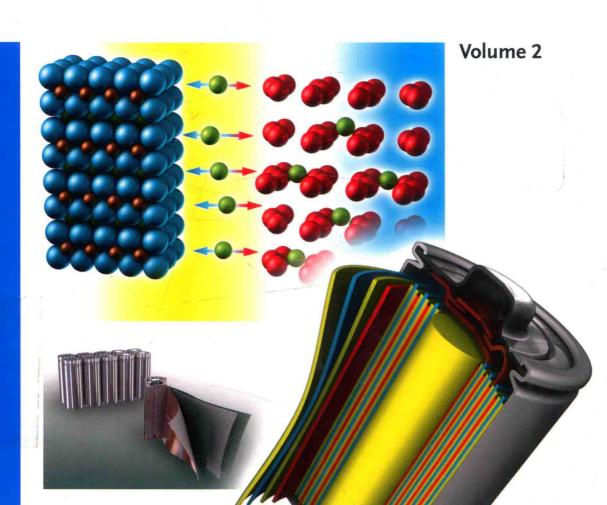
Claus Daniel and Jürgen O. Besenhard (Editors)



# Handbook of Battery Materials

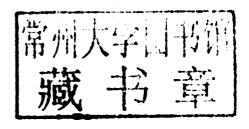
Second, Completely Revised and Enlarged Edition



#### Edited by Claus Daniel and Jürgen O. Besenhard

### Handbook of Battery Materials

Second, Completely Revised and Enlarged Edition





WILEY-VCH Verlag GmbH & Co. KGaA

#### The Editor

#### Dr.-Ing. Claus Daniel

Oak Ridge National Laboratory MS6083 P.O. Box 2008 Oak Ridge, TN 37831-6083 USA 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

Into Deutsche Nationalibiliotnek
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>>.

© 2011 Wiley-VCH Verlag & 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.

Typesetting Laserwords Private Limited,
Chennai

Printing and Binding betz-druck GmbH,
Darmstadt

Cover Design Formgeber, Eppelheim

Printed in the Federal Republic of Germany Printed on acid-free paper

Print ISBN: 978-3-527-32695-2

Edited by Claus Daniel and Jürgen O. Besenhard

Handbook of Battery Materials

#### Related Titles

Lui, R.-S., Zhang, L., Sun, X., Lui, H., Zhang, J., (eds.)

## Electrochemical Technologies for Energy Storage and Conversion

2011

ISBN: 978-3-527-32869-7

Garcia-Martinez, J. (ed.)

## Nanotechnology for the Energy Challenge

2010

ISBN: 978-3-527-32401-9

Stolten, D. (ed.)

#### Hydrogen and Fuel Cells Fundamentals, Technologies and Applications

2010

ISBN: 978-3-527-32711-9

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

Hirscher, M. (ed.)

#### Handbook of Hydrogen Storage

New Materials for Future Energy Storage

2010

ISBN: 978-3-527-32273-2

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

#### Electrocatalysis of Direct Methanol Fuel Cells

From Fundamentals to Applications

2009

ISBN: 978-3-527-32377-7

Ozawa, K. (ed.)

## Lithium Ion Rechargeable Batteries

Materials, Technology, and New Applications

2009

ISBN: 978-3-527-31983-1

Vielstich, W., Gasteiger, H. A., Yokokawa, H. (eds.)

#### Handbook of Fuel Cells

Advances in Electrocatalysis, Materials, Diagnostics and Durability, Volumes 5 & 6

2009

ISBN: 978-0-470-72311-1

Mitsos, A., Barton, P. I. (eds.)

## Microfabricated Power Generation Devices

Design and Technology

2009

ISBN: 978-3-527-32081-3

#### Dedication: Jürgen O. Besenhard (1944-2006)

The first edition of the "Handbook of Battery Materials" was edited by Professor Jürgen Otto Besenhard. Jürgen Besenhard began his scientific career at the time, when the era of lithium batteries came up. With his strong background in chemistry and his outstanding ability to interpret and understand the complex phenomena behind the many exploratory research findings on lithium batteries in the late 1960s and early to mid 1970s, Jürgen Besenhard was able to attribute "performance" to material properties. His early work is evidence for this:

- Understanding of reversible alkali metal ion intercalation into graphite anodes (J. Electroanal. Chem., 53 (1974) 329 and Carbon, 14 (1976) 111)
- 2) Understanding of reversible alkali metal ion insertion into oxide materials for cathodes (*Mat. Res. Bull.*, 11 (1976) 83 and *J. Power Sources*, 1 (1976/1977) 267)
- 3) First reviews on lithium batteries (J. Electroanal. Chem., 68 (1976) 1 and J. Electroanal. Chem., 72 (1976) 1)
- Preparation of lithium alloys with defined stoichiometry in organic electrolytes at ambient temperature (*Electrochim. Acta*, 20 (1975) 513).

