Hydrogen storage and complex hydrides

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Solid material for hydrogen storage

- Metal and complex hydrides
- Chemical hydrides
- Nanoporous structures

Source: DoE 2007
Storage as hydrides

\[ M(s) + \frac{x}{2} H_2 \rightarrow MH_x(s) + \text{energy} \]

Interstitial metal hydride
(Metal with hydrogen atoms in octahedral-tetrahedral holes)

Complex hydride

Sabrina Sartori, Summer School, Reykjavik, August 17-21, 2010
PCI of intermetallic (AB\textsubscript{x}H\textsubscript{n}) compound

Enthalpy of formation

\[ \ln\left(\frac{P_{eq}}{P_{0}}\right) = \frac{\Delta H}{R} \cdot \frac{1}{T} - \frac{\Delta S}{R} \]

Zuettel (2003)
Exercise

The desired value of enthalpy of formation of our hydride to reach an equilibrium pressure of 1 bar at 27 °C?

1) Considering $\Delta S_f = -130 \text{ JK}^{-1}\text{mol}^{-1} \text{H}_2$ for all metal-hydrogen systems

2) Answer in kJ mol $^{-1} \text{H}_2$

$$\ln\left(\frac{P_{eq}}{P_{eq}^0}\right) = \frac{\Delta H}{R} \cdot \frac{1}{T} - \frac{\Delta S}{R}$$
More stable \hspace{10mm} less stable

Zuettel (2003)

Sabrina Sartori, Summer School, Reykjavik, August 17-21, 2010
Complex hydrides promising candidates

- > 5 wt% hydrogen:
  - LiAlH$_4$: 10.6 wt%
  - NaAlH$_4$: 7.5 wt%
  - Mg(AlH$_4$)$_2$: 9.3 wt%
  - LiNH$_2$/Li$_2$NH reactions (11.5 wt%)
  - LiBH$_4$ (18.5 wt%), NaBH$_4$ (10.7 wt%)
  - Ammonia-Borane systems: e.g. H$_3$NBH$_3$ (19.6 wt%)

- Why not used: problems of thermodynamic and kinetics. Not reversible at moderate conditions. Complicated desorption of H$_2$

- Additives (Bogdanović et al., 1997):
  - Reversible (NaAlH$_4$ with Ti-additives).
  - Reduced desorption temperature.
High-energy ball-milling...

...brings about a broad variety of defects
Breaking crystallinity, creating new surfaces, mass transfer = enhanced reactivity of materials towards hydrogen
Using neutrons to "see" hydrogen

In contrast to X-ray, neutrons are scattered by the nuclei of the atoms. X-ray data tends to give erroneously short metal-hydrogen distances and incertainties in determination of hydrogen coordinates.
Structural characteristics

- Anions: AlH$_4^-$, AlH$_6^{3-}$, BH$_4^-$, MgH$_3^-$ etc. Covalent bonded.

- Metal ions: Alkaline, alkaline earth or 3$d$ elements. Ionic bonded.
The variation in the crystal structures of $\text{MAIH}_4$ arise from the difference in the size of the alkali cations of Li, Na and K, which result in coordination numbers of 5, 8 and 10, respectively.

Dehydrogenation and rehydrogenation- Undoped alanates

Desorption ALANATES, e.g. NaAlH$_4$ (7.5 wt%):

$3 \text{NaAlH}_4 \rightarrow \text{Na}_3\text{AlH}_6 + 2 \text{Al} + 3 \text{H}_2$ 3.7w% 180-230°C

$\text{Na}_3\text{AlH}_6 \rightarrow 3 \text{NaH} + \text{Al} + 3/2 \text{H}_2$ 1.9wt% 230-250°C

$\text{NaH} \rightarrow \text{Na} + \frac{1}{2} \text{H}_2$ 1.9wt% 425°C

*The reaction temperatures depend strongly on the heating rate*
Study of dehydrogenation LiAlD$_4$ - *in-situ* PXD

Brinks, Hauback, Fjellvåg, Norby (2003)

