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DOE Hydrogen Program

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

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This presentation does not contain any proprietary or confidential information

Overview

Timeline

Project start date – FY05
Project end date – FY10
Percent complete – ~40%

Barriers Addressed

- Long-term reliability of complex hydrides by pressure cycling and thermal aging with gaseous impurity mixed hydrogen charge. (Li_3AlH_6-$3LiNH_2$ mixed phase and Li_2NH-$LiNH_2$ systems in FY07)
- Studies on phase transitions (during heating) and vaporization thermodynamics of Mg- and Ca-Borohydrides.

Budget

Total project funding (5yrs.) : $ 1.5 M (Requested)
DOE share (5yrs.) : $ 1.2 M

Contractor share (5yrs.) : $ 301 K

Funding received in FY06 : $ 200 K

Funding received in FY07 (so far) : $ 130 K

Partners

Active Current Collaboration

- Sandia National Laboratories, CA – *L. Klebanoff, Eva Ronnebro*
- *General Electric Corp. – Dr. J.C. Zhao*
- IPNS, Argonne National Laboratory, Chicago IL
  - J. Richardson, E. Maxey, and A Huq
- Univ. of Utah, Salt Lake City UT- *Dr. Z. Fang*

Future Collaboration

- *Jet Propulsion Laboratory (Caltech)- Dr. Robert C. Bowman, Pasadena CA*
- *NIST, Gaithersburg, Maryland- Dr. Terry Udovic*
- *Brookhaven National Laboratories, NY – Dr. James Reilly*
- *University of Rome-Prof. Rosario Cantelli*
- *University of Hawaii- Prof. Craig Jensen*
- *European Commission - DG Joint Research Centre - Institute for Energy, Westerduinweg 3, NL-1755 LE Petten- Dr. Constantina Filiou*

UNR-MHCoE Research Program Objectives

A. Impact of Impurities on Long term Durability of the Complex Hydrides

The primary focus of UNR research is to determine the effects of gaseous trace impurities (ppm levels of O_2, CO, H_2O, NH_3 etc. in H_2) in complex hydrides/precursors after prolonged hydrogen pressure cycling and relatively short term thermal aging. Accelerated laboratory tests designed at UNR can simulate these conditions providing insights into the long term reliability of complex hydrides and their precursors.

Relevance to DOE-MHCoE: **In practical applications, trace impurities in hydrogen gas will have an impact on the hydrogen loading capacities during periodic recharging with fresh hydrogen. UNR facilities are also being utilized by the MHCoE Center partners.**

Progress till FY 2007: **Effects of using industrial hydrogen for 1100 cycles in Li_2NH-$LiNH_2$ system were reported. Pressure cycling (~500 cycles) using 100 ppm level O_2 impurity in UHP H_2 as well as thermal aging (CO impurity) of mixed phase Li_3AlH_6-$LiNH_2$ have been completed.**

Plan for FY 2008: **We will continue these pressure cycling and aging studies on UNR materials, and other destabilized complex hydrides.**

B. Fundamental Mechanistic Studies on Complex Hydrides

Vaporization Thermodynamics: **To understand vaporization behavior of complex hydrides/precursors and identify vapor species at moderate temperatures under vacuum using a Gravimetric Torsion Effusion apparatus.**

Structural and Mechanistic Studies (X-ray and Neutron): **X-ray and neutron scattering mechanistic studies (in-situ and ex-situ) on complex hydrides to elucidate phase evolution during hydrogen sorption/desorption and structural changes during phase transitions.**

Relevance to DOE-MHCoE: **In-situ structural changes during hydriding and dehydriding can reveal phase transition and reaction mechanisms that are important for future development. Also, during desorption, knowledge of vaporization thermodynamics provides insights into hydrides that may decompose at operating temperatures.**

Progress till FY 2007: **In-situ neutron diffraction during deuteriding/de-deuteriding of Li_2ND-$LiND_2$ mechanisms have been reported (defect structure mechanism studies are ongoing). Disproportionation behavior during heating (moderate vacuum) of $Mg(BH_4)_2$ has been studied.**

Plan for FY 2008: **Continue the activities on crystal structure, vapor pressure. We have added new tasks on determining binary phase diagrams for destabilized complex hydrides.**

Plan and Approach

A. Trace Impurity Impact on Long term Durability of the Complex Hydrides.

1. Gaseous Impurities and Tested Materials

The impurities that are being tested are: O_2, CO, H_2O, CH_4, and NH_3(~100 ppm) mixed with UHP H_2. The hydrides that were studied were Li_2NH-$LiNH_2$ and Li_3AlH_6-$LiNH_2$ mixed phase. Future studies will include $Ca(BH_4)_2$, $Mg(BH_4)_2$, and other potential destabilized hydrides being developed by MHCoE center partners.

2. Equipment and Testing Methodology (UNR)

UNR now has a fully functional low pressure (~2 bar) and high pressure (~120 bar) cycling apparatus that can operate up to ~400°C. The chosen materials are subjected to predetermined number of pressure cycles (500-1000) with a fresh charge of impurity-mixed UHP H_2. For example, with Li_3AlH_6-$LiNH_2$ mixed phase, we have pressure cycling with 100 ppm O_2 and thermal aging with 100 ppm CO. In the future, other impurities will be tested if these materials show promise.

A fully automatic Sievert's apparatus is used for obtaining isotherms of the cycled hydrides (before and after cycling) for quantifying changes in hydrogen capacities.

B. Fundamental Mechanistic Studies on Complex Hydrides

1. Vaporization Thermodynamics

A Gravimetric Torsion Effusion apparatus is used to obtain total and partial pressures of evolved vapor species during heating (moderate vacuum). Possible routes of disproportionation were determined during this dehydriding process. Studies on $Mg(BH_4)_2$ are in progress and other selected hydrides will be studies in FY '08.

2. Structural and Mechanistic Studies (X-ray and Neutron Diffraction)

Using XRD (at UNR), dynamic structural information of phase evolution is obtained as a function of temperature at a constant pressure or at constant temperature with increasing hydrogen pressure in complex hydrides. In addition, ex-situ XRD of cycled hydrides are performed to identify new phases and structural changes. In-situ neutron scattering experiments by interfacing Sievert's apparatus for dynamic kinetic studies are proposed for later in FY '07, and early part of FY '08.

Technical Accomplishments in FY 2007

- **Alanate-Amide (Li_3AlH_6-$LiNH_2$) Binary Hydride**
  1. Thermal Aging at 325°C (~9500 Torr) for 125 hours with 100 ppm CO/H_2 showed minimal hydrogen capacity loss.
  2. Pressure Cycling with 100 ppm O_2/H_2 shows ~0.6 wt.% H_2 loss after ~540 cycles.
  3. From equilibrium isotherms up to ~10^4 Torr, van't Hoff plot was obtained (ΔH=-69.5 $kJ \cdot mol^{-1}$ H_2)
  4. There is evidence of Li_3AlN_2 formation at 325°C after 12 hours (under He atmosphere).
  5. In-situ XRD from RT to 325°C revealed that both Li_3AlH_6 and $LiNH_2$ were stable up to ~190°C and decomposed to Li_2NH, Al, and LiH. Li_2O impurity content did not change significantly.
  6. Rehydrogenation of the disproportionated sample was feasible at 325°C and 2 bar H_2 up to 1 hour; however Li_3AlN_2 formed after 20 hours.

- **Imide-Amide (Li_2NH-$LiNH_2$) Impurity Effects**
  1. Isotherms obtained at 325°C with 100 ppm CO/H_2 showed complete reversibility of Li_2NH-$LiNH_2$ system. Insignificant loss of hydrogen capacity was observed in spite of CO impurity.
  2. While obtaining a standard desorption isotherm, it was observed that at 325°C, the total hydrogen desorbed did not go below 2 wt.% H_2; however, at 200°C, it approached 0.5 wt.% H_2.

- **Phase Transitions in $Ca(BH_4)_2$ and $Mg(BH_4)_2$**
  1. At RT, the as-synthesized showed α-$Ca(BH_4)_2$ and CaB_6 as the major phases. XRD patterns between 200-300°C show a phase transition from α-$Ca(BH_4)_2 \rightarrow \beta$-$Ca(BH_4)_2$ (structure refinement is in progress). It was observed that beyond 300°C, low angle β-$Ca(BH_4)_2$ Bragg peaks disappeared.
  2. No phase transition was observed in $Mg(BH_4)_2$ from 25°C -250°C (in He atmosphere).

- **Vapor Pressure Measurement of $Mg(BH_4)_2$**
  1. Between 10^{-4}-10^{-5} Torr and temperatures up to 250°C, it was observed that $Mg(BH_4)_2$ disproportionates almost fully to H_2 (Avg. Mol. Wt. of effusing gas: 2.4 g/mol) with residual Mg (s).

Publications and Presentations

Journal Publications May 2006 - April 2007

1. *A. Huq, J.W. Richardson, E.R. Maxey, D. Chandra, W-M. Chien,* "Structural studies of Li_3N using Neutron Powder Diffraction," J. Alloys and Compounds, *Article in Press 2007 JALCOM–D05-00350R1, (2006)* (Elastic in-situ neutron scattering at IPNS, Argonne-MHCoE program), Full length Paper in print 2007.

2. *W-M. Chien, J. Lamb, D. Chandra, A. Huq, J. Richardson Jr. and E. Maxey,* "Phase Evolution of Li_2ND, LiD and $LiND_2$ in Hydriding/dehydriding of Li_3N," *Journal of Alloys and Compounds,* 9 pages Very *recently Accepted paper in Print* (Feb. 2007).

Proceedings May 2006 - April 2007

3. *W. Chien, J. Lamb and D. Chandra*, "Structural Behavior and Pressure Cycling Effect Studies of Li-Based Complex Hydrides," *TMS 2007 Extraction, Processing, Structure and Properties Proceedings, CD Structure Materials Division*, pp 143-149, 2007
4. *W-M. Chien, D. Chandra, A. Huq, J. W. Richardson, Jr., E. Maxey, S. Fakra and M. Kunz*, "Deuteriding and Low Temperature Structural Studies of Li-Based Complex Hydrides," *Materials Science &Technology (MS&T) 2006: FUNDAMENTAL AND CHARACTERIZATION*, Volume 1, 501-507, 2006.

