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Merit Review and Peer Evaluation Meeting Registration
Washington, D.C June 7-11, 2010

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

Dhanesh Chandra, PI
Research Associates and Students:
Josh Lamb, Wen-Ming Chien, Narendra Pal (Graduate Student),
Jeff Olson (undergraduate student)
Materials Science and Engineering Division
Chemical and Metallurgical Engineering, MS 388
University of Nevada, Reno (*UNR*)
Klaus Yvon*, Radovan Cerny*, Delphine Phanon*, and Nicolas Penin*
***University of Geneva**
Jean-Claude Crivello, Michel Latroche**, Michelle Gupta, Uni. of Paris-Sud, **CNRS, Paris**
IEA Collaborators

May 30, 2010

Overview

Timeline

Project start date – FY05
Project end date – FY10
Percent complete – ~96%

Barriers Addressed

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

Budget

Total project funding (5yrs.) : $ 1.920,352

DOE share (5yrs.) : $ 1.536,278

Contractor share (5yrs.) : $ 384,074

Funding received in FY2007 : $ 520,000 (includes instrument)

Funding received in FY2008: $ 350,000

Funding received in FY2009: $ 391,278

MHCoE Partners

Active Current Collaboration

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

Future Collaboration

- ***NIST Gaithersburg, Maryland - Dr. Terry Udovic***
- ***Brookhaven National Laboratories, NY – Dr. James Reilly***
- ***Oak Ridge National Laboratory- Dr. Gilbert Brown***

Relevance

General

- ***"Grand Challenge" Program:*** Launched by DOE for R&D of hydrogen storage technologies - designed to meet targets for commercially viable vehicular systems.
- ***Metal Hydrides Center of Excellence MHCoE):*** Three Centers of Excellence exist; we work on on-board hydrogen storage technical barriers.
- ***Study Topics at Uni. of Nevada, Reno (UNR):*** (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).

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

1. *Objectives:*

- Effect of ppm and higher level impurities in H_2 gas.
- Li-N-H light weight based compounds used to evaluate long-term durability.
- To develop new materials with *enhanced hydriding properties, by modifying or controlling reaction pathways.*
- To develop longer cycle life complex hydrides, with lower hydrogen release temperatures and improved kinetics.

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

- ***System Weight and volume:*** Identified *materials systems: Li-N-H, Li-Al-N-H and other light weight materials for studies.*
- ***Durability:*** *Addressed these issues by using industrial hydrogen as well as various individual impurity gas mixtures in hydrogen gas.*
- ***Charging /Discharging:*** *Reaction pathways found.*
- ***Life cycle assessments:*** *Addressed environmental impact of hydrogen storage via impurity gas effect ; example N_2,O_2, H_2O, CO, CO_2, NH_3 and other gases.*

Approach

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

- ***Light-weight Li-N-H system has ~10.5 wt.%H-capacity and long cycle life:*** During loading of pure hydrogen in Li3N, 5 compounds form, depending on the conditions.

  In fully loaded condition the major phase is $LiNH_2$ (8.78 wt.%H) along with residual LiH (~12 wt.%H) phase which adds up to ~10.5 wt.%H.

- ***This study is expected to have Broader Impact on hydride research:*** Research is expected to give insight to other hydrides (mixtures of amides-alanates, amide-magnesium hydrides and others). In addition, mixing H_2 with N_2 changes the thermodynamic paths leading to significant changes in cycle ability.

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, N_2 in H_2gas) 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 (last period's work).*

- ***Update:*** Effects of using Nitrogen gas as an impurity in hydrogen gas to enhance the reversible hydrogen capacity have shown promise, and are presented here.

- ***Objectives:*** Specifically, the emphasis of this year's study was to evaluate the following (Best Results:*80/20):

  1. Long-term effects of four Nitrogen Mixtures with Hydrogen and compare with H_2 alone:

     (1) H_2-No Nitrogen (2) H_2-100 ppm Nitrogen (3) *80/20 molar H_2/N_2 (4) 50/50 molar H_2/N_2 (5) 25/75 molar H_2/N_2

  2. New Phase Evolution – $Li_{1.5}NH_{1.5}$
  3. Modeling – $Li_{1.5}NH_{1.5}$ and Li_4NH

C. **Addressing Charging/Discharging Rates and Applied Thermodynamic Studies**

- ***Difficulties in Interpreting Our Earlier Neutron and X-ray diffraction Data:*** These difficulties implied understanding of the phase equilibria of the system. So, *CALPHAD* thermodynamic modeling calculations were performed.

- ***Pressure-Composition Isotherms:*** Thermodynamic and Structural analyses performed to obtain phase stability information, and formation of new phases. Agreements between experimental and thermodynamic results found.

Summary of Previous year's Accomplishments

Li-N-H System (Gas Impurity effects)

- **Completed 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:**

Phase Fields Obtained from equilibrium Li-N-H Ternary Phase Diagrams (From 2009 Presentation Slide 10)				
225°C	$Li_3N(s) + H_2(g) \rightarrow$	$Li_3N(s) + Li_2NH(s) + Li(l) \rightarrow$	$Li_2NH(s) + LiH(s) + Li(l) \rightarrow$	$Li_2NH + LiH$ + gas
9 atm.		≤ 3 wt.% H	$\geq\sim 3 \leq 5$ wt.% H	$\geq\sim 5 \leq 9.5$ wt.% H
25°C	$Li_3N(s) + H_2(g) \rightarrow$	$Li_3N(s) + Li_2NH(s) + Li_4NH(s) \rightarrow$	$Li_2NH(s) + LiH(s) + Li_4NH(s) \rightarrow$	$Li_2NH + LiH$ + gas
9 atm.		$\leq \sim 2.5$ wt.% H	$\geq\sim 2.5 \leq 5$ wt.% H	$\geq\sim 5 \leq 9.5$ wt.% H

- **Li_4NH phase at room temperature; stable up to ~5 wt.%H and peritectically decomposes at 25°C.**
- **The amount of LiH phase formed under equilibrium loading of hydrogen was determined.**
- **New higher hydrogen capacity (5.8 wt.%H) cubic phase of $Li_{2-x}NH_{1+x}$ (x=1/2) type was found.**
- **X-ray diffraction pattern was also obtained of this solid solution intermediate phase.**
- **Improved kinetics were observed at higher pressures in the Li-N-H system.**

Summary of This Year's Accomplishments

Li-N-H System (New results on *Gas Impurity effects)*

- ***Significant Result*** → **Nitrogen gas compensation during cycling improved H-capacity. (Earlier studies revealed significant loss of N_2 from the solids during cycling)**
- ***Hydrogen Absorption Capacity*** → **Varied depending on the amount of N_2 mixed with H_2 ; in particular H_2/N_2 = 80/20 molar ratio yields ~10 wt.%H absorption.**
- ***ppm Level N_2 Added Improves H-Capacity*** → **Even 100ppm N_2 in H_2 significantly improved the hydrogen absorption as a function of number of cycles (~8 wt.%H); much more than with just H_2.**
- ***Terminal Phase During Desorption 80/20 H_2/H_2*** → **Significant increase in Li_2NH phase and decrease in the LiH phase (as compared to pure H2 loading).**

Applied Thermodynamics and Crystallographic Studies

- ***New Phase Detected Experimentally:*** **An intermediate phase $Li_{1.5}NH_{1.5}$ (F-43m), a= 05.027 Å, and vol.=127.04 Å^3. determined.**

  General formula = $Li_{2-x}NH_{1+x}$ @ x=1/2 at H-5.8 wt.%; forms between imide (x=0) and amide (x=1) phases.

