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Direct preparation of $LiBH_4$ from pre-treated LiH + B mixture at high pressure

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ABSTRACT

$LiBH_4$ was prepared from LiH + B mixture at 300–500 °C with a hydrogen pressure of 35 MPa. The LiH + B mixture was pretreated by ball milling under 10 MPa hydrogen pressure for 10 h. The results showed that ball-milling treatment is favorable for the formation of $LiBH_4$, which could reduce the reaction temperature for about 200 °C. A small quantity of $LiBH_4$ could be found in the pre-treated sample. The formation of $LiBH_4$ from LiH + B mixture is a kinetically hindered progress and a diffusion-control reaction. $LiBH_4$ formed at 400 °C could release 6.59 wt.% H_2 when it was heated from room temperature to 500 °C. The yield of $LiBH_4$ is about 59.4%.

1. Introduction

Hydrogen is an environmentally friendly synthetic fuel, but the storage remains a challenge especially for mobile applications. To find efficient and economic methods for storing hydrogen is critical to realizing the hydrogen economy. The US Department of Energy (DOE) is supporting research to demonstrate viable materials for on-board hydrogen storage. The DOE goals are focused on achieving a storage system of 6 wt.% H_2 and 45 kg H_2 m^{-3} by 2010 and developing a system reaching 9 wt.% H_2 and 81 kg H_2 m^{-3} by 2015 [1,2].

Nanostructured carbon materials [3] and complex hydrides are a new class of lightweight materials for hydrogen storage. Since the first publication on the reversible Ti catalyzed $NaAlH_4$ and Na_2LiAlH_6 by Bogdanović and Schwickardi [4] in 1997 complex hydrides gained a lot of attention in the hydrogen community. One of the primary classes of materials currently under consideration for solid-state on board hydrogen storage material, are ionic compounds often with group 1 or 2 cations (e.g., Li, Na, and Mg), and an anionic "complex" of light metals and hydrogen (e.g., $[BH_4]^-$ and $[AlH_4]^-$). Interest in low-Z complex hydrides, such as metal borohydries [5–7], $M^{n+}(BH_4)_n$, and metal alanates, $M^{n+}(AlH_4)_n$, stems from their inherent ability to contain large amounts of hydrogen by weight (up to 18.5 wt.% in $LiBH_4$).

In particular, $LiBH_4$ with a theoretical gravimetric hydrogen density of 18.5 wt.% is a very interesting material, nevertheless the thermodynamic, kinetic and reversibility deficiencies limit it from practical application. Therefore, many efforts have focused on incorporating additives, such as metals, metal halides, oxides, sulfides, hydrides, nanoporous scaffolds to thermodynamically destabilize $LiBH_4$ toward lowered desorption temperatures. However, reversibility of $LiBH_4$ gains little attention. In chemical industry, $LiBH_4$ is usually synthesized by a wet chemical reaction method using diethyl ether or isopropylamine as solvent, by a metathesis of $NaBH_4$ with Li halides or chlorides [8,9]. As organic solvent has side-effect on products and is perilous to handle, a cleaner and more efficient way to regenerate $LiBH_4$ is in great need.

The practical use of such metal complexes is limited due to both thermodynamic and kinetic deficiencies, and reversibility of those metal complexes have not yet been well resolved. For example, $LiBH_4$ can be formed according to reaction (1) under a pressure of 35 MPa hydrogen and 600 °C [10]:

$$LiH + B + (3/2)H_2 \rightarrow LiBH_4 \quad (1)$$

The enthalpy and entropy for reaction (1) is calculated to be $\Delta_r H^0 = 66.6\ \mathrm{kJ\,mol^{-1}}\ H_2$ and $\Delta_r S^0 = 97.4\ \mathrm{J\,K^{-1}\,mol^{-1}}\ H_2$, respectively [11]. From a thermodynamic point of view, hydrogen absorption in LiH with boron forming $LiBH_4$ should be possible at 1 bar hydrogen pressure and room temperature, and conclusively the reaction is simply kinetically hindered [12]. Thus, more activated mixture of LiH and B may result in a lower reaction temperature.

