Discovery and Development of Metal Hydrides for Reversible On-board Hydrogen Storage

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Sandia National Laboratories
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Project ID: ST_03_Allendorf

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Overview of Sandia Program

Timeline

- Project started in March ‘05
- Project end June 2010
- Percent complete 80%

Barriers

- A. System Weight & Volume, B. Cost, C. Efficiency, D. Durability
- E. Charge/discharge rates
- P. Lack of Understanding of Hydrogen Physisorption and Chemisorption

SNL R&D Budget

- FY08 Funds: $2.4M
- Planned FY09 Funds: $2.3M

MHCoE Partners

- BNL, JPL, NIST, ORNL, SRNL, Caltech, GA Tech, OSU, PITT, Stanford, UH, UIUC, UNR, UNB, Utah, HRL, UTRC

Collaborators

- V. Ozolins (UCLA), J. Herberg (LLNL), Y. Filinchuk (ESRF), C. Wolverton (Northwestern), J-H Her (U. Maryland)

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the US Department of Energy’s National Nuclear Security Administration under contract DE-AC04-94AL85000
Sandia Team (~ 6 FTEs)

Technical POC and MHCoE Director: Lennie Klebanoff

Core Technical Team

Mark Allendorf: Theory, Theory Group Coordinator
Eric Majzoub: PEGS theory, experiments (Sandia/UMSL)
Tim Boyle: Nanoconfinement (liquid-phase syntheses)
Mutlu Kartin: New materials (borohydrides, amides)
Vitalie Stavila: New materials (borohydrides, ammine complexes)
Joe Cordaro: New materials (nanoconfinement, bulk syntheses)
Weifang Luo: New materials, since 03/02/2009
Ewa Rönnebro: Departed 02/20/2009

Other Key Contributors
Rich Behrens, Leo Seballos, Ida Nielsen

Ph.D. Students
Rebecca Newhouse (UC Santa Cruz), Godwin Severa (U. Hawai’i),
David Peaslee (UMSL)
Discover, develop and validate “reversible” on-board metal hydride storage materials with potential to meet the DOE 2010 targets and a clear path to meeting the 2015 targets. Use theory-directed synthesis with characterization.

**Prediction of crystal structure prototypes:**
- Prototype Electrostatic Ground State (PEGS) technique for structure predictions and rapid ΔH estimates
- First-principles Density Functional Theory (DFT) is used for accurate thermodynamics calculations

**Synthesis/sample preparation:**
- Solid-state and solution routes
- High-energy ball-milling (SPEX)
- Hot-sintering at high-P (600°C, 2000 bar)

**Understanding structural properties / Probing hydrogen release reaction mechanisms / Additives/dopants/catalysts modification:**
- Powder/Synchrotron XRD, Neutron diffraction, STMBMS, PCT/Sieverts, Raman, FTIR, TGA/DSC, TEM, SEM, EDAX, EELS
Status in June 2008:

- Modeled structure and thermodynamics in alkali-, and transition metal(TM)-borohydrides using PEGS / first-principles DFT
- Used quantum chemical methods to calculate bond energies of alane complexes (in support of BNL AlH₃ regeneration studies)
- Modeling of alanate energetics in solution initiated

Focus during FY08/FY09:

- Impact of *closo*-borates formation on thermodynamics of Li-, Ca- and Mg-borohydrides
- Reaction pathways in complex multi-component systems
- Role of gas phase in determining reaction pathways
- Continue the coordination of MHCoE Theory Group (Allendorf)
Collaboration -- SNL / GA Tech / U. Pittsburg

Phase equilibrium calculations can provide valuable insight into complex hydride decomposition chemistry

- **Gas phase:**
  - Fuel-cell poisons (e.g. NH₃)
  - Storage capacity, reversibility
  - Safety (e.g., H₂O or O₂ reactions)
  - Possible kinetic role

- **Condensed phase:**
  - Multiple stable products
  - Parasitic reactions
  - Effects of T, P, reaction stoichiometry

- **Useful results of equilibrium modeling:**
  - Identify most stable products
  - Predict undesirable gas-phase species
  - System design and optimal operating conditions

Metal Hydride Theory Needs to Address Multiple Phases and Gas Composition

Ki Chul Kim & David Sholl (GA Tech.)
Bo Zhang & Karl Johnson (U. Pittsburgh)
Mark Allendorf (SNL)
Comprehensive Multi-phase Equilibrium Modeling is Advancing Our Understanding of Metal Hydride Systems

