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Crystal Gateway Marriott, Arlington, VA May 20, 2009

DOE Hydrogen Program

Effect of Trace Elements on Long-Term Cycling/Aging Properties and Thermodynamic Studies 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 – ~80%

Barriers Addressed

A. System Weight and Volume
D. Durability/Operability
E. Charge/Discharge Rates

Budget

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

Contractor share (5yrs.) : $ 301 K

Funding received in FY07 : $ 250 K
(Includes funding for major equipment)

Funding received in FY08: $ 100 K
So far

Funding for FY09: As Planned

MHCoE Partners

Active Current Collaboration

- Sandia National Laboratories, CA – *L. Klebanoff, E. Ronnebro (now at PNNL)*
- *Ohio State University – Dr. J.C. Zhao*
- Oak Ridge National Laboratory, Neutron Center, Dr. *A. Huq*
- *University of Geneva, Switzerland, Prof K. Yvon, Prof. R. Cerny, Dr. D. Phanon, Dr. N. Penin*
- *University of Rome, Prof. R. Cantelli*
- *University of Paris/CNRS- Dr. M. Latroche*

Future Collaboration

- *NIST Gaithersburg, Maryland - Dr. Terry Udovic*
- *Brookhaven National Laboratories, NY – Dr. James Reilly*
- *European Commission - DG Joint Research Centre - Institute for Energy, Petten- Dr. Constantina Filiou*

Relevance

A. General:

- The "Grand Challenge" program launched by DOE for research and development of hydrogen storage technologies was designed to meet targets for commercially viable systems for vehicular applications.
- Research is being conducted at different three hydrogen storage Centers of Excellence, amongst them is our *Metal Hydrides Center of Excellence* to address issues of board hydrogen storage technical barriers.
- At Uni. of Nevada, Reno (UNR) we address topics related to: (1) System weight and volume, (2) Durability/operability, and (3) Charging and discharging Rates and *part* of life cycle assessment addressing the environmental impact for hydrogen storage (excluding costs).

B. Impact of Impurities on Long-term Durability and Understanding Reaction Pathways of the Complex Hydrides

1. Objectives:

- Determination of the effect of ppm level impurities in H_2 gas, and impurities and defect in light-weight storage materials.
- Li-N light weight based compounds used to evaluate long-term durability,
- Understanding the reaction pathways for both *developing new materials with enhanced hydriding properties, modifying or controlling reaction pathways for improved performance*
- Results obtained in this research are expected to have direct impact on addressing of the barriers to improve the kinetics, lower hydrogen release temperatures, and longer cycle life.

2. Relevance to Addressing On-board Hydrogen Storage Specific Technical barriers:

1. System Weight and volume: Identified *materials systems: Li-N-H, Li-Al-N-H and other light weight materials for studies.*
2. Durability: *Addressed these issues by using industrial hydrogen as well as various individual impurity gas mixtures in hydrogen gas.*
3. Charging /Discharging: *Reaction pathways found; the work is in progress*
4. Life cycle assessments: *Addressed only the environmental impact for hydrogen storage via relating to effects of oxygen, water vapor and related gas effects.*

Approach

A. Basis for Selection of Li-N-H system Was To Address the barrier on System weight:

- **Light-weight Li-N-H system with ~10.5 wt.%H capacity at the start of the program.**
- **Results are expected to have broader implications to give insight to other hydrides (mixtures of amides-alanates, amide-magnesium hydrides and others).**

B. Durability/Operability and Life cycle environmental effects

- ***Trace Impurity Impact on Long-term Durability:*** **In practical applications, trace impurities in commercial hydrogen gas (such as dispensed at future H_2 gas stations) will have an impact on the hydrogen loading capacities during periodic recharging with fresh hydrogen.**
- ***Approach:*** **To determine the effects of gaseous trace impurities (ppm levels of O_2, CO, H_2O, CH_4, NH_3 etc. in H_2) on complex hydrides after prolonged *hydrogen pressure cycling and thermal aging. Note: NH_3 is not a common impurity in H_2 gas itself, but there is an potential of ppm level emission at higher temperatures, so we checked its environmental effect.***
- ***Update:*** **Effects of using *industrial hydrogen* up to 1100 cycles in Li-N-H system are already 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. These results may be extrapolated to higher cycles.**

C. Addressing Charging/Discharging Rates and Applied Thermodynamic Studies

- **Our earlier in-situ neutron and x-ray diffraction experiments were difficult to interpret, as far as phase equilibria was concerned. Some phases appeared at room temperature and in the in–situ experiments at higher temperatures. So, applied thermodynamic calculations were performed.**
- **Also, controlled loading of H_2 in Li_3N using Sievert's apparatus and analyzing the products by x-ray diffraction yielded very important phase stability information, and formation of new phases. Thermodynamic calculations using *CALPHAD* method agree with the experimental results.**

Key Accomplishments

Li-N-H System (*Gas Impurity effects)*

- **Made progress in cycling tests on Li-N-H system to determine the effect of various gaseous impurities in H_2 (100 ppm level of O_2, CO, H_2O, CH_4, NH_3) to simulate the charge/discharge with fresh H_2 in Li-N-H hydrides.**
- **The effect of NH_3 gas impurity – isothermal (255°C) and isobaric aging at 6.2 bar H_2 performed using 100 ppm NH_3 in H_2 revealed no loss in hydrogen capacity.**

Applied Thermodynamics and Crystallographic Studies

- **Critical phase reaction pathways determined using *progressive incremental loading of hydrogen* in Li_3N, supported by the *CALPHAD* developed Li-N-H Phase diagrams (only phase fields are outlined here- note there is possibility of Li_4NH phase at 255°C, yet to be confirmed):**

$$At\ 225^o C: Li_3N(s) + H_2 \rightarrow Li_2NH(s) + Li_3N(s) + Li(l)(\leq\sim 3wt.\%H) \rightarrow$$
$$Li_2NH(s) + LiH + Li(l)(\sim 3 \leq 5wt.\%H) \rightarrow Li_2NH(s) + gas + LiH(s)(\sim 5 \leq 9.5wt.\%H)$$

$$At\ 25^o C: Li_3N(s) + H_2 \rightarrow Li_3N(s) + Li_2NH(s) + Li_4NH(s)(\leq\sim 2.5wt.\%H) \rightarrow$$
$$Li_2NH(s) + LiH(s) + Li_4NH(s)(\sim 2.5 \leq 5wt.\%H) \rightarrow Li_2NH(s) + gas + LiH(s)(\sim 5 \leq 9.5wt.\%H)$$

