Hydrogen Absorption Properties of Li-Mg-N-H System

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ABSTRACT

Isothermal hydrogen absorption properties of the ball milled mixture of 3$Mg(NH_2)_2$ and 8LiH after dehydrogenation at 200 °C under high vacuum were investigated at two different temperatures of 150 and 200 °C. The pressure –composition isotherm (PCT) curve at 200 °C revealed a two-plateaus-like behavior, while the PCT curve at 150 °C showed a single-plateau-like behavior. The hydrogenated phases were composed of LiH and $Mg(NH_2)_2$ under 9 MPa at 200 °C, while those were observed as mixed phases of LiH and $LiNH_2$ at 150 °C without any trace of $Mg(NH_2)_2$ in XRD measurements. These results indicate that there are 2 step hydrogenation processes corresponding to high and low pressures at 200 °C, but the kinetics at 150 °C is too slow to proceed with the second hydrogenating step at high pressure region.

KEYWORDS: Hydrogen storage materials (A), Gas-solid reactions (B), High-energy ball milling(B), Mechanochemical synthesis (B), Thermal analysis (D)

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1. Introduction

Since the hydrogen storage (H-storage) properties of the Li-N-H system was reported by Chen et al.[1] as a new family of promising hydrogen storage materials, many relevant studies have been performed to understand and improve their H-storage properties all over the world[2~13]. As a result of those investigations, the similar hydrogen storage systems i.e. Li-Mg-N-H systems have been independently designed by Luo[14], Leng et al.[15], Xiong et al.[16] and Nakamori et al.[17] at almost the same time. The Li-Mg-N-H systems are essentially composed of magnesium amide $Mg(NH_2)_2$ and lithium hydride LiH as the H-storage state, and the difference among these materials is only in the molar ratio of $Mg(NH_2)_2$ and LiH, that is,

$$3\,Mg(NH_2)_2 + 6\,LiH \leftrightarrow 3\,Li_2Mg(NH)_2 + 6\,H_2 \qquad (1)$$

$$3\,Mg(NH_2)_2 + 8\,LiH \leftrightarrow 4Li_2NH + Mg_3N_2 + 8\,H_2 \qquad (2)$$

$$3\,Mg(NH_2)_2 + 12\,LiH \leftrightarrow 4\,Li_3N + Mg_3N_2 + 12\,H_2. \qquad (3)$$

The reactions (1), (2) and (3) have been respectively reported by Luo and Xiong et al., Leng et al. and Nakamori et al. Although the hydrogen capacity increases from 5.6 to 9.1 mass% with the increasing ratio of LiH to $Mg(NH_2)_2$, the temperature for the complete hydrogen desorption increases from about 150 to more than 500 ºC with the increasing ratio due to their stabilities. In our group, special attention has been paid to the system with the 3:8 molar ratio of $Mg(NH_2)_2$ and LiH as one of the most promising hydrogen storage systems, because it was expected to have a relatively high hydrogen capacity (6.9 mass%) and a relatively lower operating temperature (< 200 ºC) on the basis of the ammonia mediated reaction model[7]. In our experiments, only the hydrogen desorption properties under a zero hydrogen partial pressure have been reported with respect to the 3:8 system so far[15].

In this paper, we report experimental results on the isothermal hydrogen absorption properties of the reaction (2), in which the PCT profiles in H-absorption process under a waiting time of 1 h were determined at 150 and 200 ºC, and finally the phase transformation in this system during hydrogenation is briefly discussed.

2. Experimental

The starting materials, LiH (95 mass% purity) and MgH_2 (90 mass% purity) were purchased from Sigma Aldrich. Main impurities in LiH are Li_2O and LiOH, while those in MgH_2 are ~9 mass% of non-reacting Mg and ~1 mass% of MgO. In this work, $Mg(NH_2)_2$ was mechanochemically synthesized from MgH_2 powder by ball milling in pure NH_3 (0.4 MPa) gas. The mechanical milling was performed for 12 h at room temperature by using a rocking mill equipment (SEIWA GIKEN Co., Ltd. RM-10) with a frequency of 10 Hz. The mixture of $3Mg(NH_2)_2$ and 8LiH was prepared by using a planetary ball mill equipment (Fritsch, P7) with 400 rpm for 2 h at room temperature. Prior to measurements of the PCT curve, dehydrogenation of the sample was performed by heat-treatment at 200 ºC for 12 h under high vacuum below $1x10^{-4}$ Pa.

