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## Stability and Reversibility of LiBH<sub>4</sub>

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LiBH<sub>4</sub> is a complex hydride and exhibits a high gravimetric hydrogen density of 18.5 wt %. Therefore it is a promising hydrogen storage material for mobile applications. The stability of LiBH<sub>4</sub> was investigated by *pcT* (pressure, concentration, and temperature) measurements under constant hydrogen flows and extrapolated to equilibrium. According to the van 't Hoff equation the following thermodynamic parameters are determined for the desorption: enthalpy of reaction  $\Delta_r H = 74 \text{ kJ mol}^{-1} \text{ H}_2$  and entropy of reaction  $\Delta_r S = 115 \text{ J K}^{-1} \text{ mol}^{-1} \text{ H}_2$ . LiBH<sub>4</sub> decomposes to LiH + B +  $\frac{3}{2} \text{H}_2$  and can theoretically release 13.9 wt % hydrogen for this reaction. It is shown that the reaction can be reversed at a temperature of 600 °C and at a pressure of 155 bar. The formation of LiBH<sub>4</sub> was confirmed by XRD (X-ray diffraction). In the rehydridized material 8.3 wt % hydrogen was desorbed in a TPD (temperature-programmed desorption) measurement compared to 10.9 wt % desorbed in the first dehydrogenation.

### 1. Introduction

Hydrogen is an environmentally friendly synthetic fuel when produced from renewable energy,<sup>1</sup> but the storage remains a challenge especially for mobile applications. On one side the energy density (heating value) of hydrogen per mass is very high (141.8 MJ kg<sup>-1</sup>),<sup>2</sup> but on the other hand the energy density per volume is low (11.6 MJ m<sup>-3</sup>) for H<sub>2</sub> gas at standard conditions. The challenge of hydrogen storage is to find a lightweight storage material with a high hydrogen density. Furthermore the storage should operate at considerable conditions preferably at temperatures between 0 and 100 °C and pressures between 1 and 10 bar.<sup>1</sup>

A new class of lightweight materials for hydrogen storage are complex hydrides and since the first publication on the reversible Ti catalyzed NaAlH<sub>4</sub> and Na<sub>2</sub>LiAlH<sub>6</sub> by Bogdanovic and Schwickardi<sup>3</sup> in 1997 complex hydrides gained a lot of attention in the hydrogen community. The gravimetric hydrogen density of NaAlH<sub>4</sub> is 7.5 wt %. Since this publication, the role of the Ti catalyst is controversial and still not fully understood.<sup>4</sup> Streukens et al.<sup>5</sup> showed that the titanium doping also significantly alters the thermodynamics of the system.

From the point of view of gravimetric hydrogen density, LiBH<sub>4</sub> is even more interesting than NaAlH<sub>4</sub>. It has been shown that LiBH<sub>4</sub> desorbs half of its hydrogen content (9 wt %) when heated to 600 °C (with a heating rate of 2 °C min<sup>-1</sup> and desorbed into vacuum).<sup>6,7</sup>

For almost all the intermetallic hydrides the entropy of reaction is  $\Delta S = 130 \text{ J K}^{-1} \text{ mol}^{-1} \text{ H}_2$  corresponding to the change of entropy from molecular hydrogen gas to dissolved solid hydrogen.<sup>7</sup> The stability of the hydride can therefore be described and compared by the enthalpy of reaction only. For

complex hydrides, the situation is somewhat more complicated and the entropy of reaction seems to be lower and variable for different complex hydrides. On the basis of theoretical calculations, it was estimated that  $100 \leq \Delta S \leq 130 \text{ J K}^{-1} \text{ mol}^{-1} \text{ H}_2$ .<sup>8</sup> For the determination and comparison of the stability of complex hydrides the enthalpy  $\Delta_r H$  and also the entropy of reaction  $\Delta_r S$  have to be considered.