Jürgen Besenhard's research interests were almost unlimited. After he received a Full Professorship at the University of Münster (Germany) in 1986 and especially after 1993, when he assumed the position as head of the Institute of Chemistry and Technology at Graz University of Technology in Austria, he expanded his activities to countless topics in the field of applied electrochemistry. But his favorite topic, "his dedication," has always been "Battery Materials."

Jürgen Otto Besenhard was an exceptional and devoted scientist and he leaves behind an enduring record of achievements. He was considered as a leading authority in the field of lithium battery materials. His works will always assure him a highly prominent position in the history of battery technology.

Prof. Besenhard was also a highly respected teacher inside and outside the university. Consequently, it was only natural that he edited a book, which attempted to give explanations, rather than only summarizing figures and facts. The "Handbook of Battery Materials" was one of Jürgen Otto Besenhard's favorite projects. He knew that materials are the key to batteries. It is the merit of Claus Daniel and the publisher Wiley, that this project will be continued.

May this new edition of the "Handbook of Battery Materials" be a useful guide into the complex and rapidly growing field of battery materials. Beyond that, it is my personal wish and hope that the readers of this book may also take the chance to review Prof. Besenhard's work. Jürgen Otto Besenhard has been truly one of the fathers of lithium batteries and lithium ion batteries.

Münster, Germany, July, 2011

Martin Winter

## Preface to the Second Edition of the Handbook of Battery Materials

For Kijan and Stina

The language of experiment is more authoritative than any reasoning, facts can destroy our ratiocination – not vice versa.

Count Alessandro Volta, 1745–1827 Inventor of the Battery

You are looking at the second edition of the Handbook of Battery Materials. It has been 12 years since the first edition edited by Prof. Jürgen Besenhard was published.

This second edition is dedicated in memory of world renowned Prof. Jürgen Besenhard who was a pioneer in the field of electrochemical energy storage and lithium batteries. As a young scientist in the field of electrochemical energy storage, I am humbled to inherit this handbook from him.

Over the last decade, driven by consumer electronics, power tools, and recently automotive and renewable energy storage, electrochemical energy storage chemistries and devices have been developed at a never before seen pace. New chemistries have been discovered, and continued performance increases to established chemistries are under way. With these developments, we decided to update the handbook from 1999. The new edition is completely revised and expanded to almost double its original content.

Due to the fast pace of the market and very quick developments on large scale energy storage, we removed the chapter on *Global Competition*. It might be outdated by the time this book actually hits the shelves. Chapters from Parts I and II from the first edition on *Fundamentals and General Aspects of Electrochemical Energy Storage, Practical Batteries*, and *Materials for Aqueous Electrolyte Batteries* have been revised for the new edition to reflect the work in the past decade. Part III on *Materials for Alkali Metal Batteries* has been expanded in view of the many research efforts on lithium ion and other alkali metal ion batteries. In addition, we added new Parts IV on *New Emerging Technologies* and V on *Performance and Technology Development* with chapters on *Metal Air, Catalysts, and Membranes, Sulfur, System Level Modeling, Mechanics of Battery Materials*, and *Electrode Manufacturing*.

In our effort, we strongly held on to Prof. Besenhard's goal to "fill the gap" between fundamental electrochemistry and application of batteries in order to provide a "comprehensive source of detailed information" for "graduate or higher level" students and "those who are doing research in the field of materials for energy storage."

I would like to thank all authors who contributed to this book; Craig Blue, Ray Boeman, and David Howell who made me apply my experience and knowledge from a different area to the field of electrochemical energy storage; and Nancy Dudney who continues to be a resourceful expert advisor to me.

Finally, I thank my wife Isabell and my family for the many sacrifices they make and support they give me in my daily work.

