

# LiBH<sub>4</sub> a new hydrogen storage material

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## Abstract

The challenge in the research on hydrogen storage materials is to pack hydrogen atoms or molecules as close as possible. The density of liquid and solid hydrogen is 70.8 and 70.6 kg m<sup>-3</sup>, respectively. Hydrogen absorbed in metals can reach a density of more than 150 kg m<sup>-3</sup> (e.g. Mg<sub>2</sub>FeH<sub>6</sub>) at atmospheric pressure. However, due to the large atomic mass of the transition metals the gravimetric hydrogen density is limited to less than 5 mass%. Light weight group 3 metals, e.g. Al, B, are able to bind four hydrogen atoms and form together with an alkali metal an ionic or at least partially covalent compound. These compounds are rather stable and often desorb the hydrogen only above their melting temperature. Complex hydrides like NaAlH<sub>4</sub>, when catalyzed, decompose already at room temperature. We have investigated LiBH<sub>4</sub>, a complex hydride which consists of 18 mass% of hydrogen. The hydrogen desorption from LiBH<sub>4</sub> was successfully catalyzed with SiO<sub>2</sub> and 13.5 mass% of hydrogen were liberated starting already at 200 °C.

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## 1. Introduction: hydrogen storage

The volumetric and gravimetric density of hydrogen in a storage material is crucial for mobile applications. Hydrogen can be stored by six different methods and phenomena:

- high pressure gas cylinders (up to 800 bar);
- liquid hydrogen in kryogenic tanks (at 21 K);
- adsorbed hydrogen on materials with a large specific surface area (at  $T < 100$  K);
- absorbed on interstitial sites in a host metal (at ambient pressure and temperature);
- chemically bond in covalent and ionic compounds (at ambient pressure);
- oxidation of reactive metals, e.g. Li, Na, with water.

The most common storage systems are high pressure gas cylinders with a maximum pressure of 20 MPa. New light weight composite cylinders have been developed which support pressure up to 80 MPa and therefore, the hydrogen reaches a volumetric density of 36 kg m<sup>-3</sup>, approximately half as much as in its liquid state. The safety of pressurized cylinders is an issue of concern especially in highly populated regions. Liquid hydrogen is stored in cryogenic tanks at 21.2 K and ambient pressure. Due to the low

critical temperature of hydrogen (33 K) liquid hydrogen can only be stored in open systems. The volumetric density of liquid hydrogen is 70.8 kg m<sup>-3</sup>, and large volumes where the thermal losses are small can reach hydrogen to system mass ratio close to one. The highest volumetric densities of hydrogen are found in metal hydrides. Fig. 1 shows the volumetric versus gravimetric hydrogen density of some selected materials. Many metals and alloys are capable of reversibly absorbing large amounts of hydrogen. Charging can be done using molecular hydrogen gas or hydrogen atoms from an electrolyte. Molecular hydrogen is dissociated at the surface prior to absorption, two H atoms recombine to H<sub>2</sub> in the desorption process. The host metal dissolves some hydrogen as a Sieverts type solid solution ( $\alpha$ -phase). As the concentration  $c_H$  of H in the metal is increased, the H–H interaction becomes locally important and nucleation and growth of the hydride phase ( $\beta$ ) start.

The thermodynamic aspects of the hydride formation from gaseous hydrogen is described by pressure–composition isotherms ( $p$  $c$  $T$  curves, Fig. 2). While the two phases coexist, the isotherms show a flat plateau, the length of which determines the amount of H<sub>2</sub> stored. In the pure  $\beta$ -phase, the H<sub>2</sub> pressure rises steeply with the concentration. The two-phase region ends at the critical temperature  $T_c$ , above which no phase transition from  $\alpha$ - to  $\beta$ -phase is observed. The equilibrium pressure  $p_{eq}$  as a function of

