Hydrogen Desorption Mechanism in a Li−N−H System by Means of the Isotopic Exchange Technique

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The hydrogen desorption mechanism in the reaction from $LiH + LiNH_2$ to $Li_2NH + H_2$ was examined by thermal desorption mass spectrometry, thermogravimetric analysis, and Fourier transform IR analyses for the products replaced by LiD or $LiND_2$ for LiH or $LiNH_2$, respectively. The results obtained indicate that the hydrogen desorption reaction proceeds through the following two-step elementary reactions mediated by ammonia: $2LiNH_2 \rightarrow Li_2NH + NH_3$ and $LiH + NH_3 \rightarrow LiNH_2 + H_2$, where hydrogen molecules are randomly formed from four equivalent hydrogen atoms in a hypothetical $LiNH_4$ produced by the reaction between LiH and NH_3 according to the laws of probability.

Introduction

Hydrogen has been targeted as an ultimate fuel for transportation systems in the future due to its abundance and environmental friendliness. For use of hydrogen as one of the secondary energies, it is necessary to develop high-performance hydrogen storage materials.[1,2] Most of the chemical hydrides composed of light elements such as sodium alanate systems,[3−5] borohydride systems,[6−10] amide systems,[11−21] and so on inevitably possess a quite high hydrogen capacity, so systematic investigations have vigorously been in progress all over the world.

Among them, metal−nitrogen−hydrogen (Metal−N−H) systems have been regarded as one of the most attractive hydrogen storage systems. Actually, lithium nitrides (Li_3N) can absorb/desorb a large amount of hydrogen by the following two consecutive reactions:

$$Li_3N + 2H_2 \leftrightarrow Li_2NH + LiH + H_2 \leftrightarrow LiNH_2 + 2LiH \quad (1)$$

Theoretically, a reversible hydrogen of 10.4 wt % ($2H_2/(Li_3N + 2H_2)$) is accessible in these two reactions. So far, we have investigated the hydrogenating/dehydrogenating properties of the ball milled mixture of $LiNH_2$ and LiH with a small amount of $TiCl_3$ as catalyst according to the following reaction:[14]

$$LiNH_2 + LiH \leftrightarrow Li_2NH + H_2 \quad (2)$$

The reason is that reaction 2 can absorb/desorb ∼6.5 wt % of hydrogen at a much lower temperature due to the smaller enthalpy change, ΔH, than the left part in reaction 1. In addition, we have already reported on the mechanism of the hydrogen desorption reaction (2).[17]

Concerning the mechanism of reaction 2, Chen et al. have claimed that H in $LiNH_2$ is positively charged while H in LiH is negatively charged, so that the strong affinity between $H^{\delta+}$ and $H^{\delta-}$ gives rise to a hydrogen molecule.[13] This model

suggests hydrogen gas desorption due to the direct molecule−molecule interaction, in which the LiH and $LiNH_2$ molecules should be liberated from two solid phases. On the other hand, we have proposed that the hydrogen desorption reaction (2) could proceed through the following two-step elementary reaction mediated by ammonia:[17]

$$2LiNH_2 \rightarrow Li_2NH + NH_3 \quad (3)$$

and

$$LiH + NH_3 \rightarrow LiNH_2 + H_2 \quad (4)$$
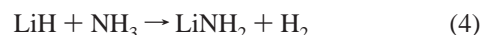
The difference between the above two models lies in whether ammonia does or does not mediate reaction 2.

In this report, we give a microscopic description concerning the hydrogen desorption mechanism in reaction 2 and verify the validity of our proposed model by comparison with experimental data obtained by means of an isotopic exchange technique, where LiD or $LiND_2$ is replaced by respectively LiH or $LiNH_2$ in the milled composites of $LiNH_2$ and LiH.

