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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 $-253\,^\circ\mathrm{C}$, 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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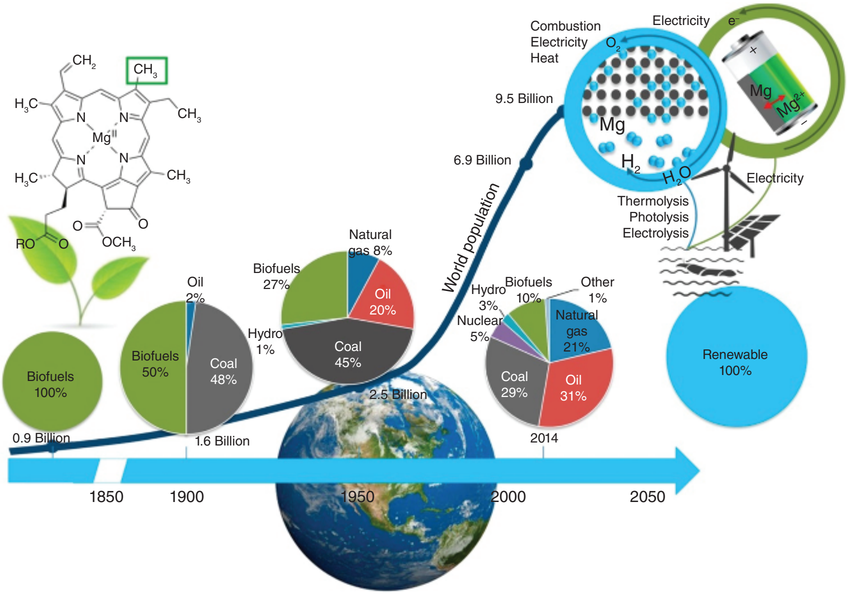

Figure 1.1 The role of Mg-based materials in hydrogen storage and batteries. Source: Reproduced with permission from Sun et al. [5] Copyright 2018, Elsevier.

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

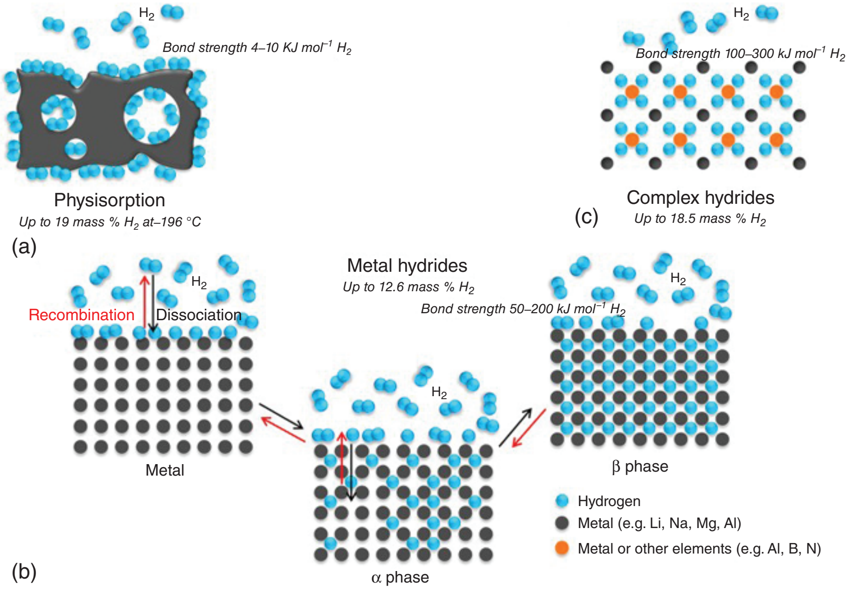

Figure 1.2 An overview of essential metal hydrides for hydrogen storage applications. Source: Reproduced with permission from Sun et al. [8]. Copyright 2018 Elsevier.

