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# Significantly improved dehydrogenation of LiBH<sub>4</sub> destabilized by TiF<sub>3</sub>

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The hydrogen storage properties of LiBH<sub>4</sub> ball milled with TiF<sub>3</sub> were investigated. It was found that the LiBH<sub>4</sub>-TiF<sub>3</sub> mixture exhibited significantly improved dehydrogenation properties. For example, the LiBH<sub>4</sub>-TiF<sub>3</sub> (mole ratio: 3 : 1) sample started to release hydrogen at around 100 °C, and the hydrogen desorption capacity reached 5.0 wt% at 250 °C. Furthermore, the dehydrogenated product can be partially rehydrogenated at 100 atm H<sub>2</sub> and 350 °C. X-Ray diffraction (XRD), infrared (IR) spectroscopy and X-ray photoelectron spectroscopy (XPS) characterizations revealed that the decreased dehydrogenation conditions in the LiBH<sub>4</sub>-TiF<sub>3</sub> system resulted from an exothermic reaction of 3LiBH<sub>4</sub> + TiF<sub>3</sub> → 3LiF + TiB<sub>2</sub> + B + 6H<sub>2</sub>, which improved both its thermodynamics and kinetics. As the above reaction is exothermic, the reverse reaction is not feasible, further investigations indicated that the rehydrogenation may be due to the formation of another borohydride.

## Introduction

The hydrogen storage program was proposed and began investigation several decades ago.<sup>1,2</sup> With the ever-increasing demand for clean and renewable energy sources as a long-term solution for a secure energy future, tremendous efforts have been devoted to the research and development of hydrogen storage materials in the past few decades.<sup>3-7</sup> Up to now, several classes of candidate hydrogen storage materials, including metal hydrides,<sup>3,4</sup> polymers<sup>8</sup> and chemical hydrides<sup>9-12</sup> and organometallic complexes,<sup>13</sup> *etc.*, have been developed and investigated. Among them, LiBH<sub>4</sub> is a promising hydrogen storage material due to its high hydrogen storage capacities (18.3 wt%, 121 kg m<sup>-3</sup>) which are well above the US Department of Energy's (DOE) target for transportation applications by 2015 (9.0 wt% and 91 kg m<sup>-3</sup>).<sup>14,15</sup> However, its main evolution of gas starts at 380 °C, and the rehydrogenation can be achieved only under conditions of 15–30 MPa H<sub>2</sub> pressure and 650 °C.<sup>16</sup>

To meet all the demands required for commercial vehicular applications, the dehydrogenation/rehydrogenation of LiBH<sub>4</sub> needs to be improved. In 2003, Züttel *et al.* reported that SiO<sub>2</sub>

may be used as a catalyst for the dehydrogenation of LiBH<sub>4</sub>, lowering the temperature of hydrogen evolution to 300 °C.<sup>17</sup> Then, destabilization and nanocrystallization of LiBH<sub>4</sub><sup>18</sup> were extensively used for the purpose of improving its thermodynamic and kinetic properties. The destabilization involves modifying the thermodynamics of hydrogenation/dehydrogenation reactions by using additives to form compounds or alloys in the dehydrogenated state.<sup>19</sup> Literature protocols showed that many additives, including metals,<sup>20</sup> hydrides,<sup>20-22</sup> chlorides,<sup>22</sup> oxides<sup>23</sup> and other materials, such as carbon<sup>24</sup> or their mixtures,<sup>14,25-27</sup> can improve the dehydrogenation and rehydrogenation properties of LiBH<sub>4</sub>. Up to now, the most effective composite material reported is LiBH<sub>4</sub> + 0.2MgCl<sub>2</sub> + 0.1TiCl<sub>3</sub>, which releases 5 wt% of hydrogen from 60 °C to 400 °C and can be rehydrogenated to 4.5 wt% at 600 °C.<sup>27</sup> Meanwhile, first principle calculations were employed and a reasonable thermodynamic guideline, which is beneficial for both assessing the validity and prediction of the destabilization reactions, was proposed.<sup>19,28</sup>

It has been reported that titanate salts can promote the dehydrogenation and rehydrogenation properties of LiBH<sub>4</sub> and its related multicomounds.<sup>22,26,27,29</sup> However, the LiBH<sub>4</sub>-TiF<sub>3</sub> system was not systemically investigated and the role of TiF<sub>3</sub> is not quite clear. In this paper, the binary composite was studied, superior dehydrogenation performance was observed and the role of TiF<sub>3</sub> in destabilizing LiBH<sub>4</sub> is discussed. The initial desorption properties for the system were evaluated using Sievert's methods

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## Broader context

It is already known that titanate salts can promote the dehydrogenation and rehydrogenation properties of LiBH<sub>4</sub>. In this paper, a promising hydrogen storage binary composite of LiBH<sub>4</sub>-TiF<sub>3</sub> was reported. It was found that LiBH<sub>4</sub> can react with TiF<sub>3</sub> to release hydrogen at about 100 °C based on an exothermic reaction of 3LiBH<sub>4</sub> + TiF<sub>3</sub> → 3LiF + TiB<sub>2</sub> + B + 6H<sub>2</sub>, which improved both its thermodynamics and kinetics.