- $220^\circ$C
  - LiD + Al

- $160^\circ$C
  - Li$_3$AlD$_6$ + Al

- $130^\circ$C
  - LiAlD$_4$

\[ 3\text{LiAlH}_4 = \text{Li}_3\text{AlH}_6 + 2\text{Al} + 3\text{H}_2 \] $150^\circ$C (R1) 5.3 wt%

\[ \text{Li}_3\text{AlH}_6 = 3\text{LiH} + \text{Al} + 3/2\text{H}_2 \] $210^\circ$C (R2) 2.6 wt%

\[ 3\text{LiH} + 3\text{Al} = 3\text{LiAl} + 3/2\text{H}_2 \] $350^\circ$C (R3) 2.6 wt%
Li$_3$AlD$_6$

- Isolated octahedra $\text{AlD}_6^{3-}$:
  - Al-D: 1.754 and 1.734 Å.
- Li: 6-coordinated:
  - Li-D: 1.892-2.120 Å.

The structure can be described as a distorted bcc structure of $\text{AlD}_6^{3-}$ units with all tetrahedral sites filled with Li.

Brinks, Hauback (2003)

Each Li atom is connected to two corners and two edges of $\text{AlD}_6^{3-}$ octahedra with in total six D atoms in the coordination sphere.
Mixed alanates $\text{Na}_2\text{LiAID}_6$ and $\text{K}_2\text{NaAlH}_6$

- Synthesized from $\text{NaAID}_4 + \text{LiAID}_4$
- Synthesized by ball milling $\text{KH} + \text{NaAlH}_4$
- Both $Fm-3m$.
- Different size of octahedron $\text{AlD}_6^{3-}$ and $\text{LiD}_6^{-}$
  - K in tetrahedral sites
  - Na in octahedral sites

Isostructural to $\text{Na}_2\text{LiAID}_6$

$\text{Na}_2\text{LiAID}_6$

$\text{K}_2\text{NaAlH}_6$

Theoretical 3.5 wt%  Theoretical 2.2 wt%

Brinks, Hauback, Jensen, Zidan (2005)
Sørby, Brinks, Fossdal, Thorshaug, Hauback (2006)
**TiF₃ in Na₂LiAlH₆: thermal data**

- **Na₂LiAlH₆**: (Diss enthalpy) $\Delta H^0 = 56.4$ kJ/mol H₂ (more stable)
- **Na₃AlH₆**: $\Delta H^0 = 47$ kJ/mol H₂ (Bogdanovic 2000)

Reversible (2.8 wt%) decomposition, sample rehydrogenated in 1-2 h at 200 °C

$$\text{Na}_2\text{LiAlH}_6 = 2\text{NaH} + \text{LiH} + \text{Al} + 3/2\text{H}_2$$

Fossdal, Brinks, Hauback (2005)

**Adjustment of the stability of complex hydrides by anion substitution (H/F). Na₃AlH₆ₓF₆₋ₓ less stable than Na₃AlH₆**
Mg(AlH$_4$)$_2$

- Isolated AlH$_4$· tetrahedra.
- Mg surrounded by 6 H.
- MgH$_6$ octahedra share one corner with each of six AlH$_4$· tetrahedra.
- Sheet like structure along c-axis.
- Al – H: 1.561, 1.671 Å.

Sheets interconnected by van der Waals forces

Mg(AlH$_4$)$_2$: Solvent-free and fast synthesis

reversibility not sufficient (kbar pressures for rehydrogenation at RT)

Fichtner et al. (2003)
Fossdal, Brinks, Fichtner, Hauback (2005)
Additives in alanates

P7 ball milling apparatus

ball milling (Fritsch P6) in Ar, high-pressure vial with pressure/temperature monitoring system (evico magnetics)
Effect of additives – NaAlH$_4$ +Ti-compounds

The undoped NaAlH$_4$ sample at 160 °C delivers H$_2$ at an almost negligible rate and, even at 200 °C, the H$_2$ evolution takes 22-24 h until completion. In contrast samples doped with Ti(OBu)$_4$ is completed at 160 °C within 6-8 h and at 180 and 200 °C within 2-3 and 1 h respectively.

