# Development of Metal Hydrides at Sandia National Laboratories

*Presented by*

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***Sandia National Laboratories***

*Livermore, California*

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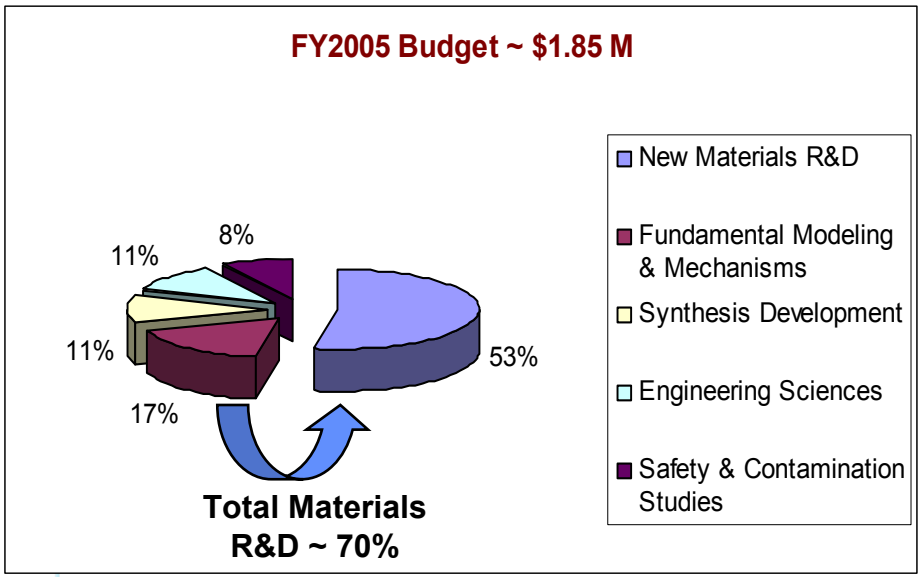
This presentation does not contain any proprietary information

**Project ID# STP62**

# 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.*

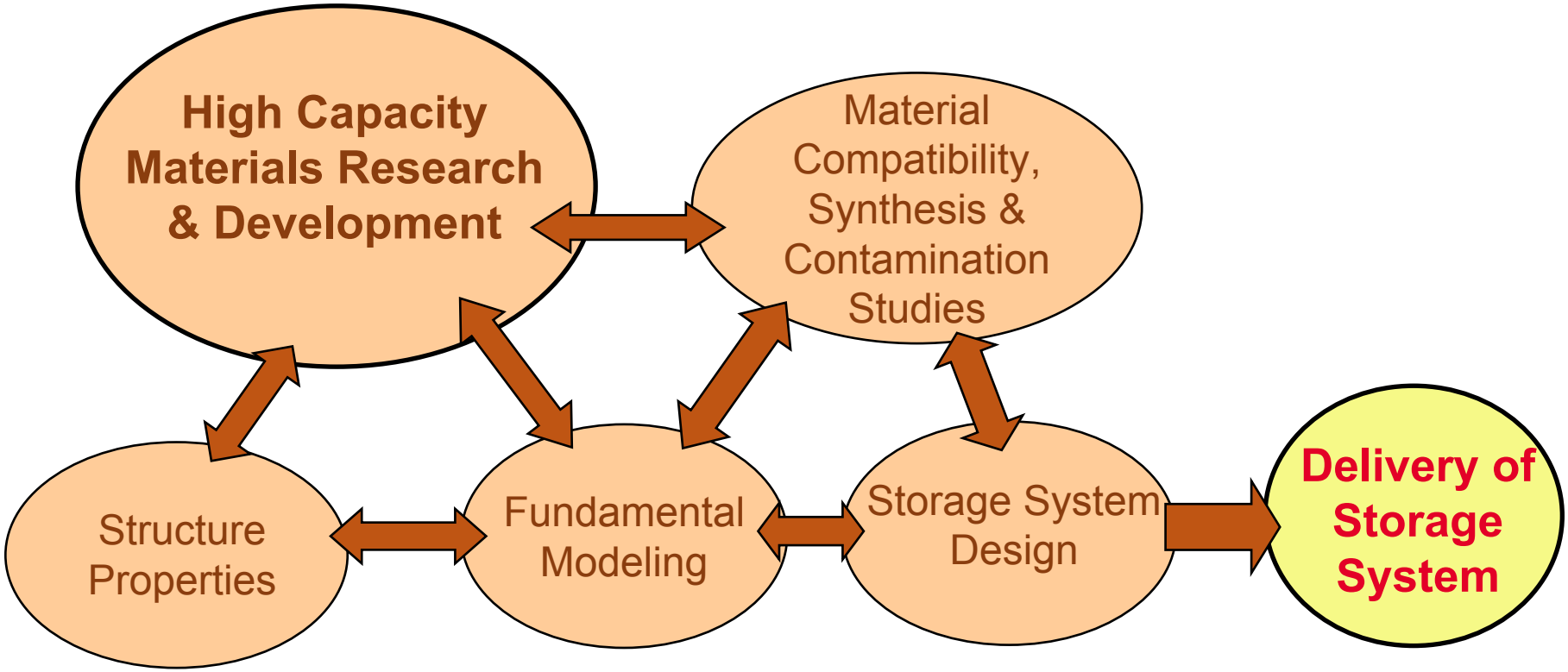
## Sandia Team (~ 6 FTEs)

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 : $\equiv N$, $Li_3N$**

**1st Step:**

$$LiNH_2 + LiH \underset{1\ atm}{\overset{300^oC}{\rightleftharpoons}} Li_2NH + H_2$$

**6.5 wt%**

**2nd step:**

$$Li_2NH + LiH \underset{0.05\ atm}{\overset{300^oC}{\rightleftharpoons}} Li_3N + H_2$$

**5 wt%**

**Two steps in total:**

**11.5 wt%**

**Major limitations**:

- Temperature too high
- Pressure too low

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

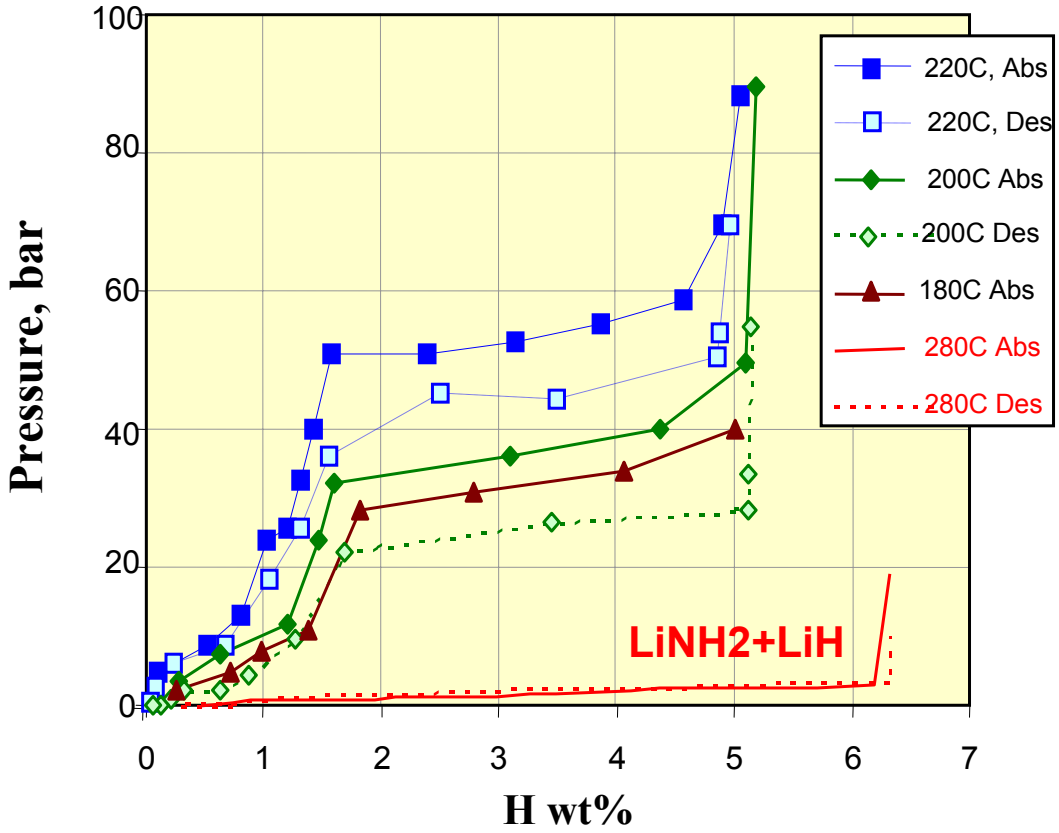
New system:

Partial Mg substitution

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

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

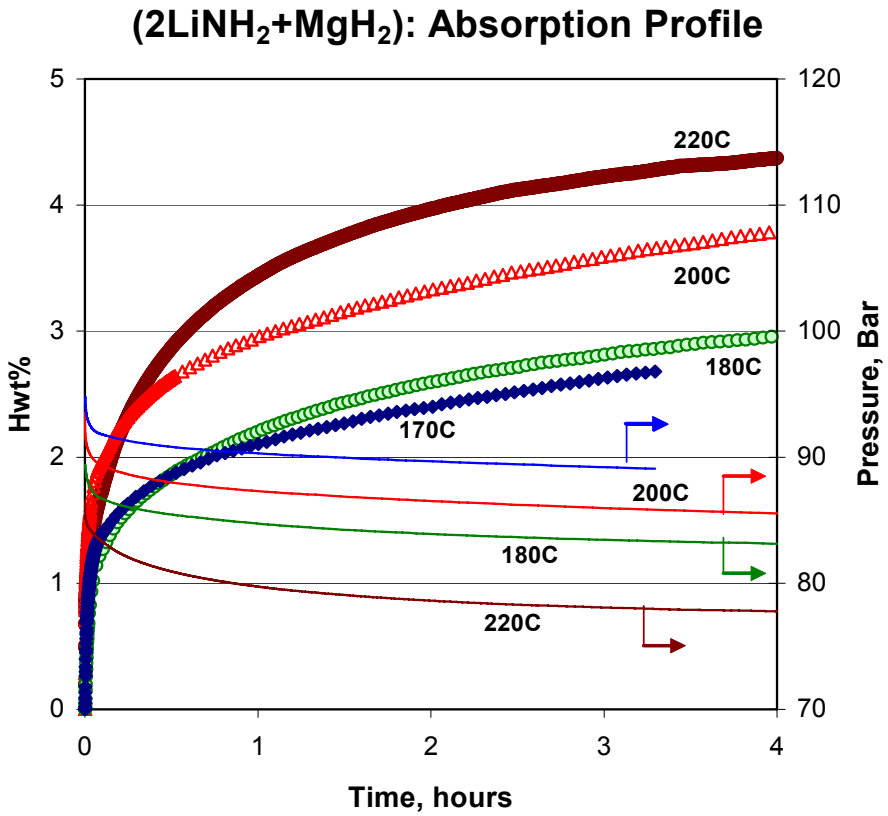
# (A1)Thermodynamic characterization - Luo

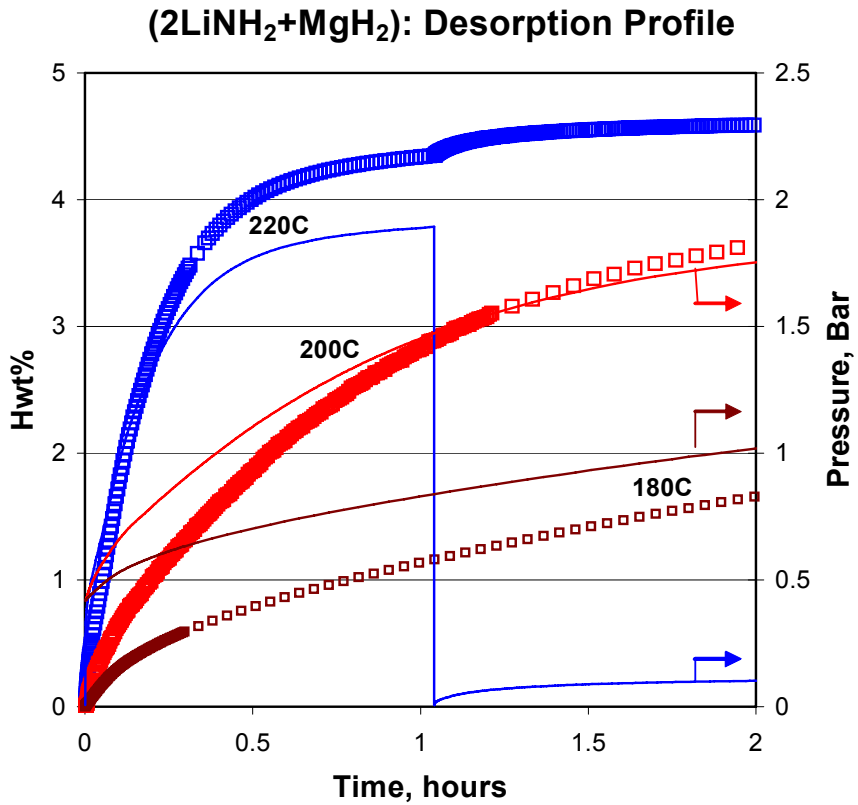



Isotherms were measured at:

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

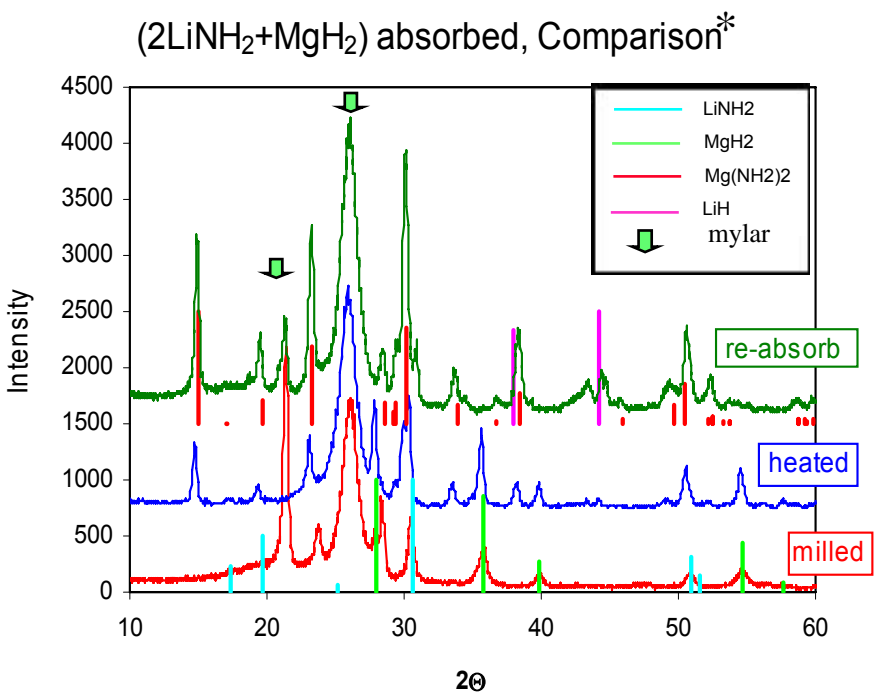
# (A2) Sorption profile - Luo

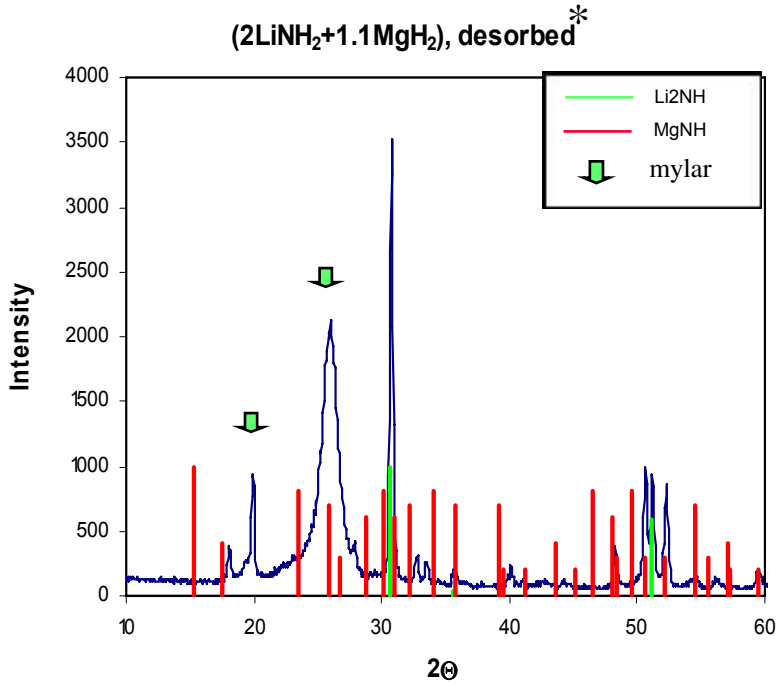



- *85% of desorption completed in 0.5h at 220°C*
- *Sorption rate decreases with decreasing temperature*

