

*DOE 2006 Hydrogen Program Annual Review, Washington D.C.
Crystal Gateway Marriot, Arlington, VA - May 16-19, 2006*

Effect of Trace Elements on Long-Term Cycling and Aging Properties of Complex Hydrides for Hydrogen Storage

Dhanesh Chandra

**Metallurgical and materials Engineering, MS 388
University of Nevada, Reno (UNR)
Reno NV 89557**

Date: 04-20-06

This presentation does not contain any proprietary or confidential information

Overview

Timeline

Project start date – FY05
Project end date – FY10
Percent complete – ~20%

Budget

Total project funding (5yrs.) : \$ 1.5 M
(Requested)
DOE share (5yrs.) : \$ 1.2 M
Contractor share (5yrs.) : \$ 301 K
Funding received in FY05 : \$ 75K
Funding received in FY06 : \$ 200 K

Barriers Addressed

- Long-term reliability of complex hydrides developed by MHCoe partners (when charged with hydrogen with gaseous impurities)- First studies on Li_3N
- Hydrogen sorption mechanisms in non catalyzed and catalyzed Li-based complex hydrides
- Ca and Mg borohydrides – in-situ structural studies

Partners

Current Collaborations

- Sandia National Laboratories, CA
- IPNS, Argonne National Laboratory, Chicago, IL
- Florida Solar Energy Center, Cocoa Beach, FL

Future Collaborations

- *Jet Propulsion Laboratory (Caltech), Pasadena, CA*
- *NIST, Gaithersburg, Maryland*
- *Brookhaven National Laboratories, NY*
- *Univ. of Utah, Salt Lake City, UT*
- *University of Rome, Rome, Italy*
- *University of Hawaii*

Objectives

Overall Objective

- The primary objective of the UNR Project is to determine the effects of gaseous impurities (ppm levels of O₂, CO, H₂O etc.) in the H₂ upon long-term hydriding/dehydriding of complex hydrides and a related secondary objective is to determine the mechanisms of degradation.
- The relevance to the DOE MHCoe program is that, in practical applications, trace impurities in hydrogen gas will have an impact on the hydrogen loading capacities during periodic recharging with fresh hydrogen. Prolonged charge/discharge of hydrides in actual use may be performed by accelerated laboratory tests which are extremely useful to understand the reliable use of hydrogen fuel. These approaches are being used for Complex hydrides and may be extended to other hydrides.

2005

- MHCoe Program had just started in 2005 and we had just started the research. When we started the program Li₃N showed promise, so we initiated our studies on this material which is a precursor to study other promising complex hydrides.

2006 (Oct.2005- Sept.2006)

- **Thermodynamic Studies:**
 - Extrinsic Hydrogen Charging/Discharging effects:** Perform experiments on pressure cycling of Li₃N to study impurity effects using industrial grade hydrogen (similar to that available of a hydrogen dispensing gas station) by constructing pressure cycling apparatus.
 - Vaporization Thermodynamics of Precursor Materials:** To show if there is undesirable gas phases evolving during evacuation. (Disproportionation and other effects).
 - Differential Scanning Calorimetry** for in-situ hydriding testing
- **Crystal Structure Studies:**
Neutron and X-ray Diffraction Mechanistic Studies on Complex Hydrides such as Li₃N (in-situ neutron studies and ex-situ studies), and use the experience to conduct near term research on Mg-Li-N-H, Ca or Mg borohydrides hydrides.

Plan and Approach

Cycling Studies and their Approach

Determination of Temperature and Pressure Range to Perform long-term pressure cycling (~1000 cycles) on Li amide/imide hydrides to evaluate degradation of hydrogen charging/discharging properties.

1. Main Impurities to be Tested

The impurities planned to be tested are as follows: (1) Industrial grade hydrogen (2) O₂ (3) CO (4) H₂O. We will use 100 ppm impurity in UHP Hydrogen gases (in consultation with Codes and Standards group at NREL).

2. Testing Methods Developed (UNR)

Extrinsic non equilibrium accelerated testing apparatus developed for Hydrogen loading and unloading

3. Number of Hydriding Cycles

We subjected Li amide/imides for ~1100 charge/discharge cycles with fresh of charges of hydrogen, every cycle using industrial grade hydrogen with O₂, CO, H₂O, and other impurities.

4. Approach to Check Impurity effects Thermodynamically

Subject hydrides to non-equilibrium pressure cycles using UHP hydrogen with known amount of impurity, Use Sievert's apparatus to obtain equilibrium isotherms (before and after cycling))

Hydrogen Pressure : ~2 atm. (for the initial experiments) and then Evacuate.

Time for Charging and Discharge: 0.5 hours each; Temperature: 255°C. Then performed X-ray diffraction, ex-situ in this case, and obtain structural information such as formation of new phases.

5. Vapor Pressure Measurements

Use Gravimetric Torsion Effusion apparatus and obtain total and partial pressure of vapors evolving during heating of materials. Thermodynamics of vaporization may be obtained. Information such as evolution of other gases besides hydrogen during dehydriding process.

6. In-situ Monitoring - Mechanistic Crystallographic Studies

Information obtained: Phase changes as a function of Temperature at a constant pressure to obtain dynamic formation of phases being formed in Complex hydrides by neutron diffraction methods.

Executive Summary of Technical Accomplishments

➤ Results from Impurity Cycling of Li_3N Complex Hydrides

Loss of Capacity: 1101 impurity pressure cycles performed on $\text{Li}_3\text{N}/\text{LiNH}_2/\text{Li}_2\text{NH}$ with industrial grade impure Hydrogen gas at 255°C showed ~2.3 wt.% decrease in Hydrogen capacity – X-ray diffraction Characterization, which is in progress, show formation of Li_2O (~30%) besides other expected phases.

➤ Results from Neutron and Synchrotron Studies:

1. Study of Three Commercial Li_3N Precursor Compounds (Room Temperature Study)

Quantitative Phase Determination Mass Fraction of Residual High Pressure β phase in α phase in (as received Li_3N): **Neutrons: ~49 wt % β phase and Synchrotron X-rays: ~45 wt % β phase**

$\beta \rightarrow \alpha$ Phase Transition Starts @ ~473K and ends at ~690K.. Metastable β to α transformation was not reversible on cooling. A manuscript is in review with *Journal of alloys and Compounds based on these results.*

2. In-situ Neutron Diffraction Research with Pure α - Li_3N

2a. Deuteriding: Simultaneous formation LiND_2 , LiD and Li_2ND at 200°C . Quantitative analyses aid in the thermodynamic evaluation of coefficients in equations.

2b. De-deuteriding:

A. Li_2ND concentration increases and LiND_2 decreases at 250°C

B. Li_2ND and LiND_2 concentration increases are associated with LiD concentration decreases at 320°C

Please Note: Dr. Chen (Singapore) showed complete desorption of $\text{Li}_2\text{N}/\text{LiH}$ at ~430°C.; *Nature, vol.420,Nov.2002,303.*

C. In-situ Neutron Diffraction Research with $\alpha+\beta$ Li_3N (starting Material). Deuteriding at 200°C showed similar results.

➤ Vapor Pressure Studies (Torsion Effusion Knudsen Cell method)

