ELECTROCHEMICAL ENERGY STORAGE AND CONVERSION

Electrolytes for Electrochemical Supercapacitors

Cheng Zhong • Yida Deng • Wenbin Hu
Daoming Sun • Xiaopeng Han • Jinli Qiao
Jiujun Zhang

CRC Press
Taylor & Francis Group

Electrolytes for Electrochemical Supercapacitors

Edited by

Cheng Zhong • Yida Deng • Wenbin Hu
Daoming Sun • Xiaopeng Han • Jinli Qiao
Jiujun Zhang

CRC Press
Taylor & Francis Group
Boca Raton London New York

CRC Press is an imprint of the
Taylor & Francis Group, an informa business

CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

Printed on acid-free paper
Version Date: 20151218

International Standard Book Number-13: 978-1-4987-4755-4 (Hardback)

Library of Congress Cataloging-in-Publication Data

Names: Zhong, Cheng (Electrical engineer), editor.
Title: Electrolytes for electrochemical supercapacitors / editors, Cheng Zhong, Yida Deng, Wenbin Hu, Daoming Sun, Xiaopeng Han, Jinli Qiao, Jiujun Zhang.
Description: Boca Raton : Taylor & Francis, 2016. | Series: Electrochemical energy storage and conversion | Includes bibliographical references and index.
Identifiers: LCCN 2015048071 | ISBN 9781498747554 (alk. paper)
Subjects: LCSH: Supercapacitors--Materials. | Electrolytes. | Electrolytic capacitors.
Classification: LCC TK7872.C65 E46 2016 | DDC 621.31/5--dc23
LC record available at http://lccn.loc.gov/2015048071

Visit the Taylor & Francis Web site at
http://www.taylorandfrancis.com

and the CRC Press Web site at
http://www.crcpress.com

Electrolytes for Electrochemical Supercapacitors

ELECTROCHEMICAL ENERGY STORAGE AND CONVERSION

Series Editor: Jiujun Zhang
National Research Council Institute for Fuel Cell Innovation
Vancouver, British Columbia, Canada

Published Titles

Electrochemical Supercapacitors for Energy Storage and Delivery: Fundamentals and Applications
Aiping Yu, Victor Chabot, and Jiujun Zhang

Proton Exchange Membrane Fuel Cells
Zhigang Qi

Graphene: Energy Storage and Conversion Applications
Zhaoping Liu and Xufeng Zhou

Electrochemical Polymer Electrolyte Membranes
Jianhua Fang, Jinli Qiao, David P. Wilkinson, and Jiujun Zhang

Lithium-Ion Batteries: Fundamentals and Applications
Yuping Wu

Lead-Acid Battery Technologies: Fundamentals, Materials, and Applications
Joey Jung, Lei Zhang, and Jiujun Zhang

Solar Energy Conversion and Storage: Photochemical Modes
Suresh C. Ameta and Rakshit Ameta

Electrochemical Energy: Advanced Materials and Technologies
Pei Kang Shen, Chao-Yang Wang, San Ping Jiang, Xueliang Sun, and Jiujun Zhang

Electrolytes for Electrochemical Supercapacitors
Cheng Zhong, Yida Deng, Wenbin Hu, Daoming Sun, Xiaopeng Han, Jinli Qiao, and Jiujun Zhang

Series Preface

The goal of the *Electrochemical Energy Storage and Conversion* book series is to provide comprehensive coverage of the field, with titles focusing on fundamentals, technologies, applications, and the latest developments, including secondary (or rechargeable) batteries, fuel cells, supercapacitors, CO_2 electroreduction to produce low-carbon fuels, electrolysis for hydrogen generation/storage, and photoelectrochemistry for water splitting to produce hydrogen, among others. Each book in this series is self-contained, written by scientists and engineers with strong academic and industrial expertise who are at the top of their fields and on the cutting edge of technology. With a broad view of various electrochemical energy conversion and storage devices, this unique book series provides essential reading for university students, scientists, and engineers, and allows them to easily locate the latest information on electrochemical technology, fundamentals, and applications.

