Helmholtz-Zentrum
Geesthacht
Zentrum für Material- und Küstenforschung

Final Draft
of the original manuscript:

Saldan, I.:

A prospect for LiBH4 as on-board hydrogen storage

In: Central European Journal of Chemistry (2011) Springer

DOI: 10.2478/s11532-011-0068-9

Central European Journal of **Chemistry**

A prospect for $LiBH_4$ as on-board hydrogen storage

Review

I. Saldan

Helmholtz-Zentrum Geesthacht, Institute of Materials Research,

Geesthacht 21502, Germany

Abstract: In contrast to the traditional metal hydrides, in which hydrogen storage involves the reversible hydrogen entering/exiting of the host hydride lattice, $LiBH_4$ release hydrogen via decomposition that produces segregated LiH and amorphous B phase. This is obviously the reason why lithium borohydride applications in fuel cell meet so far only one requirement – high hydrogen storage capacity. Nevertheless its thermodynamics and kinetics studies are very active today and some efficient ways to meet furl cell requirements might be done through lowering temperature for hydrogenation/dehydrogenation and suitable catalyst. It is expected some improvements can help us to use $LiBH_4$ in on-board hydrogen storage.

Keywords: *$LiBH_4$ · Hydrogen storage capacity · Thermodynamics · Kinetics*

1 Introduction

Hydrogen can be one of the alternative energy carriers, which should replace the traditional fossil fuels in a nearly future. The direct production of this new fuel would be made by electrolysis of water and under combustion of hydrogen only water will have been obtained too. The hydrogen energy content is equal to 142 MJ/kg what is much larger than petroleum – about 47 MJ/kg. Therefore the hydrogen chemical energy would be feasible to use for combustion engines and fuel cells. A modern, commercially available car with a range of 400 km burns about 24 kg of petrol in a combustion engine; to cover the same range, 8 kg hydrogen are needed for the combustion engine version or only 4 kg hydrogen for an electric car with a fuel cell. But one of the most discouraging challenges for widespread use of hydrogen as a fuel is the absence of a commercially viable hydrogen storage technology. Only a hydrogen storage material with ~ 9 wt.%H_2 gravimetric and ~ 80kg H_2/m^3 volumetric density in fuel cell can replace petroleum fuel vehicle on the large scale [1].

In this paper the state of the art and some outlooks on thermodynamics and kinetics of $LiBH_4$ as the reversible hydrogen storage material adapted to the fuel cell application have been reviewed.

Dr. Ivan Saldan*
Helmholtz-Zentrum Geesthacht, Institute of Materials Research, Max-Planck St. 1, Geesthacht, 21502 GERMANY
Fax: ++49 4152 -87 -2625 Office: ++49 4152 -87 -2689 e-mail: ivan_saldan@yahoo.com

2 Theoretical predictions to meet fuel cell requirements

Although the progress in the fuel cell technology appears to be eventually real, a viable method of on-board hydrogen storage is still under studying. In order to have advantage of petrol and diesel, hydrogen storage material should operate at temperatures 243–323 K with fast (< 5 min) reversibility (~ 90%) during at least 500 cycles [2]. From thermodynamic point of view reversible decomposition of $LiBH_4$ at moderate conditions ($P(H_2) \leq 100$ bar; T ~ 300 K) means reaction enthalpy around ~ 25–35 kJ/mol H_2. Therefore the development of different methods to adjust hydrogen storage material to the suitable thermodynamic properties is very crucial.

2.1 Thermal decomposition of $LiBH_4$

Complex hydrides, including light metal (Li), have sufficient gravimetric hydrogen storage capacity which is very suitable for fuel cell vehicles. This is the main reason why lithium complex hydrides such as $LiNH_2$ (with ~ 8.8 wt.% H_2) and $LiBH_4$ (with ~ 18.5 wt.% H_2) are being studied by many research groups. Particularly, the latter can desorb theoretically about ~ 13.5 wt.% H_2 by reaction (1), because LiH is too stabile (up to 1173K [3,4]):

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

The experimental value of enthalpy for this reaction is about ~ 68.6 kJ/mol H_2, therefore the temperature for hydrogen release is close to ~ 680 K [5]. The thermal desorption of $LiBH_4$ shows us a structural transition around ~ 380 K and melting point at ~ 550 K.

The precise theoretical observation of the $LiBH_4$ stability at absolute zero temperature as well as the most possible its intermediates at heat treatment are discussed in [6]. Based on existence of alkali-metal B-H inorganic compounds it was assumed that the LiB_3H_8, LiB_6H_6 and $LiB_{12}H_{12}$ should have the same crystal structure as CsB_3H_8 [7], $K_2B_6H_6$ [8] and $K_2B_{12}H_{12}$ [9], respectively. The stability of all possible intermediates such as $Li_2B_nH_n$ ($5 \leq n \leq 12$) was predicted using first principle calculation. The output compounds had different symmetry depending on the structure of $[B_nH_n]$ clusters. Moreover the theoretical results indicated the cubic and monoclinic types of structure for $Li_2B_{12}H_{12}$ and based on cohesive energy value, which was larger for the last, only $Li_2B_{12}H_{12}$ with $P2_1/n$ structure was considered as possible intermediate. The calculated enthalpy of $LiBH_4$ formation (with orthorhombic *Pnma*

Dr. Ivan Saldan*
Helmholtz-Zentrum Geesthacht, Institute of Materials Research, Max-Planck St. 1, Geesthacht, 21502 GERMANY
Fax: ++49 4152 -87 -2625 Office: ++49 4152 -87 -2689 e-mail: ivan_saldan@yahoo.com

symmetry; with zero-point energy correction) was equal to –56 kJ/mol H_2 [10]. And only $Li_2B_nH_n$ ($10 \le n \le 12$) compounds showed more negative value: –87; –79; –125 kJ/mol H_2 for $Li_2B_{10}H_{10}$; $Li_2B_{11}H_{11}$; $Li_2B_{12}H_{12}$, correspondently [6]. Taking into account relationship between the formation enthalpy and the mole fraction of H_2 the authors concluded that the most possible intermediates for $LiBH_4$ decomposition should be $LiB_{12}H_{12}$ and the total hydrogenation/dehydrogenation process for lithium borohydrides can be written as follow:

$$LiBH_4 \leftrightarrow \frac{1}{12}Li_2B_{12}H_{12} + \frac{5}{6}LiH + \frac{13}{12}H_2 \leftrightarrow LiH + B + \frac{3}{2}H_2 \qquad (2)$$

In this case the calculated enthalpy (without zero-point energy correction) and hydrogen content for first and second steps were 56 kJ/mol H_2 & ~ 10 wt.% H_2 and 125 kJ/mol H_2 & ~ 4 wt.% H_2, correspondently. The most interesting result was that the calculated enthalpy for the first step in process (2) is lower of that for the direct dehydriding reaction (1). These theoretical calculations on the energy of monoclinic $Li_2B_{12}H_{12}$ provided the upper-limit value for the thermodynamic stability. Moreover, it was predicted by phonon density of states that bending modes for $Li_2B_{12}H_{12}$ with $P2_1/n$ structure have lower frequencies than those of $LiBH_4$ (*Pnma*). Lithium borohydride desorbs hydrogen at temperatures above the melting point. The latent heat of fusion is 0.078 eV per formula unit [11] and similar values were expected for $Li_2B_nH_n$. Among the all considered closo-type dianions the $[B_{12}H_{12}]^{2-}$ was the most stable:

$$n\,B + \frac{n}{2}H_2 + 2\,e^- \leftrightarrow [B_nH_n]^{2-} \qquad (3)$$

It means that $Li_2B_{12}H_{12}$ should be present at hydrogenation/dehydrogenation process for $LiBH_4$ as an intermediate phase.

Because of the fact that B_2H_6 compound can be released during desorption of borohydrides [12], another reaction mechanism for the rehydrogenation of $LiBH_4$ was proposed in [13]:

$$LiH + B + \frac{3}{2}H_2 \leftrightarrow LiH + \frac{1}{2}B_2H_6 \leftrightarrow Li^+H^- + \frac{1}{2}(BH_3)_2 \leftrightarrow Li^+[BH_4]^- \qquad (4)$$

It is possible that hydrogen desorption and absorption can occur for lithium borohydride at low temperature and pressure by using an intermediate compound.

In recent work [14] $LiBH_4$ decomposition was studied by synchrotron radiation powder X-ray diffraction (SR-PXD) and solid state CP/MAS NMR at variable temperature. The experimental results showed evidence of the presence three new phases, which were not similar to those theoretically predicted in [6]. Two phases denoted as I and II which would be formed by partial dehydrogenation with slightly lower hydrogen content than stoichiometric

Dr. Ivan Saldan*
Helmholtz-Zentrum Geesthacht, Institute of Materials Research, Max-Planck St. 1, Geesthacht, 21502 GERMANY
Fax: ++49 4152 -87 -2625 Office: ++49 4152 -87 -2689 e-mail: ivan_saldan@yahoo.com

$LiBH_4$. This observation was explained by similar the Li and B coordination in phases I and II to that in $LiBH_4$. But the limited SR-PXD data has not allowed yet a complete structural analysis neither for I nor II phase. Boron NMR revealed a minor signal at $\delta(^{11}B) \approx -3.5$ ppm (0.3%) that was suggested to another phase existence; most probably it was a complex between water and $LiBH_4$ other words as an impurity, which was not identified by SR-PXD.

In experimental work [15] the thermodynamic parameters for reaction (1) were precisely determined by van't Hoff equation: $\Delta H = 74$ kJ/mol H_2 and $\Delta S = 115$ J/K mol H_2. It means that decomposition temperature (T_d) for $LiBH_4$ at 1 bar hydrogen pressure can be 643 K. These thermodynamic properties obviously are not appropriate for general criteria under fuel cell application. Moreover, the reversibility for (1) reaction together with very slow kinetics should be improved too.

2.3 Partially cation substitution in $LiBH_4$

Recent experiment suggests that tetragonal configuration of BH_4 complexes is strongly distorted [10]. Analyses for the electronic structure and the Born effective charge tensors indicated that Li atoms are ionized as Li^+ cations. A boron atom constructs sp^3 hybrids and forms covalent bonds with surrounding H atoms. The Γ-phonon frequencies originated from the internal B-H bending and stretching vibrations of BH_4 complexes reproduced by the molecular approximation, suggested the strong bonding of BH_4. These bonding properties are expected to be held even at high temperature but in another structure – hexagonal $P6_3mc$. It was proposed that a charge compensation by Li^+ cation would be a key feature for the stability of the internal bonding of $[BH_4]^-$ anions. Therefore a suppression of the charge transfer by the partial substitution Li atoms by other light metals would be effective to decrease thermodynamic stability of whole $LiBH_4$ compound.

Firstly the correlation between B-H atomistic vibrations in $[BH_4]^-$ anion and melting temperatures (T_m) of MBH_4 (M=Li, Na, K) were clarify in [16]. Stretching modes of B–H bonds (v_1 and v_3) modes are due to changes in the distance between the B and H atom; the bending modes (v_2 and v_4) – the change in the angles between the H-B-H bonds (fig.1). On the one hand bending mode v_2 the Raman shifts decrease in order of $LiBH_4 > NaBH_4 > KBH_4 > RbBH_4 > CsBH_4$; on the other hand the Raman shifts of the stretching mode v_1 decrease in the order of $NaBH_4 > KBH_4 > RbBH_4 > CsBH_4$. The smaller value on stretching mode and

Dr. Ivan Saldan*
Helmholtz-Zentrum Geesthacht, Institute of Materials Research, Max-Planck St. 1, Geesthacht, 21502 GERMANY
Fax: ++49 4152 -87 -2625 Office: ++49 4152 -87 -2689 e-mail: ivan_saldan@yahoo.com

related spectra at around 2200–2400 cm^{-1} of $LiBH_4$ comparing to those of $NaBH_4$ and KBH_4 should be due to the less-density orthorhombic structure [17] that is different with respect to crystal structure of $NaBH_4$ and KBH_4 (*Fm*3*m*).