Reaction Model

If the ammonia-mediated reaction model is valid, two kinds of H atoms should exist in the original system with respect to reaction 4; that is, one is in LiH and the other is in NH_3. For example, when we employ the ball-milled mixture of lithium deutride LiD and $LiNH_2$ as the original system of reaction 2, it is expected that a mixture of isotopic gases with some different ratios of $H_2:HD:D_2$ is desorbed with increasing temperature under nonequilibrium conditions according to the following several models, which are proposed in consideration of the H atom selectivity rule to make H_2 molecule emission.

Model 1 is that the probability of forming H_2, HD, or D_2 molecules from H and D atoms in LiD and NH_3 simply obeys the laws of probability without any distinctions between H and D atoms, just like the release of isotopic gases after the hypothetical formation of $LiNDH_3$

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$$NH_3 + LiD \rightarrow {}^1/_2LiNH_2 + {}^1/_2LiNHD + {}^1/_2H_2 + {}^1/_2HD \quad (5)$$
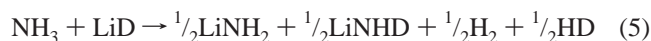
Model 2 is that the D atom in LiD remains in lithium amide, like forming LiNHD without releasing HD as a gas molecule

$$NH_3 + LiD \rightarrow LiNHD + H_2 \quad (6)$$
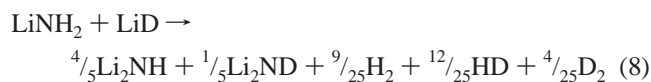
Model 3 is that the D atom in LiD releases from the original solid state as HD gas

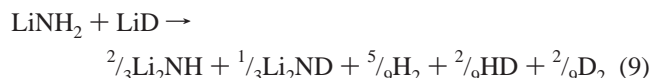$$NH_3 + LiD \rightarrow LiNH_2 + HD \quad (7)$$
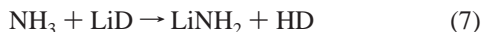
At the next step, the produced Li amides containing protium and/or deuterium atoms in reactions 5−7 decompose into the corresponding lithium imides, Li_2NH or Li_2ND, and emit the corresponding ammonia molecules, NH_3, NH_2D, NHD_2, or ND_3. Then these molecules react with the leaving LiD and transform into the corresponding Li amides and H_2, HD, and D_2 gases. As a result of the following successive steps, the corresponding Li imides and hydrogen gases in the model-dependent ratio can be evaluated. This evaluation is complicated, and details are given in the Appendix. As a result, the corresponding reactions can be expressed as follows

Model 1:

$$LiNH_2 + LiD \rightarrow$$
$${}^4/_5Li_2NH + {}^1/_5Li_2ND + {}^9/_{25}H_2 + {}^{12}/_{25}HD + {}^4/_{25}D_2 \quad (8)$$

Model 2:

$$LiNH_2 + LiD \rightarrow$$
$${}^2/_3Li_2NH + {}^1/_3Li_2ND + {}^5/_9H_2 + {}^2/_9HD + {}^2/_9D_2 \quad (9)$$

and

Model 3:

$$LiNH_2 + LiD \rightarrow Li_2NH + HD \quad (10)$$

The above three models are really based on two elementary reactions (3) and (4) mediated by ammonia.

On the other hand, according to the model proposed by Chen et al.,[13] the corresponding hydrogen desorbing reaction is given by the same description as reaction 10. Moreover, if the isotopic gases are randomly desorbed after hypothetically forming a Li_2-NDH_2 molecule between LiD and $LiNH_2$ according to the laws of probability without any distinctions between H and D atoms, the reaction can be written as follows

Model 4:

$$LiNH_2 + LiD \rightarrow {}^2/_3Li_2NH + {}^1/_3Li_2ND + {}^1/_3H_2 + {}^2/_3HD \quad (11)$$
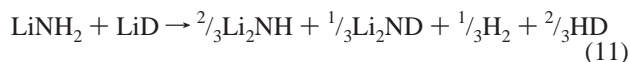
Here, it should be noted that the isotope effect of deuterium for hydrogen was ignored in the above description, because the desorption properties of deuterium gas from the ball-milled mixture of LiD and $LiND_2$ were almost the same as those of hydrogen gas from the mixture of LiH and $LiNH_2$. Similarly, when we employ the ball-milled mixture of LiH and $LiND_2$ as the original system of reaction 2, we notice that the reaction descriptions for models 1−4 can be given by an exchange of H for D, and vice versa, in reactions 8−11 according to the above ignorance of the isotope effect.

