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Merit Review and Peer Evaluation Meeting Registration**
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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 H₂ 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 H₂ 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 O₂, CO, H₂O, CH₄, NH₃ etc. in H₂) on complex hydrides after prolonged *hydrogen pressure cycling and thermal aging*. Note: NH₃ is not a common impurity in H₂ 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 O₂ impurity in UHP H₂ as well as thermal aging (CO impurity) of mixed phase Li₃AlH₆-LiNH₂ have been completed. These results may be extrapolated to higher cycles.

C. Addressing Charging/Discharging Rates and Applied Thermodynamic Studies

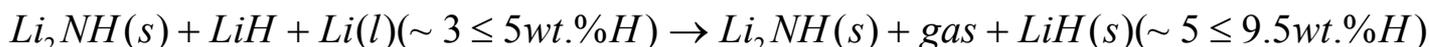
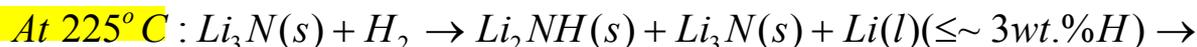
- Our earlier in-situ neutron and x-ray diffraction experiments were difficult to interpret, as far as phase equilibria was concerned. Some phases appeared at room temperature and in the in-situ experiments at higher temperatures. So, applied thermodynamic calculations were performed.
- Also, controlled loading of H₂ in Li₃N 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.

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 H₂ (100 ppm level of O₂, CO, H₂O, CH₄, NH₃) to simulate the charge/discharge with fresh H₂ in Li-N-H hydrides.
- The effect of NH₃ gas impurity – isothermal (255°C) and isobaric aging at 6.2 bar H₂ performed using 100 ppm NH₃ in H₂ revealed no loss in hydrogen capacity.

Applied Thermodynamics and Crystallographic Studies

- Critical phase reaction pathways determined using *progressive incremental loading of hydrogen* in Li₃N, supported by the CALPHAD developed Li-N-H Phase diagrams (only phase fields are outlined here- note there is possibility of Li₄NH phase at 255°C, yet to be confirmed):



- Determined formation of the Li₄NH 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

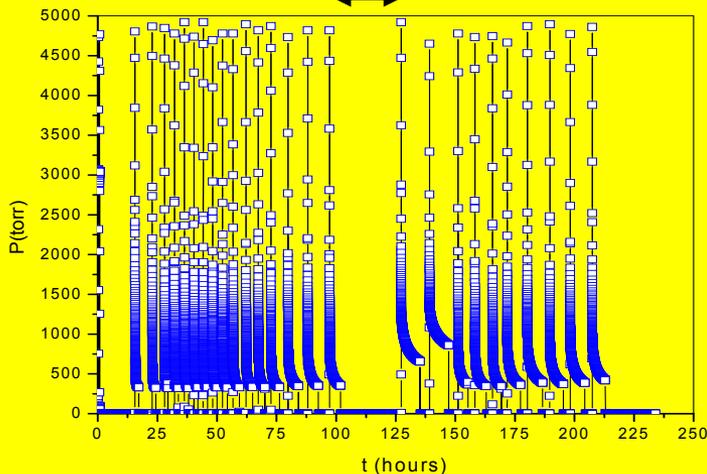
Sample Pressure Cycling Data of Complex Hydrides. Monitoring of Kinetics During Pressure Cycling at UNR

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 H₂. 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 - LiNH₂-Li₂NH

Cycling Interrupted Under Vacuum



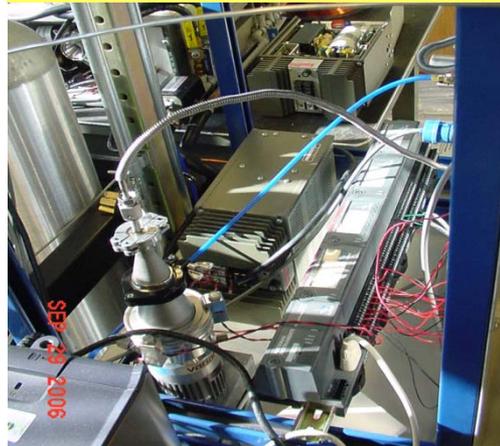
Instruments Used

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 H₂ Pressure Cycling apparatus -2 bar H₂ (back Panel)



