Guidelines for Developing Amide-Based Hydrogen Storage Materials

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An effective method for developing amide-based high-performance hydrogen storage materials is to prepare appropriate combinations of amides and hydrides. We have proposed that a mixture of an amide with a low decomposition temperature and a hydride showing rapid reaction to ammonia would be an appropriate combination. According to this proposal, the mixture of $Mg(NH_2)_2$ (Mg amide) and LiH (Li hydride) was investigated. The dehydriding temperature of the mixture of $Mg(NH_2)_2$ and 4·LiH is lower than that of the mixture of $LiNH_2$ (Li amide) and 2·LiH. A method for preventing ammonia release is increasing the LiH ratio in the mixtures, which results in a reduction in the amount of desorbed hydrogen. The homogeneous dispersion between $Mg(NH_2)_2$ and LiH might be also an important factor for preventing ammonia release.

1. Introduction

Hydrogen has attracted considerable attention as a new energy carrier for the development of clean and eco-friendly energy systems. For this purpose, hydrogen storage materials with high hydrogen densities (greater than 5–6 mass%) and low dehydriding temperatures (lower than 373 K) are important targets of the extensive developments.[1–3]

One of the candidates for hydrogen storage materials is the amide system. For example, $LiNH_2$ (Li amide) together with LiH (Li hydride) desorb hydrogen as follows:[4,5]

$$LiNH_2 + 2·LiH \leftrightarrow Li_2NH + LiH + H_2$$
$$\leftrightarrow Li_3N + 2·H_2 \quad (1)$$
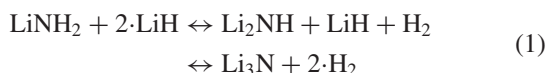
In the first- and second-step reactions, more than 5.2 and 5.4 mass% of hydrogen can be stored, which surpass the desired gravimetric hydrogen density. However, the dehydriding temperatures are approximately 470 and 700 K, respectively,[5] which are higher than the desirable temperatures. Therefore, the destabilizing of amide-based hydrogen storage materials in order to decrease the dehydriding temperature is one of the important research directions. For this purpose, the hydriding and dehydriding properties of various related systems, *e.g.* Li–Na–N–H,[6] Li–Mg–N–H,[7–12] Li–Ca–N–H,[11] Na–Mg–N–H[13] and Ca–N–H,[5,11,14] have been extensively investigated. Another important research direction is to clarify the method for preventing ammonia release.

In this study, from these two viewpoints, we investigate the stability of $M(NH_2)_x$ (M amide, $x = 1$ for $M =$ Li and Na, $x = 2$ for $M =$ Mg) and reactivity between MH_y (M hydride, $y = 1$ for $M =$ Li and Na, $y = 2$ for $M =$ Mg) and ammonia in order to choose an appropriate combination for decreasing the dehydriding temperature. We, then study the mixing ratio of the chosen amide and hydride for preventing ammonia

release. Here, we focus on Li, Na and Mg as light elements for M in order to maintain high gravimetric hydrogen density.

2. Experimental

$LiNH_2$, $NaNH_2$ (Na amide) and $Mg(NH_2)_2$ (Mg amide) were prepared as follows: Approximately 100 mg of MH_y (purchased from Cerac Co., Ltd. for LiH (99%) and Aldrich Co., Ltd. for NaH (95%) and MgH_2 (90% of hydride and 10% of Mg metal)) was manually milled by using an agate mortar and pestle; subsequently, it was placed inside a Mo crucible in a glove box filled with purified argon gas (dew point below 180 K). The crucible containing MH_y was then sealed within a reaction tube equipped with a connection valve for the evacuation and introduction of ammonia gas. After evacuation at 1×10^{-4} Pa, 0.5 MPa of ammonia gas (5N) was introduced into the reaction tube and heated. The details of the preparing conditions (heating temperature and time) are described in Section 3.1.3. The reactions are expressed as follows:

$$MH + NH_3 \rightarrow MNH_2 + H_2 \quad (M = Li, Na) \quad (2)$$
$$MH_2 + 2·NH_3 \rightarrow M(NH_2)_2 + 2·H_2 \quad (M = Mg) \quad (2)'$$
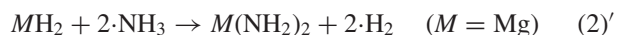
During the synthesis, we can measure the reactivity between MH_y and ammonia gas.