- Gibbs Free Energy minimization
- FactSage package (commercial software)
- Thermodynamic data sources:
  - Gas phase: *JANAF Tables*
  - Gas-phase $B_nH_m - B_{10}H_{14}$
- Custom hydride data base
  - Li-B-C-Mg condensed phases
  - $\Delta H_f^\circ (298) \Delta S^\circ (298)$, $C_p(T)$
    - DFT + phonon calculation
    (Kim & Sholl results, 2008)
- Examples of possible calculations:
  - Constant $(T,p)$, $(T,V)$, $(T,H)$
  - Phase diagrams
  - Thermodynamics of individual reactions

Polynomial fit to $C_p$ for MgH$_2$
Data from DFT and phonon calculation
(Kim & Sholl, 2008)
LiNH₂ (+ LiH): Prediction of Significant Gas-phase Impurities

Nominal reactions:

- \( \text{LiNH}_2 \leftrightarrow 0.5\text{Li}_2\text{NH} + 0.25\text{N}_2 + 0.75\text{H}_2 \)
- \( \text{LiNH}_2 + \text{LiH} \leftrightarrow \text{Li}_2\text{NH} + \text{H}_2 \)
- \( 2\text{LiNH}_2 \leftrightarrow \text{Li}_2\text{NH} + \text{NH}_3 \)

Conditions for calculation:

- 1 mole LiNH₂ (+1 mole LiH)
- Constant T, Constant V (10 L)
- Gas phase: \( \text{H}_2, \text{NH}_3, \text{N}_2, \text{Li}, \text{Li}_2, \text{LiH} \)

Results:

- \( \text{N}_2 \) and \( \text{NH}_3 \) predicted to be significant byproducts
- LiH addition:
  - Scavenges nitrogen to enhance \( \text{H}_2 \) yield
  - Reduces \( \text{NH}_3 \), but only at \( T > 360 \degree \text{C} \)
- Experiments confirm \( \text{NH}_3 \) formation but suggest kinetic barrier to \( \text{N}_2 \) formation

Future Work: Model Equilibria for Most Important Metal Hydride Materials

- Model phase equilibria for general hydride categories:
  - Hydride + C
  - Nitrogen-containing hydrides
  - Boron-containing hydrides

- Model the following destabilized reactions:
  - \(2\text{LiNH}_2 + \text{C} \rightarrow \text{Li}_2\text{CN}_2 + 2\text{H}_2\) \(\Delta U(0 \text{ K}) = 31.4 \text{ kJ/mol H}_2\)
  - \(2\text{C} + \text{Mg(BH}_4)_2 \rightarrow \text{MgB}_2\text{C}_2 + 4\text{H}_2\) \(\Delta U(0 \text{ K}) = 43.1 \text{ kJ/mol H}_2\)
  - \(\text{BN} + 4\text{Mg(BH}_4)_2 \rightarrow 3\text{MgH}_2 + \text{MgB}_9\text{N} + 13\text{H}_2\) \(\Delta U(0 \text{ K}) = 51.2 \text{ kJ/mol H}_2\)

- Incorporate multiple gas-phase species approach into U. Pittsburgh / Georgia Tech screening code
  
  -- see more details in ST08 by K. Johnson (Univ. Pittsburgh)
  -- see our additional slide #30

- Journal article describing results is in preparation
Alkali-TM-(BH₄)ₓ Explored for Low-Temperature Desorption

Investigation of LiSc(BH₄)₄ Validates PEGS method with TM-borohydrides

Collaboration -- SNL / JPL / Caltech / UCLA

- Solid-state NMR indicates formation of ScB₂, [B₁₂H₁₂]²⁻ on desorption
- PEGS predicted structures:
  - Sc(BH₄)₃: C₂₂₂₁
  - Sc₂[B₁₂H₁₂]₃: Cm
  - LiSc(BH₄)₄: I-4

Complicated decomposition pathway predicted using PEGS structures consistent with experimental measurements


Exploring:
- NaTi(BH₄)₄
- Na₂Ti(BH₄)₅
- LiTi(BH₄)₄
- Li₂Ti(BH₄)₅

Theoretical and Experimental Search for Alkali-Ti-(BH₄)ₓ

Collaboration -- SNL / UTRC

- Stabilize Ti(BH₄)₃ through addition of alkali metals, and/or confinement in nano-frameworks

Synthesis:

\[
\begin{align*}
\text{TiX}_4 + \text{LiBH}_4 & \rightarrow \text{Ti(BH}_4)_3 \quad (X=\text{Cl, Br})^* \quad \text{Completed} \\
\text{Ti(BH}_4)_3 + \text{MBH}_4 & \rightarrow \text{MTi(BH}_4)_4 \quad (M=\text{Li, Na}) \quad \text{In progress}
\end{align*}
\]