Pressure Cycling apparatus -2 bar H₂



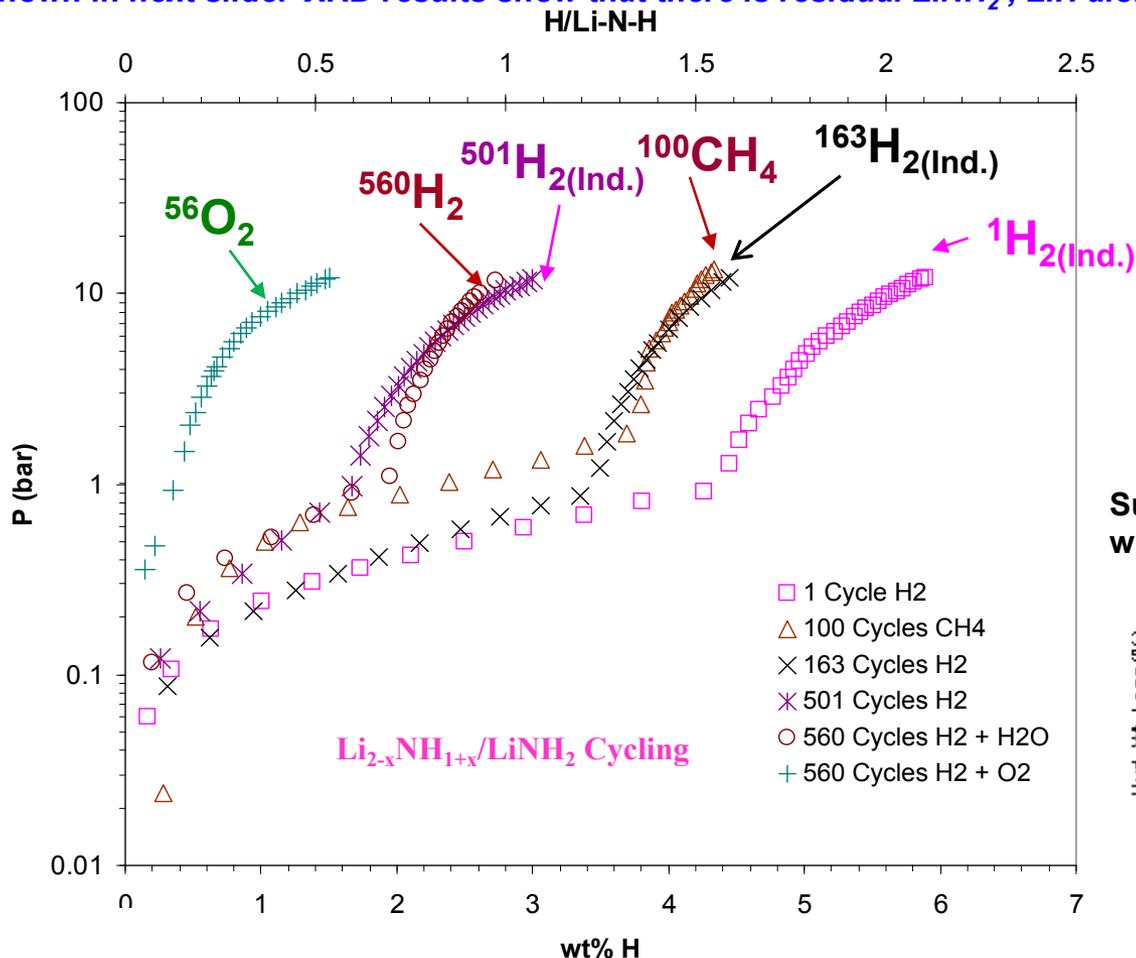
Summary Isotherms Taken Before and After $\text{Li}_{2-x}\text{NH}_{1+x}$ - LiNH_2 Cycling (No catalyst) with Industrial Hydrogen, and 100 ppm levels of O_2 , H_2O , CH_4 in UHP H_2 to show the effect of impurities from previous years (included for updating purposes)

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 $\text{H}_2 \rightarrow$ 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 .



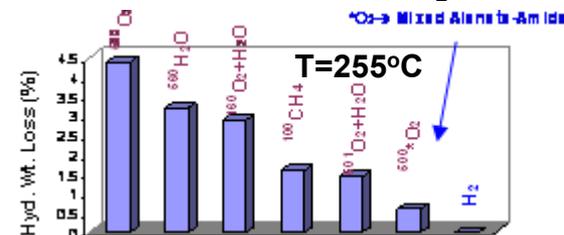
No. of Cycles



Impurity Gas in H_2

H_2 (Ind.) = Industrial Hydrogen

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



Isotherms Li_3N-H_2 with and without low levels of NH_3

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 $350^\circ C$ or so, there may be problems.

