Hydrogen Desorption Processes in Li-Mg-N-H Systems

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Abstract

Li-Mg-N-H systems composed of $Mg(NH_2)_2$ and LiH with various ratios can reversibly store a large amount of hydrogen under the temperature condition above 150 °C. These composites with 3:6, 3:8 and 3:12 ratio of $Mg(NH_2)_2$ and LiH have been independently reported by four groups as promising candidates of high performance hydrogen storage materials possessing the reversibility and the high capacity. In any cases, an interaction between NH_3 and LiH plays an important role for the progress of hydrogen desorbing and absorbing reactions. For the hydrogen desorption process, the NH_3 molecule generated from $Mg(NH_2)_2$ reacts with LiH, forming $LiNH_2$ and H_2. Especially, under an equilibrium condition, in-situ diffraction results indicated that the single phase of $LiNH_2$·MgNH ($LiMgN_2H_3$) could be generated other than the separated two phases. As a next step, the NH_3 molecule generated from $LiNH_2$ reacts with LiH, desorbing H_2. As a result, the dehydrogenated phase was evaluated to be Li_2NH·MgNH ($Li_2MgN_2H_2$) or separated two phases, in which the final phase should depend on the experimental conditions. Thus, if the amount of LiH is enough to react with NH_3, the hydrogen desorption processes are described by the NH_3 generation from the corresponding amides and the imide.

Introduction

In order to realize high capacity hydrogen storage systems with respect to volumetric and gravimetric density, we have focused on the nano composites of light elements such as lithium, magnesium, nitrogen, boron and carbon for the hydrogen storage materials [1-11]. These systems have two independent weak points for hydrogen storage. One is thermodynamic properties, the other is kinetic properties on the hydrogen absorption/desorption reactions. So far, we have reported several materials as the promising hydrogen storage system which has been prepared to overcome those weak points, by some approaches such as adding suitable catalysts, using the ball milling methods and choosing suitable composites.

Li-Mg-N-H systems have been focused on as one of the most promising hydrogen storage systems, since Chen's report [12]. A lot of researchers have reported on thermodynamics, kinetics and structural properties of the systems as the hydrogen storage mediates [1-7, 13-19]. With respect to the Li-N-H system, we have suggested and proved the ammonia mediated reaction mechanism on the hydrogen desorption reaction [3, 4]. That is, the reaction is successively progressed by 2-elementary reactions; one is that $2LiNH_2$ decomposes to Li_2NH and ammonia; the other is that the generated NH_3 reacts with LiH and transforms into $LiNH_2$ and H_2. In the case of the Li-Mg-N-H system, the mechanism would be essentially the same as the Li-N-H system. However it's little complicated to totally understand the reaction processes, because various phases are observed by several research groups [16-19]. In this work, we discuss the hydrogen desorption processes of the Li-Mg-N-H systems in order to simply explain.

Experimental Procedure

Starting materials of LiH and MgH_2 with 95% purity were purchased from Sigma-Aldrich. $Mg(NH_2)_2$ was synthesized by ball-milling MgH_2 under a pure NH_3 atmosphere, the details of which have been described elsewhere [7]. Three kinds of the Li-Mg-N-H samples with the LiH/$Mg(NH_2)_2$ molar ratios (Li/Mg) of 6/3, 8/3, and 12/3 were prepared by ball-milling for 2 h under a 1.0 MPa H_2 atmosphere, using a planetary ball milling apparatus (Fritsch, P7) with 400 rpm. For the milling treatment, the mixed powders of 300 mg and 20 pieces of steel balls with a diameter of 7 mm were set into a Cr-steel pot with a volume of ~25 mL. All the material handlings were performed in a glovebox filled with purified argon to keep a low water vapor concentration (the dew point is lower than −80 °C) and a low oxygen concentration (less than 1 ppm) during the operation. The purification was performed using a gas recycling purification system (Miwa MFG Co., Ltd., MPP60W). The thermal gas desorption properties of the mixture

were examined by thermal desorption mass spectroscopy (TDMS) (Anelva, M-QA200TS) combined with thermogravimetry (TG) (Rigaku, TG8120) upon heating to 500 °C at a ramp rate of 5 °C/min. This equipment was especially set inside the glovebox filled with purified argon so that the samples were never exposed to the air atmosphere. The identification of structure was carried out by the powder X-ray diffraction (XRD) method with Cu Kα radiation (Rigaku, RINT-2100).

