Improved Hydrogen Generation Performance via Hydrolysis of MgH₂ with Nb₂O₅ and CeO₂ Doping

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Rapid formation of magnesium hydroxide passivation layer during hydrolysis of MgH₂ seriously blocks its application as a hydrogen generation material. MgH₂ is also susceptible to oxidation. MgH₂ with Nb₂O₅ and/or CeO₂ doping has been prepared via high energy ball milling in this work with the aim of enhancing the hydrolysis performance and oxidation resistance. The phase compositions, microstructure and hydrogen evolution properties have been systematically investigated. Nb₂O₅ and CeO₂ particles with particle size in the range of ~20–200 nm are uniformly dotted on the surface of MgH₂ matrix after ball milling. It is found that Nb₂O₅ shows better facilitating effects than CeO₂ on the hydrolysis performance of MgH₂. As-milled MgH₂+10%Nb₂O₅ and MgH₂+10%CeO₂ samples generate ~705 and 474 mL g⁻¹ of hydrogen in distilled water within 60 min, respectively. Introducing MgCl₂ in water can also significantly enhance the hydrolysis reaction kinetics and conversion rate. As-milled MgH₂+10%Nb₂O₅ sample shows a hydrogen yield of 1222 mL g⁻¹ in 5% MgCl₂ solution, corresponding to a conversion rate of 74.6%. However, air exposed MgH₂+10%Nb₂O₅ sample hardly generates any hydrogen in MgCl₂ solution. CeO₂ can modify the oxidation resistance to some extent. MgH₂ with CeO₂ doping can still produce ~250 mL g⁻¹ of hydrogen after 24 h air exposure.

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1. Introduction

In the context of traditional energy shortage and environmental concern, hydrogen is regarded as an ideal renewable energy carrier due to its high energy density, abundant sources and water as the only form of emission.^{1–3)} Convenient hydrogen generation, storage and usage are three essential aspects for large scale applications of hydrogen. Generating hydrogen in a simple, pollution-free and inexpensive way is still challenging.^{4,5)}

Biomass conversion, water electrolysis and photo catalysis are usually adopted hydrogen generation ways.^{6–9)} However, the storage of compressed gaseous hydrogen is necessary. Pressurized hydrogen in bulky tanks can not meet the requirements for many mobile and portable applications.^{10,11)} Generating hydrogen on-site by the hydrolysis reaction of metals and metal hydrides is a promising strategy to serve as energy source similar to batteries. Encouragingly, the metal hydrides usually have a gravimetric energy density at least one order of magnitude higher.

Metals and metal hydrides including Mg, MgH₂, Al and NaBH₄ *et al.*^{12–14)} have been extensively investigated. Although the hydrolysis process of NaBH₄ is controllable and safe, the recovery rate of its byproduct is extremely low. With respect to Al, its hydrolysis reaction usually needs high temperature and additives.^{15,16)} Mg and Mg hydrides have been reported to produce hydrogen spontaneously in water at room temperature.¹⁷⁾ The advantages of MgH₂ as a hydrogen generator include inexpensiveness, non-pollution of the byproduct and desirable hydrogen production yield. The hydrolysis reaction of MgH₂ in water can be described by the following equation.¹⁸⁾

The theoretical hydrogen yield is calculated to be ~1820 mL g⁻¹ (~15.2 mass%) based on the reaction equation. However, quickly formed dense Mg(OH)₂ layer on the matrix surface always hinders the further hydrolysis of internal MgH₂.¹⁹⁾

The strategies usually adopted to promote the hydroxide layer exfoliation include ball milling with various kinds of additives, raising the temperature of water and optimizing aqueous solution.^{20–22)} It has been reported that ball milled MgH₂+CaH₂ composite shows superior hydrolysis kinetics and a conversion yield of 60% after 20 min of hydrolysis.²³⁾ CaH₂ is found to be able to break the hydroxide layer during hydrolysis reaction. Introducing Cl⁻ ions in water can accelerate the hydrolysis reaction to some extent.²⁴⁾ It is found that MgH₂ can produce 1310 mL g⁻¹ of hydrogen within 5 min in 4.5% NH₄Cl solution at 60°C.¹⁹⁾

