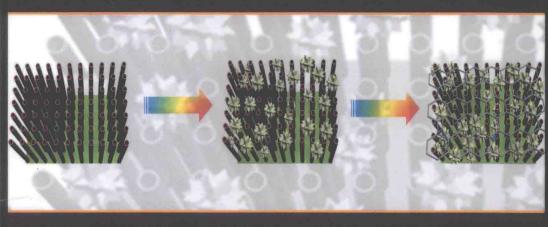
ADVANCED ELECTRODE MATERIALS



Edited By

Ashutosh Tiwari, Filiz Kuralay

and Lokman Uzun



WILEY

Advanced Electrode Materials

Edited by

Ashutosh Tiwari, Filiz Kuralay and Lokman Uzun





Copyright © 2017 by Scrivener Publishing LLC. All rights reserved.

Co-published by John Wiley & Sons, Inc. Hoboken, New Jersey, and Scrivener Publishing LLC, Beverly, Massachusetts.

Published simultaneously in Canada.

No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning, or otherwise, except as permitted under Section 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, (978) 750-8400, fax (978) 750-4470, or on the web at www.copyright.com. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201) 748-6011, fax (201) 748-6008, or online at http://www.wiley.com/go/permission.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives or written sales materials. The advice and strategies contained herein may not be suitable for your situation. You should consult with a professional where appropriate. Neither the publisher nor author shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

For general information on our other products and services or for technical support, please contact our Customer Care Department within the United States at (800) 762-2974, outside the United States at (317) 572-3993 or fax (317) 572-4002.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic formats. For more information about Wiley products, visit our web site at www.wiley.com.

For more information about Scrivener products please visit www.scrivenerpublishing.com.

Cover design by Russell Richardson

Library of Congress Cataloging-in-Publication Data:

ISBN 978-1-119-24252-9

Printed in the United States of America

Among the hot topics concerning advanced materials are recent advances in electrode materials because of their importance not only in developing new biosensors but also in designing efficient batteries, fuel cells and, of course, energy storage and conversion systems. Therefore, we have tried to compile various valuable aspects of this hot topic as a part of the Advanced Materials Series.

In this book, a narrative is presented of recent advances in electrode materials and their novel applications, which are a cross section of advanced materials. Electrochemistry is a widely used branch of chemistry which combines chemical and electrical effects. It provides the advantages of high sensitivity, high performance and low cost. In electrochemistry, a well-designed electrode material is the key to many applications. Therefore, we have summarized different electrodes used in various fields for enhancing the quality of electrochemical systems. We begin with a chapter regarding advances in electrode materials, particularly those based on energy storage, since an electrode is one of the important parts of electrochemical capacitors as well as energy storage and conversion products. The major classes of suitable electrode materials used for capacitors are commonly activated nanoporous carbon, graphene, carbon nanotubes, conducting polymers, metal oxides and polymer composites, which have been extensively reported on in the literature.

Diamond-based electrodes have garnered great attention for use in electrochemical systems. Therefore, detailed techniques used in chemical vapor deposition (CVD) to generate polycrystalline and nanocrystalline diamond layers are also covered, along with methodologies employed to dope the diamond phase in order to obtain an electrically conductive material. Then, the use of diamond-based layers for the assembly of electrodes is summarized to inform readers in areas related to the environment and renewable energies, including food and pharmaceutical analysis, soil and water purification, supercapacitors, Li-ion cells and fuel cells. Recent advances in tungsten oxide/conducting polymer hybrid assemblies for electrochromic applications have taken place which emphasize the importance

of developing new technologies that can be used for electrochromic applications. Tungsten oxide (WO3) has emerged as one of the key materials for electrochromic devices since it exhibits the best electrochromic activity among transition metal oxides. The introduction of WO,/conducting polymer-based hybrid materials has prompted the development of nanocomposites with properties unmatched by conventional counterparts. The interdisciplinary research involving materials science, bioelectrochemistry and electrochemistry is still the hallmark of many technological and fundamental breakthroughs. The effectiveness of surfactant-free metal nanoparticles as "abiotic" catalysts in biotechnology are outlined, based on systems harvesting energy from biological sources for various sensing and wireless information-processing devices for biomedical, homeland and environmental monitoring applications. In another chapter, polyoxometalates (POMs) based on concepts of biosensors for renewable energy applications are summarized. POMs are a well-known class of discrete early transition metal-oxide clusters with a variety of sizes, shapes, compositions and physical and chemical properties, which undergo reversible multivalence reductions/oxidations. Electrochemical sensors based on ordered mesoporous carbons are also highlighted since they provide high sensitivity and selectivity.

