

Short communication

# A hybrid method for hydrogen storage and generation from water

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Received 28 April 2007; received in revised form 11 May 2007; accepted 11 May 2007

Available online 18 May 2007

## Abstract

This communication describes a new hybrid method for storing hydrogen in solid inorganic hydride materials as well as producing it from water based on the reaction between  $\text{LiOH}/\text{LiOH}\cdot\text{H}_2\text{O}$  and  $\text{LiH}$ . As a hydrogen storage method, the release and uptake of hydrogen in this method are accomplished via a series of simple reactions with good kinetics within a practically reasonable temperature range. The reversible hydrogen storage capacity of the material system is 6–8.8 wt.% at  $<350^\circ\text{C}$ . This capacity is one of the highest among all other metal hydrides known to date in the same temperature range. As a hydrogen production method, 100% of hydrogen generated by this method comes from water by its reaction with alkali metal oxides. This method is also an environmentally friendly alternative to the current commercial processes for hydrogen production. The preliminary thermodynamic calculation on energy required for complete regeneration shows that the current system is energetically favorable.

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*Keywords:* Hydrogen storage; Hydrogen production; Metal hydride; Regeneration; Energy balance

## 1. Introduction

Hydrogen is undoubtedly one of the key alternatives to replace petroleum products as a clean energy carrier for both transportation and stationary applications. Interest in hydrogen has grown dramatically since 1990, and many advances in hydrogen production and storage technologies have been made during the past decade [1]. However, there are still a number of critical scientific and technological problems to be overcome before any large-scale utilization of hydrogen could occur.

A major challenge for using hydrogen as a fuel today is to develop efficient and effective methods for hydrogen storage that can not only store hydrogen safely but also supply it where it is needed and when it is needed. One of the methods for hydrogen storage is based on chemical reactions of solid inorganic hydrides that release hydrogen [2–17]. This method can be classified into two groups: (1) simple or complex metal hydrides and reactions that may be reversible on-board a vehicle by which hydrogen generation and storage take place by a simple reversal of the chemical reaction as a result of modest changes in the temperature and pressure. Sodium alanate-based ( $\text{NaAlH}_4$ )

complex metal hydrides are an example [2,5–7]; (2) chemical storage by which the hydrogen generation reaction is not reversible under modest temperature/pressure changes. Hydrolysis of alkali and alkali-earth metal based borohydrides is the example of this group [14,17]. All these approaches, however, face formidable technical hurdles. For the former, the kinetics of either dehydrogenation or hydrogenation reactions are often too poor or the temperature of these reactions are too high to be feasible for practical applications [8–12]. In contrast, for the latter, the main technical difficulty is that most such hydrides react with water vigorously rendering the rate of hydrogen releasing reaction difficult to control [13–17]. Further, the reaction products of many promising chemical hydrides such as  $\text{NaBH}_4$ , are not recyclable; in other words, they become solid wastes.

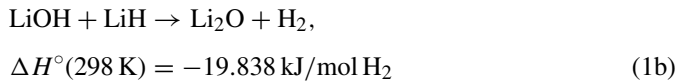
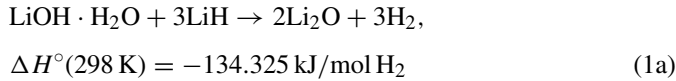
In the present communication, we describe a hybrid approach for hydrogen storage by which the release and uptake of hydrogen are reversible via a series of simple reactions based on the reaction between  $\text{LiOH}/\text{LiOH}\cdot\text{H}_2\text{O}$  and  $\text{LiH}$  with good kinetics within a practically reasonable temperature range ( $<350^\circ\text{C}$ ). In particular, the recharge of hydrogen is accomplished by reaction with water, rather than high pressure  $\text{H}_2$  gas. Although the reaction of  $\text{LiH}$  with water has been studied in a number of published research in the literature [18–21], the utility of these reactions for hydrogen storage, especially the reaction cycles that involves these reactions making it possible for reversible

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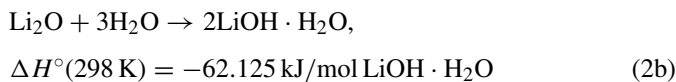
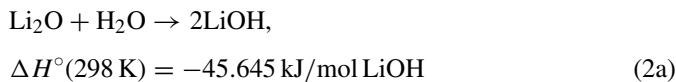
hydrogen storage and generation, have not been explored in the past.

