Research Progress in Magnesium-Based Solid Hydrogen Storage

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Abstract. The materials produced with magnesium for hydrogen storage have the highest potential for growth and have received huge attention because of their low cost, large supply, and excellent hydrogen storage capacity. However, because to its steady hydrogen absorption and emission thermodynamics and slow kinetics, this material's use in hydrogen storage is constrained. Hydrogen uptake and release of materials are thermodynamically stable and slow kinetic, because hydrogen molecules have a high dissociation energy on the surface of Mg, while hydrogen atoms have a slow diffusion rate in the magnesium lattice, which limits its application. Therefore, a large number of research works have focused on the thermal/kinetic modification of magnesium-based materials recently, and has made significant progress. In this paper, the modification methods of the above materials are analyzed, with emphasis on the mechanism of absorption and release of hydrogen, and the influence of alloying, nano crystallization and catalyst addition on optimizing and improving the material properties. Finally, research results are summarized, and the future development direction is discussed.

Keywords: solid hydrogen storage, MgH_2, magnesium-based hydrogen storage material, hydrogen absorption, discharge performance.

1. Introduction

Hydrogen is a kind of zero-carbon energy, and it has the advantages of large reserves, storable, zero emission and so on. It is considered as an ideal substitute for fossil energy sources, and its energy density is up to 142 MJ kg^{-1} [1]. Hydrogen burns to produce water (and a small amount of nitrogen oxide), which can be used to produce hydrogen. Hydrogen can be efficiently converted into different forms of energy (such as electricity and heat), and for renewable energy storage, it is an ideal carrier. In addition, Hydrogen element is the most abundant one in the universe and one of the most common elements on Earth. Among them, the total heat generated from the combustion is nearly 9,000 times that of the earth's fossil energy [2], Can almost achieve long-term energy demand.

The development of hydrogen energy faces many challenges for example, hydrogen production cost and application cost, among which the biggest challenge is efficient hydrogen storage technology, which is also the key to whether hydrogen energy can be widely used. At present, the main hydrogen storage methods are low temperature liquid hydrogen, solid material storage and high-pressure storage. The US Department of Energy's most stringent standard for materials is 6.5 wt% mass hydrogen storage density and 0.05kg H_2/L volume capacity [3]. In addition to requiring high weight and volume capacity, fast adsorption kinetics at near ambient temperatures, high reversibility, high stability and high-cost effectiveness are ideal systems that should have [4].

Magnesium-based solid hydrogen storage is to form a stable compound MgH_2 in the form of magnesium and hydrogen to achieve the goal of storing hydrogen atoms. The enthalpy of hydrogen absorption reaction of Mg is changed to-74.4kJ/mol H_2, and the entropy is changed to-135.4kJ/mol H_2 [5]. The enthalpy of the MgH_2 dehydrogenation reaction changes to 74.7kJ/mol H_2, and the entropy changes to 130 kJ / mol H_2 [6], With the high thermodynamic stability and the strong force of the Mg-H ionic bond, an energy barrier of up to 3.35 eV is needed to overcome to destroy the Mg-H bond [7]. This requires the compound to fully absorb hydrogen above 300 degrees Celsius, so the kinetics is slower at a temperature below 300°C. At present, some achievements have been made in improving the magnesium-based hydrogen storage performance in the aspects of alloying, nano

crystallization and catalyst addition. In this paper, the above research progress is summarized and prospected.

2. Modification of the Magnesium-based Hydrogen Storage Material

2.1. Alloying

Because MgH_2 standard hydrogen enthalpy to 75kJ·mol^{-1} H_2, high thermodynamic stability, which makes the decomposition of hydrogen is difficult, after adding transition metal alloying, thermodynamic stability can drop, which can reduce the temperature of hydrogen absorption, the phase boundary of single-phase or multiphase magnesium hydrogen storage alloy can be generated by the alloy of Mg and transition metal, and can also provide huge amount of active absorption sites therefore, the performance of Mg /MgH_2 system is improved [8].