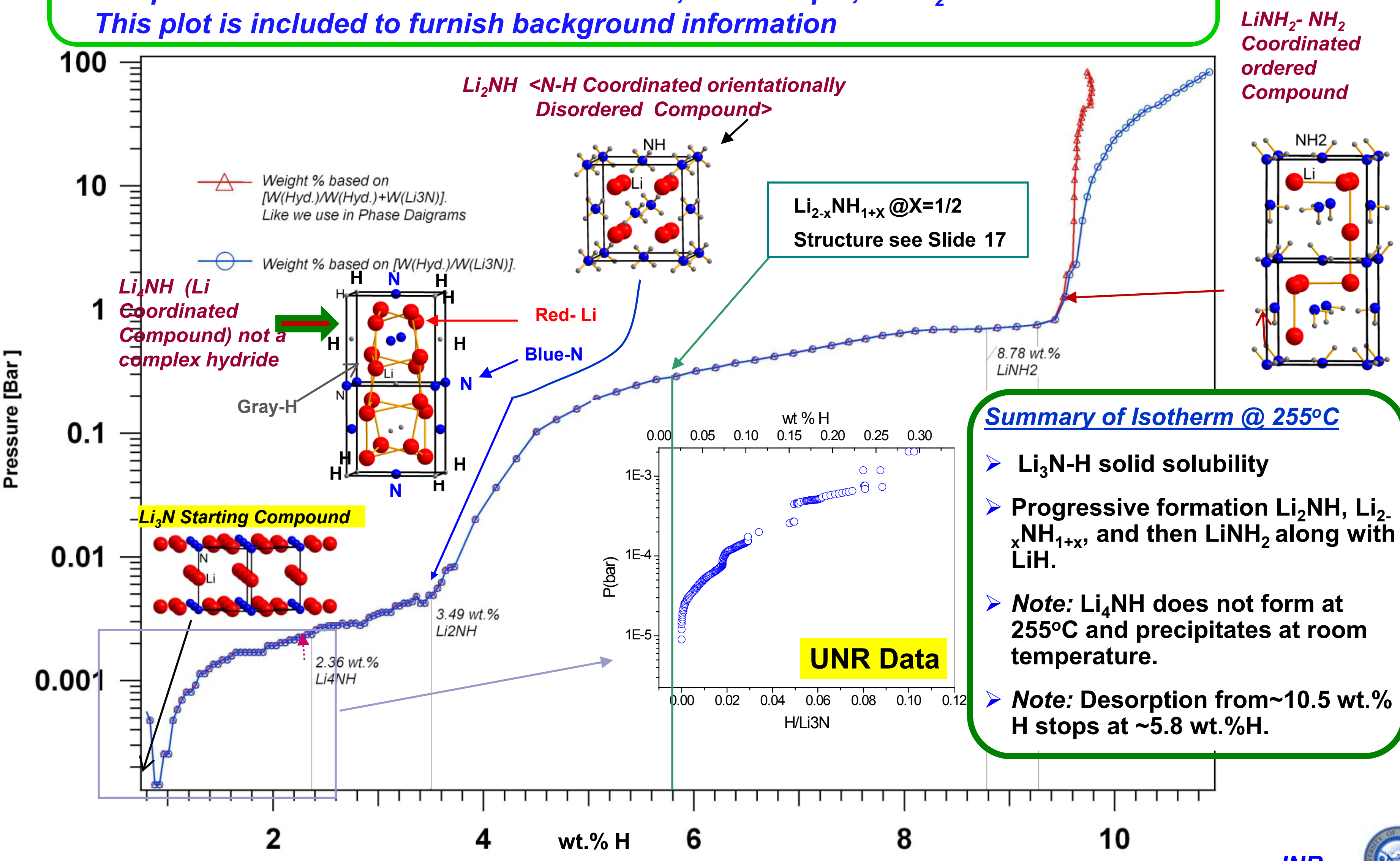
  Modeling performed on this compound

  Other investigators have reported another cubic phase, but details or compositions were not reported (*W. David et al.*).
- ***In-situ synchrotron x-ray diffraction Studies:*** **To elucidate phase equilibria details, work in progress.**
- ***Modeling Results:*** **Band structure, density of states, Electron Localized function determined of the $Li_{1.5}NH_{1.5}$ phase and compared with others.**

  Published in *Phys Rev B in 2010* (IEA collaboration)
- ***CALPHAD Modeling of Li-N-H System:*** **Critical phase reaction pathways determined with *progressive incremental loading of hydrogen* in Li_3N.**

Technical Accomplishments and Progress -1

- *Isotherm (Abs.) 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. This plot is included to furnish background information*



Summary of Isotherm @ 255°C

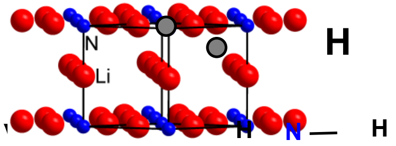
- **Li_3N-H solid solubility**
- **Progressive formation Li_2NH, $Li_{2-x}NH_{1+x}$, and then $LiNH_2$ along with LiH.**
- ***Note:* Li_4NH does not form at 255°C and precipitates at room temperature.**
- ***Note:* Desorption from~10.5 wt.% H stops at ~5.8 wt.%H.**

Phase Evolution Summary of the Li-N-H system

Li_3N

↓

Li_3N (ss)



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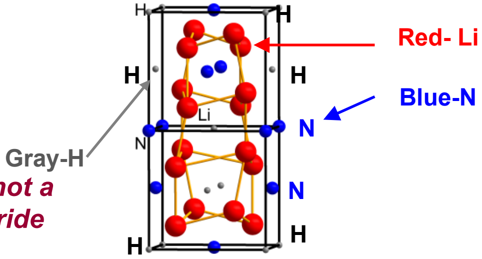
Li_4NH

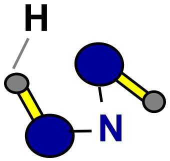
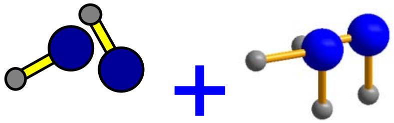
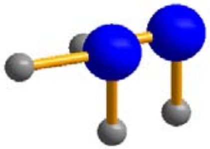
Li_4NH (Li Coordinated Compound) not a complex hydride



$LiNH_4$ Composition: 2.46 wt.%H

General Formula For Complex Hydrides ⇒ $Li_{2-x}NH_{1+x}$

↓

1st Complex Hydride **$Li_{2-x}NH_{1+x}$ @x=0 = Li_2NH** 	**N-H Disordered Bonds** **Structure: Slide 16**	**3.48 wt.%H**
↓ 2nd Complex Hydride **$Li_{1.5}NH_{1.5}$ @x=1/2**  **SS= Solid Solution compound* **x=1/2**	**N-H+N-H_2 Intermediate Compound** **Ordering at x=1/2** **Structure Slide 17**	**3.48 to ~5.8 wt.% H**
3rd Complex Hydride ↓ **$LiNH_2$ @x=1** 	**N-H_2 Ordered Bonds** **Structure: Slide 16**	**8.78 wt.%H**

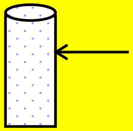
$Li_3N \rightarrow Li_3N$ (ss) $\rightarrow Li_4NH \rightarrow Li_2NH \rightarrow Li_{1.5}NH_{1.5} \rightarrow LiNH_2$

LiH → *SS→ 5.8 wt.%H*

METAL HYDRIDE CENTER OF EXCELLENCE

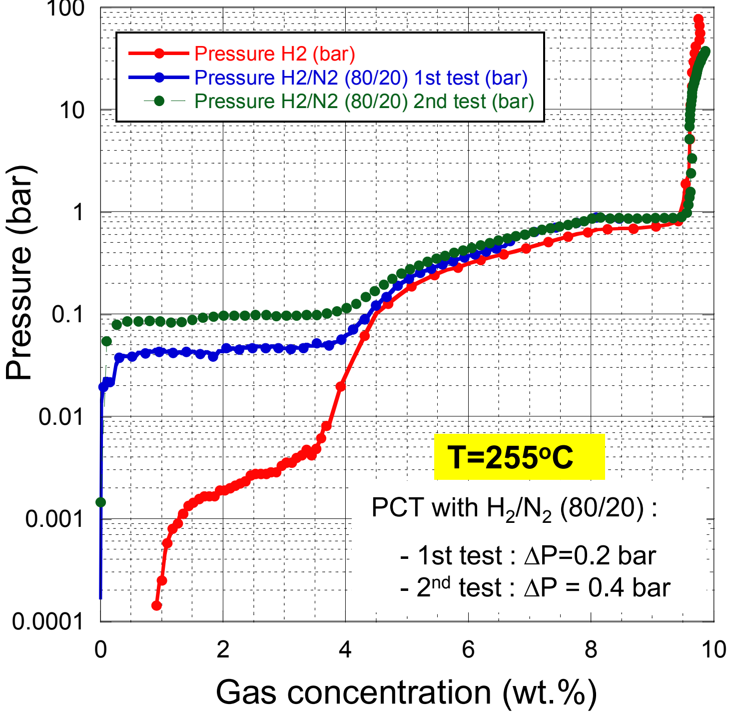
Comparison of PCI curves obtained under hydrogen and H_2/N_2 - 80/20 at 255°C

