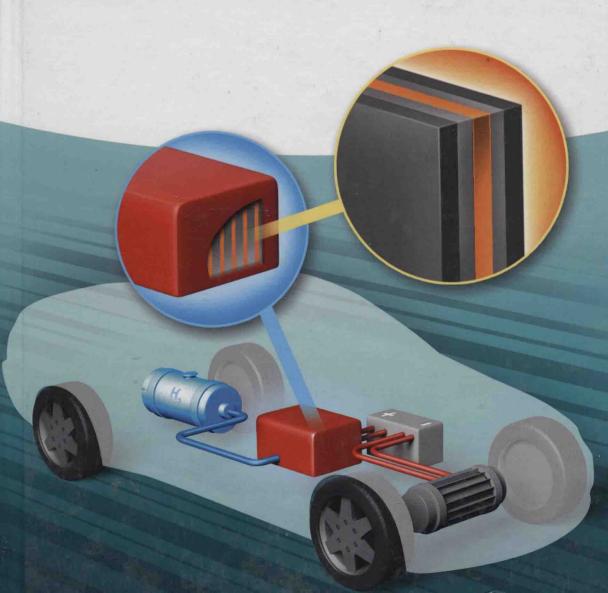
Edited by Zhongwei Chen, Jean-Pol Dodelet,

# Non-Noble Metal Fuel Cell Catalysts



Edited by Zhongwei Chen, Jean-Pol Dodelet, and Jiujun Zhang

## Non-Noble Metal Fuel Cell Catalysts





#### Editors

#### Prof. Zhongwei Chen

University of Waterloo Dept. of Chem. Engineering 200 University Avenue West N2L 3G1 NK Canada

#### Prof. Jean-Pol Dodelet

INRS
Energie, Matériaux et Télécommunications
Boulevard Lionel Boulet 1650
J3X 1S2 NK
Canada

#### Dr. Jiujun Zhang

National Res. Council Canada Inst. for Fuel Cell Innovation Westbrook Mall 4250 V6T 1W5 NK Canada All books published by Wiley-VCH are carefully produced. Nevertheless, authors, editors, and publisher do not warrant the information contained in these books, including this book, to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

#### Library of Congress Card No.: applied for

#### British Library Cataloguing-in-Publication

A catalogue record for this book is available from the British Library.

### Bibliographic information published by the Deutsche Nationalbibliothek

The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <a href="http://dnb.d-nb.de">http://dnb.d-nb.de</a>.

© 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Boschstr. 12, 69469 Weinheim, Germany

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form — by photoprinting, microfilm, or any other means — nor transmitted or translated into a machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

Print ISBN: 978-3-527-33324-0 ePDF ISBN: 978-3-527-66493-1 ePub ISBN: 978-3-527-66492-4 mobi ISBN: 978-3-527-66491-7 oBook ISBN: 978-3-527-66490-0

Cover-Design Formgeber, Mannheim, Germany Typesetting Laserwords Private Limited, Chennai, India Printing and Binding Markono Print Media Pte Ltd, Singapore

Printed on acid-free paper

Edited by Zhongwei Chen, Jean-Pol Dodelet, and Jiujun Zhang

Non-Noble Metal Fuel Cell Catalysts

#### Related Titles

Jiang, S. P., Yan, Y. (eds.)

#### Materials for High-Temperature Fuel Cells

Series: Materials for Sustainable Energy and Development Series edited by Lu, G. Q. M.

2013

ISBN: 978-3-527-33041-6

Stolten, D., Emonts, B. (eds.)

#### Fuel Cell Science and Engineering

Materials, Processes, Systems and Technology 2 Volumes

2012

ISBN: 978-3-527-33012-6

Park, J.-K. (ed.)

# Principles and Applications of Lithium Secondary Batteries

2012

ISBN: 978-3-527-33151-2

Zhang, J., Zhang, L., Liu, H., Sun, A., Liu, R.-S. (eds.)

# Electrochemical Technologies for Energy Storage and Conversion

2011

ISBN: 978-3-527-32869-7

Daniel, C., Besenhard, J. O. (eds.)