Presentations at National and International Meetings May 2006 - April 2007

1. *D. Chandra* "Extrinsic Effects of Impurities on Long-Term Behavior of Complex Hydrides," Session F: H-18 Wednesday Jan. 31st. 2007, International Energy Agency Task 22 - January 2007 Experts Meeting, Hosted by Sandia National Laboratory, January 28 to Feb 1st, 2007 Monterey Plaza Hotel, Monterey, California
2. *W. Chien, J. Lamb and D. Chandra*, "Structural Behavior and Pressure Cycling Effect Studies of Li-Based Complex Hydrides," Presentation at TMS 2007 Annual Meeting & Exhibition, Orlando, Florida, USA, February 25-March 1, 2007.
3. *D. Chandra, W-M. Chien, J. Lamb*, "Pressure Cycling Studies of Li-based Complex Hydrides," Presentation at the MRS Annual Meeting in Boston, MA November 27-December 1 2006.
4. *W-M. Chien, D. Chandra, A. Huq, J. W. Richardson, Jr., E. Maxey, S. Fakra and M. Kunz*, "Structural and Hydriding Behaviors Neutron Studies on Li-Based Hydrogen Storage Materials," Poster Presentation, 2006 American Conference on Neutron Scattering - St. Charles, IL, June 18-22, 2006. (Abstract, pp. 88).
5. *W-M. Chien, D. Chandra, J. Lamb, A. Huq, J. W. Richardson, Jr., E. Maxey, S. Fakra and M. Kunz,* "Neutron and Synchrotron Structure Evaluation of Li3N During Hydriding and Dehydriding" Poster Presentation, 2006 Denver X-ray Conference - Denver, Colorado, August 7-11, 2006. (Abstract, pp. 5).
6. *W-M. Chien, D. Chandra, A. Huq, J. W. Richardson, Jr., E. Maxey, S. Fakra and M. Kunz,* "Deuteriding and Low Temperature Structural Studies of Li-Based Complex Hydrides" Poster Presentation, Materials Science &Technology 2006 Conference and Exhibition – October 15-19, 2006 – Duke Energy Center – Cincinnati, OH, USA. (Abstract, pp. 39).
7. *W.M. Chien, D.Chandra, A. Huq, J. Richardson Jr., E. Maxey, M. Kunz, S. Fakra*, "Phase Evolution of Li_2ND LiD and $LiND_2$ in Hydriding/Dehydriding of Li_3N," MH2006-International Symposium on Metal-Hydrogen Systems-Fundamentals and Applications, Lahaina, Maui, Hawaii, October 1-6, 2006. Paper#373. (Abstract, pp. 97).

Experimental Apparatuses for Pressure Cycling and Thermal Aging

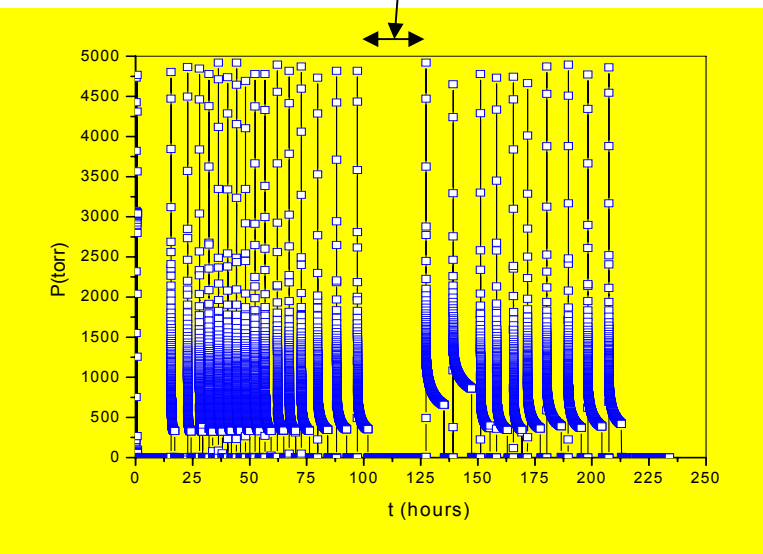
Impurity Impact

Instruments Available

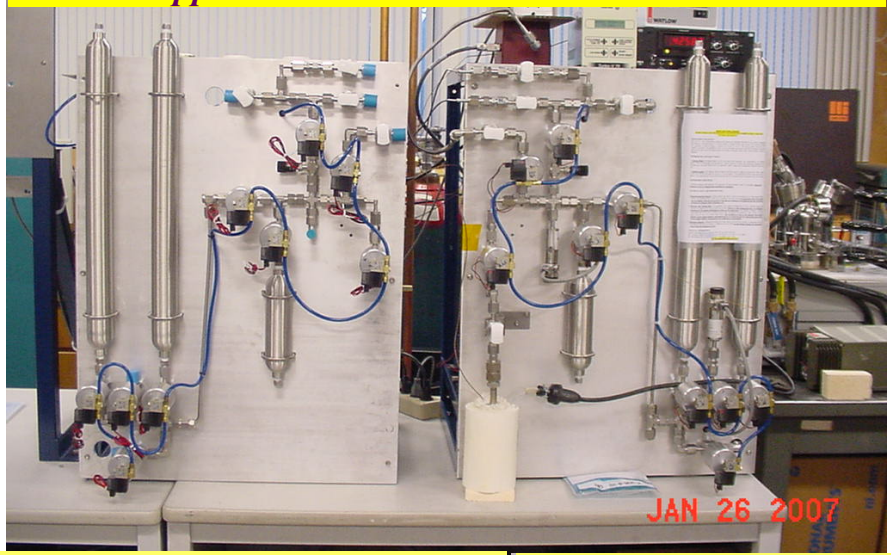
Sample Pressure Cycling Data of Complex Hydrides. Monitoring of Kinetics During Pressure Cycling at UNR

Automatic Pressure Cycling Apparatus at UNR Showing >20 pressure cycles - $LiNH_2$-Li_2NH

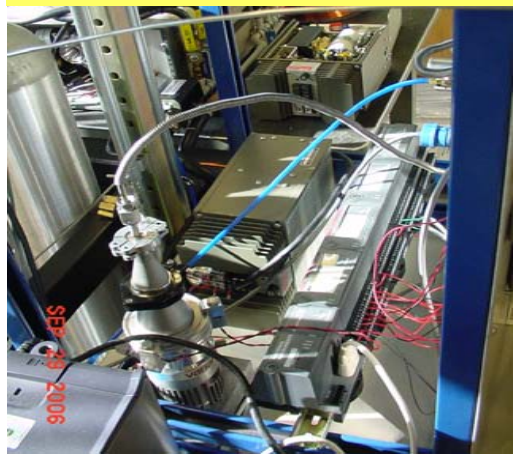
Cycling Interrupted Under Vacuum



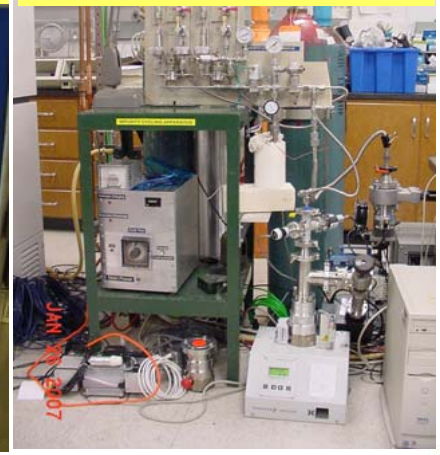
Dual -120 Bar Pressure Cycling Apparatus and Sievert's Apparatus Combined Front Panels



120 bar H_2 Pressure Cycling apparatus -2 bar H_2 (back Panel)



Pressure Cycling apparatus -2 bar H_2

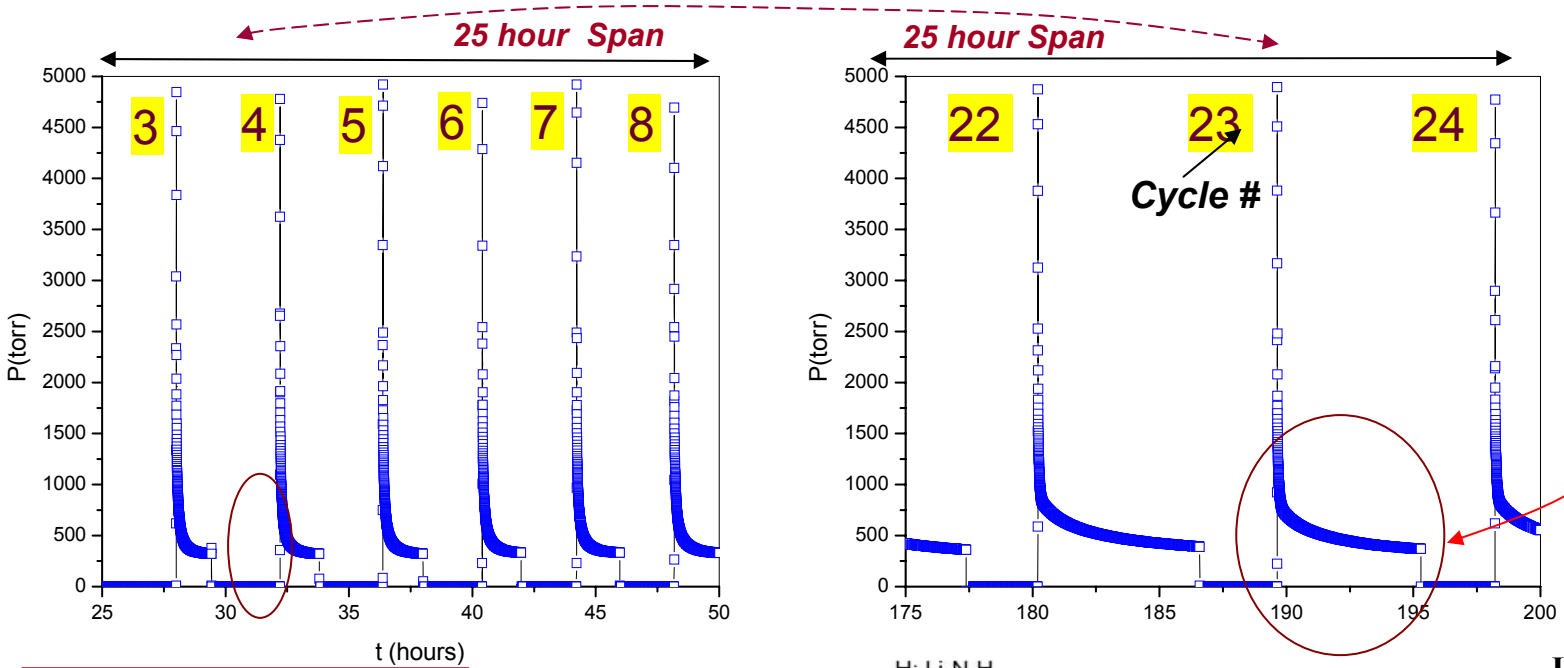


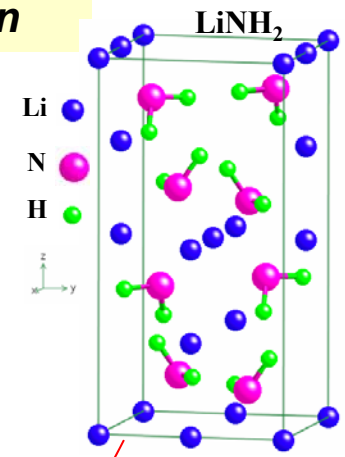
Sievert's Apparatus

Experimental Details of Pressure Cycling

Sample Data to Show Change in Kinetics During Pressure Cycling of Li_2NH - $LiNH_2$

