Development of Metal Hydrides at Sandia National Laboratories

Presented by

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Livermore, California

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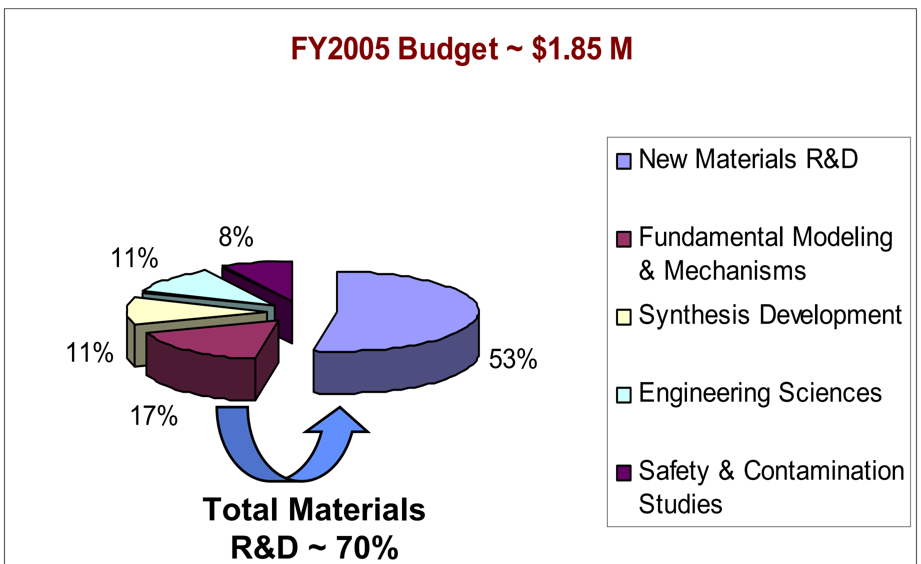
This presentation does not contain any proprietary information

Project ID# ST2

Overview

Timeline

- Project started in the early 1990s'
- Reviewed and renewed every FY through Annual Operation Plans
- Incorporated into MHCoE January 2005
- Percent complete ~ 50% for FY05



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

Partners

- MHCoE collaborators include Caltech, ORNL, JPL, UNR, Stanford U, U of Utah, U Hawaii, U of PITT, SRNL, HRL, UIUC, CMU, GE, NIST, BNL, Intematix
- Gary Sandrock operates IEA/Task-17, maintains the Hydride Information Center databases and collaborates with BNL
- Singapore U., Tohoku U., UCLA, U. Geneva, LLNL

Objectives

- ***Develop new reversible hydrogen storage materials that meet or exceed DOE FreedomCAR 2010 and 2015 goals,***
- ***Identify reversible hydrides that exceed the hydrogen capacity of Mg modified Li amides in FY05.***

Sandia Team (~ 6 FTEs)

Ray Baldonado
Bob Bastasz
Tim Boyle
Yongkee Chae
Paul Crooker*
Sherrika Daniel*
Karl Gross (consultant)
Steve Karim

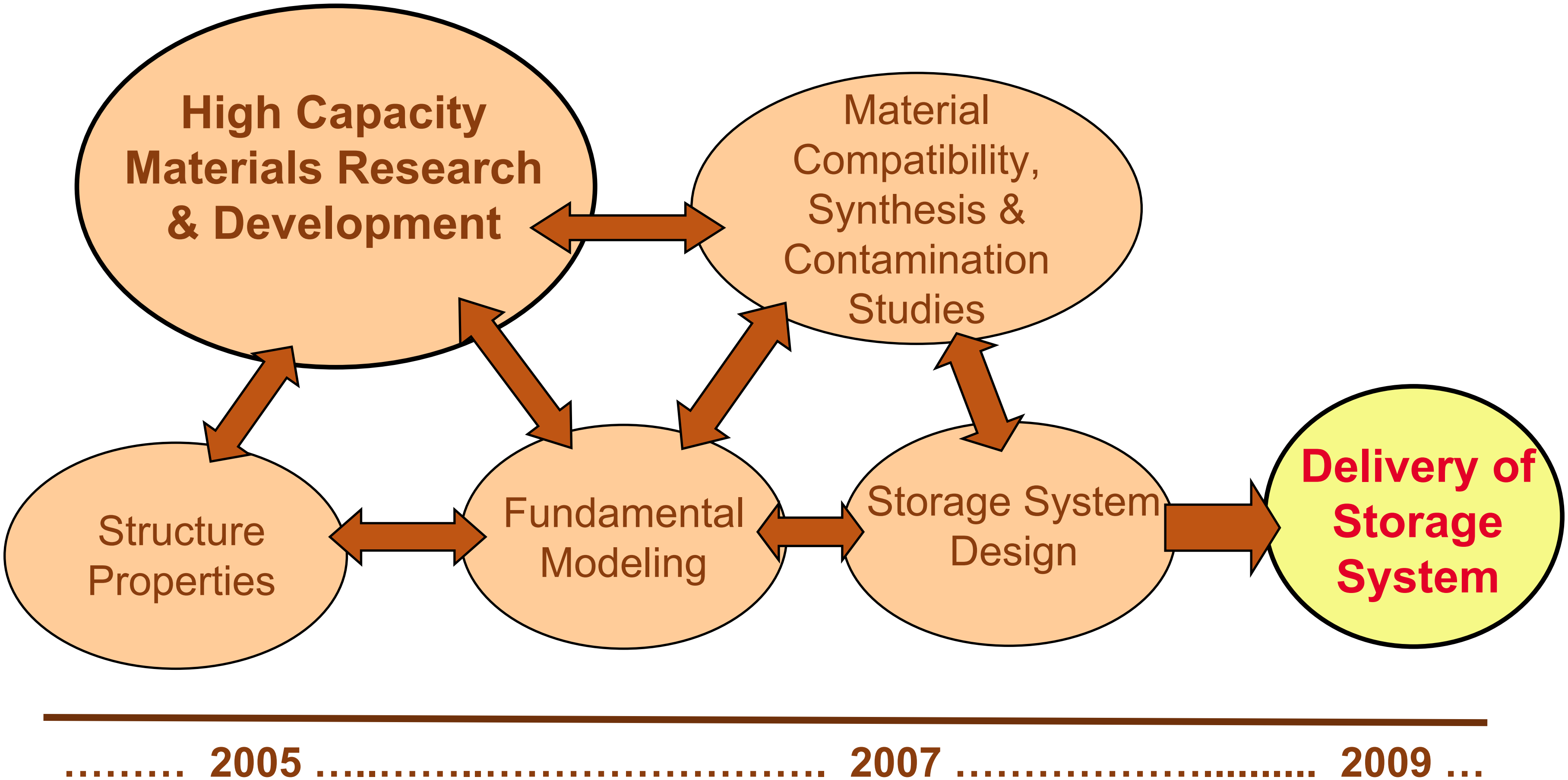
Jay Keller
Weifang Luo
Eric Majzoub
Tony McDaniel
Marcina Moreno
Vidvuds Ozolins (consultant)
Ewa Ronnebro*
Gary Sandrock (consultant)

Ken Stewart
Roland Stumpf
Konrad Thuermer
Jim Voigt
Karl Wally*
Jim Wang
Ken Wilson
Nancy Yang

* New Team Members

Approach

Science-based materials development



I. New Hydrogen Storage Materials

A. *Low temperature Mg modified Li amides*

Amide : $-NH_2$, $LiNH_2$ | **Imide : >NH, Li_2NH** | **Nitride : ⋮N, Li_3N**

[1] 1st Step:

$LiNH_2 + LiH \overset{300^oC}{\underset{1\ atm}{\Leftrightarrow}} Li_2NH + H_2$ **6.5 wt%**

2nd step:

$Li_2NH + LiH \overset{300^oC}{\underset{0.05\ atm}{\Leftrightarrow}} Li_3N + H_2$ **5 wt%**

Two steps in total:

11.5 wt%

Major limitations:

- Temperature too high
- Pressure too low

New system:

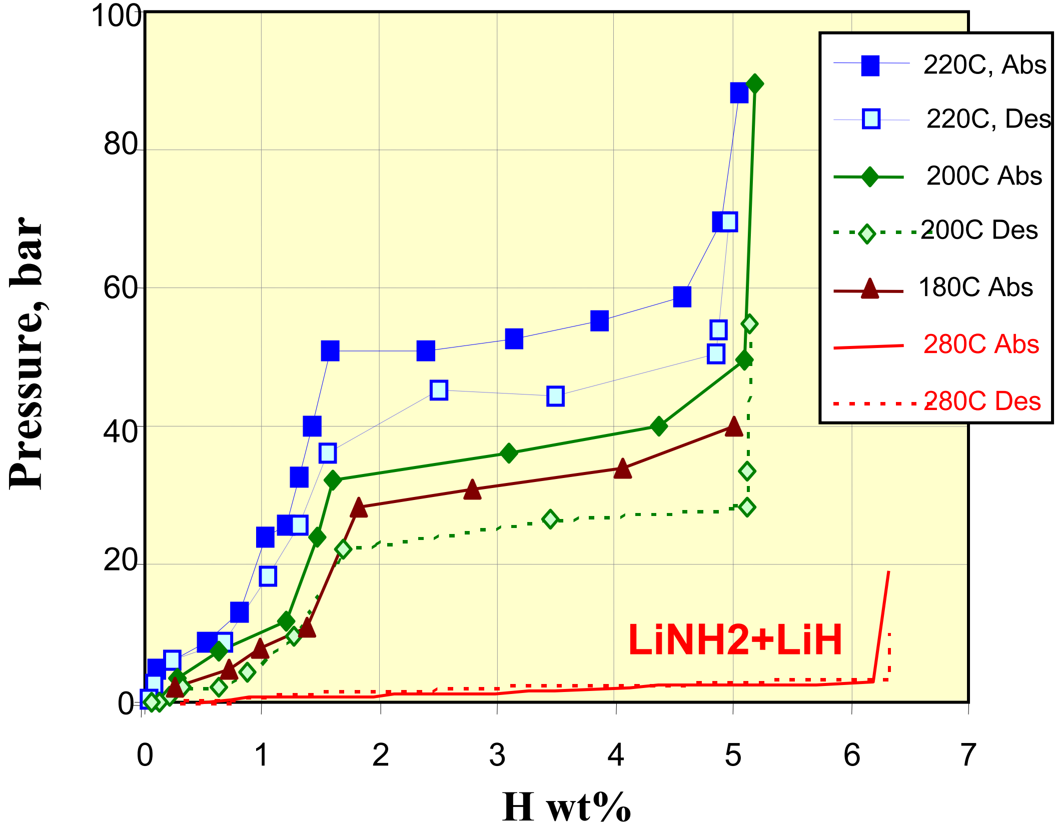
Partial Mg substitution

Chen, P. et al, *Nature* vol. **420**, (2002) 302.

