

Letter

Impregnation method for the synthesis of Li–N–H systems

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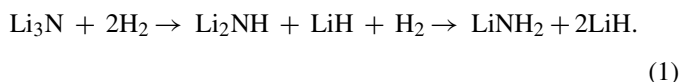
Abstract

We demonstrated the feasibility of an impregnation method for the synthesis of Li_2NH (Li-imide) and LiNH_2 (Li-amide) for application as novel candidates for hydrogen storage materials. A metallic Li foil placed on a Ni foam was heated under Ar atmosphere and then impregnated homogeneously into the Ni foam without changing the bulk morphology of the foam. The morphology of the foam was retained after nitrogenation of the impregnated Li (formation of Li_3N) as well as after ten repeated hydrogenation and dehydrogenation reactions (reversible formation of Li_2NH and LiNH_2). It was noted that the hydrogenation reaction after the nitrogenation was drastically promoted by the addition of a small amount of Co powder on the metallic Li foil prior to the impregnation. Therefore, it is found that the impregnation method is useful to handle the Li–N–H systems as hydrogen storage materials because the bulk morphology is retained.

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Keywords: Impregnation; Lithium; Amide; Imide; Hydrogen storage material**1. Introduction**

Solid-state hydrogen storage materials have been extensively investigated thus far [1–4]. A candidate material is the Li–N–H system comprising Li_2NH (Li-imide) and LiNH_2 (Li-amide) as well as their related hydrides [5–11]. Li_2NH and LiNH_2 can be synthesized by the hydrogenation of Li_3N according to the following reactions:



Eq. (1) proceeds by solid–gas reactions in the conventional manner using the powder metallurgical method. We have also focused on non-conventional methods by using specific elemental properties of Li as a primary component of Li_2NH and LiNH_2 .

One of the non-conventional methods is “evaporation” by using a high vapour pressure of Li [12]. Here, the metallic Li is heated under vacuum to deposit an evaporated film onto a metallic substrate. The metallic Li film is then nitrogenated and hydrogenated to prepare the film of Li_2NH and LiNH_2 in accordance with Eq. (1).

The other new method is “impregnation” by using a low melting temperature of Li. The impregnation method has been extensively employed for many kinds of structural and functional materials to improve their properties. The applications of structural materials to concretes [13,14] and plasters [15] for mechanical strengthening are well known. Examples of functional materials are Pt and Au catalysts impregnated into Al_2O_3 foams, which have been developed for the selective oxidation of CO [16]. Further, the impregnation method has been recently applied to improve the cathode and anode performances in solid oxide fuel cells [17].

In this report, we report the application of the impregnation method for the synthesis of Li_2NH and LiNH_2 for the first time. The main purpose of our study is to clarify the feasibility of handling the hydrides with bulk morphologies even after the repeated hydrogenation and dehydrogenation reactions. This property of morphology retention even after repeated hydrogenation and dehydrogenation is expected to be advantageous for hydrogen storage applications, such as suppression of small-particle scattering, prevention of sintering (maintenance of high surface areas), and retention of high reactivity.

2. Experimental

The Ni foam (Sumitomo Electric Industries, Ltd., porosity with 98%, pore size around 500 μm , thickness and diameter with about 1.5 and 10 mm, respectively) is selected as a matrix for impregnation. In a glove box circulating with

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catalytically purified Ar, a metallic Li foil with 99.9%-purity was placed on top of the Ni foam installed in a steel reaction cell having a diameter of 15 mm. The cell was sealed and then heated up to 500 °C for 4 h under Ar atmosphere. During the process, the Li foil melts and impregnates into the Ni foam. While the samples were placed inside the cell, the metallic Li impregnated into the Ni foam was nitrogenated under 0.2 MPa of nitrogen with 99.99995%-purity at 220 °C for 3 h and then hydrogenated under 1.5 MPa of hydrogen with 99.99999%-purity at 300 °C for 10 h, in order to obtain Li_2NH (Li-imide) and LiNH_2 (Li-amide). The dehydrogenation of the hydrogenated sample was carried out under vacuum (approximately 0.05 Pa) at 250 °C for 10 h. The reactions of hydrogenation (1.5 MPa of hydrogen at 300 °C for 10 h) and dehydrogenation (vacuum at 250 °C for 10 h) were repeated up to 10 times. A schematic drawing of the setup is shown in Fig. 1.