## 2. Description of the method

Fig. 1 is a schematic illustration of the hybrid method. For hydrogen generation, lithium hydride and lithium hydroxide monohydrate ( $\text{LiOH}\cdot\text{H}_2\text{O}$ ) or lithium hydroxide ( $\text{LiOH}$ ) are reacted according to Eq. (1):



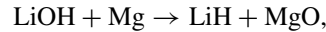
Reactions (1a) and (1b) produce, respectively, up to 8.8% and 6.3% of hydrogen between near room temperature to 350 °C. Owing to its reactivity and solubility in water, one of the reactants of (1), lithium hydroxide monohydrate ( $\text{LiOH}\cdot\text{H}_2\text{O}$ ) or lithium hydroxide ( $\text{LiOH}$ ), can be regenerated by reacting the product of (1),  $\text{Li}_2\text{O}$ , with water at room temperature based on Eq. (2):



It is noted here that aqueous solubility of  $\text{LiOH}$  is 12.8 g  $\text{L}^{-1}$  (9.6  $\text{LiOH}/\text{H}_2\text{O}$  molar ratio) at 20 °C, and it increases with increasing of the temperature [22].

One mole of  $\text{LiOH}\cdot\text{H}_2\text{O}$  or  $\text{LiOH}$  of the products of (2) can be reused for the hydrogen production by (1). The other one mole of  $\text{LiOH}$  can be used for reproduction of lithium hydride, which can be accomplished in several different approaches. One of these approaches is by the reaction of  $\text{LiOH}$  with magnesium metal as shown in Eq. (3). The reaction product,  $\text{LiH}$ , can then be used in the  $\text{H}_2$  production reaction (1). Of course, it is necessary to separate  $\text{LiH}$  from the products of reaction (3) before it can

be further used. Further discussion on the separation of  $\text{LiH}$  will be presented later in this communication.



$$\Delta H^\circ(298\text{ K}) = -204.642\text{ kJ/mol LiH} \quad (3)$$

Clearly, reactions 1a, 1b, 2a, 2b and 3 constitute a hydrogen generation and regeneration cycle. From a hydrogen storage perspective, it is an off-board reversible storage technique as oppose to storage techniques that recharge reversible reactions on-board using high pressure hydrogen gas. The most unique feature of this method is that the recharge of hydrogen is accomplished using water.

Fig. 1 and reactions 1a, 1b, 2a, 2b and 3 also demonstrate that hydrogen can be produced from water using several exothermic reactions provided there is a supply of magnesium metal (or using other methods) for regeneration of  $\text{LiH}$ . Therefore, this is also an alternative hydrogen production method.

It should be noted that Groups IA and IIA elements such as Na, Ca, Mg, K, and Ba would undergo reactions similar to (1) and (2). Therefore, they can also be used for hydrogen generation and storage. However, lithium is a better choice due to its light weight and high hydrogen content of its hydrogen containing compounds. Many other metal hydrides, such as  $\text{MgH}_2$ ,  $\text{AlH}_3$ ,  $\text{NiH}_2$ , and  $\text{TiH}_2$ , would undergo reactions similar to (1). However, the regeneration of their respective hydroxides using reactions similar to (2) is difficult because the reactions of their oxides with water are thermodynamically unfavorable. Therefore, lithium hydride and lithium oxide ( $\text{Li}_2\text{O}$ ) are uniquely suited for hydrogen generation and regeneration on the basis of (1) and (2).

