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 H_2 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

DOE

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 (AlH_3)

- **BNL(POC)**
- SRNL
- JPL
- 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 H_2 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 H_2 storage

Project D - Alane (AlH_3)

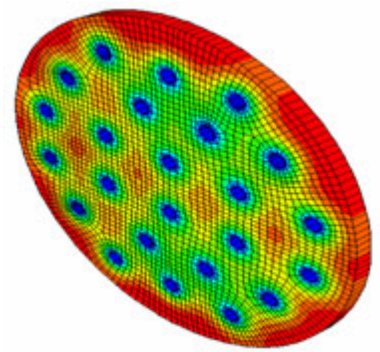
Understand desorption and regeneration properties of alane for H_2 storage

See talk by: Jason Graetz, BNL

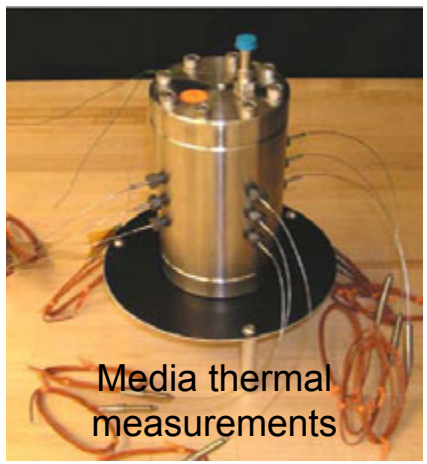
Project E: Engineering Design, Analysis and Test