The researchers made magnesium-based hydrogen storage alloys of Ni, Ti, In, Al, Ag, Si, Ga, Ce, Ca, Cd in specific proportions. Comparing the enthalpy change and hydrogen storage amount, alloy can reduce the enthalpy change to a certain extent. The storage number of alloys is generally significantly reduced, refer to Table 1.

Table 1. Characteristics of magnesium alloy [7]

Alloy	Δ H (kJ mol −1H_2)	Hydrogen storage capacity (%)
Mg2Ni	64.5	3.6
Mg3Cd	65.5	2.8
Mg0.95In0.05	68.1	5.3
Mg3Ag	68.2	2.1
Mg2Si	36.4	5.0
Mg5Ga2	68.7	5.7
Mg2Fe(H6)	87.0	5.5
Mg80Ce18Ni2	63.0	3.32
Mg3PrNi0.1	80.7	3.23
Mg3La	81.0	2.89
Mg3LaNi0.1	-	2.73
Mg2Cu	72.6	2.53

In conclusion, alloying can reduce the enthalpy of hydrogen storage materials and the thermodynamic and kinetic properties are improved at the cost of greatly sacrificing hydrogen capacity. In the process of hydrogenation, due to the bond fracture between Mg and other elements, its reversibility is poor, and the cycle stability of the system will also decrease [8].

2.2. Catalyst

The catalyst can dissociate H in the process of Mg/MgH_2, and provide the active site for the adsorption and diffusion. The dissociation energy on the magnesium surface can be reduced by catalyst, and the interaction of the unsaturated d / f electron shell with the valence electron layer of H can cause a decrease of Mg-H bond energy [9], thus makes the kinetic properties of the material reaction improved. Cui et al. synthesized series of core-shell structure of Mg-TM nanocomplexes [10]. The catalytic dehydrogenation properties were ranked as magnesium-titanium, magnesium-niobium, magnesium-nickel, magnesium-vanadium, magnesium-cobalt, magnesium-molybdenum [11]. Core-shell Mg@TM system was prepared by vapor deposition, and the nano-shell coating on MgH_2 particles was formed, which the adsorption/dehydrogenation kinetics of Mg/MgH2 was greatly improved. The fastest hydrogen absorbing composite is Mg@Ni (Fig. 1).

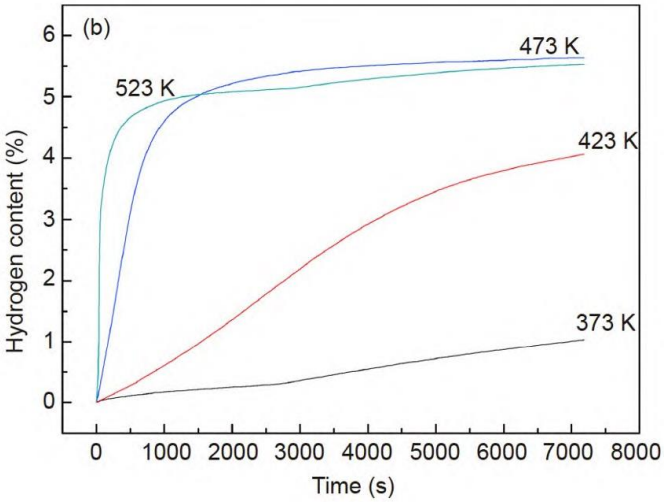

Figure 1. Isothermal hydrogen absorption kinetic curves of Mg @ Ni composite [11]

Intermetallic compounds are also highly efficient catalysts, and Chen et al. found that MoNi alloy improved the performance of magnesium-based materials [12]. MgH_2-MoNi, the composite can absorb / pump 6.7% hydrogen at 60s and 10 min of 300°C H_2. Metal chlorides, fluorides, hydrides, borides, nitrides, and carbonides also have significant catalytic effects, respectively. Ti3C2-MgH_2 has the best improvement effect. The MgH_2 + 5%Ti3C2 composite can generate 6.2% of H_2 internally [13]. Metal oxides have also been extensively studied [14]. Addition of TiVO3.5 can observably reduce the temperature of MgH_2 and improve the kinetic performance of the reaction. MgH_2+10% TiVO3.5 samples at 250°C for 10 min, 5.0% hydrogen injection internally, and 3.9% hydrogen absorption in 5s at 5 MPa hydrogen pressure, 100°C. The catalyst properties of the added hydrogen storage materials are summarized in table 2.