Structure of $[\text{B}_{12}\text{H}_{12}]^{2-}$ Salts Predicted with PEGS and Confirmed with XRD

**Synthesis:**

$$\text{Cs}_2[\text{B}_{12}\text{H}_{12}] \xrightarrow{-\text{Cs}^+} [\text{H}_3\text{O}]_2[\text{B}_{12}\text{H}_{12}]$$

$$[\text{H}_3\text{O}]_2[\text{B}_{12}\text{H}_{12}] \xrightarrow{-\text{CO}_2, -\text{H}_2\text{O}} \text{M}[\text{B}_{12}\text{H}_{12}] \cdot x\text{H}_2\text{O} \quad (\text{M}=\text{metal ion})$$

$$\text{M}[\text{B}_{12}\text{H}_{12}] \cdot x\text{H}_2\text{O} \xrightarrow{-x\text{H}_2\text{O}} \text{M}[\text{B}_{12}\text{H}_{12}]$$

Evidence of diborane and closo-borates formation during borohydride desorption reactions prompts further analysis of $[\text{B}_{12}\text{H}_{12}]^{2-}$ salts*

**Synthesis:**

$$\text{Cs}_2[\text{B}_{12}\text{H}_{12}] \xrightarrow{-\text{Cs}^+} [\text{H}_3\text{O}]_2[\text{B}_{12}\text{H}_{12}]$$

$$[\text{H}_3\text{O}]_2[\text{B}_{12}\text{H}_{12}] \xrightarrow{-\text{CO}_2, -\text{H}_2\text{O}} \text{M}[\text{B}_{12}\text{H}_{12}] \cdot x\text{H}_2\text{O} \quad (\text{M}=\text{metal ion})$$

$$\text{M}[\text{B}_{12}\text{H}_{12}] \cdot x\text{H}_2\text{O} \xrightarrow{-x\text{H}_2\text{O}} \text{M}[\text{B}_{12}\text{H}_{12}]$$

**Theory Predicted Structure**

$$C2/c \quad \text{Ca}[\text{B}_{12}\text{H}_{12}]$$

**Calculated vs. Observed powder-XRD of Ca$[\text{B}_{12}\text{H}_{12}]$**

**Collaboration -- SNL / NIST**

<table>
<thead>
<tr>
<th>Compound</th>
<th>PEGS Structures</th>
<th>SNL/NIST Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$<em>2$[B$</em>{12}$H$_{12}$]</td>
<td>C2/m (#12)</td>
<td>Pa-3</td>
</tr>
<tr>
<td>Na$<em>2$[B$</em>{12}$H$_{12}$]</td>
<td>P2$_1$/n (#14)</td>
<td>P2$_1$/n</td>
</tr>
<tr>
<td>Ca[B$<em>{12}$H$</em>{12}$]</td>
<td>C2/c (#15)</td>
<td>C2/c</td>
</tr>
<tr>
<td>Mg[B$<em>{12}$H$</em>{12}$]</td>
<td>C2/m (#12)</td>
<td>Amorphous</td>
</tr>
<tr>
<td>Sc$<em>2$[B$</em>{12}$H$_{12}$]$_3$</td>
<td>Cm (#8)</td>
<td>Amorphous</td>
</tr>
</tbody>
</table>

Ref:  
First-principles DFT calculations determine compound thermodynamics while Gibbs’ free energy calculations determine reaction critical temperature \( (T_c = T_{1\text{bar}} \text{ of } H_2) \), \( \Delta H \) and thermodynamically possible products.

**Desired desorption products for \( \text{Ca}(BH_4)_2 \) and \( \text{Mg}(BH_4)_2 \) are \( \text{CaB}_6 \) and \( \text{MgB}_2 \)

**But:**

- \( \text{Mg}[B_{12}H_{12}] \) formation *lowers* capacity of \( \text{Mg}(BH_4)_2 \) from 14.9 to 8.1 wt% \( H_2 \)
- \( \text{Ca}[B_{12}H_{12}] \) formation *lowers* capacity of \( \text{Ca}(BH_4)_2 \) from 9.6 to 6.3 wt% \( H_2 \)

