Metal Hydride Center of Excellence

Lennie Klebanoff, Director (presenting)

Jay Keller, Deputy Director

This presentation does not contain any proprietary information

Project ID# ST 13
Outline

• Summary of MHCoE Organization, Participants, Activities

• Sandia Program Overview
  – Li/X Amide Materials for H₂ Storage
  – Discovering New Complex Hydrides
  – Summary of Accomplishments for FY 2006
  – Summary of Future Work 2006 and 2007
  – Response to Reviewer Comments from 2005 Review
  – Publications and Presentations
New MHCoE Project Structure

Coordinating Council (2006)
Greg Olson (HRL), Craig Jensen (UH), Lennie Klebanoff (SNL), Jay Keller (SNL)
Jim Wegrzyn (BNL), Ian Robertson (UIUC), Bruce Clemens (Stanford)

Project Groups

A
- Destabilized Hydrides
  - HRL(POC)
    - Caltech
    - JPL
    - Stanford
    - U. Hawaii
    - U. Pitt/CMU
    - UIUC
    - U. Utah
    - Intematix
    - NIST

B
- Complex Anionic Materials
  - SNL(POC)
    - GE
    - U. Hawaii
    - UIUC
    - JPL
    - ORNL
    - NIST
    - Intematix
    - UNR

C
- Amides/Imides (M-N-H)
  - SNL(POC)
    - GE
    - U. Utah
    - UNR
    - ORNL
    - U. Hawaii
    - JPL

D
- Alanes (AlH₃)
  - BNL(POC)
    - GE
    - U. Hawaii
    - SNL

E
- Engineering Analysis & Design
  - SRNL(POC)
    - NIST
    - JPL
    - GE
    - SNL

MHCoE Budget: $6.33M FY’06
Project A – Destabilized Hydrides

Develop strategies for reducing H₂ storage thermal requirements, improve hydride kinetics

See talk by: Greg Olson, HRL

Project B - Complex Anionic Materials

Predict, synthesize and evaluate promising new complex hydride materials
Project C - Amides/Imides

Assess viability of amides, imides for on-board H₂ storage

Project D - Alane (AlH₃)

Understand desorption and regeneration properties of alane for H₂ storage

See talk by: Jason Graetz, BNL
Project E: Engineering Design, Analysis and Test

Provide engineering, analysis and design supporting DOE system performance goals. Provide engineering based materials targets

See poster by: SRNL

Thermal Modeling

Media thermal measurements
Collaboration is Key to MHCoE

Materials Development

Mechanisms & Modeling

System Design & Engineering

2010 Material
Project Groups Milestone Chart

Milestone Chart has been implemented Center-wide:

- Progress checked quarterly against milestones, aids planning tracks technical risk, rolls up to MYRDDP Milestones

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<thead>
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<th>Organization</th>
<th>Task Description</th>
<th>Timeline begins FY05 (10/1/2004) and ends FY12 (9/30/12). Each cell is 6 months in duration for which the start date is shown below.</th>
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<td>MHCoE Center Milestones</td>
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<td>A. Destabilized Hydrides</td>
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<td>B. Complex Anionic Materials (Borohydrides &amp; Alanates)</td>
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<td>C. Amide/Imides (M-N-H Systems)</td>
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<td>E. Engineering Analysis &amp; Design</td>
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<td>Portfolio Reallocation Decision Point (Project bars)</td>
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<td>Output (Task bars)</td>
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**Sandia Program Overview**

**Timeline**
- Project started in March ‘05
- Project end ~ 2010
- Percent complete ~ 20% for project duration

**Barriers**
*MYPP Section 3.3.4.2.1 On-Board Storage Barriers*
- A. – G. Cost, Weight & Volume, Efficiency, Durability, Refueling Time, Codes & Standards, Life Cycle & Efficiency Analyses
- M. Hydrogen Capacity and Reversibility
- N. Lack of Understanding of Hydrogen Physisorption and Chemisorption
- O. Test Protocols and Evaluation Facilities
- P. Dispensing Technology

