

Short communication

## Recent development on hydrogen storage properties in metal–N–H systems

T. Ichikawa<sup>a</sup>, H.Y. Leng<sup>a</sup>, S. Isobe<sup>b</sup>, N. Hanada<sup>a</sup>, H. Fujii<sup>a,\*</sup>

<sup>a</sup> Materials Science Center, N-BARD, Hiroshima University, Higashi-Hiroshima 739-8526, Japan

<sup>b</sup> Graduate School of Advanced Sciences of Matter, Hiroshima University, Higashi-Hiroshima 739-8530, Japan

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### Abstract

In this paper, we review our recent results on hydrogen storage properties in light metals(M)–nitrogen(N)–hydrogen(H) systems prepared by mechanochemical method. At first, the composite mixture of LiH and LiNH<sub>2</sub> doped with TiCl<sub>3</sub> as a catalyst was prepared by ball milling for 2 h under a H<sub>2</sub> gas pressure of 1 MPa. The TDS profile indicated that ~6 mass% H<sub>2</sub> was desorbed by the reaction  $\text{LiH} + \text{LiNH}_2 \leftrightarrow \text{Li}_2\text{NH} + \text{H}_2$  in the temperature range from 150 to 250 °C under a He gas flow at a heating rate of 5 °C min<sup>-1</sup>, but the H-desorption equilibrium pressure  $P_{\text{H}_2}$  was ~0.1 MPa at 250 °C. This temperature is too high for onboard use, indicating that further improvement is necessary to destabilize the above H-storage reaction. For that, we clarified the H-desorption mechanism by the isotopic exchange experiments, on the basis of which we designed a new Li–Mg–N–H composite system with the reaction  $8\text{LiH} + 3\text{Mg}(\text{NH}_2)_2 \leftrightarrow 4\text{Li}_2\text{NH} + \text{Mg}_3\text{N}_2 + 8\text{H}_2$ . This composite materials desorbed ~7 mass% H<sub>2</sub> in the range from 120 to 200 °C and the H-desorption equilibrium pressure  $P_{\text{H}_2}$  was higher than 5 MPa at 200 °C, indicating that this system has an excellent potential for onboard applications.

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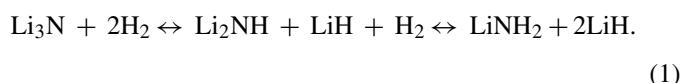
**Keywords:** Hydrogen storage; Metal amide/imide; Mechanochemical treatment; Composite

### 1. Introduction

For utilizing hydrogen energy in near future as one of the secondary energies, it is important to establish suitable hydrogen storage and transportation technologies. One of the key technologies on that way is the development of high-performance hydrogen storage (H-storage) materials. It is well-known that conventional metal hydrides can more densely store hydrogen than in liquid or high-pressure gas hydrogen. However, those hydrides are too heavy for commercial application. To overcome the disadvantage, some chemical hydrides composed of light elements like alanate systems [1–3], borohydride systems [4,5], amide–imide systems [6–12] have been targeted and developed as promising materials for practical use all over the world.

On the amide–imide, so called metal–N–H, systems, since the discovery of the Li<sub>3</sub>N system for H-storage by Chen et al. [6], much attention has been paid as onboard H-storage. According to the Chen's report, a large amount of hydrogen (10.4 mass%) were reversibly stored in Li<sub>3</sub>N by the following two-step

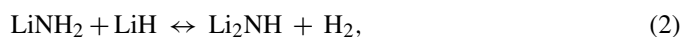
reactions:



However, the standard enthalpy change of the first-step reaction in the reaction (1) can be calculated to be  $-148 \text{ kJ mol}^{-1}$  H<sub>2</sub> from each standard enthalpy of formation [7], the magnitude is so large that a very high temperature over 430 °C is required for complete recovery of Li<sub>3</sub>N from the hydrogenated state. On the other hand, the second reaction has a much smaller enthalpy change calculated to be  $-44.5 \text{ kJ mol}^{-1}$  H<sub>2</sub> [7] and still a large amount of hydrogen storage capacity of 6.5 mass%. Therefore, it is worthy to examine the H-storage properties of Li<sub>2</sub>NH as one of the suitable H-storage materials for onboard use.

