

Modified Lithium Borohydrides for Reversible Hydrogen Storage

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In an attempt to develop lithium borohydrides as reversible hydrogen storage materials with high hydrogen storage capacities, the feasibility of reducing the dehydrogenation temperature of the lithium borohydride and moderating rehydrogenation conditions was explored. The lithium borohydride was modified by ball milling with metal oxides and metal chlorides as additives. The modified lithium borohydrides released 9 wt % hydrogen starting from 473 K. The dehydrided modified lithium borohydrides absorbed 7–9 wt % hydrogen at 873 K and 7 MPa. The modification with additives reduced the dehydriding starting temperature from 673 to 473 K and moderated the rehydrogenation conditions from 923 K/15 MPa to 873 K/7 MPa. XRD and SEM analysis revealed the formation of an intermediate compound that might play a key role in changing the reaction path, resulting in the lower dehydriding temperature and reversibility. The reversible hydrogen storage capacity of the oxide-modified lithium borohydrides decreased gradually during hydriding/dehydriding cycling. One of the possible reasons for this effect might be the loss of boron during dehydrogenation, but this can be prevented by changing the dehydriding path using appropriate additives. The additives reduced the dehydriding temperature and improved the reversibility, but they also reduced the hydrogen storage capacity. The best compromise can be reached by selecting appropriate additives, optimizing the additive loading, and using new synthesis processes other than ball milling.

1. Introduction

Alkali metal borohydrides such as LiBH_4 and NaBH_4 are lightweight materials that contain large amounts of hydrogen. The theoretical gravimetric and volumetric hydrogen storage capacities (18.5 wt %, 121 kg/m^3 and 10.6 wt %, 98.7 kg/m^3 , respectively) are well above the U.S. Department of Energy (DOE) benchmark for transportation applications¹ (7.5 wt % and 65 kg/m^3), even taking into account the weight and volume of the containment system. Lithium borohydride could be a superior hydrogen storage material if hydrogen absorption could be reversed at moderate conditions. Borohydrides are also relatively inexpensive and can be produced from abundant natural borax deposits.^{2,3} Unfortunately, these materials are very stable. For example, heating above 673 K, that is, above its melting point, is required to release the majority of the hydrogen from LiBH_4 .⁴ Also, the rehydrogenation conditions are too harsh for practical application. However, the solid hydrogen storage potential of these materials warrants investigation into possible methods to resolve or alleviate these two major problems.

Fedneva et al.⁴ investigated LiBH_4 by DTA (differential thermal analysis). The thermogram of LiBH_4 showed three endothermic effects: at 381–385, 541–559, and 756–765 K. The endothermic effect at 381–385 K is reversible and corresponds to LiBH_4 polymorphic transformation. The second peak at 541–559 K corresponds to LiBH_4 fusion, accompanied by a slight decomposition, which liberates approximately 2% of the hydrogen in the compound. The main evolution of gas starts at 653 K and liberates 80% of the hydrogen in LiBH_4 . The cause of the small effect at 756–765 K is uncertain, but it coincides with the liberation of 50% of the theoretical hydrogen content in LiBH_4 .

In 1980, Alain Muller⁵ reported that 5 g of LiBH_4 decomposed and released 13.8 wt % hydrogen at 723 K and 10^{-2} mmHg (1.3 Pa) pressure within 24 h by the reaction $\text{LiBH}_4 \rightarrow \text{LiH} + \text{B} + \frac{3}{2}\text{H}_2$ with a reaction enthalpy of -24.8 kcal/(mol of H_2). After dehydrogenation, the sample was able to absorb 11.8 wt % (6.65 L) of hydrogen at 923 K and 15 MPa within 48 h. To improve the dehydrogenation and subsequent rehydrogenation processes, 10 wt % aluminum powder was mixed mechanically with LiBH_4 . The mixed material then liberated 12.4 wt % hydrogen at 723 K and 1 Pa within 24 h. Subsequently, 15.2 wt % hydrogen was recharged onto the decomposed material at 923 K and 15 MPa within 12 h. However, the extremely slow reversibility lasted for only two cycles. The dehydriding and rehydriding temperatures were too high. Recently, Zuttler reported that 25% LiBH_4 ball milled with 75% SiO_2 liberated 9 wt % (based on the weight of LiBH_4 in the mixture) hydrogen starting from 523 K through the reaction $\text{LiBH}_4 \rightarrow \text{LiH} + \text{B} + \text{H}_2$. He indicates that the reaction is partially reversible, but provided no detailed data in the report.⁶ Orimo studied the Raman spectra of NaBH_4 , KBH_4 , and LiBH_4 and suggested that the stability of LiBH_4 or LiNH_2 can be reduced by partial cation substitution using smaller-sized and/or higher-valence cations with higher electronegativities such as Mg.⁷ By adding Mg into LiBH_4 at a ratio of $\text{Li}/\text{Mg} = 9:1$ through ball milling, the dehydriding temperature was reduced from 850 to 820 K.⁸ Vajo reported that the ball-milled mixture $\text{LiH} + 0.5\text{MgB}_2 + 0.03\text{TiCl}_3$ absorbed 9 wt % at 350 °C and 100 bar and desorbed 8 wt % hydrogen at 450 °C without counting the weight of the catalyst TiCl_3 . The true capacities based on the total weight of the mixed material were 7.84 and 6.96 wt % for hydrogen absorption and desorption, respectively. Using $\text{LiH} + 0.5\text{MgB}_2 + 0.03\text{TiCl}_3$ as the experimental sample for the measurement of P – C – T (pressure–composition–temperature) isotherms, Vajo concluded that the rehydroge-