Although the reverse reaction in the LiBH<sub>4</sub>-TiF<sub>3</sub> system is not thermodynamically favoured, as indicated by the exothermic nature of the dehydrogenation reactions, the dehydrogenated products can be partially rehydrogenated at 350 °C and 100 atm H<sub>2</sub> pressure due to the formation of a new borohydride.

and a thermogravimetric/differential thermal analysis mass spectrometer (TG/DTA-MS). Powder X-ray diffraction (XRD), infrared (IR) spectroscopy and X-ray photoelectron spectroscopy (XPS) were used to determine the sample phase and the dehydrogenation and rehydrogenation pathway. Results show that the onset of hydrogen desorption is only about 100 °C and the LiBH<sub>4</sub>-TiF<sub>3</sub> mixture (3 : 1) can release 5.0 wt% and 6.4 wt% hydrogen below 250 °C and 500 °C, *i.e.* both the thermodynamic and the kinetic properties of LiBH<sub>4</sub> can be improved when destabilized by TiF<sub>3</sub>. The dehydrogenated sample can also be partially rehydrogenated at 100 atm H<sub>2</sub> and 350 °C. Furthermore, the enthalpy change of the dehydrogenation reaction was calculated, the role of TiF<sub>3</sub> in decreasing the dehydrogenation of LiBH<sub>4</sub> and the rehydrogenation ability were discussed.

## Experimental

The source materials were obtained commercially, namely LiBH<sub>4</sub> 95% (Alfa Aesar, USA) and TiF<sub>3</sub> (Alfa Aesar, USA) were used without further purification, with all handling procedures conducted under an argon atmosphere. Approximately 0.5 g mixtures of LiBH<sub>4</sub>-TiF<sub>3</sub> with various mole ratios of 50 : 3 (S1), 5 : 1 (S2), 3 : 1 (S3) and 2 : 1 (S4) were mechanically milled for 15 min (planetary QM-1SP2) under argon.

Hydrogen release property measurements were performed by Sievert's method from ambient temperature to 600 °C at a 2 °C min<sup>-1</sup> heating rate and by thermogravimetric/differential thermal analysis (TG/DTA, STA 449C) connected to a mass spectrometer (MS, QMS 403) using a heating rate of 10 °C min<sup>-1</sup> under a 1 atm argon atmosphere. Typical sample quantities were 5–10 mg, which is sufficient for getting accurate results due to the high sensitivity of the employed equipment. The rehydrogenation of the LiBH<sub>4</sub>-TiF<sub>3</sub> sample was carried out on a home-made Sievert's apparatus under 10 MPa hydrogen pressure and 350 °C for 12 h. The pressure-concentration-temperature (PCT) measurements were carried out on a Sievert's apparatus, a named gas reaction controller (GRC, Advanced Materials Corp., USA). For the PCT desorption measurement, the sample was first evacuated at room temperature, and then a starting hydrogen pressure (purity 99.9999%) of 30 atm was applied to the container to about 30 atm. After that, the sample was heated to the desired temperatures. During the desorption, the pressure of the system was measured with a pressure gauge. The equilibrium time for each point was 120 s. The equilibrium time is the default period of time in our program to judge the equilibrium; unless the monitored pressure changes within that period of time (120 s), the program will not go to the next pressure point. Finally, the weight of this volume is calculated and the pressure is plotted as a function of the desorbed amount of hydrogen (in weight percent). The powder X-ray diffraction (XRD, Rigaku D/max 2400) measurements were conducted to confirm the phase structure. Powders were spread and measured on a Si single crystal. Amorphous polymer tape was used to cover the surface of the powder to avoid oxidation during the XRD measurement. Fourier transform infrared spectroscopy (FT-IR, Magna-IR 550 II, Nicolet) analyses were conducted to confirm the reversible formation of B-H bond. The products were pressed with KBr and then loaded in a sealed chamber for the measurement. The oxidation state of the titanium and boron components were

analyzed using X-ray photoelectron spectroscopy (XPS, PHI-5000C ESCA) on a RBD upgraded system (PerkinElmer) with Mg K $\alpha$  radiation ( $h\nu = 1253.6$  eV). The binding energy values correspond to the carbon C 1s core level at 284.6 eV.