# (A3) XRD characterization - Luo & Majzoub



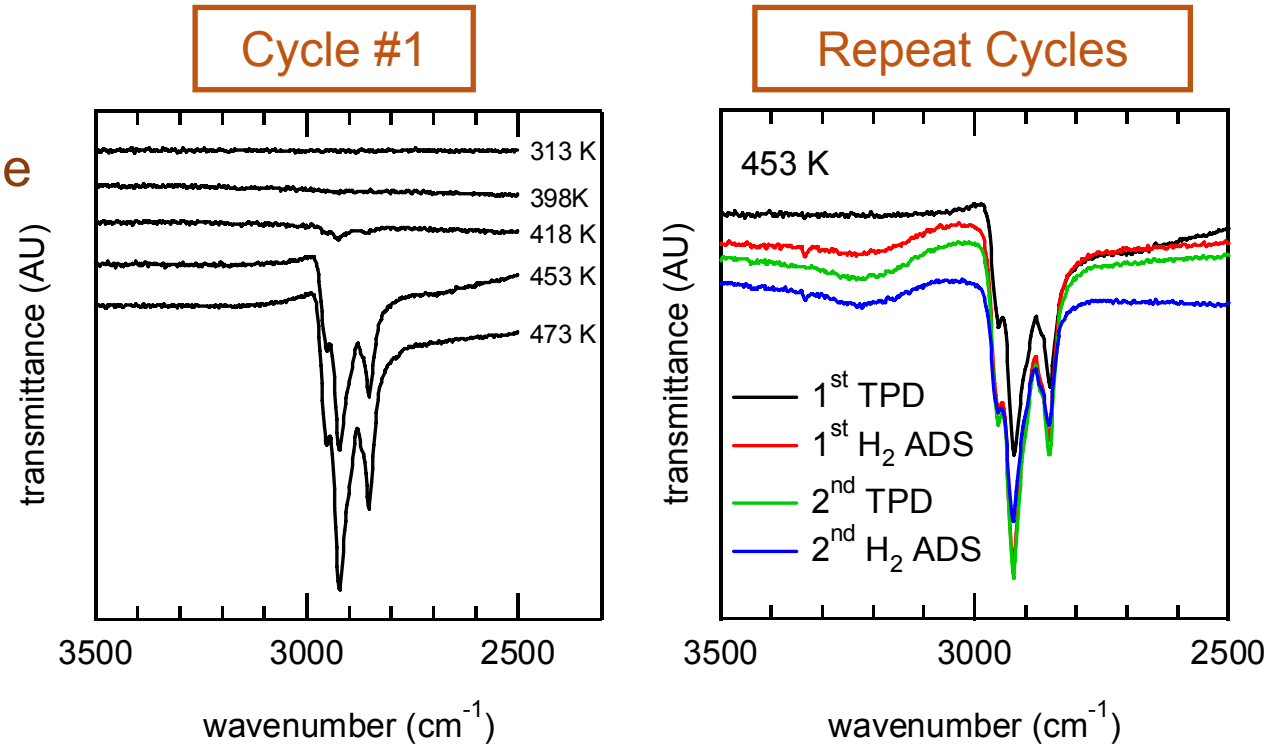

* Mylar was used to protect sample from being contaminated during XRD scanning

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

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

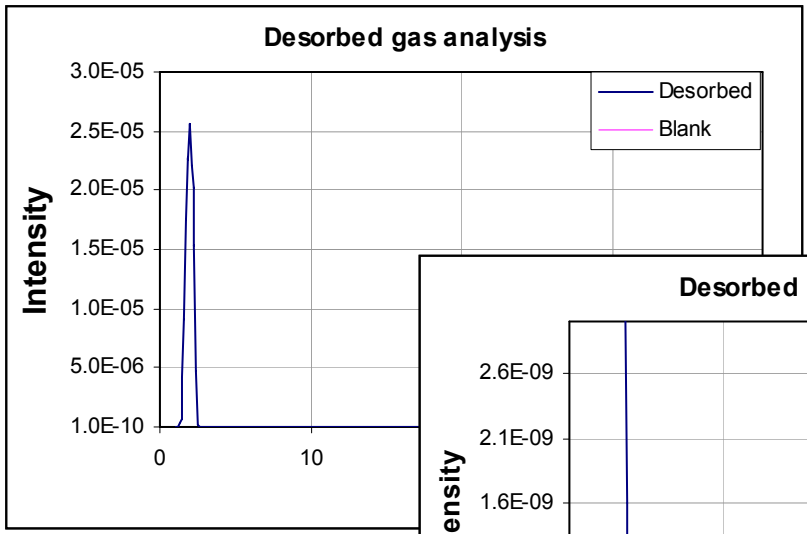
# (A4) Diffuse Reflectance Infrared Spectroscopy Measurements– McDaniel & Chae

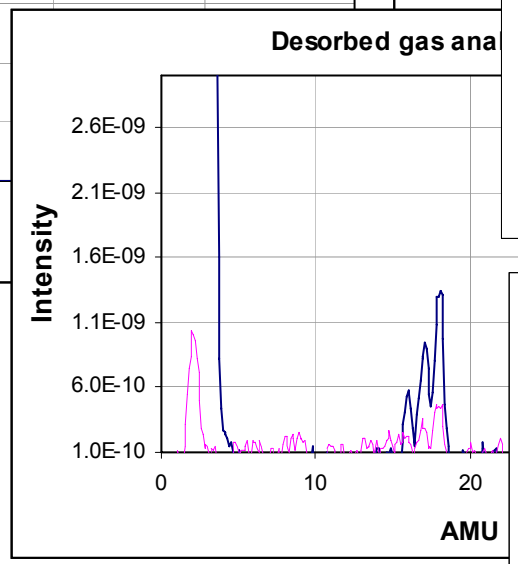
- First desorption cycle material "as milled"
- Second desorption cycle followed $H_2$ adsorption
  - 8 MPa
  - 473 K
  - 120 minutes
- $H_2$ desorption
  - 130 KPa
  - 5 K $min^{-1}$ ramp

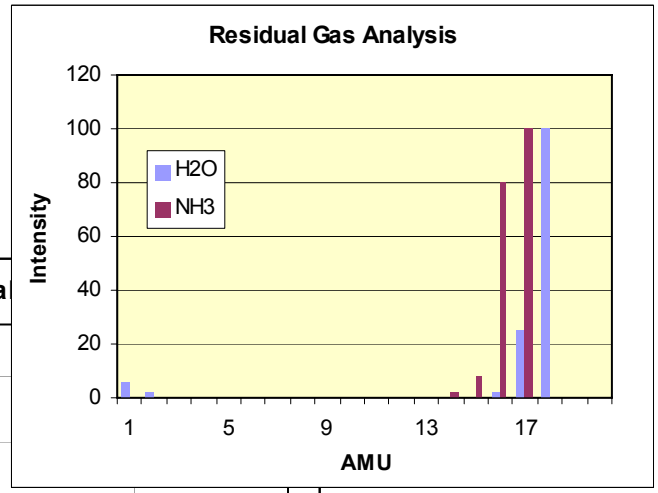


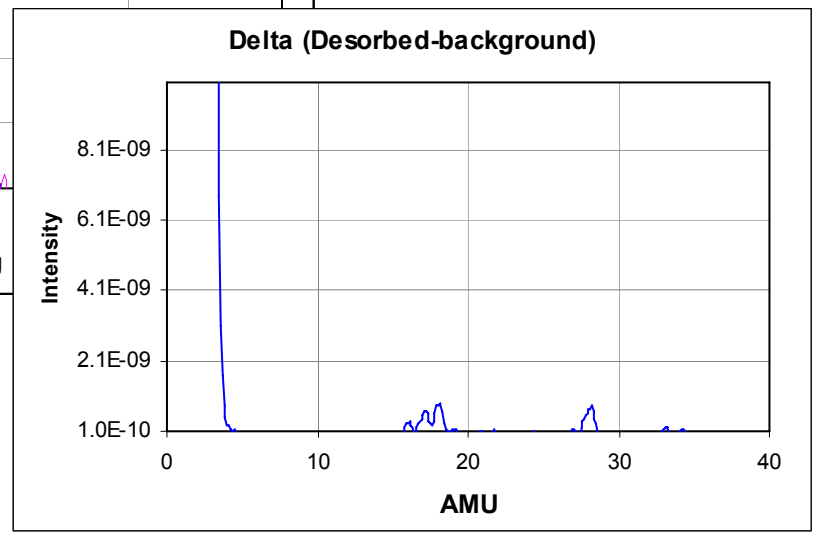

***N-H vibrational features appeared upon first heating of freshly milled sample. Structural changes in material stabilized on subsequent ads-des cycles.***