Recently there were different experimental works on the destabilisation of LiBH<sub>4</sub> as for example with MgH<sub>2</sub>,<sup>9</sup> C,<sup>10</sup> LiNH<sub>2</sub>,<sup>11,12</sup> and modification of LiBH<sub>4</sub> with TiO<sub>2</sub>, TiCl<sub>3</sub>, ZrO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>, SnO<sub>2</sub>, and other additives.<sup>13,14</sup> Alapati et al.<sup>8,15</sup> made theoretical calculations on the stability of destabilized LiBH<sub>4</sub>. To compare the stability of the destabilized and modified LiBH<sub>4</sub>, it is necessary to compare the values with the stability of pure LiBH<sub>4</sub>.

In the literature only a few values for the standard enthalpy of formation  $\Delta_f H^0$  (Li + B + 2H<sub>2</sub> → LiBH<sub>4</sub> [reaction 1]) and standard enthalpy of reaction  $\Delta_r H^0$  (LiBH<sub>4</sub> → LiH + B +  $\frac{3}{2} \text{H}_2$  [reaction 2]) are found. Davis et al.<sup>16</sup> determined  $\Delta_f H^0 = -184.7 \text{ kJ mol}^{-1}$  by reacting the compounds with hydrochloric acid. From experimental values of the enthalpy of formation of LiBH<sub>4</sub> (-194.0 kJ mol<sup>-1</sup>) and LiH (-90.7 kJ mol<sup>-1</sup>) determined by reacting the compounds with hydrochloric acid Smith et al.<sup>17</sup> calculated  $\Delta_r H^0 = 68.9 \text{ kJ mol}^{-1} \text{ H}_2$  and  $\Delta_r S^0 = 100.3 \text{ J K}^{-1} \text{ mol}^{-1} \text{ H}_2$  for reaction 2.

The U.S. National Institute of Standards and Technology (NIST)<sup>18</sup> gives the following values for the enthalpy of formation and entropy for LiBH<sub>4</sub>,  $\Delta_f H^0 = -190.46 \text{ kJ mol}^{-1}$  and  $S^0 = 75.88 \text{ J K}^{-1} \text{ mol}^{-1}$ , and for LiH,  $\Delta_f H^0 = -90.63 \text{ kJ mol}^{-1}$  and  $S^0 = 20.03 \text{ J K}^{-1} \text{ mol}^{-1}$  resulting in  $\Delta_r H^0 = 66.6 \text{ kJ mol}^{-1} \text{ H}_2$  and  $\Delta_r S^0 = 97.4 \text{ J K}^{-1} \text{ mol}^{-1} \text{ H}_2$  for reaction 2.

Miwa et al.<sup>19</sup> studied the stability of LiBH<sub>4</sub> by first principles calculations, and they estimated the heat of formation considering only the total energies as -194 kJ mol<sup>-1</sup> and including the zero-point energies to -160 kJ mol<sup>-1</sup>. With the heat of formation for LiH of -153 (-162) kJ mol<sup>-1</sup> H<sub>2</sub> with (without)

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the zero-point energy contributions the enthalpy of reaction of LiBH<sub>4</sub> from LiH, B, and H<sub>2</sub> was predicted as −56 (−75) kJ mol<sup>−1</sup> H<sub>2</sub> with (without) the zero-point energies.

Nakamori et al.<sup>20</sup> investigated the stability of metal borohydrides M(BH<sub>4</sub>)<sub>n</sub> (*n* = 1–4) by first-principles calculations, and they found that the charge transfer from M<sup>n+</sup> cations to (BH<sub>4</sub>)<sup>−</sup> anions is a key feature for the stability of M(BH<sub>4</sub>)<sub>n</sub>. There exists a correlation between the heat of formation Δ<sub>f</sub>H° of M(BH<sub>4</sub>)<sub>n</sub> and the Pauling electronegativity of the cation χ<sub>P</sub>, which they represented by the linear relation, Δ<sub>f</sub>H° = 247.4χ<sub>P</sub> − 388.3 kJ mol<sup>−1</sup> of BH<sub>4</sub> resulting in Δ<sub>f</sub>H° = −146 kJ mol<sup>−1</sup> for LiBH<sub>4</sub> with χ<sub>P</sub> = 0.98 for lithium.

There are few reports on the reversibility of LiBH<sub>4</sub> in the literature. In a patent of Muller et al.<sup>21</sup> the rehydrogenation is mentioned to preferably be carried out at a temperature comprised between 600 and 650 °C and at a pressure between 100 and 200 bar. Orimo et al.<sup>22</sup> showed the B–H atomistic vibrations in LiBH<sub>4</sub> by Raman spectroscopy of the rehydrogenated compound reacted at a temperature of 600 °C and a pressure of 350 bar hydrogen.