W. Luo, J. Alloys and Comp., 381 (2004) 284-287.

Y. Nakamori, S. Orimo, J. Alloys and Compounds, 370 (2004) 271-275.

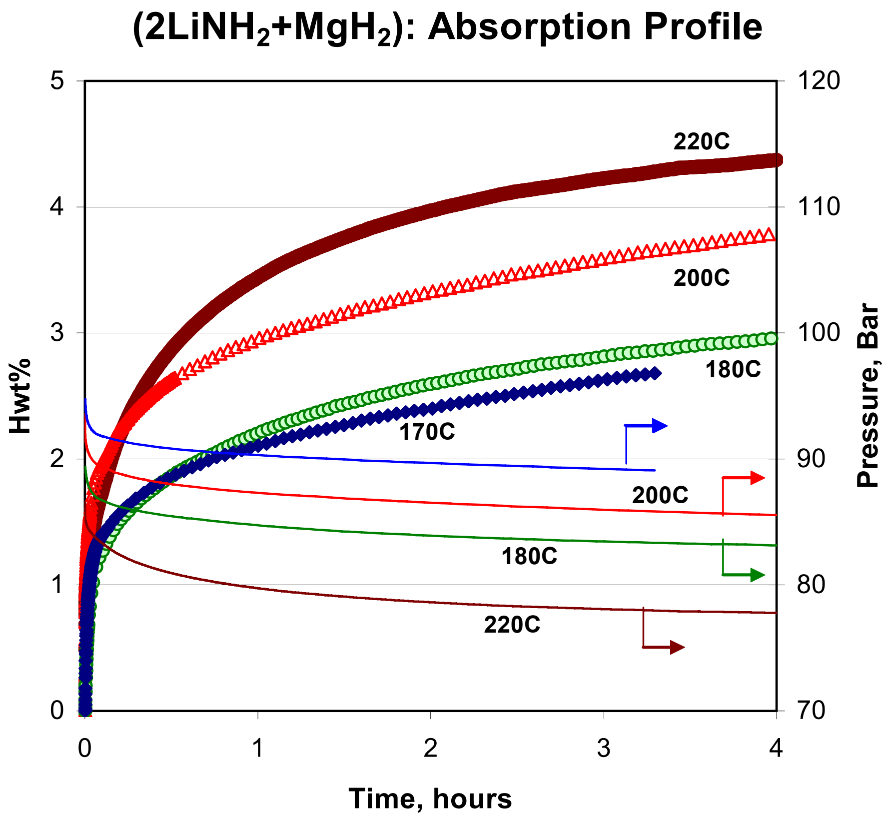
(A1)Thermodynamic characterization - Luo

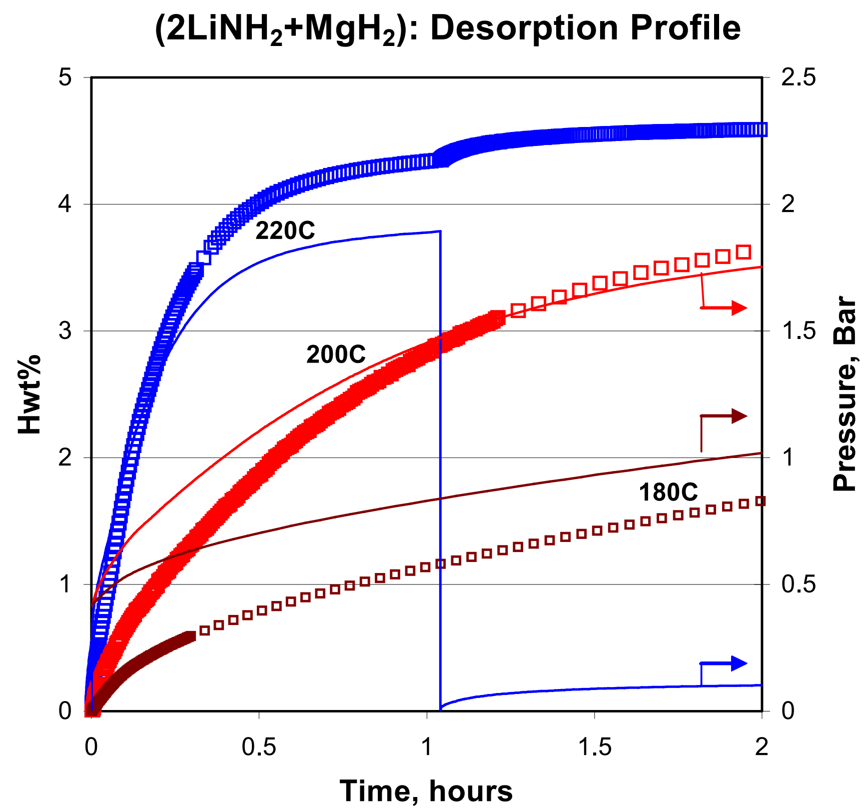


Isotherms were measured at:

- 220, 200, 180°C for absorption and desorption.
- Plateau pressure much higher than the one without Mg-substitution.

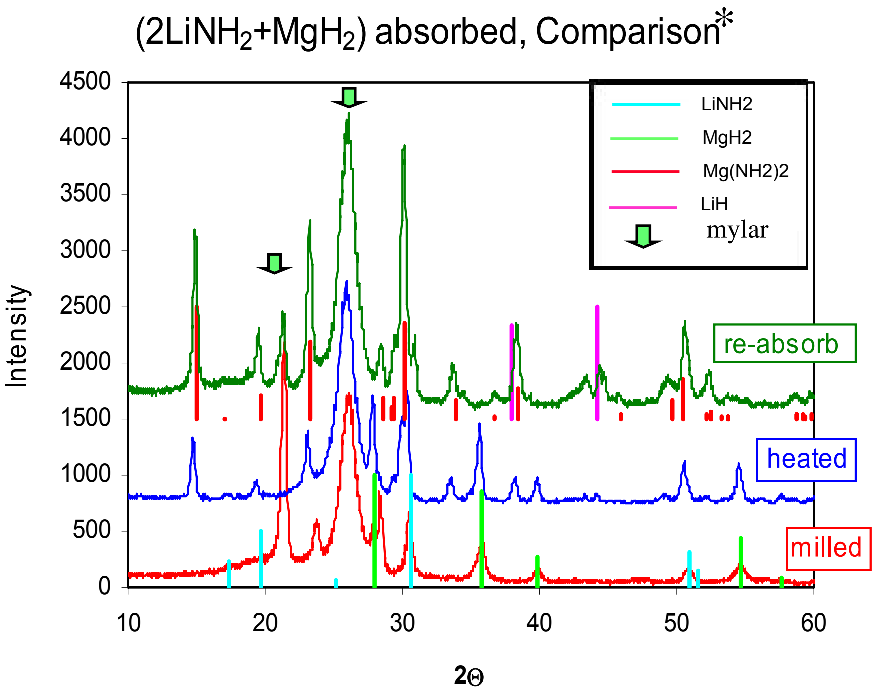
(A2) Sorption profile - Luo

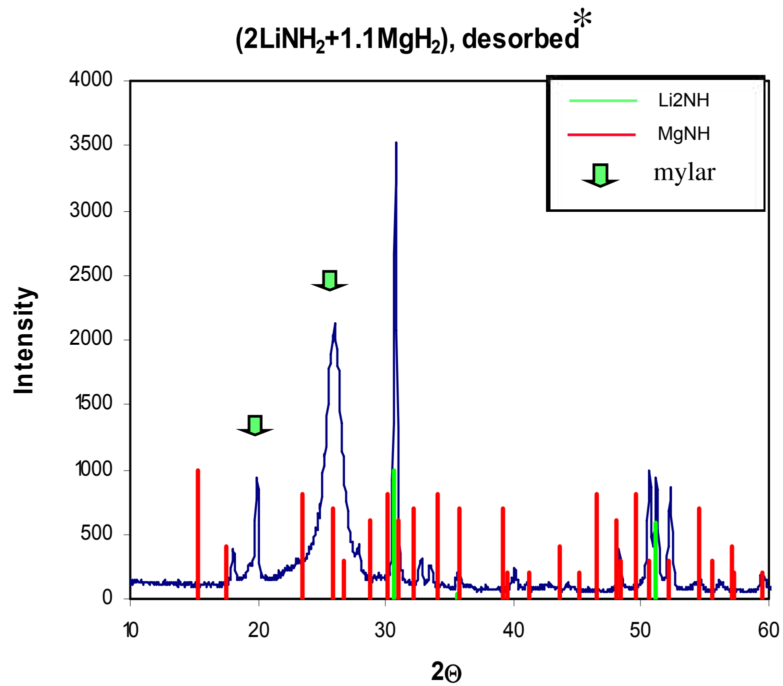




- *85% of desorption completed in 0.5h at 220°C*
- *Sorption rate decreases with decreasing temperature*

(A3) XRD characterization - Luo & Majzoub





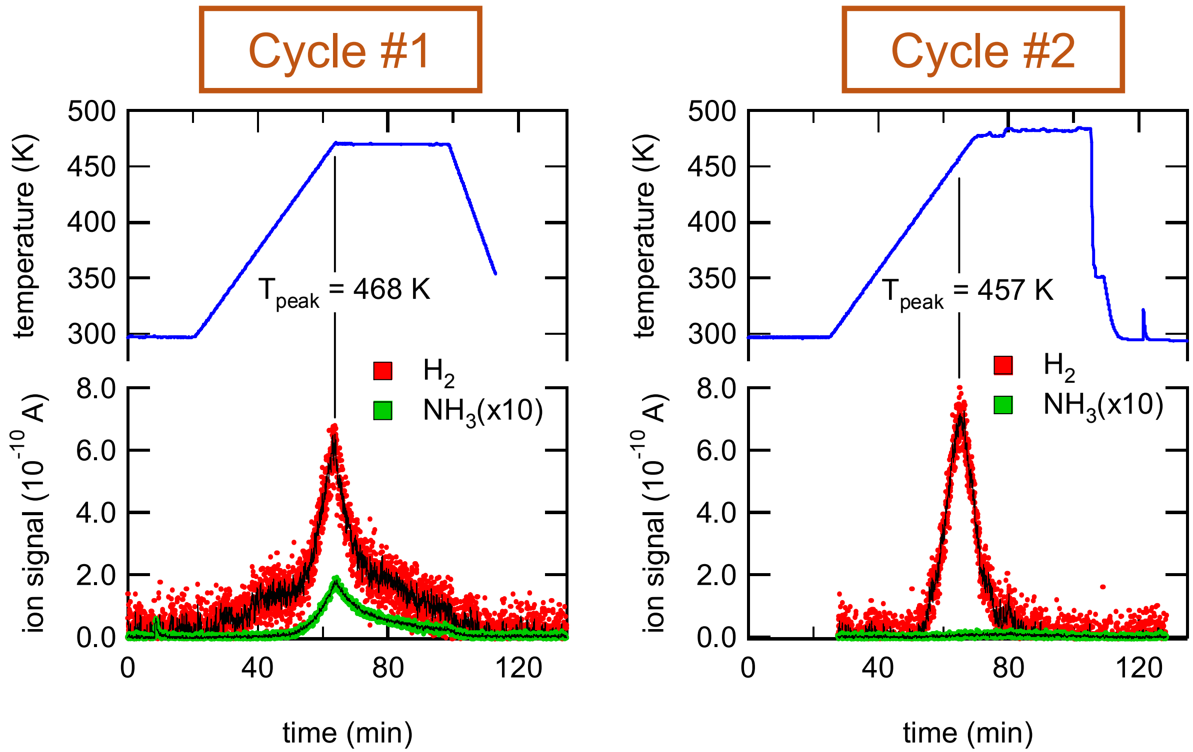
* Mylar was used to protect sample from being contaminated during XRD scanning

A new reaction path was proposed based on the material characterization results:

$$2LiNH_2 + MgH_2 \longrightarrow Li_2Mg(NH)_2 + 2H_2 \rightleftharpoons 2LiH + Mg(NH_2)_2$$

(A4) TPD-MS measurements – McDaniel & Chae

- First desorption cycle material "as milled"
- Second desorption cycle followed H_2 adsorption
  - 8 MPa
  - 473 K
  - 120 minutes
- H_2 desorption
  - 130 KPa
  - 5 K min^{-1} ramp

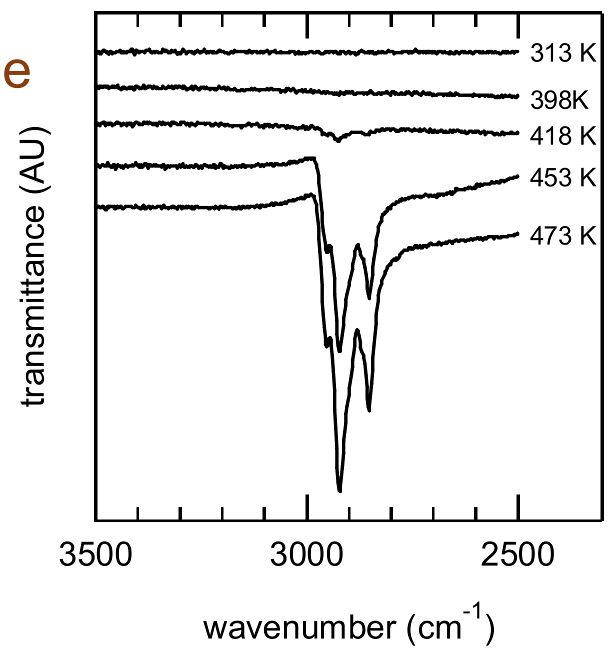


NH_3 desorption on first heating indicates chemical instability of milled material. Absent of low temperature "shoulder" on H_2 desorption peak in second cycle indicates structural changes in heated material.