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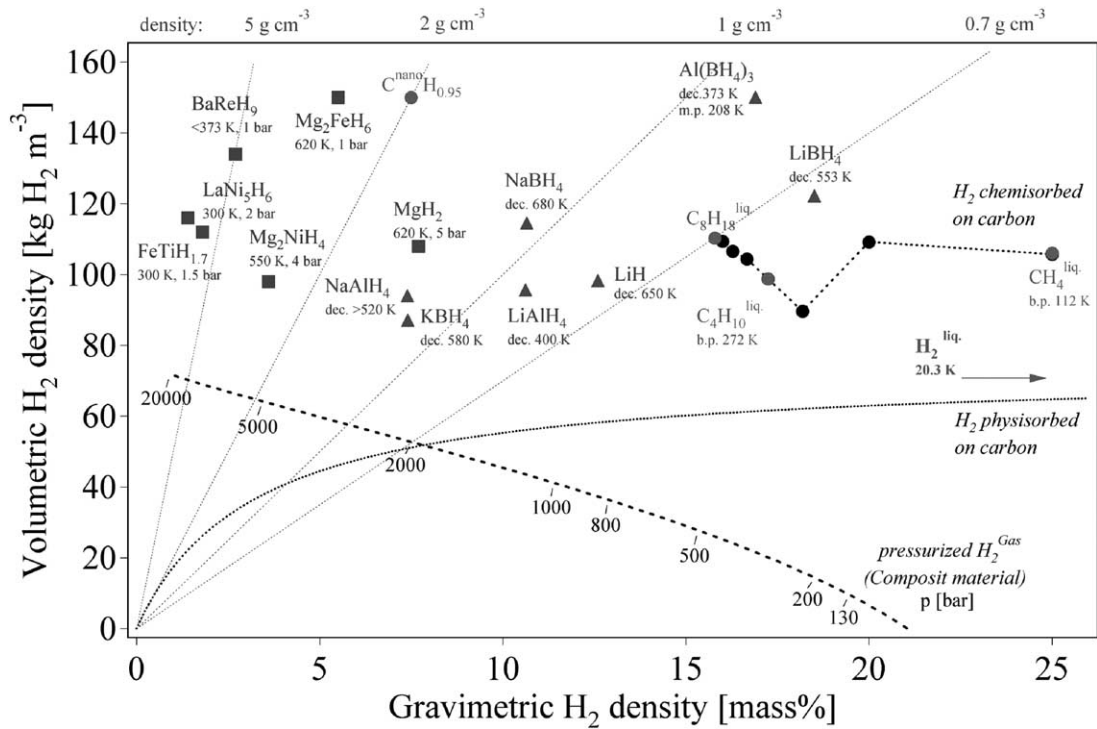


Fig. 1. Volumetric and gravimetric hydrogen density of some selected hydrides [1,2].  $\text{Mg}_2\text{FeH}_6$  shows the highest known volumetric hydrogen density of  $150 \text{ kg m}^{-3}$ , which is more than the double of liquid hydrogen.  $\text{BaReH}_9$  has the largest H/M ratio of 4.5, i.e. 4.5 hydrogen atoms per metal atom.  $\text{LiBH}_4$  exhibits the highest gravimetric hydrogen density of 18 mass%.

temperature is related to the changes  $\Delta H$  and  $\Delta S$  of enthalpy and entropy, respectively, by the Van't Hoff equation:

$$\ln\left(\frac{p_{\text{eq}}}{p_{\text{eq}}^0}\right) = \frac{\Delta H}{R} \frac{1}{T} - \frac{\Delta S}{R} \quad (1)$$

As the entropy change corresponds mostly to the change from molecular hydrogen gas to dissolved solid hydrogen, it

amounts approximately to  $S^0 = 130 \text{ J K}^{-1} \text{ mol}^{-1}$  for all metal–hydrogen systems. The enthalpy term characterizes the stability of the metal–hydrogen bond. To reach an equilibrium pressure of 1 bar at 300 K  $\Delta H$  should amount to  $19.6 \text{ kJ mol}_H^{-1}$ .

Metallic hydrides consist of transition metals and the lanthanides and the actinides. The structure of these hydrides are fundamentally similar to those of the metals.

