

Dehydriding and rehydriding properties of $\text{Mg}(\text{NH}_2)_2\text{-LiH}$ systems

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Abstract

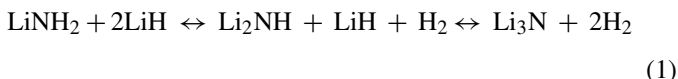
The dehydriding and rehydriding properties of the mixtures of $3\text{Mg}(\text{NH}_2)_2 + n\text{LiH}$ ($n = 6, 8, \text{ and } 12$) were investigated by pressure–composition (p – c) isotherm and X-ray diffraction (XRD) measurements in order to clarify the effects of the LiH ratio n on the properties. The amounts of the hydrogen desorbed from the mixtures with $n = 6, 8, \text{ and } 12$ were 5.4, 5.1, and 4.5 mass%, respectively; this indicates that the amounts on a unit mass basis decrease with increasing n . However, the molar ratios of the desorbed hydrogen to the mixtures estimated from the amounts were almost equal, and also the features of the p – c isotherms were similar to each other. Moreover, the $\text{Li}_2\text{Mg}(\text{NH})_2$ and LiH phases were observed in XRD profiles of all the mixtures after p – c isotherm measurements. These results suggest that the dehydriding reaction of the mixtures of $3\text{Mg}(\text{NH}_2)_2 + n\text{LiH}$ ($n = 6, 8, \text{ and } 12$) under hydrogen pressure is not dominantly affected by the value of n . On the other hand, the amounts of the ammonia desorbed from the mixtures detected by mass spectroscopy decreased with increasing n .
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1. Introduction

The use of hydrogen-based energy in practical applications such as fuel cell vehicles requires the development of safe and efficient hydrogen storage technology. Although metal hydrides hold promise for hydrogen storage because of their high volumetric hydrogen densities, those developed so far do not possess sufficient gravimetric hydrogen densities for automobile use. Therefore, much attention has been paid to hydrogen storage materials composed of light-element complex hydrides such as NaAlH_4 [1–3], $\text{LiNH}_2\text{-LiH}$ [4–11], $\text{LiBH}_4\text{-LiNH}_2$ [12,13] in recent years.

The $\text{LiNH}_2\text{-LiH}$ system has been reported as a promising candidate for hydrogen storage and the reversible reactions with hydrogen are shown in the following equation:



The reactions occur in two steps and more than 10 mass% of hydrogen is absorbed/desorbed in the overall reactions. How-

ever, the dehydriding temperatures of the first- and second-step reactions are still too high and the dehydriding plateau pressures are low for practical applications [4]. Many relevant studies on similar hydrogen storage systems such as Li-Mg-N-H [14–20], Li-Na-N-H [11], Li-Ca-N-H [15], and Mg-Na-N-H [21] have been performed to improve the dehydriding properties of the $\text{LiNH}_2\text{-LiH}$ system. As a result of those studies, it has been reported that the Li-Mg-N-H systems with various molar ratios such as $3\text{Mg}(\text{NH}_2)_2 + n\text{LiH}$ ($n = 6, 8, \text{ and } 12$) possess lower dehydriding temperatures than those of the $\text{LiNH}_2\text{-LiH}$ system. We have proposed the dehydriding reaction of the $3\text{Mg}(\text{NH}_2)_2 + 12\text{LiH}$ system under hydrogen pressure based on the results of the pressure–composition (p – c) isotherm and X-ray diffraction (XRD) measurements [20]. In the plateau region on the p – c isotherm, $\text{Mg}(\text{NH}_2)_2$, $\text{Li}_4\text{Mg}_3(\text{NH}_2)_2(\text{NH})_4$, and LiH phases coexist and the molar ratio of the $\text{Li}_4\text{Mg}_3(\text{NH}_2)_2(\text{NH})_4$ phase increases (while those of $\text{Mg}(\text{NH}_2)_2$ and LiH phases decrease) with the amount of the desorbed hydrogen. On the other hand, the mixture of $\text{Li}_{4+x}\text{Mg}_3(\text{NH}_2)_{2-x}(\text{NH})_{4+x} + (8-x)\text{LiH}$ ($0 \leq x \leq 2$) is formed in the sloping region on the p – c isotherm.