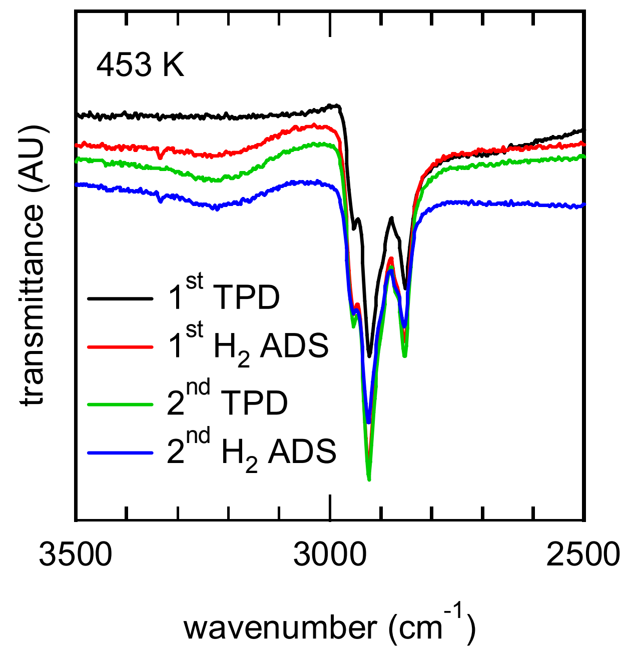
(A5) Diffuse Reflectance Infrared Spectroscopy Measurements– McDaniel & Chae

- First desorption cycle material "as milled"
- Second desorption cycle followed H_2 adsorption
  - 8 MPa
  - 473 K
  - 120 minutes
- H_2 desorption
  - 130 KPa
  - 5 K min^{-1} ramp

Cycle #1

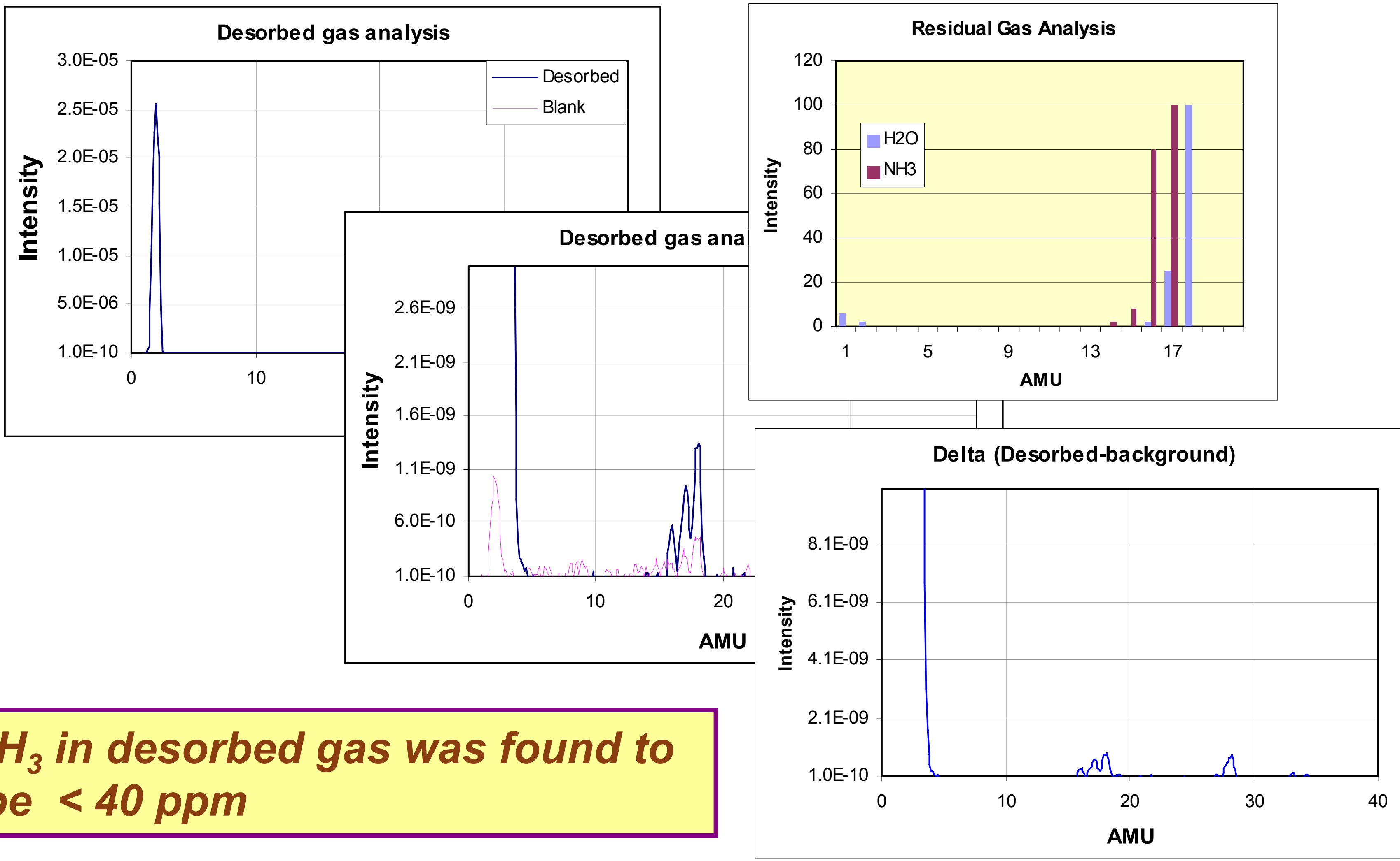


Repeat Cycles



N-H vibrational features appeared upon first heating of freshly milled sample. Structural changes in material stabilized on subsequent ads-des cycles.

(A6) Desorbed gas analysis– Luo



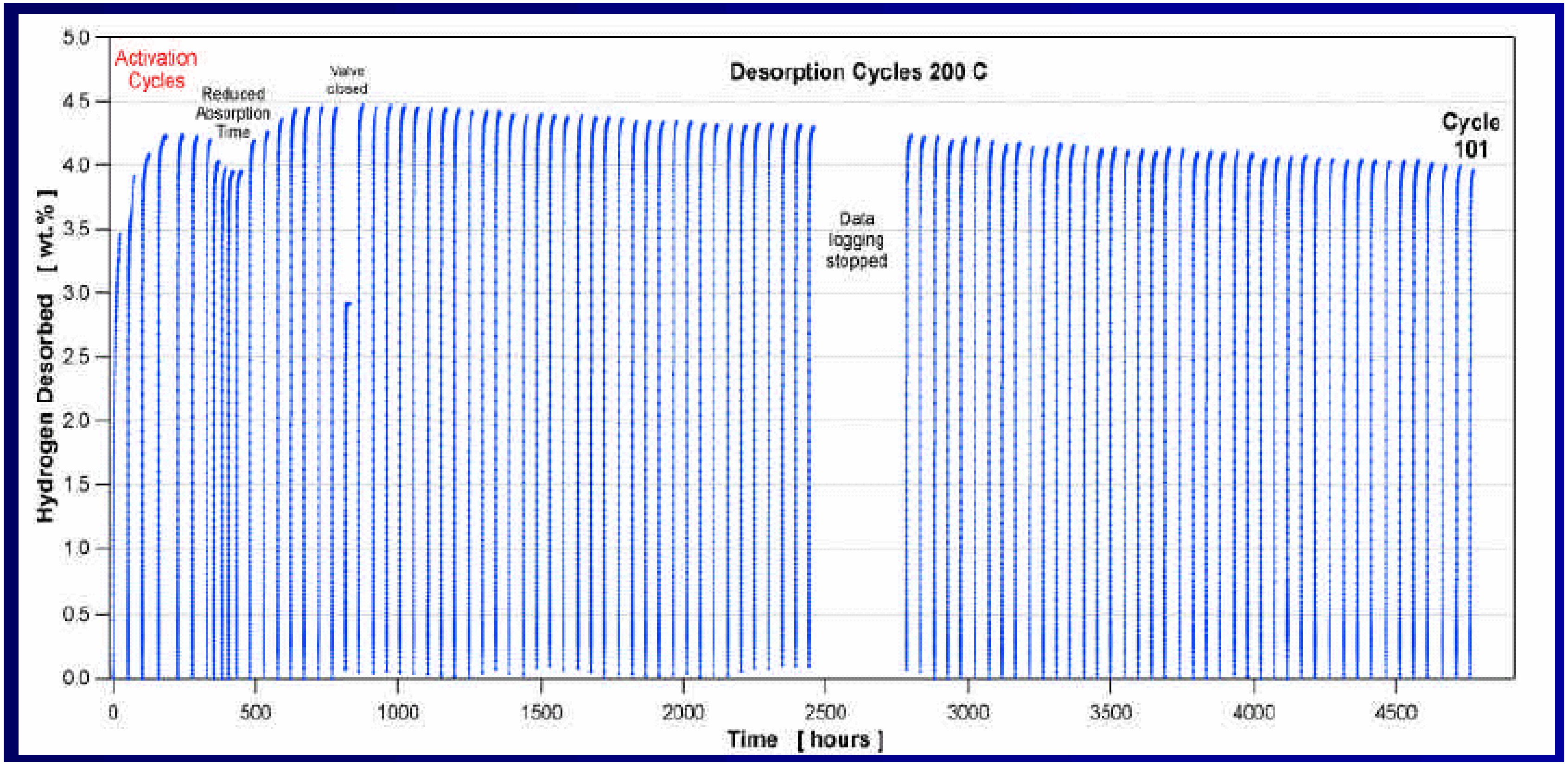
NH_3 in desorbed gas was found to be < 40 ppm

(A7) Ammonia Issues - Luo

- Ammonia formation:
  - *Is possible from self-decomposition of amide at higher temperatures than hydrogen formation*
  - *Could be inhibited by thorough mixing with sufficient amount of hydrides*
- Potential methods to eliminate ammonia formation:
  - *Optimize operational temperature*
  - *Optimize amide/hydride ratio*
- Potential methods to remove ammonia in H_2 stream:
  - *Add ammonia filter or trap before enter fuel cell system*