<table>
<thead>
<tr>
<th>Possible Reactions</th>
<th>Theoretical wt% ( H_2 )</th>
<th>( \Delta H^{300K} )</th>
<th>( T_c (°C) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Mg}(BH_4)_2 \rightarrow \text{MgB}_2 + 4H_2 )</td>
<td>14.9</td>
<td>38.8</td>
<td>75</td>
</tr>
<tr>
<td>( 6\text{Mg}(BH_4)<em>2 \rightarrow \text{Mg}[B</em>{12}H_{12}] + 5\text{MgH}_2 + 13H_2 )</td>
<td>8.1</td>
<td>29.3</td>
<td>20</td>
</tr>
<tr>
<td>( 3\text{Ca}(BH_4)_2 \rightarrow \text{CaB}_6 + 2\text{CaH}_2 + 10H_2 )</td>
<td>9.6</td>
<td>40.8</td>
<td>94</td>
</tr>
<tr>
<td>( 6\text{Ca}(BH_4)<em>2 \rightarrow \text{Ca}[B</em>{12}H_{12}] + 5\text{CaH}_2 + 13H_2 )</td>
<td>6.3</td>
<td>39.2</td>
<td>99</td>
</tr>
</tbody>
</table>

A predicted desorption pathway of \( \text{Ca}(BH_4)_2 \) involves \( \text{Ca}[B_{12}H_{12}] \), and is therefore consistent with loss of capacity on each cycle observed in sorption experiments.
Entropy of H₂ gas (130 J/Kmol H₂ at 20 °C, 1 bar) commonly dominates. Products with fewer anions or tightly bound bulk phase reduce the number of low frequency phonon branches and decreases ΔS to ~ 100 J/K mol H₂ for the following reactions:

### New Candidate Destabilized Reactions:

<table>
<thead>
<tr>
<th>Predicted Reactions</th>
<th>Theoretical wt% H₂</th>
<th>ΔH₃₀₀K kJ/mol H₂</th>
<th>Tₑ (°C)</th>
<th>SNL Data: wt% H₂ (350°C, 4h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5Mg(BH₄)₂ + 2LiBH₄ → Li₂[B₁₂H₁₂] + 5MgH₂ + 13H₂</td>
<td>8.4</td>
<td>24.4</td>
<td>-29</td>
<td>6.0</td>
</tr>
<tr>
<td>5Mg(BH₄)₂ + Ca(BH₄)₂ → Ca[B₁₂H₁₂] + 5MgH₂ + 13H₂</td>
<td>7.7</td>
<td>25.7</td>
<td>-18</td>
<td>4.4</td>
</tr>
<tr>
<td>5Ca(BH₄)₂ + 2LiBH₄ → Li₂[B₁₂H₁₂] + 5CaH₂ + 13H₂</td>
<td>6.7</td>
<td>37.9</td>
<td>83</td>
<td>6.2</td>
</tr>
</tbody>
</table>

**Kinetic barriers for new reactions are unknown**

**Experimental Comparison of 5Ca(BH₄)₂ + 2LiBH₄ vs Ca(BH₄)₂ Systems:**

Although the kinetics improved slightly and the desorption temperature was lowered ~50 °C, a significant capacity loss via cycling still remains.
# Theory Milestones

<table>
<thead>
<tr>
<th>Month/year</th>
<th>Milestone or Go/No-Go decision: <strong>Al-Adduct Theory</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>May-08 ✓</td>
<td>Milestone: Complete BAC calculations of alane-amine complexes</td>
</tr>
<tr>
<td>Sep-08 ✓</td>
<td>Milestone: Complete BAC calculations on alane-adduct complexes</td>
</tr>
<tr>
<td>Dec-08 ✓</td>
<td>No-go: Model reactions of alane-amine surface interactions</td>
</tr>
<tr>
<td>May-09</td>
<td>Milestone: Complete calculations on alanate-amine complexes</td>
</tr>
<tr>
<td>Sep-09</td>
<td>Milestone: Complete calculations on alanate-ether adducts</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Month/year</th>
<th>Milestone or Go/No-Go decision: <strong>Alanate/Borohydride Theory</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Jan-09 ✓</td>
<td>Milestones: (1) Structural modeling of TM-containing borohydrides. (2) Extension of PEGS method to nanoparticle hydrides</td>
</tr>
<tr>
<td>Feb-09 ✓</td>
<td>* No-go: Discontinue surfactant templating for nano-scale alanates/borohydrides</td>
</tr>
<tr>
<td>Jul-10</td>
<td>Milestone: Finish alkali-TM borohydride structure and stability calculations</td>
</tr>
<tr>
<td>Nov-10</td>
<td>Go/no-go: Discontinue alkali-TM borohydrides if no suitable materials found</td>
</tr>
</tbody>
</table>

* -- see our additional slide #31
Discovery and Characterization of New Materials

Status in June 2008:

- Determined the phase transitions of Ca(BH$_4$)$_2$ polymorphs at different temperatures (see our additional slide #32)
- Demonstrated the partial reversibility of Ca(BH$_4$)$_2$ at 100 bar and 350°C
- Initiated additive screening for Ca(BH$_4$)$_2$
- Theory predicted bi-alkali borohydrides, AK(BH$_4$)$_2$ (A= Li, Na), were synthesized but not pursued further due to poor thermodynamics

Focus during FY08/FY09:

- Elucidate the reaction mechanism and decomposition products of Ca(BH$_4$)$_2$
- Complete Ca(BH$_4$)$_2$ additive study, $\Delta$H determination: Make go/no-go decision
- Syntheses and characterization of PEGS-predicted closo-borates and new BH$_4$/NH$_3$, BH$_4$/NH$_2$, BH$_4$/AlH$_4$ systems
- Re-hydrogenation of Mg(BH$_4$)$_2$ utilizing Sandia high-pressure capability (see our additional slide #33, see ST07-UH)
- Incorporation of hydride materials in catalyzed nano-framework structures (NFS) to improve kinetics (see our additional slide #34, see ST10-UTRC)
Effect of Additives on Cycling Capacity and Kinetics of Ca(BH$_4$)$_2$

- 30 different additives screened
- ~6 wt% H$_2$ released in 1 hour at 350 °C
- Additives do not significantly improve kinetics of Ca(BH$_4$)$_2$
- Significant capacity loss observed on subsequent cycles

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

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

- Additives do not significantly improve kinetics of Ca(BH$_4$)$_2$
- Significant capacity loss observed on subsequent cycles
"$B_nH_m$" species formed during the dehydrogenation

11B MAS-NMR reveals the presence \([B_nH_m]\) species and their accumulation upon cycling

Separate experiments show that Ca\([B_{12}H_{12}]\) cannot be hydrogenated or dehydrogenated under the conditions tested

---

**Ca\((BH_4)\_2\) with Additive-A**

\[\omega_r = 13 \text { kHz}\]

14.7 ppm 16.2 ppm -33.0 ppm

**Ca\((BH_4)\_2\) with Additive-B**

\[\omega_r = 15 \text { kHz}\]

\[\omega_r = 15 \text { kHz}\]

---

Reference compounds: Ca\([B_{12}H_{12}]\) at 450°C
Ca\([B_{12}H_{12}]\) at 350°C
K\(_2\)[B\(_{10}H_{10}\)]
K\(_2\)[B\(_{12}H_{12}\)]
Although the thermodynamics for Ca(BH$_4$)$_2$ are reasonable (measured $\Delta H_{\text{desorption}} = 20 – 30$ kJ/mol H$_2$ by DSC)*, we have made a decision to “down-select” Ca(BH$_4$)$_2$ as a hydrogen storage material, because:

- It is only partially reversible due to “$B_nH_m$” formation
- It is kinetically limited
- Catalysts do not improve the rate of hydrogen desorption below 300 ºC
- The observed maximum desorption capacity, up to 350 ºC, is less than ~7 wt %

∴ We will not pursue Ca(BH$_4$)$_2$ further as a hydrogen storage material

* -- see our additional slide #37
**New M(BH₄)ₙ-NH₃ Materials Synthesized and Characterized**

**Motivation:** Based on promising results reported for Mg(BH₄)₂·2NH₃ (Zhao *et al.*), other metal-borohydride-ammonia systems were investigated.

The BH₄-NH₃ compounds display increased air- and moisture stability compared to the initial borohydrides.

- **Ca(BH₄)₂·NH₃**, **MgCa(BH₄)₄·NH₃**, and **LiCa(BH₄)₃·NH₃** adducts release significant amounts of NH₃ upon heating, confirmed by gas phase analysis.

- New systems based on transition metals (e.g. Ti(III)) are currently under investigation.

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-- see other details on the Ca(BH₄)₂-NH₃ system in STP37 by G. Brown (ORNL)
# Experimental Milestones