In the present work, the p – c isotherm and XRD measurements of the mixtures of the $3\text{Mg}(\text{NH}_2)_2 + n\text{LiH}$ ($n = 6, 8, \text{ and } 12$) were performed in order to clarify the effects of the LiH ratio n on

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the dehydriding and rehydriding properties. Furthermore, the ammonia gas desorption during dehydrogenation of the mixtures was examined using thermal desorption mass spectroscopy.

2. Experimental

The starting materials of LiH (purity 95%) and MgH₂ (purity 98%) were purchased from Sigma–Aldrich and AVOCADO, respectively. Mg(NH₂)₂ was synthesized by the reaction of MgH₂ with ammonia gas as follows [22]: in a glove-box filled with purified argon gas (dew point below 180 K), MgH₂ was put into a Mo crucible and then the crucible was placed in a reaction tube equipped with a connection valve for evacuation and introduction of ammonia gas. After evacuation, 0.5 MPa of ammonia gas (purity 99.999%) was introduced into the reaction tube and the tube was heated at 603 K for 12 days. The mixtures of 3Mg(NH₂)₂ + nLiH (*n* = 6, 8, and 12) were prepared using an agate pestle and mortar by hand. Then, the mixtures were mechanically milled for 2 h under a hydrogen pressure (purity 99.9999%) of 1 MPa using a planetary ball mill (Fritsch P-5).

The dehydriding/rehydriding properties and the ammonia gas desorption during dehydrogenation of the mixtures were examined by the *p*–*c* isotherm measurement, XRD analysis (Rigaku RINT-TTR), and thermal desorption mass spectroscopy (Anelva M-QA200TS). The conventional volumetric method with a Sieverts apparatus (Suzuki Shokan Co., Ltd.) was used to obtain *p*–*c* isotherms at 523 K. The equilibrium criterion during *p*–*c* isotherm measurement was set as follows:

$$\Delta A_H < 0.05 \quad (2)$$

with

$$A_H (\text{mass}\%) = \frac{M_H}{M_M} \times 100 \quad (3)$$

where ΔA_H is the amount of the absorbed/desorbed hydrogen (A_H) during a day, and M_H and M_M represent the mass of the absorbed/desorbed hydrogen and the mixtures of 3Mg(NH₂)₂ + nLiH (*n* = 6, 8, and 12), respectively. The XRD measurements were carried out with Cu K α radiation at room temperature, and the diffraction patterns were analyzed by the Rietveld method using a computer program RIETAN [23]. Thermal desorption mass spectroscopy was performed under helium gas flow with a heating rate of 5 K/min and the equipment was installed inside the glove box.

3. Results and discussion

3.1. Dehydriding properties of 3Mg(NH₂)₂ + nLiH (*n* = 6, 8, and 12)

Fig. 1 shows the *p*–*c* isotherms of the mixtures of 3Mg(NH₂)₂ + nLiH (*n* = 6, 8, and 12) during dehydriding at 523 K. Total amounts of the hydrogen desorbed from the mixtures with *n* = 6, 8, and 12 were 5.4, 5.1, and 4.5 mass%, respectively. Although the amounts on a unit mass basis decrease with increasing *n*, the molar ratios of hydrogen molecule desorbed from mixtures of 3Mg(NH₂)₂ + nLiH (*n* = 6, 8, and 12) to the mixtures, H₂/(3Mg(NH₂)₂ + nLiH) (*n* = 6, 8, and 12), estimated from the amounts are almost equal (5.8/1, 5.9/1, 5.9/1, respectively). Two distinct regions, a plateau region (A–B in Fig. 1) and a sloping region (B–C in Fig. 1), can be seen on the isotherms of all the mixtures. The plateau pressures were almost equal (around 7 MPa) and approximately 2/3 of total amount of the desorbed hydrogen was desorbed with the plateau on the isotherms. In addition, the remainder (approximately 1/3) was desorbed in the sloping region on the isotherms. These features of the isotherms, which are similar to those of the