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nation enthalpy of LiBH_4 was reduced by 25 kJ/(mol of H_2). The kinetics was extremely slow: reaching equilibrium took 100 h.⁹

Most borohydride research has focused on “on-demand” hydrogen sources, which rely on an irreversible catalyzed hydrolysis reaction. The theoretical hydrogen yield by hydrolysis is only 7.6 wt %, and a considerable amount of water must be supplied. Ruthenium was used as the catalyst. Also, the issue of the safe and cost-effective disposal or recycling of the hydrolysis byproduct NaBO_2 has not yet been resolved.¹⁰

A reversible borohydride material capable of releasing and reabsorbing hydrogen at moderate conditions similar to those employed for a standard metal hydride would represent a major breakthrough in hydrogen storage technology. Motivated by the high theoretical gravimetric and volumetric capacity, systematic investigations were conducted to modify commercially available LiBH_4 for reversible hydrogen storage. A number of potential additives were screened, and several of them were found to reduce the thermal decomposition temperature and improve the reversibility at relatively moderate conditions. Material characterizations showed an interaction of the borohydride with the additives, which helps in understanding the dehydrogenating/rehydrogenating processes. The detailed results are reported herein.

2. Experimental Section

The LiBH_4 powder (95% purity) and the additive powder (99.9–99.99% purity) were purchased from Sigma-Aldrich and used directly without any pretreatment.

For sample preparation, in an argon glovebox, 2 g of LiBH_4 and the appropriate additive powder mixture was placed in a 25-mL hardened steel grinding bowl containing three 11-mm-diameter tungsten carbide balls. (The weight ratio of the balls to the powder was 32:2.) The sealed grinding bowls were removed from the argon glovebox and put on a Frisch-7 planetary ball mill for 5–10 h of milling at 600 rpm. After milling, the dehydrogenating temperatures of the modified borohydrides were first screened on a Perkin-Elmer TG/DTA thermal analyzer. Then, 0.5 g of selected modified LiBH_4 powders was transferred to a Sieverts apparatus, a volumetric device with 500 Pa (5 mbar) back-pressure, for temperature-programmed desorption (TPD) measurements. The temperature was ramped from ambient to 973 K at a rate of 5 K/min. The rehydrogenations were conducted at 873 K and 7 MPa (99.9999% hydrogen) in the same Sieverts apparatus. The hydrogen absorption and desorption capacities were calculated according to the total weight of the modified borohydrides including the weight of the additives. Borohydrides that showed promising results were investigated by X-ray diffraction (XRD) in a Philips X'Pert Pro X-ray diffractometer to determine their crystal structure and phase composition in different states: as milled, dehydrided, and rehydrided. The morphologies and additive distributions of the new materials were analyzed with a Hitachi S3600N scanning electron microscope (SEM) equipped with an energy dispersion spectrometer (EDS). The composition of the dehydrogenating gas stream was analyzed with a Pfeiffer ThermoStar mass spectrometer in ambient environment.

3. Results and Discussion

3.1. Dehydrogenation of the Modified LiBH_4 Materials.

In the initial TG/DTA screening, eight oxides and chlorides were added to LiBH_4 through ball milling. Five additives, namely, TiO_2 , TiCl_3 , ZrO_2 , V_2O_3 , and SnO_2 , were effective in reducing the temperature of rapid decomposition and increasing the desorption rate at low temperature compared to commercial

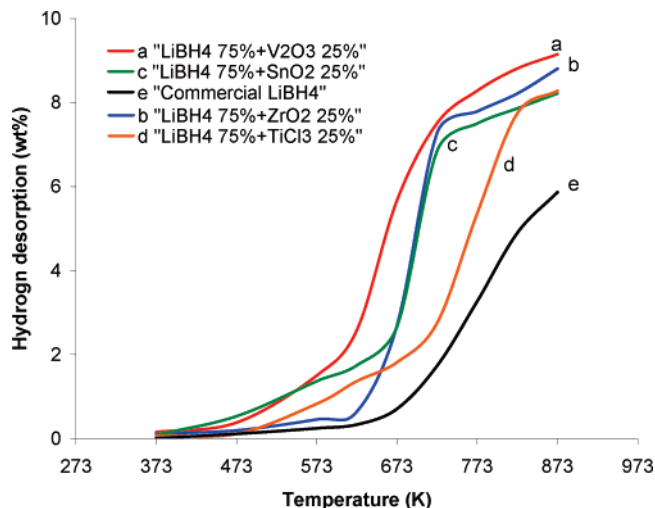


Figure 1. Comparison of the modified LiBH_4 materials with the commercial LiBH_4 .