Although NH_3 may not be a contaminant in commercial hydrogen gas, we decided to check its effects by purposely mixing NH_3 in H_2 , and pressure cycle at $255^\circ C$

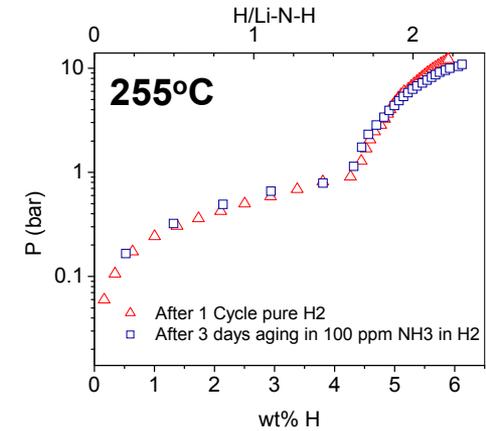
Summary of Results

Thermodynamic: Figure- top right

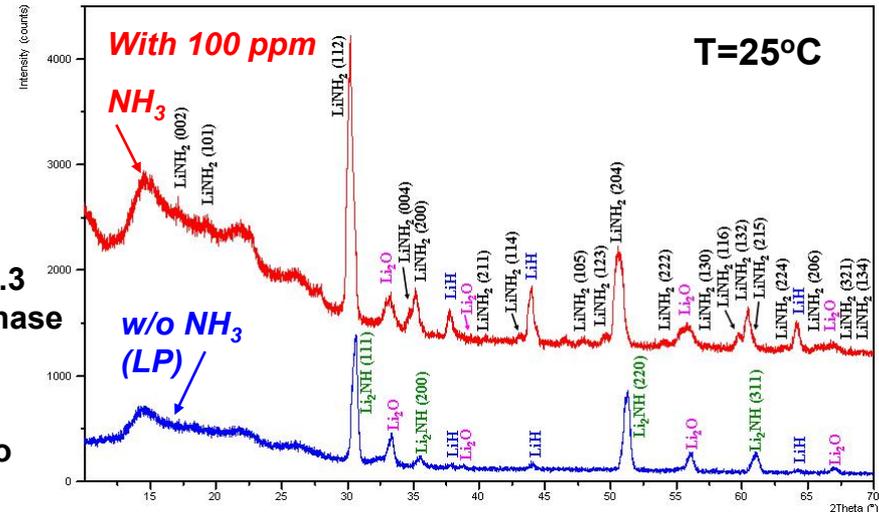
1. Isotherm taken without any NH_3 present in the H_2 gas (reference- red triangles)
2. The isotherm (blue squares) obtained with 100 ppm NH_3-H_2 72 hours ($255^\circ C$ at 6.3 bar) thermally aged sample showed virtually no change in the hydrogen capacity. (more aging experiments are being performed)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

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

1. Patterns (blue) without NH_3 (taken at low pressure, LP, $\ll 1.3$ 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.