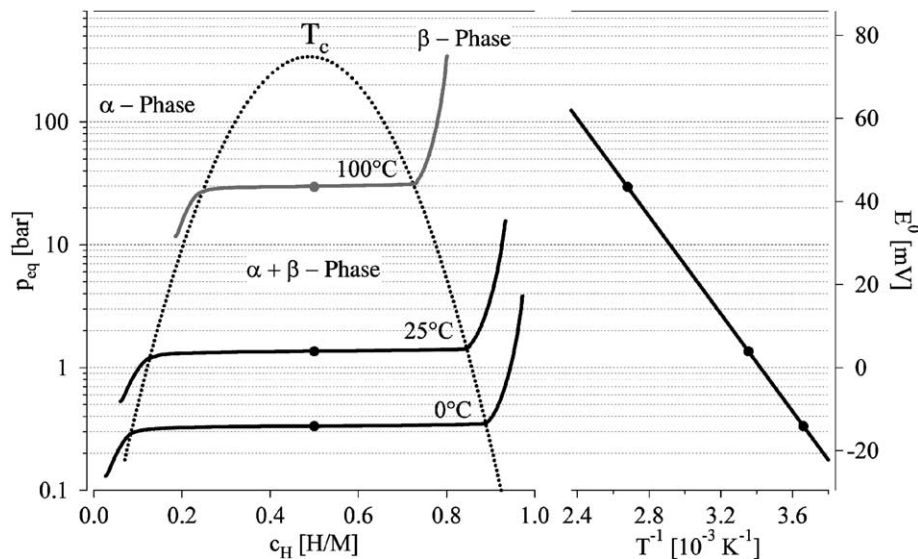


Fig. 2. The  $pT$  isotherms (left-hand side) for a hypothetical metal hydride. Corresponding Van't Hoff plot on the right-hand side.

Table 1  
Physical properties of selected complex hydrides

Formula	$M$ (g mol <sup>-1</sup> )	$\rho$ (g cm <sup>-3</sup> )	$T_m$ (°C)	$T_{dec}$ (°C)	$x$ (mass%)	Reference
LiBH <sub>4</sub>	21.784	0.66	268	380	18.4	[8]
NaBH <sub>4</sub>	37.83	1.074	505	400	10.6	[27]
LiAlH <sub>4</sub>	37.95	0.917	>125	125	9.5	[27]
KBH <sub>4</sub>	53.94	1.178	585	500	7.4	[27]
NaAlH <sub>4</sub>	54.0	1.27	178	210	7.4	[5]
Mg <sub>2</sub> NiH <sub>4</sub>	111.3	2.72		280	3.6	[29]
Mg <sub>2</sub> FeH <sub>6</sub>	110.5	2.72		320	5.4	[28]
Mg <sub>3</sub> MnH <sub>7</sub>	134.9	2.30		280	5.2	[28]
BaReH <sub>9</sub>	332.5	4.86		<100	2.7	[28]

$M$ : molecular mass,  $\rho$ : density,  $T_m$ : melting point,  $T_{dec}$ : decomposition temperature,  $x$ : gravimetric hydrogen density.

Due to the lattice expansion upon hydrogen sorption, the metal often loses some of its high symmetry, and as a consequence of the coexistence of the  $\alpha$ -phase and anisotropically expanded  $\beta$ -phase, lattice defects and internal strain fields are formed, which end in a decrepitation of brittle host metals such as intermetallic compounds. The H atoms vibrate around their equilibrium position, perform local motions and long range diffusion. Metal hydrides intercalate a maximum of one to two hydrogen atoms per metal atom. Due to the large molecular mass of the transition metals the gravimetric hydrogen density of the metal hydrides is limited to less than 8 mass%.

The groups 1–3 light metals, e.g. Li, Mg, B, Al, build a large variety of metal–hydrogen complexes. They are especially interesting because of their light weight and the number of hydrogen atoms per metal atom which in many cases is two. The main difference of the complex hydrides to the above described metallic hydrides is the transition to an ionic or covalent compound of the metals upon hydrogen absorption. Table 1 shows the physical properties of some selected complex hydrides.