2 mol% Ti(OBu)$_4$  
2 mol% TiCl$_3$  
Dehydrogenation from RT to 270 °C

Bogdanovic et al. (1997)
Effect of mol % TiCl$_3$ in NaAlH$_4$ (ball milled)

H$_2$ absorption (from NaH + Al)
T=125°C, P=8 MPa = 80 bar

H$_2$ desorption (from NaAlH$_4$)
T=125°C

Multiple order-of-magnitude increases in kinetics. Decrease desorption temperatures

Bogdanovic et al. (1997); Sandrock et al. (2002); Srinivasan, Brinks, Hauback, Jensen (2004)
Doped NaAlH$_4$

150 °C desorption - kinetics

120 °C

Via wet chem.

Dehy at 3 temp.

b.m. under H$_2$ for 10h

NaAlH$_4$+2mol%Ti(OBu)$_4$
PCI at 160 °C for 6 different mol% doping level of Ti

1st plateau
NaAlH₄

2nd plateau
Na₃AlH₆

Bogdanovic et al., (2007)
Others additives NaAlH₄

In comparison to TiCl₃-doped NaAlH₄, ScCl₃ and CeCl₃ dopants reduce hydrogenation times by a factor of 2 at high pressure and by a factor of 10 at low pressure.

As TiCl₃ is the best Ti-precursor compound (together with Ti-nanoparticles), trichlorides of the first-row transition metals are investigated as alternative dopants. ScCl₃ results highly efficient, both with respect to storage capacity and kinetics.

Bogdanovic at al. (2006)
## Borohydrides

<table>
<thead>
<tr>
<th>Hydrogenated form</th>
<th>Dehydrogenated form</th>
<th>Hydrogen capacity</th>
<th>Decompo. temp., °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>wt. %</td>
<td>g H₂/L</td>
</tr>
<tr>
<td>LiBH₄</td>
<td>LiH + B</td>
<td>13.9</td>
<td>93</td>
</tr>
<tr>
<td>2 LiBH₄ + MgH₂</td>
<td>3 LiH + MgB₂</td>
<td>11.4</td>
<td>46</td>
</tr>
<tr>
<td>2 LiBH₄ + Al</td>
<td>2 LiH + AlB₂</td>
<td>8.6</td>
<td></td>
</tr>
<tr>
<td>7 LiBH₄ + 1.75 Mg₂Sn + 0.25 Sn</td>
<td>Li₃Sn₂ + 3.5 MgB₂</td>
<td>6.3</td>
<td>46</td>
</tr>
<tr>
<td>NaBH₄</td>
<td>NaH + B</td>
<td>7.9</td>
<td>85.5</td>
</tr>
<tr>
<td>2 NaBH₄ + MgH₂</td>
<td>3 NaH + MgB₂</td>
<td>7.6</td>
<td>62</td>
</tr>
<tr>
<td>Be(BH₄)₂</td>
<td>Be + 2B</td>
<td>20.8</td>
<td>126</td>
</tr>
<tr>
<td>Mg(BH₄)₂</td>
<td>Mg + 2B</td>
<td>14.9</td>
<td>113</td>
</tr>
<tr>
<td>Ca(BH₄)₂</td>
<td>2/3 CaH₂ + 1/3CaB₆</td>
<td>9.7</td>
<td>108</td>
</tr>
<tr>
<td>Ca(BH₄)₂ + MgH₂</td>
<td>CaH₂ + MgB₂</td>
<td>8.3</td>
<td></td>
</tr>
<tr>
<td>Zn(BH₄)₂</td>
<td>Zn + 2B*</td>
<td>8.5</td>
<td></td>
</tr>
<tr>
<td>Al(BH₄)₃</td>
<td>Al + 3B*</td>
<td>16.9</td>
<td>121</td>
</tr>
<tr>
<td>Sc(BH₄)₃</td>
<td>ScB₂ + B (?)</td>
<td>13.5</td>
<td></td>
</tr>
<tr>
<td>Ti(BH₄)₃</td>
<td>TiB₂ + B*</td>
<td>13.1</td>
<td></td>
</tr>
<tr>
<td>Mn(BH₄)₂</td>
<td>Mn + 2B</td>
<td>9.5</td>
<td></td>
</tr>
<tr>
<td>Zr(BH₄)₄</td>
<td>ZrB₂ + 2B (?)</td>
<td>10.7</td>
<td>108</td>
</tr>
</tbody>
</table>