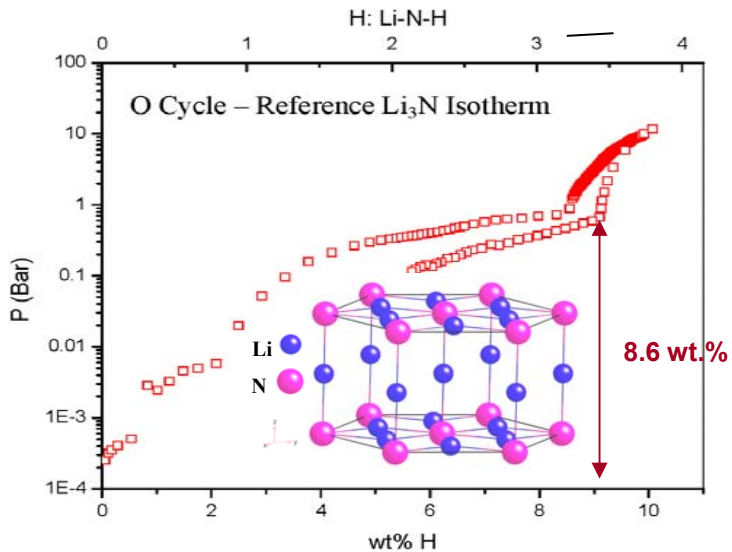
Capability: 120 Bar **Pressure cycling @ 255°C (3-8 and 22-24 cycles) Shown**

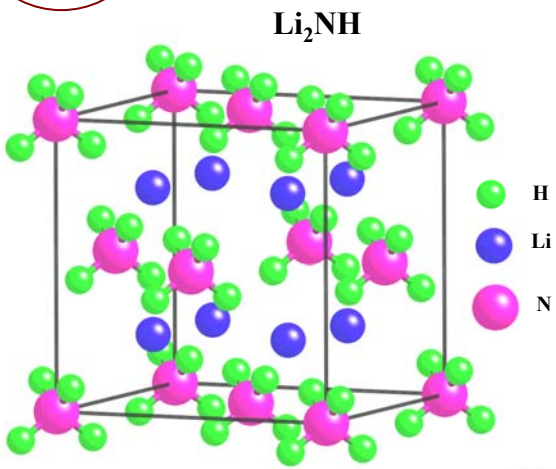




Importance:

One can visually see the changes in kinetics as a function of pressure cycles on the computer display. Selected portions of cycling data are shown for clarity.





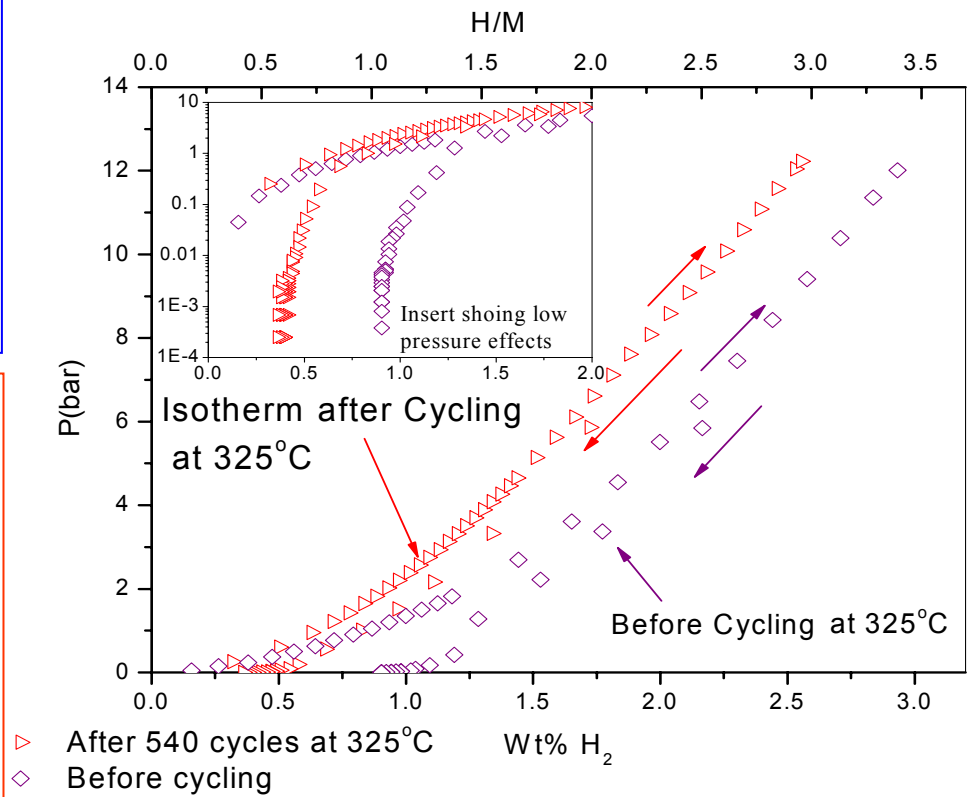
Pressure Cycling: Effect of Impurity (100ppm O_2 impurity in UHP H_2) Gas {Li_3AlH_6+3$LiNH_2$ (4% $TiCl_2$ + $^1/_3AlCl_3$)} at 325°C

Experiment

1. Cycling performed on Li_3AlH_6-$LiNH_2$ binary using impure hydrogen described above: 540 pressure cycles performed using 100 ppm O_2 mixed with UHP hydrogen. Catalyzed sample from MHCoE partner at Univ. of Utah.
2. Equilibrium Isotherm taken before and after 540 pressure cycles at 325°C.

Results

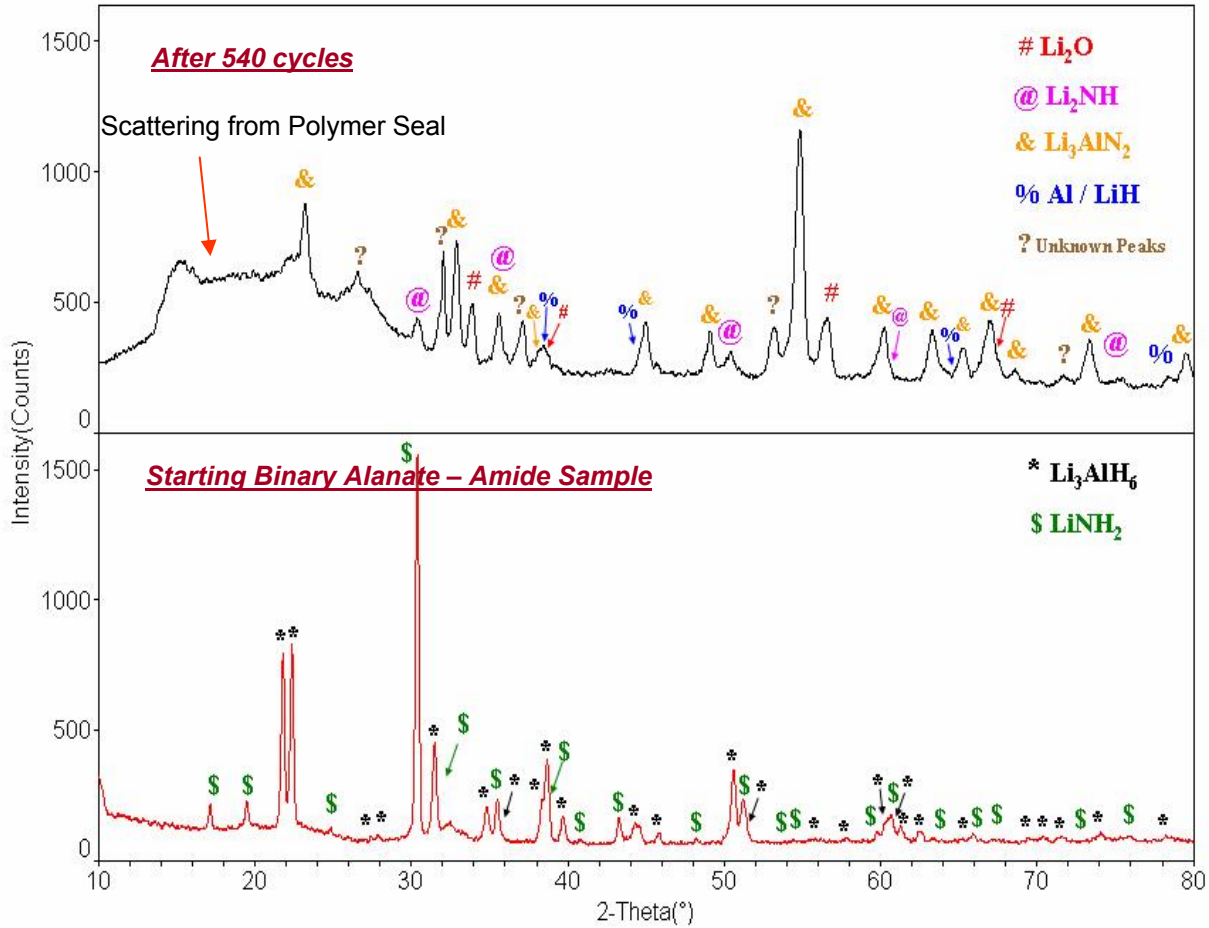
- After 540 pressure cycles (325°C, 2 bar), a loss of ~0.6 wt.% H_2 capacity was observed in Li_3AlH_6-3$LiNH_2$ system.
- When compared with Li_2NH-$LiNH_2$ system (~2.6% wt. % H_2 loss after ~500 cycles) in industrial H_2 (H_2O~32 ppm, O_2~10ppm), the (H_2) capacity loss in this system is lower (under similar cycling conditions). This may be due to presence of other impurities in the industrial H2 gas .
- The Li_2NH, Li_3AlN_2 and Li_2O are major phases. Smaller amounts of LiH or Al phases are also present.
- The loss in H_2 storage capacity can be mainly attributed to formation of Li_2O, and LiH/Al.
- Overall, the H_2 capacity losses are not very significant due oxygen alone.



Significance

- The small loss in H_2 (~0.6 wt.% H_2) capacity in Li_3AlH_6-3$LiNH_2$ system after 540 cycles is encouraging.
- Formation of Li_3AlN_2 is confirmed however it may be hydrided at higher pressures.

Ex-Situ X-Ray Diffraction Analyses: Effect of Impurity (100ppm O_2 impurity in UHP H_2) Gas Upon Pressure Cycling of {Li_3AlH_6+3$LiNH_2$ (4% $TiCl_2$ + $^1/_3AlCl_3$)} at 325°C



Experiment

- XRD characterization of pressure cycled hydride (before and after).

*$Li_3AlH_6 \leftrightarrow 3LiH + Al + 3/2H_2$ (2.4 wt.%) $\Delta H^0 = 32\ kJ/molH_2$

*$3LiNH_2 + 3LiH \leftrightarrow 3Li_2NH + 3H_2$ (4.9 wt%) $\Delta H^0 = -45\ kJ/molH_2$

Results

- XRD results show that there is residual Li_2NH along with Li_3AlN_2 and Li_2O as major phases, and LiH or Al phases are present.
- It is interesting to see the Imide phase after cycles and possible presence of Al metal

Significance

- After cycling there is still the Li_2NH phase present, besides the Li_2O, and the new Li_3AlN_2 phase.