## Results & discussions

The LiBH<sub>4</sub>-TiF<sub>3</sub> samples were prepared through ball milling. The temperature programmed desorption (TPD) profile in Fig. 1 shows the hydrogen desorption properties of the ball-milled LiBH<sub>4</sub> and LiBH<sub>4</sub>-TiF<sub>3</sub> mixtures. For commercial LiBH<sub>4</sub>, no hydrogen is released until 300 °C, but for LiBH<sub>4</sub>-TiF<sub>3</sub> (mole ratio: 3 : 1), the majority of the hydrogen is released below 290 °C. It is clear that the decomposition properties of LiBH<sub>4</sub> can be significantly improved by TiF<sub>3</sub> addition. Meanwhile, it can be observed from the dehydrogenation properties of LiBH<sub>4</sub>-TiF<sub>3</sub> with different mole ratios (Fig. 2) that when there is sufficient TiF<sub>3</sub> (mole ratio of LiBH<sub>4</sub> : TiF<sub>3</sub>  $\geq$  3 : 1), the dehydrogenation starts from 100 °C and ends at about 290 °C, while insufficient TiF<sub>3</sub> will lead to partial decomposition at temperatures >290 °C.

After heating to 600 °C, a total release of 11.9 wt% hydrogen was observed for commercial LiBH<sub>4</sub>, which is 65.0% of its theoretical hydrogen capacity. However, for LiBH<sub>4</sub>-TiF<sub>3</sub>

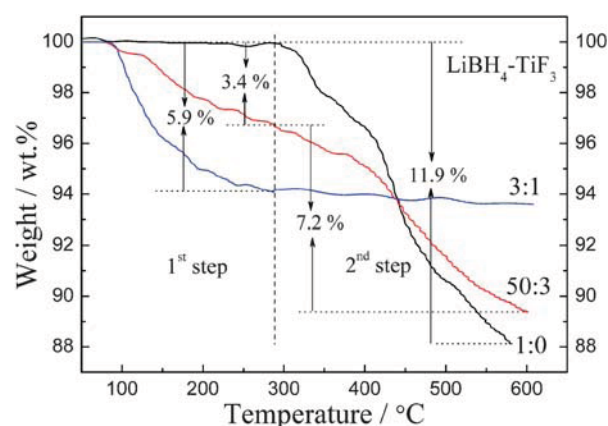


Fig. 1 TPD of the commercial LiBH<sub>4</sub> and LiBH<sub>4</sub>-TiF<sub>3</sub> mixtures, with mole ratios of 50 : 3 and 3 : 1. The heating rate is 2 °C min<sup>-1</sup>.

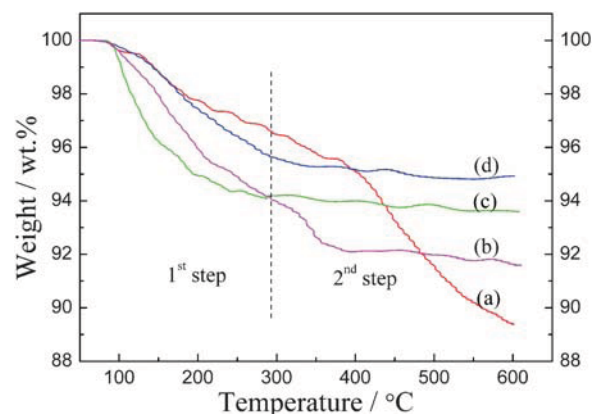
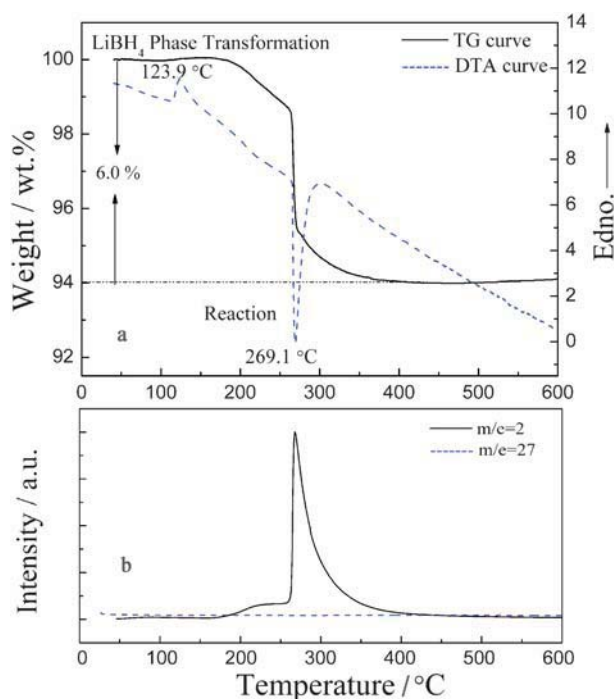


Fig. 2 TPD of the LiBH<sub>4</sub>-TiF<sub>3</sub> mixtures with mole ratios of 50 : 3 (a), 5 : 1 (b), 3 : 1 (c), 2 : 1 (d). The heating rate is 2 °C min<sup>-1</sup>.