Hydrogen absorption properties of the dehydrogenated sample were examined by a hand made compact Sievert's type apparatus, which is schematically shown in Figure 1. The apparatus is composed of a reservoir tank, a sample cell, two pressure sensors A and B, and two valves, which are connected with stainless steel tubes. The PCT examinations were performed under two different isothermal conditions of 150 and 200 °C, which was accurately controlled within ±0.1 °C by a temperature controller (Shinko Technos Co. Ltd., Temperature Control unit). The volume of the reservoir tank V_{RES}, including the pressure sensor A, is ~ 78 cm^3, while the sample cell with pressure sensor B is ~ 10 cm^3. Before performing the PCT examination, the total volume of V_{HT} and V_{RT}, and its ratio were measured. The pressure sensors (Druck Ltd. DPI280) were expressed to be very accurate in the wide range from 0.100 to 15.000 MPa. In the present study, we used the NIST12 software as an equation of state corresponding to hydrogen gaseous phase to calculate hydrogen concentration absorbed in the sample, which is provided by the National Institute of Standards and Technology (NIST), USA.

The amount of the hydrogen absorption was evaluated according to the following procedures. After the dehydrogenated sample of ~ 0.13 g was set into the sample cell with the volume V_{HT} in Fig. 1, the sample cell and the reservoir tank were evacuated down to $1x10^{-4}$ Pa, and the sample part was heated up to 150 or 200 °C. After that, for each hydrogenating step, gaseous hydrogen (99.99999 % purity) was introduced into the reservoir tank up to 10 MPa by opening the V_1 valve, and then the V_2 valve, which combines with the sample cell and the reservoir tank, was opened. After passing several minutes, the V_2 valve was again closed and the pressures were monitored by both the pressure sensors for 1 h. Generally, the kinetics of hydrogenation and dehydrogenation on the Li-N-H system, where the reaction proceeds with a disproportionation, is considered to be so slow that the waiting time for the each measuring point in the PCT curve has to be long enough for reaching an equilibrium condition. In this work, we terminated the waiting time at 1 h. Finally, the amount of hydrogen absorption was determined from the difference between the pressures before opening the V_2 valve and after waiting for 1h. We tried to determine the PCT curve in the H-desorption process as well, but failed to get the reliable PCT data at lower temperature than 200 °C because of a slow kinetics in the H-released process under a finite H_2 pressure without catalyst. Then, the hydrogen desorption properties of the samples before and after the PCT experiments were examined by a thermal desorption mass spectroscopy (TDMS, Anelva, M-QA200TS) combined with thermogravimetry (TG, Rigaku, TG8120) in the heating process up to 450 °C at a heating rate of 5 °C/min under a highly pure helium (purity > 99.9999%) flow.

In this work, all the experimental processes from the sample preparation to the examination of H-storage properties were performed in the glovebox filled with a purified argon gas without exposing the sample to air at all. The identification of phases in the samples was carried out by X-ray powder diffraction (XRD) with Cu Kα radiation (Rigaku, RINT-2500).

3. Results and Discussion

Pressure-composition isotherm (PCT) curves of hydrogen absorption at 150 and 200 °C under the condition of the 1 h waiting time are shown in Figure 2. Here, the PCT examinations at 200 °C were independently twice performed by using the samples from different batches. Unfortunately, those examinations can not be regarded as “the real PCT measurement”, because the waiting time of 1 h was not long enough for reaching equilibrium condition of hydrogen absorption. However, the PCT curves obtained in this work give outline of the real PCT profile and basic information for improving the fundamental reaction as one of the practical hydrogen storage systems.