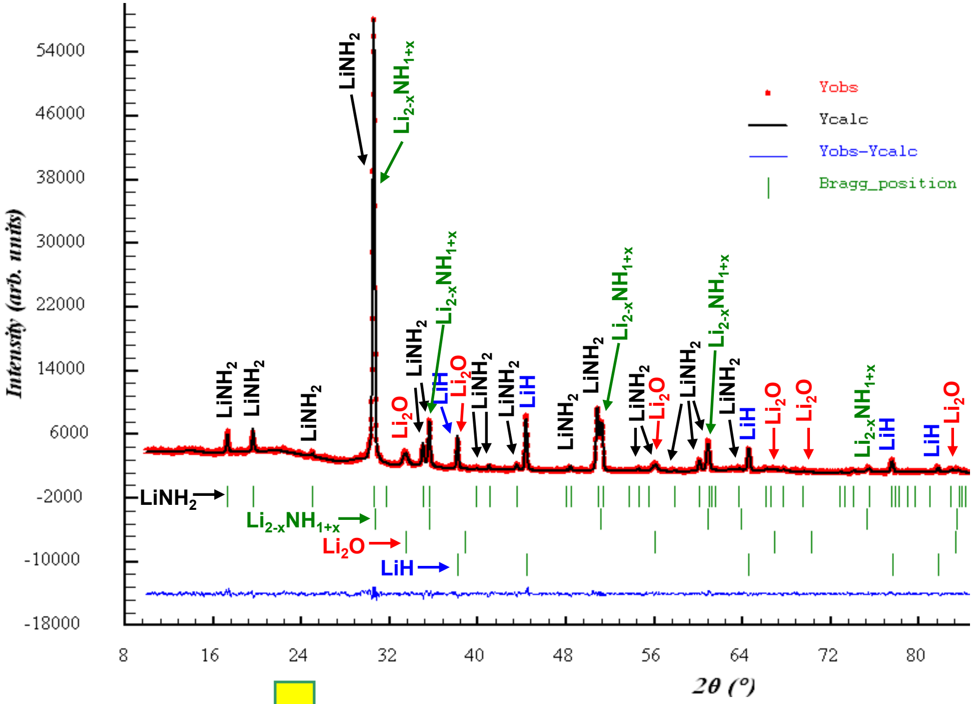
Sample Vial



Homogeneous White Powder with N_2/H_2 mixtures–No Slag-mass : 33 mg after the experiment.

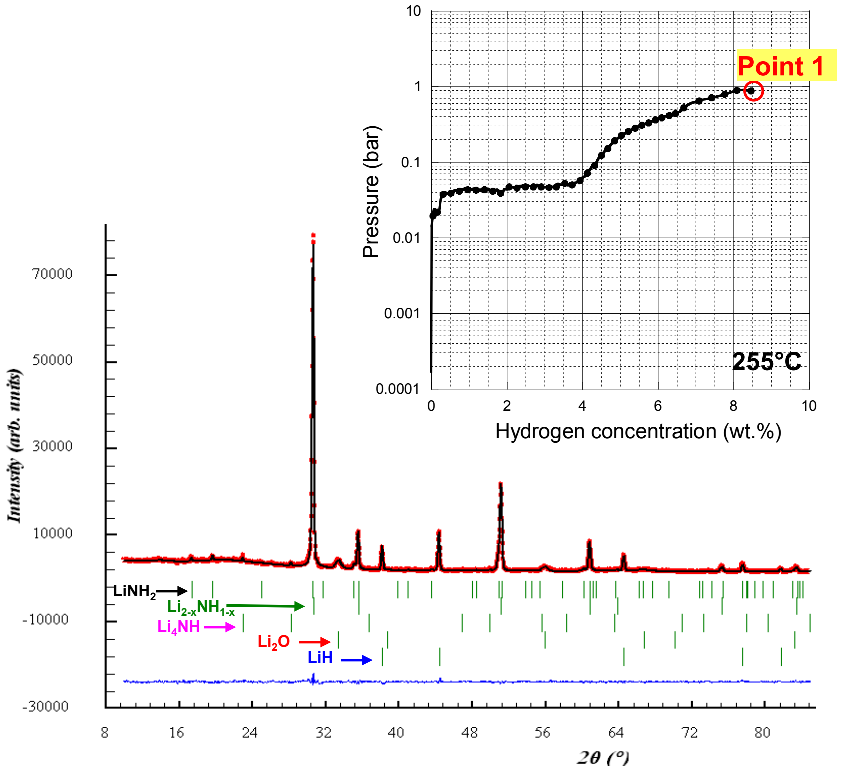
- Equilibrium pressure (up to ~4 wt.%H) is increased using N_2/H_2 mixtures as compared to pure H_2 (in Red).
- Cycling results show good absorption properties (Please see Slide 11)

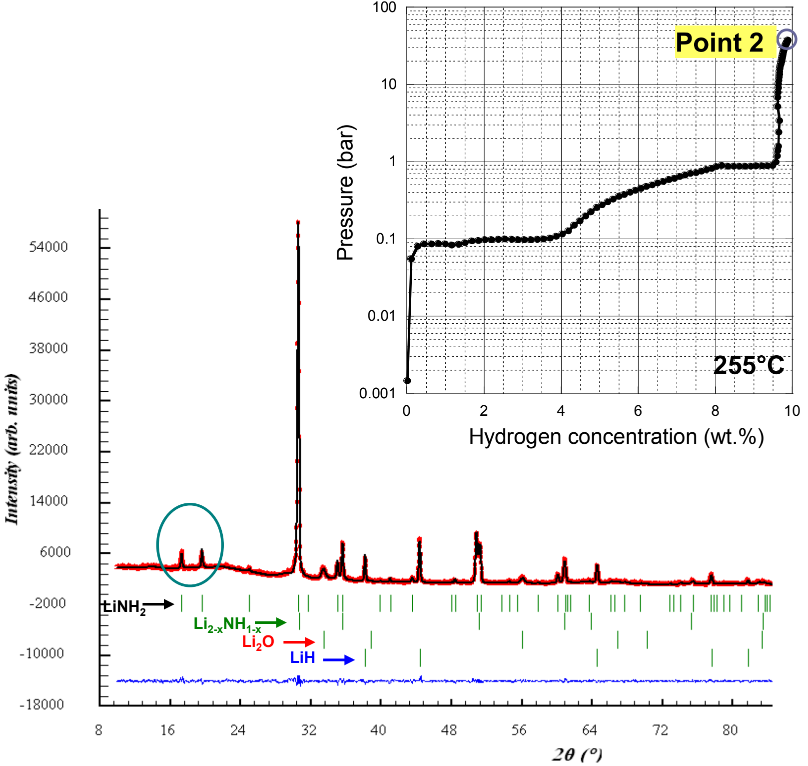




wt.% $LiNH_2$	wt.% Li_2NH	wt.% $Li_{2-x}NH_{1+x}$	wt.% Li_3N	wt.% Li_2O	wt.% LiH	wt.% Li_4NH	a $Li_{2-x}NH_{1+x}$ (Å)	Occ. Li	Occ. H
66	0	1 Fm-3m	0	5.5	27.5	0	5.0458	1.14	1.86

Phase evolution obtained Using H_2/N_2 (80/20)