Although this new approach for hydrogen storage has the potential, several scientific and technological challenges remain. First of all, understanding the reaction mechanisms and hence controlling the rate of dehydrogenation is crucial for applying this method in practical situations. Secondly, a key factor that will determine the future prospects of this technology is the energy efficiency of the entire cycle. It was estimated that for a hydrogen-storage technology to be practically viable the total energy required for the regeneration of the reactants must be no more than 1.6 times of the energy content of the hydrogen produced [23]. In this communication, experimental verifications of the dehydrogenation reactions, the process of the uptake of hydrogen, and basic concepts of the method for regeneration of lithium hydride are presented.

## 3. Experimental

The starting materials, lithium hydroxide ( $\text{LiOH}$ , 98%), lithium hydroxide monohydrate ( $\text{LiOH}\cdot\text{H}_2\text{O}$ , 98%), lithium hydride ( $\text{LiH}$ , 95%), magnesium powder ( $\text{Mg}$ , 98%) were purchased from Aldrich Chemical. All of the starting materials were used as received without any further purification. To prevent samples and raw materials from undergoing oxidation and/or hydroxide formation, they were stored and handled in an argon-filled glove box equipped with a recirculation system.

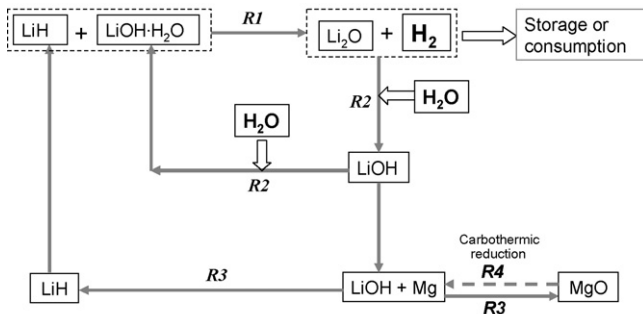


Fig. 1. A Schematic of the reaction cycles for hydrogen storage and generation from water.

The mixtures of LiOH/LiH in the present communication were mechanically milled in an SPEX 8000 high-energy mill under argon atmosphere for 30 min. After milling, the samples were transferred to a glove box. The thermal hydrogen release properties of the mixtures were determined by a thermogravimetry analyzer (TGA) (Shimadzu TA50) upon heating to 350 °C at a heating rate of 5 °C min<sup>-1</sup> and holding at this temperature for 40 min. To avoid any exposure of the sample to air, this equipment was set inside the argon-filled glove box equipped with a recirculation system.

The identification of reactants and reaction products in the mixture before and after thermogravimetric analysis was carried out using a Siemens D5000 model X-ray diffractometer with Ni-filtered Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). A scanning rate of 0.02° s<sup>-1</sup> was applied to record the patterns in the 2 $\theta$  range of 10–90°. In addition, it is noted that the amorphous-like background in the XRD patterns is attributed to the thin plastic films that were used to cover the powders.

A scanning electron microscope (SEM) with EDAX was used to characterize the particle size and chemical composition of the samples after different processing. SEM samples were prepared by attaching a small amount of the powders in a carbon-based conductive tape in the glove box.

## 4. Experimental verification

### 4.1. Dehydrogenation reactions

To demonstrate the basic concepts of the method described above, we used thermogravimetric analysis (TGA) and X-ray diffraction (XRD) methods to verify the reaction path and products. Fig. 2a shows the TGA curve of the H<sub>2</sub> release reaction (1a). It was carried out by mixing LiH and LiOH·H<sub>2</sub>O powder with a molar ratio of 3:1 under carefully controlled conditions to avoid reaction during mixing. The sample was then immediately analyzed using TGA under argon atmosphere with a heating rate of 5 °C min<sup>-1</sup>. It can be seen that a total of 8.5 wt.% of hydrogen was released within the examined temperature range. The maximum amount of H<sub>2</sub> that can be produced by (1a) would be 8.8 wt.%. Fig. 2a also shows that the dehydrogenation is accomplished in two steps. The first step between room temperature to 70 °C corresponds to reaction (4) and the second step between