Oak Ridge, TN, July 2011

Claus Daniel

#### **List of Contributors**

#### Jörg H. Albering

Graz University of Technology Institute for Chemical Technology of Inorganic Materials Stremeyrgasse 16/III 8010 Graz Austria

#### Marius Amereller

University of Regensburg Institute of Physical and Theoretical Chemistry Universitätsstr. 31 93053 Regensburg Germany

#### Michel Armand

Université de Montréal Département de Chimie C.P. 6128 Succursale Centre-Ville Montréal Québec H3C 3J7 Canada

#### Josef Barthel

University of Regensburg Institute of Physical and Theoretical Chemistry Universitätsstr. 31 93053 Regensburg Germany

#### Dietrich Berndt

Am Weissen Berg 3 61476 Kronberg Germany

#### Jürgen Otto Besenhard

Graz University of Technology of Inorganic Materials Stremayrgasse 16/III 8010 Graz Austria

#### Leo Binder

Graz University of Technology Institute for Inorganic Chemistry Stremayrgasse 9 8010 Graz Austria

#### Peter Birke

Christian-Albrechts University Technical Faculty Chair for Sensors and Solid State Ionics Kaiserstr. 2 24143 Kiel Germany

#### H. Böhm

AEG Anglo Batteries GmbH Söfliger Str. 100 889077 Ulm Germany

#### Werner Böhnstedt

Daramic Inc. Erlengang 31 22844 Norderstedt Germany

#### Peter G. Bruce

University of St. Andrews School of Chemistry North Haugh St. Andrews, KY16 9ST Scotland

#### Myoungdo Chung

Sakti3 Incorporated Ann Arbor, MI USA

#### Claus Daniel

Oak Ridge National Laboratory Oak Ridge, TN 37831-6083 USA

and

University of Tennessee Department of Materials Science and Engineering Knoxville, TN 37996 USA

#### Daniel H. Doughty

Battery Safety Consulting Inc. 139 Big Horn Ridge Dr. NE Albuquerque, NM 87122 USA

#### Josef Drobits

Technische Universität Wien Institut für Technische Elektrochemie Getreidemarkt 9/158 1060 Wien Austria

#### Christoph Fabjan

Technische Universität Wien Institut für Technische Elektrochemie Getreidemarkt 9/158 1060 Wien Austria

#### Wujun Fu

Center for Nanophase Materials Sciences Oak Ridge National Laboratory Oak Ridge TN 37831 USA

#### Nobuhiro Furukawa

Sanyo Electric Co., Ltd. **Electrochemistry Department** New Materials Research Center 1-18-3 Hashiridani Hirahata City Osaka 573-8534 Japan

#### Diane Golodnitsky

Tel Aviv University Department of Chemistry Tel Aviv 69978 Israel

#### Heiner Jakob Gores

University of Regensburg Institute of Physical and Theoretical Chemistry Universitätsstr. 31 93053 Regensburg Germany

and

WWU Münster (Westfälische Wilhelms-Universität Münster) MEET - Münster Electrochemical **Energy Technology** Corrensstraße 46 48149 Münster Germany

#### Fiona Gray

University of St Andrews School of Chemistry The Purdie Building North Haugh St Andrews Fife KY16 9ST UK

#### Robert Hartl

University of Regensburg Institute of Physical and Theoretical Chemistry Universitätsstr. 31 93053 Regensburg Germany

#### Robert A. Huggins

Christian-Albrechts-University Kaiserstr. 2 24143 Kiel Germany

#### HyonCheol Kim

Sakti3 1490 Eisenhower Place Building 4 Ann Arbor, MI 48108

#### Kimio Kinoshita

Lawrence Berkeley Laboratory **Environmental Energy** Technology Berkeley, CA 94720 USA

#### Akiya Kozawa

ITE Battery Research Institute 39 Youke, Ukino Chiaki-cho Ichinomiyashi Aichi-ken 491 Japan

#### Jianlin Li

Oak Ridge National Laboratory Materials Science and Technology Division Oak Ridge, TN 37831-6083 USA

#### Chengdu Liang

Center for Nanophase Materials Sciences Oak Ridge National Laboratory Oak Ridge, TN 37831 USA

#### Zengcai Liu

Center for Nanophase Materials Sciences Oak Ridge National Laboratory Oak Ridge, TN 37831 USA

