

Jianxin Zou, Yanna NuLi, Zhigang Hu, Xi Lin,
and Qiuyu Zhang

Magnesium-Based Energy Storage Materials and Systems



Magnesium-Based Energy Storage Materials and Systems

Magnesium-Based Energy Storage Materials and Systems

*Jianxin Zou
Yanna NuLi
Zhigang Hu
Xi Lin
Qiuyu Zhang*

Authors

Prof. Jianxin Zou

Shanghai Jiao Tong University
Dongchuan Road 800
Minxing District
Shanghai
CH, 200240

Prof. Yanna NuLi

Shanghai Jiao Tong University
Dongchuan Road 800
Minxing District
Shanghai
CH, 200240

Prof. Zhigang Hu

Shanghai Jiao Tong University
Dongchuan Road 800
Minxing District
Shanghai
CH, 200240

Dr. Xi Lin

Shanghai Jiao Tong University
Dongchuan Road 800
Minxing District
Shanghai
CH, 200240

Dr. Qiuyu Zhang

Shanghai Jiao Tong University
Dongchuan Road 800
Minxing District
Shanghai
CH, 200240

Cover: © Roman Samokhin/Shutterstock;
© Andriy Onufriyenko/Getty Images

■ 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>>.

© 2024 WILEY-VCH GmbH, Boschstraße 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: 978-3-527-35226-5

ePDF ISBN: 978-3-527-84259-9

ePub ISBN: 978-3-527-84260-5

oBook ISBN: 978-3-527-84261-2

Typesetting Straive, Chennai, India

Contents

Preface *ix*

Acknowledgments *xi*

1 Overview *1*

- 1.1 Introduction to Mg-based Hydrogen and Electric Energy Storage Materials *1*
- 1.2 Overview of Mg-based Hydrogen Storage Materials and Systems *2*
- 1.3 Overview of Mg-ion Batteries *5*

2 Hydrogen Absorption/Desorption in Mg-based Materials and Their Applications *9*

- 2.1 The Characterizations of Mg-based Hydrogen Storage Materials *9*
 - 2.1.1 An Introduction to the Crystal Structure of Mg and MgH₂ *9*
 - 2.1.2 Thermodynamic Mechanisms for the Hydrogen Absorption/Desorption of Mg/MgH₂ *9*
 - 2.1.3 Kinetic Mechanisms for the Hydrogen Absorption/Desorption of Mg/MgH₂ *10*
- 2.2 Methods for Improving the Hydrogen Storage Performance of Mg-based Materials *14*
 - 2.2.1 Alloying *14*
 - 2.2.2 Catalyzing *18*
 - 2.2.3 Nano-structuring *21*
 - 2.2.4 Combining with Complex Hydrides *28*
 - 2.2.4.1 Combining with Metal Amides *28*
 - 2.2.4.2 Combining with Metal Boronhydrides or Alanates *30*
- 2.3 Synthesis Technologies for Mg-based Hydrogen Storage Materials *33*
 - 2.3.1 Preparation Methods of Mg-based Alloys *33*
 - 2.3.1.1 Melting-based Methods *35*
 - 2.3.1.2 Hydrogen Combustion Synthesis (HCS) *35*
 - 2.3.1.3 Mechanical Alloying, Compactions and Severe Plastic Deformation (SPD) Methods *37*
 - 2.3.1.4 Hydriding Chemical Vapor Deposition (HCVD) *39*