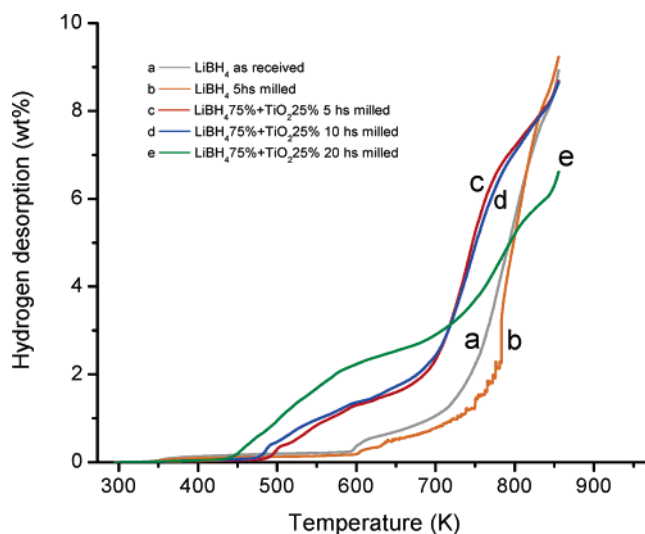


Figure 2. TPD of the TiO_2 -modified and commercial LiBH_4 materials.

LiBH_4 (see Figure 1). The materials 75% LiBH_4 + 25% TiO_2 , 75% LiBH_4 + 25% V_2O_3 , 75% LiBH_4 + 25% ZrO_2 , 75% LiBH_4 + 25% SnO_2 , and 75% LiBH_4 + 25% TiCl_3 each desorbed 8–9 wt % hydrogen from 448 to 473 K.

To verify the influence of the ball milling on the lithium borohydride dehydrogenation, a sample of commercial LiBH_4 was ball milled for 5 h without any additives. Figure 2 shows the TPD data for commercial LiBH_4 , ball-milled LiBH_4 , and TiO_2 -modified LiBH_4 samples. Commercial LiBH_4 decomposes starting from approximately 598 K at a very low rate. At about 723 K, the decomposition accelerates appreciably, resulting in a final release of 9 wt % hydrogen at about 873 K. A comparison of the commercial LiBH_4 with 5-h-milled LiBH_4 shows that the ball milling alone does not reduce the dehydrogenating temperature or improve the dehydrogenating kinetics. The modified material 75% LiBH_4 + 25% TiO_2 liberates the same amount of hydrogen (9 wt %) as the commercial LiBH_4 , but does so starting at 473 K for the samples milled for 5–10 h and at 448 K for that milled for 20 h. The effect of the TiO_2 in reducing the dehydrogenating temperature is obvious. It is recognized that extending the milling time does little to reduce the dehydrogenating temperature, but does decrease the hydrogen capacity. For example, the 20-h-milled 75% LiBH_4 + 25% TiO_2 releases only 6.9 wt % hydrogen at 873 K. A possible reason for this behavior will be discussed later in this article.

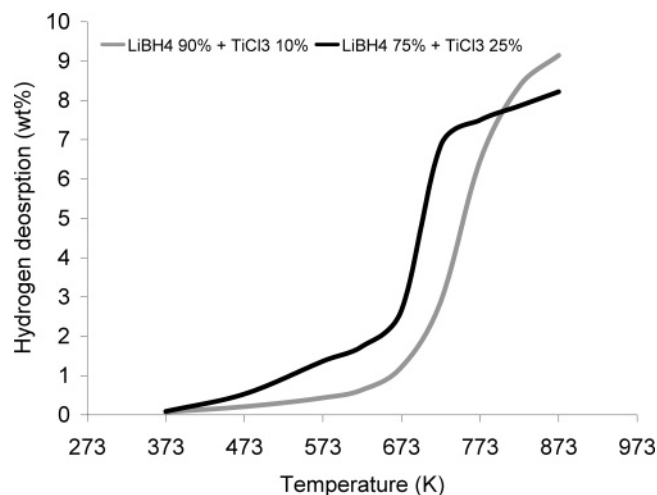


Figure 3. Effect of the additive TiCl_3 on the dehydrogenation behavior of LiBH_4 .

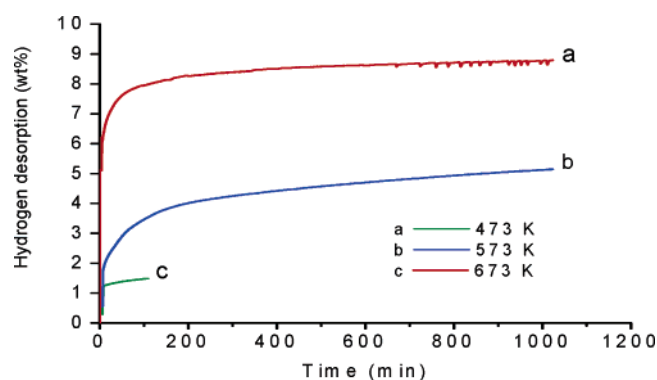


Figure 4. Dehydrogenation of 75% LiBH_4 + 25% TiO_2 at 473, 573, and 673 K.