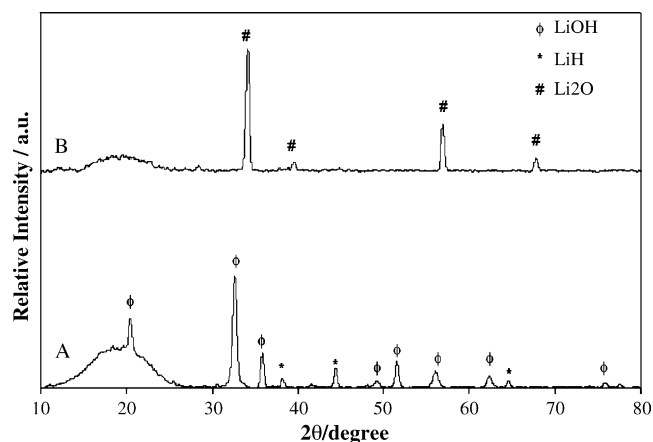


Fig. 3. X-ray diffraction patterns from the reaction of a LiOH·H<sub>2</sub>O + LiH mixture after partial and complete dehydrogenation. Curve A, after dehydrogenation at 50 °C; curve B, after dehydrogenation at 350 °C.

120 and 350 °C corresponds to reaction (1b).



$$\Delta H^\circ(298 \text{ K}) = -96.648 \text{ kJ/mol H}_2 \quad (4)$$

In order to determine the reaction paths of reaction (1a), i.e. the intermediate reactions, two approaches were taken. First, Reactions (1b) and (4) are proposed as the intermediate reactions because the molar balance of these reactions matches with the weight loss steps present in the TGA curve in Fig. 2a. To further confirm each reaction step, the products after partial and complete dehydrogenation at specific temperatures were analyzed using XRD. Fig. 3A shows the XRD pattern of the product after dehydrogenation at 60 °C for 10 min, in which the peaks that are marked with “φ” are indexed to LiOH, and those marked with asterisk are indexed to be LiH. This confirms that the first dehydrogenation step corresponds to Reaction (4). After complete dehydrogenation at 350 °C, the reaction products converted to Li<sub>2</sub>O (Fig. 3B), which corresponds to reaction (1b).

It is noted that reaction (4) is in essence the hydrolysis reaction of LiH. TGA data for this reaction showed that the weight loss is quite fast, and accompanied by a spike in the sample temperature (around 50 °C). This is consistent with the strongly exothermic nature of this reaction

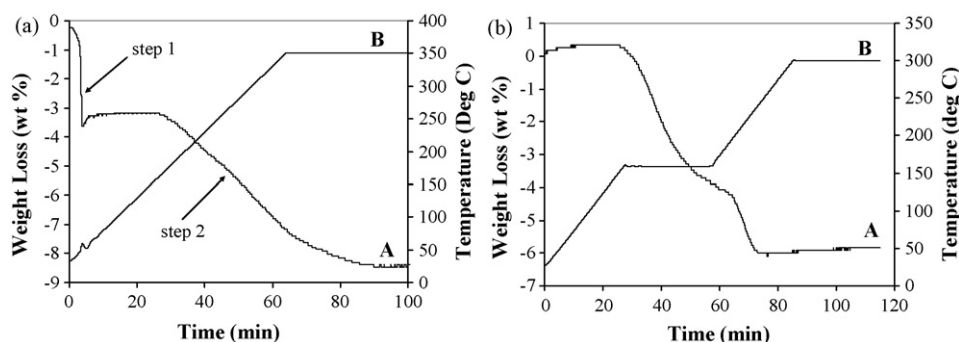


Fig. 2. (a) TGA curves for the reaction of LiOH·H<sub>2</sub>O + 3LiH mixture. (b) TGA curves for the reaction of LiOH + LiH mixture. In both figures, curve A shows the hydrogen generation by this reaction under atmospheric-pressure argon and a heating rate of 5 °C min<sup>-1</sup>. Curve B shows the temperature profile.