MgH_2 is formed, the reversible reaction between magnesium and hydrogen can be described by the following equation: $MgH_2(s) \rightarrow Mg(s) + H_2(g)$. For this reaction, the measured changes of enthalpy (ΔH) and entropy (ΔS) are $74.1 \pm 0.4\,kJ\,mol^{-1}$ and $133.4 \pm 0.7\,J\,K^{-1}\,mol^{-1}$, which entails an equilibrium pressure of 1 bar at 283 °C. Therefore, when selecting hydrogen storage materials, the ΔH and the ΔS of hydrogenation and dehydrogenation are among the most important parameters. Such values can be easily derived from the PCT isotherms using the van't Hoff plot. Beside thermodynamic considerations, the kinetic properties of MgH_2 are also pivotal when selecting a suitable hydrogen storage system. In fact, achieving the fastest hydrogenation/dehydrogenation kinetics is an indispensable goal for MgH_2. Alloying, catalyzing, nano-structuring, and combining with complex hydrides, are among the most effective strategies to improve the hydrogen storage kinetics and thermodynamics of MgH_2 [8].

In practice, Mg-based materials must be processed and placed in a hydrogen storage tank (HST) for efficient storage and transportation of hydrogen. However, when processed into pellets and packed in HSTs, Mg-based alloys suffer from sluggish hydrogen desorption kinetics, which largely impedes their practical applications, due to the large enthalpy change of hydrogen desorption reaction and the low powder thermal conductivity of Mg-based alloys [14]. And this phenomenon unfortunately becomes more significant in large-scale Mg-based HSTs. To enhance the hydrogen desorption kinetics of large-scale Mg-based HSTs, appropriate types of heating are indispensable to provide a high heating efficiency [15, 16]. Currently, direct electrical heating is one conventional way to heat Mg-based HSTs; however, it becomes strenuous to apply due to the limited heat-exchange surfaces and accumulated heat during the hydrogen absorption process with the increase of the HST scale. Heat transfer fluid (HTF) tube is another more efficient way to heat Mg-based HSTs with more uniform control of the local temperature due to the increased heat exchange areas [17–19]. Before carrying out real experiments, numerical simulations are always applied to assist the design of high-efficiency HSTs.

Magnesium hydride can also be used to produce hydrogen through hydrolysis with water, offering a doubled gravimetric capacity of 15.2 wt% and a high volumetric capacity of $150\,g\,l^{-1}$ [20]. The hydrolysis of magnesium materials refers to the reactions of Mg and MgH_2 with aqueous solution to produce more hydrogen and insoluble magnesium hydroxide at room temperature under standard atmospheric environment. Beside instant high gravimetric capacity and volumetric capacity, the hydrolysis of Mg and MgH_2 shows distinct advantages, including low material cost, abundant Mg resources, non-pollution oxidation by-products, moderate reaction temperature, and mature Mg recycling technology [21]. Therefore, hydrolysis of Mg-based materials is a promising technology for the development of portable hydrogen fuel cells. Nevertheless, the insoluble and dense $Mg(OH)_2$ passivation layer deposited on the surface of Mg or MgH_2 could minimize the diffusion of water molecules into inner particles for continuous hydrogen production, thus resulting in undesirable and uncontrollable hydrolysis performance [22]. To address such issues, the addition of catalysts can help to improve hydrogen generation. In addition, control of temperature, pH values, salt solution, etc. can also be effective.

1.3 Overview of Mg-ion Batteries

The current indispensability of economical and sustainable energy storage prospers battery research nowadays. Since their invention in 1991, Li ion batteries (LIBs) have become the state-of-the-art energy storage technology, which exerts widespread applications in portable devices, electrical vehicles, and grid energy storage. However, LIBs are limited by their capacity and energy density, approaching the theoretical limits of intercalation chemistry, as well as the ever-increasing consumption of expensive Li resources. Beyond Li-ion batteries, because of owning a higher volumetric capacity ($3833\,\mathrm{mA\,h\,cm^{-3}}$ for Mg versus $2046\,\mathrm{mA\,h\,cm^{-3}}$ for Li) and dendrite-free metal anode, rechargeable Mg-ion batteries are a promising alternative for high-density energy storage applications (Figure 1.3) [24]. However, RMBs remain underdeveloped due to the absence of high-performance electrolytes, cathodes, and anodes for any practical applications.

