ChemComm

Cite this: Chem. Commun., 2012, 48, 5509-5511

www.rsc.org/chemcomm

COMMUNICATION

Efficient catalysis by MgCl₂ in hydrogen generation *via* hydrolysis of Mg-based hydride prepared by hydriding combustion synthesis[†]

Zelun Zhao, ‡ Yunfeng Zhu and Liquan Li*

Received 1st April 2012, Accepted 14th April 2012 DOI: 10.1039/c2cc32353b

Magnesium chloride efficiently catalyzed the hydrolysis of Mg-based hydride prepared by hydriding combustion synthesis. Hydrogen yield of 1635 mL g^{-1} was obtained (MgH₂), *i.e.* with 96% conversion in 30 min at 303 K.

To resolve the worldwide environmental and energy crisis, hydrogen energy is considered as an ideal clean energy vector with zero CO₂ emission to replace traditional fossil energy, especially for on-board fuel cell applications.¹ However, the production and storage technology of hydrogen is a remaining barrier in the development of hydrogen energy economy.² Magnesium hydride is one promising hydrogen storage material due to its high hydrogen storage capacity (7.6 wt%), cheap price, abundant resource and low environmental impact.³ The major challenge in application of MgH₂ as hydrogen storage material is the poor thermodynamics in hydriding and dehydriding reactions with the reaction temperatures usually as high as 573 K.⁴ Recently, hydrogen production *via* hydrolysis of MgH₂ has attracted more and more attention because of the theoretical hydrogen yield, which is as high as 1703 mL g^{-1.5}

MgH₂ shows thermodynamic instability during hydrolysis reaction,⁶ while the poor kinetics does not meet practical requirements, which is caused by the passive Mg(OH)₂ layer produced on the surface of MgH₂. The reaction kinetics could be enhanced by reducing the pH value of the solution by adding acids⁷ or acidic salts such as ammonium salts.8 But these additions corrode the reactor and refuelling is needed during application. Mg-based hydride composites such as Mg-La-H,9 Mg-Ca-H10 were also used to generate hydrogen via hydrolysis with improved kinetics, e.g., 88.3% conversion in 21 min for Mg-La-H, 80% conversion in 30 min for Mg-Ca-H. Although these composites can improve the kinetics, it is still not satisfactory because of the lower theoretical hydrogen yield of these additives (474 mL g^{-1} for LaH₃, 1065 mL g^{-1} for CaH₂). Additionally, some impurities in the by-product, such as La(OH)₃ and Ca(OH)₂, are not easy to separate in the recycling process.

In the present work, the Mg-based hydride (Mg and Ni in a molar ratio of 99:1) prepared by hydriding combustion synthesis (HCS)¹¹ was chosen to generate hydrogen via hydrolysis. Mechanical milling (MM) of Mg-based hydride was performed to improve its hydrolysis property.¹² As indicated in Fig. 1 (dashed line), when the Mg-based hydride was immersed in pure water, it released 192 mL g^{-1} of hydrogen with a high generation rate within initial 3 minutes. However, after that, the rate was slowed down quickly. The low rate is mainly attributed to the passive Mg(OH)₂ layer formed on the surface of MgH₂. The solid line in Fig. 1 shows the kinetic curve of hydrogen generation via hydrolysis of the Mg-based hydride in $0.5 \text{ mol } L^{-1} \text{ MgCl}_2$ solution. The yield of hydrogen reached 927 mL g⁻¹ within initial 3 min, which is about five times larger than that in pure water. Our results revealed that introduction of MgCl₂ in solution could break the passive layer of Mg(OH)₂. The reason can be explained by a suitable pH value of MgCl₂ solution (pH = 8.91) when $[Mg^{2+}]$ was 0.5 mol L^{-1} , which is lower than that of saturated Mg(OH)₂ solution (pH = 10.44). After that, a high rate of hydrogen generation kept for another 10 min, and then the hydrolysis almost completed after nearly 30 min. The result indicated that the hydrogen yield reached 1635 mL g^{-1} and the hydrolysis conversion of 96% was obtained.