It is considered that the additives play a significant role both in enabling lower-temperature hydrogen desorption and in releasing more hydrogen than commercial borohydride at the same temperature. Zuttler⁶ reported that about 50% theoretical hydrogen content (~ 9 wt %) is liberated from LiBH_4 catalyzed by SiO_2 starting at 473 K. Given the mixture ratio of 25 wt % LiBH_4 and 75 wt % SiO_2 , the actual hydrogen desorption of the total amount of mixed material is far less than 9 wt %. In the experiments reported here, about 9 wt % hydrogen was released from the modified LiBH_4 -based materials (including the weight of the additive), and the dehydrogenation was initiated at 473 K. It is proposed that a possible overall LiBH_4 dehydrogenation reaction is $2\text{LiBH}_4 \rightarrow 2\text{LiH} + 2\text{B} + 3\text{H}_2$ because LiH is very stable up to 1173 K.^{6,7} This reaction liberates 13.79 wt % of the hydrogen from LiBH_4 . Upon addition of 25 wt % TiO_2 , the hydrogen released from our modified material 75% LiBH_4 + 25% TiO_2 is theoretically 10.34 wt %. Practically, the average dehydrogenation capacity of our modified LiBH_4 materials containing 25 wt % additives is about 9 wt %. This is understandable because of hydrogen evolution during ball milling that is caused by the interaction of LiBH_4 and TiO_2 . This issue is discussed further in the XRD analysis section.

Reducing the additive loading increases the hydrogen desorption capacity, but it also raises the dehydrogenation temperature. Figure 3 shows a dehydrogenation comparison of the materials 75% LiBH_4 + 25% TiCl_3 and 90% LiBH_4 + 10% TiCl_3 . As expected, the hydrogen desorption capacity increased from 8.2 to 9.2 wt % at 873 K as the TiCl_3 loading was reduced from 25% to 10%. However, the rapid dehydrogenation temperature increased from 373 to 523 K. The reaction kinetics also suffered. A similar

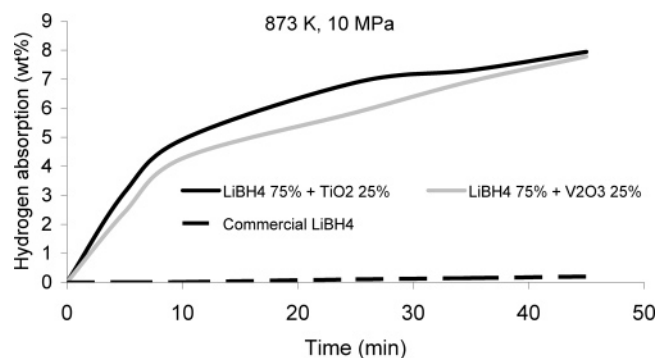


Figure 5. Hydrogen absorption of the dehydrided materials 75% LiBH_4 + 25% TiO_2 and 75% LiBH_4 + 25% V_2O_3 .

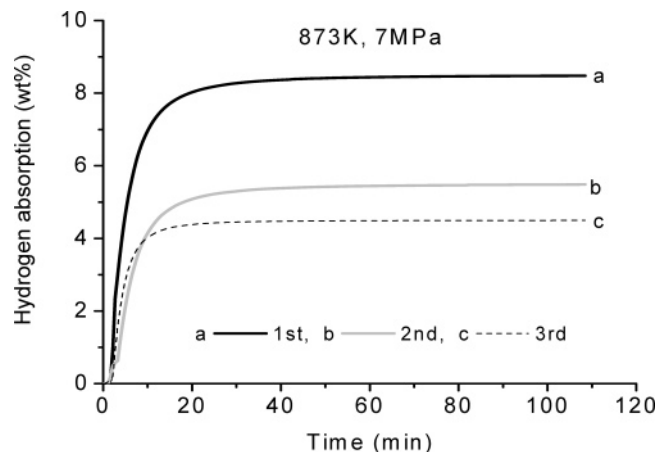


Figure 6. Isothermal hydrogen absorption of the material 75% LiBH_4 + 25% TiO_2 .

conclusion was made on the basis of a comparison of the materials 75% LiBH_4 + 25% TiO_2 and 90% LiBH_4 + 10% TiO_2 in our experiments. Obviously, there is a tradeoff issue, so the most reasonable compromise should be pursued.