Jiujun Zhang
National Research Council of Canada
Richmond, British Columbia

Preface

The electrochemical supercapacitor (ES), also known as a supercapacitor, ultracapacitor, or electrochemical capacitor, is a special type of capacitor that can have relatively high-energy density when compared to conventional dielectric capacitors and electrolytic capacitors. As an electrochemical energy storage/conversion device the ES has several advantages, such as fast charging–discharging capability, immense power density, wide operating temperature ranges, and long service lifetimes. As a result, ESs have been found to be readily applicable in a wide variety of important applications such as hybrid and electrical vehicles, portable electronics, backup power supplies, aircraft, and smart grids. In particular, they can play a significant role in the effective use of intermittent energies from renewable sources.

Although ESs are now available in commercial markets, they still face some challenges, such as relatively low-energy density compared to both batteries and fuel cells. This low-energy density will limit their wide applications in many high energy–demanding systems, and also cause high manufacturing cost. In recent years, there have been tremendous efforts focusing on the development of novel electrode materials and electrolytes as well as electrode/electrolyte configurations to improve the energy density for the next generation of supercapacitors.

For fundamental aspects, in Conway's excellent pioneering book (*Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications*), published in 1999, he provided a comprehensive discussion of the science of ESs in the twentieth century. In 2013, Yu et al. published *Electrochemical Supercapacitors for Energy Storage and Delivery: Fundamentals and Applications* and Béguin et al. published *Supercapacitors: Materials, Systems, and Applications*, covered comprehensive science and technology, as well as coverage of the latest developments of ESs including electrical double-layer capacitors and pseudocapacitors. The critical roles of both ES electrode materials and electrolytes in improving energy density are emphasized in these books.

On the basis of our recent review paper published in *Chemical Society Reviews* (2015, 44: 7484–7539), we have largely extended this paper's content and completed this book covering the key aspects of novel and advanced electrolyte systems and compositions. This book focuses on both the fundamental and technological aspects of all kinds of ES electrolytes. The effects of electrolytes on ES performance are highlighted. Some comparisons among different electrolytes in terms of their associated ES performance are presented. This book also discusses the compatibility issue or interactions between ES electrolytes, active components such as electrode materials, and inactive components such as current collectors, binders, additives, and separators. The book also illuminates the practical aspects of designing and optimizing electrolyte systems for improving ES performance. We have a strong desire to have this book be beneficial for the research and development activities of academic researchers, graduate/undergraduate students, industry professionals, and manufacturers of electrode/electrolyte systems, and also for other electrochemical energy devices such as batteries, and end users of these devices.

We acknowledge and express our sincere thanks to the contributions of all those who involved in preparing and developing this book. We also express our appreciation to CRC Press for giving us this great opportunity to lead this book project, particularly to Allison Shatkin, Jill Jurgensen, and Ariel Crockett for their guidance and support in the book preparation process. Finally, we are also grateful for the support of the National Natural Science Foundation for Distinguished Young Scholars of China (no. 51125016), and the National Natural Science Foundation of China (no. 51472178).

If there are any technical errors in the book, we would deeply welcome any constructive comments for further improvement.

Editors

Cheng Zhong is an associate professor in the School of Materials Science and Engineering at Tianjin University. Prior to joining the faculty at Tianjin University, he worked as an associate professor in the State Key Laboratory of Metal Matrix Composites, Department of Materials Science and Engineering at Shanghai Jiao Tong University. He earned his BSc and PhD in materials science from Fudan University in 2004 and 2009, respectively. Dr. Zhong's recent research interests focus on the development of electrochemical metallurgy methods for preparing micro/nanostructured materials for electrochemical and electrocatalysis applications.