### 2. H-storage properties of the mixture of LiNH<sub>2</sub> and LiH prepared by ball milling

As a series of systematic studies on the metal–N–H systems, we firstly focused on the second-step reaction in the reaction (1);



\* Corresponding author. Tel.: +81 82 424 5747; fax: +81 82 424 7486.

E-mail address: [hfuji@hiroshima-u.ac.jp](mailto:hfuji@hiroshima-u.ac.jp) (H. Fujii).

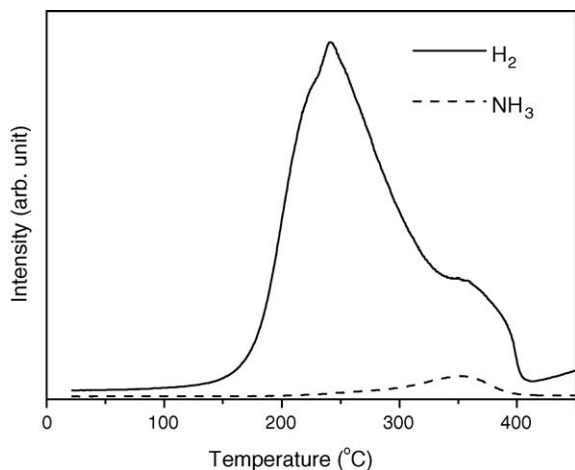


Fig. 1. TDS profiles for  $\text{H}_2$  and  $\text{NH}_3$  from the ball milled mixtures of  $\text{LiH} + \text{LiNH}_2$  examined under a helium flow at a heating rate of  $5^\circ\text{C min}^{-1}$ .

Both the  $\text{LiNH}_2$  and  $\text{LiH}$  were commercially purchased in this work. The mixture was ball milled by a planetary-type equipment (Fritch P7) under a  $\text{H}_2$  gas atmosphere of 1 MPa for 2 h. The thermal desorption spectrum (TDS) from the product is shown in Fig. 1. We can see that the  $\text{H}_2$  gas is desorbed between 150 and  $400^\circ\text{C}$ , while the  $\text{NH}_3$  gas is only desorbed in high temperature region around  $350^\circ\text{C}$ , synchronizing with the  $\text{H}_2$  gas desorption profile. Usually, it is known that the  $\text{NH}_3$  gas is emitted by the following decomposition reaction on heating process;



Here, the enthalpy change for releasing  $\text{NH}_3$  is endothermic, which is calculated to be  $84\text{ kJ mol}^{-1} \text{ NH}_3$  [7]. Therefore, the  $\text{NH}_3$  emission from the mixture around  $350^\circ\text{C}$  might be due to thermal decomposition of remaining  $\text{LiNH}_2$  that did not react with  $\text{LiH}$  because of slow reaction kinetics.

To improve the reaction kinetics, we doped a small amount of  $\text{TiCl}_3$  (1 mol%) as a catalyst in the 1:1 mixture of  $\text{LiNH}_2$  and  $\text{LiH}$  and milled for 2 h as well [8]. The TDS profiles from the  $\text{TiCl}_3$ -doped composite for  $\text{H}_2$  and  $\text{NH}_3$  are shown in Fig. 2 together with the result of thermogravimetry (TG) measurement. We can see that a large amount of hydrogen ( $\sim 6\text{ mass}\%$ ) are desorbed in the range of  $150\text{--}250^\circ\text{C}$  at a heating rate of  $5^\circ\text{C min}^{-1}$ . This indicates that the reaction kinetics is dramatically improved by doping 1 mol%  $\text{TiCl}_3$ , similar to the sodium alanate system [1–3] and all the  $\text{LiNH}_2$  are completely consumed by reacting with  $\text{LiH}$  until  $300^\circ\text{C}$  and transformed into  $\text{Li}_2\text{NH}$  and  $\text{H}_2$ . Consequently, the emission of  $\text{NH}_3$  gas could not be detected within our experimental accuracy. The reversibility was tested by repeating dehydrogenation and rehydrogenation at  $220^\circ\text{C}$  for 12 h under high vacuum and 3 MPa  $\text{H}_2$  until 10 cycles. The results indicated that the cycle retention was excellent. However, our PCI measurement gave an equilibrium pressure  $P_{\text{H}_2} = 0.1\text{ MPa}$  at  $250^\circ\text{C}$  [15], indicating that the desorption temperature is too high for onboard H-storage.

