

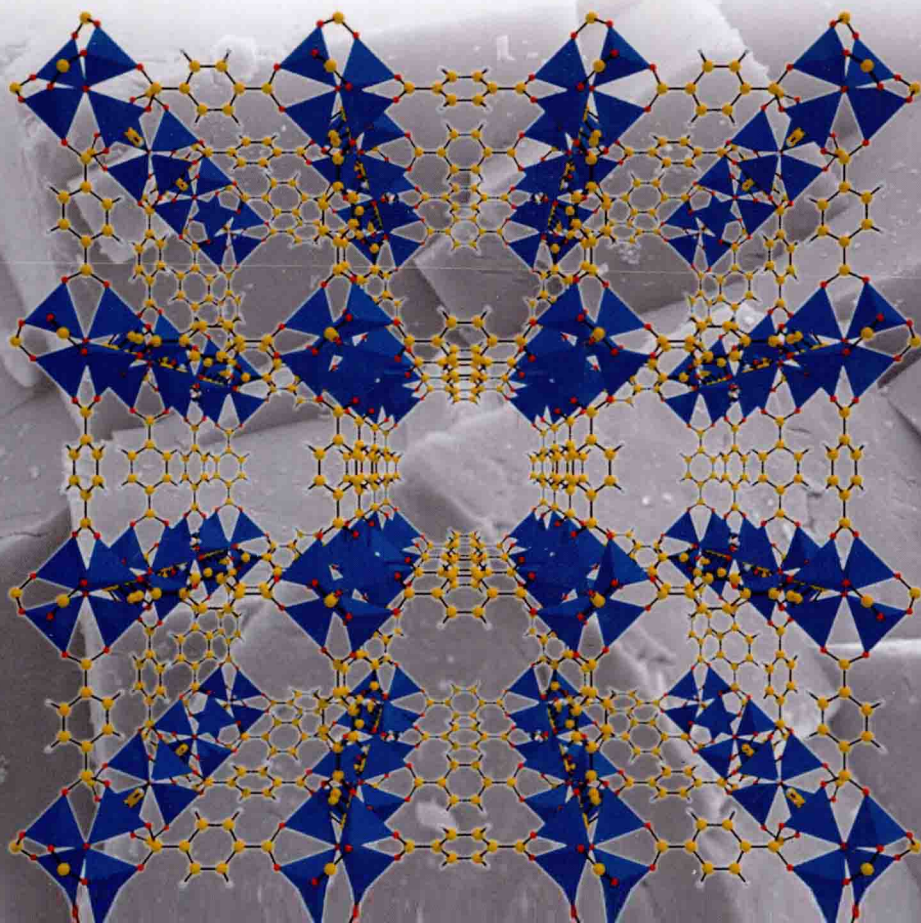
Edited by Michael Hirscher

 WILEY-VCH

Handbook of Hydrogen Storage

New Materials for Future Energy Storage

With a Foreword by Katsuhiko Hirose



Edited by
Michael Hirscher

Handbook of Hydrogen Storage

New Materials for Future Energy Storage



WILEY-VCH Verlag GmbH & Co. KGaA

The Editor

Dr. Michael Hirscher

Max-Planck-Institut für
Metallforschung
Heisenbergstr. 3
70569 Stuttgart

Cover

Crystal structure of metal-organic framework MOF-5 constructed of ZnO_4 tetrahedra and carboxylate ligands. Background showing a scanning electron microscope picture of cubic MOF-5 crystals.

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>.

© 2010 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

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 Thomson Digital, Noida, India

Printing and Binding betz-druck GmbH, Darmstadt

Cover Design Adam-Design, Weinheim

Printed in the Federal Republic of Germany

Printed on acid-free paper

ISBN: 978-3-527-32273-2

Edited by
Michael Hirscher

**Handbook of Hydrogen
Storage**

Further Reading

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

Microfabricated Power Generation Devices

Design and Technology

2009

ISBN: 978-3-527-32081-3

Züttel, A., Borgschulte, A., Schlapbach, L. (eds.)

