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

Ewa Rönnebro and Eric Majzoub
Sandia National Laboratories
June 12, 2008

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Sandia Program Overview

**Timeline**
- Project started in March ‘05
- Project end ~ 2010
- Percent complete 60%

**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**
- $1.96M in FY ‘07
- $2.01M in FY ‘08

**MHCoE Partners**
- Caltech, ORNL, JPL, UNR, Stanford, UIUC, Utah, UH, PITT, SRNL, HRL, CMU, GE, NIST, BNL, Intematix, UTRC, UNB

**Collaborators**
- V. Ozolins (UCLA), K. Yvon (U. Geneva), J. Herberg (LLNL), Y. Filinchuk (ESRF)
- C. Wolverton (Northwestern)

Note: Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States 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

Ewa Rönnebro: Proj. B POC, new materials
Eric Majzoub: PEGS theory, experiments (Sandia/UMSL)
Mark Allendorf: Theory, Theory Group Coordinator
Tony McDaniel: High-throughput screening
Ethan Hecht: High-throughput screening
Mutlu Ulutagay-Kartin (since 12/07)
Vitalie Stavila (since 1/08)

Ph.D. Students

Godwin Severa: U. Hawai’i
Rebecca Newhouse, Leo Seballos: UC Santa Cruz

Other Key Contributors

Bob Bastasz, Tim Boyle, Andy Lutz, Bill Houf
Discovering New Complex Hydride Materials

Experimental

- Established a synthesis route that combines high-energy milling followed by hot-sintering under high H₂-pressures:
  - Metal + Binary Hydride + H₂ → Complex Hydride
  - Boride + Binary Hydride + H₂ → Metal Borohydride
  (Normal run: P < 700 bar, T < 450°C)

- New Start (7/1/2007): Improving kinetics, cycling life and desorption properties by incorporation of hydride materials in nanoframeworks. Teaming with UTRC (lead)

Theory

- The Prototype Electrostatic Ground State (PEGS) technique for structure determination and ΔH estimates

- Provide MHCoE partners with theoretical support
  -- provide Al-N bond energies for AlH₃ regeneration studies (BNL).
Status in March 2007:

- Ca(BH$_4$)$_2$ partially reversible at 700bar and 400-450°C
- New compounds found in the ternary Ge and Mn systems, but H-content too low
- Theory predicted bialkali borohydrides

Focus during FY07/FY08:

- Focus on re-hydriding Ca(BH$_4$)$_2$ at lower P and T
- Synthesis of PEGS-predicted bialkali borohydrides
- Re-hydriding low-temperature borohydrides utilizing our high-pressure capability. Teaming with Craig Jensen (UH) (in additional slides)
Ca(BH$_4$)$_2$ as H-storage Material

**Motivation:** In FY06, theory predicts Ca(BH$_4$)$_2$ has nearly ideal thermodynamics ($\Delta H \sim 40$ kJ/mol H$_2$), 9.6 wt. %

Ozolins, Majzoub and Wolverton, in preparation

**Status 3/07:**

\[
\text{CaB}_6 + 2\text{CaH}_2 + 10 \text{H}_2 \rightarrow 3\text{Ca(BH}_4\text{)}_2 @700\text{bar, } 400^\circ\text{C, } 48\text{hours}
\]

- Starting with anticipated decomposition products implies reversibility

**This year:**

**What is the decomposition reaction mechanism?**

**Can Ca(BH$_4$)$_2$ be re-hydrided at lower pressures and temperatures?**

- Partial reversibility observed during in situ synchrotron studies at Brookhaven by Job Rijssenbeek, Yan Gao, Ewa Rönnebro, J.-C. Zhao, unpublished data (2007)

- Partial reversibility of 3.8 wt% at 350°C and 90 bar reported from TGA by J.H. Kim et al, Scripta Materialia, **58**, 481 (2008)
Identified Crystal Structures of $\alpha$, $\alpha'$, $\beta$ Ca(BH$_4$)$_2$ Polymorphs