The samples were characterized by optical microscopy and scanning electron microscopy observations, X-ray diffraction measurement (Cu K α) and laser Raman spectroscopy (532 nm-laser), while maintaining the bulk morphologies of the samples. The total hydrogen content of the hydrogenated sample was precisely measured by hydrogen analysis (the thermal conductivity detector of hydrogen extracted by heating and fusion in inert gas).

3. Results and discussion

The optical microscopy and scanning electron microscopy images of the Ni foam before and after the impregnation process are shown in Fig. 2(a and b), respectively. The metallic Li was homogeneously impregnated into the Ni foam without changing the original bulk morphology of the foam.

Moreover, Fig. 3(a–e) shows the images of the samples after (a) nitrogenation, (b) hydrogenation, (c) dehydrogenation, (d) 10th-rehydrogenation and (e) 10th-dehydrogenation, respectively. It is particularly emphasized that the observed bulk morphologies are retained perfectly after nitrogenation as well as after 10 repeated hydrogenation and dehydrogenation reactions. The scanning electron microscopy images reveal

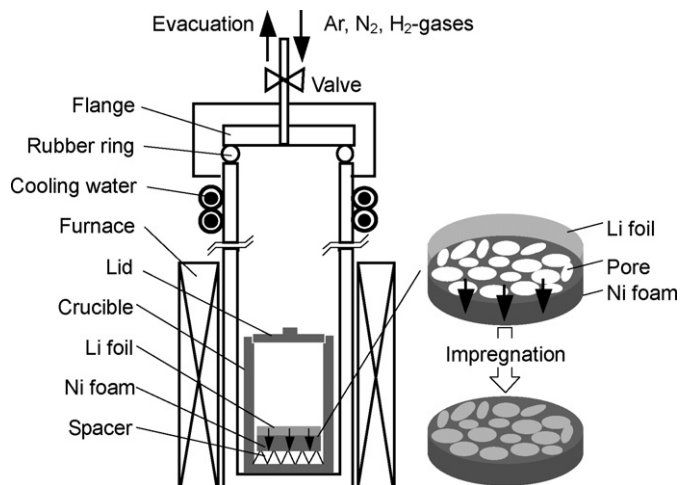


Fig. 1. Schematic drawing of the setup for the impregnation method. A metallic Li foil was placed on top of the Ni foam for the impregnation. A bellows-shaped Ni foil was used as "Spacer" for avoiding any direct contact between the Ni foam and the bottom of the crucible.

that there is no obvious detaching of the samples during the reactions.

X-ray diffraction profiles of all the samples corresponding to Fig. 3 are shown in Fig. 4(a–e). In Fig. 4(a), we can determine the diffraction peaks from Li_3N ; in Fig. 4(b), the peaks disappear, thereby indicating the progress of Eq. (1). There is no evidence of reactions between Li (or Li–N) and Ni as the form. Because the X-ray diffraction profiles from Li_2NH and LiNH_2 are quite similar to each other, we cannot find any obvious changes in Fig. 4(b–e). Thus, the laser Raman spectroscopy was carried out to identify the phases formed in each step.