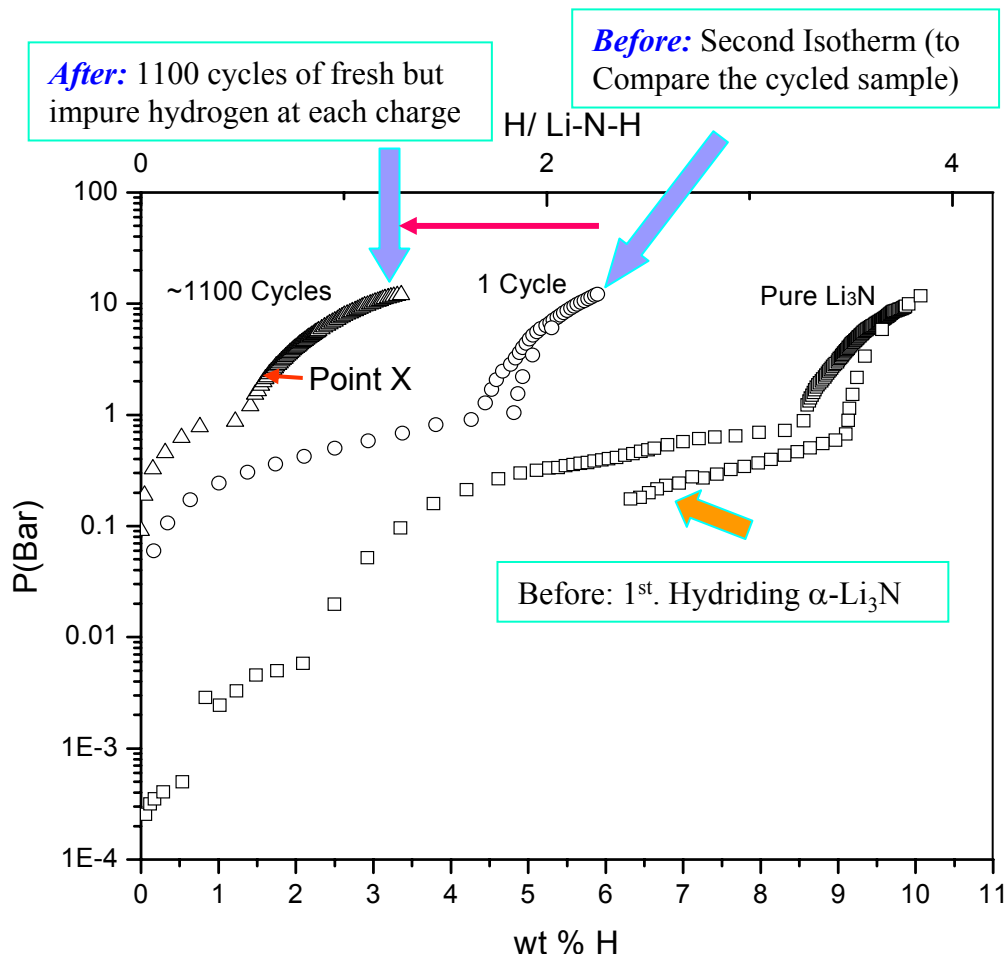
Release of Li or Li_3N and other Vapors in the system that are detrimental to plumbing of the engineered system in long term use of Fuel Cell and other components; such as reactivity of Li with fuel cell's catalyst Pt interfaces. We found release of Li gas along with Li_3N gas during heating due to disproportionation of the precursor Li_3N . Based on these we plan to perform new studies with GE on Mg borohydrides.

➤ In-situ DSC Hydriding of Complex Hydrides

Preliminary Results (in collaboration with Florida Solar Research Center, show endothermic/exothermic reaction as function of temperature that correlation of these results wit the x-ray/neutron diffraction results are in progress.

Thermodynamic Results - Effect of Impurities Upon Pressure Cycling

The Changes in Hydrogen capacity Due to pressure cycling of Li_3N at 255°C at ~ 2 atm. using Industrial grade Hydrogen – Equilibrium Isotherms are shown obtained using UNR's Sievert's Apparatus



After: 1100 cycles of fresh but impure hydrogen at each charge

Before: Second Isotherm (to Compare the cycled sample)

Before: 1st. Hydriding $\alpha\text{-Li}_3\text{N}$

Description:

- Equilibrium Isotherm before cycling (very 1st. Cycle on Pure Li_3N (right).
- Second cycle isotherm amide/imide (actually consider this as the 1st. Cycle for comparison)
- Isotherm after 1101 cycles with charges of industrial hydrogen (represented as ~ 1100 cycles).

Results:

Thermodynamics: After 1100 Pressure cycles at 255°C at $p = \sim 2$ atm. we lost hydrogen capacity of ~ 2.3 wt.%.

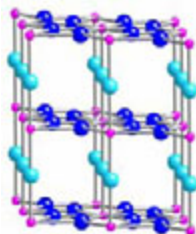
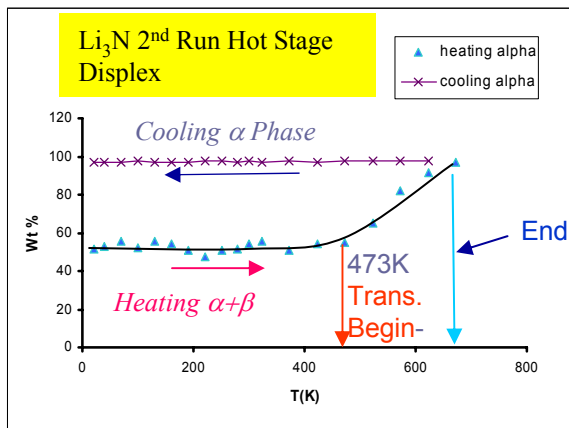
Reason for Loss of Capacity: Preliminary XRD semi quantitative Rietveld analyses of this sample at "Point X" after cycling show LiH ($\sim 15.2\%$), Li_2O (30.5%), Li_2NH ($\sim 54.3\%$)

Importance: Formation of Li_2O is detrimental to amide/ imide systems. Detailed studies on O_2 impurity important for $\text{MgH}_2\text{-Li}_2\text{NH}$ system for future studies. (LiH formation discussed later)

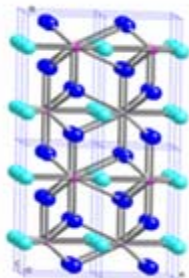
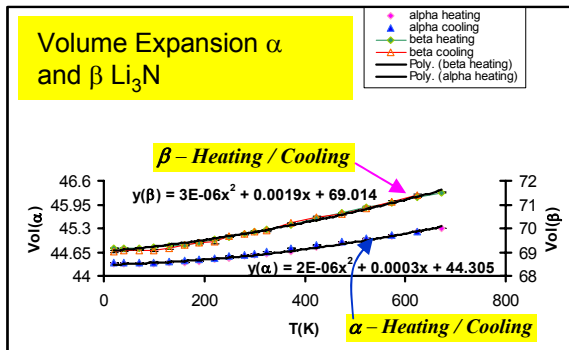
Nominal Gas Analyses From Supplier of Industrial Hydrogen gas: Hydrogen min % (v/v) 99%, Water ~ 32 ppm, O_2 ~ 10 ppm, N_2 ~ 400 ppm, Total Hydrocarbons: 10 ppm, CO_2 ~ 10 ppm, CO ~ 10 ppm, Argon ? may be present, reads as oxygen. The residual gas from the cylinder will be post analyzed.



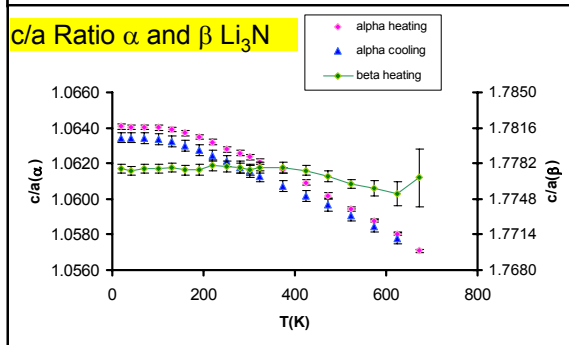
Crystal Structure Mechanistic Studies of Precursor - Neutron Diffraction Data



α Li₃N
Phase
Hexagonal
– P6/mmm
(191)



β Li₃N
Phase
Hexagonal
– P6₃/mmc
(194)



Explanation of the Figures (left)

1. The Commercial Li₃N has α and β phases present.
2. To remove the β phase we heated the sample from 10 K to ~ 660 K, in-situ (without hydrogen) while collecting neutron diffraction data. (Plot on top)
3. Volume expansion and c/a ratio were measured as a function of temperature (bottom plots)

Results:

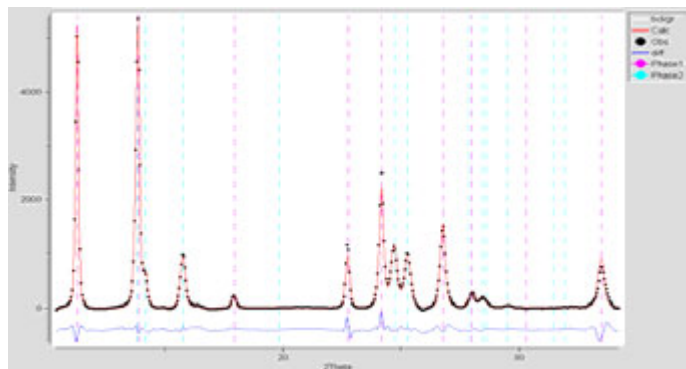
- Commercial Li₃N contains a and b phases
- The Conversion of β → α Li₃N starts at 473 K and is almost complete at ~ 677K (~2% or so β phase remains)
- Further details can be found in a forthcoming publication

Importance:

These results will help in assessing the expansion and contraction in pure materials as a function of temperature for baseline studies on amide/imide precursor.