In-situ synchrotron data from ESRF, Ca(BH$_4$)$_2$ made by desolvating an Aldrich sample

$$(\alpha, \beta) \rightarrow (\alpha', \beta) \xrightarrow{-H_2} \text{desorption products}$$

$160 \, ^\circ\text{C}$

$350 \, ^\circ\text{C}$

$\alpha \rightarrow \alpha'$ at ~$160^\circ\text{C}$

$\beta$-phase does not transform into $\alpha'$, and decomposes at $350^\circ\text{C}$ to release $H_2$

$\alpha'$-phase forms above $160^\circ\text{C}$. Decomposes at $350^\circ\text{C}$ to release $H_2$

The polymorphs have different stability depending on temperature, and can be manipulated with additives

Also see ST37 D. Chandra, U. Nevada-Reno

Y. Filinchuk, E. Rönnebro, D. Chandra, submitted
11B MAS-NMR Reveals \( \text{Ca}(\text{BH}_4)_2 \) Decomposition Products

- Desorption at 320 °C leads to \( \text{CaB}_6 \) and \( \text{CaH}_2 \)
- Desorption at 450 °C leads to \( \text{CaB}_6 \) and probably a-B

Confirmed decomposition products, and found intermediate species

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\( \omega_r = 12-13 \text{ kHz} \)

\( \text{a-Boron (ref.)} \)

\( \text{CaB}_6 \text{(ref.)} \)

Desorbed at 320 °C

Desorbed at 450 °C

\( \text{Ca}(\text{BH}_4)_2 \) as made (uncatalyzed)

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likely \( \text{CaB}_{12} \text{H}_{12} \)

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-- see more details in ST34 by R. Bowman, JPL

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Hwang, Bowman, Kim, Reiter, Zan, Rönnebro

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 ppm

100 80 60 40 20 0 -20 -40 -60 -80 -100
Investigated Effect of Additives on Desorption Kinetics of Ca(BH₄)₂

Additives change desorption kinetics and released H₂

Desorption curves collected in Sievert’s apparatus

~7 wt. % H rapidly desorbed at 360 °C

Four different additives A-D of 2 mol% dopant level, compared to no additive
Additives Aid Reversibility of Ca(BH$_4$)$_2$ at lower P and T

Re-hydrided at 350°C and 120 bar to ~4.5wt% (A) in 12 hours

~3.5 wt% H re-hydrided in 1 hour

Additive B
Additive A
No Additive

Time (min)

Wt% H

3x improvement in hydrogenation kinetics with additives

Ewa Rönnebro, Vitalie Stavila, Mutlu Ulutagay-Kartin, manuscript in progress
**New LiK(BH₄)₂ Synthesized**

**Motivation:** Improving thermodynamics by changing cationic matrix

Ball Milled: \( \text{LiBH}_4 + \text{KBH}_4 \rightarrow \text{LiK(BH}_4\text{)}\text{_2} \quad (10.6 \text{ H wt.\%})

- XRD shows new phase plus ~10% KBH₄, no LiBH₄
- Stable orthorhombic structure calculated as low-energy structure

Nuclear Magnetic Resonance

(Hwang, Bowman et al)

- Confirms no LiBH₄, in agreement with XRD

- TGA did not show \( \text{H}_2 \) evolution below 500°C

∴ Do Not Pursue Further

Synthesis of \( \text{LiK(BH}_4\text{)}\text{_2} \) reported by P. Edwards et al, ISHE, Richmond, VA, 2007
High-Throughput Screening (HiTS) of Catalysts

Tony McDaniel
Mutlu Ulutagay-Kartin
Ethan Hecht

Completed Initial Proof of Principle Experiments using micro-hotplate reactors:

- Demonstration of in-situ calorimetry, H₂ cycling diagnostics
- Synthesis of NaAlH₄ from ball-milled Al + NaH precursors + H₂
- In-situ demonstration of NaAlH₄ catalysis by Ti

- Developed software architecture required for combinatorial work

Solved problems associated with hotplate reliability, but other hardware reliability issues emerged when examining higher T materials.