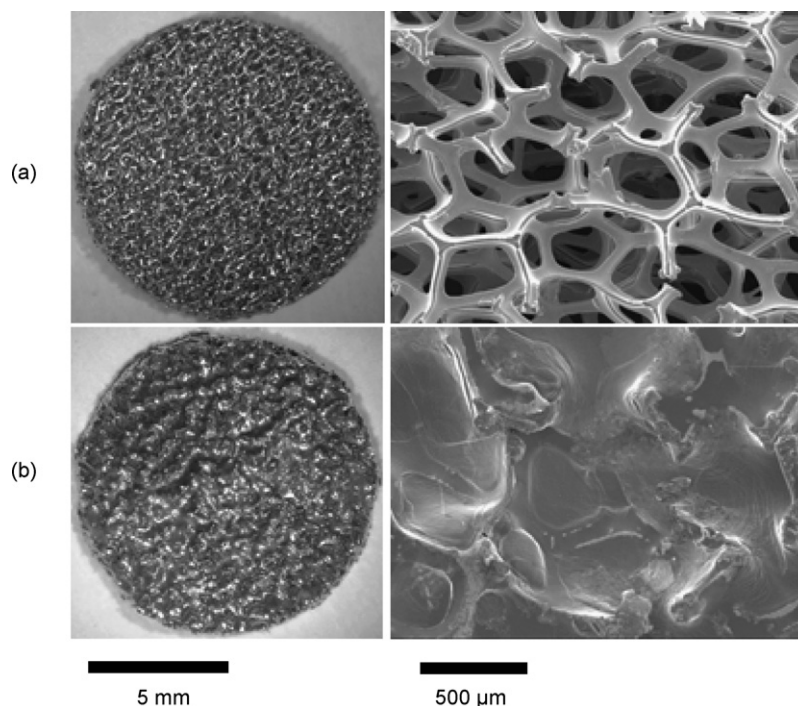


Fig. 2. Optical microscopy (left) and scanning electron microscopy (right) images of the Ni foam (a) before and (b) after the impregnation process. The conditions for the preparation can be seen in the text.

