Contents

Preface *XIII*
List of Contributors *XV*

1 **Electrocatalysts for Acid Proton Exchange Membrane (PEM) Fuel Cells – an Overview** *1*
Michael Bron
1.1 Introduction *1*
1.2 Acid PEM Fuel Cell Background and Fundamentals *2*
1.2.1 Acid PEM Fuel Cell Overview – History, Status, and Advantages *2*
1.2.2 Acid PEM Fuel Cell Reactions – Thermodynamics and Kinetics *4*
1.3 Acid PEM Fuel Cell Catalysis for Cathode O_2 Reduction Reaction *9*
1.3.1 Electrochemical Thermodynamics of O_2 Reduction Reaction *10*
1.3.2 Pt-Based Catalysts for the Oxygen Reduction Reaction *10*
1.3.3 Electrochemical Kinetics and Mechanism of the O_2 Reduction Reaction Catalyzed by Pt Catalysts *16*
1.4 Catalyst Challenges and Perspective in Acid PEM Fuel Cells *18*
1.4.1 Pt Catalyst Cost Analysis and Major Challenges *18*
1.4.2 Sustainability *19*
1.4.3 Major Technical Challenges for Non-noble Metal Catalysts and Mitigation Strategies *19*
1.4.4 Non-noble Metal Catalyst Overview *20*
1.5 Conclusion *22*
References *22*

2 **Heat-Treated Transition Metal-N_xC_y Electrocatalysts for the O_2 Reduction Reaction in Acid PEM Fuel Cells** *29*
Frédéric Jaouen
2.1 Introduction *29*
2.1.1 Why the Search for Non-precious Metal Catalysts for O_2 Reduction? *29*
2.1.2 Activity, Power Performance, and Durability Constraints on Me/N/C Catalysts *33*
2.1.3 Milestones Achieved by Me/N/C Catalysts over the Last 50 Years *37*

2.1.3.1 Milestone 1 37
2.1.3.2 Milestone 2 38
2.1.3.3 Milestone 3 39
2.1.3.4 Milestone 4 39
2.1.3.5 Milestone 5 39
2.2 Synthesis Approaches for Heat-Treated Me/N/C Catalysts 40
2.2.1 The Supported-Macrocycle Approach 41
2.2.2 The Templating Method 42
2.2.3 The Foaming Agent Approach 43
2.2.4 The N Molecule or Metal–Ligand Approach 45
2.2.5 The N–Polymer Approach 48
2.2.6 Gaseous N-Precursor Approach (NH_3 and CH_3CN) 50
2.2.7 Thermally Decomposable Metal-Organic Frameworks (MOF) 52
2.3 Important Parameters for Highly Active Me/N/C Catalysts 54
2.3.1 Pyrolysis Temperature 54
2.3.1.1 Metal Macrocycles Supported on Carbon and Pyrolyzed in Inert Atmosphere 54
2.3.1.2 Separate Metal and Nitrogen Precursors or Metal–Ligand Complexes Impregnated on a Carbon Support and Pyrolyzed in Inert or Reactive Atmosphere 56
2.3.2 The Transition Metal 57
2.3.2.1 Binary Metal Catalysts 58
2.3.2.2 Metal Concentration 59
2.3.3 The Nitrogen Content and Speciation by X-ray Photoelectron Spectroscopy (XPS) 61
2.3.4 The Carbon Support/Host 64
2.4 Nature of the Active Sites 73
2.4.1 Time-of-Flight Secondary Ion Mass Spectroscopy 73
2.4.2 X-ray Absorption Spectroscopy and Extended X-ray Absorption Fine Structure 75
2.4.2.1 Studies on Pyrolyzed Macrocycles 76
2.4.2.2 Studies on Catalysts Synthesized from Separate Metal, N and C Precursors 77
2.4.3 Mössbauer Spectroscopy 79
2.4.3.1 Studies on FePc and Fe- Porphyrin, Unpyrolyzed or Pyrolyzed at $T < 500\,°C$ 80
2.4.3.2 Studies on Fe Macrocycles Pyrolyzed at $T \geq 700\,°C$ 81
2.4.3.3 Studies on Fe–N–C Catalysts Obtained by Pyrolysis of Separate Fe, N, and C Precursors 85
2.4.4 Turnover Frequency and Site Density 91
2.5 Electrochemical Investigation by RDE/RRDE Methods 94
2.5.1 RDE and the Thin Film Problem: Model and Experiment 94