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

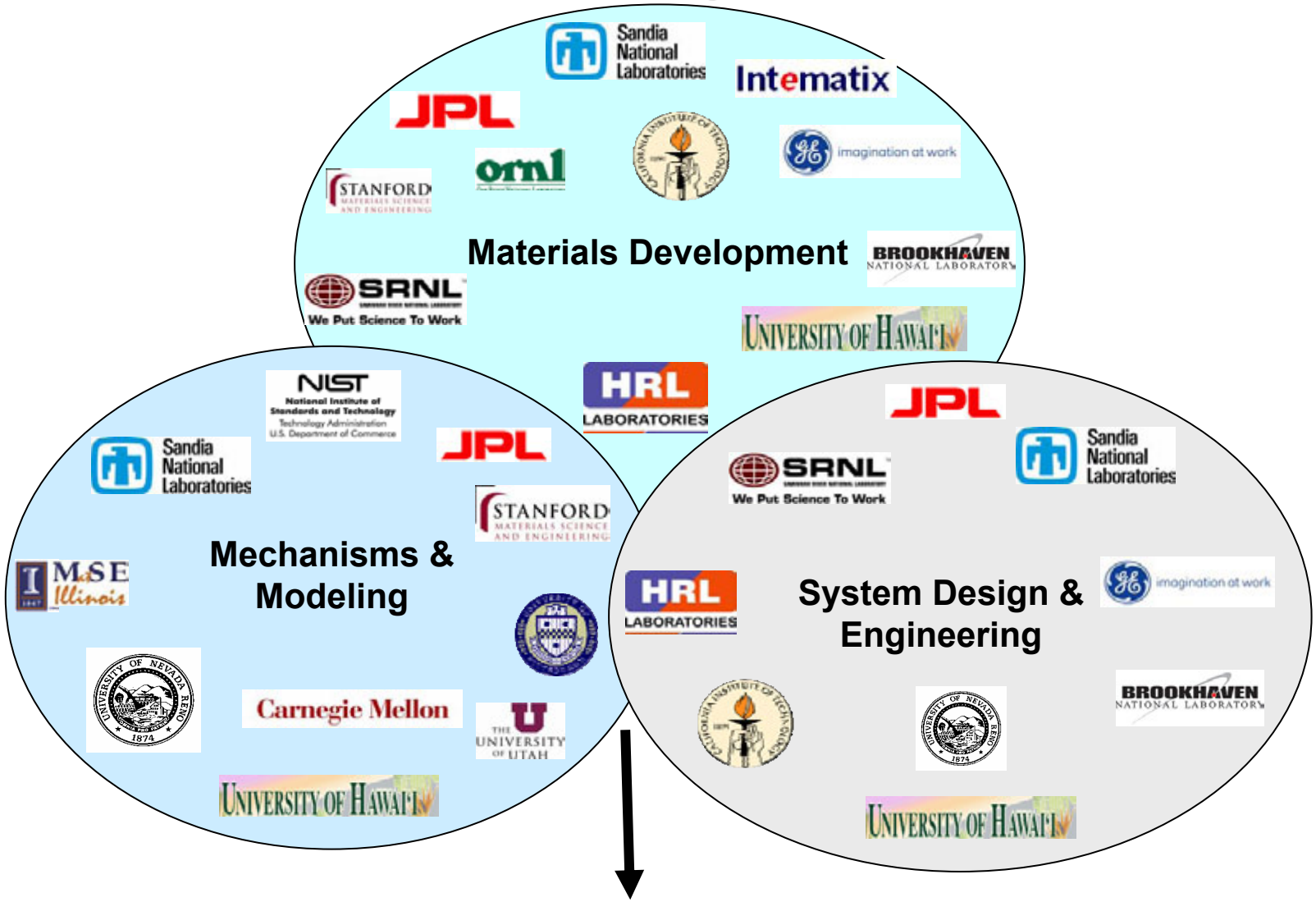
See poster by: SRNL



Thermal Modeling



Collaboration is Key to MHCoE

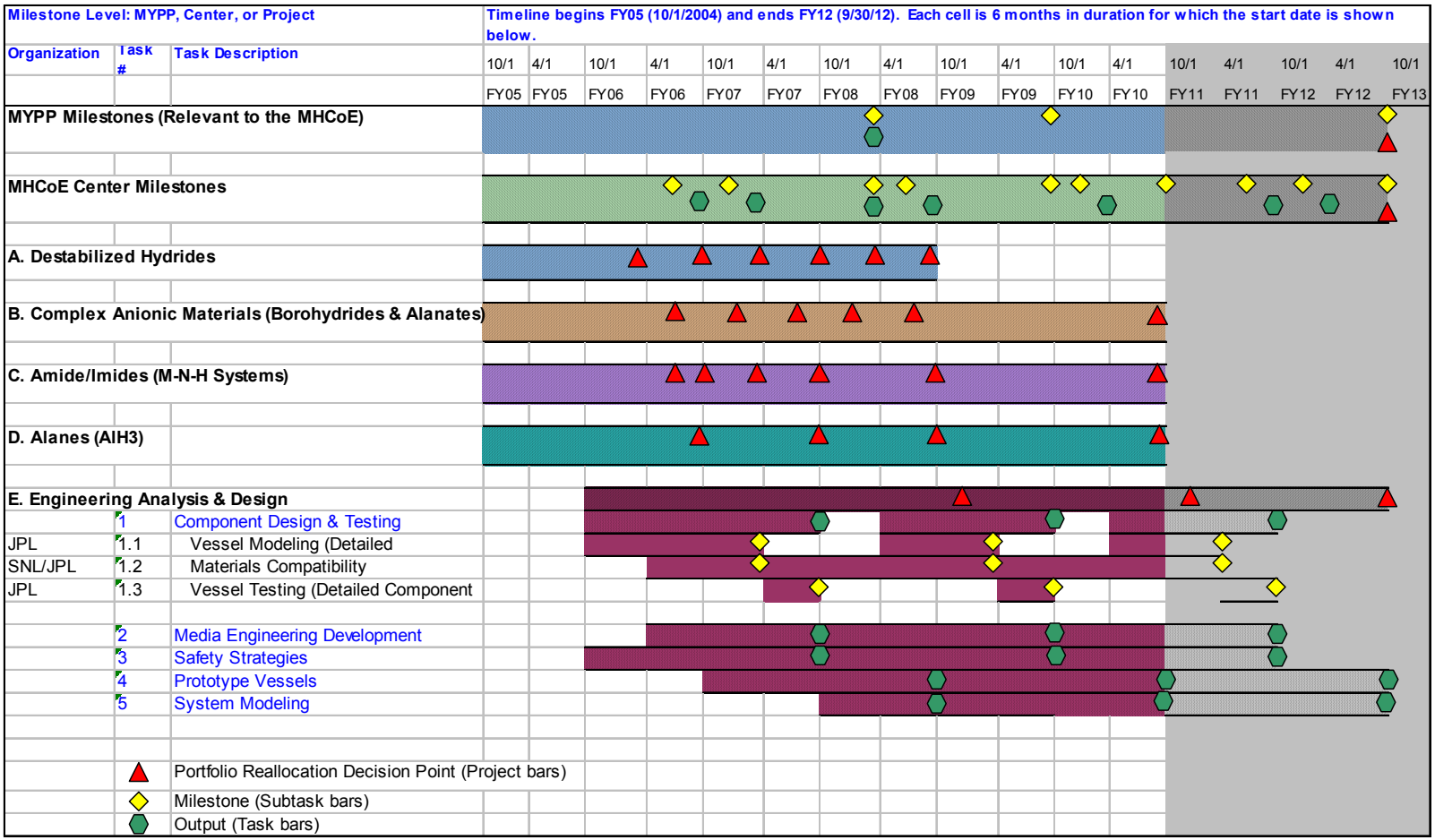


2010 Material

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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Sandia Program Overview

Timeline

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

Budget

$1.99M in FY '05

$2.26M in FY '06

Collaborators

National U. of Singapore, Tohoku U., UCLA, U. Geneva, LLNL, UOP, UTRC, IFE

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

MHCoE Partners

Caltech, ORNL, JPL, UNR, Stanford U., U. of Utah, U. Hawaii, U. Pitt, SRNL, HRL, UIUC, CMU, GE, NIST, BNL, Intematix

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
- Sandia Program Overview
  - **Li/X Amide Materials for H_2 Storage**
    Weifang Luo (PI), Lennie Klebanoff (Presenting)
  - **Discovering New Complex Hydrides**
  - **Summary of Accomplishments for FY 2006**
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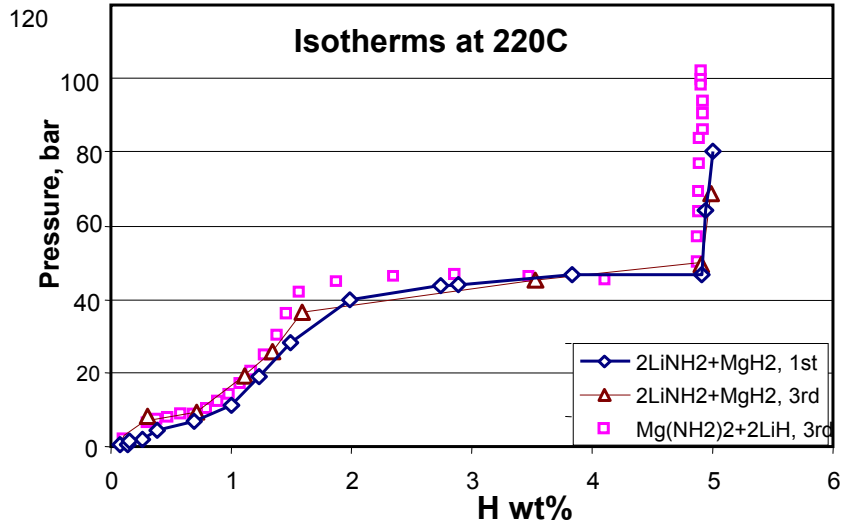
Li/X Amides

Status in May 2005:

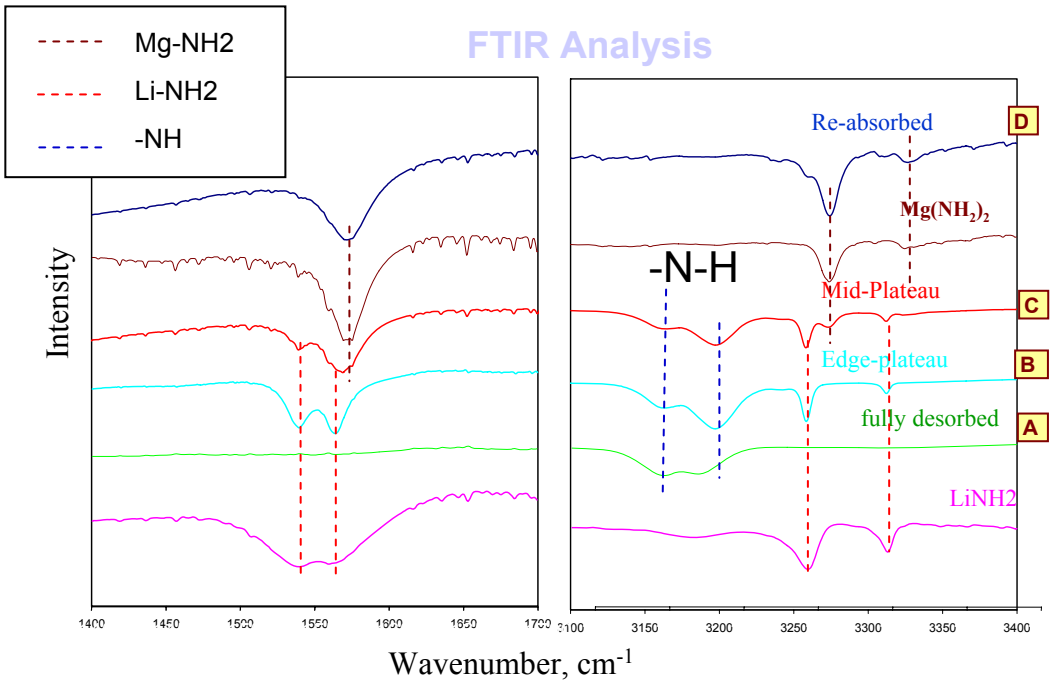
- Li/Mg amide Isotherms measured (40 bar at 220 C)
- Time-dependent absorption/desorption measured for Li/Mg amide
- Completed initial cycling measurements (~100 cycles) for Li/Mg amide
- A speculative new reaction path proposed



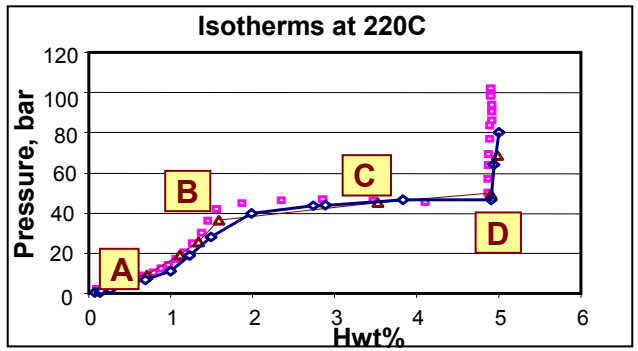
Accomplishments in FY 2006:

- Determined reaction pathway for Li/Mg amide by FTIR and XRD
- Quantified NH_3 release accompanying H_2 desorption from Li/Mg Amide
- Examined an alternative to Mg: $2LiNH_2 + LiAlH_4$
- 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, Cr_2O_5 for catalysis of Li/Mg system (slight effect found)