In this paper the enthalpy Δ<sub>r</sub>H and entropy Δ<sub>r</sub>S of reaction of desorption according to reaction 2 are determined by *pcT* (pressure, concentration, and temperature) measurements. Only LiBH<sub>4</sub> without any catalyst was measured due to the fact that additives can influence the thermodynamics of the mixture as, e.g., observed for Ti doped NaAlH<sub>4</sub>.<sup>5</sup> The logarithm of the equilibrium pressure *p*<sub>eq</sub> divided by standard pressure *p*<sub>0</sub> = 1.013 25 bar as a function of the inverse temperature is represented in a van 't Hoff plot, and Δ<sub>r</sub>H and Δ<sub>r</sub>S are determined according to the van 't Hoff equation:

$$\ln\left(\frac{p_{\text{eq}}}{p_0}\right) = \frac{\Delta_r H}{R} \cdot \frac{1}{T} - \frac{\Delta_r S}{R}$$

The slope of the straight line is proportional to Δ<sub>r</sub>H and the axis intercept is proportional to Δ<sub>r</sub>S.

To get closer to the equilibrium pressure, the measurements done at a flow of 2, 1, and 0.1 cm<sup>3</sup>(STP) min<sup>−1</sup> are extrapolated to the equilibrium pressure at a flow of 0 cm<sup>3</sup>(STP) min<sup>−1</sup>. ln(*p*<sub>eq</sub>/*p*<sub>0</sub>) is plotted as a function of the hydrogen flow and linearly extrapolated to a flow of 0 cm<sup>3</sup>(STP) min<sup>−1</sup>. The linear dependence of ln(*p*<sub>eq</sub>/*p*<sub>0</sub>) on the flow is in accordance with a kinetics model of hydrogen absorption and desorption in Ti doped NaAlH<sub>4</sub>.<sup>23</sup> Furthermore it is shown that LiBH<sub>4</sub> once dehydrogenated can be rehydrogenated at a high pressure and temperature. The rehydrogenation of LiBH<sub>4</sub> is confirmed by X-ray diffraction (XRD) and by temperature-programmed desorption (TPD).

## 2. Experimental Section

LiBH<sub>4</sub> was purchased from Sigma-Aldrich (purity ≥ 95% gas-volumetric) and handled solely under inert gas conditions in an argon glovebox. For the *pcT* measurements 250 mg of LiBH<sub>4</sub> was filled in a stainless steel autoclave, air tightly closed and transferred to the *pcT* apparatus. Prior to the measurement the sample was evacuated at room temperature to a vacuum of better than 5 × 10<sup>−3</sup> mbar. The starting hydrogen pressure (purity 99.999%) was applied to the autoclave, and the sample was heated to the desired temperature. The temperatures were between 400 and 520 °C and thus well above the melting point of LiBH<sub>4</sub> that is reported to be at 268 °C.<sup>6</sup> The *pcT* measurement was started by releasing the hydrogen gas out of the system via a mass flow controller/meter set to a constant flow (2, 1, and 0.1 cm<sup>3</sup>(STP) min<sup>−1</sup>, respectively). During desorption the

pressure of the system is measured with a pressure gauge. The total desorbed volume of hydrogen (hydrogen from the sample and system volume at standard conditions) can be calculated by integrating the flow with time. From this value the contribution due to the system volume has to be subtracted. 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). With a *pcT* system volume of approximately 33 cm<sup>3</sup> and the supposition that all hydrogen is desorbed (1.54 cm<sup>3</sup>-(STP) hydrogen/(1 mg of LiBH<sub>4</sub>) for reaction 2), one experiment takes at the most about 8.5 h for a flow of 2 cm<sup>3</sup>(STP) min<sup>−1</sup> when the desorption is started at a pressure of 20 bar and 20 times more for a flow of 0.1 cm<sup>3</sup>(STP) min<sup>−1</sup>.