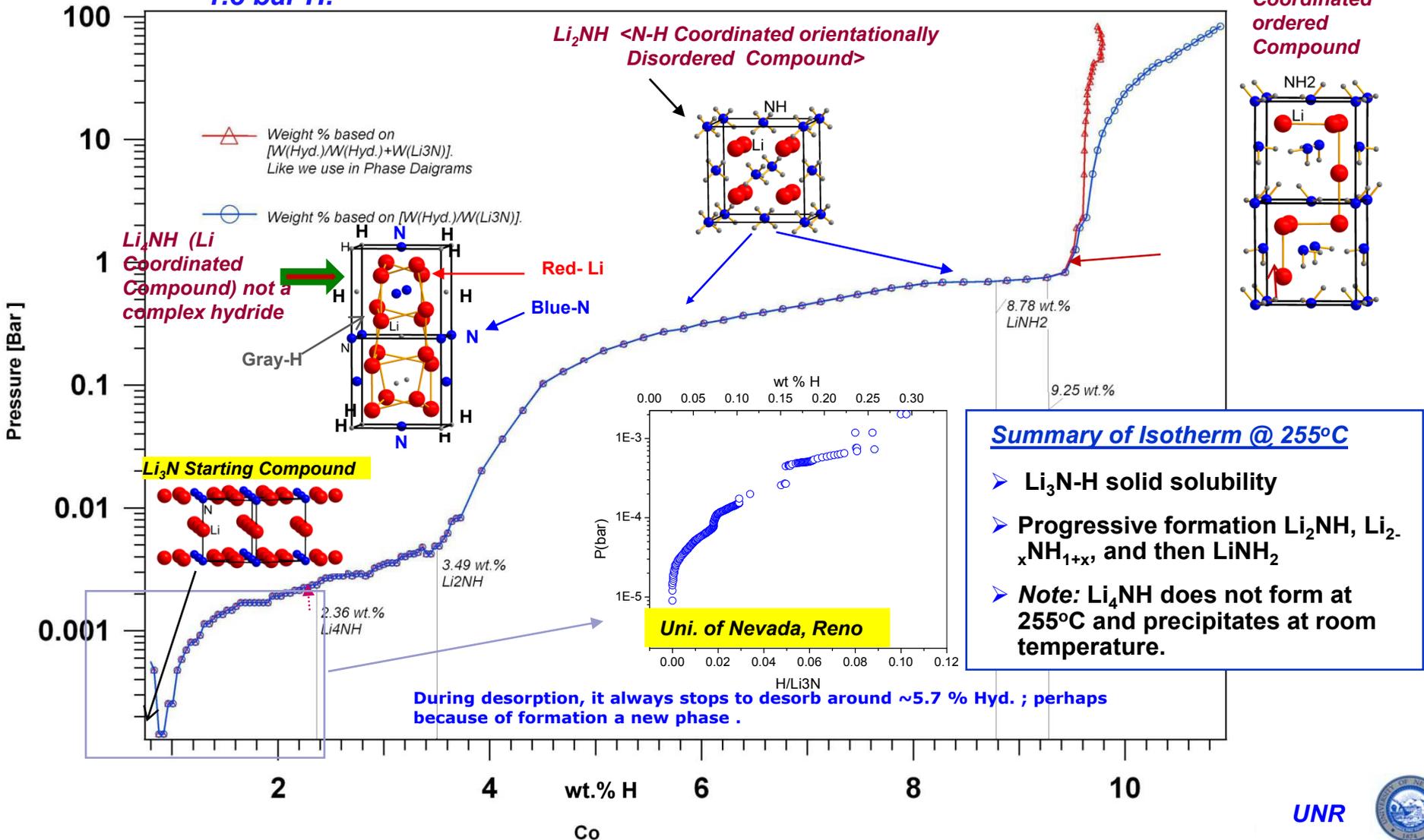


XRD patterns from Hydrides with and without NH_3 additions - corresponding the isotherms shown above.



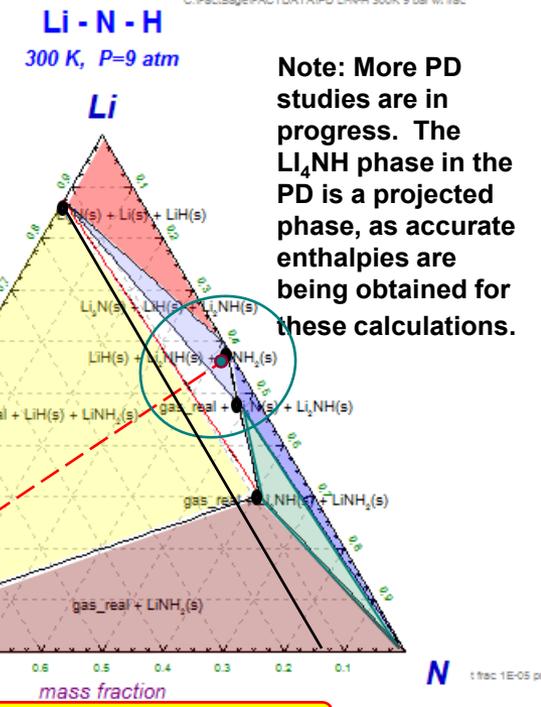
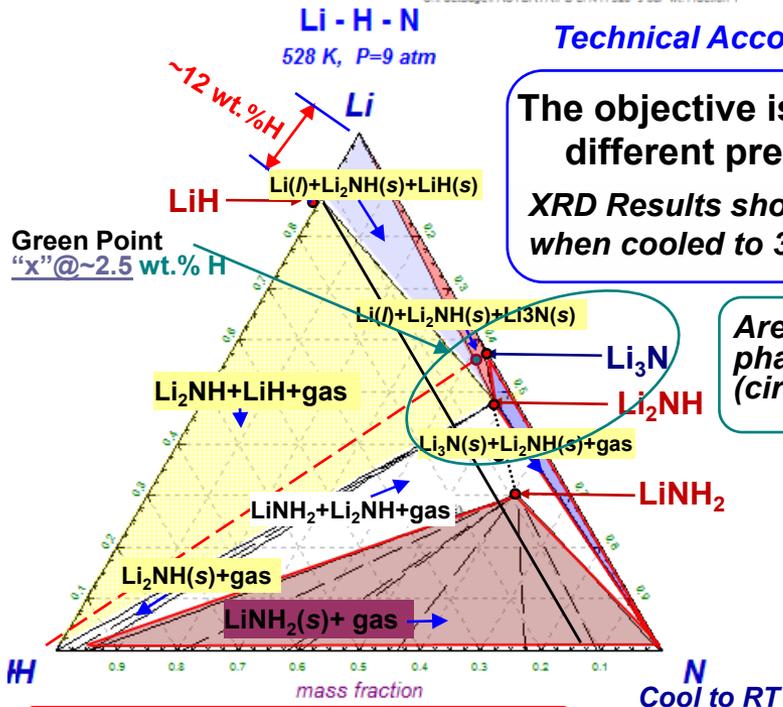
Isotherm obtained from $\text{Li}_3\text{N-H}$ at 255°C (at Uni. of Geneva)

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.