Experimental Procedures

The starting materials LiH (95%) and LiD (95%) were purchased from Sigma-Aldrich, and $LiNH_2$ (95%) was from Stem Chemicals. The $LiND_2$ powder used in this work was synthesized from LiD by ball milling under a ND_3 atmosphere according to the following reaction:

$$LiD + ND_3 \rightarrow LiND_2 + D_2 \quad (4')$$
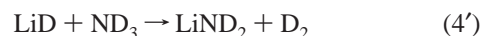
This method was already reported as one of the synthesizing methods of $LiNH_2$ from LiH by ball milling under NH_3 atmosphere.[22]

To achieve nanometer-scale contact among $LiNH_2$, LiD (or $LiND_2$, LiH), and 1 mol % $TiCl_3$, the mixtures were mechanically ball milled (P7, Fritsch) at 400 rpm under a hydrogen atmosphere of 1 MPa (99.9999%) at room temperature for 2 h. The reason we added a small amount of $TiCl_3$ to the mixtures in this work is to prevent NH_3 emission through reaction 2 by improving the reaction kinetics. Prior to 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 inner volume of ~30 cm^3. All the sample treatments were performed in an argon glovebox purified by a gas recycling purification system (MP-P60W, Miwa MFG CO., Ltd.) to minimize the oxygen and water pollutions.

The gas desorption properties of ball-milled mixtures were examined by thermal desorption mass spectroscopy measurements (TDMS; M-QA200TS, Anelva) with an increasing temperature from room temperature to 450 °C at a heating rate of 20 °C/min. The TDMS equipment is especially designed and built up for using it inside the glovebox, which permitted simultaneous determinations by TDMS measurement, thermogravimetry, and differential thermal analysis (TG and DTA; TG8120, Rigaku) without exposing the samples to air at all. Additionally, we have already checked by preliminary examination that it is possible to relatively estimate the ratios of amount of the isotopic gases, H_2, HD, and D_2 desorbed by the TDMS measurement.

In addition to the above thermal analysis, Fourier transform infrared spectroscopy measurement (FT-IR; Spectrum One, Perkin-Elmer) was performed by a pellet method to estimate the ratio of Li_2NH to Li_2ND in the dehydrogenated product, where the pellet containing 1 wt % samples in KBr was set in the BaF_2 folder filled with purified argon to avoid exposing the samples to air at all.

Results and Discussion

To clarify the mechanism of hydrogen desorption reaction from the microscopic point of view, we performed the TDMS measurements for two kinds of the ball-milled mixtures of LiD + $LiNH_2$ and LiH + $LiND_2$, which are shown in parts a and b of Figure 1, respectively. A mixture of H_2, HD, and D_2 can be found as the desorbed gas, and the onset and peak temperatures in the TDMS profiles are almost the same for all the isotopic gases, indicating no significant isotope effect on gaseous desorption reaction. From Figure 1a, the ratio of the areas of the TDMS profiles corresponding to the mass numbers 2 (=H_2), 3 (=HD), and 4 (=D_2) is estimated to be 9.0:13.1:2.9 for the mixture of LiD and $LiNH_2$, which is close to the ratio of H_2:HD:D_2 = 9:12:4 evaluated by model 1. Furthermore, the ratio for the mixture of LiH and $LiND_2$ is estimated to be 2.1:13.9:9.0 as shown in Figure 1b, which is almost in reverse order of that in Figure 1a. This result suggests that model 1 is acceptable as well.