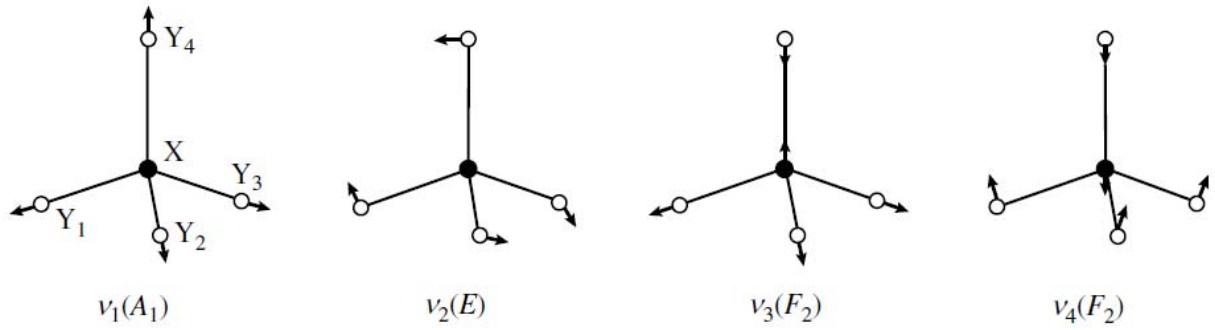

Fig.1 Schema of atomistic vibrations in XY_4 group; X is B atom, Y – H atom.

It is expected to have linear relationship between earth metals and atomistic vibration of $[BH_4]^-$ anions in their correspondent borohydrides. Obviously metals of the first group in Periodic Table have the same type of influence on $[BH_4]^-$ anions but only with the difference in the value.

The differential scanning calorimetry (DSC) profiles of MBH_4 (M = Li, Na, K) during heating up to 900 K under 1 bar hydrogen pressure has been done in [16]. Taking into account endothermic peaks only for melting reaction (structural transformation take place at ~ 380K for $LiBH_4$; ~10K for $NaBH_4$; and ~1.5K for KBH_4) one can conclude that melting temperature (T_m) increases in order of $LiBH_4$ < $NaBH_4$ < KBH_4 (fig.2). Similar behavior present also for T_d (fig.2). Since decrease of stretching modes ν_1 and bending modes ν_2 (exception for $LiBH_4$ because of structure) and increase of T_m and T_d in the order $LiBH_4$; $NaBH_4$; KBH_4; $RbBH_4$; $CsBH_4$ take place, it can be concluded that smaller cation size or higher valence cation with larger electronegativity would be preferred for lower T_d of MBH_4 compounds. Behavior of the curves (fig.2) can be explained by a small changing in cell parameters of borohydrides as a total result of different influences between cation and anion in polarized molecules.

In recent work [18] a correlation between the T_d and the Pauling electronegativity (χ_p) was observed experimentally for $M(BH_4)_n$, where M was rare-earth and transition metal. Moreover, a good correlation between estimated enthalpy for $M(BH_4)_n$ decomposition and the observed T_d, was presented as confirmation to predict stability of borohydrides. Other words, the thermodynamic stability of $LiBH_4$ can be reduced by partial substitution of Li on another

Dr. Ivan Saldan*
Helmholtz-Zentrum Geesthacht, Institute of Materials Research, Max-Planck St. 1, Geesthacht, 21502 GERMANY
Fax: ++49 4152 -87 -2625 Office: ++49 4152 -87 -2689 e-mail: ivan_saldan@yahoo.com

light element with less metallic in nature and subsequently the B-H bonds may be weakened and T_d should be decreased.

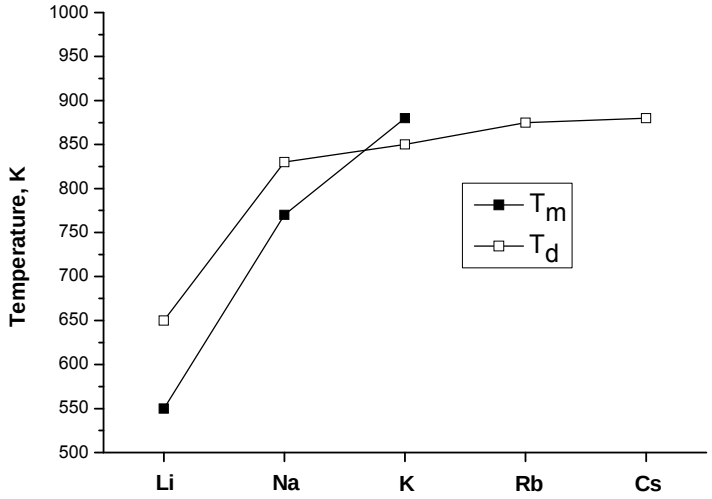

Fig.2. Dependence of melting and decomposition temperatures (T_m and T_d, correspondently) for MBH_4 (M = Li; Na; K; Rb; Cs) compounds.

But today there are only a few experimental data on partial cation substituted $LiBH_4$ ($LiK(BH_4)_2$ [18-22] and $LiSc(BH_4)_4$ [22]) which showed that partial substitution of Li by another element from 1a group in Periodic Table could not decrease T_d. Therefore it is expected that reduction of T_d could be for cation substituted $LiBH_4$ by transition elements though hydrogen gravimetric capacity of this new compound will be also reduced [23].

2.4 Partially H-atom substitution inside $[BH_4]^-$ anion

Since H- and F atom are very similar on size and valence, H→F substitution inside BH_4 tetrahedron may be possible. And these compounds, called as "hydridofluoride", in most cases have the same crystal structure as their corresponding hydrides. Moreover thermodynamic properties can be changed gradually by progressive H→F substitution. The direct reaction of hydrogen on a mixture of Na with Mg or NaF with Mg allowed to synthesize both orthorhombic $NaMgH_3$ and $NaMgH_2F$, respectively [24]. Another example was $Na_3AlH_2F_4$ made from NaF, Al in the presence of TiF_3 [25]. For $NaMgH_{3-x}F_x$ compounds their enthalpy of formation increases with increasing *x* value [26]; while in case of

Dr. Ivan Saldan*
Helmholtz-Zentrum Geesthacht, Institute of Materials Research, Max-Planck St. 1, Geesthacht, 21502 GERMANY
Fax: ++49 4152 -87 -2625 Office: ++49 4152 -87 -2689 e-mail: ivan_saldan@yahoo.com

$Na_{12}Al_4H_{24-x}F_x$ – results in gradually enthalpy reducing. A changing of ΔH from $LiBH_4$ to $LiBF_4$ would be interesting to observe too.

In recent work [27] the decomposition reaction of $LiBH_4$ with F anion doping was investigated by first-principles calculations. The computed cell parameters of $LiBH_4$ were in good agreement with the experimental data (space group *Pnma*, *a*=57.17858(4), *b*=54.43686(2), *c*=56.80321(4) Å [28]). According to the calculation H→F, substitution can be possible for $LiBH_4$ at its formation (as $LiBH_{4-x}F_x$) and under its decomposition for LiH (as $LiH_{1-y}F_y$). A 1×2×1 $LiBH_4$ supercell consisting of 48 atoms ($Li_8B_8H_{32}$), a 1×2×1 LiH supercell containing 16 atoms (Li_8H_8), and a crystallographic unit cell containing 12 atoms to represent α-boron were constructed to study $LiBH_4$ decomposition. Five possible theoretical reactions under decomposition of $Li_8B_8H_{32-x}F_x$ (x= 1–4), including persisting its substitutional feature in LiH lattice, combining with Li cation to generate segregated LiF phase, combining with B to generate gaseous BF_3, bonding with H to generate gaseous HF, or forming gaseous F_2 by coupling with another F, were presented:

$$Li_8B_8H_{32-x}F_x \rightarrow Li_8H_{8-x}F_x + 8\ B + 12\ H_2 \quad (5)$$

$$Li_8B_8H_{32-x}F_x \rightarrow Li_{8-x}H_{8-x} + Li_xF_x + 8\ B + 12\ H_2 \quad (6)$$

$$Li_8B_8H_{32-x}F_x \rightarrow Li_8H_8 + x/3\ BF_3 + (8-x/3)\ B + (12-x/2)\ H_2 \quad (7)$$

$$Li_8B_8H_{32-x}F_x \rightarrow Li_8H_8 + H_xF_x + 8B + (12-x)\ H_2 \quad (8)$$

$$Li_8B_8H_{32-x}F_x \rightarrow Li_8H_8 + 8B + x/2\ F_2 + (12-x/2)\ H_2 \quad (9)$$

In fig.3 the calculated decomposition enthalpy of $Li_8B_8H_{32-x}F_x$ (x = 1–4) depending on H→F substitution is present.

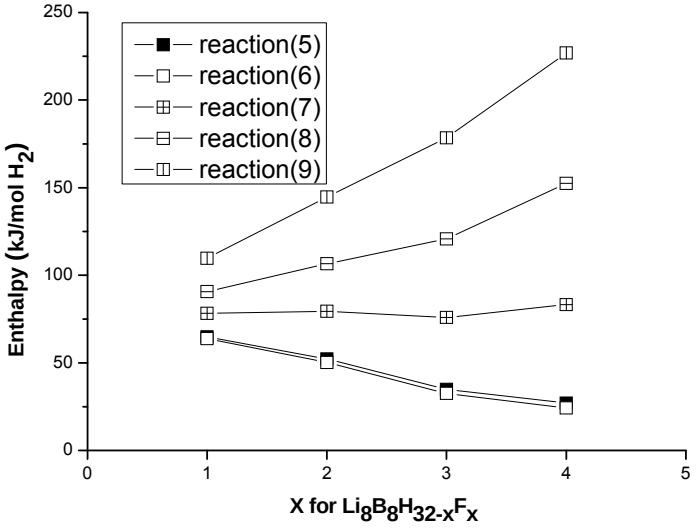

Fig.3 Calculated decomposition enthalpy of $Li_8B_8H_{32-x}F_x$ (x = 1–4) at the reactions (5-9).

Dr. Ivan Saldan*
Helmholtz-Zentrum Geesthacht, Institute of Materials Research, Max-Planck St. 1, Geesthacht, 21502 GERMANY
Fax: ++49 4152 -87 -2625 Office: ++49 4152 -87 -2689 e-mail: ivan_saldan@yahoo.com

According to the calculation, reactions (5) and (6) are more favorable than others. It means that possibility of generation of gaseous fluorine phases (BF_3; HF; F_2) at $Li_8B_8H_{32-x}F_x$ (x = 1–4) decomposition should be excluded. The tendency of reaction enthalpy decreasing with H→F substitution increasing for (5) reaction can be explained by F substitution in both $Li_8B_8H_{32-x}F_x$ and $Li_8H_{8-x}F_x$. The formation enthalpies of these F-substituted hydrides are much more negative than those of the pure counterparts, but with an absolute decrease in $Li_8H_{8-x}F_x$ larger than that in $Li_8B_8H_{32-x}F_x$. The value of enthalpy decomposition for $LiBH_4$ with and without zero-point energy corrections were 60.9 kJ/mol H_2 and 77.7 kJ/mol H_2, respectively, which is in a good agreement with those reported in [3-5,10,15].