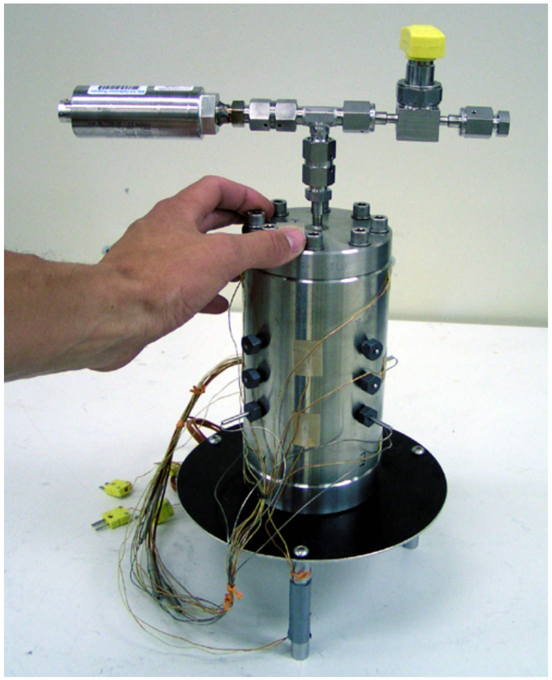
Ammonia desorption can be controlled by engineering design

(A8) Cycle test to 101 cycles - Gross



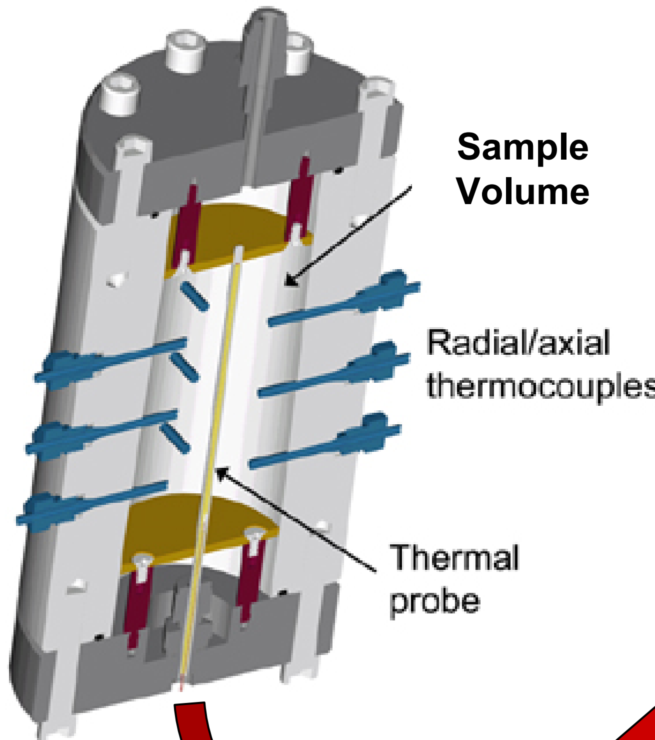
Capacity loss: 0.005wt% per cycle

(A9) Thermal Properties Measurements
Hardware configuration – Crooker & Dedrick

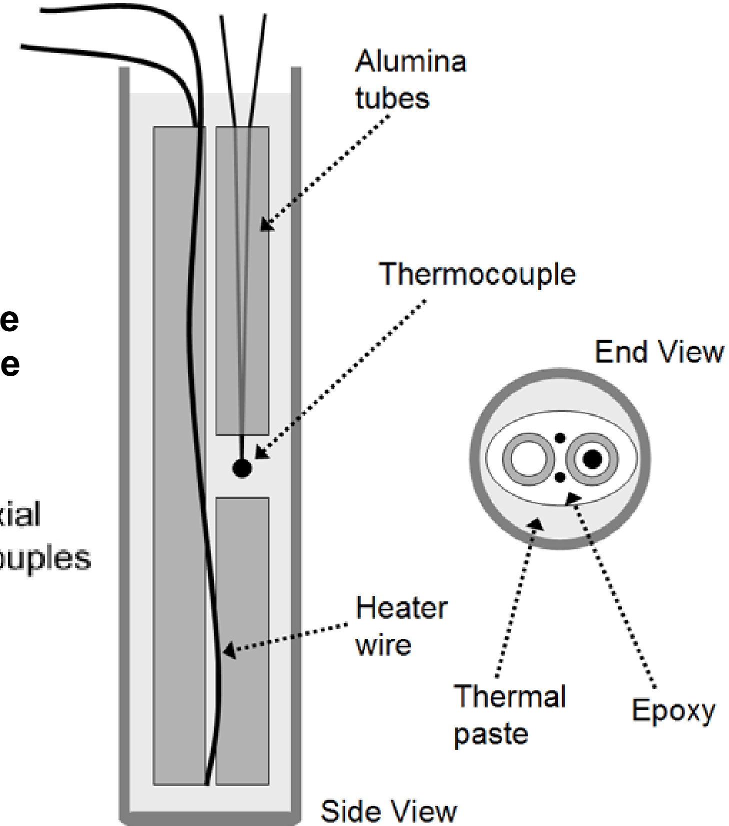


Loaded with ~ 130 grams ball-milled $LiNH_2$-MgH_2

Optimized to measure K_{th} up to ~5 W/m-K



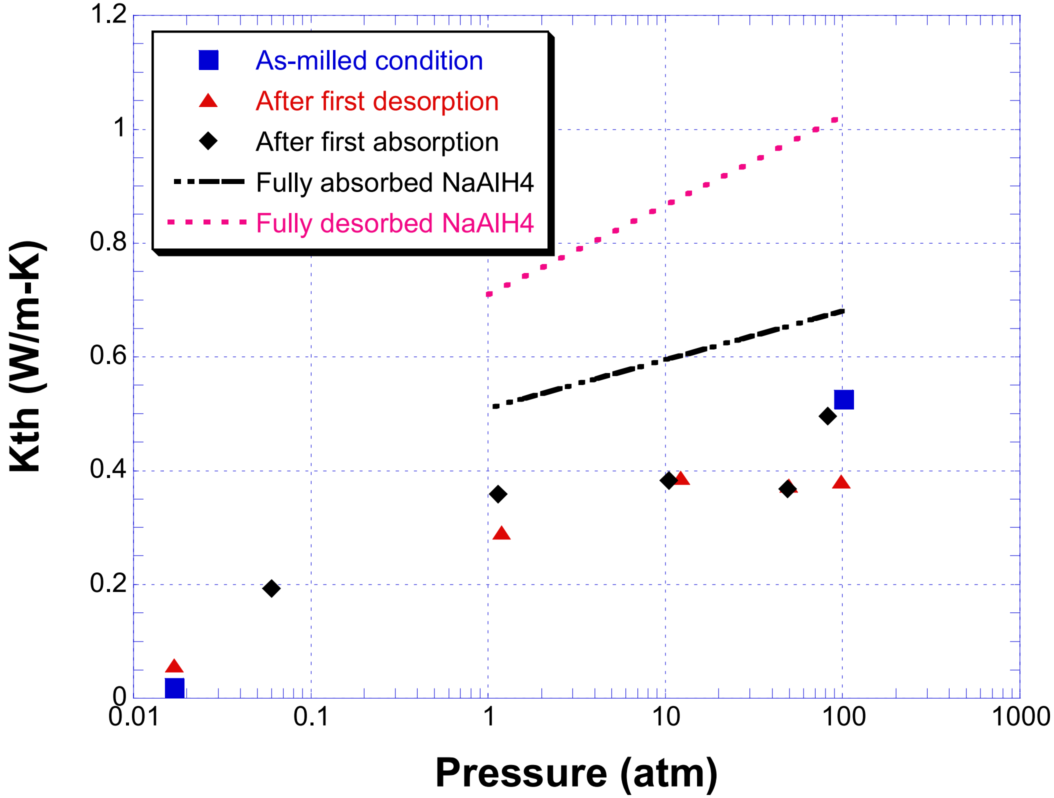
Solid model



Probe design

(A10) Preliminary K^{th} results – Crooker

$2LiNH_2 + MgH_2 \longrightarrow Li_2Mg(NH)_2 + 2H_2 \rightleftarrows 2LiH + Mg(NH_2)_2$



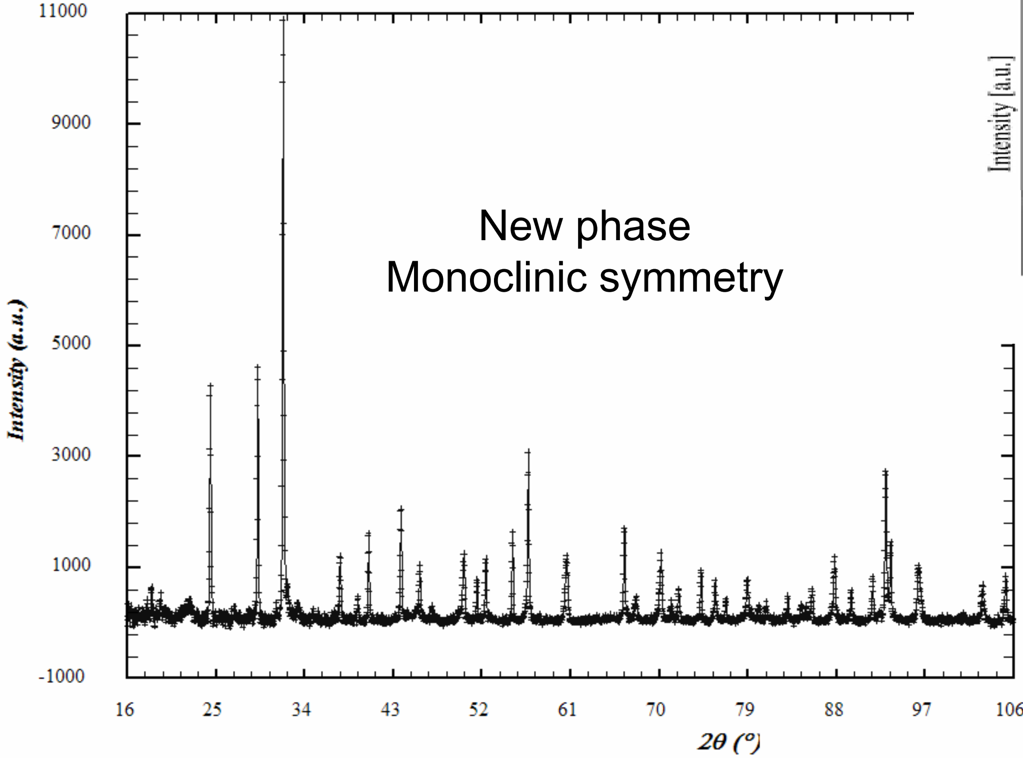
Thermal conductivity of $LiNH_2$+MgH_2 material increases with gas pressure and similar to those of sodium alanates.

