Synthesis of Nanophase Materials for Thermodynamically Tuned Reversible Hydrogen Storage

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Overview

Timeline
• Project start date: October 1, 2004
• Project end date: December 31, 2010
Percent complete: 90%

Budget
• Total project funding
  DOE share $1M (5 yrs)
  Contractor share $250k (5 yrs)
• Funding for FY07
  DOE share $200k
  Contractor share $50k
• Funding for FY08
  DOE share $200k
  Contractor share $50k

Barriers
(B) Weight and volume of on board hydrogen storage systems
(M) Reversibility of high capacity solid state storage materials
(N) Kinetics (fueling/refueling times) associated with current solid state storage materials

Partners
Interactions/ collaborations:
John Vajo, HRL Laboratories
Vitalie Stavila, Sandia Natl. Lab.
Karl Johnson, Univ. Pittsburgh
David Sholl, Georgia Inst. Tech.
J.C. Zhao, GE/Ohio State Univ.
Terry Udovic, NIST
Joseph Reiter, JPL
Craig Jensen, U. Hawaii
To assess whether thermodynamically tractable reactions based on hydride destabilization, that should be reversible but appear not to be, are kinetically limited.

To enable short hydrogenation times associated with refueling, that will require short solid-state and gas-solid diffusion path lengths.

To address the problems associated with large, light-metal-hydride enthalpies (hydrogen fueling/refueling temperatures) and develop strategies to address thermodynamic issues surrounding the use of these materials through hydride destabilization. Systems of interest determined through “computational screening” by MHCoE partner members.

To understand issues related to grain growth and surface/interface energies, which are vital in order to understand the kinetics of hydrogenation/dehydrogenation reactions.
Approach

- Ball milling of destabilization candidates and gravimetric dehydrogenation and hydrogenation evaluation of thermodynamically appropriate systems, using Sieverts apparatus systems at Caltech and at JPL.
- Analysis of borohydride reaction pathway intermediates, like closo-boranes to see if these structures can be destabilized.
- DFT calculations of specific hydride destabilization formation enthalpies and reaction enthalpies.
- X-ray diffraction for determining reaction product phases.
- NMR analysis (at the Caltech Solid State NMR facility) to determine bonding and phase formation in systems that lack long range crystallographic order.
- Transmission electron microscopy (at the Caltech Kavli Nanoscale Institute and the Material Science TEM facilities) and energy filtered imaging to determine microstructural evolution and phase inhomogeneities in scaffold based systems.
Technical accomplishments: Investigation of 2LiBH$_4$-MgH$_2$ under H$_2$ back pressure via NMR

Background:

• Inconsistencies in determining closo-dodecaborane (MB$_{12}$H$_{12}$) formation. B$_{12}$H$_{12}$ appeared to be ubiquitous in metal borohydride reactions$^{1,2}$ and scaffold experiments of LiBH$_4$$^3$.
• But original destabilization system, 2LiBH$_4$-MgH$_2$, showed reversibility (no NMR of B$_{12}$H$_{12}$) while it has been assumed that B$_{12}$H$_{12}$ intermediates are stable.
• Several studies$^{4-5}$ showed the importance of H$_2$ back pressure to avoid direct decomposition of LiBH$_4$, the case where the hydrogen capacity drops as the discharge/charge cycle goes due to the interference from the stable MB$_{12}$H$_{12}$.
• Uncertainty as to whether B$_{12}$H$_{12}$ suppressed in presence of high (4 bar) backpressure or whether B$_{12}$H$_{12}$ phase destabilized during cycling.
• Our recent work indicated that closo-borane extremely stable, so
• Case revisited to assess phase formation at high and moderate (1.5 bar) backpressure to probe limits of that show that modest back-pressure inadequate to suppress B$_{12}$H$_{12}$ formation.

Technical accomplishments: Can B\textsubscript{12}H\textsubscript{12} be destabilized?

