Design of Novel Multi-Component Metal Hydride-Based Mixtures for Hydrogen Storage

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Overview

Timeline
- Project Start Date: 9/1/08
- Project End Date: 8/31/13 (1 year no-cost extension to 8/31/14)
- ~100% complete

Budget
- Total Project Value: $2,714,400
- Cost Share: $554,400
- DOE Share: $2,160,000
- DOE Funding Spent*: $2,092,372
  *as of 3/31/14

Barriers
- Barriers addressed
  - O. Lack of Understanding of Hydrogen Physisorption and Chemisorption
  - A. System Weight and Volume
  - E. Charging/Discharging Rates

Partners
- Northwestern University
- UCLA
- Ford Motor Company
- Project lead: Northwestern University
Relevance – Objectives and Approach

Our project: Combinations of materials to form novel multicomponent reactions

Hydrogen Storage Measurements and Auto Perspective
Yang and Veenstra, Ford; Hwang (NMR), Caltech

Computational Prediction of Novel Reactions
Wolverton, NU; Ozolins, UCLA

Kinetics/Catalysis/Synthesis Experiments
Kung, NU
Shore, Ohio St.

NORTHWESTERN UNIVERSITY
UCLA
Ford
Computational Screening of Reactions – Thermodynamics and Kinetics

• Tools for Computational Prediction of New Materials/Reactions
  – (High-Throughput) Density Functional Theory:
    • Open Quantum Materials Database (OQMD) - Wolverton
  – Crystal Structure Prediction:
    • Prototype Electrostatic Ground State (PEGS) – Majzoub and Ozolins
  – Prediction of Decomposition Pathways:
    • Grand Canonical Linear Programming (GCLP) – Ozolins and Wolverton

Note: None of these tools were developed in the current project. They were either developed previously or in other projects, but utilized/leveraged here.
Computational Screening of Reactions – Thermodynamics and Kinetics

We have used DFT+computational tools to look for reactions in many systems:

- **Li-Mg-N-H** (Advanced Materials 19, 3233 (2007))
- **Li-Al-N-H** (in prep, 2013)
- **Mg-B-N-H** (in press, 2014)
- **Ca-B-N-H** (Phys. Rev. B 84, 134103 (2011))
- **Li-Mg-Ca-B-H** (J. Amer. Chem. Soc. 131, 230 (2009))
- **Li-Mg-B-N-H** (unpublished)

Rather than doing this one system at a time...
Can we just compute all possible storage reactions, involving all known crystalline phases?
High-Throughput Discovery of **All Possible Storage Reactions**

**Open Quantum Materials Database (OQMD)**

- **Open** – An online (oqmd.org), freely available database…
- **Quantum** – … of self-consistently DFT-calculated properties…
- **Materials** – … for ~30,000 experimentally observed and 250,000 hypothetical structures…
- **Database** – … built on a standard and extensible database framework.

Scan over hundreds of possible alloy systems; For each system, need to compute (quickly) ground state hull of all combinations of known phases at all stoichiometries.

Saal, Kirklin, Aykol, Meredig, and Wolverton "*Materials Design and Discovery with High-Throughput Density Functional Theory: The Open Quantum Mechanical Database (OQMD)*", JOM 65, 1501 (Nov. 2013)
Technical Accomplishments:
High-Throughput Discovery of All Possible Thermodynamic Storage Reactions

How many thermodynamically-allowed $H_2$ storage reactions are there?

- Any compound in the ICSD with elements from
  \{H, Li, B, N, Na, Mg, Al, Si, K, Ca, Sc, Ti\} (and unit cell < 60 atoms)
  832 total phases considered, 171 contained hydrogen

- **Total Reactions**
  4212 reactions (with $\Delta H < 150$ kJ/mol $H_2$)

- **Reactions w/ good enthalpy**
  434 reactions with $\Delta H$ between 20-40 kJ/mol $H_2$

- **Reactions w/ high capacity**
  108 reactions with > 6 wt. % $H_2$
  43 reactions with > 8 wt. % $H_2$

- **Reactions w/ good enthalpy and high capacity**
  22 reactions with $\Delta H$ 20-40 kJ/mol $H_2$, > 6 wt. %
  7 reactions with $\Delta H$ 20-40 kJ/mol $H_2$, > 8 wt. %
Technical Accomplishments (previous):
Novel, High-Capacity Predicted Reactions

- High-throughput computational screen through all possible high capacity reactions with suitable thermodynamics in Li-Mg-B-N-H quinary.
- We focus on the reactions in bold (grayed out reactions were known previously and have been studied experimentally)