As shown in Fig. 2, we notice that a two-plateaus-like structure appears in the PCT curves at 200 °C. Two-plateaus pressures should be lower than 1 MPa and 6 MPa, respectively, because the much longer waiting time leads to the much lower equilibrium pressure. On the other hand, such a two-plateaus-like behavior is not found in the PCT curve at 150 °C, where the equilibrium pressure seems to be lower than 1 MPa as well, corresponding to the lower plateau-like pressure at 200 °C. Although the waiting time of 1 h is not long enough to reach the equilibrium pressure, the difference of the PCT curves between 150 and 200 °C seems to be essential. Particularly, the hydrogen concentration in the PCT curve at 200 °C reaches up to 5.5 mass% at the H_2 gas pressure of 9 MPa, but that at 150 °C reaches to only 3.5 mass% at the same pressure.

The hydrogen concentration of 5.5 mass% at 200 °C under 9 MPa is lower than the expected value (~ 6.9 mass%) from the reaction (2). To clarify the reason, the TDMS and TG spectra were examined for the sample after dehydrogenating at 200 °C for 12 h under a high vacuum below $1\text{x}10^{-4}$ Pa. As is shown in Figure 3 (a), a small amount of hydrogen (~1.2 mass%) are desorbed at higher temperature than 250 °C, indicating incomplete dehydrogenation of the 3:8 milled mixture by heat-treatment at 200 °C for 12 h under the high vacuum condition, and a small amount of hydrogen has remained in the samples. Therefore, the amount 5.5 mass% observed in Fig. 2 at 200 °C can be regarded to be fully hydrogenated under 9 MPa. However, the amount of 3.5 mass% at 150 °C can be regarded not to completely be hydrogenated.

In addition, the hydrogen desorption properties of the sample after the PCT examinations at 150 and 200 °C under 9 MPa were examined in this work. As is shown in Figs. 3 (b) and (c), it is confirmed by the corresponding weight loss of about 7 mass% in the heating process up to 450 °C that the sample is almost fully hydrogenated at 200 °C under 9 MPa, while the weight loss after the PCT examination at 150 °C under 9 MPa is only 5 mass%, indicating incomplete hydrogenation. However, it is to be noted that the onset temperature of hydrogen desorption after hydrogenation at 150 °C is lower than that at 200 °C.

To identify the phases in both the hydrogenated samples after the examination of the PCT curves at 200 and 150 °C, their structural properties were examined by the XRD measurements. The XRD profiles after hydrogenating the samples at 200 and 150 °C were shown in Figures 4(b) and (c), respectively. In this figure, the XRD profile (a) is also shown for the dehydrogenated sample at 200 °C before examining the PCT curve. Although the dehydrogenated sample should be composed of the mixed phases of Li_2NH and Mg_3N_2, only the Li_2NH phase can be found in Fig.4 (a). Actually, the previous results indicated that the dehydrogenated state of this product was the mixed phases of Li_2NH and Mg_3N_2 after the dehydrogenation at 400 °C[15]. Therefore, this indicates that the crystal growth of the Mg_3N_2 phase was not achieved yet after the dehydrogenation at 200 °C because $Mg(NH_2)_2$ before dehydrogenation synthesized by the mechanochemical method possessed nano-structure or amorphous structure and revealed no structural feature in the XRD profile[15]. With respect to the rehydrogenated samples, the mixed phases of LiH and $Mg(NH_2)_2$ is found in the hydrogenated sample after the examination of the PCT profiles at 200 °C as is evident from Fig. 4 (b), indicating a good reversibility. On the other hand, it is seen that the hydrogenated sample after examining the PCT curve at 150 °C is mainly composed of LiH, $LiNH_2$ or Li_2NH without any traces of $Mg(NH_2)_2$. Although a small amount $Mg(NH_2)_2$ remains nano-crystalline feature unchanged after examining the PCT curve at 150 °C and it is difficult to discriminate the $LiNH_2$ and Li_2NH phases from the difference in the XRD profiles, the hydrogen desorption properties in Fig. 3(c) suggest that the phases of the sample after hydrogenating at 150 °C under 9 MPa were mainly composed of LiH and $LiNH_2$.