Conducting polymer-based electrochemical DNA biosensing is also detailed in the book. Electrode materials for fuel cells lead to important reactions such as oxygen evolution reactions (OER), hydrogen evolution reactions (HER), and oxygen reduction reactions (ORR). In metal-air batteries and fuel cells, the most sluggish reaction is the ORR reaction, which is the bottleneck of numerous electrochemical reactions. Key electrocatalytic reactions occur at the cathode of a proton exchange membrane fuel cell (PEMFC). Therefore, inexpensive materials that have high activity, stability, and resistance to methanol crossover effects for ORR-HOR and OER reactions have been summarized in one of the chapters. In another chapter, a study of phosphate polyanion electrodes and their performance with glassy electrodes for potential application in lithium-ion solid-state batteries is presented in order to stress the importance of new generation solidstate batteries. Then, in a related area, conducting polymer-based hybrid nanocomposites for lithium batteries are given. In this chapter, host-guest and core-shell hybrid nanocomposites based on conducting conjugated polymers and inorganic compounds, which are considered active components of the lithium batteries, are reported. Later on, electrode materials for fuel cell applications are categorized and evaluated in two separate parts as catalyst supports and anode/cathode catalysts. Platinum (Pt)-based catalysts make fuel cell technology less cost-effective due to the limited supply and high cost of Pt. Thus, research on the cost reduction of fuel cells is dealt with either by optimization of existing Pt catalysts or development of Pt or non-Pt alloy catalysts with new and improved electronic structures. Novel photoelectrocatalytic electrode materials for fuel cell reactions are also summarized, with the main focus of the chapter being the recent progress of novel photoresponsive electrodes as anode catalysts for improving the photoelectrocatalytic activity of low molecular weight alcohols oxidation under light irradiation. Finally, advanced nanomaterials for the design and construction of anode materials for microbial cells are detailed at the end of the book.

The invaluable efforts of distinguished researchers from ten different countries with seventeen different affiliations have helped build a comprehensive book from the perspective of advanced materials. By including information presented by such a wide range of authors we hope to contribute to the understanding of students and researchers as well as industrial partners from different fields.

Editors AshutoshTiwari, PhD, DSc Filiz Kuralay, PhD Lokman Uzun, PhD September 2016

Contents

Pr	eface			XV
Pa	art 1	State	e-of-the-Art Electrode Materials	
1	Adva	ınces in	Electrode Materials	3
	J. Sc	ołoduch	10, J. Cabaj and D. Zając	
	1.1	Advar	nced Electrode Materials for	
		Molec	cular Electrochemistry	4
		1.1.1	Graphite and Related sp ² -Hybridized	
			Carbon Materials	4
		1.1.2	Graphene	6
			1.1.2.1 Graphene Preparation	6
			1.1.2.2 Engineering of Graphene	7
		1.1.3	Carbon Nanotubes	8
			1.1.3.1 Carbon Nanotube Networks for	
			Applications in Flexible Electronics	9
		1.1.4	Surface Structure of Carbon Electrode Materials	11
	1.2	Electr	ode Materials for Electrochemical Capacitors	12
		1.2.1	Carbon-based Electrodes	12
		1.2.2	Metal Oxide Composite Electrodes	13
		1.2.3	Conductive Polymers-based Electrodes	15
		1.2.4	Nanocomposites-based Electrode Materials for	
			Supercapacitor	16
	1.3	Nanos	structure Electrode Materials for Electrochemical	
		Energ	y Storage and Conversion	16
		1.3.1	Assembly and Properties of Nanoparticles	17
	1.4	Progre	ess and Perspective of Advanced Electrode	
		Materi	ials	18
	Ackı	nowledg	gments	19
	Refe	rences		10