<table>
<thead>
<tr>
<th>Month/year</th>
<th>Milestone or Go/No-Go decision</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Oct-08</strong></td>
<td>Go: Successfully coated the catalyzed NFS substrate with metal hydride via solution route. Milestone: Complete PCT isotherms for Ca(BH₄)₂ to determine reaction enthalpy</td>
</tr>
</tbody>
</table>
| **Jan-09** | Milestone: Synthesize Ca(BH₄)₂/NH₃ system  
No-go: On further work on Ca(BH₄)₂/NH₃ system  
Milestone: Complete STMBMS characterization of Ca(BH₄)₂  
No-go: La-doped CaB₆, but the efforts shifted towards C-doping of MgB₂ |
| **Mar-09** | Milestone: Lowering of Ca(BH₄)₂ desorption temperature  
No-go decision made on Ca(BH₄)₂ |
| **April-09** | Milestone: Complete additive screening study of MHCoE borohydride  
Milestone: Discover new borohydride related materials **In progress** |
| **May-09** | Go/no-go on A-TM-(BH₄)ₓ: Reversibility of alkali transition metal borohydrides |
| **June-09** | Go/no-go: Continue with mixed Caₙ₋ₓMₓ(BH₄)₂ materials if reversibility has been shown at improved P and T compared to Ca(BH₄)₂  
Go/no-Go: to incorporate the hydride material into the NFS *via* a solid-state route, (50% loading of a hydride material with a hydrogen storage capacity greater than 5% in NFS) |
| **Sep-09** | Milestone: Incorporation of hydride material in catalyzed nano-frameworks |
| **Oct-09** | Milestone: Complete additive screening study of MHCoE of mixed amide/borohydride |
Summary of Accomplishments

Theory:
- Developed phase equilibria theoretical technique, applied to LiNH₂ (+LiH) and (LiBH₄ + C)
- Predicted structures of [B₁₂H₁₂]²⁻ intermediates and their effect on reaction pathways
- PEGS structure predictions of transition-metal borohydrides

Calcium Borohydride:
- Completed additive screening of Ca(BH₄)₂ and studied the cycling behavior
- Revealed that BₙHₘ species limit the reversibility of Ca(BH₄)₂
- Probed reaction pathway and kinetics of Ca(BH₄)₂ using STMBMS (see our additional slides #38, 39)
- Made No-Go decision on Ca(BH₄)₂

New Materials:
- Synthesized [B₁₂H₁₂]²⁻ salts with various cations to examine their influence on the hydrogen release in borohydride systems in conjunction with theoretical predictions (see our additional slide #36)
- Synthesized new MM'(BH₄)ₓ/(NH₃)ᵧ and MM'(BH₄)ₓ/(NH₂)ᵧ compounds and assessed their hydrogen storage properties (see our additional slide #40)
- Synthesized Ca(AlH₄)/(BH₄) and predicted high symmetry solid-state structure (see our additional slide #41)
- Examined C-dopant effects on MgB₂ hydrogenation (see our additional slide #35)
- Initiated the incorporation of Ca(BH₄)₂ in a C-aerogel and characterized hydrogen release
Future Work in 2009

Theory:
- Model phase equilibria for promising metal hydride materials
- Complete calculations on alanate-ether adducts
- Examine phase stability and the reactions of TM-containing borohydrides
- Conduct PEGS search for mixed-anion borohydride materials

New Materials:
- Synthesis and characterization of PEGS predicted new BH$_4$/NH$_3$, BH$_4$/NH$_2$ and BH$_4$/AlH$_4$ compounds
  (see our additional slides #40,41)
- Explore new mixed-metal borohydride systems

Incorporation of Hydrides into Nano-frameworks:
- Metal borohydride incorporation into nano-frameworks via solution routes
- Characterize metal borohydride incorporation into catalyzed and uncatalyzed nano-frameworks
  (see ST10-UTRC)
# Collaborations

## MHCoE Partners:
- **BNL:** J. Wegrzyn, J. Graetz
- **Caltech:** S.-J. Hwang, C. Ahn
- **HRL:** J. Vajo, P. Liu
- **GA Tech:** D. Sholl
- **JPL:** J. Reiter, J. Zan
- **NIST:** T. Udovic, U. Kettner
- **OSU:** J.-C. Zhao
- **SRNL:** D. Anton, R. Zidan
- **U. Hawai‘i:** C. Jensen
- **U. Illinois:** I. Robertson, D. Johnson
- **UNR:** D. Chandra
- **U. Pitt:** K. Johnson
- **U. Utah:** Z. Fang
- **UTRC:** X. Tang, D. Mosher, S. Opalka

## Other Collaborations:
- **ESRF:** Y. Filinchuk
- **LLNL:** J. Herberg
- **Northwestern:** C. Wolverton
- **UCLA:** V. Ozolins
- **U. Geneva:** K. Yvon
- **U. Maryland:** J.-H. Her
Additional Slides
SNL Major Technical Emphases
2009/2010

2008/2009

- Borohydrides: 45%
- New Materials: 25%
- Theory: 20%
- Nano: 10%

2009/2010

- New Materials: 40%
- Borohydrides: 20%
- Theory: 20%
- Nano: 10%

Improvement of Current Materials
**Motivation:** MHCoE Theory (Sholl) predicts LiBH$_4$ + C has favorable desorption thermodynamics (ΔH = 45.1 kJ/mol H$_2$)

