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

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Overview

Timeline
• Project Start Date: 9/1/08 (Funding started Feb. 09)
• Project End Date: 8/31/13
• ~60% complete

Budget
• Total Budget: $2714K
  – DOE Share: $2160K
  – Contractors Share: $554K
• Funding for FY11: $200K
• Planned FY12: $400K

Barriers
• Barriers addressed
  – P. 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 - Project Objectives

• Our project: Combine materials from distinct categories to form novel multicomponent reactions

• Examples of systems to be studied include mixtures of complex hydrides and chemical hydrides and novel multicomponent complex hydride materials and reactions
Approach

Our approach involves a powerful blend of:
1) H₂ Storage measurements and characterization, 2) State-of-the-art computational modeling, 3) Detailed catalysis experiments, 4) In-depth automotive perspective
Technical Accomplishments: Experimental Screening & Testing of Theoretical Predictions

Approach:
- Computation
- Materials Synthesis & Testing
- Catalyst Screening

Guiding Questions:
- Is there experimental evidence of a new reactant structure (e.g., Mg-B-N-H)?
- What is the experimentally observed desorption pathway?
- How do these results compare with predictions?

Experimental Objectives:
- Synthesize, characterize, and test promising storage reactions predicted by computation
- Interface with kinetics-focused work to provide materials of interest for catalysis studies and assist in detailed testing of catalyzed reactions.

Predicted Compositions of Interest

<table>
<thead>
<tr>
<th>Predicted Compositions of Interest</th>
<th>Experimental Status</th>
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<tbody>
<tr>
<td>(NH₄)₂B₁₂H₁₂</td>
<td>Material received from OSU (Zhao)</td>
</tr>
<tr>
<td>5Mg(BH₄)₂ + 2LiBH₄</td>
<td>Material prepared &amp; experiments initiated</td>
</tr>
<tr>
<td>Mg(BH₄)₂</td>
<td>Deferred given existing literature data</td>
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= current experimental focus
$2\text{LiBH}_4 + 5\text{Mg(BH}_4\text{)}_2$ : Desorption and Partial Reversibility

Partial reversibility observed.

Optimization of reversible conditions still TBD

(2000 psi/138 bar, 350 °C recharge)

Partial reversibility observed.
Optimization of reversible conditions still TBD
2LiBH₄ + 5Mg(BH₄)₂ : Phase Evolution

XRD indicates initially similar to physical mixture, evolution in 2-3 steps:

- ~200-250 °C : Mg(BH₄)₂ & (possibly) LiBH₄ consumption
- ~250-300 °C : Continued Mg(BH₄)₂ consumption, formation of MgB₂ or possibly MgH₂
- Possible 3rd step over 350 °C : continued MgB₂ formation, other unidentified phase?
**Effect of 3 wt. % Co-activated carbon on the dehydrogenation of 2LiBH₄-5Mg(BH₄)₂**

Gas-phase IR indicated no borane release from catalyzed hydride.

3 wt % Co-AC catalyst (70 wt.% catalyst) accelerated the rate of dehydrogenation.

CH₄

B-H stretching

No catalyst

AC

3 wt. % Co-AC

AC heated with H₂

**A**

**A**
LiBH$_4$ decomposition is observed below 250°C when catalyzed with carbon.
Phys. Mixture of 2 wt. % Ni-AC catalyst further facilitates dehydrogenation of LiBH$_4$.

- AC alone greatly enhanced LiBH$_4$ dehydrogenation.
- The more AC, the faster the rate.
- Addition of Ni further improved dehydrogenation kinetics.
- Future work includes using infusion technique.
LiBH\textsubscript{4} dehydrogenation
Model for Mass Transport

\[
\begin{align*}
(LiBH_4)\text{solid} & \rightarrow \frac{1}{12}(Li_2B_{12}H_{12})\text{solid} + \frac{5}{6}(LiH)\text{solid} + \frac{13}{12}(H_2)\text{gas} \\
& \rightarrow (B)\text{solid} + (LiH)\text{solid} + \frac{3}{2}(H_2)\text{gas}
\end{align*}
\]

1. \(LiBH_4: H_2 : LiH \rightarrow \text{equilibrium} \rightarrow C^1[\text{defects}]\)
2. \(LiBH_4: H_2 : Li_2B_{12}H_{12} \rightarrow \text{equilibrium} \rightarrow C^2[\text{defects}]\)

\[
\nabla C = \frac{C^1[\text{defects}] - C^2[\text{defects}]}{d}
\]

\[
J = -D\nabla C
\]
Native defect concentration gradient

\[ J = -D \nabla C \]

The BH₃ vacancy has the largest concentration gradient.

But how about D?

Low-energy defects: H and Li vacancy pair

Low-energy defects: Li vacancy and interstitial pair
Can [BH$_3$] diffuse through LiBH$_4$?

After taking BH$_3$ from the original BH$_4$ negative unit, a negative H forms, which lies exactly at the original BH$_4$ position. The negative H does not combine to the neighboring BH$_4$ unit.