FTIR Reveals Chemical Pathway



$2LiNH_2 + MgH_2 \rightarrow$

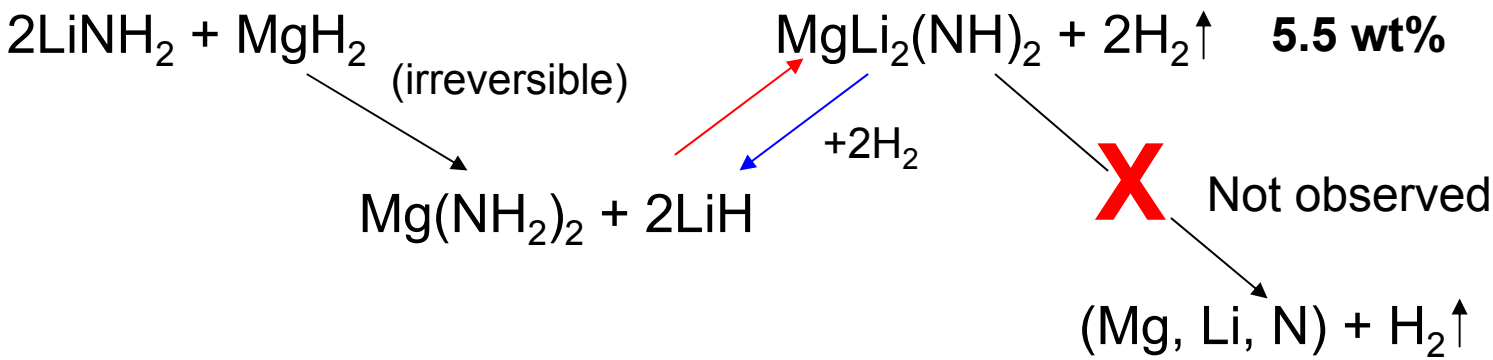


FTIR Assignments (supported by XRD):

1. Fully H_2 desorbed: -N-H character (imide)
2. Fully H_2 re-absorbed: $Mg(NH_2)_2$ (amide)
3. Starting material ($2LiNH_2 + MgH_2$) not recovered

Li/Mg Amide Reaction Pathway Elucidated

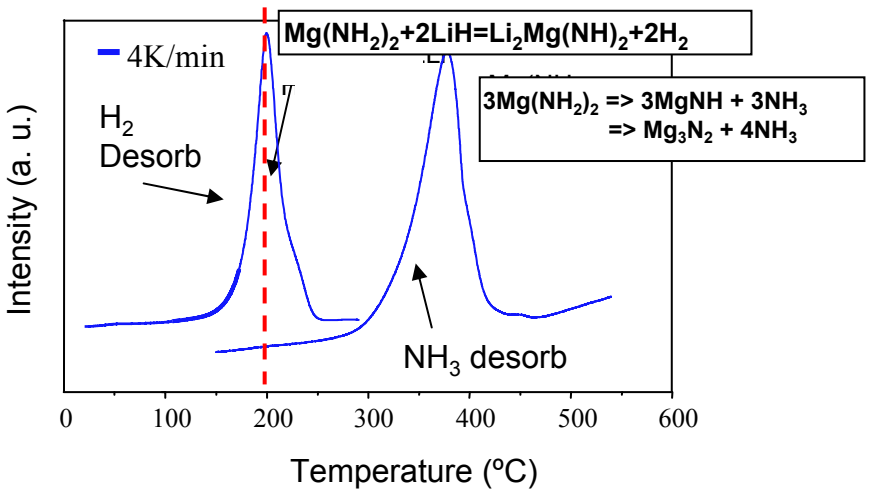
Observed Pathway:



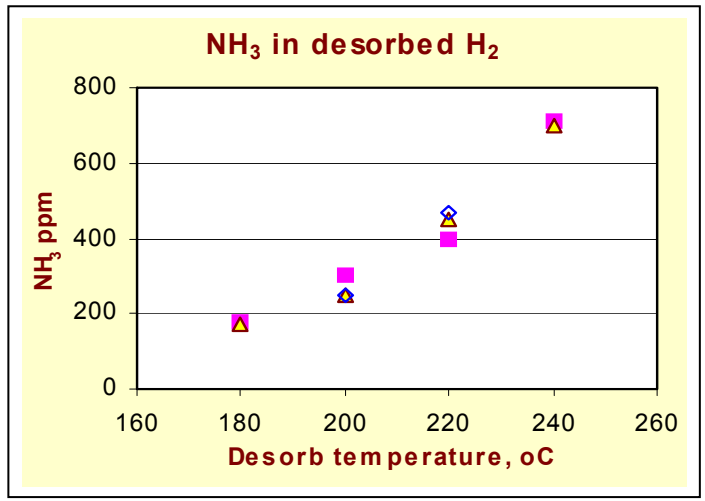
- **Irreversible transformation of ($2LiNH_2 + MgH_2$) into $Mg(NH_2)_2$**
- **$Mg(NH_2)_2$ a risk for NH_3 release (capacity loss, FC catalyst poisoning)**
- **Ti, ZnO, Pd, Pt, Ni, Cr_2O_5 catalysis effect found to be slight (SNL)**

Hydrogen in imide is inaccessible

NH_3 Release Quantitatively Determined



* Z. Xiong, et al, *J. Alloys and Compounds*, 398 (2005) 235-239.

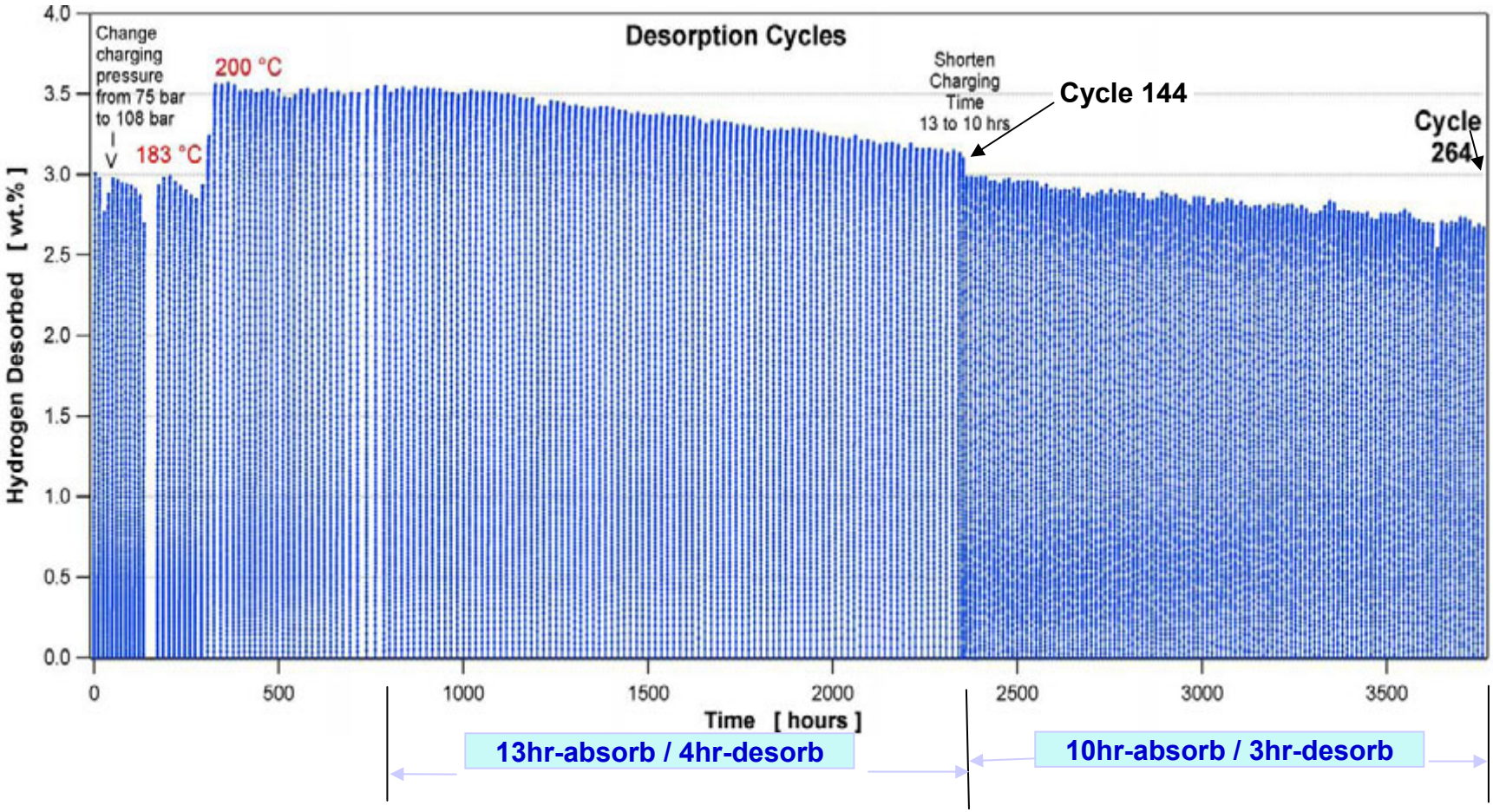


Draeger Tube was used to quantify NH_3 in H_2
Uncertainty: ± 60 ppm

Material loss due to NH_3 release: ~ 3% of original storage capacity over 200 cycles, with 300ppm NH_3