Precursor Material-Li₃N Quantitative Synchrotron X-ray Diffraction Results

X-Ray (Synchrotron LBNL) Sample Li₃N From Supplier S



β phase:

Space group: P6₃/mmc

a = 3.552(1) Å, c = 6.311(3) Å

N 1/3 2/3 1/4

Li(1) 0 0 1/4

Li(2) 1/3 2/3 0.583

H. J. Beister, S. Haag, R. Kniep, K. Strossner, and K. Syassen, *Angew. Chem. Int. Ed. Engl.*, 27 (1988), No. 8, 1101-1103.

α phase:

Space group: P6/mmm

a = 3.648(1) Å, c = 3.875(1) Å

N 0 0 0

Li(1) 0 0 1/2

Li(2) 1/3 2/3 0

Rabenau and H. Schulz,

J. Less-Common Metals, 50 (1976), 155-159.

Nature of this Room Temperature Study

1. To evaluate the impurity phases in commercial precursor Li₃N material. There is a residual high pressure β phase present in α-Li₃N in significant quantities .
2. Three samples from major commercial vendors were obtained.
3. Quantitative Synchrotron X-ray Diffraction. A sample plot shown on the left shows a typical pattern. Also the atom positions in the lattice.

Results:

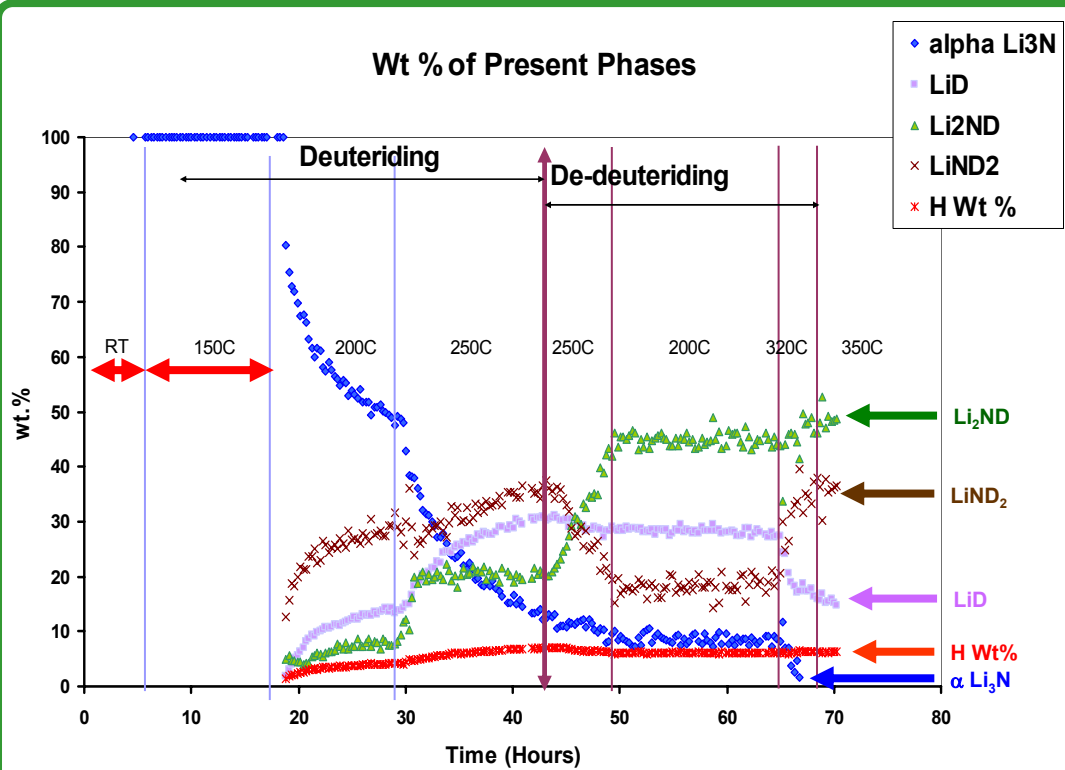
1. Samples from major suppliers were almost has the same amount of impurity of β phase; except for Sample S.
2. Lattice parameters at room temperature were also nearly the same (pl. see below)

Samples	Lattice Parameters at room temperature				Wt.% of Phase	
	α Phase		β Phase		α Phase	β Phase
	a (Å)	c (Å)	a (Å)	c (Å)		
Sample A	3.5890(5)	3.8086(6)	3.5131(7)	6.2433(23)	54.67	45.33
Sample C	3.5862(3)	3.8070(5)	3.5091(4)	6.2370(11)	54.29	45.71
Sample S	3.5881(3)	3.8095(5)	3.5123(5)	5.2436(14)	59.18	40.82

Importance: To explore if one can obtain a Li₃N phase during desorption in amide-imide system that will give ~11 wt.% hydrogen recovery. Currently under moderate conditions we get only ~5.5-6%. Details of the starting phase properties are important to understand mechanisms.



Weight% of Phases Formed During Deuteriding of Pure α -Li₃N and Subsequent Removal of Deuterium



During Loading of Deuterium

- At 200°C: The amount of LiND₂ is higher than that of Li₂ND (Once Li₂ND forms, it immediately transforms to LiND₂ in presence of deuterium gas). LiD also formed the plot (left)
- At 250°C: the kinetics of formation of Li₂ND and LiD increased substantially as the temperature was increased from 200° to 250°C. Note the rapid decrease in the amount of α -Li₃N.

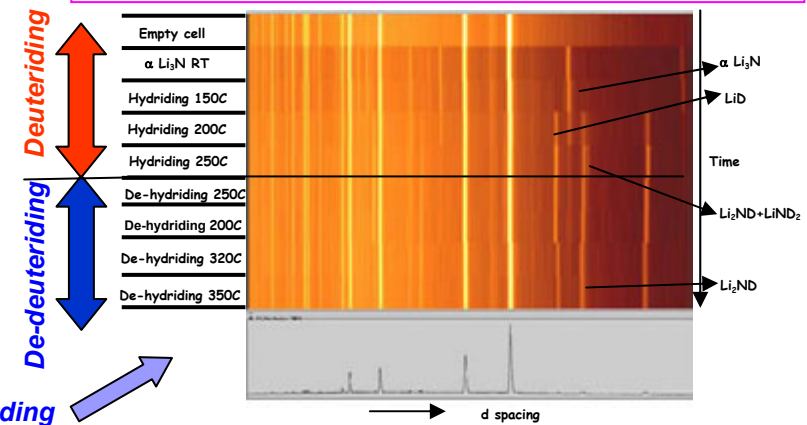
During Unloading of Deuterium (Brown line)

- At 250°C: LiND₂ → Li₂ND but the amount of LiD phase did not change significantly.
- Increase from 200 to 320°C: We observe a decrease in LiD and increase in LiND₂. (Pl. note: we are evacuating!)

Importance:

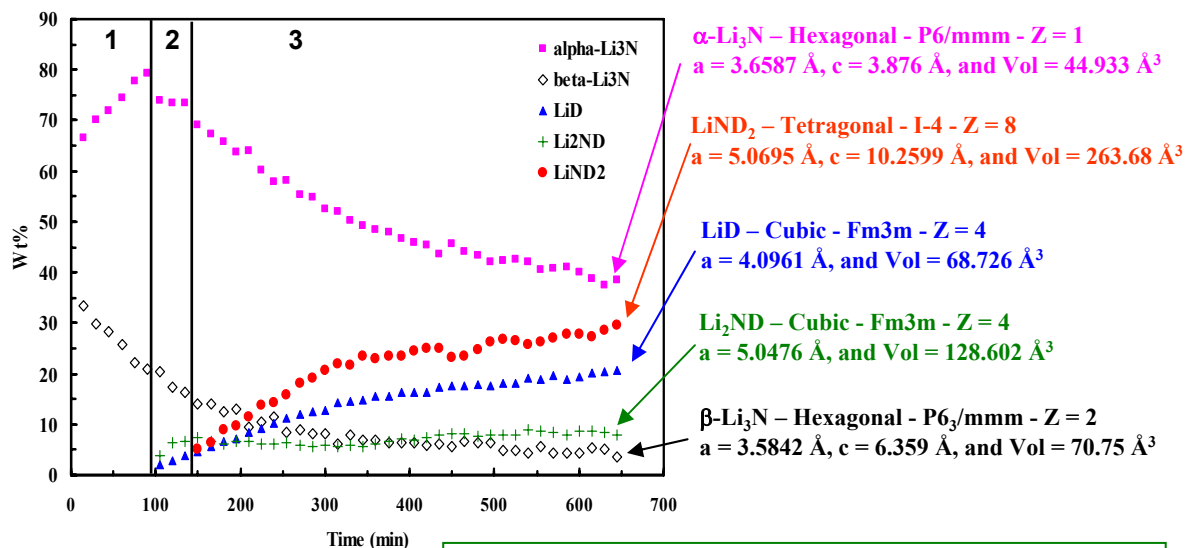
Decrease in the amount of LiD as the temperature is increased to 320°C suggests phase transitions (with no deuterium added-under vacuum).