Simultaneously, the TG experiments revealed that a weight loss from the ball-milled LiD + $LiNH_2$ sample reached up to 7.2% shown in Figure 2a by heating to 350 °C. If the isotopic
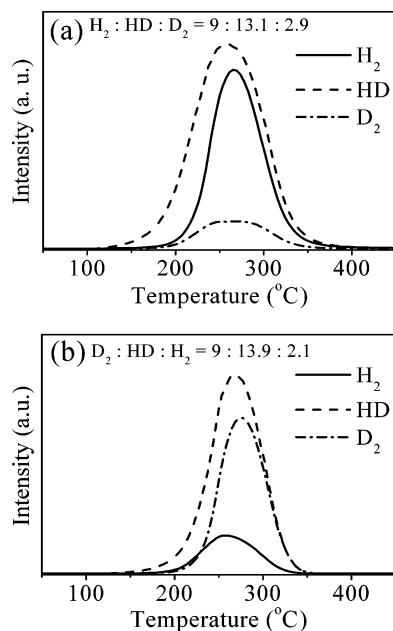
Figure 1. TDMS profiles from the ball-milled mixtures of (a) LiD + LiNH$_2$ and (b) LiH + LiND$_2$ examined under a helium flow at a heating rate of 20 °C/min.
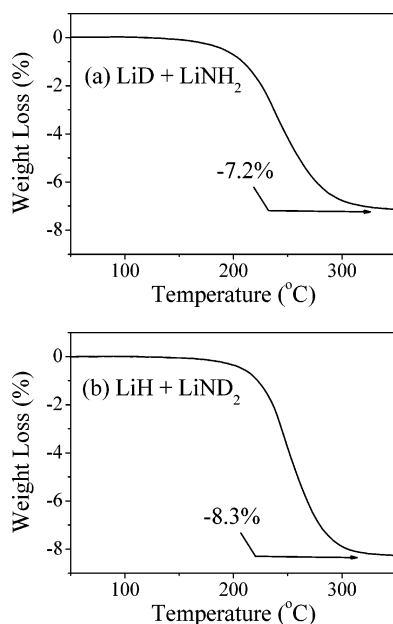

Figure 2. TG profiles from the ball-milled mixtures of (a) LiD + LiNH$_2$ and (b) LiH + LiND$_2$ examined under a helium flow at a heating rate of 20 °C/min.

Figure 3. FT-IR spectra for the gas desorbed samples from the ball-milled mixtures of LiD + LiNH$_2$ and LiH + LiND$_2$. In this figure, FT-IR spectra are shown for the samples with the ratios of 4:1, 1:1, and 1:4 for Li$_2$NH and Li$_2$ND as references.

gases are desorbed with the ratios of H$_2$:HD:D$_2$ expected from the models 1, 2, and 4, we can deduce a weight loss from the LiH + LiND$_2$ sample by reversing the ratios of H$_2$:HD:D$_2$ for the models 1, 2, and 4. Consequently, the values of the expected weight losses are calculated to be 8.2%, 9.0%, and 9.0%, respectively, according to the corresponding models. The result obtained from TG measurement for LiH + LiND$_2$ indicates that the weight loss reaches up to 8.3% as shown in Figure 2b, suggesting that model 1 is also acceptable.

However, we should take into account that TiCl$_3$ used as a dopant for smoothly proceeding reaction 2 can be reduced to the metallic state by ball milling with a strongly reducing agent such as a hydride. From earlier work on alanates,[23] it is known that thus formed Ti0 may act as a chemisorption site for hydrogen. 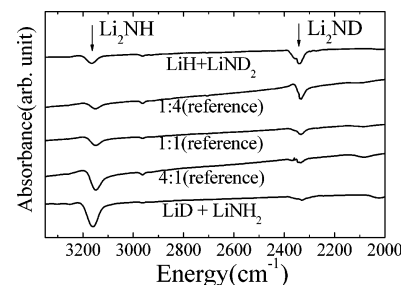As a consequence, an isotopic scrambling effect may strongly affect the H$_2$:HD:D$_2$ ratio, leading to an excess of HD in the mixture.