Hydrogen as a Future Energy Carrier

2008

ISBN: 978-3-527-30817-0

Sundmacher, K., Kienle, A., Pesch, H. J., Berndt, J. F., Huppmann, G. (eds.)

Molten Carbonate Fuel Cells

Modeling, Analysis, Simulation, and Control

2007

ISBN: 978-3-527-31474-4

Hynes, J. T., Klinman, J. T., Limbach, H.-H., Schowen, R. L. (eds.)

Hydrogen-Transfer Reactions

4 Volumes

2007

ISBN: 978-3-527-30777-7

Malanowski, N., Heimer, T., Luther, W., Werner, M. (eds.)

Growth Market Nanotechnology

An Analysis of Technology and Innovation

2006

ISBN: 978-3-527-31457-7

Olah, G. A., Goeppert, A., Prakash, G. K. S.

Beyond Oil and Gas: The Methanol Economy

2006

ISBN: 978-3-527-31275-7

Kockmann, N. (ed.)

Micro Process Engineering

Fundamentals, Devices, Fabrication, and Applications

2006

ISBN: 978-3-527-31246-7

Foreword

Our children need your great ideas and effort for hydrogen storage technologies innovations.

Sustainable/Hydrogen society construction rely on your brain and hand of research.

Katsuhiko Hirose, Project General Manager, Strategic Planning Department, Fuel Cell System Engineering Division, Toyota Motor Corporation

The human race has a long history of desiring mobility. I believe that is why even in the Stone Age and Bronze Age people traveled long distances to exchange information and goods.

In the last century this mobility expanded dramatically through the invention of the automobile and the use of oil as its fuel. This combination of oil and automobile seemed perfect until it became an environmental problem. Local environmental issues were partly solved by the introduction of catalysts and precise emission control through the tremendous efforts of catalyst material scientists and engineers. However, automobiles are again facing very high hurdles such as global warming and energy security issues.

In 2008 the world experienced the great shock of high oil prices. Not only the automobile industry but also everyday lives are massively affected by high oil prices. The cause was not the previously predicted scenario (peak oil), the problem was brought about without the collapse of any oil fields, just high oil prices created in the market. We have recognized that we now need to accelerate efforts to move away from oil as an automobile fuel and, at the same time, meet future requirements for reduced carbon dioxide emissions. There are only a few technologies able to achieve these targets while meeting user requirements such as low cost, long range travel and quick, easy refueling capabilities.

Hydrogen is the most promising technology and the automobile industry has spent billions of dollars to bring it onto the roads. As a result, vehicle technologies have reached very high levels, out-performing the current internal combustion engines two- or three-fold in terms of thermal efficiency, and at the same time reaching current vehicle levels of cold start capability down to -30°C and other performance targets. However, the biggest and most difficult issue remaining is cost reduction of the technologies to current vehicle levels, which is essential for hydro-

gen to be popular enough to solve both the energy security and carbon dioxide issues. There had seemed to be a similar pattern of cost reduction for fuel cell stacks and components to that for current technologies, since they both include steps such as reducing the number of parts and improving performance to reduce size and materials usage. However, hydrogen storage is a little bit different. Currently, the only available technology is a carbon fiber reinforced plastic composite high-pressure tank system, but this technology leaves several problems for future cost reduction. The quantities of expensive materials used constrain potential cost reduction and the large cylindrical shape limits installation of the tank in conventional vehicles.

The world's major automotive companies have announced fuel cell vehicle commercialization from 2015. The automotive industry recognizes that hydrogen storage still needs innovative ideas and materials in order to transform it into a popular technology for the future. The important requirements for hydrogen storage technologies are energy efficiency, size and weight, as well as easy adaptation to supply infrastructures and cost.

This problem cannot be solved by either academia or industry alone, so scientists and engineers must work together to achieve this difficult but indispensable task. I believe the current good collaboration will bring this about and we will be able to leave a clean, green globe for our children.