B. Modified Complex Hydrides
Investigation of bi-alkali alanates

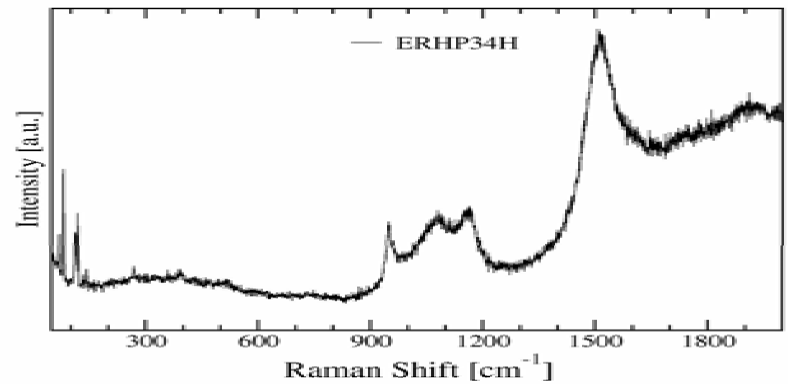
- Pressed pellets of hand mixed or ball milled samples were tested at high pressures up to 136 MPa and temperatures up to 450C facility.
- bi-alkali alanates of various molar ratios were tested:
  - *Li-K, Li-Mg, Li-Ca, Li-Ti, Mg-Ti, etc….*
  - *New bi-alkali Li-K alanate formed @ 68 MPa and 330C*
    - *Starting mixture of $LiAlH_4$ + 2KH or LiH + 2KH + Al*
    - *Pellets expanded and showed in white color*
- Investigation of $Li(Al_{1-x}B_x)H_4$, $Na(Al_{1-x}B_x)H_4$, etc…systems are in progress

Properties of new Li-K alanates - Ronnebro

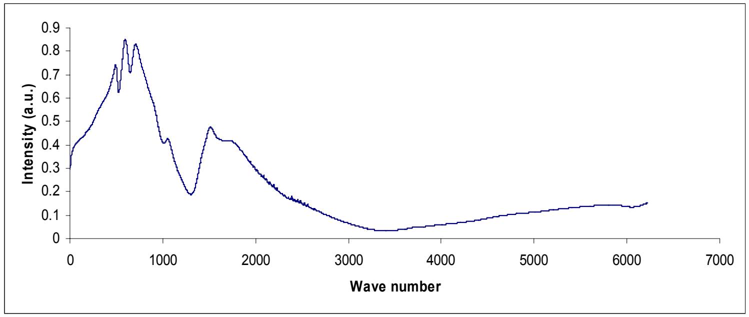
Powder X-ray diffraction pattern



Raman spectra



FTIR



Structural, kinetic and thermodynamic properties are under investigation

C. Modified Borohydrides

(collaboration between Sandrock & BNL)

Can Hydrogen Driven Metallurgical Reactions be used to make nanocomposites for "stimulating" the Borohydrides?

$LiBH_4 \Leftrightarrow LiH + B + 3/2\ H_2$ (13.9 wt. % H)

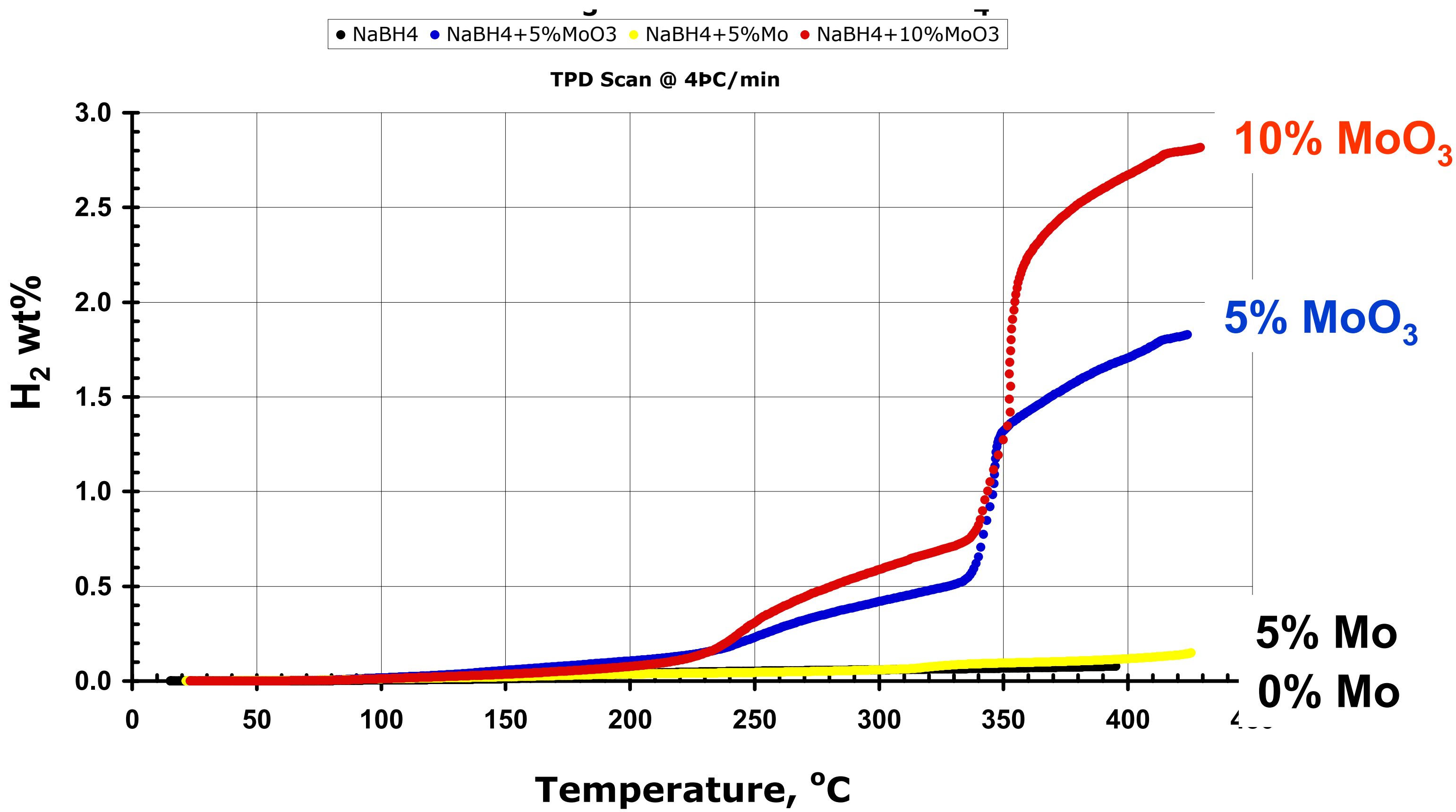
$NaBH_4 \Leftrightarrow NaH + B + 3/2\ H_2$ (8.0 wt. % H)

Possible Oxide Precursor Reactions (schematic):

$NaBH_4 + MoO_3 \Rightarrow NaBH_4 + Mo + (Na_2O \text{ or } B_2O_3 \text{ or } H_2O)$

$NaBH_4 + Mo \Leftrightarrow NaH + MoB_x + H_2$

Effect of Mo & MoO_3 on NaBH4 - Sandrock



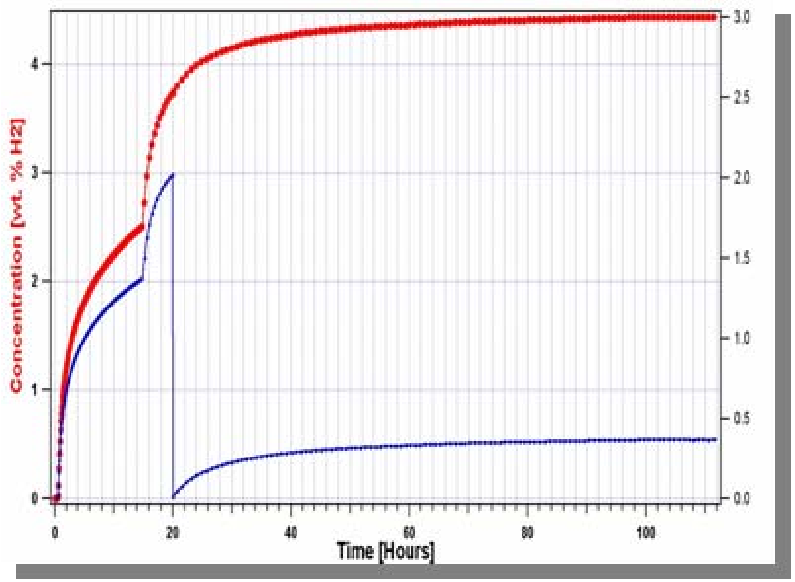
Mo is not the best addition for $NaBH_4$ reversibility because the Mo-borides are too stable.

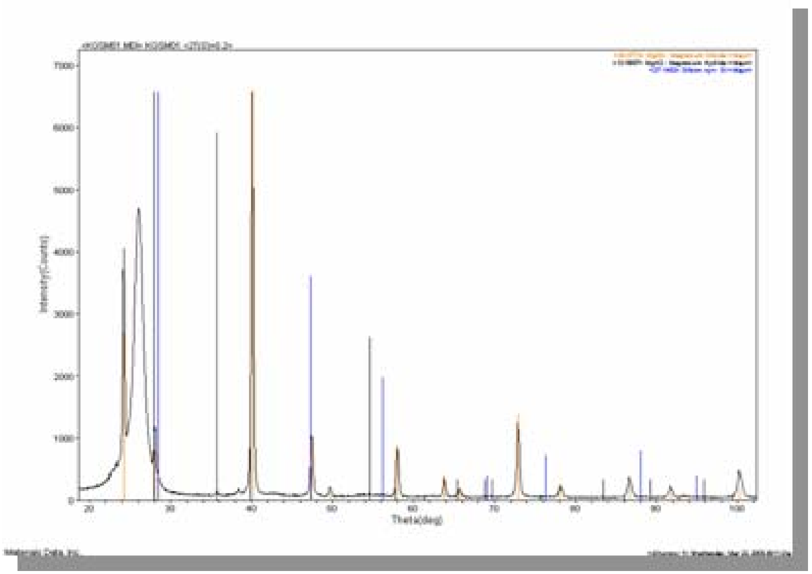
D. Destabilized Mg hydride – Gross

(in collaboration with HRL)

MgH_2 Has 7.6 wt.% hydrogen - but too stable for FCV applications

Much more favorable thermodynamics: $2MgH_2 + Si \Rightarrow Mg_2Si + 2H_2$





- ***Reversibility being tested using High-pressure station***
- ***4.5 wt% hydrogen was release on desorption at 360°C***
- ***XRD after desorption showed 100% conversion to Mg_2Si***

E. Aluminum hydrides (AlH_3)

(collaboration of Sandrock & BNL)

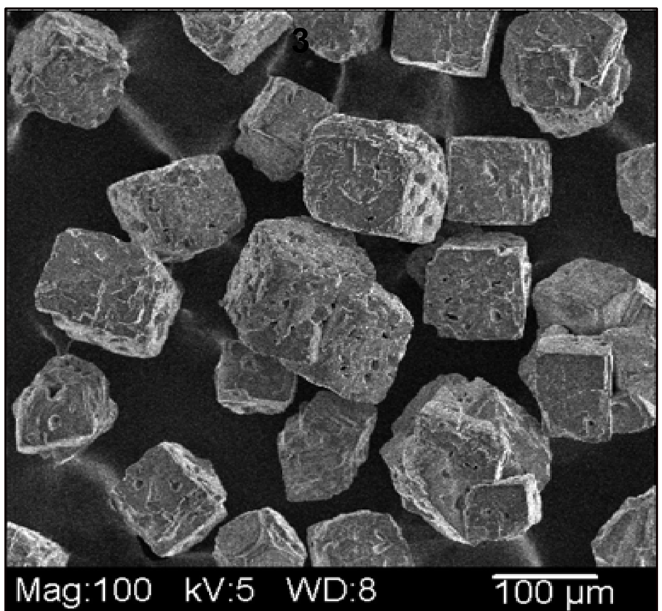
$$\alpha\text{-}AlH_3 \longrightarrow Al + 3/2\ H_2$$