vi Contents

2	Dia	mond-based Electrodes	2	
	Em	anuela Tamburri and Maria Letizia Terranova		
	2.1	Introduction	23	
	2.2	Techniques for Preparation of Diamond Layers	28	
		2.2.1 HF-CVD Diamond Synthesis	30	
		2.2.2 MW-CVD Diamond Synthesis	3.	
		2.2.3 RF-CVD Diamond Synthesis	3	
	2.3	Why Diamond for Electrodes?	32	
	2.4	Diamond Doping	33	
		2.4.1 In Situ Diamond Doping	34	
		2.4.2 Ion Implantation	37	
	2.5	Electrochemical Properties of Doped Diamonds	37	
	2.6	Diamond Electrodes Applications	39	
		2.6.1 Water Treatment and Disinfection	39	
		2.6.2 Electroanalytical Sensors	4(
		2.6.3 Energy Technology	45	
		2.6.3.1 Supercapacitors	45	
		2.6.3.2 Li Ion Batteries	49	
		2.6.3.3 Fuel Cells	51	
	2.7	Conclusions	52	
	Refe	erences	53	
2	D	at Adams and Transition On the Control of the Publisher		
3		ant Advances in Tungsten Oxide/Conducting Polymer	(1	
		rid Assemblies for Electrochromic Applications	61	
		dem Dulgerbaki and Aysegul Uygun Oksuz Introduction	62	
	3.2 History and Technology of Electrochromics3.3 Electrochromic Devices		63	
	3.3		63	
		3.3.1 Electrochromic Contrast	64	
		3.3.2 Coloration Efficiency	64	
		3.3.3 Switching Speed 3.3.4 Stability	65	
		3.3.5 Optical Memory	65	
	3 /	Transition Metal Oxides	65	
	3.5		67	
		Conjugated Organic Polymers	67	
	3.7	Hybrid Materials	69	
	3.8	Electrochromic Tungsten Oxide/Conducting	70	
	5.0	Polymer Hybrids	77.1	
	3.9	Conclusions and Perspectives	71	
		nowledgments	95	
		erences	99	
	TICIC	1011003	99	

4				-free Nanomaterials for rgy Conversion Systems:	
				s to Bionanotechnology	103
				W. Napporn and Kouakou B. Kokoh	
	4.1			rode Materials Design: Preparation and	
	Tex			n of Metal Nanoparticles	104
				Strategies for Metal Nanoparticles	
		11.11.1		tion: General Consideration	104
		4.1.2		d Synthetic Methods without Organic	
		11112		les as Surfactants	109
	4.2	Electr		Performances Toward Organic	
			ules Oxid		114
				catalytic Properties of Metal Nanoparticles	
				ine Medium	114
			4.2.1.1	Electrocatalytic Properties Toward	
				Glycerol Oxidation	114
			4.2.1.2	Electrocatalytic Properties Toward	
				Carbohydrates Oxidation	116
		4.2.2	Spectro	electrochemical Characterization of the	
			Electrod	le–Electrolyte Interface	118
			4.2.2.1	Spectroelectrochemical Probing of	
				Electrode Materials Surface by	
				CO Stripping	118
			4.2.2.2	Spectroelectrochemical Probing of	
				Glycerol Electrooxidation Reaction	120
			4.2.2.3	Spectroelectrochemical Probing of	
				Glucose Electrooxidation Reaction	121
		4.2.3	Electroc	hemical Synthesis of Sustainable	
			Chemica	als: Electroanalytical Study	123
		4.2.4		hemical Energy Conversion: Direct	
			.4	drates Alkaline Fuel Cells	128
	4.3	Metal		icles at Work in Bionanotechnology	131
		4.3.1		anoparticles at Work in Closed-biological	
				ons: Toward Implantable Devices	131
		4.3.2		on of Implantable Biomedical and	
				tion Processing Devices by Fuel Cells	133
	4.4	Concli			136
		nowledg	gments		137
	Note				137
	Refe	rences			138

Part 2 Engineering of Applied Electrode Materials

5	Poly	oxomet	talate-based Modified Electrodes for				
	Elec	trocata	lysis: From Molecule Sensing to Renewable				
	Ener	gy-rela	ited Applications	149			
	Cri	Cristina Freire, Diana M. Fernandes, Marta Nunes and					
	Mariana Araújo						
			duction	150			
	5.2	POM:	s and POMs-based (Nano)Composites	151			
			Polyoxometalates	151			
			Polyoxometalate-based (Nano)Composites	154			
			General Electrochemical Behavior of POMs	157			
	5.3	POM:	s-based Electrocatalysis for Sensing Applications	160			
		5.3.1	Reductive Electrocatalysis	161			
			5.3.1.1 Nitrite Reduction	161			
			5.3.1.2 Bromate Reduction	167			
			5.3.1.3 Iodate Reduction	168			
			5.3.1.4 Hydrogen Peroxide Reduction Reaction	170			
		5.3.2		173			
			5.3.2.1 Dopamine and Ascorbic Acid Oxidations	173			
			5.3.2.2 L-Cysteine Oxidation	177			
	5.4	POMs	s-based Electrocatalysis for Energy Storage and				
		Conve	ersion Applications	178			
		5.4.1	Oxygen Evolution Reaction	179			
		5.4.2	Hydrogen Evolution Reaction	183			
			Oxygen Reduction Reaction	185			
			uding Remarks	191			
		nowledg		193			
			reviations and Acronyms	193			
	Refe	rences		196			
6			nical Sensors Based on Ordered				
			Carbons	213			
	Xiangjie Bo and Ming Zhou						
		Introd		213			
	6.2	Electro	ochemical Sensors Based on OMCs	217			
	6.3		ochemical Sensors Based on Redox				
			tors/OMCs	222			
	6.4		ochemical Sensors Based on NPs/OMCs	226			
		6.4.1					
			Metal NPs/OMCs	228			