**Budget**
- $1.99M in FY ‘05
- $2.26M in FY ‘06

**Collaborators**

**MHCoE Partners**
Sandia Team (~ 6 FTEs):

Director Change: Wang → Klebanoff

Core Technical Team

Weifang Luo
Andy Lutz
Eric Majzoub
Tony McDaniel
Ewa Ronnebro
Roland Stumpf

Other Key Contributors

Mark Allendorf, Bob Bastasz, Tim Boyle, Bill Houf
Karl Gross (Hy-Energy)
Outline

• Summary of MHCoE Organization, Participants, Activities
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  – Li/X Amide Materials for H₂ Storage
    *Weifang Luo (PI), Lennie Klebanoff (Presenting)*
  – Discovering New Complex Hydrides
  – Summary of Accomplishments for FY 2006
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Li/X Amides

Status in May 2005:

- Li/Mg amide isotherms measured (40 bar at 220 C)
- Time-dependent absorption/desorption measured for Li/Mg amide
- Completed initial cycling measurements (~100 cycles) for Li/Mg amide
- A speculative new reaction path proposed

Accomplishments in FY 2006:

- Determined reaction pathway for Li/Mg amide by FTIR and XRD
- Quantified NH₃ release accompanying H₂ desorption from Li/Mg Amide
- Examined an alternative to Mg: \(2\text{LiNH}_2 + \text{LiAlH}_4\)
- Began engineering study for this class of materials (cycling life, expansion)
- Conducted contamination (air exposure) tests for Li/Mg amide
- Assessed Ti, ZnO, Pd, Pt, Ni, Cr₂O₅ for catalysis of Li/Mg system (slight effect found)
FTIR Reveals Chemical Pathway

FTIR Assignments (supported by XRD):

1. Fully H₂ desorbed: -N-H character (imide)
2. Fully H₂ re-absorbed: Mg(NH₂)₂ (amide)
3. Starting material (2LiNH₂ + MgH₂) not recovered
Li/Mg Amide Reaction Pathway Elucidated

**Observed Pathway:**

\[ 2\text{LiNH}_2 + \text{MgH}_2 \rightarrow \text{MgLi}_2(\text{NH})_2 + 2\text{H}_2 \text{ (irreversible)} \]

\[ \text{Mg(NH}_2)_2 + 2\text{LiH} \]

\[ \text{Mg(NH}_2)_2 + 2\text{H}_2 \rightarrow 5.5 \text{ wt\%} \]

\[ \text{(Mg, Li, N) + H}_2 \rightarrow \text{X} \text{ (Not observed)} \]

- Irreversible transformation of \(2\text{LiNH}_2 + \text{MgH}_2\) into \(\text{Mg(NH}_2)_2\)
- \(\text{Mg(NH}_2)_2\) a risk for \(\text{NH}_3\) release (capacity loss, FC catalyst poisoning)
- Ti, ZnO, Pd, Pt, Ni, \(\text{Cr}_2\text{O}_5\) catalysis effect found to be slight (SNL)

**Hydrogen in imide is inaccessible**
**NH₃ Release Quantitatively Determined**

![Graph showing NH₃ release with temperature](image)


Material loss due to NH₃ release: ~ 3% of original storage capacity over 200 cycles, with 300ppm NH₃

Irreversible loss of (2LiNH₂ + MgH₂) starting material observed

Draeger Tube was used to quantify NH₃ in H₂
Uncertainty: ± 60 ppm
(2LiNH$_2$+MgH$_2$): Cycle Life at 200$^\circ$C

Slow kinetics, capacity affected by charging time

After 264 Cycles, 23% of storage capacity is lost
Difficulties with Li/Mg Amide

- Hydrogen in imide is not accessible
- Storage material volatilizes by NH$_3$ release
- Significant loss of storage capacity observed with cycling
- Slow kinetics, not significantly improved by catalysis

We suggest reducing the experimental effort on Li/Mg Amides, and assess theoretical options for enabling this class of material
**Synthesized New Li-Al-N-H Compound**

\[ 2\text{LiNH}_2 + \text{LiAlH}_4 \rightarrow \text{Li}_3\text{AlN}_2 + 4\text{H}_2 \quad \text{9.5 wt. % (theo.)} \]

**Synthesis Forward:**

**Ball Milling:** \( 2\text{LiNH}_2 + \text{LiAlH}_4 \rightarrow [\text{Li-Al-N-H}] \)

- Spontaneous release at RT of \( \text{H}_2 \), exothermic reaction

[Li-Al-N-H] structural characterization:
- Evidence for Al-N bonding
- 4-coordinated Al, \([\text{LiAlH}_{4-x}\text{N}_x]\), stable complex

**Synthesis Backward:**

\[ \text{Li}_3\text{AlN}_2 + 2\text{H}_2 \rightarrow \text{LiNH}_2 + 2\text{LiH} + \text{AlN} \]

