Hydrogen storage in light complex hydrides

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Solid material for hydrogen storage

- Metal and complex hydrides
- Chemical hydrides
- Nanoporous structures

The goals are changing and also the achievements in high-temp PEM etc (meaning higher temperatures for H-desorption will be acceptable).

Sartori Sabrina, Summer School on Materials for the Hydrogen Society, Reykjavik, June 19-23, 2008
Storage as hydrides

\[ M(s) + \frac{x}{2} \, H_2 \leftrightarrow M\text{H}_x(s) + \text{energy} \]

Interstitial metal hydride

Complex hydride

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• **Alanates (Al):** NaAlH$_4$, LiAlH$_4$, KAlH$_4$, Mg(AlH$_4$)$_2$, mixed alanates (Na$_2$LiAlH$_6$, K$_2$LiAlH$_6$);  
  - Structures;  
  - Undoped alanates;  
  - Effect of additives;  
  - Dehydrogenation/rehydrogenation

• **Amides/imides (N)**  
  - Structures;  
  - Dehydrogenation/rehydrogenation

• **Borohydrides (B)**  
  - Structures;  
  - Dehydrogenation/rehydrogenation  
  - mixed systems
### The Challenge: Goals for hydrogen storage

<table>
<thead>
<tr>
<th>Storage Parameter</th>
<th>2010 Target</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>System Gravimetric Capacity:</strong></td>
<td></td>
</tr>
<tr>
<td>Usable, specific-energy from H₂ (net useful energy/max system mass)</td>
<td>2 kWh/kg</td>
</tr>
<tr>
<td>(0.06 kg H₂/kg system or 6 wt.%)</td>
<td></td>
</tr>
<tr>
<td><strong>System Volumetric Capacity:</strong></td>
<td></td>
</tr>
<tr>
<td>Usable energy density from H₂ (net useful energy/max system volume)</td>
<td>1.5 kWh/L</td>
</tr>
<tr>
<td>(0.045 kg H₂/L system)</td>
<td></td>
</tr>
<tr>
<td><strong>Durability/Operability</strong></td>
<td></td>
</tr>
<tr>
<td>• Operating ambient temperature</td>
<td>-30/50 °C (sun)</td>
</tr>
<tr>
<td>• Min/max delivery temperature</td>
<td>-40/85 °C</td>
</tr>
<tr>
<td>• Cycle life (1/4 tank to full)</td>
<td>1000 Cycles</td>
</tr>
<tr>
<td>• Min delivery pressure from tank; FC=fuel cell, ICE=internal combustion engine</td>
<td>4 FC/35 ICE Atm (abs)</td>
</tr>
<tr>
<td><strong>Charging/Discharging Rates</strong></td>
<td></td>
</tr>
<tr>
<td>• System fill time (for 5 kg H₂)</td>
<td>3 min</td>
</tr>
<tr>
<td>• Min full flow rate</td>
<td>0.02 (g/s)/kW</td>
</tr>
<tr>
<td>• Transient response 10%–90% and 90%–0%</td>
<td>0.75 s</td>
</tr>
</tbody>
</table>

- **2010:** ≥ 6 wt%
- **2015:** ≥ 9 wt%
Status of hydrogen storage systems
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
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.
Synchrotron powder X-ray diffraction

Swiss-Norwegian Beamline (BM01)

- Heating under evacuation 1 °C/min.
- Diffraction data collected every 2 min

Dehydrogenation reaction studied by *in situ* SR-XRD
Structural characteristics

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

- Metal ions: Alkaline, alkaline earth or $3d$ elements. Ionic bonded.
Combined neutron and X-ray diffraction

**NaAlD$_4$**
- **AlD$_4^-$** tetrahedra
  - Al-D: 1.626 Å (at 295 K).
- **Na$^+$**: surrounded by 8 D atoms from 8 different AlD$_4^-$:
  - Na-D: 2.439, 2.431 Å.

