Synthesis and partial dehydrogenation of the impregnated lithium borohydride, LiBH_4

Masaharu MENJO, Hai-Wen LI, Motoaki MATSUO, Kazutaka IKEDA and Shin-ichi ORIMO[†]

Institute for Materials Research, Tohoku University, 2-1-1, Katahira, Aoba-ku, Sendai 980-8577

LiBH_4 with high hydrogen density has been attracting great interest as one of potential candidates of advanced hydrogen storage materials. A feasible way to overcome problematic issues on dehydrogenation of LiBH_4 , such as formation of fine powders and overflow by melting, is expected to synthesize bulk LiBH_4 by applying the “impregnation method”. In the present study, LiBH_4 on a Ni foam with porosity of 98% homogeneously impregnated the foam at 573 K without changing the original bulk morphology of the foam. The morphology of the impregnated LiBH_4 was also well retained, even after a partial dehydrogenation at 873 K. Some Ni borides were found to be newly formed depending on the heating (dehydrogenation) conditions, and the formation probably dominates the microstructure and dehydrogenation property of the impregnated LiBH_4 .

©2009 The Ceramic Society of Japan. All rights reserved.

Key-words : Hydrogen storage, Impregnation, Complex hydride, Borohydride, Boride

[Received December 9, 2008; Accepted February 19, 2009]

1. Introduction

Development of advanced hydrogen storage materials is a critical research topic for various hydrogen energy applications.¹⁾ Metal borohydrides $M(\text{BH}_4)_n$ (n (valence of metal M) = 1–4), some of the complex hydrides, with high hydrogen densities have been attracting great interest as potential candidates of advanced hydrogen storage materials.^{2)–10)} For instance, LiBH_4 , composed of Li^+ cation and $[\text{BH}_4]^-$ complex anion, can store about 13.8 mass% of hydrogen based on the following reversible reactions:^{11),12)}

Upon heating (from the left to the right side of the reaction (1)), LiBH_4 melts at around 550 K²⁾ and then decomposes into LiH and B above 700 K accompanying the dehydrogenation (hydrogen desorption) reaction. It has been found that the dehydrogenation temperatures can be decreased by partial or full substitutions of Li by other appropriate metals or ions.^{2),13)}

Here, there are two problematic issues regarding the reaction (1) from the viewpoint of practical applications: One is formation of fine powders of the components, LiBH_4 , LiH, and B, after the reaction (possibly causing, for example, surface poisoning and lowering heat conductivity). Another is “overflow” of the melted LiBH_4 from sample containers.

A feasible way to overcome these issues is to synthesize bulk LiBH_4 by applying the “impregnation method” as an advanced material processing for complex hydrides. We have previously applied this method to LiNH_2 .^{14),15)} The bulk LiNH_2 which impregnated Ni foam (impregnated LiNH_2) did not change into the fine powders and it retained the bulk morphology even after ten reversible reactions, storing about 6 mass% of hydrogen.

In the present paper, we report the preliminary results on the synthesis of the impregnated LiBH_4 and the dehydrogenation property by heating.

2. Experimental

A schematic drawing of the setup is shown in Fig. 1. Ni foam (Sumitomo Electric Industries, Ltd., porosity of 98%, pore size of 100–500 μm , thickness and diameter of about 1.5 mm and 10 mm, respectively) was used as a matrix for impregnation, as in the previous study on LiNH_2 .^{14),15)} In a glove box with circulating catalytically purified argon (dew point below 183 K), pellet-shaped LiBH_4 (Aldrich Co., Ltd., 95.0% purity) placed on top of the Ni foam was installed in a reaction container. The container was sealed and then heated up to 573 K for 120 min under a hydrogen (99.9999%-purity) pressure of 0.5 MPa. During the process, the pellet-shaped LiBH_4 melted and impregnated the Ni foam. The samples before and after the impregnation were characterized by optical and scanning electron microscopy observa-

Fig. 1. Schematic drawing of the setup for the impregnation method. Pellet-shaped LiBH_4 is placed on top of the Ni foam for impregnation. By heating, this pellet melts and impregnates the Ni foam. A bellows-shaped Ni foil is used as a “spacer” to avoid any direct contact between the Ni foam and the bottom of the crucible.

[†] Corresponding author: S. Orimo; E-mail: orimo@imr.tohoku.ac.jp

tions, gas chromatography (heating rate of 5 K/min up to 873 K, Ar flow), Raman spectroscopy (532-nm laser), and powder X-ray diffraction measurement (Cu K α). The samples were always handled in the glove box without exposure to air.