For complete hydrogenation, need:
- High \( \text{H}_2 \) pressure (120 bar)
- High T (330C)
- Long Time (3 days to 5.17 wt %)

*In collaboration with Ping Chen (NUS)*
Amides: FY 06 Accomplishments

• Determined reaction pathway for \((2\text{LiNH}_2+\text{MgH}_2)\)

• Quantitatively measured \(\text{NH}_3\) contamination of desorbed \(\text{H}_2\) from Li/Mg (~420 ppm \(\text{NH}_3\) at 220C)

• Measured extended cycling life of Li/Mg amide: Desorption capacity strongly depends on absorption history.

• Synthesized new Li-Al-N-H compound, characterized composition

• Conducted hydrogenation studies of \(\text{Li}_3\text{AlN}_2\), ~4 H atoms can be absorbed per \(\text{Li}_3\text{AlN}_2\), with high pressure, high temperature and slow kinetics.

• Obtained first engineering results (expansion pressure) for Li/Mg Amide

• Conducted air exposure tests for Li/Mg amide: stable after 10 min exposure to dried/wet air at 220C
Future Amide Work in FY2006/2007

FY 2006:

• Use theory to assess possible modifications to Li/Mg amide system

• Acquire more data on structure of [Li-Al-N-H] complex, identify product from ball milling 2LiNH₂ and LiAlH₄. Use theory to guide strategy for lowering thermodynamic stability of [Li-Al-N-H] complex

FY 2007:

• As guided by theory, perform further exploratory studies on modified amide systems

2007 amide effort will be reduced and redirected to novel preparations of borohydrides
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    *Ewa Rönnebro and Eric Majzoub (presenting)*
    
    Tim Boyle, Sherrika Daniel-Taylor, Roland Stumpf
  – New Materials Synthesized: K₂LiAlH₆, Borohydrides, Na-Si-H
  – Monte Carlo Modeling of Hydride Stability, Thermodynamic Calculations
  – Discovering New Complex Hydrides
  – Summary of Accomplishments for FY 2006
  – Summary of Future Work 2006 and 2007
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Status in May 2005

- Established synthesis route for high-pressure sintering of metal hydrides
- Discovered K$_2$LiAlH$_6$, needed characterization
- Need for rapid assessment of candidate materials when crystal structures are unknown
- New borohydride materials needed

Accomplishments in 2006

- Optimized synthesis route and characterize K$_2$LiAlH$_6$
- Synthesized high-capacity borohydrides
- Discovered new metal hydrides by hot-sintering under high-hydrogen pressures
- Developed Monte Carlo technique for estimating reaction enthalpies for candidate materials,
- Performed calculations for hydrogen release from borohydrides
Finding New Complex Hydrides

• The 2010 specifications require new hydride materials

• Our approach to new materials discovery
  – Seek new material systems by new combinations of elements
  – Developed rapid theoretical assessment capability
Discovering New Complex Hydride Materials

**Experiment**

- Established a synthesis route that combines high-energy milling (SPEX) followed by hot-sintering under high H$_2$-pressures:

  \[
  \text{Metal + Binary Hydride + H}_2 \rightarrow \text{Complex Hydride} \\
  (P < 2000\text{bar}, T < 500\text{C})
  \]

- Established a solvent-based exchange route for preparing borohydrides:

  \[
  \text{MCl}_x + x\text{NaBH}_4 \rightarrow \text{M(BH}_4)_x + x\text{NaCl} \\
  (\text{DME, THF}...) 
  \]

**Theory**

- Developed a Monte Carlo technique which provides minimum energy structures for subsequent enthalpy estimates
- Full thermodynamics calculated for promising materials
Nine New Materials Synthesized

High-pressure hot-sintering
- $K_2LiAlH_6$
- Ca-B-H
- Mg-B-H
- Na-Si-H

Solvent-based chemistry
- $Ca(BH_4)_2(THF)_2$
- $Ti(BH_4)_3(DME)$
- $Sc(BH_4)_2(THF)_2$
- $Al(BH_4)_3 (py)$
- $Mg(BH_4)_2(THF)_2$

Other sintering techniques in the literature: U. Geneva (Switzerland), MPI (Germany), Stockholm University (Sweden), IFE (Norway), SRNL (USA), U. Tohoku (Japan)
A New Bialkali Alanate Discovered

• We wanted to find an alanate with higher H-content and better sorption properties than sodium alanate (NaAlH₄).
• In FY’05 these bialkali alanate systems were investigated:
  - Li-K-Al-H (successful synthesis)
  - Li-Mg-Al-H
  - Li-Ca-Al-H
  - Li-Ti-Al-H
  - Mg-Ti-Al-H

Potential for >6wt% Hydrogen

• In FY’06 the synthesis route was optimized by mixing LiAlH₄ + 2KH and treating at 700 bar H₂-pressure and 320ºC for 1 day.