**KAID$_4$**
- **AlD$_4^-$** isolated tetrahedra
  - Al-D: 1.618 Å (at 295 K).
- **K$^+$**: surrounded by ten D atoms:
  - K-D: 2.596 Å (at 295 K).

**LiAlD$_4$**
- **AlD$_4^-$** tetrahedra connected via Li.
- **Li$^+$**: surrounded by a trigonal bipyramid of 5 D atoms from 5 different AlD$_4^-$:
  - Li-D: 1.831 – 1.978 Å.
  - Al-D: 1.604 – 1.637 Å.

Hauback, Brinks, Jensen, Murphy, Maeland (2003)

Hauback, Brinks, et al. (2005)

Hauback, Brinks, Fjellvåg (2002)
Li₃AlD₆

- Isolated octahedra AlD₆³⁻:
  - Al-D: 1.754 and 1.734 Å.
- Li: 6-coordinated:
  - Li-D: 1.892-2.120 Å.

Each Li atom is connected to two corners and two edges of AlD₆³⁻ octahedra with in total six D atoms in the coordination sphere.

The structure can be described as a distorted bcc structure of AlD₆³⁻ units with all tetrahedral sites filled with Li

Brinks, Hauback (2003)
**Mg(AlH₄)₂**

- Isolated AlH₄⁻ tetrahedra.
- Mg surrounded by 6 H.
- MgH₆ octahedra share one corner with each of six AlH₄⁻ tetrahedra.
- Sheet like structure along c-axis.
- Al – H: 1.561, 1.671 Å.

- Mg(AlH₄)₂: Solvent-free and fast synthesis
- Details of thermal and isothermal decomposition of Mg(AlH₄)₂
- Scale-up strategies promising, but reversibility not sufficient

Sheets interconnected by van der Waals forces

Fichtner et al. (2003)
Fossdal, Brinks, Fichtner, Hauback (2005)
Mixed alanates $\text{Na}_2\text{LiAlD}_6$ and $\text{K}_2\text{NaAlH}_6$

- Synthesized from $\text{NaAlD}_4 + \text{LiAlD}_4$
- Synthesized by ball milling $\text{KH} + \text{NaAlH}_4$.
- SR-PXD + PND
- Both $Fm-3m$.
- Different size of octahedron $\text{AlD}_6^-$ and $\text{LiD}_6^-$
- fcc geometry of $\text{AlD}_6^-$
  - $\text{K}$ in tetrahedral sites
  - $\text{Na}$ in octahedral sites

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

$$a = 7.3848(1) \text{ Å}$$

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

$$a = 8.118(1) \text{ Å}$$

Brinks, Hauback, Jensen, Zidan (2005)
Sørby, Brinks, Fossdal, Thorshaug, Hauback (2006)
Dehydrogenation and rehydrogenation - Undoped alanates

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

\[ 3 \text{NaAlH}_4 \rightarrow \text{Na}_3\text{AlH}_6 + 2 \text{Al} + 3 \text{H}_2 \quad 3.7\text{w}\% \quad 180-230^\circ\text{C} \]

\[ \text{Na}_3\text{AlH}_6 \rightarrow 3 \text{NaH} + \text{Al} + 3/2 \text{H}_2 \quad 1.9\text{wt}\% \quad 230-250^\circ\text{C} \]

\[ \text{NaH} \rightarrow \text{Na} + \frac{1}{2}\text{H}_2 \quad 1.9\text{wt}\% \quad 425^\circ\text{C} \]

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

$\text{LiAlD}_4 \rightarrow 220^\circ \text{C} \quad \text{LiD} + \text{Al}$

$\text{Li}_3\text{AlD}_6 + \text{Al} \rightarrow 160^\circ \text{C}$

$\text{LiAlD}_4 \rightarrow 130^\circ \text{C}$

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

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

$3\text{LiH} + 3\text{Al} = 3\text{LiAl} + 3/2\text{H}_2 \quad 350^\circ \text{C} \quad (\text{R3}) \quad 2.6 \text{ wt}\%$