Reaction 6 from V. Ozolins, E. H. Majzoub and C. Wolverton, JACS (2008) shown in table below suggests destabilization route: (6\textsuperscript{*}) Li\textsubscript{2}B\textsubscript{12}H\textsubscript{12} + 6MgH\textsubscript{2} -> 6MgB\textsubscript{2} + 2LiH + 11H\textsubscript{2} but NMR indicates that no MgB\textsubscript{2} formed and that all dehydrogenation from initial MgH\textsubscript{2}

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**Table 2. Predicted Decomposition Reactions for Borohydrides\textsuperscript{a}**

<table>
<thead>
<tr>
<th>reaction</th>
<th>wt % (kg H\textsubscript{2}/kg)</th>
<th>vol density (g H\textsubscript{2}l)</th>
<th>$\Delta H , ^0 \text{K}$</th>
<th>$\Delta H , ^{300} \text{K}$</th>
<th>$\Delta S , ^{300} \text{K}$</th>
<th>$T_c$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(4) Li\textsubscript{2}B\textsubscript{12}H\textsubscript{12} + 2CaH\textsubscript{2} → 2CaB\textsubscript{6} + 2LiH + 7H\textsubscript{2}</td>
<td>5.9</td>
<td>67</td>
<td>43.1</td>
<td>51.1</td>
<td>128.2</td>
<td>123</td>
</tr>
<tr>
<td>(5) Li\textsubscript{2}B\textsubscript{12}H\textsubscript{12} + 6Mg → 6MgB\textsubscript{2} + 2LiH + 5H\textsubscript{2}</td>
<td>3.3</td>
<td>40</td>
<td>53.4</td>
<td>60.2</td>
<td>112.0</td>
<td>259</td>
</tr>
<tr>
<td>(6\textsuperscript{*}) Li\textsubscript{3}B\textsubscript{12}H\textsubscript{12} + 6MgH\textsubscript{2} → 6MgB\textsubscript{2} + 2LiH + 11H\textsubscript{2}</td>
<td>7.1</td>
<td>53</td>
<td>52.4</td>
<td>60.1</td>
<td>123.3</td>
<td>215</td>
</tr>
<tr>
<td>(7) MgB\textsubscript{12}H\textsubscript{12} + 5MgH\textsubscript{2} → 6MgB\textsubscript{2} + 11H\textsubscript{2}</td>
<td>7.5</td>
<td>86</td>
<td>42.1</td>
<td>50.0</td>
<td>123.9</td>
<td>128</td>
</tr>
<tr>
<td>(8) CaB\textsubscript{12}H\textsubscript{12} + CaH\textsubscript{2} → 2CaB\textsubscript{6} + 7H\textsubscript{2}</td>
<td>6.3</td>
<td>85</td>
<td>38.6</td>
<td>47.0</td>
<td>130.7</td>
<td>86</td>
</tr>
<tr>
<td>(9) CaB\textsubscript{12}H\textsubscript{12} + 3MgH\textsubscript{2} → 3MgB\textsubscript{2} + CaB\textsubscript{6} + 9H\textsubscript{2}</td>
<td>7.0</td>
<td>91</td>
<td>45.2</td>
<td>53.2</td>
<td>126.7</td>
<td>144</td>
</tr>
</tbody>
</table>
Technical accomplishments: Can B$_{12}$H$_{12}$ be destabilized? cont’d

Given the apparent ubiquity of B$_{12}$H$_{12}$ formation as shown below for example in the work that describes the improved kinetics of LiBH$_4$ in a carbon scaffold as shown from our analysis below, some effort was expended in probing for evidence that this phase might be destabilized.

An assessment of other reactions suggested in the paper by Ozolins, et al were run in order to probe for destabilization reactions, were not successful in destabilizing the B$_{12}$H$_{12}$ phase.

Reaction 4 in that paper:  
\[
\text{Li}_2\text{B}_{12}\text{H}_{12} + 2\text{CaH}_2 \rightarrow 2\text{CaB}_6 + 2\text{LiH} + 7\text{H}_2
\]
was run in both directions at 400°C, no hydrogen was released.

