Complex metal hydrides for reversible hydrogen storage

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Hydrogen as a fuel

- Hydrogen gas has almost three times energy content of gasoline (120 MJ/kg vs. 44 MJ/kg)
- $H_2$ Fuel Cells reach >80% efficiency in combined heat and power generation and >50% in electrical
- No natural source of hydrogen; difficult/expensive to produce
- Low density of $H_2$ gas and liquid => low volumetric energy content
- Volumetric compression and storage is problematic

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Energy Storage Workshop, Santa Clara, CA, April 29, 2010
Metal hydrides represent a class of materials with volumetric densities higher than gaseous or liquid hydrogen.

Volume Comparisons for 4 kg Vehicular $\text{H}_2$ Storage

- $\text{Mg}_2\text{FeH}_6$: 26L
- $\text{LaNi}_5\text{H}_6$: 33L
- $\text{H}_2$ (liquid): 57L
- $\text{H}_2$ (200 bar): 110L

Complex metal hydrides

Material Capacity vs. Temperature

[Diagram showing various metal hydrides and their capacities and temperatures]

N. Stetson & G. Sandrock (DOE)
Metal borohydrides represent a class of materials with high gravimetric and volumetric hydrogen densities.

<table>
<thead>
<tr>
<th></th>
<th>Density (g/cm³)</th>
<th>Hydrogen density (kg/m³)</th>
<th>Hydrogen density (mass%)</th>
<th>Heat of formation, ΔH, (kJ/mol)</th>
<th>Melting / Decomposition* T, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiBH₄</td>
<td>0.66</td>
<td>122.1</td>
<td>18.5</td>
<td>-194</td>
<td>278</td>
</tr>
<tr>
<td>NaBH₄</td>
<td>1.07</td>
<td>114.5</td>
<td>10.7</td>
<td>-191</td>
<td>505</td>
</tr>
<tr>
<td>Mg(BH₄)₂</td>
<td>0.78</td>
<td>147.4</td>
<td>14.9</td>
<td>-226</td>
<td>295*</td>
</tr>
<tr>
<td>Ca(BH₄)₂</td>
<td>1.07</td>
<td>124.1</td>
<td>11.6</td>
<td>-302</td>
<td>310*</td>
</tr>
<tr>
<td>Al(BH₄)₃</td>
<td>0.79 (liq.)</td>
<td>133.5</td>
<td>16.9</td>
<td>-131</td>
<td>-64</td>
</tr>
<tr>
<td>Zr(BH₄)₄</td>
<td>1.18</td>
<td>126.2</td>
<td>10.7</td>
<td>-398</td>
<td>29*</td>
</tr>
</tbody>
</table>

2LiBH₄ $\xrightarrow{\Delta}$ 2LiH + 2B + 3H₂  $w_{t\%}H = 13.9$

3Ca(BH₄)₂ $\xrightarrow{\Delta}$ 2CaH₂ + CaB₆ + 10H₂  $w_{t\%}H = 9.6$

Mg(BH₄)₂ $\xrightarrow{\Delta}$ MgB₂ + 4H₂  $w_{t\%}H = 14.9$


S. Orimo, Y. Nakamori, J.R. Eliseo, A. Züttel, C.M. Jensen, *Chem. Rev.*, 2007, 107, 4111.
Reversible borohydrides

$$M(BH_4)_x \leftrightarrow M + xB + 2xH_2$$

Selected examples:

- $2LiBH_4 \leftrightarrow 2LiH + 2B + 3H_2$
  - Züttel et al. Scr. Mater., 2007, 56, 823

- $Mg(BH_4)_2 \leftrightarrow MgB_2 + 4H_2$
  - Severa et al. Chem. Commun. 2010, 46, 421

- $3Ca(BH_4)_2 \leftrightarrow 2CaH_2 + CaB_6 + 10H_2$

Problems & Challenges:

- high dehydrogenation temperatures
- high pressure required for rehydrogenation
- contamination of $H_2$ gas with boron hydrides
- loss of capacity upon cycling
- stable intermediates ($[B_{12}H_{12}]^{2-}$, etc.)