In this paper, $LiBH_4$ is prepared via the pre-activated mixture of LiH and B under 35 MPa H_2 and 300–500 °C. To achieve such a high hydrogen pressure, a double stage hydrogen compressor is used in our work which can produce high-pressure ultrapure hydrogen with a pressure over 70 MPa and purity of 99.9999%, the working mechanism of

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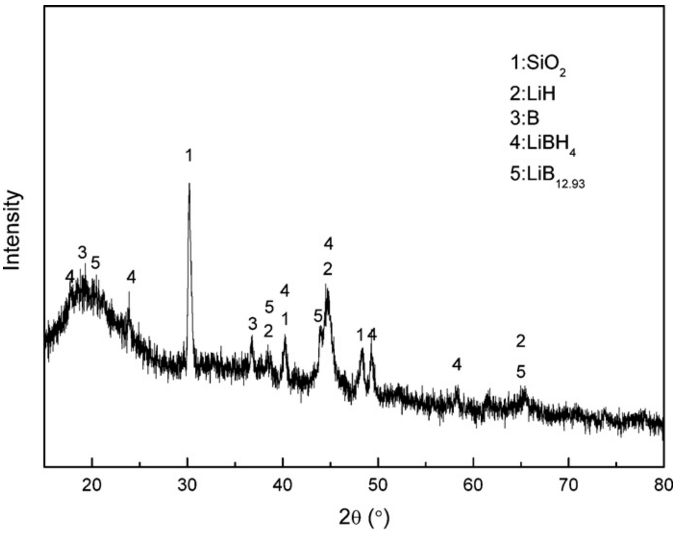

Fig. 1. The XRD pattern of LiH + B mixture after ball-milling for 10 h at a hydrogen pressure of 10 MPa, SiO_2 was used to calibrate the position of diffraction peaks.

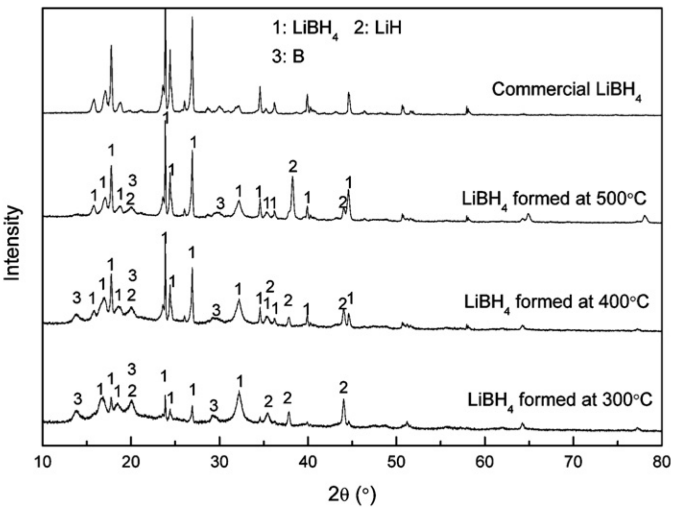

Fig. 2. The XRD patterns of pre-treated LiH + B composite maintained at different temperatures and at a hydrogen pressure of 35 MPa for 10 h.

the compressor has been described in our previous work [13].

2. Experimental details

The initial materials, $LiBH_4$ (16949-15-8, 95%), LiH (7580-67-8, 98%) and B (7440-42-8, 95–97%) were purchased from Aldrich Chemical and used as received. Influence of impurities in the initial materials on the final experimental results was not taken into consideration. To prevent samples and raw materials from undergoing oxidation and/or hydroxide formation, they were stored and handled in an argon-filled glovebox (Mbraun MB200B). LiH and B with a molar ratio of 1:1 and a total weight of about 1.5 g were placed into a stainless vessel with steel balls. The ball-to-powder ratio was 60:1. The vessel was first evacuated and then filled with 10 MPa hydrogen and ball-milled for 10 h. Finally, the treated sample was introduced to a high pressure reactor and heated to target temperatures, and maintained the temperature constantly under a hydrogen pressure of 35 MPa for 10 h.

The thermal gas desorption properties of the mixtures were determined by thermogravimetry (TG) analyzer (Netzsch STA449F3) upon heating to 500 °C at a heating rate of 5 °C/min. The flow rate of argon (99.99% purity) was maintained at 40 mL/min during the entire heating process. Structure analysis was carried out using a Rigaku D/max-3B X-ray diffractometer using Cu Kα radiation at room temperature. The XRD measurements were carried out by using a specially designed sample holder to prevent the contact of the sample with air. The hydriding/dehydriding tests on the prepared samples (~0.5 g) were carried out on a Sievert's type apparatus.