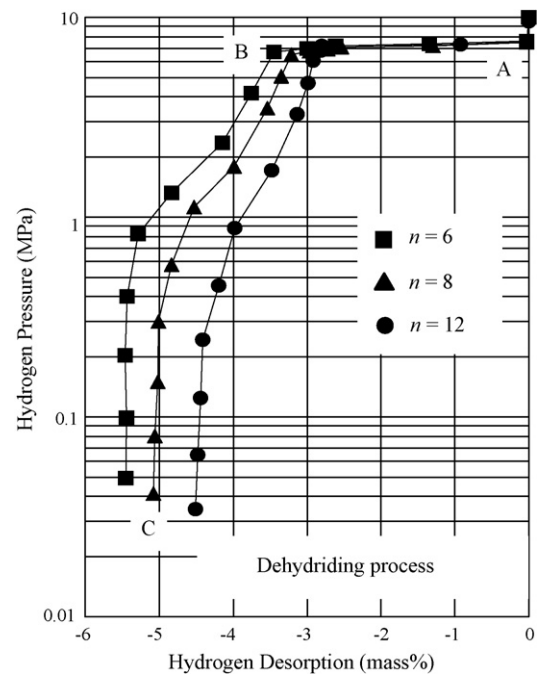
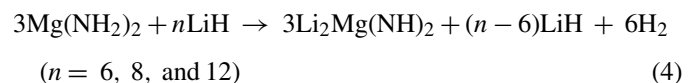


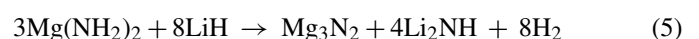
Fig. 1. The *p*–*c* isotherms of the mixtures of 3Mg(NH₂)₂ + nLiH (*n* = 6, 8, and 12) during dehydriding at 523 K. Points A, B, and C mark the beginning of plateau region, the end of plateau region, and the end of sloping region on the isotherms, respectively.

3Mg(NH₂)₂ + 6LiH system reported by Luo and coworkers [14], imply that the dehydriding reactions under hydrogen pressure of the 3Mg(NH₂)₂ + nLiH (*n* = 6 and 8) systems are similar to that of the 3Mg(NH₂)₂ + 12LiH system as proposed in our previous work [20].

The powder XRD profiles of the mixtures of the 3Mg(NH₂)₂ + nLiH (*n* = 6, 8, and 12) after *p*–*c* isotherm measurements (point C in Fig. 1) are shown in Fig. 2. Here, the amorphous-like background in the diffraction profiles is due to the tape used to avoid the exposure of the sample to air during the XRD measurement. The diffraction peaks of Li₂Mg(NH)₂ [14,20] and LiH phases are seen in the profiles of all the mixtures. The diffraction intensity of the LiH phase increased with increasing *n* and it was revealed by Rietveld analysis of the diffraction profiles that the molar ratio of the LiH phase to the Li₂Mg(NH)₂ phase increases with increasing *n*. Based on this result of XRD measurement, the amounts of the desorbed hydrogen, and chemical valences of Li, Mg, N, and H, the dehydriding process of the 3Mg(NH₂)₂ + nLiH (*n* = 6, 8, and 12) systems under hydrogen pressure is proposed as follows:



The dehydrogenation of 3Li₂Mg(NH)₂ + (n – 6)LiH (*n* = 6, 8, and 12) systems was not observed at 523 K (Figs. 1 and 2); this indicates that the dehydriding reactions of 3Mg(NH₂)₂ + nLiH (*n* = 8 and 12) systems as shown in the following equations [17,19] occur at higher temperatures:



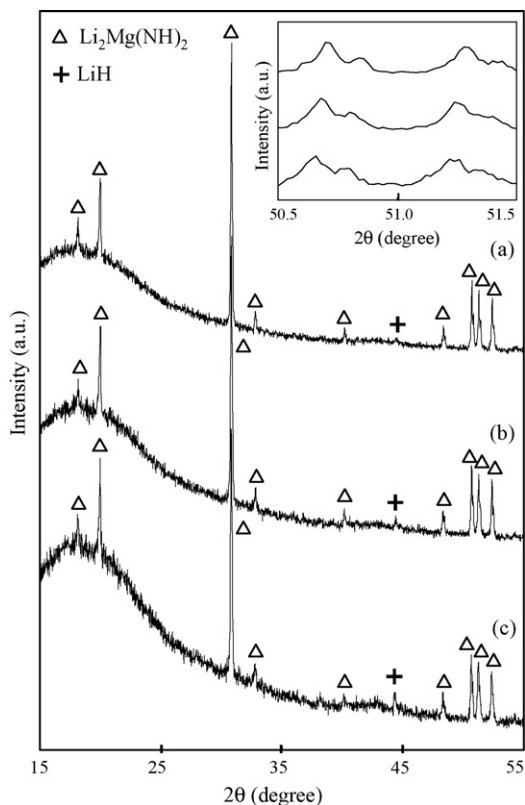


Fig. 2. Powder X-ray diffraction profiles of the mixtures of (a) $3\text{Mg}(\text{NH}_2)_2 + 6\text{LiH}$, (b) $3\text{Mg}(\text{NH}_2)_2 + 8\text{LiH}$, and (c) $3\text{Mg}(\text{NH}_2)_2 + 12\text{LiH}$ after dehydrogenation as the p - c isotherm measurements were carried out to point C in Fig. 1, respectively. Open triangles and crosses show the peak positions of the $\text{Li}_2\text{Mg}(\text{NH}_2)_2$ phase and the LiH phase, respectively. The enlargement profiles of the region from 50.5° to 51.5° are shown in the inset.



On the other hand, the peak positions of the $\text{Li}_2\text{Mg}(\text{NH}_2)_2$ phase slightly shift to lower angles with increasing n . For example, the enlargement profiles of the region from 50.5° to 51.5° are shown in the inset. The lattice parameters and the lattice volume of the $\text{Li}_2\text{Mg}(\text{NH}_2)_2$ phase estimated from Fig. 2a–c are summarized in Table 1. The lattice parameters and the lattice volume very slightly increase with increasing n , although the volume expansion is less than 0.3%.

Fig. 3 shows thermal desorption mass spectra of ammonia desorbed during dehydrogenation of the mixtures of $3\text{Mg}(\text{NH}_2)_2 + n\text{LiH}$ ($n = 6, 8, \text{ and } 12$). Although the ammonia desorption was detected for all the mixtures, the signal

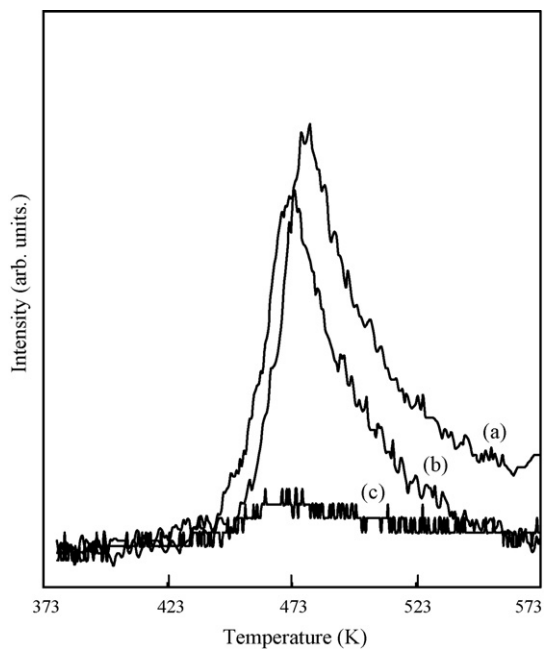


Fig. 3. Thermal desorption mass spectra of ammonia desorbed from the mixtures of (a) $3\text{Mg}(\text{NH}_2)_2 + 6\text{LiH}$, (b) $3\text{Mg}(\text{NH}_2)_2 + 8\text{LiH}$, and (c) $3\text{Mg}(\text{NH}_2)_2 + 12\text{LiH}$, respectively.

intensity decreased with increasing n . In particular, the signal intensity of the desorbed ammonia for $3\text{Mg}(\text{NH}_2)_2 + 12\text{LiH}$ was much smaller than those for $3\text{Mg}(\text{NH}_2)_2 + 6\text{LiH}$ and $3\text{Mg}(\text{NH}_2)_2 + 8\text{LiH}$. This result suggests that the increase of n has an effect on decreasing the amount of ammonia desorbed from the mixture of $3\text{Mg}(\text{NH}_2)_2 + n\text{LiH}$. We are investigating the ammonia desorption from the mixtures of $3\text{Mg}(\text{NH}_2)_2 + n\text{LiH}$ ($n = 6, 8, \text{ and } 12$) under hydrogen pressure by FT-IR spectroscopy.

