Advancements in Metal Hydride Materials for Hydrogen Storage

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Abstract. Hydrogen energy is attracting the attention of scientists because of its high energy density and low environmental pollution in the world trend of clean energy use. In addition, the basis for the use of hydrogen energy is its secure, cost-effective, and efficient storage. After decades of devotions by experts, many high-performance hydrogen storage materials have been created. The poor hydrogen storage capacity, challenging hydrogen storage circumstances, slow hydrogen storage speed, and potential safety concerns remain, nonetheless, with the present hydrogen storage materials. Metal hydride materials, which have a high hydrogen storage density and safe reactions, have so steadily been a research focus in recent years. In this paper, magnesium-based materials and titanium-based materials are selected as the representatives of metal hydride materials, and their hydrogen storage mechanisms, common modification methods, and the advanced research progress of these methods are reviewed. Through the analysis of data, the hydrogen storage properties and the respective characteristics of each modified hydrogen storage material are rigorously presented. The key technical limitations and possible improvement directions of these materials are summarized, and the future application prospects and development trends of hydrogen storage materials are predicted at the end.

Keywords: Hydrogen storage capacity, magnesium-based materials, titanium-based materials, hydrogenation, dehydrogenation kinetics, activation energy.

1. Introduction

In today's world, environmental issue has become a major concern for governments. The U.S. government joined the Paris agreement in 2016 and pledged to reduce greenhouse gas emission levels to 80% of 2005 levels in the next 10 years. China, as a developing country, remains committed to environmental protection, promised to reach its highest carbon emissions in 2030 and finally decline to carbon neutrality 30 years later; while the U.S. has a more aggressive goal, advancing its carbon neutrality target to 2050 [1]. In order to achieve such a goal, human beings need to adjust the energy structure, gradually promote the enormous scale application of clean energy, as well as reducing the consumption of traditional fossil fuels.

Hydrogen has the smallest relative molecular mass of any gas monomer, but it has a very high calorific value of 142 mJ/kg, which is almost three times the calorific value of the same mass of gasoline. Compared with other energy sources, hydrogen only emits water after combustion, and no other greenhouse gases or toxic gases, making it the cleanest energy source is known on earth [2]. Therefore, based on the above advantages of hydrogen and the global energy growth trend, the use of hydrogen as a form of energy combustion or electricity production has become a hotspot of the energy industry [2].

Hydrogen storage is the basis for the utilization of hydrogen energy. At present, the mainstream hydrogen storage methods are liquified hydrogen storage, compressed hydrogen storage, and materials-based storage [3]. Among them, compressed hydrogen storage is quite widespread in real life, and this technology is also applied to the storage of other gases like oxygen. However, this approach puts high demands on the pressure resistance of the container. It also does not have a high storage capacity. For example, the weight of hydrogen storage in high-pressure cylinders commonly found in hydrogen stations is only 1wt%. In addition, high pressure also brings safety issues such as easy leakage of hydrogen gas and the explosion of the container. In terms of the liquified hydrogen storage, although this method has a small container size and fast hydrogenation and release, liquified hydrogen storage needs to consume a lot of energy to cool down because of the low boiling point of hydrogen (20.37 K). The low-temperature storage also requires excellent adiabatic properties of the container. These disadvantages make liquified hydrogen storage costly and limit its commercial application.

The material-based storage has advantages that the above two methods do not have. This method has a higher density of hydrogen storage and is convenient to transport. Furthermore, the storage conditions of this approach are milder, making it safer and thus less costly. The material-based storage can be classed as liquid form and solid form. Solid-state materials can be further split into chemisorption materials and physisorption materials [4]. This paper will focus on metal hydride materials, which are a type of chemisorption material. The mechanism of hydrogen storage in metal hydrides is illustrated in Figure 1. Metal hydride materials have the wide range of commercial application scenarios, such as solid-state hydrogen storage tanks for long-distance transportation or as a source of hydrogen storage for buildings or vehicles, due to the benefits of its large capacity for hydrogen storage, easy portability, good safety, and low cost.

