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Hydrogen storage properties of Li–Mg–N–H systems

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Abstract

The hydriding and dehydriding reactions of $M(\mathrm{NH_2})_y$, where $M = \mathrm{Li} - x$ at.% Mg ($x = 0$–100 and $y = 1$–2), were examined for the purpose of developing reversible hydrogen storage materials. At the start of the reaction, the dehydriding temperatures of $\mathrm{LiNH_2}$ with partial Mg substitutions drastically decrease with an increase in the Mg concentrations, to approximately 370 K with $x = 30$. Moreover, the reversible dehydriding and rehydriding reactions of $\mathrm{Mg(NH_2)_2}$, in which 9.1 mass% of hydrogen can be stored, were successively investigated. The reversible hydriding and dehydriding reactions of $M(\mathrm{NH_2})_y$ are useful for the development of hydrogen storage materials for fuel cell applications.

Keywords: Complex hydride; Hydrogen storage; Lithium; Magnesium; Amide; Imide

1. Introduction

Chen et al. have reported that lithium imide ($\mathrm{Li_2NH}$) and lithium amide ($\mathrm{LiNH_2}$) exhibit reversible hydriding and dehydriding reactions [1,2], expressed as follows:

$$\mathrm{LiNH_2 + 2LiH \Leftrightarrow Li_2NH + LiH + H_2 \Leftrightarrow Li_3N + 2H_2} \quad (1)$$

The dehydriding reaction caused by the decomposition of $\mathrm{LiNH_2}$ into $\mathrm{Li_2NH}$ (left-to-right direction of the first reaction of Eq. (1)) begins at approximately 423–473 K in vacuum [1–3] and at approximately 550 K in argon [4,5] . These temperatures are higher than the desired temperatures, particularly, for the polymer electrode fuel cell, which is typically below 373 K. Therefore, the decrease in the dehydriding temperatures of amides (and imides) is an important research direction. One of the effective methods is the partial substitution of cations; for example, Li can be substituted by Mg, which is an element with a larger electronegativity [4–6].

In this study, we first examine the hydriding and dehydriding reactions of $\mathrm{LiNH_2}$ with/without partial Mg substitutions. In addition, the notable hydriding and dehydriding reactions of $\mathrm{Mg(NH_2)_2}$ mixed with an appropriate molar of LiH were also investigated.

2. Experimental

Samples were prepared by the following two methods: Method-1, mixtures of Li and Mg powders (both with 99.9% purity) were heat-treated under 0.1 MPa of argon in order to prepare $\mathrm{Li} - x$ at.% Mg alloys ($x = 0$, 10, 30, and 50). Subsequently, the alloys were nitrided at 833 K under 0.1 MPa of nitrogen (99.99995% purity) for 1 h, and successively hydrided at 573–623 K under 35 MPa of hydrogen (99.99999% purity) for 2 h. Method-2, $\mathrm{Li_3N}$ and $\mathrm{Mg_3N_2}$ were independently prepared by gas-phase nitrogenation of metallic Li and Mg, respectively. The mixtures of $\mathrm{Li_3N}$–20 at.% $\mathrm{Mg_3N_2}$ 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.

The samples prepared were examined by powder X-ray diffraction measurement (PANalytical, X'Pert, Cu Kα) and thermal desorption spectroscopy detected by gas chromatog-

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raphy (GL Science, GC323, argon flow under 0.1 MPa at a heating rate of 10 K/min). All the samples were handled in a glove box filled with purified argon (dew point below 180 K) during the preparations/measurements. This handling manner is important in order to avoid the desorption of ammonia [7].

3. Results and discussion

3.1. $LiNH_2$ with/without partial Mg substitutions

Fig. 1 shows the dehydriding reactions of $LiNH_2$ with/without partial substitutions of Li by Mg, as prepared by Method-1. The dehydriding reaction of $LiNH_2$ without partial Mg substitutions (left-to-right direction of the first reaction of Eq. (1)) begins at approximately 550 K at a heating rate of 10 K/min under argon [4,5]. At the start of the reaction, with partial Mg substitutions, the dehydriding temperatures drastically decrease to approximately 370 K with $x = 30$ in $M = \mathrm{Li} - x$ at.% Mg, as shown in the inset. The optimized concentration of Mg is predicted to be approximately $x = 30$.

The powder X-ray diffraction profiles of $LiNH_2$ with/without partial Mg substitutions are shown in Fig. 2. According to Eq. (1), the sample without substitution consists of the mixture of $LiNH_2$ and LiH. It should be emphasized that some of the diffraction peaks shift with an increase in the Mg concentrations, due to the actual substitution of Li by Mg. In addition, the $Mg(NH_2)_2$type phase (the crystal structure is similar to $LiNH_2$ [8]) are also observed in the samples with partial Mg substitutions.

3.2. $Mg(NH_2)_2$ mixed with LiH

We have predicted that the mixtures of magnesium amide and lithium hydride (or their nitrides), in addition to the partial substitutions described in Section 3.1, exhibit similar effects to enhance the dehydriding reaction. A possible reaction of $Mg(NH_2)_2$ is expressed as follows [9,10]:

$$3Mg(NH_2)_2 + 12LiH \Leftrightarrow 4Li_3N + Mg_3N_2 + 12H_2 \qquad (2)$$

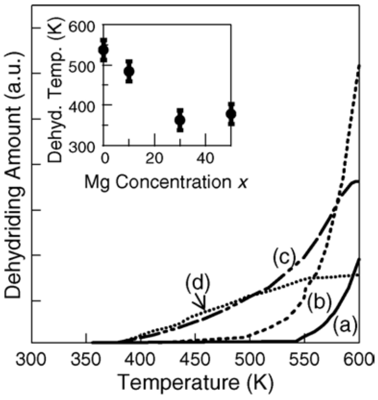

Fig. 1. Dehydriding amount of $M(NH_2)_y$ with $M = \mathrm{Li} - x$ at.% Mg: (a) $x = 0$, (b) $x = 10$, (c) $x = 30$, and (d) $x = 50$, at a heating rate of 10 K/min under 0.1 MPa of argon. The samples were prepared by Method-1. The inset shows the initial dehydriding temperature as a function of the Mg concentration x.