# (A5) Desorbed gas analysis– Luo



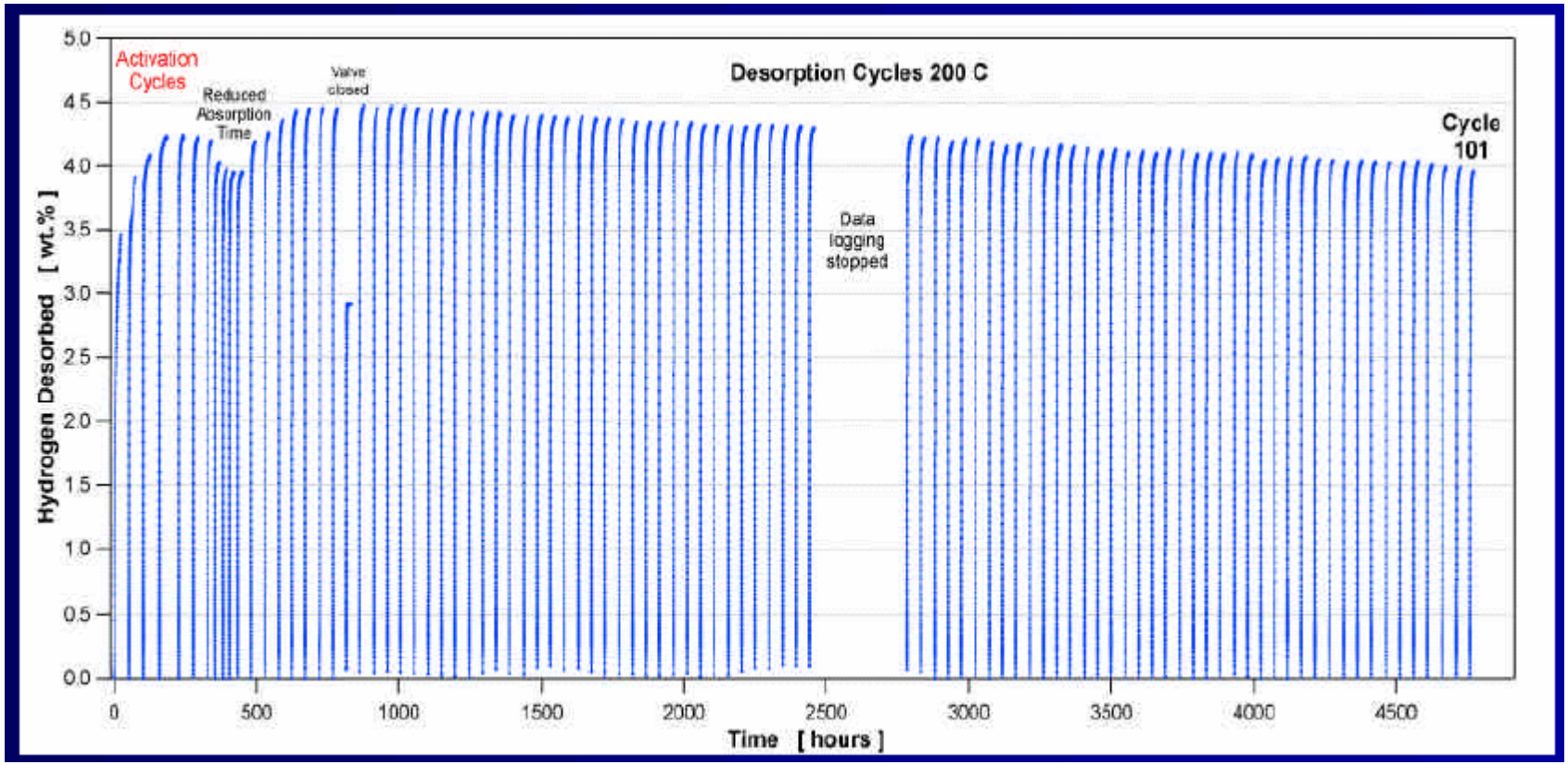

***$NH_3$ in desorbed gas was found to be < 40 ppm***

# (A6) 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***

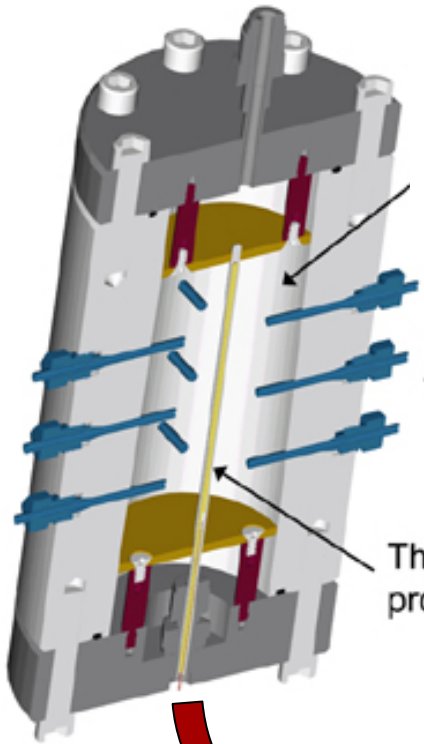
# (A7) Cycle test to 101 cycles - Gross

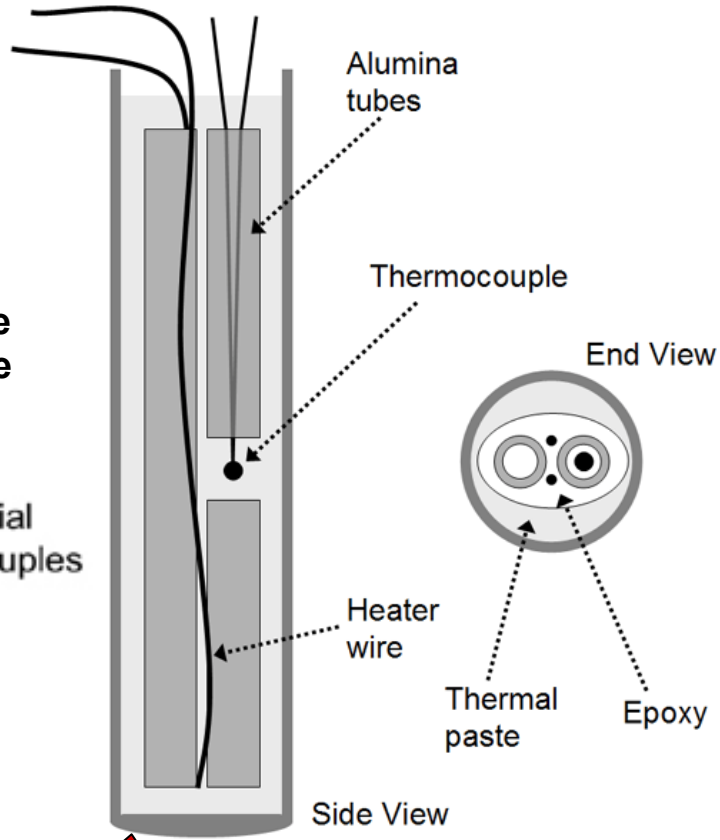



**Capacity loss: 0.005wt% per cycle**

# (A8) Thermal Properties Measurements
## Hardware configuration – Crooker & Dedrick

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



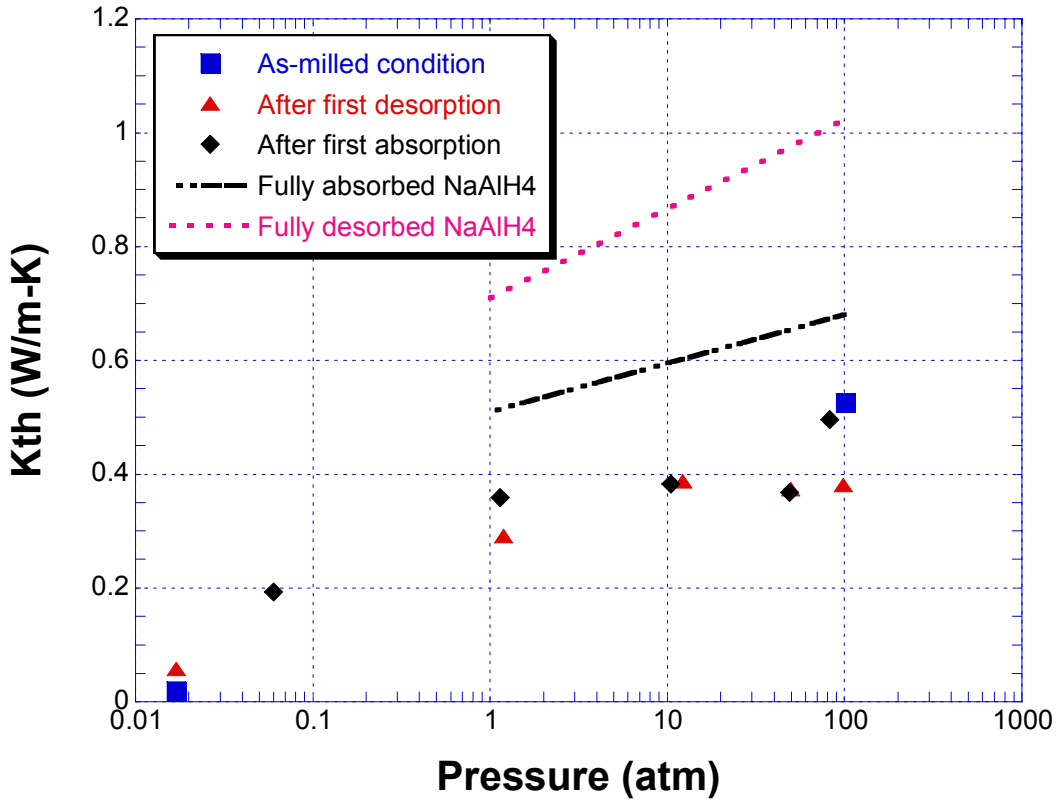




**Optimized to measure $K_{th}$ up to ~5 W/m-K**

Solid model → Probe design

# (A9) Preliminary $K^{th}$ results – Crooker

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



