (carbon monoxide, methoxy, formaldehyde and formate) on the surface are still unclear [54]. Clarification of such information is not only interesting in terms of the surface science, but is also essential for a better understanding of the reaction mechanisms on Pt catalysts in direct methanol fuel cells (DMFC). Mechanisms of electrocatalytic reactions often involve various kinds of adsorbed species as reactants, intermediates, poisons, supporting electrolytes, and solvent molecules. Such competitive adsorption complicates the interpretation of the overall reaction. Therefore, the identification of different adsorbates involved during an electrochemical process is of primary concern. Electrooxidation of methanol on a Pt(111) surface is an interesting case in view of the adsorbates involved during reaction, because the current–potential curve shows the significant influence of specific anion adsorption [20–23]. The reaction is

most suppressed in sulfuric acid solution, but proceeds smoothly in perchloric acid or fluoric acid solution. Furthermore, the reaction rate of methanol oxidation on a Pt(111) surface is the lowest among low index surfaces [24] in sulfuric acid solution. This indicates that the oxidation reaction is most retarded on a Pt(111) surface in sulfuric acid solution. The development of infrared reflection absorption spectroscopy (IRAS) has enabled in situ observation of adsorbed species during electrocatalytic reactions [25–29]. However, vibrational spectroscopy provides little information regarding the long-range structure and symmetry of the adsorbed species. Therefore, a combination of vibrational spectroscopy and electron diffraction is required to provide this information [30–32].

In this chapter, we deal with the adsorption of CO and electrolyte anions on a Pt(111) surface during the electrooxidation of methanol in sulfuric and perchloric acid solutions. In order to obtain local structural information during the reaction, the reaction was quenched by immersing the surface into an ultra-high vacuum (UHV) environment. The surface was then studied using IRAS and low-energy electron diffraction (LEED). For the methanol oxidation reaction in both sulfuric and perchloric acid solutions, the difference in reaction rates is discussed in terms of the local structure on the surface. The $(\sqrt{7} \times \sqrt{7}) - R19.1^\circ$ structure was obtained by IRAS and LEED studies on the immersed surface, due to the coadsorption of CO derived from methanol with bisulfate.

14.2 The Preparation and Spectroscopic Characterization of Fuel Cell Catalysts

14.2.1 Catalyst Preparation by Electroless Plating and Direct Hydrogen Reduction Methods: Practical Application for High Performance PEFC

Sample Preparation

Six catalysts were prepared (catalyst 1 to catalyst 6). Carbon black (CB; Vulcan XC-72R) was used as a substrate for catalyst 1 to catalyst 6. Ultrapure (milli-Q) water was used. Catalysts 1 to 4 and catalysts 5 to 6 were prepared by electroless plating and hydrogen direct reduction methods, respectively.

Catalyst 1.—First, 0.2 g of CB was ultrasonicated in 20 mL of 1.4 mM $\text{PdCl}_2/0.1 \text{ M HCl}$ solution for 0.5 h. Water was added to the solution and the supernatant fluid was removed, with the cycle being continuously repeated to collect all the supernatant. Next, 25 mL of platinum electroless plating solution containing 50 mg of PtCl_2 , 80 mg of NH_4Cl , and 6 mL of 38% NH_4OH in 19 mL of water (the solution pH was adjusted by addition of 38% NH_4OH and NH_4Cl to 10.5) was added to the solution and mechanically stirred for a few minutes, after which 0.65 g of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ was added for chemical reduction at 313 K for 30 min [7].

Catalyst 2.—Twenty millilitres of 0.1 M SnCl_2 /0.1 M HCl was aged for 3 days; 0.2 g of CB was then ultrasonicated in the solution for 1.5 h. After centrifugation, 20 mL of 1.4 mM PdCl_2 /0.1 M HCl solution was added to the solution and ultrasonicated for 0.5 h. Water was added to the solution, and the supernatant fluid was removed. As described for catalyst 1, 25 mL of platinum electroless plating solution was then added to the solution and mechanically stirred for a few minutes. Finally, 0.65 g of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ was added for reduction at 313 K for 30 min [7].

Catalyst 3.—First, 0.2 g of CB was ultrasonicated in 20 mL of 1.4 mM PdCl_2 /0.1 M HCl solution for 0.5 h. Water was added to the solution, and the supernatant fluid was removed. Fifty millilitres of platinum electroless plating solution containing 0.3 g of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, 0.2 g of NaOH, and 6 mL of 38% NH_4OH in 44 mL of water was then added to the solution and mechanically stirred for a few minutes. Finally, 0.65 g of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ was added for reduction at 318 K for 30 min.

Catalyst 4.—First, 1.26 g of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ was dissolved in 100 mL of water, and the solution pH was adjusted to 7 by adding Na_2CO_3 . The solution pH was subsequently lowered to 3 by adding NaHSO_3 . The solution was then gently warmed until it became colorless. The solution pH was raised to 6 by adding Na_2CO_3 , and a white precipitate of $\text{Na}_6\text{Pt}(\text{SO}_3)_4$ was then obtained. The precipitate was filtered and washed vigorously with water, then dried at 353 K for 2 h. Next, 0.4 g of the $\text{Na}_6\text{Pt}(\text{SO}_3)_4$ was dissolved in 50 mL of 1 M H_2SO_4 and diluted to 150 mL with water; 80 mg of CB was suspended in water and agitated at 353 K. Platinum electroless plating solution was added to the solution dropwise with constant stirring at 353 K. Fifty millilitres of 30% H_2O_2 was then slowly added to the solution with stirring at 353 K for 1 h [11].

Catalysts 5 and 6.— Twenty milligram (catalyst 5) and 9 mg (catalyst 6) of K_2PtCl_4 were dissolved in 100 mL of milli-Q water, and 28 mg (catalyst 5) and 81 mg (catalyst 6) of CB were suspended in the solution, respectively. Each solution was purged with Ar gas using the bubbling technique before introduction of the hydrogen. Then hydrogen gas was introduced by bubbling with stirring for direct reduction at 300 K for 5 min. The solutions were held overnight. Other platinum salts such as PtCl_2 can be used with similar processing methods. The particle size (and size distribution) can be controlled by adjusting the concentrations of platinum salts in solution [18].

Characterizations of the Catalysts

CV and TEM

CV measurements were carried out at room temperature in a three-electrode electrochemical cell. The working electrode was a gold disk on which the catalysts were mixed with water and dried. Pt gauze and a Hg/HgSO_4 electrode were used as counter and reference electrodes, respectively. A Toho technical

research polarization unit PS-07 potentiostat/galvanostat was used for these measurements. 0.5 M H_2SO_4 , which was purged by N_2 , was used as the electrolyte. The electrodes were activated by cycling the electrode potential between 0.05 and 1.55 V versus SHE at 50 mV/s, and were then measured using CV. The platinum surface areas per 1 mg (Pt/C) were deduced by calculating the electrochemical surface areas [13].

TEM measurements were carried out on Philips Tecnai F20 and JEOL JEM-2010F systems. Samples were deposited on 3 mm² copper grids covered with a continuous film of carbon. X-ray powder diffraction patterns were measured on a Bruker AXS, D8 Advance.

Membrane electrode assemblies (MEAs) for a standard PEFC test cell (Eiwa) were made by hot-pressing pretreated Nafion 112 membranes along with the catalyst (catalysts 1–6 and a commercial 50 wt% Pt catalyst (Tanaka Kikinzoku, TEC10E50E) supported by CB). The catalyst layers were put on carbon papers, which were coated with polytetrafluoroethylene (PTFE) and CB. The catalysts were preliminarily mixed with 5 wt% Nafion 117 solution. The catalyst loadings were typically 1 mgPt/cm² for catalysts 1 to 4 and 0.60 and 0.12 mgPt/cm² for catalysts 5 and 6, respectively. Hydrogen gas was supplied to the anode at 1.4 L/min. Oxygen gas was fed to the cathode at 2.6 L/min. The catalysts were preheated to 353 K, and the cell temperature was maintained at 353 K.

Electroless Plating Catalysts (Catalysts 1 to 4)

The CV curves from four different catalysts (1 to 4) in Fig. 14.1 are approximately similar to that of the polycrystalline Pt surface. However, each voltammogram has its own characteristic features. For the CVs of catalyst 1 and catalyst 2, peaks from hydrogen oxidation/reduction at 50–200 mV were unresolved, whereas for catalysts 3 and 4, the peaks are well developed. The well-resolved peaks from catalyst 3 and catalyst 4 are typical of those from a polycrystalline platinum electrode, with peaks at 0.125 and 0.27 V. Therefore, it was predicted from these CVs that the platinum particles of catalyst 3 and catalyst 4 exhibit a well-defined low index surface plane.

Comparisons of active platinum surface areas per 1 mg Pt/C for catalysts 1 to 4 indicate that the values, 50 and 55 cm²/mg for catalyst 1 and catalyst 2, respectively, are remarkably smaller than the others. That for catalyst 3 is approximately twice (110 cm²/mg) as large as those for catalyst 1 and catalyst 2. Catalyst 4 showed the largest value at 320 cm²/mg.

TEM images of the four catalysts are shown in Fig. 14.2. The images were used to measure the platinum particle size on the CBs of each catalyst. The size of catalyst 1 was relatively large, at approximately 10–30 nm in diameter. For catalyst 2, 2 nm or smaller platinum particles aggregated to form 20–40 nm lump clusters. The size of catalyst 3 particles was widely distributed around 2–10 nm. For catalyst 4, platinum did not produce a particular particle but yielded unique network structures on the CBs. When the images of catalyst

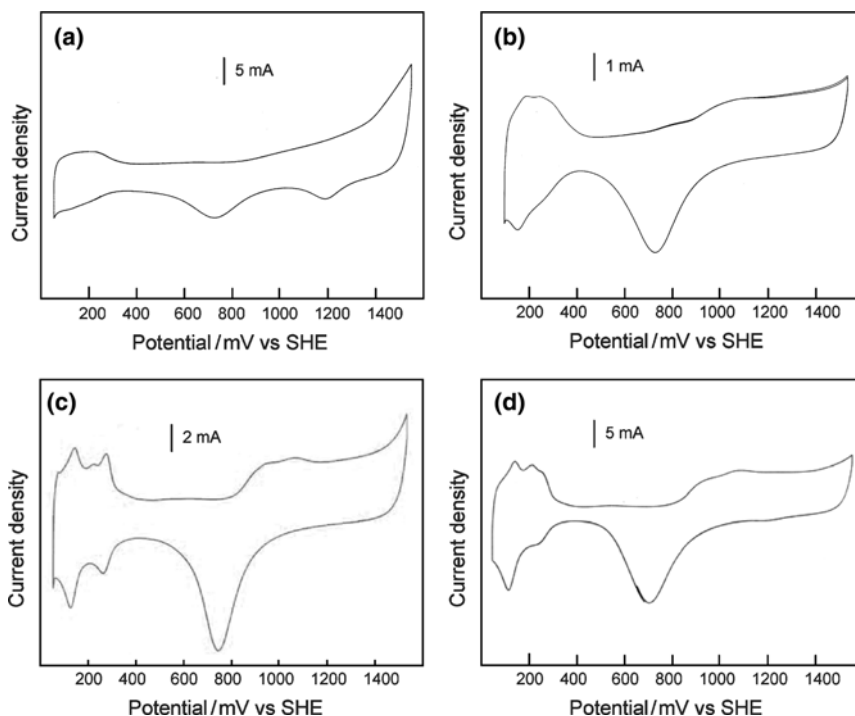


Fig. 14.1. Cyclic voltammograms of (a) catalyst 1, (b) catalyst 2, (c) catalyst 3 and (d) catalyst 4. Electrolyte: 0.5 M H_2SO_4 , scan rate: 50 mV/s ([19], copyright Wiley Inter-Science)

3 and catalyst 4 were enlarged in scale, lattice stripes of platinum could be clearly observed. The lattice stripe distances were distributed in the range of 0.22–0.24 nm, which is in good accordance with that of the Pt(111) lattice plane distance. In contrast, the selected area electron diffraction (SAED) patterns of the particles in catalyst 1 and catalyst 2 gave only scattered diffuse spots, because the particles were too thick for the electron beam to penetrate. There was no electron diffraction pattern of Pd observed.

Direct Hydrogen Reduction Catalysts (Catalysts 5 to 6)

The CV curves from catalyst 5 and 6 shown in Fig. 14.3 are also typical of CV from a polycrystalline platinum electrode, with peaks at 0.125 and 0.27 V. The electrochemical platinum surface areas of these catalysts are 280 and 120 cm^2/mg for catalyst 5 and catalyst 6, respectively, and are larger than those for catalysts 1 and 2. However, these values cannot be directly compared, because the catalyst loadings were not the same; the catalyst loading for catalysts 1 to 4 is 1.0 mgPt/cm^2 , while those for catalysts 5 and 6 are 0.6 and 0.12 mgPt/cm^2 , respectively.

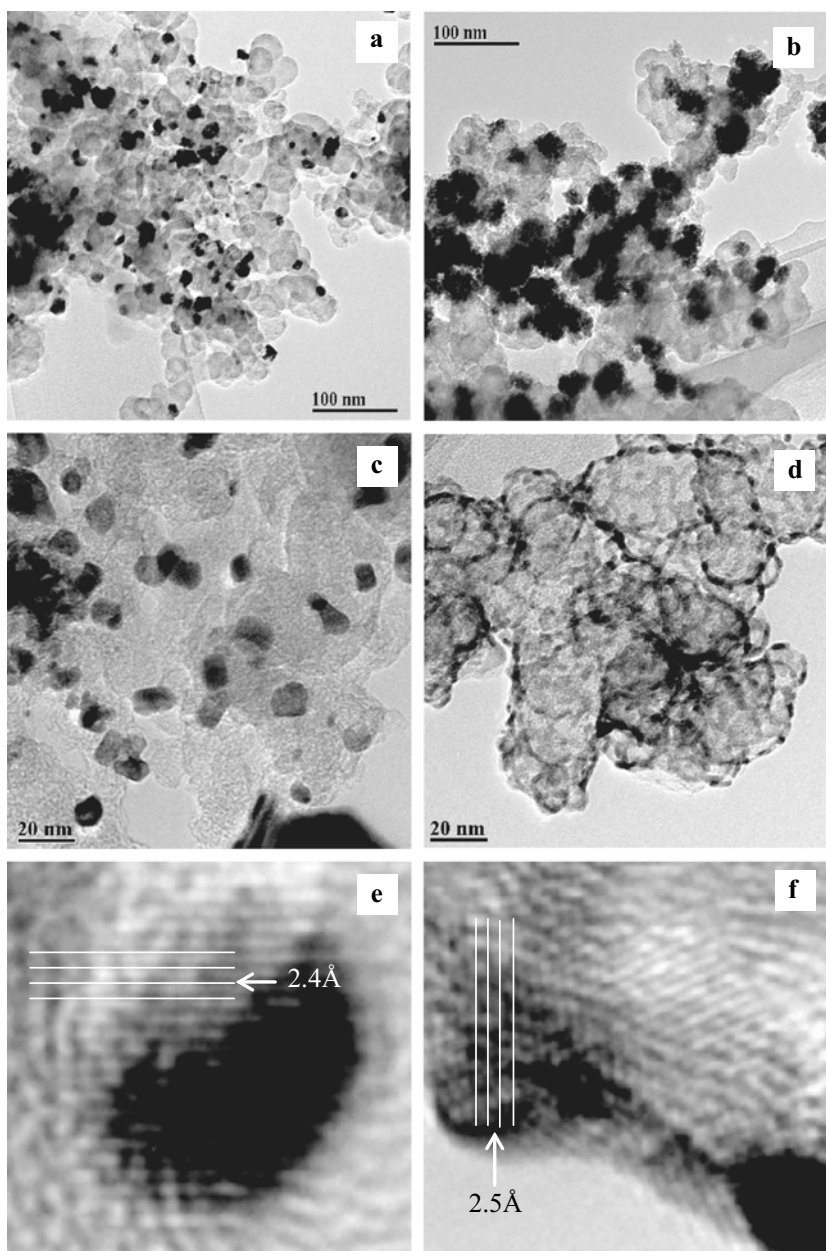


Fig. 14.2. TEM images of (a) catalyst 1, (b) catalyst 2, (c) catalyst 3, (d) catalyst 4, (e) high zoomed catalyst 3, and (f) high zoomed catalyst 4 ([19], copyright Wiley Inter-Science)

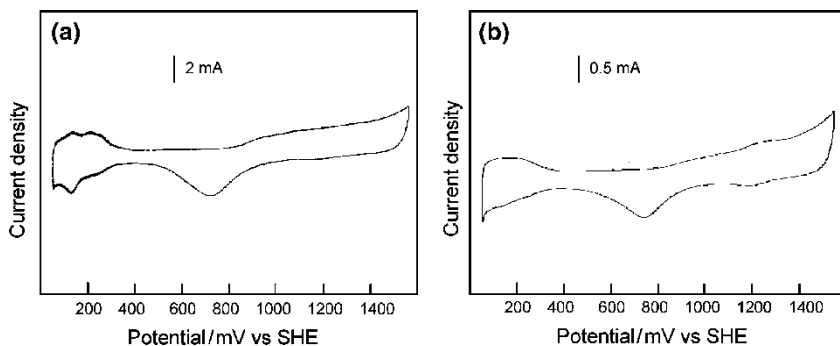


Fig. 14.3. Cyclic voltammograms of (a) catalyst 5 and (b) catalyst 6. Electrolyte: 0.5 M H_2SO_4 , scan rate: 50 mV/s ([19], copyright Wiley Inter-Science)

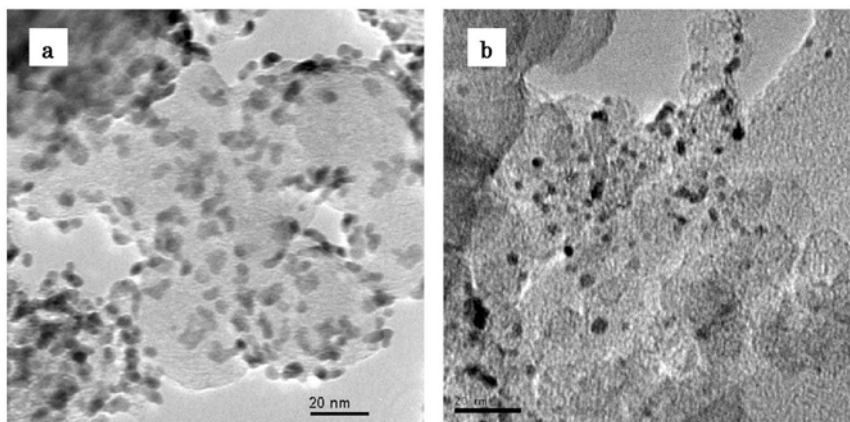


Fig. 14.4. TEM images of (a) catalyst 5 and (b) catalyst 6 ([19], copyright Wiley Inter-Science)

TEM images for catalysts 5 and 6 are shown in Fig. 14.4. The particle size of catalyst 5 was relatively small, approximately in the range of 2–5 nm, whereas that of catalyst 6 was in the range of 1–4 nm, which is much smaller than the other catalysts. If we consider the above catalyst Pt loadings (Pt amount against CB) for catalysts 1 to 4 and catalysts 5 and 6, we could explain that the large active surface area (from CV) of catalysts 5 and 6 is caused by the small particle size distribution compared with that of catalysts 1 to 3. Likewise, comparison of the surface area of catalyst 5 with catalyst 6 shows that the former has a larger surface area than the latter, despite the larger particle size. The large surface area (catalyst 5) is explained by the large Pt loading amount against CB. It is, however, quite difficult to compare absolute values of surface area of catalysts from CV and TEM measurements.

