

Rechargeable hydrogen storage in nanostructured mixtures of hydrogenated carbon and lithium hydride

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A hydrogen storage ability caused by the interaction between nanostructured carbon ($C^{\text{nano}}H_x$) and lithium hydride (LiH) is demonstrated, which should be recognized as Li-C-H system in the H-storage materials. Especially, the 2:1 mixture of $C^{\text{nano}}H_x$ and LiH exhibited promising hydrogen storage properties with a rechargeable hydrogen capacity of more than 4 mass% below 350 °C, preserving the nanostructural feature in the mixture even after hydrogen release. On the other hand, the 1:2 and 1:1 mixtures exhibited the crystal growth of Li_2C_2 after hydrogen desorption, leading to poorer hydrogen rechargeability. © 2005 American Institute of Physics.

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For realizing hydrogen energy systems in the near future, it is necessary to develop sustainable hydrogen storage (H-storage) systems using high-performance H-storage materials.^{1,2} Recently, much attention has been paid to some different kinds of H-storage materials composed of light elements,³⁻⁵ because the hydrogen capacities of conventional H-storage alloys are limited by its own weight. Particularly, the nanostructural carbon materials have been expected as one of the ultimate systems for H-storage due to the cheap price, the abundant resource, and the simple handling.⁶⁻⁸ On the other hand, some chemical hydrides, based on lithium (Li), sodium (Na), or magnesium (Mg) as light elements, have been also attracted as promising H-storage materials for applicable use.^{4,5,9}

Hydrogen desorption properties from a mixture (ball milled for 2 h under 1 MPa hydrogen) of $C^{\text{nano}}H_x$ (ball milled for 80 h under 1 MPa hydrogen)¹⁰ and LiH (purchased from Sigma-Aldrich with 95% purity, powder) with the 2:1 molar ratio are shown in Fig. 1 (first cycle), which were examined by means of a thermogravimetry and mass spectroscopy (TG-MS) equipment installed inside a glovebox filled with purified argon. The large weight loss of 8.4 mass% upon heating up to 500 °C is caused by gas desorption of mainly hydrogen peaked around 350 °C and a small amount of methane and ethane. In principle, each hydride in the mixture desorbs hydrogen gas in the heating process. LiH needs a high temperature of more than 600 °C for thermal decomposition, while $C^{\text{nano}}H_x$ reveals hydrogen and hydrocarbon desorbing profiles widely ranged from 300 to 800 °C.¹⁰⁻¹² However, the hydrogen desorption in the ball-milled mixture progress at much lower temperature than that in their own hydrides. In addition, simultaneously performed differential thermal analysis indicated that the above hydrogen desorbing reaction was clearly endothermic. So, we could expect that the ball-milled mixture reveals a rechargeable H-storage behavior. Figure 1 shows the hydrogen desorption properties of the mixture for a few dehydrogenating and rehydrogenating

cycles. The H-recharged product under 3 MPa at 350 °C for 8 h desorbs only hydrogen gas with a two-peak structure corresponding to about 5 mass% without any hydrocarbon emission in the temperature range from 150 to 500 °C. After dehydrogenating the product at 350 °C under a high vacuum, further heating up to 500 °C revealed a weight loss of less than 1 mass% in the TG-MS profiles, indicating almost complete dehydrogenation below 350 °C.

Prior to the discussion on mechanism of the above H-storage ability, we would mention the motivated experimental facts as follows. On the basis of the report on H-storage properties of the lithium nitride (Li_3N) by Chen *et al.*,⁹ we have started investigating the Li-N-H chemical reaction of $LiNH_2 + LiH \leftrightarrow Li_2NH + H_2$ as one of the candidates for H-storage.¹³ In our experiments, it has been clarified that, after lithium amide ($LiNH_2$) decomposes into lithium imide

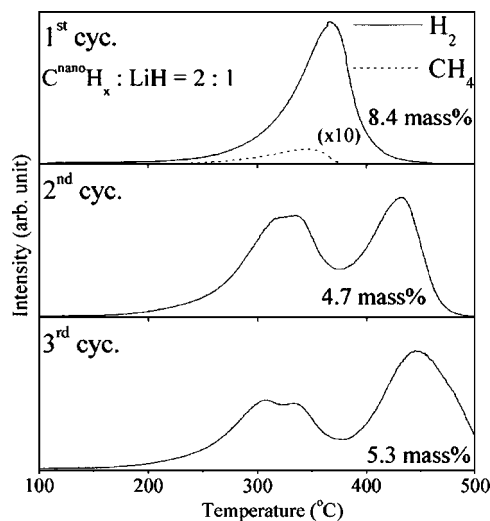


FIG. 1. MS profiles for hydrogen H_2 and methane CH_4 gases from the ball-milled 2:1 mixture of hydrogenated nanostructural carbon $C^{\text{nano}}H_x$ and lithium hydride LiH after repeating the first through third dehydrogenation and rehydrogenation cycles. Weight loss of the mixtures after heating up to 500 °C is given. All data were taken at a heating rate of 5 °C/min.