2.3.2	Synthesis of Mg-based Materials with Special Structure and Morphology	41
2.3.2.1	Synthesis of Core–Shell Structured Mg-based Materials	41
2.3.2.2	Synthesis of Nanostructured Mg-based Materials	44
2.3.2.3	Synthesis of Amorphous Mg-based Materials	46
2.4	Advanced Characterization Techniques	46
2.4.1	Synchrotron Radiation	46
2.4.2	In-situ TEM	47
2.4.3	Neutron Diffraction	48
2.4.4	Theoretical Simulations	50
2.5	Fundamentals and Applications of Mg-based Hydrogen Storage Tanks	52
2.5.1	An Introduction to Mg-based Hydrogen Storage Tanks	52
2.5.2	Numerical Modeling	54
2.5.2.1	Heat Transfer Equations	54
2.5.2.2	Mass Transfer Equations	55
2.5.3	Thermal Enhancement Methods	57
2.5.3.1	Powder Compaction	57
2.5.3.2	Metal Skeleton	58
2.5.3.3	Heat Transfer Pipe	58
2.5.3.4	Phase Change Material (PCM)	58
2.5.3.5	Thermochemical Material (TCM)	59
2.5.4	Practical Applications	59
3	Hydrolysis of Mg-based Hydrogen Storage Materials	61
3.1	Hydrolysis Processes of Mg/MgH ₂	62
3.2	Control of Hydrolysis Processes	63
3.2.1	Modification of Reaction Mediate	63
3.2.1.1	Modifying pH Value	63
3.2.1.2	Effects from Other Cations and Anions	66
3.2.2	Adding Catalytic Additives	69
3.2.2.1	Metal Halides	69
3.2.2.2	Metal Oxides, Sulfides and Hydrides	72
3.2.2.3	Carbon Additives	73
3.2.3	Introduction of MgH ₂ based Nanostructures	73
3.2.4	Controlling Hydrolysis Process by Alloying	74
3.2.4.1	Alloying with Active Metals	74
3.2.4.2	Alloying with Metals with Higher Corrosion Potential	75
3.2.4.3	Alloying with Si	77
3.3	Controllable Hydrolysis Systems	77
4	Electrolytes for Mg Batteries	81
4.1	Liquid Electrolytes	81
4.1.1	Aqueous Liquid Electrolytes	81

4.1.1.1	Alkaline Solutions	82
4.1.1.2	Neutral Saline Solutions	82
4.1.1.3	Seawater and Seawater/Acid Mixed Solutions	83
4.1.2	Organic Liquid Electrolytes	84
4.1.2.1	Grignard-based Electrolytes	84
4.1.2.2	HMDS-based Electrolytes	86
4.1.2.3	MgCl ₂ -AlCl ₃ (MACC) Based Electrolytes	86
4.1.2.4	Mg(TFSI) ₂ -based Electrolytes	87
4.1.2.5	Boron-centered Electrolytes	89
4.1.2.6	Other Organic Electrolytes	91
4.2	Solid and Quasi-solid State Electrolytes	93
4.2.1	Solid-state Electrolytes	93
4.2.2	Quasi-solid State Electrolytes	95
5	Cathodes and Anodes for Mg Batteries	97
5.1	Intercalation-type Cathode Materials	97
5.1.1	Chevrel Phase, CP (Mo ₆ T ₈ ; T = S, Se, Te) Cathode Materials	97
5.1.2	V ₂ O ₅ - Mg ²⁺ Insertion-Type Cathode Materials	100
5.1.2.1	Effect of Morphology on V ₂ O ₅	101
5.1.2.2	Effect of Layer Spacing on V ₂ O ₅	102
5.1.3	Molybdenum Oxide (MoO ₃) and Uranium Oxide (α-U ₃ O ₈) - Mg ²⁺ Insertion-type Cathode Materials	105
5.1.3.1	Molybdenum Oxide (MoO ₃) Insertion-type Cathode Materials	105
5.1.3.2	Uranium Oxide (α-U ₃ O ₈) Insertion-type Cathode Materials	106
5.1.4	Layered Structure Cathode Materials	107
5.1.4.1	Layered Oxide Cathode	107
5.1.4.2	Layered Sulfides/Selenide Cathode	108
5.1.4.3	Other Layered Cathode	109
5.1.5	Spinel Structure Cathode Materials	109
5.1.5.1	Spinel Oxide Cathode	109
5.1.5.2	Spinel Sulfide Cathode	110
5.1.6	Olivine Structure Cathode Materials	110
5.1.7	NASICON Structure Cathode Materials	111
5.1.8	Carbon-based Materials	114
5.1.9	MT ₂ (M = Metal, T = S, Se) Type Intercalation Cathode Materials	115
5.2	Conversion-type Cathode Materials	117
5.2.1	Chalcogenides	118
5.2.2	Mg—O ₂ Batteries	120
5.2.3	Mg—S Batteries	122
5.2.4	Mg—Se Batteries	126
5.2.5	Mg—Te Batteries	126
5.2.6	Mg—I ₂ Batteries	126
5.3	Organic Cathodes	127
5.3.1	Carbonyl Compounds	127