#### Arumugam Manthiram

The University of Texas at Austin Materials Science and **Engineering Program** Austin, TX 78712 USA

#### Alexander Maurer

University of Regensburg Institute of Physical and Theoretical Chemistry Universitätsstr. 31 93053 Regensburg Germany

#### James McBreen

Brookhaven National Laboratory Department of Applied Science Upton, NY 1973 USA

#### Dominik Moosbauer

University of Regensburg Institute of Physical and Theoretical Chemistry Universitätsstr. 31 93053 Regensburg Germany

and

Gamry Instruments, Inc. 734 Louis Drive Warminster, PA 18974 USA

#### Partha P. Mukherjee

Oak Ridge National Laboratory Computer Science and Mathematics Division Oak Ridge, TN 37831 USA

#### Theivanayagam Muraliganth

The University of Texas at Austin Materials Science and **Engineering Program** Austin, TX 78712 USA

#### Chaitanya K. Narula

University of Tennessee Materials Science and Technology Division Physical Chemistry of Materials Oak Ridge, TN 37831 USA

and

Department of Materials Science and Engineering Knoxville, TN 37966 USA

#### Koji Nishio

Sanyo Electric Co., Ltd. **Electrochemistry Department** New Materials Research Center 1-18-3 Hashiridani Hirahata City Osaka 573-8534 Japan

#### Sreekanth Pannala

Oak Ridge National Laboratory Computer Science and Mathematics Division Oak Ridge, TN 37831 USA

#### **Emanuel Peled**

Tel Aviv University Department of Chemistry Tel Aviv 69978 Israel

#### Jack Penciner

Tel Aviv University Department of Chemistry Tel Aviv 69978 Israel

#### Karsten Pinkwart

Fraunhofer Institut für Chemische Technologie (ICT) Angewandte Elektrochemie Josef-von-Fraunhofer-Str. 7 76327 Pfinztal Germany

#### James J. Reilly

Brookhaven National Laboratory Department of Sustainable **Energy Technologies** Upton, NY 11973 USA

#### Ann Marie Sastry

Sakti3 1490 Eisenhower Place Building 4 Ann Arbor, MI 48108

and

University of Michigan Departments of Mechanical Biomedical and Materials Science and Engineering 2300 Hayward Street Ann Arbor, MI 48109 USA

#### Robert Spotnitz

Battery Design LLC 2277 Delucchi Drive Pleasanton, CA 94588 USA

#### Shin-ichi Tobishima

Gunma University Department of Chemistry and Biochemistry Faculty of Engineering 1-5-1 Tenjin-cho Kiryu, Gunma, 376-8515 Japan

#### Iens Tübke

Fraunhofer Institut für Chemische Technologie Angewandte Elektrochemie Josef-von-Fraunhofer-Str. 7 76327 Pfinztal Germany

#### John A. Turner

Oak Ridge National Laboratory Computer Science and Mathematics Division Oak Ridge, TN 37831 USA

#### Chia-Wei Wang

Sakti3 1490 Eisenhower Place **Building 4** Ann Arbor, MI 48108

#### Werner Weppner

Christian-Albrechts University Technical Faculty Chair for Sensors and Solid State Ionics Kaiserstr. 2 24143 Kiel Germany

#### Martin Winter

Graz University of Technology of Inorganic Materials Stremayrgasse 16/III 8010 Graz Austria

#### David L. Wood III

Oak Ridge National Laboratory Materials Science and **Technology Division** Oak Ridge, TN 37831-6083 USA

#### Jun-ichi Yamaki

Kyushu University Institute for Materials Chemistry and Engineering 6-1 Kasuga-koen Kasuka-shi 816-8508 Japan

#### Kohei Yamamoto

Fuji Electrochemical Co. Washizu, Kosai-shi Shizuoka-ken 431 Japan

#### Masaki Yoshio

Saga University Faculty of Science and Engineering Department of Applied Chemistry 1 Honjo Saga 8408502 Japan

#### Ji-Guang Zhang

Pacific Northwest National Laboratory **Energy and Environment** Directory Richland, WA 99352 USA