#### Handbook of Battery Materials

Second, Completely Revised and Enlarged Edition

2 Volumes

2011

ISBN: 978-3-527-32695-2

Aifantis, K. E., Hackney, S. A., Kumar, R. V. (eds.)

# High Energy Density Lithium Batteries

Materials, Engineering, Applications

2010

ISBN: 978-3-527-32407-1

Liu, H., Zhang, J. (eds.)

#### Electrocatalysis of Direct Methanol Fuel Cells

From Fundamentals to Applications

2009

ISBN: 978-3-527-32377-7

#### Preface

In the context of economic development and improvement in human living conditions, developing advanced technologies for energy storage and conversion has become a hot topic today. Polymer electrolyte membrane (PEM) fuel cells are one kind of important clean energy-converting devices that have drawn a great deal of attention in recent years due to their high efficiency, high energy density, and low or zero emissions, as well as their several important areas of application such as transportation, stationary and portable power, and micro-power. However, two major technical challenges, namely, high cost and low reliability/durability, have been identified as the major obstacles hindering the commercialization of PEM fuel cells. Fuel cell catalysts, such as platinum (Pt)-based catalysts and their associated catalyst layers, are the major factors related to these challenges. To overcome the challenges, exploring new catalysts, improving catalyst activity and stability/durability, and reducing catalyst cost are currently the major approaches in fuel cell technology and commercialization.

Regarding the cost reduction of Pt-based catalysts, non-noble metal catalysts, the next generation PEM fuel cell catalysts slated to replace expensive Pt, have been recognized as the sustainable solution for the commercialization of PEM fuel cells. In more recent years, intensified research and development in this area has been carried out by the world fuel cell community. To facilitate this effort, a book specifically focusing on this area is definitely necessary. This book contains comprehensive and systematic information on non-noble metal electrocatalysts for oxygen reduction reactions in both acid and alkaline PEM fuel cells with emphasis on (i) the fundamentals of electrochemical oxygen reduction catalysis with non-noble metal catalysts within acid and alkaline PEM fuel cells; (ii) the synthesis, characterization, activity validation, and modeling of various kinds of non-noble metal electrocatalysts; and (iii) the integration of the non-noble metal electrocatalysts into fuel cells and validation of their performance.

This book is written by a group of top scientists in the field of fuel cell catalysts, who not only have excellent academic records but also industrial expertise in the use of fuel cells. The book contains the latest updated information on R&D achievements and understanding in electrocatalysts for oxygen reduction reactions in both acid and alkaline PEM fuel cells. Some important R&D directions toward commercialization of both types of fuel cells are also discussed. In order to help readers understand the science and technology

of the fuel cell catalysis, some important and representative figures, tables, photographs, and a comprehensive list of reference papers are presented in this book.

We believe that this book should be extremely useful to researchers and engineers who are working in energy/fuel cell industries. We sincerely hope that through reading this book, the reader will easily be able to locate the latest information on the fundamentals and applications of the catalysis of the oxygen reduction reaction in the next generation of fuel cells. It is expected that this book could be used as a reference for college/university students including undergraduates and graduates, and scientists and engineers who work in the areas of energy, electrochemistry science/technology, fuel cells, and electrocatalysis.

We would like to acknowledge with deep appreciation all of the efforts of all the contributors in writing their chapters. We also wish to thank Dr. Heike Nöthe, Senior Project Editor at STMS Books for extensive help and support.

If technical errors are found in this book, we and all the contributors would deeply appreciate the readers' constructive comments for correction and further improvement.