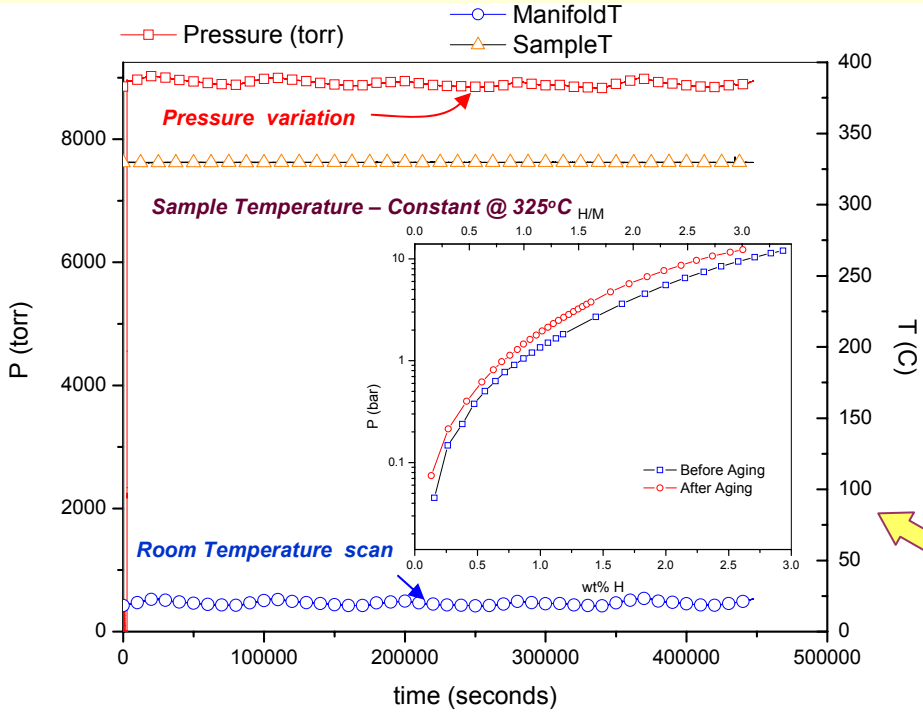
*References

C.M Andrei, H.W. Brinks, B.C. Hauback et al. J. Alloys and compds,395 307-312, 2005

J. Lu, Z. Z. Fang, and H.Y. Sohn, J. Phys. Chem. B 110(29), 14236-14241, 2006

Thermal Aging: Effect of Impurity (100ppm CO impurity in UHP H_2) Gas {Li_3AlH_6+3$LiNH_2$ (4% $TiCl_2$ + $^1/_3AlCl_3$)} at 325°C

Impurity Impact



Pressure data taken every 5 seconds, every 256 data point is shown for clarity

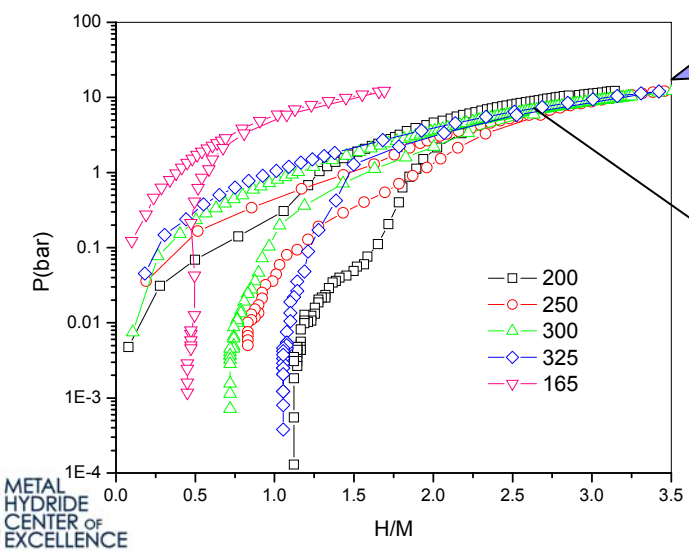
Experiment

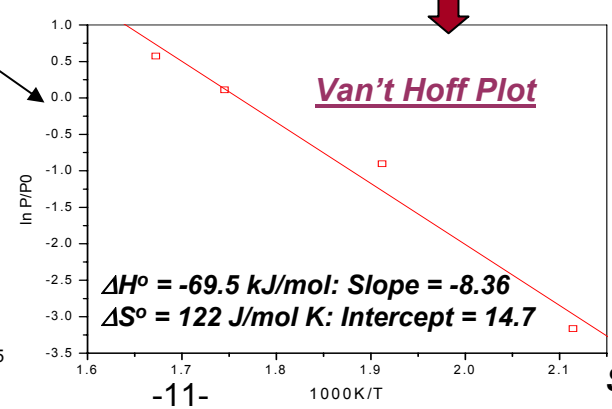
1. Absorption isotherms of $3LiNH_2$-Li_3AlH_6 before and after thermal aging at 325°C at ~ 9500 Torr for 125 hours using 100 ppm level of carbon monoxide in UHP hydrogen (shown in inset). Top–left
2. Absorption/desorption Isotherms (up to 9500 torr) taken at different using UHP Hydrogen (*no impurities*) – bottom left.

Results

1. *Thermal aging Impurity Tests:* Negligible increase in pressure observed after 125 hours of aging at 325°C. Thermal aging data is shown in Figure in red (squares), showing negligible change in the capacity. Periodic fluctuation in hydrogen pressure is due to room temperature fluctuation; but this is always expected.
2. *P-C-T Measurements:* Low pressure isotherms (up to 10 bar hydrogen and up to 325°C).
3. From van't Hoff Plot ΔH°= -69 kJ/mol

Absorption/Desorption isotherms on $3LiNH_2$ - Li_3AlH_6



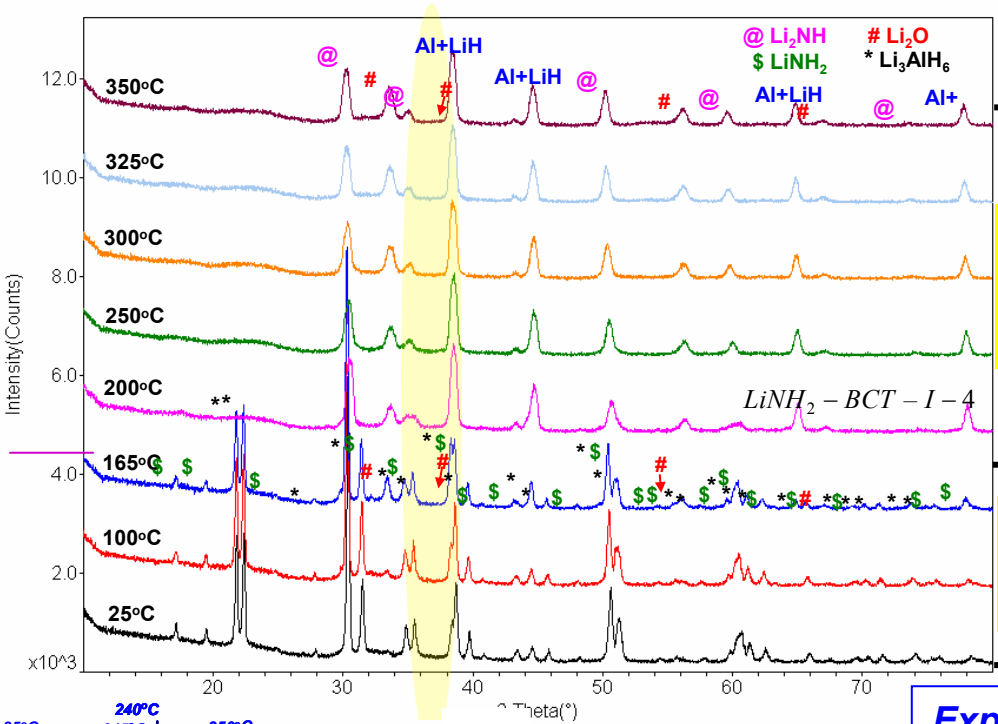


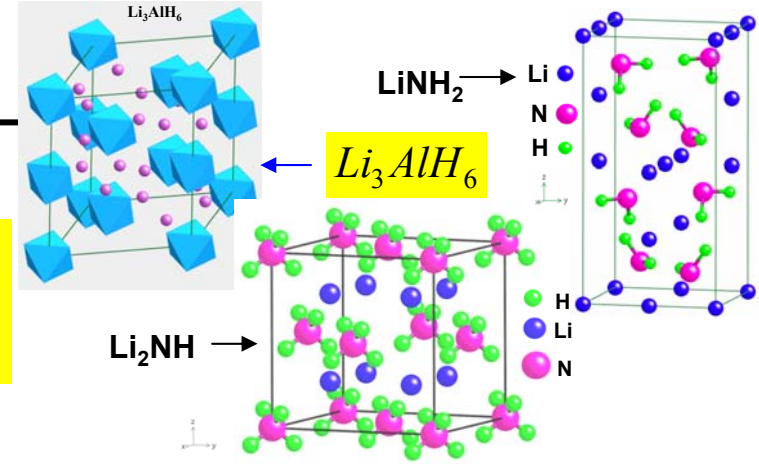
Significance

Thermally aged $3LiNH_2$-Li_3AlH_6 with CO impurity does not show any significant loss of hydrogen.

In-situ De-hydriding from RT to 350°C (under He atmosphere): Li_3AlH_6- $3LiNH_2$

Mechanistic Studies



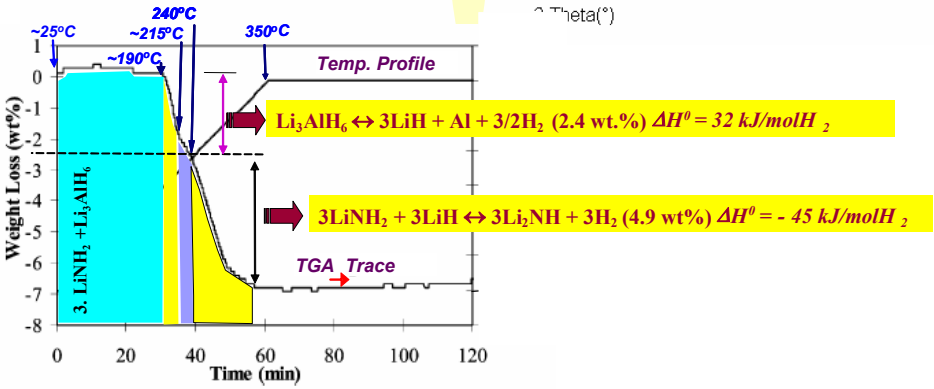


References:

Li_2NH: T. Noritake, H. Nozaki, M. Aoki, S. Towata, G. Kitahara, Y. Nakamori and S. Orimo, *J. Alloys Compd.* 393 (2005), 264-268.

$LiNH_2$: -K. Miwa, N. Ohba, S. Towata, Y. Nakamori, and S. Orimo *Physical Review*, B71(2005), 195109.

Li_3AlH_6: H.W. Brinks and B.C. Hauback *J. Alloy and Compd.*, 354 (2003), 143-147.



TGA Data from MHCoE Partner, University of Utah (Dr. Fang)

References

C.M Andrei, H.W. Brinks, B.C. Hauback et al. J. Alloys and compds,395 307-312, 2005

J. Lu, Z. Z. Fang, and H.Y. Sohn, J. Phys. Chem. B 110(29), 14236-14241, 2006

Experiment

To *determine Phase Stability* by Increasing Temperature of Li_3AlH_6-$3LiNH_2$ Binary Hydride by in-situ dehydriding.

