

M-N-H Systems for High-Performance Hydrogen Storage (M = Alkaline and Alkaline Earth Metal)

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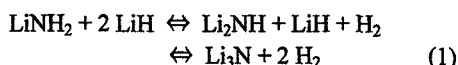
Non-transition metal complex hydrides, M-N-H systems, are recently regarded as potential candidates for high-performance hydrogen storage. The reversible dehydriding and rehydriding reactions of $\text{Mg}(\text{NH}_2)_2$ were successively investigated by mixing with an appropriate molar of LiH, in which more than 9 mass% of hydrogen can be stored. On the other hand, the mixtures of $\text{Mg}(\text{NH}_2)_2$ and MgH_2 desorb ammonia with increasing temperatures, similar to the decomposition reaction of $\text{Mg}(\text{NH}_2)_2$ alone. Therefore, LiH should be mixed with $\text{Mg}(\text{NH}_2)_2$ in order to suppress the desorption of ammonia, and to enhance the desorption of hydrogen.

Keywords: Hydrogen storage, Solid-gas reaction, Magnesium, Lithium, Amide

1. INTRODUCTION

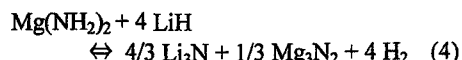
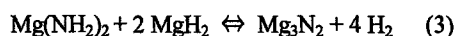
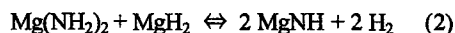
The hydrogen storage material is one of the important key issues for realizing the environment-friendly hydrogen energy system [1]. Recently, considerable attention has been paid to M-N-H systems for development of high-performance hydrogen storage [2-14].

For example, the mixture of LiNH_2 and 2 molars of LiH have been reported by Chen et al. [2], and the hydrogen storage (dehydriding) reactions were explained as follow;



The both reactions correspond to more than 5 mass% of hydrogen. The dehydriding reaction begins at approximately 423–473 K and 550 K in vacuum [2-4] and in argon [5-6], respectively. However, the reported temperatures are still higher than those desired, especially for polymer electrode fuel cells for which it is typically below 373 K.

We have already reported that an effective method for destabilization of LiNH_2 is to partially substitute Li by elements with larger electronegativity, such as Mg [5]. When the reaction begins, the dehydriding temperatures decrease to approximately 370 K with an increase in Mg concentration for MNH_2 with $M = \text{Li}-30 \text{ at.\%Mg}$ [6]. Therefore, it was predicted that $\text{Mg}(\text{NH}_2)_2$ exhibit similar effects to enhance the dehydriding reaction. A possible reaction of $\text{Mg}(\text{NH}_2)_2$ is expressed as follows [9,10],



In this study, we investigated the hydriding and dehydriding properties of $\text{Mg}(\text{NH}_2)_2$. Based on the experimental results, we propose good combination between amide and hydride for developing high-performance hydrogen storage materials in M-N-H systems.

2. EXPERIMENTAL

2.1 Sample preparation

Samples were prepared by the following two methods: *Method-1*) $\text{Mg}(\text{NH}_2)_2$ was prepared by reaction between MgH_2 and ammonia at 613 K for 1 week. Conceivable reactions are as follows:



$\text{Mg}(\text{NH}_2)_2$ thus prepared was mixed with 1 molar of MgH_2 , 2 molars of MgH_2 , to investigate the possible reactions of Eqs. (2)(3). *Method-2*) Li_3N and Mg_3N_2 were independently prepared by gas-phase nitrogeation of metallic Li and Mg, respectively. The mixtures of 4 molars of Li_3N and 1 molar of Mg_3N_2 were then heated up to 833 K under 0.1 MPa of nitrogen for 2 h, and successively, the nitrides were hydrided at 523 K under 35 MPa of hydrogen for 4 h to prepare $\text{Mg}(\text{NH}_2)_2$ mixed with 4 molars of LiH according to Eq. (4).

2.2 Sample characterization

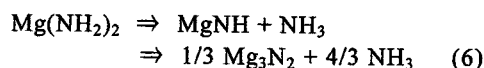
The dehydriding and hydriding reactions were examined by powder X-ray diffraction

measurement (PANalytical, X'PERT, Cu-K α), thermal desorption spectroscopy (TDS) detected by gas chromatography (GL Science, GC323, argon flow under 0.1 MPa with a heating rate of 10 K/min), and thermogravimetry and differential thermal analysis (TG-DTA, Bruker AXS, TG-DTA 2000SA, Ar flow under 0.1 MPa with a heating rate of 10 K/min). The sample was placed in a gas-tight container (equipped with gas-exchanging and heating unit for the TDS measurements) in the glove box to avoid the exposure to air, except for the TG-DTA measurements.