In conclusion, the results obtained are summarized as follows: The PCT profile at 200 °C in the Li-Mg-N-H system has a two-plateaus-like behavior and reaches to fully hydrogenated state under 9 MPa H_2. The hydrogenated sample after examining the PCT profile at 200 °C was composed of LiH and $Mg(NH_2)_2$ indicating a good reversibility. On the other hand, the PCT curve at 150 °C shows a single plateau-like behavior but does not reach to fully hydrogenated state within several hours under H_2 pressures up to

9 MPa. Those suggest that the hydrogenation process of the Li-Mg-N-H system is composed of 2 different steps, and the second step difficultly progresses at low temperature of 150 °C. The mechanism of the hydrogenation on the Li-Mg-N-H system in detail would be discussed in elsewhere[18].

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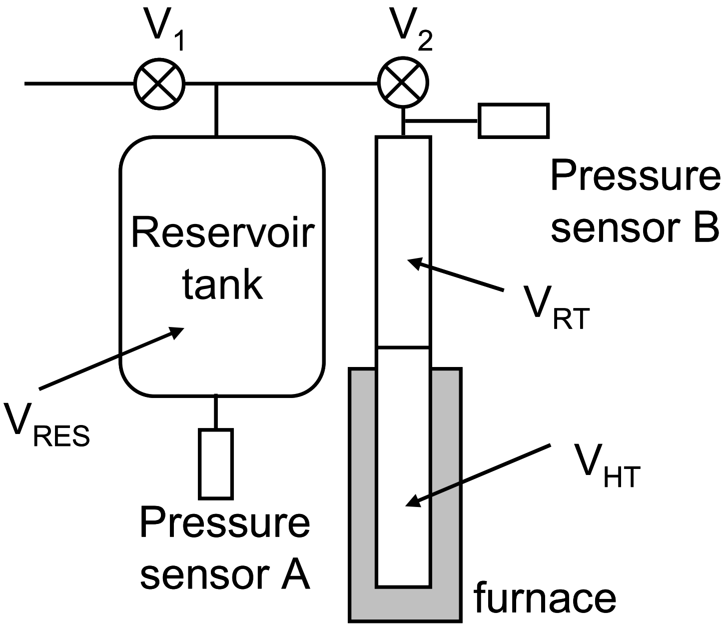
Captions

Figure 1: Schematic figure of hand made compact Sievert's type apparatus, in which isothermal hydrogen absorption properties of the dehydrogenated sample were examined.

Figure 2: Pressure-composition isotherm (PCT) curves of hydrogen absorption at 150 and 200 °C

Figure 3: Hydrogen desorption mass spectrum (dashed line) and the corresponding weight loss (solid line) for the dehydrogenated sample at 200 °C under high vacuum for 12h (a), the rehydrogenated sample by the PCT measurement at 200 °C (b) and at 150 °C (c) on the mixture of $3Mg(NH_2)_2$ and 8LiH, in which the thermal analyses was performed under a pure helium flow at a 5 ºC/min heat rate.

Figure 4: XRD profiles of the dehydrogenated sample at 200 °C under high vacuum for 12h (a), the rehydrogenated sample by the PCT measurement at 200 °C (b) and at 150 °C (c) on the mixture of $3Mg(NH_2)_2$ and 8LiH. The broad peak around 20° is due to grease used to fix the powder on the sample holder.