Oxidation is another critical problem with MgH₂ as a hydrogen production material, which deteriorates the hydrogen evolution kinetics and conversion rate obviously. MgO layer severely blocks the contact between MgH₂ and water. Considering the brittleness and redox characteristics, Nb₂O₅ and CeO₂ are selected as additives to modify the hydrolysis performance and oxidation resistance of MgH₂ in this work. MgH₂+10%Nb₂O₅, MgH₂+10%CeO₂ and MgH₂+5%Nb₂O₅+5%CeO₂ composites are prepared by ball milling in Ar. The phase compositions, microstructure and hydrolysis performance in both distilled water and MgCl₂ solution of milled samples are systematically studied. Special attention is also paid to the hydrolysis kinetics of air exposed samples. It is found that Nb₂O₅ shows better facilitating effects than CeO₂ on the hydrolysis of MgH₂. However, MgH₂ with Nb₂O₅ doping suffers serious oxidation during air exposure. CeO₂ can modify the anti-oxidation property of MgH₂ to some extent.

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2. Experimental

2.1 Material preparation

MgH_2 (Alfa Aesar, $\sim 44\ \mu\text{m}$, 98% purity), Nb_2O_5 (Alfa Aesar, -325 mesh, 99.99% purity) and CeO_2 (Alfa Aesar, -325 mesh, 99.99% purity) powders were used as starting materials without any further processing. Pure MgH_2 , $\text{MgH}_2+10\%\text{Nb}_2\text{O}_5$, $\text{MgH}_2+10\%\text{CeO}_2$ and $\text{MgH}_2+5\%\text{Nb}_2\text{O}_5+5\%\text{CeO}_2$ (mass%) were ball milled in an inert argon atmosphere for 3 h using a SPEX 8000D ball mill. 1 g of each sample was introduced in a tungsten carbide vial sealed under pure argon and containing 20 g steel balls, corresponding to a ball to powder weight ratio of 20:1. To avoid overheating during ball milling process, an interval of 15 min was performed after each milling of 15 min. All the loading and weighing were performed in a glove box under the protection of high purity argon to avoid oxidation as much as possible. To investigate the oxidation resistance of MgH_2 -based hydrolysis materials with Nb_2O_5 and CeO_2 doping, the as-milled pure MgH_2 , $\text{MgH}_2+10\%\text{CeO}_2$, $\text{MgH}_2+10\%\text{Nb}_2\text{O}_5$ and $\text{MgH}_2+5\%\text{Nb}_2\text{O}_5+5\%\text{CeO}_2$ samples were also exposed to the ambient air for 24 h.

2.2 Characterization and measurement

The hydrolysis equipment employed in this work is shown schematically in Fig. 1. Water replacement method was adopted to measure the hydrolysis kinetics of as-milled samples in distilled water and 5.0% MgCl_2 solution (at%). The equipment consists of two parts, one for the hydrolysis reaction and the other for gas measurement. The flask was put into a water bath, where the temperature was constantly maintained at 20°C during overall hydrolysis reaction. For each sample, about 0.2 g of powder was transferred into the 150 mL flask. Then, 90 mL distilled water or 5% MgCl_2 solution was injected into the flask. The hydrogen yields and conversion rates of all samples were calculated according to the hydrolysis of 1 g sample.

The phase compositions of as-milled samples were measured by X-ray diffraction (XRD, Bruker D8 diffractometer). Scanning electron microscopy (SEM, ZEISS MERLIN Compact) equipped with an energy dispersive spectroscopy (EDS) was applied to characterize the microstructure of the as-milled and air exposed samples. The microstructure of as-milled samples was also observed by TEM (FEI Tecnai G2 F30).

Fig. 1 Schematic diagram for the hydrogen production from hydrolysis of as-milled samples in distilled water or MgCl_2 solution.

Fig. 2 XRD patterns of as-received MgH_2 , ball milled MgH_2 , $\text{MgH}_2+10\%\text{Nb}_2\text{O}_5$, $\text{MgH}_2+10\%\text{CeO}_2$ and $\text{MgH}_2+5\%\text{Nb}_2\text{O}_5+5\%\text{CeO}_2$.