5.3.2	Organosulfur Compounds	129
5.3.3	Nitrogen-based Compounds	130
5.4	Anodes for Mg Batteries	132

6	Conclusions and Outlook	137
----------	--------------------------------	------------

List of Abbreviations 139

Chapter 1 139

Chapter 2 139

Chapter 3 141

Chapter 4 141

Chapter 5 142

References 145

Index 161

Preface

In recent years, the importance of renewable energy sources has become increasingly evident as the whole world is facing the challenges of climate change, severe environmental pollution, and the urgent demand for sustainable development. While renewable energy offers great potential for a cleaner and greener future, it also presents certain challenges, particularly in terms of its intermittency, low energy intensity, and the need for efficient energy storage systems. One of the most significant challenges in renewable energy is its fluctuating nature. Solar and wind power, for example, are highly dependent on weather conditions and can vary in their availability. To mitigate this issue, large-scale energy storage techniques have to be developed, which involve storing surplus energy during periods of high production and releasing it during times of low production for renewable energies. Two promising candidates for such energy storage are electricity and hydrogen, as they are clean, sustainable, and independent of geological conditions.

On one hand, compressed hydrogen storage technology and liquid-state storage suffer from high costs, high energy consumption from compression/liquefaction, and safety issues. In contrast, hydrogen storage in solid-state form has been regarded as a viable alternative since it is possible to store more hydrogen per unit volume than that of liquid or high-pressure hydrogen gas while maintaining high safety of operation. Among different hydrogen storage materials, magnesium-based materials have shown significant advantages in this regard. For instance, it possesses high hydrogen storage capacity (up to ~ 7.6 wt% and 110 g l^{-1} for MgH_2), abundant resources, and low cost, making it a promising option for hydrogen storage and transportation.

On the other hand, rechargeable magnesium-ion batteries (RMBs) are also emerging as a promising alternative for high-density energy storage systems beyond lithium-ion batteries (LIBs), because of their high volumetric capacity and dendrite-free metal anodes.

Nevertheless, there is no such book available till now that links fundamental knowledge in magnesium-based hydrogen storage materials and magnesium batteries to the basic applications in energy storage devices. While there is such an abundance of research papers, reviews, perspectives, and monographs published in relation to magnesium-based energy storage materials, these publications are almost exclusively for senior researchers in the field of energy materials, with few providing an introductory ramp to readers of a wide range of interests.

This book aims to fill the gap mentioned above. It provides a comprehensive understanding of magnesium-based energy storage materials and their systems, linking the fundamental concepts to the actual challenges encountered in real-life applications.

Shanghai, China
February 2024

Jianxin Zou

Acknowledgments

The authors would like to express their gratitude for the support received from the National Key Research and Development Program of China (Grant No. 2022YFB3803700), the National Natural Science Foundation (Grant No. 52171186), and the Center of Hydrogen Science, Shanghai Jiao Tong University.

Shanghai, China

Jianxin Zou

1

Overview

1.1 Introduction to Mg-based Hydrogen and Electric Energy Storage Materials

The heavy reliance on fossil fuels has incurred serious environmental consequences because of the resultant carbon dioxide (CO₂) emissions into the atmosphere, which are, however, driven by the accelerating energy demands due to global civilization and economic development [1]. The access to abundant, cheap, and clean energy has become our most essential foundation for economic prosperity and human civilization. Among all other new alternative clean energy sources, such as solar, biomass, and nuclear sources, hydrogen has been widely recognized as a clean, renewable, and high-density energy carrier [2]. Although it is believed to be the long-term solution for the world energy supply, the current hydrogen storage and transportation technologies remain the bottleneck challenge to be tackled [3]. Therefore, developing safe, effective, and economical technologies to store and transport hydrogen is an essential step to make it more competitive with respect to other fuels.