Irreversible loss of ($2LiNH_2$ + MgH_2) starting material observed

$(2LiNH_2+MgH_2)$: Cycle Life at 200°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

$$2LiNH_2 + LiAlH_4 \xrightarrow{(?)} Li_3AlN_2 + 4H_2 \quad 9.5\ wt.\ \%\ (theo.)$$

Synthesis Forward:

Ball Milling: $2LiNH_2 + LiAlH_4 \rightarrow$ [Li-Al-N-H]

- **Spontaneous release at RT of H_2, exothermic reaction**

[Li-Al-N-H] structural characterization:

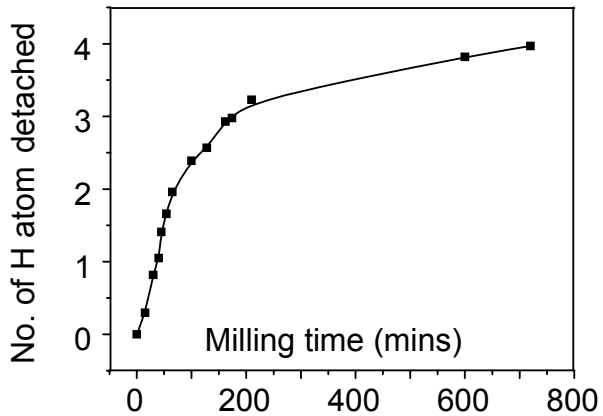
- **Evidence for Al-N bonding**
- **4-coordinated Al, [$LiAlH_{4-x}N_x$], stable complex**

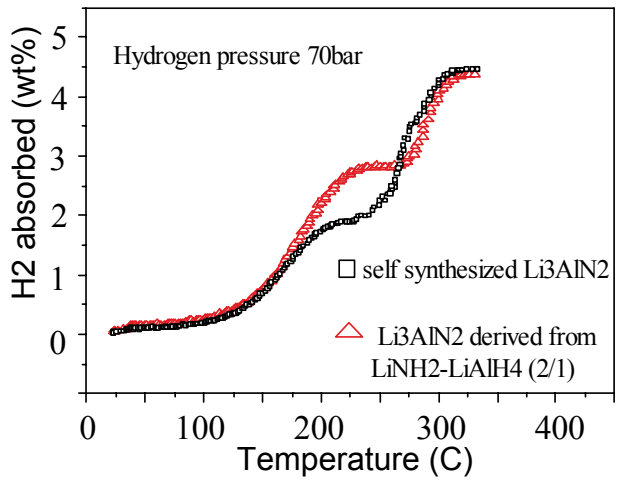
Synthesis Backward:

$$Li_3AlN_2 + 2H_2 \rightarrow LiNH_2 + 2LiH + AlN$$

For complete hydrogenation, need:

- **High 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 ($2LiNH_2+MgH_2$)
- Quantitatively measured NH_3 contamination of desorbed H_2 from Li/Mg (~420 ppm 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 Li_3AlN_2, ~4 H atoms can be absorbed per Li_3AlN_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 $2LiNH_2$ and $LiAlH_4$. 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
  - **Status 2005, Plans 2006**
  - **New Materials Synthesized: K_2LiAlH_6, Borohydrides, Na-Si-H**
  - **Monte Carlo Modeling of Hydride Stability, Thermodynamic Calculations**
  - **Discovering New Complex Hydrides**
  - **Summary of Accomplishments for FY 2006**
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Status in May 2005

- Established synthesis route for high-pressure sintering of metal hydrides
- Discovered K_2LiAlH_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_2LiAlH_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 < 2000bar, T < 500C)

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

(DME, THF…)

$$MCl_x + xNaBH_4 \rightarrow M(BH_4)_x + xNaCl$$

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

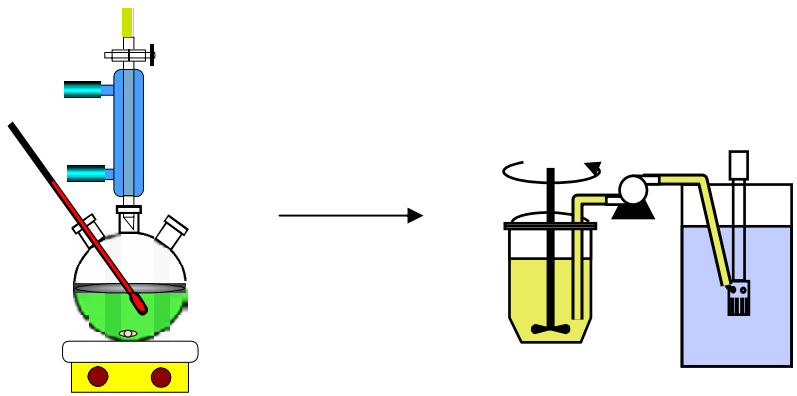
- K_2LiAlH_6
- Ca-B-H
- Mg-B-H
- Na-Si-H

Sandia High-pressure Station

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

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)
- $Mg(BH_4)_2(THF)_2$



Solution Route

Shear Mixer

A New Bialkali Alanate Discovered

- We wanted to find an alanate with higher H-content and better sorption properties than sodium alanate ($NaAlH_4$)
- In FY'05 these bialkali alanate systems were investigated:

Potential for >6wt% Hydrogen

- **Li-K-Al-H (successful synthesis)**
- **Li-Mg-Al-H**
- **Li-Ca-Al-H**
- **Li-Ti-Al-H**
- **Mg-Ti-Al-H**

} No reaction observed

- In FY'06 the synthesis route was optimized by mixing $LiAlH_4$+2KH and treating at 700 bar H_2-pressure and 320ºC for 1 day.

Other known bialkali alanates in the literature: Na_2LiAlH_6 and K_2NaAlH_6

J. Huot, S. Boily, V. Guther, R. Schulz, J. Alloys Compd., 383 (1999) 304.
W. Brinks, B.C. Hauback, C.M. Jensen, R. Zidan, J. Alloys Comp., 392 (2005) 27.
J. Graetz, Y. Lee, J.J. Reilly, S. Park, T. Vogt, Phys. Rev. B, v.71, (2005) 184115.