Technical Accomplishments and Progress - 5

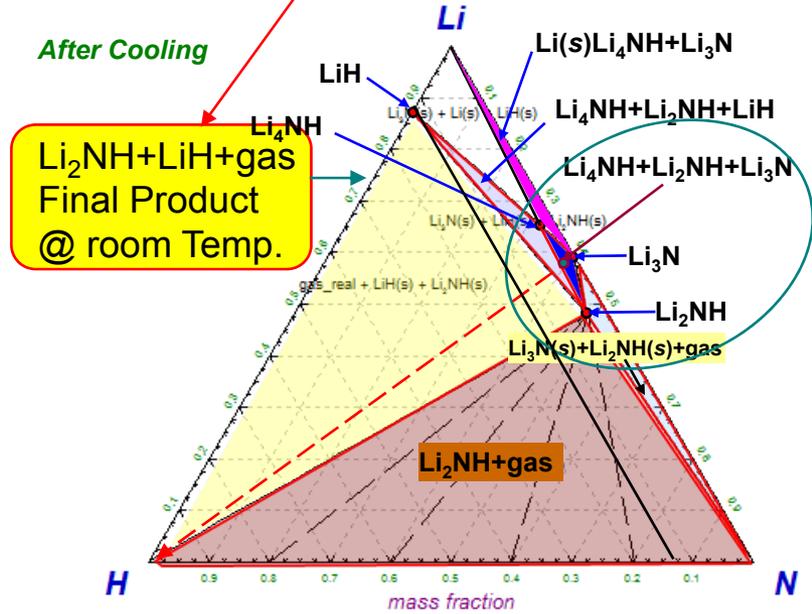
The objective is show stability of phases at different pressures and Temperatures
 XRD Results show no LiNH_2 up to $\sim 8.5\text{wt.}\% \text{ H}$ when cooled to 300K under no H_2 pressure



$\text{Li}_2\text{NH} + \text{LiH} + \text{gas}$ @ 528K, 9atm.

$\text{Li}_2\text{NH} + \text{LiNH}_2 + \text{LiH}$ @ 300K, 9 atm.

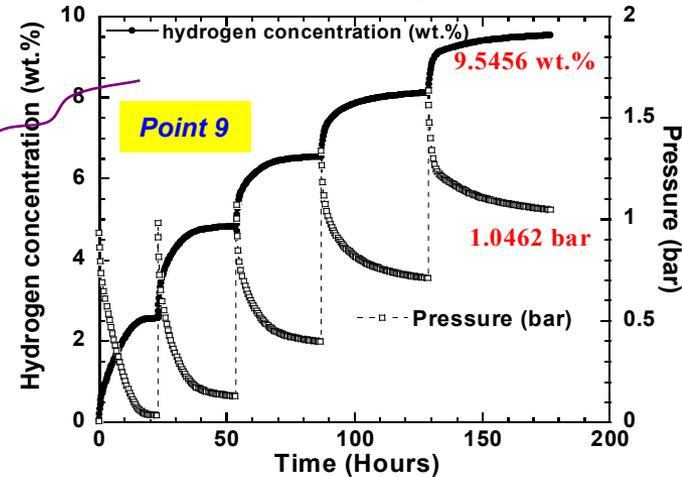
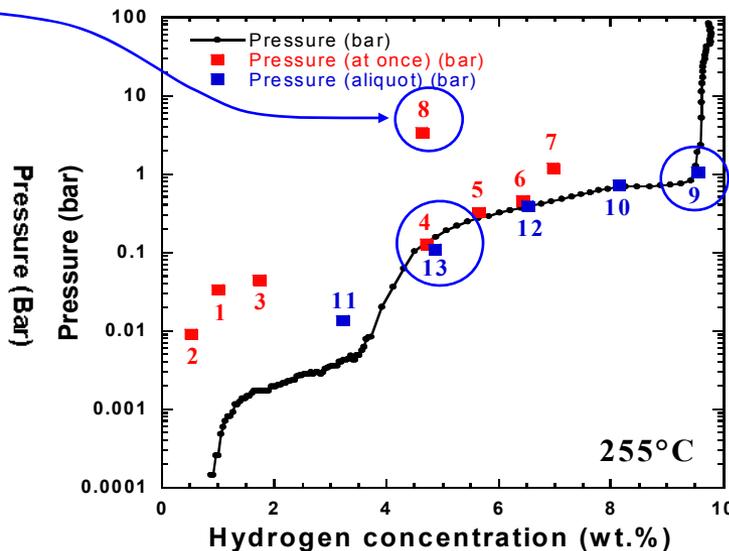
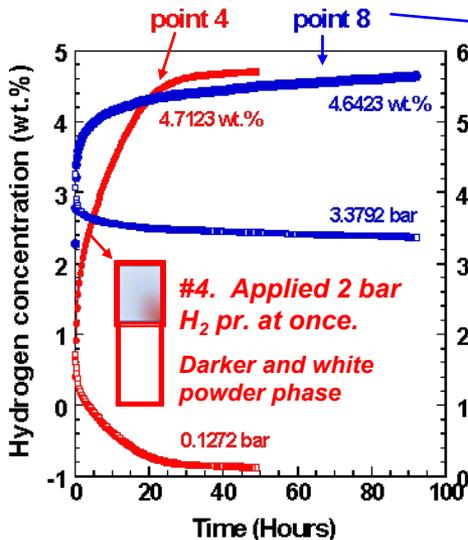
- Example of Reaction Pathways at point "x" $\sim 2.5 \text{ wt.}\% \text{ H}$**
- Depended on Temp. and pressure history of the Li-N-H system.
 - The stable phases when cooled to room temperature are different.
 - Calculated/exptl./estimated Li-N-H diagram shows:
 - $\text{Li}_2\text{NH}(s) + \text{Li}_3\text{N} + \text{Li}(\text{liq.})$ @ 225°C, 9 atm. (top left PD)
 - $\text{Li}_3\text{N}(s) + \text{Li}_2\text{NH}(s) + \text{LiH}(s)$, (cooled to 25°C, 9 atm.)
 - $\text{Li}_2\text{NH}(s) + \text{Li}_4\text{NH} + \text{LiH}(s)$ (25°C, with all gaseous H_2 removed under ambient argon pr. (bottom right)