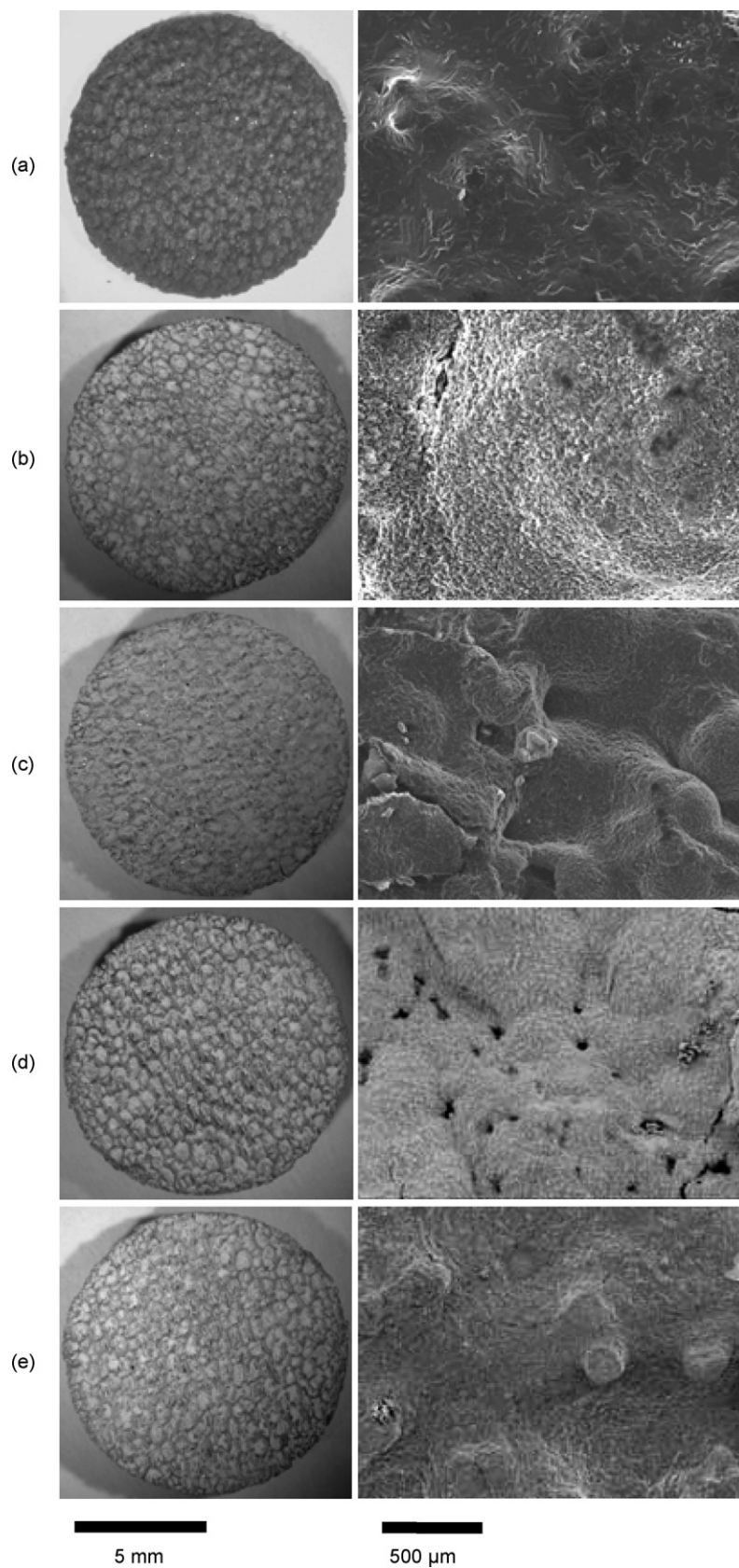


Fig. 3. Optical microscopy (left) and scanning electron microscopy (right) images of the Ni foam after (a) nitrogenation, (b) hydrogenation, (c) dehydrogenation, (d) 10th-rehydrogenation and (e) 10th-dehydrogenation, respectively.

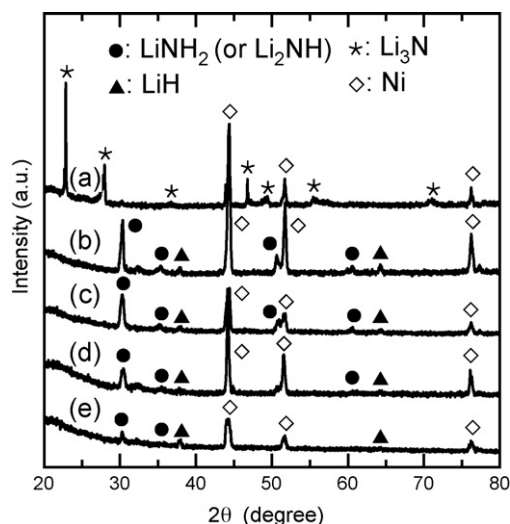


Fig. 4. X-ray diffraction profiles of the samples (corresponding to those shown in Fig. 3) after (a) nitrogenation, (b) hydrogenation, (c) dehydrogenation, (d) 10th-rehydrogenation and (e) 10th-dehydrogenation, respectively. Broad uphill at about 20° originates from glass substrates used for measurements, and there is no evidence of reactions between Li (or Li–N) and Ni as the form.

As shown in Fig. 5(a), there is no N–H stretching mode in Li_3N . However, after hydrogenation, the N–H stretching modes from LiNH_2 can be detected, as shown in Fig. 5(b and d), which are the samples after the 1st- and 10th-(re)hydrogenation, respectively. Moreover, a stretching mode that is different from that in LiNH_2 can be detected, as shown in Fig. 5(c and e), which are the samples after the 1st- and 10th-dehydrogenation, respectively. Therefore, the hydrogenation and dehydrogenation reactions employed in the study are experimentally estimated to be the following reversible reactions: “ $\text{Li}_2\text{NH} + \text{LiH} + \text{H}_2 \leftrightarrow \text{LiNH}_2 + 2\text{LiH}$,” at least in the surface area of the sample impregnated in the Ni foam.

