Short communication

Hydrogen absorption/desorption behaviors over a quaternary Mg–Ca–Li–N–H system

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Abstract

Hydrogen storage in a quaternary Mg–Ca–Li–N–H system has been investigated by XRD, FT-IR, TPD and PCI. Results showed that hydrogen desorption occurred at temperature about 50 °C, and peaked at ∼178 °C under a heating rate of 2 °C min^{-1}. The reversibility of hydrogen storage was observed and the maximum hydrogen storage capacity of about 2.7 wt.% was reached at 220 °C and 75 atm. However, the plateau pressure for hydrogen desorption is relatively low (∼0.3 atm). Structural identifications reveal that a new phase with tetragonal structure positioned at 31.8° and 51.3° of XRD peaks was generated during hydrogen absorption/desorption.
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1. Introduction

The development of hydrogen-fueled vehicles and portable electronics requires novel functional materials that can store sufficient amount of hydrogen at moderate temperature and relatively low pressures with small volume, lightweight, and fast kinetics for recharging [1,2]. In this aspect, considerable research works have been done in the past three decades in order to develop practical viable materials [3–7]. However, the energy densities and/or reaction kinetics of the existing hydrogen storage materials are below the criteria needed for practical applications.

Recently, a new series of hydrogen storage materials, named metal–N–H system have been developed [8–11]. Chen et al. reported that the lithium nitride/imide system could reversibly absorb/desorb 11.5 wt.% of H$_2$ at temperature above 150 °C [8]. Further investigations demonstrated that ternary systems such as Mg(NH$_2$)$_2$–2LiH and LiNH$_2$–CaH$_2$ exhibit high hydrogen storage capacity with improved thermodynamics [9,10]. All these results indicate that the metal–N–H based materials are promising candidates for the onboard hydrogen storage. However, the

operating temperatures of these hydrogen materials are relatively high (>150 °C). Further investigations should be done to optimize the overall hydrogen storage performances.

It has been reported that the operation temperature of the Li–Ca–N–H system is obvious lower than that of the Li–N–H system [9], but its reversible hydrogen storage capacity also is lower than that of Li–N–H at the same time. In this paper, in order to improve the thermodynamic property and reversible hydrogen storage capacity, the mixture Mg(NH$_2$)$_2$, Ca(NH$_2$)$_2$ and LiH (1:1:4) was prepared and their structure and hydrogen storage properties were studied and reported.

2. Experimental

LiH was purchased from Sigma–Aldrich. Mg(NH$_2$)$_2$ and Ca(NH$_2$)$_2$ were synthesized on site by reacting metallic Mg or Ca with NH$_3$, respectively. The preparation methods of Mg(NH$_2$)$_2$ and Ca(NH$_2$)$_2$ are described for details in Ref. [12]. The Mg–Ca–Li–N–H sample was prepared by mechanically milling the mixture of Mg(NH$_2$)$_2$, Ca(NH$_2$)$_2$ and LiH in a molar ratio of 1:1:4 for 20 h using a SPEX 8000 high-energy mill with a stainless milling ball (*d* = 20 mm). Certain amounts of hydrogen were released during ball milling due to the reaction between Mg(NH$_2$)$_2$, Ca(NH$_2$)$_2$ and LiH, which are equivalent to about three H atoms per Mg(NH$_2$)$_2$–Ca(NH$_2$)$_2$–4LiH

(1.5H$_2$, ∼1.9 wt.%) by weighing the samples before and after ball milled. It was also confirmed by measuring the pressure of the released hydrogen. All the samples before and after hydrogenation/dehydrogenation were always handled in the glove box filled with purified argon.

The temperature-dependence of hydrogen desorption of Mg–Ca–Li–N–H sample was carried on the home-made temperature-programmed desorption (TPD, with purified Ar as carrier gas) system with an on-line mass spectrometer (MS) and gas chromatograph (GC) attached. About 100 mg sample was loaded and tested. At the same time, the out-let gas was also detected by an ammonia (NH$_3$) sensitive reagent (Co(NO$_3$)$_2$ solution) to identify any trace of NH$_3$. Temperature was raised gradually from 25 to 280 °C at 2 °C min^{-1}.

The amounts of hydrogen desorption/absorption with increasing temperature and pressure-composition isotherms (PCI) at 220 °C were measured by an automatic Sieverts-type apparatus (Advanced Materials Co.). The sample of about 450 mg was used each time. The release and soak modes were applied in determining the amounts of hydrogen desorbed/absorbed over the sample. Temperature was raised to 250 °C at 2 °C min^{-1} for desorption and to 220 °C at 1 °C min^{-1} for absorption, respectively.

Differential scanning calorimetry (DSC) measurements of the fresh and re-hydrogenated samples were conducted on a Netzsch DSC 204 HP unit. Ar was applied as carrier gas and heated at the rate of 2 °C min^{-1}. A Perkin-Elemer FT-IR-3000 unit was applied to identify the N–H vibration in all samples. DRIFT mode was adopted.