Although the TPD data provide an overall picture of the dehydrogenation process in a wide temperature range, isothermal dehydrogenation studies are normally used to judge material performance characteristics such as storage capacity and kinetics at the desired temperature. The isothermal dehydrogenation properties of the material 75% LiBH_4 + 25% TiO_2 are shown in Figure 4. It appears that the dehydrogenation process follows first-order kinetics. There are two stages in the dehydrogenation process: fast dehydrogenation in the first short period and very slow dehydrogenation thereafter. The material desorbed about 8.0 wt % hydrogen within the first 100 min at 673 K. However, hydrogen desorption continued for about 10 h before the reaction was completed, adding 0.5 wt % hydrogen for a total of 8.5 wt % desorption. The material desorbed about 4.5 and 1.5 wt % hydrogen at 573 and 473 K, respectively. This shows that the hydrogen desorption is a temperature-dependent process.

3.2. Rehydrogenation of the Modified LiBH_4 Materials.

In Muller's work,⁵ the modified material 90 wt % LiBH_4 + 10 wt % Al desorbed 12.4 wt % hydrogen at 723 K within 12 h in the first dehydrogenation, but the dehydrided material could not be recharged to its original capacity. The second dehydrogenation yielded only 5 wt % hydrogen. The effect of the second rehydrogenation was almost negligible, absorbing only 0.6 wt % hydrogen. To study the dehydrogenation/rehydrogenation reversibility of the modified borohydrides, the material 75% LiBH_4 + 25% TiO_2 was selected for hydriding and dehydrogenation cycling tests. After being dehydrogenated at 873 K for 1 h, the materials 75%

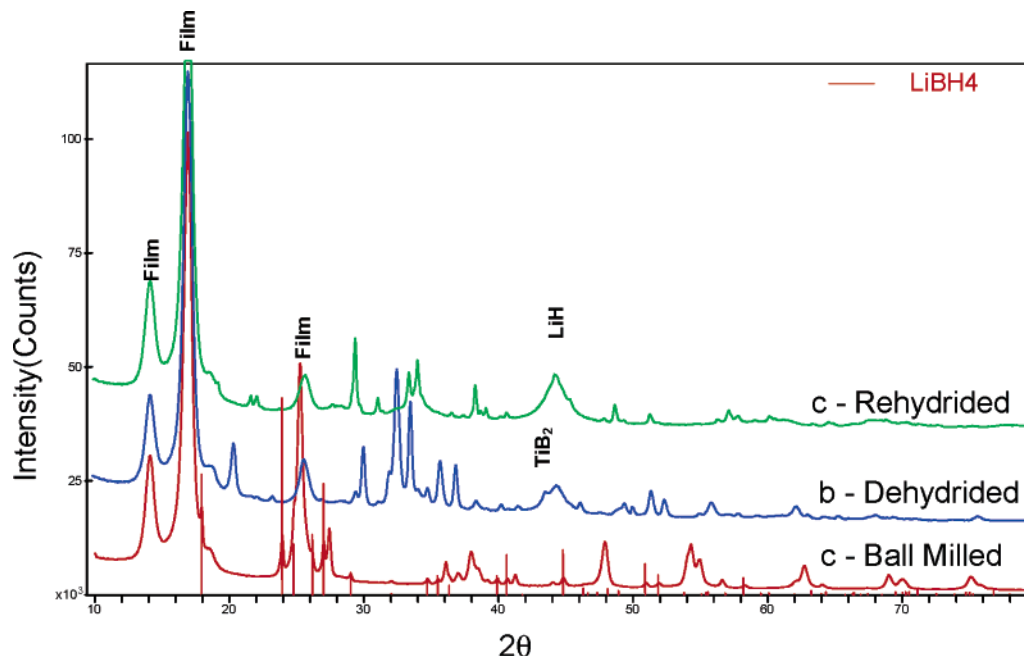


Figure 7. XRD spectra of the material 75% LiBH₄ + 25% TiO₂ in different states.

LiBH₄ + 25% TiO₂ and 75% LiBH₄ + 25% V₂O₃ were rehydrided at 873 K and 10 MPa. As Figure 5 shows, the dehydrided materials LiBH₄ + 25% TiO₂ and 75% LiBH₄ + 25% V₂O₃ absorb 7.8 and 7.9 wt % hydrogen, respectively, within 45 min. The rehydrogenation capacity increased to 8 wt % when the absorption time was prolonged to 1 h. This shows that the new LiBH₄ materials are reversible at the conditions tested. Obviously, the rehydriding temperature and pressure are still too high. However, it is believed that the elevated conditions can be moderated by adjusting the compositions and tuning the thermodynamic stability of the modified LiBH₄ materials. Figure 6 shows the repeated isothermal rehydrogenation of the material 75% LiBH₄ + 25% TiO₂ at 873 K and 7 MPa. The hydrogen absorption capacity decreases from 8.25 to 5.6 and 4.2 wt % in the second and third hydrogenations, respectively. To investigate the possible causes, XRD and mass spectrum analyses were conducted.