Brinks, Hauback, Fjellvåg, Norby (2003)

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Thermolysis of KAlH$_4$ releases hydrogen and it consist on three steps of dehydrogenation,

\[ 3 \text{KAlH}_4 \rightarrow \text{K}_3\text{AlH}_6 + 2\text{Al} + 3\text{H}_2 \text{ (2.9 wt.%) at 300 ºC} \] (1)
\[ \text{K}_3\text{AlH}_6 \rightarrow 3\text{KH} + \text{Al} + 3/2\text{H}_2 \text{ (1.4 wt.%)} \] (2)
\[ 3\text{KH} \rightarrow 3\text{K} + 3/2\text{H}_2 \text{ (1.4 wt.%)} \] (3)

In step 1, KAlH$_4$ decomposes to K$_3$AlH$_6$, followed by decomposition to KH in step 2. KAlH$_4$ was found to be reversible without a catalyst. In situ diffraction investigations of KAlH$_4$ powders published by Mamatha et al. J. Alloys Comp. (2006) revealed the appearance of unidentified phases during decomposition.
Mg(AlH₄)₂ – In situ PXD

Mg(AlH₄)₂ → MgH₂ + 2Al + 3H₂  135-163 °C (R1) 7.0 wt%
(without the involvement of AlH₆³⁻, as an intermediate phase)

MgH₂ + 2Al → AlₓMgᵧ + AlₐMgb + H₂  270-310 °C (R2) 2.3 wt%

Fossdal, Brinks, Fichtner, Hauback (2005)
Additives in alanates

ball milling apparatus
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.

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

\[ \text{H}_2 \text{ absorption} \quad T=125^\circ \text{C}, \ P=8 \text{ MPa} \]

\[ \text{H}_2 \text{ desorption} \quad T=125^\circ \text{C} \]

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$_4$
PCT at 160 °C for 6 different mol% doping level of Ti

Bogdanovic et al., (2007)
Van’t Hoff plot

![Van’t Hoff plot](image-url)
Effect of TiCl$_3$ in NaAlH$_4$ (ball milled)

Improve significantly reversibility (NaAlH$_4$). Up to 4.5 wt% cyclic H-capacity
$\text{NaAlH}_4 + \text{TiCl}_3$

- The effect of the additives \textbf{NOT} understood:
  - Dopant or catalyst?
  - Solid solution or secondary phase?

<table>
<thead>
<tr>
<th>Solid solution</th>
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</thead>
<tbody>
<tr>
<td>$\text{Na}_{1-3x}\text{Ti}_x\text{AlH}_4$</td>
</tr>
<tr>
<td>$\text{NaAl}_{1-x}\text{Ti}_x\text{AlH}_4$</td>
</tr>
<tr>
<td>Could improve kinetics in grains.</td>
</tr>
<tr>
<td>PXD: Changes in unit-cell dimension of $\text{NaAlH}_4$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Heterogenous catalyst</th>
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</thead>
<tbody>
<tr>
<td>Catalyzing hydrogen splitting/combination and/or diffusion of metal-containing species.</td>
</tr>
<tr>
<td>PXD: Detection of secondary Ti-containing phases.</td>
</tr>
</tbody>
</table>
## Nature of additives – NaAlH₄ + Ti-compounds