2.5.2 Activity for H_2O_2 Reduction or Oxidation: a Major Difference from Pt-Based Catalysts 99
2.5.3 The pH Effect: Another Look at the Turnover Frequency of Different Active Sites 103
2.6 Conclusions 105
Acronyms 106
Acknowledgments 106
References 107

3 Modified Carbon Materials for O_2 Reduction Reaction Electrocatalysts in Acid PEM Fuel Cells *119*
Deepika Singh, Jesaiah King, and Umit S. Ozkan
3.1 Introduction 119
3.2 Doped Carbon Materials 119
3.2.1 Nitrogen-Doped Carbons 121
3.2.1.1 N-Doped CNTs and CNFs 122
3.2.1.2 N-Doped Fullerene 124
3.2.1.3 Carbon Nitrides 124
3.2.1.4 Graphitic Carbon Nitride 125
3.2.1.5 N-Doped Graphene 125
3.2.2 Doping with Other Heteroatoms 127
3.3 Doped Carbons as ORR Catalysts 130
3.3.1 Nitrogen-Doped Carbon Materials Prepared without a Metal 139
3.4 Conclusions 140
Acknowledgment 141
References 141

4 Transition Metal Chalcogenides for Oxygen Reduction Electrocatalysts in PEM Fuel Cells *157*
Kunchan Lee, Nicolas Alonso-Vante, and Jiujun Zhang
4.1 Introduction 157
4.2 Non-noble Metal Chalcogenide Electrocatalysts for Oxygen Reduction Reaction 160
4.3 Synthesis Methods for Non-noble Metal Chalcogenides 163
4.3.1 Nonorganic Solvent Methods 164
4.3.2 Organic Solvent Methods at Low Temperature 165
4.4 Oxygen Reduction Reaction on Non-noble Metal Chalcogenides 168
4.4.1 Mechanism of Oxygen Reduction Reaction 168
4.4.2 Theoretical Approach for ORR Mechanism 172
4.5 Methanol Tolerance 175
4.6 Fuel Cell Measurements 177
4.7 Conclusions 178
References 179

5 Transition Metal Oxides, Carbides, Nitrides, Oxynitrides, and Carbonitrides for O_2 Reduction Reaction Electrocatalysts for Acid PEM Fuel Cells *183*
Akimitsu Ishihara, Hideto Imai, and Ken-ichiro Ota
5.1 Introduction *183*
5.2 Transition Metal Nitrides and Carbonitrides as Cathode Catalysts *185*
5.3 Stability of Oxides in Acid Electrolyte *186*
5.4 Non-noble Metal Oxide-Based Cathode Catalysts *187*
5.4.1 Stability of Group 4 and 5 Metal Oxide-Based Catalysts *187*
5.4.2 Formation of Complex Oxide Layer Containing Active Sites *188*
5.4.3 Substitutional Doping of Nitrogen *189*
5.4.4 Creation of Oxygen Defects without Using Carbon and Nitrogen *191*
5.4.5 Oxidation of Compounds Including Carbon and Nitrogen *193*
5.4.6 Performance of Single Cell with Oxide-Based Cathodes *197*
5.5 Conclusions *198*
Acknowledgments *198*
References *199*