3.3. XRD Analysis of the Modified LiBH₄ Materials. To identify the phase compositions during dehydrogenation and rehydrogenation, the material 75% LiBH₄ + 25% TiO₂ was investigated by XRD in three different states: ball-milled, dehydrided, and rehydrided. The XRD spectrum of the 5-h-ball-milled 75% LiBH₄ + 25% TiO₂ shows a structural change (see Figure 7a). The crystal structure of TiO₂ has partially changed from anatase to rutile. In addition to the expected LiBH₄ and TiO₂, traces of TiB₂ and LiB₃O₅ have formed through the possible interaction between LiBH₄ and TiO₂ during ball milling. The XRD data confirmed partial LiBH₄ decomposition and the combination of Ti with B. It is proposed that the intermediate compound TiB₂ dispersed within the matrix might provide a pathway for the reversible dehydriding/rehydriding reaction. Its interesting role might be to facilitate the B–H bond dissociation and recombination process. The material 75% LiBH₄ + 25% TiO₂ can be expressed as LiBH₄ + 0.09TiO₂. According to this molar ratio, most of the LiBH₄ is not able to react with TiO₂ during ball milling. In most of our measurements, the oxide-/chloride-modified LiBH₄ materials desorbed 8–9 wt % hydrogen, which is equal to one-half of the theoretical capacity of LiBH₄.

The XRD results for the dehydrided material 75% LiBH₄ + 25% TiO₂ are shown in Figure 7b. It appears that the LiBH₄ decomposes into LiH, LiOH, TiB₂, and trace amounts of Li₇B₆ during hydrogen evolution. The additive TiO₂ disappears. The XRD spectrum does not indicate the visible presence of boron as the reaction $2\text{LiBH}_4 \rightarrow 2\text{LiH} + 2\text{B} + 3\text{H}_2$ would suggest.⁵ More likely, LiBH₄ might react with TiO₂, resulting in the formation of LiH; LiOH; and, more meaningfully, intermediate compounds such as TiB₂. It is possible that some boron segregates from LiBH₄ as amorphous clusters without reacting with titanium. The intermediate phases might make the dehydrogenation reversible at relatively moderate conditions. The hypothetical reversible reaction is given as $6\text{LiBH}_4 + 2\text{TiO}_2 \rightarrow 2\text{LiH} + 4\text{LiOH} + 2\text{TiB}_2 + 2\text{B} + 9\text{H}_2$. The contribution of the additive TiO₂ might be to form intermediate boron compounds that promote the decomposition of LiBH₄, resulting in low-temperature dehydriding and facilitating the recombination leading to reversibility. It is not the intention of this work to prove the mechanism using the limited data presented here. The possible existence of the compound Ti₇B₆ has not been verified. More material characterizations and particularly designed experiments have to be conducted to understand the actual reactions.

The XRD results for the rehydrided material 75% LiBH₄ + 25% TiO₂ are shown in Figure 7c. The intensities of the identifiable peaks are very low, which indicates that the materials are either in short-range disorder or in amorphous states. The recombined LiBH₄ is not detectable in our XRD experiments, although its existence is evidenced by our rehydriding and subsequent dehydriding measurements (Figures 4–6). The expected recombined LiBH₄ could be in an amorphous state. Similar results have been reported by other laboratories.⁸ The visible peaks are identified as the TiB₂, Li₇B₆, and possibly Li₃BO₃. The additive TiO₂ is not identifiable in the XRD spectrum of the rehydrided material. However, the intermediate compound TiB₂ persists in both dehydrided and rehydrided states. It is interesting to note that TiO₂ partially decomposes into TiB₂ during the ball milling and dehydriding process. The intermediate compounds derived from oxide additives, such as TiB₂ in 75% LiBH₄ + 25% TiO₂, might play a role in reducing the