1. Results of phase transformations during hydriding of α -Li₃N as a function of temperature and time obtained from in-situ neutron diffraction analyses.
2. Plot above shows non equilibrium situation of adding hydrogen to α -Li₃N; the sections shown are isothermal regions of (a) deuteriding and (b) de-deuteriding
3. Obtaining the amount of D/H absorbing in the solids (deduced amount by back calculations). Data points taken every 15 minutes.



Neutron Diffraction patterns taken at different temperatures during Deuteriding

Isothermal In-situ Neutron Hydriding of Li_3N Showing Variation of Wt.% Phases at 200°C



In-situ Hydriding – Starting Materials is $\alpha + \beta \text{Li}_3\text{N}$

Neutron Diffraction Data taken every 15 minutes at 200°C isothermally (left) at 2 bar deuterium pressure.

General Comments on Isothermal Hydriding at 200°C

- As the experiment is started initially (region 1) only the $\beta\text{-Li}_3\text{N}$ transforms to $\alpha\text{-Li}_3\text{N}$.
- In region 2, the hydride phases begin to appear; only Li_2ND and LiD form.
- Other hydride phase, LiND_2 , was formed in region 3.
- In this case of $\alpha + \beta \text{Li}_3\text{N}$ results are similar to those obtained using only $\alpha\text{-Li}_3\text{N}$ (compare results from previous slide). Note change in the amount of $\beta\text{-Li}_3\text{N}$.
- The amount of LiD and LiND_2 increased with time. Note the decrease in the amount of $\alpha\text{-Li}_3\text{N}$ during hydriding.

Importance:

Although detailed kinetic studies were not performed it can be noted that this processes is kinetically slow as seen in the plot (left).

Results:

Plot of Wt.% Phase vs time at 200°C during hydriding showing:

Region 1: $\beta\text{-Li}_3\text{N} \rightarrow \alpha\text{-Li}_3\text{N}$

Region 2: $\beta\text{-Li}_3\text{N} \rightarrow \alpha\text{-Li}_3\text{N}$

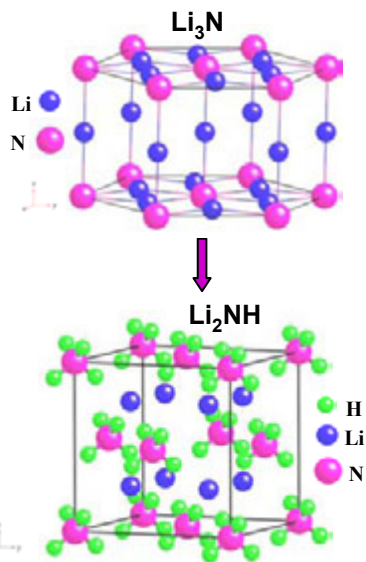
$\alpha\text{-Li}_3\text{N} \rightarrow \text{Li}_2\text{ND} + \text{LiD}$

Region 3: $\beta\text{-Li}_3\text{N} \rightarrow \alpha\text{-Li}_3\text{N}$

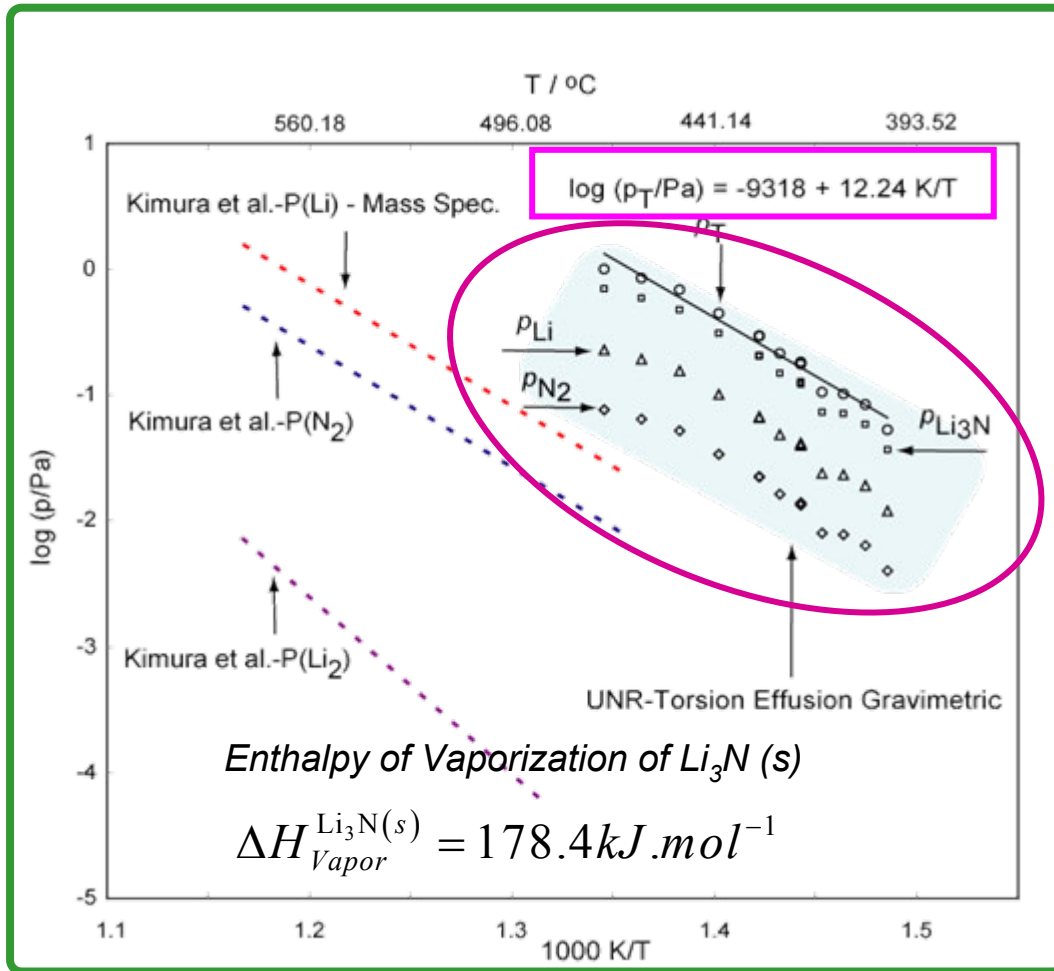
$\alpha\text{-Li}_3\text{N} \rightarrow \text{Li}_2\text{ND} + \text{LiD}$

$\text{Li}_2\text{ND} \rightarrow \text{LiND}_2 + \text{LiD}$

Amount of $\text{LiND}_2 + \text{LiD}$ Increases significantly as compared to Li_2ND .



Vapor Pressure and Disproportionation of Li_3N



➤ Significance:

Around room temperature the pressures are very low, so could not obtain the data. Small amount of Li_3N , or Li vapor may evolve during high temperature evaporation; Care should be taken the sample chamber have no Pt, Molybdenum sample cells are good for these materials.

➤ Vapor Pressures of $\alpha\text{-Li}_3\text{N}$ are very low

□ Dissociation of Solid Li_3N during Vaporization show very low vapor pressures for example:

@ $410^\circ\text{C} \rightarrow 1.01 \times 10^{-6} \text{ atm} \cdot (0.102 \text{ Pa})$
 @ $470^\circ\text{C} \rightarrow 9.94 \times 10^{-6} \text{ atm} \cdot (1 \text{ Pa})$

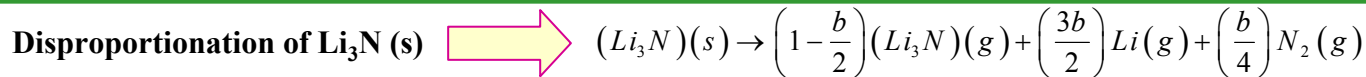
➤ The equilibrium Pressure equation shown in the Figure (top left) partial pressure equations are shown on the next page.