To investigate the dehydriding properties, the mixtures of $M(NH_2)_x$ and MH_y were prepared by the following two methods: *Method-1)* First, nitrides were prepared by gas-phase nitrogenation of metal M. The mixture of nitrides (M_3N_x and M_3N_y) was mechanically mixed for 24 h by planetary ball milling (Fritsch P-7) with 20 steel balls (7 mm in diameter) in a hardened steel vial (30 cm³ in volume) under purified argon gas at 0.1 MPa. The mixture was then hydrided for 4 h at 523 K under hydrogen gas at 35 MPa such as the hydriding reaction (from right to left) of eq. (5). *Method-2)* The prepared $M(NH_2)_x$ and purchased MH_y were mechanically mixed by planetary ball milling for 4 h under hydrogen gas at 1 MPa.

$M(NH_2)_x$ and mixture of $M(NH_2)_x$ and MH_y were

examined by powder X-ray diffraction measurement (PAN-alytical X'Pert with an X-ray wavelength of 0.154 nm and a synchrotron radiation beam with an X-ray wavelength of 0.08 nm in SPring-8 (BL19B2)), thermogravimetry (Rigaku, TG8120) and mass spectroscopy (Anelva M-QA200TS). The samples were always handled in a glove box filled with purified argon or helium gas. The details of the experimental procedure have been described elsewhere.[7,8,15,16]

3. Results and Discussion

3.1 Guideline for effective reaction between $M(NH_2)_x$ and MH_y

3.1.1 Dehydriding process

As a guideline for choosing the appropriate composition, we focused on the dehydriding process, which has been described by Hu *et al.*[17] and Ichikawa *et al.*,[18] as follows: In the first step, $M(NH_2)_x$ decompose to $M_{2/x}NH$ (M imide) and then to M_3N_x (M nitride) continuously with increasing temperature as follows:

$$M(NH_2)_x \rightarrow x/2{\cdot}M_{2/x}NH + x/2{\cdot}NH_3$$
$$\rightarrow 1/3{\cdot}M_3N_x + 2x/3{\cdot}NH_3 \qquad (3)$$
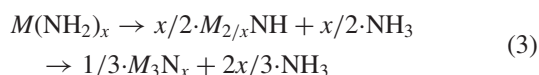
In this reaction, only ammonia can be desorbed. However, in the second step, ammonia reacts with MH_y resulting in only hydrogen being desorbed:

$$y{\cdot}NH_3 + MH_y \rightarrow M(NH_2)_y + y{\cdot}H_2 \qquad (4)$$

On the other hand, Chen *et al.*[19] have reported another dehydriding process of the mixture of $LiNH_2$ and LiH; in this process, the hydrogen in $LiNH_2$ is partially positively charged ($H^{\delta+}$). However, in LiH it is negatively charged ($H^{\delta-}$). The redox pair of $H^{\delta+}$ and $H^{\delta-}$ combines to form molecular hydrogen (H_2), and simultaneously, $N^{\delta-}$ and $Li^{\delta+}$ combine to form Li_3N. The process of the dehydriding reaction is currently under discussion. However, we focused on reactions (3) and (4) because these two reactions certainly proceed at least separately.[20] Based on reactions (3) and (4), we proposed that the mixture of $M(NH_2)_x$ with a low decomposition temperature and MH_y showing rapid reaction to ammonia is one of the appropriate combinations.