6 Theoretical Modeling of Non-noble Metal Electrocatalysts for Acid and Alkaline PEM Fuel Cells *205*
Eben Dy and Zheng Shi
6.1 Introduction *205*
6.2 Mechanisms of ORR *205*
6.2.1 Role of the Catalyst *206*
6.2.2 Effect of pH *208*
6.3 Simple Metal–N_4 Macrocycles *212*
6.4 Heat-Treated Transition Metal Nitrogen–Carbon Precursors (M-N_x/C) *216*
6.5 Functionalized Graphitic Materials *221*
6.5.1 Doped Graphene Materials *222*
6.5.2 Doped Carbon Nanotube Materials *227*
6.5.3 Metal-Functionalized Graphene Materials *229*
6.6 Conducting Polymers *232*
6.7 Outlook *235*
References *236*

7 Membranes for Alkaline Polyelectrolyte Fuel Cells *243*
Jing Pan, Chen Chen, and Lin Zhuang
7.1 Introduction *243*
7.2 Two Main Challenges of APEs *244*
7.2.1 Pursuing High Conductivity as well as Low Swelling Degree *244*
7.2.2 High Chemical Stabilities of Cation Groups *244*
7.3 APEs Reported in the Literature *245*
7.3.1 Heterogeneous APE Membranes *246*

7.3.1.1 Ion-Solvating Polymers 246
7.3.1.2 Organic–Inorganic Hybrid APE Membranes 247
7.3.1.3 Composite APE Membrane 248
7.3.2 Homogeneous APE Membranes 249
7.3.2.1 Film-Modified APEs 249
7.3.2.2 Polymer-Modified APEs 250
7.3.2.3 Monomer-Polymerized APE 250
7.4 Strategies for Improving the Ionic Conductivity of APE 254
7.5 Efforts of Improving the Chemical Stability of the Cationic Functional Group 258
7.5.1 Cationic Groups with Conjugated Structure 258
7.5.2 Cationic Groups with Strong Electron Donor 260
7.6 Research on the Chemical Stability of APE Backbone 261
7.7 Conclusions and Perspective 261
References 264

8 Electrocatalysts for Alkaline Polymer Exchange Membrane (PEM) Fuel Cells – Overview *271*
Rongzhong Jiang and Deryn Chu
8.1 Introduction 271
8.2 Alkaline Fuel Cell Overview – History, Status, and Advantages 272
8.3 Alkaline Fuel Cell and Alkaline PEM Fuel Cell – Thermodynamics and Kinetics 274
8.3.1 Thermodynamics of H_2/O_2 Fuel Cell Reactions in Alkaline Electrolyte 274
8.3.2 Kinetics of O_2 Reduction in Alkaline Fuel Cells 276
8.3.3 Mechanisms of Oxygen Reduction at Noble Metal Surface 279
8.3.4 Mechanisms of Oxygen Reduction at Non-noble Metal Surface 282
8.3.5 Kinetics and Mechanisms of H_2 Oxidation 284
8.4 Silver-Based Materials for Cathode Electrocatalysts in Alkaline PEM Fuel Cells 286
8.4.1 Starting Materials and Synthesis Strategies for Silver-Based Electrocatalysts 287
8.4.1.1 Chemical Synthesis of Powder Ag Catalysts 288
8.4.1.2 Some Synthetic Methods for Porous Ag Membranes and Porous Electrodes 291
8.4.2 Physical and Electrochemical Characterizations 291
8.4.2.1 X-ray Powder Diffraction (XRD) 291
8.4.2.2 X-ray Photoelectron Spectroscopy (XPS) 293
8.4.2.3 Transmission Electron Microscopy (TEM) 293
8.4.2.4 Electrochemical Method 295
8.4.3 Silver-Based Catalysts for Alkaline PEM Fuel Cells 297
8.5 Catalysts for Oxidation of a Broad Range of Fuels for Alkaline PEM Fuel Cells 298
8.5.1 Non-carbon Fuels and Specific Catalysts for Their Oxidation 298