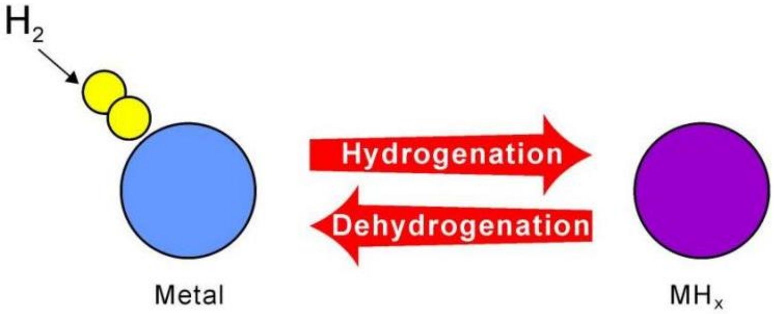

Figure 1. The mechanism of metal storage

Among metal hydride materials, research on magnesium-based and titanium-based hydrogen storage materials has become a current hot topic due to their excellent hydrogen storage properties and wide sources of raw materials. In terms of magnesium-based materials, this paper focuses on the effect and principle of action of two modification methods, namely alloying, and nanosizing, and introduces the current advanced materials. In terms of titanium-based materials, the impacts of the different metal’s additions on the hydrogen storage performance of Ti-Fe alloys are introduced. The principles of hydrogen storage performance enhancement of two advanced materials are summarized so that readers can understand the logic of metal hydride material development and the future development direction in a more organized manner.

2. Mg-Based Materials

This material has a particularly high theoretical mass hydrogen storage density at 7.6 wt% and its theoretical bulk density of hydrogen storage is up to 110 kg/m^3 [5]. These qualities make it a high-quality hydrogen storing substance that has garnered a lot of interest, while the manufacturing cost is low due to the abundant reserves of magnesium on the earth. Compared with other metal atoms, magnesium is lighter and safer. Based on the above advantages, Mg-based materials have great potential to store hydrogen in vehicles, fuel cells, and residential areas.

The hydrogenation reaction of Mg-based materials consists of three steps: hydrogen molecule dissociation and adsorption on the Mg surface, hydrogen atom diffusion within Mg, and solid hydride nucleation and growth. (MgH_2), and the inverse reaction is dehydrogenation. Because of the Mg-H bond's remarkable thermodynamic stability, both hydrogenation and dehydrogenation temperatures exceed 300 °C [6]. Meanwhile, the slow rate of hydrogen atoms dissociation on the magnesium surface and the slow rate of hydrogen atom diffusion in MgH_2 result in slow dehydrogenation and hydrogenation rates. These two facts lead to its slow dehydrogenation and hydrogenation rate, which greatly limits mg-based hydrogen storage materials’ practical applications. Therefore, for decades, many scientists have devoted themselves to improving mg-based materials’ hydrogen storage performance, and significant progress has been achieved in this area.

2.1. Alloying

Among various modification methods, alloying is of great importance nowadays. By incorporating additional transition metals into Mg-based materials, the thermodynamic and kinetic reaction rate can be greatly increased, lowering the hydrogen storage temperature and accelerating hydrogen absorption and dehydrogenation [6]. Mg-Ni alloy is a typical alloy hydrogen storage material mentioned above, and its hydride $MgNiH_2$ can release hydrogen below 250°C [7]. Nowadays, the introduction of small amounts of rare earth elements Re (e.g., La, Y, Ce) to the Mg-Ni alloy has turned out to be a popular method for the improvement of Mg-Ni materials. This method enables the introduction of more interfacial channels for hydrogen atoms diffusion [8]. As a result, it contributes to the enhancement of the diffusion rate of hydrogen atoms in MgH2.

Yan et al. introduced Y in Mg-Ni to prepare $Mg_{95-x}Y_5 Ni_x$ (x=5, 10, 15) alloy materials by vacuum furnace method [8]. After three hydrogenation and dehydrogenation cycles, the alloy material's X-Ray diffraction analysis (XRD) measurements indicated that it had a nanocrystalline structure made up of MgH_2, Mg_2NiH_4, and YH_3. However, during the dehydrogenation process, YH_3 was the only component that does not released hydrogen but act as a catalyst for the release of hydrogen from the other two hydrates, MgH_2 and Mg_2NiH_4 [8]. Among the three elements contained in the alloy, the Ni content has a strong connection to the hydrogen adsorption and dehydrogenation reaction rate and reaction conditions of the alloy materials.