Conclusion

Up to ~200°C, the binary phases are stable. In-situ dehydriding proceeds according to overall solid state reaction beyond 150°C:

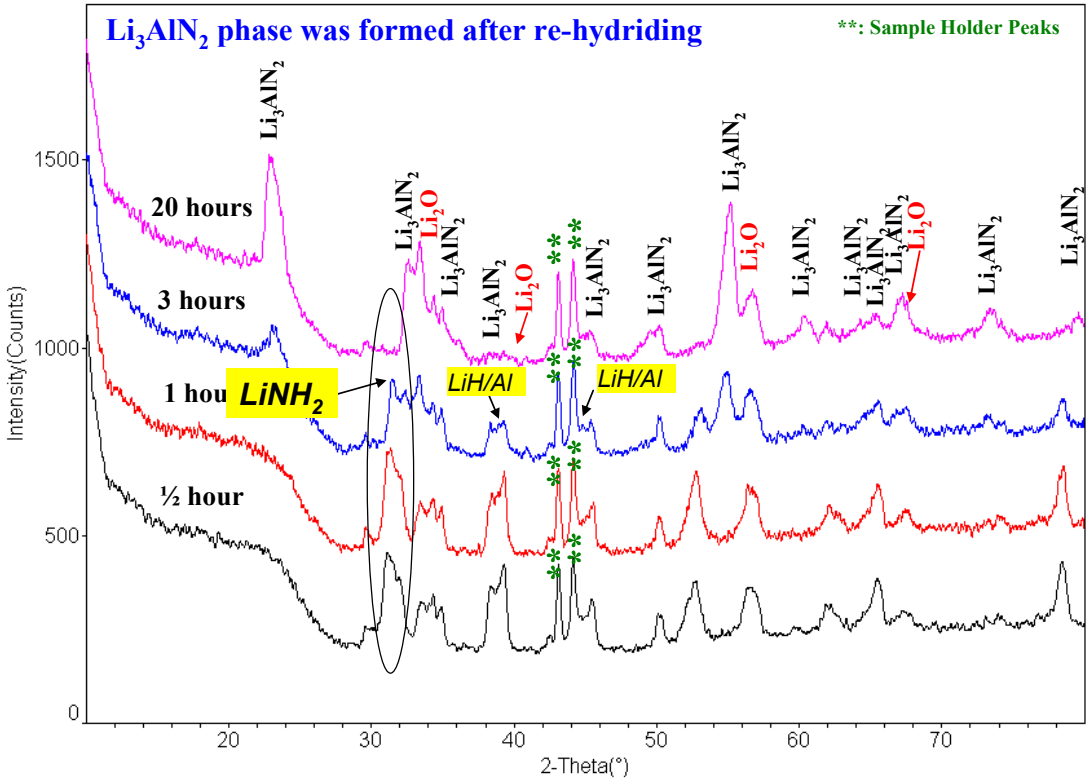
Li_3AlH_6+$3LiNH_2$↔Al+$3Li_2NH$+$^9/_2H_2$ ~7.1wt.%.

Intermediate reactions are shown along with the TGA Figure- left. It appears that Al precipitates out along with LiH phase.

METAL HYDRIDE CENTER OF EXCELLENCE

In-situ *Rehydriding* Binary Li_3AlH_6-$3LiNH_2$ (~7.1 wt%) - (4% $TiCl_2$ - $^1/_3AlCl_3$)

Mechanistic Studies



Experiment

After desorption we re-hydrided the desorbed mixtures of the original $3LiNH_2$-Li_3AlH_6. The sample was aged in the X-ray Diffractometer and many patterns taken at different intervals. Only some patterns are shown in this Figure taken at 325°C under 2 bar hydrogen pressure recoding from ½ hour to 20 hours.

Results

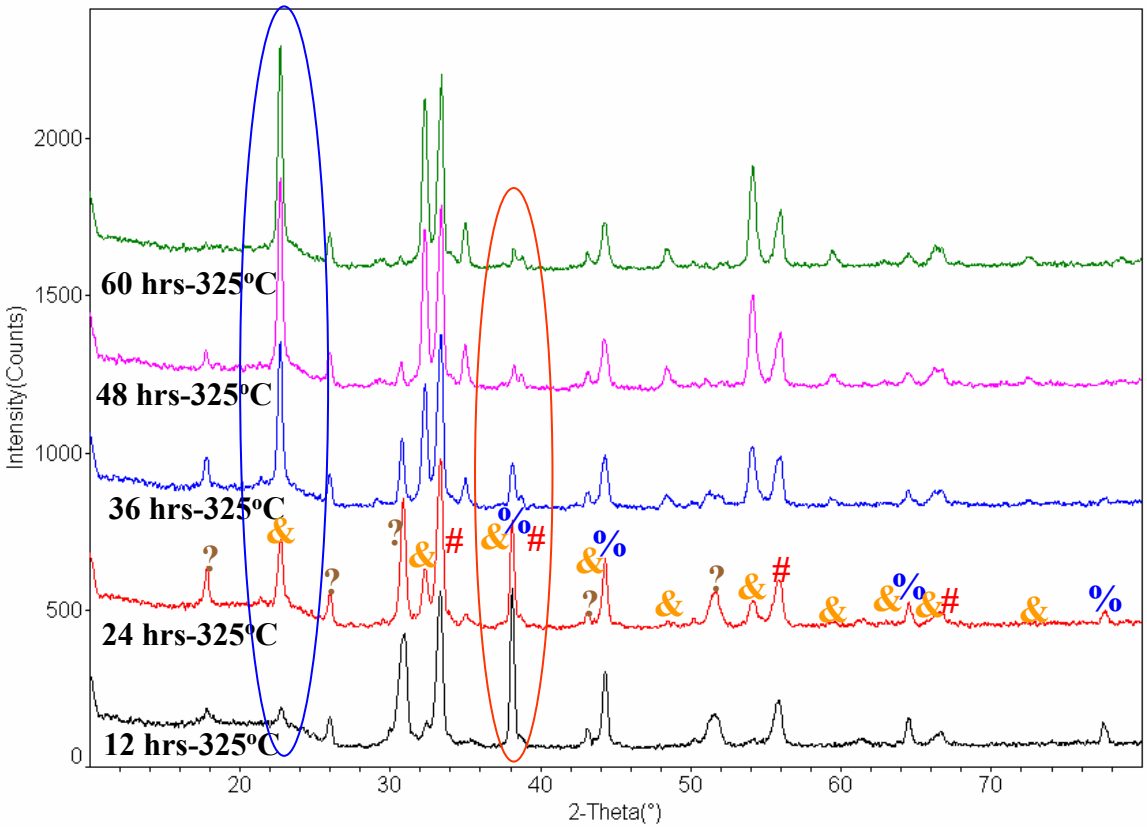
Re-hydriding of $3LiNH_2$-Li_3AlH_6 of the disproportionated phases that contained mainly Li_2NH, LIH, and Al as material phases at 325°C under 2 bar hydrogen.

Results show that initially $LiNH_2$ (amide) phase forms along with other phases, but later after 20 hours of aging a new Li_3AlN_2 phase forms as shown above.

Significance

- Amide phase reformation during in-situ rehydriding shows reversibility.
- Li_3AlN_2 does not appear to effect reversibility at ~10 bar pressures.

XRD- Isothermal (325°C) Aging of Li_3AlN_2 Phase (Dehydrided Binary Li_3AlH_6-$3LiNH_2$) up to 60 hours in He Atmosphere

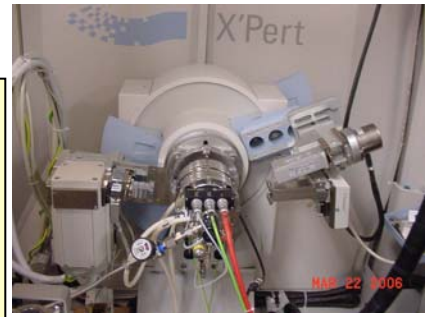


& Li_3AlN_2

% Al / LiH

Li_2O

? Unknown Peaks



Experiment

To determine if new nitride phases forms instantaneously or slowly during as a function of time at 325°C

Results

1. A new phase Li_3AlN_2 (designated as "&") forms. Intensity of the Bragg peaks of this phase increases from 12 to 60 hours. Thus this phase forms slowly as the time is increased. (Please Note: in the blue circled area of the Bragg peaks are at ~22° 2θ)
2. Al and LiH Bragg Peaks decreased in intensity with increasing time; thus amount of Al and LiH phases decrease as function of time. (Please Note: in the red circled area the Bragg peaks are at ~38° 2θ)

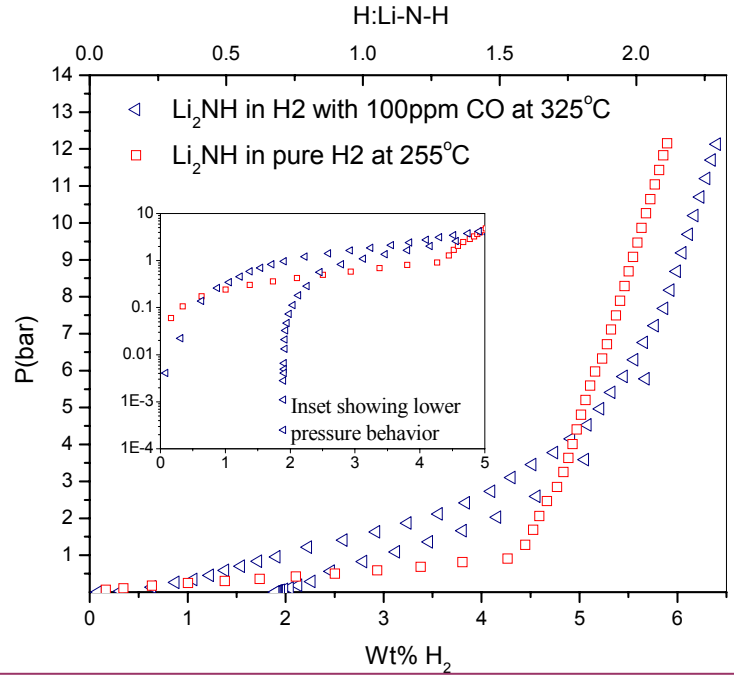
Please Note: This experiment is independent conducted, and is not the same as the results in the previous slide.