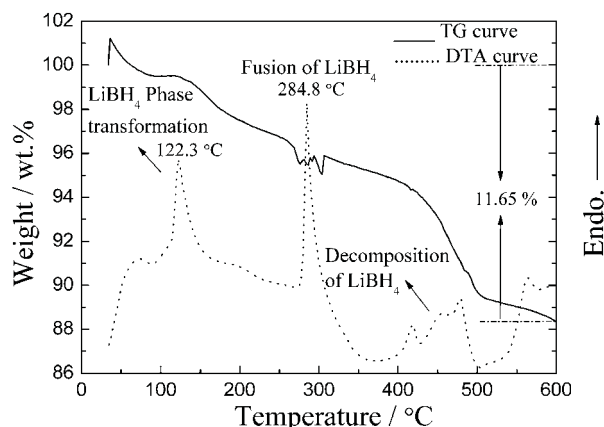
(mole ratio: 3 : 1), the weight loss reached 5.9 wt% at 290 °C, corresponding to 83.2% of the hydrogen in LiBH<sub>4</sub>. Therefore, TiF<sub>3</sub> addition can promote the decomposition of LiBH<sub>4</sub>.

Fig. 3 shows the thermogravimetric/differential thermal analysis (TG/DTA) curves for LiBH<sub>4</sub>-TiF<sub>3</sub> (mole ratio: 3 : 1). One step with a total weight loss of 6.0 wt% was observed in the TG curve, which agrees well with the TPD result in Fig. 1. It is also confirmed by the synchronous mass spectroscopy (MS) profile that the gas released is pure H<sub>2</sub>. The DTA curve has an endothermic peak at 123.9 °C corresponds to the phase transformation of LiBH<sub>4</sub>. The exothermic peak at 269.1 °C is ascribed to a chemical reaction of LiBH<sub>4</sub> with TiF<sub>3</sub>, resulting in the dehydrogenation of LiBH<sub>4</sub>. This reaction starts at a low temperature with low kinetics but becomes violent at 269.1 °C. However, a two-step weight loss with a total capacity of 11.65 wt% was observed in the TG/DTA curves for LiBH<sub>4</sub>-TiF<sub>3</sub> (mole ratio: 50 : 3) (Fig. 4), which agrees well with the TPD result in Fig. 1. Furthermore, the DTA curve showed three endothermic peaks. The endothermic peaks at 122.3 °C, 284.8 °C, and 400–500 °C may correspond to the phase transformation, fusion, and decomposition of LiBH<sub>4</sub>, respectively.<sup>26</sup> It is clear that insufficient TiF<sub>3</sub> will lead to excess LiBH<sub>4</sub>, which decomposes above 290 °C.

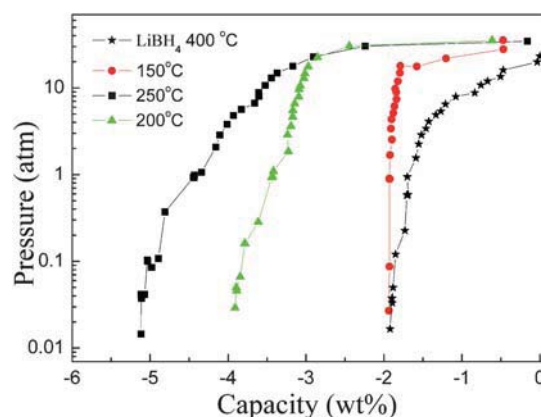
Pressure-composition-temperature (PCT) desorption curves for LiBH<sub>4</sub> at 400 °C and LiBH<sub>4</sub>-TiF<sub>3</sub> (mole ratio: 3 : 1) at 150 °C, 200 °C, and 250 °C are shown in Fig. 5. Firstly, no flat plateau can be observed in the curves, which is different from the behavior of the traditional metal hydrides. This is specific to this kind of composite as its equilibrium pressure is probably above 30 bar the maximum pressure of our equipment. Secondly, the fact that the desorption capacity of the compound increases with



**Fig. 3** (a) TG/DTA curves for a LiBH<sub>4</sub>-TiF<sub>3</sub> mixture (mole ratio: 3 : 1), and (b) synchronous MS profiles of  $m/e = 2$  (H<sub>2</sub>),  $m/e = 27$  (B<sub>2</sub>H<sub>6</sub>). The heating rate is 10 °C min<sup>-1</sup>.



**Fig. 4** TG/DTA curves for a LiBH<sub>4</sub>-TiF<sub>3</sub> mixture (mole ratio: 50 : 3). The heating rate is 10 °C min<sup>-1</sup>.