3.1.2 Decomposition reactions of $M(NH_2)_x$

The decomposition reactions of $M(NH_2)_x$ were examined by thermogravimetry; the results are shown in Fig. 1. The weight loss in $M(NH_2)_x$ was clearly observed at approximately 625, 670 and 600 K for $M =$ Li, Na and Mg, respectively. The value of the weight loss at 750 K for each sample is listed in Table 1. The calculated values of the weight loss corresponding to the decomposition reaction from $M(NH_2)_x$ to $M_{2/x}NH$ [reaction from left to center of eq. (3)] and from $M(NH_2)_x$ to M_3N_x [reaction from left to right of eq. (3)] are also shown in Table 1. The weight loss in $LiNH_2$ at 750 K is 36 mass%, which corresponds to the calculated value of the weight loss for the decomposition reaction to Li_2NH (Li imide). After heating up to 750 K, Li_2NH and small amount of $LiNH_2$ were observed in the powder X-ray diffraction profile, as shown in the inset of Fig. 1. The weight loss in $NaNH_2$ at 750 K is more than 50 mass%, which is greater than the calculated value. After measurement, the evaporation of the sample was visually
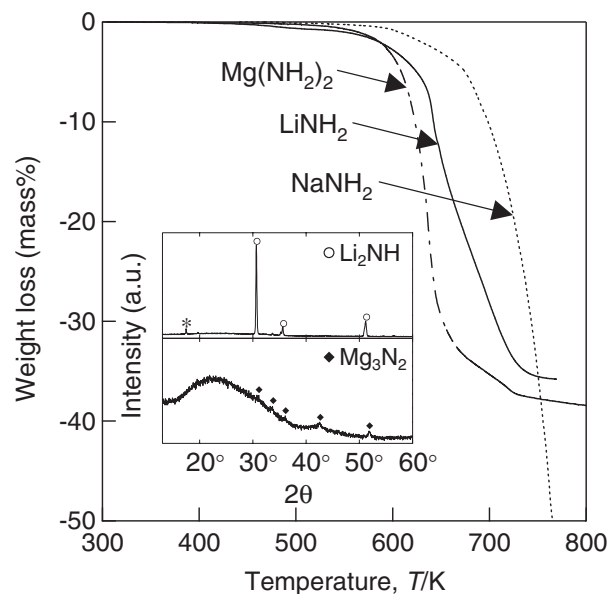

Fig. 1 Thermogravimetry of $M(NH_2)_x$ for $M =$ Li, Na and Mg under helium flow at 0.1 MPa with a heating rate of 5 K/min. The inset shows the powder X-ray diffraction profile after the dehydriding reaction of $LiNH_2$ and $Mg(NH_2)_2$. The X-ray wavelength is 0.154 nm. The open circles, asterisk and closed diamonds indicate the peak positions of Li_2NH, $LiNH_2$ and Mg_3N_2.

Table 1 The measured values of weight loss of $M(NH_2)_x$ for $M =$ Li, Na and Mg at 750 K in thermogravimetry shown in Fig. 1. The calculated values corresponding to the decomposition reaction from $M(NH_2)_x$ to $M_{2/x}NH$ [reaction from left to center of eq. (3)] and from $M(NH_2)_x$ to M_3N_x [reaction from left to right of eq. (3)] are also shown as references.

$M(NH_2)_x$	Weight loss (mass%)		
	Measured by TG	Calculated according to eq. (3)	
		$M(NH_2)_x$ to $M_{2/x}NH$	$M(NH_2)_x$ to M_3N_x
$LiNH_2$	36	37.8	49.4
$NaNH_2$	50~	21.8	29.1
$Mg(NH_2)_2$	38	30.2	40.3

observed in $NaNH_2$. On the other hand, the weight loss in $Mg(NH_2)_2$ is approximately 38 mass%, which corresponds to the calculated value of the weight loss for the decomposition reaction to Mg_3N_2. In fact, Mg_3N_2 was detected in the X-ray diffraction profile, as shown in the inset of Fig. 1. Based on these results, $Mg(NH_2)_2$ was chosen as the appropriate amide because it had a lower decomposition temperature and evolved larger amounts of desorbed ammonia as compared with $LiNH_2$ and $NaNH_2$.