3.2. Rehydriding property of $3\text{Mg}(\text{NH}_2)_2 + 12\text{LiH}$

The p - c isotherms of the mixture of $3\text{Mg}(\text{NH}_2)_2 + 12\text{LiH}$ during dehydriding and rehydriding at 523 K are shown in Fig. 4. The reversible hydrogenation/dehydrogenation of the mixture at 523 K was confirmed by the isotherms. The isotherm during rehydriding was similar to that during dehydriding although small hysteresis was observed for the two regions (A and B in Fig. 4). The isotherms imply that the reaction of the mixture of $3\text{Mg}(\text{NH}_2)_2 + 12\text{LiH}$ with hydrogen proposed in our previous work [20] occurs reversibly.

Table 1
Lattice parameters and the lattice volume of the $\text{Li}_2\text{Mg}(\text{NH}_2)_2$ phase observed in the diffraction profiles of the mixtures of $3\text{Mg}(\text{NH}_2)_2 + n\text{LiH}$ ($n = 6, 8, \text{ and } 12$) after dehydrogenation (a–c)

	Lattice parameters (\AA)			Lattice volume (\AA^3)
	<i>a</i>	<i>b</i>	<i>c</i>	
$3\text{Mg}(\text{NH}_2)_2 + 6\text{LiH}$	9.776 (1)	4.988 (1) Fig. 2	5.197 (1)	253.4 (1)
$3\text{Mg}(\text{NH}_2)_2 + 8\text{LiH}$	9.781 (1)	4.989 (1)	5.200 (1)	253.7 (1)
$3\text{Mg}(\text{NH}_2)_2 + 12\text{LiH}$	9.784 (1)	4.992 (1)	5.202 (1)	254.1 (1)

Standard deviations are given in parentheses.

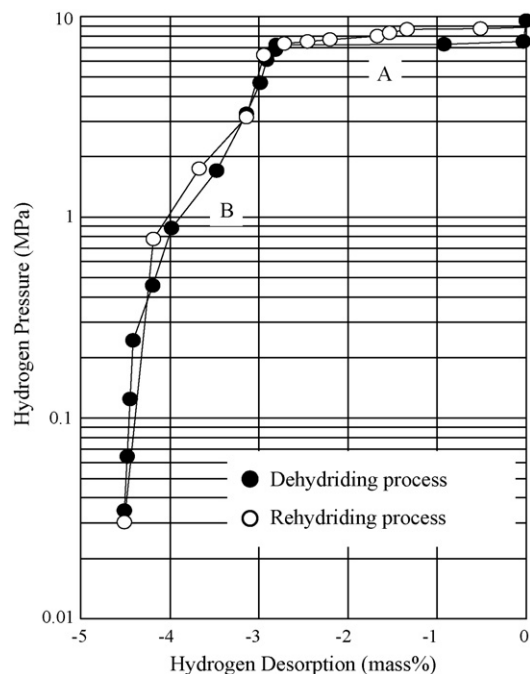


Fig. 4. The p - c isotherms of the mixture of $3\text{Mg}(\text{NH}_2)_2 + 12\text{LiH}$ during dehydrating and rehydrating at 523 K.

4. Conclusions

The dehydrating and rehydrating properties of the mixtures of $3\text{Mg}(\text{NH}_2)_2 + n\text{LiH}$ ($n = 6, 8,$ and 12) were investigated by p - c isotherm and XRD measurements in order to clarify the effects of the LiH ratio n on the properties. The amounts of the hydrogen desorbed from the mixtures with $n = 6, 8,$ and 12 on a unit mass basis decreased with increasing n . However, the molar ratios of the desorbed hydrogen to the mixtures were almost equal, and also the features of the p - c isotherms were similar to each other. Moreover, the $\text{Li}_2\text{Mg}(\text{NH}_2)_2$ and LiH phases were observed in XRD profiles of all the mixtures after the p - c isotherm measurements. These results suggest that the dehydrating reaction of the mixtures of $3\text{Mg}(\text{NH}_2)_2 + n\text{LiH}$ ($n = 6, 8,$ and 12) under hydrogen pressure is not dominantly affected by the value of n . On the other hand, the signal intensity of ammonia desorbed from the mixtures detected by thermal desorption mass spectroscopy decreased with increasing n ; this implies that the increase of n