Hydrogen can also be stored indirectly in reactive metals like Li, Na, Al, or Zn. These metals easily react with water to the corresponding hydroxide and liberate the hydrogen from the water. Since water is the product of the combustion of hydrogen with oxygen or air it can be recycled in a closed loop and react with the metal. Finally, the metal hydroxides can be thermally reduced to the metals in a solar furnace [2,3].

In this paper, we report about recent new developments on the hydrogen desorption from the complex hydride LiBH<sub>4</sub> into the gas phase.

## 2. Experimental

The compounds were purchased from Fluka Chemie AG in Switzerland (Sigma–Aldrich Fine Chemicals) [4]: lithium borohydride (LiBH<sub>4</sub>) no. 62460 (pract.;  $\geq 95\%$  gas-volumetric). The samples were handled solely in the argon glove box. The LiBH<sub>4</sub>-powder was transferred into the Mark-tubes with an inner diameter of 1 mm in the argon glove box and

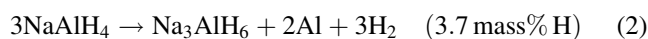
sealed on top with putty and later on the tubes were closed by melting the glass in a gas flame. The structure at room temperature was investigated by means of synchrotron radiation at the Swiss Light Source (SLS) with a high resolution powder diffractometer (Debye–Scherrer geometry). The photon energy was set to 8.15 eV ( $\lambda = 1.52 \text{ \AA}$ ).

The desorption experiments were carried out in a stainless steel cylinder. Approximately 200–300 mg of LiBH<sub>4</sub> was used for each desorption experiment. The desorbed gas was measured by means of a mass flow controller (Brooks instruments, 5850E, maximum flow 5 standard cm<sup>3</sup> min<sup>-1</sup>), with a maximum full scale error of 1%.

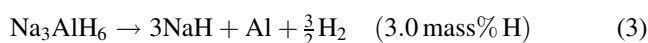
### 2.1. Complex hydrides

The hydrogen in the complex hydrides is located in the corners of a tetraeder with boron or aluminum in the center. The negative charge of the anion, [BH<sub>4</sub>]<sup>-</sup> and [AlH<sub>4</sub>]<sup>-</sup> is compensated by a cation, e.g. Li or Na. The hydride complexes of borane, the tetrahydroborates M(BH<sub>4</sub>), and of alane the tetrahydroaluminate M(AlH<sub>4</sub>) are interesting storage materials, however, they were known to be stable and decompose only at elevated temperatures and often above the melting point of the complex.

Bogdanovic and Schwickardi [5] presented in 1996 for the first time adsorption and desorption pressure–concentration isotherms of catalyzed NaAlH<sub>4</sub> at temperatures of 180 and 210 °C. The isotherms exhibit an absence of hysteresis and a nearly horizontal pressure plateau. Furthermore, the catalyzed system reversibly absorbed and desorbed hydrogen up to 4.2 mass% and the mechanism of the two-step reaction was described. A more detailed study of the NaAlH<sub>4</sub> with an improved catalyst was published in 2000 by Bogdanovic et al. [6]. A desorption hydrogen pressure of 2 bar at 60 °C was found and the enthalpy for the dissociation reaction was determined to be 37 and 47 kJ mol<sup>-1</sup> for the first dissociation step of Ti-doped NaAlH<sub>4</sub>:



and the second



respectively. Therefore, the equilibrium hydrogen pressure at room temperature is approximately 1 bar. Furthermore, the reaction is reversible, a complete conversion to product was achieved at 270 °C under 175 bar hydrogen pressure in 2–3 h [7].

The first report of a pure alkali metal tetrahydroboride appeared in 1940 by Schlesinger and Brown [8] who synthesized the lithiumtetrahydroboride (lithiumborohydride) ( $\text{LiBH}_4$ ) by the reaction of ethyllithium with diborane ( $\text{B}_2\text{H}_6$ ). The direct reaction of the corresponding metal with diborane in etheral solvents under suitable conditions produces high yields of the tetrahydroborides [9]:



where  $\text{M} = \text{Li}, \text{Na}, \text{K}$ , etc. Direct synthesis from the metal, boron and hydrogen at 550–700 °C and 30–150 bar  $\text{H}_2$  has been reported to yield the lithium salt, and it has been claimed that such a method is generally applicable to groups IA and IIA metals [10]. The reaction involving either the metal or the metal hydride, or the metal together with triethylborane in an inert hydrocarbon has formed the basis of a patent



where  $\text{M} = \text{Li}, \text{Na}, \text{K}$ , etc.