December 2009

Katsuhiko Hirose

Preface

The limited fossil fuel resources and the environmental impact of their use require a change to renewable energy sources in the near future. For mobile application an efficient energy carrier is needed that can be produced and used in a closed cycle. Presently, hydrogen is the only energy carrier that can be produced easily in large amounts and in an appropriate time scale. Electric energy, either from renewable energies, for example, solar and wind, or future fusion reactors, can be used to produce hydrogen from water by electrolysis. The combustion of hydrogen leads again only to water and the cycle is closed. A comprehensive overview of the hydrogen cycle was given recently in the book “Hydrogen as a Future Energy Carrier” edited by Züttel *et al.* [1].

For individual motor car traffic, currently, three concepts are discussed by major auto manufacturers, fuel-cell vehicles, extended-range electric vehicles and battery-electric vehicles, for example, see the GM road map [2, 3] in Figure 1. The use of these three technologies depends on the application field and is related to the different energy densities of these energy carriers (see Figure 2). To achieve a driving range of 500 km for a conventional vehicle with today's Diesel technology requires a tank system weighing approximately 43 kg with a volume of 46 L. A zero-emission vehicle driven by a fuel cell with hydrogen will need a 700 bar high-pressure tank system of about 125 kg and 260 L to achieve the same driving range. A battery-electric vehicle will require an energy storage system (comprising battery cells, heat management and power electronics) which, using the most advanced Li-ion-battery technology (energy density 120 Wh kg^{-1}), would weigh almost 1000 kg with a volume of 670 L. This value assumes that the total electric energy of the battery is used, which would significantly reduce the cycle life of the device. More realistic is a maximum usage of 80% of the stored energy. The loading of a battery will take between several hours at a high-voltage high-current station and about one day at a conventional 230 V power socket with 16 A. Fast charging stations (about 50 kW, 30 to 90 min reloading), on the other hand, would require a very considerable infrastructure investment of several billion euros for a European nation such as France or Germany, comparable to a hydrogen infrastructure. The refueling of the high-pressure hydrogen vessel will take about 3 min, which is comparable to the Diesel tank. Furthermore, a hydrogen storage system for a driving range of 500 km will cost about 3000 US\$ if produced in

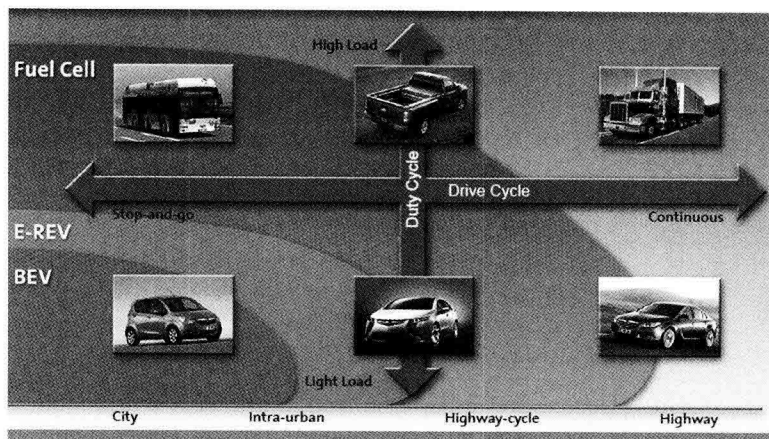


Figure 1 Application map for various electric vehicle technologies, from battery-electric vehicles (BEV), extended-range electric vehicles (E-REV) to fuel-cell vehicles, considering driving distance and load [2, 3].

high volumes. A comparable battery system would be in the price range of 50 000 US\$.

According to these constraints, a battery-electric vehicle (BEV) would be the choice for light-weight vehicles and driving ranges up to 150 km. Extended-range electric vehicles (E-REV) could be the solution for users who only occasionally need longer driving ranges, up to 500 km. However, for long driving ranges or high load the fuel-cell vehicle possesses clear advantages due to zero emission in all operating

