

Edited by François Béguin and Elzbieta Frackowiak

Supercapacitors

Materials, Systems, and Applications

Series Editor:
G.Q. Max Lu



Edited by
François Béguin and Elżbieta Frąckowiak

Supercapacitors

Related Titles

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

Fuel Cell Science and Engineering

Materials, Processes, Systems and Technology

2012

ISBN: 978-3-527-33012-6

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

Park, J.-K.

Principles and Applications of Lithium Secondary Batteries

2012

ISBN: 978-3-527-33151-2

Ozawa, K. (ed.)

Lithium Ion Rechargeable Batteries

Materials, Technology, and New Applications

2009

ISBN: 978-3-527-31983-1

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

Handbook of Battery Materials 2nd completely revised and enlarged edition

2011

ISBN: 978-3-527-32695-2

O'Hayre, R., Colella, W., Cha, S.-W., Prinz, F. B.

Fuel Cell Fundamentals

ISBN: 978-0-470-25843-9

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

Edited by François Béguin and Elżbieta Frąckowiak

Supercapacitors

Materials, Systems, and Applications



**WILEY-
VCH**

WILEY-VCH Verlag GmbH & Co. KGaA

The Editors

Prof. François Béguin

Poznan University of Technology
Faculty of Chemical Technology
u1. Piotrowo 3
Poznan, 60-965
Poland

Prof. Elzbieta Frąckowiak

Poznan University of Technology
Institute of Chemistry and Technical Electrochemistry
u1. Piotrowo 3
Poznan, 60-965
Poland

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 Data

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 <<http://dnb.d-nb.de>>.

© 2013 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: 978-3-527-32883-3
ePDF ISBN: 978-3-527-64669-2
ePub ISBN: 978-3-527-64668-5
mobi ISBN: 978-3-527-64667-8
oBook ISBN: 978-3-527-64666-1

Materials for sustainable energy and development (Print) ISSN: 2194-7813

Materials for sustainable energy and development (Internet) ISSN: 2194-7821

Typesetting Laserwords Private Limited, Chennai, India

Printing and Binding Markono Print Media Pte Ltd, Singapore

Cover Design Simone Benjamin, McLeese Lake, Canada

Printed in Singapore
Printed on acid-free paper

Editorial Board

Members of the Advisory Board of the “Materials for Sustainable Energy and Development” Series

Professor Huiming Cheng
Professor Calum Drummond
Professor Morinobu Endo
Professor Michael Grätzel
Professor Kevin Kendall
Professor Katsumi Kaneko
Professor Can Li
Professor Arthur Nozik
Professor Detlev Stöver
Professor Ferdi Schüth
Professor Ralph Yang

Contents

Series Editor Preface	<i>XVII</i>
Preface	<i>XIX</i>
About the Series Editor	<i>XXI</i>
About the Volume Editors	<i>XXIII</i>
List of Contributors	<i>XXV</i>

1	General Principles of Electrochemistry	1
	<i>Scott W. Donne</i>	
1.1	Equilibrium Electrochemistry	1
1.1.1	Spontaneous Chemical Reactions	1
1.1.2	The Gibbs Energy Minimum	1
1.1.3	Bridging the Gap between Chemical Equilibrium and Electrochemical Potential	3
1.1.4	The Relation between E and ΔG_r	3
1.1.5	The Nernst Equation	4
1.1.6	Cells at Equilibrium	5
1.1.7	Standard Potentials	5
1.1.8	Using the Nernst Equation – Eh–pH Diagrams	6
1.2	Ionics	6
1.2.1	Ions in Solution	6
1.2.1.1	Ion–Solvent Interactions	7
1.2.1.2	Thermodynamics	8
1.2.2	The Born or Simple Continuum Model	8
1.2.2.1	Testing the Born Equation	9
1.2.3	The Structure of Water	9
1.2.3.1	Water Structure near an Ion	11
1.2.3.2	The Ion–Dipole Model	11
1.2.3.3	Cavity Formation	12
1.2.3.4	Breaking up the Cluster	12
1.2.3.5	Ion–Dipole Interaction	12
1.2.3.6	The Born Energy	13
1.2.3.7	Orienting the Solvated Ion in the Cavity	13