<table>
<thead>
<tr>
<th>Additives</th>
<th>a (Å)</th>
<th>c (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaAlH₄</td>
<td>5.0232(1)</td>
<td>11.3483(2)</td>
</tr>
<tr>
<td>+ 6% TiCl₃</td>
<td>5.0231(1)</td>
<td>11.3481(2)</td>
</tr>
<tr>
<td>+ 6% TiCl₄</td>
<td>5.0234(1)</td>
<td>11.3493(2)</td>
</tr>
<tr>
<td>+ 6% TiF₃</td>
<td>5.0234(1)</td>
<td>11.3493(2)</td>
</tr>
<tr>
<td>NaH+Al+2%Ti(OBu)₄ @ 7 cycles</td>
<td>5.0233(1)</td>
<td>11.3498(2)</td>
</tr>
<tr>
<td>NaAlD₄</td>
<td>5.0090(1)</td>
<td>11.3069(2)</td>
</tr>
<tr>
<td>NaAlD₄ + 6% TiCl₄</td>
<td>5.0102(1)</td>
<td>11.3113(3)</td>
</tr>
</tbody>
</table>

- NaAlH₄ + TiCl₃/TiCl₄/TiF₃/Ti(OBu)₄
- No significant changes in unit-cell dimensions of NaAlH₄
  - No significant solid-solution of Ti into NaAlH₄

Brinks, Jensen, Srinivasan, Hauback, Sun, Murphy (2004)
Others additives NaAlH$_4$

As TiCl$_3$ is the best Ti-precursor compound (together with Ti-nanoparticles), trichlorides of the first-row transition metals are investigated as alternative dopants. ScCl$_3$ results highly efficient, both with respect to storage capacity and kinetics.

In comparison to TiCl$_3$-doped NaAlH$_4$, ScCl$_3$ and CeCl$_3$ dopants reduce hydrogenation times by a factor of 2 at high pressure and by a factor of 10 at low pressure.

Bogdanovic at al. (2006)
Sodium Alanate

- Synthesis of NaAlD$_4$ with improved kinetics and reversibility (4 wt% H$_2$)

- Improved synthesis of catalyst: Ti$_{13}$*6THF

- 2NaAlH$_4$+LiH+2mol%TiF$_3$ leads to the formation of reversible Na$_2$LiAlH$_6$ (2.8 wt%)

- Adjustment of the stability of complex hydrides by anion substitution (H/F). Na$_3$AlH$_{6-x}$F$_x$ less stable than Na$_3$AlH$_6$
LiAlD$_4$ with additives

**Thermal desorption spectroscopy**

Three separate peaks of hydrogen desorption in agreement with the 3 decomposition steps

- VCl$_3$ reduces the desorption temperature more efficiently
- 3TiCl$_3$·AlCl$_3$ decomposes more LiAlD$_4$ into Li$_3$AlD$_6$ during ball-milling (from PXD data)


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LiAlD$_4$ with additives - *In-situ* SR PXD

2 % VCl$_3$

- VCl$_3$ and TiCl$_3$·1/3AlCl$_3$ reduce desorption temperature by 60 and 50 °C respectively.
- Amount and type of additive important for the decomposition.


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TiF$_3$ in Na$_2$LiAlH$_6$: thermal data

- Na$_2$LiAlH$_6$: (Diss enthalpy) $\Delta H^0 = 56.4$ kJ/mol H$_2$ (more stable)
- Na$_3$AlH$_6$: $\Delta H^0 = 47$ kJ/mol H$_2$ (Bogdanovic 2000)

Reversible decomposition, sample rehydrogenated in 1-2 h at 200 °C

Na$_2$LiAlH$_6 = 2$NaH + LiH + Al + 3/2H$_2$

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$\textbf{K}_2\text{NaAlH}_6$: Stability

+ 1 mol% TiF$_3$

- Reaction reversible
- Very stable
- Fast desorption kinetics (60 min at 325°C and 90 min at 280°C)

$\Delta H^\circ = 98.2 \text{ kJ/mol-H}_2$

$\Delta S^\circ = 149.9 \text{ J/K mol-H}_2$

Sørby, Brinks, Hauback (2006)
LiNH₂, Mg(NH₂)₂ and Li₂ND(H) can be described as (pseudo-)fcc packing of amide/imide anions with cations in tetrahedral sites. Pure, well-crystalline MgND is hard to obtain from decomposition of Mg(ND₂)₂.