Not operational. DOE/MHCoE Coordinating Council reviewed options for materials screening, decided to pursue other methods. ∴ HiTS discontinued.
<table>
<thead>
<tr>
<th>Month/year</th>
<th>Milestone or Go/No-Go decision</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mar-08</td>
<td>Milestone: Show reversibility of Ca(BH$_4$)$_2$ at lower pressures and temperatures. <strong>Accomplished.</strong></td>
</tr>
<tr>
<td><strong>✓</strong> Mar-08</td>
<td>Milestone: Acquire data on new materials and catalyst searches with HiTS methodology. <strong>Not accomplished, activity discontinued</strong></td>
</tr>
<tr>
<td>Sep-08</td>
<td>Milestone: Complete Pressure-Composition-Temperature isotherms for Ca(BH$_4$)$_2$ to determine reaction enthalpy</td>
</tr>
<tr>
<td>Mar-09</td>
<td>Go/no-go on Ca(BH$_4$)$_2$: Characterize and improve Ca(BH$_4$)$_2$ kinetics properties with additives (Teaming with JPL, Caltech, NIST)    Milestone: Discover new borohydride related materials (Teaming with U. Ohio and U. Utah)</td>
</tr>
<tr>
<td>May-09</td>
<td>Milestone: Lowering of Ca(BH$_4$)$_2$ desorption temperature Go/no-go on AkTm(BH$_4$)$_x$: Reversibility of alkali transition metal borohydrides (Teaming with U. Hawaii)</td>
</tr>
<tr>
<td>Sep-09</td>
<td>Milestone: Incorporation of hydride material in catalyzed nanoframeworks (Teaming with UTRC)</td>
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</table>
Status in March 2007:

- Validated PEGS method with known compounds
- Predicted stable bialkali borohydrides with PEGS

Focus during FY07/FY08:

- Predicting structures and thermodynamics of Ca(BH₄)₂, NaK(BH₄)₂, and other promising compounds
- Quantitative evaluation of PEGS versus ICSD
- Explore use of PEGS with alkali-transition metal borohydrides such as LiSc(BH₄)₄ (teaming with JPL and Caltech)
- Use quantum chemical methods to calculate bond energies of alane complexes (in support of BNL AlH₃ regeneration studies)
Crystal Structures For Materials Discovery Using PEGS or Database Searching

**PEGS** - Prototype Electrostatic Ground States
- Global optimization of electrostatic energy
- Potential energy smoothing
- Model anions as rigid units


**Database searching**
- Few hits for some compounds
- A new material may have a new crystal structure

**First-principles density functional theory (DFT)** is used for accurate energies and thermodynamics calculations

**PEGS provides high-quality structures using the basic physical principles governing atomic interactions in complex hydrides**
PEGS Method Produces Best Candidate for Mg(BH$_4$)$_2$ Ground State

Experimental Mg(BH$_4$)$_2$ Crystal Structures

LT $P6_1$, 30 f.u./conv cell
HT $Fdd$,$d$, 64 f.u./conv cell


$\bar{I}4m2$ 4 f.u. primitive cell

V. Ozolins, E. H. Majzoub, C. Wolverton

PEGS prediction LT $I\bar{4}m2$

PEGS structure implies metastability of synthesized Mg(BH$_4$)$_2$

Preferred decomp: Mg(BH$_4$)$_2$ $\rightarrow$ 1/6 MgB$_{12}$H$_{12}$ + 5/6 MgH$_2$ + 13/6 H$_2$

(MgB$_{12}$H$_{12}$ also predicted with PEGS method)
PEGS Predicts Weakly Metastable NaK(BH$_4$)$_2$

PEGS provides several high-symmetry candidates that may be observed as polymorphs

<table>
<thead>
<tr>
<th>Space Group</th>
<th>E-E$_0$ [meV/f.u.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>146 $R3$</td>
<td>+110</td>
</tr>
<tr>
<td>148 $R\bar{3}$</td>
<td>+80</td>
</tr>
<tr>
<td>156 $P3m1$</td>
<td>+76</td>
</tr>
<tr>
<td>166 $R\bar{3}m$</td>
<td>0.0</td>
</tr>
</tbody>
</table>

NaK(BH$_4$)$_2$ predicted to be mildly unstable
(-3kJ/mol at T = 0K) No ZPE included!