#### X. Gregory Zhang

Independent consultant 3 Weatherell Street Ontario M6S 1S6 Canada

#### Xiangchun Zhang

Sakti3 Incorporated Ann Arbor, MI USA

#### Sandra Zugmann

University of Regensburg Institute of Physical and Theoretical Chemistry Universitätsstr. 31 93053 Regensburg Germany

#### Contents

Preface XXVII
List of Contributors XXIX

## Part I Fundamentals and General Aspects of Electrochemical Energy Storage 1

1	Thermodynamics and Mechanistics 3
	Karsten Pinkwart and Jens Tübke
1.1	Electrochemical Power Sources 3
1.2	Electrochemical Fundamentals 6
1.2.1	Electrochemical Cell 6
1.2.2	Electrochemical Series of Metals 9
1.2.3	Discharging 11
1.2.4	Charging 12
1.3	Thermodynamics 13
1.3.1	Electrode Processes at Equilibrium 13
1.3.2	Reaction Free Energy $\Delta G$ and Equilibrium Cell Voltage $\Delta \varepsilon_{00}$ 14
1.3.3	Concentration Dependence of the Equilibrium Cell Voltage 15
1.3.4	Temperature Dependence of the Equilibrium Cell Voltage 16
1.3.5	Pressure Dependence of the Equilibrium Cell Voltage 18
1.3.6	Overpotential of Half Cells and Internal Resistance 19
1.4	Criteria for the Judgment of Batteries 21
1.4.1	Terminal Voltage 21
1.4.2	Current-Voltage Diagram 21
1.4.3	Discharge Characteristic 22
1.4.4	Characteristic Line of Charge 22
1.4.5	Overcharge Reactions 23
1.4.6	Coulometric Efficiency and Energy Efficiency 24
1.4.7	Cycle Life and Shelf Life 24
1.4.8	Specific Energy and Energy Density 25
1.4.9	Safety 25
1.4.10	Costs per Stored Watt Hour 26
	References 26

2	Practical Batteries 27
	Koji Nishio and Nobuhiro Furukawa
2.1	Introduction 27
2.2	Alkaline-Manganese Batteries 27
2.3	Nickel-Cadmium Batteries 30
2.4	Nickel-MH Batteries 36
2.5	Lithium Primary Batteries 43
2.5.1	Lithium–Manganese Dioxide Batteries 43
2.5.2	Lithium-Carbon Monofluoride Batteries 52
2.5.3	Lithium-Thionyl Chloride Batteries 54
2.6	Coin-Type Lithium Secondary Batteries 55
2.6.1	Secondary Lithium–Manganese Dioxide Batteries 55
2.6.2	Lithium-Vanadium Oxide Secondary Batteries 60
2.6.3	Lithium–Polyaniline Batteries 62
2.6.4	Secondary Lithium-Carbon Batteries 62
2.6.5	Secondary Li-LGH-Vanadium Oxide Batteries 63
2.6.6	Secondary Lithium–Polyacene Batteries 64
2.6.7	Secondary Niobium Oxide-Vanadium Oxide Batteries 64
2.6.8	Secondary Titanium Oxide–Manganese Oxide Batteries 65
2.7	Lithium-Ion Batteries 66
2.7.1	Positive Electrode Materials 66
2.7.2	Negative Electrode Materials 70
2.7.3	Battery Performances 75
2.8	Secondary Lithium Batteries with Metal Anodes 78
	References 80
	Further Reading 84
	Part II Materials for Aqueous Electrolyte Batteries 87
3	Structural Chemistry of Manganese Dioxide and Related
	Compounds 89
	Jörg H. Albering
3.1	Introduction 89
3.2	Tunnel Structures 90
3.2.1	$\beta$ -MnO <sub>2</sub> 90
3.2.2	Ramsdellite 91
3.2.3	$\gamma$ -MnO <sub>2</sub> and $\varepsilon$ -MnO <sub>2</sub> 93
3.2.4	$\alpha$ -MnO <sub>2</sub> 100
3.2.5	Romanèchite, Todorokite, and Related Compounds 102
3.3	Layer Structures 104
3.3.1	Mn <sub>5</sub> O <sub>8</sub> and Similar Compounds 105
3.3.2	Lithiophorite 106
3.3.3	Chalcophanite 108
3.3.4	$\delta$ -MnO <sub>2</sub> Materials 109
3.3.5	10 Å Phyllomanganates of the Buserite Type 114
6.000.000	