1.2.3.8	The Leftover Water Molecules	14
1.2.3.9	Comparison with Experiment	14
1.2.3.10	The Ion–Quadrupole Model	14
1.2.3.11	The Induced Dipole Interaction	14
1.2.3.12	The Results	15
1.2.3.13	Enthalpy of Hydration of the Proton	15
1.2.4	The Solvation Number	16
1.2.4.1	Coordination Number	16
1.2.4.2	The Primary Solvation Number	16
1.2.5	Activity and Activity Coefficients	16
1.2.5.1	Fugacity (f')	16
1.2.5.2	Dilute Solutions of Nonelectrolytes	16
1.2.5.3	Activity (a)	17
1.2.5.4	Standard States	17
1.2.5.5	Infinite Dilution	18
1.2.5.6	Measurement of Solvent Activity	18
1.2.5.7	Measurement of Solute Activity	18
1.2.5.8	Electrolyte Activity	18
1.2.5.9	Mean Ion Quantities	19
1.2.5.10	Relation between f , γ , and γ	19
1.2.6	Ion–Ion Interactions	20
1.2.6.1	Introduction	20
1.2.6.2	Debye–Huckel Model for Calculating ψ_2	21
1.2.6.3	Poisson–Boltzmann Equation	22
1.2.6.4	Charge Density	22
1.2.6.5	Solving the Poisson–Boltzmann Equation	23
1.2.6.6	Calculation of $\Delta\mu_{i-1}$	24
1.2.6.7	Debye Length, K^{-1} or L_D	24
1.2.6.8	The Activity Coefficient	24
1.2.6.9	Comparison with Experiment	26
1.2.6.10	Approximations of the Debye–Huckel Limiting Law	26
1.2.6.11	The Distance of Closest Approach	27
1.2.6.12	Physical Interpretation of the Activity Coefficient	27
1.2.7	Concentrated Electrolyte Solutions	27
1.2.7.1	The Stokes–Robinson Treatment	27
1.2.7.2	The Ion-Hydration Correction	28
1.2.7.3	The Concentration Correction	28
1.2.7.4	The Stokes–Robinson Equation	29
1.2.7.5	Evaluation of the Stokes–Robinson Equation	29
1.2.8	Ion Pair Formation	29
1.2.8.1	Ion Pairs	29
1.2.8.2	The Fuoss Treatment	30
1.2.9	Ion Dynamics	32
1.2.9.1	Ionic Mobility and Transport Numbers	32
1.2.9.2	Diffusion	33

1.2.9.3	Fick's Second Law	33
1.2.9.4	Diffusion Statistics	35
1.3	Dynamic Electrochemistry	36
1.3.1	Review of Fundamentals	36
1.3.1.1	Potential	36
1.3.1.2	Potential inside a Good Conductor	37
1.3.1.3	Charge on a Good Conductor	37
1.3.1.4	Force between Charges	37
1.3.1.5	Potential due to an Assembly of Charges	37
1.3.1.6	Potential Difference between Two Phases in Contact ($\Delta\phi$)	38
1.3.1.7	The Electrochemical Potential ($\bar{\mu}$)	39
1.3.2	The Electrically Charged Interface or Double Layer	39
1.3.2.1	The Interface	39
1.3.2.2	Ideally Polarized Electrode	40
1.3.2.3	The Helmholtz Model	40
1.3.2.4	Gouy–Chapman or Diffuse Model	42
1.3.2.5	The Stern Model	43
1.3.2.6	The Bockris, Devanathan, and Muller Model	45
1.3.2.7	Calculation of the Capacitance	48
1.3.3	Charge Transfer at the Interface	49
1.3.3.1	Transition State Theory	49
1.3.3.2	Redox Charge-Transfer Reactions	50
1.3.3.3	The Act of Charge Transfer	53
1.3.3.4	The Butler–Volmer Equation	55
1.3.3.5	I in Terms of the Standard Rate Constant (k^0)	56
1.3.3.6	Relation between k^0 and I_0	56
1.3.4	Multistep Processes	57
1.3.4.1	The Multistep Butler–Volmer Equation	57
1.3.4.2	Rules for Mechanisms	58
1.3.4.3	Concentration Dependence of I_0	59
1.3.4.4	Charge-Transfer Resistance (R_{ct})	60
1.3.4.5	Whole Cell Voltages	60
1.3.5	Mass Transport Control	61
1.3.5.1	Diffusion and Migration	61
1.3.5.2	The Limiting Current Density (I_L)	62
1.3.5.3	Rotating Disk Electrode	64
	Further Reading	64
2	General Properties of Electrochemical Capacitors	69
	<i>Tony Pandolfo, Vanessa Ruiz, Seepalakottai Sivakkumar, and Jawahr Nerkar</i>	
2.1	Introduction	69
2.2	Capacitor Principles	70
2.3	Electrochemical Capacitors	71
2.3.1	Electric Double-Layer Capacitors	75