✓ NaK(BH$_4$)$_2$ synthesized
✓ XRD confirms predicted new phase (metastable)

MAS NMR indicates new chemical environment for Na and K.
∴ New compound formed

J. Herberg, LLNL
PEGS Finds High-Symmetry Candidate for LiSc(BH$_4$)$_4$

Ball milled: ScCl$_3$ + 4LiBH$_4$ → LiSc(BH$_4$)$_4$ + 3LiCl (14.5 H wt. %)

Rxn takes place, but:
- X-ray diffraction inconclusive on structure
- NMR indicates new phase
- ICSD search has very few structure candidates

PEGS applicable to transition metal borohydrides with some covalent character
PEGS Ca(BH$_4$)$_2$ Search Explains Experimental Observations

PEGS-structure of $\beta$-Ca(BH$_4$)$_2$
Confirmed by Rietveld refinements

Temperature dependence of $\alpha$ and $\beta$ polymorphs

Preliminary calculation shows $\alpha$-to-$\beta$ transition

- PEGS finds four high-symmetry structures for Ca(BH$_4$)$_2$
- All appear to be observed in X-ray diffraction – new polymorphs!
- Rietveld refinements indicate we have found the correct beta phase structure

E. Majzoub and E. Rönnebro, manuscript submitted
Found Promising Adducts for Liquid-phase Alane Regeneration

*A MHCoE collaboration between SNL and BNL*

We need accurate $H_3Al—NR_3$ complexation energies to optimally choose $NR_3$

Our solution: Bond Additivity Correction Methods
- Sandia in-house codes based on Gaussian 03 suite
- Corrects systematic errors in computed energies
- More accurate than DFT/B3LYP
- Chemical accuracy ($\pm 1 – 2$ kcal/mol for heats of formation)
- Provides temperature-dependent thermodynamics

Comparison of BAC methods with standard DFT used by chemists

<table>
<thead>
<tr>
<th>Method</th>
<th>Avg. error</th>
<th>Test set (heats of formation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BAC-MP4</td>
<td>1.25</td>
<td>93 species</td>
</tr>
<tr>
<td>BAC-G2</td>
<td>0.69</td>
<td>143 species</td>
</tr>
<tr>
<td>DFT/B3LYP</td>
<td>3.11</td>
<td>148 species</td>
</tr>
</tbody>
</table>

*$\text{kcal/mol}$
Pyridine, Pyrazine Are Promising Adducts

TEDA-bound AlH$_3$ is too stable – what other amines to try?

Computed Al-N complexation energies (BAC-MP2), kJ/mol at 298 K

<table>
<thead>
<tr>
<th>1:1 Complexes</th>
<th>Al-N BDE</th>
<th>1:2 Complexes</th>
<th>Al-N BDE</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlH$_3$.NMe$_3$</td>
<td>147.6 (108.1)</td>
<td>AlH$_3$.2NMe$_3$</td>
<td>217.9 (145.9)</td>
</tr>
<tr>
<td>AlH$_3$.NEt$_3$</td>
<td>118.6 (89.1)</td>
<td>AlH$_3$.2NEt$_3$</td>
<td>158.7 (90.9)</td>
</tr>
<tr>
<td>AlH$_3$.TEDA</td>
<td>156.3 (115.4)</td>
<td>AlH$_3$.2TEDA</td>
<td>233.8 (155.4)</td>
</tr>
<tr>
<td>AlH$_3$.Quinuclidine</td>
<td>159.9 (118.4)</td>
<td>AlH$_3$.2Quinuclidine</td>
<td>236.7 (156.0)</td>
</tr>
<tr>
<td>AlH$_3$.pyridine</td>
<td>135.2 (109.2)</td>
<td>(AlH$_3$)$_2$.pyrazine</td>
<td>110.4</td>
</tr>
<tr>
<td>AlH$_3$.pyrazine</td>
<td>125.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Red: BAC-MP2; Blue: DFT/B3LYP (McGready et al.)