3.1.3 Reactivity between MH_y and ammonia

The reactivity between the MH_y and ammonia was investigated in order to choose the appropriate MH_y in the second step for the generation of only desorbed hydrogen, according to eq. (4). For this purpose, manually milled MH_y were heated under ammonia at 0.5 MPa. In the powder X-ray diffraction profiles, it was observed that MH_y were converted into $M(NH_2)_y$ for $M =$ Li, Na and Mg, according to eq. (4), as shown in Fig. 2. The reaction temperature and reaction time for the progression of the reaction of eq. (4) to completion are listed in Table 2. If the reaction temperature is lower than that required for the completion of the reaction,
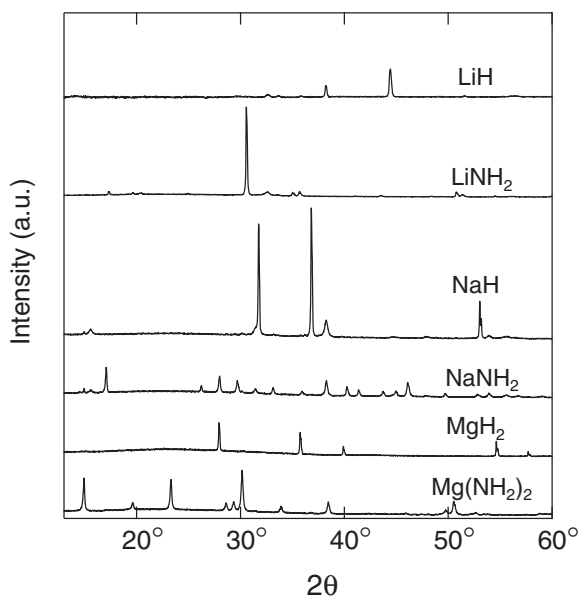
Fig. 2   Powder X-ray diffraction profiles of MH_y, and MH_y reacted with ammonia at 0.5 MPa (M = Li, Na and Mg). The reaction temperature and reaction time are shown in Table 2. The X-ray wavelength is 0.154 nm. All samples were identified as containing a single phase of LiH, LiNH$_2$, NaH, NaNH$_2$, MgH$_2$ and Mg(NH$_2$)$_2$.

Table 2   Reaction conditions between MH_y and ammonia at 0.5 MPa, according to eq. (4). The appropriate temperature and time for the progress of the reaction to completion were determined from the confirmation of $M(NH_2)_y$ as products in the powder X-ray diffraction profile and from no pressure change, respectively.

MH_y	Temp., T/K	Time, t/h
LiH	493	12
NaH	573	48
MgH$_2$	613	168

not only $M(NH_2)_y$ but also the starting material, MH_y, were observed in the powder X-ray diffraction profile. On the other hand, if the reaction temperature is higher, $M_{2/y}$NH (M imide) were also observed in the powder X-ray diffraction profile due to the decomposition reaction of $M(NH_2)y$, according to eq. (3)[7] (not shown). Therefore, the temperatures listed in Table 2 are the most appropriate ones for the progression of the reaction of eq. (4) under ammonia at 0.5 MPa to completion. The reaction time in Table 2 was determined from the pressure; no pressure change indicates that the reaction progressed to completion. Based on these results, we can conclude that LiH reacts with ammonia faster even at lower temperature than NaH and MgH$_2$ react. Hence, LiH would be better for MH_y, which is mixed with $M(NH_2)_x$.