In order to model solid solutions between $LiBH_4$ and $LiBF_4$, the adopted procedure in [29] contemplated the following steps: (1) classification, by symmetry equivalence, of all the possible configurations obtained at the same F content; (2) full geometry optimization, to compute vibrational and thermodynamic properties of the Li–B–H–F structures; (3) calculation of ΔH, ΔS and ΔG at T = 298K and P = 0.1013250 MPa for the reaction:

$$(1-a/16)\ LiBH_4 + (a/16)\ LiBF_4 \rightarrow (1/4)\ Li_4B_4H_{16-a}F_a \qquad (10)$$

Value *a* showed the number of F ions which can substitute H inside the unit cell ($0 \le a \le 16$). The quantum-mechanical data of mixed compounds were used to derive the ΔH curve (fig.4) by thermodynamic modeling according to the equation:

$$\Delta H_{mix} = x(1-x)[L_0 + L_1(2x-1)] \qquad (11)$$

Value *x* is the molar fraction of $LiBF_4$ and L_0 = 62438 $Jmol^{-1}$ and L_1 = − 9750 $Jmol^{-1}$ were the interaction parameters.

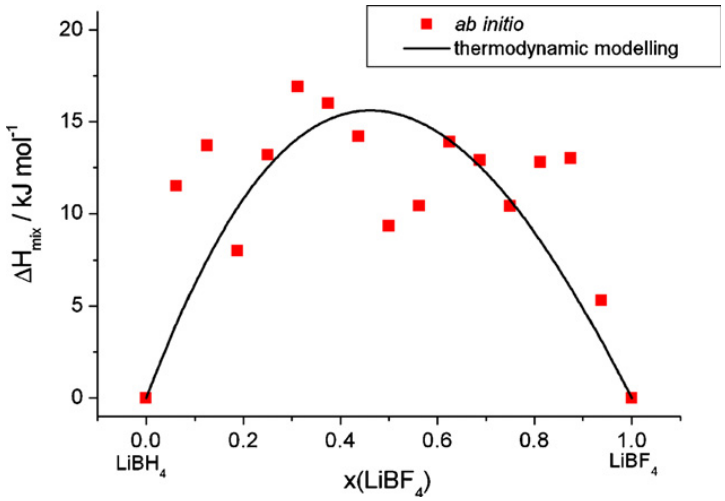

Fig.4. Calculated excess enthalpy of mixing as a function of composition in the orthorhombic $LiBH_4$–$LiBF_4$ solid solution at 298K and 1bar (line) in comparison with the results from first principles calculations (squares).

Dr. Ivan Saldan*
Helmholtz-Zentrum Geesthacht, Institute of Materials Research, Max-Planck St. 1, Geesthacht, 21502 GERMANY
Fax: ++49 4152 -87 -2625 Office: ++49 4152 -87 -2689 e-mail: ivan_saldan@yahoo.com

The main conclusion of this theoretical calculation was that at room temperature changes in enthalpy for all compositions from the pure hydride to the pure fluoride were positive. This indicates no formation of mixed $LiBH_4$–$LiBF_4$ compounds at room temperature and 1 bar of pressure.

In experimental work [30] only $LiBH_4$ and MgF_2 have been found as the main products of mechanochemical interaction between LiF and MgB_2. Nevertheless in this work NEXAFS data is the next strong hint of $LiBH_{4-x}F_x$ existence after ATR–FTIR observations in [31] for LiF–MgB_2 system. In the next studies possible fluorine substitution for hydrogen atom inside $[BH_4]^-$ anion will be proposed by another experimental methods (e.g. wet chemical). Some similar $[BH_4]^-$ anion modification have been already experimentally confirmed for $[BH_3OH]^-$, $[BH_3OR]^-$ and $[BH_3NH_2]^-$ in [32], [33] and [34], respectively.

2.5 Reactive hydride composites based on $LiBH_4$

In principle, two or more hydrides can chemically react with each other if total heat of the mixture formation has exothermic effect. And the value of the mixture reaction enthalpy can be altered by selecting certain hydride-reagents. The method produces a new composite called as "Reactive Hydride Composite" (RHC). If thermodynamically possible to create a mixture of $LiBH_4$ with another light hydride to decrease its T_d and at the same time remain the high hydrogen content it can be one of the solutions to obtain appropriate reversible hydrogen storage material in fuel cell.

One the most noticeable RHC example is the mixture of $LiBH_4$ with MgH_2 experimentally studied in [35]:

$$LiBH_4 + \frac{1}{2}MgH_2 \rightarrow LiH + \frac{1}{2}MgB_2 + 2H_2 \qquad (12)$$

This reaction (10) yielded maximum ~ 11.5 wt.%H_2 and reversibly – more than 9 wt.%H_2. Thermodynamical properties were estimated by van't Hoff equation: ΔH = 40.5 kJ/mol H_2 and ΔS = 81.3 J/K molH_2. These data show that reaction (12) can be carried out at 498 K temperature under 1 bar hydrogen pressure. Because of the equilibrium pressure for MgH_2/Mg system is higher than for the RHC at above 633 K it means that reaction (12) should be change to another one as follows:

Dr. Ivan Saldan*
Helmholtz-Zentrum Geesthacht, Institute of Materials Research, Max-Planck St. 1, Geesthacht, 21502 GERMANY
Fax: ++49 4152 -87 -2625 Office: ++49 4152 -87 -2689 e-mail: ivan_saldan@yahoo.com

$$LiBH_4 + \frac{1}{2}Mg \rightarrow LiH + \frac{1}{2}MgB_2 + \frac{3}{2}H_2 \quad (13)$$

It is known that hydrogenation of Mg is exothermic therefore the enthalpy for reaction (13) is expected to be less than for reaction (12).

Other possible reactions with these light hydrides were predicted in recent theoretical work [36]:

$$4\ LiBH_4 + MgH_2 \rightarrow 4\ LiH + MgB_4 + 7\ H_2 \quad (14)$$

$$7\ LiBH_4 + MgH_2 \rightarrow 7\ LiH + MgB_7 + \frac{23}{2}H_2 \quad (15)$$

The calculated enthalpy by DFT for reaction (14) and (15) were 53.5 kJ/mol H_2 and 55.1 kJ/mol H_2, respectively. But any experimental results were not obtained for these reactions which can yield a maximum of ~ 12.5 wt.%H_2 and ~ 13 wt.%H_2 at completion for (14) and (15), correspondently. Another example of HRC with similar expectations is mixture of $LiBH_4$ with CaH_2:

$$6\ LiBH_4 + CaH_2 \rightarrow 6\ LiH + CaB_6 + 10H_2 \quad (16)$$

The DFT calculation estimated reaction (16) as possible with enthalpy 47.0 kJ/mol H_2 and maximum theoretical capacity ~ 12 wt.%H_2.

The mixture $LiBH_4$ with $LiNH_2$ experimentally can produce hydrogen up to ~ 7.8 wt.%H_2 at 522 K under 1 bar hydrogen pressure [37,38]:

$$LiBH_4 + 2\ LiNH_2 \rightarrow Li_3BN_2 + 4\ H_2 \quad (17)$$

The calculated reaction enthalpy was 24 kJ/mol H_2 and theoretically 11.9 wt.%H_2 was predicted [36]. But really under heating this composite forms quaternary hydride ($Li_4BN_3H_{10}$; space group $I2_13$; cell parameter a = 10.679(1)–10.672(1) Å [39]) as intermediate phases which decompose at room temperature. This is why the phase composition of the RHC is very sensitive to ambient conditions.

Hydrides of transition metals demonstrate lower gravimetric density of hydrogen with respect to light metal hydrides. Nevertheless, from thermodynamic point of view it is interesting to predict possibilities of new RHC based on $LiBH_4$ with at least ScH_2 and TiH_2. The DFT calculations in [36] gave some reactions which worth of our attention:

$$LiBH_4 + \frac{1}{2}ScH_2 \rightarrow LiH + \frac{1}{2}ScB_2 + 2H_2 \quad (18)$$

The theoretical results showed that reaction (18) can release ~ 8.9 wt.%H_2 on completion and their calculated reaction enthalpy should be 34.7 kJ/mol H_2. Similar reaction can be possible with TiH_2:

Dr. Ivan Saldan*
Helmholtz-Zentrum Geesthacht, Institute of Materials Research, Max-Planck St. 1, Geesthacht, 21502 GERMANY
Fax: ++49 4152 -87 -2625 Office: ++49 4152 -87 -2689 e-mail: ivan_saldan@yahoo.com

$$LiBH_4 + \frac{1}{2}TiH_2 \rightarrow LiH + \frac{1}{2}TiB_2 + 2H_2 \quad (19)$$

DFT calculations indicated 6.5 kJ/mol H_2 and the theoretical maximum hydrogen content can be only ~ 8.7 wt.% H_2.

It is no surprise that the mixtures $LiBH_4$ with transition metals hydrides give lower hydrogen gravimetric density, though their thermodynamic data are not worse as regards to mixture $LiBH_4$ with light metals hydrides. Since all above mentioned reactions were observed only theoretically, their experimental examination would be useful studies to get answer how much hydrogen can be load/unload for these new RHCs at moderate conditions.

2.6 Carbon influence on $LiBH_4$ dehydrogenation/rehydrogenation

It is known, that carbon can react with hydrogen to produce hydrocarbons. But every allotropic carbon modification with specific own structure should have different thermodynamics for reaction with hydrogen. Graphite is expected more difficult to react with hydrogen than activated carbon or carbon black. Nevertheless graphite in nano-scale as nano-fibers and Li- K-intercalated graphite were studied with regards to hydrogen storage materials [40,41]. Theoretically graphite can store hydrogen at 65meV/H_2 through the dramatic swelling of interlayer separation where one hydrogen molecule can be placed on the top of every graphite hexagon (~ 7.7wt.%H_2). But hydrogen intercalation causes a big interlayer relaxation (in ~ 1.70 times) therefore optimal H_2 adsorption distance is far too large for energetically favorable adsorption of hydrogen molecule between two graphene sheets inside graphite [40]. In order to increase possibility for graphite interaction with hydrogen the alkali-doping of graphite nanofibers was introduce in some recent works [41,42]. Calculations showed stronger hydrogen adsorption on Li-intercalated graphite with respect to K-intercalated one. Only physical adsorption had been located, the binding energy of which is relatively higher at 0 K and become near zero at 298 K. Thus un-cyclable hydrogen is actually not adsorbed on alkali atoms but only by defects of graphite, so called “carbon edge sites”, where hydrogen adsorption is thermodynamically very favorable [41]. These defects were produced by the repeated heat treatment at 523 K for 12h [42]. After absorption/desorption cycling for both Li- and K-doped graphite nano-fibers H_2O impurity was present at thermogravimetry and it can be the reason why no hydrogen adsorption was observed for Li-

Dr. Ivan Saldan*
Helmholtz-Zentrum Geesthacht, Institute of Materials Research, Max-Planck St. 1, Geesthacht, 21502 GERMANY
Fax: ++49 4152 -87 -2625 Office: ++49 4152 -87 -2689 e-mail: ivan_saldan@yahoo.com

doped graphite. But for K-doped graphite only 1.3 wt.% H_2 was achieved near at room temperature. It should be dissociatively adsorbed hydrogen, or other words, chemical adsorbed hydrogen, because thermodynamically very difficult to desorb hydrogen atoms from these carbon edge sites.