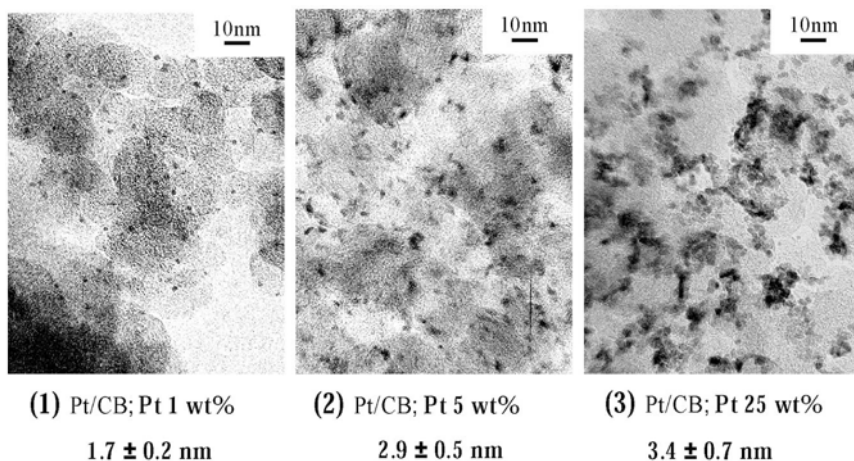


Fig. 14.5. TEM images of (1) Pt/CB; Pt 1 wt%, (2) Pt/CB; Pt 5 wt%, (3) Pt/CB; Pt 25 wt%. Mean particle size of (1), (2), and (3) is 1.7(2), 2.9(5), and 3.4(7) nm, respectively

The CB in catalysts 5 and 6 was used without any purification treatment. When H_2SO_4 or HNO_3 acid solution were used for purification of the CB supports prior to hydrogen reduction, large Pt particles were loaded on to the CB supports. Acid treatment of CB causes significant etching of CB at oxidized carbon sites so that rapid growth of Pt particles proceeded. On the other hand, mild activation of CB, that is, thermal treatment in an Ar atmosphere at 573 K for 5 h, yielded highly dispersed fine Pt particles. Figure 14.5 shows TEM images of the direct hydrogen reduction catalyst samples, which were processed with such thermal pretreatment. The Pt loading amount for the direct hydrogen reduction catalysts, (1), (2), and (3), which were pretreated by Ar cleaning, are 1, 5, and 25 Pt wt%, respectively. The TEM results indicate that the Pt particles have uniform particle size distribution, and that lower loading of Pt (1 wt%) gives rise to smaller Pt particle size (1.7 nm). The mean particles size for samples (1), (2), and (3) are 1.7(0.2), 2.9(0.5), and 3.4(0.7) nm, respectively. The thermal pretreatment of CB at 573 K in an Ar atmosphere eliminates contaminated hydrocarbons from the CB surface, resulting in wide exposure of clean homogeneous active sites without contaminated hydrocarbons. Pt particles have isolated distribution as individual particles for sample (1) at 1 wt%, whereas each Pt particle is aggregated into larger particles for the higher loaded samples (2) and (3). Figure 14.6 shows the results of powder x-ray diffraction for the three direct hydrogen reduction samples. The 2θ maxima of the (111) reflection peak are 40.18, 39.95, and 39.92, for 1, 5, and 25 wt%, respectively. From the 2θ values, the nearest neighbor distances of the fcc Pt lattice were calculated to be 0.2749, 0.2764, and 0.2766 nm, respectively. Since that of the bulk Pt crystal is 0.2774 nm,

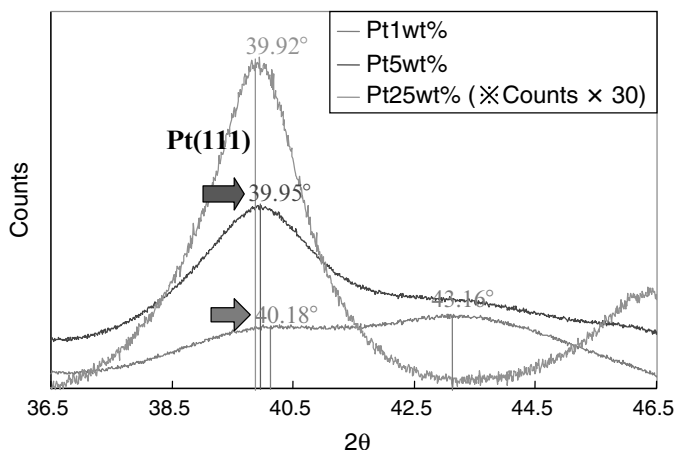


Fig. 14.6. 2θ values of Pt(111) peak maximum of (1) Pt/CB, 1 wt%, (2) Pt/CB, 5 wt% and (3) Pt/CB, 25 wt%. The value at 43.16° is the peak from CB support

the Pt–Pt distance of the ultra-fine particles is substantially smaller in these finely divided structures. The smaller particle size exhibits a smaller Pt–Pt distance. This is not an unlikely result, because the top-layer Pt–Pt distance of bulk Pt crystal is normally shortened and surface reconstruction takes place due to the existence of excess surface electrons. The electron rich structure of a highly dispersed smaller particle size Pt catalyst could exhibit high cell performance, due to its enhanced reduction ability.

Cell Performance

Electroless Plating Catalysts

Figure 14.7 shows the results of cell performance for catalysts 1 to 6 and a commercial 50 wt% Pt catalyst supported by CB (Tanaka Kikinzoku, TEC10E50E). Both catalyst 1 and catalyst 2 show power densities of 0.03 W/cm^2 , which is insufficiently low, and the voltages fall suddenly with the increase in current. In contrast, catalyst 3 and catalyst 4 display excellent power densities of 1.16 and 0.94 W/cm^2 , respectively, with only a gradual decrease in voltage with increase in the current. It is concluded that the use of much larger Pt particles (30–40 nm), as in catalyst 1 and catalyst 2, is unfavorable for obtaining high efficiency output performance.

Direct Hydrogen Reduction Catalysts

On the other hand, the power density of catalyst 5 is excellent at 1.24 W/cm^2 , with only a gradual fall in voltage with current increase, whereas that of catalyst 6, at 0.75 W/cm^2 , is relatively low, and the voltage falls with increase

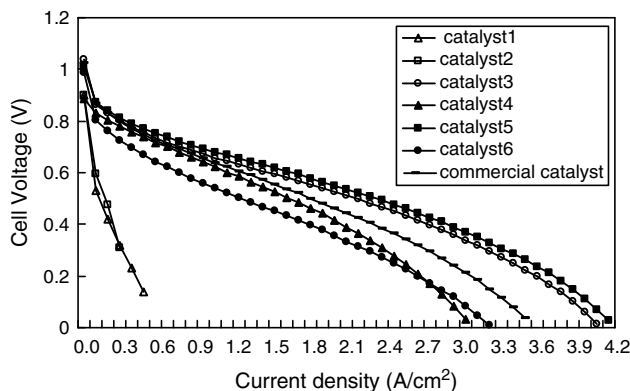


Fig. 14.7. Cell performances of CB-supported catalysts 1 to 4, hydrogen direct reduction catalysts 5 to 6 and commercial catalyst ([19], copyright Wiley Inter-Science)

in the current. The power density of catalysts 3, 4, and 5 is much higher than that of the CB-supported commercial catalyst at 0.90 W/cm^2 . However, the Pt loading amount on CB for catalyst 6 is no more than 0.12 mg/cm^2 . If the power density of catalysts 1 to 6 is plotted per unit platinum weight, the power density of catalyst 6 becomes abnormally large. The catalysts prepared by the hydrogen reduction method showed excellent power output when prepared using ultra-pure water (milli-Q water) with Ar purge before hydrogen gas introduction. The use of normal grade water with no Ar purge reduced the power output by approximately one half. Thus, Pt catalysts obtained by different solution pretreatments display remarkable differences in output power.

Both preparation methods of electroplating and direct hydrogen reduction can be carried out in a single batch. It is possible for catalysts to be mixed with electrolyte solution in the same vessel, which simplifies the preparation procedures.

14.2.2 In Situ IRAS Studies of Methanol Oxidation on Fuel Cell Catalysts

One of the serious issues of direct methanol fuel cells (DMFC) is its small power output, which is approximately one tenth that of a hydrogen fuel cell. One significant reason for the lower power output is CO poisoning [33–35]. In order to improve the output efficiency of DMFCs, it is crucial to elucidate mechanisms for methanol oxidation on real fuel cell catalysts, such as fine Pt particles supported on carbon black or carbon nanotubes. It is uncertain whether the mechanisms of methanol oxidation on Pt fuel cell catalysts are similar to those on well-defined Pt(111). It is well known that the Ru/Pt (1:1) catalyst shows much better power output or efficiency than a Pt catalyst [36].

OH radicals are selectively adsorbed on Ru sites and CO, present by poisoning of the catalyst, reacts with the OH to form CO₂, which can then desorb from the catalyst surface. Ru/Pt catalysts are now widely used as anode catalysts in DMFC. However, the surface distribution of Ru atoms is still unclear, and the detailed reaction mechanisms are not straightforward.

The catalyst samples supported by CB (Vulcan XC-72R) were coated on Au polycrystalline electrodes (10 mm ϕ). The catalyst samples used were commercial catalysts (Tanaka Kikinzoku Co.) with Pt 45 wt% and PtRu 38 wt% loadings. The electrolyte solutions used were 0.5 M H₂SO₄ or 0.1 M HClO₄ + 0.1 M methanol. Since methanol on Pt particles can readily decompose CO at any electrode potential, a background interferogram file was measured for the H₂SO₄ or HClO₄ solution without methanol. In order to introduce methanol continuously onto the Pt catalyst surfaces, a 0.8 mm ϕ hole was drilled through the bottom face of the BaF₂ optical prism. Electrolyte solution was sucked from this hole through a tube and pumped out, so that the electrolyte solution flowed continuously to the catalyst particles on the Au disk electrode. Figure 14.8 shows CV curves for the Pt catalyst supported on CB/Au disk electrode in (a) 0.5 M H₂SO₄ and (b) 0.5 M H₂SO₄ + 0.1 MCH₃OH solutions. In Fig. 14.8a, the CV curves (a₁) and (a₂) depict the result from the polycrystalline Au electrode and Pt catalyst coated Au electrode, respectively. Since no significant current was seen in the (a₁) curve, the Au electrode surface is found to be electrochemically inactive. A typical result after several potential cycles is given in Fig. 14.8b. It is clear that hydrogen redox peaks are evident in Fig. 14.8b. This indicates that CO poisoning has only partially proceeded on the catalyst surface, and new active sites are created after the main oxidation reaction at 600–800 mV.

Figure 14.9 shows in situ IRAS results of the Pt/Ru(1:1) catalyst in 0.1 M HClO₄ + 0.1 MCH₃OH as a function of electrode potential. A background (reference) spectrum was obtained using 0.1 M HClO₄ without CH₃OH at 0 V. The splitting absorption band appears at around 2021 cm⁻¹ at 0 mV. The higher frequency bands observed at 2021, 2023, 2025, and 2026 cm⁻¹ in the 0 to +200 mV range are assigned to CO adsorbed on top of a Pt atom site. The shoulder bands that appear at the lower frequency side, around 2010 cm⁻¹, are attributed to CO adsorbed on a Ru atom site. These bands appear even at negative potentials, down to less than -400 mV, although the intensity of those bands is extremely small. The low intensity indicates that the CO coverage on Pt/Ru is very small and that most of the remaining Pt/Ru sites are covered by atomic hydrogen and cationic water molecules (H₃O⁺(H₂O)_n). On the other hand, it cannot be neglected that CO is produced by the reduction of CO₂, which cannot be eliminated from the milli-Q solution. CO on Ru has the highest band intensity at 50 mV, when the CO₂ band at 2342 cm⁻¹ starts to appear. When the Pt catalyst without Ru is used, the band (2278 cm⁻¹) starts to appear at 100 mV, as shown in Fig. 14.10. The ¹³CO₂ band in Fig. 14.10 appears at 2278 cm⁻¹, because ¹³CH₃OH was used. Figure 14.11 compares the intensities of PtCO, RuCO, and CO₂ (evolution

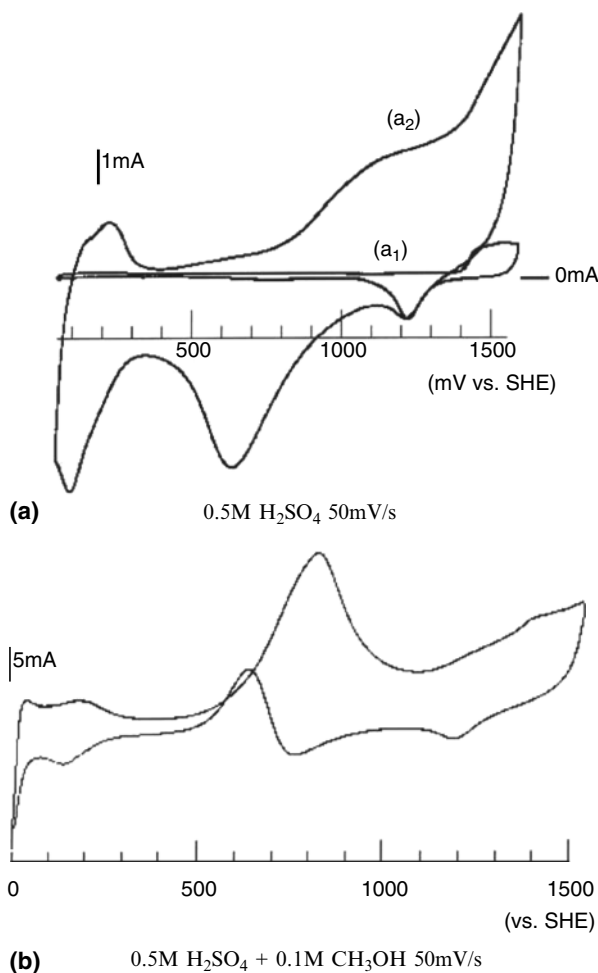


Fig. 14.8. Cyclic voltammograms of Pt commercial catalyst in (a) 0.5 M H_2SO_4 and (b) 0.5 M H_2SO_4 + 0.1 M CH_3OH solutions. Scan speed was 50 mV/s

product) at various potentials. It is clear that CO/Pt and OH/Ru start to react at 50 or 100 mV, resulting in the evolution of CO_2 . When the Pt catalyst without Ru is used, the reaction shifts by 50 mV to more positive (anodic side) potential. This indicates that the Pt/Ru catalyst plays an important role in improving power output.

It is unknown, whether CO is the sole reaction intermediate species from methanol [37–39]. A band indicating the presence of formate on the Pt catalyst sample could be successfully obtained at a potential of 100 mV, as shown in Fig. 14.12. The bands at 1504 and 1339 cm^{-1} are assignable to OCO_{asym} and OCO_{sym} stretching absorptions, respectively. Taking into consideration the fact that the ordinal methanol decomposition reaction at a fuel cell anode

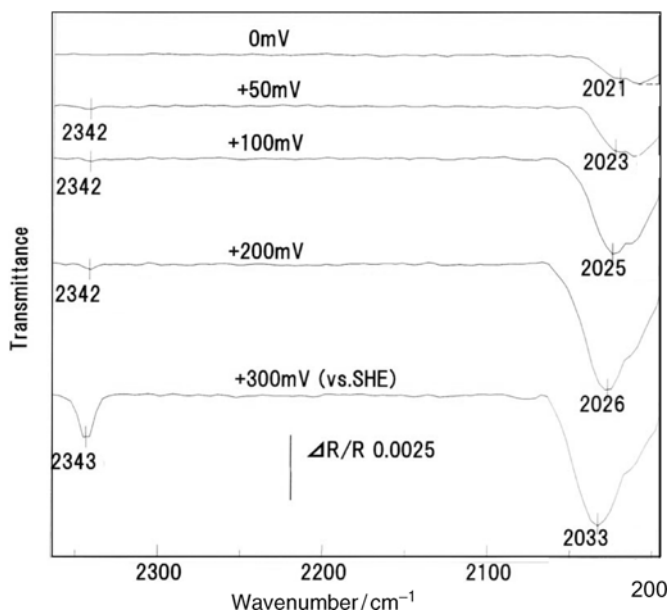


Fig. 14.9. In situ IRAS of Pt/Ru commercial catalyst in CO purged H_2SO_4 solution as a function of electrode potential

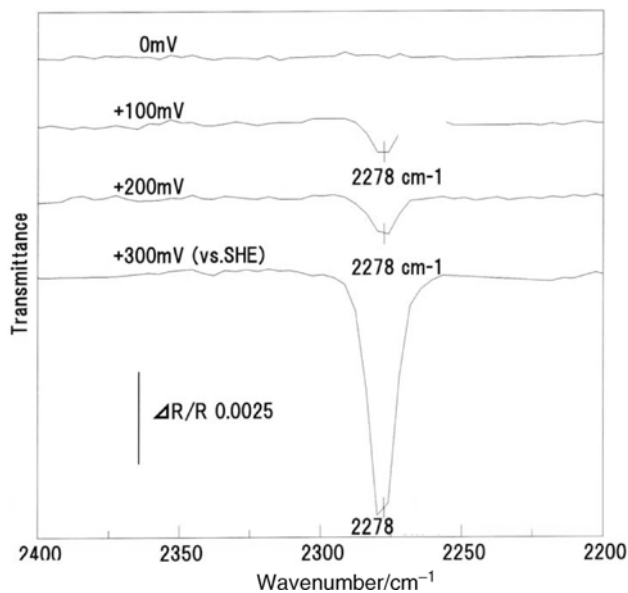


Fig. 14.10. In situ IRAS of Pt commercial catalyst in 0.1 M HClO_4 + 0.1 M CH_3OH as a function of electrode potential. Background spectrum from 0.1 M HClO_4 at 0 mV