3. RESULTS AND DISCUSSION

3.1 Mg(NH₂)₂ mixed with MgH₂

First, the decomposition process of Mg(NH₂)₂ was examined by TG-DTA, as shown in Fig. 1 (a). The weight loss begins at approximately 400 K, and the decomposition reactions clearly occur at approximately 630 K and 720 K, corresponding to 25 mass% and 32 mass% of weight losses, respectively. After heating up to 873 K, only Mg₃N₂ was detected in the X-ray diffraction profile, as shown in the inset of Fig. 1. The two-step decomposition process of Mg(NH₂)₂ can be explained as follows:



he possible dehydriding reactions (left-to-right directions) in Eqs. (2) and (3) were examined by TG-DTA, and the results are also shown in Fig. 1 (b) and (c). The weight loss reactions clearly occur at approximately 630 K and 720 – 750 K.

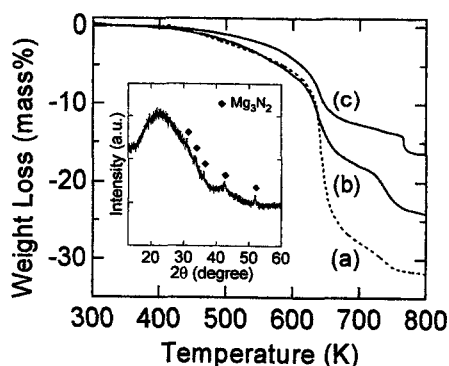


FIG. 1 Thermogravimetries of (a) Mg(NH₂)₂ mixed without MgH₂, (b) Mg(NH₂)₂ mixed with 1 molar of MgH₂ and (c) Mg(NH₂)₂ mixed with 2 molar of MgH₂ in argon flow at 0.1 MPa with a heating rate of 10 K/min. The samples were prepared by *Method-1*). The inset shows the powder X-ray diffraction profile after the measurement of (a) i.e., Mg(NH₂)₂ without MgH₂. The peak positions of Mg₃N₂ in ref. [15] were represented by closed diamonds.

The weight losses are approximately 24 mass% and 16 mass% for the Mg(NH₂)₂ with 1 molar of MgH₂ and the Mg(NH₂)₂ with 2 molar of MgH₂, respectively. However, these values are much larger than the estimated dehydriding reactions, 4.9 mass% and 7.4 mass% according to Eqs. (2) and (3), suggesting that not only hydrogen but also ammonia was desorbed during heating. Judging from these results, we infer that the mixture of Mg(NH₂)₂ and 1 molar of MgH₂ (or 2 molar of MgH₂) also decomposes similar to that of only Mg(NH₂)₂; first into MgNH at approximately 630 K, and then into Mg₃N₂ up to approximately 720 K.

3.2 Mg(NH₂)₂ mixed with LiH

In order to confirm the reaction according to Eq. (4), the sample was prepared by *Method 2*) (right-to-left direction of Eq. (4)). As shown in Fig. 2, the diffraction peaks of Mg₃N₂ and Li₃N were observed in the sample before hydriding reaction. Only the diffraction peaks corresponding to the mixture of Mg(NH₂)₂ and LiH were actually observed after the hydriding reaction. Moreover, only the diffraction peaks corresponding to the mixture of Mg₃N₂ and Li₃N were observed after the dehydriding reaction (left-to-right direction of Eq. (4)) in vacuum up to 750 K. These results indicated that the hydriding and dehydriding reactions proceed completely in accordance with Eq. (4).

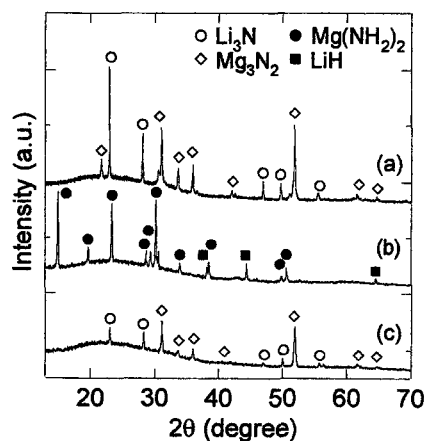


FIG. 2 Powder X-ray diffraction profiles of the samples prepared by *Method-2*); (a) before the hydriding reaction (right-term of Eq. (4)), (b) after the hydriding reaction (left-term of Eq.(4)), and (c) after the dehydriding reaction (again, right-term of Eq. (4)). The open circles, open diamonds, closed circles and closed squares show the peak positions of Li₃N, Mg₃N₂, Mg(NH₂)₂ and LiH in refs. [16], [15], [17] and [18], respectively.