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Hydrogen release from Ca(BH$_4$)$_2$

with Ewa Rönnebro and Mutlu Kartin (Sandia)

**Additive Effect on Ca(BH$_4$)$_2$**

Desorption

**Life-cycle of Ca(BH$_4$)$_2$ with 4wt% PdCl$_2$ Additive**

**Results:**

- Additives have a significant effect on H$_2$ release from Ca(BH$_4$)$_2$
- Significant capacity loss observed upon cycling
Significant improvement in hydrogen desorption of Mg(BH$_4$)$_2$ was observed in the presence of the TiF$_3$/ScCl$_3$ additive.
Hydrogen release from \( \text{Mg(BH}_{4}\text{)}_{2} \)

**Desorption of \( \text{Mg(BH}_{4}\text{)}_{2} \) ball-milled with 5mol% \( \text{TiF}_{3} \) and 5mol% \( \text{ScCl}_{3} \)**

- Up to 14 wt% \( \text{H}_{2} \) released upon heating to 600 °C
- At 90 MPa and 390 °C rehydrogenation of 49% for the sample with additives and 66% for the un-doped sample with additives was observed

11B MAS NMR 
\( \omega_{r} = 15 \text{ kHz} \)

Desorption at 600 °C

Energy Storage Workshop, Santa Clara, April 29, 2010
MgB$_2$ almost exclusively formed upon heating up to 600 °C
Additives distributed relatively uniformly throughout the boride sample
Modeling Complex Equilibria

In collaboration with M.D. Allendorf (Sandia) and Prof. Sholl’s group (Georgia Tech)

DFT (enthalpy, entropy, heat capacity) and FactSage (thermochemical calculations)

\[
\text{LiBH}_4(s) \rightarrow \frac{5}{6}\text{LiH(s)} + \frac{1}{12}\text{Li}_2\text{B}_{12}\text{H}_{12}(s) + \frac{13}{12}\text{H}_2(g)
\]

\[
\text{Mg(BH}_4)_2(s) \rightarrow \frac{5}{6}\text{MgH}_2(s) + \frac{1}{6}\text{MgB}_{12}\text{H}_{12}(s) + \frac{13}{6}\text{H}_2(g)
\]

Evidence of diborane and closo-polyborate cluster formation during borohydride desorption reactions prompted further analysis of $[\text{B}_{12}\text{H}_{12}]^{2-}$ salts.

The Prototype Electrostatic Ground State (PEGS) technique was used for structure determination and $\Delta H$ estimates.

Calculations were performed by Prof. E. Majzoub (University of Missouri, St. Louis).


### Borohydride reactions:

<table>
<thead>
<tr>
<th>Predicted Reactions</th>
<th>Theoretical wt% H$_2$</th>
<th>$\Delta H_{300K}$ kJ/mol H$_2$</th>
<th>$T_c$ (°C)</th>
<th>Experimental Data: wt% H$_2$ (350 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5\text{Mg(BH}_4\text{)}_2 + 2\text{LiBH}_4$</td>
<td>8.4</td>
<td>24.4</td>
<td>-29</td>
<td>6.0</td>
</tr>
<tr>
<td>$5\text{Mg(BH}_4\text{)}_2 + \text{Ca(BH}_4\text{)}_2$</td>
<td>7.7</td>
<td>25.7</td>
<td>-18</td>
<td>4.4</td>
</tr>
<tr>
<td>$5\text{Ca(BH}_4\text{)}_2 + 2\text{LiBH}_4$</td>
<td>6.7</td>
<td>37.9</td>
<td>83</td>
<td>5.2</td>
</tr>
</tbody>
</table>
[B$_{12}$H$_{12}$]$^{2-}$ Destabilization

CaB$_{12}$H$_{12}$ $\xrightarrow{\Delta}$ no CaB$_6$ up to 700 °C

CaB$_{12}$H$_{12}$ + CaH$_2$ $\xrightarrow{\Delta}$ CaB$_6$ + H$_2$

The presence of CaH$_2$ decreases the temperature required to form CaB$_6$ by $\approx$200 °C; the magnitude of the destabilizing effect is similar to the one observed in metal borohydrides.
Are \([B_{12}H_{12}]^{2-}\) species reversible?

The predicted enthalpies of the LiBH\(_4\), Mg(BH\(_4\))\(_2\) and Ca(BH\(_4\))\(_2\) dehydrogenation reactions to form MgB\(_{12}H_{12}\) and CaB\(_{12}H_{12}\) suggest that the reverse processes are feasible.

\[
\begin{align*}
\text{Li}_2\text{B}_{12}\text{H}_{12} + 10 \text{LiH} & \xrightarrow{+13\text{H}_2} 12\text{LiBH}_4 & \Delta H^{300K} = -44.4 \text{ kJ/mol}^* \\
\text{Na}_2\text{B}_{12}\text{H}_{12} + 10 \text{NaH} & \xrightarrow{+13\text{H}_2} 12\text{NaBH}_4 & \Delta H^{300K} = -? \\
\text{MgB}_{12}\text{H}_{12} + 5 \text{MgH}_2 & \xrightarrow{+13\text{H}_2} 6\text{Mg(BH}_4)_2 & \Delta H^{300K} = -29.3 \text{ kJ/mol}^* \\
\text{CaB}_{12}\text{H}_{12} + 5 \text{CaH}_2 & \xrightarrow{+13\text{H}_2} 6\text{Ca(BH}_4)_2 & \Delta H^{300K} = -39.2 \text{ kJ/mol}^*
\end{align*}
\]