( $\Delta H^\circ$  (298 K) =  $-96.648 \text{ kJ mol}^{-1} \text{ H}_2$ ). In practice, extra heat exchanger with high heat extraction rate would be required to prevent thermal runaway in large mass application. However, because the water molecule in lithium hydroxide monohydrate is in crystalline form, the rate of (4) is much slower than that of the reaction between LiH and water directly. On the other hand, some catalysts may be used to control the rate of reaction (4), for example, Pt-LiCoO<sub>2</sub> was found to be an excellent catalyst for controlling the rate of hydrolysis of NaBH<sub>4</sub> [24].

The experiment also demonstrated that when LiOH instead of LiOH·H<sub>2</sub>O is used, 6.0 wt.% of hydrogen can be released under 300 °C (Fig. 2b), based on reaction (1b). X-ray diffraction analysis was carried out on the raw materials as well as on the products of this reaction. In Fig. 4, pattern A, which represents the XRD result for the sample before dehydrogenation (reaction (1b)), is attributed to the phases of the reactants LiOH and LiH. Pattern B shows the XRD result for the sample after dehydrogenation clearly indicating that LiOH and LiH are absent in the samples by being consumed by the reaction. In this pattern, all the peaks can be indexed to be that of Li<sub>2</sub>O, which indicate that the reaction (1b) is complete.

#### 4.2. Uptake of hydrogen and regeneration of the reactants

To demonstrate the uptake of hydrogen, Li<sub>2</sub>O from (1) is reacted with water according to Eq. (2). Patterns C and D of Fig. 4 show the XRD result of the product of (2). Clearly, LiOH or LiOH·H<sub>2</sub>O, which is one of the reactants of the hydrogen producing reaction (1), is reproduced by (2). In other words, the dehydrogenation product is partially re-hydrogenated.

The complete regeneration of the reactants for reaction (1), however, also needs the replenishment of LiH. Using the product of (1), lithium hydride can be produced in a number of

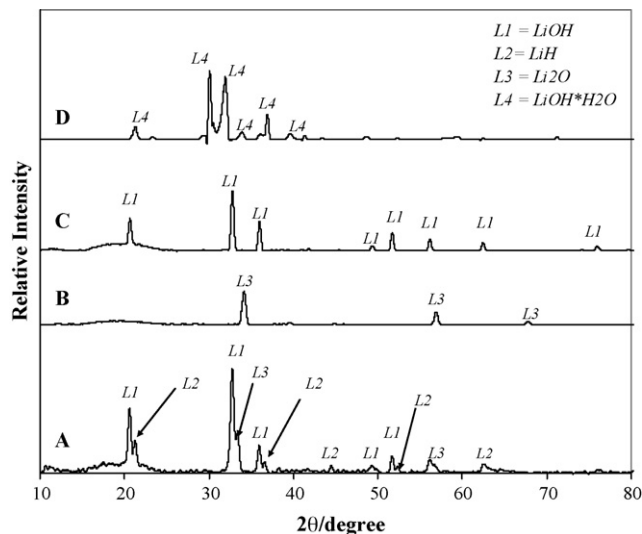


Fig. 4. X-ray diffraction patterns from the reaction of a LiOH + LiH mixture after milling, dehydrogenation, and rehydrogenation by reacting the dehydrogenated products with water. Curve A, after milling. Curve B, after dehydrogenation at 100–350 °C. Curve C, after reacting the dehydrogenated products with water and dried in vacuum at 80 °C overnight. Curve D, after reacting the dehydrogenated products with water and naturally dried in air at room temperature.