Results and Discussions

Figure 1 shows the TDMS results of samples with several ratios of LiH and $Mg(NH_2)_2$. In the all profiles, hydrogen was mainly desorbed from the sample with small emission of ammonia. Figure 2 shows the powder XRD results of samples, which were after heat treatment under vacuum condition up to 500 °C, as the phases after the dehydrogenation. In the cases of "Li/Mg = 8/3 and 6/3", Li_2NH and Mg_3N_2 phases were observed in the both XRD results. In the case of "Li/Mg = 12/3", Li_2NH and LiMgN phases were assigned in the XRD profiles. The hydrogen desorption reactions were reported to proceed as following equations [6, 13-15];

$$\mathbf{6}\ LiH + 3Mg(NH_2)_2 \rightarrow 3Li_2MgN_2H_2 + 6H_2, \quad (1)$$

$$\mathbf{8}\ LiH + 3Mg(NH_2)_2 \rightarrow 4Li_2NH + Mg_3N_2 + 8H_2, \quad (2)$$

$$\mathbf{12}\ LiH + 3Mg(NH_2)_2 \rightarrow 4Li_3N + Mg_3N_2 + 12H_2. \quad (3)$$

Here, about the reaction (3) can be followed to next step (4) making ternary nitride LiMgN due to thermodynamic properties [20].

$$Li_3N + Mg_3N_2 \rightarrow LiMgN \quad (4)$$

According to these hydrogen desroption reaction formulas, the XRD result of "Li/Mg = 8/3 and 12/3" were quite reasonable. On the other hand, the result of "Li/Mg = 6/3" did not agree with the previous report [14, 15]. We expected that the reason is due to decomposition accompanied with ammonia emission (5) at high temperature condition.

$$Li_2MgN_2H_2 \rightarrow Li_2NH + 1/3Mg_3N_2 + 1/3NH_3 \quad (5)$$

In fact, the ammonia signal was observed around 400 ~ 500 °C in the profiles of TDMS as shown in Figure 3. Conclusively, above results indicated that the hydogenated and dehaydrogenated states could be discribed in the way of reactions (1), (2) and (3) in the Li-Mg-N-H system with every molar ratio of LiH and $Mg(NH_2)_2$.

Next, we discuss the transformation of the phases during the dehydrogenating reaction processes in the Li-Mg-N-H systems. About this issue, we would like to refer to some experimental results reported by several groups. By Rijssenbeek et al. [16], in the case of "Li/Mg = 6/3", three new imide crystal structures were determined by using high-resolution X-ray and neutron diffraction and identified a new family of imides with formula $Li_{4-2x}Mg_x(NH)_2$ (up to 6 wt.% of H_2, at ~220 °C). Luo et al. reported on the

case of “Li/Mg = 6/3” and characterized the products at several points on the P-C isotherm and proposed the reactions [17], as follows;

$$Mg(NH_2)_2 + 2LiH \leftrightarrow Li_2MgN_2H_{3.2} + 1.4H_2, \quad (6)$$

$$Li_2MgN_2H_{3.2} \leftrightarrow Li_2Mg(NH)_2 + 0.6H_2. \quad (7)$$

In the case of “Li/Mg = 8/3”, Nakamura et al. determined the phase of $Li_{2.6}MgN_2D_{1.4}$ as a dehydrogenated state (in vacuum condition, at 200 °C) by using synchrotron radiation (SR)-X-ray and neutron diffraction [18]. For “Li/Mg = 6/3, 8/3, 12/3” systems, Aoki et al. performed PC-isotherm measurements only for the dehydrogenation at 250 °C and observed complex imide $Li_2Mg(NH)_2$ as a dehydrogented state by SR-XRD [19]. Out of consideration of all experimental results, the reaction steps of the Li-Mg-N-H system can be explained as below.