➤ UNR data (400-470°C) is circled in the Figure (left). Kimura et al. (1980) reported data (466-586°C) but their pressure appear lower than ours. In general our data as well Kimura's data show relatively low vapor pressures.

➤ Although the vapor pressure is low, but we observed that the vapors partially disproportionate to Li_3N , Li and N gas phases.

➤ At higher temperature around 470°C Liquid Li forms leading to reaction with the Pt-20%Rh Knudsen cell by formation Intermetallics or Grain Boundary diffusion. X-ray Diffraction study of the residual powder showed significant amount of Li_3N and a small amount of Li-Pt intermetallic phase.

Li₃N Vapor Pressure Data Analyses



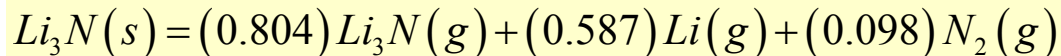
Calculated Average Molecular Weight (MW_{AVG}) of the Effusing Gas Species

Measured MW_{AVG} = 26.15 g·mol⁻¹
(this is 25% < MW_{Li₃N} = 34.83 g·mol⁻¹)

$$M_{AVG} = \frac{2\pi RT}{(2K)^2} \cdot \left(\frac{dw/dt}{\theta}\right)^2 \left[\frac{(a_1 f_1 d_1) + (a_2 f_2 d_2)}{(a_1 c_1) + (a_2 c_2)}\right]^2 = \sum_{i=1}^n [m_i M_i^{1/2}]^{-2}$$

$$M_{AVG}^{CALC} = \left[\frac{\left(1 - \frac{b}{2}\right)(M_{Li_3N})^{0.5} + \left(\frac{3b}{2}\right)(M_{Li})^{0.5} + \left(\frac{b}{4}\right)(M_{N_2})^{0.5}}{\left(1 - \frac{b}{2}\right)(M_{Li_3N}) + \left(\frac{3b}{2}\right)(M_{Li}) + \left(\frac{b}{4}\right)(M_{N_2})} \right]^{-2}$$

In this case: b = 0.391



➤ We find the constant 'b' by equating the calculated and experimentally molecular weight, the partial pressures of the gas species can then be given by:

$$p_{Li_3N} = \frac{\left(1 - \frac{b}{2}\right)(M_{Li_3N})^{0.5}}{\left(1 - \frac{b}{2}\right)(M_{Li_3N})^{0.5} + \left(\frac{3b}{2}\right)(M_{Li})^{0.5} + \left(\frac{b}{4}\right)(M_{N_2})^{0.5}} \quad p_{Li_3N} = 0.406 P_T \quad \log(p_{Li_3N}) = -9318.39 + 12.24/T$$

$$p_{Li} = \frac{\left(\frac{3b}{2}\right)(M_{Li})^{0.5}}{\left(1 - \frac{b}{2}\right)(M_{Li_3N})^{0.5} + \left(\frac{3b}{2}\right)(M_{Li})^{0.5} + \left(\frac{b}{4}\right)(M_{N_2})^{0.5}} \quad p_{Li} = 0.445 P_T \quad \log(p_{Li}) = -9318.35 + 12.24/T$$

$$p_{N_2} = \frac{\left(\frac{b}{4}\right)(M_{N_2})^{0.5}}{\left(1 - \frac{b}{2}\right)(M_{Li_3N})^{0.5} + \left(\frac{3b}{2}\right)(M_{Li})^{0.5} + \left(\frac{b}{4}\right)(M_{N_2})^{0.5}} \quad p_{N_2} = 0.149 P_T \quad \log(p_{N_2}) = -9318.83 + 12.24/T$$

Total Pressure (P_T) Equation: log(P_T) = -9318 + 12.24/T (from slide 11)

Preliminary In-situ Hydriding Mechanisms of Li_3N Using DSC

Collaboration with Dr. Darlene Slattery and Dr. Mike Hampton (Florida Solar Energy Center, Cocoa Beach)

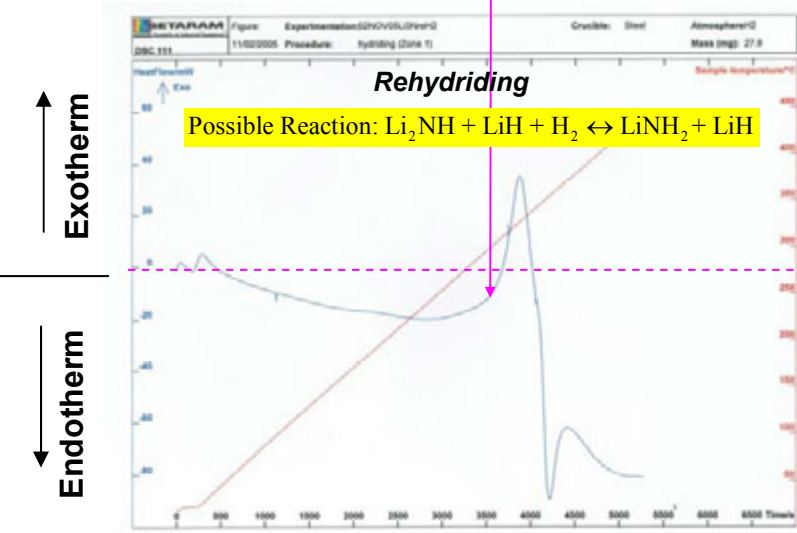
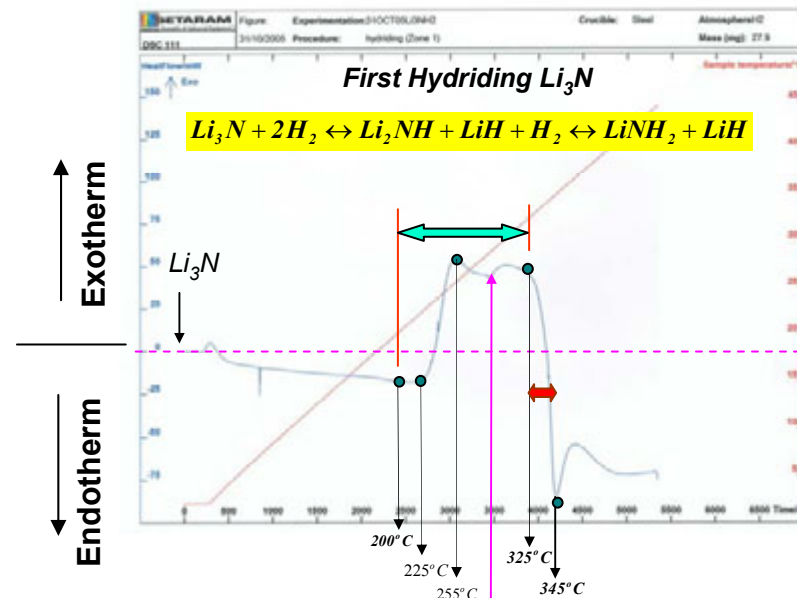
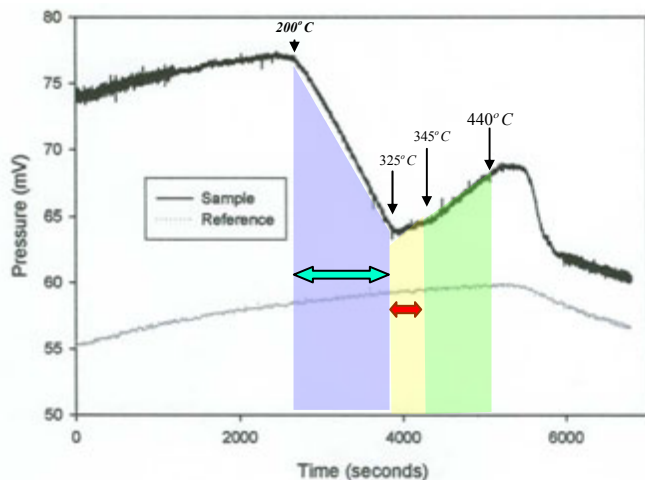
➤ Prof. Ping Chen (2002) performed pioneering experiments showing gravimetric data which showed a steep increase in hydrogen absorption starting $\sim 170^\circ\text{C}$ to $\sim 200^\circ\text{C}$. (*P.Chen et al. Nature 420,p302,2002)

❑ In-situ DSC Plots obtained by hydriding at 5 atmospheres during heating in the DSC at Florida Solar Energy Center. (right)

❑ DSC Scan shows that $\sim 225^\circ\text{C}$ hydrogen absorption begins suggested by the exothermic reaction peak. It appears that the hydrogen absorption continues up to approximately 325°C . It can be noted that the pressure decreased from 200 to 325°C (please see Pressure vs Time/Temp. Figure below).