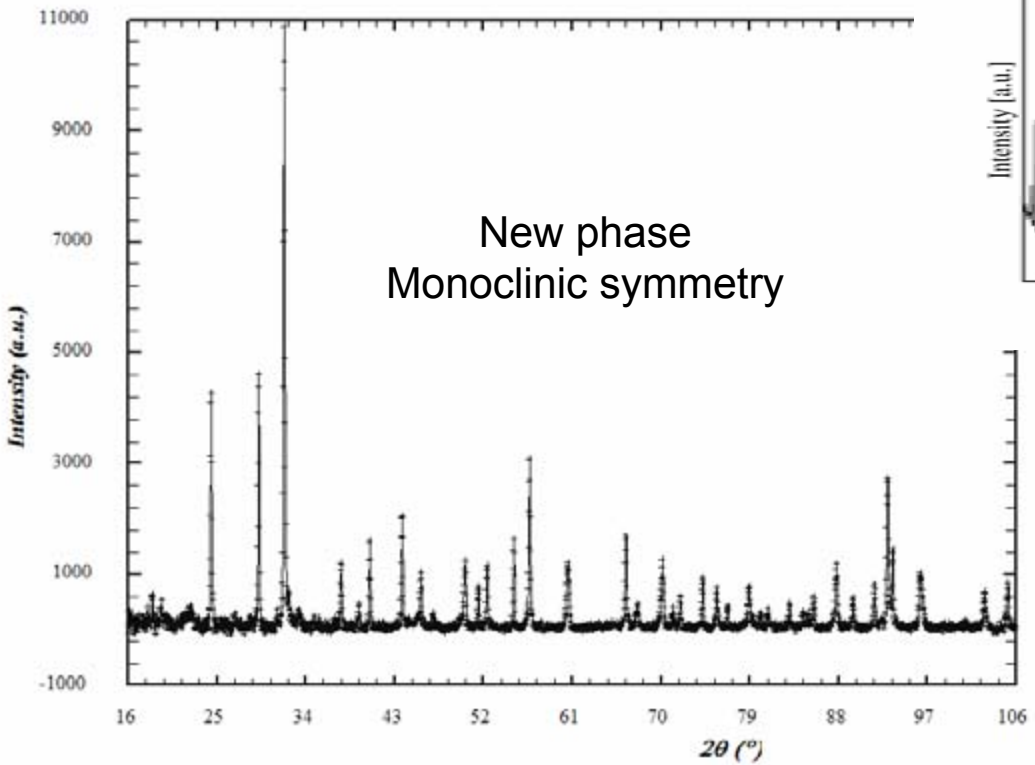

***Thermal conductivity of $LiNH_2$+$MgH_2$ material increases with gas pressure and similar to those of sodium alanates.***

# 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 LiAlH4 + 2KH or LiH + 2KH + Al*
    - *Pellets expanded and showed in white color*
- Investigation of Li(Al1-xBx)H4, Na(Al1-xBx)H4, etc…systems are in progress

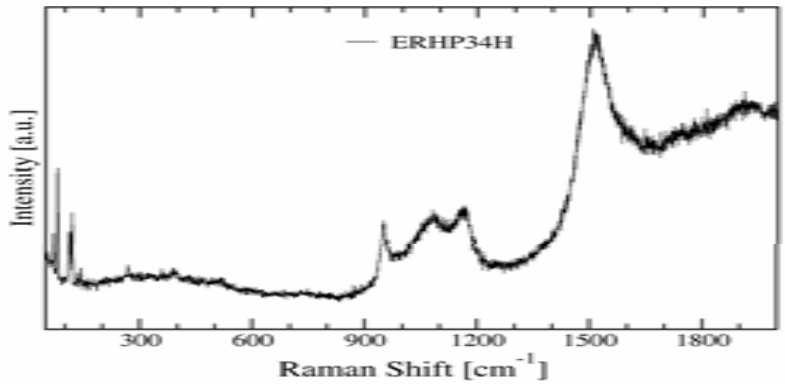
# Properties of new Li-K alanates - Ronnebro

Powder X-ray diffraction pattern

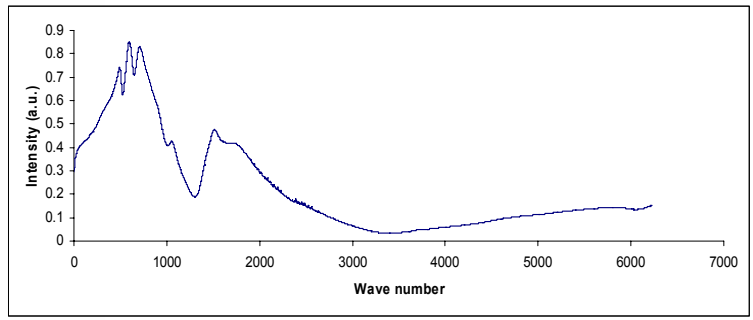



New phase
Monoclinic symmetry

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)

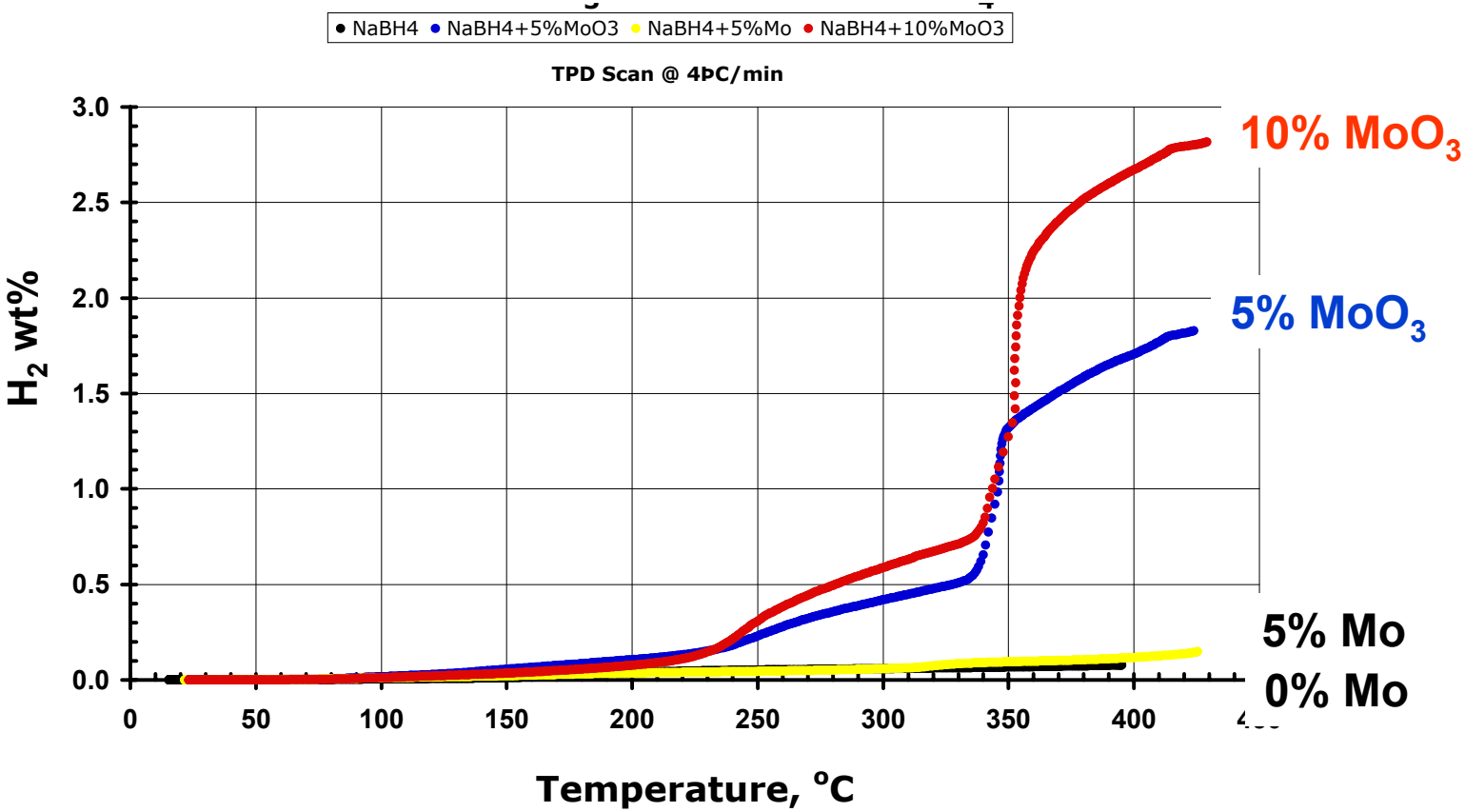
$NaBH_4 \Leftrightarrow NaH + B + 3/2\ H_2$ (8.0 wt. % H)