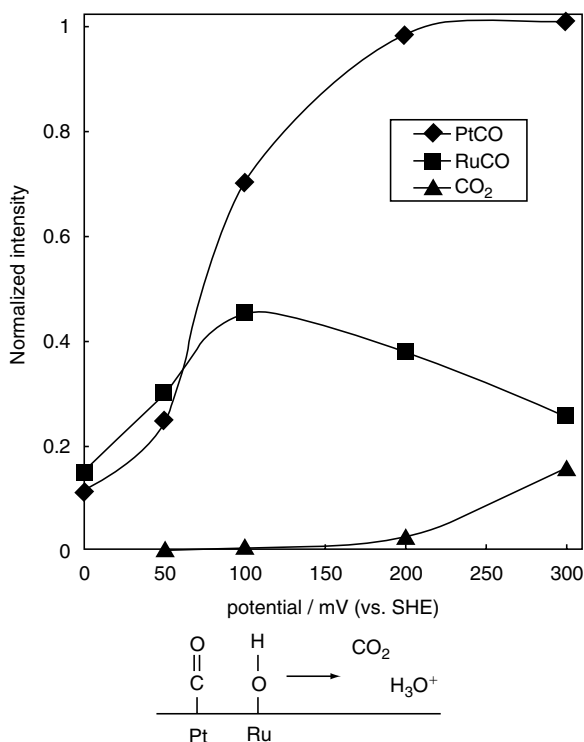


Fig. 14.11. Comparisons of intensities of PtCO, RuCO, and CO₂ as a function of electrode potential

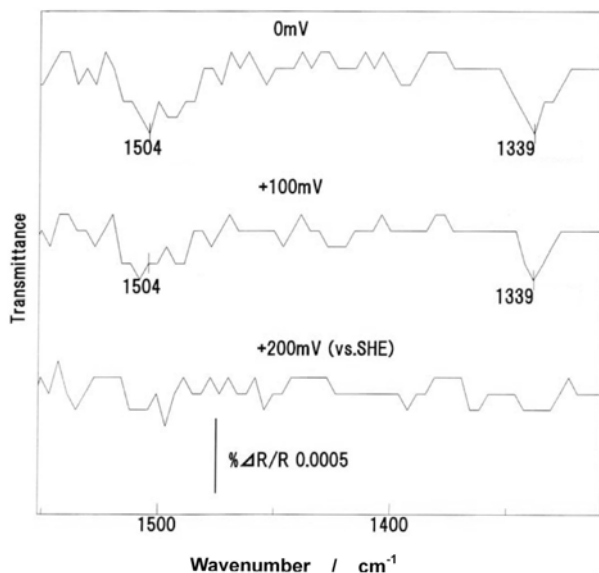


Fig. 14.12. In situ IRAS of commercial Pt catalyst in 0.1 M HClO₄ + 0.1 M CH₃OH as a function of electrode potential, Background is from 0.1 M HClO₄ at 0 mV

catalyst occurs at a potential in the 0 to +100 mV range, a parallel reaction path mechanism, by way of both CO and formate, could be possible a reaction mechanism pathway for methanol oxidation on catalyst surfaces.

14.3 Spectroscopic Studies of Methanol Oxidation on Pt Surfaces

14.3.1 Electrooxidation of Methanol on Pt(111) in Acid Solutions: Effects of Electrolyte Anions during Electrocatalytic Reactions

Experimental Procedures

The electrooxidation of methanol on a Pt(111) surface in both sulfuric acid and perchloric acid solutions was investigated by combined apparatus under both UHV and electrochemical environments. In sulfuric acid solution, a strong lateral interaction was observed between adsorbed bisulfate and CO derived from methanol. Coadsorption of CO derived from methanol with bisulfate ion yielded a $(\sqrt{7} \times \sqrt{7}) - R19.1^\circ\text{-CO-bisulfate}$ structure. In perchloric acid solution, however, no lateral interaction between adsorbed CO and perchlorate was observed. The difference in the reaction rates of methanol oxidation in both solutions was explained by these specific anion adsorption effects.

Experiments were conducted with combined electrochemical and UHV apparatus, and the procedures used were the same as those previously reported [31, 32]. After preparation of a clean Pt(111) surface under UHV, the sample was immersed into an aqueous solution containing either (1) 0.1 M HClO_4 saturated with CO, (2) 0.5 M H_2SO_4 saturated with CO, (3) 0.5 M H_2SO_4 with 0.1 M of methanol, or (4) 0.1 M HClO_4 with 0.1 M of methanol. Following polarization at a certain potential, the sample was emersed to UHV for LEED and IRAS measurements. The IRAS measurements were carried out in the auxiliary chamber using a Perkin-Elmer 1720X Fourier transform infrared spectrometer with a liquid nitrogen-cooled MCT detector. The IRAS spectra were usually obtained with a resolution of 8 cm^{-1} . All measurements were carried out at room temperature. Solutions were prepared using Milli-Q water (18.3 M Ω , Millipore), high-purity perchloric and sulfuric acid solutions (Ultrapur, Cica-Merk), high-purity CO gas (Takachiho Chemical Ind.) and anhydrous methanol (Wako Ind.). The reference electrode used was the standard hydrogen electrode (SHE).

CO Adsorption and Oxidation on Pt(111)

Prior to methanol electrooxidation, the adsorption of CO on Pt(111) was investigated, because CO is known to be an important intermediate in the methanol electrooxidation reaction. Figure 14.13A shows the current-potential curve for Pt(111) in a CO saturated 0.5 M H_2SO_4 solution, in

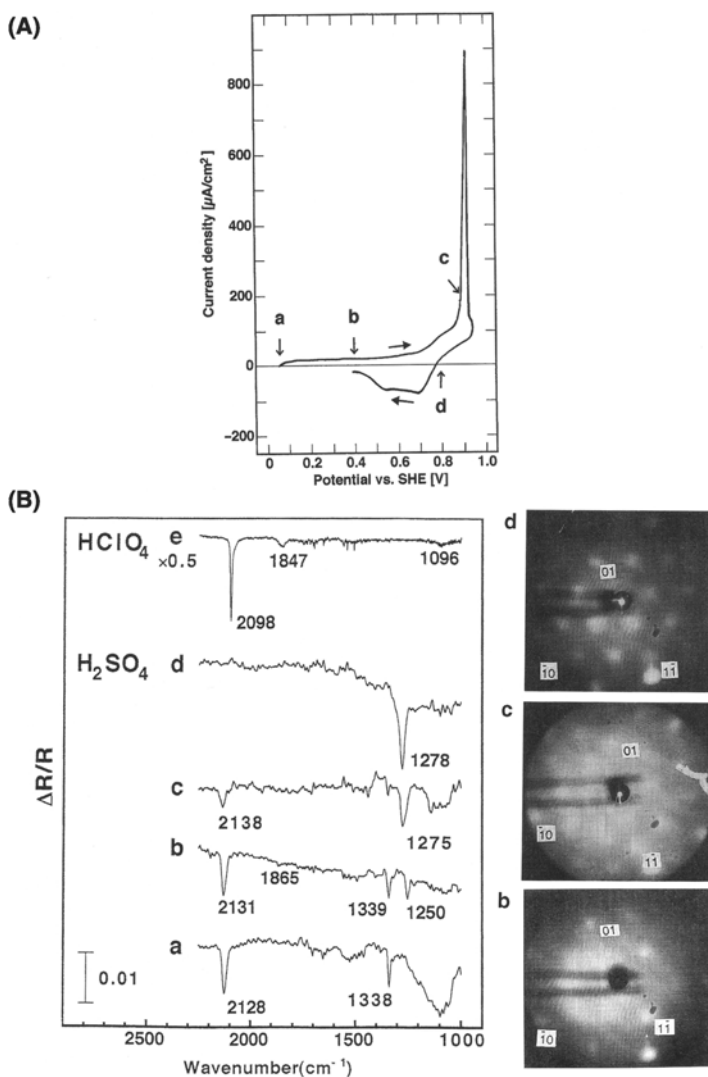


Fig. 14.13. (A) Current–potential curve: Pt(111) in CO saturated 0.5 M H_2SO_4 at 50 mV/s. LEED and IRAS measured at points a–d (0.05, 0.4, 0.9, and 0.8 V versus SHE, respectively) are shown in (B). (B) IRAS and LEED patterns: (a–d) Pt(111) emerged from CO saturated 0.5 M H_2SO_4 at 0.05, 0.4, 0.9, and 0.8 V versus SHE, respectively; (e) Pt(111) emerged from CO saturated 0.1 M HClO_4 at 0.02 V versus SHE. Primary electron beam energy was (b) 100 eV, (c) 97 eV, and (d) 104 eV ([48], copyright Elsevier Science)

which the points a, b, c, and d correspond to the emersed potentials referred from the IRAS and LEED results given in Fig. 14.13B. The potential sweep rate was 0.05 V/s. Hydrogen adsorption and desorption currents completely disappeared in the curve, indicating that adsorbed CO saturated the surface. In the anodic sweep, an oxidation current for the adsorbed CO started to appear at 0.7 V and developed with a sharp peak at 0.91 V. The oxidation of CO supplied from solution continued until ca. 0.8 V under the cathodic sweep. In order to characterize the surface structure during CO oxidation, the UHV emersion technique combined with IRAS and LEED observations was performed. Figure 14.13B shows the IRAS and LEED results for Pt(111) emersed from a CO saturated 0.5 M sulfuric acid solution at 0.05, 0.4, and 0.9 V (anodic sweep) and 0.8 V (cathodic sweep), respectively. At 0.05 V (Fig. 14.13B, spectrum a) and 0.4 V (Fig. 14.13B, spectrum b), strong absorptions for adsorbed CO were observed in the IRAS spectra. The bands at ca. 2130 and 1865 cm^{-1} are assignable to linear and bridged CO absorptions, respectively. The absorption bands obtained by the present *ex situ* IRAS study are higher than the widely known values reported by *in situ* observation in solution or under UHV [40–42]. The higher absorption shifts of CO (2130 cm^{-1}) than the previous results are ascribed to less back donation to CO, as a result of coadsorbed bisulfate, similar to CO on oxygen coadsorbed metal surfaces. The bands at 1339 and 1250 cm^{-1} are assigned to the absorption of adsorbed bisulfate [43]. While the lower frequency band at 1240–1280 cm^{-1} has been well established for Pt(111)-($\sqrt{3} \times \sqrt{3}$) - R30°-bisulfate [31], the higher absorption band at 1339 cm^{-1} for adsorbed bisulfate has not been reported before [31, 43–46]. The interaction between bisulfate and CO causes the reorientation of adsorbed bisulfate, yielding a higher absorption band at 1339 cm^{-1} . The band at 1339 cm^{-1} corresponds to the highest frequency vibration of the bisulfate νSO stretching. The mode with C_{2v} symmetry produced a strong dipole moment change. The IRAS spectra of $\text{SO}_3 + \text{H}_2\text{O}$ adsorption on a Pt(111) surface under UHV also showed both 1339 and 1250 cm^{-1} bands. At these potentials, the LEED pattern shows a disordered ($\sqrt{3} \times \sqrt{3}$) pattern (Fig. 14.13B, spectrum b). At 0.9 V in the anodic sweep, the band at 1275 cm^{-1} for ($\sqrt{3} \times \sqrt{3}$) - R30°-bisulfate was developed at the expense of the bands for CO at 2131 cm^{-1} and bisulfate at 1339 cm^{-1} . The occurrence of a rapid oxidation reaction at this potential was supported by the fact that a remarkable steep oxidation current of CO to CO_2 was observed. Therefore, residual CO species, indicated by the absorption at 2138 cm^{-1} , were still present at emersion. At this potential, a disordered ($\sqrt{3} \times \sqrt{3}$) - R30° LEED pattern was also obtained (Fig. 14.13B, spectrum c).

At 0.8 V in the cathodic sweep, where the oxidation of CO is completely terminated (Fig. 14.13B, spectrum d), no adsorbed CO remained after emersion, but the adsorbed bisulfate is dominant, as seen in the IRAS spectra. Simultaneously, the LEED pattern shows a clear ($\sqrt{3} \times \sqrt{3}$) - R30° pattern. The single absorption of bisulfate ion at 1278 cm^{-1} , together with the clear LEED pattern of ($\sqrt{3} \times \sqrt{3}$) - R30°, is in good accordance with previous

results obtained in a CO-free solution [30]. The lack of CO oxidation in the cathodic sweep is ascribed to the formation of an ordered $(\sqrt{3} \times \sqrt{3}) - \text{R}30^\circ$ -bisulfate layer and the blocking of CO adsorption sites. Pt(111) emerged from a CO saturated 0.1 M perchloric acid solution (sulfuric acid-free electrolyte solution) was also examined. When the surface was emerged, a sharp band for linear CO at 2098 cm^{-1} and a broad band for bridged CO at 1847 cm^{-1} were observed over a wide potential range. A typical result for the emerged surface at 0.05 V is shown in Fig. 14.13B, spectrum e. The peak at 2098 cm^{-1} was fairly sharp with a FWHM of less than 8 cm^{-1} . Notably, these band positions for CO coincided with those observed under UHV [42]. The results indicated no interaction between adsorbed CO and perchlorate. The electrooxidation of CO on Pt(111) in sulfuric acid solution is summarized as follows. The coadsorption of CO and bisulfate shows a strong lateral interaction. The change in the LEED pattern, followed by the removal of adsorbed CO due to oxidation, supports the structural change of the adsorbed bisulfate. The resulting bisulfate layer showed a stable and ordered $(\sqrt{3} \times \sqrt{3}) - \text{R}30^\circ$ -bisulfate structure. The stable anion layer prohibits CO re-adsorption for electrooxidation.

Methanol Oxidation on Pt(111)

To date, strong anion adsorption effects in relation to methanol oxidation on a Pt(111) electrode have been insisted by several researchers [20–23], and the effect of the electrolyte anion on the reaction rate has been widely discussed. In the present study, we focused on the surface structure of adsorbed species during the course of methanol oxidation. The current–potential curve for Pt(111) in a 0.5 M sulfuric acid solution containing 0.1 M methanol is shown in Fig. 14.14A. An oxidation current was observed for methanol above 0.5 V. The current–potential curve for Pt(111) in a 0.1 M perchloric acid solution containing 0.1 M methanol is also shown in Fig. 14.14B. The current density for methanol oxidation in perchloric acid solution was approximately twice as large as that in sulfuric acid solution, as seen in Fig. 14.14A and B. These results are in good accordance with previous reports [20–23]. For a sulfuric acid solution containing 0.1 M methanol and confined to a potential below 0.5 V, the features of the current–potential curve were extremely similar to those for a methanol-free sulfuric acid solution [25]. Clear peaks for hydrogen and anion adsorption or desorption were steadily observed together with so-called anomalous sharp spikes at 0.45 V. This indicates that bisulfate ions are adsorbed on Pt(111) prior to methanol oxidation. The suppression of the oxidation current in sulfuric acid solution is ascribed to strong interactions between Pt atoms and bisulfate ions, as discussed in the previous section. In order to obtain structural information during the reaction, the surface during methanol electrooxidation was emerged to UHV at several potentials, then studied using IRAS and LEED. Figure 14.14C presents the ex situ IRAS and LEED results, of which the emerged potentials are indicated in the current–potential curve in Fig. 14.14A. At 0.3 V (Fig. 14.14C, spectrum a), neither

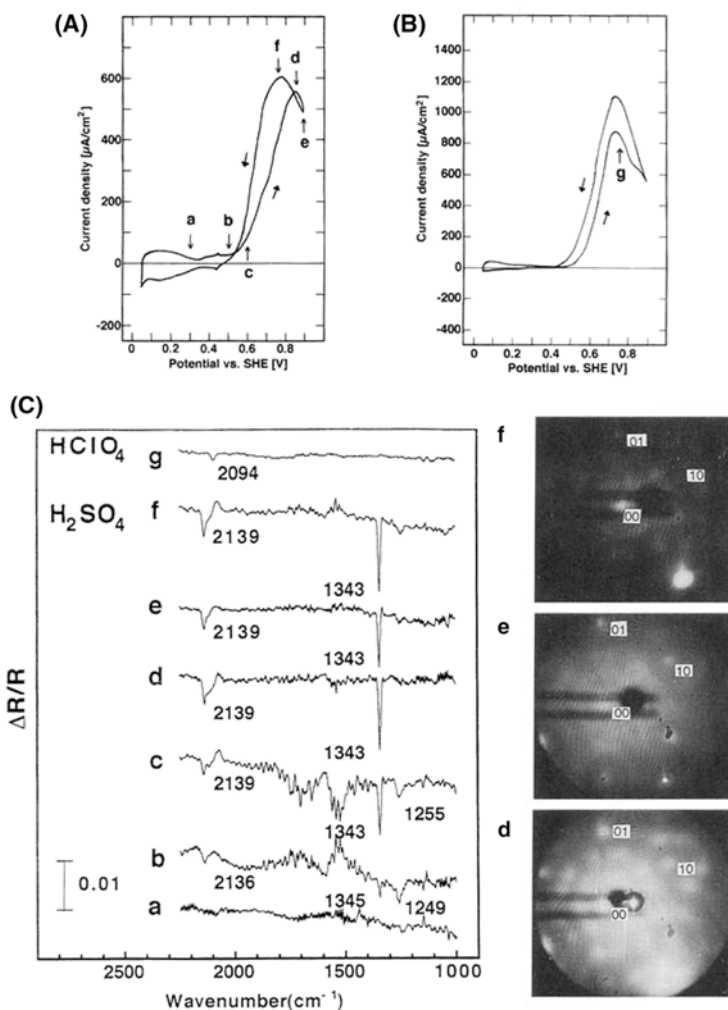


Fig. 14.14. (A) Current–potential curve: Pt(111) in 0.5 M H_2SO_4 + 0.1 M CH_3OH at 50 mV/s. LEED and IRAS measured at points a–f (0.3, 0.5, 0.6, 0.85, 0.9, and 0.73 V versus SHE, respectively) is shown in (C). (B) Current–potential curve: Pt(111) in 0.1 M HClO_4 + 0.1 M CH_3OH at 50 mV/s. IRAS measured at points g (0.76 V versus SHE) is shown in (C). (C) IRAS and LEED patterns: (a–f) Pt(111) emerged during electrooxidation in 0.5 M H_2SO_4 + 0.1 M CH_3OH at 0.3, 0.5, 0.6, 0.85, 0.9 and 0.73 V versus SHE, respectively; (g) Pt(111) emerged during electrooxidation in 0.1 M HClO_4 + 0.1 M CH_3OH at 0.76 V versus SHE. Primary electron beam energy was (d) 79 eV, (e) 77 eV, and (f) 78 eV ([48], copyright Elsevier Science)