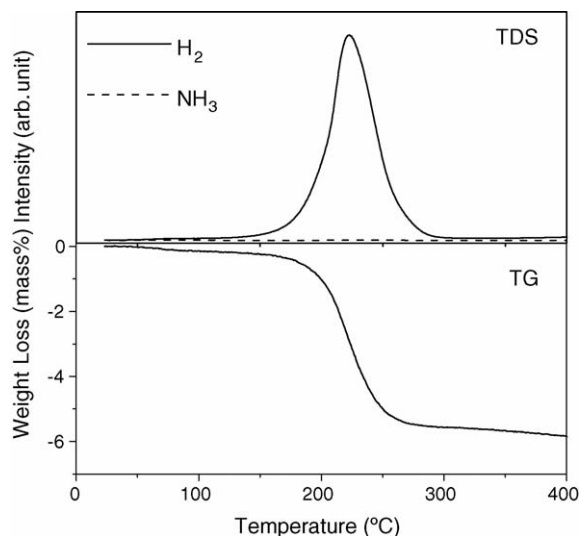
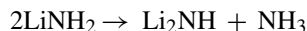


Fig. 2. TDS for  $\text{H}_2$  and  $\text{NH}_3$  and TG profiles from the ball milled mixtures of  $\text{LiD} + \text{LiNH}_2 + \text{TiCl}_3$  (1 mol%) examined under a helium flow at a heating rate of  $5^\circ\text{C min}^{-1}$ .

### 3. Reaction mechanism for hydrogen desorption from the 1:1 mixture of $\text{LiNH}_2$ and $\text{LiH}$

For improving the reaction (2) and lowering the H-desorption temperature under  $P_{\text{H}_2} = 0.1\text{ MPa}$ , it is important to clarify the reaction mechanism for hydrogen sorption in the reaction (2). As described in the previous paper [7], we have proposed that the hydrogen desorption reaction was progressed by the following two elemental reactions (3) and (4) mediated by an  $\text{NH}_3$  molecule:



and



On the other hand, Chen et al. [9] have claimed another mechanism, where H in  $\text{LiNH}_2$  is positively charged while H in  $\text{LiH}$  is negatively charged, so that the strong affinity between  $\text{H}^{\delta+}$  and  $\text{H}^{\delta-}$  predominantly leads to a generation of hydrogen molecule. This model suggests hydrogen gas desorption due to the direct molecule–molecule interaction, in which the  $\text{LiH}$  and  $\text{LiNH}_2$  molecules should be liberated from two solid phases. The difference between the above two models lies in whether the  $\text{NH}_3$  molecule does mediate or not in the proceeding of the reaction (2).

In this work, to clarify the hydrogen desorption mechanism in the reaction (2), we have performed the TDS and FT-IR measurements for the products prepared by an isotopic exchange technique, where  $\text{LiD}$  or  $\text{LiND}_2$  is replaced by, respectively,  $\text{LiH}$  or  $\text{LiNH}_2$  in the  $\text{TiCl}_3$ -doped 1:1 composite mixture of  $\text{LiH}$  and  $\text{LiNH}_2$  [13].

The TDS profiles for isotopic hydrogen gases from two kinds of the ball milled mixtures of  $\text{LiD} + \text{LiNH}_2$  and  $\text{LiH} + \text{LiND}_2$  are shown in Fig. 3(a and b), respectively. A mixture gas composed of  $\text{H}_2$ ,  $\text{HD}$  and  $\text{D}_2$  is emitted as a desorption gas, and the onset and peak temperatures in the TDS profiles are almost the same