For the TPD experiment 100 mg of LiBH<sub>4</sub> was used and was heated with a ramp of 0.5 °C min<sup>−1</sup> from room temperature to 600 °C. To reduce the foaming of the LiBH<sub>4</sub> when heating and desorbing into vacuum at a temperature above the melting point, the TPD measurements were made at a constant pressure of 1 bar H<sub>2</sub>. The pressure of the system was controlled by a mass flow controller/meter connected to the vacuum, and the desorbed amount of hydrogen was measured with the same mass flow controller/meter.

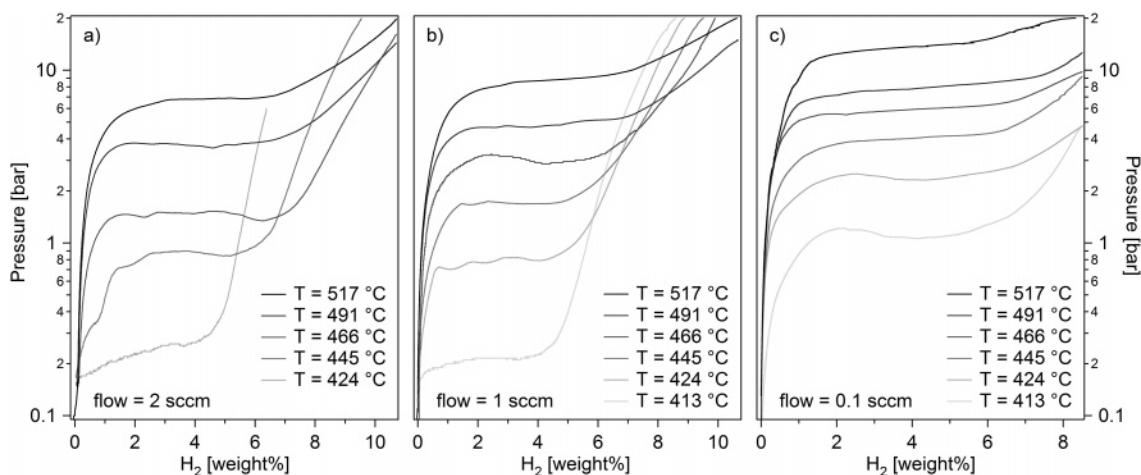
The rehydrogenation was made at a pressure of approximately 155 bar H<sub>2</sub> (purity 99.999%) at a temperature of 600 °C for 200 min and then slowly cooled to room temperature with a rate of 0.5 °C min<sup>−1</sup>.

For the XRD measurements closed glass capillaries (diameter, 0.8 mm; wall thickness, 0.01 mm) containing the samples were prepared in the glovebox and measured in an X'Pert Pro diffractometer from Panalytical with Cu K<sub>α</sub> radiation (λ = 1.5418 Å) using an incident beam X-ray mirror in combination with a linear detector system (X'Celerator). To see the influence of the capillaries on the measurement, an empty capillary was measured.

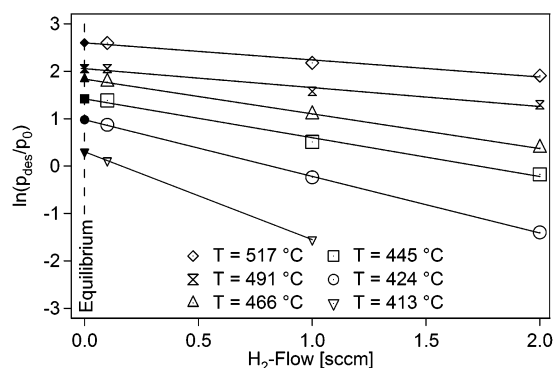
## 3. Results and Discussion

Six *pcT* isotherms in a temperature range from 410 to 520 °C were measured for three different hydrogen flows (2, 1, and 0.1 cm<sup>3</sup>(STP) min<sup>−1</sup>) and are shown in Figure 1.