3. Results and Discussions

3.1 Phase compositions and microstructure characteristics of as-milled samples

XRD patterns of as-received pure MgH_2 and ball milled samples are presented in Fig. 2. For as-received MgH_2 , only Bragg peaks from $\beta\text{-MgH}_2$ are observed. After ball milling, Bragg peaks concentrated around 25.6° , 31.4° and 37.7° from $\gamma\text{-MgH}_2$ are also observed. For $\text{MgH}_2+10\%\text{Nb}_2\text{O}_5$ sample, Bragg peaks from $\gamma\text{-MgH}_2$, $\beta\text{-MgH}_2$ and Nb_2O_5 are observed. Any reaction between MgH_2 and Nb_2O_5 during ball milling is not observed by XRD. It is also the case for $\text{MgH}_2+10\%\text{CeO}_2$ sample. In addition, the XRD pattern of ball milled $\text{MgH}_2+5\%\text{Nb}_2\text{O}_5+5\%\text{CeO}_2$ sample consists of Bragg peaks from $\gamma\text{-MgH}_2$, $\beta\text{-MgH}_2$, Nb_2O_5 and CeO_2 . Nb_2O_5 and CeO_2 do not react with each other during ball milling process.

Figure 3(a) and (b) display the backscattered electron micrographs of as-received and ball milled pure MgH_2 , respectively. Curl MgH_2 becomes irregular and much finer after ball milling for 3 h. Figure 3(c)–(d) show the backscattered electron micrographs of ball milled $\text{MgH}_2+10\%\text{Nb}_2\text{O}_5$ sample. The size of ball milled particles is less than $10\ \mu\text{m}$ as shown in Fig. 3(c). Abundant Nb_2O_5 particles with particle size much less than $1\ \mu\text{m}$ are observed on the MgH_2 matrix surface. Similar phenomenon is also observed in ball milled $\text{MgH}_2+10\%\text{CeO}_2$ and $\text{MgH}_2+5\%\text{Nb}_2\text{O}_5+5\%\text{CeO}_2$ samples as displayed in Fig. 3(e)–(h), in which a large number of super fine CeO_2 or $\text{CeO}_2/\text{Nb}_2\text{O}_5$ particles distribute on the MgH_2 surface.

Figure 4(a)–(d) present the typical TEM images of ball milled pure MgH_2 , $\text{MgH}_2+10\%\text{Nb}_2\text{O}_5$, $\text{MgH}_2+10\%\text{CeO}_2$ and $\text{MgH}_2+5\%\text{Nb}_2\text{O}_5+5\%\text{CeO}_2$ samples, respectively. For $\text{MgH}_2+10\%\text{Nb}_2\text{O}_5$ and $\text{MgH}_2+10\%\text{CeO}_2$ samples as illustrated in Fig. 4(b) and (c), irregular secondary phase particles with particle size in the range of tens of nm to $\sim 200\ \text{nm}$ uniformly distribute in MgH_2 matrix. With respect to $\text{MgH}_2+5\%\text{Nb}_2\text{O}_5+5\%\text{CeO}_2$ sample, plenty of secondary phase particles embedded in MgH_2 matrix are also clearly observed. However, the size of secondary phase particles obviously changes. There are many much finer secondary particles with particle size of $\sim 20\ \text{nm}$ embedding in the matrix

Fig. 3 (a) and (b) are backscattered electron micrographs of as-received and as-milled pure MgH_2 , respectively. (c)–(d), (e)–(f) and (g)–(h) are backscattered electron micrographs of ball milled $\text{MgH}_2+10\%\text{Nb}_2\text{O}_5$, $\text{MgH}_2+10\%\text{CeO}_2$ and $\text{MgH}_2+5\%\text{Nb}_2\text{O}_5+5\%\text{CeO}_2$, respectively.

together with some secondary phase particles with particle size in the range of $\sim 100\text{--}200\text{ nm}$. It is speculated that the frequent rubbing between Nb_2O_5 and CeO_2 during high energy ball milling process boosts their own fragmentation and refinement.