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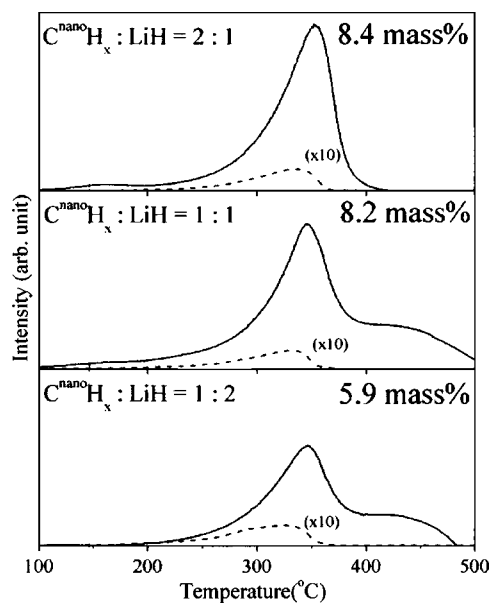


FIG. 2. MS profiles for hydrogen gas and methane gas from the ball-milled mixtures of hydrogenated nanostructural carbon $C^{\text{nano}}H_x$ and lithium hydride LiH with different molar ratios of 1:2, 1:1, and 2:1. Weight loss from the mixtures after heating up to 500 °C for the MS measurement is given. All data were taken in the heating rate of 5 °C/min.

(Li_2NH) and ammonia (NH_3), the extremely stable LiH easily reacts with the emitted NH_3 and releases hydrogen according to the reaction, $LiH + NH_3 \rightarrow LiNH_2 + H_2$, which suggests the destabilization of the strong Li-H ionic bond in LiH by interacting with a polar molecule NH_3 . It has been experimentally confirmed that this reaction proceeds even at room temperature under ball-milling conditions because the reaction is exothermic at standard condition.¹⁴ Thus, it can be deduced that the reaction between LiH and NH_3 is caused by the interaction between the protide (H^-) in LiH and the proton (H^+) in NH_3 .^{14,15} This deduction naturally brings us to the following concept that H^+ in the extremely stable $C^{\text{nano}}H_x$ product could interact with H^- in LiH—analogue to the reaction between LiH and NH_3 —if close contact between them in nanometer scale could be realized, which could lead to hydrogen desorption from a mixture of $C^{\text{nano}}H_x$ and LiH.

For realizing the above concept, we examined the hydrogen desorption properties for the ball-milled mixtures of $C^{\text{nano}}H_x$ and LiH with three different molar ratios of 2:1, 1:1, and 1:2, where the $C^{\text{nano}}H_x$ product used in this work was prepared by ball milling using zirconia balls under 1 MPa H_2 atmosphere.¹⁰ The MS profiles of these mixtures for hydrogen and hydrocarbon desorptions are shown in Fig. 2. The results indicate that the hydrogen desorption profiles of all the mixtures exhibit similar behavior at lower temperatures than 400 °C. The onset and peak temperatures of hydrogen desorption are, respectively, ~150 and ~350 °C for all of the ball-milled mixtures. Thus, these results indicate that both stable hydrides are destabilized by the interaction between the $C^{\text{nano}}H_x$ and LiH at lower temperature than the hydrogen desorption temperatures of each product. Furthermore, it is noted that the highest ratio of $C^{\text{nano}}H_x$ to LiH leads to the best H_2 -desorption properties because the weight loss after heating increases and the hydrogen desorption temperature decreases with the increasing the molar ratio of $C^{\text{nano}}H_x$ to LiH as shown in Fig. 2. In addition, we examined the hydrogen desorption properties for the 4:1 mixture in the