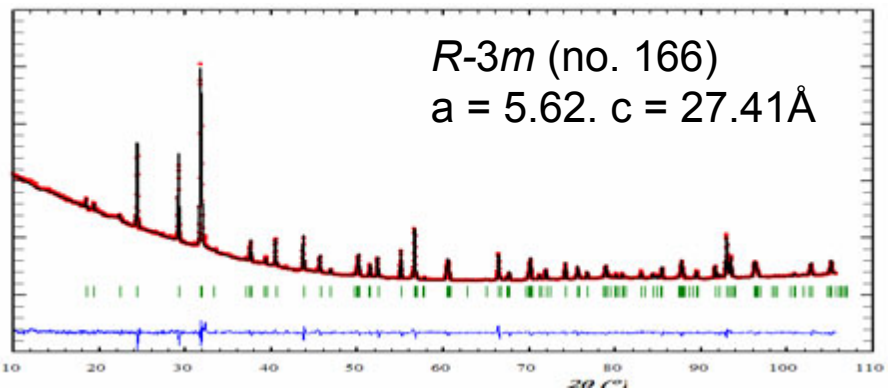
Characterized K_2LiAlH_6

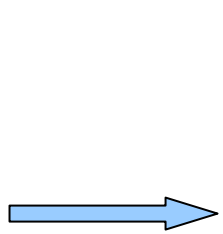
$LiAlH_4 + 2KH \rightarrow K_2LiAlH_6$ at 700 bar and 320C

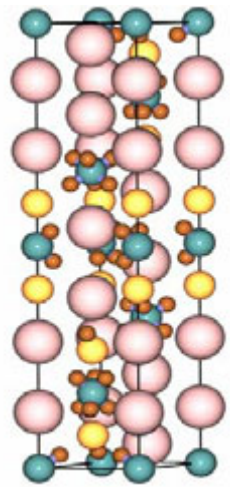
- Hydrogen storage properties:
  Desorption >200C; Absorption >320C and 100bar H_2
  $K_2LiAlH_6 \leftrightarrow 2KH + LiH + Al + 3/2H_2$ (2.5 wt % theo.)
  Slow kinetics

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

Plot from Rietveld refinement







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 $Ca(BH_4)_2$ has promising thermodynamics

$Ca(BH_4)_2$ contains 9.6 wt% (theo.) hydrogen

- Attempted synthesis route: **$CaB_6+2CaH_2+10H_2 \rightarrow 3Ca(BH_4)_2$**
  (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 CaB_6+2CaH_2:
  - Absorption >350C at 100bar H_2
  - 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

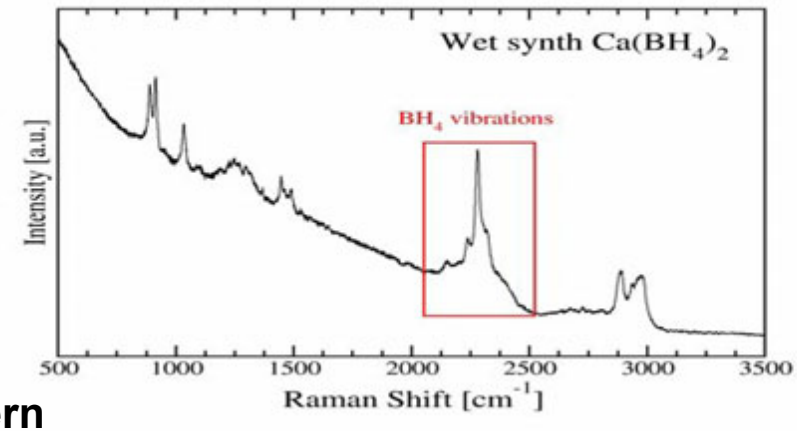
$$MCl_x + x\,NaBH_4 \xrightarrow{\text{DME, THF...}} M(BH_4)_x + xNaCl$$

Metal borohydrides synthesized in FY06:

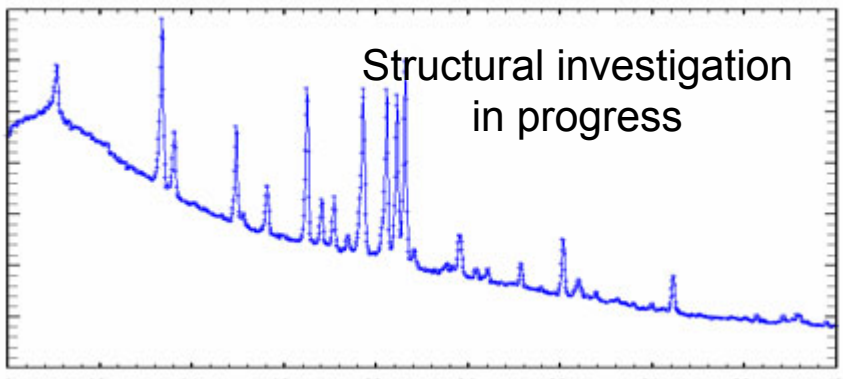
$Ti(BH_4)_3(DME)$
$Sc(BH_4)_3(THF)_2$
$Al(BH_4)_3(py)$
$Mg(BH4)_2(THF)_2$
$CaBH_4(THF)_2$

Solvent-free products being investigated

Raman Spectrum



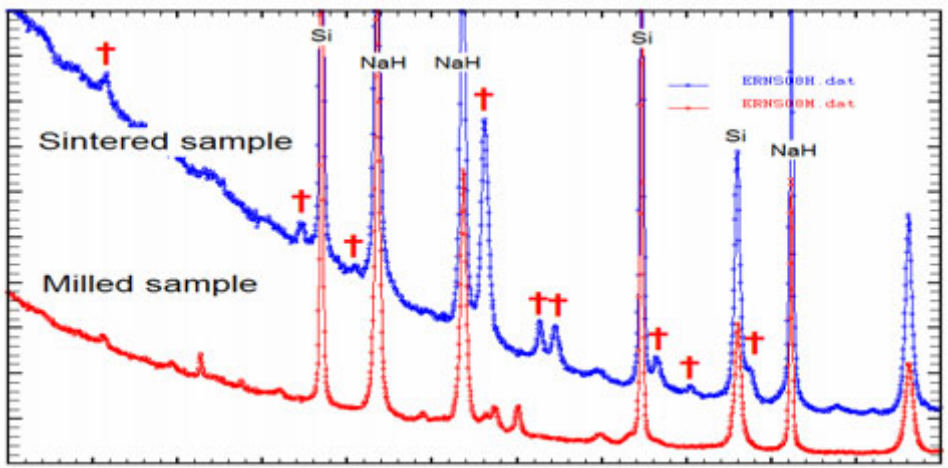
XRD Pattern



Evidence for First Na-Si-H Compound

2NaH + Si → [Na-Si-H] (high-pressure sintering)

- **Investigation of $[SiH_6]^{2-}$ stabilization by Li^+, Na^+ or 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**



XRD pattern

† = New phase

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

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

METAL HYDRIDE CENTER OF EXCELLENCE

Sandia National Laboratories

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 H_2-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:

$$Ca(BH_4)_2 \rightarrow 1/3CaB_6 + 2/3\ CaH_2 + 10/3\ H_2$$

(unknown structure)

For enthalpy estimates:

- ignore phonon contribution
- ignore PV term for hydrogen gas

Predicting Hydride Thermodynamics

New Alternative Technique

Database

- Inorganic crystal structure database
- ICSD data base contains 80,000 inorganic structures
- Looking for AB_2X_8 yields ~100 inequivalent test structures

Monte Carlo

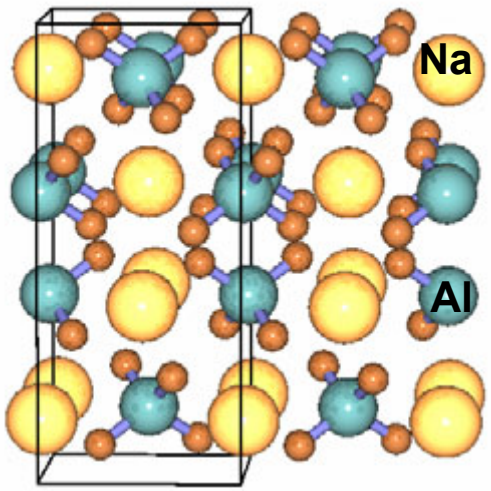
- Global optimization
- Simulated annealing
- Electrostatic interactions
- MH_x anion is a rigid unit