Other known bialkali alanates in the literature: Na₂LiAlH₆ and K₂NaAlH₆

Characterized $K_2LiAlH_6$

$LiAlH_4 + 2KH \rightarrow K_2LiAlH_6$ at 700 bar and 320°C

• Hydrogen storage properties:
  Desorption >200°C; Absorption >320°C and 100bar $H_2$
  $K_2LiAlH_6 \leftrightarrow 2KH + LiH + Al + 3/2H_2$ (2.5 wt % Theo.)
  Slow kinetics

• $K_2LiAlH_6$ is isostructural with HT-$K_2LiAlF_6$
• Structure supported by ab-initio calculations

Plot from Rietveld refinement

$R-3m$ (no. 166)
$a = 5.62$, $c = 27.41$Å

Note: Not the same phase as J. Graetz et al, Phys. Rev. B, v. 71, (2005) 184115
First Solid-state Synthesis of Ca-B-H Compound

Motivation: Theory predicts Ca(BH₄)₂ has promising thermodynamics

Ca(BH₄)₂ contains 9.6 wt% (theo.) hydrogen

• Attempted synthesis route: \[ \text{CaB}_6 + 2\text{CaH}_2 + 10\text{H}_2 \rightarrow 3\text{Ca(BH}_4)_2 \] (700bar, 400C (high-pressure sintering))

• Characterization by XRD, Raman, DSC&TGA and Neutron Diffraction
In-situ XRD in progress to confirm composition

• Preliminary hydrogen sorption properties for CaB₆+2CaH₂:
  – Absorption >350C at 100bar H₂
  – Desorption >250C
  – Kinetics slow (~2 weeks for charging) and <1wt% reversible, but theory predicts higher wt% for calcium borohydride

Collaborations with
JPL/LLNL (NMR), U. Illinois (TEM), In-situ XRD (U. Nevada), NIST (NPD)
Five Metal Borohydrides Made by Solvent-based Route

\[
\text{MCl}_x + x\text{NaBH}_4 \xrightarrow{\text{DME, THF...}} \text{M(BH}_4)_x + x\text{NaCl}
\]

Metal borohydrides synthesized in FY06:

- Ti(BH\(_4\))\(_3\) (DME)
- Sc(BH\(_4\))\(_3\) (THF)\(_2\)
- Al(BH\(_4\))\(_3\) (py)
- Mg(BH\(_4\))\(_2\) (THF)\(_2\)
- CaBH\(_4\) (THF)\(_2\)

Solvent-free products being investigated

Raman Spectrum

XRD Pattern

Structural investigation in progress
Evidence for First Na-Si-H Compound

2NaH + Si $\rightarrow$ [Na-Si-H] (high-pressure sintering)

- Investigation of $[\text{SiH}_6]^2-$ stabilization by $\text{Li}^+$, $\text{Na}^+$ or $\text{Ca}^{2+}$
- XRD reveals new phases in Na-Si-H system
  - Hydrogen content being investigated by neutron spectroscopy and NMR
  - Different phases appear depending on reaction conditions

Collaborations with
NIST (NPD),
JPL&LLNL (NMR)
U. Utah (reactive milling)
HRL (milling)

\[ XRD \text{ pattern} \]
\[ \uparrow = \text{New phase} \]
FY 2006 Accomplishments: Alanates, Borohydrides, New Materials

**Alanates**
- A new alanate, $K_2LiAlH_6$, was used to develop new discovery strategies
- Determined structure of $K_2LiAlH_6$ and investigated hydrogen sorption properties
- Ab-initio calculations verified the crystal structure

  --The work on alanates will not continue since these materials cannot meet the DOE specifications

**Borohydrides**
- Solid-state synthesis of new borohydrides was demonstrated to be feasible in the Ca-B-H and Mg-B-H systems
- Synthesized several metal borohydrides by solvent based exchange reaction