3. Results and discussion

The optical and scanning electron microscopy images of the Ni foam before and after the impregnation are shown in Fig. 2, respectively. The images indicate that LiBH₄ homogeneously impregnated the Ni foam without changing the original bulk morphology of the foam. Overall dehydrogenation property by heating was analyzed by gas chromatography. As shown in Fig. 3, the impregnated LiBH₄ has a narrower dehydrogenation temperature range comparing with that of the conventional LiBH₄. Also, small and irregular dehydrogenation reaction around 650

K, probably coming from the overflow of the melted LiBH₄ from the sample containers, cannot be detected in the impregnated LiBH₄. Moreover the bulk morphology was well retained after the heating, as summarized in Fig. 4. Thus, the two problematic issues mentioned in Introduction might be possibly solved by applying the “impregnation method” to LiBH₄. (The change of the microstructures also observed in Fig. 4 relates to the formation of Ni borides, explained later.)

Raman spectroscopy detecting B–H bonding and vibration features is quite useful to investigate LiBH₄ and the derived complex hydrides.^{2),16)–18)} The actual Raman spectra of the samples corresponding to the images shown in Figs. 4(a)–(e) are summarized in Fig. 5. By the comparison with the calculated phonon density of state (DOS) shown in the inset of Fig. 5,^{16)–18)} the spectra can be identified as either LiBH₄ or Li₂B₁₂H₁₂. The spectrum of LiBH₄ in the sample after the heating at 773 K (Fig. 5(b)) is the almost same as that in the sample just after the impregnation (Fig. 5(a)). On the other hand, different spectra can be clearly detected in the samples after the heating at 873 K (Figs. 5(c)–(e)).

Before impregnation

After impregnation

5 mm

500 μ m

Fig. 2. Optical microscopy (left) and scanning electron microscopy (right) images of the Ni foam, before and after the impregnation of LiBH₄, respectively. LiBH₄ homogeneously impregnated the Ni foam without changing the original bulk morphology of the foam.

Fig. 3. Profiles of gas chromatography corresponding to dehydrogenation reactions of (a) the impregnated LiBH₄ and (b) the conventional LiBH₄. Small and irregular peaks around 650 K only detected in (b) are probably coming from the “overflow” of the melted LiBH₄ from the sample containers.

Fig. 4. Optical microscopy (left) and scanning electron microscopy (right) images; (a) after impregnation of LiBH₄ (same to the lower image in Fig. 2), after the heating at (b) 773 K for 5 min, 873 K for (c) 5 min, (d) 60 min, and (e) 120 min under a hydrogen pressure of 1 MPa, respectively. The bulk morphology was well retained after the heating.

Fig. 5. Raman spectra of the samples corresponding to those shown in Figs. 4(a)–(e). By the comparison with the calculated phonon density of state (DOS) shown in the inset,^{16)–18)} the spectra can be identified as either LiBH_4 or $\text{Li}_2\text{B}_{12}\text{H}_{12}$. (a) and (b) correspond to the spectra of LiBH_4 , and (c)–(e) mainly of $\text{Li}_2\text{B}_{12}\text{H}_{12}$. (The intensity of (a) and (b) was decreased by 20% and 50%, respectively.)

These spectra originate from $\text{Li}_2\text{B}_{12}\text{H}_{12}$, composed of Li^+ cation and $[\text{B}_{12}\text{H}_{12}]^{2-}$ complex anion, formed according to the following reaction:^{17)–20)}

This result suggests that the decomposition and partial dehydrogenation reactions (2) occurred at 873 K.

Each the sample was crushed into powder in the glove box, and powder X-ray diffraction measurement was carried out. The results are summarized in Fig. 6, and agree well with those of the Raman spectroscopy; that is, the diffraction peaks from LiBH_4 disappeared by heating at 873 K. It can be noted that due to the reaction of the Ni foam and B from LiBH_4 and/or $\text{Li}_2\text{B}_{12}\text{H}_{12}$, diffraction peaks of some Ni borides (Ni_3B , Ni_2B , and Ni_4B_3) newly formed depending on the heating (dehydrogenation) conditions. The formation of the Ni borides is considered to dominate not only the microstructure observed in Fig. 4 and but also the specific dehydrogenation property described above. Systematic investigations including the promotion of the reversible dehydrogenation and rehydrogenation of the impregnated LiBH_4 is highly required.

Fig. 6. Powder X-ray diffraction profiles of the samples corresponding to those shown in Figs. 4(a)–(e) and 5(a)–(e). Broad uphill at about 20° originates from glass substrate used for measurement. Some Ni borides were found to be newly formed depending on the heating (dehydrogenation) conditions.