bisulfate nor CO was adsorbed on the platinum surface. At 0.5 V (Fig. 14.14C, spectrum b), where the oxidation of methanol has just started to occur, the absorption for linear CO was observed at 2136 cm^{-1} , together with those for bisulfate at 1345 and 1249 cm^{-1} . Correspondingly, the LEED results showed a disordered $(\sqrt{7} \times \sqrt{7}) - \text{R}19.1^\circ$ pattern at these potentials. The bands for bisulfate at 1249 and 1345 cm^{-1} are again assignable to bisulfate and reoriented bisulfate, respectively, as discussed in the previous section. The anodic potential sweep produced an increase in the methanol oxidation current and the band intensity of linear CO and reoriented bisulfate (Fig. 14.14C, spectra c and d). At 0.85 V (Fig. 14.14C, spectrum d), where the reaction rate was the highest for the anodic sweep, the band for bisulfate at 1250 cm^{-1} was hardly observed, and the reoriented bisulfate band at 1343 cm^{-1} dominated with remarkably sharp bandwidth. At the same time, the LEED pattern showed a clear $(\sqrt{7} \times \sqrt{7}) - \text{R}19.1^\circ$ pattern. Therefore, the $(\sqrt{7} \times \sqrt{7}) - \text{R}19.1^\circ$ pattern results from CO and a reoriented bisulfate coadsorbed structure. Furthermore, the anodic sweep showed a slight decrease in reaction rate, and the $(\sqrt{7} \times \sqrt{7}) - \text{R}19.1^\circ$ -bisulfate-CO structure then partially disappeared (Fig. 14.14C, spectrum e); ex situ IRAS spectra exhibited a corresponding decrease in intensity for the bands at 2139 and 1343 cm^{-1} . However, a cathodic sweep from 0.9 V recovered the ordering of the $(\sqrt{7} \times \sqrt{7}) - \text{R}19.1^\circ$ -bisulfate-CO structure. At 0.73 V (Fig. 14.14C, spectrum f), where the reaction rate was the highest, the intensity of both IR absorption peaks for CO and coadsorbed reoriented bisulfate was the largest. Also, LEED results recovered a clear $(\sqrt{7} \times \sqrt{7}) - \text{R}19.1^\circ$ pattern at 0.73 V. It is important to note that the higher ordering of the $(\sqrt{7} \times \sqrt{7}) - \text{R}19.1^\circ$ -bisulfate-CO structure, and the disappearance of the band at 1250 cm^{-1} , are coincident with the larger reaction rate. In addition, a clear $(\sqrt{7} \times \sqrt{7}) - \text{R}19.1^\circ$ pattern was reproducible from the methanol-containing solution, but has never been obtained from a CO saturated (methanol-free) solution at any potential. Comparing the present IRAS results in Fig. 14.13B and Fig. 14.14C, it is noted that $\theta_{\text{bisulfate}}/\theta_{\text{CO}}$ is much greater in the methanol-containing solution than it is in the methanol-free solution. An excess of bisulfate ion over CO is required to form the $(\sqrt{7} \times \sqrt{7}) - \text{R}19.1^\circ$ -bisulfate-CO phase. It is surprising that methanol oxidation was not terminated, but steadily observed despite the presence of the adsorbed bisulfate layer. The result is in marked contrast with the fact that CO adsorption and oxidation are prohibited by the stable $(\sqrt{3} \times \sqrt{3}) - \text{R}30^\circ$ -bisulfate phase in a methanol-free solution. A possible explanation for the difference between methanol-containing and methanol-free solutions is that the $(\sqrt{7} \times \sqrt{7}) - \text{R}19.1^\circ$ -bisulfate-CO phase is stabilized by the methanol-containing solution. The CO adsorption site in the $(\sqrt{7} \times \sqrt{7})$ phase plays an important role as a reaction site (active center), although the bisulfate adsorption site in the $(\sqrt{7} \times \sqrt{7})$ phase dominates the surface. When the surface was emerged from perchloric acid solution at a potential where the oxidation reaction of methanol proceeded, a single absorption band of CO derived from methanol appeared at 2094 cm^{-1} . The result at 0.76 V is

shown in Fig. 14.14C, spectrum g. In contrast to the results for sulfuric acid solution, the band for adsorbed perchlorate was hardly observed, even at a potential where the largest reaction current was attained. The band for perchlorate at 1234 cm^{-1} did not appear until 0.9 V. LEED measurements were also performed, but showed no ordered structure over the whole potential range. Therefore, the difference in the current–potential curves of both solutions is explained by the degree of interaction between adsorbed CO and anions on Pt(111). No interaction was observed between adsorbed CO and perchlorate ion. In sulfuric acid solution, methanol strongly interacted with adsorbed bisulfate ions. The oxidation reaction rate in sulfuric acid solution was well correlated to the coverage of the $(\sqrt{7} \times \sqrt{7}) - \text{R}19.1^\circ$ –bisulfate–CO phase. In contrast, the $(\sqrt{3} \times \sqrt{3}) - \text{R}30^\circ$ –bisulfate phase behaved as a poison in that it blocks the reaction.

14.3.2 Methanol Oxidation Mechanisms on Pt(111) Surfaces

UHV Studies

Methanol surface chemistry is important to fields of application, in particular, the development of fuel cells. One of the important issues to be overcome for DMFC is poisoning by CO produced from methanol at the surface of a Pt electrocatalyst. Detailed knowledge is required for the effect of poisoning on the reactivity of the catalysts with methanol, as well as the influence of coadsorbates, for the development of practical CO-tolerant electrodes. It is therefore essential to determine in detail the reaction mechanisms for methanol oxidation on Pt catalysts from both a fundamental and an applied perspective. Studies of methanol oxidation have been extensively reported by various methods including IRAS [47–49], high-resolution electron energy loss spectroscopy (HREELS) [50], photoelectron spectroscopy [51], and temperature-programmed desorption (TPD) [52]. While the formation of formaldehyde and formate has not been detected so far on Pt surfaces, recent reports by Domen et al. and Matsumoto et al. [52–54] indicate that formaldehyde and formate are stabilized on the surface as reaction intermediates when an oxygen-precovered surface is annealed. However, reasons for the rapid decomposition of formaldehyde and the reaction mechanism are still unclear. They also showed that a methanol molecule is stable on bare Pt(111) at a temperature of 160 K, where water molecules start to desorb from the Pt(111) surface. Methanol molecules are stabilized on a smooth Pt(111) surface until 200 K, whether water molecules are coadsorbed or not. Upon further temperature increase, methanol molecules decompose to CO.

In order to simulate an electrode surface polarized at positive electrode potential, a Pt(111) surface was modified by oxygen and subjected to subsequent H_2O adsorption and annealing. Pt(111) – $2 \times 2 - \text{O}$ or $3 \times 3 - \text{OH}(\sqrt{3} \times \sqrt{3})$ structures were routinely produced. Methanol oxidation was examined on those model electrode surfaces, and the IR results are presented in Fig. 14.15.

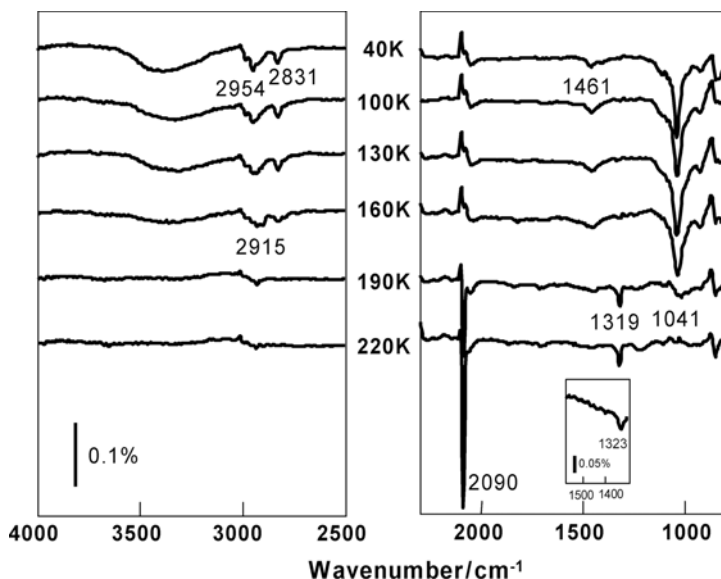


Fig. 14.15. IRAS of methanol decomposition on $\sqrt{3} \times \sqrt{3}$ (or 3×3)-OH pre-dosed Pt(111) surface as a function of temperature under UHV. Inset: In situ IRAS of methanol decomposition on Pt(111) electrode in 0.1 M HF solution at 800 mV(NHE)

On the former 2×2 -Pt(111)-O surface, absorption bands appeared at 1631 and 1273 cm^{-1} and were attributed to adsorbed formaldehyde. For $\sqrt{3} \times \sqrt{3}$ or 3×3 -Pt(111)-OH + H_2O , the band at 1319 cm^{-1} was assigned to formate (δOCO). As shown in the inset of Fig. 14.15, a band for formate was successfully observed on a Pt(111) electrode surface at a sufficiently positive potential, higher than 800 mV (NHE), in HF solution. In contrast, the band for formaldehyde was not detected, although unclear absorptions appear at $1600 - 1700\text{ cm}^{-1}$, which could be assigned to νCO , δHOH , and νHCO .

In Situ Studies

A number of reports have shown that spectroscopic evidence for reaction intermediates of methanol oxidation reactions is not sufficient to establish the reaction mechanisms [54]. As reaction intermediates, CO, formate, formaldehyde, formic acid, methoxide and formyl are representative. However, since most of the molecules, except for CO, show very small infrared intensity cross sections, the absorption intensities of the molecules are too weak to properly identify possible intermediates. Strong intensities from the bands of H_3O^+ asymmetric bending or H_2O scissoring vibrations also interfere with band assignments. In this respect, the previous reports should be taken into account in the discussion of reaction intermediates [55].

As described in the previous section, the potential at which methanol oxidation to CO or CO₂ starts to occur is dependent upon the Pt catalyst morphology or geometry. Methanol, present on a completely flat Pt(111) electrode surface with less step density, shows no reaction until 0.5 V (NHE), where OH species predominates on a positively polarized surface in HF solution. In contrast, methanol on a polycrystalline or ultra-fine particle Pt catalyst indicates that oxidation reactions generating CO molecules occur at any negative electrode potentials. Therefore, background Fourier transform interferogram data must be collected in a solution without methanol. Oxidation from methanol to any intermediate molecule, including CO, takes place at any electrode potential. Furthermore, recent surface enhanced infrared reflection absorption spectroscopy (SEIRAS) and in situ IRAS studies showed that the formate can be observed definitely on OH-covered positively polarized electrode surfaces.

It is well known that adsorption and reaction of a molecule takes place at a step site rather than a terrace site. This is explained by the fact that the work function value at a step site is lower than that of a terrace site by approximately 0.2 eV, and a step is an electron-deficient site [56]. As an example, methanol oxidation to CO and CO₂ on Pt surfaces was examined in conjunction with different electrode surfaces with terrace or step sites. There have been disputes concerning dual path mechanisms of methanol oxidation on Pt surfaces. According to the dual path mechanism, methanol is oxidized by way of CO or unknown intermediates X, where X = formate, formaldehyde, methoxy, etc.

It is worthy to note that the potential at which methanol starts to decompose to CO or CO₂ is extremely dependent upon the Pt surface morphology, as shown in Figs. 14.16 and 14.17. When the Pt(111) electrode has wide terrace surfaces with no steps or any defect site, and exhibits a perfect (111) surface, the potential at which the CO peak starts to appear is retarded until 500 mV. However, when the Pt(111) electrode has steps in addition to terraces, the potential of methanol oxidation to CO is drastically reduced to 200 mV. It is well known that step sites exhibit a more positive local potential than that of terrace sites, by 300–400 mV [56]. When polycrystalline Pt or Pt cluster particles are used for methanol oxidation, the CO peak appears at any negative potential. Thus, it could be deduced that a step site provides the surface with a lower work function value locally, and accordingly exhibits increased reactivity with a less positive potential polarization than that for a terrace site.

Reaction Mechanisms

From the discussions of the above UHV and in situ studies, the methanol oxidation mechanism on Pt fuel cell catalysts is described as follows. It is not quite certain whether Pt fuel cell anode catalysts under active conditions show a similar oxidation mechanism or not, because there are so many differences in both systems; fuel cells are driven in atmospheric or higher pressure

500mM methanol oxidation in 0.1M HF

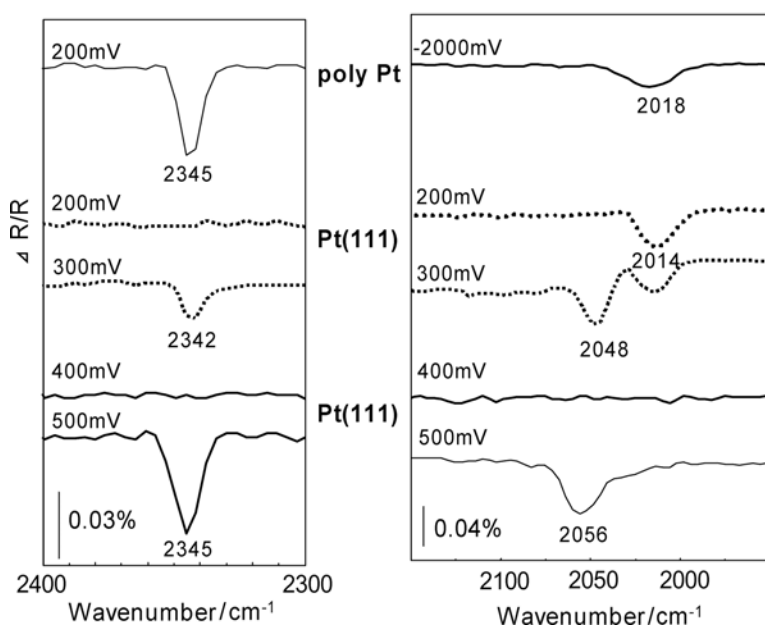


Fig. 14.16. IRAS of (a) polycrystalline Pt(111), (b) Pt(111) with step and Pt(111) without step in 0.1 M HF + 0.5 M CH₃OH

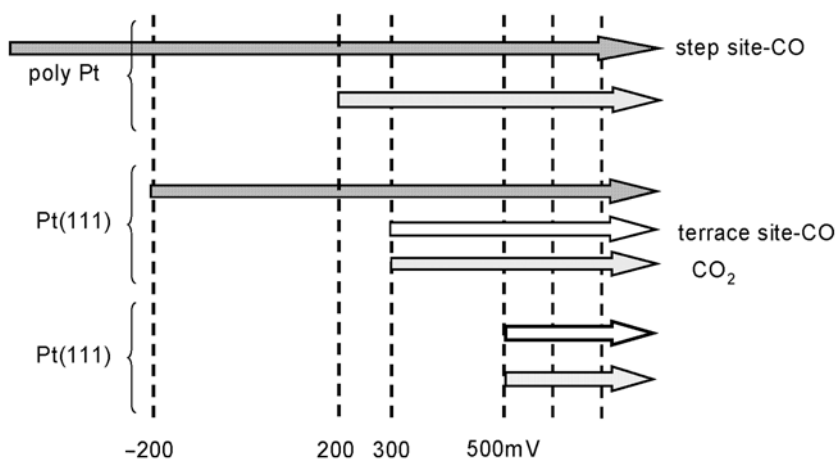


Fig. 14.17. Comparison of electrode potential at (a) polycrystalline Pt, (b) Pt(111) with step and (c) Pt(111) without step where CO or CO₂ absorption bands start to appear in 0.1 M HF + 0.5 M CH₃OH

conditions, electrolyte polymer molecules or ions are in contact with the Pt catalysts, and the concentrations of H_2O and pH are not specified in the case of fuel cells, etc. In spite of such different conditions, it is thought that methanol oxidation takes place by almost similar mechanisms, regardless of Pt morphological differences.

In the negative electrode potential range where hydrogen evolution normally occurs, atomic hydrogen and cationic water molecules are strongly adsorbed and cover the catalyst surface. Therefore, methanol molecules cannot reach the catalyst surface. However, a small amount of CO, which is a decomposition product of methanol, continuously appears at any negative potential in the IRAS spectra. This indicates that at the boundaries of over-layer anionic water domains, methanol molecules can reach defect or edge sites of the catalyst, resulting in decomposition to CO. At the hydrogen stripping potential of 50–100 mV, where cationic water molecules as well as atomic hydrogen start to desorb from the surface, OH radicals from the solution are created on the surface. CO adsorbed on the catalyst with an OH radical is combined into a CO_2 molecule on the surface, as indicated by the appearance of CO_2 in the IRAS spectra. Ordinal DMFC catalysts show an anodic potential of 50–100 mV when steady state operation is attained. In a DMFC, there are two routes for methanol to decompose into CO_2 . One is by way of CO, and the other is by direct reaction of methanol with OH_{ad} , producing formate molecules. Introduction of concentrated and diluted methanol would accelerate the CO path and the formate path, respectively. When Pt/Ru is used as an anodic catalyst, the potential at which the CO_2 band starts to appear shifts to the negative side by 50–100 mV. This explains why the output power increases with the use of Pt/Ru catalysts. Furthermore, as the electrode potential is increased to the more positive side, methanol decomposition progresses with greater speed. This is why the output voltage of a DMFC is reduced with larger current application.

As far as the IRAS measurements are concerned, there are no other bands except for CO, CO_2 , formate and water molecule. There are many conditions relating to optimal cell power: methanol concentration, electrode potential, solution pH, Ru amount in the Pt/Ru catalyst, etc. It is necessary to investigate the optimal conditions to obtain maximum power output for a DMFC. For example, accumulation of OH radicals on the catalyst surface at more negative potentials would contribute to an increase in output power.

14.4 Conclusions

Catalysts prepared by electroless plating and by direct hydrogen reduction show higher power densities than those of commercial catalysts. Those catalysts with excessively large Pt particle size show poor power densities, and are therefore not suitable as fuel cell catalysts. The amount of Pt loading on CB per unit MEA area can be reduced to as low as 0.1 mg/cm^2 without significant

reduction in power output when a direct hydrogen reduction catalyst is used. These catalysts displayed many potential advantages, simple preparation procedure, cell cost, and high cell performance, with regard to DMFC or PEFC. There are two definite routes for a methanol molecule to oxidize on Pt catalysts. One is by CO path, and the other is by way of formate route. Because OH radicals are the key molecules that accelerate CO and methanol oxidation, DMFC electrode catalysts should be functional to yield OH radicals at more negative potential as possible.