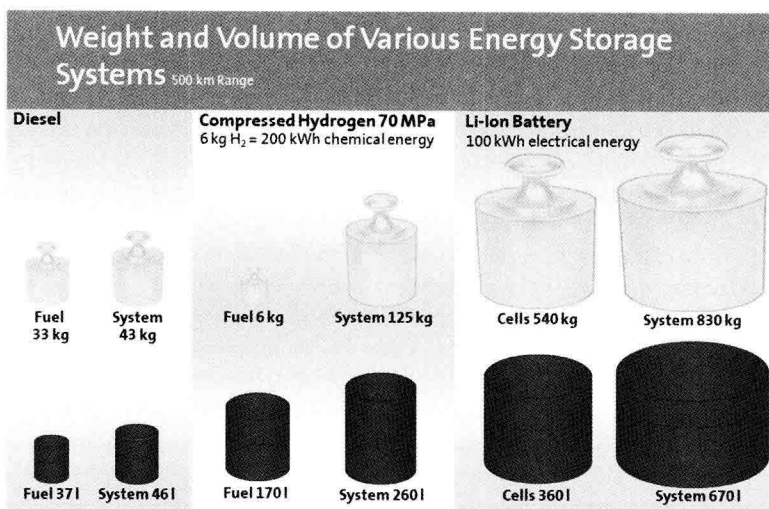


Figure 2 Weights and volumes of different energy carriers and systems used in vehicles to achieve a total driving range of 500 km [2, 3].

conditions and fast refueling times. Figure 1 shows an application map for the various technologies.

Nevertheless, current technologies, such as compressed gas or liquefied hydrogen, have severe disadvantages (especially in volumetric terms) compared to fossil fuels and the storage of hydrogen in light-weight solids could be the solution to further enhance the energy density of hydrogen tanks. The benchmark for all these solid-state systems needs to be an improvement over a 70 MPa tank system. In particular, fundamental knowledge of the atomistic processes is required to design optimized novel materials with new physical properties.

For automotive application of solid state absorbers, there are, more or less, two operating regimes envisaged to achieve such a technology breakthrough:

- 1) Room temperature storage at pressures up to 35 MPa
- 2) Cryogenic storage at pressures up to 5 MPa.

This handbook gives a comprehensive overview of novel solid hydrogen storage materials, highlighting their main advantages and drawbacks. The first chapter is devoted to the storage of hydrogen in a pure form giving the state-of-the-art for compressed and liquid hydrogen. In Chapter 2 adsorption materials for hydrogen storage by physisorption of hydrogen molecules are analyzed for possible cryo-adsorption systems. Chapter 3 describes the potential of clathrate hydrates as storage materials. Chapter 4 gives a review of conventional hydrides, including techniques to improve them by nanostructuring. Chapters 5–9 are devoted to novel light-weight materials, ranging from complex hydrides; amides, imides and mixtures; tailoring of reaction enthalpies; ammonia, borane and related compounds; and aluminum hydride. Finally, Chapter 10 concentrates on nanoparticles, mainly in systems confined by scaffold materials.

December 2009

Michael Hirscher

References

- 1 Züttel, A., Borgschulte, A., and Schlapbach L.,(eds) (2008) *Hydrogen as a Future Energy Carrier*, Wiley-VCH, Weinheim.
- 2 von Helmolt, R. and Eberle, U. (2007) *J. Power Sources*, **165**, 833–843.
- 3 Johnen F.T., von Helmolt, R., and Eberle, U. Conference Proceedings "Technical Congress 2009" of the German Vehicle Manufacturers' Association VDA.

List of Contributors

Philipp Adelhelm

Utrecht University
Inorganic Chemistry and Catalysis
Debye Institute for Nanomaterials
Science
Sorbonnelaan 16
3584 CA Utrecht
The Netherlands

Felix Baitalow

TU Bergakademie Freiberg
Department of Energy Process
Engineering and Chemical Engineering
Fuchsmuehlenweg 9
Building 1
09596 Freiberg
Germany

Martin Dornheim

GKSS Research Centre Geesthacht
Institute of Materials Research
Max-Planck-Straße 1
21502 Geesthacht
Germany

Michael Felderhoff

Max-Planck-Institut für
Kohlenforschung
Kaiser-Wilhelm-Platz 1
45470 Mülheim/Ruhr
Germany