ICSD

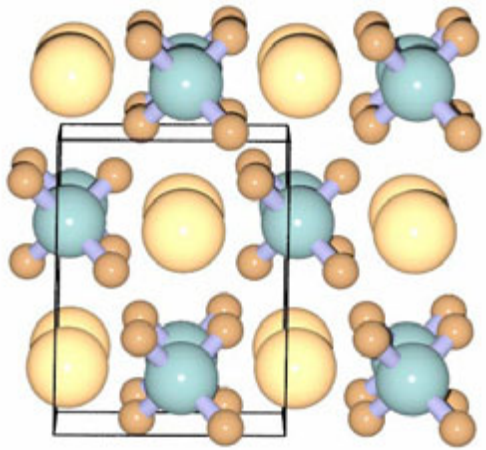
MC

Energy of Structure at T=0K

Monte Carlo Approach Initially Validated Using $NaAlH_4$



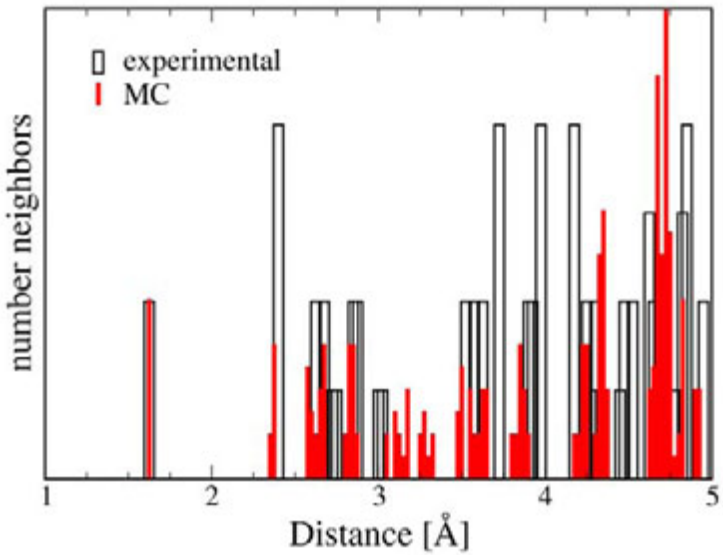
Experiment



MC

($NaAlH_4$ structure known *Belskii, et al., Russ. J. Inorg. Chem., 28, (1983)*)

Total Pair Distribution Function

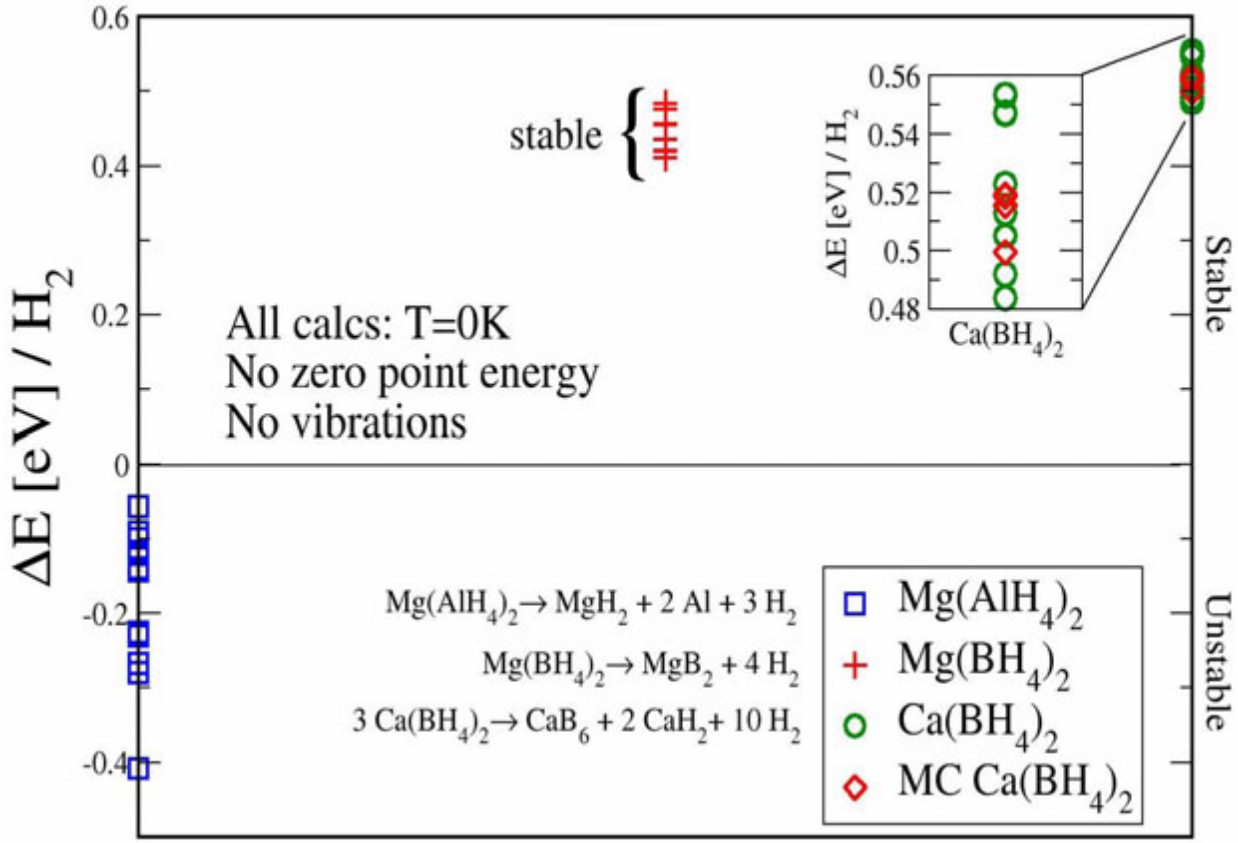


Structure	Z	eV/fu[meV]
Experiment	4	-19.424
MC	2	-19.360

- MC, with fewer formula units, approximates correct energy and crystal structure

Calculated Formation Energy Reveals Relative Stability of Structures

0.5eV/H_2 = 50kJ/mol H_2



Thus, MC technique also validated with borohydrides

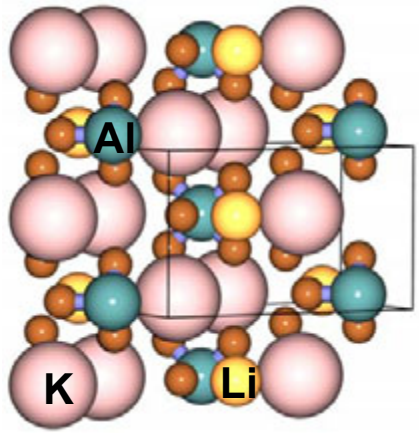
MC Code With Orthorhombic Unit Cell in Bialkali Alanate

VASP calculations from structures for K_2LiAlH_6

Structure	Z	eV/fu[meV]
**Rietveld/*K_2LiAlF_6	6	-30.700
MC	2	-30.633
*K_3MoF_6	4	-30.589