- **Determined formation of the Li_4NH phase at room temperature; this phase is stable up to ~5 wt.%H and is peritectically decomposed phase observed @25°C:** $Li_2NH(s) + Liq. \rightarrow Li_4NH(s)$
- **Details of the amount of LiH phase formed under equilibrium loading of hydrogen presented.**
- **New higher hydrogen capacity cubic phase of $Li_{2-x}NH_{1+x}$ type was found (details are subject of a manuscript).**
- **Improved kinetics observed at higher pressures in the Li-N-H system.**

Experimental Apparatuses for Pressure Cycling and Thermal Aging

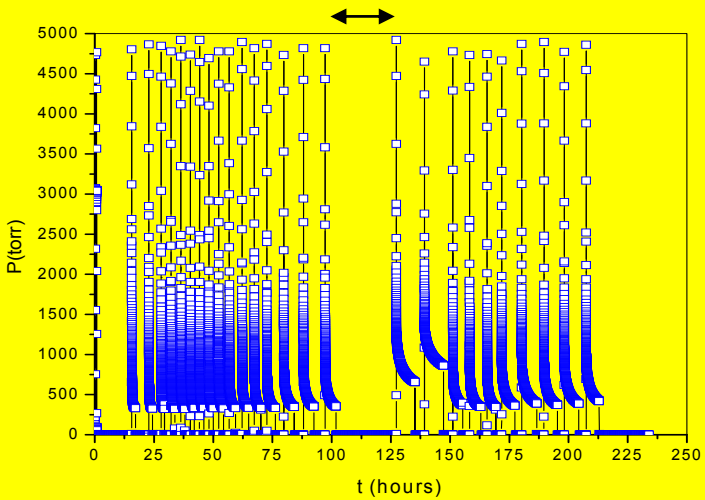
Sample Pressure Cycling Data of Complex Hydrides. Monitoring of Kinetics During Pressure Cycling at UNR

Equipment and Testing Methodology (University of Nevada, Reno (UNR).

- **UNR has 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 pre-determined number of pressure cycles (500-1500) with fresh charge of impurity mixed UHP H_2. In addition we have fully automatic Sievert's apparatuses, and in-situ hydrogen x-ray diffraction capabilities (not shown), HP DSC, TGA etc.**

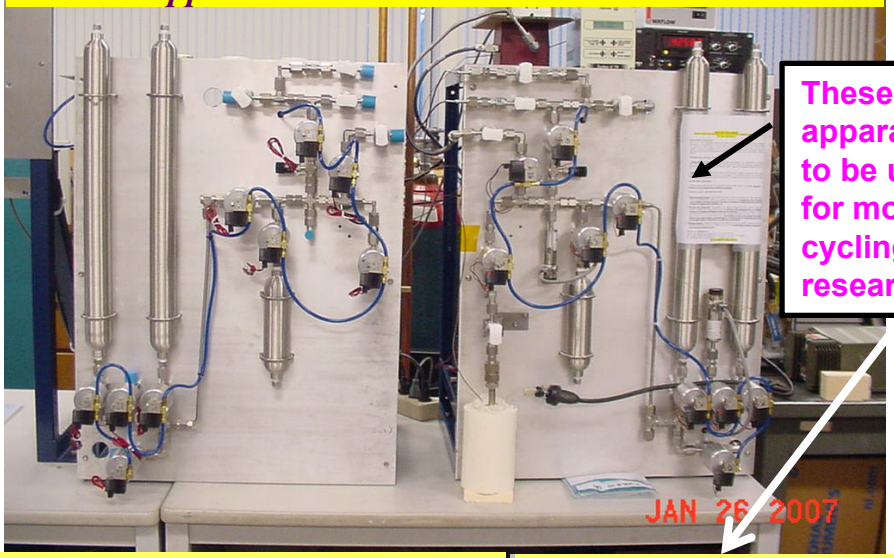
Automatic Pressure Cycling Apparatus at UNR Showing >20 pressure cycles - $LiNH_2$-Li_2NH