2.3.1.1	Double-Layer and Porous Materials Models	75
2.3.1.2	EDLC Construction	77
2.3.2	Pseudocapacitive Electrochemical Capacitors	86
2.3.2.1	Electronically Conducting Polymers	87
2.3.2.2	Transition Metal Oxides	93
2.3.2.3	Lithium-Ion Capacitors	98
2.4	Summary	100
	Acknowledgments	101
	References	101
3	Electrochemical Techniques	111
	<i>Pierre-Louis Taberna and Patrice Simon</i>	
3.1	Electrochemical Apparatus	111
3.2	Electrochemical Cell	111
3.3	Electrochemical Interface: Supercapacitors	114
3.4	Most Used Electrochemical Techniques	115
3.4.1	Transient Techniques	115
3.4.1.1	Cyclic Voltammetry	115
3.4.1.2	Galvanostatic Cycling	117
3.4.2	Stationary Technique	119
3.4.2.1	Electrochemical Impedance Spectroscopy	119
3.4.2.2	Supercapacitor Impedance	124
	References	129
4	Electrical Double-Layer Capacitors and Carbons for EDLCs	131
	<i>Patrice Simon, Pierre-Louis Taberna, and François Béguin</i>	
4.1	Introduction	131
4.2	The Electrical Double Layer	132
4.3	Types of Carbons Used for EDLCs	135
4.3.1	Activated Carbon Powders	135
4.3.2	Activated Carbon Fabrics	137
4.3.3	Carbon Nanotubes	138
4.3.4	Carbon Aerogels	138
4.4	Capacitance versus Pore Size	138
4.5	Evidence of Desolvation of Ions	141
4.6	Performance Limitation: Pore Accessibility or Saturation of Porosity	148
4.6.1	Limitation by Pore Accessibility	148
4.6.2	Limitation of Capacitor Performance by Porosity Saturation	150
4.7	Beyond the Double-Layer Capacitance in Microporous Carbons	153
4.7.1	Microporous Carbons in Neat Ionic Liquid Electrolyte	153
4.7.2	Extra Capacitance with Ionic Liquids in Solution	157
4.7.3	Ions Trapping in Pores	159
4.7.4	Intercalation/Insertion of Ions	161
4.8	Conclusions	162
	References	163

5	Modern Theories of Carbon-Based Electrochemical Capacitors	167
	<i>Jingsong Huang, Rui Qiao, Guang Feng, Bobby G. Sumpter, and Vincent Meunier</i>	
5.1	Introduction	167
5.1.1	Carbon-Based Electrochemical Capacitors	167
5.1.2	Elements of EDLCs	169
5.2	Classical Theories	172
5.2.1	Compact Layer at the Interface	172
5.2.2	Diffuse Layer in the Electrolyte	173
5.2.3	Space Charge Layer in the Electrodes	175
5.3	Recent Developments	176
5.3.1	Post-Helmholtz Models with Surface Curvature Effects	176
5.3.1.1	Models for Endohedral Capacitors	176
5.3.1.2	Models for Hierarchically Porous Carbon Materials	185
5.3.1.3	Models for Exohedral Capacitors	187
5.3.2	EDL Theories Beyond the GCS Model	189
5.3.3	Quantum Capacitance of Graphitic Carbons	191
5.3.4	Molecular Dynamics Simulations	192
5.3.4.1	EDLs in Aqueous Electrolytes	193
5.3.4.2	EDLs in Organic Electrolytes	196
5.3.4.3	EDLs in Room-Temperature ILs	197
5.4	Concluding Remarks	201
	Acknowledgments	202
	References	203
6	Electrode Materials with Pseudocapacitive Properties	207
	<i>Elżbieta Frąckowiak</i>	
6.1	Introduction	207
6.2	Conducting Polymers in Supercapacitor Application	208
6.3	Metal Oxide/Carbon Composites	212
6.4	Pseudocapacitive Effect of Heteroatoms Present in the Carbon Network	214
6.4.1	Oxygen-Enriched Carbons	215
6.4.2	Nitrogen-Enriched Carbons	216
6.5	Nanoporous Carbons with Electrosorbed Hydrogen	222
6.6	Electrolytic Solutions – a Source of Faradaic Reactions	226
6.7	Conclusions – Profits and Disadvantages of Pseudocapacitive Effects	231
	References	233
7	Li-Ion-Based Hybrid Supercapacitors in Organic Medium	239
	<i>Katsuhiko Naoi and Yuki Nagano</i>	
7.1	Introduction	239
7.2	Voltage Limitation of Conventional EDLCs	239
7.3	Hybrid Capacitor Systems	242

7.3.1	Lithium-Ion Capacitor (LIC)	243
7.3.2	Nanohybrid Capacitor (NHC)	247
7.4	Material Design for NHC	248
7.5	Conclusion	254
	Abbreviations	255
	References	255
8	Asymmetric and Hybrid Devices in Aqueous Electrolytes	257
	<i>Thierry Brousse, Daniel Bélanger, and Daniel Guay</i>	
8.1	Introduction	257
8.2	Aqueous Hybrid (Asymmetric) Devices	259
8.2.1	Principles, Requirements, and Limitations	259
8.2.2	Activated Carbon/PbO ₂ Devices	262
8.2.3	Activated Carbon/Ni(OH) ₂ Hybrid Devices	267
8.2.4	Aqueous-Based Hybrid Devices Based on Activated Carbon and Conducting Polymers	269
8.3	Aqueous Asymmetric Electrochemical Capacitors	272
8.3.1	Principles, Requirements, and Limitations	272
8.3.2	Activated Carbon/MnO ₂ Devices	274
8.3.3	Other MnO ₂ -Based Asymmetric or Hybrid Devices	278
8.3.4	Carbon/Carbon Aqueous Asymmetric Devices	279
8.3.5	Carbon/RuO ₂ Devices	280
8.4	Tantalum Oxide–Ruthenium Oxide Hybrid Capacitors	282
8.5	Perspectives	282
	References	283
9	EDLCs Based on Solvent-Free Ionic Liquids	289
	<i>Mariachiara Lazzari, Catia Arbizzani, Francesca Soavi, and Marina Mastragostino</i>	
9.1	Introduction	289
9.2	Carbon Electrode/Ionic Liquid Interface	291
9.3	Ionic Liquids	292
9.4	Carbon Electrodes	297
9.5	Supercapacitors	298
9.6	Concluding Remarks	302
	Ionic Liquid Codes	303
	Glossary	304
	References	305
10	Manufacturing of Industrial Supercapacitors	307
	<i>Philippe Azaïs</i>	
10.1	Introduction	307
10.2	Cell Components	309
10.2.1	Electrode Design and Its Components	309
10.2.1.1	Current Collector	309