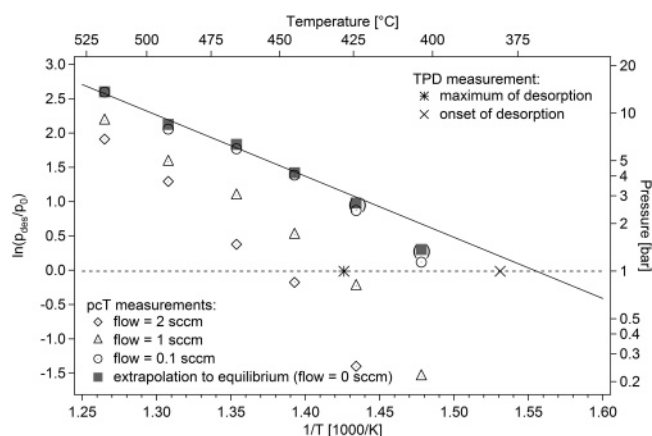
The measurements at high temperatures were started at a pressure of 20 bar, and some measurements at lower temperatures were started at lower pressures because the plateau pressures were expected to be at much lower pressures than 20 bar. For flows of 2 and 1 cm<sup>3</sup>(STP) min<sup>−1</sup> the desorbed amount of hydrogen is 10.6 wt %, and for a flow of 0.1 cm<sup>3</sup>(STP) min<sup>−1</sup> 8.5 wt % this smaller value is probably due to the error of the mass flow controller/meter whose relative error is bigger for small flows. For each temperature, relatively flat plateaus were observed and the width of the plateaus is decreasing with decreasing temperature. The plateau pressure of desorption *p*<sub>des</sub> for each isotherm was taken in the middle of each plateau. For each temperature the plateau pressures depend on the applied hydrogen flow and are decreasing with increasing flow, indicating that the kinetics of the material is slow. If ln(*p*<sub>des</sub>/*p*<sub>0</sub>) (*p*<sub>0</sub> = 1.013 25 bar) is plotted as a function of the hydrogen flow, a straight line can be fitted to the measured points and the plateau pressures can be extrapolated to the equilibrium pressure *p*<sub>eq</sub> located at a flow of 0 cm<sup>3</sup>(STP) min<sup>−1</sup> (Figure 2). All the results are shown in Figure 3 in which empty symbols correspond to the measured plateau pressures and the filled symbols are the extrapolated equilibrium pressures *p*<sub>eq</sub>. A straight line is fitted to the extrapolated equilibrium pressures at the highest temperatures. The two points at temperatures of 413 and 424 °C are below the fitted line. This can be due to the fact that the



**Figure 1.** *pcT* isotherms measured at a constant hydrogen flow of (a) 2, (b) 1, and (c) 0.1 cm<sup>3</sup>(STP) min<sup>-1</sup> (sccm in the figure).



**Figure 2.**  $\ln(p_{\text{des}}/p_0)$  plotted as a function of the hydrogen flow (empty symbols) and linearly extrapolation to the equilibrium pressure  $p_{\text{eq}}$  located at a flow of 0 cm<sup>3</sup> (STP) min<sup>-1</sup> (sccm in the figure; filled symbols).



**Figure 3.** van 't Hoff plot of the plateau pressures for the desorption of LiBH<sub>4</sub> (sccm represents cm<sup>3</sup>(STP) min<sup>-1</sup>).  $\ln(p_{\text{des}}/p_0)$  is plotted as a function of the inverse temperature  $1/T$ .

kinetics of the material is too slow and that the equilibrium is not reached at this temperature. By applying the van 't Hoff equation the following values for the enthalpy and entropy of reaction were found:  $\Delta_r H = 74 \text{ kJ mol}^{-1} \text{ H}_2$  and  $\Delta_r S = 115 \text{ J K}^{-1} \text{ mol}^{-1} \text{ H}_2$ .

These values are higher than the standard enthalpies and entropies of reaction given so far in the literature. Because the dehydrogenation reaction was not catalyzed but dehydrogenated from the pure LiBH<sub>4</sub> and the reaction seems to be very slow, it cannot be excluded that the equilibrium is not fully reached although the fitted points are well-located on straight lines for the extrapolation to equilibrium and on the van 't Hoff plot.

Furthermore, the values are determined at a temperature between 445 and 517 °C, and they do not need necessarily to be the same as the values determined for the standard temperature (25 °C). The equilibrium temperature at the standard pressure given by  $T_{\text{eq}} = \Delta_r H / \Delta_r S$  (cf. van 't Hoff equation) is 370 °C, as can be seen in Figure 3.