X-ray diffraction (XRD) was performed on a Bruker D8-advance X-ray diffractometer with Cu Kα radiation at 40 kV and 40 mA and equipped with an in-situ cell to identify the structural changes during hydrogenation/dehydrogenation.

3. Results and discussion

Temperature-programmed desorption (TPD) curve of the Mg–Ca–Li–N–H mixture just after ball milling (fresh sample) was first measured and shown in Fig. 1(a). It can be seen that hydrogen release from the mixture started at ∼50 °C and peaked at ∼178 °C, which is relatively lower than that of Li–Ca–N–H sample and close to that of Li–Mg–N–H sample [9]. Only hydrogen was released in the tested temperature range by the detection of MS and Co(NO$_3$)$_2$ solution. Fig. 1(b) shows quantitatively the hydrogen absorption/desorption over the Mg–Ca–Li–N–H mixture with temperatures. With increasing temperature from 50 to 250 °C, the amount of hydrogen desorption increases gradually. In the temperature range 125–240 °C, the rate of hydrogen desorption is relatively fast, which agrees well with the observation of TPD measurement. The total amount of hydrogen desorption is about 2.96 wt.% (∼5H). Together with three H atoms detached from the mixture during ball milling, totally eight H atoms break away from the starting chemicals. The dehydrogenated sample was cooled down to 0 °C and then re-hydrogenated under ∼75 atm of H$_2$ with increasing temperature. The starting temperature for hydrogen absorption is about 75 °C, which is obvious lower than that of Li–Mg–N–H sample [9]. The
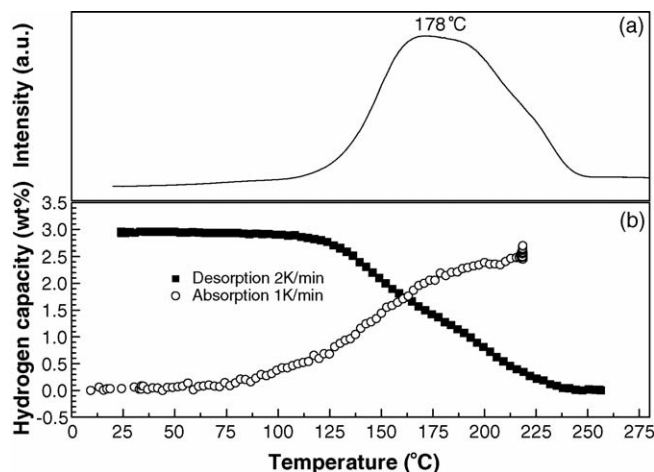

Fig. 1. TPD and temperature dependences of hydrogen absorption/desorption of the Mg–Ca–Li–N–H mixture. (a) TPD; (b) hydrogen absorption/desorption with increasing temperature.

amount of hydrogen absorption is about 2.7 wt.% (∼4H) after holding the mixture at ∼220 °C for 1 h. According to the above volumetric release test, the chemical composition of the starting materials and the amount of hydrogen released during ball milling, the overall dehydrogenation equation can be interpreted as follows:

$$Mg(NH_2)_2 + Ca(NH_2)_2 + 4LiH$$
$$\rightarrow Li_4MgCaN_4H_4 + 4H_2 \quad 5.0 \text{ wt.\%} \quad (1)$$
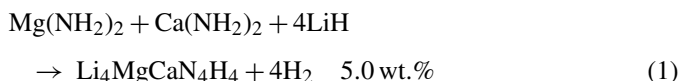
approximately half of the desorbed H can be reunited with the sample under the present testing conditions. Further investigations are needed to analyze the reversibility of the other half of detached hydrogen.

To further investigate the gas–solid reaction characteristic of the Mg–Ca–Li–N–H mixture, PCI curve was measured at 220 °C and illustrated in Fig. 2. It can be confirmed that ∼2.7 wt.% hydrogen can be reversibly absorbed/desorbed, which is close to the amount of hydrogen desorption of 2.96 wt.% from the fresh sample. As absorbing hydrogen, PCI curve shows two plateau
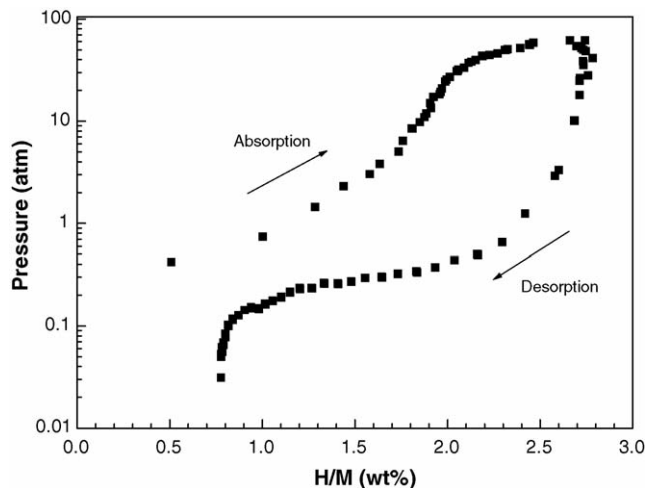