**New Hydrogen Storage Materials**
- Developed synthesis strategies for rapidly assessing promising hydride materials
- Sintering under high-hydrogen pressures resulted in new Na-Si-H phases
Future Work in FY2006/2007

FY 2006:

Borohydrides
• Characterize new borohydrides prepared by solid-state, solvent methods.
• Explore reversibility

Na-Si-H, Ca-Si-H
• Optimize solid-state synthesis routes at the high-pressure station to increase yield and to discover new materials
• Investigate structural and hydrogen sorption properties
• Go/no-go decision in Dec-06 depends on the potential of the new materials

FY 2007:

Borohydrides
• Synthesize bialkali borohydrides and explore reversibility of (Ca, Mg, Sc, Ti, Al etc) borohydrides based on theoretical predictions

Synthesis of New Complex Anionic Materials
• Discover new complex anionic materials by sintering under high H₂-pressure and down-select the most promising materials
Developed Rapid Assessment Method Based on Monte Carlo Techniques

**Motivation:**

- Develop Monte Carlo technique for estimating reaction enthalpies for candidate materials
- Overcome ICSD limitations on available structures

Example:

\[ \text{Ca}(\text{BH}_4)_2 \rightarrow \frac{1}{3}\text{CaB}_6 + \frac{2}{3}\text{CaH}_2 + \frac{10}{3}\text{H}_2 \]

(unknown structure)

For enthalpy estimates:

- ignore phonon contribution
- ignore PV term for hydrogen gas
Predicting Hydride Thermodynamics

Database
- Inorganic crystal structure database
- ICSD data base contains 80,000 inorganic structures
- Looking for AB$_2$X$_8$ yields ~100 inequivalent test structures

New Alternative Technique

Monte Carlo
- Global optimization
- Simulated annealing
- Electrostatic interactions
- MH$_x$ anion is a rigid unit

Energy of Structure at T=0K
Monte Carlo Approach Initially Validated Using NaAlH$_4$


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<th>Structure</th>
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<th>eV/fu[meV]</th>
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<tr>
<td>MC</td>
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<td>-19.360</td>
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</table>

- MC, with fewer formula units, approximates correct energy and crystal structure
Calculated Formation Energy Reveals Relative Stability of Structures

0.5eV/H₂ = 50kJ/mol H₂

Thus, MC technique also validated with borohydrides
## MC Code With Orthorhombic Unit Cell in Bialkali Alanate

VASP calculations from structures for $\text{K}_2\text{LiAlH}_6$

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<th>Structure</th>
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<th>eV/fu[meV]</th>
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<td><em>K$_3\text{MoF}_6$</em></td>
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</table>

*ICSD structures  **Experimental structure

- All other ICSD structures much higher in energy than $K_3\text{MoF}_6$
- MC energy lower than most ICSD structures and only requires 2 formula units per cell
Promising Hydrogen Pressures at 300K
Predicted for Mg(BH$_4$)$_2$ and Ca(BH$_4$)$_2$

$\text{Mg}(\text{BH}_4)_2 \rightarrow \text{MgB}_2 + 4\text{H}_2$ at $T>260\text{K}$
$\text{Mg}(\text{BH}_4)_2 \rightarrow 1/2\text{MgB}_4 + 1/2\text{MgH}_2 + 7/2\text{H}_2$ at $T<260\text{K}$

$3\text{Ca}(\text{BH}_4)_2 \rightarrow \text{CaB}_6 + 2\text{CaH}_2 + 4\text{H}_2$

- Based on >30 ICSD trial structures, GGA, PAW, harmonic approximation
- Caveats: preliminary calculation, imaginary phonons, thermal expansion

$9.6\%$ H$_2$ at T>260K

$14.8\%$ H$_2$ at T>260K

**Mg(BH$_4$)$_2$ and Ca(BH$_4$)$_2$** might be reversible at useful P/T
FY 2006 Accomplishments: Hydride Modeling

• New method for enthalpy estimate of complex metal hydrides:
  - Monte Carlo simulated annealing
  - Advantages over ICSD when structures are limited (e.g. mixed compounds)

• MC method validated with known systems:
  - Sodium alanate
  - Calcium borohydride (energy equivalent to ICSD)
  - Bialkali alanate

• Theoretical modeling showed favorable plateau pressures for Ca(BH$_4$)$_2$ and Mg(BH$_4$)$_2$
FY 2006:

Finalize the MC Code Improvements:
- MCM (Monte Carlo with Minimization)
- Basin hopping routine to more quickly find low energy structures

FY 2007:

Explore Specific Compounds
- Bialkali borohydrides
- Suggest new compounds that seem promising and perform full phonon calculations
Status Relative to DOE Targets

- DOE technical targets for gravimetric capacity
  - 2010: 6 wt% (system), 9-13 wt% (material)
  - 2015: 9 wt% (system), 13-16 wt% (material)

- $2\text{LiNH}_2+\text{MgH}_2$: 5.0 wt% (material) as measured
- $\text{K}_2\text{LiAlH}_6$: 2.5 wt% (material) as measured
- $\text{Ca}(\text{BH}_4)_2$: 9.6 wt% (material) theoretical
- $\text{Mg}(\text{BH}_4)_2$: 14.8 wt% (material) theoretical
- $\text{A-Si-H (A=Li, Na, Ca)}$: ~ 6-12 wt% (mat.)

Volumetric and other key properties are unknown at present.
Review of Future 2006 Work

Amides
• Use theory to assess possible modifications to Li/Mg amide system
• Complete study of [Li-Al-N-H] complex

Borohydrides
• Characterize new borohydrides
• Explore reversibility

Na-Si-H, Ca-Si-H
• Optimize solid-state synthesis routes
• Investigate structural and hydrogen sorption properties
• Go/no-go decision in Dec-06
Review of Future 2007 Work

**Borohydrides**
- Synthesize predicted bialkali borohydrides and explore their reversibility

**Synthesis of New Complex Anionic Materials**
- Discover new complex anionic materials by sintering under high H$_2$-pressure

**Hydride Modeling**
- Finalize the MC code improvements
- Explore Bialkali borohydrides

**Rapid Thermal Processing**
- Establish a rapid thermal processing route to discover and characterize novel amides/nitrides, borohydrides, complex hydrides, etc.
Establishing Rapid Thermal Processing Capability

**Motivation:** Hydrogen storage needs a breakthrough material

**Approach:** (existing Sandia technology)

**High-Pressure Rapid Thermal Processing**

- **Mini Hotplates (~ 1mm dia.)**
  - Rapid thermal processing of complex hydride precursors (700°C, 350 bar)
    - **powders, slurries, liquids,** …
  - Trap metastable states and strained morphologies
  - Catalyst studies
  - In-situ gas-phase analysis

- **Precise Control of Melt Condition**
  - Millisecond response times
  - Real-time calorimetry (in situ DSC)

FY’06

- Alanates 10%
- Amides 20%
- Synthesis of new complex hydrides 20%
- Theory 20%
- Borohydrides 20%
- Eng. properties 10%

FY’07

- Rapid thermal processing: materials discovery 20%
- Synthesis of new complex hydrides 20%
- Theory 20%
- Borohydrides 30%
- Eng. properties 5%
- Amides 5%

FY’06:
- Amides 20%
- Synthesis of new complex hydrides 20%
- Eng. properties 10%
- Borohydrides 20%

FY’07:
- Borohydrides 30%
Summary

**MHCoE:** Established a fully collaborating interdisciplinary organization

**Amides:** Examined Li/Mg system, redirecting experimental activity to novel synthetic methods

**Complex Hydrides:** Synthesized many new compounds, shifting focus to borohydrides

**Theory:** Developed theoretical methodology for finding promising candidate materials
Extra Slides
Critical Problems and Issues

Although progress has been made, critical issues remain…..

Weight Capacity: Experimental materials do not meet the DOE 2010 storage targets

Kinetics: Experimental materials do not display kinetics consistent with 2010 DOE targets

Stability: Known materials do not have cycling lifetimes consistent with 2010 DOE performance specifications
High-pressure Rapid Thermal Processing Combined With In-Situ Diagnostics

• Design miniature reactor for extreme operating conditions
  – $P > 350$ bar, $T_{\text{max}} = 700$ $^\circ$C
• Rapid thermal processing
  – melt and quench on millisecond time scales (controlled independently)
    • trap metastable states and strained morphologies
• Characterize adsorption/desorption cycles in situ (no sample transfer)
  – Calorimetry (DSC and/or DTA)
  – Thermal desorption with TCD
• Efficient multiplexing using arrays of sample chambers on a single chip
  – Combinatorial analysis