❑ At 325°C the pressure appears to increase and also in the DSC we observe a steep change from exothermic to endothermic regions ($325\text{-}345^\circ\text{C}$). Thus, we believe that there is a hydrogen release, perhaps with a concurrent phase transformation in presence of hydrogen.

❑ In the second DSC scan (right- bottom) we show that hydriding begins at $\sim 275^\circ\text{C}$; research in progress.



Future Work (FY06-FY07)

1. Continue work on Effect of Impurities on Specific contaminants on Complex Hydrides

- Continue Work on 100 ppm Oxygen, CO, CO₂, H₂O etc. Pressure Hydriding of Li₃N, LiNH₂/MgH₂, or other complex hydrides MgH₂/LiBH₄, MgBH₄. We will start the high pressure 120 bar pressure cycling work on MgH₂/Li₂NH (with Sandia) in FY 07, the apparatus is expected to complete by late September FY06. The experience developed during this Li₃N cycling experiments will be useful for high pressure cycling of Mg-Li-N-H and other complex hydrides.

2. Complete Cycling Apparatus Fabrication and Automation

- Optimize Pressure Cycling Apparatus for Different Types of Hydrides (Please see slide 15 for a photo of cycling apparatus - right side). Add work stations for thermal cycling and automate the system by National Instruments - work in progress.
- 120 Bar High Pressure Hydrogen Cycling of LiNH₂-MgH₂ (Sandia - MHCoe partners) High pressure apparatus is current under construction.

3. In-Situ Hydriding/dehydriding X-ray diffraction Studies

- Start Ca Borohydride In-situ Hydriding-X-ray Diffraction work (Sandia - *Mechanistic Studies*) in FY'06. PANalytical X-ray Diffraction system (Slide 15) - left with hot hydrogen stage (10 bars pressure maximum) will be used for this purpose.

4. In-Situ Neutron Diffraction at IPNS Argonne / NIST Maryland

- Continue In-situ Neutron Studies on Deuteration of Catalyzed complex hydrides - Mechanistic Studies from MHCoe group; including new Ca Borohydride study. Please see Slide 16 for details of the apparatus at Argonne. NIST apparatus is not shown here.

5. Vapor Pressure Studies on Mg(BH₄)₂ - GE Collaboration

- Determine thermodynamics of vaporization by measuring vapor pressures of Mg(BH₄)₂, as this material has very high capacity of hydrogen (~15 wt%) as shown in Slide 17. Torsion Effusion Apparatus shown in Slide 18 will be used for this purpose. This is available at UNR, except new Mo Knudsen cell will be fabricated.

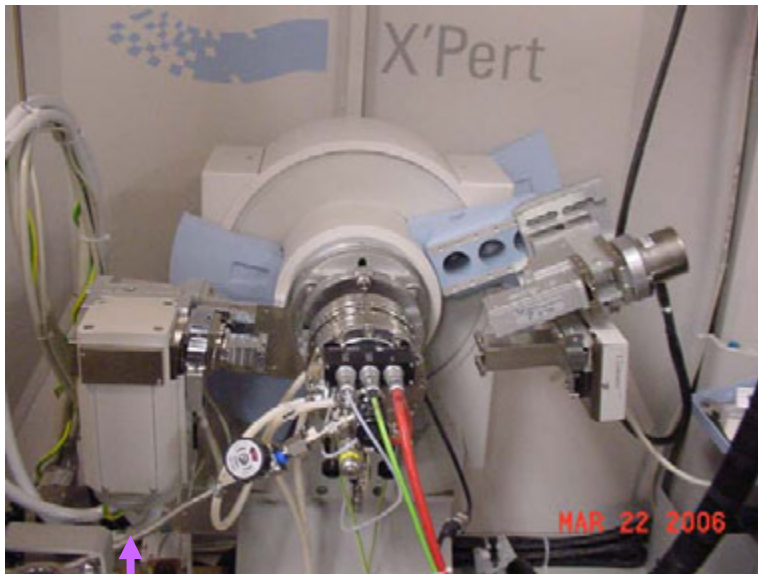
6. Hydrogen Lattice Dynamics Studies on Complex Hydrides- Prof. Cantelli, Uni. of Rome - IPHE Proposal

- "Hydrogen Dynamics, Lattice interactions, and Atomic-scale Structure of Complex/Chemical Hydrides" will be a subject of IPHE research topic for mid-2007. This proposed study is on lattice dynamics of complex hydrides, such as amides, imides, and other hydrides. This collaborative study between Cantelli-Rome, Italy and Chandra, Jensen-USA includes spectroscopes that will allow understanding of the H dynamics, like muons (an Italian group), neutrons (Italy and perhaps Denmark), anelasticity (Cantelli's group), and the local structure like positrons (Italy and Japan).

Apparatuses For Pressure/Thermal Cycling at UNR

UNR's Pressure Impurity Cycling apparatus (right bottom) and Partially finished Multi-channel Pressure Impurity cycling (Top right) In-situ Hydriding X-ray Diffraction Stage (left)

Hydrogen Tubing to High Temperature PANalytical X-ray Diffractometer

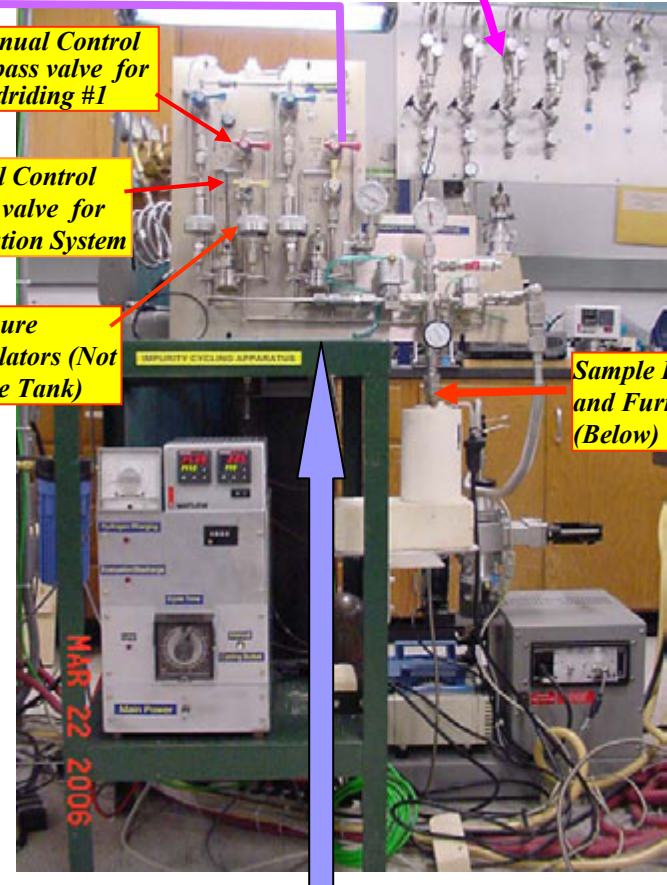


Manual Control Bypass valve for Hydriding #1

Manual Control Bypass valve for Evacuation System

Pressure Regulators (Not on the Tank)

Sample Holder and Furnace (Below)