Fig. 2 shows the cyclic curve of hydrogen generation *via* hydrolysis of Mg-based hydride with the MgCl₂ catalyst. After each hydrolysis reaction cycle, the reaction solution with



Fig. 1 Kinetic curves of hydrogen generation *via* hydrolysis of Mg-based hydride prepared by HCS + MM: solid line, in 0.5 mol L^{-1} MgCl₂; dashed line, in pure water at 303 K.

College of Materials Science and Engineering, Nanjing University of Technology, 5 Xinmofan Road, Nanjing, Jiangsu, P.R. China. E-mail: lilq@njut.edu.cn; Tel: +86-25-83587255

[‡] Electronic supplementary information (ESI) available: Experimental details, characterization of samples, Scheme S1, Fig. S1–S3. See DOI: 10.1039/c2cc32353b
‡ Graduate student.



Fig. 2 Cyclic curve of hydrogen generation *via* hydrolysis of Mg-based hydride with the MgCl₂ catalyst (the hydrogen yield data collected within 30 min in each cycle).

the catalyst was separated from the deposited solid by-product. Then the collected solution was reused for the next reaction cycle without adding MgCl₂. After nine cycles, the yield of hydrogen generation reached 1600 mL g⁻¹ (94% conversion) in 30 min. As compared to the first cycle, the decrease in hydrogen yield was about 35 mL g⁻¹ (2% decrease in conversion). The result indicates that MgCl₂ in solution has a good catalytic effect in the hydrolysis of Mg-based hydride and could be recycled with little degradation.

 $MgCl_2$ is a standard solution found in any corrosion laboratory and is used to determine the susceptibility against stress corrosion cracking (standard ASTM method), because it attacks the grain boundary of the oxide or the passive layer of the metal under investigation. Thus $MgCl_2$ attacks the grain boundary of $Mg(OH)_2$ formed at the surface and disintegrates the formed layer.¹³ Fig. 3 shows the hydrogen yields *via* hydrolysis of Mg-based hydride prepared by HCS in 1.0 mol L⁻¹ NaCl and 0.5 mol L⁻¹ MgCl₂ solutions with the same molarities of Cl⁻. The large hydrogen yield difference indicates that the magnesium ion has an important role in our hydrolysis system.

Fig. S1 (ESI[†]) shows the pH value changes during the hydrolysis reactions given in Fig. 3. At the beginning, the pH value increased rapidly either in 0.5 mol L^{-1} MgCl₂ solution or in 1.0 mol L^{-1} NaCl solution. After several minutes, compared with the near constant of 10.44 in NaCl solution,



Fig. 3 Hydrogen yields in the hydrolysis of Mg-based hydride prepared by HCS in $MgCl_2$ solution and in NaCl solution with the same molarities of Cl^- at 303 K.

the pH value in $MgCl_2$ solution decreased to 8.95 at about 30 min, which was in accordance with that of $MgCl_2$ solution before reaction. After that, the pH value kept near 8.95, which agreed with the hydrogen yield curve after 30 min as shown in Fig. 3.

The pH value was decreased according to eqn (1) when $MgCl_2$ was added into the solution, which promotes the dissolution of $Mg(OH)_{2su}$ and $Mg(OH)_{2aq}$ ($Mg(OH)_{2su}$ and $Mg(OH)_{2aq}$ denote $Mg(OH)_2$ formed on the surface of MgH_2 and that formed in the solution, respectively). The dissolution of $Mg(OH)_{2su}$ results in the formation of the fresh surface of MgH_2 exposed to the solution, which then reacts with water and HCl according to eqn (2). Thus two moles of hydrogen are produced for every mole of MgH_2 reacted. Now once the passive film of $Mg(OH)_{2su}$ formed and slowed down the hydrogen release, HCl will destroy the formed passive layer according to eqn (3). At the same time, the Mg^{2+} from $Mg(OH)_{2su}$ and MgH_2 complements the Mg^{2+} consumed in the formation of $Mg(OH)_{2su}$ to keep the low pH value of the solution.