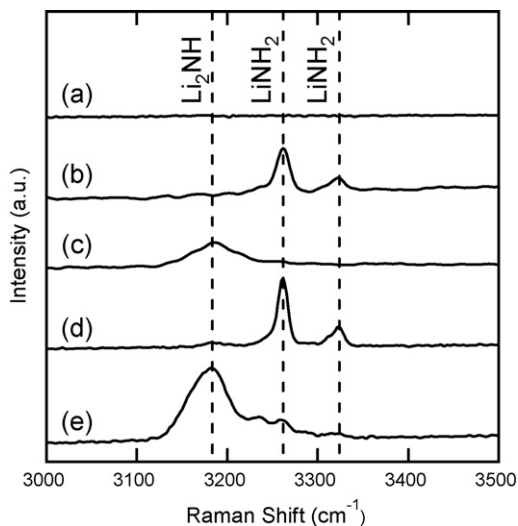


Fig. 5. Raman spectra of the samples (corresponding to those shown in Fig. 3) after (a) nitrogenation, (b) hydrogenation, (c) dehydrogenation, (d) 10th-rehydrogenation and (e) 10th-dehydrogenation, respectively.

Table 1

Comparison between the theoretical and experimental values of the total hydrogen contents of the samples after 1st- and 10th-rehydrogenations

Hydrogenation process	Hydrogen content (mass%)	
	Theoretical	Experimental
1st	9.2	2.9
10th	9.2	6.4
1st (with Co addition)	8.8	8.5

Furthermore, the value of the sample “with Co addition” is also shown.

Table 1 shows the total hydrogen contents of the hydrogenated samples. The theoretical value of the hydrogen content of LiNH_2 with the Ni foam is approximately 9.2 mass%, when considering the porosity of the Ni foam. The contents are 2.9 and 6.4 mass% for the samples after the 1st- and 10th-rehydrogenations, respectively, suggesting that (1) the samples under the present conditions were not completely hydrogenated and (2) the hydrogenation fraction increases after the hydrogenation and dehydrogenation reactions. In order to catalytically promote the hydrogenation reaction, the Co powder (less than $<2\ \mu\text{m}$, 1 at% to the Li amount) was added on the Li foil before the impregnation process. The rest of the process is the same as the above. Further, as shown in Table 1, the hydrogen content of the hydrogenated sample with Co addition drastically increases up to 8.5 mass% just after the 1st-hydrogenation; this is very close to the theoretical value of the hydrogen content – approximately 8.8 mass% – obtained by considering the Ni foam and 1 at% Co to the amount of Li. Apparently, the hydrogenation reaction was promoted by the addition of a small amount of the Co powder.

Experimental studies are now performed on the hydrogen storage functions, including the formation property of ammonia and its possible suppression by the bulk morphology using the Ni foam, of the impregnated Li–N–H systems without/some other transition metal powders.

4. Summary

The feasibility of the impregnation method for the synthesis of Li_2NH and LiNH_2 for application as novel candidates for hydrogen storage materials was demonstrated in this report. Ni foam with a porosity of 98% was selected as a matrix for impregnation, and the metallic Li foil melted and impregnated into the Ni foam homogeneously. The sample was nitrogenated and then hydrogenated to obtain Li_2NH and LiNH_2 . The bulk morphology of the Ni foam was retained after impregnation, nitrogenation, and even after ten repeated hydrogenation and dehydrogenation reactions. The hydrogenation reaction was drastically promoted by the addition of a small amount of Co powder on the metallic Li foil; this contrasts with the incomplete hydrogenation reaction of the sample that occurs without any addition. In this manner, it is found that impregnation method is useful to handle the Li–N–H systems as hydrogen storage materials since the bulk morphology is retained.

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