Lithium tetrahydroboride is a salt-like, hygroscopic, crystalline material with a reported melting point at 275 [8] or 278 °C and density 0.681 or 0.66  $\text{g cm}^{-3}$  at 25 °C. At 0 °C, its vapor pressure is much less than  $10^{-5}$  mbar, and the salt neither decomposes nor sublimates. The heat of formation of the compound has been measured [11–13], and the heat capacity was determined from 15 to 303 K. The usual thermodynamic functions have been tabulated for 15–300 and 0–2000 K (for a hypothetical solid). At 298.15 K the values are as follows:  $\Delta H_f^\circ = -194.44 \text{ kJ mol}^{-1}$ ,  $\Delta F_f^\circ = -128.96 \text{ kJ mol}^{-1}$ ,  $S^\circ = 75.91 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $c_p = 82.60 \text{ J K}^{-1} \text{ mol}^{-1}$ .

The stability of metal tetrahydroborides has also been discussed in relation to their percentage ionic character, and those compounds with less ionic character than diborane are expected to be highly unstable [14]. Steric effects have also been suggested to be important in some compounds [15,16]. The special feature exhibited by the covalent metal hydroborides is that the hydroboride group is bonded to the metal atom by bridging hydrogen atoms similar to the bonding in diborane, which may be regarded as the simplest of the so-called “electron-deficient” molecules. Such molecules possess fewer electrons than those apparently required to fill all the bonding orbitals, based on the criterion that a normal bonding orbital involving two atoms contains two electrons. The molecular orbital bonding scheme for diborane has been discussed extensively [16].

Fedneva et al. [17] investigated  $\text{LiBH}_4$  by means of thermal analysis (DTA). The thermogram of  $\text{LiBH}_4$  showed three endothermic effects: at 108–112, 268–286, and 483–492 °C. The endothermic effect at 108–112 °C is reversible and corresponds to polymorphic transformation

of  $\text{LiBH}_4$ . The second peak at 268–286 °C corresponds to the fusion of  $\text{LiBH}_4$ . The fusion is accompanied by a slight decomposition, which liberates approximately 2% of the hydrogen in the compound. The main evolution of gas starts at 380 °C and liberates 80% of the hydrogen in  $\text{LiBH}_4$ . The reason for the small effect at 483–492 °C is according to the authors uncertain. However, it coincides with the liberation of 50% of the hydrogen.

Stasinevich and Egorenko [18] investigated the alkali metal tetrahydroborides by means of thermal analysis in hydrogen at pressures up to 10 bar. The decomposition of the compounds can proceed in one of the following directions:



or



The thermal decomposition, at least in the early stages, is reversible, as is shown by the decomposition temperature being higher in the presence of hydrogen than in the vacuum or inert gas [19,20] and also by the existence [20,21] of a rapid isotopic exchange between tetrahydroboride and deuterium at  $T > 350$  °C. The decomposition temperature obtained for various hydrogen pressures lead to the following enthalpy and entropy for  $\text{LiBH}_4$ :  $\Delta H_f^\circ = -177 \text{ kJ mol}^{-1}$ ,  $S^\circ = 238 \text{ J K}^{-1}$ .

The change in free energy (isobaric) for the formation of the alkali metal tetrahydroborides from the elements have been published [22,23]:



$$\Delta G_T = -194.2 + 0.219T \text{ kJ mol}^{-1} \quad (9)$$



$$\Delta G_T = -103.4 + 0.150T \text{ kJ mol}^{-1} \quad (11)$$

The lattice energy of the crystalline compound is estimated from heats of formation to be 779  $\text{kJ mol}^{-1}$  [24].

