Cyclic Hydrogenation and Dehydrogenation Property of LiNH_2 Impregnated into Ni Foam

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Cyclic hydrogenation and dehydrogenation property of LiNH_2 impregnated into the Ni foam was experimentally investigated, comparing with that of conventional LiNH_2 powder. The amount of dehydrogenation from the impregnated sample after activating was 4.3 mass% (without the weight of the Ni foam), and remained 3.3 mass% after the 49th cycle of hydrogenation and dehydrogenation, while the amount from the powder sample drastically decreased down to 0.5 mass% until only the 11th cycle. The main origin of the superior cyclic property of the impregnated sample was attributed to the suppression of sintering, mainly due to release of the exothermic heat during the hydrogenation supported by the frames of the Ni foam. [doi:10.2320/matertrans.MA201012]

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1. Introduction

Development of advanced hydrogen storage materials is a critical research topic for various hydrogen energy applications. Complex hydrides with high hydrogen densities have been attracting great interest as potential candidates for advanced hydrogen storage materials.¹⁾ For instance, LiNH_2 (lithium amide), composed of Li^+ cation and $[\text{NH}_2]^-$ complex anion, can store 5.2 mass% of hydrogen based on the following reversible reaction.²⁻⁶⁾

We have previously demonstrated the feasibility of an impregnation method for the synthesis of LiNH_2 and Li_2NH (lithium imide) systems to overcome some issues on powder sample, such as scattering and sintering of powders, from the viewpoint of practical applications.^{7,8)} We confirmed that the bulk morphology with a coin shape was well retained for the impregnated sample after the nitrogeneration (formation of Li_3N) and the cyclic hydrogenation and dehydrogenation (reversible formation of LiNH_2 and Li_2NH) up to 10 cycles. In this report, the cyclic hydrogenation and dehydrogenation property more than 10 cycles was experimentally investigated, and then the different cyclic properties between the impregnated sample and powder one were discussed.

2. Experimental Procedures

Impregnation samples were prepared using the apparatus as schematically drawn in Fig. 1, and the procedure was the same as that in the previous reports;⁷⁻⁹⁾ a Ni foam (porosity of 98%, pore size of 100–500 μm , foam size of 10 mm diameter by 1.5 mm thickness, respectively) was used as a matrix for the impregnation. In a glove box with circulating catalytic

Fig. 1 Schematic drawing for the impregnation method. Li foil was placed on top of the Ni foam for the impregnation. By heating, Li foil was melted and impregnated into the Ni foam. A bellows-shaped Ni foil was used as a spacer to avoid any direct contact between the Ni foam and the bottom of the crucible.⁷⁻⁹⁾

cally purified argon, a metallic Li foil (99.9% purity) placed on top of the Ni foam was installed in a reaction container. The container was sealed and then heated up to 773 K for 240 min under an argon pressure of 0.2 MPa for the impregnation, following by the nitrogeneration at 493 K for 180 min under a nitrogen pressure of 0.2 MPa.

The impregnated Li_3N was set in a pressure-composition-temperature (PCT) measuring apparatus. To activate the surface, the impregnated Li_3N was heat-treated at 573 K for 180 min under a hydrogen pressure of 1.5 MPa and then evacuated at 573 K for 420 min, which were repeated twice. After the activation treatment, the cyclic hydrogenation and dehydrogenation were carried out under the same conditions of the activation. For comparison, the conventional Li_3N

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powder (80 mesh, 99.9% purity) was examined under the same procedures as the case of the impregnated Li_3N . The morphology and microstructure were observed by optical and scanning electron microscopy. The N-H bonding and vibration features were examined by the Raman spectroscopy (532-nm laser, at room temperature) to identify the phase of LiNH_2 and Li_2NH .

3. Results and Discussion

The PCT curves from the (a) impregnated sample and (b) powder one during the dehydrogenation (from the left to right side of the reaction (1)) at 573 K are shown in Fig. 2. The starting points of all the PCT curves were adjusted to zero as the amount of dehydrogenation. The PCT curves of the first cycle both from the impregnated sample and from the powder one show the equilibrium pressures of around 0.2 MPa and the amounts of dehydrogenation of 4.3 mass% (derived from the calculation of $\text{H}/(\text{LiNH}_2 + 2\text{LiH})$, without the weight of the Ni foam). These PCT curves are similar to that from the previous report,²⁾ in which the equilibrium pressure was around 0.2 MPa and the amount of dehydrogenation at 558 K was 6.5 mass% ($\text{H}/(\text{LiNH}_2 + 2\text{LiH})$), corresponding to 4.8 mass% ($\text{H}/(\text{LiNH}_2 + 2\text{LiH})$). (The slight deviation from the present results possibly originated from the different experimental conditions, such as the measuring temperature, the installed amount of the sample and the size of the reaction cell.)