10.2.1.2	Activated Carbons for Supercapacitors	312
10.2.1.3	Industrial Activated Carbons for Industrial Supercapacitors	317
10.2.1.4	Particle Size Distribution of Activated Carbons and Its Optimization	320
10.2.1.5	Binders	322
10.2.1.6	Conductive Additives	325
10.2.2	Electrolyte	326
10.2.2.1	Electrolyte Impact on Performance	327
10.2.2.2	Liquid-State Electrolyte and Remaining Problems	340
10.2.2.3	Ionic Liquid Electrolyte	341
10.2.2.4	Solid-State Electrolyte	343
10.2.3	Separator	343
10.2.3.1	Separator Requirements	343
10.2.3.2	Cellulosic Separators and Polymeric Separators	343
10.3	Cell Design	345
10.3.1	Small-Size Components	347
10.3.2	Large Cells	347
10.3.2.1	High-Power Cells	348
10.3.2.2	Energy Cells	350
10.3.2.3	Pouch Cell design	351
10.3.2.4	Debate on Cell Design: Prismatic versus Cylindrical Cells	351
10.3.2.5	Aqueous Medium Cells	351
10.4	Module Design	352
10.4.1	Large Modules Based on Hard-Type Cells	353
10.4.1.1	Metallic Connections Between Cells	354
10.4.1.2	Electric Terminal for Module	354
10.4.1.3	Insulator for Module	354
10.4.1.4	Cell Balancing and Other Information Detection	356
10.4.1.5	Module Enclosure	357
10.4.2	Large Modules Based on Pouch-Type Cells	357
10.4.3	Large Modules Working in Aqueous Electrolytes	359
10.4.4	Other Modules Based on Asymmetric Technologies	360
10.5	Conclusions and Perspectives	362
	References	363
11	Supercapacitor Module Sizing and Heat Management under Electric, Thermal, and Aging Constraints	373
	<i>Hamid Gualous and Roland Gallay</i>	
11.1	Introduction	373
11.2	Electrical Characterization	374
11.2.1	C and ESR Measurement	374
11.2.1.1	Capacitance and Series Resistance Characterization in the Time Domain	374
11.2.1.2	Capacitance and Series Resistance Characterization in the Frequency Domain	375

11.2.2	Supercapacitor Properties, Performances, and Characterization	376
11.2.2.1	Capacitance and ESR as a Function of the Voltage	376
11.2.2.2	Capacitance and ESR as a Function of the Temperature	378
11.2.2.3	Self-Discharge and Leakage Current	378
11.2.3	“Ragone Plot” Theory	381
11.2.3.1	Match Impedance	383
11.2.3.2	Power Available for the Load, Ragone Equation	384
11.2.4	Energetic Performance and Discharging at Constant Current	387
11.2.5	Energetic Performance and Discharging at Constant Power	389
11.2.6	Energetic Performance and Discharging at Constant Load	394
11.2.7	Efficiency	394
11.3	Thermal Modeling	395
11.3.1	Thermal Modeling of Supercapacitors	397
11.3.2	Conduction Heat Transfer	397
11.3.3	Thermal Boundary Conditions	399
11.3.4	Convection Heat Transfer Coefficient	401
11.3.5	Solution Procedure	402
11.3.6	BCAP0350 Experimental Results	404
11.4	Supercapacitor Lifetime	410
11.4.1	Failure Modes	411
11.4.2	Temperature and Voltage as an Aging Acceleration Factor	411
11.4.3	Physical Origin of Aging	413
11.4.4	Testing	415
11.4.5	DC Voltage Test	415
11.4.6	Voltage Cycling Test	417
11.5	Supercapacitor Module Sizing Methods	418
11.6	Applications	420
11.6.1	Power Management of Fuel Cell Vehicles	421
11.6.1.1	Problem Statement	421
11.6.1.2	Fuel Cell Modeling	421
11.6.1.3	Supercapacitors Modeling	422
11.6.2	The Power Management of a Fuel Cell Vehicle by Optimal Control	422
11.6.2.1	Optimal Control without Constraint	423
11.6.2.2	The Hamilton–Jacobi–Bellman Equation	423
11.6.3	Optimal Control with Inequality Constraints on the Fuel Cell Power and on the Fuel Cell Power Rate	427
11.6.3.1	Constraints on the Fuel Cell Power	427
11.6.3.2	Constraints on the Fuel Cell Power Rate	427
11.6.4	Power Management of Fuel Cell Vehicle by Optimal Control Associated to Sliding Mode Control	429
11.6.5	Conclusion	433
	References	434

