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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/liquefication, 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 $110\,\mathrm{g\,l^{-1}}$ 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.

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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 (CO_2) 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 °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 ($110\,\mathrm{g\,l^{-1}}$) storage densities [7]. Moreover, magnesium hydrides have been also used as a one-time hydrogen carrier, where their water hydrolysis

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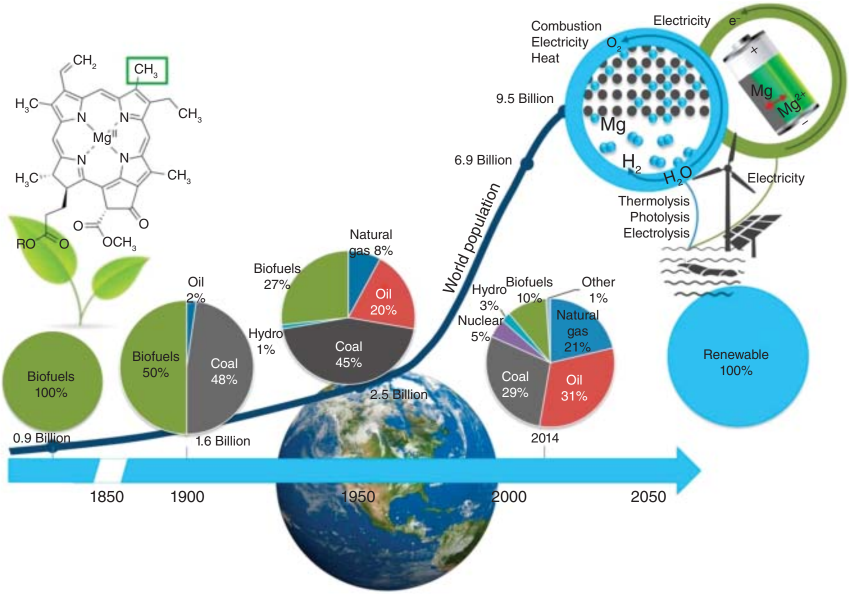

Figure 1.1 The role of Mg-based materials in hydrogen storage and batteries. Source: Reproduced with permission from Sun et al. [5] Copyright 2018, Elsevier.

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 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 °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

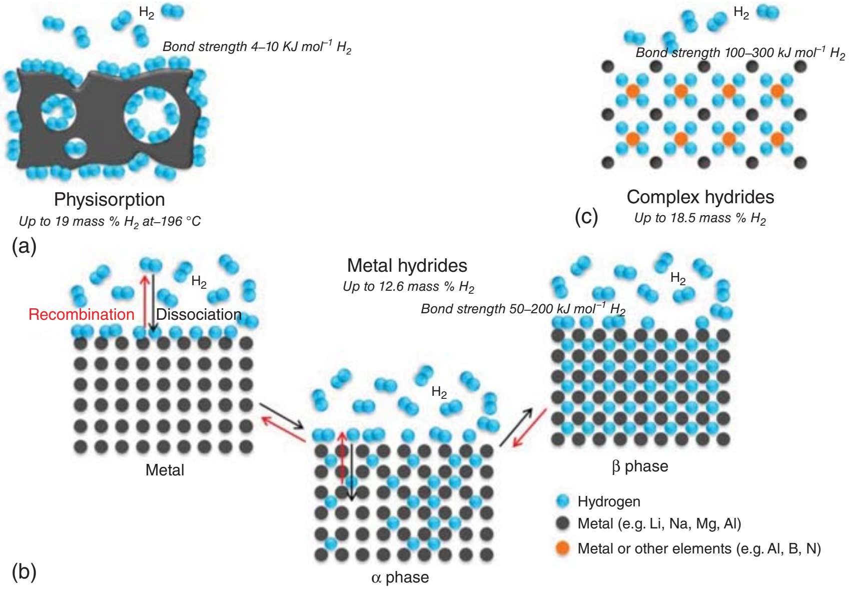

Figure 1.2 An overview of essential metal hydrides for hydrogen storage applications. Source: Reproduced with permission from Sun et al. [8]. Copyright 2018 Elsevier.