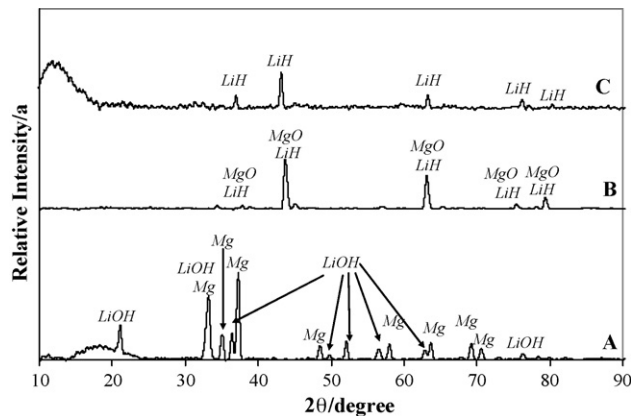


Fig. 5. X-ray diffraction patterns from the reaction of a LiOH + Mg mixture: (A) after milling, (B) after heat to 500 °C at argon atmosphere for 2 h, (C) after further heated up to 700 °C under Ar/H<sub>2</sub> (H<sub>2</sub> partial pressure is 2 psi) mixture gas, followed by the collection of the liquid.

different ways including the electrolysis of Li<sub>2</sub>O or LiCl and followed by the hydrogenation of lithium metal. A more preferable approach that does not require hydrogen from other sources is to use magnesium metal to react with LiOH based on reaction (3). The experimental confirmation of R(3) is shown in Fig. 5. The products of reaction (3) include LiH and MgO which must be separated. Depending on the difference between the melting temperature (680 °C) and decomposition temperature (>720 °C) [25] of LiH, the reaction products of reaction (3) may be separated when the temperature is controlled at appropriate level (680–720 °C). The equilibrium pressure of H<sub>2</sub> was about 0.5 psi at 700 °C for the decomposition of LiH to Li and H<sub>2</sub>, which implies that even a very small amount of H<sub>2</sub> could suppress the further decomposition of LiH. Thus, to separate LiH from MgO, the product of reaction (3) was heated up to 700 °C under Ar/H<sub>2</sub> (H<sub>2</sub> partial pressure is 2 psi) mixture gas, followed by the collection of the liquid. Because the XRD patterns for LiH and MgO are almost overlapped each other, EDAX was applied to distinguish these two powders. Fig. 6 shows the EDAX characterization for the products of reaction (3) before and after separation. It clearly indicates that, LiH can be separated from MgO by heating the mixture to 700 °C under Ar/H<sub>2</sub> mixture gas. After separation, LiH will then be used in reaction (1) to produce H<sub>2</sub>, while MgO will be subjected to a reduction process that produces Mg metal from MgO.

## 5. Discussion

With regard to the reversibility of the hydrogen uptake and release reactions, the above information clearly shows that the method introduced in this communication is different from that of the conventional method of using reversible solid hydride materials. For conventional reversible hydrogen storage materials, a given reaction is reversible for either the release or uptake of hydrogen under controlled conditions. Reaction (1) for releasing hydrogen according to the hybrid method described in this communication, however, is not reversible under normal conditions [17]. Instead, the recharge of hydrogen according to this