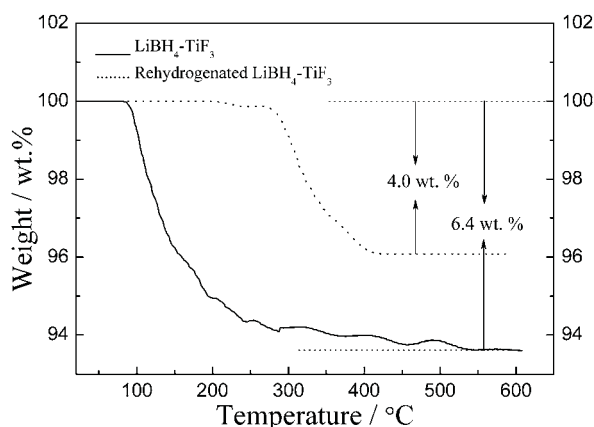


**Fig. 5** PCT desorption curves of the commercial LiBH<sub>4</sub> at 400 °C and LiBH<sub>4</sub>-TiF<sub>3</sub> mixture (mole ratio: 3 : 1) at various temperatures.

increasing temperature indicates its relatively poor kinetics. Finally, the mixture can release 4.4 wt%, 3.4 wt%, and 2.0 wt% hydrogen to 1 atm at 150 °C, 200 °C, and 250 °C, respectively, while only 1.7 wt% hydrogen is released for pure LiBH<sub>4</sub> at 400 °C. It is clear that the kinetic property for the hydrogen desorption from LiBH<sub>4</sub> was improved.

The product of the LiBH<sub>4</sub>-TiF<sub>3</sub> mixture (mole ratio: 3 : 1) dehydrogenated at 350 °C for 2 h was rehydrogenated at 350 °C and 10 MPa H<sub>2</sub>. Its TPD result (Fig. 6) shows that the dehydrogenated product can be partially rehydrogenated, and exhibits improved rehydrogenation conditions than that of pure LiBH<sub>4</sub>.<sup>30</sup> However, the hydrogen capacity at 500 °C was decreased to 4.0 wt%, and the onset hydrogen desorption temperature is about 300 °C, much higher than that of the original mixture. Meanwhile, additional charge-recharge was tested for the first rehydrogenated sample. After dehydrogenation at 450 °C for 2 h, the first reformed mixture was rehydrogenated at 350 °C and 10 MPa H<sub>2</sub> for 12 h. However, only less than 1 wt% hydrogen desorption was achieved, suggesting that the reversibility for the rehydrogenated product is poor. Hence, it is predicted that the rehydrogenation pathway was not the reverse reaction of dehydrogenation.

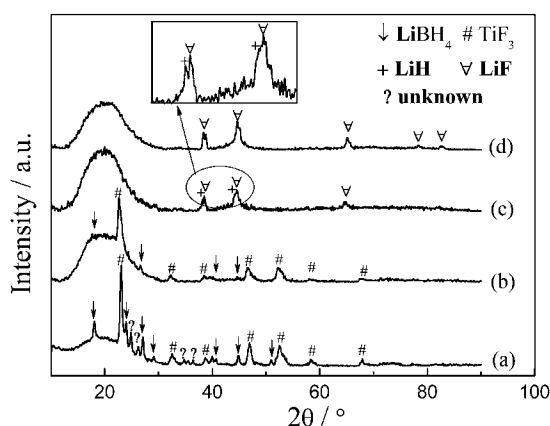
To understand the dehydrogenating/rehydrogenating process for the LiBH<sub>4</sub>-TiF<sub>3</sub> mixtures, X-ray diffraction (XRD) and



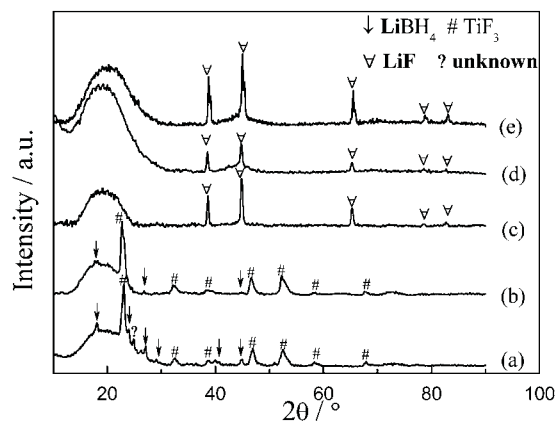
**Fig. 6** TPD of  $\text{LiBH}_4\text{-TiF}_3$  mixtures (mole ratio: 3 : 1) and its rehydrogenated sample. The heating rate is  $2^\circ\text{C min}^{-1}$ .

infrared (IR) spectroscopy measurements were conducted. The XRD patterns for the milled samples before and after dehydrogenation at  $600^\circ\text{C}$  are shown in Fig. 7. For the as-prepared  $\text{LiBH}_4\text{-TiF}_3$  mixtures, only  $\text{LiBH}_4$  and  $\text{TiF}_3$  were found in the XRD patterns, implying that the ball milling creates a physical mixture. For the dehydrogenated samples, the  $\text{LiBH}_4$  and  $\text{TiF}_3$  peaks disappeared. New phases of  $\text{LiH}$  and  $\text{LiF}$  were observed for the  $\text{LiBH}_4\text{-TiF}_3$  (mole ratio: 50 : 3) mixture, while only the  $\text{LiF}$  phase is present for the  $\text{LiBH}_4\text{-TiF}_3$  (mole ratio: 3 : 1) mixture. Similar results can be observed for  $\text{LiBH}_4\text{-TiF}_3$  mixtures with different mole ratios (Fig. 8). In the case of the rehydrogenated sample, no desirable  $\text{LiBH}_4$  was observed, but only  $\text{LiF}$  (Fig. 8). The IR results (Fig. 9) for  $\text{LiBH}_4$  and the milled  $\text{LiBH}_4\text{-TiF}_3$  (mole ratio: 3 : 1) together with its dehydrogenated and rehydrogenated samples show that the peaks for B-H in the milled  $\text{LiBH}_4\text{-TiF}_3$  mixture are similar to the commercial  $\text{LiBH}_4$ , which reconfirmed the physical mixture of the ball milling. Meanwhile, the disappeared B-H bond after the dehydrogenation at  $350^\circ\text{C}$  reappeared in the regenerated sample, indicating the partial reformation of the B-H bond during the rehydrogenation process.