4. Conclusions

Preliminary results on the synthesis of the bulk LiBH_4 which impregnated into Ni foam (impregnated LiBH_4) and the dehydrogenation property by heating were reported. Pellet-shaped LiBH_4 homogeneously impregnated the Ni foam at 573 K without changing the original bulk morphology of the foam, which was also well retained after the partial dehydrogenation at 873 K. The impregnated LiBH_4 has the narrower dehydrogenation temperature range comparing with that of the conventional LiBH_4 . Also, small and irregular dehydrogenation reaction around 650 K, probably coming from the overflow of the melted LiBH_4 from the sample containers, cannot be detected in the impregnated LiBH_4 . Thus, the two problematic issues mentioned in Introduction might be possibly solved by applying the “impregnation method” to LiBH_4 . Some Ni borides (Ni_3B , Ni_2B , and Ni_4B_3) were found to be newly formed depending on the heating (dehydrogenation) conditions, and the formation probably dominates the microstructure and dehydrogenation property of the impregnated LiBH_4 .

Acknowledgements This work was financially supported by Global COE Program “Materials Integration, Tohoku University,” and by the Collaboration Research with Electric Power Development Co., Ltd., (J-Power). The authors would like to acknowledge to Mr. T. Haga and Mr. T. Kikuchi for their helpful discussions.

References

- 1) S. Orimo, Y. Nakamori, J. R. Eliseo, A. Züttel and C. M. Jensen, *Chem. Rev.*, **107**, 4111–4132 (2007).
- 2) Y. Nakamori and S. Orimo, *J. Alloys Comp.*, **370**, 271–275 (2004).
- 3) L. Schlapbach and A. Züttel, *Nature*, **414**, 353–358 (2001).
- 4) A. Züttel, P. Wenger, S. Rentsch, P. Sudan, Ph. Mauron and Ch. Emmenegger, *J. Power Sources*, **118**, 1–7 (2003).
- 5) W. Grochala and P. P. Edwards, *Chem. Rev.*, **104**, 1283–1316 (2004).
- 6) M. Au and A. Jurgensen, *J. Phys. Chem. B*, **110**, 7062–7067 (2006).
- 7) M. Au, A. Jurgensen and K. Zeigler, *J. Phys. Chem. B*, **110**, 26482–26487 (2006).
- 8) X. B. Yu, Z. Wu, Q. R. Chen, Z. L. Li, B. C. Weng and T. S. Huang, *Appl. Phys. Lett.*, **90**, 034106-1–3 (2007).
- 9) H.-W. Li, K. Kikuchi, Y. Nakamori, N. Ohba, K. Miwa, S. Towata and S. Orimo, *Acta Mater.*, **56**, 1342–1347 (2008).
- 10) T. Sato, K. Miwa, Y. Nakamori, K. Ohoyama, H.-W. Li, T. Noritake, M. Aoki, S. Towata and S. Orimo, *Phys. Rev. B*, **77**, 104114-1–8 (2008).
- 11) A. Züttel, S. Rentsch, P. Fischer, P. Wenger, P. Sudan, Ph. Mauron and Ch. Emmenegger, *J. Alloys Comp.*, **356–357**, 515–520 (2003).
- 12) S. Orimo, Y. Nakamori, G. Kitahara, K. Miwa, N. Ohba, S. Towata and A. Züttel, *J. Alloys Comp.*, **404–406**, 427–430 (2005).
- 13) Y. Nakamori, K. Miwa, A. Ninomiya, H.-W. Li, N. Ohba, S. Towata, A. Züttel and S. Orimo, *Phys. Rev. B*, **74**, 045126-1–9 (2006).
- 14) T. Hao, M. Matsuo, Y. Nakamori and S. Orimo, *J. Alloys Comp.*, **458**, L1–L5 (2008).
- 15) M. Menjo, T. Hao, M. Matsuo, Y. Nakamori and S. Orimo, *J. Japan Inst. Metals*, **72**, 163–167 (2008).
- 16) K. Miwa, N. Ohba, S. Towata, Y. Nakamori and S. Orimo, *Phys. Rev. B*, **69**, 245120-1–8 (2004).
- 17) S. Orimo, Y. Nakamori, N. Ohba, K. Miwa, M. Aoki, S. Towata and A. Züttel, *Appl. Phys. Lett.*, **89**, 021920-1–3 (2006).
- 18) N. Ohba, K. Miwa, M. Aoki, T. Noritake, S. Towata, Y. Nakamori, S. Orimo and A. Züttel, *Phys. Rev. B*, **74**, 075110-1–7 (2006).
- 19) H.-W. Li, K. Kikuchi, T. Sato, Y. Nakamori, N. Ohba, M. Aoki, K. Miwa, S. Towata and S. Orimo, *Mater. Trans.*, **49**, 2224–2228 (2008).
- 20) S. J. Hwang, R. C. Bowman, Jr., J. W. Reiter, J. Rijssenbeek, G. L. Soloveichik, J. C. Zhao, H. Kabbour and C. C. Ahn, *J. Phys. Chem. C*, **112**, 3164–3169 (2008).