Reaction 8, CaB$_{12}$H$_{12}$ + CaH$_2$ -> 2CaB$_6$ + 7H$_2$ was run from right to left at >90 bar pressure with no hydrogen uptake that could be measured. We note however that V. Stavila of Sandia National Lab. was able to run this reaction but temperatures of >450°C were required.

In addition, reaction 14 from that paper:  
\[
\text{Ca(BH}_4)_2 \rightarrow \text{CaB}_{12}\text{H}_{12} + 5\text{CaH}_2 + 13\text{H}_2
\]
was run from right to left with no hydrogen uptake that could be measured.

In addition, reaction 15 from that paper:  
\[
3\text{Ca(BH}_4)_2 \rightarrow \text{CaB}_6 + 2\text{CaH}_2 + 10\text{H}_2
\]
was run in both directions and partial reversibility was seen when the reaction is run from left to right (60%) but no reaction was seen in going from right to left.

Characteristic -12 ppm peak from Li$_2$B$_{12}$H$_{12}$ shown from scaffold dehydrogenated LiBH$_4$ from “Enhanced Hydrogen Storage Kinetics of LiBH$_4$ in Nanoporous Carbon Scaffolds, A. F. Gross, J. J. Vajo,” S. L. Van Atta, and G. L. Olson, J. Phys. Chem. C (2008), 112, 5651-5657
Technical accomplishments: Investigation of initial $2\text{LiBH}_4-\text{MgH}_2$ reaction under $\text{H}_2$ back pressure via NMR

6 samples analyzed via NMR for this work:

1. LCS-109: The as-prepared $2\text{LiH} + \text{MgB}_2$ mixture after milling for 1 hr.
2. LCS-109ua: Half of the as-prepared sample LCS-109 after the first hydrogenation.
3. LCS-109ub: The same sample after dehydrogenation into 4 bar $\text{H}_2$.
4. LCS-109uc: The rehydrogenation of LCS-109ub after it had been dehydrogenated in 4 bar $\text{H}_2$.
5. LCS-109ud: The other half of sample LCS-109ua after dehydrogenation into vacuum.

Figure at right shows temperature ramp (dotted trace) and uptake plots for samples into 4 bar hydrogen backpressure or into vacuum.
Technical accomplishments: Investigation of $2\text{LiBH}_4$-$\text{MgH}_2$ under $\text{H}_2$ back pressure via NMR (cont’d)

- NMR shows intermediate formation due to direct decomposition of $\text{LiBH}_4$ is directly responsible for the degraded performance of the hydrogen storage system.
- 4 bar $\text{H}_2$ back pressure suppress the $\text{Li}_2\text{B}_{12}\text{H}_{12}$ formation.
- Alternative reaction route for $\text{M(BH}_4)_n$ alone without $\text{MH}_2$ has not been fully studied. $\text{H}_2$ back pressure study might be helpful.

### Phases identified and quantified by NMR

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\text{MgB}_2$</th>
<th>$\text{LiBH}_4$</th>
<th>a-B</th>
<th>$\text{B}<em>{12}\text{H}</em>{12}$ related</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCS-109</td>
<td>0.98</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LCS-109a</td>
<td>0.01</td>
<td>0.96</td>
<td>0.02</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>LCS-109b</td>
<td>0.95</td>
<td></td>
<td></td>
<td>0.05</td>
</tr>
<tr>
<td>LCS-109c</td>
<td>0.01</td>
<td>0.94</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>LCS-109d</td>
<td>0.04</td>
<td>0.14</td>
<td>0.29</td>
<td>0.53</td>
</tr>
<tr>
<td>LCS-109e</td>
<td>0.02</td>
<td>0.23</td>
<td>0.18</td>
<td>0.58</td>
</tr>
</tbody>
</table>

Negligible amount of intermediate formed.
To better assess the physicochemical property of metal dodecaborates (MB$_{12}$H$_{12}$, M=Li, K, Ca, Mg, etc), during desorption of metal borohydrides, the dynamics was probed by static variable-temperature NMR spectroscopy.