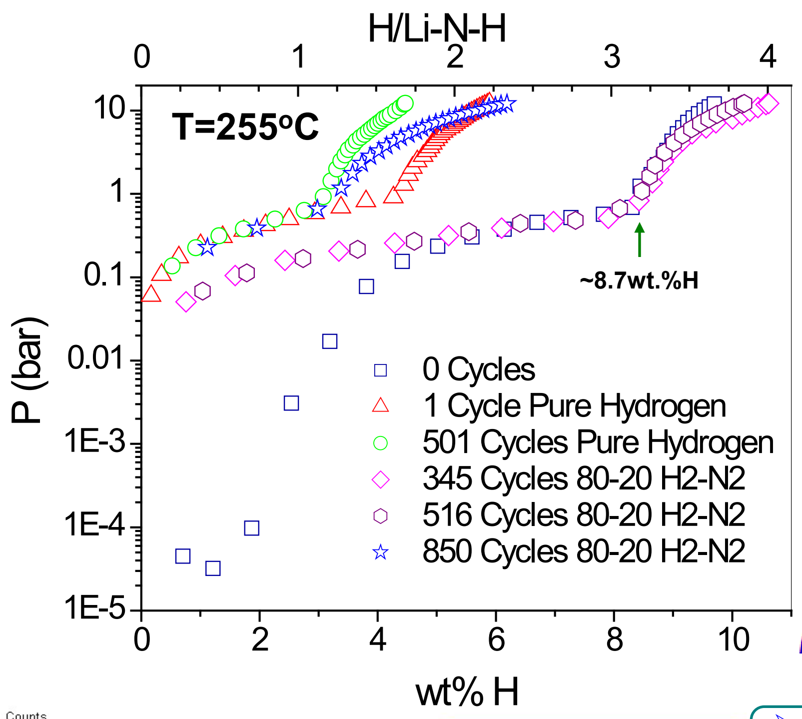


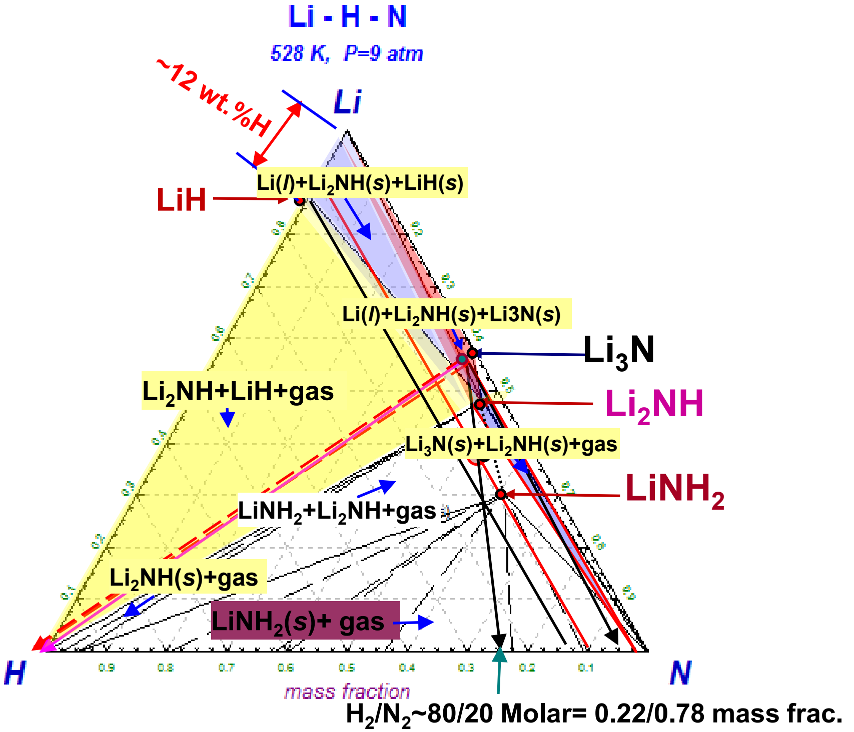
	wt.% $LiNH_2$	wt.% Li_2NH	wt.% $Li_{2-x}NH_{1+x}$	wt.% Li_3N	wt.% Li_2O	wt.% LiH	wt.% Li_4NH	*a* $Li_{2-x}NH_{1+x}$ (Å)	Occ. Li	Occ. H
Point 1	31	0	30 Fm-3m	1.5	6.5	31	0	5.0471	1.24	1.76
Point 2	66	0	1 Fm-3m	0	5.5	27.5	0	5.0458	1.14	1.86

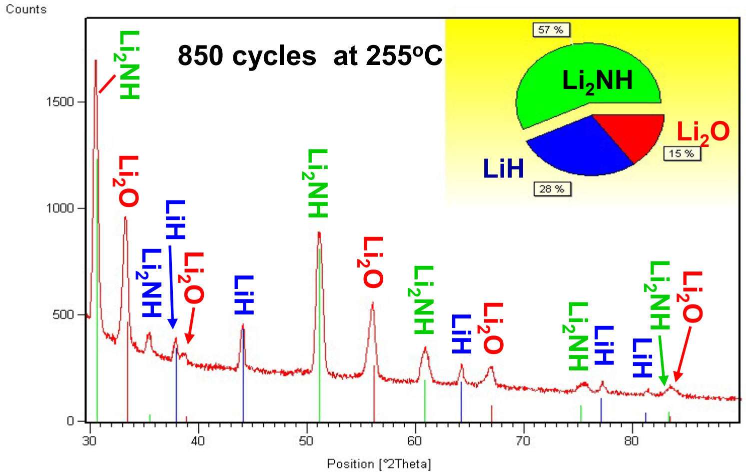
1. Partial loading of H to observe the phases formed showed that at ~8.2 wt.%H, 2 phases $LiNH_2$ $Li_{1.5}NH_{1.5}$ and LiH formed (isotherm intentionally terminated).

2. Fully loaded (isotherm –right) the $Li_{1.5}NH_{1.5}$ virtually disappears and increases the amount of Li_2NH

Increased H-capacity with higher N_2 Content by using 80/20 H_2/N_2 Mixtures During Pressure cycling

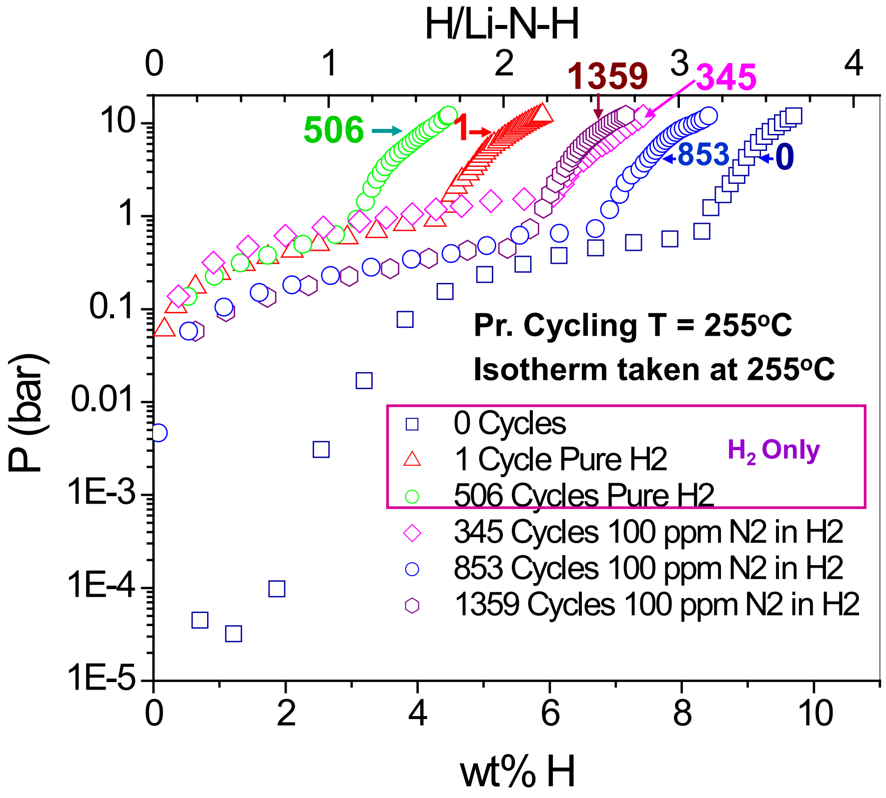






- ***80/20 molar H_2/N_2 shows High H-capacity:*** **The 345 and 516 cycles show as good a capacity of ~10 wt.% as the starting isotherm 0-cycle, which is remarkable.**
- ***Possible reason for Decrease in H-capacity after 850 cycles:*** **XRD pattern (left) shows increased oxide formation; O_2 might have been accidentally introduced in the system during transferring the sample holder after the 516th cycle (from the cycling machine to the Sieverts apparatus). This 850 cycles experiment needs to be repeated.**
- ***Replenishing the lost N_2 from Li-N-H compounds:*** **Prior results showed loss of nitrogen possibly due to evacuation /loading cycles.**

