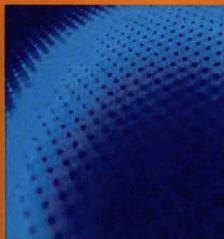
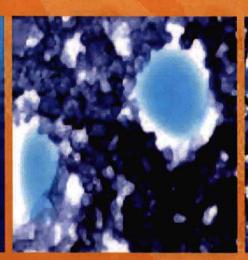
edited by S. R. S. Prabaharan M. S. Michael







Nanotechnology in Advanced Electrochemical Power Sources

Nanotechnology in Advanced Electrochemical Power Sources

edited by S. R. S. Prabaharan M. S. Michael



Published by

Pan Stanford Publishing Pte. Ltd. Penthouse Level, Suntec Tower 3 8 Temasek Boulevard Singapore 038988

Email: editorial@panstanford.com

Web: www.panstanford.com

British Library Cataloguing-in-Publication Data

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

Nanotechnology in Advanced Electrochemical Power Sources

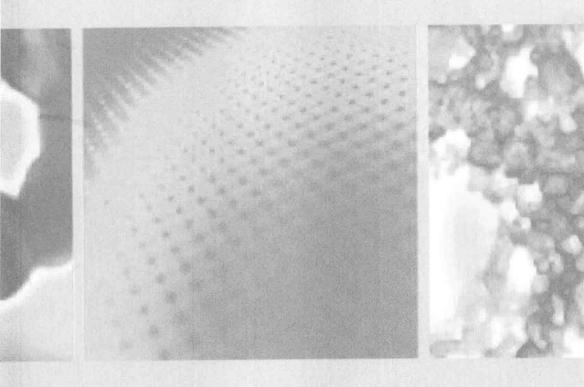
Copyright © 2015 Pan Stanford Publishing Pte. Ltd.

All rights reserved. This book, or parts thereof, may not be reproduced in any form or by any means, electronic or mechanical, including photocopying, recording or any information storage and retrieval system now known or to be invented, without written permission from the publisher.

For photocopying of material in this volume, please pay a copying fee through the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA. In this case permission to photocopy is not required from the publisher.

ISBN 978-981-4241-43-4 (Hardcover) ISBN 978-981-4303-05-7 (eBook)

Printed in the USA



Nanotechnology in Advanced Electrochemical Power Sources

Senior Authors

Atsuo Yamada

Department of Engineering, Building 5-607, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Elzbieta Frackowiak

Institute of Chemistry and Technical Electrochemistry, Poznan University of Technology, 60-965 Poznan, Piotrowo 3. Poland

Itaru Honma

Institute of Multidisciplinary Research for Advanced, Tohoku University, 2-1-1, Katahira, Sendai, Miyagi 980-8577, Japan

Iunichi Kawamura

Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, Katahira 2-1-1, Aobaku, Sendai, Japan

Katsuhiko Naoi

Institute of Symbiotic Science and Technology, Tokyo University of Agriculture & Technology, Tokyo, Japan

Kwang-Bum Kim

Department of Materials Science and Engineering, Yonsei University, 134 Shinchon-dong, Seodaemun-gu, Seoul 120-749, Korea

Maximilian Fichtner

Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), P.O. Box 3640, D-76021 Karlsruhe, Germany

Nail Suleimanov

Zavoisky Physical-Technical Institute of Russian Academy of Sciences, 420029 Kazan, Russian Federation

Robert Dominko

National Institute of Chemistry, Hajdrihova 19, SI-1000 Ljubljana, Slovenia, and ALISTORE-ERI, 80039 Amiens Cedex, France

Shinichi Komaha

Department of Applied Chemistry, Tokyo University of Science, Kaaurazaka 1-3, Shinjuku, Tokyo 162-8601, Japan

S R S Prabaharan

School of Electronics Engineering, VIT University, Chennai Campus, Vandalur-Kelambakkam Road, Chennai, 600 127, India

Sylvain Franger

Physico-Chimie de l'Etat Solide. Institut de Chimie Mol'eculaire et des Mat'eriaux, d'Orsav, UMR CNRS 8182, Universit'e Paris XI, 91405 Orsav cedex. France

Teunis van Ree

Department of Chemistry, University of Venda, Thohoyandou, 0950 South Africa

Yuping Wu

New Energy and Materials Laboratory (NEML), Department of Chemistry, Fudan University, Shanghai 200433, China

Foreword

Electrochemical energy storage is regarded as a vital means of providing portable power to the mankind in variety of ways. The current trend in developing advanced power/energy sources has rendered impetus to advancement as anticipated by scientists and engineers around the world. Thus, tremendous research opportunities exist in both government and private funded activities all over the world. To facilitate that nanotechnology has complemented laurels to enhance such opportunities to meet the anticipated demand by improving the existing storage limits of battery system especially lithium-containing batteries of present and the future technologies and supercapacitors.