Effect of Pressure on Kinetics and Formation of LiNH₂ Phase

Kin_Li3N_9

PCT-2 - Measure PCT - 5 aliquot of 1 bar - 166mL



Point No.9: White Powder with LiNH₂ phase predominant

Experiment

- To determine the effect of pressure on loading the same amount of hydrogen (~4.6 wt.%)
- To determine phase evolution of LiNH₂

Summary

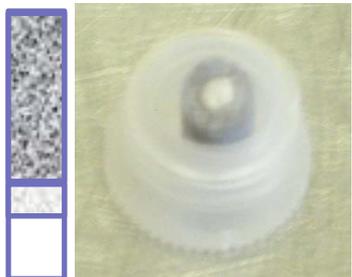
Related the Figure –top left

- 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
- 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 ₃ N	wt.% Li ₂ O	wt.% LiH	wt.% Li ₄ NH
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

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



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, $\sim 0.002\text{-}0.003$ bar (results not shown for brevity).

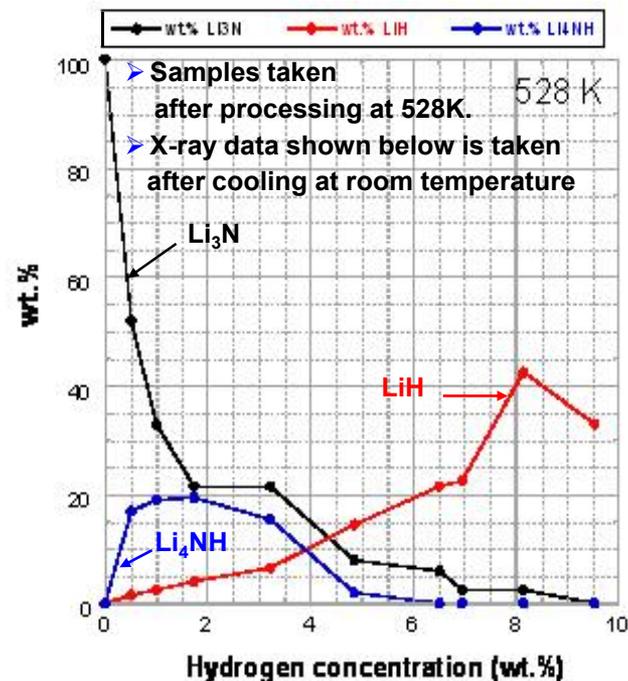
Results

- 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 $\text{Li}_2\text{NH}+\text{Liq.}$ 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 .

Summary

- The Li_4NH decomposes peritectically: $\text{Li}_2\text{NH}(\text{s}) + \text{Liq.} \rightarrow \text{Li}_4\text{NH}(\text{s})$ 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. Zharebtsov, 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).