January 2014

Dr. Zhongwei Chen, Waterloo, Ontario, Canada Dr. Jean-Pol Dodelet Montreal, Quebec, Canada Dr. Jiujun Zhang Vancouver, British Columbia, Canada

#### List of Contributors

#### Nicolas Alonso-Vante

IC2MP-CNRS 7285 University of Poitiers 4 Michel Brunet Street 86022 Poitiers France

#### Koichiro Asazawa

Daihatsu Motor Co., Ltd.
Frontier technology R&D
Department
R&D Division
3000 Yamanoue
Ryuo
Gamo
Shiga 520-2593
Japan

#### Michael Bron

Martin Luther University Halle-Wittenberg Faculty of Natural Sciences II Department of Chemistry von-Danckelmann-Platz 4 06120 Halle Germany

#### Rui Cai

Chinese Academy of Sciences State Key Laboratory of Catalysis Dalian Institute of Chemical Physics 457 Zhongshan Road Dalian 116023 China

#### Chen Chen

Wuhan University College of Chemistry and Molecular Sciences Luojia Hill Street Wu Chang Wuhan 430072 China

#### Zhongwei Chen

University of Waterloo
Department of Chemical
Engineering
Waterloo Institute for
Nanotechnology
Waterloo Institute for Sustainable
Energy
200 University Avenue West.
Waterloo
Ontario
N2L 3G1
Canada

#### Deryn Chu

U.S. Army Research Laboratory Sensors and Electron Devices Directorate 2800 Powder Mill Road Adelphi MD 20783-1197 USA

#### Wenling Chu

Chinese Academy of Sciences State Key Laboratory of Catalysis Dalian Institute of Chemical Physics 457 Zhongshan Road Dalian 116023 China

#### Eben Dy

National Research Council Canada Institute for Fuel Cell Innovation 4250 Wesbrook Mall V6T 1W5 Vancouver BC Canada

#### **Drew Higgins**

University of Waterloo Department of Chemical Engineering Waterloo Institute for Nanotechnology Waterloo Institute for Sustainable Energy 200 University Avenue West. Waterloo Ontario N2L 3G1 Canada

#### Hideto Imai

NISSAN ARC Ltd. **Energy-Device Analysis** Department 1 Natsushima Yokosuka Iapan

#### Akimitsu Ishihara

Yokohama National University Green Hydrogen Research Center 79-5 Tokiwadai Hodogaya-ku Yokohama Japan

#### Frédéric Jaouen

Université de Montpellier II Institut Charles Gerhardt Montpellier Laboratory of Aggregates, Interfaces and Materials for Energy CNRS-UMR 5253 2 Place Eugène Bataillon 34095 Montpellier France

#### Rongzhong Jiang

U.S. Army Research Laboratory Sensors and Electron Devices Directorate 2800 Powder Mill Road Adelphi MD 20783-1197 USA

#### Jesaiah King

The Ohio State University Department of Chemical and Biomolecular Engineering Koffolt Laboratories 140 W. 19th Ave. Columbus OH 43210 USA

#### Kunchan Lee

Showa Denko K.K. Institute for Advanced and Core Technology 1-1-1. Ohnodai Midori-ku, Chiba-shi Chiba 267-0056 Japan

#### Qing Li

Materials Physics and Applications Division Los Alamos National Laboratory P.O. Box 1663 Mailstop D429 Los Alamos NM 87545 USA

#### Ken-ichiro Ota

Yokohama National University Green Hydrogen Research Center 79-5 Tokiwadai Hodogaya-ku Yokohama Japan

#### Umit S. Ozkan

The Ohio State University Department of Chemical and Biomolecular Engineering Koffolt Laboratories 140 W. 19th Ave. Columbus OH 43210 USA

#### Jing Pan

Wuhan University College of Chemistry and Molecular Sciences Luojia Hill Street Wu Chang Wuhan, 430072 China

#### Tomokazu Sakamoto

Daihatsu Motor Co., Ltd. Frontier technology R&D Department **R&D** Division 3000 Yamanoue Ryuo Gamo Shiga 520-2593 Japan

#### Zheng Shi

National Research Council Canada Institute for Fuel Cell Innovation 4250 Wesbrook Mall V6T 1W5 Vancouver BC Canada

#### Deepika Singh

The Ohio State University Department of Chemical and Biomolecular Engineering Koffolt Laboratories 140 W. 19th Ave. Columbus OH 43210 USA

