
Contents

Preface	V
List of Contributors	XVII
List of Abbreviations	XXI
1 Historical Overview and Fundamental Aspects of Molecular Catalysts for Energy Conversion	
<i>T. Okada, T. Abe, and M. Kaneko</i>	1
1.1 Introduction: Why Molecular Catalysts? A New Era of Biomimetic Approach Toward Efficient Energy Conversion Systems.....	1
1.2 Molecular Catalysts for Fuel Cell Reactions	2
1.2.1 Oxygen Reduction Catalysts	3
1.2.2 Fuel Oxidation Catalysts	13
1.3 Molecular Catalysts for Artificial Photosynthetic Reaction	17
1.3.1 Water Oxidation Catalyst	18
1.3.2 Reduction Catalyst	18
1.3.3 Photodevices for Photoinduced Chemical Reaction in the Water Phase	25
1.4 Summary	29
References	30
2 Charge Transport in Molecular Catalysis in a Heterogeneous Phase	
<i>M. Kaneko and T. Okada</i>	37
2.1 Introduction	37
2.2 Charge Transport (CT) by Molecules in a Heterogeneous Phase ..	38
2.2.1 General Overview	38
2.2.2 Mechanism of Charge Transport	39
2.3 Charge Transfer by Molecules Under Photoexcited State in a Heterogeneous Phase	46

2.3.1	Overview	46
2.3.2	Mechanism of Charge Transfer at Photoexcited State in a Heterogeneous Phase	47
2.4	Charge Transfer and Electrochemical Reactions in Metal Complexes	50
2.4.1	Charge Transfer in Metal Complexes	50
2.4.2	Charge Transfer at Electrode Surfaces	53
2.4.3	Oxygen Reduction Reaction at Metal Macrocycles	55
2.5	Proton Transport in Polymer Electrolytes	59
2.5.1	Proton Transfer Reactions	59
2.5.2	Proton Transport in Polymer Electrolytes	60
2.6	Summary	62
	References	63
3 Electrochemical Methods for Catalyst Evaluation in Fuel Cells and Solar Cells		
	<i>T. Okada and M. Kaneko</i>	67
3.1	Introduction	67
3.2	Electrochemical Measuring System for Catalyst Research in Fuel Cells	68
3.2.1	Reference Electrode	68
3.2.2	Rotating Ring-Disk Electrode	69
3.2.3	Gas Electrodes of Half-Cell Configuration	74
3.2.4	Fuel Cell Test Station	76
3.2.5	Electrochemical Methods for Electrocatalysts	79
3.3	Electrochemical Measuring System for Heterogeneous Charge Transport and Solar Cells	86
3.3.1	Testing Method of Charge Transport in Heterogeneous Systems	86
3.3.2	Evaluation of Charge Transport by Redox Molecules Incorporated in a Heterogeneous Phase	88
3.3.3	AC Impedance Spectroscopy to Evaluate Charge Transport, Conductivity, Double-Layer Capacitance, and Electrode Reaction	89
3.3.4	I-V Characteristics of Solar Cells	93
3.3.5	Impedance Spectroscopy to Evaluate Multistep Charge Transport of a Dye-Sensitized Solar Cell	94
3.4	Summary	97
	References	101
4 Molecular Catalysts for Fuel Cell Anodes		
	<i>T. Okada</i>	103
4.1	Introduction	103
4.2	Concept of Composite Electrocatalysts in Fuel Cells	105
4.3	Methanol Oxidation Reaction	107

4.3.1	Mechanism of Methanol Oxidation Reaction	107
4.3.2	New Electrocatalysts for Methanol Oxidation Reaction	108
4.3.3	Structure of Composite Catalysts	112
4.4	Formic Acid Oxidation Reaction	118
4.4.1	Mechanism of Formic Acid Oxidation	118
4.4.2	Formic Acid Oxidation on Composite Catalysts	119
4.5	CO-Tolerant Electrocatalysts for Hydrogen Oxidation Reaction	123
4.5.1	Electrochemical and Fuel Cell Testing	123
4.5.2	Durability Testing	127
4.5.3	Structural Characterization	127
4.6	Summary	134
	References	134
5 Macrocycles for Fuel Cell Cathodes		
	<i>K. Oyaizu, H. Murata, and M. Yuasa</i>	139
5.1	Introduction	139
5.2	Molecular Design of Macrocycles for Fuel Cell Cathodes	141
5.3	Diporphyrin Cobalt Complexes and Related Catalysts	142
5.3.1	Diporphyrin Cobalt Complexes	142
5.3.2	Polypyrrole Cobalt Complexes	144
5.3.3	Cobalt Thienylporphyrins	149
5.4	Porphyrin Assemblies Based on Intermolecular Interaction	153
5.5	Multinuclear Complexes as Electron Reservoirs	158
5.6	Summary	159
	References	160
6 Platinum-Free Catalysts for Fuel Cell Cathode		
	<i>N. Koshino and H. Higashimura</i>	163
6.1	Introduction	163
6.2	Drawbacks of Using Pt as Catalysts in PEFC	164
6.3	Mechanistic Aspects of Oxygen Reduction by Cathode Catalyst	165
6.4	Platinum-Free Catalysts for Fuel Cell Cathode	166
6.4.1	Metal Particles	167
6.4.2	Metal Oxides, Carbides, Nitrides, and Chalcogenides	168
6.4.3	Carbon Materials	171
6.4.4	Metal Complex-Based Catalysts	172
6.4.5	Catalysts Designed from Dinuclear Metal Complexes	177
6.5	Summary	180
	References	181
7 Novel Support Materials for Fuel Cell Catalysts		
	<i>J. Nakamura</i>	185
7.1	Introduction	185
7.2	Performance of Electrocatalysts Using Carbon Nanotubes	187
7.2.1	H ₂ -O ₂ Fuel Cell	187