To clarify whether the scrambling effect is strong or not, we examined the FT-IR measurement to determine the ratio of amount of Li$_2$NH to Li$_2$ND in the product after the desorption of isotopic gases from the ball-milled mixtures, because the FT-IR results should not be affected by the scrambling effect, which originated in the chemisorbed state on the metallic Ti. As was described in the above reaction models, the ratio of the amount of Li$_2$NH to Li$_2$ND was evaluated to be 4:1, 2:1, 1:0, or 2:1 for the model 1, 2, 3, or 4, respectively, in the dehydrogenated products. Figure 3 shows the IR absorbance for the gas desorbed samples. As references, the absorbance of mere mixtures of Li$_2$-NH and Li$_2$ND with the molar ratios of 4:1, 1:1, and 1:4 are also shown in Figure 3. We notice that two peaks corresponding to the N−H and N−D stretching modes are located at ∼3150 and ∼2350 cm^{-1}, respectively. The ratios of the peak area for the references were, respectively, 8.7:1.3, 6.3:3.7, and 3.1:6.9, indicating that the peak area corresponding to N−H mode should be equivalent to be ∼1.7 times larger than those of N−D mode. Therefore, we can evaluate the number of N−D modes in the dehydrogenated mixture of LiD + LiNH$_2$ as being ∼1.7 times larger than the real values of its peak area. As a result of calibration, the relative ratios of Li$_2$NH to Li$_2$ND in the degassed samples from the ball-milled mixtures of LiD + LiNH$_2$ and LiH + LiND$_2$ could be obtained to be 3.9:1 and 1:3.8, respectively. These values are very close to those expected from model 1. Therefore, we conclude that the scrambling effect is not so strong in this system. All the above results indicate that model 1 is acceptable as a mechanism of hydrogen desorption.

Conclusion

In this work, we have investigated the hydrogen desorption mechanism in the reaction from LiH + LiNH$_2$ to Li$_2$NH + H$_2$ by replacing LiD or LiND$_2$ for LiH or LiNH$_2$. From the TDMS and TG measurements, we have relatively evaluated the amounts of H$_2$, HD, and D$_2$ desorbed from the mixtures of LiD + LiNH$_2$ and LiH + LiND$_2$ and confirmed that model 1, in which the hydrogen desorption reaction 2 is controlled by the two-step elementary reaction mediated by ammonia, is valid. Additionally, FT-IR analysis of the N−H and N−D stretching modes in the dehydrogenated products of LiD + LiNH$_2$ and LiH + LiND$_2$ verified that the isotope scrambling effect on a chemisorption site for hydrogen was not so strong. This model 1 microscopically suggests that LiH and NH$_3$ molecules react and momentarily form such a LiNH$_4$ molecule in the hydrogen desorption process.
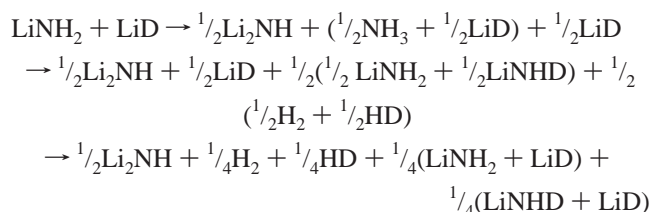
Finally, it is to be noted that the above discussion is concerned with the hydrogen desorption mechanism under nonequilibrium conditions without reverse reaction from gaseous hydrogen.

Under equilibrium conditions, the reverse reaction corresponding to hydrogen absorption should be taken into account to describe the hydrogen gas desorption process. Therefore, more complicated considerations should be introduced to discuss the hydrogen sorption reaction in the closed system. These works are now in progress.
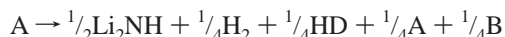
Appendix