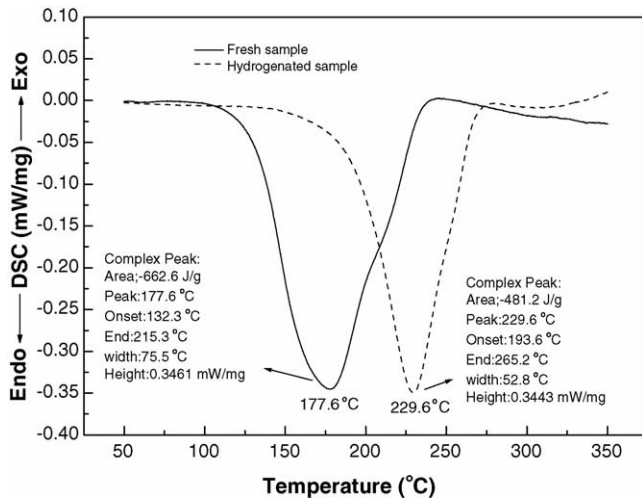Fig. 2. PCI curve of the Mg–Ca–Li–N–H mixture at 220 °C.

Fig. 3. DSC of the fresh and hydrogenated samples of the Mg–Ca–Li–N–H mixture.

Fig. 4. FT-IR spectra of the Mg–Ca–Li–N–H mixture at different states.

regions. One is lower than 1 atm, which is similar to the overall behavior of Li–Ca–N–H system [9], and the other is above 45 atm, which is closed to that of Li–Mg–N–H sample [9,10]. However, as desorbing hydrogen, PCI curve of the mixture can be divided into three parts consisting of a higher pressure region with large slope, a plateau region ($\sim$0.3 atm) and a low pressure region, respectively, which resembles to hydrogen desorption behavior of Li–N–H sample [8] and/or Li–Ca–N–H sample [9].

In addition, the heat effects of the fresh and re-hydrogenated samples of the Mg–Ca–Li–N–H mixture were studied by DSC (Fig. 3). It can be seen that hydrogen desorption from the Mg–Ca–Li–N–H mixture is of endothermic nature, which indicates hydrogen absorption/desorption over the Mg–Ca–Li–N–H mixture may be reversible. For the fresh sample, the endothermic hydrogen desorption starts at $\sim$50 °C and peak at 177.6 °C, which is in good agreement with the result of TPD. The total heat effect of hydrogen desorption calculated is about 44.1 kJ mol^{-1}-H$_2$. As to the re-hydrogenated sample, the endothermic peak temperature is 229.6 °C, which is higher than that of the fresh sample. However, the total heat effect is about 36.5 kJ mol^{-1}-H$_2$, which is lower than that of the fresh sample. The above results indicate that the hydrogen desorption from the hydrogenated sample may need higher temperature to overcome higher energy barrier than that of the fresh sample, but the hydrogen desorption from the hydrogenated sample should be thermodynamically favored at lower temperatures.