The stability of metal hydrides can be changed by partial substitution of the consisting elements. Due to the delocalized electrons in metals substituted elements influence the overall stability of the interstitial hydrogen atoms. The electrons in ionic compounds are strongly localized, therefore, other routes have to be developed to destabilize the complex hydrides.

### 3. Results and discussion

The structure of  $\text{LiBH}_4$  is orthorhombic in agreement with the one by Harris and Meibohm [25]. The unit cell contains four molecules and has the dimensions  $a = 7.1730 \text{ \AA}$ ,  $b = 4.4340 \text{ \AA}$ ,  $c = 6.7976 \text{ \AA}$  at 25 °C (Fig. 3). The calculated density of  $\text{LiBH}_4$  is  $0.669 \text{ g cm}^{-3}$ . The arrangement of lithium and tetrahydroboride ions satisfies the space group  $Pnma$  (#62). Each  $\text{Li}^+$ -ion is surrounded by four  $[\text{BH}_4]^-$ -ions

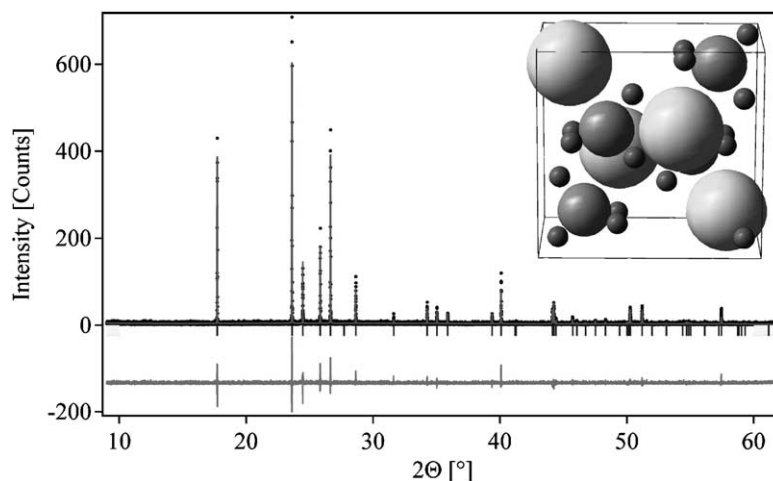


Fig. 3. Synchrotron powder diffraction spectrum (Debye–Scherrer) of polycrystalline  $\text{LiBH}_4$ . Space group  $Pnma$  (#62),  $a = 7.1730(1) \text{ \AA}$ ,  $b = 4.4340(1) \text{ \AA}$ ,  $c = 6.7976(1) \text{ \AA}$ ,  $V = 216.20 \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho = 0.669(2) \text{ g cm}^{-3}$ ,  $R_{\text{Bragg}} = 6.94\%$ ,  $R_{\text{wp}} = 7.68\%$  and  $\chi^2 = 0.58$ . The inset shows a drawing of the orthorhombic unit cell containing four  $\text{LiBH}_4$ , the size of the atoms corresponds to 25% of their covalent radii.

in a tetrahedral configuration. The  $[\text{BH}_4]$  tetrahedrons are strongly deformed, two hydrogen atoms are at a bond length of  $d(\text{B}-\text{H}) = 1.30 \text{ \AA}$ , one at  $d(\text{B}-\text{H}) = 1.28 \text{ \AA}$  and one at  $d(\text{B}-\text{H}) = 1.44 \text{ \AA}$ . Pistorius [26] investigated the phase diagram of  $\text{LiBH}_4$  over a large temperature and pressure range and found a structural transition from the orthorhombic phase at low temperature to a tetragonal phase around  $105 \text{ }^\circ\text{C}$ . However, the structural transition around  $100 \text{ }^\circ\text{C}$  is accompanied by a hydrogen desorption and therefore not only the structure but also the composition changes slightly. The thermal desorption spectra of pure  $\text{LiBH}_4$  shown in Fig. 4a exhibits a slight hydrogen desorption between  $100$  and  $200 \text{ }^\circ\text{C}$  of  $0.3 \text{ mass\%}$  or approximately  $1.5\%$  of the total hydrogen content of the compound which is in good agreement with the observation of Fedneva et al. [17]. The fusion was observed around  $270 \text{ }^\circ\text{C}$  without liberation of hydrogen. At  $320 \text{ }^\circ\text{C}$  the first significant hydrogen desorption peak starts and liberates an additional  $1 \text{ mass\%}$  of hydrogen. This first desorption goes over to a