3. Results and discussion

Fig. 1 shows the XRD pattern of LiH + B mixture after ball-milling for 10 h at a hydrogen pressure of 10 MPa, which reveals that a small quantity of $LiBH_4$ was formed during ball-milling process. Fig. 2 shows the XRD patterns of the samples formed at 300 °C, 400 °C and 500 °C, respectively. It can be seen from Fig. 2 that LiH still abound in large quantity for the sample formed at 300 °C. As reaction temperature increases, the diffraction intensity of $LiBH_4$ increases. The samples formed at 400 °C and 500 °C contain $LiBH_4$, minor LiH and B. XRD patterns of both samples are quite the same to each other, which indicated higher reaction temperatures have little beneficial effect. So we draw a conclusion that $LiBH_4$ can be directly formed from LiH and B under 400 °C and a hydrogen pressure of 35 MPa, which is about 200 °C lower than the value reported in literature [10]. As no catalyst was applied, ball milling treatment under high hydrogen pressure should be the key factor which brings down the reaction temperature. Moreover, our previous experiments revealed that pre-treatment under Ar atmosphere could not achieve the same results (not included here). Therefore, ball-milling pre-treatment under high hydrogen pressure may activate the mixtures rather than just remove inert outer layer of the reactants.

Generally speaking, the break of B–B bond and the formation of B–H bond are the reaction barrier to reaction (1) [12]. Based on this consideration, additives that will react with boron to form instable intermediates received considerable attraction. It has been reported that $LiBH_4$ can be formed from AlB_2 and LiH at moderate temperature and hydrogen pressure due to the low stability of AlB_2, but $LiBH_4$ is absent when AlB_2 is replaced by boron under the same condition [14]. The enthalpy of formation of AlB_2 is calculated to be 16 kJ mol^{-1} by density functional calculations [15]. However, the stability of the $LiBH_4$/Al system is comparable to that of pure $LiBH_4$. The small destabilization due to the AlB_2 can even be compensated at higher temperatures by an entropy decrease of $\Delta S = -S^0(\mathrm{Al}) - (1/2)S^0(\mathrm{B}) + S^0(\mathrm{AlB_2}) = -14\,\mathrm{J\,mol^{-1}\,K^{-1}}$. Hence the thermodynamic driving force is similar for both systems [14,16]. So the enabled hydrogenation using AlB_2 instead of B is probably a kinetic effect, which indicates improving the kinetics properties is the key task in synthesizing $LiBH_4$. Many previous studies [17–19] on high-energy ball milling of metallic materials have shown that considerable enthalpies can be stored in the ball-milled metals. The stored enthalpy can be as high as 5–10 kJ mol^{-1} and has been attributed to the presence of high-density structural defects and a large area of grain boundaries. Atoms at the defect sites and grain boundaries have higher energies than those located at the perfect lattice sites, and thus have higher activity. The activation energy will be decreased if the transformation from LiH–B to $LiBH_4$ starts from these active sites.

The reaction among LiH, B and hydrogen is a solid–solid–gas reaction. From a kinetic point view, the reaction suffers both from inert boron and solid diffusion. In this paper, high energy ball-milling is adopted as a pre-treatment, which has several advantages. Ball-milling makes the particles of the complexes much smaller; and induces mechanical-alloying effect on LiH and B to reduce solid diffusion pathway; eliminates passivation layer of LiH and B powder and deoxidizes the surface oxides. These reasons are responsible for the decrease of reaction temperature and formation of a small quantity of $LiBH_4$ during ball milling under high pressure as shown in Fig. 1. Similar results had also been reported by Agresti and Khandelwal [20] and Çakanyıldırım and Gürü [21].

When solid reactants have a particle shape as in the present study, the kinetics of gas/solid and liquid/solid reactions can normally be investigated based on a shrinking-core model [22,23]. Possible governing steps that control the reaction kinetics of the

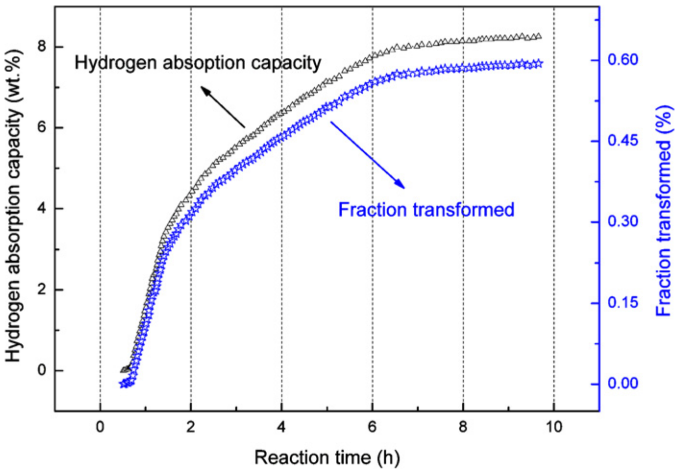

Fig. 3. The transformed fraction of $LiBH_4$ as a function of reaction time. The hydrogen absorption capacity is deduced from the hydrogen pressure reduction of the reactor as a function of reaction time.