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



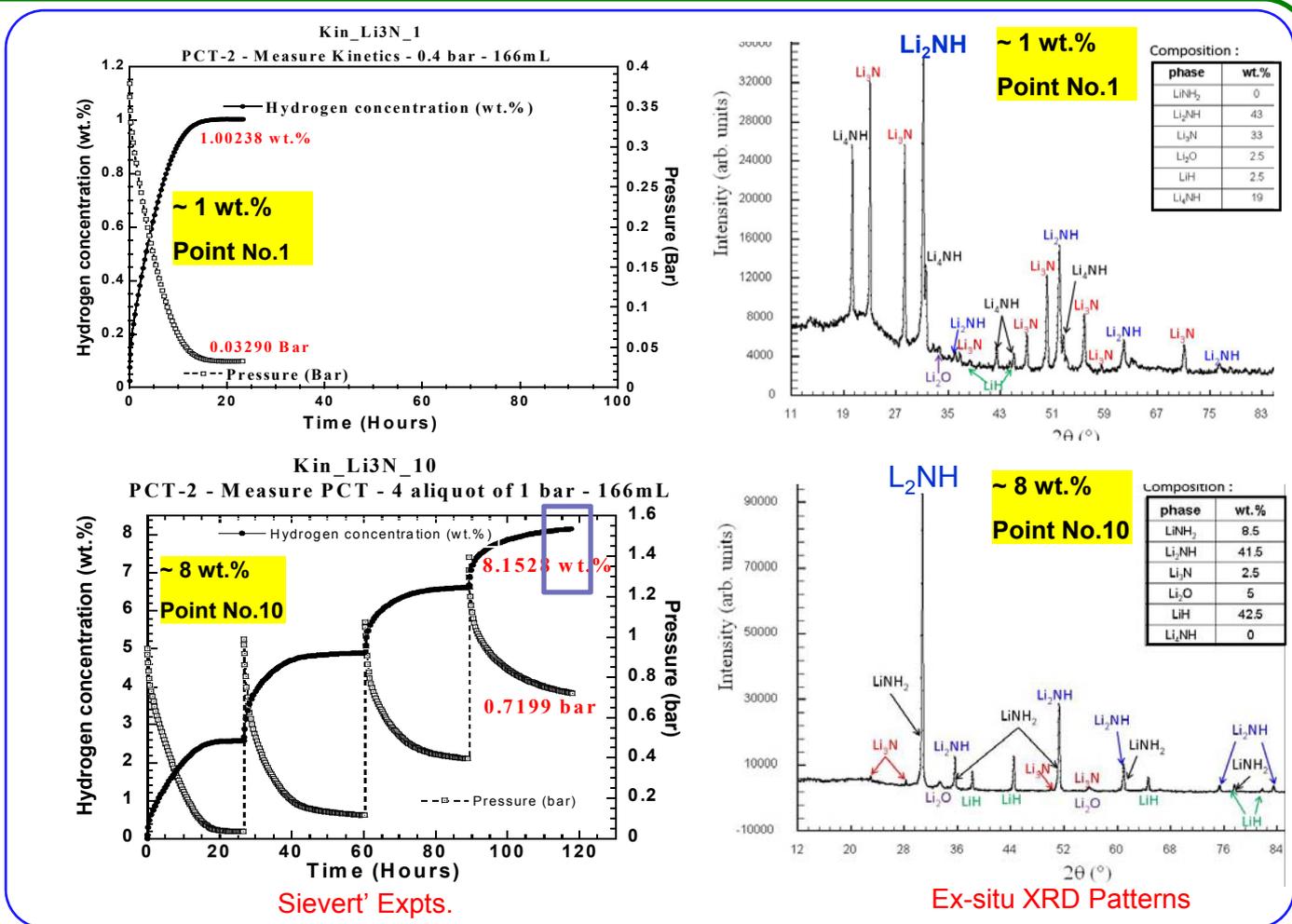
Phase Evolution after Loading ~1 wt.% and ~8 wt.% H in Li₃N (Ex-situ Experiments)

Experiment

To determine stability of Li₄NH phase at various amounts of hydrogen loading.

Results

- Maximum amount of Li₄NH phase was present at point No.1 indicated in the PCT.



Summary

- The Li₄NH Phase forms at lower concentrations of hydrogen up to ~4.89 wt.% H (point 13 in the PCT)
- There is no Li₄NH phase at ~8 wt.% H as indicated in the table.



Li_{2-x}NH_{1+x} and LiNH₂ Phase Evolution During Loading of Hydrogen in Li₃N

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.