12	Testing of Electrochemical Capacitors	437
	<i>Andrew Burke</i>	
12.1	Introduction	437
12.2	Summaries of DC Test Procedures	437
12.2.1	USABC Test Procedures	439
12.2.2	IEC Test Procedures	440
12.2.3	UC Davis Test Procedures	441
12.3	Application of the Test Procedures to Carbon/Carbon Devices	443
12.3.1	Capacitance	443
12.3.2	Resistance	443
12.3.3	Energy Density	448
12.3.4	Power Capability	449
12.3.5	Pulse Cycle Testing	453
12.4	Testing of Hybrid, Pseudocapacitive Devices	456
12.4.1	Capacitance	456
12.4.2	Resistance	456
12.4.3	Energy Density	459
12.4.4	Power Capability and Pulse Cycle Tests	460
12.5	Relationships between AC Impedance and DC Testing	460
12.6	Uncertainties in Ultracapacitor Data Interpretation	465
12.6.1	Charging Algorithm	466
12.6.2	Capacitance	466
12.6.3	Resistance	466
12.6.4	Energy Density	467
12.6.5	Power Capability	467
12.6.6	Round-Trip Efficiency	469
12.7	Summary	469
	References	469
13	Reliability of Electrochemical Capacitors	473
	<i>John R. Miller</i>	
13.1	Introduction	473
13.2	Reliability Basics	473
13.3	Cell Reliability	474
13.4	System Reliability	478
13.5	Assessment of Cell Reliability	481
13.5.1	Experimental Approach Example	484
13.6	Reliability of Practical Systems	491
13.6.1	Cell Voltage Nonuniformity	492
13.6.2	Cell Temperature Nonuniformity	494
13.7	Increasing System Reliability	499
13.7.1	Reduce Cell Stress	499
13.7.2	Burn-in of Cells	501
13.7.3	Use Fewer Cells in Series	501
13.7.4	Use “Long-Life” Cells	501

13.7.5	Implement Maintenance	502
13.7.6	Add Redundancy	502
13.8	System Design Example	503
13.8.1	Problem Statement	503
13.8.2	System Analysis	504
13.8.3	Cell Reliability	506
	References	507
14	Market and Applications of Electrochemical Capacitors	509
	<i>John R. Miller</i>	
14.1	Introduction: Principles and History	509
14.2	Commercial Designs: DC Power Applications	510
14.2.1	Bipolar Designs	510
14.2.2	Cell Designs	512
14.2.3	Asymmetric Designs	513
14.3	Energy Conservation and Energy Harvesting Applications	516
14.3.1	Motion and Energy	516
14.3.2	Hybridization: Energy Capture and Reuse	518
14.3.3	Energy Conservation and Efficiency	521
14.3.4	Engine Cranking	521
14.4	Technology Combination Applications	523
14.4.1	Battery/Capacitor Combination Applications	523
14.5	Electricity Grid Applications	523
14.5.1	Storage and the Utility Grid	523
14.6	Conclusions	524
	References	525
	Index	527

Series Editor Preface

The Wiley Series on New Materials for Sustainable Energy and Development

Sustainable energy and development is attracting increasing attention from the scientific research communities and industries alike, with an international race to develop technologies for clean fossil energy, hydrogen and renewable energy as well as water reuse and recycling. According to the REN21 (Renewables Global Status Report 2012 p. 17) total investment in renewable energy reached \$257 billion in 2011, up from \$211 billion in 2010. The top countries for investment in 2011 were China, Germany, the United States, Italy, and Brazil. In addressing the challenging issues of energy security, oil price rise, and climate change, innovative materials are essential enablers.

In this context, there is a need for an authoritative source of information, presented in a systematic manner, on the latest scientific breakthroughs and knowledge advancement in materials science and engineering as they pertain to energy and the environment. The aim of the *Wiley Series on New Materials for Sustainable Energy and Development* is to serve the community in this respect. This has been an ambitious publication project on materials science for energy applications. Each volume of the series will include high-quality contributions from top international researchers, and is expected to become the standard reference for many years to come.

This book series covers advances in materials science and innovation for renewable energy, clean use of fossil energy, and greenhouse gas mitigation and associated environmental technologies. Current volumes in the series are:

- Supercapacitors. Materials, Systems, and Applications
- Functional Nanostructured Materials and Membranes for Water Treatment
- Materials for High-Temperature Fuel Cells
- Materials for Low-Temperature Fuel Cells
- Advanced Thermoelectric Materials. Fundamentals and Applications
- Advanced Lithium-Ion Batteries. Recent Trends and Perspectives
- Photocatalysis and Water Purification. From Fundamentals to Recent Applications

In presenting this volume on Supercapacitors, I would like to thank the authors and editors of this important book, for their tremendous effort and hard work in completing the manuscript in a timely manner. The quality of the chapters reflects well the caliber of the contributing authors to this book, and will no doubt be recognized and valued by readers.