H-capacity (g) = 10.1 wt%

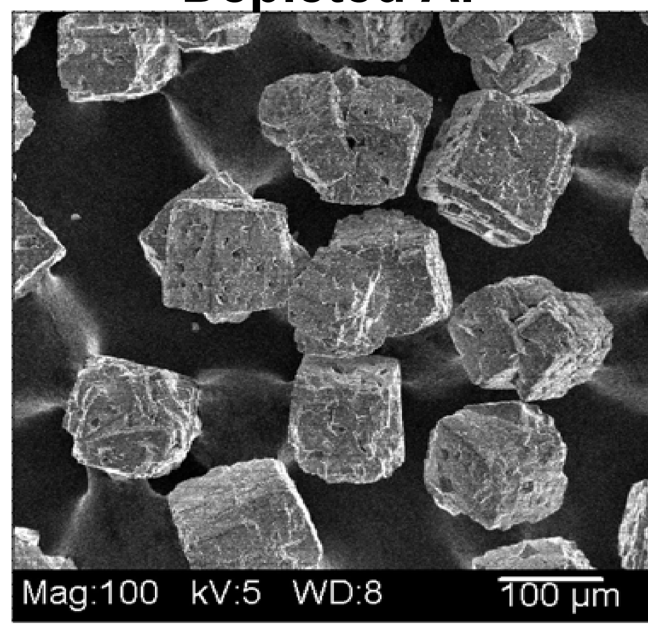
H-capacity (v) = 149 kg/m^3

ΔH_{des} = 7.6 kJ/mol H_2

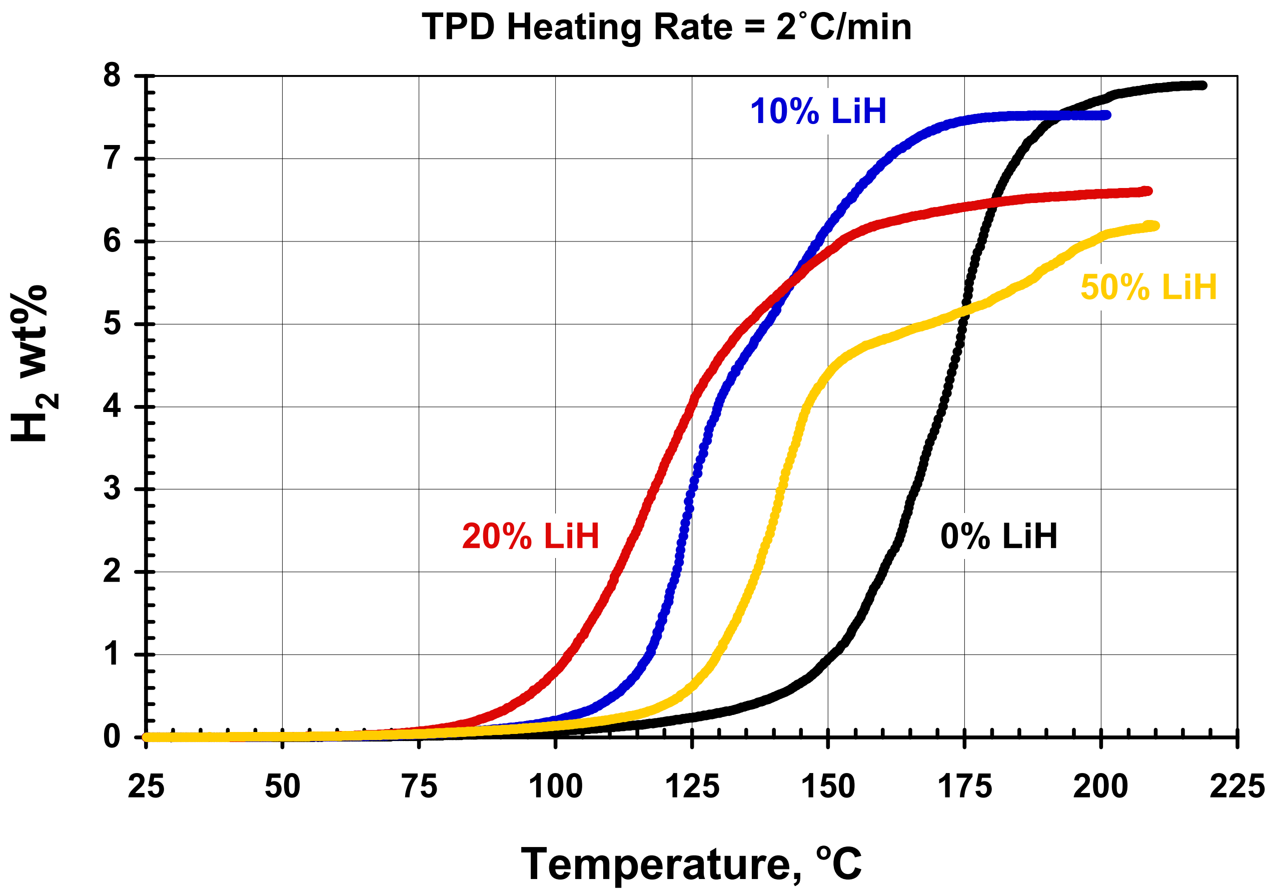
AlH_3



Depleted Al



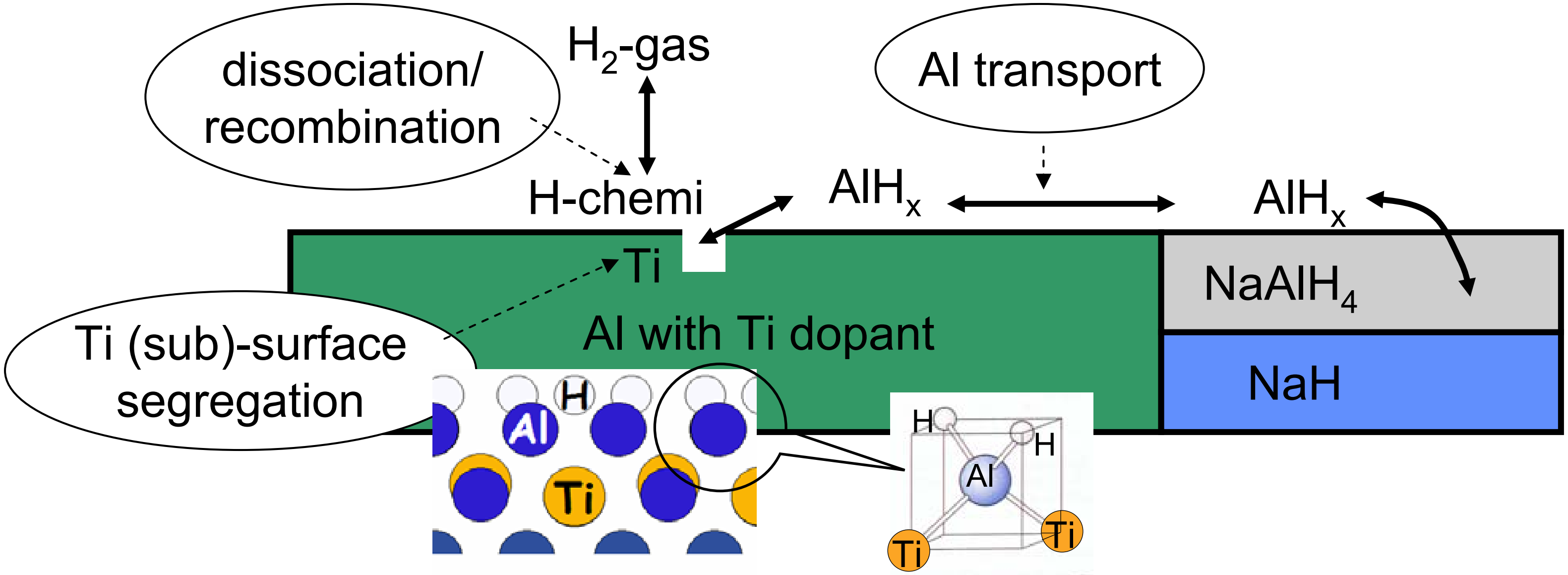
Effect of LiH doping via TPD – Sandrock



Desorption temperature can be reduced by adding more LiH

II. Fundamental Mechanisms & Modeling

(1) Surface alloy catalytic model of $NaAlH_4$ - Stumpf



- **H_2 chemistry is autocatalytic: H promotes (sub-) surface Ti**
- **Sub-surface Ti creates "activated" sp3-like Al surface atoms with stronger H affinity and reduced H_2 sorption barriers**
- **Exposed Ti offers chemisorbed H_2 binding site and vanishing barriers**
- **AlHx provides long range Al transport**
- **Results for Sc are similar to those for Ti**

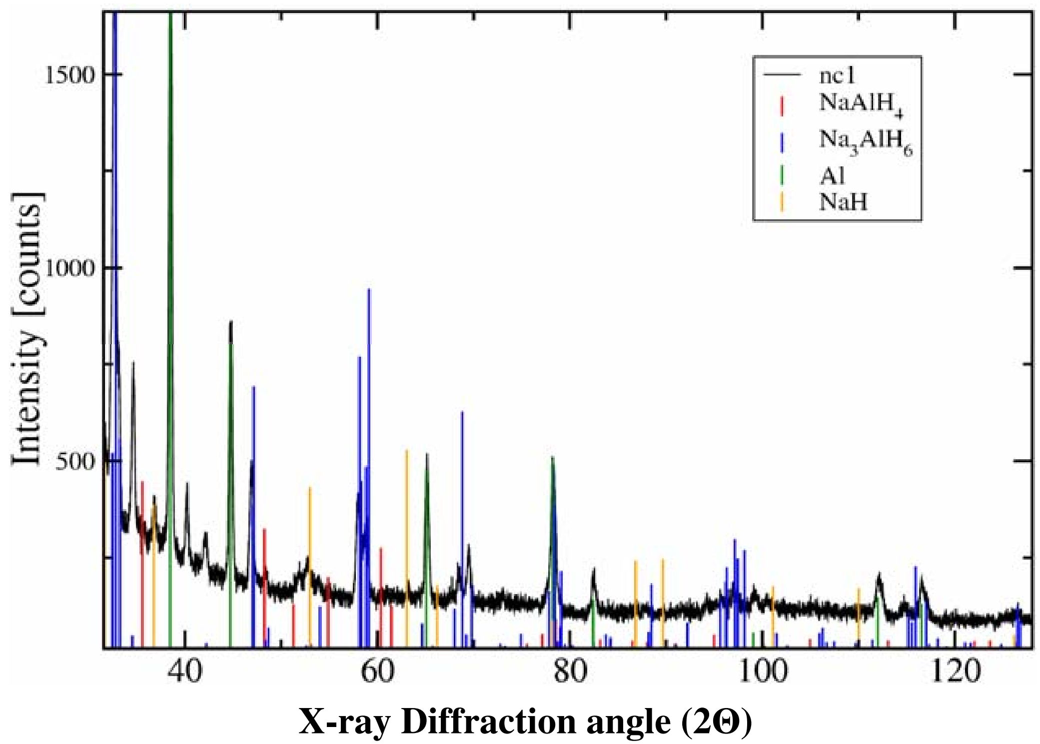
Surface alloys of simple and transition metals are promising new catalysts for H chemistry