Cycling Interrupted Under Vacuum



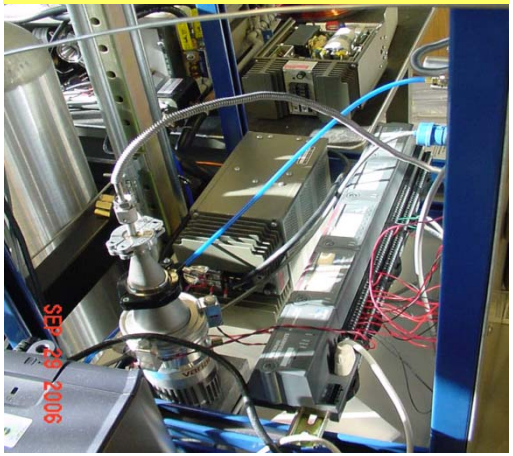
Instruments Used

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



These apparatuses to be used for more HP cycling research

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



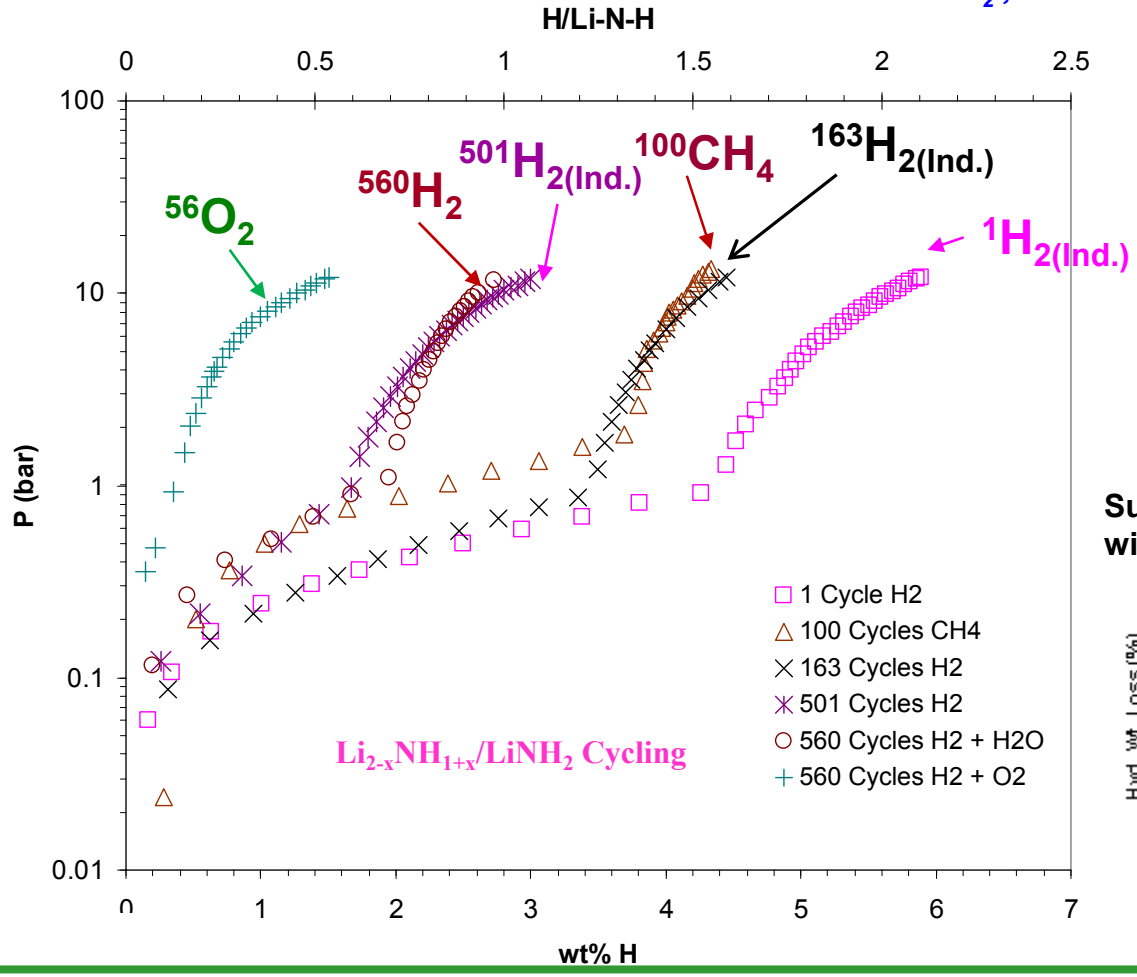
Pressure Cycling apparatus -2 bar H_2

Summary Isotherms Taken Before and After $Li_{2-x}NH_{1+x}$- $LiNH_2$ Cycling (No catalyst) with Industrial Hydrogen, and 100 ppm levels of O_2 , H_2O, CH_4 in UHP H_2 to show the effect of impurities from <u>previous years</u> (included for updating purposes)

Results

Pressure Cycling : **Significantly more losses with O_2 and H_2O impurities observed.**
(Desorption cycles not shown for clarity)

Thermal aging: 100 ppm NH_3, with $H_2 \rightarrow$ virtually no *loss in H_2 capacity for the imide–amide system ; shown in next slide. XRD results show that there is residual $LiNH_2$, LiH along with Li_2O .*



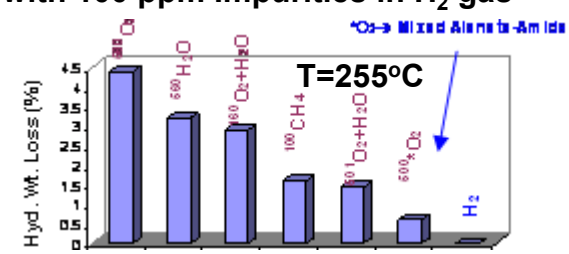
No. of Cycles

$^{56}O_2$

Impurity Gas in H_2

$H_{2\ (Ind)}$= Industrial Hydrogen

Summary: Weight loss After Cycling with 100 ppm Impurities in H_2 gas



Ammonia-Hydrogen Aging Effects

Experiment

There was concern that NH_3 emissions in the hydriding or dehydriding imide-amide system. We were very concerned, and estimated very small ppm levels at this temperature. At higher temperatures 350°C or so, there may be problems.

Although NH_3 may not be a contaminant in commercial hydrogen gas, we decided to check it effects by purposely mixing NH_3 in H_2, and pressure cycle at 255°C

Summary of Results

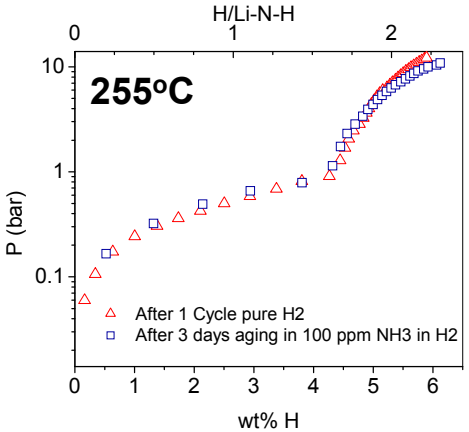
Thermodynamic: Figure- top right

1. Isotherm taken without any NH_3 present in the H_2 gas (reference- red triangles)
2. The isotherm (blue squares) obtained with 100 ppm NH_3-H_2 72 hours (255°Cat 6.3 bar) thermally aged sample showed virtually no change in the hydrogen capacity. (more aging experiments are being performed)
3. It is concluded that ppm levels of NH_3 are not harmful to the Li-N-H system at 225°C with these conditions.

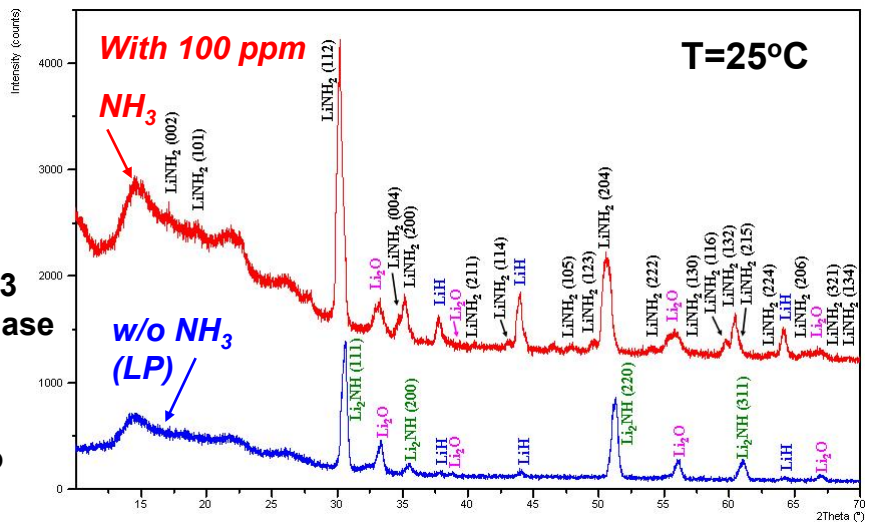
Crystal Structure (Ex-situ x-ray diffraction Studies):

1. Patterns (blue) without NH_3 (taken at low pressure, LP, <<1.3 bar) showed predominantly Li_2NH phase, some impurity phase Li_2O, as expected.
2. Patterns (red) with 100 ppm NH_3 @ 6.3 bar showed mainly, $LiNH_2$, LiH, and small amount of Li_2O phase. These are also expected phases under the pressure conditions.