The dehydriding reaction (left-to-right direction of Eq. (4)) was also examined by thermal desorption spectroscopy, as shown in Fig. 3. The dehydriding reaction begins at approximately 500 K and a sharp peak appears at approximately 680 K. Using gas chromatography, we have confirmed that the gas component from the sample is only hydrogen, without the formation of ammonia. From the result of thermogravimetry (not shown), the amount of desorbed hydrogen is approximately 8 mass% up to 700 K at a heating rate of 10 K/min under 0.1 MPa of argon, which corresponds to 89% of the estimated value (9 mass%) according to Eq. (4). Figure 3 also expresses the effects of milling together with catalysts prior to the hydriding reaction in *Method-2*). The sharp peak drastically decreases from 680 K to 540 K by 1 h-milling together with 1 mol% Ti. The milling conditions with catalysts will be optimized.

The preliminary results indicated that Eq. (4) contains at least two reaction steps as follows: In the first step, Li_3N reacts with hydrogen to form $\text{Li}_2\text{NH}/\text{LiNH}_2$ and $\text{LiH}/2 \text{ LiH}$ then, in the second step, $\text{Li}_2\text{NH}/\text{LiNH}_2$ reacts with Mg_3N_2 . Detailed mechanism of the reversible hydriding and dehydriding reaction of Eq. (4) is now being investigated by synchrotron radiation X-ray diffraction and neutron diffraction experiments.

Similar reactions of Eq. (4) have been also reported by National University of Singapore [11], Sandia National Laboratory [12] and Hiroshima University [13].

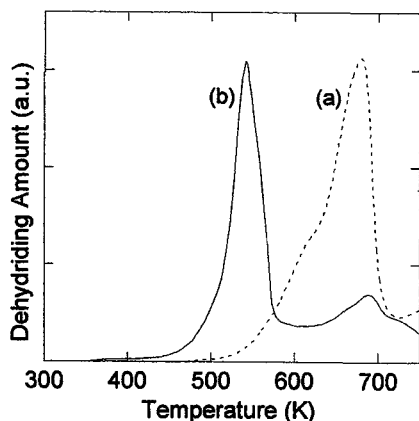


FIG. 3 Dehydriding profiles of the samples prepared by *Method-2*); (a) after the hydriding reaction (left-to-right direction of Eq. (4)), at a heating rate of 10 K/min under 0.1 MPa of argon. The sample (b) was 1 h-milled together with 1 mol% Ti prior to the hydriding reaction in *Method-2*).

3.3 Combination between amide and hydride

An effective method for development of hydrogen storage properties for *M-N-H* system is to choose good combination between amide and hydride. Among various combination, we have chosen $\text{Mg}(\text{NH}_2)_2$ mixed with LiH , which shown lower dehydriding reaction up to now.

The dehydriding reactions of the mixture of $\text{Mg}(\text{NH}_2)_2$ and MgH_2 cannot be confirmed, at least under the present condition with a heating rate of 10 K/min under 0.1 MPa of argon. The intrinsic reason is the limited kinetics of reaction between MgH_2 and ammonia to form $\text{Mg}(\text{NH}_2)_2$. As shown in ref. [10] in detail, it required approximately 1 week to form $\text{Mg}(\text{NH}_2)_2$ from MgH_2 completely, indicating that the reaction of MgH_2 with ammonia is in the order of day. On the other hand, it was reported that the reaction of LiH with ammonia is ultra-fast (25 ms) [14]. Therefore, LiH should be mixed with $\text{Mg}(\text{NH}_2)_2$ in order to suppress the desorption of ammonia, and to enhance the desorption of only hydrogen.

It should be emphasized that the dehydriding reaction of the mixture of $\text{Mg}(\text{NH}_2)_2$ and 4 molars of LiH begins at approximately 420 K under the present condition, while that of the mixture of LiNH_2 and 2 molars of LiH began at approximately 550 K with a heating rate of 10 K/min under 0.1 MPa of argon by gas chromatography [5]. The difference is due to the lower decomposition temperature of $\text{Mg}(\text{NH}_2)_2$ as compared to that of LiNH_2 , with respect to the formation of ammonia. Moreover, the mixed LiH could suppress the desorption of ammonia from $\text{Mg}(\text{NH}_2)_2$, and enhance the desorption of only hydrogen. From above results, we propose that amides with lower decomposition temperature and hydrides with faster reaction kinetics with ammonia should be chosen for developing high-performance hydrogen storage materials in *M-N-H* systems.

4. CONCLUSIONS

The reversible dehydriding and rehydriding reactions of $\text{Mg}(\text{NH}_2)_2$ were successively investigated by mixing with an appropriate molar of LiH , in which more than 9 mass% of hydrogen can be stored. On the other hand, with increasing temperature, the mixtures of $\text{Mg}(\text{NH}_2)_2$ and MgH_2 desorb ammonia, similar to the decomposition reaction of $\text{Mg}(\text{NH}_2)_2$ alone. Therefore, LiH should be mixed with $\text{Mg}(\text{NH}_2)_2$ in order to suppress the desorption of ammonia, and to enhance the desorption of only hydrogen, which due to the "ultra-fast" reaction of LiH with ammonia from $\text{Mg}(\text{NH}_2)_2$, unlike MgH_2 .

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