First of all, the electrolytes for RMBs play a crucial role in bridging the electrodes and transferring electroactive species via ionic transport, and the ideal electrolytes should possess not only compatibility with the electrodes, but also electrochemical and thermodynamic stability and safety in the energy storage system [7]. In general, the RMB electrolytes can be classified into liquid- and solid-state (quasi-solid-state) electrolytes. Liquid electrolytes can be classified into aqueous and organic electrolytes. Aqueous electrolytes include alkaline solutions (e.g. magnesium perchlorate with magnesium hydroxide), neutral saline solutions

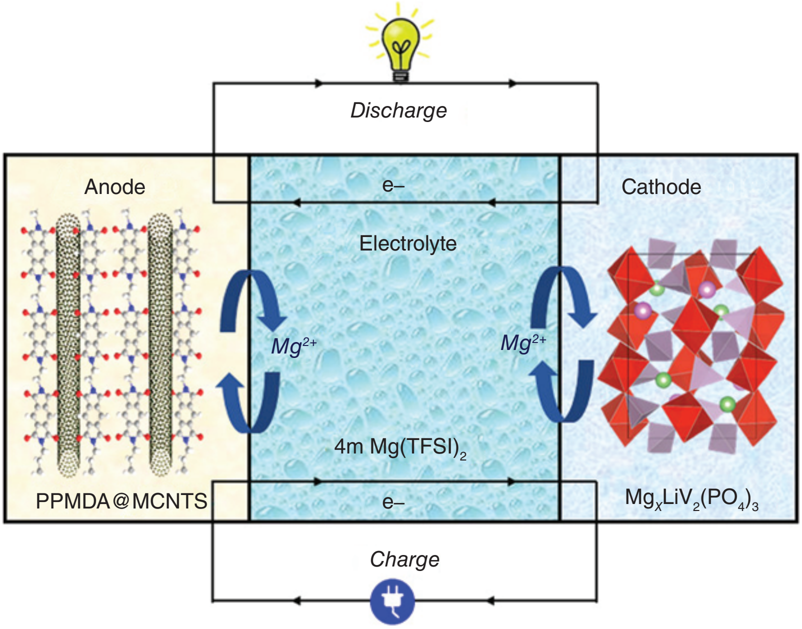

Figure 1.3 Illustration of rechargeable Mg-ion batteries (RMBs). Source: Reproduced with permission from Wang et al. [24]. Copyright 2017 American Chemical Society.

(NaCl solution), and seawater and seawater with acid (H_2SO_4). Organic electrolytes include Grignard-based, boron-based, $(HMDS)_2Mg$-based, and boron-centered electrolytes. However, one key challenge with MIBs in organic liquid electrolytes is their strong chemical reactivity toward electrolyte components (e.g. salt, solvent, additives) due to their low electronegativity [25]. Solid and quasi-solid electrolytes have been considered one of the most promising alternatives, because of their distinct advantageous properties over liquid electrolytes, such as good safety, excellent non-volatility, and superior flexibility. In general, solid electrolytes can be classified into inorganic solid electrolytes (ISEs), solid polymer electrolytes (SPEs), and composite polymer electrolytes (CPEs). Quasi-solid electrolytes (QSSEs) are often confused with SPEs, also known as gel polymerized electrolytes (GPEs), such as PEO/SiO_2 and poly(tetrahydrofuran)-based GPE (PTHF-based GPE). However, solid and quasi-solid electrolytes remain in a nascent stage and suffer from low ionic conductivity.