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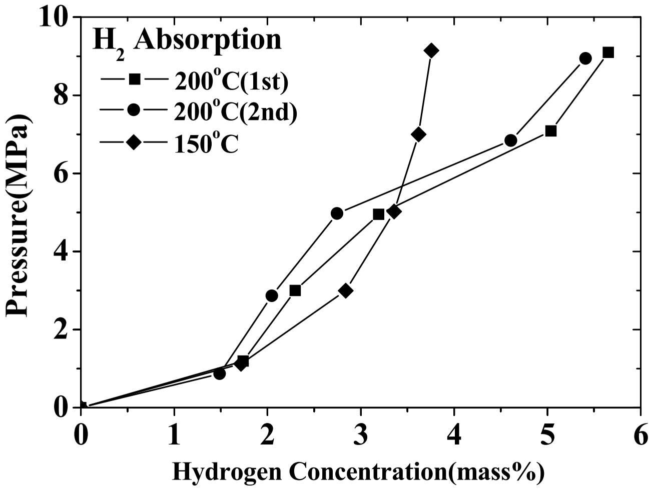

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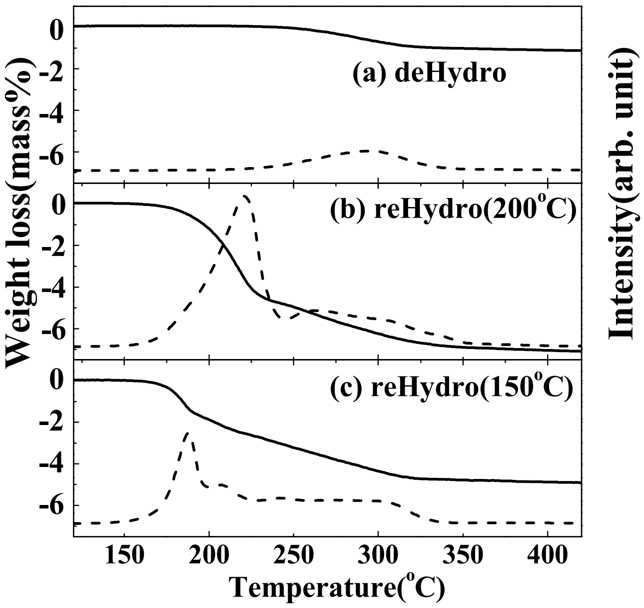

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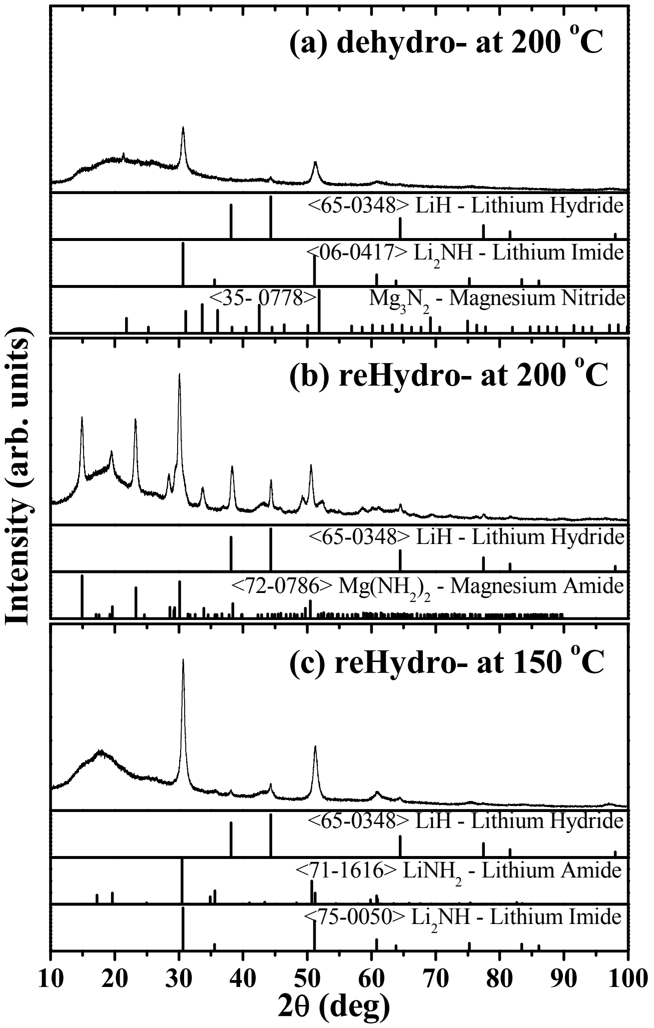

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