Isotherms Li_3N-H_2 with and without low levels of NH_3

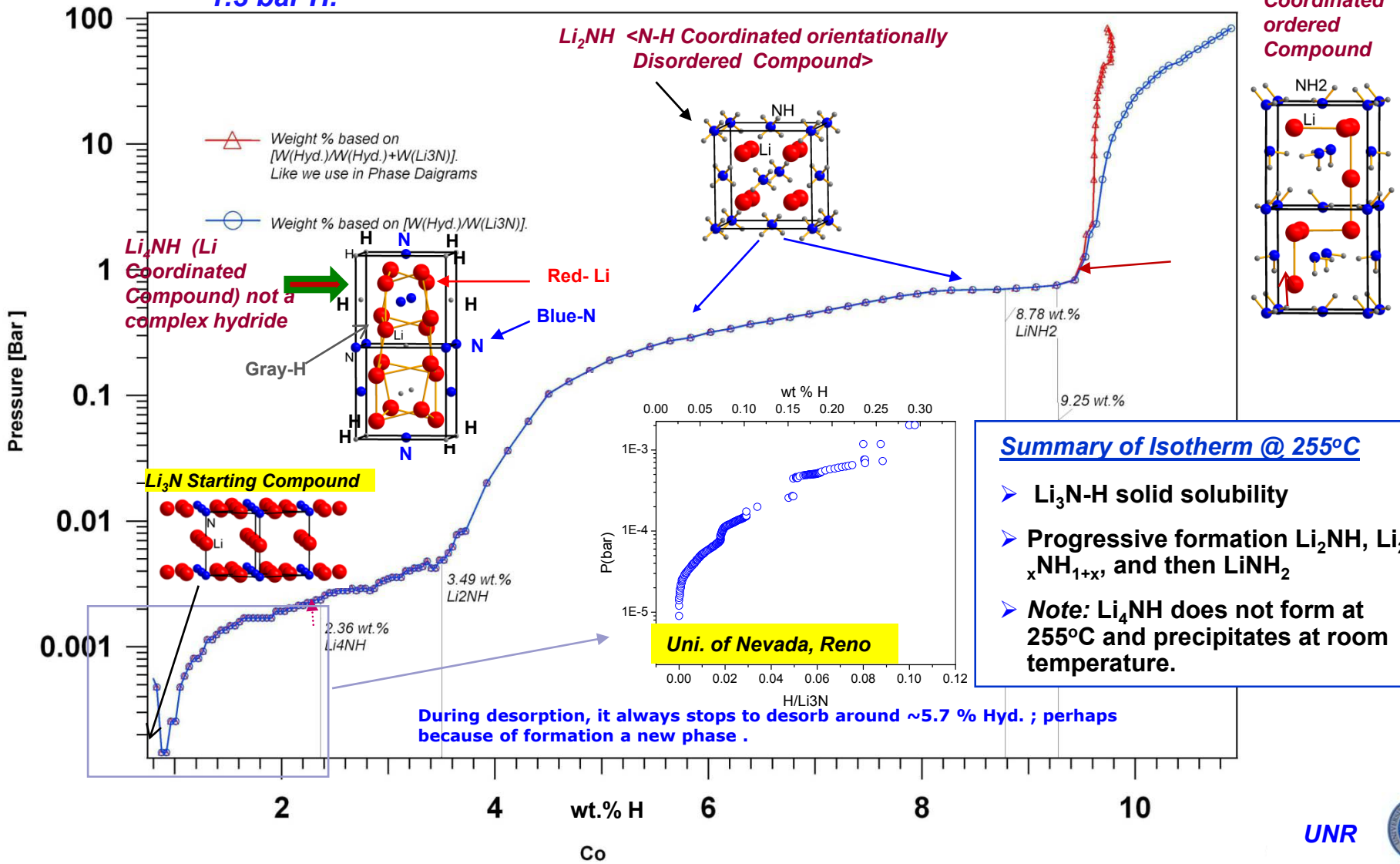


XRD patterns from Hydrides with and without NH_3 additions - corresponding the isotherms shown above.



Isotherm obtained from Li_3N-H at 255°C (at Uni. of Geneva)

The low pressure isotherm (inset) was obtained at UNR, Reno, showing compositions of different Phases formation; for example, $LiNH_2$ forms at 1.3 bar H.



During desorption, it always stops to desorb around ~5.7 % Hyd. ; perhaps because of formation a new phase .

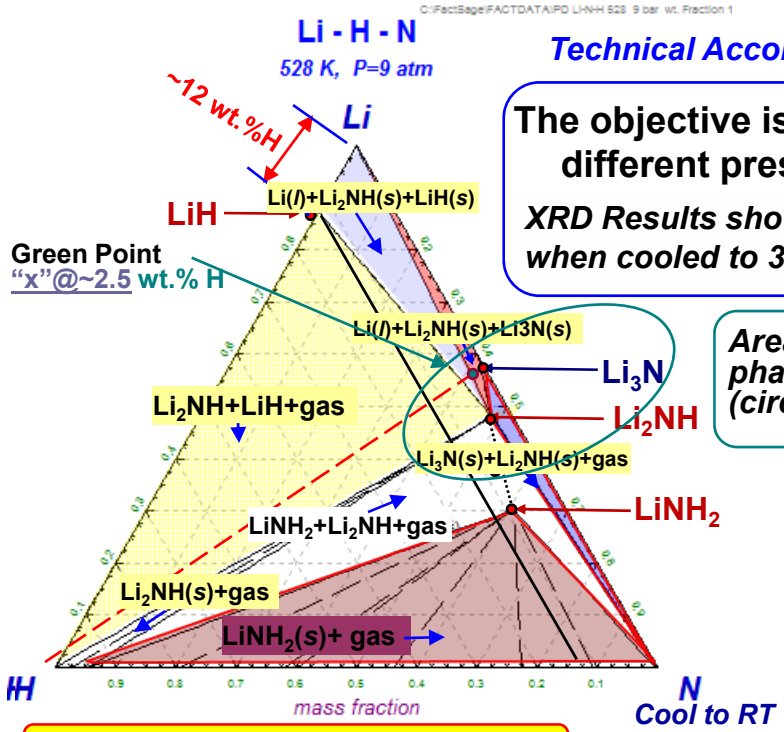
Summary of Isotherm @ 255°C

- **Li_3N-H solid solubility**
- **Progressive formation Li_2NH, $Li_{2-x}NH_{1+x}$, and then $LiNH_2$**
- ***Note:* Li_4NH does not form at 255°C and precipitates at room temperature.**