A *pcT*-absorption measurement was made from 0 to 20 bar at a temperature of 500 °C at a flow of 1 cm<sup>3</sup>(STP) min<sup>-1</sup>, but no plateau could be seen. An absorption was made at a higher pressure and a higher temperature as discussed later.

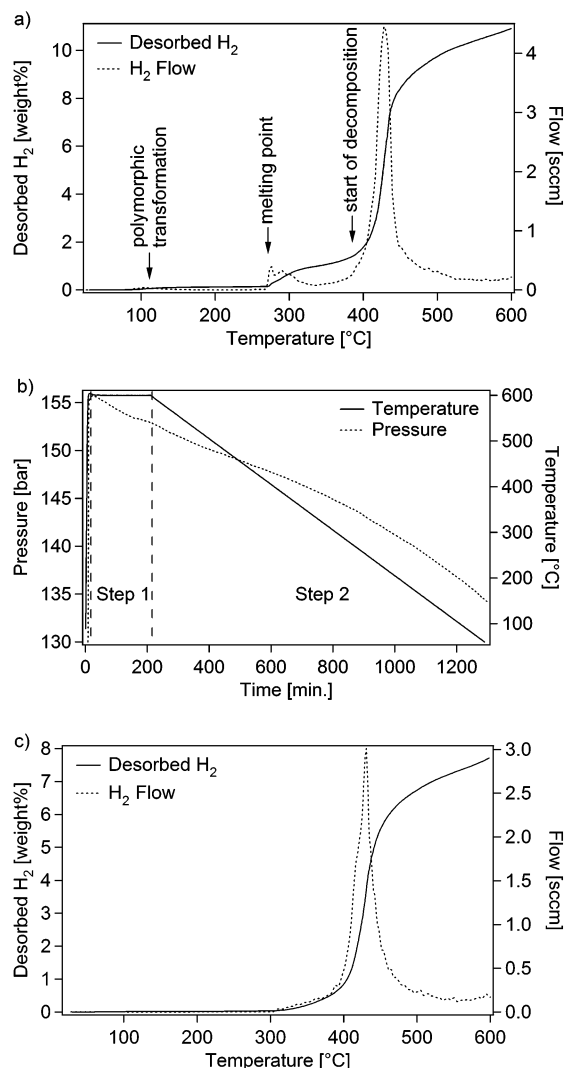
A TPD spectrum of the as-purchased LiBH<sub>4</sub> is shown in Figure 4a. The first desorption peak occurs at approximately 110 °C, where the polymorphic transformation occurs and 0.1 wt % hydrogen is desorbed. The second desorption peak occurs around the melting point of LiBH<sub>4</sub> at 268 °C and where an additional 1 wt % hydrogen is desorbed. The maximum of the major dehydrogenation is around 430 °C, where most of the hydrogen evolves, and up to a temperature of 600 °C, 10.9 wt % hydrogen is desorbed. The desorption is not complete because reaction 2 yields a theoretical value of 13.8 wt %. The thermal desorption spectrum of LiBH<sub>4</sub> shown in Figure 4a exhibits a hydrogen liberation curve which is in good agreement with the observations of Fedneva et al.<sup>24</sup> The temperature of the maximal desorption (430 °C) is plotted in the van 't Hoff plot of Figure 3 (star). It is clearly seen that with a heating rate of 0.5 °C min<sup>-1</sup> the desorption is not in equilibrium. The onset of the desorption peak is around 380 °C (cross) this is near the equilibrium temperature of 370 °C.

The desorption product can be rehydrogenated at a hydrogen pressure of 155 bar and a temperature of 600 °C, as shown in Figure 4b. At lower temperatures the hydrogen uptake decreases and finally stops at about 450 °C. The decreasing of the pressure at lower temperatures is due to the fact that the system is cooled.

The TPD spectrum of the rehydrogenated LiBH<sub>4</sub> according to the process shown in Figure 4b is shown in Figure 4c. Up to a temperature of 600 °C 8.3 wt % hydrogen was desorbed compared to 10.9 wt % for the starting material. Contrary to LiBH<sub>4</sub> from the supplier the rehydrogenated LiBH<sub>4</sub> never showed a hydrogen release at the melting point. This could be due to the liberation of residual solvents of the as purchased product which has a purity of only  $\geq 95\%$ .