Using DFT calculation in [36] for $LiBH_4$ mixtures with carbon in solid phase non-hydrocarbon species the enthalpy value ~ 31.8 kJ/mol H_2 and hydrogen capacity ~ 12 wt.%H_2 at completion can be achieved by reaction:

$$LiBH_4 + C \rightarrow LiBC + 2\ H_2 \qquad (20)$$

In practice carbon nano-tubes was used to check this reaction [43]. No CH_4 was detected by mass spectroscopy during hydrogenation/dehydrogenation of $LiBH_4$ mixtures with carbon nano-tubes (C_{nano}; Shenzhen Nanotech Port Co., Ltd., China). System $LiBH_4/C_{nano}$, where C_{nano} was introduced as multi-wall carbon nanotubes (MWCNTs) was expected to show better thermodynamic properties with respect to RHCs. In this experimental work $LiBH_4/C_{nano}$ with different mass ratios (2:1; 1:1 and 1:2) were mechanically milled under inert gas for 1h. For all mixtures the thermogravimetry showed that initial temperature for hydrogen desorption were ~ 520 K and the main temperature peaks were ~ 733 K; ~ 648 K and ~ 633 K for 2:1; 1:1 and 1:2 $LiBH_4/C_{nano}$ mixtures, respectively. And the hydrogen storage capacity was: ~ 11; ~ 8.55 and ~ 6 wt.%H_2 for the same direction of the mixtures. The 1:2 mass ration $LiBH_4/C_{nano}$ mixture was partly rehydrogenated at 673 K under 100 bar hydrogen pressure and the main hydrogen desorption peak was on 10 K lower than for the first desorption though hydrogen release was only 1.26 wt.%H_2. XRD analysis of 1:2 mass ration $LiBH_4/C_{nano}$ mixture showed $LiBH_4$ and C; Li_2C_2, C and LiOH; Li_2C_2, C and LiH for milled, dehydrogenated and rehydrogenated samples, respectively. Therefore the reaction paths were proposed as follows:

$$LiBH_4 + C \rightarrow \frac{1}{2} Li_2C_2 + B + 2\ H_2 \rightarrow LiH + C + B + \frac{3}{2}\ H_2 \qquad (21)$$

Carbon in form of non-hydrocarbon species is expected to moderate thermodynamics for $LiBH_4$ decomposition/formation by reaction (20) though the reaction paths are not determined yet. Nevertheless the influence of carbon on $LiBH_4$ reversible decomposition is visible, because neither graphite nano-fibers nor MWCNTs can react directly with hydrogen.

From thermodynamic point of view these carbon species can be involved even in the RHCs reactions and some of them have been calculated by DFT in [36]. Reaction (12) theoretically can be performed more easily when 1 mol of carbon would be added:

Dr. Ivan Saldan*
Helmholtz-Zentrum Geesthacht, Institute of Materials Research, Max-Planck St. 1, Geesthacht, 21502 GERMANY
Fax: ++49 4152 -87 -2625 Office: ++49 4152 -87 -2689 e-mail: ivan_saldan@yahoo.com

$$LiBH_4 + \frac{1}{2} MgH_2 + C \rightarrow \frac{1}{2} MgB_2C_2 + LiH + 2\ H_2 \quad (22)$$

Calculations had given 39.9 kJ/mol H_2 of reaction enthalpy and 8.6 wt.%H_2 of maximum gravimetric density. This enthalpy value is better than for reaction (12) though hydrogen storage capacity is gone out of the necessary limit. The next similar example could be reaction with CaH_2:

$$LiBH_4 + \frac{1}{2} CaH_2 + C \rightarrow \frac{1}{2} CaB_2C_2 + LiH + 2\ H_2 \quad (23)$$

The reaction is thermodynamically feasible and even in comparison with reaction (16) the calculated enthalpy is lower (~ 45.9 kJ/molH_2). But again theoretical gravimetric density is also decreased (7.3 wt.%H_2). And at the end, two possible reactions involving ScH_2 were predicted as thermodynamically very interesting:

$$LiBH_4 + \frac{1}{2} ScH_2 + \frac{1}{2} C \rightarrow \frac{1}{2} ScB_2C + LiH + 2\ H_2 \quad (24)$$

$$LiBH_4 + \frac{1}{2} ScH_2 + C \rightarrow \frac{1}{2} ScB_2C_2 + LiH + 2\ H_2 \quad (25)$$

Because of increasing RCHs weight on carbon mass the total hydrogen storage capacity is decreased to 7.9 wt.%H_2 and 7.0 wt.%H_2, but the calculated values of enthalpy are quite good – 37.6 kJ/mol H_2 and 36.9 kJ/mol H_2 for (24) and (25), respectively. Energy comparing for these reactions together with (18) showed that all reactive enthalpies are very close each other that priory means these carbon modifications more obviously as catalytic effects on RHCs mixtures.

2.7 Promising approaches and reactions of $LiBH_4$ regards to fuel cell application

From all above mentioned chapters the main approaches to meet fuel cell application of $LiBH_4$ can be combined as follows:

(1) For thermodynamically stable $LiBH_4$ the partial substitution of Li^+ on less ionized metallic atom can be a good example to destabilize interaction between cation and anion. However, it is expected decrease of the hydrogen storage capacity.

(2) Because of low weight of F-atoms and theoretically observed their influence on $Li_8B_8H_{32-x}F_x$ ($1 \leq x \leq 4$) thermodynamic properties, it can be an efficient example among other possible partial H-atom substitution inside $[BH_4]^-$ anion.

Dr. Ivan Saldan*
Helmholtz-Zentrum Geesthacht, Institute of Materials Research, Max-Planck St. 1, Geesthacht, 21502 GERMANY
Fax: ++49 4152 -87 -2625 Office: ++49 4152 -87 -2689 e-mail: ivan_saldan@yahoo.com

(3) RHCs based on $LiBH_4$ is a great good idea because under changing of thermodynamics the hydrogen storage capacity of the composite can be maintained.

(4) In spite of decreasing total hydrogen storage capacity for RHC mixtures with carbon nanofibers the satisfied thermodynamic properties is retained. In addition, these carbon modifications might be discussed as catalytic effects on hydrogen sorption.

Taking into account above mentioned reaction enthalpy and hydrogen storage capacity (equations 12-25) only three reactions (17, 18 and 20) can be observed as promising ways for real $LiBH_4$ on-board application. For better general view the graph with total reaction enthalpy versus theoretical hydrogen content has been built in fig.5.

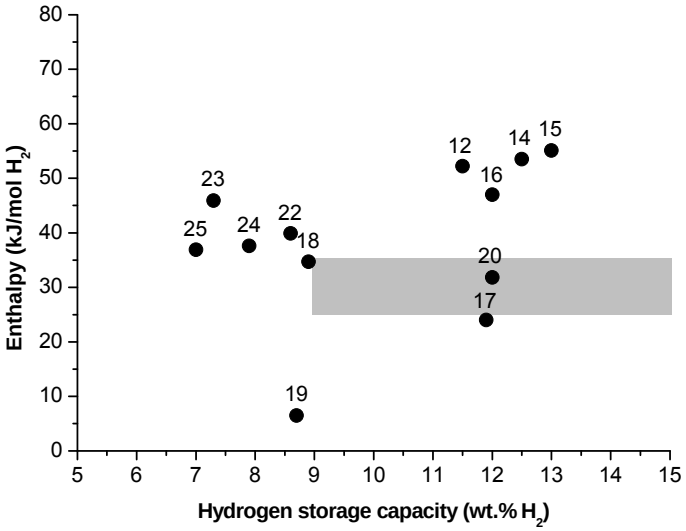

Fig.5. The reaction enthalpy (calculated by DFT without zero-point energy correction [36]) at 300 K per 1 mol H_2 of (12-25) reactions versus theoretical hydrogen storage capacity. Gray rectangular square describes fuel cell requirements.

Interaction between $LiBH_4$ and $LiNH_2$, RHC reaction between $LiBH_4$ and ScH_2 as well carbon interaction with lithium borohydride (equation 17, 18 and 20, correspondently) have the best compromise between thermodynamics and hydrogen gravimetric density. Therefore they should be studied in detail and their answers for other fuel cell requirements must be done as soon as possible.

Dr. Ivan Saldan*
Helmholtz-Zentrum Geesthacht, Institute of Materials Research, Max-Planck St. 1, Geesthacht, 21502 GERMANY
Fax: ++49 4152 -87 -2625 Office: ++49 4152 -87 -2689 e-mail: ivan_saldan@yahoo.com

3 Experimental results of $LiBH_4$ reversible decomposition

There are a lot of experimental results on $LiBH_4$ regarding to its application in fuel cell however today there is no example which can be tested in practice. Truly say, some strong tendencies/certain approaches to describe and solve the problems are not so visible. In this chapter the main directions, which can be successful, of the purpose to make $LiBH_4$ based material adopted with working conditions in fuel cell have been collected.

3.1 Binary $LiBH_4$–$LiNH_2$ and ternary $LiBH_4$–$LiNH_2$–MgH_2 mixtures

The system of $LiBH_4$–$LiNH_2$ in molar ration 1:2 were studied experimentally in [37,38] and reaction mechanism (Eq.17) was confirmed by [44]. The quantities of desorbed hydrogen were experimentally deduced as approximately 7.9–9.5 wt.%H_2. The dehydriding reaction of $LiBH_4$ proceeds at approximately 800 K, while that of the mixture of $LiBH_4$ + $2LiNH_2$ proceeds at approximately 650 K. This indicates that the dehydriding temperature of $LiBH_4$ reduces by 150 K by mixing 2 mol of $LiNH_2$. The exothermic peak was observed at a slightly higher temperature of the dehydriding reaction of the mixture, but it could be due to the solidification of the product and not due to the exothermic dehydriding reaction of the mixture itself.

The two-step hydrogen absorption for Li_3N to form $LiNH_2$ + 2 LiH with theoretical hydrogen capacity ~ 10.4 wt.%H_2, was shown in [45]:

$$Li_3N + 2\ H_2 \rightarrow Li_2NH + LiH + H_2 \leftrightarrow LiNH_2 + 2\ LiH \qquad (26)$$

However only second reaction step can be reversible under practical conditions and releases around ~ 5.2 wt.%H_2. By eliminating an extra LiH in this reversible reaction, the hydrogen storage capacity increases to ~ 6.5 wt.%H_2:

$$LiNH_2 + LiH \leftrightarrow Li_2NH + 2\ H_2 \qquad (27)$$

These reversible hydrogen reactions (Eq. 26-27) were precursors before detail investigation of $LiBH_4$–$LiNH_2$ system in [46,47].