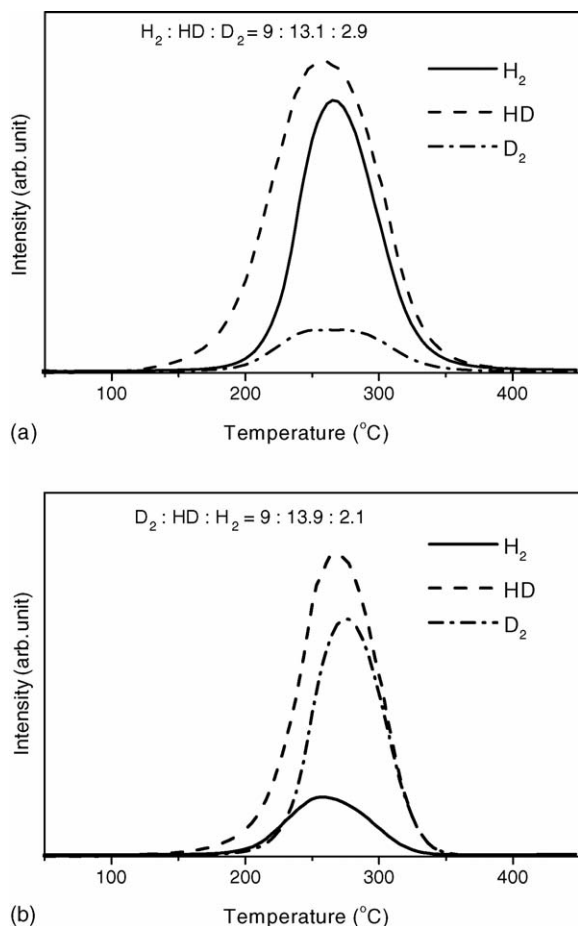


Fig. 3. TDS profiles for isotopic gases from the ball milled mixtures of (a) LiD + LiNH<sub>2</sub> and (b) LiH + LiND<sub>2</sub> examined under a helium flow at a heating rate of 20 °C min<sup>-1</sup>.

for all the isotopic gases, indicating no significant isotope effect on gaseous desorption reaction. From Fig. 3(a), the ratio of the areas of the TDS profiles corresponding to the mass numbers 2 (=H<sub>2</sub>), 3 (=HD) and 4 (=D<sub>2</sub>) is estimated to be 9.0:13.1:2.9 for the mixture of LiD and LiNH<sub>2</sub>, while the ratio for the mixture of LiH and LiND<sub>2</sub> is estimated to be 2.1:13.9:9.0 as shown in Fig. 3(b), which is almost in reverse order of that in the mixture of LiD and LiNH<sub>2</sub>.

Furthermore, we performed the FT-IR measurements to determine the molar ratios of Li<sub>2</sub>NH to Li<sub>2</sub>ND in the product after desorbing isotopic gases from the ball milled mixtures of LiD + LiNH<sub>2</sub> and LiH + LiND<sub>2</sub> doped 1 mol% TiCl<sub>3</sub> as a catalyst. The results of IR absorbance are shown in Fig. 4 together with those of mere mixtures of Li<sub>2</sub>NH and Li<sub>2</sub>ND with the molar ratios of 4:1, 1:1 and 1:4 as references. We notice that two peaks corresponding to the N–H and N–D stretching modes are located at ~3150 and ~2350 cm<sup>-1</sup>, respectively. The ratios of the peak areas for the references were, respectively, 8.7:1.3, 6.3:3.7 and 3.1:6.9. This indicates that the peak area corresponding to N–H mode should be equivalent to be ~1.7 times as large as that of N–D mode. Therefore, we can evaluate the real amount of Li<sub>2</sub>ND in the dehydrogenated products as being ~1.7 times as large as the measurable peak area. By using this calibration factor of 1.7, the relative molar ratios corresponding to Li<sub>2</sub>NH and

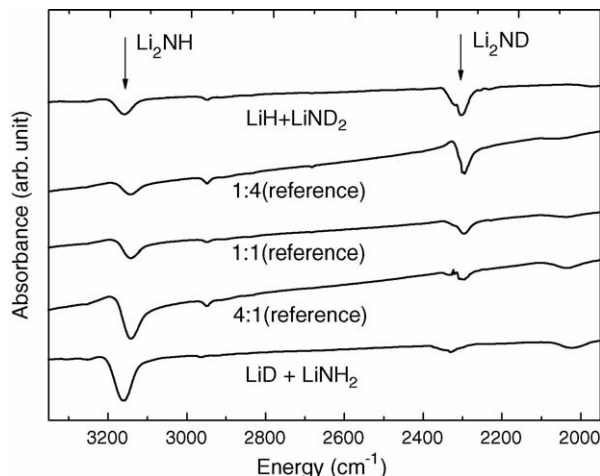


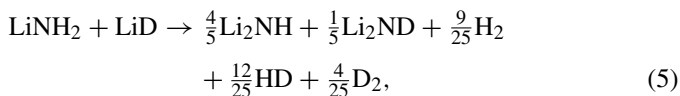
Fig. 4. FT-IR spectra after desorbing isotopic gases from the ball milled mixtures of LiD + LiNH<sub>2</sub> and LiH + LiND<sub>2</sub>. In this figure, FT-IR spectra are shown for some standard samples with the ratios of 4:1, 1:1 and 1:4 for Li<sub>2</sub>NH and Li<sub>2</sub>ND as references.