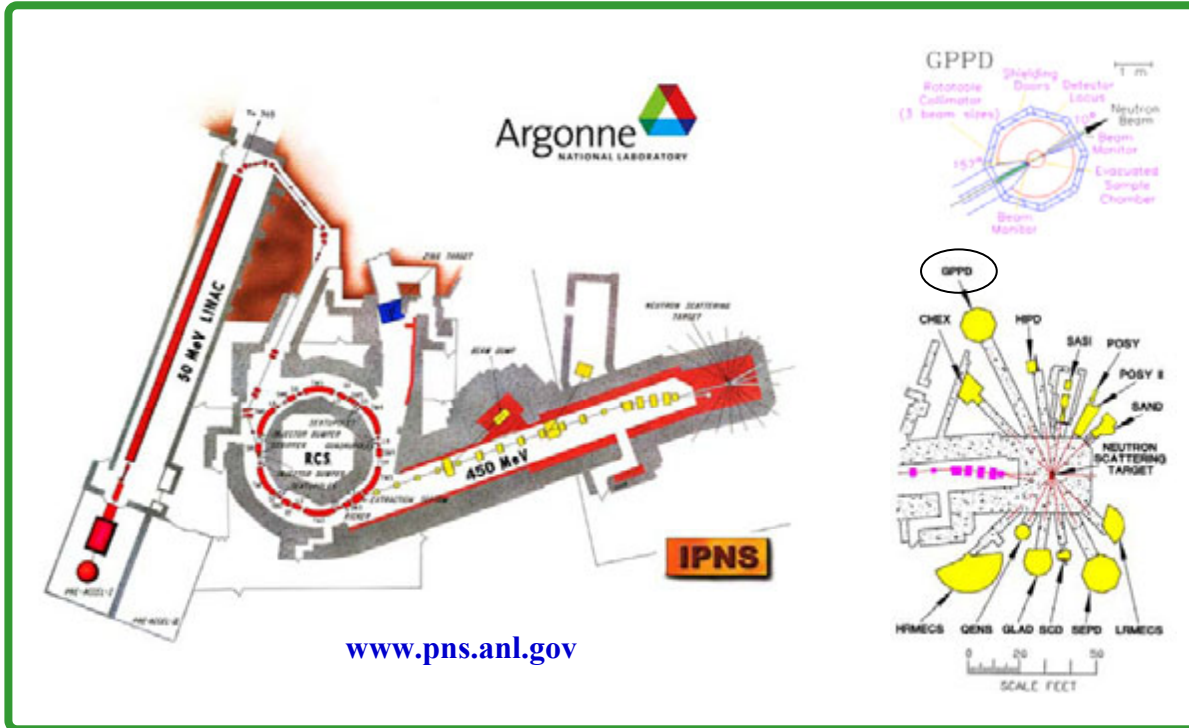
This Diffractometer shown above will be used in-situ hydriding experiments. This has an Anton Parr heating stage with pressure capability of 10 atmospheres of hydrogen.

To be used for in-situ hydriding catalyzed calcium Borohydride (Sandia National Laboratories) collaborative research.

Semiautomatic Pressure Cycling Apparatus used for 1100 hydriding/dehydriding cycles on α -Li₃N at UNR

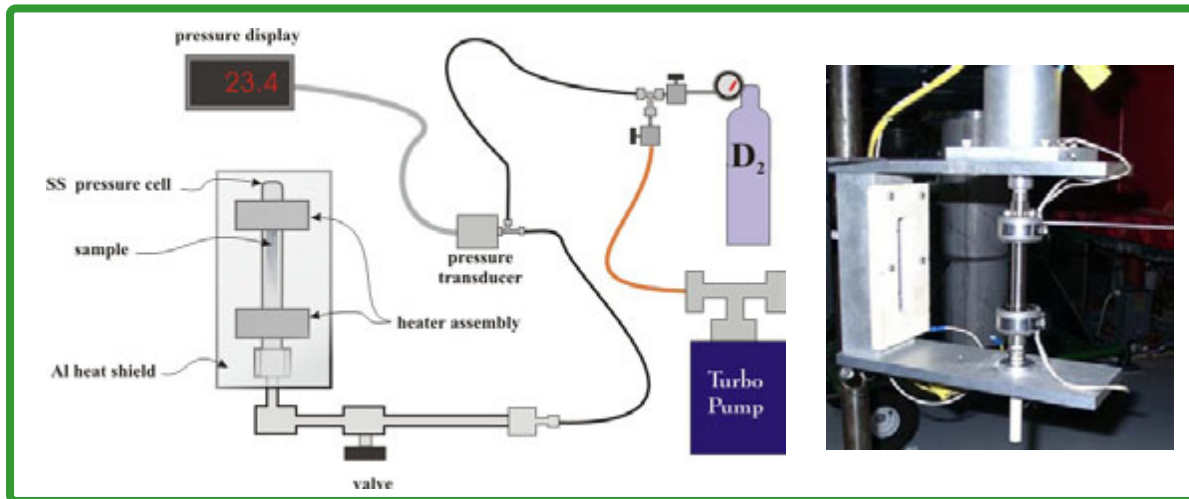


In-situ Neutron Diffraction Apparatus



Structural Characterization Facility

Neutron diffraction experiments will be carried at IPNS Argonne National laboratory and NIST (Maryland). The photo to the top left shows the general schematic of the facility of IPNS, Argonne.



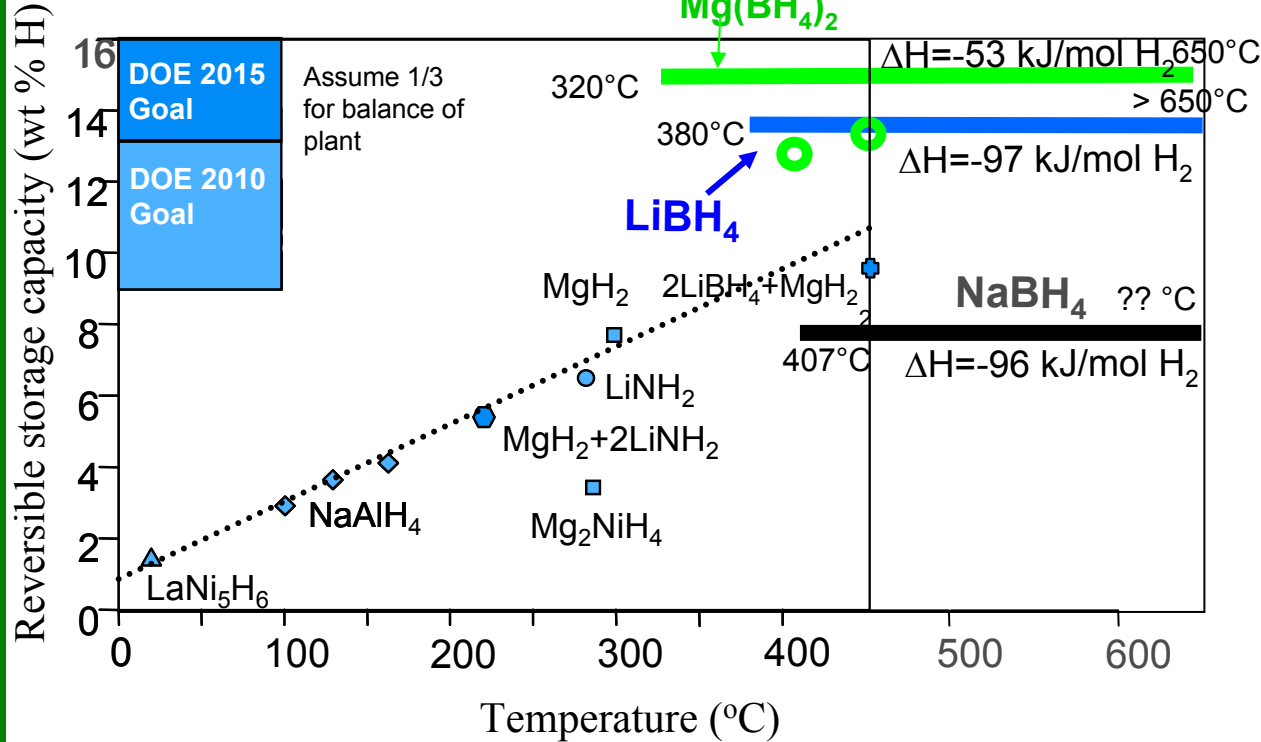
In-situ Hydriding Sample Holders with heating capability:

Neutron diffraction Hydriding Sample Holder set up that is being used for our project at IPNS. Two types of sample settings are shown; one bottom-left; and newer sample holder of Superalloy on the right with heating capability.

Vapor pressures Studies on Mg borohydrides



Mg(BH₄)₂ & Other Metal Hydrides – Collaboration with GE
 The figure below has been furnished by Dr. J.C. Zhao - GE



Significance of this work:

The Mg(BH₄)₂ has ~15% hydrogen capacity, with low $\Delta H \sim -53$ kJ/mol is an interesting materials is a good candidate for future work in starting FY2006. Our MHCoe partner, (GE – Collaboration with Dr. J.C. Zhao.), requested to us to measure vaporization Thermodynamics of Mg Borohydrides. Vaporization thermodynamics for this system of Hydrogen is not well established.