* ICSD structures **Experimental structure

VASP relaxed Monte Carlo Structure

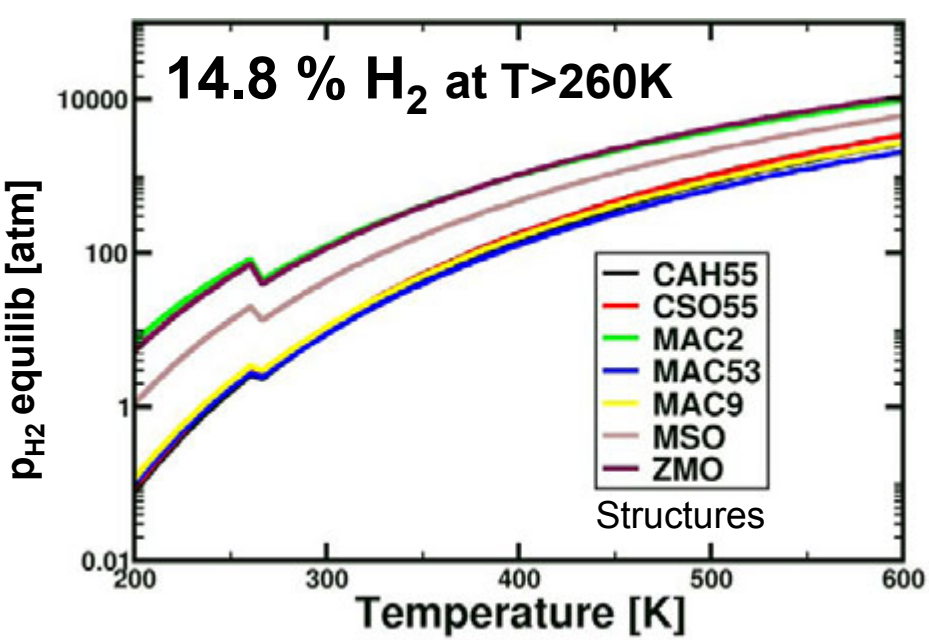


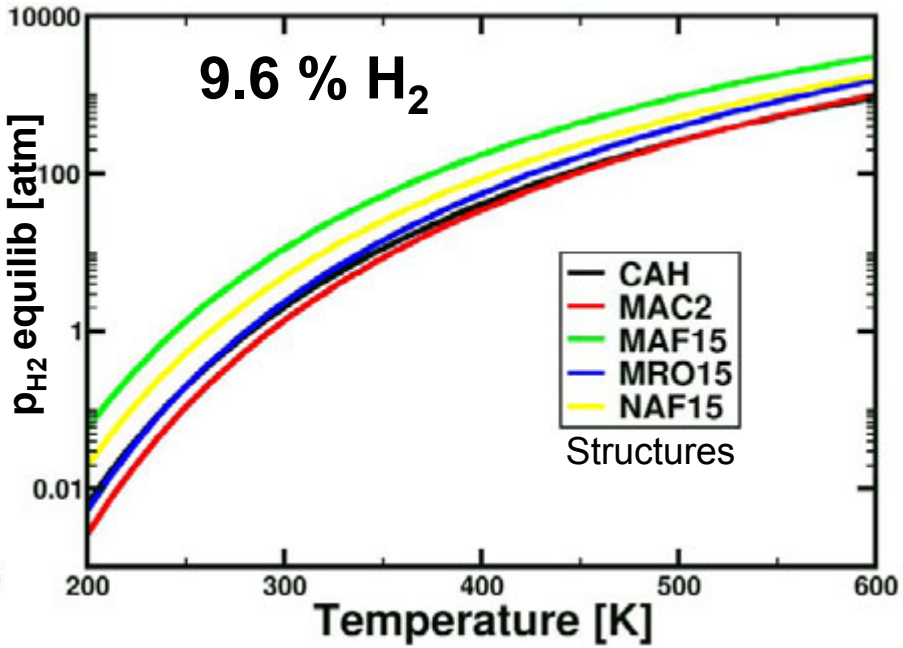
- All other ICSD structures much higher in energy than K_3MoF_6
- MC energy lower than most ICSD structures and only requires 2 formula units per cell

Promising Hydrogen Pressures at 300K Predicted for $Mg(BH_4)_2$ and $Ca(BH_4)_2$

$Mg(BH_4)_2 \rightarrow MgB_2 + 4H_2$ at T>260K
$Mg(BH_4)_2 \rightarrow 1/2MgB_4 + 1/2MgH_2 + 7/2H_2$ at T<260K

$3Ca(BH_4)_2 \rightarrow CaB_6 + 2CaH_2 + 4H_2$





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

$Mg(BH_4)_2$ 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 $Mg(BH_4)_2$

FY2006/2007 Future Work: Hydride Modeling

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)

- $2LiNH_2+MgH_2$: 5.0 wt% (material) as measured
- K_2LiAlH_6: 2.5 wt% (material) as measured
- $Ca(BH_4)_2$: 9.6 wt% (material) theoretical
- $Mg(BH_4)_2$: 14.8 wt% (material) theoretical
- 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.

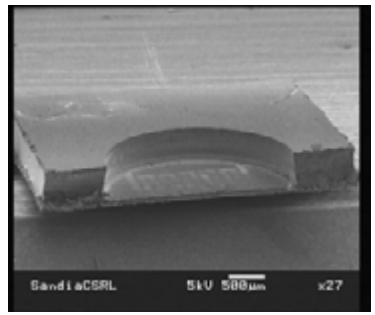
Establishing Rapid Thermal Processing Capability

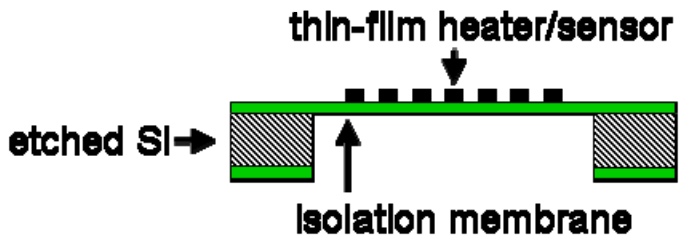
Motivation: Hydrogen storage needs a breakthrough material

Approach: (existing Sandia technology)

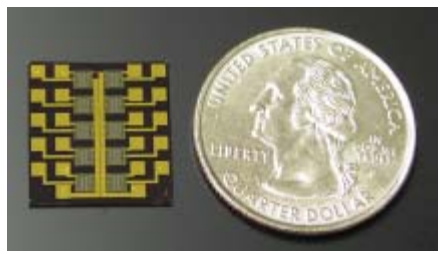
High-Pressure Rapid Thermal Processing

- Mini Hotplates (~ 1mm dia.)
  - Rapid thermal processing of complex hydride precursors (700C, 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)