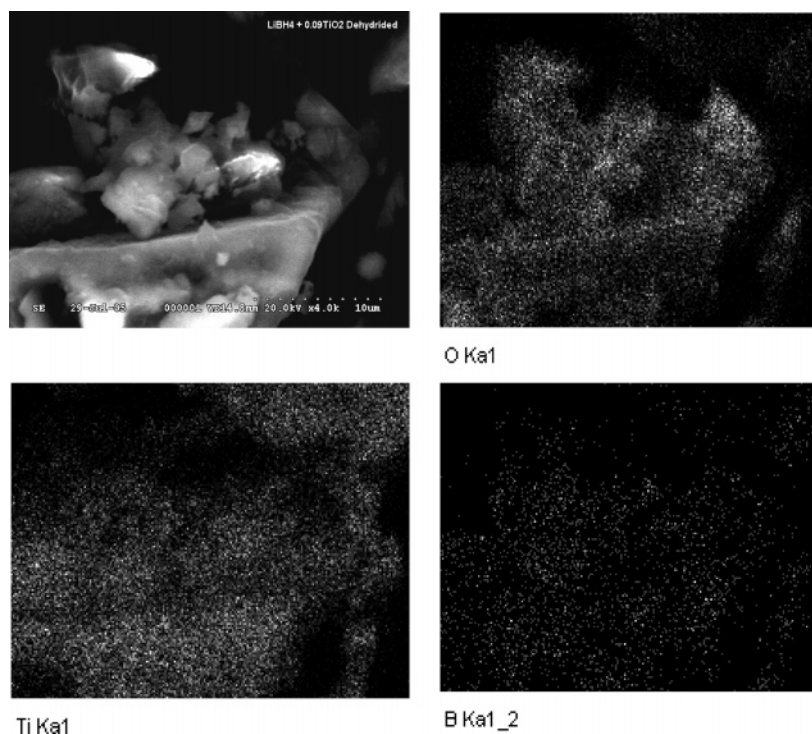
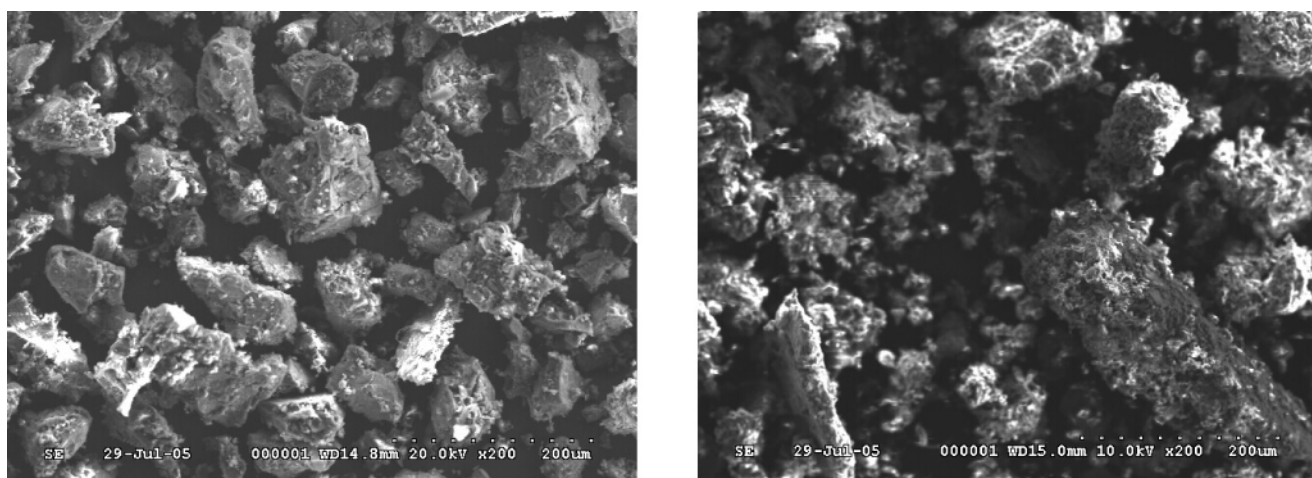


Figure 8. EDX element maps of the material 75% LiBH_4 + 25% TiO_2 ($\times 4000$).



(a) As dehydrided ($\times 200$)

(b) As rehydrided ($\times 300$)

Figure 9. SEM morphologies of the dehydrided and rehydrided material 75% LiBH_4 + 25% TiO_2 ($\times 300$).

decomposition temperature and providing reversibility for lithium borohydride materials. There is also another possibility that rehydrogenation produces a new Li-B-H-Ti complex that has a lower stability and better reversibility than the original LiBH_4 . More experiments and characterization might provide clues to address this possibility.

3.4. SEM Observation and EDX Mapping of the 75% LiBH_4 + 25% TiO_2 Material. To verify the distribution and decomposition of the additive TiO_2 , SEM and EDX mapping were carried out. After a sample had been dehydrided at 873 K, the disassociation of titanium and oxygen through the decomposition of TiO_2 was observed in the element maps of the dehydrided material 75% LiBH_4 + 25% TiO_2 (see Figure 8). Titanium can combine with boron to form TiB_2 as suggested by the XRD data in Figure 7. A similar segregation of titanium and oxygen was also observed in the rehydrided materials 75% LiBH_4 + 25% TiO_2 in our experiments. The dehydrided and

rehydrided samples of 75% LiBH_4 + 25% TiO_2 exhibited porous and layered features with the coarsen particles size shown in Figure 9.

3.5. Mass Spectral Analysis of the Gas Stream from Decomposition of the Commercial LiBH_4 . Mass spectral analysis indicates that the decomposition gas stream from commercially available LiBH_4 consists mainly of hydrogen with trace amounts of BH_3 and H_2O , see Figure 10. The H_2O most likely comes from moisture absorbed during sample transfer. However, BH_3 formation, even in trace amounts, causes permanent loss of the boron, resulting in a gradual decrease of the hydrogen storage capacity during dehydriding/rehydriding cycling. We have not yet conducted mass spectral analysis on any modified LiBH_4 . However, it is possible that the formation of BH_3 can be prevented by selecting appropriate additives and changing the reaction path in the modified LiBH_4 materials. The results of such investigations will be reported later.