In this context, the book entitled Nanotechnology in Advanced Electrochemical Power Sources is timely which encompasses chapters contributed by various world renowned experts in the field of lithium-containing battery electrodes, electrolytes and supercapacitors. State-of-the-art understanding pertaining to nanoscale aspects of the above mentioned advanced energy storage devices has been the focus of this volume. While the fundamental issues relating to the device performance of various positive and negative electrode materials for instance, olivine and silicate cathodes, highcapacity anodic materials such as Sn alloys, silicon and conversion type electrode, modified electrode with CNTs, graphene-based supercapacitors, hierarchically designed porous air cathodes and their nanoscale advantages in terms of device performances are also covered. There are 12 full length chapters including a dedicated chapter on Li-air secondary batteries, a futuristic endeavor in developing a high energy density battery having theoretical specific capacity closest to gasoline. The intended audience of this book includes students, materials scientists, electrical engineers, new

comers who would like to learn the nuances of the exhilarating branch having enormous societal advantages for the mankind.

B.V.R. Chowdari

BRCewde

National University of Singapore. Former president of IUMRS, President MRS (Singapore) Executive Director NUS-India Research initiatives and Chairman of ICMAT conferences

Preface

The challenge to provide adequate power supplies to the human race on an indefinite basis without causing long-term damage to the environment requires versatile means of energy conversion and storage. The advances in large-scale original equipment manufacturer (OEM) gadgets, smart cellular phones, tablet computers (tabs), power-hungy long-range communication devices, and modern-day electric mobility systems (plug-in electric cars, for instance) demand for huge power and energy in the form of rechargeable energy storage systems. Electrical energy storage thus becomes vital today than at any time in the human history. The recent evolution of nanotechnology may provide opportunities to meet the anticipated demand by improving the existing storage limits of battery system. especially Li-ion batteries, supercapacitors, and upcoming novel energy storage system namely Li-air rechargeable batteries. The engineering of new materials, and especially at the nanoscale, has become imperative to achieve enhanced energy and power efficiency to meet these challenges of energy storage systems. This book incorporates state-of-the-art understanding pertaining to nanoscale aspects of advanced energy storage devices such as Liion batteries. Li-air batteries, and electrochemical supercapacitors. It focuses on various fundamental issues related to the device performance of various positive and negative electrode materials. with special reference to their nanoscale advantages. It also includes fundamentals and processing techniques with regard to synthesis, characterization, physical and electrochemical properties, and applications of nanoscale materials pertaining to advanced electrochemical power sources. The goal of this book is to render an update of the current advancement in the field of electrochemical power sources with special reference to nanotechnology. A vari-

ety of advanced nanomaterials, such as transition metal oxides. phosphates, silicates, and conversion electrodes, together with carbonaceous materials that include carbon nanotubes, nanorods, and mesoporous carbons, are discussed by notable authorities of this exhilarating field. The book presents a balanced mix of theoretical and experimental approaches adopted over these years in the advancement of lithium-based power sources (Li-ion and Li-Air) and electrochemical capacitors. The book is a compact reference source for students, scientists, engineers, and specialists in various fields, including electron devices, electrochemistry, electrical engineering, nanotechnology, and solid state physics.

> S. R. S. Prabaharan M. S. Michael Summer 2014

Contents

Se	nior	Author	S	xiii		
Fo	Foreword					
Pr	eface	2		xvii		
	100			1		
1		Redox Reaction in Size-Controlled Li _x FePO ₄				
		Atsuo Yamada				
	1.1	Backg	ground	2		
	1.2	Binary Phase Diagram				
	1.3	Size Effect versus Surface Effect				
	1.4	Air Po	pisoning	6		
	1.5	Caref	ul Verification of Phase Diagram	9		
		1.5.1	Electrochemical Approach	9		
		1.5.2	Structural Approach	10		
		1.5.3	Consistency between Electrochemical and			
			Structural Data	16		
		1.5.4	Thermodynamic Approach	19		
	1.6	Sumn	nary	21		
_	Orth	osilisa	te-Based Cathode Materials for Lithium-Ion			
2	Batteries					
	Robert Dominko					
		2.1 Background				
	2.2			24 27		
	2.2		ture–Property Relationship	27		
			X-Ray Diffraction Investigation			
	2.2		⁶ Li MAS NMR Investigation	29 31		
		10				
	2.4		rochemical Properties (<i>In situ</i> Structural Studies:	00		
		XKD a	and XAS)	32		