Li<sub>2</sub>ND in the products after degassing the ball milled mixtures of LiD + LiNH<sub>2</sub> and LiH + LiND<sub>2</sub> were finally estimated to be 3.9:1 and 1:3.8, respectively.

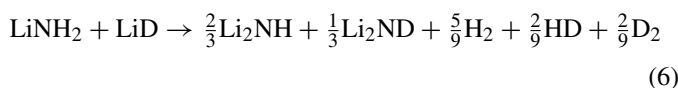
On the basis of the above results, we have to verify whether the NH<sub>3</sub> molecule does mediate or not in the proceeding of the reaction (2).

If we stand on the model proposed by Chen et al. the desorbing gas from the mixture should be only HD gas, but not H<sub>2</sub> or D<sub>2</sub> gases. However, we should take into account that TiCl<sub>3</sub> used as a catalyst for smooth proceeding of the reaction (2) can be reduced to the metallic state by ball milling with a reducing agent such as a hydride LiH [14]. As a consequence, an isotope scrambling effect may strongly affect the H<sub>2</sub>:HD:D<sub>2</sub> ratio, leading to desorption of H<sub>2</sub> and D<sub>2</sub> gases from the mixture [3]. Therefore, by only the analyses of the desorbing gas it is difficult to identify whether the molecule–molecule reaction does really occur or not. On the other hand, the molar ratio of Li<sub>2</sub>NH and Li<sub>2</sub>ND determined by the FT-IR measurements after desorbing isotopic gases should not be affected by the scrambling effect, because the effect is originated in the chemisorbed state on the metallic Ti. According to Chen's model, only the Li<sub>2</sub>NH phase should be detected by FT-IR measurement.

Next, if we stand on the ammonia mediated model, then LiNH<sub>2</sub> first decomposes into Li<sub>2</sub>NH and NH<sub>3</sub>, and the liberalized NH<sub>3</sub> reacts with LiD, releasing the isotopic gases. In the second reaction process, the following three models could be possibly considered reflecting the difference between the characters of D and H atoms. Model 1 is that the generation of H<sub>2</sub>, HD or D<sub>2</sub> molecule from H and D atoms in LiD and NH<sub>3</sub> simply obeys the laws of probability without any distinctions between H and D atoms. In this case, we can evaluate the following chemical reaction equation by a little bit complicated calculation. The details are abbreviated here (see Ref. [13]).



Model 2 is that the D atom in LiD specially remains in lithium imide;

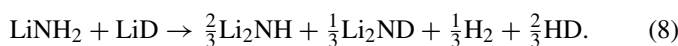


Model 3 is that the D atom in LiD is specially released from the original solid state as the DH gas;



Here, it is noted that the reaction (7) gives the same expression as the model proposed by Chen et al. [9] without the  $\text{NH}_3$  mediation.

Moreover, we should take into account another case that the isotopic gases are randomly desorbed after hypothetically forming  $\text{Li}_2\text{NDH}_2$  molecule by collision between the LiD and  $\text{LiNH}_2$  molecules as an instant state as direct molecule–molecule reaction. In this case, the reaction can be written as follows,



In the above expressions, we notice that the isotope effect of deuterium for hydrogen is ignored. The reason is because the desorption properties of deuterium gas from the ball milled mixture of LiD and  $\text{LiND}_2$  were almost the same as those of hydrogen gas from the mixture of LiH and  $\text{LiNH}_2$ .