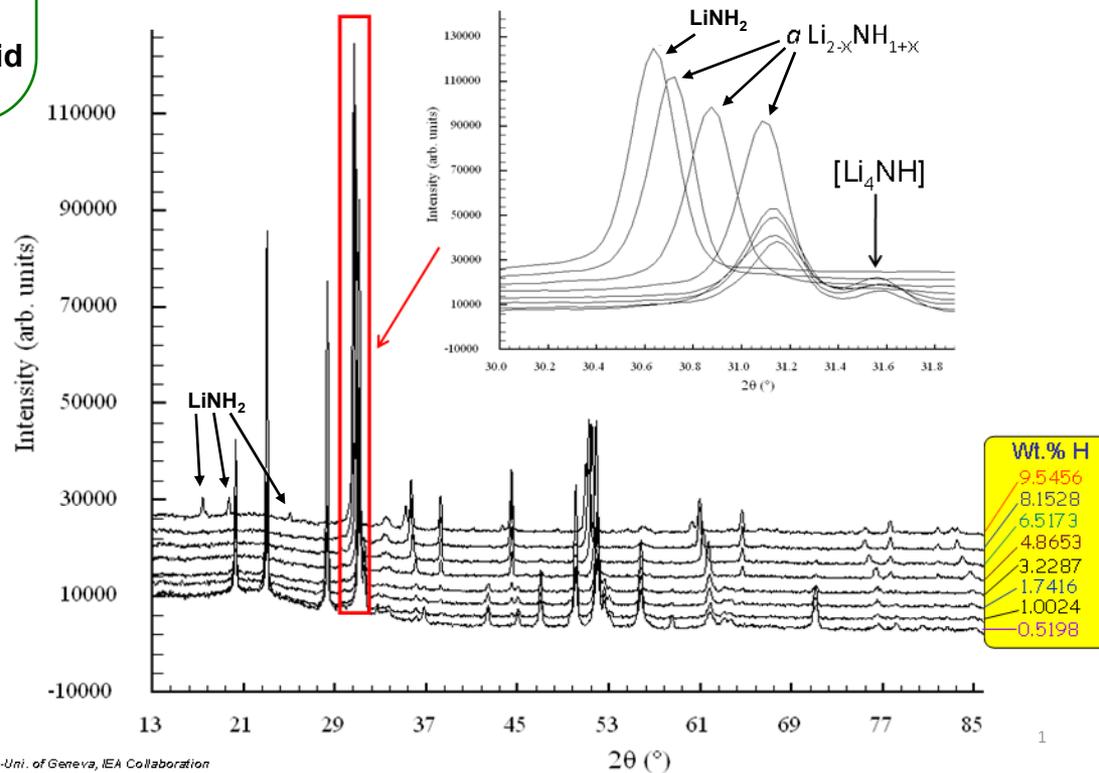
It should be noted that these experiments were done in controlled manner such the pressure did rise above ~1 to 1.2 bar at each loading.

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 LiNH₂ phase does not form until about ~9 wt.%H. Some isolated peaks for LiNH₂ are shown in the pattern.
4. At about 9 wt.% there is equilibrium between Li_{2-x}NH_{1+x} and LiNH₂

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 Genève

IEA Collaboration, Primary Contact: Prof. K. Yvon, PI's sabbatical leave research 2008 **Type of Institution:** University
Extent: Research related to US DOE H₂ 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 H₂ 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 H₂ 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 H₂ 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 H₂ 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 O₂, CO, CO₂, H₂O, CH₄, NH₃, and others mixed with UHP H₂) 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 newly 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*

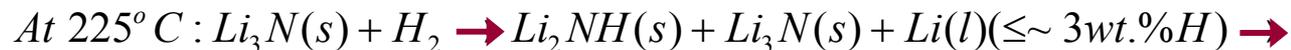
- ❑ We will continue IEA collaboration with Uni. of Geneva, Paris/CNRS, and Rome. We have started collaboration with the EU team on developing catalyst for the Li based hydride systems. We at (UNR) had discussions with the DG Joint Research Centre - Institute for Energy, Holland.

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 H₂-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 O₂, CO, CO₂, H₂O, NH₃, CH₄, in H₂, revealed O₂ and H₂O 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 Li₃N-H that exhibit three primary phase boundaries. stable phases at different H wt.% ranges are given below based on experiments:



- 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: $\text{Li}_2\text{NH}(s) + \text{Liq.} \rightarrow \text{Li}_4\text{NH}(s) @ 25^\circ\text{C}$
- 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 $\text{Li}_{2-x}\text{NH}_{1+x}$ 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.

Acknowledgements

We are very grateful to the US DOE-MHCoE for the support of this Project.

We thank Dr. Gary Sandrock for his valuable comments on NH₃ issues in in amide-amide system.

We are also grateful to researchers from K. Yvon, R. Cerny, N. Penin, and D. Phanon, M. Latroche R. Cantelli, and Y. Filinchuk for their valuable contributions, and support of the facilities for this research during the PI's sabbatical leave work.

We thank E. Ronnebro (now at PNNL), and J.C. Zhao of OSU for collaboration Mg-and Ca-Borohydride. We also thank Dr. A. Huq of ORNL for her collaboration on neutron diffraction studies.