When the cycle numbers increases, however, the difference in the PCT curves between the impregnated sample and powder one becomes obvious; that is, the amount of dehydrogenation from the powder sample drastically decreases. The variations of the amount of dehydrogenation as a function of cycle numbers for the impregnated sample and powder one are plotted in Fig. 3. The former one remains 3.3 mass% after the 49th cycle, which is equivalent to approximately 80% of the value of the first cycle. On the other hand, the latter one decreases down to 0.5 mass% until only the 11th cycle, and then it reaches to 0.4 mass% after the 19th cycle, which is less than 10% of the value of the first cycle.

In order to clarify the origin of the different cyclic properties, the local structure regarding the complex anions was evaluated by the Raman spectroscopy. The Raman spectra for the impregnated sample after the dehydrogenation of the 49th cycle and that for the powder one after the 19th cycle are summarized in Fig. 4. The Raman shift of 3180 cm^{-1} in the impregnated sample is dominantly coming from Li_2NH , due to the well dehydrogenation from LiNH_2 to Li_2NH . On the other hand, the spectra at 3260 cm^{-1} and 3320 cm^{-1} in the powder sample are from LiNH_2 , indicating that the dehydrogenation hardly proceeded. These results are consistent with those of the PCT curves and the variations of the amount of dehydrogenation for the samples as shown in Fig. 2 and 3, respectively.

The morphologies of the samples used for the Raman spectroscopy were investigated by optical and scanning electron microscopy as shown in Fig. 5. The original bulk morphology with a coin shape with a rough surface morphology is apparently well retained for the impregnated

Fig. 2 PCT curves from the (a) impregnated sample and (b) powder one during the dehydrogenation at 573 K. The PCT curve of the first cycle from the impregnated sample is almost the same as that from the powder sample. With the increase in cycle numbers, the difference between the two samples became obvious.

Fig. 3 Variations of the amount of dehydrogenation as a function of cycle numbers for the impregnated sample and powder one. The amount of dehydrogenation from the impregnated sample remains 3.3 mass% after the 49th cycle, while the amount from the powder sample decreases down to 0.5 mass% until only the 11th cycle.

sample. The powder sample is, on the other hand, found to be densely (almost no small pores and open spaces) sintered to form the conical shape coming from the inner shape of the crucible as a sample container.

Fig. 4 Raman spectra for the impregnated sample and powder one after the cyclic hydrogenation and dehydrogenation. The Raman shift of 3180 cm^{-1} in the impregnated sample is dominantly coming from Li_2NH , and the spectra in the powder sample are from LiNH_2 .

Impregnated sample after the 49th cycle

Powder sample after the 19th cycle

Fig. 5 Optical (left) and scanning electron microscopy (right) images of the impregnated sample and powder one after the cyclic hydrogenation and dehydrogenation. The original bulk morphology with a coin shape with a rough surface morphology is apparently well retained for the impregnated sample. The powder sample is densely sintered to form the conical shape.

Sintering is one of the critical factors to degrade the cyclic hydrogenation and dehydrogenation property for LiNH_2 ;¹⁰⁾ the dehydrogenation of LiNH_2 at higher temperature (673 K) generates sintered particles covered with inactive and impervious skin layers. This may correspond to the isolation of hydrogen from the sintered sample, resulting in degradation of the hydrogenation and dehydrogenation property. In order to suppress sintering and to improve the cyclic property, it is necessary to release the exothermic heat, corresponding to 66.1 kJ/mol in the standard enthalpy,²⁾ during the hydrogenation from Li_2NH to LiNH_2 . For the impregnated sample, LiNH_2 is surrounded with the frames of the Ni foam, which are expected to suppress sintering. This is because the thermal conductivity of Ni (67.3 W/mK at 573 K ¹¹⁾) is much higher than that of LiNH_2 (0.45 W/mK at room temperature¹²⁾). For the powder sample, however, the exothermic heat during the hydrogenation is remained in the sample due to the low thermal conductivity of LiNH_2 and it results in sintering. LiNH_2 impregnated into Ni foam can be therefore expected to be advantageous for hydrogen storage applications.

The ammonia emission from the system as a by-product during dehydrogenation leads to the loss of the constituent nitrogen, which is another factor to degrade the cyclic hydrogenation and dehydrogenation property.¹³⁾ It is required to analyze the ammonia emission from the impregnated sample to clarify the reason for the gradual degradation of the amount of dehydrogenation, which is being examined in progress.

4. Conclusions

Cyclic hydrogenation and dehydrogenation property of LiNH_2 impregnated into the Ni foam was experimentally investigated, comparing with that of conventional LiNH_2 powder. The amount of dehydrogenation from the impregnated sample after the activation treatment was $4.3\text{ mass\%}$ (without the weight of the Ni foam), and remained $3.3\text{ mass\%}$ after the 49th cycle. On the other hand, the amount from the powder sample significantly decreased down to $0.5\text{ mass\%}$ until only the 11th cycle. The main origin of the superior cyclic property of the impregnated sample was attributed to the suppression of sintering, mainly due to release of the exothermic heat during the hydrogenation supported by the frames of the Ni foam.

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