Michael Hirscher

Max-Planck-Institut für
Metallforschung
Heisenbergstr. 3
70569 Stuttgart
Germany

Jacques Huot

Université du Québec à Trois-Rivières
Institut de Recherche sur l'Hydrogène
3351 des Forges
PO Box 500, Trois-Rivières (QC) G9A
5H7
Canada

Takayuki Ichikawa

Hiroshima University
Institute for Advanced Materials
Research
1-3-1 Kagamiyama
Higashi-Hiroshima, 739-8530
Japan

Petra E. de Jongh

Utrecht University
Inorganic Chemistry and Catalysis,
Debye Institute for Nanomaterials
Science
Sorbonnelaan 16
3584 CA Utrecht
The Netherlands

Manfred Klell

Hydrogen Center Austria
Inffeldgasse 15
A-8010 Graz
Austria

Florian Mertens

TU Bergakademie Freiberg
Department of Physical Chemistry
Leipziger Str. 29
09596 Freiberg
Germany

Barbara Panella

ETH Zurich
Institute for Chemical and
Bioengineering, Department of
Chemistry and Applied Biosciences,
Hönggerberg
8093 Zürich
Switzerland

and

Max-Planck-Institut für
Metallforschung
Heisenbergstr. 3
70569 Stuttgart
Germany

Cor J. Peters

Delft University of Technology
Faculty of Mechanical, Maritime
and Materials Engineering
Department of Process and Energy
Laboratory of Process Equipment
Leeghwaterstraat 44
2628 CA Delft
The Netherlands

and

The Petroleum Institute
Department of Chemical Engineering
P.O. Box 2533
Abu Dhabi
United Arab Emirates

Sona Raeissi

Shiraz University
Chemical and Petroleum Engineering
Department
Shiraz 71345
Iran

Alireza Shariati

Shiraz University
Chemical and Petroleum Engineering
Department
Shiraz 71345
Iran

Claudia Weidenthaler

Max-Planck-Institut für
Kohlenforschung
Kaiser-Wilhelm-Platz 1
45470 Mülheim/Ruhr
Germany

Gert Wolf

TU Bergakademie Freiberg
Department of Physical Chemistry
Leipziger Str. 29
09596 Freiberg
Germany

Ragaiy Zidan

Savannah River National Laboratory
Energy Security Directorate
Aiken
SC 29803
USA

Contents

Foreword	V
Preface	XV
List of Contributors	XIX

1	Storage of Hydrogen in the Pure Form	1
	<i>Manfred Klell</i>	
1.1	Introduction	1
1.2	Thermodynamic State and Properties	1
1.2.1	Variables of State	2
1.2.2	T-s-Diagram	4
1.2.2.1	Joule–Thomson Coefficient	5
1.2.3	Properties	5
1.3	Gaseous Storage	8
1.3.1	Compression and Expansion	10
1.3.2	Tank Systems	12
1.3.3	High Pressure Infrastructure	13
1.4	Liquid Storage	15
1.4.1	Liquefaction	15
1.4.2	Thermodynamic Analysis	17
1.4.2.1	Pressure Build-Up	21
1.4.2.2	Boil-Off	23
1.4.2.3	Cooling and Filling	24
1.4.2.4	Back-Gas	27
1.4.3	Tank Systems	28
1.4.4	Distribution Facilities	30
1.5	Hybrid Storage	30
1.5.1	Supercritical Storage	31
1.5.2	Hydrogen Slush	32
1.6	Comparison of Energy Densities	32
1.7	Conclusion	35
	References	36