*Formation of diborane observed.
Synthesis tetrahydroborate

Direct reaction in ethereal solvents:

\[ 2\text{MH} + \text{B}_2\text{H}_6 \rightarrow \text{MBH}_4 \]

Direct synthesis from the metal, boron and hydrogen:

\( (550-700 \, ^0\text{C}, \, 30-150 \, \text{bar}) \)

\[ \text{M} + \text{B} + 2\text{H}_2 \rightarrow \text{MBH}_4 \]

Metathesis reaction:

\[ \text{MgCl}_2 + 2\text{MBH}_4 \rightarrow \text{Mg(BH}_4)_2 + 2\text{MCl} \]
LiBH$_4$

- Dehyd. LiBH$_4$ = LiH + B + 3/2 H$_2$ \quad (13.9 \text{ wt%})
  - $P_{eq}$ = 1 bar @ 410°C
  - Reversibility at 600 °C and 350 bar
  - Slow kinetics < 600°C (can be improved by additives or by #)
- NaBH$_4$ and KBH$_4$ more stable (670/830°C)

# LiBH$_4$ “destabilized” by stabilizing the products
- LiBH$_4$ + ½ Mg = LiH + ½ MgB$_2$ + 3/2 H$_2$ (des. Temp. reduced by 30 K)
- LiBH$_4$ + ½ MgH$_2$ = LiH + ½ MgB$_2$ + 5/2 H$_2$ (rehyd. at T< 300 °C, 50 bar)
- Cycled at 330°C
- TiCl$_3$, VCl$_3$ used as catalyst

Low- and high-temperature structures of LiBH$_4$
Dehydrogenation reactions

Alkali metal borohydrides:

\[
\begin{align*}
M(BH_4) & \rightleftharpoons MH + B + 3/2H_2 \\
A(BH_4) & \rightleftharpoons AB + 2H_2
\end{align*}
\]

Alkaline earth borohydrides:

\[
\begin{align*}
M(BH_4)_2 & \rightleftharpoons MH_2 + 2B + 3H_2 \\
M(BH_4)_2 & \rightleftharpoons MB_2 + 4H_2 \\
M(BH_4)_2 & \rightleftharpoons 2/3MH_2 + 1/3MB_6 + 10/3H_2
\end{align*}
\]
Thermal desorption from LiBH$_4$

Various heating rates (0.5-6 °C min$^{-1}$)

several intermediate steps
-110 °C polymorphic transformation
- 280 °C melting
- 490 °C hydrogen LiBH$_2$ (50%)
- at 680 °C des of 3 of the 4 H

Li$_2$B$_{12}$H$_{12}$ cluster confirmed by Raman and XRD
Borohydrides

Pro: High gravimetric storage density (wt.% H₂)

Cons: Alkali (e.g. LiBH₄): thermodynamically too stable
alkaline earth: kinetically too slow
transition metal: unstable and/or irreversible
Diborane B₂H₆ release

??? SOLUTION ???

Make new borohydrides or modify existing ones
Elements, for which tetrahydroborate (BH$_4$) complexes exist

<table>
<thead>
<tr>
<th>Group</th>
<th>Period</th>
<th>Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>H, He</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>Li, Be, Na, Mg</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Kr</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>Rb, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, Xe</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>Ba, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>Lu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Po, At, Rn</td>
</tr>
<tr>
<td>7</td>
<td>7</td>
<td>Rf, Db, Sg, Bh, Hs, Mt,Ds, Rg, Uub, Uut, Uuo</td>
</tr>
</tbody>
</table>

*Lanthanoids

**Actinoids

* = Filled in blue
** = Filled in red
---
Exercise @ find relation heat of formation borohydrides versus Pauling electronegativities of cations