A study of hydrogen and ammonia release from the series of reactant mixtures $(LiBH_4)_{1-x}(LiNH_2)_x$ was performed in [46]. It was found that maximum hydrogen and minimum ammonia release do occur at x = 0.667 that corresponds to the composition $LiB_{0.33}N_{0.67}H_{2.67}$. In addition, non-equilibrium phase diagram to show occurrence of the

Dr. Ivan Saldan*
Helmholtz-Zentrum Geesthacht, Institute of Materials Research, Max-Planck St. 1, Geesthacht, 21502 GERMANY
Fax: ++49 4152 -87 -2625 Office: ++49 4152 -87 -2689 e-mail: ivan_saldan@yahoo.com

various crystalline phases (α; β; γ; δ with melting temperatures at 150–190; 75–90; ~ 45; ~ 50 ºC, respectively) and their correlation with released gases (H_2 and NH_3) was constructed. Experimental results confirmed that at ~ 250 ºC almost entirely hydrogen gas (~ 11.0 wt.%H_2 and ~ 1.6 wt.%NH_3) was desorbed from molten $(LiBH_4)_{0.333}(LiNH_2)_{0.667}$ mixture. Improved hydrogen from the mixture was successfully proposed by incorporation of small amount of noble metal (Pd; Pt) in [47]. For example, in samples of $LiB_{0.33}N_{0.67}H_{2.67}$ with 0.29 mol % Pt (Pt/Vulcan carbon) the midpoint of hydrogen release was reduced by –90 °C. Hydrogen release becomes detectable by mass spectrometry at temperatures ~ 115 °C, and the onset of significant weight loss in Ar or He gas begins at ~ 150 °C. The quantity of ammonia produced during dehydrogenation is substantially reduced. There appears to be a sizable temperature interval below ~ 210 °C in which H_2 is released with little or no accompanying NH_3 production. Also it was mentioned that the total quantity of NH_3 released depends on how much of the dehydrogenation is conducted below NH_3-producing temperatures. Calorimetric results indicated that the dehydrogenation process is exothermic in both additive-free and additive-containing $LiB_{0.33}N_{0.67}H_{2.67}$. Therefore rehydrogenation by pressurized hydrogen gas is appeared to be thermodynamically unfavorable. Only ~ 15% of the released hydrogen was recovered by 91 bar hydrogen pressure at relatively low temperatures. The authors of [47] give some assumption that there is no direct evidence for recovery of the α-phase and possibly because of hydrogen absorption occurs through the formation of hydride species, such as LiH, $LiNH_2$, or Li_2NH. The mechanism by which noble metals promote hydrogen release is speculative now. Calorimetric measurements also suggest that additives do not produce large changes in thermodynamics, supporting the view that improved hydrogen release arises predominantly from faster low-temperature kinetics. Similar kinetic effect was observed for $Li_4BN_3H_{10}$ by $NiCl_2$ in [48]. In the absence of the catalyst, this composition simultaneously releases H_2 and NH_3 in roughly equal quantities by weight at temperatures above 240 °C. When Ni in the form of $NiCl_2$ is added as a dehydrogenation catalyst, only the H_2 release temperature is reduced by 122 °C while NH_3 release still occurs at the higher temperature. This result clearly demonstrates that because of the catalyst two gases are evolved in two distinct decomposition reactions that are coincident in uncatalysed $Li_4BN_3H_{10}$. This is not a result of a single decomposition reaction but rather is two separate H_2 and NH_3 decompositions.

Another examples of mixed complex hydrides together with binary metal hydride look as a complicated ternary mixture [48-50] although they had shown quite good properties with

Dr. Ivan Saldan*
Helmholtz-Zentrum Geesthacht, Institute of Materials Research, Max-Planck St. 1, Geesthacht, 21502 GERMANY
Fax: ++49 4152 -87 -2625 Office: ++49 4152 -87 -2689 e-mail: ivan_saldan@yahoo.com

purpose of fuel cell application. To enhance the properties of mentioned above binary mixtures the ternary system $LiBH_4$–$LiNH_2$–MgH_2 was chosen in [48]. The choice of 1:2:1 stoichiometry was based on several factors: (1) the constituent hydrides and their binary mixtures all possess high gravimetric/volumetric capacities; (2) mixtures containing MgH_2 are known to suppress ammonia release from nitrogen-containing hydrides such as $LiNH_2$; (3) a stable lightweight compound (Li–Mg–B–N) known as a potential dehydrogenated product phase contains Mg, B, N in stoichiometry 1:1:2 as follow from the stoichiometric mixture. Experiments had shown that the unique desorption for the ternary mixture has reaction mechanism which is not simple superposition of the known binary mixtures:

$$3\ LiNH_2 + LiBH_4 \rightarrow Li_4BN_3H_{10} \quad (28)$$

$$2\ Li_4BN_3H_{10} + 3\ MgH_2 \rightarrow 3\ Mg(NH_2)_2 + 2\ LiBH_4 + 6\ LiH \quad (29)$$

$$2\ Li_4BN_3H_{10} + 3\ MgH_2 \rightarrow 3\ Li_2Mg(NH)_2 + 2\ LiBH_4 + 6\ H_2 \quad (30)$$

$$Mg(NH_2)_2 + 2\ LiH \leftrightarrow Li_2Mg(NH)_2 + 2\ H_2 \quad (31)$$

$$3\ Li_2Mg(NH)_2 + 2\ LiBH_4 \rightarrow 2\ Li_3BN_2 + Mg_3N_2 + 2\ LiH + 6\ H_2 \quad (32)$$

$$2\ Li_3BN_2 + Mg_3N_2 + LiBH_4 \rightarrow 3\ LiMgBN_2\ (\text{unknown phase}) + 4\ LiH \quad (33)$$

$$LiMgBN_2\ (\text{unknown phase}) \rightarrow LiMgBN_2\ (\text{Tetragonal}) \quad (34)$$

$$2\ LiH \rightarrow Li + H_2 \quad (35)$$

Reaction by equations (28-29) appears during ball milling and at heating up to ~ 100 °C when $Li_4BN_3H_{10}$ was molten. Further heating to 180 °C results in the release of ~ 2.0 wt.%H_2 and corresponds to equation (30). In temperature interval 180–225 °C desorbed hydrogen increases to ~ 4.0 wt.%H_2 by reaction (31). The next major hydrogen release occurs between 255–375 °C that corresponds to equation (32), thus totally ~ 8.2 wt.%H_2 was found. There is no hydrogen release in temperature range 330-485 °C, where an unknown phase was detected and two reactions could have place by equations (33-34). And the last hydrogen desorption event was shown at 500–575 °C by reaction (35). Through a wide-ranging experimental and first-principle computational analysis in [48] the self-catalyzing mechanism arose from a set of coupled ancillary reactions that yield both a homogenizing ionic liquid phase ($Li_4BN_3H_{10}$) and product nuclei for a subsequent reversible hydrogen-storage reaction ($Mg(NH_2)_2$/LiH system) had been demonstrated. These effects combine to yield enhanced low-temperature desorption kinetics and a significant reduction in ammonia liberation relative to the state of the art binary constituent mixtures. In order to establish the impact of MgH_2 in $LiBH_4$–$LiNH_2$–MgH_2 system the ternary mixture $LiBH_4(LiNH_2)_2(MgH_2)_x$ ($0 \leq x \leq 1$) had been studied in [49]. As a conclusion $LiBH_4(LiNH_2)_2(MgH_2)$ show the least ammonia release (<0.1

Dr. Ivan Saldan*
Helmholtz-Zentrum Geesthacht, Institute of Materials Research, Max-Planck St. 1, Geesthacht, 21502 GERMANY
Fax: ++49 4152 -87 -2625 Office: ++49 4152 -87 -2689 e-mail: ivan_saldan@yahoo.com

wt.%NH_3) and the biggest value of hydrogen desorption (~ 4.0 wt.%H_2) at low-temperature event (~ 160 °C).

The next promising example of ternary mixture can be $LiBH_4$–$Mg(NH_2)_2$–LiH system. The mixtures of this with stoichiometry of 0.05:1:2; 0.1:1:2; 0.2:1:2 and 0.3:1:2 were thoroughly investigated in [50]. Kinetic and thermodynamic improvements in the hydrogen sorption properties of the binary $Mg(NH_2)_2$–LiH system were achieved by introducing a small amount of $LiBH_4$. Hydrogen release at ~ 140 °C and uptake at ~ 100 °C was accelerated by two times, while the temperature of equilibrium pressure at 1 bar decreases by 20 °C to ~ 70 °C. The in situ formed solid solution between $LiBH_4$ and $LiNH_2$ with weaked N–H bonds may be attributed to the enhancement of the hydrogen sorption kinetics.

In conclusion a general characteristic of $LiBH_4$–$LiNH_2$ system can be described by general equation in groundbreaking work [51]:

$$\frac{y}{x} M^1H_x + M^2(NH_2)_y \rightarrow \frac{y}{x} M^1(NH)_{x/2} + M^2(NH)_{y/2} + y\ H_2 \qquad (36),$$

where M^1 and M^2 are alkali or alkaline-earth metals. The main principle is interaction between negatively charged hydrogen $[H]^-$ in ionic hydrides (e.g. in LiH, NaH) or partially negatively charged hydrogen $[H]^{\delta-}$ in complex hydrides (e.g. in ($[BH_4]^-$, $[AlH_4]^-$) with partially positively charged hydrogen $[H]^{\delta+}$ in covalent hydrides (e.g. in $LiNH_2$, NH_3, H_2S), so called “electron donor-acceptor” mechanism:

$$[H]^{\delta+} + [H]^{\delta-} \rightarrow 2\ [H]^0 \rightarrow H_2 \qquad (37)$$

This proposed reaction mechanism provide a reasonable explanation for destabilizing metal hydrides from energy point of view and can be applied as a theoretical guidance for the screening of potential hydrogen storage materials.

3.2 $LiBH_4$–MH_2 (M = Sc, Mg, Ce) as reactive hydride composites

Among MH_2 (M = Sc, Ce, Mg,) scandium hydride may appear to be rather unpromising, since the experimentally observed reaction enthalpy for decomposition of ScH_2, CeH_2 and MgH_2 was estimated to be ~ 258 [52]; ~ 193.3 [53] and ~ 76.1 [54] kJ/mol H_2, respectively. But this thermodynamically stable hydride (ScH_2) can react with $LiBH_4$ and exothermically produce ScB_2 and LiH under ~ 1 bar equilibrium hydrogen pressure at 330 K

Dr. Ivan Saldan*
Helmholtz-Zentrum Geesthacht, Institute of Materials Research, Max-Planck St. 1, Geesthacht, 21502 GERMANY
Fax: ++49 4152 -87 -2625 Office: ++49 4152 -87 -2689 e-mail: ivan_saldan@yahoo.com

(Eq.18). $LiBH_4$–ScH_2 system is one of the best promising examples of RHCs regards to fuel cell application though not thoroughly studied so far.

In a contrast, $LiBH_4$–MgH_2 system is very well developed by group of Prof. John Vajo [55-58] and Prof. Rüdiger Bormann [59-64] independently. In fact, the idea of RHC was proposed by second group and verified mostly for $2LiBH_4$–MgB_2. Indeed, magnesium hydride as a reactive additive, enables simultaneously to retain hydrogen capacity and exothermically react with $LiBH_4$, produces new compound – MgB_2 (Eq.12). Mechanically milled mixtures of $LiBH_4$ with MgH_2 with molar ratio 2:1 are shown to store hydrogen above ~ 8 wt.%H_2 reversibly and extrapolation of isotherm predicted equilibrium hydrogen pressure of ~ 1 bar at approximately ~ 450 K. Individual decomposition of $LiBH_4$ and MgH_2 was observed at higher temperatures and low pressures ($T \geq 720$ K and $P \leq 3$ bar) whereas simultaneous desorption of H_2 from $LiBH_4$ and formation of MgB_2 took place at $T \approx 670$ K and a hydrogen pressure around ~ 5 bar [64]. Strong influence of stoichiometry on the reaction pathway and cycling kinetics has been observed in [65]. That fact was associated with the initial reaction of deuterium at the surface of the sample, but the rate of the subsequent reaction was decreased because the high $LiBD_4$ content material may result in the encapsulation of MgD_2 within LiD matrix, hindering the mass transport required for further reaction.

In recent paper [66] the reaction pathway for interaction $LiBH_4$ with M (M = Mg, Ti, Sc) was proposed from thermodynamic point of view:

$$LiBH_4 + \frac{1}{2}M \rightarrow \frac{3}{4}LiBH_4 + \frac{3}{8}MH_2 + \frac{1}{8}MB_2 + \frac{1}{4}LiH \rightarrow \frac{1}{2}MB_2 + LiH + \frac{3}{2}H_2 \quad (38)$$

But only in case of Mg the reaction (38) with subsequent (12) experimentally were performed at 1 bar hydrogen pressure and temperatures 640-670 K that produced ~ 8.8 wt.%H_2 during 100 h [67]. It means that for Ti and Sc reaction (38) controlled by some kinetic barriers (possible by the high temperature melting of M) and for them formation of new stable phases (MB_2 and LiH) is not simultaneous with $LiBH_4$ decomposition. Nevertheless a kinetic effect on $LiBH_4$ decomposition by Ti and Sc (and other transition metals) were observed and resulted in lowering of T_d. It should be denoted that in case of Mg reaction (38) is totally reversible and during cycling some kinetic improvements also take place.