2	Physisorption in Porous Materials	39
	<i>Barbara Panella and Michael Hirscher</i>	
2.1	Introduction	39
2.2	Carbon Materials	44
2.3	Organic Polymers	48
2.4	Zeolites	50
2.5	Coordination Polymers	51
2.6	Conclusions	58
	References	59
3	Clathrate Hydrates	63
	<i>Alireza Shariati, Sona Raeissi, and Cor J. Peters</i>	
3.1	Introduction	63
3.2	Clathrate Hydrate Structures	64
3.3	Hydrogen Clathrate Hydrate	66
3.4	Kinetic Aspects of Hydrogen Clathrate Hydrate	73
3.5	Modeling of Hydrogen Clathrate Hydrates	74
3.6	Future of Hydrogen Storage	76
	References	77
4	Metal Hydrides	81
	<i>Jacques Huot</i>	
4.1	Introduction	81
4.2	Elemental Hydrides	82
4.2.1	Ionic or Saline Hydrides	82
4.2.2	Covalent Hydrides	82
4.2.3	Metallic Hydrides	83
4.3	Thermodynamics of Metal Hydrides	83
4.3.1	Introduction	83
4.3.2	Low Concentration	85
4.3.3	High Concentration	86
4.4	Intermetallic Compounds	88
4.4.1	Thermodynamics	88
4.4.1.1	Miedema's Model	89
4.4.1.2	Semi-Empirical Band Structure Model	91
4.4.2	Crystal Structure	92
4.4.3	Electronic Structure	94
4.5	Practical Considerations	94
4.5.1	Synthesis	95
4.5.2	Activation	95
4.5.3	Hysteresis	96
4.5.4	Plateau Slope	97
4.5.5	Reversible Capacity	98
4.5.6	Hydrogenation Kinetics	98
4.5.7	Cycle Life	99

4.5.8	Decrepitation	99
4.6	Metal Hydrides Systems	100
4.6.1	AB ₅	100
4.6.2	TiFe	101
4.6.3	AB ₂ Laves Phases	102
4.6.4	BCC Solid Solution	103
4.7	Nanocrystalline Mg and Mg-Based Alloys	104
4.7.1	Hydrogen Sorption Kinetics	105
4.7.2	Reduction of the Heat of Formation	107
4.7.3	Severe Plastic Deformation Techniques	108
4.8	Conclusion	109
4.8.1	Alloys Development	109
4.8.2	Synthesis	110
4.8.3	System Engineering	110
	References	110
5	Complex Hydrides	117
	<i>Claudia Weidenthaler and Michael Felderhoff</i>	
5.1	Introduction	117
5.2	Complex Borohydrides	118
5.2.1	Introduction	118
5.2.2	Stability of Metal Borohydrides	118
5.2.3	Decomposition of Complex Borohydrides	119
5.2.4	Lithium Borohydride, LiBH ₄	120
5.2.4.1	Synthesis and Crystal Structure	120
5.2.4.2	Decomposition of LiBH ₄	120
5.2.5	Sodium Borohydride, NaBH ₄	122
5.2.5.1	Synthesis and Crystal Structure	122
5.2.5.2	Decomposition of NaBH ₄	122
5.2.6	Potassium Borohydride KBH ₄	122
5.2.7	Beryllium Borohydride Be(BH ₄) ₂	123
5.2.8	Magnesium Borohydride Mg(BH ₄) ₂	123
5.2.8.1	Synthesis and Crystal Structure	123
5.2.8.2	Decomposition	123
5.2.9	Calcium Borohydride Ca(BH ₄) ₂	124
5.2.9.1	Synthesis and Crystal Structure	124
5.2.9.2	Decomposition	125
5.2.10	Aluminum Borohydride Al(BH ₄) ₃	126
5.2.10.1	Synthesis and Crystal Structure	126
5.2.10.2	Decomposition	126
5.2.11	Zinc Borohydride Zn(BH ₄) ₂	126
5.2.12	NaBH ₄ as a Hydrogen Storage Material in Solution	126
5.2.12.1	Regeneration of Decomposed NaBH ₄ in Solution	128
5.3	Complex Aluminum Hydrides	128
5.3.1	Introduction	128