Predicted heat of formation borohydrides $\Delta H_{\text{boro}}$

- $\text{LiBH}_4 = -161 \text{ kJ mol}^{-1}$ BH$_4$
- $\text{CuBH}_4 = 76$
- $\text{NaBH}_4 = -155$
- $\text{KBH}_4 = -198$
- $\text{Zr(BH}_4)_4 = -54$
- $\text{Hf(BH}_4)_4 = -61$

- $\frac{1}{n}M + B + 2H_2 \rightarrow \frac{1}{n}M(\text{BH}_4)_n$, $\frac{1}{n}M(\text{BH}_4)_n$

- $\text{Mg(BH}_4)_2 = -71$
- $\text{Zn(BH}_4)_2 = 15$
- $\text{Sc(BH}_4)_3 = -72$
Sabrina Sartori, Summer School, Reykjavik, August 17-21, 2010

thermodynamically unstable

with $X_p \geq 1.6$


$\Delta H$ (kJ/mol BH$_4$)

$\chi_p$
$n \text{ LiBH}_4 + \text{MCl}_n \rightarrow \text{M(BH}_4\text{)}_n + n \text{ LiCl}$

Exercise @ find relation desorption temperature vs Pauling electronegativity

Thermal desorption of M(BH4)n

$\Delta H_{\text{des}}$ indicator for searching the material with appropriate stability for hydrogen storage material

$$M(BH_4)_n \rightarrow MH_m + nB + \left(\frac{4n-m}{2}\right)H_2$$

we can find relation between $\Delta H_{\text{des}}$ and $T_d$

Stability vs. electronegativity

Charge compensation by \(M^{n+}\) is a key feature for the stability of \(M(BH_4)_n\) and hydrogen desorption temperature decreases with increasing of Pauling electronegativity \(\chi_p\) of M.

Any solution?
Double-cation borohydrides!

H.-W. Li et al., J. Alloys and Comp. 2007
Adjustment of thermodynamical stabilities by combination of two metals with different electronegativities

\[ MCl_n + mLiBH_4 \rightarrow MLi_{m-n}(BH_4)_m + nLiC \]

H.-W. Li et al., J. Alloys and Comp. 2007
Thermal desorption

\[ \chi_p = \frac{1.4 + 1.0(m - 4)}{1 + (m - 4)} \]

\[ \text{Zr} \text{(BH}_4\text{)}_4 \]
\[ \text{ZrLi} \text{(BH}_4\text{)}_5 \]
\[ \text{ZrLi}_2 \text{(BH}_4\text{)}_6 \]

H.-W. Li et al., J. Alloys and Comp. 2007
The search for novel metal borohydrides

Mixed metal borohydrides

LiK(BH$_4$)$_2$, LiMg(BH$_4$)$_3$

LiSc(BH$_4$)$_4$
NaSc(BH$_4$)$_4$
KSc(BH$_4$)$_4$

LiZn$_2$(BH$_4$)$_5$
NaZn(BH$_4$)$_3$
NaZn$_2$(BH$_4$)$_5$

Mixed metal borohydrides

Anion substitution

Li(BH$_4$)$_{1-x}$Cl$_x$

(Hummelshøj et al., 2008 CAMD Summer School, TDU)
Local Coordination Screening (LCS) approach

CAMD 2008 Summer School
Center for Atomic Scale Materials Design
Technical University of Denmark, Kongens Lyngby, Denmark

Search for novel metal borohydrides

Systems with alloy composition

\[ M_1 M_2 (BH_4)_{2-5} \]

M1 = alkali metal
M2 = alkali, alkaline earth or 3d/4d transition metal

757 compositions have been simulated

22 stable alloys with promising decomposition energies

The Approach

Configuration space and template structures $\rightarrow$ Initial screening

\[ M_1 M_2 (BH_4)_x \]

\[ M1 \in \{Li, Na, K\} \quad x=2 \quad M2 \in \{Li, Na, K\} \]

\[ x=3,4 \quad M2 \in \{Li, Na, K, Mg, Al, Ca, Sc-Zn, Y-Mo, Ru-Cd\} \]

Exception: \( Al(BH_4)_3 \)

**literature search, structures reported** $\rightarrow$ templates structures with tetrahedral (T) - for the smallest Li and Mg - and octahedral (O) - for the larger Na, K and Ca - coordination of BH\(_4\) groups to the metal atoms were used.