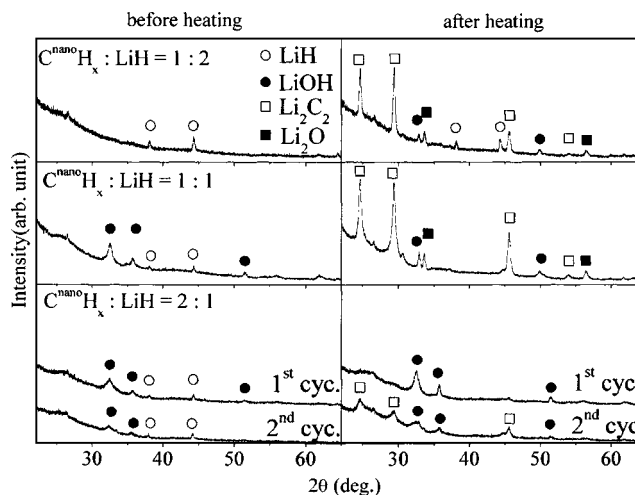


FIG. 3. XRD profiles using $Cu K\alpha$ radiation before and after heating up to 500 °C for the ball-milled mixtures of hydrogenated nanostructural carbon $C^{\text{nano}}H_x$ and lithium hydride LiH with the molar ratios of 1:2, 1:1, and 2:1. The peaks expressed by solid circle (\bullet) are indexed as lithium hydroxide (LiOH), which are generated by water vapor contamination from air during the XRD measurements.

expectation of much better H-storage properties. The results indicated only weight loss of 4 mass% below 500 °C, because the amount of the LiH powder should not be enough to react with $C^{\text{nano}}H_x$ completely. Therefore, the remaining hydrogen (3–4 mass%) would be desorbed from the $C^{\text{nano}}H_x$ itself at a much higher temperature.

To clarify the difference in H-storage properties among the above three ball-milled mixtures, the x-ray diffraction (XRD) examination was performed and the details are shown in Fig. 3. In all of the mixtures before heating up to 500 °C, only the LiH phase can be recognized as a worthy component, whereas $C^{\text{nano}}H_x$ reveals no characteristic XRD profile because of its own nanostructure.^{8,10–12,16,17} In contrast, we can see the crystal growth of the Li_2C_2 phase in the 1:2 and 1:1 mixtures after heating up to 500 °C, whereas there is no clear Li_2C_2 peak and no other valuable peaks in the 2:1 mixture. These results indicate that even after $C^{\text{nano}}H_x$ reacts with LiH, releasing hydrogen by heating up to 500 °C, the 2:1 mixture preserves a similar nanostructural feature, Li_xC^{nano} , to the host carbon-based product, which leads to good rechargeable H-storage properties, while the 1:2 and 1:1 mixtures reveal the crystal growth of the Li_2C_2 phase as a main phase after heating up to 500 °C, which leads to worse H-storage rechargeability, because the Li_2C_2 phase is too stable to absorb hydrogen at moderate pressures and temperatures. Actually, we could succeed in the sufficient rehydrogenation of more than 4 mass% for only the 2:1 mixture under 3 MPa hydrogen at 350 °C among three trials. Unfortunately, the cycle properties in the 2:1 mixture at 350 °C are not satisfactory as practical systems of H-storage because of the appearance of the Li_2C_2 phase in the dehydrogenated state after the second cycle as shown in Fig. 3, which might lead to the deterioration of the H-storage ability in this product. However, this deterioration would be avoided by controlling the reaction at a much lower temperature.

As another aspect, it should be considered that the intercalation of the Li atom into the graphene layer of $C^{\text{nano}}H_x$ took place during ball milling of the 2:1 mixture for 2 h, which was expected to induce the destabilization of the strong C-H bonding.¹⁸ However, the results obtained so far

did not show any evidence of the appearance of such intercalation yet. In any case, the above results indicate that the ability for the H-storage in the ball-milled mixture of LiH and C^{nano}H_x is caused by preserving the nanostructural feature in the carbon-based materials.

In conclusion, we have demonstrated the H-storage properties in the mixture of C^{nano}H_x and LiH prepared by mechanical ball milling. Particularly, the 2:1 mixture in the molar ratio shows the best rechargeability for H-storage among our trials. Although the ways to prepare the ball-milled mixture are not optimized at present, it has been clarified that it is possible to destabilize the strong C-H bonding in C^{nano}H_x—as well as the strong Li-H ionic-bond in LiH—by a close contact between them in nanometer scale, and to rechargeably store a large amount of hydrogen of more than 5 mass% by preserving nanostructural feature in the host carbon material. So far, the opinions show a lack of optimism about the ability of H-storage due to both the physisorption and chemisorption in nanostructural carbons.^{19–23} However this type of destabilization seems to be induced in all kinds of nanostructural carbon materials^{7,24} such as a single-walled carbon nanotube, graphite nanofiber, activated carbon, and so on. Therefore, it is of interest to investigate the destabilization of chemisorbed hydrogen in all of the nanostructural carbon-based materials for H-storage in detail.