Finally, I would like to thank the editorial board members. I am grateful to their excellent advice and help in terms of examining coverage of topics and suggesting authors, and evaluating book proposals.

I would also like to thank the editors from the publisher Wiley-VCH with whom I have worked since 2008, Dr Esther Levy, Dr Gudrun Walter, and Dr Bente Flier for their professional assistance and strong support during this project.

I hope you will find this book interesting, informative and valuable as a reference in your work. We will endeavour to bring to you further volumes in this series or update you on the future book plans in this growing field.

Brisbane, Australia
31 July 2012

G.Q. Max Lu

Preface

Currently, our planet faces huge challenges related to energy. How to reduce CO₂ emissions and fossil fuel consumption? How to introduce renewable energies in the energy mix? Of course these are not new questions, but simply, until the end of the last century, no one cared about the scarcity of fossil fuels even if some warnings appeared during the successive oil crises.

The answer to the above questions is energy saving as well as energy management. It is exactly the role that can be played by electrochemical capacitors, so-called supercapacitors, because of their ability to store larger amounts of energy than the traditional dielectric capacitors. Such exceptional properties originate from the nanometric scale capacitors built from the polarized electrode material and a layer of attracted ions on its surface. The thickness of the electrode–electrolyte interface is directly controlled by the size of ions. Supercapacitors are able to harvest energy in very short periods (less than one minute) and to subsequently provide burst of energy when needed. They are now a reality in the market, where they are applied in automotive and stationary systems, and allow energy savings ranging from 10 to 40%. They can also play a role in the stabilization of current when intermittent renewable energies are introduced in the energetic mix.

Although supercapacitors are now commercially available, they still require improvements, especially for enhancing their energy density. It requires a fundamental understanding of their properties and exact operating principles, in addition to improving electrode materials, electrolytes past and integration in systems. All these topics led to a very strong motivation of academics and industry during the decade.

When Max Lu invited us to suggest a book in his series *Materials for Sustainable Energy and Development*, we immediately thought about Supercapacitors. Indeed, since the fantastic pioneer book *Electrochemical supercapacitors: Scientific Fundamentals and Technological Applications* published by B.E. Conway in 1999, no other comprehensive book was dealing extensively with the topic of supercapacitors, and until now the book is generally referred in almost all scientific publications concerning this subject. During the past 10 years new ideas appeared, such as a better description of what is really the double-layer in these systems and hybrid and asymmetric capacitors, requiring a comprehensive review.

Our book entitled *Supercapacitors: materials and systems* does not intend to substitute but be a complement to the Conway's book taking advantage of the developments which appeared in the past decade. It is dedicated to researchers and engineers involved with supercapacitor science, its developments, and implementation. The book is also intended for graduate and undergraduate students wanting to special in energy storage systems.

For these reasons, it has been written in collaboration with scientists world-wide renowned in supercapacitors science and also with contributors from the industry. The book includes 14 chapters: 3 being dedicated to general principles of electrochemistry, electrochemical characterization techniques and general properties of supercapacitors in order to allow reading the book without any prerequisite knowledge; 3 to fundamentals, general properties, and modelling of electrical double-layer capacitors, and pseudo-capacitors; 3 to new trends such as asymmetric and hybrid capacitors, and the use of ionic liquid electrolytes; 2 to manufacturing and modules sizing; 3 to testing, reliability, and applications of supercapacitors. Each chapter aims at giving the most detailed information using familiar terms.

We are very happy and proud that we could gather, in this book, the greatest names in supercapacitors science and technology. All are colleagues and friends who we met in international conferences or with whom we have had the pleasure to collaborate. They all kindly accepted to devote their time for contributing chapters; we sincerely and warmly thank them for their help. We also would like to thank our friend Max Lu for giving us this wonderful opportunity and also the Wiley staff for being patient. Finally, we would like to dedicate this book to our solve parents who would be very proud to see our small contribution in helping solve humanity problems.