#### Hirohisa Tanaka

Daihatsu Motor Co., Ltd. Frontier technology R&D Department R&D Division 3000 Yamanoue Ryuo Gamo Shiga 520-2593 Japan

#### Gang Wu

Materials Physics and Applications Division Los Alamos National Laboratory P.O. Box 1663 Mailstop D429 Los Alamos NM 87545 USA

#### Jiujun Zhang

National Research Council Canada Institute for Fuel Cell Innovation Westbrook Mall 4250 Vancouver BC V6T 1W5 Canada

#### Lin Zhuang

Wuhan University College of Chemistry and Molecular Sciences Luojia Hill Street Wu Chang Wuhan, 430072 China

#### Contents

Preface	XIII	
List of C	ontributors	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 O2 Reduction Reaction 9	
1.3.1	Electrochemical Thermodynamics of O2 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 <sub>2</sub> 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 <sub>x</sub> C <sub>y</sub> Electrocatalysts for the	
	O <sub>2</sub> 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 <sub>2</sub> 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 32	

۷۱	Contents

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 (NH3 and CH3CN) 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 ≥ 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 <sub>2</sub> O <sub>2</sub> 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 <sub>2</sub> 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
1.4	Oxygen Reduction Reaction on Non-noble Metal Chalcogenides 168
4.4.1	Mechanism of Oxygen Reduction Reaction 168
1.4.2	Theoretical Approach for ORR Mechanism 172
4.5	Methanol Tolerance 175
4.6	Fuel Cell Measurements 177
4.7	Conclusions 178
	References 179