References

1. P.G. Patil, J. Power Sources **37**, 171 (1992)
2. H.P. Dhar, J. Electroanal. Chem. **357**, 237 (1993)
3. A.J. Appleby, F.R. Foulkes, *Fuel Cell Handbook* (Van Nostrand Reinhold, New York, 1989)
4. S. Gottesfeld, T.A. Zawodzinski, in *Advances in Electrochemical Science and Engineering*, vol. 5, ed. by R.C. Alkire, H. Gerischer, D.M. Kolb, C.W. Tobias (Wiley-VCH, Weinheim, 1997), p. 195
5. K. Yu, J. Ding, J. Ren, S. Cheng, K.Y. Tsang, J. Mater. Chem. **14**, 506 (2004)
6. *Handbook of Fuel Cells—Fundamentals, Technology and Applications* (John Wiley & Sons, 2003)
7. Z. Liu, X. Lin, J.Y. Lee, W. Zhang, M. Han, L.M. Gan, Langmuir **18**, 4054 (2002)
8. W. Li, C. Liang, W. Zhou, J. Qiu, Z. Zhou, G. Sun, Q. Xin, J. Phys. Chem. **107**, 6292 (2003)
9. L.Z. Lee, M. Han, L.M. Gan, W. Chen, Langmuir **20**, 181 (2004)
10. W. Li, C. Liang, W. Zhou, Z. Wei, G. Sun, Q. Xin, J. Qiu, H. Han, Carbon **40**, 791 (2002)
11. M.K. Ravikumar, A.K. Shukla, J. Electrochem. Soc. **143**, 2601 (1996)
12. H. Bonnemann, W. Brijoux, R. Brinkmann, E. Dinjus, T. Joußen, B. Korall, Angew. Chem. Int. Ed. Engl. **30**, 1312 (1991)
13. D.A. Stevens, J.R. Dahn, J. Electrochem. Soc. **150**, A770 (2003)
14. K. Yamada, K. Yasuda, N. Fujiwara, Electrochem. Commun. **5**, 892 (2003)
15. E.S. Steigerwalt, G.A. Deluga, D.E. Cliffl, J. Phys. Chem. B **105**, 8097 (2001)
16. N. Fujiwara, K. Yasuda, T. Ioroi, Z. Siroma, Y. Miyazaki, Electrochim. Acta **47**, 4079 (2002)
17. V. Hacker, E. Wallnöfer, W. Baumgartner, T. Schaffer, J.O. Besenhard, H. Schröttner, M. Schmied, Electrochem. Commun. **7**, 377 (2005)
18. F.J. Vidal-Iglesias, J. Solla-Gullon, P. Rodríguez, E. Herrero, V. Montiel, J.M. Feliu, A. Aldaz, Electrochem. Commun. **6**, 1080 (2004)
19. T. Fujii, M. Ito, Fuel Cells **5**, 356 (2006)
20. C. Lamy, J.M. Leger, J. Clavilier, R. Parsons, J. Electroanal. Chem. **150**, 71 (1983)
21. N. Markovic, P.N. Ross, J. Electroanal. Chem. **330**, 499 (1992)
22. H. Kita, Y. Gao, T. Nakato, H. Hattori, J. Electroanal. Chem. **373**, 177 (1994)
23. E. Herrero, K. Franaszczuk, A. Wieckowski, J. Phys. Chem. **98**, 5074 (1994)
24. S. Motoo, N. Furoya, J. Electroanal. Chem. **330**, 499 (1992)

25. B. Beden, C. Lamy, A. Bewick, K. Kunimatsu, J. Electroanal. Chem. **121**, 343 (1981)
26. F. Kitamura, M. Takahashi, M. Ito, Chem. Phys. Lett. **123**, 273 (1986)
27. B. Beden, A. Bewick, C. Lamy, J. Electroanal. Chem. **147**, 148 (1988)
28. B. Beden, A. Bewick, C. Lamy, J. Electroanal. Chem. **150**, 505 (1988)
29. S. Matsuda, F. Kitamura, M. Takahashi, M. Ito, J. Electroanal. Chem. **274**, 305 (1989)
30. A.T. Hubbard, Chem. Rev. **88**, 633 (1988)
31. H. Ogasawara, Y. Sawatari, J. Inukai, M. Ito, J. Electroanal. Chem. **337**, 358 (1993)
32. H. Ogasawara, J. Inukai, M. Ito, Surf. Sci. Lett. **311**, L665 (1994)
33. R. Parsons, T. Van der Noot, J. Electroanal. Chem. **257**, 1 (1988)
34. A. Hamnett, Catal. Today **38**, 445 (1997)
35. A. Hamnett, in *Interfacial Electrochemistry*, ed. by A. Wieckowski (Marcel Dekker, New York, 1999)
36. H.A. Gasteiger, N. Markovic, P.N. Ross, E.J. Cairns, J. Phys. Chem. **98**, 617 (1994)
37. V.S. Bagotzky, Y.B. Vassilyev, Electrochim. Acta **12**, 1323 (1967)
38. S. Wilhelm, W. Vielstich, H.W. Buschmann, T. Iwasita, J. Electroanal. Chem. **229**, 377 (1987)
39. C. Lamy, J.M. Leger, J. Clavilier, R. Parsons, J. Electroanal. Chem. **150**, 71 (1983)
40. F. Kitamura, M. Takeda, M. Takahashi, M. Ito, Chem. Phys. Lett. **142**, 318 (1987)
41. F. Kitamura, M. Takahashi, M. Ito, Surf. Sci. **223**, 305 (1989)
42. B.E. Hayden, A.M. Bradshaw, Surf. Sci. **125**, 787 (1983)
43. Y. Sawatari, Y. Shingaya, T. Sueoka, M. Ito, Y. Osamura, Spectrochim. Acta A **50**, 1555 (1994)
44. P.W. Faguy, N. Markovic, R.R. Adzic, C.A. Fierro, E.B. Yeager, J. Electroanal. Chem. **289**, 245 (1990)
45. Y. Sawatari, J. Inukai, M. Ito, J. Electron Spectrosc. **64/65**, 515 (1993)
46. Y. Shingaya, M. Ito, J. Electroanal. Chem. **372**, 283 (1994)
47. T. Iwasita, F. Nart, J. Electroanal. Chem. **317**, 291 (1991)
48. H. Ogasawara, M. Ito, Chem. Phys. Lett. **245**, 304 (1995)
49. E.A. Batista, G.R.P. Malpass, A.J. Motheo, T. Iwasita, J. Electroanal. Chem. **571**, 273 (2004)
50. B.A. Sexton, Surf. Sci. **102**, 271 (1981)
51. B.A. Sexton, K.D. Rendulic, A.E. Hughes, Surf. Sci. **121**, 181 (1982)
52. M. Endo, T. Matsumoto, J. Kubota, K. Domen, S. Hirose, Surf. Sci. **441**, L931 (1999)
53. M. Endo, T. Matsumoto, J. Kubota, K. Domen, S. Hirose, J. Phys. Chem. B **105**, 1573 (2001)
54. Z. Liu, T. Sawada, N. Takagi, K. Watanabe, Y. Matsumoto, J. Chem. Phys. **119**, 4879 (2003)
55. T. Iwasita, W. Vielstich et al. (eds.), *Handbook of Fuel Cells*, vol. 2 (Wiley, Chichester, 2003), p. 603
56. M. Alnot, J. Eberhardt, J. Barnard, Surf. Sci. **208**, 285 (1989)

Strategies for Structural and Energy Calculation of Molecular Catalysts

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Abstract Ab initio molecular orbital calculation is becoming a powerful tool for studying molecular structures and intermolecular interactions. This chapter will begin with the explanation of computational methods for studying structures of organic metal complexes and their intermolecular interactions. The effects of basis set and electron correlation on the calculated structures and interaction energies will be also explained. The level of theory (basis set and electron correlation correction procedure) is significantly important for an accurate evaluation of structures and interaction energies. Problems of basis sets including effective core potential will also be discussed. Next classification of intermolecular forces will be explained. Intermolecular forces can be separated into two groups. One is short-range interactions such as exchange-repulsion and charge-transfer interactions. Another is long-range interactions such as electrostatic, induction and dispersion interactions. Required computational levels for evaluating these interactions will be discussed. Some examples for computational studies of organic metal complexes and related molecules will be shown. These calculations are useful for studying molecular catalysts for energy conversion systems because the catalytic reactions start from intermolecular interactions between the catalysts and reacting species. The catalytic activities depend on the molecular structure and the intermolecular interaction. Here, some applied examples will be introduced for studying molecular catalysts for fuel cells, and the strategies will be discussed for the development of new advanced molecular catalysts by the ab initio molecular orbital calculation.

15.1 Introduction

Structures and intermolecular interactions of metal complexes are important for understanding their properties as molecular catalysts. Intermolecular interaction plays important roles in controlling the recognition of reacting species by molecular catalysts. Adsorption of molecular catalysts on graphite or metal surface is also controlled by intermolecular interaction. Several experimental measurements provide valuable information on intermolecular interactions. Unfortunately, however, it is still difficult to reveal the details of intermolecular interactions only by experimental measurements. Ab initio molecular

orbital calculations provide useful information on molecular structures and intermolecular interactions. We can obtain accurate geometries of molecules by ab initio molecular orbital calculations. We can also evaluate size of interaction energy, origin of attraction and orientation dependence of the interaction energy by ab initio calculations. Sufficiently accurate interaction energies can be calculated, if a reasonably large basis set is used and electron correlation is properly corrected [1]. This chapter will begin with computational methods for calculating molecular geometries and interaction energies. The basis set and electron correlation effects will be explained. Geometries and energies obtained by ab initio molecular orbital calculations depend strongly on the used basis set and electron correlation. Choice of basis set and electron correlation procedure is essential for an accurate estimation of geometries and interaction energies. We will also briefly explain intermolecular forces. Then computational methods for calculating intermolecular interactions will be explained. In the later part of this chapter some examples for computational studies of organic metal complexes and related molecules will be explained.

15.2 Computational Methods

Commonly used ab initio molecular orbital calculation programs have geometry optimization routines. Starting from the molecular geometry defined in the input file, the programs automatically optimize the geometry by moving atom positions to decrease the energy of molecule until converging to a local minimum on the potential energy surface. The optimized geometry corresponds to the local minimum close to the initial geometry. Therefore one has to optimize geometries from sufficiently large numbers of initial geometries, if one wants to obtain the global minimum geometry.

Ab initio molecular orbital theory is a first principle method, which does not use any empirical parameters. However, ab initio molecular orbital calculations are approximation. The accuracy of the calculated structures and interaction energies depends strongly on the level of theory (basis set and electron correlation correction). Therefore the choice of basis set and electron correlation correction procedure is essential for an accurate estimation of molecular geometries and energies.

The supermolecular method is used for calculating intermolecular interaction energy. The total interaction energy (E_{total}) is calculated as the difference between the calculated energy of the dimer [$E(\text{AB})$] and the sum of the calculated energies of monomers [$E(\text{A})$ and $E(\text{B})$] as shown in the following equation:

$$E_{\text{total}} = E(\text{AB}) - [E(\text{A}) + E(\text{B})] \quad (15.1)$$

The calculated interaction energy by the supermolecular method includes basis set superposition error (BSSE) [2]. The BSSE is corrected by the counterpoise method [3]. The correction of the BSSE is essential for an accurate evaluation of weak intermolecular interactions.

15.3 Basis Set and Electron Correlation Effects on Geometry and Conformational Energy

The basis set and electron correlation effects on calculated geometries and relative energies of isomers for small organic molecules have been studied extensively [4]. Minimal basis sets (STO-3G, etc.) and split-valence basis sets without polarization functions (6-31G and 6-311G) are not suitable for geometry optimization. Optimized geometries using these basis sets often have large errors. In most cases optimized geometries of small organic molecules by second order Møller–Plesset perturbation calculations (MP2) using the 6-311G** basis are sufficiently accurate. The geometries obtained using the 6-31G* are usually close to the 6-311G** geometries. The effects of electron correlation on the optimized geometries of small organic molecules are not large. Hartree–Fock (HF) calculations underestimate the bond distance only slightly compared with calculations with electron correlation correction. In most cases the MP2/6-311G** level calculations provide sufficiently accurate relative energies for isomers of small organic molecules. This level calculation is often used for conformational analysis of small organic molecules. Electron correlation effects beyond MP2 on geometries and relative energies of small organic molecules are usually very small [5, 6].

A careful evaluation of basis set and electron correlation effects is necessary for an accurate estimation of molecular geometries and conformational energies for metal complexes. The effects of basis set on calculations of metal complexes were not so extensively studied compared with organic molecules. The effects of electron correlation on open shell metal complexes are not clear compared with closed shell organic molecules. Sometimes basis sets using effective core potential are employed for calculating metal complexes including heavy metals. Optimized geometries using effective core potential sometimes have large errors. Special care is necessary for calculations of metal complexes using effective core potentials. Density functional theory (DFT) methods were often used for calculations of metal complexes. The performance of DFT calculations is satisfactory in many cases, if reasonably reliable basis sets are used.

15.4 Intermolecular Forces

There exist several intermolecular forces between interacting molecules. Intermolecular forces can be separated into two main types. One is the long-range interactions, such as electrostatic, induction and dispersion terms, where the energy of a long-range interaction behaves as some inverse power of R ($E \sim R^{-n}$; R is the intermolecular distance). The long-range interactions have their origin in Coulombic interaction between interacting molecules. Short-range interactions include exchange-repulsion and charge-transfer interactions. Short-range interactions arise at distances where the molecular

wave functions overlap significantly. The energies of short-range interactions decrease exponentially with distance ($E \sim e^{-\alpha R}$) [7]. The distance dependence of calculated interaction energy clearly shows whether the short-range interactions (charge-transfer, etc.) are important for the attraction or not. The long-range interactions are mainly responsible for the attraction, if substantial attraction exists even when molecules are well separated. The origin of attraction of coordinate bonds is orbital–orbital interaction, as coordinate bonds are chemical bonds caused by the overlap of molecular orbitals of metal and coordinated ligand molecule.

15.5 Basis and Electron Correlation Effects on Intermolecular Interactions

Each interaction energy term requires a different level of approximation for an accurate evaluation. An evaluation of the dispersion energy is the most computationally demanding, as it requires a very large basis set and electron correlation correction. The dispersion interaction has its origin in electron correlation and molecular polarization. Small basis sets underestimate molecular polarizability and thereby underestimate the dispersion energy. Medium-size basis sets such as 6-31G* and 6-311G** are not large enough for the accurate evaluation of dispersion energy [8]. A large basis set near saturation is necessary. On the other hand, the electrostatic, induction and exchange-repulsion energies can be evaluated with moderate accuracy using medium-size basis sets. Large part of these interactions can be evaluated by HF calculations.

An accurate evaluation of weak interactions such as the π/π and CH/ π interactions requires computationally demanding high-level ab initio calculations, as the dispersion interaction is the major source of the attraction in these interactions [9,10]. Origin of attraction in physisorption of organic molecules on graphite surface is the dispersion interaction. Therefore an accurate evaluation of the physisorption energy requires high-level calculations. On the other hand, an accurate evaluation of strong interactions such as the interaction between ions and that between an ion and a neutral molecule does not require very high-level calculations. Sufficiently accurate interaction energies can be obtained using a medium-size basis set, as electrostatic and induction interactions are mainly responsible for the attraction in these interactions [11,12]. The attraction caused by coordinate bonds can also be evaluated sufficiently accurately using a medium-size basis set. The orbital–orbital interaction is the origin of attraction in the coordinate bond.

Figure 15.1 shows the basis set dependence of the calculated HF and MP2 level interaction energies for the benzene dimer (π/π interaction) [9]. The weak basis set dependence of the calculated HF-level interaction energy (mainly exchange-repulsion and electrostatic interactions) shows that the basis set dependence of the exchange-repulsion and electrostatic energies is very weak, while the MP2-level interaction energy depends strongly on the basis set.

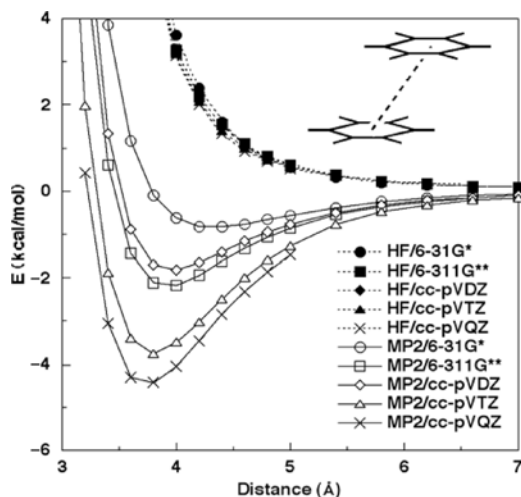


Fig. 15.1. Basis set dependence of the Hartree–Fock (*HF*) and second-order Møller–Plesset perturbation (*MP2*) level benzene dimer interaction energies

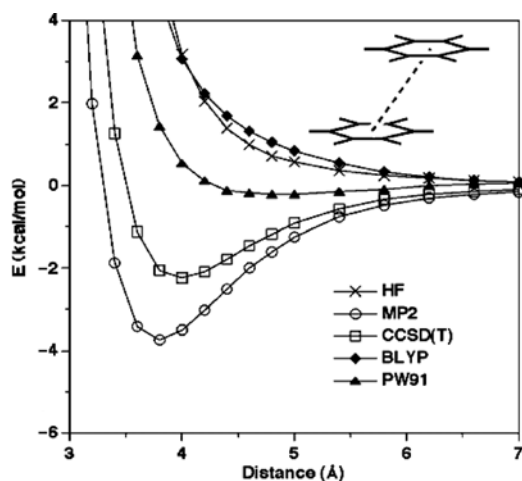
The medium-size 6-31G* and 6-311G** basis sets underestimate the attraction considerably compared with the large cc-pVQZ basis set, as these medium-sized basis sets underestimate the dispersion interaction. Effective core potential is often used for the calculations of metal complexes. The accuracy of the calculated intermolecular interaction energies using effective core potential is still not very clear. Careful evaluation of the performance of the basis set is strongly recommended before using these basis sets.

Recently reported systematic coupled-cluster calculations with single and double substitutions with inclusion of noniterative triple excitations [CCSD(T)] calculations of small organic clusters show that the CCSD(T) calculations using reasonably large basis sets reproduce the experimental binding energies quite well [1]. Calculated MP2 and CCSD(T) interaction energies for hydrogen-bonded complexes and aromatic clusters are summarized in Table 15.1. The CCSD(T) level interaction energies agree well with experimental interaction energies in the gas phase [9, 13–15].

The CCSD(T)-level electron correlation correction is highly computationally demanding. The CPU time for a CCSD(T) calculation is proportional to the seventh power of the number of basis functions, while the CPU time for an MP2 calculation is proportional to the fifth power of the number of basis functions. The MP2 calculations are widely used for electron correlation correction. The MP2-level interaction energies for hydrogen-bonded clusters and aliphatic hydrocarbon dimers are usually very close to the CCSD(T)-level interaction energies [13]. On the other hand, the MP2 calculations considerably overestimate the interaction energies for aromatic clusters (π/π interactions) [9, 15]. A comparison of HF, MP2 and CCSD(T) calculations for the benzene dimer is shown in Fig. 15.2. The calculated HF potential is repulsive.