Nowadays, hydrogen is mainly stored in three forms: compressed gas storage, liquid-state storage, and solid-state storage [4]. Compressed hydrogen storage technology, as the most mature and widely implemented storage method, suffers from difficult-to-produce and expensive carbon-fiber tanks, low volumetric energy density, and large energy consumption for hydrogen compression. Meanwhile, the liquefied hydrogen storage method requires an energetically unfavorable deep cooling to $-253\text{ }^{\circ}\text{C}$, and up to 30% energy is required for liquefaction in real applications. Beside gas and liquid storage, hydrogen storage in a solid-state form has been regarded as a viable alternative since it is possible to contain more hydrogen per unit volume than liquid or high-pressure hydrogen gas while maintaining high safety of operation.

Among different energy storage materials, magnesium and magnesium-based materials may play an important role in high-density energy storage systems (Figure 1.1) [6]. On the one hand, they have been already intensively investigated in hydrogen storage and transportation technologies because of their natural abundance and availability, as well as their extraordinary high gravimetric (7.6 wt%) and volumetric (110 g l^{-1}) storage densities [7]. Moreover, magnesium hydrides have been also used as a one-time hydrogen carrier, where their water hydrolysis

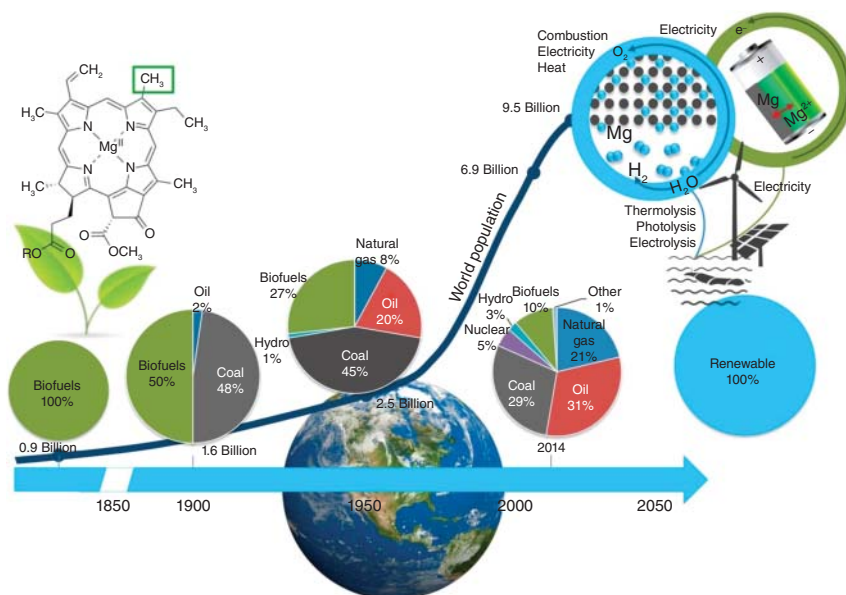


Figure 1.1 The role of Mg-based materials in hydrogen storage and batteries. Source: Reproduced with permission from Sun et al. [5] Copyright 2018, Elsevier.

can give a doubled gravimetric capacity up to 15.2 wt% and a high volumetric capacity of 150 g l^{-1} . On the other hand, rechargeable Mg-ion batteries (RMBs) can also act as a promising alternative for high-density energy storage systems beyond Li ion batteries (LIBs), because of their high volumetric capacity ($3833 \text{ mA h cm}^{-3}$) and dendrite-free metal anodes [8].

1.2 Overview of Mg-based Hydrogen Storage Materials and Systems

Hydrogen has been considered a potential clean energy vector because of its high gravimetric energy density of 33.3 kWh kg^{-1} , as compared to that of gasoline (12.4 kWh kg^{-1}) and natural gas (13.9 kWh kg^{-1}) [4]. Although highly appealing, the employment of hydrogen as an energy carrier is largely hindered by the lack of appropriate and economical storage and transportation solutions. In general, ideal hydrogen storage technologies should possess the following characteristics: (i) high volumetric and gravimetric hydrogen density; (ii) adequate recyclability; (iii) high safety; and (iv) best operated under ambient conditions [9]. Nowadays, hydrogen is mainly stored in three different forms: (i) compressed gas storage (e.g. 20, 35, and 70 MPa); (ii) liquid storage ($-253 \text{ }^\circ\text{C}$); and (iii) solid state in hydrides (e.g. metal hydrides and complex metal hydrides) [10]. It is worth noting that compressed hydrogen storage technology is currently the most mature and widely implemented storage method; however, it suffers from several major drawbacks: (i) difficult-to-produce and expensive carbon-fiber tanks; (ii) poor volumetric