In model 1, LiD reacts with $LiNH_2$ as follows

$$LiNH_2 + LiD \rightarrow \tfrac{1}{2}Li_2NH + (\tfrac{1}{2}NH_3 + \tfrac{1}{2}LiD) + \tfrac{1}{2}LiD$$
$$\rightarrow \tfrac{1}{2}Li_2NH + \tfrac{1}{2}LiD + \tfrac{1}{2}(\tfrac{1}{2}LiNH_2 + \tfrac{1}{2}LiNHD) + \tfrac{1}{2}(\tfrac{1}{2}H_2 + \tfrac{1}{2}HD)$$
$$\rightarrow \tfrac{1}{2}Li_2NH + \tfrac{1}{4}H_2 + \tfrac{1}{4}HD + \tfrac{1}{4}(LiNH_2 + LiD) + \tfrac{1}{4}(LiNHD + LiD)$$

because the probability of forming one hydrogen molecule from four hydrogen atoms in the mixture of LiH and NH_3 simply obeys the laws of probability without any discrimination between the H and D atoms. Here, to simplify the expression, the expressions, the mixtures of $LiNH_2 + LiD$ and $LiNHD + LiD$, are denoted by A and B, respectively. Therefore, we can simply describe the above reaction as follows

$$A \rightarrow \tfrac{1}{2}Li_2NH + \tfrac{1}{4}H_2 + \tfrac{1}{4}HD + \tfrac{1}{4}A + \tfrac{1}{4}B$$

and then

$$B \rightarrow \tfrac{1}{4}(Li_2NH + Li_2ND + NH_2D + NHD_2) + LiD$$
$$\rightarrow \tfrac{1}{4}(Li_2NH + Li_2ND) + \tfrac{1}{4}(\tfrac{1}{2}(LiNHD + D_2) + \tfrac{1}{2}(LiND_2 + HD)) + \tfrac{1}{4}(\tfrac{1}{6}(LiNH_2 + D_2) + \tfrac{1}{6}(LiND_2 + H_2) + \tfrac{2}{3}(LiNHD + HD)) + \tfrac{1}{2}LiD$$
$$\rightarrow \tfrac{1}{4}(Li_2NH + Li_2ND) + \tfrac{1}{4}(1/6\,H_2 + \tfrac{7}{6}HD + \tfrac{2}{3}D_2) + \tfrac{1}{4}(\tfrac{1}{6}(LiNH_2 + LiD) + \tfrac{7}{6}(LiNHD + LiD) + \tfrac{2}{3}(LiND_2 + LiD)) \rightarrow (\tfrac{1}{4}Li_2NH + \tfrac{5}{12}Li_2ND) + (\tfrac{1}{24}H_2 + \tfrac{7}{24}HD + \tfrac{1}{3}D_2) + (\tfrac{1}{24}A + \tfrac{7}{24}B)$$
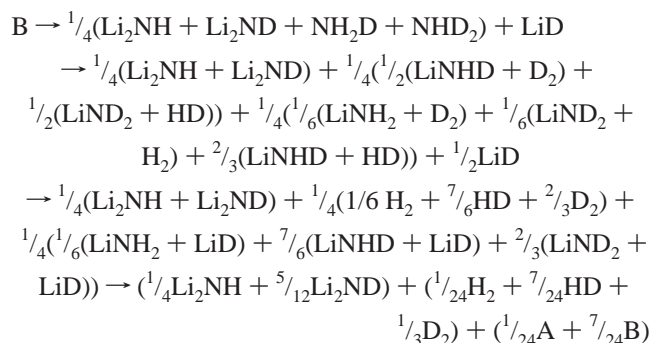
Thus, both A and B in the right-hand side contain A and B as well. Therefore, the expected total amount of the isotopic gases desorbed by proceeding the reactions A and B, which are

denoted by X_A and X_B, respectively, can be expressed by the following simultaneous equations

$$X_A = \tfrac{1}{4}H_2 + \tfrac{1}{4}HD + \tfrac{1}{4}X_A + \tfrac{1}{4}X_B$$

$$X_B = \tfrac{1}{24}H_2 + \tfrac{7}{24}HD + \tfrac{1}{3}D_2 + \tfrac{1}{24}X_A + \tfrac{7}{24}X_B$$

From the simultaneous equations, we obtain

$$X_A = \tfrac{9}{25}H_2 + \tfrac{12}{25}HD + \tfrac{4}{25}D_2$$

$$X_B = \tfrac{2}{25}H_2 + \tfrac{11}{25}HD + \tfrac{12}{25}D_2$$

Therefore, the ratio of amount of the desorbed gases $H_2:HD:D_2$ when the reaction between $LiNH_2$ and LiD proceeds is expressed to be $H_2:HD:D_2 = 9:12:4$.