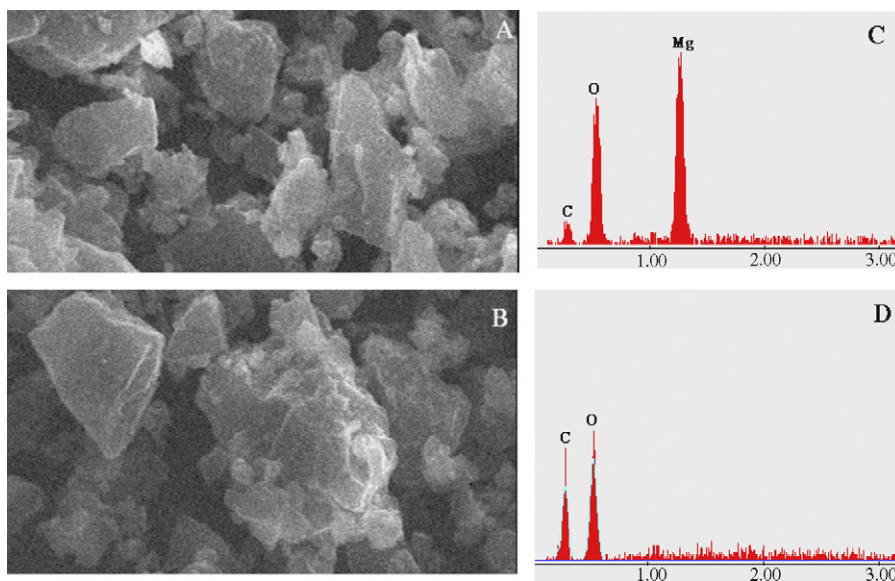


Fig. 6. SEM images and EDAX characterization for LiH/MgO mixture before and after separation. The separation was done by heating the mixture up to 700 °C under Ar/H<sub>2</sub> (H<sub>2</sub> partial pressure is 2 psi) mixture gas, followed by the collection of the liquid. (A) SEM image for LiH/MgO mixture before separation; (B) SEM image for LiH/MgO mixture after separation; (C) EDAX characterization on this image, which showed Mg signal; (D) EDAX characterization on this image, which showed that Mg signal disappeared. Combined Fig. 5 and this figure, it is clearly shown that LiH can be separated from MgO by controlling the temperature and flowing gas.

method is accomplished by separate reactions that regenerate the reactants of the hydrogen release reaction. In fact, a distinctive advantage of this method is that all the hydrogen produced by (1) can be derived 100% from water. Another important feature of the current method is that the hydrogen generation reaction (1) produces up to 8.8 wt.% of hydrogen which is higher than the reversible hydrogen storage capacity within a temperature range of <350 °C of any other known materials to date.

With respect to hydrogen production, hydrogen gas is produced commercially today by two methods: (1) the reforming of natural gas and (2) the electrolysis of water. Although the latter method generates hydrogen from water, it still relies heavily on fossil energy for generation of the electricity that is required to carry out the electrolysis process. Considerable research is underway to integrate power generation from renewable energy sources such as wind and solar energy with the electrolysis of water so that the production of hydrogen is free of the use of fossil energy. The hybrid method described in this communication provides another alternative for hydrogen production from water that is environmentally friendly provided that metallic reducing agent such as Mg can be produced by recycling MgO using renewable energy.

As shown by Fig. 1 and Reaction (3), magnesium metal is required to regenerate reactants for the hydrogen producing reaction (1). Typically, Mg metal is produced by either the electrolysis of MgCl<sub>2</sub> or the reduction of MgO. Since MgO is the byproduct of reaction (3), it must be recycled to produce Mg. The reduction of MgO can be accomplished by mixing MgO with carbon and reacting at high temperatures as shown by Eq. (5). This method, referred to as the carbothermal reaction, is an established method for magnesium metal production in the metallurgical industry. Further information on the production of Mg

using the carbothermal process can be found in Refs. [26,27].



$$\Delta_r H_5(1573 \text{ K}) = 601.7 \text{ kJ/mol Mg} \quad (5)$$

Needless to say, a large quantity of thermal energy is required to produce Mg, which can be supplied by either burning of fossil energy or the use of renewable energy. A preliminary estimation of the energy required for Mg regeneration versus the energy contained the hydrogen generated, has been carried out under ideal conditions. The results showed that the reversible cycle as described in this communication is energetically favorable. However, a detailed and reliable energy balance analysis, which is beyond the scope of this communication, must be carried out under realistic conditions involving the energy balance and efficiencies, taking into account not only the thermodynamics of the reactions but also various heat exchange steps.

## 6. Conclusions

A new hybrid method is described for storing hydrogen in solid inorganic hydride materials as well as producing it from water. As a hydrogen storage method, the release and uptake of hydrogen in this method are accomplished via a series of simple reactions with good kinetics within a practically feasible temperature range. Although these individual reactions are essentially known, this work demonstrates that these reactions can be exploited collectively to accomplish what is otherwise difficult. The reversible hydrogen storage capacity of the material system is 6–8.8 wt.% at <350 °C. As a hydrogen production method, 100% of hydrogen generated by this method comes from water by its reaction with alkali metal oxides.