Poznan
November 2012

François Bèguin and Elzbieta Frackowiak

About the Series Editor



Professor Max Lu

Editor, New Materials for Sustainable Energy and Development Series

Professor Lu's research expertise is in the areas of materials chemistry and nanotechnology. He is known for his work on nanoparticles and nanoporous materials for clean energy and environmental technologies. With over 500 journal publications in high-impact journals, including *Nature*, *Journal of the American Chemical Society*, *Angewandte Chemie*, and *Advanced Materials*, he is also coinventor of 20 international patents. Professor Lu is an Institute for Scientific Information (ISI) Highly Cited Author in Materials Science with over 17 500 citations (h-index of 63). He has received numerous prestigious awards nationally and internationally, including the Chinese Academy of Sciences International Cooperation Award (2011), the Orica Award, the RK Murphy Medal, the Le Fevre Prize, the ExxonMobil Award, the Chemeca Medal, the Top 100 Most Influential Engineers in Australia (2004, 2010, and 2012), and the Top 50 Most Influential Chinese in the World (2006). He won the Australian Research Council Federation Fellowship twice (2003 and 2008). He is an elected Fellow of the Australian Academy of Technological Sciences and Engineering (ATSE) and Fellow of Institution of Chemical Engineers (IChemE). He is editor and editorial board member of 12 major international journals including *Journal of Colloid and Interface Science* and *Carbon*.

Max Lu has been Deputy Vice-Chancellor and Vice-President (Research) since 2009. He previously held positions of acting Senior Deputy Vice-Chancellor (2012), acting Deputy Vice-Chancellor (Research), and Pro-Vice-Chancellor (Research

Linkages) from October 2008 to June 2009. He was also the Foundation Director of the ARC Centre of Excellence for Functional Nanomaterials from 2003 to 2009.

Professor Lu had formerly served on many government committees and advisory groups including the Prime Minister's Science, Engineering and Innovation Council (2004, 2005, and 2009) and the ARC College of Experts (2002–2004). He is the past Chairman of the IChemE Australia Board and former Director of the Board of ATSE. His other previous board memberships include Uniseed Pty Ltd., ARC Nanotechnology Network, and Queensland China Council. He is currently Board member of the Australian Synchrotron, National eResearch Collaboration Tools and Resources, and Research Data Storage Infrastructure. He also holds a ministerial appointment as member of the National Emerging Technologies Forum.

About the Volume Editors



Prof. François Béguin

*Poznan University of Technology,
Faculty of Chemical Technology,
Piotrowo 3, 60-965 Poznan, Poland
francois.beguin@put.poznan.pl
tel. ++48 61 665 3632
fax ++48 61 665 2571*

François Béguin is a professor at the Poznan University of Technology (Poland), where he was recently awarded the WELCOME stipend from the Foundation for Polish Science. His research activities are devoted to chemical and electrochemical applications of carbon materials, with special attention to the development of nanocarbons with controlled porosity and surface functionality for applications to energy conversion/storage and environment protection. The main topics investigated in his research group are lithium batteries, supercapacitors, electrochemical hydrogen storage, and reversible electrosorption of water contaminants. He published over 250 publications in high-ranking international journals, and his works are cited in 8300 papers, with Hirsch index 46. He is also involved in several books dealing with carbon materials and energy storage. He is a member of the International Advisory Board of the Carbon Conferences and has launched the international conferences on Carbon for Energy Storage and Environment Protection (CESEP). He is a member of the editorial board of the journal *Carbon*. He was Professor of materials science in the Orléans University (France) until 2012 and was Director of national programmes on Energy Storage (Stock-E), Hydrogen and Fuel Cells (H-PAC), and electricity management (PROGELEC) in the French Agency for Research (ANR).

**Prof. Elzbieta Frackowiak**

*Poznan University of Technology, Institute of
Chemistry and Technical Electrochemistry,*

Piotrowo 3, 60-965 Poznan, Poland

Elzbieta.Frackowiak@put.poznan.pl

tel. ++48 61 665 3632

fax ++48 61 665 2571

Elzbieta Frackowiak is a full professor at the Institute of Chemistry and Technical Electrochemistry at the Poznan University of Technology. Her main research topics are devoted to energy storage in electrochemical capacitors, Li-ion batteries, and hydrogen electrosorption. She is especially interested in the development of electrode materials (nanoporous carbons, template carbons, carbon nanotubes, graphene, etc.), composite electrodes from conducting polymers, and doped carbons and transition-metal oxides for supercapacitors, as well as in new concepts of supercapacitors based on the carbon/redox couples interface.

She serves as Chair of Division 3 “Electrochemical Energy Conversion and Storage” of the International Society of Electrochemistry (2009–2014). She is a member of International Advisory Boards – *Electrochimica Acta* from 2011 and *Energy & Environmental Science* from 2008. She was chair/cochair of a few international conferences (12th International Symposium on Intercalation Compounds (ISIC 12) Poznań, Poland, 1–5 June 2003; 2nd International Symposium on Enhanced Electrochemical Capacitors (ISEECap’11), Poznań, Poland, 12–16 June 2011; and the World CARBON conference in Krakow, 17–22 June 2012). She was the winner of the Foundation for Polish Science Prize, the so-called Polish Nobel (December 2011) and was also decorated with the Order of Polonia Restituta (December 2011) and the Order Sapienti Sat (October 2012).

She is the author of 150 publications, a few chapters, and tens of patent applications. The number of her citations is about 6000, with Hirsch index 36.