Table 15.1. Intermolecular interaction energy (E_e) of small clusters (kcal/mol)

Cluster	MP2	CCSD(T)	exp
H ₂ O–H ₂ O ^a	–4.9	–4.8	–5.0
MeOH–MeOH ^a	–5.6	–5.5	–4.6 ~ –5.9
HCOOH–HCOOH ^a	–13.8	–13.9	–13.2
HF–HF ^a	–4.4	–4.4	–4.6 ± 0.3
HCN–HF ^a	–7.4	–7.1	–6.9
C ₆ H ₆ –H ₂ O ^b	–3.4	–3.0	–3.4 ± 0.1
C ₆ H ₆ –NH ₃ ^b	–2.6	–2.2	–2.0, –2.4 ± 0.1
C ₆ H ₆ –C ₆ H ₆ ^c	–4.5	–2.5	–2.8 ± 0.4, –2.0 ± 0.2
C ₆ H ₅ Me–C ₆ H ₅ Me ^d	–6.8	–4.1	–3.6 ± 0.2

^aReference [13].^bReference [14].^cReference [9].^dReference [15].**Fig. 15.2.** Effect of electron correlation correction on the benzene dimer interaction energy

Significant electron correlation effects on the calculated potential show that a large dispersion contribution to the attraction. The MP2 calculations considerably overestimate the attraction compared with more reliable CCSD(T) calculations. Highly computationally demanding CCSD(T)-level electron correlation correction is necessary for an accurate evaluation of the interaction energy in aromatic clusters. The effects of electron correlation are not large in the calculations of the strong interactions such as the ion–ion interactions, because the electrostatic and induction interactions are the major source of attraction in these interactions [11,12].

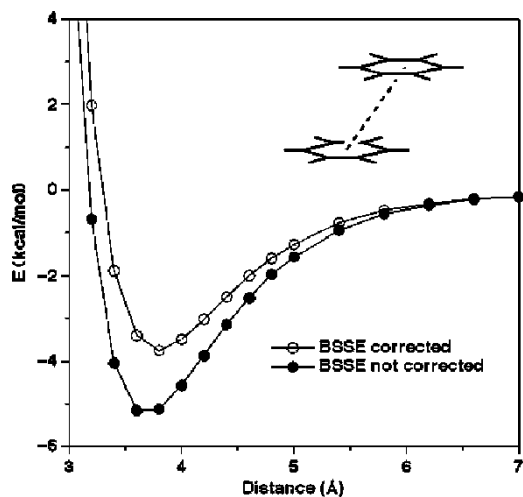


Fig. 15.3. Effects of basis set superposition error (BSSE) correction on the benzene dimer interaction energy

The calculated interaction energy by the supermolecular method includes BSSE. The BSSE is corrected by the counterpoise method. The energies of both dimer and monomers are calculated using the dimer's basis set in the counterpoise correction. The correction of BSSE is essential for accurate evaluation of weak intermolecular interactions, since the BSSE correction significantly changes the size of the calculated interaction energy. The effects of BSSE on the calculated interaction energy for the benzene dimer are shown in Fig. 15.3.

DFT calculations are often used for the evaluation of intermolecular interactions. However, DFT methods with commonly used functionals such as BLYP, B3LYP, PW91 and PBE cannot accurately evaluate dispersion energy. The intermolecular interaction energy potentials calculated with BLYP and B3LYP functionals are close to those obtained by the HF calculations. Some GGA (generalized gradient approximation) calculations such as PW91 and PBE give attractive potentials for rare-gas and hydrocarbon dimers. However, the size of the attraction is not accurate. The PW91 calculations considerably underestimate the attraction in the benzene dimer (Fig. 15.2). The attraction calculated by the PW91 method is probably not due to dispersion, since the basis set dependence of the calculated attraction is negligible [13]. The calculated attraction should strongly depend on the size of the basis set, as for the MP2 calculations shown in Fig. 15.1, if the physical origin of the attraction calculated by the PW91 method is dispersion. The negligible basis set dependence of the attraction calculated by the PW91 method shows that the calculated attraction is not dispersion energy. LSD (local spin density) calculations over bind the rare-gas and hydrocarbon dimers. The attraction by the

LSD calculations is not the dispersion interaction. DFT calculations are not suitable for evaluating the weak intermolecular interactions (π/π and CH/π interactions and physisorption on graphite), since dispersion is the major source of the attraction in these interactions. DFT calculations using medium-size basis sets provide sufficiently accurate interaction energies for the strong interaction, because DFT calculations can evaluate electrostatic and induction energies sufficiently accurately. DFT calculations can also evaluate the interactions for coordinate bonds sufficiently accurately.

15.6 Calculations of Transition Metal Complexes

We have to select correct spin state (spin multiplicity: singlet, doublet, triplet, etc.) and coordination geometry (tetrahedral, octahedral, square planar, etc.) for the calculations of transition metal complexes. The choice of correct spin state is essential for an accurate evaluation. The stable geometry of a complex depends on the spin state. A different spin state complex has a different stable structure. The geometry is optimized on the potential energy surface of the selected spin state in the calculation. If an incorrect spin state is selected, the calculated structure and interaction energies are not correct.

Careful consideration of the spin state is necessary for an accurate evaluation of structures and interactions of transition metal complexes with reacting species. The spin states of transition metal complexes often change depending on their ligands and coordination geometries. If the spin state of the transition metal complex is known from experimental measurements, molecular orbital calculations should be carried out for the observed spin state. On the other hand, an accurate *ab initio* calculation of the complex is very difficult, if the spin state is unknown. We can calculate the energy difference between different spin states of the same transition metal complex to determine the most stable spin state of the complex only by calculations in principle. But an accurate evaluation of the energy difference between different spin states is extremely difficult. Calculated energy difference between different spin states often has large error.

15.7 Examples of the *Ab Initio* Calculation for Molecular Catalysts

In this section, some examples of *ab initio* calculations on molecular catalysts used for fuel cells are explained. We will discuss the relationship between the molecular geometries and catalytic activities. Molecular catalysts such as organic metal complexes have been well known as very unique electrocatalysts for fuel cells because of their large flexibility in molecular design and their innovative functions compared to conventional metal alloy catalysts. Therefore many researches have been developing highly catalytically active organic metal

complexes for methanol oxidation reaction (MOR) and oxygen reduction reaction (ORR) in fuel cells [16–19]. The catalytic activity and electrochemical stability can be greatly improved by heat-treatment in an inert atmosphere. In general, the Co–N₄ and Co–N₂O₂ coordination structures in the organic metal complexes are believed to act as redox mediators that take part in the electrochemical MOR and/or ORR. For example, Bett et al. [18] reported macrocycles as co-catalysts of Pt for MOR. They found that Pt co-catalyzed with ruthenium tetramethylcyclam enhances the MOR in 1 M H₂SO₄ at 60°C. van Veen et al. [19] also prepared several Co–N₄ catalysts on carbon black (Vulcan XC-72R) in a similar way. They used metal complexes with various nitrogen ligands for the electrochemical ORR to examine their catalytic activities. They also confirmed that the Co–N₄ moieties remained on the carbon black after the heat-treatment at 700°C by extended x-ray absorption fine structure (EXAFS) measurements, although some metallic cobalt also appeared.

In our previous studies [20–23], we examined Pt catalysts co-catalyzed with various organic metal complexes. They are *N,N'*-mono-8-quinolyl-*o*-phenylenediamine (mqph), *N,N'*-bis(anthranilidene)ethylenediamine (anthen) and *N,N'*-bis(salicylidene)ethylenediamine (salen) complexes coordinated with transition metal ions (Co, Ni, Fe, Mo, Mn, etc.) (Fig. 15.4). We found that the mixing of the organic metal complexes with Pt catalyst noticeably enhances the electrochemical MOR in acidic media (Fig. 15.5). X-ray

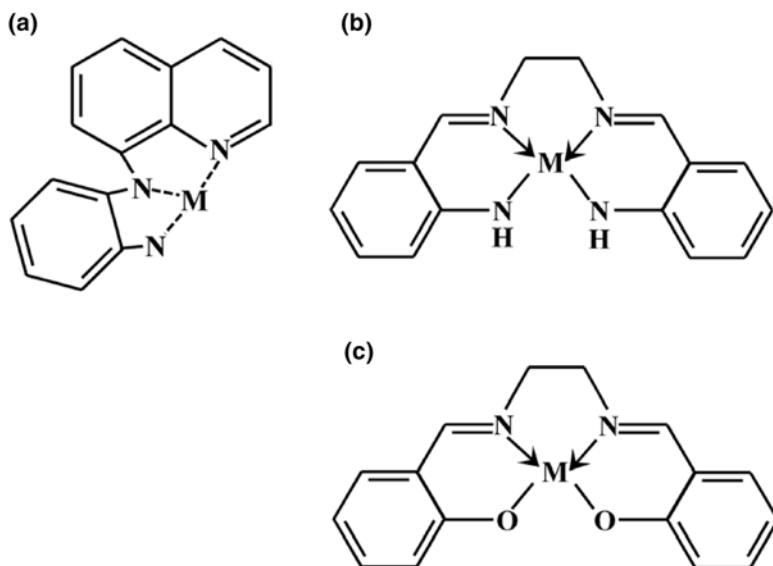


Fig. 15.4. Chemical structure of organic metal complexes tested. (a) M(mqph), (b) M(anthen) and (c) M(salen). Coordination by acetate ligands during the synthesis is omitted ([23], copyright Elsevier Limited)

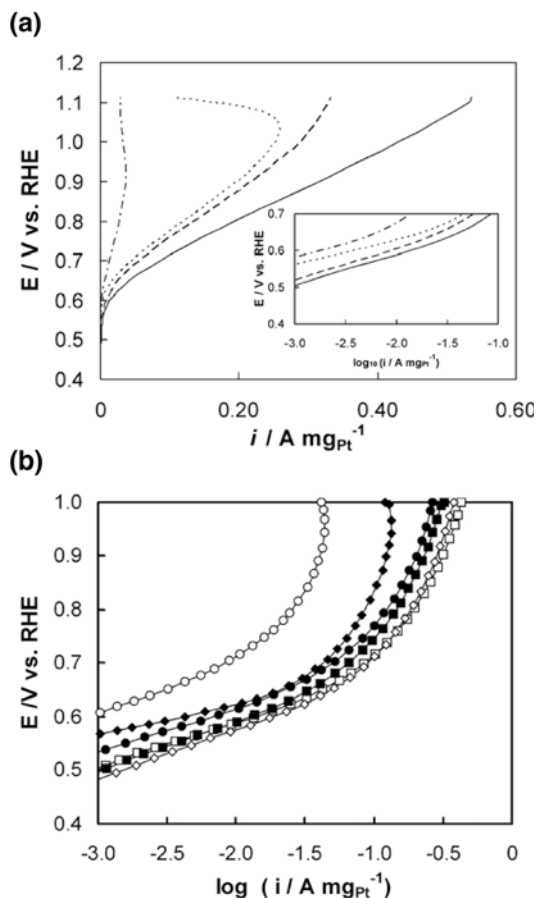


Fig. 15.5. (a) LSVs for Pt–Ni(complex)/C mixed catalysts (mixing ratio = 50/50) in 0.05 M H₂SO₄ + 1 M CH₃OH at 25°C. Potential scan rate: 1 mV s⁻¹. –, mqph; --, anthen; ···, salen; -·-, 10 wt% Pt/C(Aldrich). (b) LSVs for the Pt–Ni(mqph)/C mixed catalysts with various mixing ratios in 0.05 M H₂SO₄ + 1 M CH₃OH at 25°C. Potential scan rate: 1 mV s⁻¹. Mixing ratio: (○), 20/80; (●), 40/60, (□) 50/50, (■) 60/40, (◇) 80/20, (◆) 100/0 ([23], copyright Elsevier Limited)

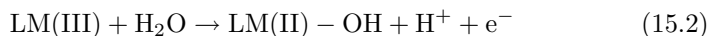
photoelectron spectroscopy (XPS) and x-ray absorption spectroscopy (XAS) measurements for the Pt–M(complex)/C mixed catalysts also showed that the M–N_xO_y structures of M(complex) remained on the graphite powder after the heat-treatment conditions at 600°C in Ar atmosphere [23], although a portion of the complex decomposed.

We tried to elucidate the MOR mechanisms by the ab initio calculation. Gaussian 03 program [24] was used for the ab initio molecular orbital calculations. The geometries of isolated organic metal complexes and their OH⁻ or CO complexes were optimized at the HF/6-31G* level. Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)

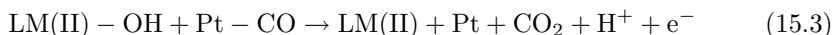
energy levels and interaction energies with OH^- and CO were calculated using the optimized geometries. The basis set superposition error (BSSE) [2] was corrected for all calculations using the counterpoise method [3]. The Ni(anthen) and Ni(salen) are square planar complexes. The Ni(mqph) is also a planar complex, although only three nitrogen atoms coordinate with the Ni. Crystal field theory suggests that square planar Ni (d^8) complex is low-spin. Therefore we assumed that the complexes are singlet in the calculations.

The assumed mechanisms of the MOR on Pt-M(complex)/C mixed catalysts are shown below:

(i) The M(complex)s play a similar role as Ru in the Pt–Ru alloy catalyst. The transition metal in M(complex) forms M–OH by the dissociation of H_2O . The M–OH oxidizes CO on the surface of Pt ((15.2)–(15.4)) [18]. (ii) The transition metal in the complex interacts with CO more strongly than Pt and it oxidizes CO by itself [17].



where L stands for the Ligand (macrocycle) and M stands for the transition metal.



Three nickel complexes were used as the model compounds. Interaction energies of the complexes with OH^- or CO were calculated to investigate the correlation between the interaction energy and the catalytic activity for electrochemical MOR on Pt–Ni(complex)/C mixed catalysts. Figure 15.6 shows the optimized geometries of the Ni complexes at the HF/6-31G* level. Figure 15.7 shows the optimized structures of the complexes with OH^- and CO. The OH^- and CO have close contacts with the Ni in the optimized geometries. In the optimized geometries for the Ni(anthen) and Ni(salen) complexes, the OH^- and CO locate above the aromatic plane, while in the Ni(mqph) complex they locate within the plane and have close contacts with Ni as the forth ligand in the square planar structure.

The interaction energies were calculated at the MP2/6-311+G** level. The calculated interaction energies (ΔE_{int}) for the complexes with OH^- and CO are shown in Fig. 15.8. The interactions of CO with the Ni(anthen) and Ni(salen) are very weak (a few kJ/mol). The very small interaction energies suggest that the orbital–orbital interaction (coordination bond) is not important in these complexes. Probably the dispersion and weak electrostatic interactions are mainly responsible for the attraction. On the other hand, the interaction of CO with the Ni(mqph) complex is significantly strong (more than 100 kJ/mol). The very strong interaction suggests that the orbital–orbital interaction plays an important role in the attraction. The interactions of OH^- with the Ni(anthen) and Ni(salen) are

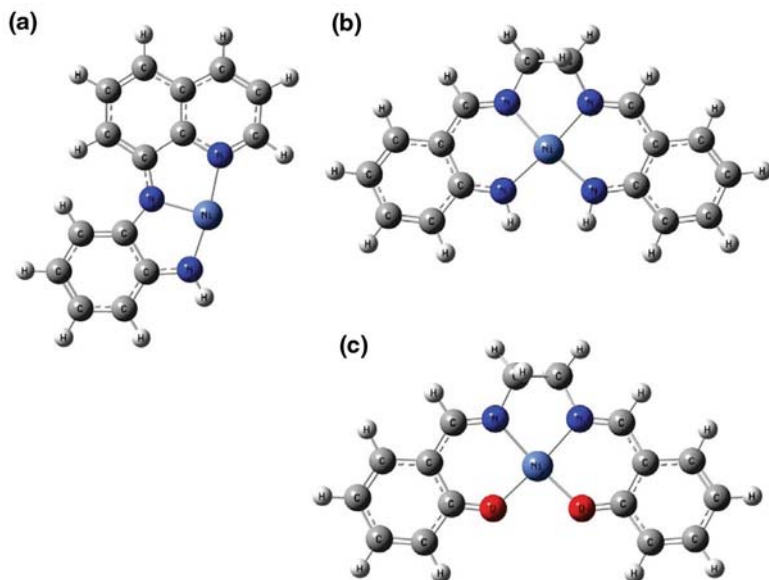


Fig. 15.6. Optimized geometries of the organic metal complexes. (a) Ni(mqph), (b) Ni(anthen) and (c) Ni(salen). HF/6-31G* ([23], copyright Elsevier Limited)

substantially stronger than those of CO due to the attractive electrostatic interaction between Ni cation and OH^- . The interaction of OH^- with Ni(mqph) is larger than those of OH^- with Ni(anthen) and Ni(salen) as in the interactions of CO. The stronger MOR activity of the Ni(mqph) complex compared with other complexes can be explained by the larger interaction energy of the complex with OH^- and CO. The larger binding energy stabilizes the OH^- species on the surface, which would enhance the oxidation of CO on metal surface in the MOR.

The LUMOs of the Ni complexes and HOMOs of OH^- and CO calculated at the HF/6-31G* level are shown in Fig. 15.9. The LUMO for Ni(mqph) localizes on the vacant site for the planar square Ni complex, which suggests that the Ni(mqph) complex will make a coordination bond with an electron donor (OH^- or CO) at this site. The optimized geometries for the Ni(mqph) complexes with OH^- and CO show that the LUMO of Ni(mqph) and HOMO of OH^- or CO overlap in the stable geometries. This suggests that the orbital-orbital interaction (coordination bond) contributes to the attraction in the complex [25]. On the other hand, the LUMOs for Ni(anthen) and Ni(salen) delocalize to the aromatic rings, suggesting that orbital-orbital interaction is not important for the attraction in these complexes.