second desorption peak starting at  $400 \text{ }^\circ\text{C}$  and reaches its maximum around  $500 \text{ }^\circ\text{C}$ . The integrated amount of hydrogen desorbed up to a temperature of  $600 \text{ }^\circ\text{C}$  is  $9 \text{ mass\%}$ , which corresponds exactly to half of the hydrogen in the starting compound. The end product has the nominal composition “ $\text{LiBH}_2$ ”. The thermal desorption spectra of  $\text{LiBH}_4$  mixed with  $\text{SiO}_2$ -powder (25:75 mass%) shown in Fig. 4b exhibits also three hydrogen desorption features, however the desorption starts at lower temperatures and  $9 \text{ mass\%}$  of hydrogen are liberated below  $400 \text{ }^\circ\text{C}$ . The first hydrogen desorption peak starts already at  $200 \text{ }^\circ\text{C}$  and the second hydrogen desorption peak starts at  $453 \text{ }^\circ\text{C}$  and is very sharp. The  $\text{SiO}_2$ -powder catalyzes the decomposition reaction of  $\text{LiBH}_4$  and lowers the temperature for all three hydrogen desorption features. Furthermore, the pure  $\text{LiBH}_4$  sample only exhibits significant desorption above  $400 \text{ }^\circ\text{C}$  in the second hydrogen desorption peak while the first hydrogen desorption peak starting at  $200 \text{ }^\circ\text{C}$  is the dominant peak of the catalyzed sample.

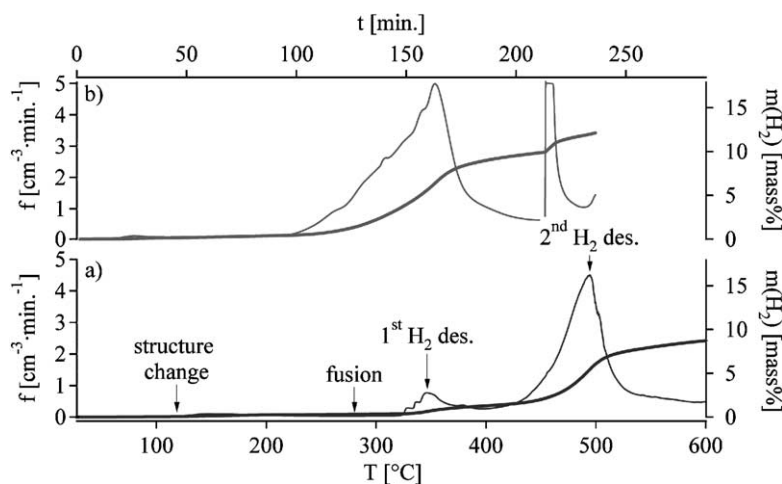


Fig. 4. Thermal desorption spectra of  $\text{LiBH}_4$ . The sample was heated after evacuation at room temperature with a heating rate of  $2 \text{ K min}^{-1}$ . The gas flow was measured as a function of time and the desorbed hydrogen was computed from the integrated gas flow: (a) pure  $\text{LiBH}_4$  and (b)  $\text{LiBH}_4$  mixed with  $\text{SiO}_2$  as catalyst.