Effect Mixing trace amount of Nitrogen (100ppm) in H_2 on the Cycle ability of Li_3N-H



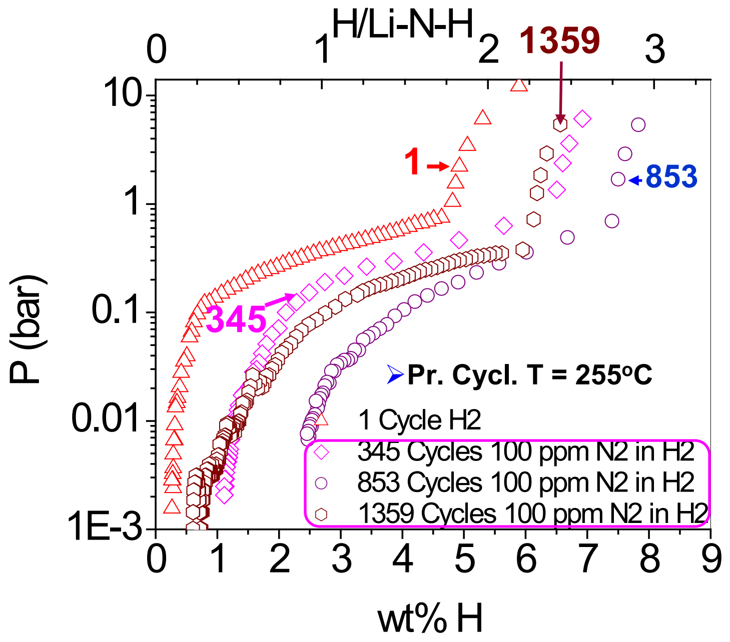
- ***Isotherm 0 (H_2):*** **Starting material-Li_3N isotherm is designated zero cycle.**
- ***Isotherm 1 (H_2): :*** **This starts at $Li_{1.5}NH_{1.5}$ +LiH and ends at $LiNH_2$.**
- ***Isotherm 506 (H_2):*** **This yields 4.2 wt.%H, with increased amount of LiH.**

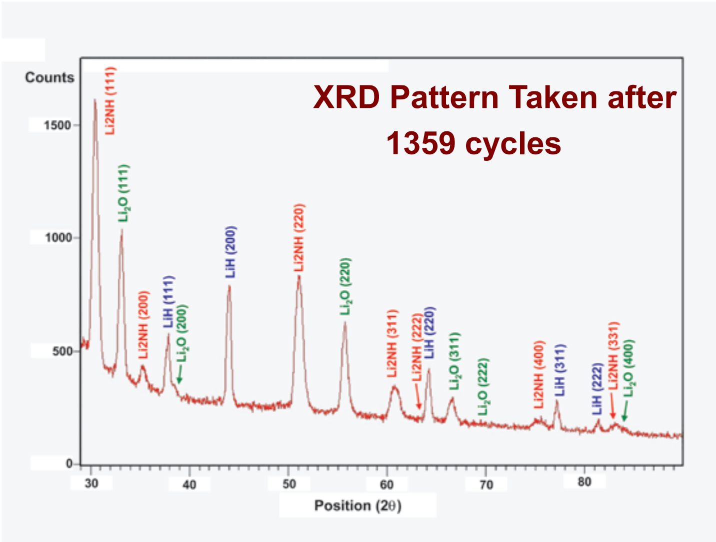
- ***Isotherm 345 (100 ppm N_2-H_2):*** **Shows 6.2 wt.% H, better than 1 cycle (5.8 wt.%H) or 506 cycles (4.2 wt.%) with only H_2.**
- ***Isotherm 853 (100 ppm N_2-H_2):*** **Increased H capacity (8.2 wt.%) as compared to the 345 cycle capacity of ~7.3 wt.%H.**
- ***Isotherm 1359 (100 ppm N_2-H_2):*** **Shows slight lowering (7 wt.%H) of capacity even with nitrogen.**

Conclusions

- **Mixing 100 ppm level of N_2 with H_2 shows much higher ultimate H-capacity as compared to even 1 cycled material with H_2 alone. All isotherms taken at 255°C.**
- **There is more Li_2NH formed in the mixed 100ppm-H_2 materials based on XRD measurements.**
- **The decrease after 1359 cycles is due to the formation Li_2O perhaps impurities in N_2 gas**

Comparison of Desorption Isotherms Obtained after Cycling H_2-100 ppm N_2

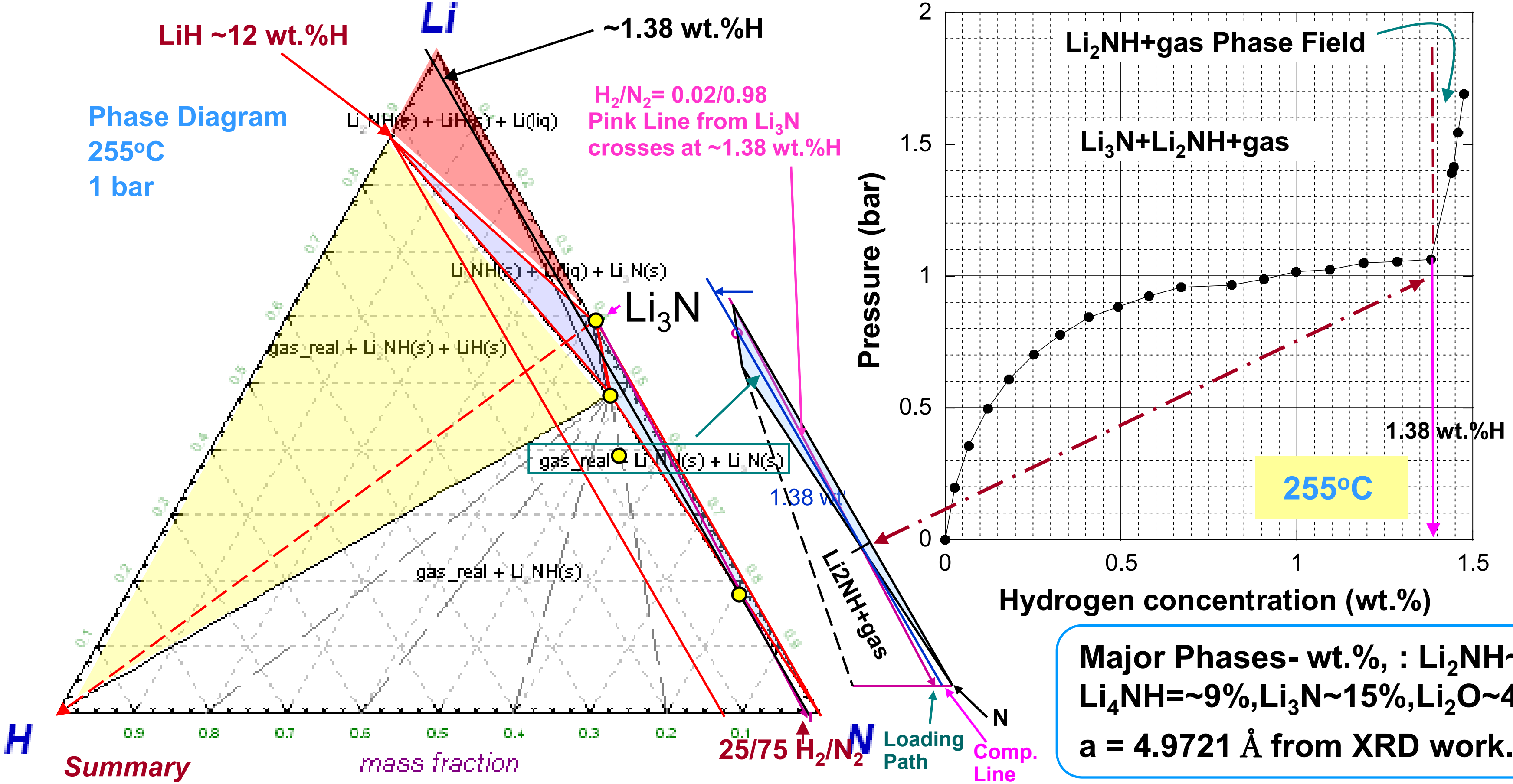




Summary:

- ***Significant Increases in H-Capacity During Desorption:*** **H- capacity much greater than 1 cycle material (H_2) and increases from 345 to 853 Pr.-cycles with H_2-100ppm N_2.**
- ***Accumulation of Li_2NH phase During Desorption cycles:*** **XRD results obtained after 1359 absorption/desorption cycles shows significantly more Li_2NH phase and less LiH phase as compared to cycling with H_2 alone. We believe that the Li_2O phase formation is due to trace O_2 impurity in N_2 gas added.**

High Nitrogen content PCI curve obtained under H_2/N_2 (25/75) pressure



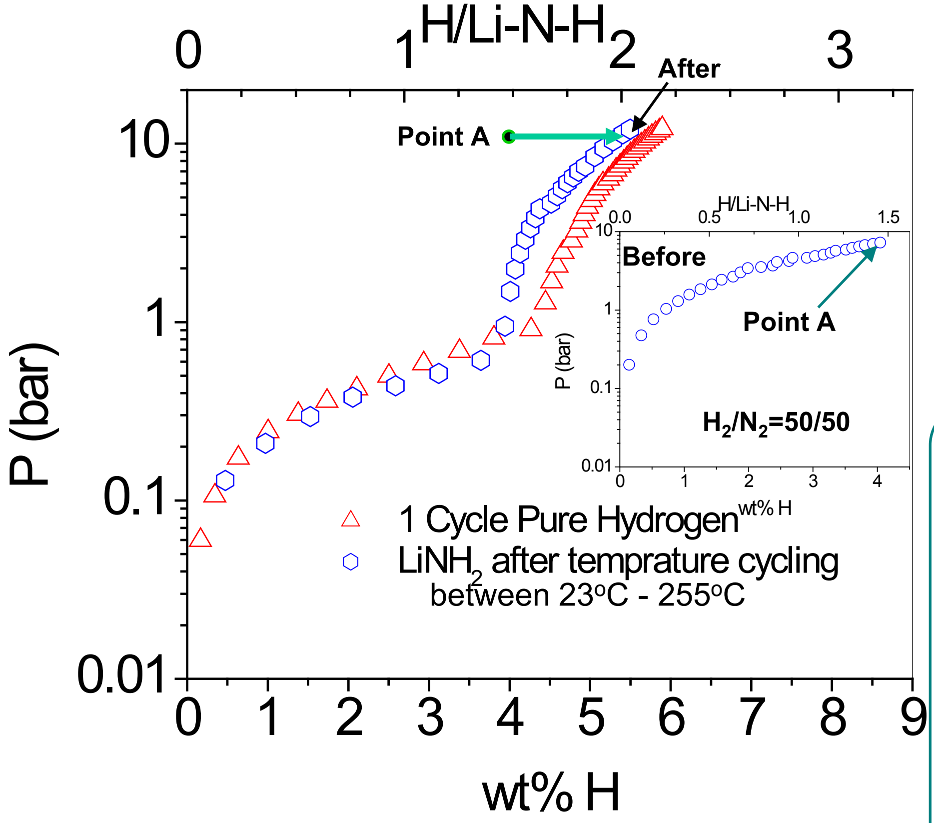
Major Phases- wt.%, : Li_2NH~70% Li_4NH=~9%,Li_3N~15%,Li_2O~4%

a = 4.9721 Å from XRD work.

Summary

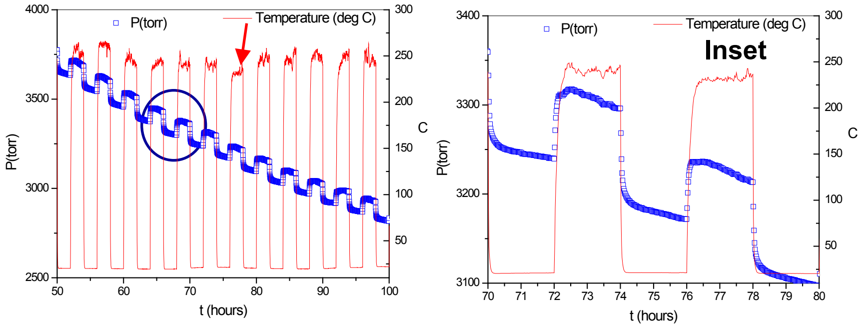
- **High partial pressure of N_2 in H_2 gas there is an abrupt change in pressure at H_2 conc. @ ~1.38 wt.%H in isotherm (right) taken with 25/75 H_2/N_2 molar or H_2/N_2= 0.02/ 0.98 wt. fraction.**
- ***CALPHAD* modeling of Li-N-H model phase diagram (left) shows a change in phase field in the Li-N-H diagram: Li_3N + Li_2NH + gas (blue region)→ Li_2NH + gas (white area) using 25/75 H_2/N_2 gas (see enlarged area –right).**
- **Li_2NH phase does not change >1.38 wt.%H, but there is more gas resulting abrupt increase in pressure.**
- **Ideally there should no LiH, but there is ~2 wt% LiH present in the final sample; due to the initial formation near the Li_3N-LiH-Li_2NH phase field in the ternary diagram.**

The Effect of Intrinsic Thermal (Temperature) Cycling on the H-capacity with starting material as $LiNH_2$ in H_2/N_2 50/50 Molar Between 23°C and 255°C



Conclusion:

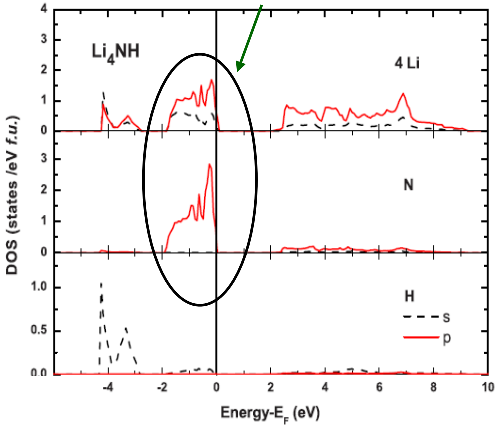
- Even high N_2 in H_2 (50/50) tends to increase H-capacity during cycling; but yields less than H_2/N_2 80/20 (see slide 11)

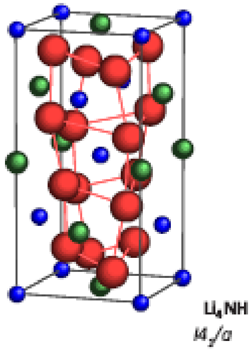


- ***Increased H-capacity:*** **Temp. cycling (top) shows a decrease in gas pressure (blue points) and clearly shows increased H-capacity, during cycling.**
- ***25 of 55 – 2 hours cycles shown (top-middle).***
- **The H- capacity increased from a ~4.0 wt% to ~4.5 wt%H after 55 thermal cycles (isotherm-Blue circles).**
- ***H-capacity: Expected to increase with further cycling.***
- **Isotherm (left-with pure H_2 in red triangles) taken after 1 cycle is included for comparison.**
- ***Large amount Li_2NH phase with H_2/N_2 cycling and some Li_2O phase (XRD)***

Summary of the Density of states of Li_4NH, Li_2NH and $LiNH_2$ showing Different Interactions