The structural changes of the Mg–Ca–Li–N–H mixture were studied by XRD and FT-IR before and after hydrogenation/dehydrogenation. Fig. 4 shows the FT-IR spectra of the Mg–Ca–Li–N–H mixture at different states. For the fresh sample, two peaks at 3293 and 3239 cm^{-1} can be attributed to Ca(NH$_2$)$_2$, and two peaks at 3313 and 3258 cm^{-1} belong to LiNH$_2$, which indicates that LiNH$_2$ was yielded by ball milling Mg(NH$_2$)$_2$, Ca(NH$_2$)$_2$ and 4LiH. This result may result from the exchange of Li$^+$ and Mg^{2+} and/or Ca^{2+} due to the higher mobility of Li$^+$ during ball milling treatment. On the other hand, a broad peak centered around 3160 cm^{-1} was generated, w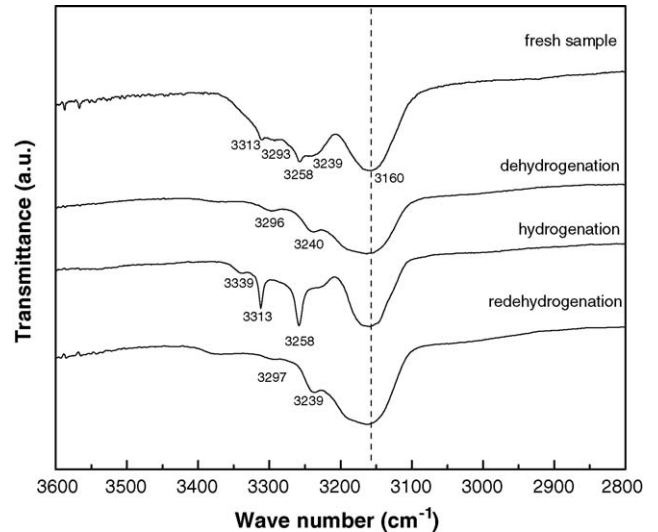hich may be attributed to the N–H stretching in a new imide-like compound of Mg–Ca–Li–N–H. The formation of this peak (3160 cm^{-1}) may be resulted from certain amount of hydrogen desorbed during ball milling treatment of Mg(NH$_2$)$_2$, Ca(NH$_2$)$_2$ and LiH. After first dehydrogenation, the peaks of LiNH$_2$ disappeared, and only the peaks at 3296 and 3240 cm^{-1} and the broad peak centered around 3160 cm^{-1} were detected, and the broad peak centered around 3160 cm^{-1} was further widened. The phenomenon implies that almost all of the mixture convert to the imide except for a very little residual of Ca(NH$_2$)$_2$. Subsequently, we re-hydrogenated the dehydrogenated sample, and clearly found that the peaks at 3313 and 3258 cm^{-1} regenerated, which indicates that the Li amide was re-yielded. At the same time, the broad peak became slightly sharp. Same FT-IR patterns were observed during repeated hydrogenation/dehydrogenation treatment.

Fig. 5 illustrates XRD patterns of the Mg–Ca–Li–N–H mixture before and after hydrogenation/dehydrogenation. It can be seen that, after ball milled, the fresh mixture exhibits partially
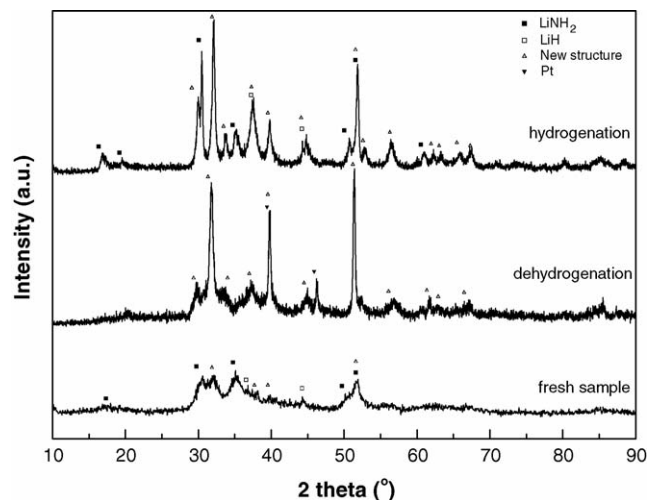

Fig. 5. XRD patterns of the Mg–Ca–Li–N–H mixture before and after dehydrogenation/hydrogenation.

amorphous characteristic and mainly consists of $LiNH_2$, LiH and a new structure. The dehydrogenated sample is mainly composed of a new structure. The new structure exhibits two stronger peaks at $31.8°$ and $51.3°$. Moreover, it was found that, with hydrogenation/dehydrogenation cycling, all peaks of XRD patterns became sharper, which implies that the crystallization of the sample is more integrated. Meanwhile, it is interesting to note that, except for the formation of $LiNH_2$ and LiH in the hydrogenated state, the new structure persists with only slight changes in the peak position. Combined with FT-IR analysis, the new structure could be attributed to the new compound of Mg–Ca–Li–N–H. Analysis reveals that the new structure may belong to tetragonal structure. However, it is difficult at this moment to determine the composition of Mg, Ca, Li, N and H in the developed structure due to the complex of elements and the complicated nature of chemical bonding. The further investigations on the structure are in progress.

4. Conclusions

In this paper, the mixture of $Mg(NH_2)_2$, $Ca(NH_2)_2$ and LiH (1:1:4) has been prepared by ball milling and the structure, hydrogen storage and thermodynamic properties have been studied. The result of temperature dependences of hydrogen absorption/desorption indicated that hydrogen (~ 2.96 wt.%) was desorbed from 50 to 280 °C. DSC study revealed the hydrogen desorption of this mixture is an endothermic reaction and the total heat effect is about 44.1 kJ mol^{-1}-H_2. PCI results showed that the reversible hydrogen storage capacity of this mixture was about 2.7 wt.% at 220 °C and 75 atm. Moreover,

the structural investigations indicated that a new compound of Mg–Ca–Li–N–H with tetragonal structure might be yielded during sample preparation and hydrogen absorption/desorption. Further work shall be done on the improvement of reversibility and the structural identification.

Acknowledgements

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