Crystal structure of Li$_2$B$_{12}$H$_{12}$

- $^{11}$B (I=3/2, quadrupole) static lineshape a sensitive measure of molecular jumping motion.
- Disappearance of powder pattern of satellite transition (peaks ±1100 ppm) and narrowing of central transition (~ 0 ppm) seen as T increases.
- Depending on cation size and crystal structure, dynamic activation energy varies widely (note difference between Li and K seen for first time).

Technical accomplishments: Destabilization of dodecaborates (MB_{12}H_{12}, M=Li, Na, K)

- In collaboration with Sandia National Laboratory (V. Stavila) conversion of MB_{12}H_{12} to M(BH_{4})_{n} via high pressure evaluated. As noted earlier, our previous attempts at lower pressure (H_{2} pressure up to 90 bar) of MB_{12}H_{12} + MH_{n} reactions unsuccessful despite estimated low thermodynamic barrier\(^{1}\)

\[
\begin{align*}
\text{Li}_{2}\text{B}_{12}\text{H}_{12} + 10 \text{LiH} & \rightarrow 12\text{LiBH}_{4} \quad \Delta H^{300K} = -44.4 \text{ kJ/mol}\* \\
\text{Na}_{2}\text{B}_{12}\text{H}_{12} + 10 \text{NaH} & \rightarrow 12\text{NaBH}_{4} \quad \Delta H^{300K} = ? \\
\text{MgB}_{12}\text{H}_{12} + 5 \text{MgH}_{2} & \rightarrow 6\text{Mg(BH}_{4}\text{)}_{2} \quad \Delta H^{300K} = -29.3 \text{ kJ/mol}\* \\
\text{CaB}_{12}\text{H}_{12} + 5 \text{CaH}_{2} & \rightarrow 6\text{Ca(BH}_{4}\text{)}_{2} \quad \Delta H^{300K} = -39.2 \text{ kJ/mol}\*
\end{align*}
\]

- SNL performed reactions using high H\(_{2}\) (930 bar) pressure at T> 550°C after high-energy ball milling over 1 hour. \(^{1}\)B MAS NMR analysis shows formation of M(BH\(_{4}\))\(_{n}\) in significant fraction (see Table for the ratio between the reactant and product). Destabilization of the closo-borane phase possible but conditions required for this are extreme.

\(^{1}\)V. Ozolins, E. H. Majzoub and C. Wolverton, JACS (2008)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Conditions</th>
<th>M(<em>{2})B(</em>{12})H(_{12})</th>
<th>MBH(_{4})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(<em>{2})B(</em>{12})H(_{12}) + 10NaH</td>
<td>500 °C, 793 bar H(_{2}), 72 h</td>
<td>9.3</td>
<td>89.6</td>
</tr>
<tr>
<td>Li(<em>{2})B(</em>{12})H(_{12}) + 10LiH</td>
<td>500 °C, 931 bar H(_{2}), 72 h</td>
<td>9.1</td>
<td>89.6</td>
</tr>
<tr>
<td>K(<em>{2})B(</em>{12})H(_{12}) + 10KH</td>
<td>500 °C, 931 bar H(_{2}), 72 h</td>
<td>7.8</td>
<td>92.2</td>
</tr>
</tbody>
</table>
• Previously believed that B\textsubscript{12}H\textsubscript{12} formation a universal problem in destabilization reactions with borohydrides that would lead to irreversible hydrogenation/dehydrogenation reactions.

• Destabilization reactions of the closo-boranes suggested by theory not achievable under normal experimental conditions.

• Conditions of high pressure and temperature (performed at Sandia National Laboratory) show that borohydride phase can be reformed.

• Closo-borane formation can be minimized by dehydrogenation into modest (4 bar) back pressure whereas dehydrogenation into vacuum or 1.5 bar pressure results in dodeca-borane formation.