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Wt.% H₂</th>
<th>Vol. H₂</th>
<th>ΔH³⁰⁰K (kJ/mol H₂)</th>
<th>ΔS³⁰⁰K (J/mol-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2(NH₄)₂B₁₂H₁₂ → 4BN + B₂₀H₁₆ + 12H₂</td>
<td>6.81</td>
<td>62</td>
<td>17</td>
<td>104</td>
</tr>
<tr>
<td>5Mg(BH₄)₂ + 2LiBH₄ → 5MgH₂ + Li₂B₁₂H₁₂ + 13H₂</td>
<td>8.37</td>
<td>66</td>
<td>24</td>
<td>104</td>
</tr>
<tr>
<td>6Mg(BH₄)₂ → 5MgH₂ + MgB₁₂H₁₂ + 13H₂</td>
<td>8.10</td>
<td>65</td>
<td>29</td>
<td>100</td>
</tr>
<tr>
<td>B₂₀H₁₆ → 20B + 8H₂</td>
<td>6.95</td>
<td>77</td>
<td>33</td>
<td>111</td>
</tr>
<tr>
<td>5MgH₂ + MgB₁₂H₁₂ → 6MgB₂ + 11H₂</td>
<td>7.46</td>
<td>81</td>
<td>44</td>
<td>115</td>
</tr>
</tbody>
</table>

- Combination of 1ˢᵗ and 4ᵗʰ reactions above gives a very high capacity reaction:

\[
2(NH₄)₂B₁₂H₁₂ \rightarrow 4BN + B₂₀H₁₆ + 12H₂ \rightarrow 4BN + 20B + 20 H₂
\]

17-33 kJ/mol H₂
11.3 wt.% H₂
103 g H₂/L
Technical Accomplishments (previous):
Interstitial $H_2$ flux in $B_{20}H_{16}$ and mass transport activation energy

- Low activation energy for interstitial $H_2$ in $B_{20}H_{16}$
- Mass transport is likely to be fast in this system while it is rate limiting in many others
- $B_{20}H_{16}$ extremely promising – first $H_2$ storage reaction of known compound with 1) high capacity, 2) good thermodynamics, and 3) predicted fast mass transport kinetics!

### Activation energy for mass transport

<table>
<thead>
<tr>
<th>Process</th>
<th>Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rehydrogenation</td>
<td>6</td>
</tr>
<tr>
<td>Dehydrogenation</td>
<td>63</td>
</tr>
</tbody>
</table>
Technical Accomplishments:

Synthesis of icosaborane-16 ($\text{B}_{20}\text{H}_{16}$) 
(subcontract with S. Shore, OSU)

- Several methods have been reported for the preparation of icosaborane-16 ($\text{B}_{20}\text{H}_{16}$) but they were carried out under extreme conditions and with low yields 9 to 15%.
- No commercial source is available.
- The method we used in this project is the modified catalytic pyrolysis of decaborane-14 ($\text{B}_{10}\text{H}_{14}$). The reported yields for this procedure range from 10 to 15% [1].

Technical Accomplishments:

Synthesis of icosaborane-16 \((B_{20}H_{16})\) – (Shore, OSU)

- The synthesis of catalyst, methylaminodimethylborane \((\text{NHMeBMe}_2)\)

\[ \text{11B NMR spectrum of MeHN=BMe}_2 \text{ in } d_8\text{-toluene} \]

\[ \text{1H NMR spectrum of MeHN=BMe}_2 \text{ in } d_8\text{-toluene} \]

- The synthesis of icosaborane-16

- The collection and characterization of icosaborane-16

\[ \text{11B NMR spectrum of icosaborane-16 in CH}_2\text{Cl}_2 \text{ (prepared in Dr. Shore’s group) } \]

( NMR peaks: 10.8, 3.7, -3.2, -5.6 )

\[ \text{11B NMR 2D spectrum of icosaborane-16}^{[2]} \]

Notes about synthesis

• We obtained 46mg product, which the yield is about 5%.
• Ran out of funds/time before characterization other than NMR could be performed.
• We have employed all of the conditions of experiment described in the published paper on the B20 synthesis but produce yields significantly less than those reported in the literature.
• Possible that the material for the catalyst, which we purchased, is not good, or perhaps problems with the temperature for making the catalyst active as listed in the literature.
Icosaborane-16 (B$_{20}$H$_{16}$) – Conclusions and Suggested Future Work

• B$_{20}$H$_{16}$ unique and potentially very interesting: Only H$_2$ storage reaction of known compound with 1) high capacity, 2) good thermodynamics, and 3) predicted fast mass transport kinetics

• Of course, there are drawbacks, but because of this unique combination of characteristics, recommend that more future work on this reaction is warranted.