List of Contributors

Catia Arbizzani

Alma Mater Studiorum
Università di Bologna
Dipartimento di Scienza
dei Metalli
Elettrochimica e Tecniche
Chimiche
Via San Donato 15
40127 Bologna
Italy

Philippe Azais

Batscap Supercapacitor
Business Unit
Odet, Ergue-Gaberic
29556 Quimper Cedex 9
France

and

Commissariat à l'Energie
Atomique (CEA)
LITEN (Laboratoire d'Innovation
pour les Technologies des
Energies Nouvelles)
17 rue des Martyrs
38054 Grenoble Cedex 9
France

Daniel Bélanger

Université du Québec à Montréal
Département de Chimie
case postale 8888
succursale centre-ville
Montréal
Québec H3C 3P8
Canada

François Béguin

Poznan University of Technology
Faculty of Chemical Technology
u1. Piotrowo 3
60-965 Poznan
Poland

Thierry Brousse

Université de Nantes
Institut des Matériaux Jean
Rouxel (IMN)
CNRS/Université de Nantes
Polytech Nantes
BP50609
44306 Nantes Cedex 3
France

Andrew Burke

University of California-Davis
Institute of Transportation
Studies
One Shields Avenue
Davis, CA 95616
USA

Scott W. Donne

University of Newcastle
School of Environmental and Life
Sciences
Office C325, Chemistry
Callaghan
New South Wales 2308
Australia

Guang Feng

Clemson University
Department of Mechanical
Engineering
Clemson, SC 29634-0921
USA

Elżbieta Frąckowiak

Poznan University of Technology
Faculty of Chemical Technology
Institute of Chemistry and
Technical Electrochemistry
u1. Piotrowo 3
60-965 Poznan
Poland

Roland Gallay

Garmanage
Clos-Besson 6
CH-1726
Farvagny-le-Petit
Switzerland

Hamid Gualous

Université de Caen Basse
Normandie
Esplanade de la Paix
BP 5186
14032, Caen Cedex 5
France

Daniel Guay

INRS-Énergie
Matériaux et
Télécommunications
1650 Boulevard Lionel Boulet
case postale 1020
Varenes
Québec J3X 1 S2
Canada

Jingsong Huang

Center for Nanophase Materials
Sciences, and Computer Science
and Mathematics Division
Oak Ridge National Laboratory
Bethel Valley Road
Oak Ridge, TN 37831-6367
USA

Mariachiara Lazzari

Alma Mater Studiorum
Università di Bologna
Dipartimento di Scienza dei Metalli
Elettrochimica e Tecniche Chimiche
Via San Donato 15
40127 Bologna
Italy

Marina Mastragostino

Alma Mater Studiorum
Università di Bologna
Dipartimento di Scienza dei
Metalli
Elettrochimica e Tecniche
Chimiche
Via San Donato 15
40127 Bologna
Italy

Vincent Meunier

Center for Nanophase Materials
Sciences, and Computer Science
and Mathematics Division
Oak Ridge National Laboratory
Bethel Valley Road
Oak Ridge, TN 37831-6367
USA

John R. Miller

JME Inc
23500 Mercantile Road, Suite L
Beachwood, OH 44122
USA

and

Case Western Reserve University
Great Lakes Energy Institute
Electrical Engineering and
Computer Science
10900 Euclid Avenue
Cleveland, OH 44106
USA

Yuki Nagano

Tokyo University of Agriculture
and Technology
School of Engineering
Division of Applied Chemistry
2-24-16 Naka-cho
Koganei
Tokyo 184-8558
Japan

Katsuhiko Naoi

Tokyo University of Agriculture
and Technology
School of Engineering, Division
of Applied Chemistry
2-24-16 Naka-cho
Koganei
Tokyo 184-8558
Japan

Jawahr Nerkar

CSIRO Energy Technology
Normanby Rd
Clayton South
Victoria 3169
Australia

Tony Pandolfo

CSIRO Energy Technology
Normanby Rd
Clayton South
Victoria 3169
Australia

Rui Qiao

Clemson University
Department of Mechanical
Engineering
Clemson, SC 29634-0921
USA

Vanessa Ruiz

CSIRO Energy Technology
Normanby Rd
Clayton South
Victoria 3169
Australia

Seepalakottai Sivakkumar

CSIRO Energy Technology
Normanby Rd
Clayton South
Victoria 3169
Australia

Patrice Simon

Unversitè Toulouse III
Institut Carnot CIRIMAT - UMR
CNRS 5085
118 route de Narbonne
31062 Toulouse
France

Bobby G. Sumpter

Center for Nanophase Materials
Sciences, and Computer Science
and Mathematics Division
Oak Ridge National Laboratory
Bethel Valley Road
Oak Ridge, TN 37831-6367
USA

Francesca Soavi

Alma Mater Studiorum
Università di Bologna
Dipartimento di Scienza dei
Metalli
Elettrochimica e Tecniche
Chimiche
Via San Donato 15
40127 Bologna
Italy

Pierre-Louis Taberna

Unversitè Toulouse III
Institut Carnot CIRIMAT - UMR
CNRS 5085
118 route de Narbonne
31062 Toulouse
France