		6.4.2		chemical Sensors Based on Noble VPs/OMCs	230
	65	Conc		11 0/ 01/12 00	233
			gments		236
		erences	Винение		236
	1010	Terrees			
7				Oxide and Metal-free Catalysts for	
				Conversion	243
				lrew G. Meguerdichian, Ting Jiang,	
	Abd			y and Steven L. Suib	
	7.1	Metal	-Nitroge	n-Carbon (M-N-C) Electrocatalysts	244
		7.1.1	Introdu	action	244
		7.1.2	Catalys	ts for Hydrogen Evolution Reaction	245
		7.1.3	Catalys	ts for Oxygen Evolution Reaction	248
		7.1.4	Catalys	ts for Oxygen Reduction Reaction	249
		7.1.5	None-h	eat-treated M-N-C Electrocatalysts	250
		7.1.6	Heat-tr	eated M-N-C Electrocatalysts	254
		7.1.7	Conclus	sion	261
	7.2	Trans	ition Met	al Oxide Electrode Materials for Oxygen	
		Evolu	tion Reac	tion, Oxygen Reduction Reaction and	
		Bifuct	ional Pur	poses (OER/ORR)	262
		7.2.1	Introdu	ction	262
		7.2.2	Oxygen	Evolution Reaction	266
				Synthesis Methodology	267
				OER Properties of Catalyst	272
			7.2.2.3		
				of TM Oxide for OER	274
		7.2.3	Oxygen	Reduction Reaction	276
			7.2.3.1		277
			7.2.3.2	. 0,	278
			7.2.3.3		278
			7.2.3.4	Theoretical Analyses of ORR Active	
				Catalysts	279
		7.2.4	Hydrogo	en Evolution Reaction	279
		7.2.5		onal Oxide Materials (OER/ORR)	281
			7.2.5.1	Bifunctional Properties of Catalyst	281
				Dopant Effects	283
				Morphology or Microstructure Analysis	283
			7.2.5.4	Synthesis Methodology	284
		7.2.6	Conclus		285
		1 . C. Amil C . S.	- WILLIAM	45/44	4.(1.)

x Contents

	7.3	Trans	sition Metal Chalcogenides, Nitrides, Oxynitrides,	
		and (Carbides	285
		7.3.1	Transition Metal Chalcogenides	285
		7.3.2	Transition Metal Nitrides	294
			Transition Metal Oxynitrides	296
			Transition Metal Carbides	298
	7.4		en Reduction Reaction for Metal-free	300
			Different Doping Synthesis Strategies	300
		7.4.2	ORR Activity in Different Carbon Source	303
			7.4.2.1 1D Carbon Nanotube Doped	303
			7.4.2.2 2D Graphene	306
		7.4.3	Oxygen Evolution Reaction	308
	Refe	erences		310
8	Stud	y of Ph	osphate Polyanion Electrodes and Their	
			e with Glassy Electrolytes: Potential Application	
	in Li	thium	Ion Solid-state Batteries	321
	S. T	erny ar	nd M.A. Frechero	
	8.1	Intro	duction	321
	8.2	Glass	Samples Preparation	323
	8.3		structured Composites Sample Preparation	324
	8.4		Powder Diffraction	325
		8.4.1	X-ray Powder Diffraction Patterns of	
			Glassy Materials	325
		8.4.2	X-ray Powder Diffraction Patterns of	
			Composites Materials	326
	8.5		nal Analysis	326
		8.5.1	Thermal Analysis of Glassy Systems	326
		8.5.2	/	329
	8.6		ty and Appearance	330
		8.6.1	Density and Oxygen Packing Density of Glassy	
		21 0 01	Materials	330
		8.6.2	Materials' Appearance	331
			8.6.2.1 Glasses	331
			8.6.2.2 Nanostructured Composites	332
	8.7		ural Features	332
		8.7.1	Glassy Materials	332
			8.7.1.1 FTIR and Raman Spectroscopy	334
		8.7.2	Nanocomposites Materials	337
	8.8		ical Behavior	342
			Glasses Materials	342
		8.8.2	Composite Materials	347