Recently Yano et al. revealed that the Pt-Ni(mqph)/C mixed catalyst works as an excellent CO-tolerant catalyst for a hydrogen oxidation reaction

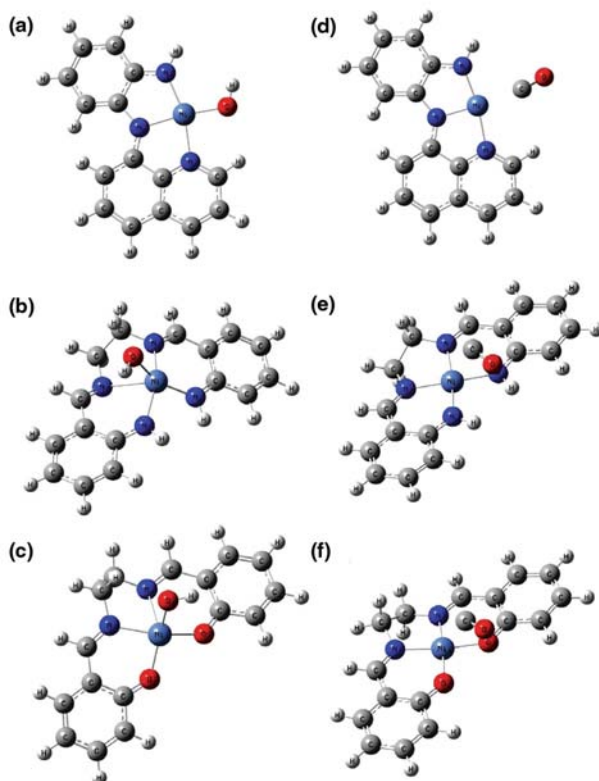


Fig. 15.7. Optimized geometries of the organic metal complexes interacting with OH^- and CO species. OH^- : (a) Ni(mqph), (b) Ni(anthen) and (c) Ni(salen). CO: (d) Ni(mqph), (e) Ni(anthen) and (f) Ni(salen). HF/6-31G* ([23], copyright Elsevier Limited)

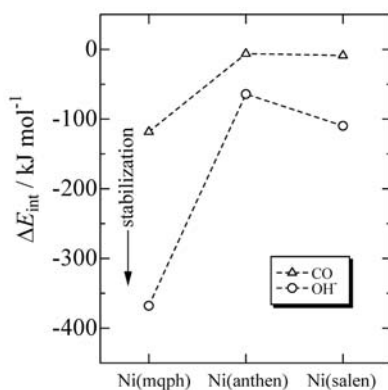


Fig. 15.8. Interaction energies ΔE_{int} of the organic metal complexes with OH^- or CO. MP2/6-311+G**// HF/6-31G* ([23], copyright Elsevier Limited)

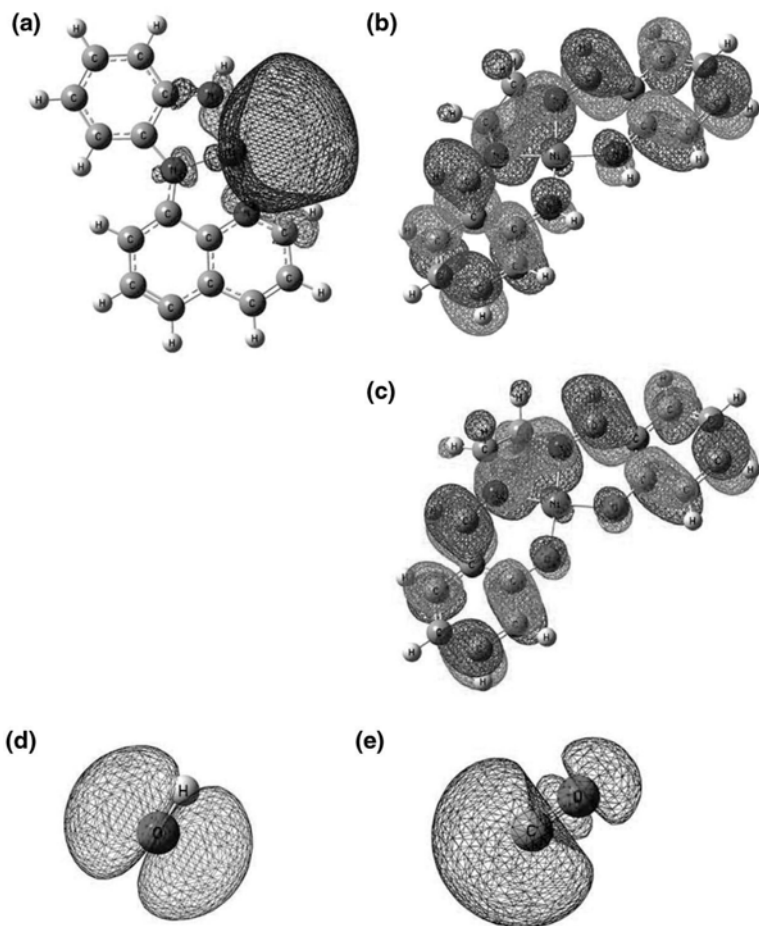


Fig. 15.9. Molecular orbital in the organic metal complexes. LUMO: (a) Ni(mqph), (b) Ni(anthen) and (c) Ni(salen). HOMO: OH⁻ and CO. HF/6-31G* ([23], copyright Elsevier Limited)

(HOR) on the fuel cell anode (Fig. 15.10) [26, 27]. Their result shows that the Pt–Ni(mqph)/C catalyst has higher CO-tolerance compared with Pt/C. It is expected that the Ni in the complex interacts with CO and the complex oxidizes CO due to the negative potential of anode where the HOR occurs. The calculated large interaction energy of Ni(mqph) with CO suggests that CO prefers to interact with the Ni(mqph), which well explains the higher CO-tolerance of Pt–Ni(mqph)/C catalyst compared with Pt/C.

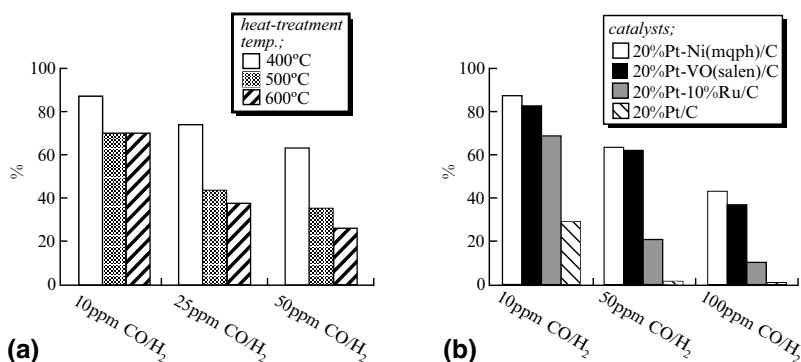


Fig. 15.10. Comparison of CO tolerance measured in a half-cell with H₂ gas containing various amount of CO at 70°C. (a) Effect of heat-treatment temperature of Pt-VO(salen)/C on the H₂ oxidation current containing various amount of CO. (b) Comparison of Pt-VO(salen)/C and Pt-Ni(mqph)/C, that were heat-treated at 400°C, with Pt/C and Pt-Ru/C for the H₂ oxidation current containing various amount of CO ([26], copyright The Royal Society of Chemistry)

15.8 Summary

Ab initio molecular orbital calculations provide valuable information on structures and interactions on molecular catalysts. Recent progress of computational methodologies and improved performance of computers enable us reliable calculations. Ab initio calculation is becoming a powerful tool for studying molecular catalysts.

References

1. T.H. Dunning Jr., J. Phys. Chem. A **104**, 9062 (2000)
2. B.J. Ransil, Chem. Phys. **34**, 2109 (1961)
3. S.F. Boys, F. Bernardi, Mol. Phys. **19**, 553 (1970)
4. W.J. Hehre, L. Radom, P.v.R. Schleyer, J.A. Pople, *Ab Initio Molecular Orbital Theory* (Wiley-Interscience, 1986)
5. K. Raghavachari, J. Chem. Phys. **81**, 1383 (1984)
6. S. Tsuzuki, K. Tanabe, J. Chem. Soc. Faraday Trans. **87**, 3207 (1991)
7. A.J. Stone, *Intermolecular Forces* (Clarendon, Oxford, 1996)
8. S. Tsuzuki, T. Uchimar, M. Mikami, K. Tanabe, J. Phys. Chem. A **102**, 2091 (1998)
9. S. Tsuzuki, K. Honda, T. Uchimar, M. Mikami, K. Tanabe, J. Am. Chem. Soc. **124**, 104 (2002)
10. S. Tsuzuki, K. Honda, T. Uchimar, M. Mikami, K. Tanabe, J. Am. Chem. Soc. **122**, 3746 (2000)
11. S. Tsuzuki, H. Tokuda, K. Hayamizu, M. Watanabe, J. Phys. Chem. B **109**, 16474 (2005)

12. S. Tsuzuki, M. Yoshida, T. Uchimaru, M. Mikami, K. Tanabe, *J. Phys. Chem. A* **105**, 769 (2001)
13. S. Tsuzuki, H.P. Luthi, *J. Chem. Phys.* **114**, 3949 (2001)
14. S. Tsuzuki, K. Honda, T. Uchimaru, M. Mikami, K. Tanabe, *J. Am. Chem. Soc.* **122**, 11450 (2000)
15. S. Tsuzuki, K. Honda, T. Uchimaru, M. Mikami, *J. Chem. Phys.* **122**, 144323 (2005)
16. J.H. Zagal, in *Handbook of Fuel Cells – Fundamentals, Technology and Applications*, vol. 2, ed. by W. Vielstich, A. Lamm, H.A. Gasteiger (John Wiley & Sons, Chichester, 2003), Chapt. 37
17. J.F. Baar, J.A.R. Veen, J.M. Eijk, T.J. Peters, N. Wit, *Electrochim. Acta* **27**, 1315 (1982)
18. J.S. Bett, H.R. Kunz, A.J. Aldykiewicz Jr., J.M. Fenton, W.E. Bailey, D.V. McGrath, *Electrochim. Acta* **43**, 3645 (1998)
19. A.L. Bouwkamp-Wijnoltz, W. Visscher, J.A.R. Veen, S.C. Tang, *Electrochim. Acta* **45**, 379 (1999)
20. T. Okada, Y. Suzuki, T. Hirose, T. Toda, T. Ozawa, *Chem. Commun.* **2001**, 2492 (2001)
21. T. Okada, Y. Suzuki, T. Hirose, T. Ozawa, *Electrochim. Acta* **49**, 385 (2004)
22. T. Okada, N. Arimura, C. Ono, M. Yuasa, *Electrochim. Acta* **51**, 1130 (2005)
23. M. Saito, H. Shiroishi, C. Ono, S. Tsuzuki, T. Okada, *J. Mol. Catal.* **248**, 99 (2006)
24. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision B.04 (Gaussian, Inc., Pittsburgh, PA, 2003)
25. K. Fukui, *Acc. Chem. Res.* **4**, 57 (1971)
26. H. Yano, C. Ono, H. Shiroishi, T. Okada, *Chem. Commun.* 1212 (2005)
27. H. Yano, C. Ono, H. Shiroishi, M. Saito, Y. Uchimoto, T. Okada, *Chem. Mater.* **18**, 4505 (2006)

Future Technologies on Molecular Catalysts

T. Okada and M. Kaneko

Abstract This chapter discusses future prospects on the role of molecular catalysts in the energy conversion technology in various fields of applications. New concepts of the molecular design are presented. In the future “hydrogen energy society,” a closed cycle consisting of hydrogen generation, storage, transmission and usage that are driven by a solar energy as the energy source is to be established. For such purpose, water photo-electrolysis, photosynthesis from CO₂ to bio-energy, electro-chemical solar cells and fuel cells should be the most promising options for hydrogen utilization. In this chapter, a dream of humans toward sustainable energy society will be discussed to stimulate the earliest realization of hydrogen economy using molecular catalysts for energy conversion systems.

16.1 Introduction

The concept of “The Hydrogen Economy” has emerged as early as the 1970s [1]. The fuel cell researchers realized the advantages of using hydrogen as fuel, and dreamed of the hydrogen infrastructure to upgrade fuel cell to the commercially viable technology. The “oil crisis” at that time directed people to the interest of alternative energy source to conventional fossil fuels, and for such demand hydrogen was an important option as the secondary energy that could be used in addition to the electric power as the most flexible, clean and distributable form of energy. The role of electrochemistry has been recognized there because hydrogen production, storage and use involve the core technology of electrochemistry [2].

In late 1980s another problem came as an issue to human economy. The “Global warming,” “Greenhouse effect” and “Climate change” are invoking much concern among people over the world, and since 1988 the Intergovernmental Panel on Climate Change (IPCC) set up by the United Nations Environment Programme (UNEP) disseminated reports not only within scientific community but also among ordinary people worldwide who have concerns on the change of global environment. The emission of carbon dioxide (CO₂)

and other greenhouse gases are a consequence of human activity using fossil energy as the primary source. Therefore, there is an urgent need to establish renewable energy system.

The two economical concepts that emerged in the end of the last century and brought into the new century merged into the term “Energy and Environment,” which now awaits the human’s challenge to resolve.

Hydrogen as clean energy is the type of medium with which the closed energy cycle can be established with the following reactions:



The forward and backward reactions correspond to water splitting (Δ = thermal, chemical, electric, or solar energy) and fuel cell reactions (Δ = electric energy), respectively. In the above system the hydrogen generation, storage, transmission and usage are the key processes to be involved.

In the present chapter, energy recycle systems based on hydrogen energy are introduced and their utilization is discussed in scope of the future “Hydrogen Energy Society.”

16.2 Road Map for Clean Energy Society

Table 16.1a shows the status of various fossil fuel energy resources identified and expected for use in human economy, together with prospected years of supply [3]. In Table 16.1b, various kinds of massive fuels are rated with various

Table 16.1. (a) Status of various fossil-fuel energy resources identified and expected (year 2005) [3]. (b) Various energy rated with various criteria

	Resources expected	Resources identified	Oil equiva- lence/ 10^{12} kg	Annual consumption in oil/ 10^{12} kg	Years of supply
Oil	2×10^{12} barrel	1.2×10^{12} barrel	160.9	3.84 (36.4%)	41
Natural gas	204×10^{12} m ³	180×10^{12} m ³	163	2.47 (23.5%)	65
Coal	6.9×10^{15} kg	909×10^{12} kg	454	2.93 (27.8%)	155
Uranium	–	4.74×10^9 kg	53.6	0.63 (6.0%)	85
Hydro	–	–	–	0.67 (6.3%)	–
Resources	Usable form		Cost	Source stability	Safety
Oil	+		+ → –	+ → –	+
Natural gas	++		+	+	+
Coal	++		+	+	+
Nuclear	+		+	–	–
Renewable energy	–		– → +	–	++

criteria. We are still much dependent on fossil fuels, and the stored energy in the form of fossil fuels appears to last for more than 100 years in total. However, people's consensus would shift to less carbon fuels, when they became aware of the finiteness of fossil fuels through the gradual uprising cost and through enforcement by some political circumstances.

Nuclear power is going to take a major role in future energy supply, and its cleanness in terms of exhaust gas is at first sight an attractive option. However, the risk of disaster and the problem of radioactive wastes are being acknowledged among people. A major disadvantage is that nuclear power plants are subject to Carnot' efficiency as long as they use thermal energy conversion processes, which causes disappointingly low total conversion efficiency of 30%. The inflexibility of operation, poor adherence to load changes and long distance of electricity transport from extreme local district to urban area through transmission lines are other problems.

The renewable energy is at present only a minor supply as compared to the increasing demands of energy consumption in the society. This option is very attractive when one considers a huge resource of natural energy such as solar energy, wind power, biomass and geothermal energy. However, from a practical and economic point of view, one can hardly expect the role of natural energy in a short-term energy strategy. What one can expect is that if high-energy conversion of solar cells such as 30% is attained, this will bring a dream to a reality (it should be noted here that at the photoexcitation center in a photosynthetic system in nature, photoinduced charge separation takes place at nearly 100% efficiency). In future energy technology, it is important to note that an energy generation plant locates in the vicinity of the community of energy demands so that the loss and mismatch in energy transmission should be minimized (onsite or distributed power source). From this point of view, solar cells and fuel cells are good candidates of power generation (Fig. 16.1) [4].

A proposed scenario is that "clean energy society" will be established in about 50 years, and until that time the present energy resources, i.e., fossil fuels and nuclear energy, should be reserved and used under strict saving technology. Hydrogen plays a central role in future energy systems, because this energy medium is generated by simple processes, easy for storage, efficient in transmission through pipelines and utilization at end-users (Fig. 16.2) [5]. How can one shorten the time of arrival of such clean energy society based on hydrogen is the issue of the future energy technology, which is represented by solar energy conversion, hydrogen generation, hydrogen mediated storage, transmission and hydrogen utilization by fuel cells. The cost and time to develop such sustainable energy technology may be huge, but deserve for challenging. A new concept energy conversion system based on molecular catalysts is expected to shorten the time to reach the goal.

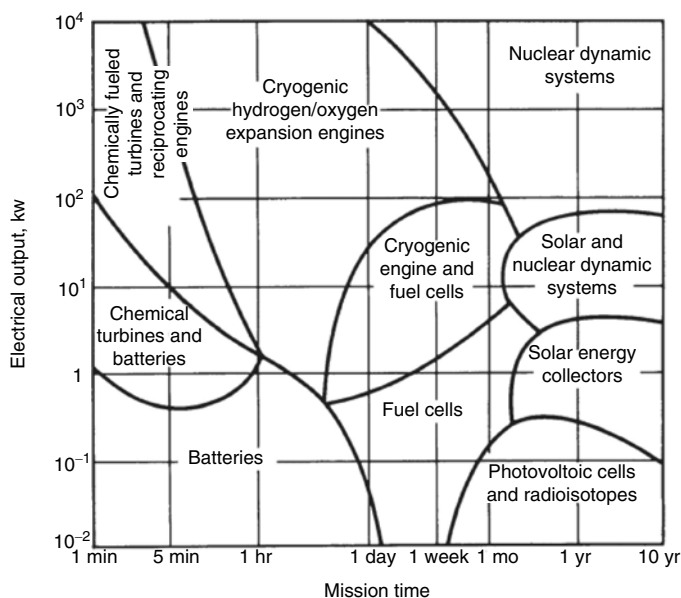


Fig. 16.1. Plots of power output and mission time, showing regions of applicability of various energy converters ([4], copyright MacGraw-Hill)

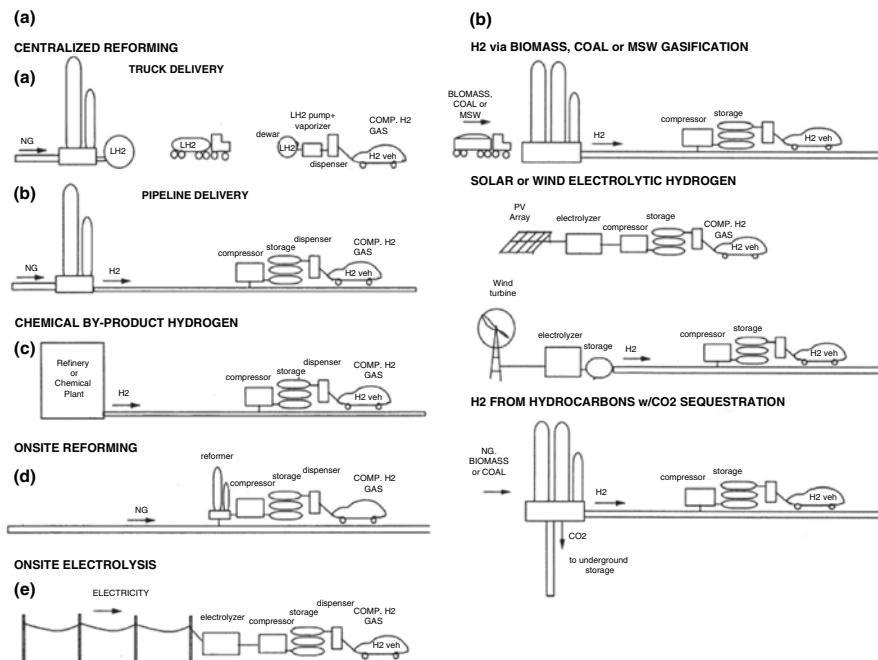


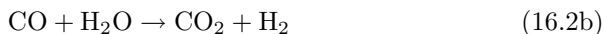
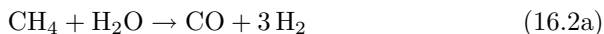
Fig. 16.2. Near-term (a) and long-term (b) hydrogen supply options for clean energy society ([5], copyright Elsevier)

16.3 Hydrogen Production

Hydrogen gas can be produced from various sources, but the most reliable source may be the abundant fossil and natural resources (natural gas, coal, or biomass). Since fossil fuels such as natural gas, oil and coal emit CO_2 when H_2 is produced, they are not very good candidate for a system to reduce CO_2 . From this point of view biomass is suited as a resource to produce H_2 in order to reduce CO_2 emission since biomass is produced by absorbing and immobilizing CO_2 in the atmosphere. In this regard biomass is a “carbon neutral” resource. It is not the aim of the present chapter to review such systems to produce H_2 from biomass. It is only to make a notice here of a system introduced shortly in Fig. 8.7 which can produce H_2 directly from biomass with a highly porous semiconductor photoanode in combination with a proton-reducing cathode generating H_2 under anaerobic conditions.