- **Nominal reaction**
  - LiBH$_4$ + C ↔ LiBC + 2H$_2$

- **Also possible:**
  - LiBH$_4$ + 2C ↔ LiBC + CH$_4$
  - LiBH$_4$ + 0.75C ↔ LiH + B + 0.75 CH$_4$

- **Conditions for each calculation**
  - 1 mole LiBH$_4$ + 1 mole C as graphite
  - Constant P (1 atm), constant T

- **Results**
  - LiH and C(s) not stable 300-640 K
    - Converted to CH$_4$ and LiBC
  - Complete conversion to LiBC+H$_2$ only at T > 540 K
  - BH$_3$ is only significant B-containing gas-phase species

-- see more details in ST08 by K. Johnson (Univ. Pittsburgh)
Motivation: Surfactant micelles offer potential for incorporation of MH in the nanoscale

- Nanoparticle Production via Surfactant Templating
  - $\text{H}_2\text{O}/\text{AOT}/\text{decane}$ solutions with $\text{NaBH}_4/\text{H}_2\text{O}$ produced ~10nm particles
  - No suitable $\text{THF}/$surfactant analogs found for alanates/borohydride inclusion
  - Problems with scalability and separation of surfactant excess prevents quantitative characterization

Method down-selected, do not pursue further
Identified Phase Transitions of Four Polymorphs of Ca(BH$_4$)$_2$

$\gamma$-phase ($\text{Pbca}$) is not predicted to be observed at any temperatures†

‡In-situ synchrotron powder diffraction of Ca(BH$_4$)$_2$


$\alpha$ to $\alpha'$ transition
$\alpha'$- to $\beta$ transition

I. Demonstrated the reversibility of the decomposition products by hydrogenation (Sandia high-pressure capability), in collaboration with U. Hawaii:

\[ \text{MgB}_2 + 4\text{H}_2 \rightarrow \text{Mg( BH}_4\_2 \quad 400 ^\circ \text{C}, 950\text{bar} \]

II. Destabilizing Mg(BH\(_4\))\(_2\) with C-doping to improve hydrogen storage properties

**Current Status:** Synthesized doped-MgB\(_2\) from Mg + B + C (dopant-level) and hydrogenated Mg\(_{2(2-x)}\)C\(_x\) precursor to form Mg(BH\(_4\))\(_2\) structure

**Synthesis:**

\[
\begin{align*}
\text{Mg} & + \\
\text{2B} & + \\
\text{dopant} & \\
\text{Argon} & \text{720 } ^\circ \text{C}
\end{align*}
\]

- Powders milled and pressed into pellets
- XRD confirmation of C-doped MgB\(_2\) from (001) peak shift
- Dopant %: 0, 2.5, 10

\[
\begin{align*}
15,000 \text{ psi H}_2 & \\
370 ^\circ \text{C} & \\
\text{XRD of 10% C-doped MgB}_2 & \text{after hydrogenation showing formation of } \beta\text{-Mg(BH}_4\_2\)
\end{align*}
\]

**Summary:** MgB\(_2\) successfully doped with C, subsequently hydrogenated to make Mg(BH\(_4\))\(_2\)

**Future Work:**

- Confirm the presence of carbon in Mg(BH\(_4\))\(_2\) (NMR, XPS)
- Improve the yield to measure the hydrogen capacity of C-doped Mg(BH\(_4\))\(_2\)
- Doping Mg(BH\(_4\))\(_2\) with transition metals
**Methods for Incorporation of Hydride Materials into NFS**

**Current Status:**
- Solution deposition of hydride materials
  - Porous materials (YSZ, C-aerogel) were treated with concentrated solutions of metal hydride
  - Varied solvent (THF, DME, pyridine), exposure time, and drying conditions
  - Results indicate that a super saturated solution can yield up to 50% incorporation by weight, however, H₂ desorption was low
- Solid-state (incipient or melting) incorporation
  - Selected three porous materials (C-aerogel, YSZ, SiO₂) and exposed to metal hydride melt
  - Used high-energy ball milling or high temperature/pressure to mix
  - Ca(BH₄)₂ wets surface of carbon aerogel but retention in the nano-framework structure has not been confirmed

**Future Work:**
- Determination of incipient wetting via melting experiments
- Solution deposition gives highest loading but effects on hydrogen desorption are marginal – propose alternative NFS or hydride materials

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Collaboration -- SNL / UTRC / Albemarle Corp.
Cycling Capacity Loss of Ca(BH$_4$)$_2$
Due to Formation of “B$_n$H$_m$” Species