For each alloy composition, 4 different template structures were used for the coordination of the BH\(_4\):

<table>
<thead>
<tr>
<th>M1</th>
<th>M2</th>
<th>M1</th>
<th>M2</th>
<th>M1</th>
<th>M2</th>
<th>M1</th>
<th>M2</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>T</td>
<td>O</td>
<td>O</td>
<td>T</td>
<td>O</td>
<td>O</td>
<td>T</td>
</tr>
</tbody>
</table>

Coordination polyhedra with either corner or edge-sharing or combination of both

Unit cell containing only ONE formula unit

Assessment of the stabilities for the 757 structures

Two selection criteria were used:

**Phase separation into binary components:**

\[ \Delta E_{\text{alloy}} = E_{\text{LiSc(BH}_4\text{)}} - (E_{\text{LiBH}_4} + E_{\text{Sc(BH}_4\text{)}}) \]

**Decomposition:**

Generic decomposition pathway, where the alloys decompose into alkali-and alkaline earth hydrides, transition metals, boron and hydrogen

\[ \Delta E_{\text{decomp}} = E_{\text{LiSc(BH}_4\text{)}} - (E_{\text{LiH}} + E_{\text{Sc}} + 4E_{\text{B}} + 7.5E_{\text{H}_2}) \]

**stability range used to select:**

\[ \Delta E_{\text{alloy}} \leq 0.0 \text{ eV/f.u. and } \Delta E_{\text{decomp}} \in \{-0.5;0.0\} \sim -0.2 \text{ eV/H}_2 \]

\[ \Delta E_{\text{alloy}} \leq 0.2 \text{ eV/f.u. and/or } \Delta E_{\text{decomp}} \leq 0.2 \text{ eV/H}_2 \text{ (alloys with only small instabilities)} \]

Calculation Procedure

Step 1:
Population of one of the four template structures with two supplied metal atoms followed by introduction of the necessary (BH4\(^-\)) groups. The ionic radii of the metals were taken from the 24 binary reference borohydrides; for BH4\(^-\), the ionic radius was adjusted according to the coordination of the group to the metal ion (face, edge, corner)

INITIAL GUESS

Iteration process

(I) Relaxation of the Hydrogen positions
(II) Contraction/expansion of unit cell volume, keeping B-H distance fixed in order to find the optimum unit cell volume
(III) Relaxation of Hydrogen positions in optimized unit cell

Step 2:
After optimization of (M1,M2) templates, the most stable structure was relaxed without constraints in a two-stage process:

- Relax atomic positions while keeping unit cell volume fixed
- Relax unit cell volume while keeping atomic positions fixed

Results

Most of the alloys are stable against decomposition BUT the majority is found to be unstable against separation into the binary components.