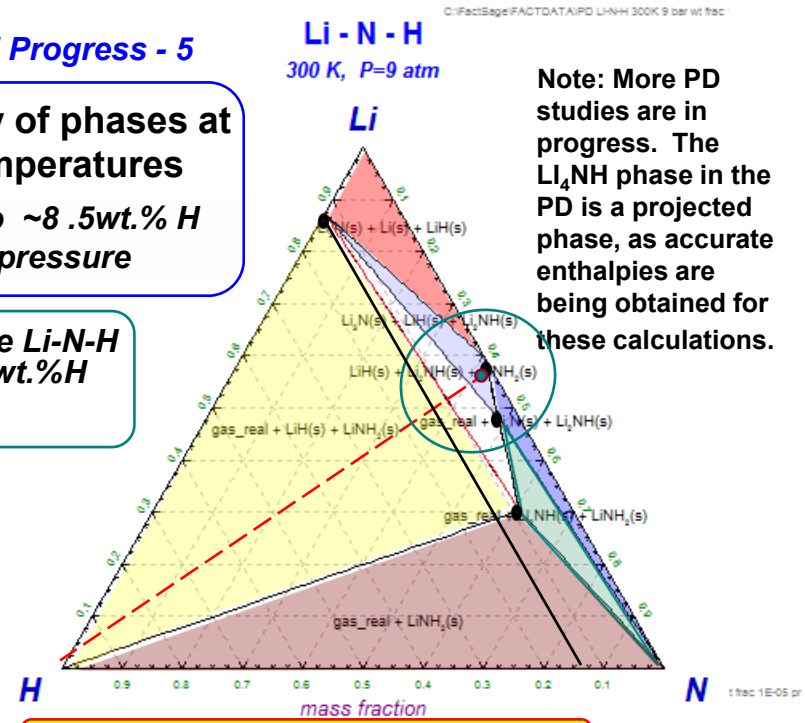
Technical Accomplishments and Progress - 5

The objective is show stability of phases at different pressures and Temperatures

XRD Results show no $LiNH_2$ up to ~8 .5wt.% H when cooled to 300K under no H_2 pressure



Area of interest in the Li-N-H phase diagram ≅ 12 wt.%H (circled areas)



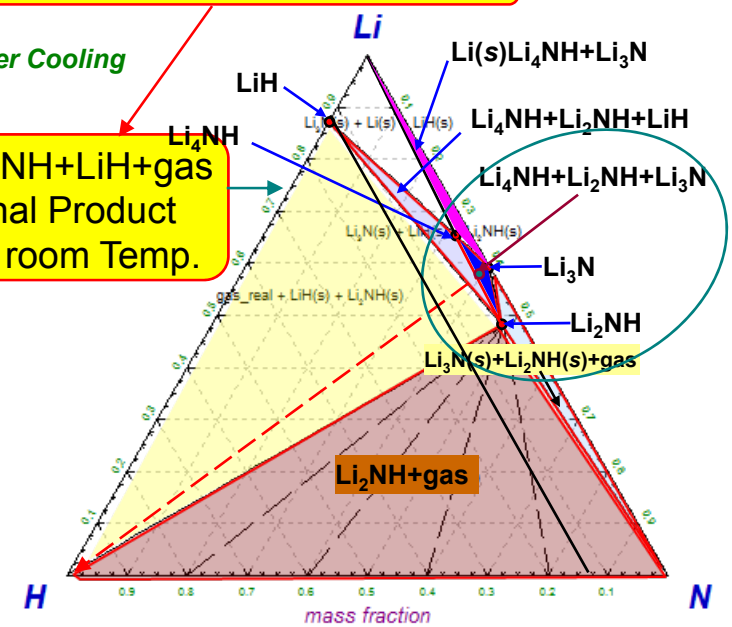
Note: More PD studies are in progress. The LI_4NH phase in the PD is a projected phase, as accurate enthalpies are being obtained for these calculations.

Li_2NH+LiH+gas @ 528K, 9atm. → Li_2NH+$LiNH_2$+ LiH @300K, 9 atm.

Cool to RT

After Cooling

Li_2NH+LiH+gas Final Product @ room Temp.



Example of Reaction Pathways at point "x" ~2.5 wt.% H

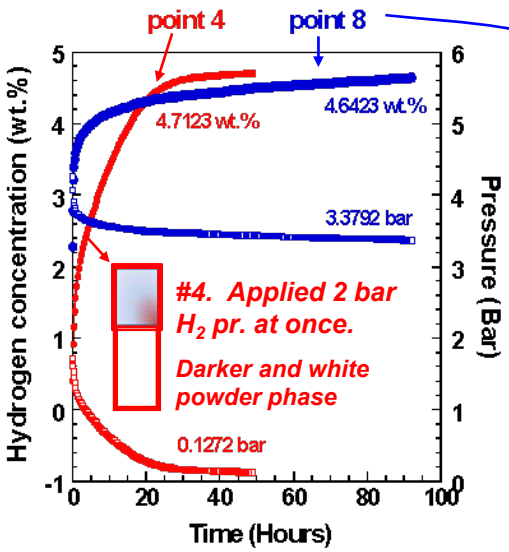
- **Depended on Temp. and pressure history of the Li-N-H system.**
- **The stable phases when cooled to room temperature are different.**
- **Calculated/exptl./estimated Li-N-H diagram shows:**

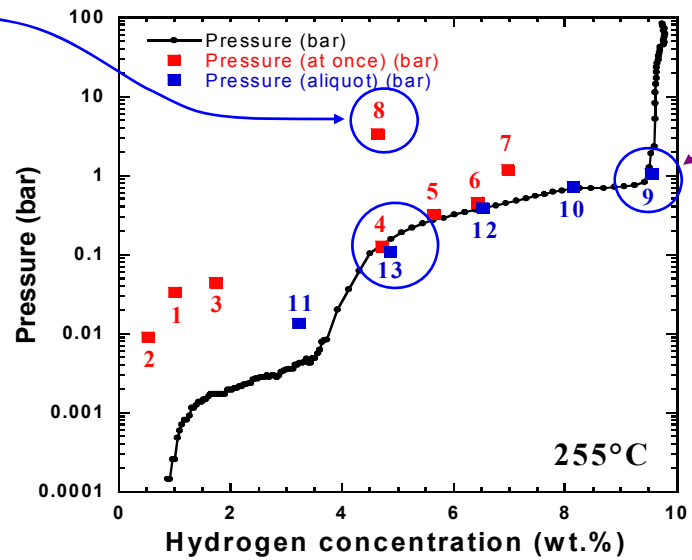
(1) *$Li_2NH(s)$ + Li_3N + Li (liq.)* @ 225°C, 9 atm. (top left PD)