Theory predicts that Ca(BH$_4$)$_2$ releases H$_2$ to form Ca[B$_{12}$H$_{12}$] upon heating

$^{11}$B MAS-NMR of Ca(BH$_4$)$_2$ with Additive-A

- CaB$_6$
- B$_n$H$_m$
- Ca(BH$_4$)$_2$

$\omega_r = 13$ kHz

XRD of Ca(BH$_4$)$_2$ with Additive-B
After 3rd Desorption

XRD indicates crystalline component is largely CaH$_2$ in desorbed product, while $^{11}$B NMR indicates the presence of amorphous CaB$_6$ and “B$_n$H$_m$” species
Can Ca[B₁₂H₁₂] Absorb/Release H₂?

**Hydrogenation:**

\[ \text{Ca[B₁₂H₁₂]} + x\text{CaH₂} + H₂ \rightarrow \text{No reaction at 400°C, 1000 bar H₂} \]

\[ \rightarrow \text{At 450°C, 1000 bar H₂ traces of Ca(BH₄)₂ form} \]

\[ \text{Ca[B₁₂H₁₂]} + H₂ \rightarrow \text{No reaction at 400°C 1000 bar H₂} \]

**Dehydrogenation:**

\[ \text{Ca[B₁₂H₁₂]} + \text{CaH₂} \]

We found that CaB₁₂H₁₂ is kinetically stable and the formation of it would hinder Ca(BH₄)₂ reversibility.
Enthalpy measurements for the decomposition have been measured using Differential Scanning Calorimetry (DSC). Pressure-Composition-Isotoherms (PCI) measurements are ongoing.

**TGA-DSC of Ca(BH₄)₂**

\[ \Delta H = 24 \text{ kJ/mol H}_2 \]

Integral 735.6 J/g

385.44 °C

Weight Loss: -6.9 %

**Desorption Isotherm at 354 °C**

Expected capacity

*Assuming H₂ is the only gaseous species released upon heating:

\[ 6\text{Ca(BH}_4\text{)}_2 \rightarrow \text{CaB}_{12}\text{H}_{12} + 5\text{CaH}_2 + 13\text{H}_2 \] (6.3 wt% H₂)

STMBMS experiments confirm that H₂ is the predominant product (see our additional slide #39)

**Ongoing measurement**
STMBMS*: A New MHCoE Capability to Elucidate Complex Reaction Processes

* Simultaneous thermo-gravimetric modulated-beam mass spectrometer

This instrument, developed for our national security work, is used to study reaction kinetics of complex systems

**Instrument details:**
- Knudsen effusion cell installed within a furnace and upon a microbalance
- Simultaneous modulated molecular beam mass spectrometer provides time-dependent species info
- High accuracy FTMS for species identification

**Data:**
- Species
- Number density
- Rate of evolution
- Partial pressure
- Temperature

Data is correlated and analyzed to determine reaction processes and kinetics

A variety of gaseous species observed during decomposition process (i.e. BH$_3$)

Lower temperature hydrogen release observed for catalyzed-Ca(BH$_4$)$_2$

H$_2$ released in multiple steps from Ca(BH$_4$)$_2$

Additives modify the kinetics and increase the amount of BH$_3$ released (~1% of H$_2$ stream)
**Motivation:** Search for new high capacity hydrogen storage materials

Ball-milled various molar-ratio mixtures of borohydride, amides and binary hydrides to form compounds with intermediate hydrogen capacities

**Selected XRD Results:**

- XRD indicates that the starting materials, $M(BH_4)_x$ and $M'(NH_2)_y$, are no longer present and new phases form.
- Raman spectroscopy indicates the presence of $(BH_4)^-$ and $(NH_2)^-$ anions, $\sim 2300$ and $\sim 3250$ cm$^{-1}$, respectively.

Characterization of hydrogen storage properties is on-going.

**Motivation:** Alanates generally have better reversibility compared to pure borohydrides

- Synthesis: $\text{LiAlH}_4 + \text{LiBH}_4 + \text{CaCl}_2 \rightarrow \text{Ca(AlH}_4)(\text{BH}_4) + 2 \text{LiCl}$
- XRD indicates no $\text{LiBH}_4$ or $\text{LiAlH}_4$
- Raman spectroscopy indicates $(\text{BH}_4)^{-}$, $(\text{AlH}_4)^{-}$ anions present in product
- Initial studies show no reversibility at 200°C, 65 bar $\text{H}_2$ pressure, experiments ongoing

**Predicted high symmetry structure**

$\text{M(AlH}_4)/(\text{BH}_4)$ are promising new hydrogen storage materials