Secondly, due to its bivalent nature, the diffusion of Mg^{2+} in solid-state cathode materials is more sluggish than monovalent cations, such as Li^+ and Na^+, resulting in a large voltage hysteresis and low magnesiation degree [26]. As such, finding suitable cathode materials with fast kinetics has become the significant challenge for developing RMBs. As already commercialized in LIBs, intercalation-type cathode materials have been attempted for magnesium batteries because of their potential to achieve high cell voltage, high energy density, and cycling stability [7]. Common intercalation-type cathode materials include Chevrel phase CP (Mo_6T_8; T = S, Se, Te) materials, V_2O_5-Mg^{2+} insertion-type materials, molybdenum oxide (MoO_3), uranium oxide (α-U_3O_8)-Mg^{2+} insertion-type materials, layered structure (e.g. V_2O_5, MnO_2, Mo_6S_8, MXene) materials, spinel structure (e.g. Mn_2O_4, Cr_2S_4, Ti_2S_4, Mn_2S_4) materials, olivine structure [$MgMSiO_4$ (M = Mn, Co, Fe)] materials, NASICON structure materials [$NaM_2^{IV}(PO_4)_3$ (M^{IV} = Ge, Ti, Zr)], carbon-based (e.g. graphite, hard carbon, soft carbon, graphene) materials, and MT_2 (M = metal, T = S, Se) type (TiS_2, $TiSe_2$, MoS_2) intercalation materials. However, conventional oxide-based cathodes face challenges with Mg intercalation chemistry due to strong electrostatic interactions within the host structures [25], which lead to polarization and low reversibility [27–32]. Beside intercalation compounds, conversion-type cathode materials are also widely investigated for RMBs, as they have the potential to achieve higher energy density and lower cost in theory [26]. Common conversion-type cathode materials include chalcogenides (e.g. CuS, Cu_2MoS_4, $CuS_{1-x}Se_x$, Ag_2S, $Cu_{2-x}Se$, Sb_2Se_3). Meanwhile, Mg–O_2 batteries, Mg–S batteries, Mg–Se batteries, Mg–Te batteries, and Mg–I_2 batteries, are also within the regime of conversion-type cathode materials. These materials take advantage of the large capacity released by structural rearrangement and chemical bond rupture during the charge and discharge process, and the resulting phase structure changes are electrochemically reversible [30, 32, 33]. In addition, redox-active organic materials can also be used for cathodes, which can be classified as n-type, p-type, or bipolar-type in terms of their capabilities to release electrons (oxidation) or receive electrons (reduction) in their neutral state during the electrochemical reaction. Common organic cathodes include carbonyl compounds (e.g. 2,5-dimethoxybenzoquinone [DMBQ], polyanthraquinone sulfides [PAQS], pyrene-4,5,9,10-tetraone [PTO], organosulfur compounds (e.g. 2,5-dimercapto-1,3,4-thiadiazole [DMcT], poly-2,2′-dithiodianiline [PDTDA]), and nitrogen-based compounds (e.g. imines [C=N], nitriles [C≡N], azo compounds (N=N)].

Lastly, direct Mg metal anodes in RMBs are also considered a major obstacle to the construction of practical RMBs because of the incompatibility of Mg metal anodes with electrolyte solutions [23]. Conventional electrolyte solutions include Mg-based electrolytes [$Mg(ClO_4)_2$, $Mg(BF_4)_2$, $Mg(PF_6)_2$, $Mg(AsF_6)_2$, etc.] and organic solvents (carbonates, nitriles, lactones, esters, etc.), which show very low compatibilities with Mg metal anodes. Therefore, Mg metal anodes cannot work reversibly in these conventional electrolyte solutions, while high-voltage/high-capacity Mg insertion-type cathodes can work because of the passivation phenomena that fully block them. In addition, magnesium is highly reactive and can react with many organic solvents and electrolyte components, leading to the formation of passivation layers and other side reactions that can degrade battery performance [34]. Replacing Mg metal anodes with alternative anodes that can work reversibly in conventional electrolyte solutions provides a promising way to develop high-performance RMBs. Indeed, a series of insertion-type materials ($Li_4Ti_5O_{12}$, $FeVO_4$, Li_3VO_4, TiO_2-B, layered $Na_2Ti_3O_7$, etc.) have been probed as anodes for MIBs but show poor diffusion kinetics because of the strong electrostatic interactions between Mg^{2+} and their surrounding anions/cations. Moreover, the relatively high reaction potential and low specific capacity of insertion anodes greatly compromise the energy density of expected high-voltage Mg batteries. In addition, Mg_xM anodes using Group IIIA, IVA, and VA elements (M) alloying with Mg could theoretically deliver high specific capacities at low alloying potentials but need to be verified.

In general, finding suitable electrode materials that can more effectively catalyze the electrode reaction and overcome the limitations of the passivation film remains the key challenge for developing high-performance RMBs. It is also worth noting that the electrodeposition of Mg metal is not fully free of dendrite formation under all conditions. Nevertheless, these attractive characteristics and distinct advantages have already made RMBs one of the most promising energy storage technologies beyond LIBs.