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Letter

Magnesium-based nanocomposites chemical hydrides

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Abstract

The hydrolysis reaction of nanostructured MgH_2 and nanocomposites MgH_2-X (X=Ca, Li, LiAlH₄) prepared by ball-milling was studied as a function of milling time and component proportion. It was found that nanocrystallinity greatly enhances the hydrolysis kinetics. Moreover, in this new class of chemical hydrides, the reaction also proceeds to full completion, contrary to some conventional chemical hydrides where the reaction stops before total completion due to the formation of passivation layers. The effect of addition of acidic solutions was also investigated.

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1. Introduction

An attractive source of hydrogen for hand-portable Proton Exchange Membrane (PEM) fuel cells is the aqueous hydrolysis of chemical hydrides. However, one major problem associated with this method of hydrogen production is the control of the hydrolysis reaction. The reaction is either too fast or even explosive for some chemical hydrides such as $LiAlH_4$ or it is too slow for practical applications in some other cases. The non-reversibility of the reaction can make this technology quite expensive and therefore, efforts should be made on reducing the overall cost of 'chemical hydride-storage tank' systems. For example, it has been known for a long time that hydrolysis of sodium borohydride (NaBH₄) could be used for generating hydrogen [1]. Recent developments of base-stabilised aqueous solutions of NaBH₄ catalyzed by ruthenium have shown some promise but problems with material cost, shelf life and recycling of products are not totally solved [2].

In a recent series of publications, Matthews et al. have investigated the production of hydrogen from complex hydrides [3,4] and from hydrolysis with steam [5]. They found that steam hydrolysis produces only hydrogen and meet the purity requirement for fuel cells applications. However, the price and availability of this type of chemical hydrides could be problematic for future applications. Therefore, there is a need for an inexpensive chemical hydride with good hydrogen release properties, low-cost and environmentally friendly.

Magnesium hydride could be considered as a candidate for the hydrolysis reaction because it can be produced at a relatively low cost. However, the hydrolysis reaction of conventional Mg hydride is incomplete and very slow because of the formation of a magnesium hydroxide layer. The hydrolysis of magnesium hydride is expressed by the following reaction.

$$MgH_2 + 2H_2O \Rightarrow Mg(OH)_2 + 2H_2$$
(1)

The hydrogen yield of this reaction is 6.5 wt.% when the weight of water is taken into account. In fuel cell applications, if the water produced by the fuel cell is redirected to the chemical hydride, then the yield increases to 15.4 wt.%. The yield of this reaction compares well with the hydrolysis of sodium borohydride which produces 7.3 wt.% if the weight of water is calculated and 21.2 wt.% if the water weight is not taken into account. Moreover, the reacted product (magnesium hydroxide) is environmentally benign.

In this paper, we present an investigation of the hy-

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drolysis of nanocomposite magnesium hydrides. In this new class of chemical hydrides, reaction kinetics are improved and often proceed to full completion, contrary to conventional chemical hydrides where reactions usually stop before total completion due to the formation of passivation layers. Tests on additions of acidic solutions were also performed.

2. Experimental details

The nanocomposites were synthesized by first mixing the raw materials inside an argon filled glove box. The mixtures were then milled for up to 20 h in a Spex 8000 model shaker mill using a vial and balls of stainless steel with a ball to powder weight ratio of 10:1. Magnesium hydride from Th. Goldschmidt (95 wt.% MgH₂, 5 wt.% Mg), lithium (Alfa, 99%), calcium (Alfa, 98.8%), and LiAlH₄ powder (Aldrich, 95%) were used.

The hydrolysis reactions were carried out in an Erlenmeyer flask provided with two openings, one for water addition and the other for hydrogen exhaust. Between 80 and 100 mg of nanocomposite was loaded into the flask and allowed to react with 10 ml of deionized water. Hydrogen release was quantified by water displacement in an inverted graduated cylinder positioned over a waterfilled tank. Measurements with acidic solutions were performed by first injecting 10 ml of deionized water and afterward, by periodic additions of 5 ml of a diluted HCl solution. The diluted HCl was prepared by mixing 1 part HCl in 100 parts of deionized water. In all measurements, the reaction mixture was continuously agitated with a magnetic stirrer.

3. Results and discussion

Fig. 1 shows the hydrogen release during hydrolysis of polycrystalline and nanocrystalline magnesium hydride. For ease of comparison, the reacted fraction as a function of time is plotted where the reacted fraction F is defined as the ratio of the volume of hydrogen released over the theoretical volume of hydrogen that could be released assuming that all material is hydrolyzed. Hydrogen discharge of polycrystalline MgH₂ is seen to be linear and quite slow. After 20 h, only 54% of the theoretical hydrogen capacity has been released. This is in striking contrast with the 20 h ball-milled magnesium hydride that has released 74% of its theoretical hydrogen capacity after 20 h of hydrolysis. Moreover, the hydrogen release of the nanocrystalline sample is much faster at the onset of the reaction. As reported previously [6], high energy milling of magnesium hydride for a period of 20 h produces a nanocrystalline structure with crystallite size of 11.9±0.1 nm and with a specific surface area of 9.9 m² g⁻¹ compared to 1.2 m² g⁻¹ for the unmilled magnesium



Fig. 1. Hydrogen release in hydrolysis of polycrystalline MgH_2 and MgH_2 milled for 20 h. The reacted fraction (*F*) is the ratio of the volume of released hydrogen over the theoretical volume of hydrogen that should be released assuming that all material is hydrolyzed.

hydride. Therefore, the high rate of reaction during the first 10 h of hydrolysis could be explained by the high specific surface area and the nanostructure. Fig. 1 shows that after 10 h of reaction the hydrolysis rate for the nanostructured magnesium hydride is similar or lower to that of the polycrystalline case, indicating the formation of a passivation layer.