Mechanical milling of LiNH₂ and LiBH₄ in varying combination ratio.
Li-amide/imide systems

Amide: -NH₂, LiNH₂
Imide: NH₂, Li₂NH
Nitride: N, Li₃N

1st Step:
LiNH₂ + LiH ↔ Li₂NH + H₂
200 °C (better with TiCl₃)

2nd Step:
Li₂NH + LiH ↔ Li₃N + H₂
320 °C

Two steps in total:
11.5 wt%

Major limitations:
• Temperature too high
• Pressure too low

New system:
Partial Mg substitution

But competitive reaction: Li-amide decomposes in 2LiNH₂ → Li₂NH + NH₃
Ammonia depletes one of the reactants and diminishes the hydrogen absorption capacity

The Li-amide/imide – systems:

New systems:

Partial Mg-substitution and Mg-amide/imides.

- LiNH$_2$ + LiH  dehydrogenation begins at approx. 277 °C (10 °C/min under Ar);
- Increasing Mg concentration, the temp. is decreased to c.a. 100 °C ;
- Mg(NH$_2$)$_2$ + 4LiH  n=4, the main weight loss below 230 °C.

• Amides of alkali or alkali-earth metals, e.g. LiNH$_2$, Mg(NH$_2$)$_2$, Ca(NH$_2$)$_2$, react with metal hydrides to release hydrogen.
• Among several combinations, reactions of Mg(NH$_2$)$_2$ with LiH have an advantage of providing a high capacity in wt%. However, the reaction mechanism is still not clear.
Reaction between Mg(NH$_2$)$_2$ and LiH in different ratios

Mg(NH$_2$)$_2$ + 2LiH $\leftrightarrow$ Li$_2$Mg(NH)$_2$ + 2H$_2$  
(n=2; 5.6 wt%  
$T_{des} > 200$ °C) [1]

3Mg(NH$_2$)$_2$ + 8LiH $\leftrightarrow$ 4Li$_2$NH + Mg$_3$N$_2$ + 8H$_2$  
(n=8/3; 6.9 wt%  
$T_{des} > 400$ °C) [2]

3Mg(NH$_2$)$_2$ + 12LiH $\leftrightarrow$ 4LiN$_3$ + Mg$_3$N$_2$ + 12H$_2$  
(n= 4; 9.1 wt%  
$T_{des} > 500$ °C) [3]

-What is an intermediate phase for each?

-Depends on the [Mg]/[Li] ratio or not ?

Reports for the 1:2 (n=2) system

\[
\begin{align*}
\text{Mg(NH}_2\text{)}_2 + 2\text{LiH} & \leftrightarrow \text{Li}_2\text{MgN}_2\text{H}_3.2 + 1.4\text{H}_2 \\
\text{Li}_2\text{MgN}_2\text{H}_3.2 & \leftrightarrow \text{Li}_2\text{Mg(NH)}_2 + 0.6\text{H}_2
\end{align*}
\]

From P-C iotherm and XRD
Luo et al (Sandia NL, USA)[4]
Rijssenbeek et al (GE, USA)[5]

Sample preparation

[Sample I]

$3\text{Mg(NH}_2\text{)}_2 + 8\text{LiH}$: ball-milled in $1 \text{MPaH}_2$ for 2h

[Sample II]

$3\text{Mg} + 8\text{LiNH}_2$: ball-milled,
dehydrogenated at $250 ^\circ \text{C}$ in vac
and rehydrogenated at $200 ^\circ \text{C}$, $10 \text{ MPa H}_2$

→ a mixture of $\text{Mg(NH}_2\text{)}_2$ and $\text{LiH}$ (+ $\text{Li-Mg-N-H}$) [1]

[Sample III, Deuterated sample]

Synthesized from $3\text{Mg} + 8\text{LiND}_2$ in a similar process to Sample II
A Li-Mg-N-D phase prepared by dehydrogenated at $200 ^\circ \text{C}$ in vac for 8h


Partly dehydrogenated

Fully hydrogenated
In situ SR-PXD for Sample I
(prepared by milling Mg(NH$_2$)$_2$ and LiH)

The patterns of the new phase from 180 °C to 240 °C
**In situ SR-PXD for Sample II**

(prepared from Mg and LiNH$_2$)

$\text{Li}_2\text{O}$

MgO

Mg(NH$_2$)$_2$

Li-Mg-N-H

LiH

New phase

110°C

150°C

210°C

250°C

290°C

Intensity / a.u.