To identify the states of the elements Ti and B, X-ray photoelectron spectroscopy (XPS) was carried out for the

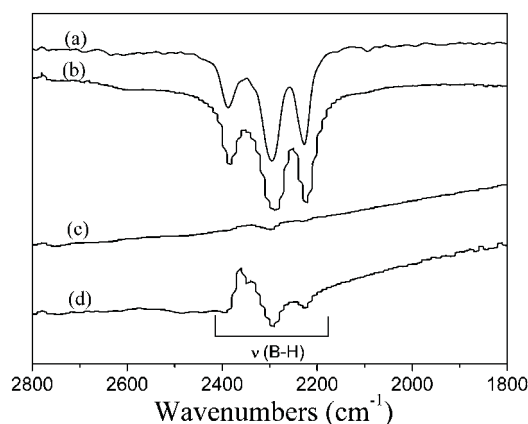


**Fig. 7** XRD patterns for the milled  $\text{LiBH}_4\text{-TiF}_3$  mixtures (a, b) before and (c, d) after dehydrogenation at  $600^\circ\text{C}$ . The mole ratios are 50 : 3 for (a, c) and 3 : 1 for (b, d).

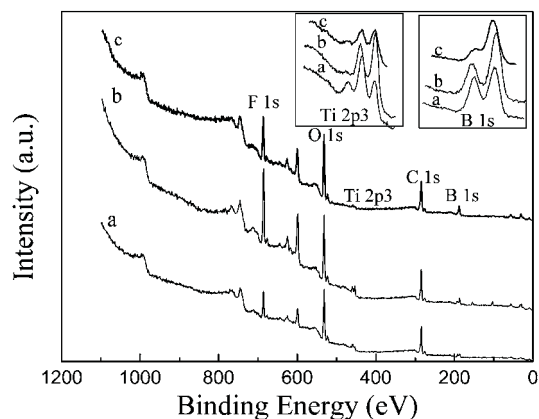


**Fig. 8** XRD patterns for the milled  $\text{LiBH}_4\text{-TiF}_3$  mixtures (a, b) before and (c, d) after dehydrogenation at  $600^\circ\text{C}$ , and (e) the rehydrogenated sample. The mole ratios are 5 : 1 for (a, c), 2 : 1 for (b, d) and 3 : 1 for (e).

dehydrogenated and regenerated  $\text{LiBH}_4\text{-TiF}_3$  (mole ratio: 3 : 1) sample. For the sample dehydrogenated at  $350^\circ\text{C}$ , as shown in Fig. 10(a), the  $\text{Ti}_{2p_{2/3}}$  binding energies at 454.2 eV and 458.9 eV are quite similar to the binding energies of  $\text{TiB}_2$  and  $\text{TiO}_2$ , respectively. Peaks centered on 187.4 and 192.0 eV are observed for boron, for which the peak at 187.4 eV may be assigned to  $\text{TiB}_2$  and the peak at 192.0 eV is assigned to  $\text{B}_2\text{O}_2$ .<sup>31-34</sup> The appearance of  $\text{TiO}_2$  and  $\text{B}_2\text{O}_2$  may be due to oxidation in air when the sample was taken out and loaded during the XPS measurement. Similar results (XPS shape and position) can be obtained for the sample dehydrogenated at  $600^\circ\text{C}$ , as shown in Fig. 10(b), in which the  $\text{Ti}_{2p_{2/3}}$  binding energies are 453.4 eV and 459.4 eV, and the  $\text{B}_{1s}$  binding energies are 187.0 eV and 192.5 eV. It is clear that the  $\text{LiBH}_4\text{-TiF}_3$  mixture produced  $\text{TiB}_2$  during the dehydrogenation. For the rehydrogenated sample, as shown in Fig. 10(c), a weak peak and a strong peak centered at 191.8 and 187.4 eV are observed for boron. The peak at 191.8 eV is assigned to  $\text{B}_2\text{O}_2$ , the peak at 187.4 eV, which is very similar to the 187.2 eV of  $\text{LiBH}_4$  (result not shown), may be assigned to regenerated borohydride. The  $\text{Ti}_{2p_{2/3}}$  binding energies are 453.5 eV and 458.7 eV, respectively. The peak at 458.7 eV is assigned to  $\text{TiO}_2$ , the peak at 453.5 eV is similar to  $\text{TiB}_2$ , but as



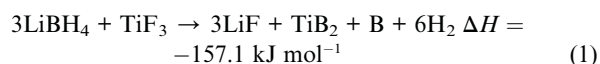
**Fig. 9** IR spectrum for commercial  $\text{LiBH}_4$  (a), a milled  $\text{LiBH}_4\text{-TiF}_3$  mixture (mole ratio: 3 : 1) (b) and the mixture dehydrogenated at  $350^\circ\text{C}$  (c) and its rehydrogenated sample (d).