• Synthesis proved difficult, with low yield.

• Future experimental work should try to validate predicted beneficial attributes of material; if validated, more focused effort should be performed to overcome any potential drawbacks (e.g., low yield synthesis, low-cost synthesis, possible kinetic limitations)
(Previous) Technical Accomplishments:
Experimental Testing of Predicted Reactions

-29 °C

\[ 5\text{Mg(BH}_4\text{)}_2 + 2\text{LiBH}_4 \rightarrow \text{Li}_2\text{B}_{12}\text{H}_{12} + 5\text{MgH}_2 + 13 \text{H}_2 \quad 8.4 \text{ wt.\% H}_2 \]

What are (non-crystalline) reaction products? Do they inhibit reversibility?

*(NMR subcontract with S. Hwang, Caltech)*
Technical Accomplishments (previous): NMR Experiments of Mixed borohydride system $2\text{LiBH}_4 + 5\text{Mg(BH}_4\text{)}_2$

Solid state NMR characterization upon $\text{H}_2$ desorption reactions

- Multinuclear and high resolution (MAS) solid state NMR experiments
- Samples include the as-milled mixture of 2:5 borohydrides and solid residue after $\text{H}_2$ desorption.
- $^1\text{H}$ and $^{11}\text{B}$ NMR show decrease of BH$_4$ (~ -41 ppm peak for both LiBH$_4$ and Mg(BH$_4$)$_2$)
- Desorbed borane species was mainly characterized by a broad -26 ppm peak (see following slides) after thermal heating above 280 C.
- Note that -26 ppm peak cannot be due to Li$_2$B$_{12}$H$_{12}$ of which resonance is expected at -15 ppm.
All $[\text{B}_n\text{H}_m]$ intermediates have higher reaction energies than MgB$_{12}$H$_{12}$. Only the reactions to MgB$_2$H$_6$ and Mg$_3$(B$_3$H$_6$)$_2$ are close to the MgB$_{12}$H$_{12}$ convex hull.

Borane species detected by $^{11}$B NMR

- Besides the sharp -17.7 ppm and a broad peak at -1 ppm (amorphous boron), the main -26 ppm peak represents the major boron species.
- Possible species for of -26 ppm peak: diborane dianion$^{2,3}$ - Li$_2$B$_2$H$_6$, MgB$_2$H$_6$
- -17.7 and -48.6 ppm: Li$_2$B$_5$H$_9$ or MgB$_5$H$_9$ like$^3$

<table>
<thead>
<tr>
<th>shift (ppm)</th>
<th>line width(Hz)</th>
<th>rel Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1.00</td>
<td>2880</td>
<td>0.15</td>
</tr>
<tr>
<td>-17.66</td>
<td>240</td>
<td>0.02</td>
</tr>
<tr>
<td>-26.50</td>
<td>2080</td>
<td>0.45</td>
</tr>
<tr>
<td>-42.45</td>
<td>545.9664</td>
<td>0.17</td>
</tr>
<tr>
<td>-42.54</td>
<td>109.0432</td>
<td>0.08</td>
</tr>
<tr>
<td>-43.94</td>
<td>1786.133</td>
<td>0.13</td>
</tr>
</tbody>
</table>

$^1$Hermanek, S. Chemical Reviews 1992, 92 (2), 325-362.


2LiBH$_4$+5Mg(BH$_4$)$_2$

- At lower temperatures, a $^{11}$B peak at -30.5 ppm appeared (200 °C).
- The peak could possibly be assigned to B$_3$H$_8$ formation. However, its formation was not in significant quantity (see green line in the stack plot), and other sharp peaks at -48.6 ppm and -17.8 ppm were accompanied.
- After heating at 200 °C, the reduction in hydrogen content measured by $^1$H NMR was less than 10% (see [H] plot). [H] plot for the new batch showed noticeable difference from the first batch that contains boron oxide in large fraction.

- Yan, Y et al proposed the following reaction route for B$_{12}$H$_{12}$$^{2-}$ formation.
- Assigning -26 ppm peak for B$_2$H$_6$$^{2-}$, and -17.8 and -48.6 ppm peaks for B$_5$H$_9$$^{2-}$, the sequence of products is inconsistent.