Similarly, with respect to the model 2, we can estimate the ratio of $H_2:HD:D_2 = 5:2:2$ by the same way as model 1 as well.

References and Notes

(1) Schlapbach, L.; Züttel, A. *Nature* **2001**, *414*, 353.
(2) Grochala, W.; Edwards, P. *Chem. Rev.* **2004**, *104*, 1283.
(3) Bogdanoviæ, B.; Schwickardi, M. *J. Alloys Compd.* **1997**, *253*, 1.
(4) Sun, D.; Srinivasan, S. S.; Kiyobayashi, T.; Kuriyama, N.; Jensen, C. M. *J. Phys. Chem. B* **2003**, *107*, 10176.
(5) T. Kiyobayashi, S. S. Srinivasan, D. Sun, and C. M. Jensen, *J. Phys. Chem. A* **2003**, *107*, 7671.
(6) Züttel, A.; Rentsch, S.; Fischer, P.; Wenger, P.; Sudan, P.; Mauron, Ph. Emmenegger, Ch. *J. Alloys Compd.* **2003**, *356*, 515.
(7) Orimo, S.; Nakamori, Y.; Züttel, A. *Mater. Sci. Eng. B* **2004**, *108*, 51.
(8) Miwa, K.; Ohba, N.; Towata, S.; Nakamori, Y.; Orimo, S. *Phys. Rev. B* **2004**, *69*, 245120.
(9) Kojima, Y.; Kawai, Y.; Nakanishi, H.; Matsumoto, S. *J. Power Sources* **2004**, *135*, 36.
(10) Li, Z. P.; Liu, B. H.; Arai, K.; Asaba, K.; Suda, S. *J. Power Sources* **2004**, *126*, 28.
(11) Chen, P.; Ziong, Z.; Luo, J.; Lin, J.; Tan, K. L. *Nature* **2002**, *420*, 302.
(12) Hu, Y. H.; Ruckenstein, E. *J. Phys. Chem. A* **2003**, *107*, 9737.
(13) Chen, P.; Xiong, Z.; Luo, J.; Lin, J.; Tan, K. L. *J. Phys. Chem. B* **2003**, *107*, 10967.
(14) Ichikawa, T.; Isobe, S.; Hanada, N.; Fujii, H. *J. Alloys Compd.* **2004**, *365*, 271.
(15) Nakamori, Y.; Orimo, S. *Mater. Sci. Eng. B* **2004**, *108*, 48.
(16) Nakamori, Y.; Orimo, S. *J. Alloys Compd.* **2004**, *370*, 271.
(17) Ichikawa, T.; Hanada, N.; Isobe, S.; Leng, H. Y.; Fujii, H. *J. Phys. Chem. B* **2004**, *108*, 7887.
(18) Leng, H. Y.; Ichikawa, T.; Hino, S.; Hanada, N.; Isobe, S.; Fujii, H. *J. Phys. Chem. B* **2004**, *108*, 8763.
(19) Luo, W. *J. Alloys Compd.* **2004**, *381*, 284.
(20) Xiong, Z.; Wu, G.; Hu, J.; Chen, P. *Adv. Mater.* **2004**, *16*, 1522.
(21) Nakamori, Y.; Kitahara, G.; Miwa, K.; Towata, S.; Orimo, S. *Appl. Phys. A* **2005**, *80*, 1.
(22) Leng, H. Y.; Ichikawa, T.; Hino, S.; Hanada, N.; Isobe, S.; Fujii, H. *J. Power Sources,* in press
(23) Gross, K. J.; Guthrie, S.; Takara, S.; Thomas, G. *J. Alloys Compd.* **2000**, *297*, 270.