To achieve a faster and more complete reaction, we added a second element which can be leached away during the electrolysis, thus exposing fresh magnesium hydride surface that react readily with water. It is known that ionic metal hydrides react readily with water and produce soluble hydroxides. Therefore, a nanocomposite of magnesium hydride with an ionic metal hydride leads to synergetic effects between the two components and faster and more complete hydrolysis reactions. Selected ionic hydrides were tested and the results of the hydrolysis experiments are presented in Fig. 2. It can be seen that for the lithium addition, the initial reaction rate is faster than in the case of pure magnesium hydride. However, the reaction quickly slows down to a smaller rate than ballmilled magnesium hydride afterwards. In the case of the LiAlH₄ addition, the general behavior of the reaction is similar to that of milled MgH₂. The most interesting case is the nanocomposite MgH2-Ca 5 at.% where the initial reaction is fast and gives a higher yield than the other reactions. After the initial period, the system decomposes at a rate similar to that of the nanocrystalline MgH₂. The results shown in Fig. 2 indicate that MgH₂-Ca is the best nanocomposite tested in the present study.

The MgH₂–Ca system was further investigated to see the effect of milling time and calcium proportion on the hydrolysis reaction. The results are presented in Fig. 3. The addition of 5 at.% of calcium to magnesium hydride and milling for 1 h produced a powder that reacted very



Fig. 2. Hydrogen release in hydrolysis of MgH₂ milled for 20 h, MgH₂– Ca 5 at.% milled for 1 h, MgH₂–Li 5 at.% milled for 1 h, and MgH₂–LiAlH₄ 5 at.% milled for 10 h. For definition of *F*, see Fig. 1.

quickly upon addition of water. On the other hand, after less than 1 h, the reaction rate was almost identical to that of pure milled magnesium hydride. This is in striking contrast to the MgH₂-Ca 5 at.% composite milled for 10 h. In this case, the hydrolysis reaction could be divided in three distinct regimes. First, a fast initial reaction which is almost instantaneous and is of the same magnitude (reacted fraction = 0.1) as that of the 20 h milled MgH_2 . This proportion is smaller than in the system MgH₂-Ca 5 at.% milled for 1 h. Afterward, the 10 h milled system enters into a second regime that last up to 4 h and where the reaction is much faster than that of the powder milled for 1 h. After 4 h of hydrolysis, the reaction rate is similar to those of the milled MgH₂ and the 1 h milled MgH₂-Ca 5 at.%. At this moment, we do not have a definitive explanation for the observed improvement of hydrolysis with milling time. Possible explanations are: structural effects due to a better distribution of calcium in the magnesium hydride matrix; creation of calcium hydride;



Fig. 3. Hydrogen release in hydrolysis of MgH₂ milled for 20 h, MgH₂– Ca 5 at.% milled for 1 h, MgH₂–Ca 5 at.% milled for 10 h, and MgH₂–Ca 20 at.% milled for 10 h. For definition of *F*, see Fig. 1.



Fig. 4. Hydrogen release in reaction of polycrystalline and nanocrystalline MgH_2 under the injection of 5 ml of diluted HCl solution. The gray bars indicate the reacted fraction if all HCl contained in the 5 ml injection reacts to produce hydrogen.

creation of complex hydride. Further experiments are needed in order to understand fully the hydrolysis reaction in this kind of nanocomposite. Fig. 3 also shows the effect of the calcium proportion. As expected, a higher proportion of calcium resulted in a faster hydrolysis reaction and completion is reached after 4 h.

In acid solution, the following reaction takes place.

$$MgH_2 + 2HCl \Rightarrow MgCl_2 + 2H_2$$
(2)

One of the advantages of this reaction over pure hydrolysis is that the end product is soluble thus making the recovery and treatment of the end product much simpler. The reaction of nanocrystalline and polycrystalline magnesium hydride to acidic solutions was tested and the results are presented in Fig. 4. In the case of the polycrystalline material, it is clear that only reaction (2) is taking place upon each addition of HCl solution. Moreover, the reaction is complete and very fast. Between HCl additions, no significant hydrolysis reaction (reaction (1)) is taking place. This is in striking difference with the nanocrystalline case where for the first 15 min both reactions (1) and (2) are taking place. Close inspection of the curves with and without acidic injection shows that there is no synergetic effect and that both reactions happen independently.

4. Conclusion

The hydrolysis reaction of MgH_2 and MgH_2 –Ca nanocomposites was studied. It was found that nanocrystalline magnesium hydride shows enhanced hydrolysis reaction compared to the conventional material. Further improvement of reaction kinetics was achieved by the nanocomposite MgH_2 –Ca 5 at.%. Investigations showed that the milling of the nanocomposite should be performed for a relatively long time in order to get a fine nanostructure which results in a fast and complete hydrolysis. Increasing the calcium content to 20 at.% results in faster kinetics and a complete hydrolysis reaction was achieved in only 4 h.

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