The XRD spectra of the as-purchased, desorbed, and rehydrogenated LiBH<sub>4</sub> are shown in Figure 5a–c, respectively. The major crystalline phase seen in the desorbed LiBH<sub>4</sub> is LiH (stars). In the spectrum of the rehydrogenated LiBH<sub>4</sub> the major phase is LiBH<sub>4</sub> (plus symbols) and LiH (stars). Compared to



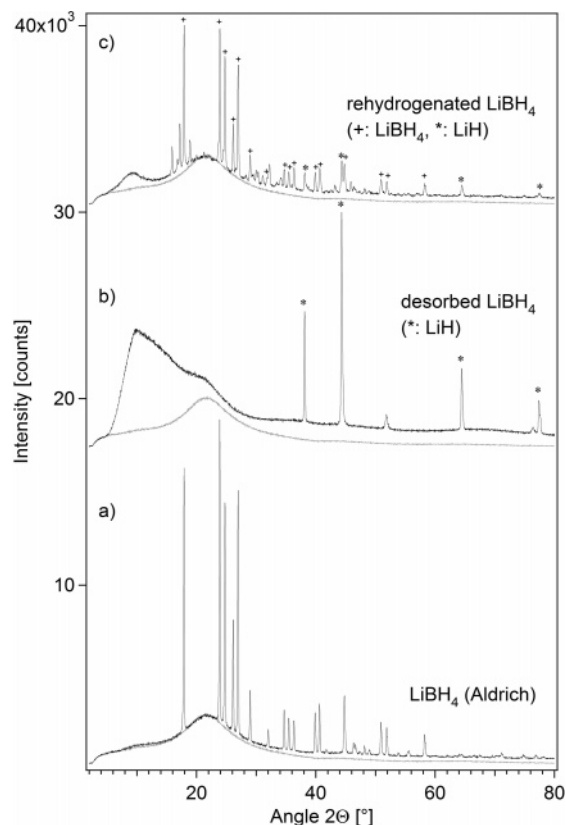


**Figure 4.** (a) TPD measurement of LiBH<sub>4</sub> from Aldrich (heating rate, 0.5 °C min<sup>-1</sup>; sccm represents cm<sup>3</sup>(STP) min<sup>-1</sup>). Three major desorption peaks are observed: at the polymorphic transformation (110 °C), at the melting point (268 °C), and at the decomposition (maximum at 430 °C). (b) Rehydrogenation reaction of desorbed LiBH<sub>4</sub> (isochoric experiment). Step 1: Isothermal heating at a temperature of 600 °C. Step 2: Cooling with a rate of 0.5 °C min<sup>-1</sup>. (c) TPD measurement of rehydrogenated LiBH<sub>4</sub> (heating rate, 0.5 °C min<sup>-1</sup>). One major desorption peak is observed at the decomposition of LiBH<sub>4</sub> (maximum at 430 °C).

the XRD of rehydrogenated LiBH<sub>4</sub> of Orimo et al.<sup>22</sup> made at a pressure of 350 bar at a temperature of 600 °C in our XRD spectrum LiBH<sub>4</sub> peaks are clearly seen. This could be due to the relatively slow cooling of the synthesized material and therefore leads to the formation of a more crystalline product. The LiH phase in the rehydrogenated LiBH<sub>4</sub> shows that the rehydrogenation reaction is not completed and that the amount of hydrogen reabsorbed can probably be improved by longer application of a high pressure. In this experiment a pressure of 155 bar was applied for 200 min and then cooled.