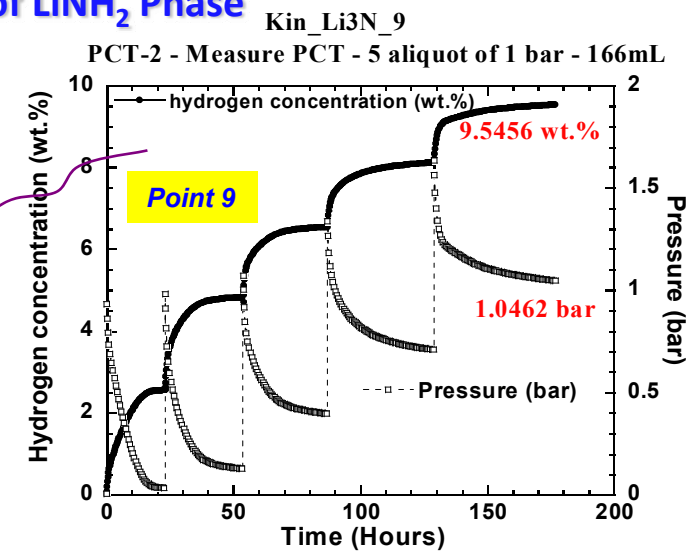
(2) *$Li_3N(s)$ + $Li_2NH(s)$ + LiH(s)*, (cooled to 25°C, 9 atm.)

(3) *$Li_2NH(s)$ + Li_4NH+ LiH (s)* (25°C, with all gaseous H_2 removed under ambient argon pr. (bottom right)

Effect of Pressure on Kinetics and Formation of $LiNH_2$ Phase





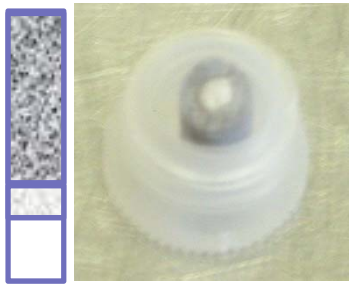


Point No.9: White Powder with $LiNH_2$ phase predominant

Experiment

1. To determine the effect of pressure on loading the same amount of hydrogen (~4.6 wt.%)
2. To determine phase evolution of $LiNH_2$

Point No.8. Photo of the Sintered Powder after Hydriding (5.2 bar applied at once)



Summary

Related the Figure –top left

1. ***Point No.8 :*** ***For a H capacity of 4.6 -4.7 wt. H (Maximum Hydrogen loading P@~0.9 bar) The $P_{equilib.} \cong 0.1272$ bar (at Point 4 in the Isotherm); we observe slower kinetics***
2. ***Point No.4 :*** ***For the same H capacity, at higher $P_{equilib.} \cong 3.38$ bar we observe significantly faster kinetics (see the Figure to the left showing three different textures of the powders obtained) Maximum Hydrogen loading pressure ~3.5 bar. LiNH2 is easier to dehydride.***

X-ray results	Hydrogen conc. (wt.%)	wt.% $LiNH_2$	wt.% $Li_{2-x}NH_{1+x}$	wt.% Li_3N	wt.% Li_2O	wt.% LiH	wt.% Li_4NH
point 4 bottom	4.7123	0	72	11	2.5	12.5	2
point 8 bottom	4.6423	50.5	8	1	2.5	38	0
point 9	9.5456	46.5	16.5	0	4	33	0

UNR-Uni. of Geneva, IEA Collaboration

Formation of new Li_4NH Phase at Room Temperature after Hydriding

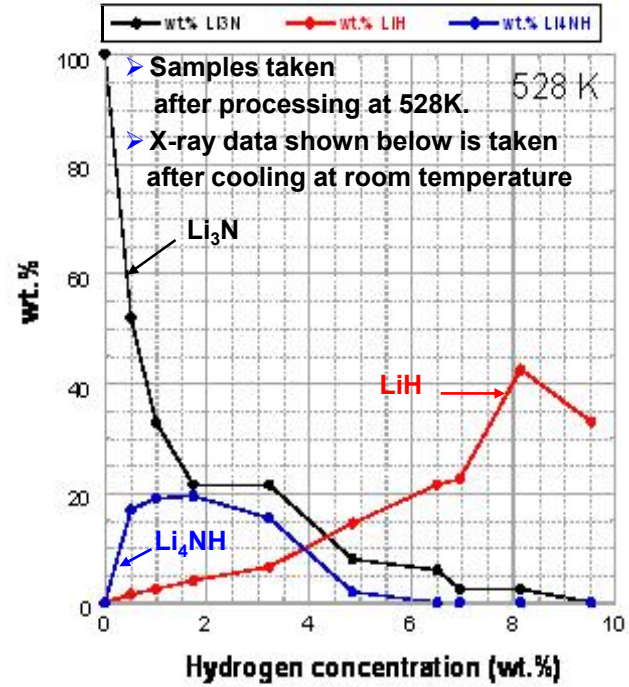
Experiments:

- To determine the Evolution of Phases by loading hydrogen in Li_3N
- In-situ x-ray diffraction experiments were also performed at UNR to observe if Li_4NH forms at 255°C at low pressures, ~0.002-0.003 bar (results not shown for brevity).

Results

- At 255°C (initially, for example @ 1 wt.%H) there is initial formation of small amount of Li (liq.)+ Li_2NH phase, and possibly Li_4NH (yet to be confirmed).
- When cooled to room temperature the Li_2NH+Liq. phase decomposes peritectically to Li_4NH.
- The variation of Li_4NH. Li_3N and LiH phases are shown in the Figure. Data obtained after cooling the samples to 25°C.

Amount of Phase as a function of Eq. Hydrogen Loading (@25°C)



Summary

- The Li_4NH decomposes peritectically: $Li_2NH(s)$+ Liq.→ Li_4NH (s) when the temperature is dropped to 25°C or below peritectic temperature.
- The Li_4NH is no longer stable above ~ 5 wt.%H.
- The structure was reported by R. Niewa and D.A. Zherebtsov, Zeitschrift Fur Kristallographie-New Crystal Structures, 217(3), 317-318 (2002), and by E. Weidner D.J. Bull and I.L. Shabalin, Chemical Physics Letters, 444(1-3), 76-79 (2007).