shrinking-core model include (i) diffusion of a gaseous species through the product layer, (ii) movement of the phase boundary, (iii) nucleation and growth of the product, or (iv) desorption or absorption of the gaseous phase at he surface of the solid particle [24]. In the case of diffusion-control reactions, the transformed fraction, f, as a function of reaction time, t, in an isothermal experiment can be expressed as

$$(1-f)^{1/3} = 1 - \frac{k_1^{1/2}}{r} t^{1/2} \tag{2}$$

where r is the original average radius of the particles, and k_1 is a rate constant. A plot of $(1-f)^{1/3}$ vs $t^{1/2}$ should be linear if the hydrogenation is indeed controlled by hydrogen diffusion.

If the formation of $LiBH_4$ is controlled by the movement of the LiH–B/$LiBH_4$ phase boundary, the transformed fraction as a function of reaction time should be [22]

$$(1-f)^{1/3} = 1 - \frac{k_2}{r} t \tag{3}$$

where k_2 is a rate constant.

For the nucleation/growth-controlled reaction, the rate equation would be [25]

$$f = 1 - \exp(-k_3 t^m) \tag{4}$$

Eq. (4) is known as a Johnson–Mehl–Avrami (JMA) equation, where m is a numerical exponent whose value can vary from 1 to 4 depending on the detail of nucleation and growth of $LiBH_4$. k_3, on the other hand, depends on the nucleation and growth rates and is therefore very sensitive to temperature. Eq. (4) could be rewritten as

$$\ln\left\{\ln\left(\frac{f}{1-f}\right)\right\} = \ln k_3 + m \ln t \tag{5}$$

Fig. 3 shows the experimental results of transformed fraction of $LiBH_4$ as a function of reaction time at 400 °C. The pre-treated composite absorbs about 8.26 wt.% of hydrogen at 400 °C, which means the yield of $LiBH_4$ is about 59.4%. And Fig. 4 shows the curves of $(1-f)^{1/3}$ vs $t^{1/2}$, $(1-f)^{1/3}$ vs t and $\ln(\ln(f/(1-f)))$ vs $\ln t$ in which the linear equation obtained via curve fitting through the least-squares method and the R-squared value is included. From Fig. 4, we can obtain that $R^2 = 0.979$, so Eq. (2) can be rewritten as

$$(1-f)^{1/3} = 1.08725 - 0.00227 t^{1/2}, \quad \text{with} \quad R^2 = 0.979 \tag{6}$$

The same approach can be used to examine other possible rate-controlling mechanisms. The obtained equations and their R-squared values are listed below.