**Fig. 10** XPS spectra for a LiBH<sub>4</sub>-TiF<sub>3</sub> mixture (mole ratio: 3 : 1) dehydrogenated at 350 °C (a), 600 °C (b) and its rehydrogenated sample (c). The insets show enlargements of the Ti 2p<sub>3</sub> and the B 1s peaks.

the reformation of the B-H bond is confirmed by IR and XPS results, this peak may be assigned to a material composed of elements Ti, B and H. The fact that TiB<sub>2</sub> cannot be identified from the XRD result in Fig. 7 is probably due to its presence in a highly dispersed, nanocrystalline and/or amorphous form.

Based on the above analysis, the reaction path for the LiBH<sub>4</sub>-TiF<sub>3</sub> mixtures is postulated to be:



The 100–290 °C decomposition step is mainly based on the equation above, which has a calculated hydrogen capacity of 7.08 wt%. The weight loss of the decomposition step above 290 °C mainly results from the decomposition of the excess LiBH<sub>4</sub>, which produces LiH, which has been confirmed by the XRD result in Fig. 7(c). This reaction might be 2LiBH<sub>4</sub> → 2LiH + 2B + 3H<sub>2</sub>.

The standard formation enthalpies for LiBH<sub>4</sub>, TiF<sub>3</sub>, LiF, and TiB<sub>2</sub> are -190,<sup>35</sup> -1435.53, -616.931, and -323.8 kJ mol<sup>-1</sup>,<sup>36</sup> respectively. Therefore, the enthalpy change for the formation of H<sub>2</sub> in reaction (1) is -26.2 kJ mol<sup>-1</sup>, and this may explain the appearance of the exothermic peak in the DTA curve very well. The standard enthalpy for the decomposition of LiBH<sub>4</sub>, namely, ~67 kJ mol<sup>-1</sup> for the formation of H<sub>2</sub>,<sup>37</sup> is endothermic. However, the new pathway is quite different, namely, exothermic, and this may be the reason why the mixture can release hydrogen at a lower temperature. However, the exothermic reaction appears to be thermodynamically unfavorable for rehydrogenation. As the regeneration of the B-H bond was confirmed by the IR spectrum, it is predicted that the rehydrogenation may be due to the formation of another borohydride.

## Conclusions

In summary, we have demonstrated that LiBH<sub>4</sub>-TiF<sub>3</sub> mixtures exhibit superior dehydrogenation performance. As TiF<sub>3</sub> can react with LiBH<sub>4</sub>, the thermodynamics and kinetics of hydrogen release from LiBH<sub>4</sub> are significantly improved, decreasing the

onset of hydrogen desorption to about 100 °C and the LiBH<sub>4</sub>-TiF<sub>3</sub> mixture (3 : 1) can release 5.0 wt% and 6.4 wt% hydrogen below 250 °C and 500 °C. Meanwhile, the dehydrogenated sample is partially reversible at 100 atm H<sub>2</sub> and 350 °C, with the hydrogen capacity for the rehydrogenated sample decreased to 4.0 wt% at 500 °C. Additionally, the reversibility was probably not due to the reverse hydrogen desorption reaction, but the formation of another new borohydride which showed worse reversibility.