Yida Deng is a professor in the School of Materials Science and Engineering, Tianjin University. He earned his PhD from Shanghai Jiao Tong University in 2006. Dr. Deng's research interests include metal and metal oxide nanostructures for electrochemical and energy applications.

Wenbin Hu is a professor and dean of the School of Materials Science and Engineering at Tianjin University. Prior to joining the faculty at Tianjin University, he worked as a professor in the Department of Materials Science and Engineering at Shanghai Jiao Tong University. He graduated from Central-South University with a BSc in 1988, and earned an MSc from Tianjin University in 1991. He earned a PhD from Central-South University in 1994. Dr. Hu is a member of the expert group on advanced structural and composite materials in the new materials field of China's 863 Program

(National High-Tech Research and Development Program). He received the support of the National Science Foundation for Distinguished Young Scholars of China in 2011. Dr. Hu's research interests focus on the design, synthesis, and characterization of advanced micro/nanomaterials for energy storage and conversion applications.

Daoming Sun is a chief technology officer at the Suzhou LiCeram Electronic Technology Co., Ltd (www.liceram.cn). He earned his PhD in physical electronics from Fudan University and holds a bachelor's degree in materials science and engineering from Xi'an University of Technology, China. His research focuses on the development of materials for electrochemical environmental sensors. Dr. Sun worked as a team leader at LiCeram, and he has successfully developed a novel high-sensitive sensor series that detects the time of wetness and corrosion current for the corrosion evaluation of metal.

Xiaopeng Han is currently a lecturer in the School of Materials Science and Engineering at Tianjin University. He earned his BSc in chemical engineering and technology from Tianjin University (2010) and PhD in material physics and chemistry from Nankai University (2015). Dr. Han's research interest focuses on functional materials with micro/nanostructures for oxygen electrocatalysis and metal-air batteries.

Jinli Qiao is a professor, PhD supervisor, and scientific core-competency leader at Donghua University, China. She earned her PhD in electrochemistry from Yamaguchi University, Japan, in 2004 before joining the National Institute of Advanced Industrial Science and Technology (AIST), Japan, as a research scientist. From 2004 to 2008, Dr. Qiao carried out seven fuel cell projects including two NEDO projects in Japan on the development of novel proton-conducting membranes, new binders for membrane electrode assembly (MEA) fabrication, and nonplatinum catalysts. From 2008 to the present, she has carried out a total of 12 projects funded by the Chinese government including NNSF of China and IACEP of the Shanghai Science and Technology Committee (SSTC). Dr. Qiao has more than 20 years of scientific research experience, particularly in the areas of electrochemical material development and energy storage and conversion including polymer electrolyte membrane (PEM) fuel cells, supercapacitors, CO_2 electroreduction, and metal-air batteries.

Jiujun Zhang is a principal research officer at the National Research Council of Canada (NRC), and a fellow of the International Society of Electrochemistry (ISE). Dr. Zhang's technical expertise areas are electrochemistry, photoelectrochemistry, spectroelectrochemistry, electrocatalysis, fuel cells (PEMFC, SOFC, and DMFC), batteries, supercapacitors, and electrolysis. Dr. Zhang earned his BS and MSc in electrochemistry from Peking University in 1982 and 1985, respectively, and his PhD in electrochemistry from Wuhan University in 1988. Starting in 1990, he carried out three terms of postdoctoral research at the California Institute of Technology, York University, and the University of British Columbia. Dr. Zhang holds more than 14 adjunct professorships, including one at the University of Waterloo, one at the University of British Columbia, and one at Peking University. To date, Dr. Zhang has approximately 400 publications with more than 16,000 citations, including 230 refereed journal papers with an *H-index* of 60, 15 edited/coauthored books, 37 book chapters, 110 conference oral and keynote/invited presentations, as well as more than 10 US/EU/WO/JP/CA patents, and has produced over 90 industrial technical reports. Dr. Zhang serves as an editor/editorial board member for several international journals as well as an editor for a book series (Electrochemical Energy Storage and Conversion, CRC Press).