8.5.1.1 Hydrogen *298*
8.5.1.2 Borohydride *298*
8.5.1.3 Hydrazine *299*
8.5.1.4 Ammonia *299*
8.5.1.5 Sulfide *300*
8.5.2 Single-Carbon Organic Fuels and Specific Catalysts for Their Oxidation *300*
8.5.2.1 Methanol *300*
8.5.2.2 Formaldehyde *301*
8.5.2.3 Formic Acid *301*
8.5.3 Organic Fuels Containing Carbon–Carbon (C–C) Bond in the Molecules and Specific Catalysts for Their Oxidation *302*
8.5.3.1 Ethanol *302*
8.5.3.2 Ethylene Glycol and Dimethyl Ether *303*
8.5.3.3 Other Organic Fuels Containing Two or More C–C Bonds in Their Molecules *305*
8.5.4 Electrochemical Kinetics and Mechanisms of Fuel Electrooxidation in Alkaline Media *305*
8.6 Major Challenges of Alkaline Fuel Cells and Alkaline PEM Fuel Cells *307*
Acknowledgments *309*
References *309*

9 Carbon Composite Cathode Catalysts for Alkaline PEM Fuel Cells *319*
Qing Li and Gang Wu
9.1 Introduction *319*
9.2 Metal-Free Carbon Catalysts *321*
9.2.1 Nitrogen Doping into Carbon *322*
9.2.2 Nitrogen-Doped Carbon Nanotube Catalysts *324*
9.2.3 Nitrogen-Doped Graphene Catalysts *325*
9.2.4 Other Heteroatom-Doped Carbon Catalysts *328*
9.3 Heat-Treated M–N–C (M: Fe, Co) Carbon Composite Catalysts *330*
9.3.1 Heating Temperatures *330*
9.3.2 Type of Transition Metals *332*
9.3.3 Nitrogen Precursors *333*
9.4 Nanocarbon/Transition Metal Compound Hybrid Catalysts *336*
9.4.1 Nanocarbon/Metal Oxides Hybrid Catalysts *337*
9.4.2 Carbon/Metal Chalcogenide Hybrid Catalysts *341*
9.4.3 Nanocarbon/Macrocycle Compound Catalysts *342*
9.5 ORR Mechanism on NPMCs in Alkaline Media *344*
9.6 NPMC Cathode Performance in Anion Exchange Membrane Fuel Cell *346*
9.7 Summary and Perspective *348*
References *349*

10 Non-precious Metal Oxides and Metal Carbides for ORR in Alkaline-Based Fuel Cells *357*
Wenling Chu, Drew Higgins, Zhongwei Chen, and Rui Cai
10.1 Introduction *357*
10.2 Metal Oxides *359*
10.2.1 Manganese Oxides *360*
10.2.2 Other Metal Oxides *362*
10.3 Perovskite-Type Oxides *364*
10.3.1 Effect of A- and B-Site Cations *365*
10.3.2 Effect of Preparation Methods *368*
10.3.3 Durability of Perovskite-Type Oxides *370*
10.3.4 Design Principles for ORR Activity on Perovskite-Type Oxides *371*
10.4 Spinel-Type Oxides *372*
10.5 Metal Carbides *377*
10.6 Conclusion and Outlook *379*
References *380*

11 Automotive Applications of Alkaline Membrane Fuel Cells *389*
Hirohisa Tanaka, Koichiro Asazawa, and Tomokazu Sakamoto
11.1 Introduction *389*
11.2 History of Alkaline Fuel Cells in Automotive Applications *392*
11.3 Fuel Used in Modern Alkaline PEM Fuel Cells in Automotive Applications *395*
11.4 Components of an Alkaline PEM Fuel Cell Membrane Electrode Assembly for Automotive Applications *398*
11.4.1 Anode Catalysts for the Direct Hydrazine Fuel Cell Vehicle *398*
11.4.2 Cathode Catalysts *404*
11.4.3 MEA Performance Using Non-noble Metal Catalysts *407*
11.5 Major Challenges to Overcome in Alkaline PEM Fuel Cells *414*
11.6 Conclusion *416*
Acknowledgments *417*
References *418*

Index *423*