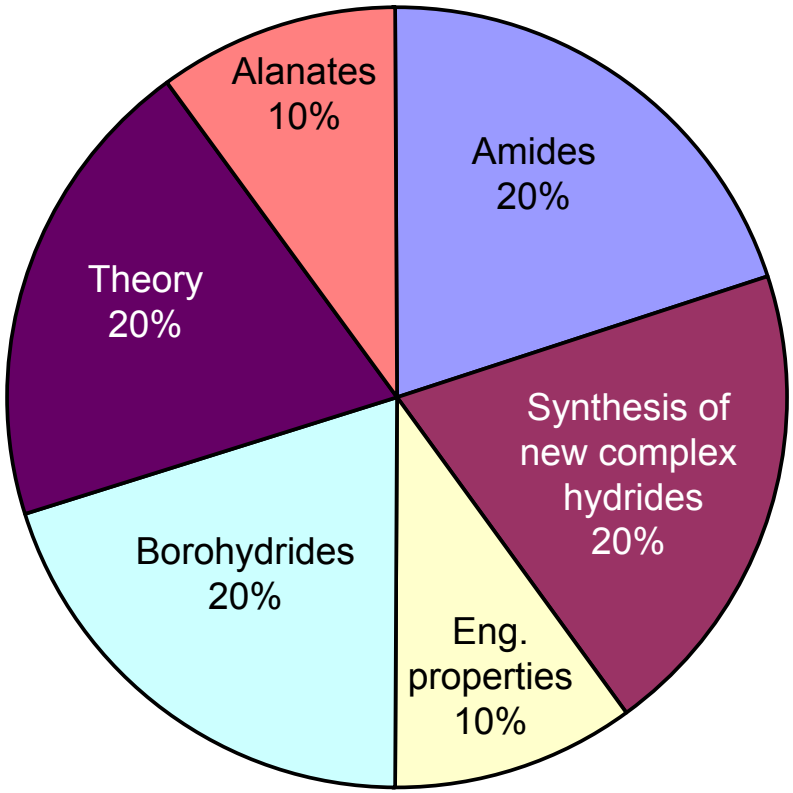


2 x 5 array of mini HPs

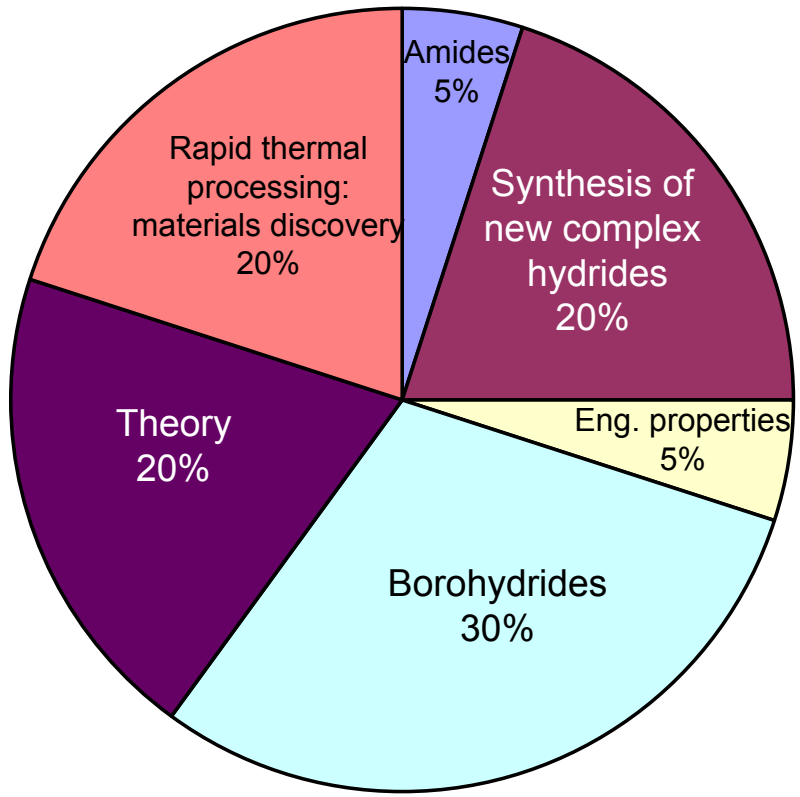


Sandia Technical Emphasis 2006/2007

FY'06



FY'07



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…..

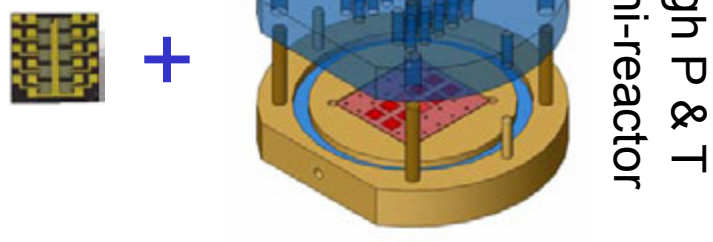
Weight Capacity: Experimental materials do not meet the DOE 2010 storage targets

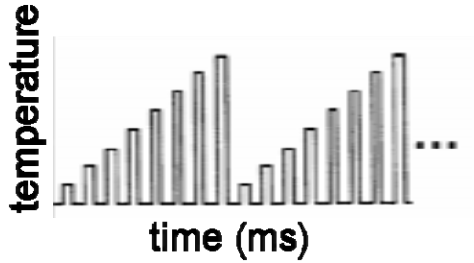
Kinetics: Experimental materials do not display kinetics consistent with 2010 DOE targets

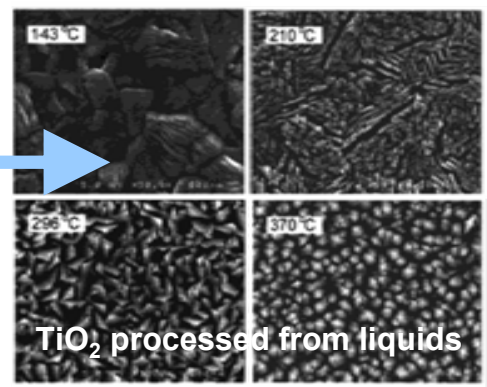
Stability: Known materials do not have cycling lifetimes consistent with 2010 DOE performance specifications

High-pressure Rapid Thermal Processing Combined With In-Situ Diagnostics

- Design miniature reactor for extreme operating conditions
  - P > 350 bar, T_{max} = 700 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







Summary: FY '06 Accomplishments

Amides

- Determined reaction pathway for ($2LiNH_2+MgH_2$)
- Quantitatively measured NH_3 contamination of desorbed H_2 from Li/Mg (~420 ppm 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 Li_3AlN_2, ~4 H atoms can be absorbed per Li_3AlN_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

Alanates

- A new alanate, K_2LiAlH_6, 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 NH_3 in amide desorption needs even more effort than presented."
  - We directly measured the contamination of NH_3 in released H_2 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 $Ca(BH_4)_2$ 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

- Structural Investigation and Hydrogen Storage Properties of a New Li,K Bialkali Alanate, E. Rönnebro, E. Majzoub, S. Sickafoose, Poster presented at Hydrogen-Metal Systems, Gordon Research Conference, Waterwille, ME, July 10-15, 2005.
- On the road to make new metal hydrides, E. Rönnebro, E. Majzoub, Oral presentation at 2006 MRS Spring Meeting, Session EE; Hydrogen Storage Materials, San Francisco, April 17-21, 2006.
- Hydrogen Storage in Sodium Alanates, E.H. Majzoub, American Crystallographic Association Annual Meeting, Orlando, Florida, June 2005.
- Global Optimization of Complex Hydride Crystal Structures, E.H. Majzoub, V. Ozolins, Materials Research Society, Spring 2006 Symposium on Materials for Hydrogen Storage, April 17-21, San Francisco, CA. Oral presentation.
- In-situ Raman Spectra of $NaAlH_4$: Evidence of Highly Stable AlH-1 Anions, E.H. Majzoub, K.F. McCarty, V. Ozolins, Materials Research Society 2004 Symposium on Materials for Hydrogen Storage, November 29 – December 3, Boston, MA. Oral presentation.

Presentations (cont'd)

- X-ray Diffraction and Raman Spectroscopy Investigation of Titanium Substitution in Sodium Aluminum Hydride, E.H. Majzoub, K.F. McCarty, V. Ozolins, 2004 TMS Annual Meeting & Exhibition, March 14-18, 2004, Charlotte, North Carolina. Oral Presentation.
- 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
- Weifang Luo, J. Wang, K. Gross, T. Boyle, P. Crooker, S. Sickafoose, K. Stewart, "Recent Development on Li-Mg-N-H Storage System", invited presentation, MRS spring meeting, San Francisco, Apr. 17-20, 2006

Publications

- Crystal structure, Raman Spectroscopy and ab-initio calculations of a new bialkali alanate K_2LiAlH_6, E. Rönnebro, E. Majzoub, paper submitted.
- Catalytically modified hydrogen properties of novel complex hydrides, Annual Report IEA, Task 17, Project H-10, K. Gross, E. Rönnebro, 2006.
- Al and 1 H MAS NMR and 27 Al Multiple Quantum Studies of Ti-doped $NaAlH_4$, J.L. Herberg, R.S. Maxwell, E.H. Majzoub, accpeted J. Al. Comp., 2005.
- Lattice dynamics of $NaAlH_4$ from high-temperature single-crystal Raman scattering and ab initio calculations: Evidence of highly stable AlH- anions, E.H. Majzoub, V. Ozolins, K.F. McCarty, Phys. Rev. B, 71, 024118, 2005.
- XRD and NMR investigation of Ti-compound formation in solution-doping of sodium aluminum hydrides: Solubility of Ti in $NaAlH_4$ crystals grown in THF, E.H. Majzoub, J.L. Herberg, R. Stumpf, S. Spangler, R.S. Maxwell., J. Al. Comp., 394, 265-270, 2005

Publications (cont'd)

- W. Luo and S, Sickafoose, "Thermodynamic and Structural Characterization of the Mg-Li-N-H Hydrogen Storage System" J. Alloys and Compounds, 407 (2006) 274-281
- W. Luo and E. Rönnebro, "Towards a viable hydrogen storage system for transportation application" J. Alloys and Compounds, 404-406 (2005) 392-395
- Z. Xiong, J. Hu, G. Wu, P. Chen, W. Luo, K. Gross and J. Wang, "Thermodynamic and kinetic investigation of the hydrogen storage in the Li-Mg-N-H system", J. Alloys and Compounds, 398 (2005) 235-239
- Weifang Luo, J. Wang, K. Gross, S. Sickafoose, P. Crooker, K. Stewart, "New Hydrogen Storage Material: Metal-N-H system", Sandia Report, in press.