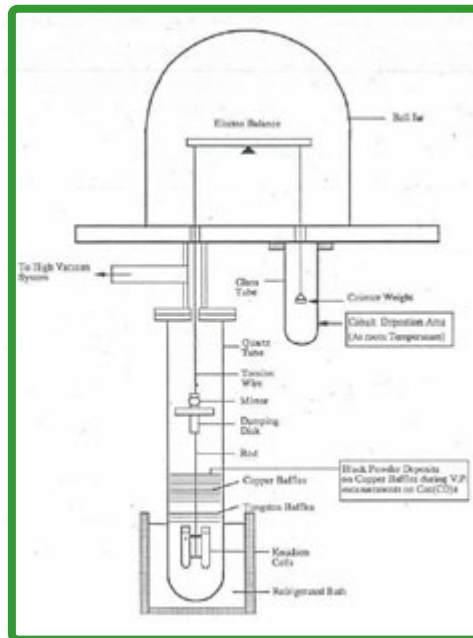
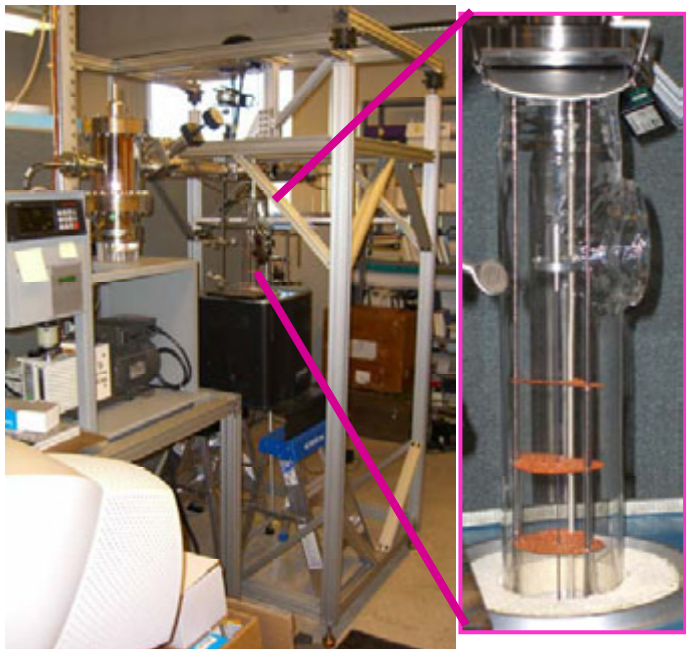
Expected Results:

Obtain equilibrium partial pressures of gases evolved from the solid phase. Develop equation ($\log P$ vs $1/T$). Enthalpy of Vaporization, Gibbs energy functions, disproportionation of solid species.

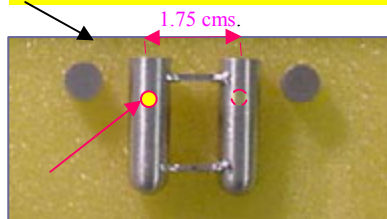
Vapor Pressure Measurement Apparatus at UNR

UNR's Torsion Effusion Gravimetric Apparatus

Cahn Balance D100 – Digital Balance



Opposed Apertures Knudsen Cells



Instrumentation:

- Torsion effusion system available at UNR (Schematic and actual apparatus shown left).

How To Measure Pressure:

A pair of Knudsen Cells with opposed orifices are suspended by a Pt-10%Ni torsion wire with known stiffness (pl. see the Figure left bottom).

A mirror placed in this assembly that records the torque induced by vapors jetting out of the cell orifices.

From the distances recorded from the mirror reflection of the meter scale, we can determine the angular displacement 'θ'

To determine total equilibrium pressure we use the following Eq.:

$$P_T = \frac{K(2\theta)}{(a_1 f_1 d_1) + (a_2 f_2 d_2)}$$

'K' is the Fiber Constant

Conditions and Sample Size:

- High vacuum (10^{-5} Torrs)
- 1 to 2 grams
- Temperature capability: -20°C to 600-700°C
- Mo Knudsen Cells to be Used

How to Measure molecular Weight of Vapors:

Measure the rate of weight loss using Cahn digital balance. The slope of the rate of weight loss curve as function of time give the molecular weight of the effusing species. Disproportionation equations (below) in the vapor phase can be determined equating the experimental M_{AVG} to the theoretical Mol. Wt. of the effusing gas species:

$$M_{AVG} = \frac{2\pi RT}{(2K)^2} \cdot \left(\frac{dw/dt}{\theta} \right)^2 \left[\frac{(a_1 f_1 d_1) + (a_2 f_2 d_2)}{(a_1 c_1) + (a_2 c_2)} \right]^2 = \sum_{i=1}^n [m_i M_i^{1/2}]^{-2}$$



Publications in 2006

1. **Review paper** “Metal Hydrides for Vehicular Applications: The State of the Art”
D. Chandra, J.J. Reilly, and R. Chellappa, *Journal of Metals*, Vol. 58, No. 2, Feb. 2006, P. 26-32.
2. **Proceeding edited** “Advanced Materials for Energy Conversion III” *A Symposium in Honor of Drs. Gary Sandrock, Louis Schlapbach and Seijirau Suda*
Editors: D. Chandra, J. Petrovic, R. Bautista and A. Imam, 2006 TMS Meeting, ISBN: 978-0-87339-610-3.
3. “Structural studies of Li_3N using Neutron Powder Diffraction ”
Ashfia Huq, Jim Richardson, Evan Maxey, Dhanesh Chandra, Wen-Ming Chien, *Journal of Alloys and Compounds*, in review, *Manuscript Number: JALCOM-D-05-00350R1*.

Presentations in 2006

- “Neutron and Synchrotron Studies on Li-Based Nitride and Hydride”
Wen-Ming Chien, Dhanesh Chandra, Ashfia Huq, James W. Richardson, Jr., Evan Maxey, Sirine Fakra, and Martin Kunz
Presented in *2006 TMS Annual Meeting*, San Antonio, Texas, USA, March 12-16, 2006
- “Time Resolved Neutron Diffraction Studies of the Hydrogen Storage Material Li_3N ”
Ashfia Huq, Jim Richardson, Evan Maxey, Dhanesh Chandra, Wen-Ming Chien
Presented in *APS (American Physical Societies) March Meeting 2006*, Baltimore, MD, USA, March 13-17, 2006

Milestone Chart for UNR

Milestone Level: MYPP, Center, or Project			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.																	
Organization	Task #	Task Description	10/1	4/1	10/1	4/1	10/1	4/1	10/1	4/1	10/1	4/1	10/1	4/1	10/1	4/1	10/1	4/1	10/1	
			FY05	FY05	FY06	FY06	FY07	FY07	FY08	FY08	FY09	FY09	FY10	FY10	FY11	FY11	FY12	FY12	FY13	
B. Complex Anionic Materials (Borohydrides & Alanates)																				
	1	Modified Complex Hydrides																		
UNR	1.2.10	In situ diffraction measurements of borohydrides																		
	2	New Hydrogen Storage Materials																		
UNR	2.2.3	In situ diffraction measurements of new hydrogen storage materials																		
C. Amide/Imides (M-N-H Systems)																				
	2	Understand reaction mechanism																		
UH (UNR & U of Rome)	3.3	Defect effect on sorption properties																		
	5	Cycle stability and contamination test																		
		Extrinsic cycling tests*																		
		*Effect of Impurities and cyclic tests on Li-Mg-N-H system																		
UNR	5.4																			
	▲	Portfolio Relocation Decision Point (Project bars)																		
	◆	Milestone (Subtask bars)																		
	●	Output (Task bars)																		

We anticipate meeting the milestones at the end of 2006, and for FY 2007

Acknowledgments

- ❑ DOE MHCoe for the support of this Project
- ❑ Dr. J. Richardson, A. Huq and E. Maxey, IPNS, Argonne National Laboratory, for the Neutron Diffraction Research
- ❑ Dr. Sirine Fakra, and Dr. Martin Kunz, Lawrence Berkeley National Laboratory, for the Synchrotron Research
- ❑ Dr. Darlene Slattery & Dr. Mike Hampton, Florida Solar Research Institute (Cocoa Beach), for DSC work