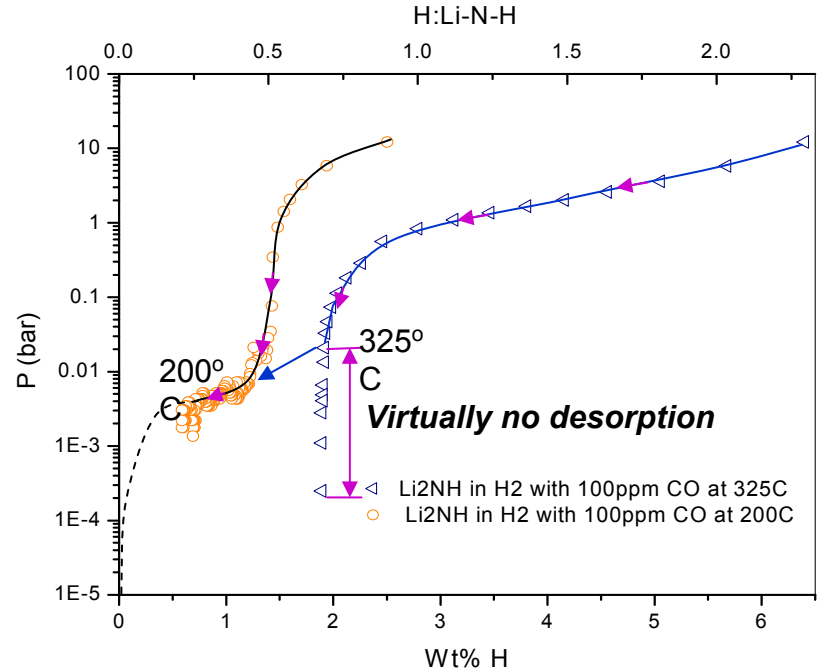
Significance

The Li_3AlN_2 Phase formation is very predominant after 60 hours of isothermal aging at 325°C; with slow formation starting at ~ 10 hours of aging.

Effect of 100ppm CO impurity in UHP Hydrogen: UNR Baseline Sample of $LiNH_2$

Impurity Impact





Experiment: **Absorption Isotherm (Left) CO- impurity PCI taken at 325°C (No cycling). Reference Isotherms shown are taken 255°C in UHP hydrogen (Red) and the one with 100 ppm carbon monoxide (blue) at 325°C. Desorption isotherm shown on the right.**

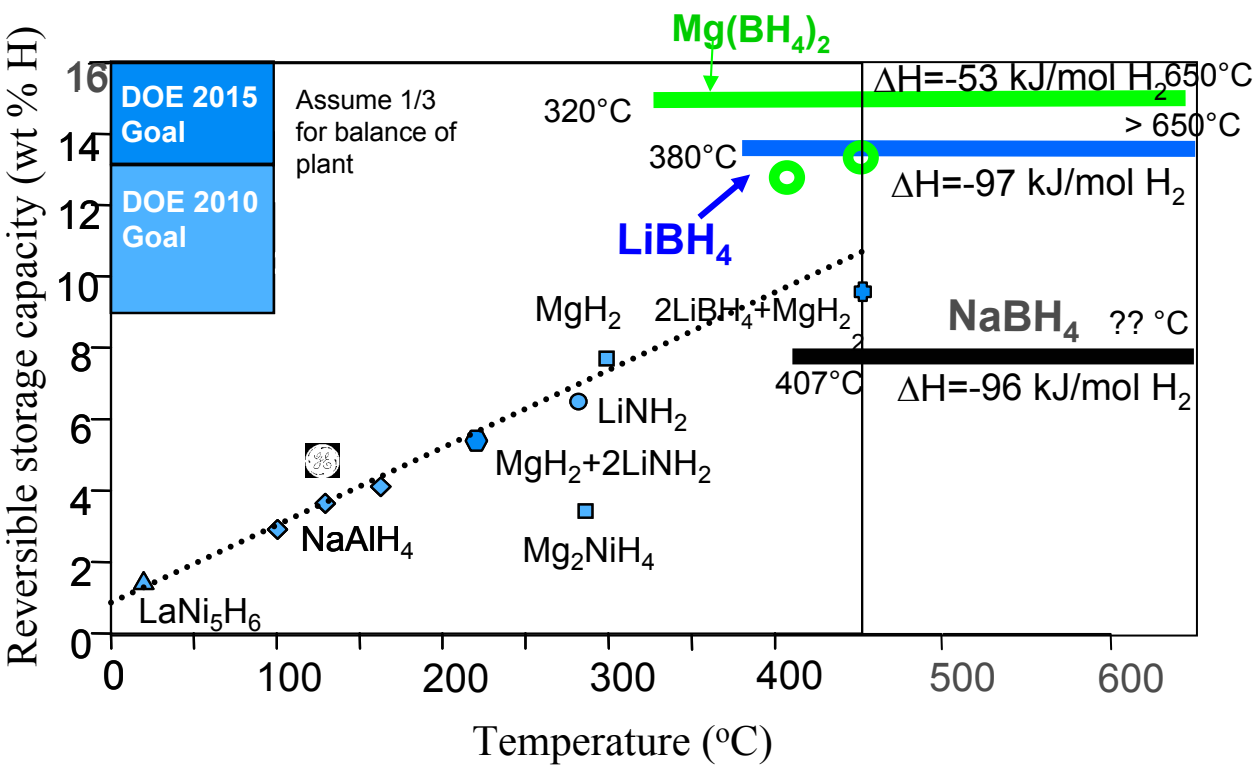
Conclusions: Carbon Monoxide Impurity Effect $LiNH_2$:

- **Thermodynamic properties do not show any significant change in Sievert's data taken with 100ppm CO+UHP H_2. These are shown by the isotherms (top left)**
- **It appears that the CO contamination is not a critical issue for the amide-imide system. (cycling not performed). Note that the isotherm taken using pure hydrogen was available from our prior work at 255°C, whereas the isotherm taken with 100 ppm CO in UHP H_2 is taken at 325°C is from our current study. This results in minor changes in the hydrogen capacities and pressures.** ***(OVERALL, NO SIGNIFICANT EFFECT).***
- **From these results it is implied that during desorption the conversion of amide ($LiNH_2$) to imide (Li_2NH) is not complete. It is beneficial if we drop the temperature down from 250°C to 200°C, during desorption, to remove more hydrogen. (Please see Figure - Top right)**

Mechanistic Studies on $Ca(BH_4)_2$ and $Mg(BH_4)_2$

Experiments

1. In-situ and ex-situ x-ray Diffraction experiments were performed $Ca(BH_4)_2$ and $Mg(BH_4)_2$ by varying the temperature to determine structural phase transitions
2. Vapor pressure measurement of $Mg(BH_4)_2$ were made to identify phase stability under vacuum (10^{-4}-10^{-5} Torr) and temperatures (up to 275°C).



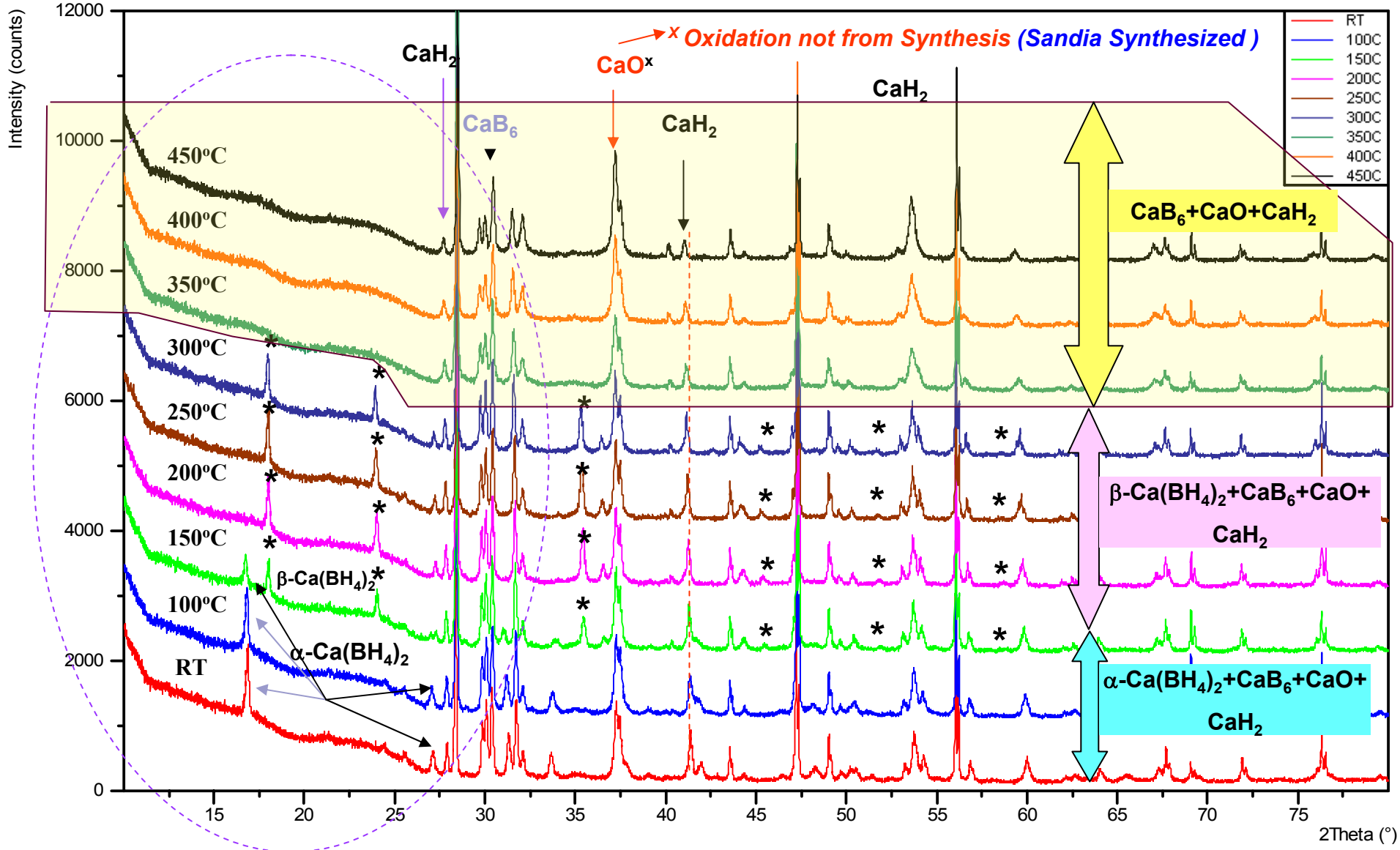
Significance

1. From the graph to the left (courtesy of GE), it is evident that $Mg(BH_4)_2$ has very high hydrogen content (~15 wt.% H_2) and lower enthalpy of hydriding (ΔH ~ -53 kJ/mol) as compared to $LiBH_4$.
2. $Ca(BH_4)_2$ is also being considered as a potential candidate and it is necessary to obtain information on structural transitions.
3. It is of interest to determine the vaporization behavior of these materials ($Mg(BH_4)_2$ is in progress and work on $Ca(BH_4)_2$ will be undertaken in FY '08)