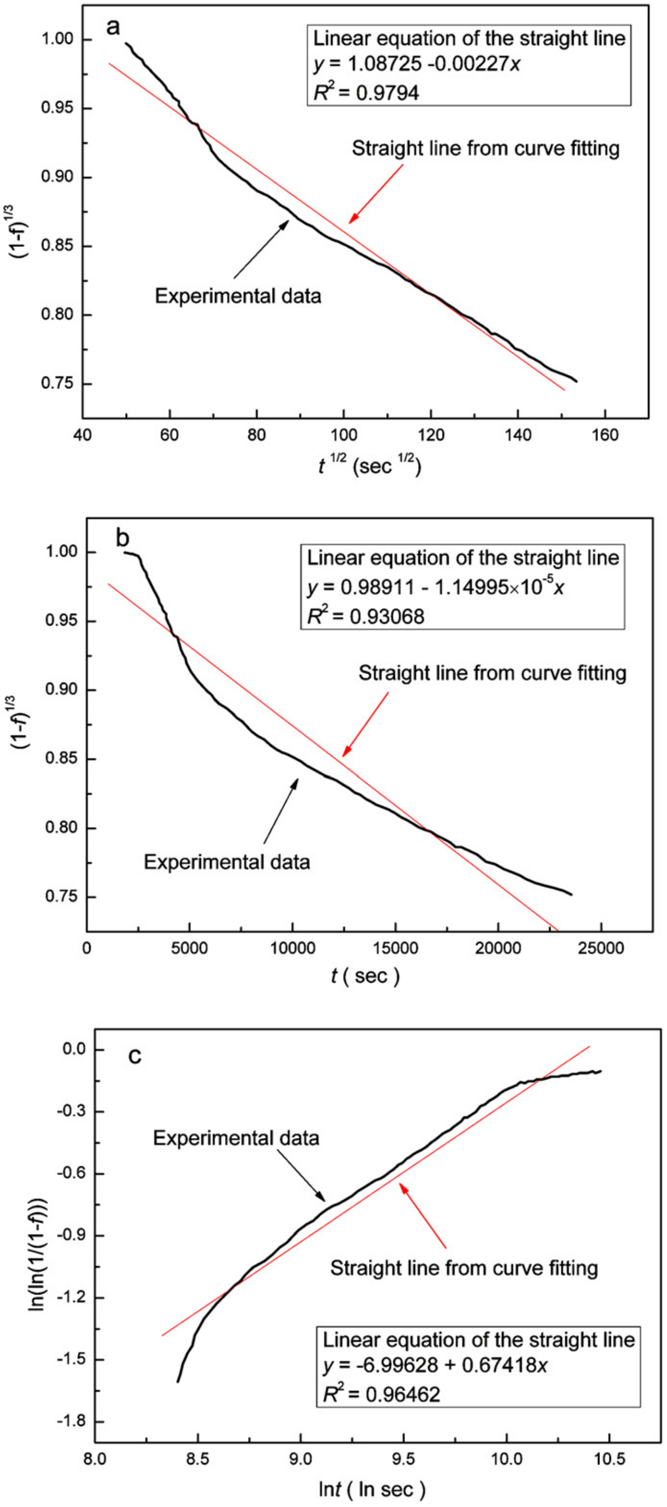

Fig. 4. The transformed fraction of $LiBH_4$, f, as function of the reaction time, t, shown in Fig. 3 is re-plotted in a chart with the axes of (a) $(1-f)^{1/3}$ vs $t^{1/2}$, (b) $(1-f)^{1/3}$ vs t and (c) $\ln(\ln(f/(1-f)))$ vs $\ln t$. The straight lines and their linear equation obtained via curve fitting of the experimental data along with the R-squared value are included for comparison.

For the case of rate-controlling step is the movement of the LiH–B/$LiBH_4$ phase boundary,

$$(1-f)^{1/3} = 0.98911 - 1.14995 \times 10^{-5} t, \quad \text{with}\, R^2 = 0.931 \tag{7}$$

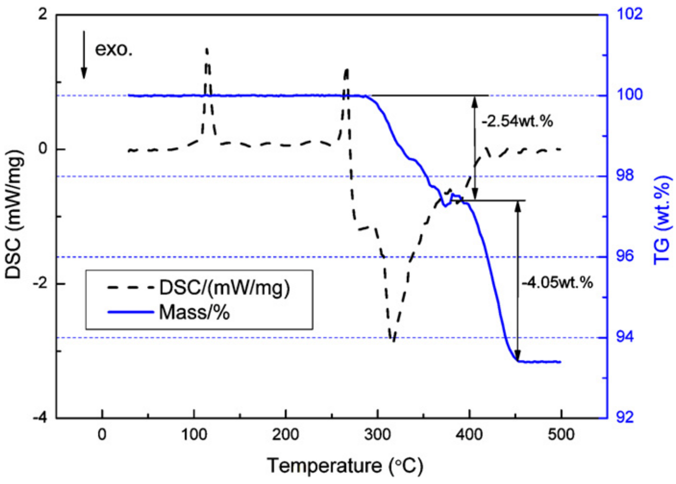

Fig. 5. TG/DSC curves of $LiBH_4$ formed at 400 °C. The heating rate is 5 °C/min.