7.2.2	DMFC	191
7.3	Why Is Carbon Nanotube So Effective as Support Material?	194
	References	197

8 Molecular Catalysts for Electrochemical Solar Cells and Artificial Photosynthesis

<i>M. Kaneko</i>		199
8.1	Introduction	199
8.2	Overview on Principles of Molecule-Based Solar Cells	200
8.2.1	Photon Absorption	201
8.2.2	Suppression of Charge Recombination to Achieve Effective Charge Separation	201
8.2.3	Diffusion of Separated Charges	202
8.2.4	Electrode Reaction	202
8.3	Dye-Sensitized Solar Cell (DSSC)	202
8.4	Artificial Photosynthesis	208
8.5	Dark Catalysis for Artificial Photosynthesis	211
8.5.1	Dark Catalysis for Water Oxidation	212
8.5.2	Dark Catalysis for Proton Reduction	213
8.6	Conclusion and Future Scopes	213
	References	214

9 Molecular Design of Sensitizers for Dye-Sensitized Solar Cells

<i>K. Hara</i>		217
9.1	Introduction	217
9.2	Metal-Complex Sensitizers	219
9.2.1	Molecular Structures of Ru-Complex Sensitizers	219
9.2.2	Electron-Transfer Processes	224
9.2.3	Performance of DSSCs Based on Ru Complexes	226
9.2.4	Other Metal-Complex Sensitizers for DSSCs	229
9.3	Porphyrins and Phthalocyanines	230
9.4	Organic Dyes	231
9.4.1	Molecular Structures of Organic-Dye Sensitizers for DSSCs	231
9.4.2	Performance of DSSCs Based on Organic Dyes	236
9.4.3	Electron Transfer from Organic Dyes to TiO ₂	237
9.4.4	Electron Diffusion Length	240
9.5	Stability	242
9.5.1	Photochemical and Thermal Stability of Sensitizers	242
9.5.2	Long-Term Stability of Solar-Cell Performance	243
9.6	Summary and Perspectives	244
	References	245

10 Fabrication of Charge Carrier Paths for High Efficiency Cells	
<i>T. Kogo, Y. Ogomi, and S. Hayase</i>	251
10.1 Introduction	251
10.2 Fabrication of Electron-Paths	252
10.3 Suppression of Black-Dye Aggregation in a Pressurized CO ₂ Atmosphere	255
10.4 Two-Layer TiO ₂ Structure for Efficient Light Harvesting	256
10.5 TCO-Less All-Metal Electrode-Type DSC	257
10.6 Ion-Path in Quasi-Solid Medium	257
10.7 Summary	260
References	260
11 Environmental Cleaning by Molecular Photocatalysts	
<i>D. Wöhrle, M. Kaneko, K. Nagai, O. Suvorova, and R. Gerdes</i>	263
11.1 Introduction	263
11.2 Oxidative Methods for the Photodegradation of Pollutants in Wastewater	264
11.2.1 Comparison of Different Methods of UV Processes for Water Cleaning	264
11.2.2 Photodegradation of Pollutants with Oxygen in the Visible Region of Light	268
11.3 Visible Light Decomposition of Ammonia to Nitrogen with Ru(bpy) ₃ ²⁺ as Sensitizer	287
11.3.1 Nitrogen Pollutants and Their Photodecomposition	287
11.3.2 Photochemical Electron Relay with Ammonia	287
11.3.3 Photochemical Decomposition of Ammonia to Dinitrogen by a Photosensitized Electron Relay	290
11.4 Visible Light Responsive Organic Semiconductors as Photocatalysts	291
11.4.1 Photoelectrochemical Character of Organic Semiconductors in Water Phase	291
11.4.2 Photoelectrochemical Oxidations by Irradiation with Visible Light	292
11.4.3 Photochemical Decomposition of Amines Using Visible Light and Organic Semiconductors	293
References	294
12 Optical Oxygen Sensor	
<i>N. Asakura and I. Okura</i>	299
12.1 Introduction	300
12.2 Theoretical Aspect of Optical Oxygen Sensor of Porphyrins	300
12.2.1 Advantage of Optical Oxygen Sensing	300
12.2.2 Principle of Optical Oxygen Sensor	301
12.2.3 Brief History of Optical Oxygen Sensors	303