Contents

1 Fundamentals of Electrochemical Supercapacitors

Cheng Zhong, Yida Deng, Wenbin Hu, Jinli Qiao, and Jiujun Zhang

CONTENTS

1.1 INTRODUCTION AND APPLICATIONS OF SUPERCAPACITORS

With the increasing consumption of globally limited fossil fuels and the resultant environmental problems such as greenhouse gas emissions and other air pollutants, there is an urgent need to engage sustainable, renewable, and clean energy sources such as the sun, winds, and tides. Since most of these sustainable (renewable) energy sources are dependent on the time of day and location, it is highly desirable to develop related energy storage devices in order to effectively harness these intermittent energy sources. Electrochemical energy storage devices, such as batteries and electrochemical supercapacitors (ESs), will play an increasingly critical role in the sustainable and large-scale use of energy from renewable sources.

ESs, also referred to as supercapacitors, ultracapacitors, or electrochemical capacitors, have received a great deal of attention due to their high power density (potentially above 10 kW kg^{-1}), long lifetime compared to batteries, and much higher energy density compared to conventional dielectric and electrolytic capacitors [1]. Depending on the charge storage mechanism, ESs can be briefly grouped into electrical double-layer capacitors (EDLCs), pseudocapacitors, and hybrid capacitors, which will be discussed further in Section 1.3. To date, EDLCs make up the majority of commercial ESs, mainly due to their technical maturity. The role of ESs among various typical electrochemical energy storage devices can be clearly seen in terms of their power density and energy density (Ragone plot) as shown in

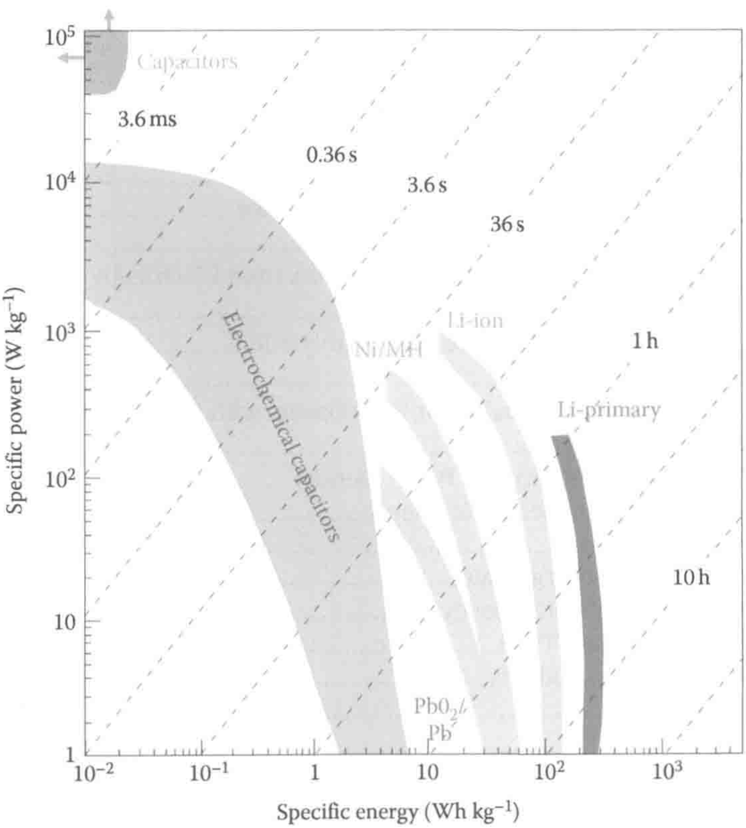

FIGURE 1.1 Ragone plots for representative energy storage devices of capacitors, batteries, and supercapacitors. (Reprinted by permission from Macmillan Publishers Ltd. *Nature Materials*, Simon, P., and Y. Gogotsi. Materials for electrochemical capacitors, 7:845–854, Copyright 2008.)