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- ¹E. Akiba, *Curr. Opin. Solid State Mater. Sci.* **4**, 267 (1999).
- ²G. Sandrock, *J. Alloys Compd.* **293**, 877 (1999).
- ³L. Schlapbach and A. Züttel, *Nature (London)* **414**, 353 (2001).
- ⁴W. Grochala and P. Edwards, *Chem. Rev. (Washington, D.C.)* **104**, 1283 (2004).
- ⁵F. Schüth, B. Bogdanović, and M. Felderhoff, *Chem. Commun. (Cambridge)* **2004**, 2249 (2004).
- ⁶A. C. Dillon, K. M. Jones, T. A. Bekkedahl, C. H. Kiang, D. S. Bethune, and M. J. Heben, *Nature (London)* **386**, 377 (1997).
- ⁷P. Chen, X. Wu, J. Lin, and K. L. Tan, *Science* **285**, 91 (1999).
- ⁸S. Orimo, G. Majer, T. Fukunaga, A. Züttel, and L. Schlapbach, *Appl. Phys. Lett.* **75**, 3093 (1999).
- ⁹P. Chen, Z. Xiong, J. Luo, J. Lin, and K. L. Tan, *Nature (London)* **420**, 302 (2002).
- ¹⁰S. Isobe, T. Ichikawa, J. I. Gottwald, E. Gomibuchi, and H. Fujii, *J. Phys. Chem. Solids* **65**, 535 (2004).
- ¹¹S. Orimo, T. Matsushima, H. Fujii, T. Fukunaga, and G. Majer, *J. Appl. Phys.* **90**, 1545 (2001).
- ¹²T. Ichikawa, D. M. Chen, S. Isobe, E. Gomibuchi, and H. Fujii, *Mater. Sci. Eng., B* **108**, 138 (2004).
- ¹³T. Ichikawa, S. Isobe, N. Hanada, and H. Fujii, *J. Alloys Compd.* **365**, 271 (2004).
- ¹⁴T. Ichikawa, N. Hanada, S. Isobe, H. Leng, and H. Fujii, *J. Phys. Chem. B* **108**, 7887 (2004).
- ¹⁵P. Chen, Z. Xiong, J. Luo, J. Lin, and K. L. Tan, *J. Phys. Chem. B* **107**, 10967 (2004).
- ¹⁶T. Fukunaga, K. Itoh, S. Orimo, M. Aoki, and H. Fujii, *J. Alloys Compd.* **327**, 224 (2001).
- ¹⁷G. Majer, E. Stanik, and S. Orimo, *J. Alloys Compd.* **356**, 617 (2003).
- ¹⁸T. Fukunaga, K. Itoh, S. Orimo, and H. Fujii, *Physica B* **311**, 95 (2002).
- ¹⁹A. Züttel, C. Nützenadel, P. Sudan, P. Mauron, C. Emmenegger, S. Rentsch, L. Schlapbach, A. Weidenkaff, and T. Kiyobayashi, *J. Alloys Compd.* **330**, 676 (2002).
- ²⁰M. Hirscher, M. Becher, M. Haluska, F. Zeppelin, X. Chen, U. Dettlaff-Weglikowska, and S. Roth, *J. Alloys Compd.* **356**, 433 (2003).
- ²¹T. Kiyobayashi, H. T. Takeshita, H. Tanaka, N. Takeichi, A. Züttel, L. Schlapbach, and N. Kuriyama, *J. Alloys Compd.* **330**, 666 (2002).
- ²²H. Kajjura, S. Tsutsui, K. Kadono, M. Kakuta, and M. Ata, *Appl. Phys. Lett.* **82**, 1105 (2003).
- ²³H. Takagi, H. Hatori, Y. Soneda, N. Yoshizawa, and Y. Yamada, *Mater. Sci. Eng., B* **108**, 143 (2004).
- ²⁴V. Skákalová, A. Quintel, Y.-M. Choi, S. Roth, M. Becher, and M. Hirscher, *Chem. Phys. Lett.* **365**, 333 (2002).

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