3.2 Hydrogen generation performance of as-milled samples

Based on the reaction between MgH_2 and water, the theoretical hydrogen yield of pure MgH_2 is calculated to be $\sim 1820\text{ mL g}^{-1}$ under the conditions of room temperature and atmospheric pressure.¹⁸⁾ Therefore, the theoretical hydrogen

yields of as-milled $\text{MgH}_2+10\%\text{Nb}_2\text{O}_5$, $\text{MgH}_2+10\%\text{CeO}_2$ and $\text{MgH}_2+5\%\text{Nb}_2\text{O}_5+5\%\text{CeO}_2$ samples are all calculated to be $\sim 1638\text{ mL g}^{-1}$. Figure 5(a) and (b) illustrate the kinetics curves of hydrogen generation via hydrolysis of as-milled samples in distilled water and 5% MgCl_2 solution, respectively. Figure 5(c) shows the corresponding conversion rates. The hydrolysis reaction kinetics and hydrogen yield of ball milled samples are highly dependent on the additives and solution.

As-received MgH_2 generates a small amount of hydrogen in both distilled water and 5% MgCl_2 solution. Its hydrogen yields in distilled water and MgCl_2 solution are ~ 86 and

Fig. 4 TEM images of (a) as-milled pure MgH_2 , (b) $\text{MgH}_2+10\%\text{Nb}_2\text{O}_5$, (c) $\text{MgH}_2+10\%\text{CeO}_2$ and (d) $\text{MgH}_2+5\%\text{Nb}_2\text{O}_5+5\%\text{CeO}_2$.

$\sim 160 \text{ mL g}^{-1}$, respectively. It is worth mentioning that, however, the hydrolysis reaction rate of MgH_2 is very fast within initial 1 min, showing its nature of rapid reaction

with water. The hydrolysis reaction is immediately interrupted once a dense Mg hydroxide passivation layer is formed.

For pure MgH_2 high-energy ball milled for 3 h, the hydrogen yield in distilled water significantly increases as shown in Fig. 5(a). It produces $\sim 397 \text{ mL g}^{-1}$ of hydrogen in 10 min, corresponding to a conversion rate of $\sim 21.8\%$. The ultimate hydrogen yield in distilled water is $\sim 445 \text{ mL g}^{-1}$. Similarly, one can observe a fast reaction rate only at the beginning of hydrolysis (within initial 2 min). As a fracture and welding process, ball milling technique can obviously decrease the particle size and increase the specific surface. Correspondingly, the hydrogen yield improves. Nevertheless, continuous Mg hydroxide layer still rapidly hinders the hydrolysis reaction, leading to an immediate interruption of hydrolysis. Moreover, ball milled $\text{MgH}_2+10\%\text{CeO}_2$ sample shows extremely similar hydrolysis kinetics as displayed in Fig. 5(a).

The hydrolysis reaction of Mg hydride at a constant temperature is mainly affected by several critical factors such as surface characteristics, matrix activity and water solution transport. The surface characteristics influences the initial hydrogen generation rate. In other words, it determines the response speed of the hydride after contact with water or water solution. The matrix activity depends on the phase constituent of the materials, which determines the type of hydrolysis reaction. Due to the insulator behavior of Mg hydride with a band gap of 5 eV ,²⁵⁾ the additives are unlikely

Fig. 5 Kinetic curves of hydrogen production from hydrolysis of as-received MgH_2 and as-milled samples in (a) distilled water and (b) 5% MgCl_2 solution at 20°C . (c) is the corresponding conversion ratios in (a) and (b).

to form galvanic cells with MgH_2 matrix. The water solution transport involves two processes: the initial water solution penetrates the surface layer into the interior of the matrix and the water solution penetrates into the magnesium hydroxide layer at the late stage of hydrolysis.