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## References

- 1 F. H. Ellinger, C. E. Holley, B. B. McIntere, D. Pavone, R. M. Potter, E. Staritzky and W. H. Zachariasen, *J. Am. Chem. Soc.*, 1955, **77**, 2647–2648.
- 2 J. J. Reilly and R. H. Wiswall, *Inorg. Chem.*, 1968, **7**, 2254–2256.
- 3 L. Schlapbach and A. Züttel, *Nature*, 2001, **414**, 353–358.
- 4 M. S. Dresselhaus and I. L. Thomas, *Nature*, 2001, **414**, 332–337.
- 5 P. Chen, Z. Xiong, J. Luo, J. Lin and K. L. Tan, *Nature*, 2002, **420**, 302–304.
- 6 N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O. Keffe and O. M. Yaghi, *Science*, 2003, **300**, 1127–1129.
- 7 P. Chen and M. Zhu, *Mater. Today*, 2008, **11**, 36–43.
- 8 S. Yuan, S. Kirklin, B. Dorney, D. Liu and L. Yu, *Macromolecules*, 2009, **42**, 1554–1559.
- 9 P. Grant, *Nature*, 2003, **424**, 129–130.
- 10 A. Züttel, S. Rentsch, P. Fisher, P. Wenger, P. Sudan, Ph. Mauron and Ch. Emmenegger, *J. Alloys Compd.*, 2003, **356–357**, 515–520.
- 11 B. Bogdanović and M. Schwickardi, *J. Alloys Compd.*, 1997, **253–254**, 1–9.
- 12 D. S. Stasinevich and G. A. Egorenko, *Russ. J. Inorg. Chem. (Transl. of Zh. Neorg. Khim.)*, 1968, **13**, 341–343.
- 13 B. Kiran, A. K. Kandalam and P. J. Jena, *J. Chem. Phys.*, 2006, **124**, 224703–224706.
- 14 M. Au and A. Jurgensen, *J. Phys. Chem. B*, 2006, **110**, 7062–7067.
- 15 [2005FY] *Annual Progress Report for the DOE Hydrogen Program*, US Government Printing Office, Washington, DC, November 2005, available at: [http://www.hydrogen.energy.gov/annual\\_progress05.html](http://www.hydrogen.energy.gov/annual_progress05.html).
- 16 E. M. Fedneva, V. L. Alpatova and V. I. Mikheeva, *Russ. J. Inorg. Chem. (Transl. of Zh. Neorg. Khim.)*, 1964, **9**, 826–827.
- 17 A. Züttel, P. Wenger, S. Rentsch, P. Sudan, Ph. Mauron and Ch. Emmenegger, *J. Power Sources*, 2003, **118**, 1–7.
- 18 A. F. Gross, J. J. Vajo, S. L. Van Atta and G. L. Olson, *J. Phys. Chem. C*, 2008, **112**, 5651–5657.
- 19 S. V. Alapati, J. K. Johnson and D. S. Scholl, *J. Phys. Chem. B*, 2006, **110**, 8769–8776.
- 20 J. Yang, A. Sudik and C. Wolverton, *J. Phys. Chem. C*, 2007, **111**, 19134–19140.
- 21 X. B. Yu, D. M. Granta and G. S. Walker, *Chem. Commun.*, 2006, 3906–3908.
- 22 M. Au, A. R. Jurgensen, W. A. Spencer, D. L. Anton, F. E. Pinkerton, S. Hwang, C. Kim and R. C. Bowman, *J. Phys. Chem. C*, 2008, **112**, 18661–18671.
- 23 X. B. Yu, D. M. Grant and G. S. Walker, *J. Phys. Chem. C*, 2008, **112**, 11059–11062.
- 24 X. B. Yu, Z. Wu, Q. R. Chen, Z. L. Li, B. C. Weng and T. S. Huang, *Appl. Phys. Lett.*, 2007, **90**, 34106.
- 25 F. E. Pinkerton and M. S. Meyer, *J. Alloys Compd.*, 2008, **464**, L1–L4.
- 26 Y. Zhang, W. Zhang, M. Fan, S. Liu, H. Chu, Y. Zhang, X. Gao and L. Sun, *J. Phys. Chem. C*, 2008, **112**, 4005–4010.

- 27 M. Au, A. Jurgensen and K. Zeigler, *J. Phys. Chem. B*, 2006, **110**, 26482–26487.
- 28 D. J. Siegel, C. Wolverton and V. Ozolins, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2007, **76**, 134102.
- 29 P. Wang, L. Ma, Z. Fang, X. Kang and P. Wang, *Energy Environ. Sci.*, 2009, **2**, 120–123.
- 30 S. Orimo, Y. Nakamori, G. Kitahara, K. Miwa, N. Ohba, S. Towata and A. Züttel, *J. Alloys Compd.*, 2005, **404–406**, 427–430.
- 31 Y. Wang and M. Trenary, *Chem. Mater.*, 1993, **5**, 199–205.
- 32 L. Schlapbach and T. Riesterer, *Appl. Phys. A: Mater. Sci. Process.*, 1983, **32**, 169–182.
- 33 R. Wang, N. Sakai, A. Fujishima, T. Watanabe and K. Hashimoto, *J. Phys. Chem. B*, 1999, **103**, 2188–2194.
- 34 J. A. Jensen, J. E. Gozum, D. M. Pollina and G. S. Girolami, *J. Am. Chem. Soc.*, 1988, **110**, 1643–1644.
- 35 P. Mauron, F. Buchter, O. Friedrichs, A. Remhof, M. Biemann, C. N. Zwicky and A. Züttel, *J. Phys. Chem. B*, 2008, **112**, 906–910.
- 36 I. Barin, *Thermochemical Data of Pure Substances*, Science Press, Beijing, 2003, vol. 2, pp. 961, 1669, 1681.
- 37 J. J. Vajo, S. L. Skeith and F. Mertens, *J. Phys. Chem. B*, 2005, **109**, 3719–3722.