Fig. 4 Schematic illustration of formation process of [B$_{12}$H$_{12}$]$^{2-}$ from [BH$_4$]$^{-}$.


Technical Accomplishments: $^{11}$B NMR calculations – Using DFT to help interpret NMR experimental data

**Collaboration w/ C. Pickard, UCL**

DFT-NMR calculations of possible $\text{Mg(BH}_4\text{)}_2$ decomposition products:

$\text{Mg(BH}_4\text{)}_2, \text{MgB}_{12}\text{H}_{12}, \text{MgB}_2\text{H}_6, \text{Mg(B}_3\text{H}_8\text{)}_2, \text{Mg}_3(\text{B}_3\text{H}_6\text{)}_2$

The theoretically calculated $^{11}$B NMR of $[\text{B}_{12}\text{H}_{12}]$ is in good agreement with the experimental measurements.

From experimental NMR measurements (Cal. Tech.), there has a strong peak around -50 ppm, which is also present in our theoretical $\text{Mg}_3(\text{B}_3\text{H}_6\text{)}_2$ NMR calculations. Thus, the agreement is in accord with our previous theoretical prediction of $\text{Mg}_3(\text{B}_3\text{H}_6\text{)}_2$ as a possible decomposition product.

The experimental NMR suggested $[\text{B}_n\text{H}_m]$ region ($\sim$-30ppm) needs further investigation (see subsequent slides).
**Technical Accomplishments**

To clarify role of possible $B_3H_8$ products, NMR experiments and calculations performed for known pure $B_3H_8$ compounds, $NaB_3H_8$ and $KB_3H_8$. Samples provided by J.C. Zhao and X. Chen, Ohio State University.

$^1H$ and $^{11}B$ MAS NMR of $MB_3H_8$

The center band line shapes of both Na and K version of $B_3H_8^-$ as well as the corresponding $^1H$ MAS NMR spectra are shown below.

- Both samples show the presence of minor contaminant ($\sim-40$ and $\sim-43$ ppm) which are nominally supposed to be $BH_4^-$ ion, and their NMR shift positions match with $NaBH_4$ and $KBH_4^-$. 
Technical Accomplishments

$^{11}$B NMR of KB$_3$H$_8$

- According to literature$^1$, while B atoms are stationary below 316 K (phase transition to isotropic phase), but NMR sees all borons equivalent due to an exchange mechanism, and our exp $^{11}$B NMR is also showing one B environment and consistent with previous reports.
- $C_Q$ and $\eta_Q$ are in agreement with literature$^2$ values (0.96 MHz and 0.76, respectively)
- $^{11}$B appears to experience bit more distortion around B coordination (higher $C_Q$ and $\eta$) compared to NaB$_3$H$_8$.
- $^{39}$K NMR was not attempted since its resonance frequency is too low at our magnet.

### Technical Accomplishments: $^{11}$B NMR – DFT calculations, collaboration with C. Pickard, UCL

$^{11}$B NMR reference standard calibration: $\delta_{\text{ref}}$

<table>
<thead>
<tr>
<th></th>
<th>MBH$_4$</th>
<th>LiBH$_4$-LT</th>
<th>LiBH$_4$-HT</th>
<th>Mg(BH$_4$)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{11}$B Chemical shielding ($\delta$) (ppm)</td>
<td></td>
<td>141.9</td>
<td>147.3</td>
<td>140.80</td>
</tr>
</tbody>
</table>

$\Delta \delta = \delta_{\text{ref}} - \delta$

$\Delta \delta_{\text{exp}} \approx -40$ ppm

$\delta_{\text{ref}} \approx 100.6$ ppm

The different $^{11}$B NMR in LiBH$_4$-HT is due to the different B-H bond length.
Technical accomplishments:

$[\text{B}_3\text{H}_8]$ $^{11}\text{B}$ NMR: calculations vs. experiments

DFT calculations of $\text{B}_3\text{H}_8$ show two $^{11}\text{B}$ peaks, consistent with the two B environments. But, experimental measurements show only one peak, due to the fast H exchange within the anion group.

Averaging these two DFT peaks are in good agreement with the experimental measurements. Thus $\text{Mg}(\text{B}_3\text{H}_8)_2$ is consistent with observed product at ~30ppm, but only present at low temperatures and in low concentrations.
With the combined NMR experiments and DFT calculations, we can assign now most of the peaks in the observed products. The current or Ref[1] measured peak ~-25ppm is still unknown. Even though Ref[1] suggests that the peak belongs to [B₂H₆], our theoretical calculations on [B₂H₆] show a different peak position.

