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
• ~30% complete

Budget

• Total Budget: $2714K
  – DOE Share: $2160K
  – Contractors Share: $554K
• Funding for FY08: $75K
• Funding for FY09: $450K
• Funding for FY10: $450K (anticipated)

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

• 3 Materials Classes (chemical, metal/complex, physisorptive) divided into DOE Centers of Excellence

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

• Systems to be studied include mixtures of complex hydrides and chemical hydrides [e.g. LiNH$_2$+NH$_3$BH$_3$] and nitrogen-hydrogen based borohydrides [e.g. Al(BH$_4$)$_3$(NH$_3$)$_3$].

• These types of combinations have only recently begun to be explored – initial results look very promising!
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: Searching for Combinations of B- and N-containing Materials

Solid Green Lines: Will show examples today
Dashed Green Lines: Will explore computationally as part of this project (promising materials/reactions will be investigated experimentally)
High-Throughput Computational Survey for Novel Reactions involving Light-Weight Elements

\[ \text{BH}_4 \quad \text{BH}_3 \quad \text{B}_{12}\text{H}_{12} \]

\[ \text{NH}_2 \quad \text{NH}_3 \quad \text{NH}_4 \]
Technical Accomplishments
Computational Methodology: DFT+GCLP
(Developed under previous work)

• Density Functional Theory
  – VASP Package
  – Static Energies, Zero-point energies,
    Vibrational Thermodynamics

• Grand Canonical Linear Programming*
  – Given the list of possible compounds,
    ALL thermodynamically reversible
    reactions are predicted automatically

• Survey compounds in ICSD involving
  first-row elements

Technical Accomplishments:
Computational Screening of the Li-Mg-B-N-H system

- The Li-Mg-B-N-H system includes most of the known high-capacity hydrides
- Constructed a database of 1\textsuperscript{st} principles free energies (including vibrations) of all (~50) known Li-Mg-B-N-H compounds:
  - Borohydrides [LiBH\textsubscript{4}, MgBH\textsubscript{4}, Li\textsubscript{2}B\textsubscript{12}H\textsubscript{12}, MgB\textsubscript{12}H\textsubscript{12}]
  - Amides/imides [LiNH\textsubscript{2}, Mg(NH\textsubscript{2})\textsubscript{2}, Li\textsubscript{2}NH, MgNH, Li\textsubscript{2}Mg(NH)\textsubscript{2}, etc.]
  - Borohydride-based compounds [Li\textsubscript{2}BNH\textsubscript{6}, Li\textsubscript{4}BN\textsubscript{3}H\textsubscript{10}, Mg(BH\textsubscript{4})\textsubscript{2}•2NH\textsubscript{3}]
  - Ammonia borane and derivatives (BH\textsubscript{3}NH\textsubscript{3}, BH\textsubscript{2}NH\textsubscript{2}, LiBH\textsubscript{2}NH\textsubscript{3}, etc.)
  - B-N-H and B-H compounds [B\textsubscript{2}H\textsubscript{6}, B\textsubscript{4}H\textsubscript{10}, B\textsubscript{16}H\textsubscript{20}, B\textsubscript{20}H\textsubscript{16}, (NH\textsubscript{4})\textsubscript{2}B\textsubscript{12}H\textsubscript{12}, etc.]
  - Reaction products: elements (Li, Mg, B, N\textsubscript{2}), hydrides (LiH, MgH2), borides (MgB\textsubscript{2}, MgB\textsubscript{4}, MgB\textsubscript{7}), nitrides (Mg\textsubscript{2}N\textsubscript{3}, Li\textsubscript{3}N, LiMgN), boronitrides (BN, Li\textsubscript{3}BN\textsubscript{2}, LiMgBN\textsubscript{2}), etc.
- Predicted new compounds using PEGS:
  - Ammoniated borohydrides
  - Metal-substituted ammonia borane derivatives
**Technical Accomplishments:** Novel, High-Capacity Predicted Reactions

- Grand-Canonical Linear Programming (GCLP) predicted reversible high-capacity reactions:

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Wt.% 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>17</td>
<td>104</td>
</tr>
<tr>
<td>5Mg(BH₄)₂ + 2LiBH₄ → 5MgH₂ + Li₂B₁₂H₁₂ + 13H₂</td>
<td>8.37</td>
<td>24</td>
<td>104</td>
</tr>
<tr>
<td>6Mg(BH₄)₂ → 5MgH₂ + MgB₁₂H₁₂ + 13H₂</td>
<td>8.10</td>
<td>29</td>
<td>100</td>
</tr>
<tr>
<td>B₂₀H₁₆ → 20B + 8H₂</td>
<td>6.95</td>
<td>33</td>
<td>111</td>
</tr>
<tr>
<td>5MgH₂ + MgB₁₂H₁₂ → 6MgB₂ + 11H₂</td>
<td>7.46</td>
<td>44</td>
<td>115</td>
</tr>
</tbody>
</table>

- Novel two-step reaction involving complex hydride with *ammonium cation*:

  -120 °C
  2(NH₄)₂B₁₂H₁₂ → 4BN + B₂₀H₁₆ + 12H₂

  +20 °C
  4BN + 20B + 20 H₂

  11.3 wt.% H₂
Technical Accomplishments: Predicted van’t Hoff diagram

![Van't Hoff diagram](image-url)
Experimental Characterization of (NH₄)₂B₁₂H₁₂

Preliminary Results:
DSC reveals endothermic step at ~ 360ºC based on 5º/min ramp

Next Steps:
Complete characterization of starting material and desorption pathway (i.e. via XRD & IR) for comparison with computation

*Material acquired from J. C. Zhao (OSU)*
Discovery of Novel Compounds in Borohydride-Amide Systems

- $\text{BH}_4$
- $\text{BH}_3$
- $\text{B}_{12}\text{H}_{12}$
- $\text{NH}_2$
- $\text{NH}_3$
- $\text{NH}_4$
Technical Accomplishments: Discovery of Novel Compounds in Borohydride-Amide Systems

- **Li$_4$(NH$_2$)$_3$(BH$_4$)** phase discovered by GM, Toyota, & Oxford:
  
  $3 \text{LiNH}_2 + \text{LiBH}_4 \rightarrow \text{Li}_4\text{(NH}_2\text{)}_3\text{(BH}_4\text{)} \quad (11 \text{ wt%})$

  -- **Benefits:**
  
  High capacity & crystalline reaction species

  -- **Limitations:**
  
  Poor kinetics, NH$_3$ release, irreversible: DFT calculated $\Delta H = 12 \text{ kJ/mol}$

- Potential for improvement in properties by replacing Li:
  
  $\text{M}_1\text{(NH}_2\text{)} + \text{M}_2\text{(BH}_4\text{)} \rightarrow \text{M}_1\text{M}_2\text{(NH}_2\text{)(BH}_4\text{)} \leftrightarrow [\text{products}] + \text{H}_2$

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**Amides**

- NaNH$_2$ [purchase]
- LiNH$_2$ [purchase]
- Mg(NH$_2$)$_2$ [synthesize]
- Ca(NH$_2$)$_2$ [synthesize]

**Borohydrides**

- NaBH$_4$ [purchase]
- LiBH$_4$ [purchase]
- Mg(BH$_4$)$_2$ [synthesize]
- Ca(BH$_4$)$_2$ [synthesize]
Technical Accomplishments:
Example TPD-MS Results from Na-B-N-H Mixture 
(i.e., 1 NaBH₄ + 1 NaNH₂)

- XRD and IR data consistent with new quaternary phase
- New low temperature hydrogen release events
- NH₃ liberation could be reduced by optimization of composition
Technical Accomplishments: PEGS+DFT Computational Prediction of a New Ca(BH\textsubscript{4})(NH\textsubscript{2}) Compound

A new Ca-B-N-H quaternary compound is predicted to be stable with respect to Ca(BH\textsubscript{4})\textsubscript{2} + Ca(NH\textsubscript{2})\textsubscript{2}
Discovery of Novel Metal Amidoborane ($\text{NH}_2\text{BH}_3$)\textsuperscript{−} Systems
Technical Accomplishments: Metal amidoboranes (MNH$_2$BH$_3$)

- High H$_2$ capacity
  - LiNH$_2$BH$_3$: 13.70 wt%
  - Ca(NH$_2$BH$_3$)$_2$: 10.10 wt%

- Low H$_2$ release $T$
  - NH$_3$BH$_3$: 110$^\circ$~200$^\circ$
  - LiNH$_2$BH$_3$: 90$^\circ$
  - Ca(NH$_2$BH$_3$)$_2$: 100$^\circ$

- Pure H$_2$ release without [N$_3$B$_3$H$_6$]

Can we find new metal amidoboranes? Can we use PEGS for the NH$_2$BH$_3$ anion? What are the thermodynamics of these reactions? What are the trends as the metal cation is varied?

Technical Accomplishments: Example: KNH$_2$BH$_3$ structure

Experimental Structure (Burrell et al.)
16 f.u.

Predicted Structure (PEGS+DFT)
2 f.u.

PEGS+DFT gives excellent predictions for the energies of amidoboranes! (PEGS+DFT energy very close to experimental structure, where known)

We have performed similar calculations for: Li, Na, K, Mg, Ca, Sc amidoboranes, finding good predictions in each case.