(2) Effect of H_2 or H ? - Majzoub & Stumpf

Experimental support for surface mechanism: dosing of Al+NaH with "atomic" H

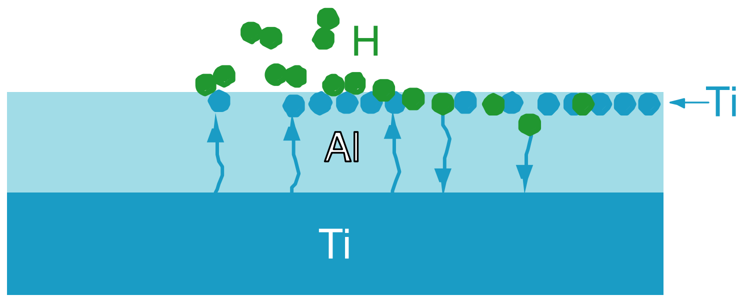
Idea: use Pd surface to crack H_2

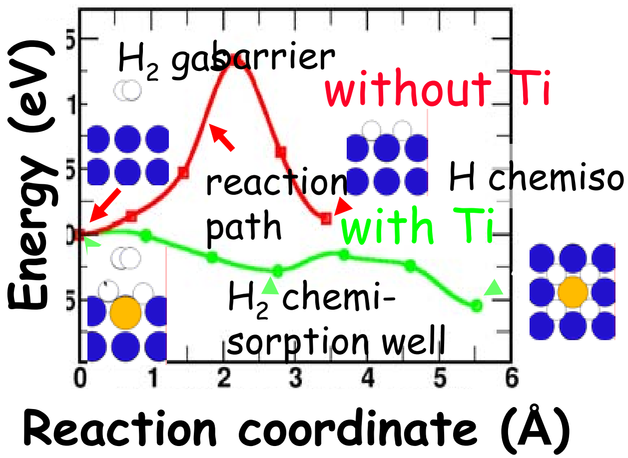
- *X-ray diffraction after 10 day exposure of Al+NaH to H_2 in contact with Pd foil shows 10% of Al+NaH converts to Na_3AlH_6 and $NaAlH_4$*
- *Control experiment without Pd shows < 1% alanate formation*



H_2 cracking ability of Pd helps hydride formation

(3A) Where is Ti ? - Bastasz



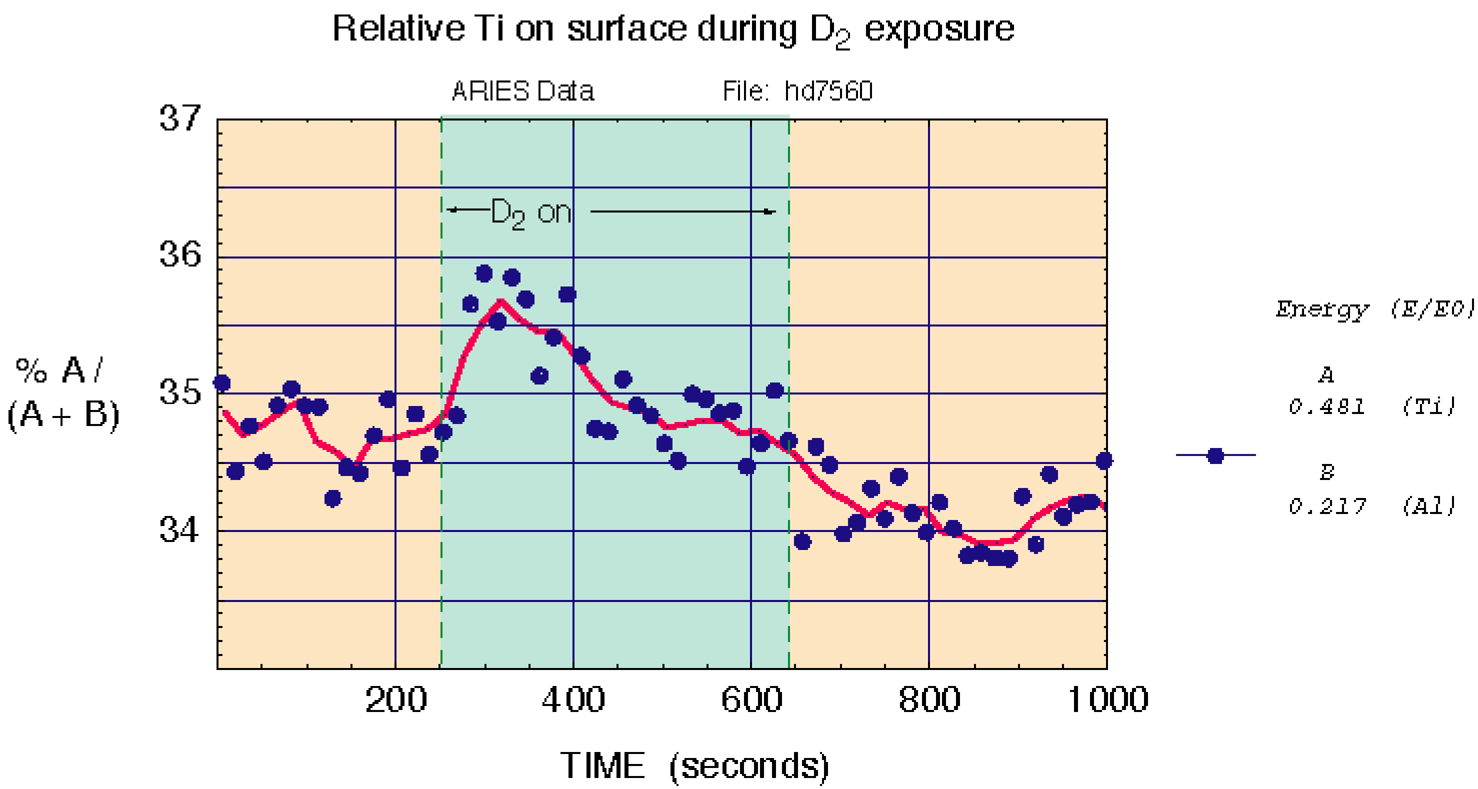


H may stabilize Ti on Al surfaces – Predictions:

- *H on surface promotes Ti segregation to near-surface sites*
- *Ti reduces H_2 adsorption barriers on Al to a fraction of an eV.*
- *Ti facilitates both uptake and release of H_2.*

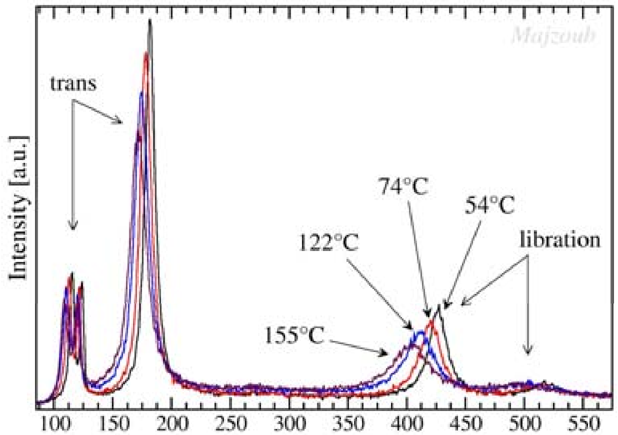
Is there experimental evidence for this?

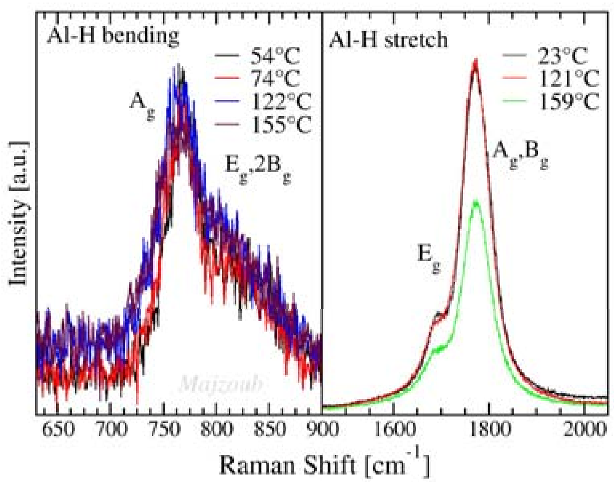
(3B) Model validation - Bastasz



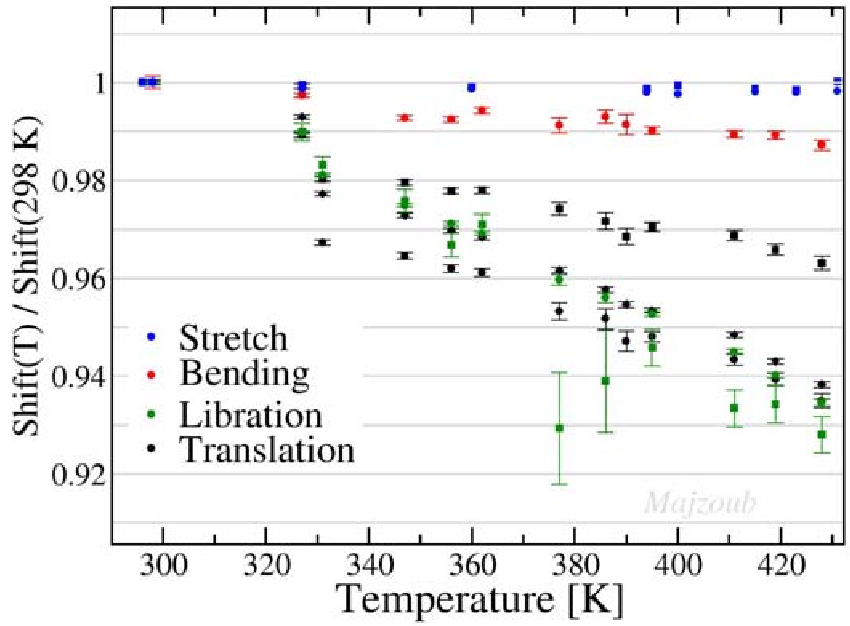
Ti/(Ti+Al) signal ratio changes indicating that Ti concentration on the surface appears to increase upon exposing sample to D_2.

(4) In-Situ Raman spectra observations - Majzoub





- Crystal modes soften up to 6-7% at Tm
- AlH_4 anion modes soften less than 1.5%
- AlH_4 anion is also stable in the melt!



Data shows a very stable AlH_4 anion.

III. Synthesis of Nanostructured Materials

Wet chemistry synthesis using NH_3 – Daniel & Boyle

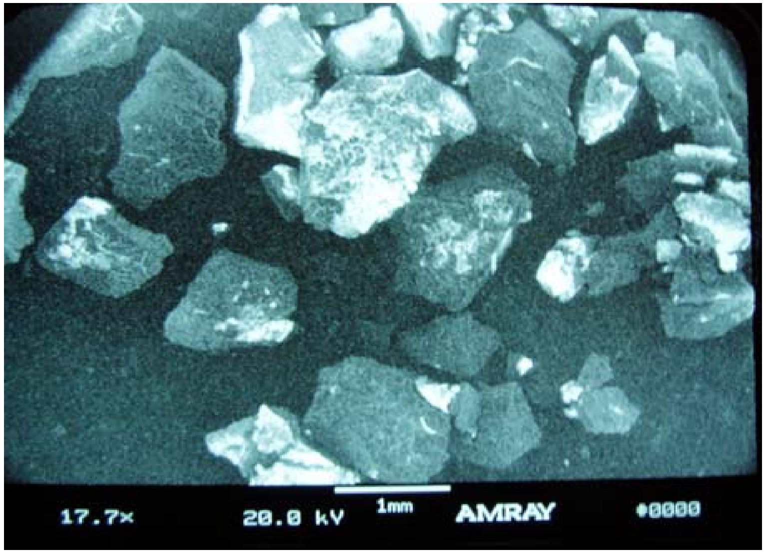


Fig. 1

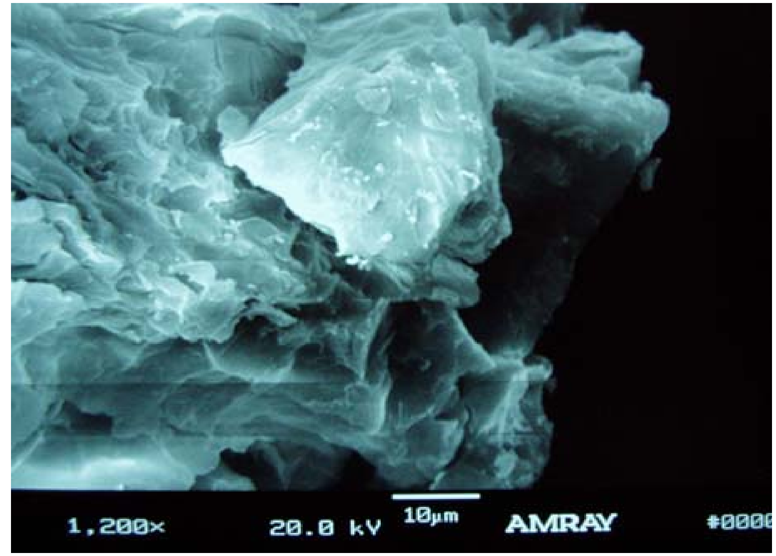


Fig. 2

Scanning Electron Microscopy (SEM) images of $Mg(NH_2)_2$ show the particle size to be ~1-2 mm. The morphology appears coarse and brittle which can be easily broken or ground.