has an effect on decreasing the amount of ammonia desorbed from the mixture of $3\text{Mg}(\text{NH}_2)_2 + n\text{LiH}$.

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References

- [1] B. Bogdanović, M. Schwickardi, *J. Alloys Compd.* 253–254 (1997) 1–9.
- [2] C.M. Jensen, K.J. Gross, *Appl. Phys. A* 72 (2001) 213–219.
- [3] G. Sandrock, K. Gross, G. Thomas, *J. Alloys Compd.* 339 (2002) 299–308.
- [4] P. Chen, Z. Xiong, J. Luo, J. Lin, K.L. Tan, *Nature* 420 (2002) 302–304.
- [5] P. Chen, Z. Xiong, J. Luo, J. Lin, K.L. Tan, *J. Phys. Chem. B* 107 (2003) 10967–10970.
- [6] Y. Nakamori, S. Orimo, *J. Alloys Compd.* 370 (2004) 271–275.
- [7] S. Orimo, Y. Nakamori, G. Kitahara, K. Miwa, N. Ohba, T. Noritake, S. Towata, *Appl. Phys. A* 79 (2004) 1765–1767.
- [8] Y.H. Hu, E. Ruckenstein, *Ind. Eng. Chem. Res.* 42 (2003) 5135–5139.
- [9] Y.H. Hu, E. Ruckenstein, *J. Phys. Chem. A* 107 (2003) 9737–9739.
- [10] T. Ichikawa, S. Isobe, N. Hanada, H. Fujii, *J. Alloys Compd.* 365 (2004) 271–276.
- [11] T. Ichikawa, N. Hanada, S. Isobe, H. Leng, H. Fujii, *J. Phys. Chem. B* 108 (2004) 7887–7892.
- [12] F.E. Pinkerton, G.P. Meisner, M.S. Meyer, M.P. Balogh, M.D. Kundrat, *J. Phys. Chem. B* 109 (2005) 6–8.
- [13] M. Aoki, K. Miwa, T. Noritake, G. Kitahara, Y. Nakamori, S. Orimo, S. Towata, *Appl. Phys. A* 80 (2005) 1409–1412.
- [14] W. Luo, *J. Alloys Compd.* 381 (2004) 284–287.
- [15] Z. Xiong, G. Wu, J. Hu, P. Chen, *Adv. Mater.* 16 (2004) 1522–1525.
- [16] Y. Nakamori, G. Kitahara, K. Miwa, S. Towata, S. Orimo, *Appl. Phys. A* 80 (2005) 1–3.
- [17] Y. Nakamori, G. Kitahara, A. Ninomiya, M. Aoki, T. Noritake, S. Towata, S. Orimo, *Mater. Trans.* 46 (2005) 2093–2097.
- [18] T. Ichikawa, K. Tokoyoda, H. Leng, H. Fujii, *J. Alloys Compd.* 400 (2005) 245–248.
- [19] H. Leng, T. Ichikawa, S. Hino, T. Nakagawa, H. Fujii, *J. Phys. Chem. B* 109 (2005) 10744–10748.
- [20] M. Aoki, T. Noritake, G. Kitahara, Y. Nakamori, S. Towata, S. Orimo, *J. Alloys Compd.* 428 (2007) 307–311.
- [21] Z. Xiong, J. Hu, G. Wu, P. Chen, *J. Alloys Compd.* 395 (2005) 209–212.
- [22] Y. Nakamori, G. Kitahara, S. Orimo, *J. Power Sources* 138 (2004) 309.
- [23] F. Izumi, in: R.A. Young (Ed.), *The Rietveld Method*, Oxford University Press, Oxford, UK, 1993 (Chapter 13).