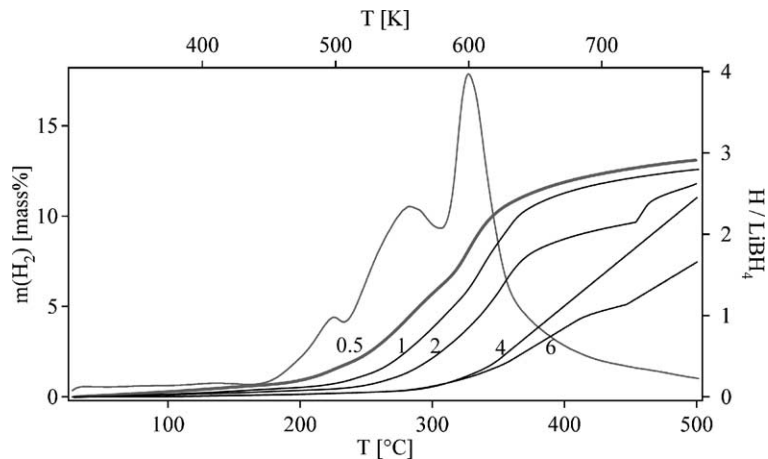
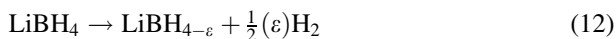


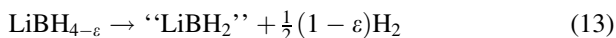
Fig. 5. Desorbed amount of hydrogen as a function of temperature for various heating rates, numbers indicate the heating rate in  $\text{K min}^{-1}$  on bottom and the hydrogen desorption flow as a function of temperature for a heating rate of  $0.5 \text{ K min}^{-1}$  on top. The sample was  $\text{LiBH}_4$  (28 mass%) mixed with  $\text{SiO}_2$ -powder.

The decomposition reaction of the catalyzed  $\text{LiBH}_4$  can be schematically described as follows:

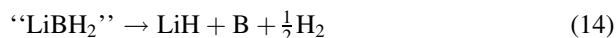
1. structural transition at  $T = 108 \text{ }^\circ\text{C}$ :



2. first hydrogen peak starting at  $T = 200 \text{ }^\circ\text{C}$ :



3. second hydrogen peak starting at  $T = 453 \text{ }^\circ\text{C}$ :



The compound  $\text{LiBH}_2$  is in quotes, since such a compound is not known yet. However, the desorption of 9 mass% indicates such a composition. Furthermore, Fedneva et al. [17] and Stasinevich and Egorenko [18] observed an endothermic effect at the composition “ $\text{LiBH}_2$ ”. Thermal desorption spectroscopy with different heating rates was applied in order to determine the activation energy of the slight hydrogen desorption process around  $100 \text{ }^\circ\text{C}$ . The logarithm of the ratio of the heating rate divided by the square of the peak temperature is a linear function of the inverse temperature if the hydrogen desorption is a first order reaction. The computed activation energy for the decomposition of  $\text{LiBH}_4$  around  $100 \text{ }^\circ\text{C}$  is  $E_A = 156 \pm 20 \text{ kJ mol}^{-1}$ .

The temperature of the major hydrogen desorption peaks strongly depends on the heating rate as shown in Fig. 5. At a small heating rate of  $0.5$  and  $1 \text{ K min}^{-1}$  three distinct desorption peaks were observed. The peak maxima correspond to  $0.33$ ,  $1.0$  and  $2.0 \text{ mol H per mol of LiBH}_4$ . This indicates that the hydrogen desorption reaction is divided in at least three steps with intermediate products. The maximum amount of desorbed hydrogen is limited to  $13.5 \text{ mass\%}$  due to the formation of lithium hydride ( $\text{LiH}$ ) which is stable up to  $900 \text{ }^\circ\text{C}$  [27].

## 4. Conclusion

We have investigated the structure and the thermal hydrogen desorption process of  $\text{LiBH}_4$  which contains  $18 \text{ mass\%}$  of hydrogen. It was found that the compound liberates hydrogen in different reaction steps and temperature regimes. The low temperature desorption from the orthorhombic phase liberates only a small amount ( $0.3 \text{ mass\%}$ ) of hydrogen. The high temperature phase liberates up to  $13.5 \text{ mass\%}$  of hydrogen ( $3 \text{ mol H per LiBH}_4$ ). A total of  $4.5 \text{ mass\%}$  of the hydrogen remain as  $\text{LiH}$  in the decomposition product. All attempts to synthesize  $\text{LiBH}_4$  from the elements at elevated conditions up to  $650 \text{ }^\circ\text{C}$  and  $150 \text{ bar H}_2$  pressure failed up to now.

## Acknowledgements

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