$\theta$/ deg
1 : 2 ratio  
\[ \text{Mg(NH}_2\text{)}_2 + 2\text{LiH} \rightleftharpoons \text{Li}_2\text{Mg} \text{(NH}_2\text{)}_2 + 2\text{H}_2 \]

Investigate by Chen, Luo et al., Zhao et al.

3 : 8 ratio  
\[ 3\text{Mg(NH}_2\text{)}_2 + 8\text{LiH} \rightleftharpoons 3\text{Li}_{(2+x)}\text{MgN}_2\text{H}_{(2-x)} + (2-3x) \text{LiH} + 3(2+x)\text{H}_2 \]

LiH rich

\[ 0 < x \leq 2/3 \quad X \text{ depends on the condition} \]
Structure of the new intermediate phase
Refinement combined PND and SR-PXD

**PND**

$R_{wp} = 7.29\%$

**SR-PXD**

$R_{wp} = 10.4\%$

Primitive cubic

$a = 5.0246(2) \text{ Å}$

$\text{Li}_{2.6}\text{MgN}_2\text{D}_{1.4}$

$\Rightarrow x \approx 0.6$ for

$\text{Li}_{(2+x)}\text{MgN}_2\text{D}_{(2-x)}$

*Li rich and D poor imide*
PCI: Mg(NH$_2$)$_2$ + nLiH (n=2, 8/3, 4)
Schematic view of the reaction process
Thermodynamic characterization

Isotherms were measured at:
- 220, 200, 180°C for absorption and desorption.
- Plateau pressure much higher than the one without Mg-substitution.

Luo (2006)
# Borohydrides

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<tbody>
<tr>
<td></td>
<td>Wt. %</td>
<td>g H₂/L</td>
<td>-ΔH, kJ/mol H₂</td>
<td>calc.</td>
</tr>
<tr>
<td>LiBH₄</td>
<td></td>
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<tr>
<td>2 LiBH₄ + MgH₂</td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>2 LiBH₄ + Al</td>
<td></td>
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</tr>
<tr>
<td>7 LiBH₄ + 1.75 Mg₂Sn + 0.25 Sn</td>
<td>Li₇Sn₂ + 3.5 MgB₂</td>
<td>6.3</td>
<td>46</td>
<td>184</td>
</tr>
<tr>
<td>NaBH₄</td>
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</tr>
<tr>
<td>2 NaBH₄ + MgH₂</td>
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<tr>
<td>Be(BH₄)₂</td>
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<tr>
<td>Mg(BH₄)₂</td>
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<td>Ca(BH₄)₂</td>
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<tr>
<td>Ca(BH₄)₂ + MgH₂</td>
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<tr>
<td>Zn(BH₄)₂</td>
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<tr>
<td>Al(BH₄)₃</td>
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<td>Sc(BH₄)₃</td>
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<td>Ti(BH₄)₃</td>
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<td>Mn(BH₄)₂</td>
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<td>Zr(BH₄)₄</td>
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*Formation of diborane observed.*
LiBH$_4$

- LiBH$_4$ = LiH + B + 3/2 H$_2$  (13.9 wt%)
  - $P_{eq} = 1$ bar @ 410°C
  - Slow kinetics < 600°C
- 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$_2$
  - LiBH$_4$ + ½ MgH$_2$ = LiH + ½ MgB$_2$ + 5/2 H$_2$
  - Cycled at 330°C
  - TiCl$_3$ used as catalyst