BAC trends agree with DFT (McGready et al.)

- 2:1 complexes (e.g. (AlH$_3$)$_2$ • pyrazine): significantly less stable
- 1:2 decomposition kinetics determined by Al-N bond in 1:1 complex

Computations of Al-O BDE are underway
### Theory Milestones FY07&FY08

<table>
<thead>
<tr>
<th>Month/year</th>
<th>Milestone or Go/No-Go decision: PEGS Theory</th>
</tr>
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<tbody>
<tr>
<td>Apr-08</td>
<td>Milestone: Complete Ca(BH₄)₂ polymorph structure determination and first-principles-calculated reaction pathways. <strong>Accomplished</strong></td>
</tr>
<tr>
<td></td>
<td>![Checkmark]</td>
</tr>
<tr>
<td>Sep-08</td>
<td>Milestone: Begin extension of PEGS method to nanoparticle hydrides</td>
</tr>
<tr>
<td>Mar-09</td>
<td>Go/no-go: Search for <em>mixed-anion</em> materials with large wt. % H</td>
</tr>
<tr>
<td>May-09</td>
<td>Go/no-go: Determine accuracy of PEGS method in nanoparticle energetics</td>
</tr>
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<th>Milestone or Go/No-Go decision: Al-Adduct Theory</th>
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<tr>
<td>May-08</td>
<td>Milestone: Complete BAC calculations of alane-amine complexes. <strong>Accomplished</strong></td>
</tr>
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<td></td>
<td>![Checkmark]</td>
</tr>
<tr>
<td>Sep-08</td>
<td>Milestone: Complete BAC calculations on alane-adduct complexes</td>
</tr>
<tr>
<td>Dec-08</td>
<td>Go/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>
**Calcium Borohydride**

- Showed partial reversibility at lower P and T: 100 bar and 350°C

- Showed drastic improvement in kinetics by choosing right additives

- Elucidated crystal structures of polymorphs using a combined theoretical/experimental approach, i.e. the PEGS-method and the Rietveld-method
New Hydrogen Storage Materials

- Synthesized LiK(BH₄)₂, do not pursue further due to poor thermodynamics
- Synthesized PEGS-predicted NaK(BH₄)₂, do not pursue further due to instability
- Re-hydrided high-capacity material by teaming with U. Hawai‘i on low-temperature borohydrides, utilizing our HP-station
- Predicted lowest-energy structure and decomposition products for Mg(BH₄)₂
- Showed that PEGS can provide transition metal borohydride structures
- Found promising adducts for liquid-phase AlH₃ regeneration based on bond-energy calculations
Future Work in FY2008

**Borohydrides**
- Determine $\Delta H$, improve kinetics and cycle life of Ca(BH$_4$)$_2$
- Synthesize borohydrides predicted by PEGS method
- Discover new borohydride related materials (teaming with U. Hawai’i, Ohio State and U. Utah)

**Nano-structured hydrides and catalyzed nanoframeworks**
- Incorporate Ca(BH$_4$)$_2$ into catalyzed nanoframeworks (with UTRC)
- Investigate kinetic improvements
- Synthesis of nanostructured complex hydrides

**Theory**
- Predict new materials with a variety of complex anions ($N_nH_n$, $B_nH_n$, etc.)
- Resolve xtal structures of polymorphic hydrides (e.g. Mg(BH$_4$)$_2$, Ca(BH$_4$)$_2$)
- Continue Al-adduct theoretical studies to optimize AlH$_3$ regeneration
Future Work in FY2009

**Borohydrides**
- Synthesize borohydride-related materials and explore their reversibility based on theoretical predictions. Continue optimizing performance of calcium borohydride and other materials

**Theory**
- Theory will continue guiding experiment and predict stable structures in promising systems, continue coordination of MHCoE Theory Group

**Nanoengineering**
- Incorporation of hydride materials in catalyzed nanoframeworks
- Explore possibilities to design alternative nanostructured metal hydrides to improve hydrogen storage properties

hydride incorporation into nanoframeworks