$$nLiH + 3Mg(NH_2)_2$$

$$\rightarrow (n\text{-}3)LiH + 3LiMgN_2H_3 + 3H_2 \quad (8)$$

$$\rightarrow (n\text{-}6)LiH + 3Li_2MgN_2H_2 + 6H_2 \quad (9)$$

$$\rightarrow (n\text{-}8)LiH + 3Li_{2.7}MgN_2H_{1.3} + 8H_2 \quad (10)$$

$$\rightarrow (n\text{-}12)LiH + 3Li_3N + 3LiMgN + 12H_2 \quad (11)$$

In first step (8), 3LiH reacts with $3Mg(NH_2)_2$, generating $3H_2$ and $3LiMgN_2H_3$, which can be regarded as a complex of Li-amide and Mg-imide. Although this single phase has not been reported yet, Aoki et al. reported the existence of $Li_{1.3}MgN_2H_{2.7}$ as quite similar phase to $LiMgN_2H_3$ [19]. Next step (9), 3LiH reacts with $3LiMgN_2H_3$, generating $3H_2$ and $3Li_2MgN_2H_2$, which can be regarded as a complex of Li-imide and Mg-imide and has been already reported by many researchers. Furthermore, 2LiH reacts with $3Li_2MgN_2H_2$ to generate $2H_2$ and $3Li_{2.7}MgN_2H_{1.3}$, which can be regarded as a complex of Li-imide and Mg-nitride, in third step (10) and seems to be equivalent phase of $Li_{2.6}MgN_2H_{1.4}$ reported by Nakamura et al. [18]. In fact, this Li-imide and Mg-nitride single phase should be reached below 200 °C if the vacuum condition was allowed. And, at much higher temperature than ~450 °C, 4LiH reacts with $3Li_{2.6}MgN_2H_{1.3}$, generating $4H_2$, $3Li_3N$ and LiMgN, which is a complex of Li-nitride and Mg-nitride. In brief, the phase transformation proceeds in the order of “Mg-amide to Mg-imide”, “Li-amide to Li-imide”, “Mg-imide to Mg-nitride” and “Li-imide to Li-nitride”. Figure 4 shows the schema of dehydrogenating processes of the Li-Mg-N-H systems. We suggest that the two kinds of phases $Mg(NH_2)_2$ and $LiMgN_2H_3$ are decreasing and increasing, respectively at the same time, because a plateau appears during step (8) in the PC-isotherm measurement [19]. On the other hand, it is suggested that the continuous transformation from $LiMgN_2H_3$ to $Li_{2.7}MgN_2H_{1.3}$, which can be written as $Li_{1+x}MgN_2H_{3-x}$, during steps (9), (10) make a slope in the PC-isotherm measurement as shown in the report by Aoki et al. [19]. About final step (11), another plateau might

appear, if the dehydrogenating involves the separation of L_3N and LiMgN during the H_2 desorption.

In our previous report, we mentioned that only the Li_2NH phase was assigned in the XRD profile for the dehydrogenated state of "Li/Mg = 8/3" at 200 °C under a vacuum condition [2], because we didn't detect the low angle peak. Therefore, at that point, we concluded that the two separated phases of Li_2NH and amorphous Mg_3N_2 were existing as the dehydrogenated phase. However, a recent work by using SR-X-ray and neutron diffraction [18] showed that the dehydrogenated phase could be assigned to the $Li_{1+x}MgN_2H_{3-x}$ single phase, which was assigned from the low angle peak corresponding to the twice larger unit cell than that of Li_2NH.