5.3.2	LiAlH_4	130
5.3.2.1	Synthesis and Crystal Structure	130
5.3.2.2	Decomposition of LiAlH_4	130
5.3.2.3	Role of Catalysts	131
5.3.3	Li_3AlH_6	132
5.3.3.1	Synthesis and Crystal Structure	132
5.3.4	NaAlH_4	133
5.3.4.1	Synthesis and Crystal Structure	133
5.3.4.2	Decomposition and Thermodynamics of NaAlH_4	133
5.3.4.3	Role of Catalysts	135
5.3.5	Na_3AlH_6	138
5.3.5.1	Synthesis and Crystal Structure	138
5.3.6	KAlH_4	139
5.3.6.1	Synthesis and Crystal Structure	139
5.3.6.2	Decomposition of KAlH_4	140
5.3.7	$\text{Mg}(\text{AlH}_4)_2$	140
5.3.7.1	Synthesis and Crystal Structure	140
5.3.7.2	Decomposition	141
5.3.8	$\text{Ca}(\text{AlH}_4)_2$	142
5.3.8.1	Synthesis and Crystal Structure	142
5.3.8.2	Decomposition of $\text{Ca}(\text{AlH}_4)_2$	143
5.3.9	$\text{Na}_2\text{LiAlH}_6$	144
5.3.10	K_2LiAlH_6	145
5.3.11	K_2NaAlH_6	145
5.3.12	$\text{LiMg}(\text{AlH}_4)_3$, LiMgAlH_6	146
5.3.12.1	Synthesis and Crystal Structure	146
5.3.12.2	Decomposition	146
5.3.13	Sr_2AlH_7	146
5.3.14	BaAlH_5	147
5.3.14.1	Synthesis and Crystal Structure	147
5.4	Complex Transition Metal Hydrides	148
5.4.1	Introduction	148
5.4.2	Properties	148
5.4.3	Synthesis	149
5.4.4	Examples of Complex Transition Metal Hydrides	150
5.5	Summary	150
	References	151
6	Amides, Imides and Mixtures	159
	<i>Takayuki Ichikawa</i>	
6.1	Introduction	159
6.2	Hydrogen Storage Properties of Amide and Imide Systems	160
6.2.1	Li–N–H System	160
6.2.2	Li–Mg–N–H Systems	161
6.2.3	Other Metal–N–H Systems	165

6.3	Structural Properties of Amide and Imide	167
6.3.1	Lithium Amide and Imide	168
6.3.2	Sodium Amide	171
6.3.3	Magnesium Amide and Imide	171
6.3.4	Other Amides and Imides	172
6.4	Prospects of Amide and Imide Systems	173
6.4.1	Kinetic Analysis and Improvement	173
6.4.2	NH ₃ Amount Desorbed from Metal–N–H Systems	176
6.4.3	Practical Properties	177
6.5	Proposed Mechanism of the Hydrogen Storage Reaction in the Metal–N–H Systems	178
6.5.1	Ammonia-Mediated Model for Hydrogen Desorption	178
6.5.2	Direct Solid–Solid Reaction Model for Hydrogen Desorption	180
6.5.3	Hydrogenating Mechanism of the Li–Mg–N–H System	181
6.6	Summary	182
	References	182
7	Tailoring Reaction Enthalpies of Hydrides	187
	<i>Martin Dornheim</i>	
7.1	Introduction	187
7.2	Thermodynamic Limitations of Lightweight Hydrides	189
7.3	Strategies to Alter the Reaction Enthalpies of Hydrides	191
7.3.1	Thermodynamic Tuning of Single Phase Hydrides by Substitution on the Metal Site	191
7.3.1.1	Lightweight Hydrides Forming Stable Compounds in the Dehydrogenated State	193
7.3.1.2	Lightweight Hydrides with Positive Heat of Mixing in the Dehydrogenated State	196
7.3.2	Thermodynamic Tuning of Single Phase Hydrides by Substitution on the Hydrogen Sites: Functional Anion Concept	199
7.3.3	Multicomponent Hydride Systems	203
7.3.3.1	Mixtures of Hydrides and Reactive Additives	203
7.3.3.2	Mixed Hydrides/Reactive Hydride Composites	207
7.4	Summary and Conclusion	210
	References	211
8	Ammonia Borane and Related Compounds as Hydrogen Source Materials	215
	<i>Florian Mertens, Gert Wolf, and Felix Baitalow</i>	
8.1	Introduction	215
8.2	Materials Description and Characterization	216
8.3	Production	219
8.4	Thermally Induced Decomposition of Pure Ammonia Borane	221
8.4.1	Pyrolysis	221
8.4.2	Decomposition in Organic Solvents	227