On the one hand, a higher Ni content can enlarge the alloy's hydrogen diffusion channels, improving the hydrogenation kinetic performance and lowering the optimal hydrogenation temperature [8]. For example, Ni_{15} reaches 90% of its maximum hydrogen capacity in 1 minute at 200°C, which is Ni_{15}’s optimal hydrogenation temperature. As a comparison, the optimal hydrogenation temperature of Ni_5 is at 300 °C, but at a slower rate than Ni_{15} at 200°C. On the other hand, Ni also has a beneficial impact on the enhancement of the kinetics of dehydrogenation. Based on the experimentally measured data, calculated by the Arrhenius equation, it has been discovered that Ni can be added to reactions to lower the activation energy needed for the dehydrogenation process, which means lowering the hydrogen dehydrogenation temperature [9]. For example, at 320°C, the whole dehydrogenation of the Ni_{15} alloy can be accomplished in five minutes. As a comparison, If the hydrogen release rate of the Ni_5 alloy reaches this value, the hydrogen needs to be released at 360°C [8].

2.2. Nanosization

Nanosization is also a valid modification method for Mg-based materials. The morphological structure of the magnesium particles created by nanosizing has significantly altered. More precisely, it has a larger specific surface area and smaller size, and the diffusion distance of hydrogen atoms becomes shorter when absorbing hydrogen, which accelerates the rate at which hydrogen is absorbed by magnesium-based materials in nano sizes, and Figure 2 illustrates how particle size affects the hydrogenation rate. Meanwhile, the majority of the hydrogen atoms in the alloy have access to its surface due to its nanosizing, which makes the Mg-H bond unstable, thus reducing the hydrogenation and dehydrogenation reaction's activation energies [10,11]. Commonly used techniques to create magnesium nanoparticles include high-energy ball milling and chemical reduction. In 2011, Joen et al. used the reduction of magnesocene ($MgCp_2$) in tetrahydrofuran solution containing polymethyl methacrylate (PMMA) with lithium, and naphthalene to prepare Mg NCs/PMMA [12]. The particle size of magnesium nanocrystals (Mg NCs) prepared by this method is about 5 nm. This is a material that can be used to isolate water and oxygen, and it can achieve rapid hydrogen adsorption in only 30 minutes at 200 °C with a hydrogen storage capacity reaching 4 wt%.

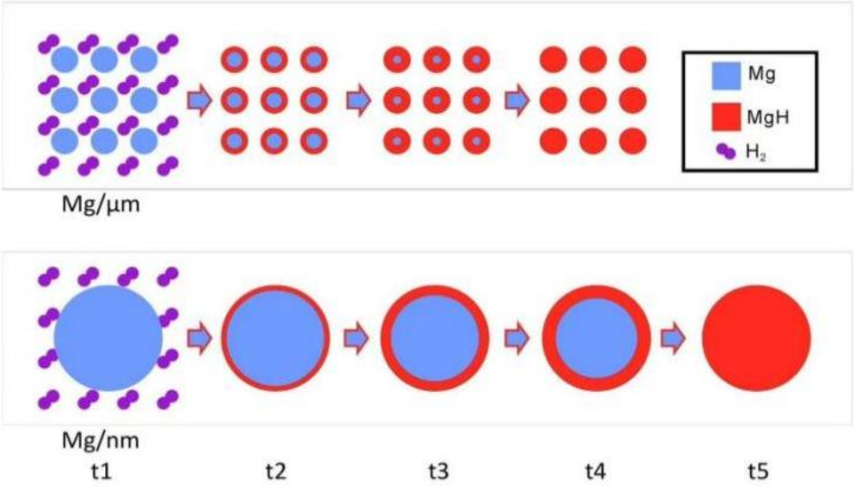

Figure 2. Effect of Particle Size of Mg on Hydrogenation Rate

Liang et al. optimized it on top of this method and successfully prepared magnesium particles with smaller particle sizes that are less than 5 nm [13]. The researchers adjusted the lithium-naphthalene mass ratio to 1:9 by using methyl magnesium chloride as a precursor which led to a maximum yield of magnesium particles at 85%. At the same time, the researchers also adjusted the ratio of PMMA to methyl magnesium chloride to 3:4, thus successfully reducing the particle size of magnesium particles [13]. The Mg NCs/PMMA composite prepared by this method had excellent hydrogen storage performance: When absorbed hydrogen at 200 °C, it can achieve rapid hydrogenation within 8 minutes and reach the maximum adsorption capacity of 4.8 wt% in 20 minutes; When released hydrogen, it only took 25 minutes to release 4.15 wt% hydrogen at 270°C [13]. The information provided above leads to the conclusion that this novel material outperforms the conventional Mg NCs/PMMA in terms of hydrogen storage capacity as well as the reaction rates.