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

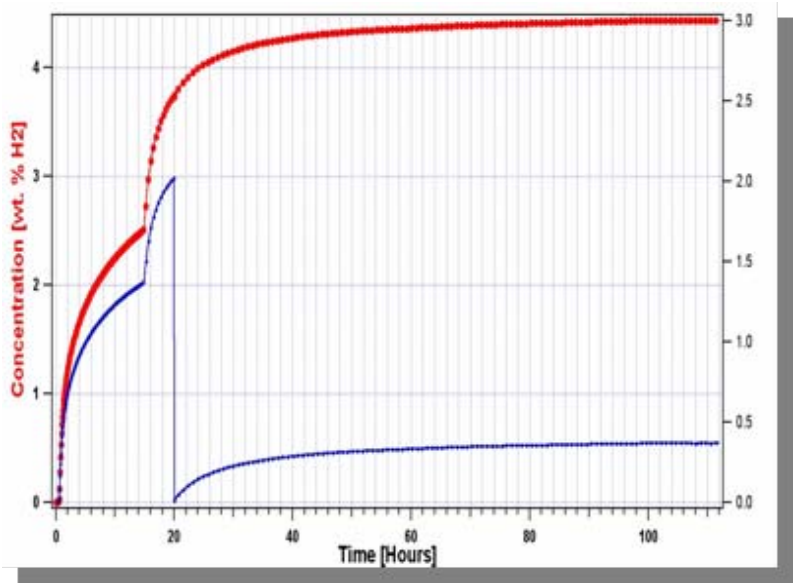


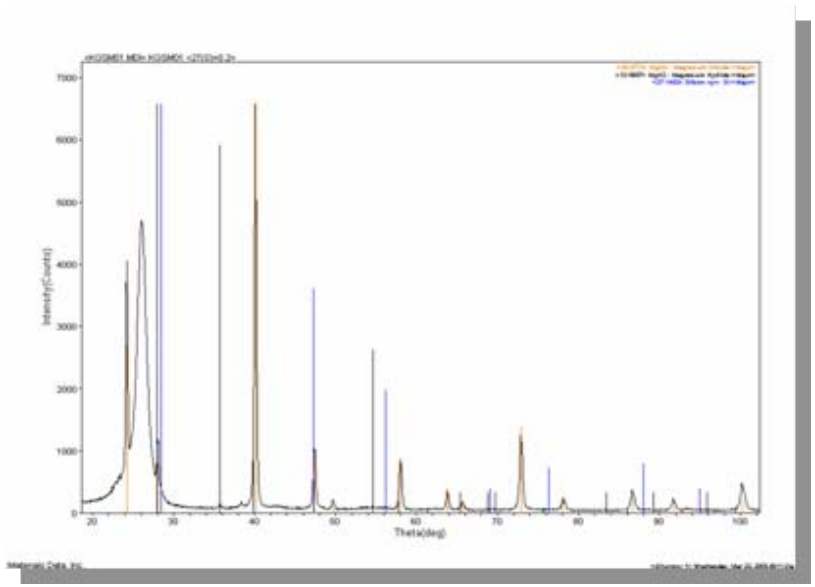

***Mo is not the best addition for $NaBH_4$ reversibility because the Mo-borides are too stable.***

# 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)*

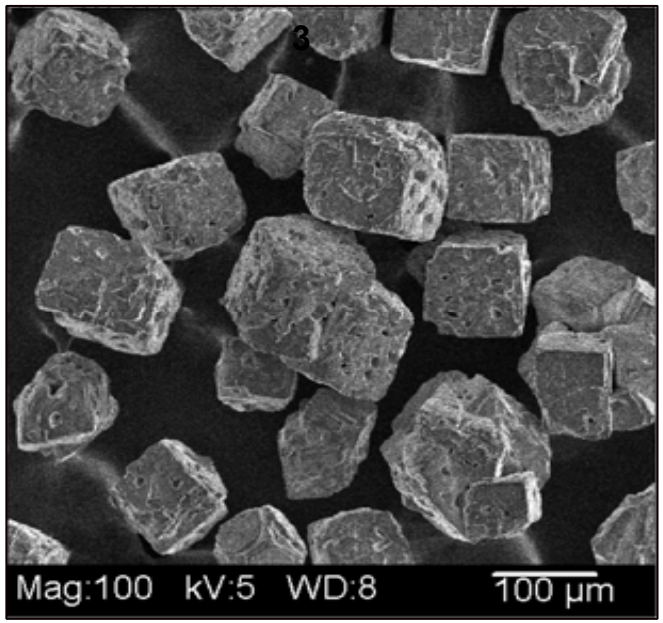
$$\alpha\text{-}AlH_3 \longrightarrow Al + 3/2\ H_2$$