The stable alloys ($\Delta E_{\text{alloy}} \leq 0.0$ eV/f.u.) cluster around certain average electronegativities of 1.3-1.4 and 1.6. The cluster around 1.3-1.4 is highly promising and it contains alloys of the following elements: Mn, (Nb), Al, Zn and Fe.
<table>
<thead>
<tr>
<th>Composition</th>
<th>wt. %</th>
<th>$\Delta E_{alloy}$ [eV/f.u.]</th>
<th>$\Delta E_{decomp}$ [eV/H$_2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNa(BH$_4$)$_2$</td>
<td>13.5</td>
<td>-0.020</td>
<td>-0.581</td>
</tr>
<tr>
<td>KZn(BH$_4$)$_3$</td>
<td>8.1</td>
<td>-0.349</td>
<td>-0.423</td>
</tr>
<tr>
<td>KAl(BH$_4$)$_4$</td>
<td>12.9</td>
<td>-0.138</td>
<td>-0.416</td>
</tr>
<tr>
<td>KCd(BH$_4$)$_3$</td>
<td>6.2</td>
<td>-0.005</td>
<td>-0.352</td>
</tr>
<tr>
<td>NaZn(BH$_4$)$_3$</td>
<td>9.1</td>
<td>-0.358</td>
<td>-0.344</td>
</tr>
<tr>
<td>LiAl(BH$_4$)$_4$</td>
<td>17.3</td>
<td>-0.391</td>
<td>-0.311</td>
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<tr>
<td>KFe(BH$_4$)$_3$</td>
<td>8.7</td>
<td>-0.116</td>
<td>-0.282</td>
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<tr>
<td>LiZn(BH$_4$)$_3$</td>
<td>10.4</td>
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<tr>
<td>NaFe(BH$_4$)$_3$</td>
<td>9.8</td>
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<td>KMn(BH$_4$)$_4$</td>
<td>10.5</td>
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<td>-0.174</td>
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<tr>
<td>NaNb(BH$_4$)$_4$</td>
<td>9.2</td>
<td>-0.128</td>
<td>-0.165</td>
</tr>
<tr>
<td>KCo(BH$_4$)$_3$</td>
<td>8.5</td>
<td>-0.089</td>
<td>-0.161</td>
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<tr>
<td>NaMn(BH$_4$)$_4$</td>
<td>11.7</td>
<td>-0.284</td>
<td>-0.131</td>
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<tr>
<td>KNi(BH$_4$)$_3$</td>
<td>8.5</td>
<td>-0.120</td>
<td>-0.116</td>
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<tr>
<td>LiFe(BH$_4$)$_3$</td>
<td>11.3</td>
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<td>-0.104</td>
</tr>
<tr>
<td>LiNb(BH$_4$)$_4$</td>
<td>10.1</td>
<td>-0.194</td>
<td>-0.097</td>
</tr>
<tr>
<td>NaCo(BH$_4$)$_3$</td>
<td>9.6</td>
<td>-0.143</td>
<td>-0.090</td>
</tr>
<tr>
<td>KRh(BH$_4$)$_4$</td>
<td>8.0</td>
<td>-0.058</td>
<td>-0.079</td>
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<tr>
<td>LiMn(BH$_4$)$_4$</td>
<td>13.3</td>
<td>-0.358</td>
<td>-0.063</td>
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<tr>
<td>NaNi(BH$_4$)$_3$</td>
<td>9.6</td>
<td>-0.164</td>
<td>-0.043</td>
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<td>NaRh(BH$_4$)$_4$</td>
<td>8.7</td>
<td>-0.033</td>
<td>-0.016</td>
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</table>
Further candidates with $0 < \Delta E_{\text{alloy}} < 0.2$ eV/f.u. and $\Delta E_{\text{decomp}} < 0.0$ eV/H$_2$