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

LiBH$_4$ AT 293K (20°C)

Orthorhombic symmetry
space group: Pnma (#62)

- $a = 7.17858(4)$ Å
- $b = 4.43686(2)$ Å
- $c = 6.80321(4)$ Å
- Vol: $216.685$ Å$^3$, $Z = 4$

LiBH$_4$ AT 408K (135°C)

Hexagonal symmetry
space group: $P6_3mc$ (#186)

- $a = 4.27631(5)$ Å
- $b = a$
- $c = 6.94844(8)$ Å
- Vol: $110.041$ Å$^3$, $Z = 2$
Dehydrogenation reactions

Alkali metal borohydrides:

\[ M(BH_4) \rightarrow MgH + B + \frac{3}{2}H_2 \]
\[ A(BH_4) \rightarrow AB + 2H_2 \]

Alkaline earth borohydrides:

\[ M(BH_4)_2 \rightarrow MH_2 + 2B + 3H_2 \]
\[ M(BH_4)_2 \rightarrow MB_2 + 4H_2 \]
\[ M(BH_4)_2 \rightarrow \frac{2}{3}MH_2 + \frac{1}{3}MB_6 + \frac{10}{3}H_2 \]
Thermal desorption from LiBH$_4$
Ca(\text{BH}_4)_2

Riktor (2007)
Mg(BH$_4$)$_2$
Mixed systems MgH$_2$ - LiBH$_4$ for changing the stability


Sartori Sabrina, Summer School on Materials for the Hydrogen Society, Reykjavik, June 19-23, 2008
Up-scaling of Solid Storage Tank

**Concept for upscaling of material production processes**

Evaluation of low cost (< 1 Euro/kg) production routes for complex hydrides using catalysed NaAlH₄ as model material

Up-scaling to kg amounts demonstrated

**Design and development of operational prototype solid storage tanks**

Laboratory tank for 0.5 kg of alanate

- Length: 40 cm / Diameter: 6 cm
- Capacity: 20 g H₂

8 kg alanate Pilot tank (currently manufactured)

- Length: 129 cm, Diameter: 34 cm.
- Capacity: 0.4 kg H₂

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Safety experiments

$t=0$ ms

$t=30$ ms

$t=320$ ms

Ti doped NaAlH$_4$

High speed images at different times are shown on the left, the corresponding infrared images are shown on the right.
Estimation for system capacities in different hydrogen storage systems

**Solid materials:**
- Good safety aspect;
- High volumetric density;
- Other projects such as NessHy/NanoHy/FlyHy learned a lot from StorHy work and indicate possibilities in improvement also in gravimetric densities

**Actual**
- Gravimetric capacity of the material: 4 wt%
- Material density: 1270 kg/m$^3$
- Porosity of the bed: 53 %
- Maximum temperature: 300 °C
- Heat transfer coefficient: 0.55 W/mK
- Operating pressure: 100 bar, design pressure 150 bar.
- Capacities of 0.0214 kg/L

**Vision**
- Porosity of the bed: 20 % (compressing the powder)
- Maximum operating pressure: 50 bars
- Maximum temperature: 215 °C
- Capacities of 0.0356 kg/L

**Improved tank?**
- Metal hydride (Mercedes 1982)
- LiBH$_4$/MgH$_2$
- NaAlH$_4$ (improved)
- NaAlH$_4$ (8 kg experimental tank)
- DOE Target (2010)

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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, which is only possible for the pure system under extreme conditions. To make the material reversible under practical conditions, it has to be added with a catalyst. Still not understood the effect of additives;
- For technical applications is not acceptable that after low-pressure rehydrogenation, the system is not rehydrogenated as quickly as prior (system without cycle stability);
- High charging rates under low pressures are still a challenge on the way to a practicable solid-state hydrogen-storage material for fuel-cell-powered cars.