VIII	Contents
	l

	Carbonitrides for O <sub>2</sub> 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
3.3	Acknowledgments 198
	References 199
	References 177
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 <sub>4</sub> Macrocycles 212
	Simple Metal-N <sub>4</sub> Macrocycles 212 Heat-Treated Transition Metal Nitrogen-Carbon Precursors
6.3 6.4	Simple Metal $-N_4$ Macrocycles 212 Heat-Treated Transition Metal Nitrogen $-$ Carbon Precursors (M- $N_x$ /C) 216
6.3 6.4 6.5	Simple Metal $-N_4$ Macrocycles 212 Heat-Treated Transition Metal Nitrogen $-$ Carbon Precursors (M- $N_x$ /C) 216 Functionalized Graphitic Materials 221
6.3 6.4 6.5 6.5.1	Simple Metal $-N_4$ Macrocycles 212 Heat-Treated Transition Metal Nitrogen $-$ Carbon Precursors (M- $N_x$ /C) 216 Functionalized Graphitic Materials 221 Doped Graphene Materials 222
6.3 6.4 6.5 6.5.1 6.5.2	Simple Metal $-N_4$ Macrocycles 212 Heat-Treated Transition Metal Nitrogen $-$ Carbon Precursors (M- $N_x$ /C) 216 Functionalized Graphitic Materials 221 Doped Graphene Materials 222 Doped Carbon Nanotube Materials 227
6.3 6.4 6.5 6.5.1 6.5.2 6.5.3	Simple Metal $-N_4$ Macrocycles 212 Heat-Treated Transition Metal Nitrogen $-$ Carbon Precursors (M- $N_x$ /C) 216 Functionalized Graphitic Materials 221 Doped Graphene Materials 222 Doped Carbon Nanotube Materials 227 Metal-Functionalized Graphene Materials 229
6.3 6.4 6.5 6.5.1 6.5.2 6.5.3 6.6	Simple Metal $-N_4$ Macrocycles 212 Heat-Treated Transition Metal Nitrogen $-$ Carbon Precursors (M- $N_x$ /C) 216 Functionalized Graphitic Materials 221 Doped Graphene Materials 222 Doped Carbon Nanotube Materials 227 Metal-Functionalized Graphene Materials 229 Conducting Polymers 232
6.3 6.4 6.5 6.5.1 6.5.2 6.5.3	Simple Metal $-N_4$ Macrocycles 212 Heat-Treated Transition Metal Nitrogen $-$ Carbon Precursors (M- $N_x$ /C) 216 Functionalized Graphitic Materials 221 Doped Graphene Materials 222 Doped Carbon Nanotube Materials 227 Metal-Functionalized Graphene Materials 229 Conducting Polymers 232 Outlook 235
6.3 6.4 6.5 6.5.1 6.5.2 6.5.3 6.6	Simple Metal $-N_4$ Macrocycles 212 Heat-Treated Transition Metal Nitrogen $-$ Carbon Precursors (M- $N_x$ /C) 216 Functionalized Graphitic Materials 221 Doped Graphene Materials 222 Doped Carbon Nanotube Materials 227 Metal-Functionalized Graphene Materials 229 Conducting Polymers 232
6.3 6.4 6.5 6.5.1 6.5.2 6.5.3 6.6 6.7	Simple Metal $-N_4$ Macrocycles 212 Heat-Treated Transition Metal Nitrogen $-$ Carbon Precursors (M- $N_x$ /C) 216 Functionalized Graphitic Materials 221 Doped Graphene Materials 222 Doped Carbon Nanotube Materials 227 Metal-Functionalized Graphene Materials 229 Conducting Polymers 232 Outlook 235 References 236
6.3 6.4 6.5 6.5.1 6.5.2 6.5.3 6.6	Simple Metal—N <sub>4</sub> Macrocycles 212 Heat-Treated Transition Metal Nitrogen—Carbon Precursors (M-N <sub>x</sub> /C) 216 Functionalized Graphitic Materials 221 Doped Graphene Materials 222 Doped Carbon Nanotube Materials 227 Metal-Functionalized Graphene Materials 229 Conducting Polymers 232 Outlook 235 References 236  Membranes for Alkaline Polyelectrolyte Fuel Cells 243
6.3 6.4 6.5 6.5.1 6.5.2 6.5.3 6.6 6.7	Simple Metal—N <sub>4</sub> Macrocycles 212 Heat-Treated Transition Metal Nitrogen—Carbon Precursors (M-N <sub>x</sub> /C) 216 Functionalized Graphitic Materials 221 Doped Graphene Materials 222 Doped Carbon Nanotube Materials 227 Metal-Functionalized Graphene Materials 229 Conducting Polymers 232 Outlook 235 References 236  Membranes for Alkaline Polyelectrolyte Fuel Cells 243 Jing Pan, Chen Chen, and Lin Zhuang
6.3 6.4 6.5 6.5.1 6.5.2 6.5.3 6.6 6.7	Simple Metal—N <sub>4</sub> Macrocycles 212 Heat-Treated Transition Metal Nitrogen—Carbon Precursors (M-N <sub>x</sub> /C) 216 Functionalized Graphitic Materials 221 Doped Graphene Materials 222 Doped Carbon Nanotube Materials 227 Metal-Functionalized Graphene Materials 229 Conducting Polymers 232 Outlook 235 References 236  Membranes for Alkaline Polyelectrolyte Fuel Cells 243 Jing Pan, Chen Chen, and Lin Zhuang Introduction 243
6.3 6.4 6.5 6.5.1 6.5.2 6.5.3 6.6 6.7 <b>7</b> 7.1 7.2	Simple Metal—N <sub>4</sub> Macrocycles 212 Heat-Treated Transition Metal Nitrogen—Carbon Precursors (M-N <sub>x</sub> /C) 216 Functionalized Graphitic Materials 221 Doped Graphene Materials 222 Doped Carbon Nanotube Materials 227 Metal-Functionalized Graphene Materials 229 Conducting Polymers 232 Outlook 235 References 236  Membranes for Alkaline Polyelectrolyte Fuel Cells 243 Jing Pan, Chen Chen, and Lin Zhuang Introduction 243 Two Main Challenges of APEs 244
6.3 6.4 6.5 6.5.1 6.5.2 6.5.3 6.6 6.7 <b>7</b> 7.1 7.2 7.2.1	Simple Metal—N <sub>4</sub> Macrocycles 212 Heat-Treated Transition Metal Nitrogen—Carbon Precursors (M-N <sub>x</sub> /C) 216 Functionalized Graphitic Materials 221 Doped Graphene Materials 222 Doped Carbon Nanotube Materials 227 Metal-Functionalized Graphene Materials 229 Conducting Polymers 232 Outlook 235 References 236  Membranes for Alkaline Polyelectrolyte Fuel Cells 243 Jing Pan, Chen Chen, and Lin Zhuang Introduction 243 Two Main Challenges of APEs 244 Pursuing High Conductivity as well as Low Swelling Degree 244
6.3 6.4 6.5 6.5.1 6.5.2 6.5.3 6.6 6.7 <b>7</b> 7.1 7.2 7.2.1 7.2.2	Simple Metal—N <sub>4</sub> Macrocycles 212 Heat-Treated Transition Metal Nitrogen—Carbon Precursors (M-N <sub>x</sub> /C) 216 Functionalized Graphitic Materials 221 Doped Graphene Materials 222 Doped Carbon Nanotube Materials 227 Metal-Functionalized Graphene Materials 229 Conducting Polymers 232 Outlook 235 References 236  Membranes for Alkaline Polyelectrolyte Fuel Cells 243 Jing Pan, Chen Chen, and Lin Zhuang Introduction 243 Two Main Challenges of APEs 244 Pursuing High Conductivity as well as Low Swelling Degree 244 High Chemical Stabilities of Cation Groups 244
6.3 6.4 6.5 6.5.1 6.5.2 6.5.3 6.6 6.7 <b>7</b> 7.1 7.2 7.2.1	Simple Metal—N <sub>4</sub> Macrocycles 212 Heat-Treated Transition Metal Nitrogen—Carbon Precursors (M-N <sub>x</sub> /C) 216 Functionalized Graphitic Materials 221 Doped Graphene Materials 222 Doped Carbon Nanotube Materials 227 Metal-Functionalized Graphene Materials 229 Conducting Polymers 232 Outlook 235 References 236  Membranes for Alkaline Polyelectrolyte Fuel Cells 243 Jing Pan, Chen Chen, and Lin Zhuang Introduction 243 Two Main Challenges of APEs 244 Pursuing High Conductivity as well as Low Swelling Degree 244