## Acknowledgements

This research is made possible partially by the financial support from the US Department of Energy (DOE) under contract number DE-FC36-05GO15069 since March 2005. The cost-share contributions by the University Utah to this project are also acknowledged.

## References

- [1] L. Schlapbach, A. Züttler, *Nature* 414 (2001) 353.
- [2] B. Bogdanovic, M. Schwickardi, *J. Alloys Compd.* 253 (1997) 1.
- [3] J. Chen, N. Kuriyama, Q. Xu, H.T. Takeshita, T. Sakai, *J. Phys. Chem. B* 105 (2001) 11214.
- [4] C.M. Jensen, K.J. Gross, *Appl. Phys. A* 72 (2001) 213.
- [5] R.A. Zidan, S. Taraka, A.G. Hee, C.M. Jensen, *J. Alloys Compd.* 285 (1999) 119.
- [6] T. Kiyobayashi, S. Srinivasan, D.L. Sun, C.M. Jensen, *J. Phys. Chem. A* 107 (2003) 7671.
- [7] J. Lu, Z.Z. Fang, *J. Phys. Chem. B* 109 (2005) 20830.
- [8] P. Chen, Z. Xiong, J. Luo, J. Lin, K.L. Tan, *Nature* 420 (2002) 302.
- [9] Z. Xiong, G. Wu, J. Hu, P. Chen, *Adv. Mater.* 16 (2004) 1522.
- [10] S.R. Johnson, P.A. Anderson, P.P. Edwards, I. Gameson, J.W. Prendergast, M. Al-Mamouri, D. Book, I.R. Harris, J.D. Speight, A. Walton, *Chem. Commun.* (2005) 2823.
- [11] W. Luo, *J. Alloys Compd.* 381 (2004) 284.
- [12] Y. Kojima, K.I. Suzuki, Y. Kawai, *J. Mater. Sci.* 39 (2004) 2227.
- [13] V.C.Y. Kong, D.W. Kirk, F.R. Foulkes, J.T. Hinatsu, *Int. J. Hydrogen Energy* 28 (2003) 1095.
- [14] V.C.Y. Kong, F.R. Foulkes, D.W. Kirk, J.T. Hinatsu, *Int. J. Hydrogen Energy* 24 (1999) 665.
- [15] M.H. Grosjean, M. Zidoune, L. Roue, J.Y. Huot, *Int. J. Hydrogen Energy* 31 (2006) 109.
- [16] R. Aiello, M.A. Matthews, D.L. Reger, J.E. Collins, *Int. J. Hydrogen Energy* 23 (1998) 1103.
- [17] J.J. Vajo, S.L. Skeith, F. Mertens, S.W. Jorgensen, *J. Alloys Compd.* 390 (2005) 55.
- [18] C. Haertling, R.J. Hanrahan Jr., R. Simth, *J. Nucl. Mater.* 349 (2006) 195.
- [19] R. Ren, A.L. Ortiz, T. Markmaitree, W. Osborn, L.L. Shaw, *J. Phys. Chem. B* 110 (2006) 10567.
- [20] M. Klanchar, B.D. Wintrose, J. Phillips, *Energy Fuels* 11 (1997) 931.
- [21] J. Phillips, M.C. Bradford, M. Klanchar, *Energy Fuels* 9 (1995) 569.
- [22] CIS-International Occupational Health and Safety Information Centre, Material Safety Data Sheet for LiOH, 2004.
- [23] <http://www1.eere.energy.gov/hydrogenandfuelcells/storage/>.
- [24] Y. Kojima, K. Suzuki, K. Fukumoto, M. Sasaki, T. Yamamoto, Y. Kawai, H. Hayashi, *Int. J. Hydrogen Energy* 27 (2002) 1029.
- [25] W. Grochala, P. Edwards, *Chem. Rev.* 104 (2004) 1283.
- [26] A. Donaldson, R.A. Cordes, *JOM* 57 (2005) 58.
- [27] G. Brooks, S. Trang, P. Witt, M.N.H. Khan, M. Nagle, *JOM* 58 (2006) 51.