			CONT	ENTS	X
	9.0	A 11_so	lid-state Lithium Ion Battery		349
			Remarks		350
		owledgi			352
		ences	Hento		352
	Refer	Circos			
9	Cond	ucting F	Polymer-based Hybrid Nanocomposites		
	as Pro	mising	Electrode Materials for Lithium Batteries		355
	O.Yu	. Posudi	ievsky, O.A. Kozarenko, V.G. Koshechko and		
	V.D.	Pokhod	enko		
	9.1	Introdu	action		356
	9.2	Electro	de Materials of Lithium Batteries Based on		
		Conduc	cting Polymer-based Nanocomposites Prepared		
			mical and Electrochemical Methods		357
			Host-guest Hybrid Nanocomposites		357
			Core-shell Hybrid Nanocomposites		361
	9.3		nochemical Preparation of Conducting		
			r-based Hybrid Nanocomposites as Electrode		
			lls of Lithium Batteries		368
			Principle of Mechanochemical Synthesis		368
			Mechanochemically Prepared Conducting		
			Polymer-based Hybrid Nanocomposite		
	45. 5		Materials for Lithium Batteries		370
		Conclus	sion		384
	Refer	ences			385
10	Energ	v Applie	cations: Fuel Cells		397
			ez Çelebi		0,77
		Introd	,		398
			st Supports for Fuel Cell Electrodes		399
			Commercial Carbon Supports		399
			Carbon Nanotube (CNT) Supports		401
			Graphene Supports		403
		10.2.4			405
		10,2,5			406
		10,2.6			408
		10.2.7			410
		10.2.8	Non-carbon Supports		411
	10.3	Anode	and Cathode Catalysts for Fuel Cells		413
			Anode Catalysts		413
		10.3.2	Cathode Catalysts		418
	10.4	Conclu	isions		420
	Refer	ences			421

11	Nove	Photoelectrocatalytic Electrodes Materials for	
		Cell Reactions	435
	Min	gshan Zhu, Chunyang Zhai and Cheng Lu	
	-	Introduction	435
	11.2	Basic Understanding on the Improved	
		Catalytic Performance of Photo-responsive Metal/	
		Semiconductor Electrodes	438
	11.3	Synthetic Methods for Metal/Semiconductor	
		Electrodes	440
		11.3.1 Electrochemical Deposition	44]
		11.3.2 Chemical Reduction Method	442
		11.3.3 Physical Mixing Method	443
		11.3.4 Hydrothermal/Solvothermal Method	444
		11.3.5 Microwave-assisted Method	445
		11.3.6 Other Preparation Methods	445
	11.4	Photo-responsive Metal/Semiconductor	
		Anode Catalysts	446
		11.4.1 TiO ₂ Nanoparticles	446
		11.4.2 One-dimensional Well-aligned TiO,	
		Nanotube Arrays	448
		11.4.3 Other Semiconductor Supports	449
	11.5	Conclusions and Future Outlook	452
	Refer	ences	453
12		ced Nanomaterials for the Design and Construction	
		ode for Microbial Fuel Cells	457
		ii, Ming Zhou and Chaokang Gu	
		Introduction	458
		Carbon Nanotubes-based Anode Materials for MFCs	459
		Graphene-based Anode Materials for MFCs	466
		Other Anode Materials for MFCs	470
		Conclusions	474
		owledgments	475
	Refere	ences	475
13	Condu	cting Polymer-based Electrochemical DNA Biosensing	485
		Kuralay	
	13.1	Introduction	486
	13.2	Electrochemical DNA Biosensors	487

			CONTENTS	X111
	13.3	Conducting Polymer-based Electrochemical		
		DNA Biosensors		489
	13.4	Conclusions and Outlook		493
	Ackn	owledgments		494
	Refer	ences		494
In	dex			501

Part 1 STATE-OF-THE-ART ELECTRODE MATERIALS