3.2   Guideline for preventing ammonia release
3.2.1   Composition ratio and homogeneous dispersion

Based on the above results, the mixture of Mg(NH$_2$)$_2$ with a low decomposition temperature and LiH showing rapid reaction to ammonia was determined as one of the best combinations. The composition ratio of Mg(NH$_2$)$_2$ and LiH was then to be determined. We believe that the composition ratio of Mg(NH$_2$)$_2$ and LiH is closely related to the prevention of ammonia release because MH_y can transform

ammonia from $M(NH_2)_x$ into hydrogen according to eq. (4). According to eq. (3), the amount of ammonia released from Mg(NH$_2$)$_2$ is twice as great as that from LiNH$_2$. Therefore, it was expected that the molar quantity of LiH should be twice that of LiNH$_2$ in the mixture of Mg(NH$_2$)$_2$ and LiH for preventing ammonia release through the dehydriding reaction such as eq. (1). The hydriding and dehydriding reactions of the mixture of Mg(NH$_2$)$_2$ and LiH were predicted as follows:

$$Mg(NH_2)_2 + 4\cdot LiH \leftrightarrow 1/3\cdot Mg_3N_2 + 4/3\cdot Li_3N + 4\cdot H_2 \quad (5)$$

According to eq. (5), 9.1 mass% of hydrogen can be stored. To investigate the actual dehydriding reaction, the mixture of Mg(NH$_2$)$_2$ and 4·LiH (in molar ratio of 1:4) was prepared by hydrogenating the mixture of nitrides [*Method-1*: right to left reaction of eq. (5)]. Figure 3 shows the results of thermogravimetry of the mixture of Mg(NH$_2$)$_2$ and 4·LiH and that of the mixture of LiNH$_2$ and 2·LiH as a reference. As expected, the main weight loss in the mixture of Mg(NH$_2$)$_2$ and 4·LiH was observed below 500 K, which is a lower temperature than that in the case of the mixture of LiNH$_2$ and 2·LiH. It was also clarified by mass spectroscopy that desorbed gas contained only hydrogen with no ammonia as shown in the inset. The weight loss in the mixture of Mg(NH$_2$)$_2$ and 4·LiH at 800 K was approximately 7 mass%, which is 77% of the calculated value. A mixture of Mg$_3$N$_2$, Li$_3$N and a small amount of LiMgN were observed as phases after completion of the dehydriding reaction under vacuum[8] (not shown). These results indicate that eq. (5) contains the intermediate phases and the dehydriding reaction of Fig. 3 proceeds up to the intermediate phase.

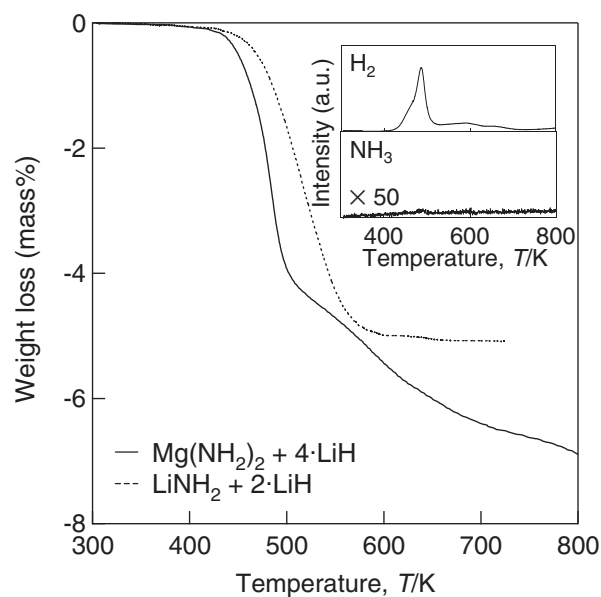Recently, the dehydriding reactions of the mixture of Mg(NH$_2$)$_2$ and LiH were reported for the other molar ratios, as follows:

Fig. 3   Thermogravimetry of the mixture of Mg(NH$_2$)$_2$ and 4·LiH under helium flow at 0.1 MPa with a heating rate of 5 K/min. The result for the mixture of LiNH$_2$ and 2·LiH is shown as a reference. The inset shows the signal of mass spectroscopy for H$_2$ and NH$_3$ of the mixture of Mg(NH$_2$)$_2$ and 4·LiH.
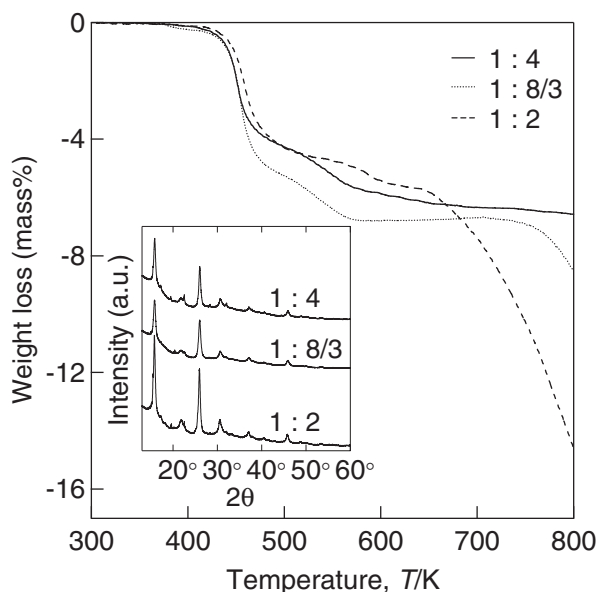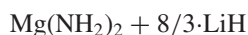
Fig. 4 Thermogravimetry of the mixtures of $Mg(NH_2)_2$ and LiH with molar ratios of 1:4, 1:8/3 and 1:2 under helium flow at 0.1 MPa with a heating rate of 5 K/min. The inset shows the powder X-ray diffraction profiles up to 513 K of the samples after the main dehydriding reaction. The X-ray wavelength is 0.08 nm.
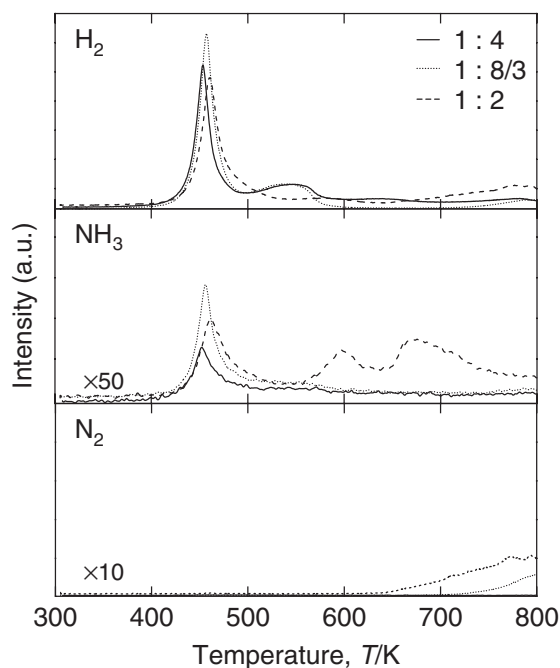

Fig. 5 Mass spectroscopy of the mixtures of $Mg(NH_2)_2$ and LiH with molar ratios of 1:4, 1:8/3 and 1:2 under helium flow at 0.1 MPa with a heating rate of 5 K/min.

$$Mg(NH_2)_2 + 8/3 \cdot LiH$$
$$\leftrightarrow 1/3 \cdot Mg_3N_2 + 4/3 \cdot Li_2NH + 8/3 \cdot H_2 \qquad (6)$$
$$Mg(NH_2)_2 + 2 \cdot LiH \leftrightarrow Li_2Mg(NH)_2 + 2 \cdot H_2 \qquad (7)$$