In case of $LiBH_4$–CeH_2 system, metallic Ce was used instead of cerium hydride, because of difficulty to obtain CeH_2 [53]. Because of total reaction enthalpy (27.6 kJ/mol H_2) from thermodynamic point of view reaction (39) occurs to be possible:

Dr. Ivan Saldan*
Helmholtz-Zentrum Geesthacht, Institute of Materials Research, Max-Planck St. 1, Geesthacht, 21502 GERMANY
Fax: ++49 4152 -87 -2625 Office: ++49 4152 -87 -2689 e-mail: ivan_saldan@yahoo.com

$$LiBH_4 + \frac{1}{6}Ce \rightarrow LiH + \frac{1}{6}CeB_6 + \frac{3}{2}H_2 \quad (39)$$

However exothermic reaction (40) with negative enthalpy value (– 193.3 kJ/mol H_2) will be happened when hydrogen is coming:

$$Ce + H_2 \rightarrow CeH_2 \quad (40)$$

Thus the two (39) and (40) reactions give us the total process (41) with enthalpy value (– 135.7 kJ/mol H_2):

$$\frac{6}{10}LiBH_4 + Ce \rightarrow \frac{6}{10}LiH + \frac{9}{10}CeH_2 + \frac{1}{10}CeB_6 \quad (41)$$

Indeed after ball milling CeH_2 was detected by XRD analysis, when for $LiBH_4$–CeH_2 system the reaction could be as follows:

$$LiBH_4 + \frac{1}{6}CeH_2 \rightarrow LiH + \frac{1}{6}CeB_6 + \frac{10}{6}H_2 \quad (42)$$

Theoretically reaction enthalpy for (42) reaction is 27.6 kJ/mol H_2 and maximal hydrogen capacity is ~ 7.3 wt.%H_2. RHCs of this system decomposed at temperatures close to melting point of pure $LiBH_4$, this is why at 446 K it is possible to reach ~ 1 bar equilibrium hydrogen pressure. In practice $LiBH_4$–CeH_2 system has a better kinetic properties as $LiBH_4$–MgH_2 and fully reversible.

In conclusion, among of a very large number of possible RHCs theoretically and experimentally predicted in [68,69] the MH_2 (M = Sc, Mg, Ce) can be promising destabilizing reagents for $LiBH_4$ with purpose of reversible hydrogen storage in fuel cell.

3.3 $LiBH_4$ nano-confinement by carbon framework

Since decomposition of $LiBH_4$ or its RHCs take place at temperatures over $LiBH_4$ melting point, the reactive powder tends to be agglomerated or sintered. This behavior to enlarge particle size leads to slow kinetics in most cases. Therefore an inert media with special design would be helpful to prevent reagents from this negative effect by confinement of nanoparticles. The first approaches of so called “nano-confinement” were observed in experimental works by MWCNTs and single-wall carbon nanotubes (SWCNTs) for MgH_2 [70], $LiBH_4$ [71] and [72] their mixtures. In all cases these carbon modifications showed improvement in H-exchange kinetics. Today there are two explanations of the effect: (1) MWCNTs or SWCNTs may act as milling aid (increase distribution of host material or even

Dr. Ivan Saldan*
Helmholtz-Zentrum Geesthacht, Institute of Materials Research, Max-Planck St. 1, Geesthacht, 21502 GERMANY
Fax: ++49 4152 -87 -2625 Office: ++49 4152 -87 -2689 e-mail: ivan_saldan@yahoo.com

adsorb possible contaminates); (2) they may form net-like structure and exert nano-confinement of reactive powder. This new approach can be a very useful tool under hydrogen release/uptake cycling where whole composite would keep unique nanostructure and thus remains constant rate of hydrogen absorption/desorption.

Idea of nano-confinement was recently proposed by carbon aerogel scaffold with pore size ~ 20 nm in [63]. The bottom-up approach where nanoparticles of hydrides are synthesized infiltrated in nano-porous inert material demonstrated several advantages: (1) increased surface area of the reactants; (2) nano-scale diffusion distances; (3) increased number of grain boundaries, which facilitate hydrogen reversible sorption. DSC measurements for $LiBH_4$–MgH_2 mixtures in molar ration 2:1 showed that nano-confined sample released ~ 4.3 wt.%H_2 (100% from theoretical) while unmodified sample only ~ 9.2 wt.%H_2 (80% from theoretical) at temperatures 530–740 K in Ar flow with 5/K rate heating. Moreover a big shift to lower temperatures and another shape of hydrogen desorption peaks may indicate some improvement of both: kinetics and thermodynamics. Unfortunately XRD analysis performed in this experimental work did not give full answer if some new phases/intermediates were present as a result of carbon interaction with $LiBH_4$ (e.g. Eqs. 20–22). Therefore identification of the intermediates would be a proof of thermodynamic effect in addition to kinetic improvements.

The same effects were observed in another experimental work [73] where nano-confined sample was prepared by direct melt infiltration of bulk $LiBH_4$–MgH_2 mixtures into the carbon aerogel. The modified sample revealed a single step of dehydrogenation and around 50 K shift in lower temperatures was detected. The results of the work showed more simple preparation of nano-confined RHCs and their improvement in H-exchange kinetics.

Obviously nano-confinement may diminish negative effect of molten $LiBH_4$ under hydrogen desorption or reabsorption, thus maybe influence on reaction mechanism of hydrogen absorption/desorption for $LiBH_4$ or its RHCs. Moreover, this new approach can be developed to become an important tool for nanotechnologies with improvement of chemical reaction yield.

Dr. Ivan Saldan*
Helmholtz-Zentrum Geesthacht, Institute of Materials Research, Max-Planck St. 1, Geesthacht, 21502 GERMANY
Fax: ++49 4152 -87 -2625 Office: ++49 4152 -87 -2689 e-mail: ivan_saldan@yahoo.com

3.4 Effect of additives under $LiBH_4$ decomposition

Appearance of experimental evidence in kinetic improvement of reversible middle-temperature complex hydrides that based on Na, Li and Al by titanium additives was the beginning of a new scientific direction made by Bogdanovic and Schwickardi [74]. Since that time a large amount of results about kinetic effects on hydrogen reactions of $LiBH_4$ or its RHCs have been done. However, because of high reactivity of $LiBH_4$, there is not so easy to find example of catalyst (additive which is not consumed by chemical reaction). In most cases proposed additives have behavior as reagents that produce intermediates but finally can not be recovered. A general catalytic mechanism for reaction between $LiBH_4$ and MX_n additive (where M is metal with n valency; X is halogene) would be presented as follows:

$$n\ LiBH_4 + MX_n \rightarrow n\ LiX + M(BH_4)_n \quad (43)$$

$$n\ LiX + M(BH_4)_n \rightarrow n\ LiX + MB_n + 2n\ H_2 \quad (44)$$

$$n\ LiX + MB_n + 2n\ H_2 \rightarrow MX_n + n\ LiH + n\ B + 2n\ H_2 \quad (45)$$

Because of higher temperature of crystallization compared to the used temperatures in [75], existence of $Ti(BH_4)_3$ as product of reaction (43) was not confirmed. However solid state reaction between $LiBH_4$ and $TiCl_3$ was observed at room temperatures with LiCl formation. Moreover, firstly was confirmed that solid LiCl can be dissolved in the structure of solid *h*-$LiBH_4$ at temperatures 373–518 K. Similar result was observed in [76] where XRD analysis with $TiCl_3$ always showed $LiBH_4$ peak with very low intensity. In 1949 reaction mechanism for interaction between $LiBH_4$ and $TiCl_4$ was proposed in [77]:

$$4\ LiBH_4 + TiCl_4 \rightarrow Ti(BH_4)_3 + 4\ LiCl + \frac{1}{2}B_2H_6 + \frac{1}{2}H_2 \quad (46)$$

It is concluded that the dehydrogenation temperatures of $Ti(BH_4)_3$ was ~ 298 K. Thus, at room temperature and ambient pressure $Ti(BH_4)_3$ decomposed by releasing hydrogen and a trace amount of gaseous B_2H_6. Therefore similar ion-exchange interactions (Eq.43) could take place in case of $LiBH_4$ with $MgCl_2$ [78], $MnCl_2$ [79] or ZnF_2 [80].

In case of HRCs based on $LiBH_4$ the additives react with $LiBH_4$ in similar way [60,62] however attendant metal hydride (e.g. MgH_2 in Eq.12) plays additional role in the kinetic improvement [81-83]. For mixture $LiBH_4$–MgH_2–$Ti\{OCH(CH_3)_2\}_4$ with molar ratio 2:1:0.1 after ball milling TiO_2 anatase was found and during 1-st hydrogen desorption Ti_2O_3 and TiB_2 appeared to be stable for further cycling [82]. XPS analysis showed that the reduction of titanium to Ti(III) was coupled to the migration of titanium species from the surface to the

Dr. Ivan Saldan*
Helmholtz-Zentrum Geesthacht, Institute of Materials Research, Max-Planck St. 1, Geesthacht, 21502 GERMANY
Fax: ++49 4152 -87 -2625 Office: ++49 4152 -87 -2689 e-mail: ivan_saldan@yahoo.com

bulk of HRC. Two main factors, related to favoring heterogeneous nucleation of MgB_2 and increase of interfacial area trough grain refinement were proposed as potential driving force for kinetic improvement. Influence of additives and microstructure refinement in $LiBH_4$–MgH_2 system were studied in [83]. Transition metal borides (e.g. ZrB_2, ScB_2, VB_2, TiB_2) are characterized by the same hexagonal lattice structure as MgB_2 with very small (0.1-3%) directional and interplanar misfit. This fact is a necessary condition for heterogeneous nucleation of MgB_2 because of lowering of interfacial energy caused by transition metal borides or subsequently by additives. A good additive distribution and its sufficient amount were found as the main reason of the efficient heterogeneous nucleation of MgB_2. However because of no changing of the limiting rate neither for hydrogen absorption (contracting volume model) nor for desorption (interfaced-controlled one-dimensional growth), caused by the additives, the latter do not show catalyst behavior.

For some metals (Al and Cr) thermodynamically favorable chemical reaction between them and $LiBH_4$ was proposed as follows [67]:

$$LiBH_4 + M \rightarrow MB_2 + 2\ LiH + 3\ H_2 \qquad (M = Al, Cr) \qquad (47)$$

In experimental work [84,85] aluminum diboride was found to form and vanish during hydrogen release/uptake. This could be the first example of catalyst for reversible $LiBH_4$ decomposition where hydrogen dissociation to atoms and recombination to H_2 molecules was accelerated by aluminum at the hydride surface.

In recent work [86] mixtures of LiH–MgB_2–X (X = TiF_4, TiO_2, TiN, TiC) in molar ratio 2:1:0.1 were studied as hydrogen storage material. Only TiF_4 had a chemical interaction with LiH similar as that was found also for TiF_3 in [87]:

$$3\ LiH + TiF_3 \rightarrow 3\ LiF + TiH_2 + \frac{1}{2} H_2 \qquad (48)$$

However for TiO_2, TiN, TiC additives no new phase formation and clear signals for TiO_2, TiN, TiC was detected by XRD, respectively. For comparison just one example of LiH–MgB_2–TiO_2(rutile) composite together with unmodified LiH–MgB_2 presented in fig. 6 and 7, correspondently. Almost the same hydrogen storage capacity was achieved in both LiH–MgB_2–TiO_2(rutile) and LiH–MgB_2, but kinetics especially for desorption was drastically improved by rutile. It is expected that behavior of TiO_2 as catalyst may be similar to that as in case of MgH_2. In [88] was concluded that uniformed distributed rutile on the surface of MgH_2 could develop hydrogenation on the surface layer of Mg which would increase the available path for hydrogen atoms by their fast diffusion into the bulk. In another experimental work

Dr. Ivan Saldan*
Helmholtz-Zentrum Geesthacht, Institute of Materials Research, Max-Planck St. 1, Geesthacht, 21502 GERMANY
Fax: ++49 4152 -87 -2625 Office: ++49 4152 -87 -2689 e-mail: ivan_saldan@yahoo.com

[89] was found that anatase form of TiO_2 is more effective than rutile because of higher surface areas which resulted in a better dispersion of active sites throughout MgH_2.