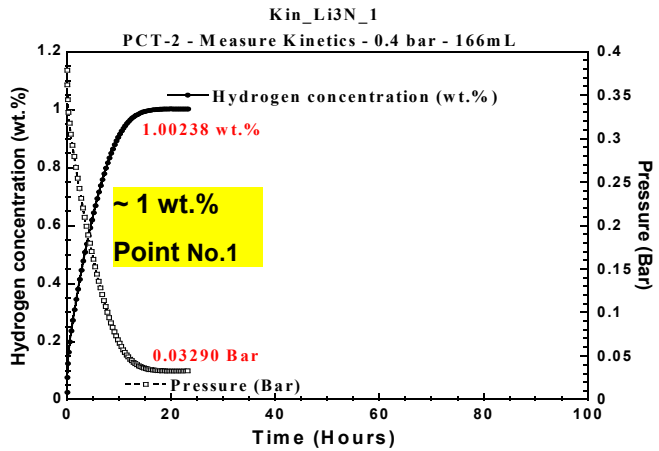
Phase Evolution after Loading ~1 wt.% and ~8 wt.% H in Li_3N (Ex-situ Experiments)

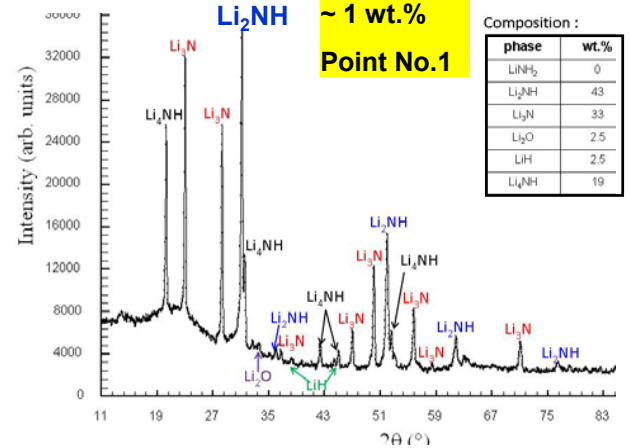
Experiment

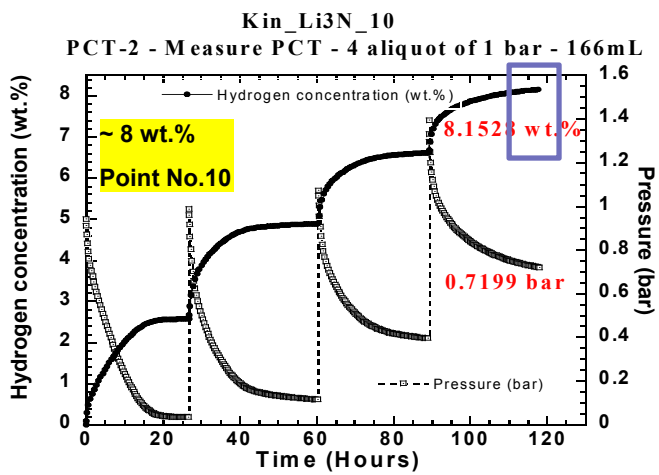
To determine stability of Li_4NH phase at various amounts of hydrogen loading.

Results

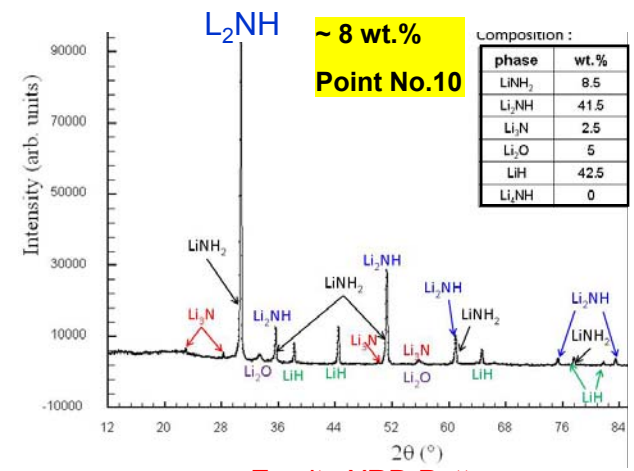
- Maximum amount of Li_4NH phase was present at point No.1 indicated in the PCT.







Sievert' Expts.



Ex-situ XRD Patterns

Summary

- The Li_4NH Phase forms at lower concentrations of hydrogen up to~4.89 wt.% H (point 13 in the PCT)
- There is no Li_4NH phase at ~8 wt.% H as indicated in the table.

$Li_{2-x}NH_{1+x}$ and $LiNH_2$ Phase Evolution During Loading of Hydrogen in Li_3N

Experiment: **Several hydrogen loading experiments were performed and XRD Patterns obtained after the experiments was terminated. The amount of hydrogen loaded was recorded as shown along with XRD patterns.**

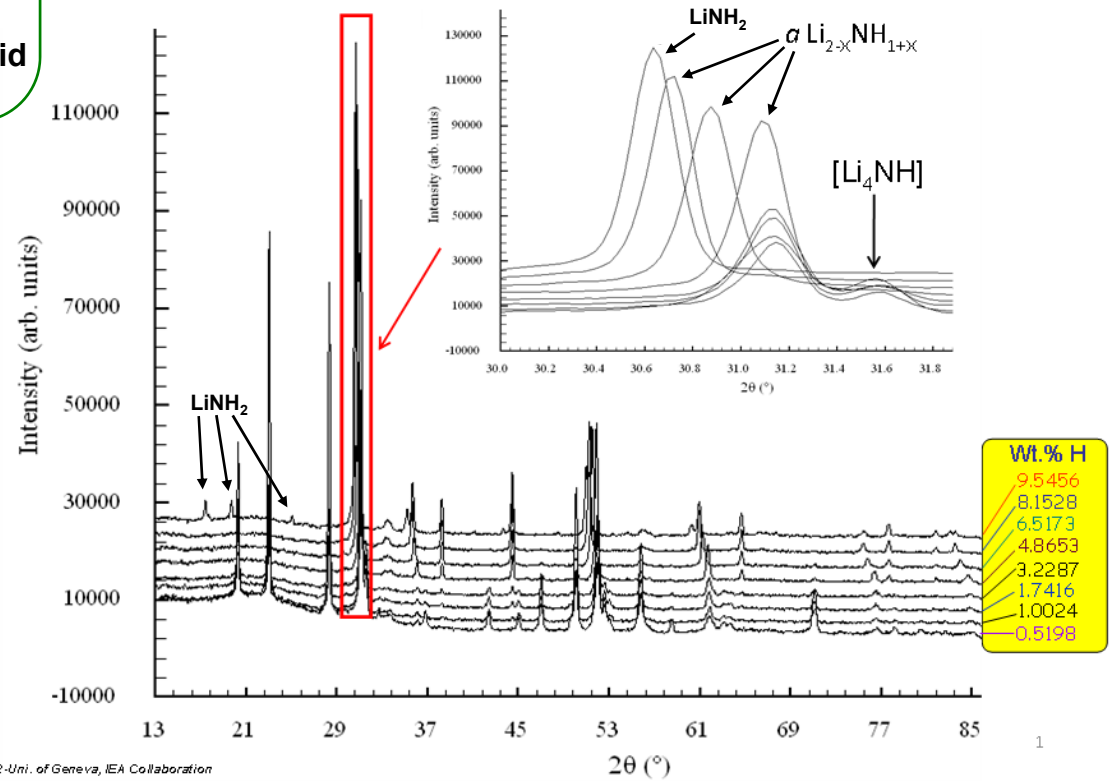
It should be noted that these experiments were done in controlled manner such the pressure did rise above ~1 to 1.2 bar at each loading.