ZnCl$_2$ assisted Dehydrogenation of 1:1 LiBH$_4$-Mg(BH$_4$)$_2$

Rationale:
- LiZn$_2$(BH$_4$)$_5$ was reported to have very low decomposition temperature,$^1$ lower than LiBH$_4$-Mg(BH$_4$)$_2$.
- However, decomposition of LiZn$_2$(BH$_4$)$_5$ leads to evolution of B$_2$H$_6$.$^1$

Objective: To investigate the effect of the addition of ZnCl$_2$ or ZnCl$_2$/carbon mixture on the decomposition of LiBH$_4$-Mg(BH$_4$)$_2$.

Approach:
- Add small quantities of ZnCl$_2$ and to see if B$_2$H$_6$ formation is suppressed.

  B$_2$H$_6$ is formed by the following reaction:
  $10$LiBH$_4$ + $5$ZnCl$_2$ = $5$Zn + $10$ LiCl + $5$B$_2$H$_6$ + $5$H$_2$
  Corresponding reaction between Mg(BH$_4$)$_2$ and ZnCl$_2$ has not been reported.

  Suppression of B$_2$H$_6$ formation will be indicated by larger quantity of low temperature H$_2$ release than that shown by the equation above.
- Explore whether carbon can also suppress B$_2$H$_6$ formation. Test 2 different types of carbon: carbon molecular sieve (Y-carbon) and graphitic carbon nitride (Carbodeon Corporation)

Results: ZnCl$_2$ addition increased H$_2$ release at low temperatures from LiBH$_4$- Mg(BH$_4$)$_2$ mixed hydrides. Comparing curves b, c, and d: more H$_2$ released with more ZnCl$_2$. 

a = LiBH$_4$

b = mixed hydride[LiBH$_4$:Mg(BH$_4$)$_2$=1:1]

c = mixed hydride + ZnCl$_2$ (BH$_4$/Zn=43.3)

d = mixed hydride + ZnCl$_2$ (BH$_4$/Zn=19.9)
Results: Evidence that indicates little or no B$_2$H$_6$ formation.

Total amount of gas released at low temperature (up to 185 °C) is much higher than that corresponding to formation of B$_2$H$_6$ and H$_2$ according to reaction A. It is consistent with reaction B.

A: 10LiBH$_4$ + 5ZnCl$_2$ = 5Zn + 10LiCl + 5B$_2$H$_6$ + 5H$_2$ (1 mole of B$_2$H$_6$ is treated as 1 mole of H$_2$)
B: 10LiBH$_4$ + 4ZnCl$_2$ = 20 H$_2$ + Zn and boron and Li decomposition products
Result: addition of carbon to ZnCl₂ further improved low temperature H₂ released from LiBH₄-Mg(BH₄)₂

- a = mixed hydride [LiBH₄:Mg(BH₄)₂ = 1:1]
- b = mixed hydride + ZnCl₂ (BH₄/Zn = 19.9)
- c = mixed hydride + ZnCl₂ + carbon-nitride (BH₄/Zn = 26.7)
- d = mixed hydride + ZnCl₂ + carbon (BH₄/Zn = 26.4)

Similar wt. % hydride in dehydriding mixture of b, c and d (78.6, 76.6 and 76.5)
Identify the kinetic barriers for re-hydrogenation of MgB₂

- What are the rate-limiting steps for MgB₂? (mass transport, nucleation, dissociation, diffusion, or others?)

We investigated the H₂ dissociation and H diffusion on the Mg-terminated MgB₂ (0001) surface
Identify the kinetic barriers for re-hydrogenation of MgB₂

<table>
<thead>
<tr>
<th></th>
<th>Barriers (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissociation</td>
<td>0.89</td>
</tr>
<tr>
<td>Diffusion</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Computational prediction of dopants that lower dissociation, diffusion barriers (or both).
Identify the kinetic barriers for re-hydrogenation of MgB$_2$

We studied the interstitial H diffusion in bulk MgB$_2$

KMC calculations results:
- $D_x = D_y = 0.22$ eV
- $D_z = 0.38$ eV

$x$, $y$ plane: parallel Mg, B layers
$z$ direction: perpendicular B layers

Low barriers for H diffusion in the bulk of MgB$_2$
Identify the kinetic barriers for re-hydrogenation of MgB$_2$