Carbon-based material is a good catalyst carrier, and has a small mass density and low price, conducive to the storage density improvement. More importantly, carbon materials can effectively inhibit the MgH_2 particles agglomeration, and also increase the cycle stability of materials [15]. It is found that the graphite additive (5 wt%) can make the composite material to achieve high stability of reversible hydrogen storage capacity in long term (about 6 wt% H_2).

Table 2. Catalyst properties of the added hydrogen storage materials [8]

Material	Tonset/°C	ΔH/kJmol$^{-1}H_2$		Ea/kJmol$^{-1}H_2$		Hydrogen wt%
		Abs	Des	Abs	Des	
MgH-4%Ni NFs	143	-	-	-	81.5	7.02
o-Nb_2O_5	195	-	74.7	-	101	6.4
2D-$TiNb_2O_7$ nanoflakes	178	-	75.2	-	100.4	7.0
MgH_2-10wt%TiC	-	-	-	-	144.62	6.01
10wt%-TiFe+5wt%-CNTs	210	-	80.6	60.7	-	6.2
MgH_2-Co/Pd@B-CNTs	198.9	-	-	-	76.66	6.67
MgH_2-10wt% TiO_2@C	205	-	73.6	38	106	6.5
MgH_2-TiO_2SCNPs/AC	163.5	-	-	-	69.2	6.5
MgH_2:Fe_3O_4@GS	262	60.62	66.34	-	90.53	6.2

2.3. Nanocrystallization

The magnesium-based materials are a kind of effective promotion Mg/MgH_2 hydrogen storage system of dynamics and thermodynamic performance strategy, nano Mg particles surface area increase, significantly increased the active site, can speed up the dissociation speed of the hydrogen particles size to the nano size, shorten the diffusion path of hydrogen atoms, more conducive to adsorption and diffusion. More importantly, the Mg-H bonds in nano-sized magnesium-based

particles become unstable and the thermodynamic properties improve significantly, as shown in fig. 2, when the particles are energetically unstable below 1nm.

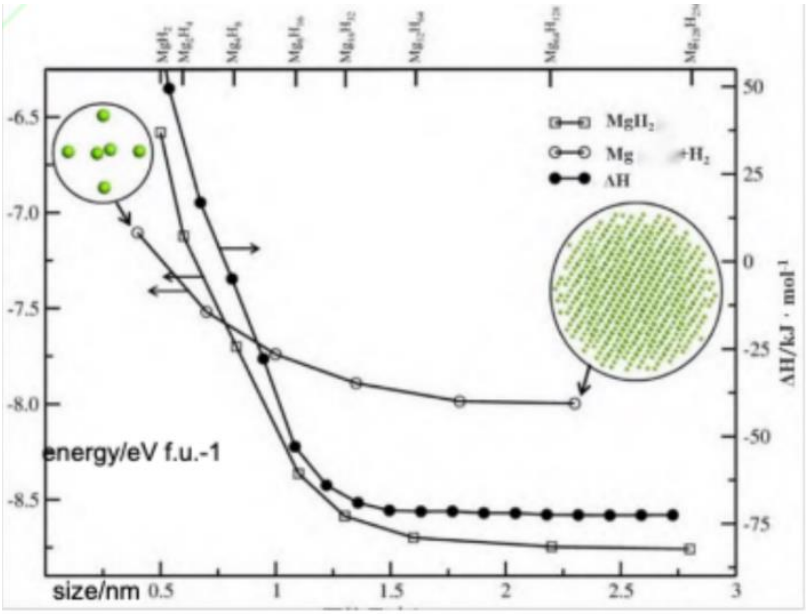

Figure 2. Particle size of the total energy of MgH_2 nanoclusters [16]