16.3.1 Natural Gas

Technologically the most plausible and reliable method to produce hydrogen at the present economy is through steam reforming and shift reaction of natural gas:



The first reaction proceeds at high temperatures (700°C to 1100°C) in the presence of a metal-based catalyst (nickel, etc.). In the second reaction additional hydrogen is recovered by a lower-temperature gas-shift reaction with the carbon dioxide produced.

World's natural gas consumption is about 24% of the total energy in 2004 (Fig. 16.3) [3]. The natural gas supply is expected to peak around the year 2030, which is 20 years after the peak of oil. The reserve estimated is 65 years use, and comparing these years of exhaust with that for oil (41 years), coal (155 years) and uranium (85 years), it is expected that the natural gas will be the major energy source in medium time outlook. As seen in Fig. 16.2, hydrogen will be produced from natural gas reforming in a near-term and long-term energy economy.

16.3.2 Renewable Energy Source

To utilize hydrogen energy as a renewable energy for hydrogen fuel cell, efficient procedure for H_2 production via water photolysis should be achieved. However, to this objective we would need longer time of research and development. In this section other renewable energy possible to substitute major part of fossil fuels is discussed. In Table 16.2 such possible energy resource is summarized.

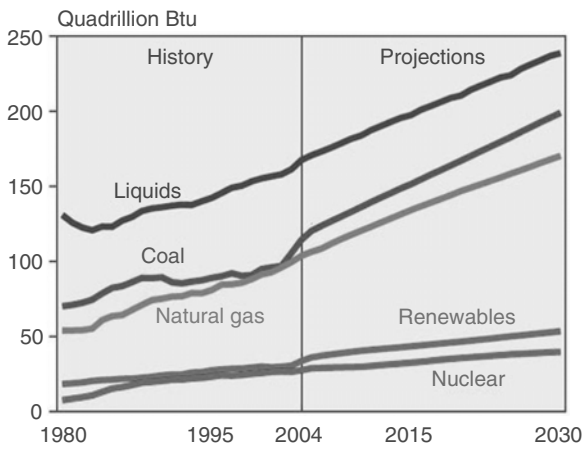


Fig. 16.3. World marketed energy use by fuel type, 1980–2030. Ref. [3]

Table 16.2. Renewable energy resource as a candidate to substitute fossil fuels

Energy	Problems	Note
Hydraulic power generation	Depends on climate and location	Small hydraulic power is attracting attention
Wind power generation	Needs supporting energy at strong window	Conditions for location
Solar cells	Si cell needs recycling LCA and NE to be examined	Market estimate in 2030 = 12GW
Artificial photosynthesis	Needs longer term for R & D	Artificial energy cycle = Future system
Biomass	NE and LCA	Possible candidate to substitute fossil fuels

Hydraulic power plant for electrical power has been used for longer times in some limited places, but it is not easy in many countries to use this in a large scale because of its limited conditions of climate and location.

Wind power plant is used now in many countries to generate electrical power. In some countries of Europe more than several percent of electrical power is already supplied by wind power (e.g., in Germany the wind power is expected to become a major source from present 14% to 45% of energy supply in 30 years). However, such a wind power has one problem to prepare and support electrical power generating system since the plant has to be stopped when the wind is strong. It is in general not sure to how much extent the electrical power can be supplied by wind power plant in future.

Solar cells especially the cells based on a Si semiconductor pn-junction look like promising in future. However, two problems exist. One is the result of market research for the year of 2030. The simulated yearly production of electrical power by solar cells in 2030 is 12 GW ($G = 10^9$) in the world based on their cost and Si resource problem, while the energy demand in the world is nearly 13 TW ($T = 10^{12}$) already in the year of 2000, probably reaching over 20 TW in 2030. Even considering that solar cells can be used for 20 years, the estimated contribution of solar cells in the total world energy demand in 2030 is only 1.2% ($= 240\text{GW}/20\text{TW}) \times 100\%$, far from substituting major part of fossil fuels by solar cells. The second problem is that the Net Energy (NE) data including also recycle energy of the solar cell is not presented yet.

An artificial photosynthesis to produce energy such as hydrogen or other fuels from solar energy and water is still not easy; we need more time of efforts in scientific research and development to support the energy demand by this technology.

The last and most possible candidate to substitute fossil fuels could be biomass that is a so-called “carbon neutral” resource. Ethanol and diesel oils are already started to be used in automobiles, but biomass itself involves also problems as mentioned in the next section. Net Energy based on Lifecycle Assessment (LCA) is of importance also for biomass, but only a few data are presented that include also recycle energy of the facilities to produce the biomass fuels.

To summarize this section of renewable energy, we should not be optimistic about renewable energy especially concerning NE problem to solve the important global warming issue.

16.3.3 Biomass

Biomass fuels such as ethanol and diesel oils produced from biomass to be used for automobiles are attracting a great deal of attention since they are regarded as carbon neutral. A large scale production of such biomass fuels have already started in many places of the world. However, the problem is not so simple. Biomass fuels are already creating big problems as follows:

(1) Growth, accumulation, and transportation of plants, and production of fuels from the biomass require not only cost but also energy. It is especially important to estimate NE (= Output energy obtained by the produced fuels – Input energy to produce the fuels) including the energy to recycle the facilities or devices and chemicals needed to produce the fuel, but actually only a few data are available concerning the NE. It has been simulated that even corn ethanol that has started to be used in automobiles in USA can produce only minus energy when using an inefficient production process, i.e., it increases CO₂ emission in that case [6]. Lifecycle Assessment is now adopted in ISO14040 (ISO = International Standard Organization) to assess the effect of human activity on environments. Evaluation of real NE produced by the

energy resource is especially important to use so called “sustainable energy resource,” but this is in principle a big issue remained for the future.

(2) The big demands to use so-called “sustainable energy” such as corn-ethanol to reduce CO₂ emission are increasing the cost of agricultural products such as corn, and the effect is exerting also on other agricultural products such as orange to raise its price. It is not a good idea to use foods for just burning to drive automobiles and other machines when we are hitting a big issue of foods shortage at this time since the world population is still increasing.

(3) Palm oils are attracting a great deal to use as a diesel oil fuel for automobiles in Europe. This enhanced conversion of forest and woods in Southeast Asia into a large scale palm farm. For this purpose big trees are often just cut down and left, or sometimes burnt down, which increases CO₂ emission even taking into account the reduction of CO₂ by using thus produced biomass fuels, as discussed sincerely now.

It is extremely important to take these problems into account. One of the approaches to avoid such issues would be to use as a biomass resource various biomass wastes that are serious pollutants for our environment but covers one third of the world energy demand per year as proposed in Chap. 8.

16.4 Hydrogen Utilization

Although the electricity is a good form of energy for the end-users, this is not always the best candidate if one looks into the factors of economic transmission or storage. Nor is it a good choice for ground transportation, air transportation and room or water heating in a house [1].

If a community had to rely on the electricity, the power generation plant should locate near the community in order to avoid the loss of long-distance transmission. However, this contradicts to the average consensus that the land cost of urban area cannot accommodate the huge power plants, which need large scale cooling system (water) and considerable space of land. Moreover, using fossil or nuclear fuels in thermal or nuclear power plants in urban area raises an issue of emission and fear of hazards.

In this sense hydrogen is a good alternative for end-use, if infrastructure is established in the urban area. The relative ease of transmission by pipeline shows an advantage over electricity (Fig. 16.4) [1], and expands the possibility for even smaller scale stations. Hydrogen can be used in the house either as fuel to produce heat (burner) or electricity (fuel cell). Another advantage is the storage, which is discussed in the next section.

Hydrogen can be used as feedstock in various industries, such as petrochemical and metal ore conversion, or in plants for chemical products. Finally conversion to electricity by fuel cell systems in various scales will be the central technology in “Hydrogen Economy.” The infrastructure of hydrogen pipelines will meet a huge demand in the future society, both in industrial sector and local communities.

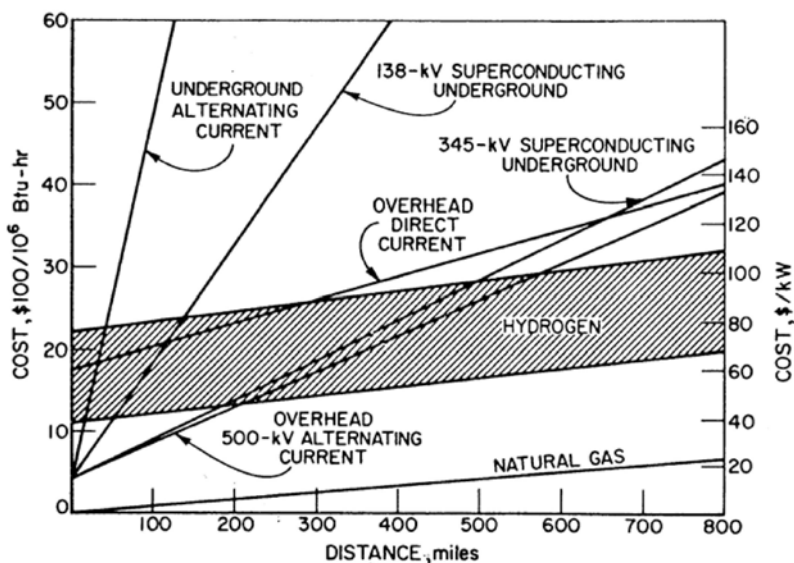


Fig. 16.4. Cost of energy transmission facilities ([1], copyright Plenum Press)

16.4.1 Hydrogen Storage

Hydrogen can be either stored as a cryogenic liquid, compressed in a high-pressure tank or stored as metal hydrides, as well as converted to many chemical compounds such as methane, ammonia, hydrazine, etc. [7]. As potential carriers of hydrogen, high hydrogen content, light weight, small volume, low-cost and nontoxic and safe medium should be the factors for the first screening especially for the fuel in transportation applications. Also fast kinetics and reversibility of H charging and discharging at low temperatures are the criteria for efficient usage of hydrogen. Unfortunately, only a few candidates can pass these criteria, and those remained are liquefied hydrogen, metal hydride and compressed hydrogen in a tank. Recently, carbon nanotubes are reported as a good support of hydrogen storage, with potentially 7 to 8 mass percent of absorption as compared to 3% to 4% for metal hydrides [8]. Modification of carbon nanotubes, e.g. by metal element inclusion, would increase the storage capacity of hydrogen, and should be challenged by future technology.

16.4.2 Energy Conversion

Hydrogen can be used for direct combustion with air in a conventional engine, to produce shaft power. For heat generation, it can either be combusted in a gas phase in a burner or combusted catalytically. However, the most efficient and promising usage is the energy conversion from chemical energy of H₂ to electricity by fuel cells, where no combustion occurs and thus free from the limitation of Carnot efficiency (Fig. 16.5) [9].

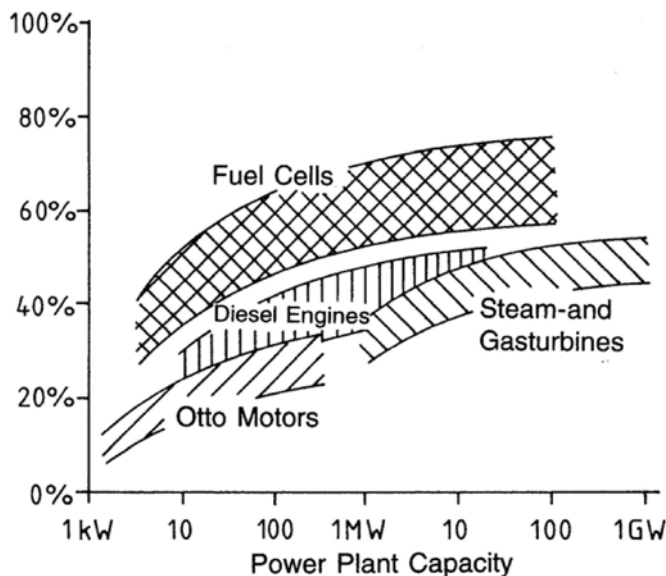


Fig. 16.5. Efficiencies of different power generators as a function of scale ([9], copyright VCH)

Using “hydrogen gas lines” as infrastructure, fuel cells operate at each house or building to supply both electricity and heat. With no pollutant emission but reusable water, fuel cells will bring about the “environmentally benign economy” as the common language in the future society. Since the large part of the voltage loss is due to the polarization of oxygen reduction reaction (ORR) at the cathode and the Ohmic resistance of the polymer electrolyte membrane, a breakthrough in both these materials is desired.

16.5 Biomimetic Approach and Role of Molecular Catalysts for Energy-Efficient Utilization

As mentioned earlier in this chapter, the photosynthesis in nature realizes a highly efficient charge separation of nearly 100% at the photoexcitation centers (photosystems I and II) by using molecule-based sensitizers. Such efficient charge separation by solar irradiation has successfully been achieved in a dye-sensitized solar cell (described in three chapters in this book) by applying a dye molecule to harvest photon energy and separate charges, the incident photon to current efficiency reaching nearly 90% at the peak of the dye absorption. Such high charge separation efficiency can be achieved only in a heterogeneous phase of a sensitizer molecule such as in a photosynthesis and an artificial solar cell where electron transfer occurs from higher singlet excitation states (S_n) to

an acceptor site (molecule) without internal conversion to the lowest excited state (S_1). Solar energy conversion by use of a sensitizer molecule is without doubt a promising approach to create sustainable energy resource.

For solar water cleavage to produce H_2 and O_2 , water oxidation is the most important and yet difficult catalysis. Also in a photosynthetic system efficient water oxidation catalysis takes place by a Mn-protein complex in an oxygen evolving center (OEC) in the photosystem II. While many artificial Mn complexes have been prepared to investigate and create efficient water oxidation catalyst, the activity of these Mn complexes has not been sufficient to utilize for a water photolysis purpose. However, Ru ammine complexes have been proved to be highly active, and so might be applicable for future artificial photosynthesis to achieve solar water cleavage to produce H_2 and O_2 .

Electro-catalysts for fuel cell anode and cathode are important fields that await an innovative molecular design. Porphyrins and phthalocyanines have been the examples of biomimetic molecular designing so far for the cathode catalyst, but future technology would call for much complex strategies: for example a picket type porphyrin in which a O_2 molecule is first entrapped in a molecular hole surrounding the active center of porphyrin [10,11], and electronic structure of O_2 is modified from triplet to singlet states, then electron transfer reaction occurs inside this hole. This will enable faster O—O bond splitting and charge transfer.

Another strategy would involve the “electron mediator” through which oxygen reduction reaction (ORR) occurs. This method uses some redox substances that allow rapid electron transfer at the electrode and then undergo rapid electron transfer with O_2 in a homogeneous phase. The nitric acid–nitric oxide redox couple is such example, with which the path of ORR is considerably altered [4]. How to realize such mediator system in a molecular basis in gas electrodes is a big challenge.

16.6 Summary

The energy and environment issues in this century will push the economy from oil and electricity to hydrogen and electricity. In order to achieve a goal of such a clean energy society, a “quantum leap” should be attained both in the infrastructure and energy technology. Molecular catalysts should be the key material to put forward such an innovative technology.

In photosynthesis and solar cells, novel design of dye-sensitizers will bring about a new breakthrough to achieve a high quantum yield in energy conversion with visible lights. Both for water oxidation in the solar water cleavage and for oxygen reduction in the fuel cell cathode, oxidation and reduction reactions of O_2 molecules become the rate determining process, and design of molecular catalysts plays a central role in promoting the kinetics and attaining the high-energy conversion efficiency.

Biomimetic approaches for the molecular design may provide significant clues in establishing a good class of catalysts, but purely artificial approaches may also be useful in the future especially for improving, e.g., the chemical stability of a molecular catalyst, which is the major issue in the application to energy conversion systems with durability.

References

1. D.P. Gregory, in *Modern Aspects of Electrochemistry*, vol. 10, ed. by J.O.M. Bockris, B.E. Conway (Plenum, New York, 1975), Chap. 5
2. J.A.G. Drake, (eds.) *Electrochemistry and Clean Energy*. Royal Soc. Chem. No. 146 (Athenaeum Press, Newcastle upon Tyne, 1994)
3. International Energy Outlook 2007, Energy Information Administration (<http://www.eia.doe.gov/oiaf/ieo/index.html>)
4. J.O.M. Bockris, S. Srinivasan, *Fuel Cells: Their Electrochemistry* (McGraw-Hill, New York, 1969)
5. J.M. Ogden, M.M. Steinbugler, T.G. Kreutz, J. Power Sources **79**, 143 (1999)
6. A.E. Farrell, R.J. Plevin, B.T. Turner, A.D. Jones, M. O'Hara, D.M. Kammen, Science **311**, 506 (2006)
7. L.O. Williams, *Hydrogen Power* (Pergamon Press, Oxford, 1980), Chap. 6
8. A.C. Dillon, K.E.H. Gilbert, P.A. Parilla, J.L. Alleman, G.L. Hornyak, K.M. Jones, M.J. Heben, Proc. 2002 U.S. DOE Hydrogen Program Rev. CP-610-32405, 2002
9. K. Kordesch, G. Simader, *Fuel Cells and Their Applications* (VCH, Weinheim, 1996), Chap. 3
10. J.P. Collman, R.R. Gagne, T.R. Halbert, J.C. Manchon, C.A. Reed, J. Am. Chem. Soc. **95**, 7868 (1973)
11. D. Ricard, B. Andrioletti, M. L'Her, B. Boitrel, Chem. Commun, 1999, 1523 (1999)

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