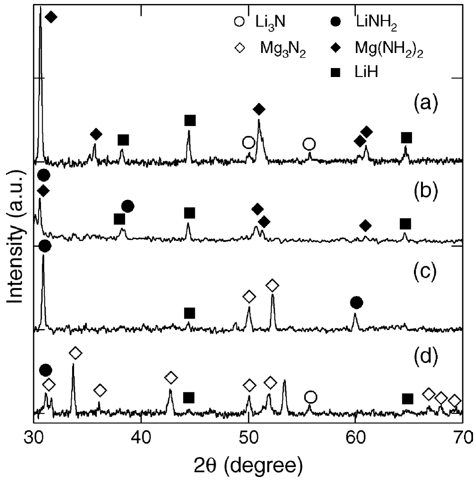

Fig. 2. Powder X-ray diffraction profiles of $M(NH_2)_y$ with $M = \mathrm{Li} - x$ at.% Mg: (a) $x = 0$, (b) $x = 10$, (c) $x = 30$, and (d) $x = 50$. The samples were prepared by Method-1.

This reaction may be composed of more than two reaction steps, similar to Eq. (1), and a total of 9.1 mass% of hydrogen can be stored in the solid state according to Eq. (2). In order to confirm the reaction according to Eq. (2), the sample was prepared by Method-2 (right-to-left direction of Eq. (2)). Only the diffraction peaks corresponding to the mixture of $Mg(NH_2)_2$ and LiH were actually observed after the hydriding reaction, as shown in Fig. 3. Moreover, only the diffraction peaks corresponding to the mixture of Mg_3N_2 and Li_3N were observed after the dehydriding reaction (left-to-right direction of Eq. (2)) in vacuum up to 750 K. These results indicate that the hydriding and dehydriding reactions proceed completely in accordance with Eq. (2).

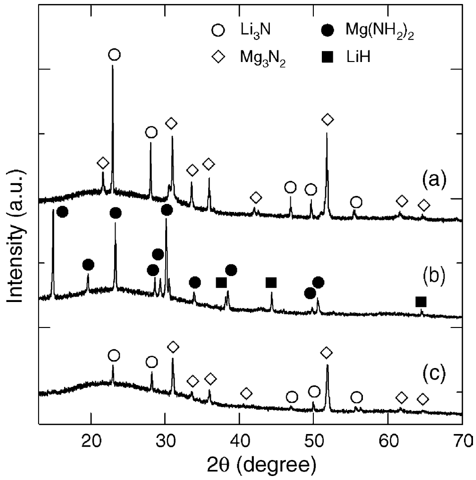

Fig. 3. Powder X-ray diffraction profiles of the samples prepared by Method-2: (a) before the hydriding reaction (right-term of Eq. (2)), (b) after the hydriding reaction (left-term of Eq. (2)), and (c) after the dehydriding reaction (again, right-term of Eq. (2)).

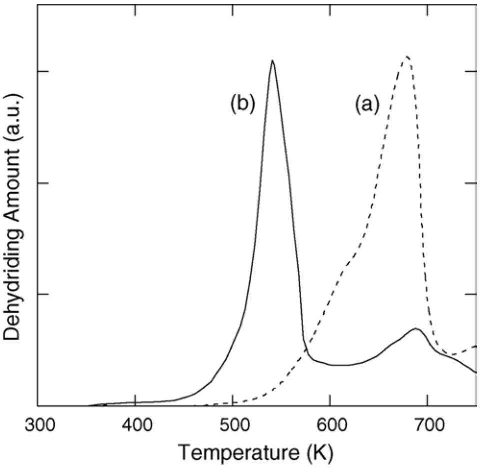

Fig. 4. Dehydriding amount of the samples prepared by Method-2: (a) after the hydriding reaction (left-to-right direction of Eq. (2)), at a heating rate of 10 K/min under 0.1 MPa of argon. The sample (b) was 1 h-milled together with 1 mol% Ti prior to the hydriding reaction in Method-2.

The dehydriding reaction (left-to-right direction of Eq. (2)) was also examined by thermal desorption spectroscopy, as shown in Fig. 4. 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 according to Eq. (2). Fig. 4 also expresses the effects of milling together with catalysts prior to the hydriding reaction in Method-2. The sharp peak drastically decreases from 680 to 540 K by 1 h milling together with 1 mol% Ti. The milling conditions with catalysts will be optimized.

Using synchrotron radiation X-ray diffraction and neutron diffraction experiments investigations on the detailed mechanism of the reversible hydriding and dehydriding reaction according to Eq. (2) and substitution effects are now underway [11,12].

4. Conclusions

The hydriding and dehydriding reactions of $M(NH_2)_y$, where $M = \mathrm{Li} - x$ at.% Mg ($x = 0$–100 and $y = 1$–2), were investigated for the development of reversible hydrogen storage materials. At the start of the reaction, with an increase in the Mg concentrations, the dehydriding temperatures of $LiNH_2$ with partial Mg substitutions drastically decrease to approximately 370 K with $x = 30$. Moreover, the reversible dehydriding and rehydriding reactions of $Mg(NH_2)_2$ were successively investigated for the first time by mixing with an appropriate molar of LiH, in which 9.1 mass% of hydrogen can be stored. The effects of milling together with the catalyst have been preliminary investigated.

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