Finally, we compare the experimental results with the above four models. The FT-IR analysis deduced that the molar ratio of  $\text{Li}_2\text{NH}$  and  $\text{Li}_2\text{ND}$  was 3.9:1 and 3.8:1 for the mixtures of LiD +  $\text{LiNH}_2$  and LiH +  $\text{LiND}_2$ , respectively, as described above. This value is close to the Model 1 for the mixture of LiD +  $\text{LiNH}_2$ . Furthermore, the molar ratio of isotopic  $\text{H}_2$ , HD and  $\text{D}_2$  gases desorbed from the ball milled mixture of LiD and  $\text{LiNH}_2$  was deduced to be 9.0:13.1:2.9. This ratio is also close to that of 9:12:4 evaluated from the Model 1. On the other hand, for the mixture of LiH and  $\text{LiND}_2$ , the ratio was also estimated to be 2.1:13.9:9.0, for isotopic  $\text{H}_2$ , HD and  $\text{D}_2$  gases, which is also close to that of 4:12:9 for the Model 1 as well. Therefore, we can conclude that the isotope scrambling effect due to catalytic effect of Ti is not so profound that the molar ratio of isotopic gases desorbed from the mixture of LiD and  $\text{LiNH}_2$  well follows the two-step elementary reaction model mediated by the  $\text{NH}_3$  molecule (Model 1).

In the  $\text{NH}_3$  mediated reaction, it should be noted that the liberalization of the  $\text{NH}_3$  molecule from the solid  $\text{LiNH}_2$  surface should occur after the  $\text{NH}_2^-$  ion might diffuse in the solid  $\text{LiNH}_2$  phase, while the  $\text{NH}_3$  molecule might be transferred just like as a free molecule between the solid phases.

#### 4. Designing for new high-performance H-storage materials in the metal–N–H systems

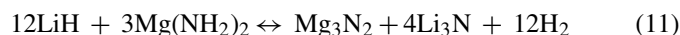
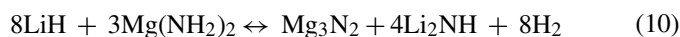
As described in our previous paper [7], since the reaction (4) from  $\text{LiH} + \text{NH}_3$  to  $\text{LiNH}_2 + \text{H}_2$  was exothermic and ultrafast, the synthesis of  $\text{LiNH}_2$  was easily performed by ball milling LiH under ammonia atmosphere at room temperature. Furthermore, in our group, some other amides  $\text{NaNH}_2$ ,  $\text{Mg}(\text{NH}_2)_2$  and

Table 1  
New possible metal–N–H systems for hydrogen storage

Number	Possible reversibly reaction for hydrogen storage	Theoretical hydrogen capacity (mass%)
1	$2\text{LiH} + \text{Mg}(\text{NH}_2)_2 \leftrightarrow \text{Li}_2\text{NH} + \text{MgNH} + 2\text{H}_2$	5.58
2	$8\text{LiH} + 3\text{Mg}(\text{NH}_2)_2 \leftrightarrow 4\text{Li}_2\text{NH} + \text{Mg}_3\text{N}_2 + 8\text{H}_2$	6.93
3	$12\text{LiH} + 3\text{Mg}(\text{NH}_2)_2 \leftrightarrow 4\text{Li}_3\text{N} + \text{Mg}_3\text{N}_2 + 12\text{H}_2$	9.15
4	$\text{MgH}_2 + \text{Mg}(\text{NH}_2)_2 \leftrightarrow 2\text{MgNH} + 2\text{H}_2$	4.88
5	$2\text{MgH}_2 + \text{Mg}(\text{NH}_2)_2 \leftrightarrow \text{Mg}_3\text{N}_2 + 4\text{H}_2$	7.40
6	$3\text{MgH}_2 + 4\text{LiNH}_2 \leftrightarrow \text{Mg}_3\text{N}_2 + 2\text{Li}_2\text{NH} + 6\text{H}_2$	7.08
7	$2\text{LiH} + \text{Ca}(\text{NH}_2)_2 \leftrightarrow \text{Li}_2\text{NH} + \text{CaNH} + 2\text{H}_2$	4.58
8	$\text{MgH}_2 + \text{Ca}(\text{NH}_2)_2 \leftrightarrow \text{MgNH} + \text{CaNH} + 2\text{H}_2$	4.10
9	$4\text{CaH}_2 + 3\text{Mg}(\text{NH}_2)_2 \leftrightarrow \text{Mg}_3\text{N}_2 + 4\text{CaNH} + 8\text{H}_2$	4.78

$\text{Ca}(\text{NH}_2)_2$  were also synthesized from their corresponding metal hydrides by ball milling under  $\text{NH}_3$  gas atmosphere [16]. On the basis of the  $\text{NH}_3$  molecule mediated reaction model, we have designed nine kinds of the H-storage reactions using some alkali and alkaline earth amides and their hydrides as listed in Table 1 as promising materials.