In order to further improving the thermodynamic and kinetic performance of Mg-based materials in nano sizes, the researchers prepared the new composite material MWCNTs-Mg NCs/PMMA by adding new Mulit-Wall Carbon Nanotubes (MWCNTs) on top of that. The data of the study showed that: when absorbed hydrogen at 200 °C, this material can achieve rapid hydrogen adsorption within 5 minutes, and finally reach a maximum hydrogenation amount of 6.7 wt% in 20 minutes. When it released hydrogen at 240 °C, it can reach 4.2 wt% in 10 minutes [13]. These results revealed that compared with Mg NCs/PMMA, this new composite material not only has a significant boost in hydrogen storage capacity but also has a faster hydrogen storage rate and lower optimal hydrogen storage temperature.

3. Ti-Based Hydrogen Storage Materials

Titanium-based is also widely studied in metal hydride hydrogen storage materials, It is mainly in alloy form, of which Ti-Fe is one of the most commonly used ti-system alloys. This material was first prepared by American researchers Silva et al. in 1974 [14]. Ti-Fe alloy can store 1.9 wt% of hydrogen, which is a significant amount [15]. Aafter activation treatment, it may store hydrogen in at ambient temperature [16]. This alloy is simple to prepare, of low cost, and safe for hydrogen storage. These factors made scientists from all over the world interested in these materials, and they produced a significant amount of meaningful work in this field. However, the Ti-Fe alloys also have some defects that cannot be neglected. The main imperfection that is it needs to be activated under harsh conditions, including high temperature (>723 K); high pressure (5-8 MPa); long activating time (200-300 min), etc. [17]. It is easily poisoned by gas impurities such as CO and O_2, for which its cycle life is greatly affected by the purity of hydrogen. The impurity gas contained in hydrogen causes its hydrogen storage performance to decline after repeated hydrogenation, making it difficult to continue for further use [18].

For the purpose of overcoming the drawbacks mentioned above, a widely accepted way is to add transition metal elements or rare earth elements to Ti-Fe alloys to replace some of the Fe. This method normally does not change the alloy's crystal structure, but changes the phase structure of the alloy so that it can improve the material's hydrogenation kinetic properties [19]. The Ti-Fe alloys' hydrogen storage performance varies with the additions of other elements in the alloy. For example, adding V to Ti-Fe alloys improves activation performance but decreases its capacity [20]. Scientists introduced Mn to Ti-Fe alloy and it can achieve hydrogen storage activation at room temperature, but the lifetime of this alloy is particularly short [21]. The addition of mixed rare earth element Mm (including Ce La Nd Pr) to the alloy creates cracks on the surface of the hydride produced by the alloy and hydrogen gas etc, which means this change can accelerate the rate of hydrogenation and dehydrogenation [22].

3.1. Adding Sm to the Alloy

Yan et al. chose to prepare a cast $Ti_1Fe_{0.8}Mn_{0.2}Sm_x$ (x=0.02, 0.04, 0.06, 0.08) hydrogen storage alloy by adding Sm elements to the Ti-Fe-Mn alloy and comprehensively examined the role of Sm in enhancing the hydrogen storage performance of the alloy at the microscopic level [23]. It was demonstrated that the alloy produced the TiFeH phase, $TiFeH_2$ phase, and $TiFe_2$ and Sm_3H_7 phases after hydrogenation. It can be concluded that $TiFeH_2$ does not absorb hydrogen during the process. From the XRD images taken by the researchers, it appears that the higher the Sm content in the alloy, the higher the $TiFeH_2$ content, resulting in less $TiFe_2$, thus allowing the Ti-Fe-Sm alloy to store more hydrogen.