For the case of rate-controlling step is nucleation and subsequent growth of $LiBH_4$,

$$\ln\left\{\ln\left(\frac{1}{1-f}\right)\right\} = -6.99628 + 0.67418\ \ln t, \quad \text{with} \quad R^2 = 0.965 \tag{8}$$

Comparisons among these relationship and their *R*-squared values indicate that the diffusion-controlled mechanism provides the best explanation for the observed reaction kinetics. First, the *R*-squared value of Eq. (6) is close to 1, which indicates the presence of a good linear relationship between $(1-f)^{1/3}$ and $t^{1/2}$. Second, the first term on the right-hand side of Eq. (6) is nearly equal to 1, which is one of the key requirements matching the theoretical equation derived from the underlying physical process. In contrast, analyses of fitting line equations of phase-boundary-controlled equation and nucleation/growth-controlled equation do not lead to satisfactory results. For the phase-boundary-controlled hydrogenation Eq. (7), the *R*-squared value deviates greatly from 1. For the nucleation/growth-controlled hydrogenation Eq. (8), its *m* value equals 0.67418, which cannot be explained by the physical process of the JMA equation. Although the JMA equation allows *m* values of 0.5 or 1 for a constant number of nuclei and a one-direction growth, and we consider 0.67418 as the approximation of 1 or 0.5, then Eq. (8) represents a hydrogenation process with $LiBH_4$ nucleated at the beginning of the reaction, and the subsequent transformation is controlled by the one-direction growth of LiH/B composite into $LiBH_4$ core, therefore the hydrogenation kinetics will be slow and the product may have dendrite structure. However, a large amount of LiBH4 is formed within 90 min as shown in Fig. 3 and the as-prepared $LiBH_4$ is observed to have fine morphology (which is not shown in this paper).

In conclusion, it should be pointed out that the present analysis only reveals that diffusion is the rate-limiting step for solid state hydrogenation of the LiH + B mixture. Whether hydrogenation proceeds with one or multiple elementary steps cannot be derived from this kinetics analysis. In fact, the mixture contains two solid reactants and hydrogen diffusion in either reactant or the necessary diffusion between LiH and B may be the rate-limiting factor.

Fig. 5 shows TG/DSC curves of $LiBH_4$ formed at 400 °C. It is clear that the $LiBH_4$ formed at 400 °C decomposed by two steps. About 2.54 wt.% weight loss occurred from 270 °C to 370 °C, another 4.05 wt.% weight loss began at about 390 °C. A total weight loss of about 6.59 wt.% is achieved when heated to 500 °C at a heating rate of 5 °C/min. The difference between maximum absorption capacity and desorption capacity attributes to the incomplete decomposition of $LiBH_4$ at 500 °C. On the other hand, the TG curve reveals that the decomposition of $LiBH_4$ is a multi-step process. The reaction equation could be the one proposed by Orimo et al. [26] as follows:

$$LiBH_4 + (1/2)Li_2B_{12}H_{12} + (5/6)LiH + (13/12)H_2 \rightarrow LiH + B + (3/2)H_2 \tag{9}$$

for the D_2/D_1 (D_2 and D_1 stand for the hydrogen desorption capacities of the second and the first stage, respectively) data of experiment (which is 1.59) is close to that of theoretical calculation (which is 1.39) according to Eq. (9). The endothermic peak at about 115 °C of DSC result can be assigned to the polymorphic transformation of $LiBH_4$. The second endothermic peak at about 262 °C corresponds to the melting of $LiBH_4$. Large exothermic peak ranges from 270 °C to 450 °C is assigned to the decomposition of $LiBH_4$ or/and other borides. The decomposition of $LiBH_4$ is supposed to be an endothermic process by Orimo et al. [10]. However, as the hydrogenation is not fully achieved, some by-products (borides) may be formed synchronously which are not detected yet. In fact, thermal properties of some metal complexes are variable. For example, an exothermic peak around 290 °C in succession to an endothermic one was found in the DSC curve of $MgH_2 + 2LiBH_4$ system by Zhang et al. [27] while no exothermic peaks were observed by Bösenberg et al. [28].

4. Conclusions

$LiBH_4$ is formed from a pretreated LiH + B mixture at 300–500 °C with a hydrogen pressure of 35 MPa. The results show that high-energy ball milling treatment under high hydrogen pressure could bring down the synthesizing temperature of $LiBH_4$ as ball milling treatment introduces high-density structural defects and a large area of grain boundaries which are favorable to improve the reaction kinetics, on the other hand, the LiH/B mixture may be well activated upon pre-treated under high hydrogen pressure. The formation of $LiBH_4$ through LiH and B is a diffusion-controlled hydrogenation process and the transformed fraction as a function of reaction duration can be expressed as $(1-f)^{1/3} = 1.08725 - 0.00227t^{1/2}$. The yield of $LiBH_4$ at 400 °C is around 59.4% and the synthesized $LiBH_4$ can release hydrogen of 6.59 wt.% in two steps.

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