 $MgCl_2 + 2H_2O \rightarrow Mg(OH)_{2aq}\downarrow + 2HCl$ (1)

$$MgH_2 + 2HCl \rightarrow MgCl_2 + 2H_2\uparrow$$
 (2)

$$Mg(OH)_{2su}\downarrow + 2HCl \rightarrow MgCl_2 + 2H_2O$$
 (3)

This research was supported by National Natural Science Foundation of China (Grant No. 51171079 and 51071085), Specialized Research Fund for the Doctoral Program of High Education (Grant No. 20093221110008) and the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

Notes and references

- (a) L. Schlapbach and A. Züttel, *Nature*, 2001, **414**, 353–354;
 (b) G. Marbán and T. Valdés-Solís, *Int. J. Hydrogen Energy*, 2007, **32**, 1626.
- 2 (a) M. Felderhoff, C. Weidenthaler, R. V. Helmolt and U. Eberle, *Phys. Chem. Chem. Phys.*, 2007, 9, 2643–2653; (b) D. K. Ross, *Vacuum*, 2006, 80, 1084–1089.
- 3 (a) B. Sakintuna, F. Lamari-Darkrim and M. Hirscher, Int. J. Hydrogen Energy, 2007, 32, 1121–1140; (b) J. Yang, A. Sudik, C. Wolverton and D. J. Siegel, Chem. Soc. Rev., 2010, 39, 656–657; (c) K.-F. Aguey-Zinsou and J.-R. Ares-Fernández, Energy Environ. Sci., 2010, 3, 526–543.
- 4 (a) C. Y. Zhu, S. Hosokai and T. Akiyama, *Cryst. Growth Des.*, 2011, **11**, 4166–4174; (b) J. F. Stampfer, C. E. Holley and J. F. Suttle, *J. Am. Chem. Soc.*, 1960, **82**, 3504–3508; (c) C. Y. Zhu, S. Hosokai, I. Mastsumoto and T. Akiyama, *Cryst. Growth Des.*, 2010, **10**, 5123–5128.
- 5 (a) E. Y. Marrero-Alfonso, A. M. Beaird, T. A. Davis and M. A. Matthews, *Ind. Eng. Chem. Res.*, 2009, **48**, 3705–3706; (b) S. Hiroi, S. Hosokai and T. Akiyama, *Int. J. Hydrogen Energy*, 2011, **36**, 1442–1447.
- 6 G. G. Perrault, J. Electroanal. Chem. Interfacial Electrochem., 1974, 51, 107–119.
- 7 (a) Y. Kojima, K. I. Suzuki and Y. Kawai, J. Mater. Sci., 2004, 39, 2227–2229; (b) S. D. Kushch, N. S. Kuyunko, R. S. Nazarov and B. P. Tarasov, Int. J. Hydrogen Energy, 2011, 36, 1321–1325; (c) J. Huot, G. Liang and R. Schulz, J. Alloys Compd., 2003, 353, L12–L15.
- 8 V. D. Makhaev, L. A. Petrova and B. P. Tarasov, *Russ. J. Inorg. Chem.*, 2008, **53**, 858–860.
- 9 (a) L. Z. Ouyang, Y. J. Xu, H. W. Dong, L. X. Sun and M. Zhu, Int. J. Hydrogen Energy, 2009, 34, 9671–9676; (b) L. Z. Ouyang,

Y. J. Wen, Y. J. Xu, X. S. Yang, L. X. Sun and M. Zhu, Int. J. Hydrogen Energy, 2010, 35, 8161–8165.

- 10 J. P. Tessier, P. Palau and J. Huot, J. Alloys Compd., 2004, 376, 180-185.
- 11 (a) H. Gu, Y. F. Zhu and L. Q. Li, *Mater. Chem. Phys.*, 2008, **112**, 218–222; (b) X. F. Liu, Y. F. Zhu and L. Q. Li, *Intermetallics*, 2007, **15**, 1582–1588.
- 12 (a) M.-H. Grosjean, M. Zidoune, J.-Y. Huot and L. Roué, Int. J. Hydrogen Energy, 2006, **31**, 1159–1163; (b) R. V. Lukashev, N. A. Yakovleva, S. N. Klyamkin and B. P. Tarasov, Russ. J. Inorg. Chem., 2008, **53**, 389–396; (c) M. H. Grosjean and L. Roué, Int. J. Hydrogen Energy, 2006, **416**, 296–302.
- 13 M. G. Fontana, in *Corrosion Engineering*, ed. S. Rao, McGraw-Hill, New York, 3rd edn, 1986, pp. 53–54.