Summary

The hydrogen desorption processes of the Li-Mg-N-H systems have been discussed in this report. Dehydrogenated states of the Li-Mg-N-H systems depend on the condition such as the amount of LiH, the temperature and pressure of hydrogen gas, because higher temperature is necessary to be proceeded into next stage (amide to imide or imide to nitride) without lithium hydride. If enough LiH reacts with Mg-amide under an equilibrium condition, the reaction steps can be explained as follows;

Mg-amide → Li-amide & Mg-imide → Li-imide & Mg-imide →
→ Li-imide & Mg-nitride → Li-nitride & Mg-nitride.

It was suggested that the reactions from "Mg-amide" to "Li-amide & Mg-imide", from "Li-amide & Mg-imide" to "Li-imide & Mg-nitride" make a plateau region, a slope region in the PC-isotherm curve, respectively. Additionally, the first step of "Mg-amide → Li-amide & Mg-imide" indicates that $Mg(NH_2)_2$ provides NH_3 with LiH, generating the Mg-imide-Li-amide single phase and H_2.

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Figure Captions

Figure 1. TDMS profiles of the mixture of LiH and $Mg(NH_2)_2$ with the LiH/$Mg(NH_2)_2$ ratios of 12/3, 8/3, 6/3, with increasing temperature up to 500 °C under a helium flow at a ramp rate of 5 °C/min.

Figure 2. XRD profiles of the mixture of LiH and $Mg(NH_2)_2$ with the LiH/$Mg(NH_2)_2$ ratios of 12/3, 8/3, 6/3 synthesized under a helium flow at 500°C.

Figure 3. Twenty times enlarged NH_3 signals in the TDMS profiles of the mixture of LiH and $Mg(NH_2)_2$ with the LiH/$Mg(NH_2)_2$ ratios 12/3, 8/3, 6/3, with increasing temperature up to 500 °C under a helium flow at a ramp rate of 5 °C/min.

Figure 4. Schema of dehydrogenating steps of the Li-Mg-N-H system

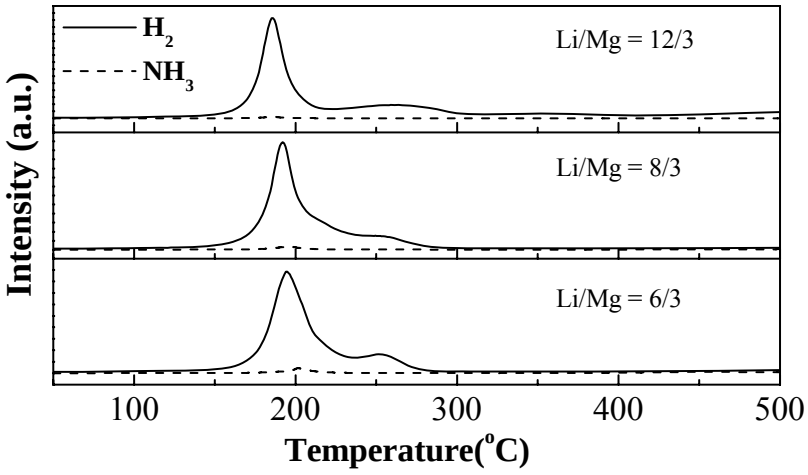
H2
NH3
Li/Mg = 12/3
Li/Mg = 8/3
Li/Mg = 6/3
Intensity (a.u.)
100
200
300
400
500
Temperature(°C)

Figure 1

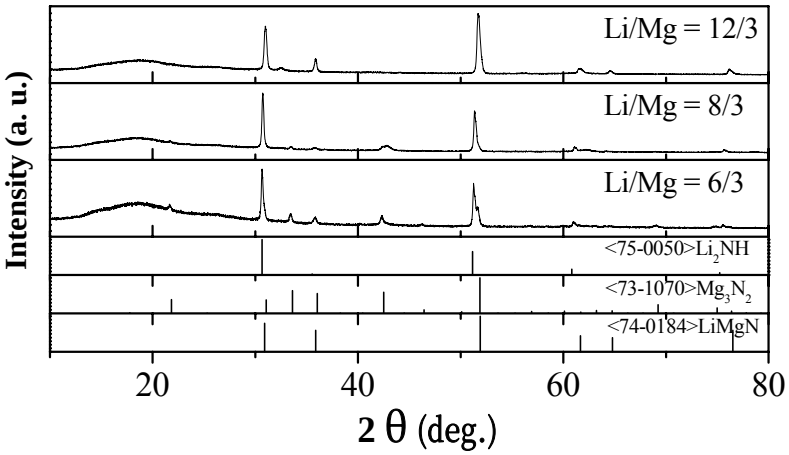
Li/Mg = 12/3
Li/Mg = 8/3
Li/Mg = 6/3
<75-0050>Li2NH
<73-1070>Mg3N2
<74-0184>LiMgN
Intensity (a. u.)
20
40
60
80
2 θ (deg.)