However, poor performance was observed due to contamination of residue solvents from wet chemistry processing.

Responses to Previous Year Reviewers' Comments

1. Overall Project Score: 3:32 – *positive feedbacks validated our approach and accomplishments in FY2004.*
2. Not enough progress made toward development of onboard storage module – *we will start the storage module development later this FY and gradually increase its efforts as the program progresses toward Phase II.*
3. Primary empirical approach to new material discovery – *we selected our tested materials based on thermodynamics, atomistic modeling and experiences (teaming between modeling and experimentation).*
4. Cost estimation is not covered – *we will initiate cost study as one of system studies in parallel to the materials discovery efforts.*
5. Difficulty of geographic separation – *we established on-line, instant communication system and regular teleconferences and face-to-face meetings for all Center partners.*

Responses to Previous Year Reviewers' Comments (continued)

6. System-based studies are needed – *we started the Center (in Jan) with engineering system as a central focus, with a ramp up of the engineering design in phase II.*
7. Make sure the performance metrics include considerations of (1) "whole storage system" weights and volumes and (2) "net" energy delivered to the vehicle – *we used this to screen our material candidates as a part of our Center system-based approach.*
8. Schedule down select of materials – *yes, we have go/no-go decision points in our AOP milestones as well as our MHCoE plan.*
9. Investment in Na-alanates? – *we stopped most tests on Na-alanates except some experiments to validate our 1st principle model.*

Future Work

Remainder of FY2005

- New Storage Materials Development
  - *Explore new complex hydrides via HP/HT process*
  - *Optimize Li-Mg-H based materials for faster kinetics and lower temperatures*
  - *Search for storage materials with optimal properties*
- Fundamental Mechanisms
  - *Conclude the modeling validation experiments on alanates*
  - *Initiate modeling and mechanisms studies on Li-Mg-H, B-Li-H and Al-H based materials*
- Chemical Synthesis Development
  - *Improve the wet chemistry process to produce pure storage materials with nano-size particles*

Future Work

Remainder of FY05 (continued)

- Engineering Science of Complex Hydrides
  - *Continue to measure engineering properties of hydrogen storage materials, e.g., thermal conductivities, volume expansion, tap density,…...etc.*
  - *Continue to study performance degradation and reliability of candidate storage materials*
  - *Initiate investigation on reactions related to safety*
- Collaboration with MHCoE Partners
  - *Lead the Metal Hydride Center of Excellence.*

Future Work

FY2006 and beyond

- New Storage Materials Development
  - *Continue to search for materials with optimal storage properties*
- Fundamental Mechanisms
  - *Continue to model newly discovered materials*
  - *Develop models to predict new materials and to guide experiments*
- Chemical Synthesis Development
  - *Continue to develop processes to produce storage materials with nano-size particles.*
- Engineering Science of newly developed Hydrides
  - *Continue to build engineering property database of hydrides.*

Presentation end

Publications

1. W. Luo, "(LiNH2-MgH2): a viable hydrogen storage system", J. Alloys and Compounds, **381**, 284-287 (2004)
2. W. Luo, K. Gross, "A kinetics model of hydrogen absorption and desorption in Ti-doped NaAlH4", J. Alloys and Compounds, **385**, 224-231 (2004)
3. Z. Xiong, J. Hu, G. Wu, P. Chen, W. Luo, K. Gross, J. Wang, "Thermodynamic and kinetic investigation on the ternary imide of $Li_2MgN_2H_2$", J. Alloys and Compounds, **in press**.
4. E. H. Majzoub, K. F. McCarty, and V. Ozolins, "Lattice dynamics of NaAlH4 from high-temperature single-crystal Raman scattering and ab initio calculations: Evidence of highly stable AlH-4 anions," Phys. Rev. **B 71**, 024118 (2005)
5. R. Bastasz, J.W. Medlin, J.A. Whaley, R. Beikler, and E. Taglauer, "Deuterium adsorption on W(100) studied by LEIS and DRS," Surface Science, volume **571** (2004) pp 31-40.
6. J. Wang and E. Ronnebro, "Hydride Developments for Hydrogen Storage," Proceedings of the 2005 Spring TMS conference, p. 19, (2005)
7. E. H. Majzoub, J. L. Herberg, R. Stumpf, S. Spangler, R.S. Maxwell, "*XRD and NMR investigation of Ti-compound formation in solution-doping of sodium aluminum hydrides: solubility of Ti in NaAlH4crystals grown in THF*," J. of Alloys and Compounds **388**, 81 (2004)
8. V. Ozolins, E. H. Majzoub, T. J. Udovic, "*Electronic structure and Rietveld refinement parameters of Ti-doped sodium alanates*," J. of Alloys and Compounds **375**, 1-10 (2004)
9. E. H. Majzoub, R. Stumpf, S. Spangler, J. Herberg, and R. Maxwell, "*Compound Formation in Ti-doped Sodium Aluminum Hydrides*," MRS Proceedings **801**, 153-158 (2004)
10. R. Stumpf, "*H-Induced Reconstruction and Faceting of Al surfaces*," Phys. Rev. Lett. **78**, 4454 (1997)
11. G. Sandrock, J. Reilly, J. Graetz, W. Zhou, J. Johnson, and J. Wegrzyn, "Accelerated thermal decomposition of AlH3 for hydrogen-fueled vehicles," Applied Physics A – Materials Science and Processing, **80**, 687–690 (2005) .

Presentations

1. R. Bastasz and J.A. Whaley, "*LEIS and DRS: Diagnostic tools for studying hydrogen on surfaces*," MRS Spring Meeting, Symposium on Materials and Technology for Hydrogen Storage and Generation, San Francisco, March 30, 2005.
2. K. Gross, W. Luo, "*Sorption Properties of novel hydrogen storage materials*", International Symposium on Matel Hydrogen Systems, Krakow, Poland, Sept. 6-9, 2004,
3. K. Gross and G. Thomas, *"Hydrogen Storage Where We Are Now and Where We Need to Go" ,* American Physical Society Annual Meeting, Montréal Canada March 20-26, 2004.
4. K. Gross and D. Dedrick, *"Advances in Hydrices for Hydrogen Storage" ,* American Physical Society Annual Meeting, Montréal Canada March 20-26, 2004.
5. K. Gross, *"Advances in Alanates for Hydrogen Storage*," NHA Annual Meeting 2004
6. K. Gross, W. Luo, "*Properties of advanced hydrogen storage materials*", Material Research Society Annual Meeting, Boston, MA, Nov. 29-Dec.2, 2004.
7. W. Luo, "*Towards a viable hydrogen storage system for transportation application*", International Symposium on Matel Hydrogen Systems, Krakow, Poland, Sept. 6-9, 2004,
8. W. Luo "*Towards A Viable Hydrogen Storage System For Transportation application*", Material Solution Conference and Exposition", Columbus, OH, Oct. 18-21, 2004.
9. W. Luo, K. Gross, E. Ronnebro, J. Wang, "*Destabilization of metal hydrides by forming nitrogen-containing compounds*", American Physical Society Annual Meeting, Los Angeles, CA, March 21-25, 2005.
10. W. Luo, K. Gross, E. Ronnebro, J. Wang, "*Metal-N-H: new promising hydrogen storage materials*", NHA Meeting, Washington DC, March 28-Apr.1, 2005
11. E. Majzoub, "*X-ray Diffraction and Raman Spectroscopy Investigation of Titanium Substitution in Sodium Aluminum Hydride*," TMS Annual Meeting 2004
12. E. Majzoub, "*In-situ Raman Spectra of NaAlH4 : Evidence of Highly Stable AlH4 Anions*," MRS 2004
13. E. Majzoub. "*In-situ Raman Spectra of NaAlH4 : Evidence of Highly Stable AlH4 Anions*," International Conference on Metal-Hydrogen Systems, Krakow, Poland, 2004
14. G. Sandrock, J. Reilly, J. Graetz, W. Zhou, J. Johnson, J. Wegrzyn, "Doping of AlH3 with alkali metal hydrides for enhanced decomposition kinetics," presented at the APS March meeting, March 21-25, 2005.

Presentations
(Continued)

15. R. Stumpf, *Promotion of H_2 Sorption at Al-Ti Alloy Surfaces in Alanate H Storage Materials*, MRS Spring Meeting, GG2.5 (2005)
16. R. Stumpf, *Basic Mechanisms of H Uptake/Release in Ti-Doped Alanate H-Storage Materials*, MS&T review, Sandia (2005)
17. R. Stumpf, K. Thürmer, R. Bastasz, *Atomistic View of the H Uptake/Release Mechanisms in the Ti-Doped Na-Al-H System*, ASM materials solutions conference, Ohio, invited talk (2004)
18. J. Wang, " *Hydride Development for Hydrogen Storage Applications,"* TMS Spring Conference, (2005)
19. J. Wang, "Hydrogen Storage Materials Research at Sandia National Laboratories," Materials Solutions Conference and Exposition, ASM Annual Meeting, Columbus, OH (2004)

Hydrogen/Material Safety

*The **most** significant hydrogen hazard associated with this project is that we are developing hydrogen storage materials with unknown properties which potentially can be very energetic. Specifically,*

- A rapid pressure rise resulting in containment failure,
- An unexpected increase in temperature of an object resulting in a burn and/or fire hazard.

Either of these could occur if some of our current materials are exposed to 1) an oxidizing atmosphere and/or 2) moisture

Hydrogen/Material Safety

Our approach to deal with these hazards are:

- Only well trained knowledgeable personnel have access to the project/laboratory and are authorized to operate the laboratory equipment,
- The quantities of material (fuel or oxidizer) are limited such that in the event of a catastrophic containment failure resulting in a rapid energy release, the resulting pressure and/or temperature rise for the system is kept well below any hazardous condition,
- Material preparation, installation and removal is performed an inert gas environment.
- All materials, when not in use, are sealed in secondary containment within the glove box and within sealed experimental vessels at 1 bar overpressure of inert dry gas.
- Sandia's well established and documented Integrated Safety Management System (ISMS) which addresses the safety aspects of new projects or changes in an existing one is fully implemented and enforced throughout all aspects of our hydrogen storage materials R&D project.