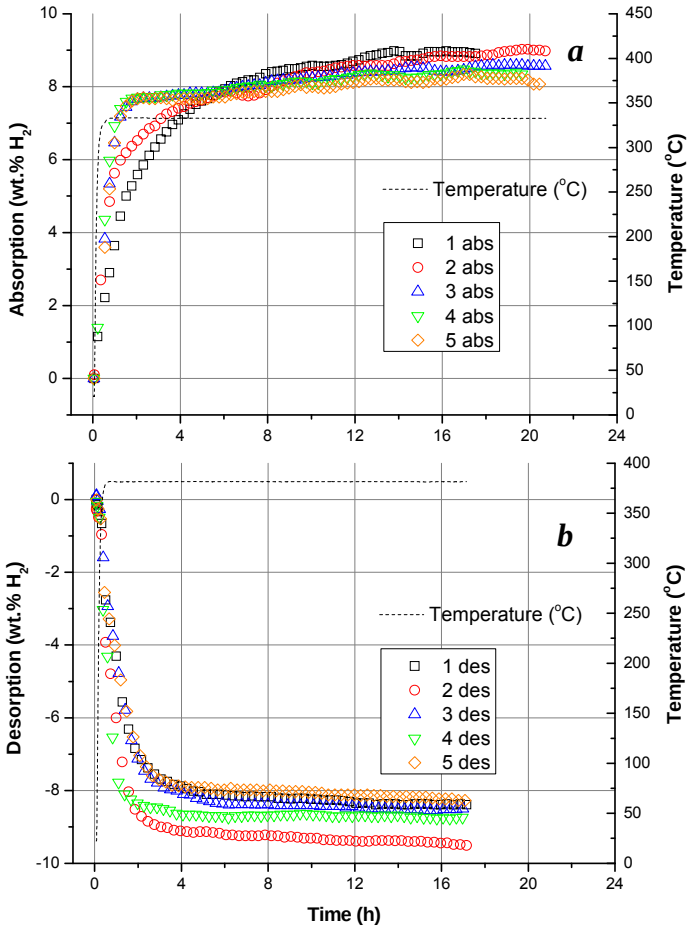

Fig.6 Hydrogen sorption for LiH–MgB_2–TiO_2(rutile) in molar ratio 2:1:0.1 during 5 cycles. Absorption was performed at 350 ºC and 50 bar of hydrogen pressure (*a*); desorption at 380 ºC and 5 bar H_2 (*b*).

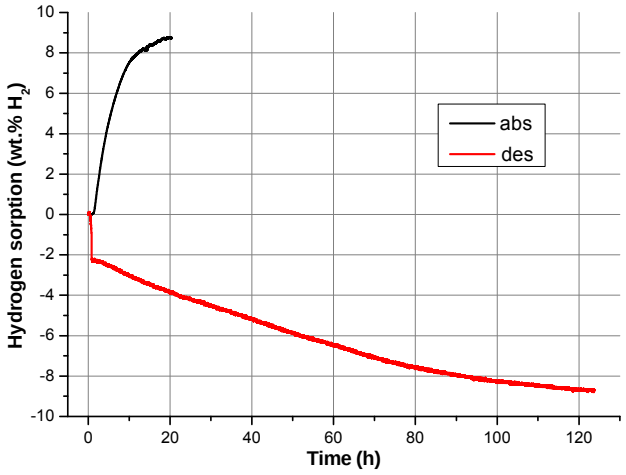

Fig.7 Hydrogen sorption for LiH–MgB_2 in molar ratio 2:1. Conditions for absorption and desorption were 350 ºC at 50 bar H_2 and 380 ºC at 5 bar H_2, respectively.

Dr. Ivan Saldan*
Helmholtz-Zentrum Geesthacht, Institute of Materials Research, Max-Planck St. 1, Geesthacht, 21502 GERMANY
Fax: ++49 4152 -87 -2625 Office: ++49 4152 -87 -2689 e-mail: ivan_saldan@yahoo.com

It should be mentioned that transition metal oxides are more promising additives for hydrogen uptake than pure transition metals though the latter have orders of magnitude higher activity to hydrogen [90-95]. Obviously, the explanation of catalytic effect by metal oxides should be found by tools of surface science. Indeed, the interaction of high surface area oxides (alumina, titania or their mixtures) with gas is concerned to heterogeneous catalysis. With respect to alumina or titania, the single phase alumina-titania solid acids [96] have stronger acid sites and greater acid site density. These facts, coupled with their high surface area produce the materials with an even greater number of acid sites per gram, making them useful heterogeneous catalysts.

4 Outlooks

Indeed $LiBH_4$ has a potential to release/uptake hydrogen at moderate conditions and the sluggish kinetics are considered to be mainly responsible for high reaction temperature [97]. Therefore practical strategies to achieve fast reaction kinetics will be the most important scientific direction with purpose of application $LiBH_4$ in fuel cell. Thus, hydrogen fuelled vehicle will be able to match the performance of that of a hydrocarbon car at comparable cost (around US$5/kWh [2]).

Acknowledgments

The author wishes to thank Drs. Martin Dorheim, Ulrike Bösenberg, Klaus Taube and José Bellosta von Colbe (Helmholtz-Zentrum Geesthacht) for useful discussions. This work was supported by the European Commission (contract MRTN-CT-2006-035366).

Dr. Ivan Saldan*
Helmholtz-Zentrum Geesthacht, Institute of Materials Research, Max-Planck St. 1, Geesthacht, 21502 GERMANY
Fax: ++49 4152 -87 -2625 Office: ++49 4152 -87 -2689 e-mail: ivan_saldan@yahoo.com

References

[1] L. Schlapbach, A. Züttel, Nature 414, (2001) 353.

[2] D.K. Ross Vacuum 80 (2006) 1084-1089.

[3] A. Züttel, S. Rentsch, P. Fesher, P. Wenger, P. Sudan, Ph. Mauron, Ch.Emmenegger, J. Alloy Comp. 356-367, (2003) 515.

[4] Yu. Nakamori, S. Orimo, J. Alloy Comp. 370, (2004) 271

[5] Smith MS, Bass GE, J. Chem Eng Data 8 (1963) 341.

[6] N. Ohba, K. Miwa, M. Aoki, T. Noritake, S. Towata, Yu. Nakamori, S. Orimo, A. Züttel, Phys. Rev. B 74, (2006) 075110

[7] H. Deiseroth, O. Sommer, H. Binder, K. Wolfer, B. Frei, Z. Anorg. Allg. Chem. 571, (1989) 21

[8] I. Kuznetsov, D. Vinitskii, K. Solntsev, N. Kuznetsov, L. Butman, Russ. J. Inorg. Chem. 32, (1987) 1803

[9] I. Tiritiris, T. Schleid, Z. Anorg. Allg. Chem. 629, (2003) 1390

[10] K. Miwa, N. Ohba, S. Towata, Yu. Nakamori, S. Orimo, Phys. Rev. B 69, (2004) 245120

[11] M. Smith, G. Bass, J. Chem. Eng. Data 8, (1963) 342

[12] E. Jeon, Y. Cho, J. Alloy and Comp. 422, (2006) 273

[13] A. Züttel, A. Borgschulte, S. Orimo, Scr. Mater. 56, (2007) 823

[14] L. Mosegaard, B. Møller, J.-E. Jørgensen, U. Bösenberg, M. Dornheim, J. C. Hanson, Y. Cerenius, G. Walker, H. J. Jakobsen, F. Besenbacher, T. R. Jensen, J. Alloys and Comp. 446–447, (2007) 301–305

[15] Ph. Mauron, F. Buchter, O. Friedrichs, A. Remhof, M.Bielmann, Ch. Zwicky, A. Züttel, J. Phys. Chem. B. 112, (2008) 906-910.

[16] J. Nakamori, Sh. Orimo, J. Alloys and Comp. 370, (2004) 271-275.

[17] Y. Filinchuk, D. Chernyshov, V. Dmitriev, Z. Kristallogr. 223, (2008) 649–659.

[18] Y. Nakamori, K. Miwa, A. Ninomiya, H. Li, N. Ohba, S. Towata, A. Züttel, S. Orimo Physical Review B 74, (2006) 045126.

[19] X.B. Xiao, W.Y. Yu, B.Yu. Tang, J. Phys.: Condens. Matter 20 (2008) 445210

[20] E. A. Nickels, M. O. Jones, W.I.F. David, S.R. Johnson, R.L. Lowton, M. Sommariva, P.P. Edwards, Angew. Chem. Int. Ed. 47, (2008) 2817 –2819

[21] Xiao-Bing Xiao, Wei-Yang Yu, Bi-Yu Tang J.Phys.: Cindens.Matter 20 (2008)445210

Dr. Ivan Saldan*
Helmholtz-Zentrum Geesthacht, Institute of Materials Research, Max-Planck St. 1, Geesthacht, 21502 GERMANY
Fax: ++49 4152 -87 -2625 Office: ++49 4152 -87 -2689 e-mail: ivan_saldan@yahoo.com

[22] H. Hagemann, M. Longhini, J. W. Kaminski, T. A. Wesolowski, R. Cerny, N. Penin, M. H. Sørby, B. C. Hauback, G. Severa, C. M. Jensen J. Phys. Chem. A 112, (2008) 7551–7555.

[23] J.S. Hummelshøj, D.D. Landis, J.Voss et al. J. Chemical Physics 131 (2009) 014101.

[24] A. Bouamrane, J.P. Laval, J.P. Soulie, J.P. Bastide, Materials Research Bulletin 35, (2000) 545–549.

[25] N. Eigen, U. Bösenberg, J. Bellosta von Collbe, T.R. Jensen, Y. Cerenius, M. Dornheim, T. Klassen, R. Bormann, J. Alloys and Comp. 477, (2009) 76-80.

[26] A. Bouamrane, C. Brauer, J.P. Soulie, J.M. Letoffe, J.P. Bastide, Thermochimica Acta 326, (1999) 37-41.

[27] L. Yin, P. Wang, Zh. Fang, H. Cheng, Chemical Physics Letters 450, (2008) 318-321

[28] J.Ph. Soulie, G. Renaudin, R. Cerny, K. Yvon, J. Alloys and Comp. 346, (2002) 200-205.

[29] M.Corno, E.Pinatel, P.Ugliengo, M.Baricco J. Alloys and Comp. doi:10.1016/j.jallcom. 2010.10.005

[30] I. Saldan, R. Gosalawit-Utke, C. Pistidda, U. Bösenberg, J.M. Ramallo-López, M. Schulze, T. Klassen, K. Suarez-Alcantara, J. Bellosta von Colbe, K. Taube, M. Dornheim J. Phys. Chem. C 2011. *To be submitted*

[31] R. Gosalawit, J.M. Bellosta von Colbe, M. Dornheim, T.R. Jensen, Y. Cerenius, Ch.M. Bonatto, M. Peschke, R. Bormann, J. Physical Chemistry C, 114 (2010) 10291-10296.

[32] T. Ruman, A. Kusnierz, A. Jurkiewicz, A. Les, W. Rode Inorg.Chem. Commun. 10 (2007) 1074-1078.