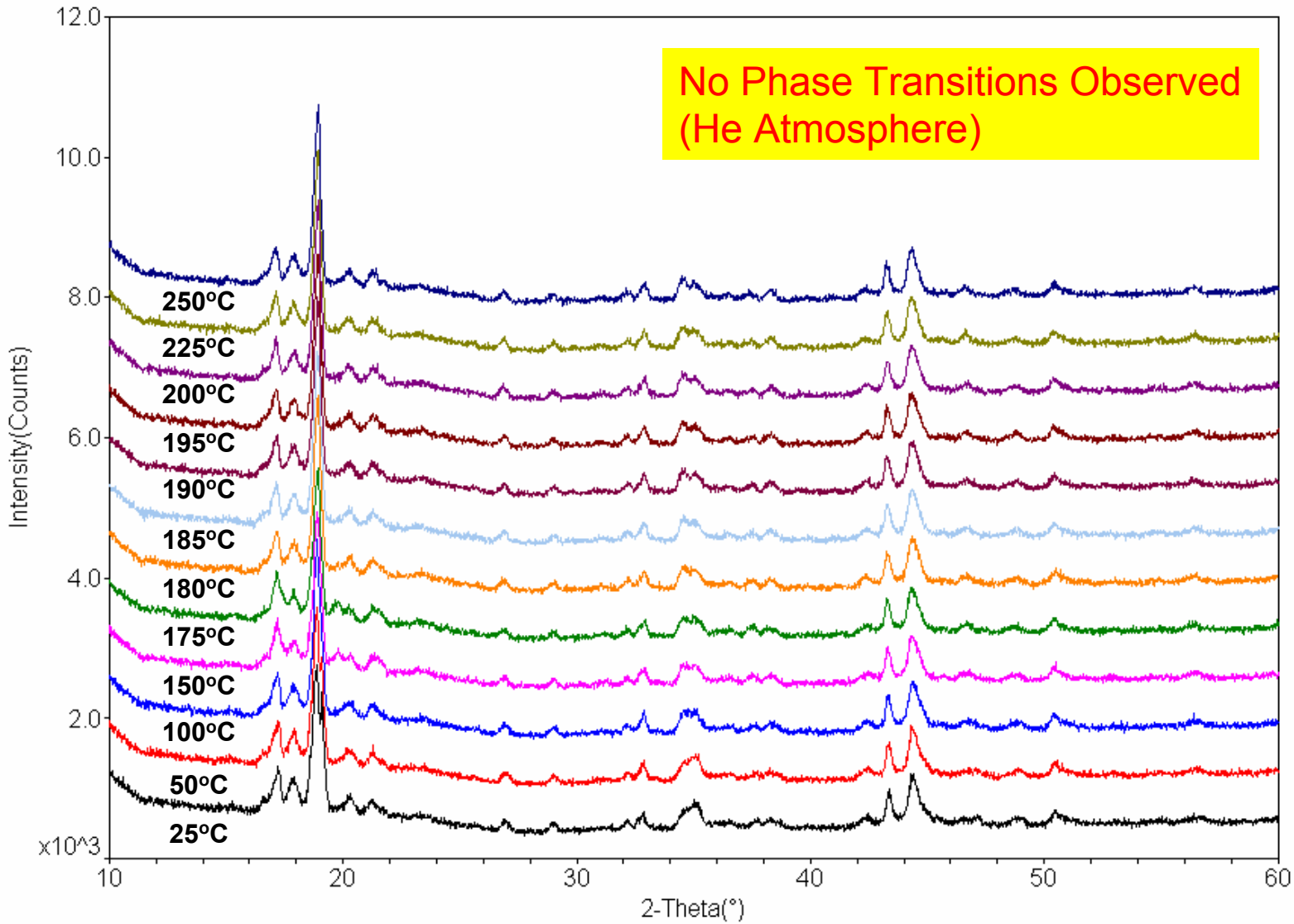
Phase Transitions in Catalyzed Sandia's $Ca(BH_4)_2$

Mechanistic Studies

- The as- synthesized sample from Sandia shows α-$Ca(BH_4)_2$ + CaB_6 phases and are stable up to 100°C. A new β-$Ca(BH_4)_2$ phase (*) forms at ~150°C and is stable up to 300°C.
- The major stable phases in the pattern are labeled in the Figure below.



Experiments Performed to Observe Phase Transitions $Mg(BH_4)_2$ during heating from 25°C to 250°C



Torsion Effusion Gravimetric Apparatus

Instrumentation:

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

Pressure Measurements:

A pair of Knudsen Cells with opposed orifices are suspended by a Pt-10%Ni torsion wire with known stiffness (Please 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.:

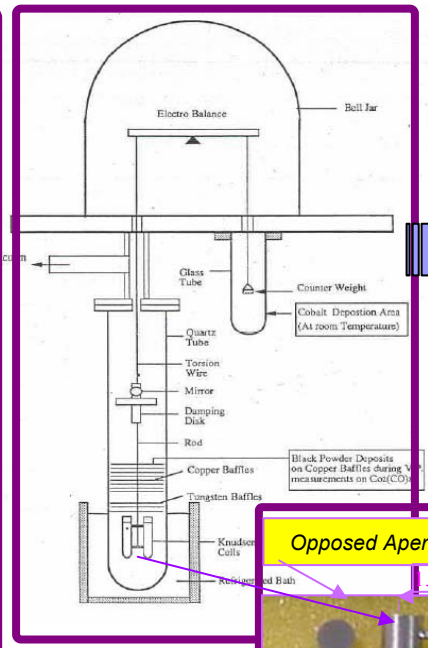
$$P_T = \frac{K(2\theta)}{(a_1 f_1 d_1)+(a_2 f_2 d_2)}$$

'K' is the Fiber Constant

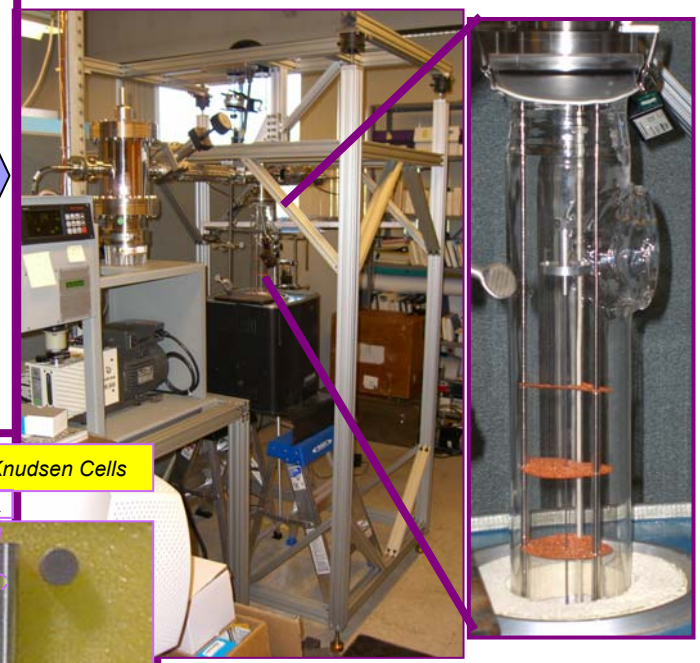
Typical Pressure, Temperature and Sample Size:

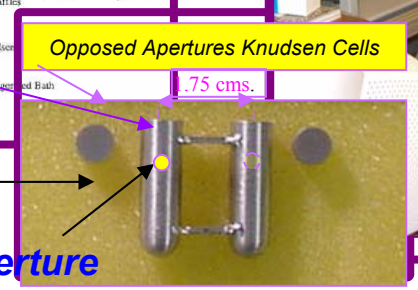
- **Turbo Pump vacuum (<10^{-5} Torrs)**
- **~ 1 gram**
- **Temperature capability: -20°C to 600-700°C**

. **Mo Knudsen Cells Used**



UNR Cahn Balance D100 – Digital Balance





Mo-Cells

Aperture

Molecular Weight Measurements 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:

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

METAL HYDRIDE CENTER OF EXCELLENCE

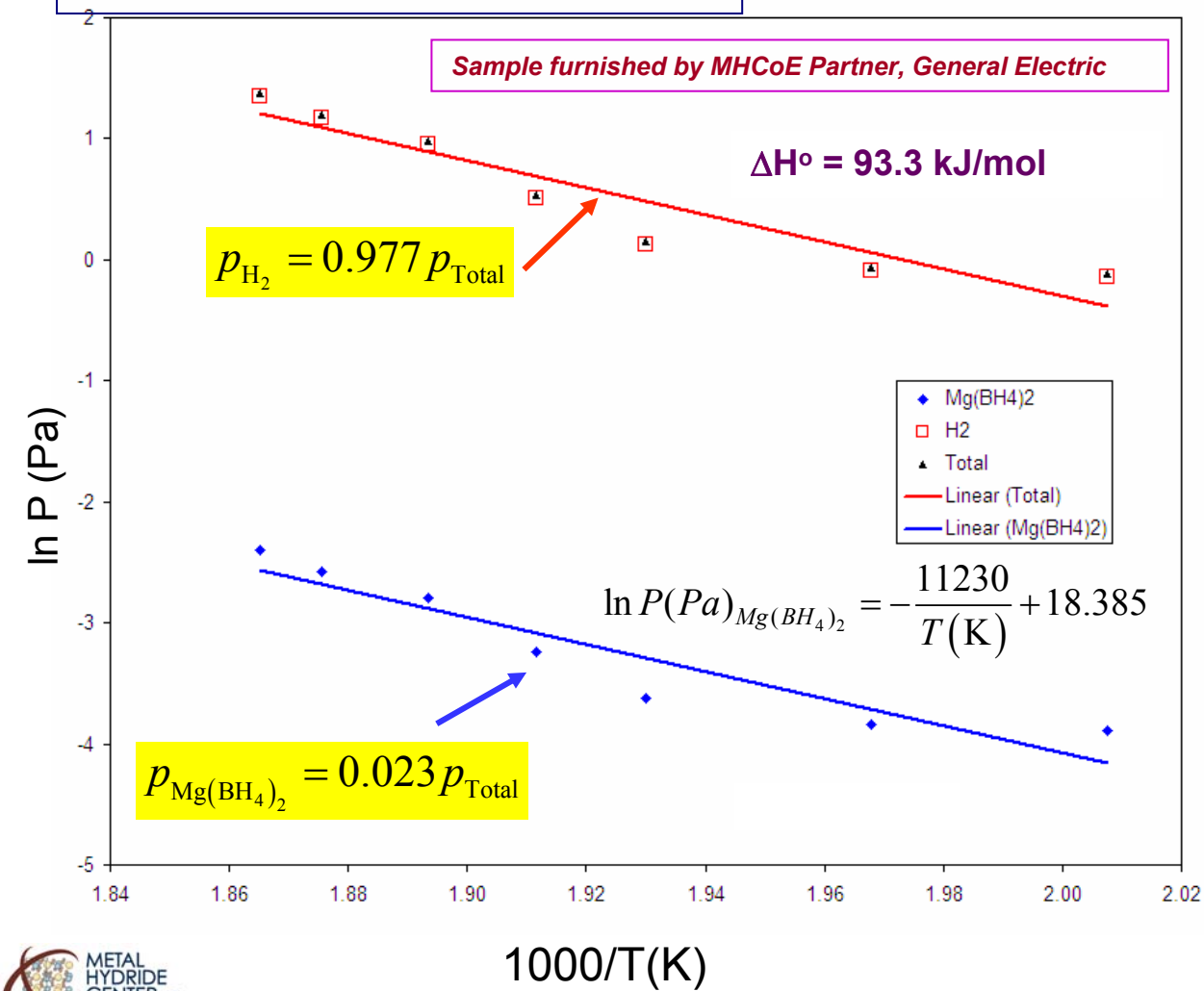
Vaporization Behavior of $Mg(BH_4)_2$

Proposed Disproportionation of $Mg(BH_4)_2$ up to 250 °C

$$Mg(BH_4)_2(s) \rightarrow 0.018\,Mg(BH_4)_2(s) + 0.982\,Mg(s) + 1.964\,B(s) + 3.928\,H_2(g)$$

Complete Decomposition of $Mg(BH_4)_2$ may occur at T > 250 °C

$$Mg(BH_4)_2(s) \rightarrow Mg(s) + 2B(s) + 4H_2(g)$$



Summary

- No detrimental cations appear to be effusing out → stable
- Partial pressure of $Mg(BH_4)_2$ is low up to ~250°C
- Average Mol. Wt. of effusing gas is 2.42 g/mol. This suggests that majority hydrogen is major component in vapor phase.
- At 225 °C

P_{H2} = 8.8×10^{-6} atm. (8.9×10^{-2} kPa

$P_{Mg(BH4)2}$ = 2.03×10^{-7} atm. (2×10^{-5} kPa)

- At T > 275 °C rapid decomposition and vigorous hydrogen release is expected.
- More work in Progress

Disproportionation Analysis for $Mg(BH_4)_2$

The average molecular weight determined from our experiments is 2.42 g/mol. This implies that the vapor phase is predominantly hydrogen.