Among these systems,  $\text{Mg}(\text{NH}_2)_2$  desorbs the largest amount of ammonia at relatively low temperature because of the smallest electronegativity [16], while LiH reacts with  $\text{NH}_3$  possessing the fastest kinetics [16]. Therefore, we assume that the most suitable material for H-storage is one of some composites of LiH and  $\text{Mg}(\text{NH}_2)_2$ . Those are designed as follows (see Table 1);



The reaction (9) of the 6:3 mixture includes the decomposition from  $\text{Mg}(\text{NH}_2)_2$  to  $\text{MgNH}$ , leading to a hydrogen capacity of 5.6 mass% as listed in Table 1, which has been examined by Luo [17] and Chen and co-workers [18,19] who estimated  $P_{\text{H}_2} = 2$  MPa at 200 °C. In addition, they claimed that the product after dehydrogenation could be assigned to be a new phase of  $\text{Li}_2\text{Mg}(\text{NH})_2$  in the XRD profile. Our recent experimental results suggest that  $\text{MgNH}$  produced in the reaction (9) by the ammonia mediated reaction might directly react with  $\text{Li}_2\text{NH}$  and transforms into a new phase of  $\text{Li}_2\text{Mg}(\text{NH})_2$  at 200–250 °C. The reaction (10) includes the decomposition from  $\text{Mg}(\text{NH}_2)_2$  to  $\text{Mg}_3\text{N}_2$  through  $\text{MgNH}$ , leading to a hydrogen capacity up to 6.9 mass% [11]. Since the  $\text{NH}_3$  generation due to the decomposition from  $\text{MgNH}$  to  $\text{Mg}_3\text{N}_2$  occurs in similar temperature regions to the decomposition from  $\text{Mg}(\text{NH}_2)_2$  to  $\text{MgNH}$ , it is possible to utilize the reaction (10) as H-storage in the similar condition to reaction (9). However, the reaction (11) accompanies with further H-desorption reaction due to the decomposition from  $\text{Li}_2\text{NH}$  to  $\text{Li}_3\text{N}$  [20]. A very high temperature over 430 °C is required for the progress of this hydrogen desorption reaction. From the above consideration, we focused on the reaction (10) to be designed as one of the suitable H-storage materials.

In details, the reaction (10) was designed by assuming the following three kinds of reactions mediated by the  $\text{NH}_3$  molecule

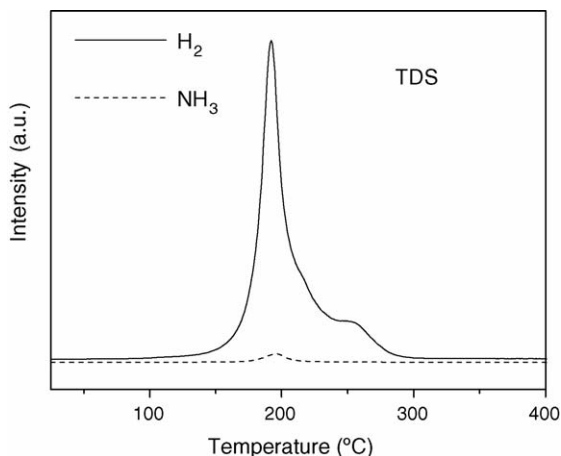


Fig. 5. TDS profiles for H<sub>2</sub> and NH<sub>3</sub> from the ball milled mixture of 8LiH + 3Mg(NH<sub>2</sub>)<sub>2</sub> under a helium flow at a heating rate of 5 °C min<sup>-1</sup>.

[11]: (1) 3Mg(NH<sub>2</sub>)<sub>2</sub> decomposes into Mg<sub>3</sub>N<sub>2</sub> and 4NH<sub>3</sub>; (2) the liberated 4NH<sub>3</sub> reacts with 4LiH and transforms into 4LiNH<sub>2</sub> and 4H<sub>2</sub>; (3) the synthesized 4LiNH<sub>2</sub> reacts with the remaining LiH and produces 4Li<sub>2</sub>NH and 4H<sub>2</sub>.