[33] J.G. Gainsford, T. Kemmitt, G.B. Jameson, S.G. Telfer Acta Cryst. C. 65 (2009) 180-181.

[34] Z. Xiong, C.K. Yong, G.Wu, P. Chen, W. Shaw, A. Karkamkar, T. Autrey, M.O. Jones, S.R. Johnson, P.P. Edwards, W.I.F. David Nature Mat. 7 (2007) 138-141.

[35] J. Vajo, S. Skeith, F. Mertens, J. Phys.Chem. B 109, (2005) 3719-3722.

[36] S. Alapati, J. Johnson, D. Sholl, Phys. Chem. Chem. Phys. 9, (2007) 1438-1452.

[37] F. Pinkerton, G. Meisner, M. Meyer, M. Balogh, M, Kundrat, J. Phys. Chem. B 109, (2005) 6

[38] M. Aoki, K. Miwa, T. Noritake, G. Kitahara, Y. Nakamori, S. Orimo, S. Towata, Appl. Phys. A. 80, (2005) 1409.

Dr. Ivan Saldan*
Helmholtz-Zentrum Geesthacht, Institute of Materials Research, Max-Planck St. 1, Geesthacht, 21502 GERMANY
Fax: ++49 4152 -87 -2625 Office: ++49 4152 -87 -2689 e-mail: ivan_saldan@yahoo.com

[39] Y. Filinchuk, K. Yvon, G. Meisner, M. Meyer, F. Pinkerton, M. Balogh, Inorg. Chem. 45, (2006) 1433

[40] N. Jacobson, B. Tegner, E. Schroder, P. Hyldgaard, B. Lundqvist, Comput. Mater. Sci., 24, (2002) 273

[41] Z. Zhu, G. Lu, S. Smith, Carbon 42, (2004) 2509

[42] F. Pinkerton, B. Wicke, C. Olk, G. Tibbetts, G. Meisner, M. Meyer, J. Herbst, J. Phys. Chem. B 104, (2000) 9460.

[43] X. Yu, Z. Wu, Q. Chen, Z. Li, B. Weng, T. Huang, Appl. Phys. Lett. 90, (2007) 034106.

[44] Y. Nakamori, A. Ninomiya, G. Kitahara, M. Aoki, T. Noritake, K. Miwa, Y. Kojima, S. Orimo J. Pow. Sour, 155, (2006), 447-455

[45] P.Chen, Z. Xiong, J.Luo, J.Lin, K.L.Tan Nature 420, (2002) 302.

[46] G. Meisner, M. Scullin, M. Balogh, F. Pinkerton, M. Meyer J. Phys. Chem. B 110, (2006) 4186-4192.

[47] F. Pinkerton, M. Meyer, G. Meisner, M. Balogh J. Phys. Chem. B 110, (2006) 7967-7974

[48] J. Yang, A. Sudik, D. J. Siegel, D. Halliday, A. Drews, R. O. Carter, III, Ch. Wolverton, G.J. Lewis, J.W. Adriaan Sachtler, J.J. Low, S. A. Faheem, D.A. Lesch, V. Ozolinš Angew. Chem. Int. Ed. 47, (2008), 882 –887

[49] A. Sudik, J. Yang, D. Halliday, A. Drews, Ch. Wolverton J. Phys. Chem. C 112 (2008), 4384-4390.

[50] J. Hu, Y. Liu, G. Wu, Zh. Xiong, Y. Sh. Chua, P. Chen Chem. Mater. 20 (2008) 4398-4402.

[51] J. Lu, Zh.Z. Fang, H.Y.Sohn Inorg. Chem., 45 (2006), 8749-8754

[52] S.V. Alapati, J. K. Johnson, D.S. Sholl J. Alloys and Comp. 446–447 (2007) 23–27

[53] S.-Ah Jin, Y.-Su Lee, J.-H. Shim, Y.W. Cho J. Phys. Chem. C 112, (2008) 9520-9524.

[54] M. Pozzo, D. Alfè Phys. Rev. B 77, (2008) 104103

[55] J. Vajo, S. Skeith, F. Mertens, J. Phys.Chem. B 109, (2005) 3719-3722

[56] J. Vajo, G.L. Olson Scripta Materialia 56 (2007) 829–834

[57] J. Vajo, T.T. Salguero, A.F. Gross, S.L. Skeith, G.L. Olson J. Alloys Comp. 446–447 (2007) 409–414

[58] J. Vajo Cur. Opin. Sol. St. Mater. Sci. doi:10.1016/j.cossms.2010.11.001 *In print.*

[59] G. Barkhordarian, T. Klassen, M. Dornheim, R. Bormann, J. Alloys and Comp. 440, (2007) L18-L21.

Dr. Ivan Saldan*
Helmholtz-Zentrum Geesthacht, Institute of Materials Research, Max-Planck St. 1, Geesthacht, 21502 GERMANY
Fax: ++49 4152 -87 -2625 Office: ++49 4152 -87 -2689 e-mail: ivan_saldan@yahoo.com

[60] Yan-Ping Zhou, Master Thesis, GKSS, Geesthacht (2007). PP. 65

[61] U. Bösenberg, S. Doppiu, L. Mosegaard, G. Barkhordarian, N. Eigen, A. Borgschulte, T.R. Jensen, Y. Cerenius, O. Gutfleisch, T. Klassen, M. Dornheim, R. Bormann, Acta Materialia 55, (2007) 3951-3958

[62] U. Bösenberg. PhD–Thesis, GKSS, Geesthacht (2009). PP.100

[63] T.K. Nielsen, U. Bösenberg, R. Gosalawit, M. Dornheim, Y. Cerenius, F. Besenbacher, T.R. Jensen ACS Nano 4, (2010) 3903-3908

[64] U. Bösenberg, D.B. Ravnsbæk, H. Hagemman, V. D'Anna, Ch. Bonatto Minella, C. Pistidda, Wouter van Beek, T.R. Jensen, Y. Cerenius, O. Gutfleisch, R. Bormann, M. Dornheim J. Phys.Chem. C . 2011 *In print*

[65] T. E.C. Price, D.M. Grant, V. Legrand, G.S. Walker. J. Hydrogen Energy 35, (2010) 4154-5161.

[66] D. J. Siegel, Ch. Wolverton, V. Ozolinš Phys. Rev B: Condens. Matter, Mater. Phys. 76, (2007), 134102

[67] J. Yang, A. Sudik, Ch. Wolverton J. Phys. Chem. C 111 (2007), 19134-19140.

[68] S.V. Alapati, J. K. Johnson, D.S. Sholl J. Phys. Chem. B, 110 (2006**)**, 8769–8776

[69] S.V. Alapati, J. K. Johnson, D.S. Sholl J. Phys. Chem. C, 112 (2008), 5258–5262

[70] C.Z.Wu, P. Wang, H.M. Cheng J. Phys. Chem. B, 109 (2005**)**, 22217

[71] Z.Z. Fang, X.D. Kang, H.B. Dai, M.G. Zhang, P. Wang, H.M. Cheng Scr. Mater., 58 (2008**)**, 922

[72] P.-J. Wang, P. Z.Z. Fang, L.-P. Ma, X.-D. Kang, P. Wang, J. Hyd. Enegy, 33 (2008**)**, 5611-5616

[73] R. Gosalawit-Utke, T. Nielsen, I. Saldan, Y. Cerenius, T.R. Jensen, T. Klassen, M. Dornheim J. Phys. Chem. C (2011) S*ubmitted*

[74] B.Bogdanovic, M. Schwickardi, J. Alloys Comp. 253-254, (1997) 1-9.

[75] L. Mosegaard, B. Møller, J.-E. Jørgensen, Ya. Filinchuk, Y. Cerenius, J. Hanson,E. Dimasi, F. Besenbacher, T. Jensen, J. Phys. Chem. C, 112, (2008) 1299-1303

[76] M. Au, A. Jurgensen, J. Phys. Chem. B 110, (2006) 7062-7067

[77] H. Hoekstra, J. Katz, J. Am. Chem. Soc. 71, (1949) 2488-2492

[78] M. Au, A. Jurgensen, K. Zeigler, J. Phys. Chem. B 110, (2006) 26482-26487

[79] R.A Varin, L. Zbroniec, J. Hyd. Energy. 35, (2010) 3588-3597

[80] M. Au, R.T. Walters, J. Hyd. Energy. 35, (2010) 10311-10316

Dr. Ivan Saldan*
Helmholtz-Zentrum Geesthacht, Institute of Materials Research, Max-Planck St. 1, Geesthacht, 21502 GERMANY
Fax: ++49 4152 -87 -2625 Office: ++49 4152 -87 -2689 e-mail: ivan_saldan@yahoo.com

[81] U. Bösenberg, U. Vainio, P. Pranzas, J. Belosta von Colbe, G. Goerigk, E. Welter, M. Dornheim, A. Schreyer, R. Bormann, Nanothech. 20, (2009) 204003.

[82] E. Deprez, M.A. Munoz-Marquez, M.A. Roldan, C. Prestipino, F.J. Palomares, Ch. Bonatto-Minella, U. Bösenberg, M. Dornheim, R. Bormann, A. Fernandez J. Phys. Chem. C 114, (2010) 3309-3317.

[83] U. Bösenberg, J.W. Kim, D. Gosslar, N. Eigen, T.R. Jensen, J. Belosta von Colbe, Y. Zhou, M. Damhs, D.H. Kim, R.Günther, Y.W. Cho, K.H. Oh, T. Klassen, R. Bormann, M. Dornheim Acta Mater. 58, (2010) 3381-3389.

[84] S.-A. Jin, J.-H. Shim, Y.W. Cho, K.-W. Yi, O. Zabara, M. Fichtner Scr. Mater. 58, (2008) 963-965.

[85] D. Blanchard, Q. Shi, B. Boothroyd, T. Vegge J. Phys. Chem. C 113, (2009) 14059-14066.

[86] I. Saldan, R. Campesi, O. Zavorotynska, G. Spoto, A. Arendarska, K. Taube, M. Dornheim J. Hyd. Energy. (2011) *To be submitted*

[87] P. Wang, L. Ma, Z. Fang, X. Kang, P. Wang Energy Environ. Sci. 2 (2009) 120-123

[88] K.S. Jung, D.H.Kim, E.Y. Lee, K.S. Lee Catalysis Today 120 (2007), 270-275

[89] D.L. Croston, D.M. Grant, G.S. Walker J. Alloys Comp. 492 (2010) 251-258

[90] V.E. Henrich, P.A. Cox, The surface science of Metal Oxides, Cambridge University Press, New York 1994

[91] R. Hummer, J.K. Norskov Surf. Sci 343 (1995) 211

[92] R. Hummer, J.K. Norskov Nature 376 (1995) 238

[93] G. Barkhordarian, T. Klassen, R. Borman J. Alloys Comp. 364 (2004) 242

[94] G. Barkhordarian, T. Klassen, R. Borman J. Phys. Chem. B 110 (2006) 11020-11024

[95] A. Borgschulte, U. Bösenberg, G. Barkhordarian, M. Dornheim, R. Borman Catalysis Today 120 (2007), 262-269

[96] G.S. Walker, E. Williams, A.K. Bhattacharya J. Mater. Sci. 32 (1997) 5583-5592

[97] H.-W. Li, Y. Yan, S. Orimo, A. Züttel, C.M. Jensen Energies 4, (2011) 185-214

Dr. Ivan Saldan*
Helmholtz-Zentrum Geesthacht, Institute of Materials Research, Max-Planck St. 1, Geesthacht, 21502 GERMANY
Fax: ++49 4152 -87 -2625 Office: ++49 4152 -87 -2689 e-mail: ivan_saldan@yahoo.com