Figure 2

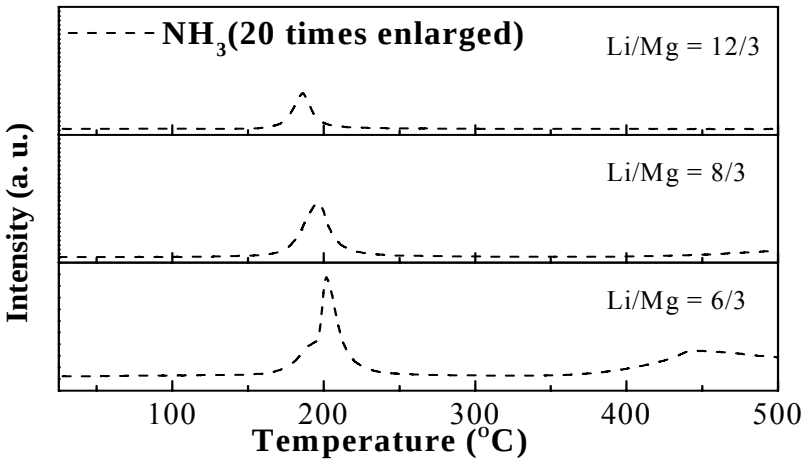
NH3(20 times enlarged)
Li/Mg = 12/3
Li/Mg = 8/3
Li/Mg = 6/3
Intensity (a. u.)
100
200
300
400
500
Temperature (°C)

Figure 3

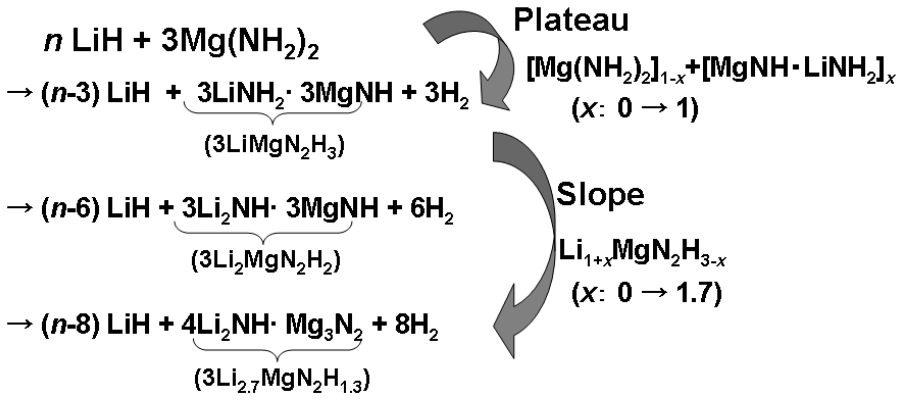
n LiH + 3Mg(NH2)2
→ (n-3) LiH + 3LiNH2· 3MgNH + 3H2
(3LiMgN2H3)
→ (n-6) LiH + 3Li2NH· 3MgNH + 6H2
(3Li2MgN2H2)
→ (n-8) LiH + 4Li2NH· Mg3N2 + 8H2
(3Li2.7MgN2H1.3)
Plateau
[Mg(NH2)2]1-x+[MgNH·LiNH2]x
(x: 0 → 1)
Slope
Li1+xMgN2H3-x
(x: 0 → 1.7)

Figure 4