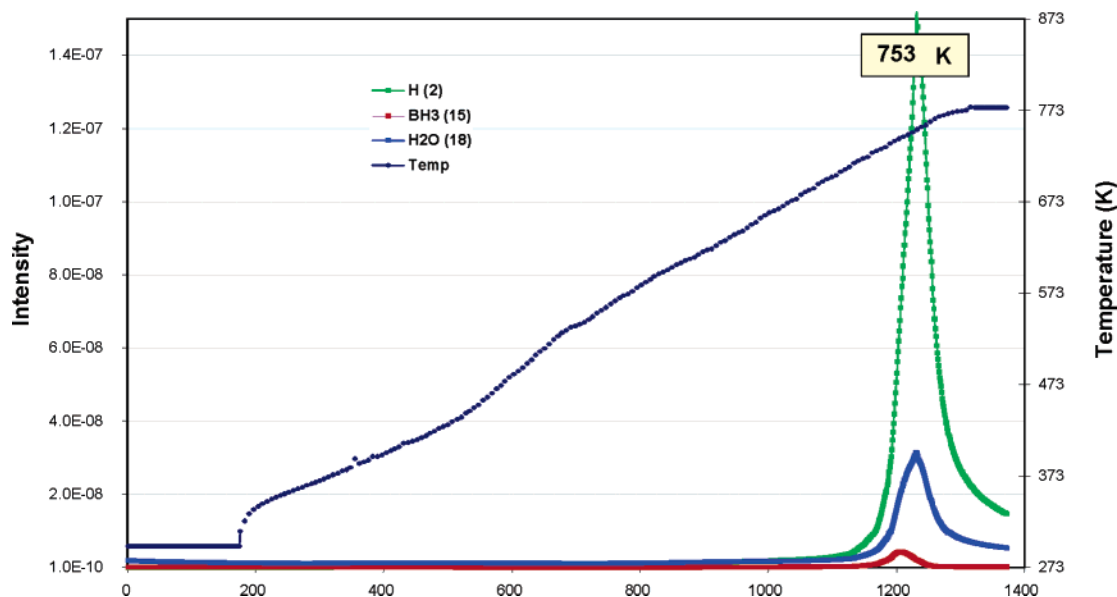


Figure 10. Mass spectra of the thermal decomposition of the material 75% LiBH_4 + 25% TiO_2 .

Conclusions

Modification of LiBH_4 with additives such as metal oxides and chlorides reduced the hydrogen desorption starting temperature from 673 to 473 K. The modified lithium borohydrides desorbed about 9 wt % hydrogen and could be recharged to 7–9 wt % hydrogen capacity at 873 K and 7 MPa. Five effective additives were identified. Material characterization indicated that the additive reacts with lithium borohydride and produces an intermediate compound that can facilitate the reversible reaction at relatively moderate conditions. The hydrogen storage capacity of the oxide-modified lithium borohydrides decreased gradually during hydriding/dehydriding cycling. One of the possible reasons for this result is the loss of boron through the formation of BH_3 that flows out with the hydrogen stream during dehydrogenation. It is believed that the boron loss can be prevented by selecting additives, forming intermediate boron compounds, and changing the reaction path. Although the additives reduce the dehydriding temperature and improve the reversibility, they also reduce the hydrogen storage capacity. The best compromise should be reached by optimization of the additive loading. Extended ball milling does little to improve dehydriding performance, but it reduces the hydrogen desorption capacity. It is believed that the additives change the thermal stability of the lithium borohydrides to some degree. It is realized that other modifiers such as metals, metal hydrides, and

compounds other than oxides and chlorides might change the B–H binding energy, resulting in the achievement of reversible dehydriding and rehydriding at reasonably moderate conditions.

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References and Notes

- (1) FY2002 Progress Report for Hydrogen, Fuel Cell and Infrastructure Technologies Program; U.S. Department of Energy, U.S. Government Printing Office: Washington, DC, 2002.
- (2) Li, Z. P.; Liu, B. H.; Suda, S. *J. Alloys Compd.* **2003**, 354, 243.
- (3) Kojima Y.; Haga, T. *Int. J. Hydrogen Energy* **2003**, 28, 989.
- (4) Fedneva, E. M.; Alpatova V. L.; Mikheeva, V. I. *Russ. J. Inorg. Chem.* **1964**, 9, 826.
- (5) Muller, A.; Havre, L.; Mathey, F.; Petit, V. I.; Bensoam, J. U.S. Patent 4,193,978, 1980.
- (6) Zuttel, A.; Rentsch, S.; Fesher, P.; Wenger, P.; Sudan, P.; Mauron, Ph.; Emmenegger, Ch. *J. Alloys Compd.* **2003**, 356–357, 515.
- (7) Nakamori, Y.; Orimo, S. *J. Alloys Compd.* **2004**, 370, 271.
- (8) Orimo, S.; Nakamori, Y.; Kitahara, G.; Miwa, K.; Ohba, N.; Towata, S.; Zuttel, A. *J. Alloys Compd.* **2005**, 404–406, 427.
- (9) Vajo, J.; Skeith, S. *J. Phys. Chem.* **2005**, 109 (9), 3719.
- (10) Millennium Cell, U.S. Patent 6534033 B1, 2003.