Predicted structure nearly degenerate with experimental structure (within 11 meV/f.u.)
Predicted structure also has two symmetrically distinct K positions, in agreement with expt.
Technical Accomplishments

Amidoborane Decomposition Products:
Dianion \([\text{NHBH} \text{NHBH}_3]^{2-}\)

- B-N-B-N bridge proposed AB decomposition product.
- DFT calculations support this proposal: \(\text{NHBH} \text{NHBH}_3\) is lowest energy decomposition intermediate (out of many possibilities calculated). Near thermoneutral for LiAB, slightly endothermic for CaAB

\(\text{Li}_2[\text{NHBH} \text{NHBH}_3]\)

J. Spielmann. etc.,

T. Autrey (private communication)
Borohydride-Ammonia Systems

\[ \text{BH}_4 \rightarrow \text{NH}_2 \]

\[ \text{BH}_3 \rightarrow \text{NH}_3 \]

\[ \text{B}_{12}\text{H}_{12} \rightarrow \text{NH}_4 \]
Technical Accomplishments:

**PEGS Predictions for Mg(BH$_4$)$_2$-$m$NH$_3$**

Prototype electrostatic ground state search (PEGS) successfully predicts energetics:


- GCLP predicts that Mg(BH$_4$)$_2$(NH$_3$)$_2$ has an **exothermic** decomposition pathway:

$$\text{Mg(BH}_4\text{)}_2\text{(NH}_3\text{)}_2 \rightarrow 2\text{BN} + \text{MgH}_2 + 7\ \text{H}_2$$

  13.6 wt. % H$_2$, $\Delta H = -21$ kJ/mol-H$_2$

- PEGS-DFT predicts monoclinic *Cm* structure, which is **2 kJ/mol** lower than *Pcab*.

$$\text{Mg(BH}_4\text{)}_2\text{(NH}_3\text{)}_2 \rightarrow 2\text{BN} + \text{MgH}_2 + 7\ \text{H}_2$$

13.6 wt. % H$_2$, $\Delta H = -21$ kJ/mol-H$_2$
Mixed-Metal Borohydride Systems
Technical Accomplishments:
PEGS+DFT Prediction of Novel Mixed-Metal Borohydride Compounds

Li/Zn and Na/Zn systems

*Ravnsbaek et al., Angew. Chemie., 48, 6659 (2009)*

**PEGS+DFT Calculations show new LiZn(BH$_4$)$_3$ phase stable;**
Experimentally-proposed LiZn$_2$(BH$_4$)$_5$ is found to be an unstable phase

**PEGS+DFT Calculations show new NaZn(BH$_4$)$_3$ phase stable;**
Experimentally-proposed NaZn$_2$(BH$_4$)$_5$ is found to be an stable phase
Exploration of Improved Catalysts
Technical Accomplishments:

**Borohydrides**

Metal catalyst for H₂ recombination

**Catalyst matrix hypothesized to:**
1. Increase hydrogen gradients on the high surface/interface area catalytic matrix, and
2. Provide nucleation sites for decomposition (by)-products and hydrogen atoms/molecules release.

**Proposed catalytic action**

**Facilitating Ca(BH₄)₂ decomposition:**
*Non-precious metal decorated carbon nanotubes (by sonic-assisted impregnation) as catalytic matrix*

**Ni or Ni-MWCNTs catalysts lowers the decomposition temperature of Ca(BH₄)₂**

We find Fe, Co, and Ni catalysts all lower the decomposition temperature (only Ni results are shown).

**Graph:**
- **Ca(BH₄)₂**
- **Ca(BH₄)₂-MWCNTs**
- **Ca(BH₄)₂-10% Ni/MWCNTs (20/80)**
- **Ca(BH₄)₂-10% Ni/MWCNTs (60/40)**
- **Ca(BH₄)₂-10% Ni**

**Derivative pressure change**

**Temperature (°C):**
- 300
- 350
- 400
- 450
- 500

**Catalyst matrix**

- Metal catalyst for H₂ recombination
Collaborations

PI’s/co-PI’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)
Future Plans

• Extend computational search for all possible promising reversible reactions in Li-Ca-B-N-H system
• Experimentally characterized storage properties/reactions of \((\text{NH}_4)_2\text{B}_{12}\text{H}_{12}\) and other predicted reactions
• Extend experimental catalyst studies to \((\text{NH}_4)_2\text{B}_{12}\text{H}_{12}\) and other predicted promising materials
• Continue computational exploration for: 1) novel BH4/NH2 compounds and reversible reactions, 2) mixed metal borohydrides, 3) AB reaction products
Summary – Project Overview

• Project focused on design of novel multi-component mixtures for hydrogen storage
• Focus on mixtures of materials from two distinct classes (e.g., reversible + irreversible)
• Systems being studied include mixtures of complex hydrides and chemical hydrides involving combinations of B- and N-containing materials
• 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
Summary – Technical Accomplishments

• Used computational methods (DFT, PEGS, GCLP) to scan through and predict all possible reactions in Li-Mg-B-N-H system with reversible thermodynamics
• New high-capacity reactions predicted, including those involving \((\text{NH}_4)_2\text{B}_{12}\text{H}_{12}\) (preliminary experimental verification underway)
• PEGS prediction of amido-borane structures. Good agreement with experiment where available (e.g., LiAB and KAB) and good prediction of structure for many other cases.
• NHBHNHBH3 dianion as AB intermediate product supported by DFT calculations
• Computational prediction and experimental observation of new mixed BH4/NH2 compounds in Na and Ca systems
• PEGS predictions for ammoniated borohydrides
• PEGS predictions for mixed-metal borohydrides
• Exploration of novel catalyst design - initial results for Ca\((\text{BH}_4)\)\(_2\)