AlH$_3$ vacancy diffusion in sodium alanate: AlH$_3$ vacancy leaves a negative H. The H then combines with the neighboring AlH$_4$ unit, thus leaving space for the vacancy to diffusion.


Very different diffusion in borohydrides vs. alanates: Mass transport in LiBH$_4$ is very low.
Mg(NH₂)₂ + Mg(BH₄)₂: Desorption Quantification and Reversibility

- Ammonia release nearly undetectable
- The dangerous compounds diborane and borazine are not detected
- Mg(NH₂)₂ + Mg(BH₄)₂ exhibits a comparatively very low desorption onset (~180°C)

- Mg(NH₂)₂ + Mg(BH₄)₂ desorbed ~8.3 wt. % at 380 °C
  - No reversibility at 250°C or 380°C (computation also supports lack of reversibility)
Mg(NH$_2$)$_2$ + Mg(BH$_4$)$_2$: Phase Evolution

- XRD: Possible new RT phase, only 1 step observed at ~150 °C
  - Low temperature signal improved vs. prior work
  - Strongest peaks overlap with substrate, baseline is high – possibly some amorphous character?
Technical Accomplishments: Experimental Testing of Predicted Compounds

Previously, no known quarternary borohydride/amide compounds in Mg-B-N-H system

\[
\text{Mg(BH}_4\text{)}_2 + \text{Mg(NH}_2\text{)}_2 \rightarrow \text{MgBNH}_6
\]

<table>
<thead>
<tr>
<th>Mg(BH$_4$)(NH$_2$)</th>
<th>$\Delta E_{\text{Static}}$</th>
<th>$\Delta H_{\text{ZPE}}^{T=0\text{K}}$</th>
<th>$\Delta H_{\text{ZPE}}^{T=300\text{K}}$</th>
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<td>-9.75</td>
<td>-8.18</td>
<td>-8.63</td>
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New, predicted compound stable w.r.t. Mg(BH$_4$)$_2$ + Mg(NH$_2$)$_2$

Technical Accomplishments

product in the decomposition of Mg-B-N-H

The pDOS of the theoretically predicted MgBH$_4$NH$_2$ is in a good agreement with the experimental IR measurements.

The decomposition products contain part of Mg(BH$_4$)$_2$ and compounds including N-B-N linear cluster, such as Mg$_3$BN$_3$.

DOWNSELECT: End work on borohydride/amide combination (due to lack of reversibility and formation of B-N bonds in product).
All \([B_nH_m] \) intermediates have higher reaction energies than \(\text{MgB}_{12}\text{H}_{12}\). Only the reactions to \(\text{MgB}_2\text{H}_6\) and \(\text{Mg}_3(\text{B}_3\text{H}_6)_2\) are close to the \(\text{MgB}_{12}\text{H}_{12}\) convex hull. \(\text{Mg}_3(\text{B}_3\text{H}_6)_2\) is a metastable intermediate in the decomposition of \(\text{Mg}(\text{BH}_4)_2\).

Y. Zhang, et. al. submitted to J. Phys. Chem. C
3 wt.% Co-AC catalyst promotes dehydrogenation of \( \text{Mg(NH}_2\text{)}_2\text{–Mg(BH}_4\text{)}_2 \) and reduces \( \text{NH}_3 \) formation

- Co–AC catalyst showed a better kinetic improvement than TiCl\(_3\).

- Gas-phase IR indicated smaller \( \text{NH}_3 \) release from catalyzed hydride.
(NH4)2B12H12: Desorption and Reversibility

2(NH4)2B12H12 ↔ 4BN + B20H16 + 12H2 ↔ 4BN + 20B + 8H2


11.3 H2 wt%

- Ammonia release nearly undetectable, and diborane and borazine are not detected

- Partial reversibility (but degrading performance) under cycling at 350°C (2000 psi H2 recharge at 350°C)
  - Small sample size for (NH4)2(B12H12) due to limited quantity may exacerbate response
(NH₄)₂(B₁₂H₁₂): Phase Evolution

- XRD indicates some unidentified phases appearing
  - Initial signal matches pretty well with ICSD (NH₄)₂(B₁₂H₁₂) structure
  - Some BN possibly formed, see peaks disappearing – at end amorphous w/substrate
- In Situ IR indicates B-N stretch above ~300 °C
Collaborations

Pl’s/co-Pl’s

Chris Wolverton (Northwestern, lead)
Harold Kung (Northwestern)
Vidvuds Ozolins (UCLA, subcontract)
Andrea Sudik (Ford, no-cost collaborator)
Jun Yang (Ford, no-cost collaborator)

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)
Future Plans

• Experimentally characterized storage properties/reactions of \((\text{NH}_4)_2\text{B}_{12}\text{H}_{12}\) and other predicted reactions; Optimize reversibility conditions for \(5\text{Mg}(\text{BH}_4)_2 + 2\text{LiBH}_4\) mixture

• Extend experimental catalyst studies to other predicted promising materials; explore optimal morphology of carbon/metal catalysts;