TiO$_2$ processed from liquids
Summary: FY ‘06 Accomplishments

Amides

• Determined reaction pathway for (2LiNH₂+MgH₂)
• Quantitatively measured NH₃ contamination of desorbed H₂ from Li/Mg (~420 ppm NH₃ at 220°C)
• Measured extended cycling life of Li/Mg amide: Desorption capacity strongly depends on absorption history.
• Synthesized new Li-Al-N-H compound, characterized composition
• Conducted hydrogenation studies of Li₃AlN₂, ~4 H atoms can be absorbed per Li₃AlN₂, with high pressure, high temperature and slow kinetics.
• Obtained first engineering results (expansion pressure) for Li/Mg Amide
• Conducted air exposure tests for Li/Mg amide: stable after 10 min exposure to dried/wet air at 220°C

Alanates

• A new alanate, K₂LiAlH₆, was used to develop new discovery strategies
  – Determined crystal structure and investigated hydrogen sorption properties
  – Ab-initio calculations verified the crystal structure

• The work on alanates will not continue since these materials cannot meet the DOE targets
Summary: FY ‘06 Accomplishments (cont.)

**Borohydrides**
- Theoretical modeling showed favorable plateau pressures for Ca(BH$_4$)$_2$ and Mg(BH$_4$)$_2$
- Solid-state synthesis of new borohydrides was demonstrated to be feasible in the Ca-B-H and Mg-B-H systems
- Synthesized several metal borohydrides by solvent based exchange reaction

**New Hydrogen Storage Materials**
- Developed synthesis strategies for rapidly assessing promising hydride materials
- The discovery process to find new hydrogen storage materials by sintering under high-hydrogen pressures resulted in new materials phases in the Na-Si-H system
Summary: FY ‘06 Accomplishments (cont.)

*Hydride Modeling:*

- New method for enthalpy estimates of complex metal hydrides:
  - Monte Carlo simulated annealing
  - Advantages over ICSD when structures are limited (e.g. mixed compounds)

- Validated with known systems:
  - Sodium alanate
  - Calcium borohydride (energy equivalent to ICSD)
  - Bialkali alanate

- Theory to be used to rapidly assess new compounds for favourable thermodynamics

- Theoretical modeling showed favorable plateau pressures for Ca(BH$_4$)$_2$ and Mg(BH$_4$)$_2$
Response to Reviewers’ Comments from 2005 Review

• “Formation of NH₃ in amide desorption needs even more effort than presented.”
  – We directly measured the contamination of NH₃ in released H₂ for the Li/Mg system, reported.

• “It is not clear what next steps will be in the Mg-modified amide systems. What are the ideas to improve the thermodynamics further?”
  – Next step required a mechanistic understanding of the pathway, reported. A theoretically guided assessment is in progress to examine options for Li/Mg amide system.

• “There is not enough effort on borohydride.”
  – We have moved a significant overall portion of our research activity, both theoretical and experimental to studying the Ca and Mg borohydride systems and have produced results in both areas. Calculated thermodynamics seem promising, and experimental attempts to synthesize Ca(BH₄)₂ are producing compounds that are under study.

• “Philosophy of selection of new materials is still based on looking for known systems from the literature that has low probability of success for the new materials discovery.”
  – We have developed a new approach (Monte Carlo) to generate new possible structures for hydrides that is very promising for guiding future synthesis work.

• “There is real concern over 6FTEs spread across 24 people.”
  – We have 3 focused, full-time Ph.D. staff members, and 6 part-time technical staff who form the core technical team.
Presentations


Presentations (cont’d)

• Weifang Luo, K. Gross, S. Sickafoose, P. Crooker, J. Wang, “Li-Mg-N-H: A viable hydrogen storage system For transportation application”, invited presentation, ICMAT-MRS meeting, Singapore, 3-8 July, 2005
• Weifang Luo, “Metal Hydride for Reversible Hydrogen Storage”, Tutorial lecture, MRS Fall meeting, Boston, Nov. 27-Dec. 02, 2005
Publications

• Crystal structure, Raman Spectroscopy and ab-initio calculations of a new bialkali alanate K₂LiAlH₆, E. Rönnebro, E. Majzoub, paper submitted.


• Al and ¹H MAS NMR and ²⁷Al Multiple Quantum Studies of Ti-doped NaAlH₄, J.L. Herberg, R.S. Maxwell, E.H. Majzoub, accepted J. Al. Comp., 2005.


Publications (cont’d)