<table>
<thead>
<tr>
<th>Composition</th>
<th>wt. %</th>
<th>$\Delta E_{\text{alloy}}$ [eV/f.u.]</th>
<th>$\Delta E_{\text{decomp}}$ [eV/H$_2$]</th>
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<tbody>
<tr>
<td>K(Na(BH$_4$)$_2$)</td>
<td>8.8</td>
<td>0.095</td>
<td>-0.825</td>
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<td>NaY(BH$_4$)$_4$</td>
<td>9.4</td>
<td>0.115</td>
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<td>NaCa(BH$_4$)$_3$</td>
<td>11.2</td>
<td>0.129</td>
<td>-0.645</td>
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<tr>
<td>LiY(BH$_4$)$_4$</td>
<td>10.4</td>
<td>0.033</td>
<td>-0.609</td>
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<tr>
<td>LiCa(BH$_4$)$_3$</td>
<td>13.2</td>
<td>0.052</td>
<td>-0.556</td>
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<tr>
<td>LiSc(BH$_4$)$_4$</td>
<td>14.5</td>
<td>0.143</td>
<td>-0.534</td>
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<tr>
<td>NaCd(BH$_4$)$_3$</td>
<td>6.7</td>
<td>0.003</td>
<td>-0.271</td>
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<td>KNb(BH$_4$)$_4$</td>
<td>8.4</td>
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<tr>
<td>NaV(BH$_4$)$_4$</td>
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<td>0.076</td>
<td>-0.188</td>
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<td>NaAg(BH$_4$)$_2$</td>
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<td>-0.177</td>
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<td>LiCd(BH$_4$)$_3$</td>
<td>7.4</td>
<td>0.102</td>
<td>-0.152</td>
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<tr>
<td>KCr(BH$_4$)$_4$</td>
<td>10.7</td>
<td>0.199</td>
<td>-0.136</td>
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<td>LiV(BH$_4$)$_4$</td>
<td>13.8</td>
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<td>-0.113</td>
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<tr>
<td>NaCr(BH$_4$)$_4$</td>
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<td>0.050</td>
<td>-0.095</td>
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<td>KPd(BH$_4$)$_3$</td>
<td>6.4</td>
<td>0.047</td>
<td>-0.095</td>
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<td>KMo(BH$_4$)$_4$</td>
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<td>0.185</td>
<td>-0.079</td>
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<td>KRu(BH$_4$)$_3$</td>
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<td>-0.061</td>
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<td>NaMo(BH$_4$)$_4$</td>
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<td>LiCr(BH$_4$)$_4$</td>
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<td>NaPd(BH$_4$)$_3$</td>
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<td>-0.014</td>
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<tr>
<td>LiCo(BH$_4$)$_3$</td>
<td>11.0</td>
<td>-0.100</td>
<td>0.019</td>
</tr>
<tr>
<td>LiNi(BH$_4$)$_3$</td>
<td>11.0</td>
<td>-0.104</td>
<td>0.069</td>
</tr>
</tbody>
</table>
Double-Cation metal borohydrides

MLi$_{m-n}$(BH$_4$)$_m$  
(Orimo, 2007)

\[ M \quad n \]
\[ \begin{array}{lcl}
\text{Zn} & 2 & \text{LiZn(BH}_4)_3 \\
\text{Al} & 3 & \text{LiAl(BH}_4)_4 \\
\text{Zr} & 4 & \text{LiZr(BH}_4)_5 \\
\end{array} \]

\text{Disproportionate upon heating}

\[ \begin{array}{lcl}
\text{LiFe(BH}_4)_3 & 1961 \\
(Li/Na)\text{Mn(BH}_4)_3,4 & 2008 \\
(Li/Na)\text{Zn(BH}_4)_3 & 1971 \\
\text{LiSc(BH}_4)_4 & 2008 \\
\text{LiZn(BH}_4)_3 & 2006 \\
\text{NaZn(BH}_4)_3 & 2008 \\
\text{NaZn}_2(\text{BH}_4)_5 & 2008 \\
\text{LiK(BH}_4)_2 & 2008 \\
\text{LiZn}_2(\text{BH}_4)_5 & 2009 \\
\text{NaZn}_2(\text{BH}_4)_5 & 2009 \\
\text{NaZn(BH}_4)_3 & 2009 \\
\text{NaSc(BH}_4)_4 & 2010 \\
\text{KZn(BH}_4)_2 & 2010 \\
\end{array} \]
**Aim**

\[ m \ NaBH_4 + TM\text{Cl}_n \rightarrow Na_{m-n} \cdot TM(BH_4)_m + n \ NaCl \]

\( TM=\text{Cd, Ti, V, Cu, Ni} \)

**Finding**

\[ \text{Na(BH}_4\text{)}_{1-x}\text{Cl}_x \]

- **Synthesis**: ball milling in Ar, 3h, 100:1
Conclusion

- At present, no solid storage material fulfils the major targets for automotive applications;

- Up to now, storage densities of ~2 wt.% are achievable on system level with complex hydrides on alanate basis (capacity of the material 4 wt%);

- Further research for novel storage materials with improved storage densities, kinetics and thermodynamic behaviour as well as for advanced system components, e.g. heat exchanger, is still required;

- For on-board storage in fuel-cell-driven vehicles, the hydrogen in the alanates needs to be reversibly charged and discharged;

- To make the material reversible under practical conditions, it has to be added with a catalyst. Still not understood the effect of additives.