The hydrolysis reaction rate of as-milled samples is very fast within initial 1~2 min as shown in Fig. 5. Accordingly, Mg hydroxide quickly forms. The hydrolysis reaction is immediately interrupted once a dense Mg hydroxide passivation layer is formed. It is particularly important for further hydrolysis of MgH_2 to accelerate the hydroxide layer exfoliation process. After high-energy ball milling, CeO_2 mainly distributes on the surface of particles. Although surface distributed CeO_2 can block the fast formation of continuous Mg hydroxide to some extent, the exfoliation effect is not significant. It is still difficult for the water or water solution to penetrate into the magnesium hydroxide layer at the late stage of hydrolysis. In addition, as-milled $\text{MgH}_2+10\%\text{CeO}_2$ sample shows a slightly higher hydrogen yield than that of as-milled pure MgH_2 as shown in Fig. 5(a). The addition of CeO_2 can act as anti-sticking agent during the ball milling process, preventing the cold welding process of the mixture to produce more defects and fresh surfaces, which can improve the surface activity and hydrolysis kinetics to some extent.

Nb_2O_5 shows better facilitating effects than CeO_2 on the hydrolysis performance of MgH_2 . $\text{MgH}_2+10\%\text{Nb}_2\text{O}_5$ sample generates a highest hydrogen yield of $\sim 705 \text{ mL g}^{-1}$ in distilled water within 60 min, which corresponds to a conversion rate of $\sim 43.1\%$. The hydrogen yield of $\text{MgH}_2+5\%\text{Nb}_2\text{O}_5+5\%\text{CeO}_2$ sample is $\sim 620 \text{ mL g}^{-1}$, which is also higher than that of $\text{MgH}_2+10\%\text{CeO}_2$ sample. After ball milling, Nb_2O_5 and CeO_2 distributed on the surface can interrupt the fast formation of Mg hydroxide. In addition, during high-energy ball milling process, Nb_2O_5 tends to be more and more embedded into MgH_2 .²⁶⁾ The interior Nb_2O_5 can effectively prevent forming a consecutive and dense Mg hydroxide on the MgH_2 surface, contributing to a deeper degree of hydrolysis and a higher conversion rate.

Introducing MgCl_2 in distilled water can enhance the reaction kinetics and hydrogen yield significantly as shown in Fig. 5(b). The hydrogen yield of ball milled pure MgH_2 sample in MgCl_2 solution after hydrolysis of 10 min is increased to $\sim 785 \text{ mL g}^{-1}$, corresponding to a conversion rate of $\sim 43.1\%$. It is also the case for $\text{MgH}_2+10\%\text{CeO}_2$, $\text{MgH}_2+10\%\text{Nb}_2\text{O}_5$ and $\text{MgH}_2+5\%\text{Nb}_2\text{O}_5+5\%\text{CeO}_2$ samples. One can also immediately conclude that the hydrolysis performance improves with the increasing of Nb_2O_5 content. The conversion rates of $\text{MgH}_2+5\%\text{Nb}_2\text{O}_5+5\%\text{CeO}_2$ and $\text{MgH}_2+10\%\text{Nb}_2\text{O}_5$ samples even reach 60.0% and 74.6%, respectively. In addition, $\text{MgH}_2+10\%\text{Nb}_2\text{O}_5$ sample shows a more continuous hydrolysis process and a higher hydrogen yield in MgCl_2 solution than ball milled pure MgH_2 as shown in Fig. 5(b).

Both Cl^- and Mg^{2+} in MgCl_2 solution account for the modified hydrolysis performance.²¹⁾ The chloride ions in solution are able to replace hydroxide ions to react with the Mg^{2+} on the sample surface (formed during hydrolysis) to form soluble MgCl_2 . Meanwhile, the Mg^{2+} in solution can react with hydroxide ions to form Mg(OH)_2 , preventing

forming a consecutive and dense Mg(OH)_2 passivation layer on the surface.

3.3 Hydrolysis performance of air exposed samples

Oxidation is another critical obstacle for the large-scale application of Mg-based hydrogen generation materials,²⁷⁾ which leads to severe deterioration of hydrogen evolution kinetics and conversion rate. Aiming at evaluating the oxidation resistance of MgH_2 -based hydrolysis materials with Nb_2O_5 and CeO_2 doping, the as-milled pure MgH_2 , $\text{MgH}_2+10\%\text{CeO}_2$, $\text{MgH}_2+10\%\text{Nb}_2\text{O}_5$ and $\text{MgH}_2+5\%\text{Nb}_2\text{O}_5+5\%\text{CeO}_2$ samples were exposed to the ambient air for 24 h. Figure 6 shows the EDS mapping of air-exposed $\text{MgH}_2+5\%\text{Nb}_2\text{O}_5+5\%\text{CeO}_2$ sample, demonstrating the distributions of Mg, Nb, Ce and O elements. According to the distributions of O and Mg elements, one can immediately conclude that the sample surface has been completely oxidized after 24 h air exposure.