**H-capacity (g) = 10.1 wt%**

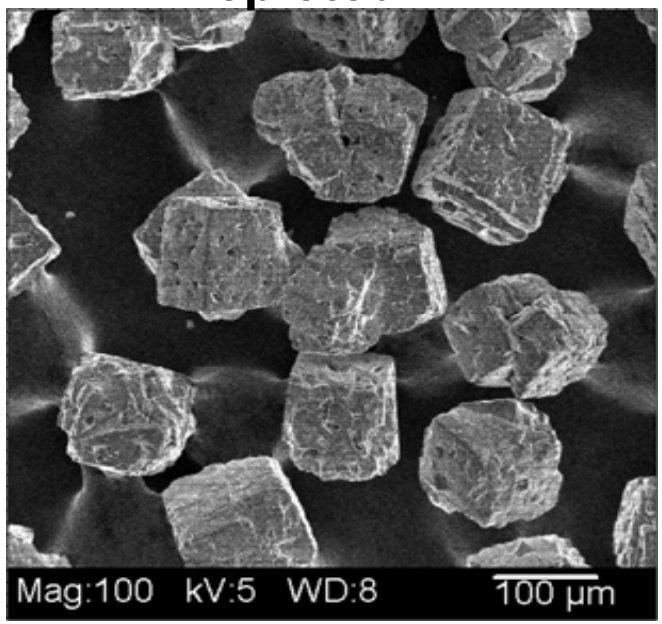
**H-capacity (v) = 149 kg/m$^3$**

**$\Delta H_{des}$ = 7.6 kJ/mol $H_2$**

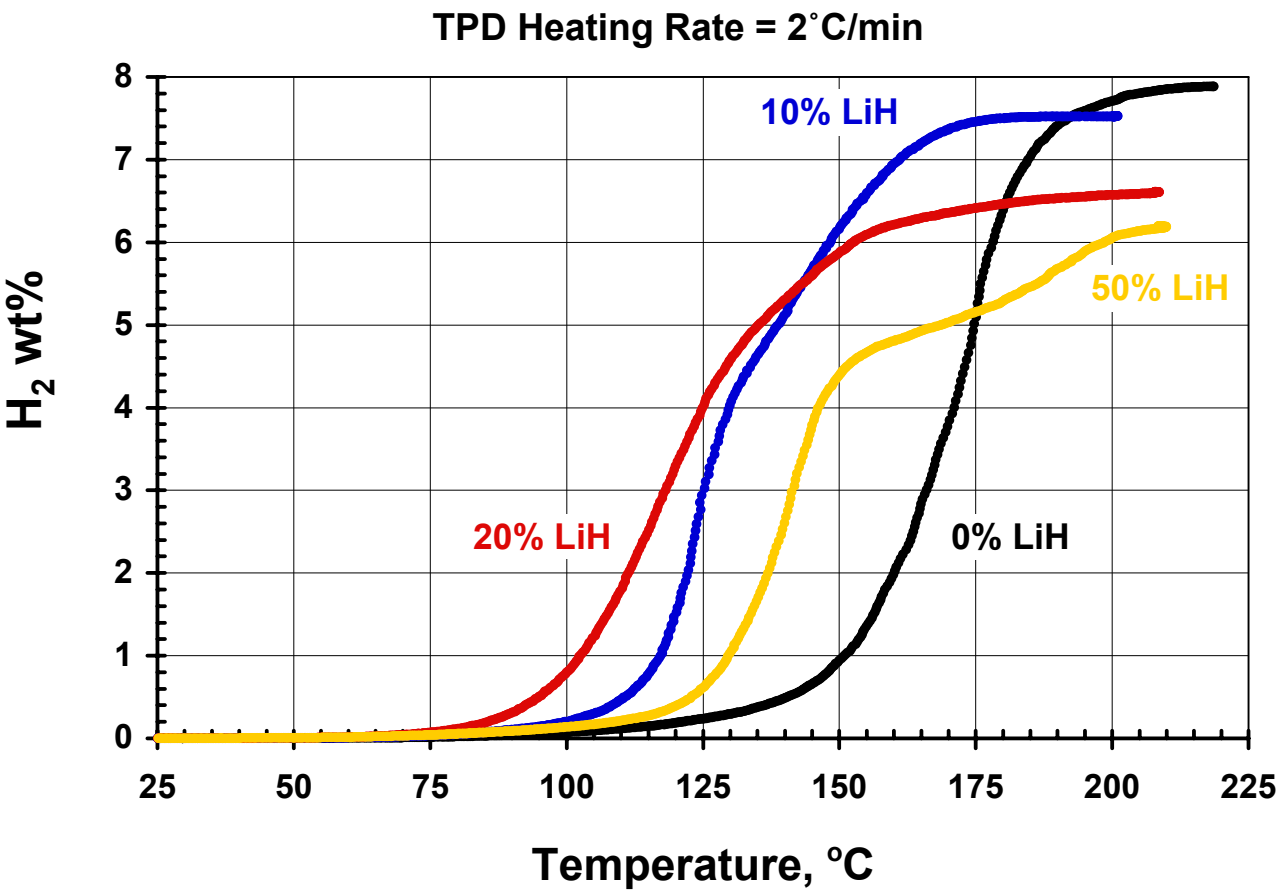
**AlH$_3$**




**Depleted Al**



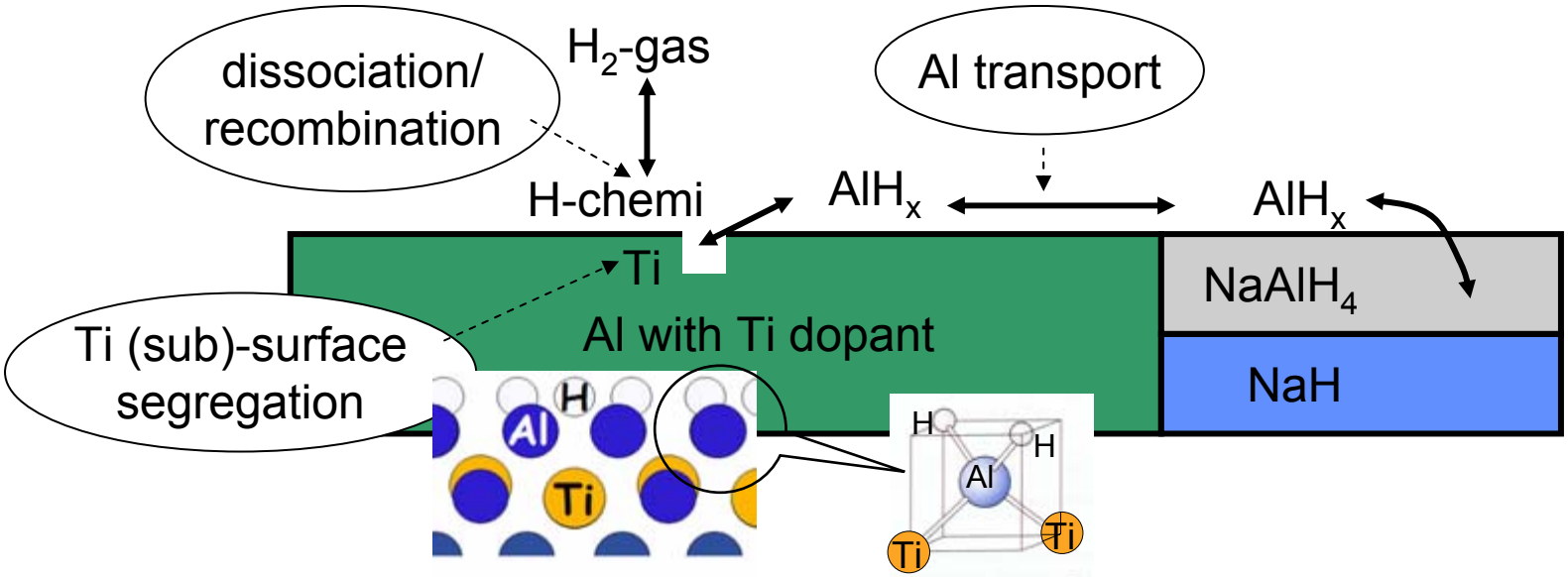
# Effect of LiH doping via TPD – Sandrock




**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

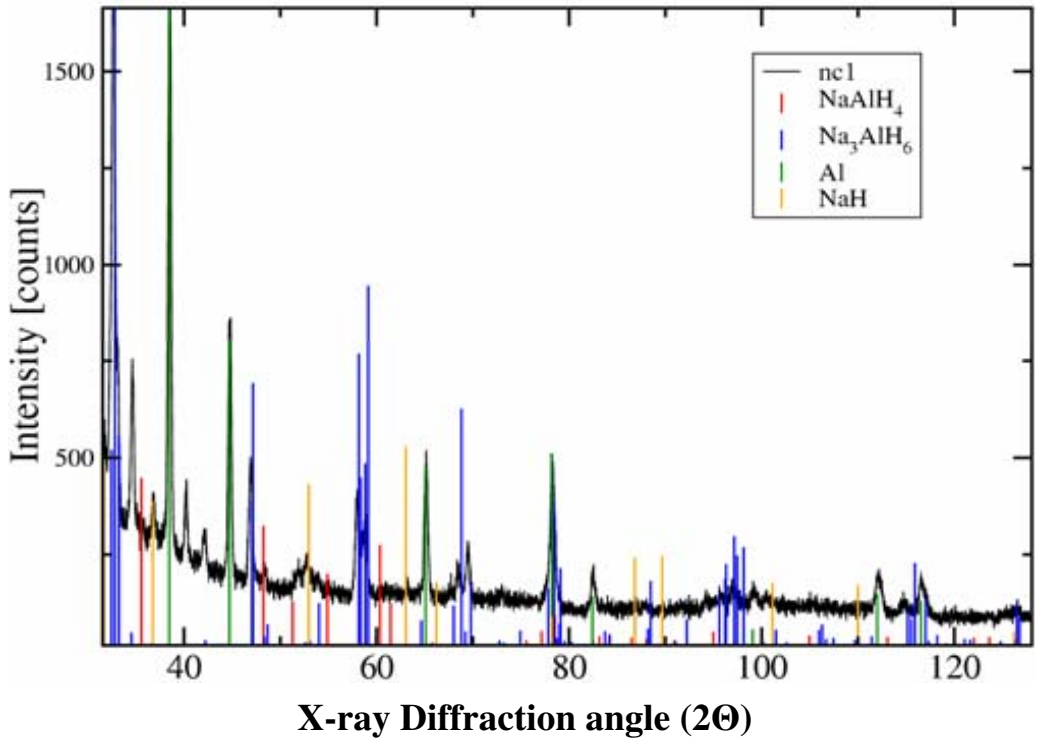
***Surface alloys of simple and transition metals are promising new catalysts for H chemistry***

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

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

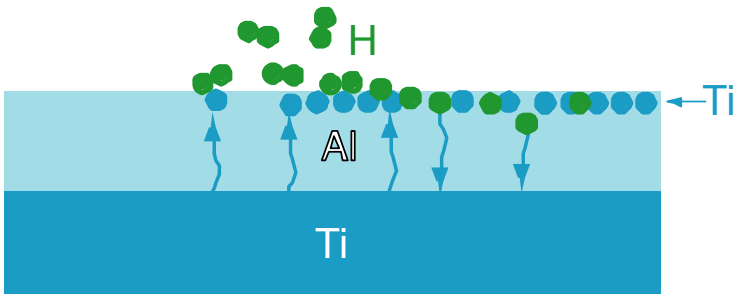
**Idea: use Pd surface to crack $H_2$**

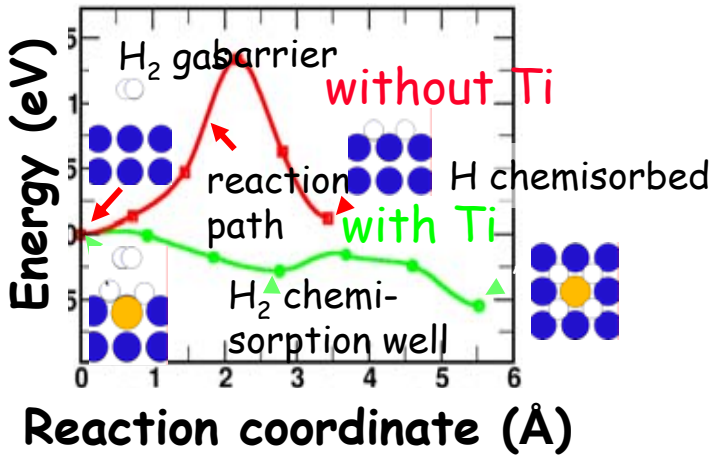
- *X-ray diffraction after 10 day exposure of Al+NaH to $H_2$ in contact with Pd foil shows 10% of Al+NaH converts to $Na_3AlH_6$ and $NaAlH_4$*
- *Control experiment without Pd shows < 1% alanate formation*