energy density (e.g. 5.6 MJ l^{-1} at 70 MPa compared to gasoline of 32.0 MJ l^{-1}); and (iii) a large energy consumption for the compression work (13–18% of hydrogen when compressed to 70 MPa) [11]. Meanwhile, the liquefied hydrogen storage method requires an energetically unfavorable deep cooling to -253°C , and up to 30% energy is required for liquefaction in real applications [12]. Moreover, due to the boiling-off phenomenon, a daily hydrogen loss of 1–2% has been considered. Therefore, the solid-state storage method has been considered an alternative and promising method (e.g. metal hydrides) for hydrogen storage and transportation due to its high achievable volumetric hydrogen density and high safety. Such metal hydrides have been discovered since 1866, when Graham affirmed the high affinity of hydrogen for Pd [13]. However, metal hydrides have been considered for hydrogen storage purposes since the 1960s.

In the past three decades, magnesium and magnesium-based materials have been intensively investigated as potential hydrogen storage carriers due to their natural abundance and availability, as well as their extraordinary high gravimetric and volumetric storage densities [5]. Among several high potential hydride systems, magnesium hydrides exert a high volumetric and gravimetric hydrogen density (110 kg m^{-3} and 7.6 wt%), making it one of the most widely studied hydrogen storage materials (Figure 1.2). It is worth noting that these values are much higher than those of compressed hydrogen, i.e. 23 kg m^{-3} at 35 MPa and 38 kg m^{-3} at 70 MPa, and 71 kg m^{-3} of liquid hydrogen (-253°C). In 1951, Wiberg first synthesized MgH_2 by heating Mg at 570°C and 20 MPa H_2 using MgI_2 catalysts directly [6]. Once

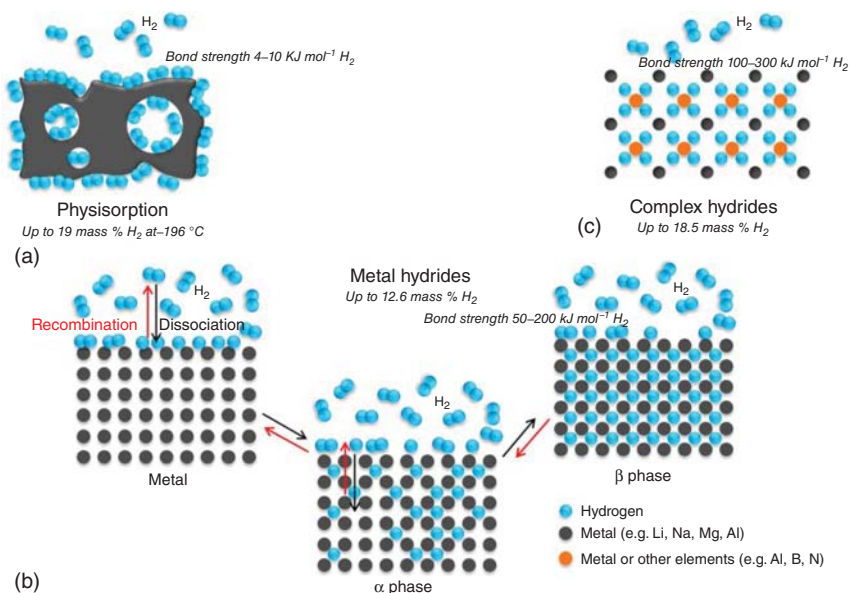


Figure 1.2 An overview of essential metal hydrides for hydrogen storage applications. Source: Reproduced with permission from Sun et al. [8]. Copyright 2018 Elsevier.