Two reaction paths can be considered for the rehydrogenation of LiBH<sub>4</sub>:

(1) One is via an intermediate compound such as LiBH<sub>2</sub> proposed by Fedneva et al.<sup>24</sup> for the desorption of LiBH<sub>4</sub>: LiBH<sub>4</sub> ↔ LiBH<sub>2</sub> + H<sub>2</sub> ↔ LiH + B + <sup>3</sup>/<sub>2</sub>H<sub>2</sub>. Orimo et al.<sup>25</sup> and Ohba et al.<sup>26</sup> proposed the dehydrogenation/hydrogenation of LiBH<sub>4</sub> via different intermediate compounds as, e.g., Li<sub>2</sub>B<sub>12</sub>H<sub>12</sub> according to the following reaction: LiBH<sub>4</sub> ↔ <sup>1</sup>/<sub>12</sub>Li<sub>2</sub>B<sub>12</sub>H<sub>12</sub> + <sup>5</sup>/<sub>6</sub>LiH + <sup>13</sup>/<sub>2</sub>H<sub>2</sub> ↔ LiH + B + <sup>3</sup>/<sub>2</sub>H<sub>2</sub>. Other proposed compounds



**Figure 5.** XRD pattern of (a) LiBH<sub>4</sub> from Aldrich, (b) desorbed LiBH<sub>4</sub>, and (c) rehydrogenated LiBH<sub>4</sub>. The gray spectra correspond to an empty glass capillary. For better readability spectra b and c are shown with an offset. Stars and plus signs correspond to the strongest LiH and LiBH<sub>4</sub> peaks, respectively.

are LiB<sub>3</sub>H<sub>8</sub> and Li<sub>2</sub>B<sub>n</sub>H<sub>n</sub> (*n* = 5–12). However, none of the structures of the proposed intermediate compounds could be identified with the minor unknown phase in our rehydrogenated LiBH<sub>4</sub> (Figure 5c).

(2) The reaction of B and H<sub>2</sub> at a high temperature to B<sub>2</sub>H<sub>6</sub> (endothermic) and subsequent reaction with LiH upon cooling down the sample:<sup>27</sup> 2LiH + 2B + 3H<sub>2</sub> → 2LiH + B<sub>2</sub>H<sub>6</sub> → 2Li<sup>+</sup>H<sup>-</sup> + (BH<sub>3</sub>)<sub>2</sub> → 2Li<sup>+</sup>[BH<sub>4</sub>]<sup>-</sup>. The synthesis of boranates from diborane and the respective metal hydrides is well-known and widely used. The wet chemical synthesis of LiBH<sub>4</sub> from LiH and B<sub>2</sub>H<sub>6</sub> in diethyl ether<sup>28</sup> and the solvent-free synthesis of NaBH<sub>4</sub> from NaH and B<sub>2</sub>H<sub>6</sub> are known.<sup>29</sup> Due to the fact that B<sub>2</sub>H<sub>6</sub> is released during the desorption of borohydrides<sup>30</sup> the hydrogen desorption of borohydrides could be according to the inverse of the reaction above.

Goerrig<sup>31</sup> claimed in 1958 that borohydrides can be directly synthesized from the elements at a temperature of 650 °C and a pressure of 150 bar hydrogen. However in this patent he did not describe the reaction path in detail. The rehydrogenation experiments of LiBH<sub>4</sub> also show that it is possible to synthesize LiBH<sub>4</sub> from the elements via LiH.

#### 4. Conclusion

We have determined experimentally the stability of LiBH<sub>4</sub> with *pT* measurements. The measurements were done with a constant hydrogen flow of 2, 1, and 0.1 cm<sup>3</sup>(STP) min<sup>-1</sup>, respectively, at constant temperatures. Because the kinetics of the material is relatively slow, the equilibrium pressures extrapolated to zero flow were used to determine the thermodynamic parameters. With the van 't Hoff equation we have calculated Δ<sub>r</sub>H = 74 kJ mol<sup>-1</sup> H<sub>2</sub> and Δ<sub>r</sub>S = 115 J K<sup>-1</sup> mol<sup>-1</sup>

H<sub>2</sub> and consequently the decomposition temperature at 1 bar of hydrogen is  $T_{\text{des}} = 370$  °C.

We could show that the desorbed LiBH<sub>4</sub> can be rehydrogenated at high pressures (155 bar) and temperatures (600 °C). TPD measurements of the rehydrogenated sample showed that for a hydrogenation time of only 200 min 8.3 wt % hydrogen could be desorbed again. XRD shows that the synthesized material is crystalline. The optimal conditions for the rehydrogenation still have to be determined. Probably the pressure and the temperature can be lowered more in order to make the rehydrogenation at milder conditions.

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