Preparation of nano-magnesium based materials, including high energy ball grinding, chemical reduction. Hydrogenation method, gas deposition and deposition method and melting method are main methods for high-energy ball grinding. But they cannot accurately control the distribution of particle size of materials within a relatively low range. In addition, the high-energy ball grinding method is easy to introduce impurities, and it is easy to cause the agglomeration and growth of materials, which makes it more appropriate to reduce the cycle stability of nano-Mg base materials by chemical reduction, hydrogenation and vapor deposition with controllable and uniform size.

The hydrogenation method directly hydrogenthe magnesium salt at 170-2 (3-8 $MPaH_2$) to 200 degrees Celsius, and the hydrogenation method usually have limitation on the materials to the nanopore of the porous material (i. e., the nanodomain). The reaction formula is:

$$Mg\ (CH) + 2H\ (g) - MgH\ (s) + 2CH\ (g) \quad (1)$$

The hydrogenation method takes the material with nanopore as the framework, controls Mg / MgH_2 within the nanometer scale, realizes effective constraint, and reduces the particles to the nanoscale to significantly improve the thermodynamic and kinetic performance. However, usually the framework will account for more than 50% of the whole system, and serious theoretical capacity loss is inevitable [8].

Chemical reduction is a bottom-up method for synthetic magnesium nanoparticles, in the presence of electronic carriers, with alkali metals, acts as a reducing agent to reduce the magnesium salt in an organic solution (tetrahydrofuran or dioxyquinoline) to obtain the magnesium nanoparticles [17-19]. Chemical reduction generates magnesium nanocrystal materials wrapped in atomic-thin and gas-selective reduced graphene oxide sheets [20]. Compared with the metal hydrides prepared by ball grinding, Mg nanocrystals is fine mono disperse nanocrystalline, and the rGO layer exhibited ideal selectivity, leaving MgH_2 free from oxygen and moisture, and improving its kinetic properties.

The vapor deposition method is based on the high temperature of instantaneous evaporation of metal. Under the action of hydrogen and other gases, metal atoms undergo a series of processes, first evaporating, then nucleating, then growing and finally condensing to obtain nanosize Mg [21]. Mg nanowires with Mg nanowires with the smallest diameter (30 nm) with a diameter range of 30 to 170 nm for 30 min at 300°C, absorbing 7.6% H_2 and releasing 6.8% H_2.

3. Conclusion

Due to its benefits, including their low price, high hydrogen storage capacity, and plentiful natural raw materials supplies, magnesium-based hydrogen storage materials are regarded as the material with the most significant advantage. The thermodynamic stability of magnesium-based materials' absorption and release, however, restricts their real application. The disadvantage of alloying is that hydrogen capacity and kinetics of hydrogenation or dehydrogenation must be sacrificed in order to modify the reaction path and lower the enthalpy. Improved dynamics for MgH_2 systems are possible, but the thermodynamic properties are essentially unaltered. Nano Mg particles play a crucial role in lowering activation energy and maintaining thermodynamic stability. Therefore, highly stable porous MOF and its derivatives are ideal carriers for future preparation of nano Mg-based materials. It is far from enough to rely solely on any of the above methods for hydrogen storage properties need to be further optimized to change the Mg/MgH_2 particles, the particle surface structure, increase the diffusion path and the interface catalytic reaction efficiency, reduce the amount of the catalyst, ensure its reversible storage ability, and improve the performance of low temperature hydrogen discharge. In the future, the dual mechanism of catalyst addition and nano modification can be used to regulate the performance of MgH_2 system, and the catalytic mechanism analysis should be strengthened to promote its practical application.

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