• Focus experimental efforts on rehydriding reactions/reversibility (subject to pressure limitations of experimental equipment)

• Focus computational efforts on kinetics, defects, diffusion/mass transport/hydrogen dissociation in promising predicted reactions

• Downselect decision: End work on borohydride/amide combinations (No reversibility from computational or experimental work; B-N bonds in product).
Summary – Technical Accomplishments

- H₂ desorption and decomposition pathways have been studied in
  - 5LiBH₄ + 2Mg(BH₄)₂ (~5.8 wt.% desorbed)
  - Mg(BH₄)₂ + Mg(NH₂)₂ (~8.3 wt.% desorbed)
  - (NH₄)₂B₁₂H₁₂ (~4.5 wt.% desorbed)
- Partial reversibility (~1-2.5 wt.%) found in 5LiBH₄ + 2Mg(BH₄)₂ and (NH₄)₂B₁₂H₁₂
- Proposed new metal-carbon catalyst: Tested on NaAlH₄, and applied to Mg(BH₄)₂ + Mg(NH₂)₂, 2LiBH₄+5Mg(BH₄)₂ and LiBH₄; Effective catalyst - lowers desorption temperature, improves dehydrogenation rate, and suppresses formation of borane and NH₃
- Downselect the mixed borohydride/amide systems as promising hydrogen storage material (lack of reversibility and B-N bonds in products)
- Predicted a new metastable Mg₃(B₃H₆)₂ intermediate in decomposition of Mg(BH₄)₂, but showed that recently-proposed Mg(B₃H₈)₂ is not stable.
- PEGS+DFT combined of experimental measurements is used in unique way to solve amorphous AlB₄H₁₁ polymeric structure (w/ JC Zhao)
- Using the predictive models of defects, kinetics of mass transport: mass transport in LiBH₄ is very low (much lower than that in NaAlH₄)
Technical Accomplishments: Experimental Testing of Predicted Reactions

\[ 5\text{Mg(BH}_4\text{)}_2 + 2\text{LiBH}_4 \xrightarrow{-29 \, ^\circ\text{C}} \text{Li}_2\text{B}_{12}\text{H}_{12} + 5\text{MgH}_2 + 13 \, \text{H}_2 \quad 8.4 \text{ wt.\% H}_2 \]

Metal NPs supported on activated carbon (AC) and good catalyst-hydride contact facilitate hydride dehydrogenation

- Catalyst to hydride ratio maintained at 0.7 while varying Co-AC and AC ratio in the catalyst.
- The more Co-AC, i.e., the more Co, the faster the dehydrogenation kinetics

- 70 wt.% Co-AC catalyst but vary Co loading on the carbon support.
- Ball-milled hydride is in much closer contact with carbon catalyst and shows accelerated dehydrogenation kinetics
Model depicting the metal/carbon catalyst facilitated dehydrogenation of complex hydride

Effect of carbon based catalyst on the dehydrogenation of different hydrides:

- Mg(NH$_2$)$_2$–Mg(BH$_4$)$_2$
- Mg(BH$_4$)$_2$–LiBH$_4$
- LiBH$_4$
Technical Accomplishments: New Theoretical Predictions

• Decomposition of Mg(BH₄)(NH₂)
• New borohydride compounds
  – Mg₃(B₃H₆)₂
  – AlB₄H₁₁
• Diffusion & mass transport (required for fast kinetics)
Recent experiments

$[\text{B}_3\text{H}_8]^-$ intermediate


$\frac{1}{3}\text{Mg(B}_3\text{H}_8)^2+\frac{2}{3}\text{MgH}_2+\frac{2}{3}\text{H}_2$

$\Delta H$ static (kJ/mol)

1/3Mg(B$_3$H$_8$)$_2$ + 2/3MgH$_2$ + 2/3H$_2$

Mg(B$_3$H$_8$)$_2$ is not a stable intermediate in the decomposition of Mg(BH$_4$)$_2$. 

PEGS-Mg(B$_3$H$_8$)$_2$

Space group: P-1 (2)
Technical Accomplishments
New metal borohydride: AlB$_4$H$_{11}$

*In collaboration with Xuenian Chen and JiCheng Zhao (OSU)*

- **AlB$_4$H$_{11}$ synthesis:**
  \[
  2\text{Al(BH}$_4$)_3+\text{B}_2\text{H}_6 \rightarrow 2\text{AlB}_4\text{H}_{11}+4\text{H}_2
  \]

- **AlB$_4$H$_{11}$ attractive properties**
  - High hydrogen content (13.5% H$_2$)
  - Moderate stability
  - Decomposition temperature ~125 °C
  - Endothermic dehydrogenation
  - Rehydrogenation at moderate conditions

- **Unknown AlB$_4$H$_{11}$ structure:** amorphous

*Can we use PEGS+DFT to predict the structure? Or at least help interpret the experimental data?*
Polymer chain is composed of Al, [BH₄], [B₃H₇] groups, which are confirmed by experimental NMR measurements.

PEGS+DFT, combined of experiment, used in unique way to solve amorphous polymeric structure.