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
3.1	Introduction 271
3.2	Alkaline Fuel Cell Overview – History, Status, and Advantages 272
3.3	Alkaline Fuel Cell and Alkaline PEM Fuel Cell – Thermodynamics
	and Kinetics 274
3.3.1	Thermodynamics of H <sub>2</sub> /O <sub>2</sub> Fuel Cell Reactions in Alkaline
	Electrolyte 274
3.3.2	Kinetics of O <sub>2</sub> Reduction in Alkaline Fuel Cells 276
3.3.3	Mechanisms of Oxygen Reduction at Noble Metal Surface 279
3.3.4	Mechanisms of Oxygen Reduction at Non-noble Metal Surface 282
3.3.5	Kinetics and Mechanisms of H <sub>2</sub> Oxidation 284
3.4	Silver-Based Materials for Cathode Electrocatalysts in Alkaline PEM
	Fuel Cells 286
3.4.1	Starting Materials and Synthesis Strategies for Silver-Based
	Electrocatalysts 287
3.4.1.1	Chemical Synthesis of Powder Ag Catalysts 288
3.4.1.2	Some Synthetic Methods for Porous Ag Membranes and Porous
	Electrodes 291
3.4.2	Physical and Electrochemical Characterizations 291
3.4.2.1	X-ray Powder Diffraction (XRD) 291
3.4.2.2	X-ray Photoelectron Spectroscopy (XPS) 293
3.4.2.3	Transmission Electron Microscopy (TEM) 293
3.4.2.4	Electrochemical Method 295
3.4.3	Silver-Based Catalysts for Alkaline PEM Fuel Cells 297
3.5	Catalysts for Oxidation of a Broad Range of Fuels for Alkaline PEM Fuel Cells 298
3.5.1	Non-carbon Fuels and Specific Catalysts for Their Oxidation 298

x	Contents	
	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