12.3	Optical Oxygen Sensor by Phosphorescence Intensity	304
12.3.1	Phosphorescent Compounds	304
12.3.2	Immobilization of Phosphorescent Molecules for Optical Oxygen Sensor and Measurement System	304
12.3.3	Optical Oxygen Sensor with Platinum Octaethylporphyrin Polystyrene Film (PtOEP-PS Film)	307
12.3.4	Optical Oxygen Sensor with PtOEP and Supports	309
12.3.5	Application of Optical Oxygen Sensor for Air Pressure Measurements	311
12.4	Optical Oxygen Sensor by Phosphorescence Lifetime Measurements	313
12.4.1	Advantages of Phosphorescence Lifetime Measurement	313
12.4.2	Phosphorescence Lifetime Measurement	314
12.4.3	Distribution of Oxygen Concentration Inside Single Living Cell by Phosphorescence Lifetime Measurement	315
12.5	Optical Oxygen Sensor T–T Absorption	318
12.5.1	Advantage of Optical Oxygen Sensor Based on T–T Absorption	320
12.5.2	Optical Oxygen Sensor Based on the Photoexcited Triplet Lifetime Measurement	320
12.5.3	Optical Oxygen Sensor Based on Stationary T–T Absorption (Stationary Quenching)	325
12.6	Summary	327
	References	327
13 Adsorption and Electrode Processes		
	<i>H. Shiroishi</i>	329
13.1	Introduction	329
13.2	Adsorption Isotherms and Kinetics	330
13.2.1	Langmuir Isotherms	330
13.2.2	Freundlich Isotherm	332
13.2.3	Temkin Isotherm	332
13.2.4	Application for Selective Reaction on Metal Surface by Adsorbate	334
13.3	Slab Optical Waveguide Spectroscopy	339
13.3.1	Principle	340
13.3.2	Application of Slab Optical Waveguide Spectroscopy	342
13.4	Methods of Digital Simulation for Electrochemical Measurements	344
13.4.1	Formulation of Electrochemical System	344
13.4.2	Finite Differential Methods	351
13.5	Digital Simulation for Polymer-Coated Electrodes	354
13.5.1	Hydrostatic Condition	355
13.5.2	Hydrodynamic Condition	357

13.6 Classical Monte Carlo Simulation for Charge Propagation in Redox Polymer	358
13.6.1 Visualization of Charge Propagation	359
13.6.2 Determination of a Charge Hopping Distance	361
References	363
14 Spectroscopic Studies of Molecular Processes on Electrocatalysts	
<i>A. Kuzume and M. Ito</i>	367
14.1 Introduction	367
14.2 The Preparation and Spectroscopic Characterization of Fuel Cell Catalysts	369
14.2.1 Catalyst Preparation by Electroless Plating and Direct Hydrogen Reduction Methods: Practical Application for High Performance PEFC	369
14.2.2 In Situ IRAS Studies of Methanol Oxidation on Fuel Cell Catalysts	377
14.3 Spectroscopic Studies of Methanol Oxidation on Pt Surfaces	382
14.3.1 Electrooxidation of Methanol on Pt(111) in Acid Solutions: Effects of Electrolyte Anions during Electrocatalytic Reactions	382
14.3.2 Methanol Oxidation Mechanisms on Pt(111) Surfaces	388
14.4 Conclusions	392
References	393
15 Strategies for Structural and Energy Calculation of Molecular Catalysts	
<i>S. Tsuzuki and M. Saito</i>	395
15.1 Introduction	395
15.2 Computational Methods	396
15.3 Basis Set and Electron Correlation Effects on Geometry and Conformational Energy	397
15.4 Intermolecular Forces	397
15.5 Basis and Electron Correlation Effects on Intermolecular Interactions	398
15.6 Calculations of Transition Metal Complexes	402
15.7 Examples of the Ab Initio Calculation for Molecular Catalysts ...	402
15.8 Summary	409
References	409
16 Future Technologies on Molecular Catalysts	
<i>T. Okada and M. Kaneko</i>	411
16.1 Introduction	411
16.2 Road Map for Clean Energy Society	412
16.3 Hydrogen Production	415
16.3.1 Natural Gas	415

XVI Contents

16.3.2 Renewable Energy Source	415
16.3.3 Biomass	417
16.4 Hydrogen Utilization	418
16.4.1 Hydrogen Storage	419
16.4.2 Energy Conversion	419
16.5 Biomimetic Approach and Role of Molecular Catalysts for Energy-Efficient Utilization	420
16.6 Summary	421
References	422
Index	423