According to eqs. (6)[9,10] and (7),[11,12] 6.9 mass% and 5.6 mass% of hydrogen, respectively, can be stored. Mixtures of $Mg(NH_2)_2$ and LiH in molar ratios of 1:4, 1:8/3 (*i.e.* 1:2.66) and 1:2 were prepared by mechanical milling (*Method-2*). The dehydriding reactions were investigated by thermogravimetry and mass spectroscopy; the results are shown in Figs. 4 and 5, and are summarized in Fig. 6. The main dehydriding temperatures are approximately 460 K in all the mixtures with various molar ratios. Moreover, up to 513 K, the powder X-ray diffraction profiles after the main dehydriding reaction are similar to each other, as shown in the inset of Fig. 4. Hence, it is evident that all the dehydriding reactions have basically the same pathway in the mixtures with various molar ratios. However, in the mixtures with molar ratios of 1:8/3[9,10] and 1:2,[11,12] the dehydriding phases have been reported to be 'the mixture of Li_2NH and Mg_3N_2' and '$Li_2Mg(NH)_2$', respectively. The details of the intermediate phases during the dehydriding reaction are now being analyzed by the Rietveld method.

In the LiH-rich phase, the amount of desorbed hydrogen up to partial dehydriding phase at appropriate condition reduced as compared to that in the $Mg(NH_2)_2$-rich phases because LiH remained (see Fig. 6). On the other hand, in the $Mg(NH_2)_2$-rich phases of Fig. 6, *i.e.* the mixtures of $Mg(NH_2)_2$ and LiH with molar ratios of 1:8/3 and 1:2, weight losses greater than the calculated values were observed, as shown in Fig. 4. In addition, ammonia gas and its decomposition gases, hydrogen and nitrogen, were detected by mass spectroscopy, and the amount of these gases increased with an increase of $Mg(NH_2)_2$, as shown in

Fig. 6 Summary of the dehydriding and hydriding reactions of the mixtures of $Mg(NH_2)_2$ and LiH with molar ratios of 1:4, 1:8/3 and 1:2. *The precise intermediate phases are being investigated.

Fig. 5. This is due to the decomposition of the intermediate phase; *e.g.*, $Li_2Mg(NH)_2$ (product of second from the left in Fig. 6) decomposed to Li_2NH, $1/3 \cdot Mg_3N_2$ and $1/3 \cdot NH_3$ (second from the right in Fig. 6) then, Li_2NH decomposed to $2/3 \cdot Li_3N$ and $1/3 \cdot NH_3$ (extreme right in Fig. 6) especially at higher temperatures. Since LiH was absent, ammonia (and also hydrogen and nitrogen) desorbed. Therefore, increasing the amount of LiH in the mixture is one of the techniques for preventing ammonia release; however, the trade off in this case is the reduction in the amount of desorbed hydrogen.

However, a small amount of ammonia was also detected in the mixture of $Mg(NH_2)_2$ and LiH with a molar ratio of 1:4 prepared by *Method-2* (see Fig. 5), whereas almost no

ammonia was detected in the mixture with the same composition ratio prepared by *Method-1* (see inset of Fig. 3). This might be due to better homogeneous dispersion between $Mg(NH_2)_2$ and LiH in the mixture prepared by *Method-1* than in the mixture prepared by *Method-2*. Beside the dispersion, surface area and morphology of $Mg(NH_2)_2$ and LiH might be also important factors for preventing ammonia release.

4. Summary

Based on the reported dehydriding process, the mixture of $Mg(NH_2)_2$ and LiH was selected as the best combinations for decreasing the dehydriding temperature. Because, $Mg(NH_2)_2$ decomposes at low temperature and LiH rapidly reacts with ammonia. The dehydriding temperature of the mixture of $Mg(NH_2)_2$ and $4 \cdot LiH$ is lower than that of the mixture of $LiNH_2$ and $2 \cdot LiH$. Increasing the amount of LiH in the mixture is one of the important techniques for preventing ammonia release; however, the trade off in this case is the reduction in the amount of desorbed hydrogen. The homogeneous dispersion between $Mg(NH_2)_2$ and LiH might be also an important factor for preventing ammonia release.

Acknowledgements

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