The addition of the Sm element can also improve the kinetic properties of the alloy in terms of hydrogenation and dehydrogenation. From the scanning electron microscopy (SEM) of the alloy taken by the researchers, it can be observed that the alloy with the addition of Sm has more interfacial channels than the traditional Ti-Fe alloy, which gives hydrogen atoms more chances in diffusion, implying that the rate of hydrogen adsorption and dehydrogenation of this alloy becomes faster [23]. More precisely, when x=0.08, the alloy can be activated within two minutes and absorb hydrogen within five minutes.

The addition of Sm element to the alloy is also beneficial to enhancing the activation properties of the alloy. Sm element is more easily combined with H, so Sm3H7 will be formed rapidly when the alloy absorbs hydrogen [23]. This will refine the alloy particles and make the alloy produce more surfaces that are in contact with hydrogen molecules and can promote the decomposition of hydrogen molecules. This will allow the alloy to be more easily activated. As reflected in the data, The alloy's energy of hydrogenation activation increases with a rise of Sm element, going from 15.2 kJ to -6.8 kJ, and the hydrogen dehydrogenation activation energy of the alloy decreases from 64.1 kJ to 48.9 kJ.

3.2. Adding Pr to the Alloy

Xu et al. from China, added Pr to the Ti-Fe alloy and studied the changes of the new alloy [24]. The researchers used XRD, SEM, and other methods to accurately study the microstructure of the alloy. It was found that the phase composition of the alloy did not change after the addition of pr to the alloy, while the crystal structure of the alloy was changed [24]. Specifically, this was reflected in the increase in the cell volume of the alloy. It can be seen that for the Ti-Fe alloys, the effect caused by the addition of Pr is different from the effect caused by the addition of general metals. This affects the alloy's hydrogen storage performances in two ways: on the one hand, the larger cell volume facilitates the entry of hydrogen into the alloy, thus enhancing the alloy's ability to store hydrogen. On the other hand, the alloy can become difficult to recover because the larger cell size may make the alloy more susceptible to pulverization during hydrogenation and dehydrogenation. It will greatly increase the cost of hydrogen storage and thus limit its commercial application. Therefore, the improvement of this method requires researchers to strike a balance between achieving high hydrogen storage capacity and controlling the degree of cell volume increase so that the material can store more hydrogen as well as have a higher number of hydrogen storage times.

4. Conclusion

This paper presents the research progress related to magnesium-based alloy materials and titanium-based alloy materials.

Mg-based materials have high hydrogen storage density, but poor kinetic and thermodynamic properties in hydrogen adsorption and dehydrogenation. Mg-Ni is a typical Mg-based alloy, and scientists have chosen to add the rare earth element Y to further improve its hydrogen storage properties. YH_3 appears in Mg-Ni-Y alloys after hydrogenation, and it does not participate in the dehydrogenation reaction, but catalyzes this reaction of other hydrides, thus significantly increasing the hydrogen release rate of the material. This finding has inspired researchers to search for new materials to prepare suitable new alloys to increase the rate of the hydrogen release reaction. However, this method also decreases the material's ability to store hydrogen.

The hydrogen capacity of the nanosized magnesium-based material is higher than that of the traditional Mg-based material. Furthermore, the hydrogenation and dehydrogenation reactions' activation energies are also lower due to the change of particle morphology structure brought by nanosizing, so its hydrogen uptake and release conditions are also milder. However, in terms of large-scale commercial applications, there is still a long way for nanosized magnesium-based materials to go, because it still needs a high temperature of more than 200 °C to absorb and release hydrogen. In general, the combination of nanosizing and alloying to prepare magnesium-based materials is expected to not only reduce the hydrogenation and dehydrogenation reactions' temperatures but also enhance the hydrogen capacity.

Titanium-based hydrogen storage materials are represented by Ti-Fe, which can achieve effective hydrogen storage at room temperature. However, it also has the restrictions of severe activation conditions and short service life. Scientists have improved its performance by adding metals to Ti-Fe. The addition of different metallic elements brings different changes, some of which can extend the alloy's hydrogen storage life and some of which can enhance the alloy's ability to activate. Therefore, the combination of these components provides the theoretical possibility to prepare Ti-based alloy hydrogen storage materials with high activation performance and long service life.

In the near future, it is believed that all these technical bottlenecks will be overcome one by one, and mankind will realize large and effective hydrogen storage under mild conditions. This technology will be applied to industrial hydrogen storage, automotive hydrogen storage, and hydrogen fuel cells, thus replacing traditional fossil energy and reducing the environmental pollution.

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