Li-H Interactions – Li_4NH





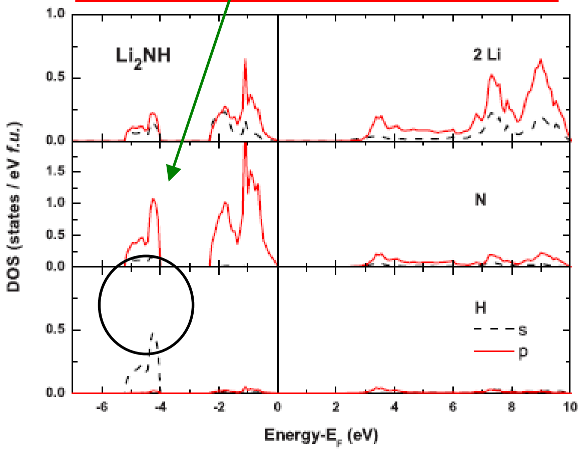
Ref. 1

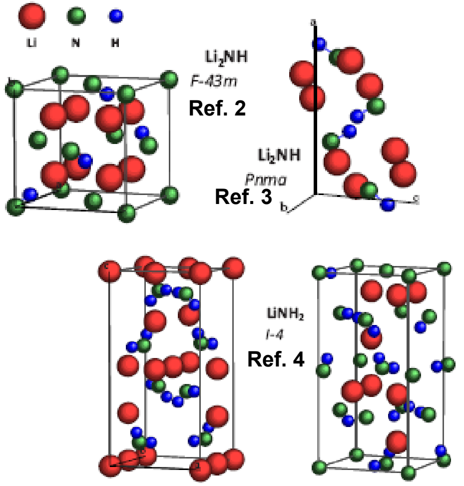
Ref 1. *J.C. Crivello, M. Gupta, R. Cerny, M. Latroche, and D. Chandra Physical reviews B 81, 104113 (2010)*

Summary:

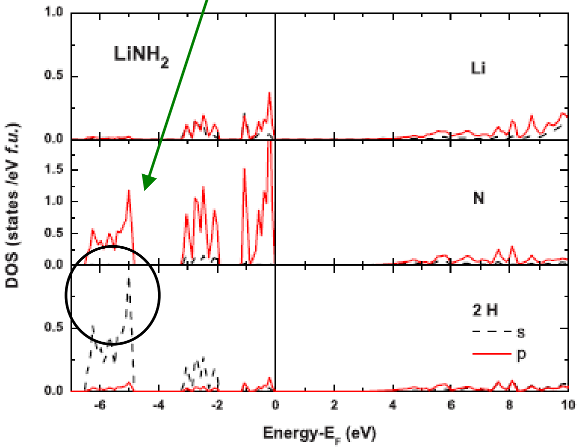
- **Modeling data of known Li_2NH, and $LiNH_2$ compared reasonably well with other investigators.**
- **Results of Li_4NH Published (*Phys. Rev. B-* ref.1)**
- ***E. Weidner et al. Chem . Phys. Letters 444.76 (2007) have also discussed the structure of Li_4NH***
- ***Note that Li_4NH is not a complex hydride, but Li Hydride –Nitride with Li-N and Li-H interactions.***

N-H Interactions - Li_2NH





N-H_2 Interactions-$LiNH_2$



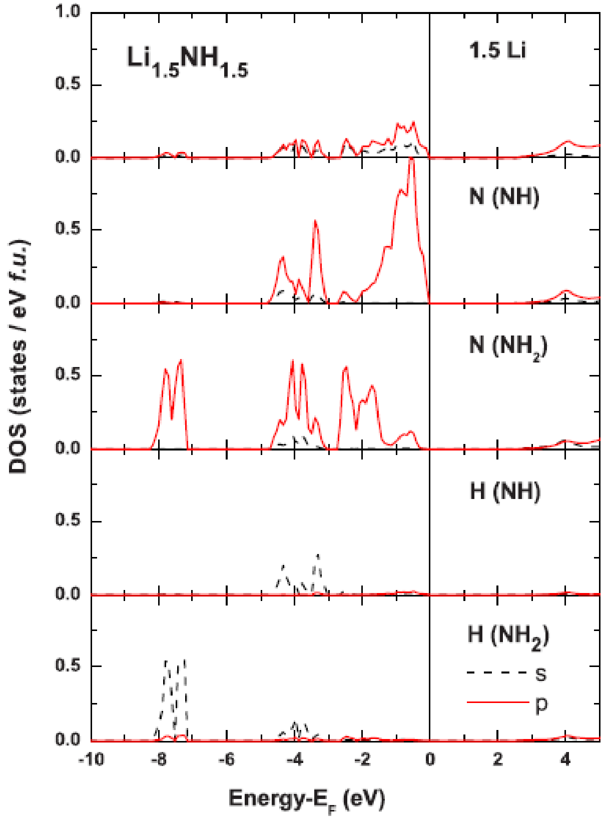
Ref. 2 K. Ohoyama, Y. Nakamori, S. Orimo, and K. Yamada, J. Phys. Soc. Jpn. 74, 483 (2005).

Ref. 3 B. Magyari-Köpe, V. Ozoliņš, and C. Wolverton, Phys. Rev. B 73, 220101(R) (2006).

Ref. 4 M. Sørby, Y. Nakamura, H. W. Brinks, T. Ichikawa, S. Hino, H. Fujii, and B. C. Hauback, J. Alloys Compd. 428, 297 (2007).

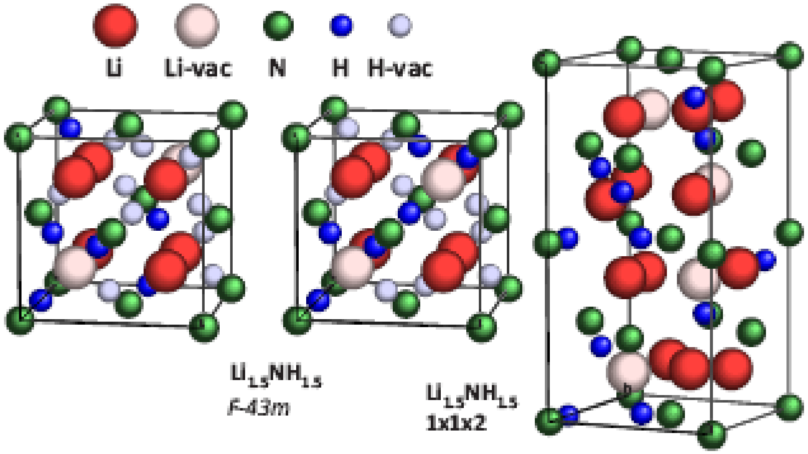
Technical Accomplishments and Progress - 11

Density of States showing both N-H and N-H_2 interactions in $Li_{1.5}NH_{1.5}$

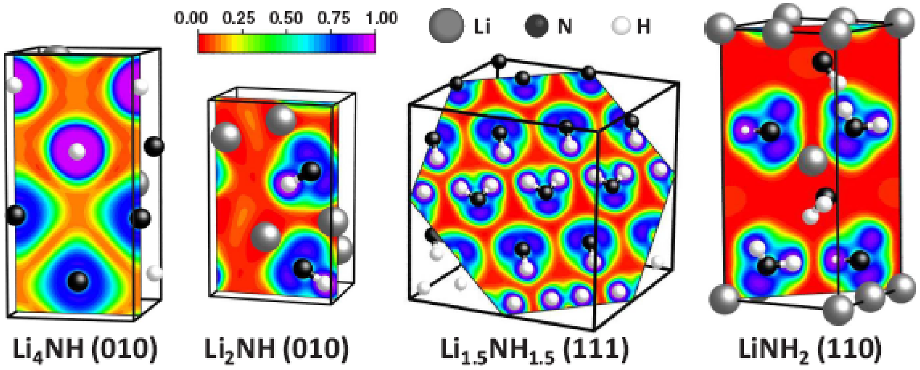


$Li_{1.5}NH_{1.5}$ DOS and Structure results from our modeling work (ref.1) show *N-H and N-H_2* interactions and ordering. Prior work of *W.I.F David et. al. J. Am. Chem. Soc, 129, 1594 (2007) is cited.*