Barriers:
- High: H$_2$ diss. on the surface
- Low: H diff. in the bulk

Doping Pd can reduce diss. barrier

<table>
<thead>
<tr>
<th>Process</th>
<th>Barriers (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Dissociation</td>
<td>0.89 eV</td>
</tr>
<tr>
<td>Pd-doped surface Diss.</td>
<td>0.17 eV</td>
</tr>
<tr>
<td>Surface Diff.</td>
<td>0.14 eV</td>
</tr>
<tr>
<td>Pd-doped surface Diff.</td>
<td>0.12 eV</td>
</tr>
<tr>
<td>H diffusion through B-Mg layers</td>
<td>0.41 eV</td>
</tr>
<tr>
<td>H diff. within B-Mg layers</td>
<td>0.22 eV</td>
</tr>
</tbody>
</table>
2LiBH$_4$+5Mg(BH$_4$)$_2$ – Conclusions and Suggested Future Work

- DFT discovery of this reaction as high capacity, and thermodynamically reversible; However, like most borohydrides, mass transport is a significant kinetic limitation to reversibility.
- **Kinetics** of high-capacity borohydride reactions almost always limiting factor - thermodynamic problems solved by appropriate combinations, i.e., 2LiBH$_4$+5Mg(BH$_4$)$_2$
- Measurements suggest that the 2LiBH$_4$+5Mg(BH$_4$)$_2$ reaction is at least partially reversible.
- Computations also suggest some strategies to reduce kinetic barriers for the hydrogenation of MgB$_2$.
- NMR experiments of 2LiBH$_4$+5Mg(BH$_4$)$_2$ show a number of intermediates or decomposition products. Many of these were identified via a combination of experiment and DFT calculations of NMR spectra.
- Future work on this system should be focused on: 1) more clearly defining the reversible (and kinetically-limited) portions of the reaction, 2) finding a suitable catalyst to overcome kinetic limitations.
Technical Accomplishments: New Theoretical Predictions

- **Kinetics** of high-capacity borohydride reactions almost always limiting factor - **thermodynamic** problems solved by appropriate combinations, i.e., \(2\text{LiBH}_4 + 5\text{Mg(BH}_4)_2\)

- **All computational efforts now focused on calculations of kinetic barriers (diffusion, mass transport, surface dissociation, etc.)**

- Diffusion & mass transport (required for fast kinetics)
  - Mass transport in LiBH\(_4\)
  - Al diffusion in B\(_{20}\)H\(_{16}\)

- H\(_2\) kinetic studies on MgB\(_2\)(0001) surfaces and bulk (see subsequent slides): dissociation and diffusion
Collaborations

PI’s/co-PI’s

Chris Wolverton (Northwestern, lead)
  Harold Kung (Northwestern)
  Vidvuds Ozolins (UCLA)
Mike Veenstra (Ford, no-cost)
  Jun Yang (Ford, no-cost)
S. G. Shore (OSU, subcontract)
S. Hwang (Caltech, subcontract)

Outside Collaborators:

D. Siegel (U. Michigan)
  E. Majzoub (UMSL)
G. Ceder, N. Marzari (MIT)
  C. Brown (NIST)
  T. Burrell (LANL)
  T. Autrey (PNNL)
F.-C. Chuang (Nat’l Sun Yat-Sen U)
  J. C. Zhao (OSU)
Summary – Technical Accomplishments

• Used computational tools and high-throughput machinery to survey high capacity, thermodynamically-reversible reactions.

• Focused efforts on two main reactions, predicted to have high capacity and suitable thermodynamics for H2 storage applications, 2LiBH4 + 5Mg(BH4)2 and B20H16.

• B20H16 extremely promising – *first known H2 storage reaction with high capacity, good thermodynamics, and computational predicted fast mass transport kinetics!*

• Theoretically predicted that mass transport in B20H16 is fast. Subcontract at OSU focused on synthesis of B20H16 compound (synthesis and NMR characterization performed; project ran out of time/funds before full desorption, kinetics, and reaction products could be performed)

• H2 desorption and decomposition pathways have been studied in \([2\text{LiBH}_4 + 5\text{Mg(BH}_4\text{)}_2]\) using NMR; reaction products consistent with theoretically predicted B2H6 anion. Using combination of experiments and DFT, able to assign almost all reaction products. Still one uncertain product (~-25ppm).

• Computational survey of dopants that lower surface dissociation or diffusion for MgB2 rehydrogenation

• Addition of ZnCl2 (and carbon) to LiBH4+Mg(BH4)2 mixture results in (slight) increase in hydrogen desorption at lower temperatures