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**‘Hot-sintering’ under high H\(_2\)-pressure**

- MB\(_{12}H_{12}\) + Metal hydride + H\(_2\)
- High-energy ball milling for 60 to 180 min
- Hydrogen pressure ≤ 100 MPa in a high-temperature reactor
- Temperature ≤ 550 \(\text{C}\)
- Reaction time: several hours to several days

\[
\begin{align*}
\Delta H^{300K} & \leq 100 \text{ MPa H}_2 \\
\leq 550 \text{ C}
\end{align*}
\]

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Under these conditions individual metal borohydrides display at least partial reversibility!
Rehydrogenation of $[\text{B}_{12}\text{H}_{12}]^{2-}$ salts

Results:
- $\text{CaB}_{12}\text{H}_{12} + 5\text{CaH}_2$ – no borohydride formation up to 500 °C and 90 MPa H₂
- $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and $\text{Na}_2\text{B}_{12}\text{H}_{12}$ – partial hydrogenation to $\text{LiBH}_4$ and $\text{NaBH}_4$ at 500 °C and 90 MPa H₂

- $\text{CaB}_{12}\text{H}_{12}$ is not susceptible to rehydrogenation reactions;
- Rehydrogenation of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and $\text{Na}_2\text{B}_{12}\text{H}_{12}$ occurs in almost quantitative yield at high temperatures and hydrogen pressures.
Neutron Vibrational Spectroscopy

Work done in collaboration with Dr. T. Udovic (NIST)

- NVS data suggest significant conversion of Li$_2$B$_{12}$H$_{12}$ and Na$_2$B$_{12}$H$_{12}$ into LiBH$_4$ and NaBH$_4$
**Motivation:** The presence of both ‘hydridic’ and ‘protic’ hydrogen atoms

\[ M^1(BH_4)_x + M^2(BH_4)_y + zNH_3 \rightarrow M^1M^2(BH_4)_{x+y}(NH_2)_z \]

- The \( BH_4^-\cdot NH_3 \) compounds display increased air- and moisture stability compared to the initial borohydrides
- \( Ca(BH_4)_2\cdot NH_3, MgCa(BH_4)_4\cdot NH_3 \) and \( LiCa(BH_4)_3\cdot NH_3 \) adducts release significant amounts of \( NH_3 \) upon heating, confirmed by gas phase analysis
- New systems based on transition metals (e.g. Ti(III) and Mn(II)) are currently under investigation
Mixed borohydride-amide materials release hydrogen at low temperatures.

Problems include poor reversibility and contamination of H₂ with NH₃.
Path to improved reversibility

Approaches to new complex metal hydrides with improved hydrogen storage characteristics:

- Selection of appropriate destabilizing agents to tune the stability of the intermediate species and render them susceptible to dehydrogenation and rehydrogenation reactions.
- Partial substitution of alkali or alkaline-earth cations with more electronegative cations (e.g. transition metals) to achieve a more efficient electron delocalization and decrease stability.

- Prediction and evaluation of new materials using computational tools.
- Synthesis and testing of promising predicted materials.
- Identification of intermediate compounds formed during dehydrogenation / rehydrogenation.
- Optimization of the cycling characteristics using destabilizing approaches and catalysis.

*Criteria: Gravimetric and volumetric densities, equilibrium pressure and temperature, fast dehydrogenation and rehydrogenation reactions*
Acknowledgements

Sandia National Laboratories:
Jay Keller, Marcina Moreno, Mark Allendorf, Eric Majzoub, Weifang Luo, Joe Cordaro, Mitch Anstey, Ewa Rönnebro (currently at PNNL), Ethan Hecht, Dennis Morrison, George Sartor, Ken Stewart

Metal Hydride Center of Excellence:
Craig Jensen (UH), John Vajo (HRL), Zak Fang (U. Utah), Channing Ann (Caltech), Joseph Reiter (JPL), Jason Zan (JPL), J.-C. Zhao (OSU), John Vajo (HRL), Dan Mosher (UTRC)

Financial Support:
U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy under the Hydrogen Storage Grand Challenge, Metal Hydride Center of Excellence (MHCoE) within DOE's National Hydrogen Storage Project