Experimentally, a mixture of Mg(NH<sub>2</sub>)<sub>2</sub> and LiH with a molar ratio of 3:8 was prepared by mechanically ball milling under a H<sub>2</sub> gas pressure of 1 MPa without any catalysts by a planetary ball mill equipment at 400 rpm for 2 h [11]. In Figs. 5 and 6, are shown the TDS profiles for H<sub>2</sub> gas as a function of temperature and TG profiles at 175 and 150 °C as a function of time, respectively. The TDS results indicate that a large amount of hydrogen (~7 mass%) are desorbed from 120 °C and the desorption peaks at 190 °C at a heating rate of 5 °C min<sup>-1</sup>. In addition, we notice that a very small amount of ammonia is also desorbed at the peak temperature of H<sub>2</sub> desorption. The TG profile exhibits that hydrogen of more than 5.5 mass% is desorbed at 175 °C within 60 min and more than 5.0 mass% at 150 °C within 120 min under a He gas flow, respectively. The reversibility of the reaction (10) was confirmed by the XRD measurement after repeating the dehydrogenation under a high vacuum and rehydrogenation under 10 MPa at 200 °C for 12 h. A preliminary PCI measurement gave an partial desorption equilibrium pressure

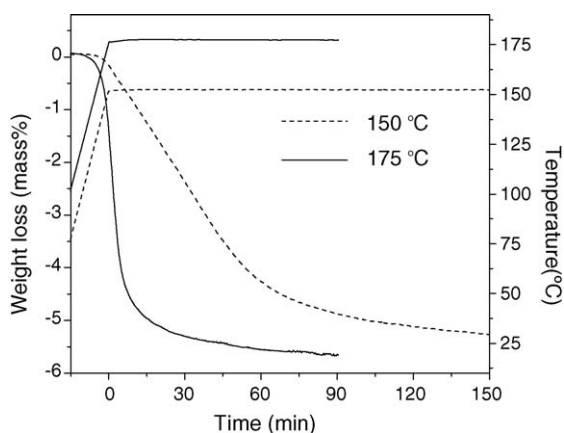


Fig. 6. Isothermal TG profiles from the ball milled mixtures of 8LiH + 3Mg(NH<sub>2</sub>)<sub>2</sub> under a helium flow at 150 and 175 °C, respectively.

$P_{\text{H}_2} \geq 5.0$  MPa at 200 °C, indicating that H-storage properties of 3Mg(NH<sub>2</sub>)<sub>2</sub> and 8LiH are much better than that of the mixture of LiNH<sub>2</sub> and LiH as we expected.

Finally, the mechanism of hydrogenation reaction of the Li–Mg–N–H system from 4Li<sub>2</sub>NH and Mg<sub>3</sub>N<sub>2</sub> to 3Mg(NH<sub>2</sub>)<sub>2</sub> and 8LiH was experimentally clarified in details [21]. Experimental results indicated that 4Li<sub>2</sub>NH was first hydrogenated into 4LiH and 4LiNH<sub>2</sub>. At the next step, 4LiNH<sub>2</sub> decomposed into 2Li<sub>2</sub>NH and 2NH<sub>3</sub>, and the liberated 2NH<sub>3</sub> reacted with (1/2)Mg<sub>3</sub>N<sub>2</sub> and produces (3/2)Mg(NH<sub>2</sub>)<sub>2</sub> phase, while the produced 2Li<sub>2</sub>NH was hydrogenated into 2LiH and 2LiNH<sub>2</sub> again. Such successive steps continued until all 4Li<sub>2</sub>NH and Mg<sub>3</sub>N<sub>2</sub> completely transformed into 8LiH and 3Mg(NH<sub>2</sub>)<sub>2</sub> by hydrogenation.

## 5. Summary

Therefore, the above results lead to the conclusion that the hydrogen absorption/desorption reactions in the metal–N–H systems reversibly progress with some multi-step ammonia mediated elementary reactions. On the other hand, the H-storage properties of the mixture composed of 6LiH and 3Mg(NH<sub>2</sub>)<sub>2</sub> have been consistently explained by the molecule–molecule reaction model between LiH and Mg(NH<sub>2</sub>)<sub>2</sub> proposed by Xiong et al. [22] without the mediation of the NH<sub>3</sub> molecule. However, the reaction model should be limited on the surfaces of both the solid phases. Therefore, it seems likely that at least the H-storage reaction mechanism in those composite materials may be originated in two or more fundamental reactions.

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