	2.5 Effect of Carbon Coating							
	2.6	Concl	usions		46			
3	Nanoscale Conversion Materials for Electrochemical Energy							
	Storage							
	Maximilian Fichtner							
	3.1	1 Introduction						
	3.2	Curre	Current Electrode Materials					
	3.3	Conve	ersion El	ectrodes	55			
	3.3.1 Concept and Examples				56			
		3.3.2	Anode l	Materials	57			
			3.3.2.1	Metal-air batteries	57			
			3.3.2.2	In Li-ion batteries	64			
		3.3.3	As Cath	ode Materials	72			
			3.3.3.1	Sulfides	73			
			3.3.3.2	Fluorides	74			
		3.3.4	Solid-St	ate Reactions in Conversion Electrodes	79			
			3.3.4.1	Thermodynamics	80			
			3.3.4.2	Kinetics	83			
	3.4	Sumn	nary		86			
4	Nanoengineered Lithium-Air Secondary Batteries:							
	Fundamental Understanding and the Current Status of							
	Development							
	M. S. Michael, Junichi Kawamura, Naoaki Kuwata,							
	and S. R. S. Prabaharan							
	4.1	.1 Introduction			90			
			/hy Li–Air Battery?					
		3 Other Metal-Air Battery Systems						
	4.4	4.4 Rechargeable Li–Air Battery System			94			
				Battery Fundamentals	94			
		4.4.2		le of Operation of Li–Air Battery	98			
				Non-aqueous Li–air system	98			
				Aqueous Li–air system	99			
			4.4.2.3	Aqueous/nonaqueous hybrid				
			a a =	electrolyte	99			
	. =			Solid-state electrolyte	100			
	4.5 Current Problems Encountered in Li–Air				400			
		Recha	argeable :	System	100			

		4.5.1 Non-aqueous Solvents	100		
		4.5.2 Gas Diffusion Electrode	106		
		4.5.3 Role of Electrocatalysts in the Li–Air System	111		
		4.5.3.1 Nano-electrocatalysts for efficient air			
		cathode	112		
	4.6	Developmental Challenges	118		
	4.7	Our Proprietary Cell Design	120		
	4.8	Summary	120		
5	Nan	o Anode Materials for Lithium-Ion Batteries	127		
	Lijur	Fu, Yi Shi, Shu Tian, Yuping Wu, and Teunis van Ree			
	5.1	The Development of Anode Materials for Lithium Ion			
		Batteries	128		
	5.2	Nanocarbon Anode Materials	128		
		5.2.1 Carbon Nanotubes	129		
		5.2.2 Carbon Nanofibers	134		
	5.3	Nano Si-Based Anode Materials	135		
	5.4	Nano Sn-Based Anode Materials	139		
		5.4.1 Metallic Sn	139		
		5.4.2 SnO ₂	142		
	5.5	Titanium Oxide-Based Nano Anode Materials	146		
		5.5.1 Anatase TiO ₂	146		
		5.5.2 Rutile TiO ₂	150		
		5.5.3 TiO ₂ (B)	151		
		5.5.4 Nano Li ₄ Ti ₅ O ₁₂	153		
	5.6	Other Oxides-Based Nano Anode Materials	156		
		5.6.1 Co-Based Oxides	156		
		5.6.2 Ni-Based Oxides	161		
		5.6.3 Cr ₂ O ₃	162		
		5.6.4 Nano MoO ₂	164		
		5.6.5 Fe-Based Oxides	167		
	5.7	Future Aspects	169		
6	Inter	face between Transition Metal Oxides-Based Electrodes			
	and Lithium Salts Electrolytes: A Physicochemical Approach				
		ain Franger			
		Introduction	178		
	62	Experimental Section			

	6.3	Physi	cochemical Approach Proposed	180			
		6.3.1	Background	180			
		6.3.2	Kinetic Equations	182			
	6.4	Confr	ontation/Discussion	184			
		6.4.1	Limitation of this Model at High Voltages				
			(>4.3 V vs. Li) Especially in Presence of				
			Propylene Carbonate	188			
		6.4.2	Limitation of this Model with the Specific				
			Surface of the Particles: the Case of the				
			Nanostructured Materials	192			
	6.5	Sumn	nary/Perspectives	194			
7	Elec	tron Sp	oin Resonance Studies of Lithium-Ion Battery				
	Mat	erials		199			
	Nail	Suleim	anov, S. R. S. Prabaharan, Dinar Abdullin,				
	and	M. S. N	Aichael				
	7.1	.1 Introduction					
	7.2	2 Electron Spin Resonance Phenomenon					
	7.3						
	Materials						
		7.3.1	Structural Imperfections of LiCoO ₂	204			
		7.3.2	ESR Investigation of $LiM_{\nu}Co_{1-\nu}O_{2}$ (M = Al, Ga	1)			
			System	205			
	7.4 ESR Investigation of NASICON Structured						
		Li ₂ Mr	$n_2(MoO_4)_3$	206			
		7.4.1	Experiment	206			
		7.4.2	ESR Analysis	208			
			7.4.2.1 Micro-scaled Li ₂ Mn ₂ (MoO ₄) ₃	208			
			7.4.2.2 Nanoscaled Li _x Mn ₂ (MoO ₄) ₃				
			(x = 0-2.0)	215			
		7.4.3	Comparison of Resonance Parameters of				
			Microscaled and Nanoscaled Li ₂ Mn ₂ (MoO ₄) ₃	216			
	7.5	Sumn	nary and Outlook	218			
8			and Graphene-Based Nanocomposites for				
	Electrochemical Energy Storage						
	Marappan Sathish and Itaru Honma						
	8.1	Introd	duction	222			