Figure 7 displays the kinetic curves of hydrogen evolution in 5% MgCl_2 solution for air exposed samples. Much inferior hydrolysis performance is observed for all air exposed samples compared with as-milled ones. Air exposed pure MgH_2 can produce only $\sim 87 \text{ mL g}^{-1}$ of hydrogen in MgCl_2 solution within 40 min, indicating an adverse effect of oxidation on hydrogen generation. The conversion rate is only $\sim 4.8\%$. However, it is much worse for air exposed MgH_2 samples with Nb_2O_5 addition. Both $\text{MgH}_2+10\%\text{Nb}_2\text{O}_5$ and $\text{MgH}_2+5\%\text{Nb}_2\text{O}_5+5\%\text{CeO}_2$ samples hardly generate any hydrogen in MgCl_2 solution during overall hydrolysis process. In contrast, MgH_2 with 10% CeO_2 addition demonstrates better hydrogen generation kinetics. After air exposure it can still produce hydrogen via hydrolysis at once. An ultimate hydrogen yield of $\sim 250 \text{ mL g}^{-1}$ is achieved, corresponding to a conversion rate of $\sim 15.3\%$.

The results show that Nb_2O_5 has an adverse effect on the oxidation resistance of MgH_2 hydrolysis reaction. Nb_2O_5 is spontaneously embedded into MgH_2 matrix during ball milling process, which has been confirmed by X-ray photoelectron spectroscopy analysis.²⁶⁾ Homogeneous Nb_2O_5 particles dotted on both the surface and subsurface of MgH_2 act as pathways assisting oxygen diffusion during air exposure. As a result, a thicker MgO layer is constructed, blocking the contact between MgH_2 and H_2O . As to CeO_2 , oxygen atoms can leave the CeO_2 lattice easily, forming a large variety of non-stoichiometric oxides.^{28,29)} In addition, CeO_2 can reduce and oxidize atoms which interact with its surface and thus oxygen vacancies can be formed and eliminated easily.³⁰⁾ Due to the redox characteristics of CeO_2 , it can prevent the formation of a continuous MgO layer on the MgH_2 surface during air exposure. The surface activity after air exposure is modified to some extent with CeO_2 addition. Accordingly, oxidized $\text{MgH}_2+10\%\text{CeO}_2$ sample can still react with water to generate hydrogen.

4. Conclusions

Mg hydrides with Nb_2O_5 and/or CeO_2 doping have been prepared by high energy ball milling in this work to improve the hydrolysis performance of MgH_2 . Any reaction among

Fig. 6 EDS mapping of air-exposed $\text{MgH}_2+5\%\text{Nb}_2\text{O}_5+5\%\text{CeO}_2$ sample, displaying the distribution of Mg, Nb, Ce and O elements.

Fig. 7 Hydrogen evolution curves from hydrolysis of air exposed samples in 5% MgCl_2 solution at 20°C.

MgH_2 , Nb_2O_5 and CeO_2 is not observed during ball milling process. It is found that ball milling can promote the hydrolysis performance of MgH_2 . Nb_2O_5 shows better

facilitating effects than CeO_2 on the hydrolysis performance of MgH_2 by promoting the hydroxide layer exfoliation. In addition, MgCl_2 also significantly promotes the hydrolysis reaction of MgH_2 . MgH_2 with Nb_2O_5 doping shows much inferior hydrogen evolution kinetics after air exposure. However, CeO_2 can modify the oxidation resistance to some extent. MgH_2 with 10% CeO_2 addition can still generate $\sim 250 \text{ mL g}^{-1}$ of hydrogen in 5% MgCl_2 solution after 24 h air exposure.

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