***$H_2$ cracking ability of Pd helps hydride formation***

# (3A) Where is Ti ? - Bastasz



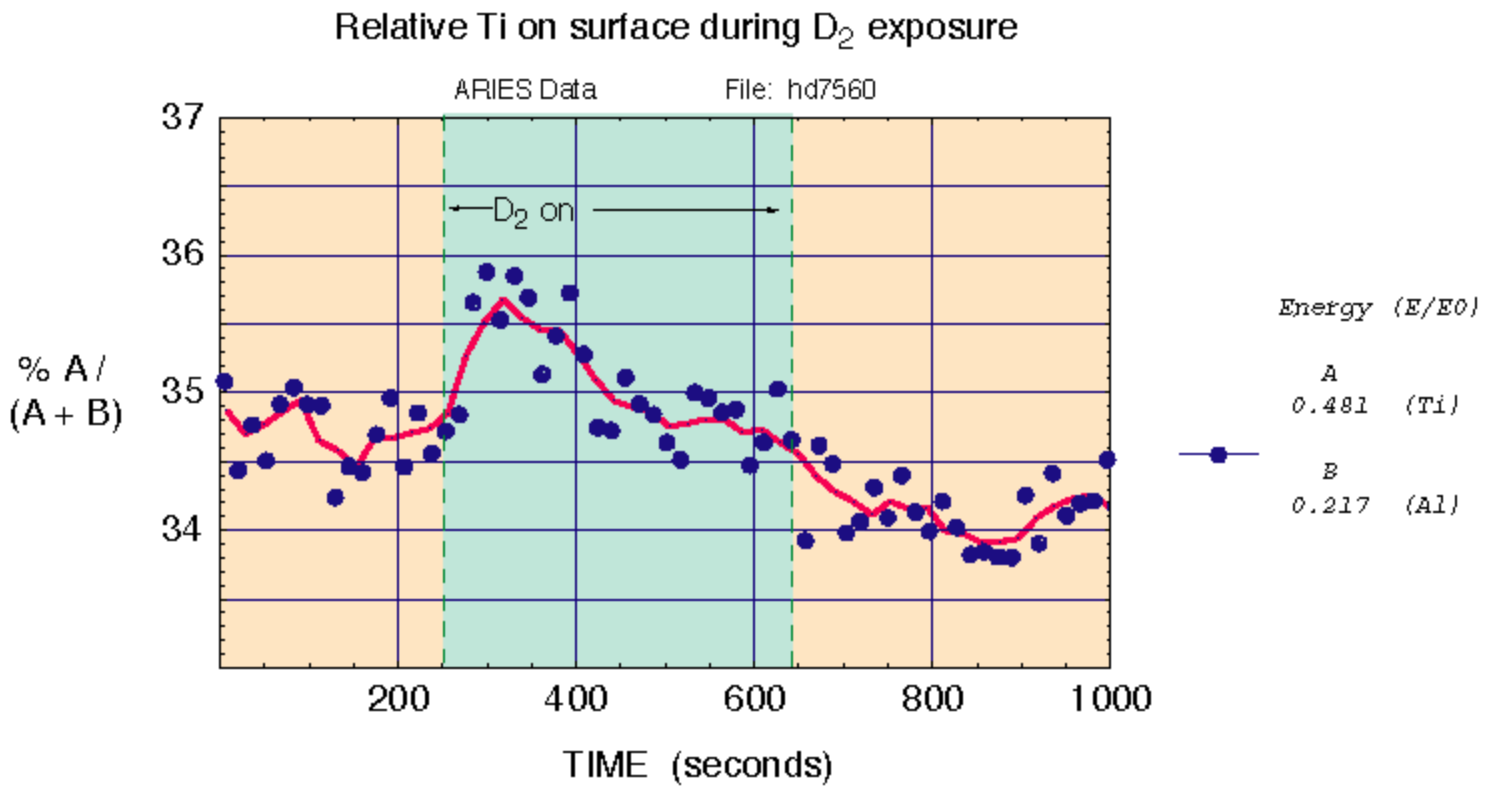




**H may stabilize Ti on Al surfaces – Predictions:**

- *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 $H_2$.*

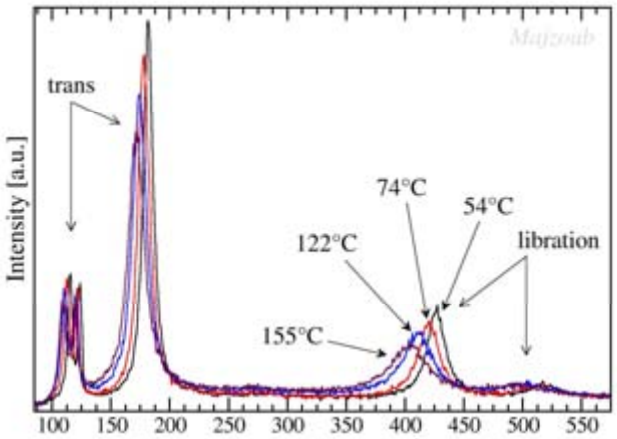
***Is there experimental evidence for this?***

# (3B) Model validation - Bastasz

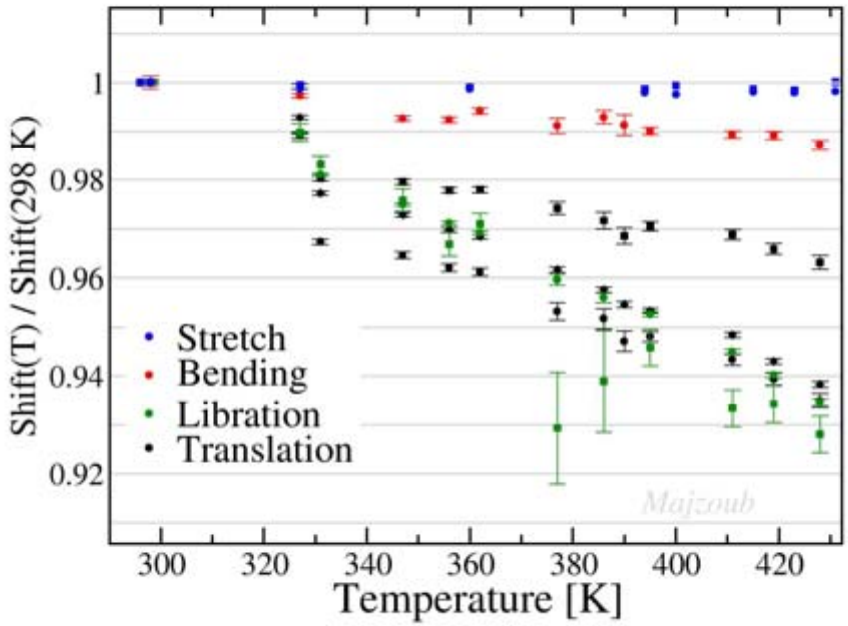



***Ti/(Ti+Al) signal ratio changes indicating that Ti concentration on the surface appears to increase upon exposing sample to $D_2$.***

# (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*

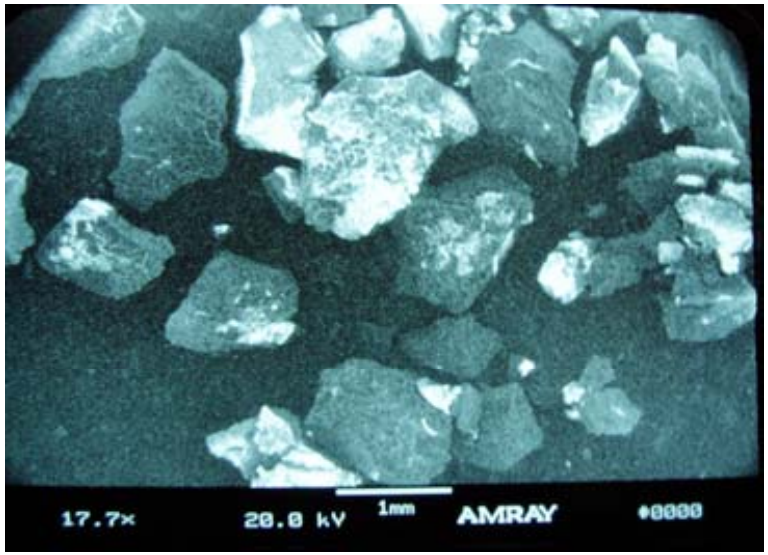



Fig. 1

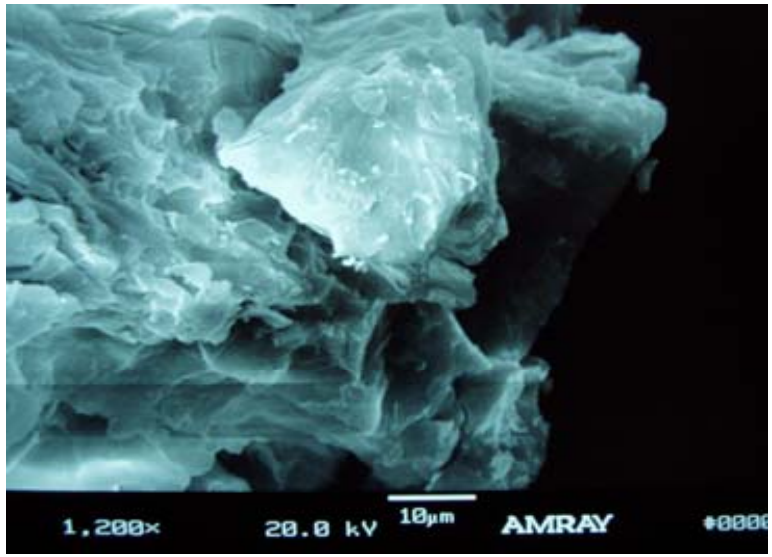



Fig. 2

**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*
- 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.*