	8.2		Nanosheets and Functionalized Graphene	224				
	0.0		ets Preparation	224				
	8.3		Nanosheets for Supercapacitors	226				
	8.4		Nanosheets for Li-Ion Battery	234				
	8.5		Nanosheets for Li–Air Battery	239				
	8.6	Summary		244				
9			ubes for Energy Storage Application	249				
		Elzbieta Frackowiak, Grzegorz Lota, and Krzysztof Fic						
		Introduct		250				
	9.2	Carbon N for Capac	anotubes/Conducting Polymers Composites itor	251				
	9.3	Carbon N	anotubes/Metal Oxides Composites for					
		Capacitor		252				
	9.4	Pseudoef	fects from Heteroatoms in the Carbon					
		Network		255				
	9.5	Pseudocapacitance Effect Related with Hydrogen						
		Electroso	rbed in Carbon	266				
	9.6	9.6 Carbon Nanotubes as a Support for Catalyst in Fuel						
		Cells		271				
	9.7	Summary	r	276				
10	Ma	nganese O	xide/Carbon Nanotube Nanocomposites for					
			cal Energy Storage Applications	281				
	Sar	g-Bok Ma	and Kwang-Bum Kim					
	10.1 Introduction							
	10.	2 Synthes	sis and Characterization of MnO ₂ /CNT					
		Nanoco	omposites	285				
		10.2.1	In situ Monitoring of Reduction Potential					
			and pH	285				
		10.2.2	UV-VIS Analysis	287				
		10.2.3	Effect of pH	287				
		10.2.4	CNT as a Reducing Agent	290				
		10.2.5	Morphology of MnO ₂ on CNT	291				
		10.2.6	Phase and Structure of MnO2 on CNT	292				
	10.	3 Electro	chemical Properties of MnO ₂ /CNT					
		Nanoco	omnosites	294				

		10.3.1	Electrock	nemical Properties of MnO ₂ Coated				
			onto CN7		294			
		10.3.2	Effect of	Initial Solution pH	296			
		10.3.3	Effect of	CNT as a Conducting Agent	298			
		10.3.4	Effect of	Heat Treatment of MnO ₂ /CNT				
			Nanocom	nposite	299			
	10.4	Nanosi	zed Lithiu	m Manganese Oxide Dispersed on				
		Carbon	Nanotube	es	303			
		10.4.1	Synthesis	s of LMO Dispersed on CNT	303			
		10.4.2	Phase an	d Structure of LMO Dispersed on				
			CNT		306			
		10.4.3	Electroch	nemical Properties of LMO				
			Disperse	d on CNT	307			
		10.4.4	Structura	al Stability of LMO Dispersed on				
			CNT		308			
	10.5	Summa	ary		312			
11	Manganese Oxides for Supercapacitors							
	Shinichi Komaba, Naoaki Yabuuchi, and							
	Tomo	Tomoya Tsuchikawa						
	11.1	Mangai	nese Oxide	es for Electrode Materials	317			
	11.2			ganese Dioxides as Electrode				
		Materia	als of Redo	ox Capacitor	321			
	11.3	From S	ymmetric	to Asymmetric Supercapacitor	328			
	11.4	Electrolyte Additives for Improvement of						
		Cyclabi			331			
	11.5	Summa	ary and Ou	tlook	335			
12	High-Voltage Electrode/Electrolyte Interface in ECs and Hybrid Capacitors 33							
	Hybrid Capacitors							
		Katsuhiko Naoi and Kazumi Chiba						
	12.1	Background						
		12.1.1	-	tage Electrode/Electrolyte	2 0 -			
			Interface		340			
			12.1.1.1	Cell voltage range of 2.5–3.0 V				
			2 M 2 V 2 W	(Region I)	344			
			12.1.1.2	Cell voltage range of 3.0–3.7 V	-			
				(Region II)	345			