The XRD pattern of the residual powder (dark brown) shows evidence of pure Magnesium. Although, we did not detect Boron, we suspect that it exists in amorphous phase. Assuming that a small amount of $Mg(BH_4)_2$ exists in the vapor just above the solid:

$$\mathrm{Mg(BH_4)_2(s)} \rightarrow (1-b)\mathrm{Mg(BH_4)_2}(g) + (b)\mathrm{Mg}(s) + (2b)B(s) + (4b)H_2(g)$$

Equations for MW of individual vapor species and average molecular weight

$$m_{H_2} = \left[\frac{(4b)M_{H_2}^{1/2}}{(1-b)M_{Mg(BH_4)_2} + (4b)M_{H_2}}\right]^{-2} \qquad m_{Mg(BH_4)_2} = \left[\frac{(1-b)M_{Mg(BH_4)_2}^{1/2}}{(1-b)M_{Mg(BH_4)_2} + (4b)M_{H_2}}\right]^{-2}$$

$$M_{avg} = \left[\frac{(1-b)M_{Mg(BH_4)_2}^{1/2} + (4b)M_{H_2}^{1/2}}{(1-b)M_{Mg(BH_4)_2} + (4b)M_{H_2}}\right]^{-2}$$

b=0.982

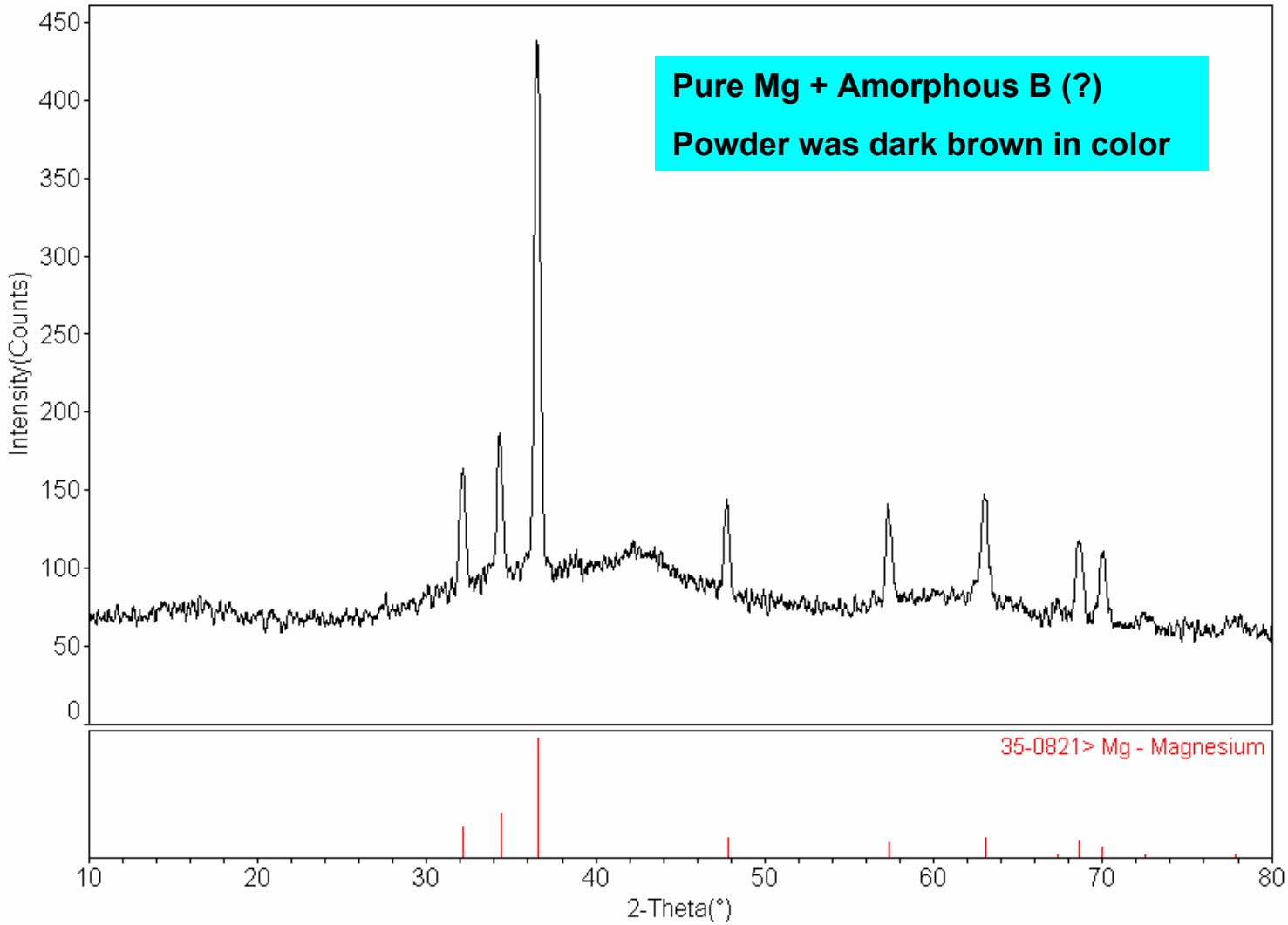
Partial Pressure

$$\frac{p_{Mg(BH_4)_2}}{p_{TOTAL}} = \left[\frac{(1-b)M_{Mg(BH_4)_2}^{1/2}}{(1-b)M_{Mg(BH_4)_2}^{1/2} + (4b)M_{H_2}^{1/2}}\right] = 0.023 \qquad \frac{p_{H_2}}{p_{TOTAL}} = \left[\frac{(4b)M_{H_2}^{1/2}}{(1-b)M_{Mg(BH_4)_2}^{1/2} + (4b)M_{H_2}^{1/2}}\right] = 0.977$$

Complete disproportionation of $Mg(BH_4)_2$ cannot be ruled out as the measured molecular weight of the effusing species is within acceptable uncertainty.

$$\mathrm{Mg(BH_4)_2(s)} \rightarrow \mathrm{Mg}(s) + (2)B(s) + (4)H_2(g)$$

XRD Pattern of Residual Powder After Vapor Pressure Measurements



Future Work (FY 2007)

1. ***Effect of Impurities on Complex Hydrides***

- Continue pressure cycling studies and determine impurity effects (100 ppm O_2, CO, CO_2, H_2O, NH_3, and others mixed with UHP H_2) on complex hydrides. High pressure cycling (upto ~120 bar) studies are in progress using the automated cycling/aging apparatus.

2. ***Mechanistic Studies - In-Situ Neutron and X-ray Diffraction Studies on Hydriding/Dehydriding***

- In-situ X-ray (UNR) and Neutron (user facilities) Diffraction studies during hydriding/dehydriding will be performed on $Mg(BH_4)_2$ and $Ca(BH_4)_2$. We also expect to obtain newly developed hydride samples from MHCoE partners and studies will be initiated on them as well.

3. ***Contribution to the MHCoE – Theory Groups***

- During the rest of the FY'07 we plan to interact with computational modeling researchers in the MHCoE group to discuss possible UNR contribution to the *theory efforts of the Center*, towards understanding of the structure and the dynamics of hydriding and dehydriding.

4. ***International collaboration with European Union (EU)***

- We have started collaboration with the EU team on developing catalysts for the Li based hydride systems. We at UNR had discussions with the DG Joint Research Centre - Institute for Energy, Westerduinweg, Holland, and agreements are being worked out by our University at this time. Detailed work at UNR is expected to start in FY 08.

Future Work (FY 2008 and Beyond)

A. Impact of Impurities on Long term Durability of the Complex Hydrides

Our work on pressure cycling and thermal aging with impurity mixed UHP H_2 will continue. The emphasis will be on complex hydrides that show the most promise. We also recommend high P-T Thermal Aging impurity mixed UHP H_2 on hydrides that are irreversible to understand surface contamination and diffusion related effects.

We plan to perform trace impurity studies on promising materials developed by different National Laboratories or MHCoE partners by the methodology already developed in our laboratory.

B. Fundamental Mechanistic Studies on Complex Hydrides

- *Vaporization Mechanisms of Complex Hydrides*
  Vapor phase disproportionation of $Ca(BH_4)_2$, $LiBH_4$, and other hydrides will be performed.
- *Phase Diagram Determination of Mixed Complex Hydrides*
  A new subtask on the development of binary experimental phase diagrams of various alanate-amide, borohydride-amide mixtures is proposed. Complementary modeling efforts using CALPHAD approach will be also undertaken. There is a need for High Pressure Differential Scanning Calorimetry for direct measurement of thermodynamic data such as enthalpy.
- *Hydrogen Lattice Dynamics Studies on Complex Hydrides (UNR- Univ. of Rome IPHE Proposal)*
  "Hydrogen Dynamics, Lattice interactions, and Atomic-scale Structure of Complex/Chemical Hydrides" has been proposed as an IPHE partnership. This study will provide insights to understand effect of defects and hydrogen dynamics in complex hydrides and elucidate catalyst mechanisms. Collaborators will include Prof. Cantelli (Rome), and Chandra-Jensen, (USA). Prof. Cantelli will perform *Anelastic spectroscopes* using deuterated Ca or Mg borohydrides. These hydrides will be prepared at UNR and shipped to Rome. Neutron diffraction studies will be performed at NIST/IPNS to correlate the anelastic data by UNR researchers.

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																	
UNR	5.4	Extrinsic cycling tests* *Effect of Impurities and cyclic tests on Li-Mg-N-H system																	
	▲	Portfolio Relocation Decision Point (Project bars)																	
	◆	Milestone (Subtask bars)																	
	●	Output (Task bars)																	

We anticipate meeting the milestones for FY 2007

Acknowledgments

- DOE-MHCoE for the support of this Project
- Dr. Zak Fang of the University of Utah for sending samples of mixed-Alantes
- Dr. Ewa Ronnebro and Dr. Lennie Klebanoff of Sandia National Laboratory for sending Ca-Borohydride samples
- Dr. J.C. Zhao of General Electric for sending Mg-Borohydride samples
- Dr. Ashfia Huq (ORNL), Dr. James Richardson, and Mr. Evan Maxey (IPNS-Argonne National Laboratory) for their help with neutron diffraction experiments. These publications are *in print* in 2007.