Summary of the Results

1. **XRD data taken at room temperature showed that a new cubic phase evolved ; $Li_{2-x}NH_{1+x}$**
2. **This phase is shown by the shifts in the cubic phase Bragg peaks in the inset above.**
3. **Under equilibrium conditions the $LiNH_2$ phase does not form until about ~9 wt.%H. Some isolated peaks for $LiNH_2$ are shown in the pattern.**
4. **At about 9 wt.% there is equilibrium between $Li_{2-x}NH_{1+x}$ and $LiNH_2$**

X-Ray Diffraction Patterns taken after hydriding at different H-compositions at 255°C and cooling the Samples to Ambient Temperature

Evolution of the XRD patterns *versus* hydrogen concentration



UNR-Uni. of Geneva, IEA Collaboration

Collaborations

University of Genéve

IEA Collaboration, Primary Contact: Prof. K. Yvon,
PI's sabbatical leave research 2008 ***Type of Institution:*** University
Extent: Research related to US DOE H_2 program working on applied crystallography and thermodynamics on LI-N-H system.

Uni. of Paris/CNRS

IEA Collaboration, Primary Contact: Dr. M. Latroche. PI's sabbatical leave research 2008, ***Type of Institution:*** University/National Lab., DOE H_2 program: ***Extent:*** Syntheses of Substituted complex hydrides

Synchrotron Center, Grenoble

Synchrotron Studies, Primary Contact: Dr. Y. Filinchuk
Type of Institution: ESRF, France, related to DOE H_2 program
Extent: in-situ Synchrotron XRD studies on complex hydrides.

University of Rome

IEA/IPHE Collaboration, Primary Contact: Prof. R. Cantelli
PI's sabbatical leave 2008, ***Type of Institution:*** University, related to
Extent: Work on characterization of Defect structure DOE H_2 program.

Sandia National Laboratories

MHCoE Collaboration, Primary Contact: Dr. L. Klebanoff , and E. Ronnebro (now at PNNL). ***Type of Institution:*** **US** National Laboratory, related to DOE H_2 program.
Extent: In-situ hydriding studies on complex hydrides

Proposed Future Work

1. *Effect of Impurities on Complex Hydrides and Defect Structure analyses*

- **Thermal aging studies (100 ppm O_2, CO, CO_2, H_2O, CH_4, NH_3, and others mixed with UHP H_2) on complex hydrides are in progress using the automated cycling/aging apparatus shown in the above slides. We now plan to study degradation behavior more closer to practical situation in vehicles.**

2. *In-Situ High Resolution X-ray Diffraction Studies on Hydriding/Dehydriding*

- **In-situ X-ray (UNR/ESRF/LBNL) will continue to obtain <u>newly</u> developed hydride samples from MHCoE partners to understand the reaction pathways towards development of improved hydrides for vehicular applications.**

3. *Collaboration with the MHCoE Theory Groups*

- **We plan to interact with computational modeling researchers in the MHCoE group to correlate experimental results towards understanding of the structure and the dynamics of hydriding and dehydriding.**

4. *International collaboration with Universities and other European Union (EU) Partners*

- **We will continue IEA collaboration with Uni. of Geneva, Paris/CNRS, and Rome. We have started collaboration with the EU team on developing catalyst for the Li based hydride systems. We at (UNR) had discussions with the DG Joint Research Centre - Institute for Energy, Holland.**

5. *Vaporization Mechanisms of Complex Hydrides*

- **Vapor phase determination towards understanding reaction of pathways/disproportionation of borohydrides.**

Summary – 1

- **In support of the DOE's MHCoE mission, some critical aspects related to long-term stability of light weight complex hydrides for vehicular applications are addressed. Durability/operability of complex hydrides was evaluated to understand the role of ppm gaseous impurities in hydrogen gas experienced during periodic filling at a *commercial hydrogen gas station* for future H_2-vehicles.**

- **Li-N based compounds are used to evaluate long-term durability, reaction pathways for both *developing new materials with enhanced hydriding properties, modifying or controlling reaction pathways for improved performance*.**

- **Pressure extrinsic cyclic testing using fresh charges of industrial hydrogen with several gaseous mixtures of 100 ppm levels of O_2, CO, CO_2, H_2O, NH_3, CH_4, in H_2, revealed O_2 and H_2O have the greatest impact.**

- **Reaction pathways to overcome barriers that exist to improve the kinetics, lower hydrogen release temperatures, and longer cycle life are being determined. An example of stepwise incremental *hydrogen* loading is shown for Li_3N-H that exhibit three primary phase boundaries. stable phases at different H wt.% ranges are given below based on experiments:**

$$At\ 225^o C: Li_3N(s) + H_2 \rightarrow Li_2NH(s) + Li_3N(s) + Li(l)(\leq\sim 3wt.\%H) \rightarrow$$
$$Li_2NH(s) + LiH + Li(l)(\sim 3 \leq 5wt.\%H) \rightarrow Li_2NH(s) + gas + LiH(s)(\sim 5 \leq 9.5wt.\%H)$$

$$At\ 25^o C: Li_3N(s) + H_2 \rightarrow Li_3N(s) + Li_2NH(s) + Li_4NH(s)(\leq\sim 2.5wt.\%H) \rightarrow$$
$$Li_2NH(s) + LiH(s) + Li_4NH(s)(\sim 2.5 \leq 5wt.\%H) \rightarrow Li_2NH(s) + gas + LiH(s)(\sim 5 \leq 9.5wt.\%H)$$

- **The above results were confirmed by Phase diagram obtained by *CALPHAD* modeling**

Summary – Cont'd

- Determined formation of the Li_4NH phase at room temperature; this phase is stable up to ~5 wt.%H and is peritectically decomposed phase: $Li_2NH(s) + Liq. \rightarrow Li_4NH(s)\ @25^oC$
- Isobaric and isothermal thermal aging at 225°C revealed that 100 ppm level of NH_3 impurity exhibited virtually no loss of hydrogen capacity, whereas CH_4 impurities have lower impact.
- There are indications that better kinetics of hydriding can be achieved at higher than equilibrium pressures.
- New non-stoichiometric $Li_{2-x}NH_{1+X}$ cubic phases with higher H-capacity found.
- ***Sabbatical leave Work:***
  Please note that the PI (D. Chandra) was on sabbatical leave at Uni. of Geneva, Uni. of Paris/CNRS, and Uni. of Rome in 2008. The crystallography and thermodynamic experiments were performed in Geneva. Additional thermodynamic work, cycling/thermal aging experiments, and in-situ x-ray diffraction work was done at Uni. of Nevada, Reno.

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