Structure and proposed models for $Li_{1.5}NH_{1.5}$



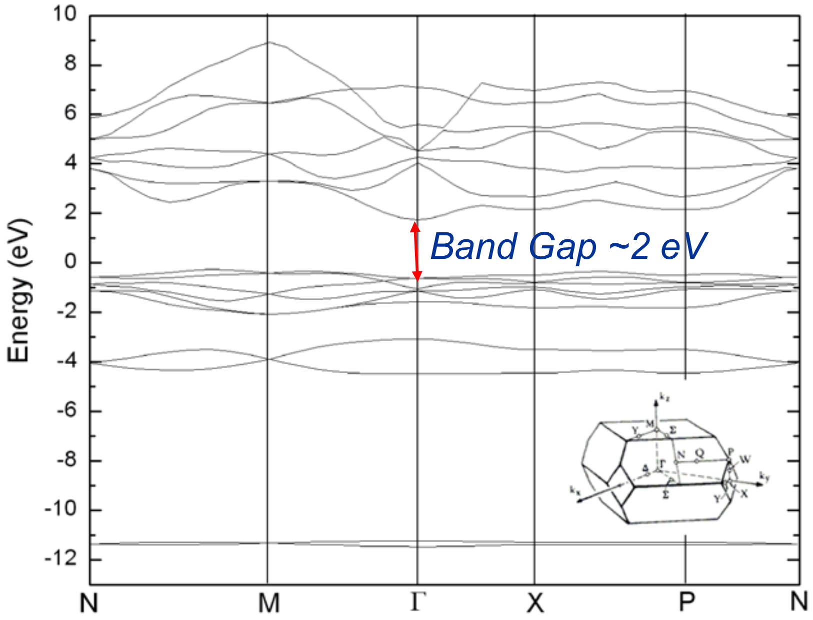
Calculated electronic localization function (ELF) for Li_4NH, Li_2NH, $Li_{1.5}NH_{1.5}$ and $LiNH_2$



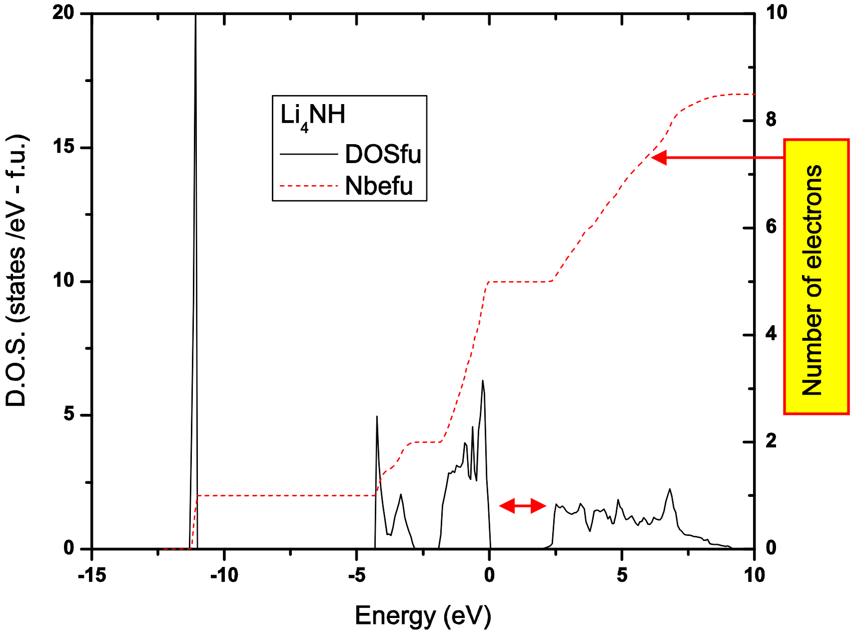
Ref 1. *J.C. Crivello, M. Gupta, R. Cerny, M. Latroche, and D. Chandra, Physical reviews B 81, 104113 (2010)*

Ab initio calculations - Li_4NH Electronic Structure (Semiconductor)

Bands Structure



Density of states



- Li_4NH is a **Li coordinated Compound (semiconductor with Band Gap ~ 2eV)**
- **Li_4NH not a complex hydride**

Collaborations

University of Genéve	IEA Collaboration, *Primary Contact:* Prof. K. Yvon, PI’s sabbatical leave research ***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, ***Type of Institution:*** University/French National Lab. ***Extent:*** Syntheses of Substituted complex hydrides and Modeling work
Synchrotron Center, Grenoble	Synchrotron Studies, *Primary Contact:* Dr. Y. Filinchuk ***Type of Institution:*** ESRF, France. ***Extent:*** In-situ Synchrotron XRD studies on complex hydrides.
University of Rome	IEA/IPHE Collaboration**,** *Primary Contact:* Prof. R. Cantelli **PI’s** sabbatical leave, ***Type of Institution:*** University ***Extent:*** Work on characterization of Defect structure DOE H_2 program.
Los Alamos National Laboratory	Heat capacity measurements *Primary Contact:* Dr. Jason Lashley ***Type of Institution:*** US National Laboratory ***Extent:*** Low temperature heat capacity measurements
Sandia National Laboratories	MHCoE Collaboration, *Primary Contacts*: Dr. L. Klebanoff , and M. Allendorf ***Type of Institution:*** US National Laboratory ***Extent:*** Modeling and MHCoE coordination on complex hydrides

Proposed Future Work

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

- **We plan to continue defect structure studies on Li_3N by introducing transition metals in Li_3N by two different methods. These defect structures are expected to reduce the Hydriding temperature.**

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.**

5. Correlation of all data and preparation of Manuscripts - *Post- DOE annual review 2010 Conference*.

- **We will finalize Journal publications after detailed analyses.**

Summary – 1

- ***Long-term stability of light weight complex hydrides for vehicular applications*:** Determine critical aspects related to durability/operability of complex hydrides.

- ***Role of ppm gaseous impurities in hydrogen gas:*** **Studies simulate periodic H_2-filling at a *commercial hydrogen gas station* for future H_2-vehicles.**

- ***Practical Issues:*** **Envision premixed 80/20 H_2/N_2 gas will be used to load the hydride bed and majority of hydrogen will be absorbed by the Li-N compounds.**

  Residual N_2 gas over-pressure is expected in the hydride tank; as lost N_2 from the Li-N-H compounds is replenished (as observed experimentally during cycling).

- ***H-Capacity Increase During Pr. Cycling:*** **Typically H-capacity deceases with hydrogen gas (alone), but we observed increased H-capacity with mixed 80/20 H_2/N_2 (molar) yielding ~10 wt.%H.**

- ***Trace amount of N_2 also increases the cycling capacity:*** **Mixing 100ppm N_2 in H_2 also significantly improves the hydrogen absorption, although 80/20 H_2/N_2 gave the best results.**

- ***Increase in Li_2NH Phase and Suppression of LiH Phase During 80/20 H_2/N_2 Pr. Cycling*:** Significant increase in the amount of Li_2NH phase in the system after cycling.

Summary – 2

Applied Thermodynamics and Crystallographic Studies

- ***New intermediate $Li_{1.5}NH_{1.5}$ identified:*** $Li_{2-x}NH_{1+x}$ at x=1/2 has a terminal composition of 5.8 wt.%H; phase forms between imide (x=0) and amide (x=1).

  This cubic phase (F-43m) lattice parameter's are a= 5.027 Å and vol. 127.04 $Å^3$. Calculated values are 5.111Å. Other investigators have reported another cubic phase, but details or compositions were not reported.

- ***Phase equilibria Studies Using In-situ synchrotron X-ray diffractions:*** Majority of work done – finalizing manuscript details.

- ***Modeling:*** Band structure, density of states, ELF's of the new $Li_{1.5}NH_{1.5}$ are compared with other Li-N-H phases; reported in publication Phys Rev B in 2010 (IEA collaboration).

- ***CALPAHD Modeling:*** Critical phase reaction pathways determined using *progressive incremental loading of hydrogen* in Li_3N.

Acknowledgements

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

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