

IV.A.1o Effect of Gaseous Impurities on Durability of Complex Li-based Hydrides for Hydrogen Storage

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Objectives

- Determination of the effect of ppm level impurities in H₂ gas as well as the effect of impurities and defects in light-weight storage materials.
- Evaluate the long-term durability of light weight Li-N-based compounds.
- Understand the reaction pathways for both developing new materials with enhanced hydriding

properties, modifying or controlling reaction pathways for improved performance.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (D) Durability/Operability
- (E) Charging/Discharging Rates
- (K) System Life Cycle Assessments
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

This project is conducting fundamental studies of light weight hydrogen storage materials, particularly of the Li-N-H system. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2010 hydrogen storage targets:

- System Gravimetric Capacity: 1.5 kWh/kg
- Storage System Cost: \$4/kWh net
- Cycle Life (1/4 tank to full): 1,000 cycles

Accomplishments

- Made progress in cycling tests on Li-N-H system to determine the effect of various gaseous impurities in H₂ (100 ppm levels 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 significant loss in hydrogen capacity.
- Critical phase reaction pathways determined using progressive incremental loading of hydrogen in Li₃N, supported by calculation of phase diagrams (CALPHAD)-developed Li-N-H phase diagrams.
- Determined formation of the Li₄NH phase at room temperature; this phase is stable up to 5 wt% H and is a peritectically decomposed phase observed at 25°C.
- Details of the amount of LiH phase formed under equilibrium loading of hydrogen determined.

- New higher capacity solid-solution cubic phase of $\text{Li}_{2-x}\text{NH}_{1+x}$ type was found.
- Improved kinetics observed at higher pressures in the Li-N-H system.



Introduction

Light weight complex metal hydrides are becoming increasingly important for hydrogen storage due to its gravimetric and volumetric capacities. Gaseous impurities (ppm levels) in ultra-high purity (UHP) hydrogen may cause loss in hydrogen capacity during cycling. Extrinsic pressure cycling and thermal aging with impure hydrogen was used to evaluate capacity changes in this project; many of the tasks are complete. These tests are important for long-term reliability of metal hydrides that is important for working towards achieving DOE technical targets for a hydrogen economy. In general, UHP hydrogen is used in the research laboratory for the development of metal hydrides. However, commercial hydrogen will always have some very low level impurities (ppm levels); typically O_2 , H_2O , CH_4 , N_2 , hydrocarbons, and others in hydrogen. Typical industrial grade hydrogen, that we used showed: “Hydrogen min % (v/v) 99%, water ~32 ppm, O_2 ~10ppm, N_2 ~400 ppm, total hydrocarbons: 10 ppm, CO_2 ~10 ppm, CO ~10 ppm, argon may be present, reads as oxygen.” We also used special 100 ppm O_2 mixed with UHP hydrogen in this study. These low level impurities affect the performance of hydrogen storage materials in the hydride beds that are installed in automobiles. The purpose of the pressure cycling experiments (with fresh charges of impure hydrogen) is to simulate the long-term performance of metal hydrides with trace amounts of impurities in the hydrogen with the above mentioned gases. In addition, it is possible that by products of the hydrogen storage (side-reactions), such as, possible generation ammonia gas may occur and affect the storage properties. The degradation of the hydriding properties are generally associated with disproportionation or decomposition of hydrides surface or bulk properties of the material during normal periodic charges of impure hydrogen. These studies are expected to lead to the understanding of mechanisms that occur after “hydrogen filling” in tanks numerous times. In another situation, for example, a hydride bed is left unused for a prolonged period of time, i.e., hydrogen is fully loaded in a hydride bed from a gas station, this type of test is called *Thermal Aging*; performed at elevated pressures and temperatures.

The objective of this research is to investigate the effect of trace impurities in complex hydrides by the principal investigator’s (PI’s) group as well as Center partners which can be potentially used for fuel cell

and other applications and aid in the development of materials solutions to potential hydrogen sorption degradation problems. The relevance to the Metal Hydride Center of Excellence program is that, trace impurities in hydrogen gas will have an impact on the hydrogen loading capacities during periodic recharging with fresh hydrogen in practical applications. These tests are being performed by accelerated laboratory testing which are extremely useful to understand the reliable use of hydrogen fuel. The PI was on sabbatical leave at the University of Geneva, University of Paris, and Università di Roma “La Sapienza” where some of the work was performed.

Approach

In this research, we are conducting experiments on cycling and aging tests of materials (as described in the above section) developed by the Center partners. Pressure cycling apparatus was constructed at UNR for hydrogen loading and unloading. The overall approach to perform cycling on currently reversible complex hydrides such as imide/amide system (using Li_3N as precursor), Li amide-alanate that has theoretical hydrogen capacity ranging from ~7 to ~10.5 wt% hydrogen. The specific tasks were to determine the changes in the pressure-composition isotherm after cycling with impure hydrogen. A reference temperature of 255°C and a hydrogen pressure range from vacuum to 2 bar was chosen, based on pioneering research of Prof. Ping Chen’s *Science* paper [1].

We have expounded on the initial results obtained last year by performing crystal structure analyses after cycling steps, by obtaining isotherms with UHP hydrogen (after cycling with impure hydrogen). Crystal structure analyses were performed as well that revealed new phase formation, yet showed hydrogen storage properties. Characterization of the phases before and after these cycling tests was performed using both static and dynamic X-ray diffraction revealed the impurity related and intrinsic impurity phases after cycling. We performed synchrotron in situ X-ray diffraction on $\text{Ca}(\text{BH}_4)_2$ in collaboration with ESRF, France, and Sandia National Laboratories. In addition, studies were performed on the sabbatical leave in Geneva, Paris and Rome, where thermodynamic phase equilibria and crystallographic studies were performed.

Results

High resolution pressure-composition isotherms were obtained on the $\text{Li}_3\text{N-H}_2$ system (Figure 1) at the University of Genève. It can be noted there the isotherm exhibits a slope or a curvature at higher hydrogen compositions indicating a possible new plateau. However, this curvature was found to be due to the use of H/M rather than H/H+M. In Figure 1 there are two

isotherms superimposed, which show no significant change at lower hydrogen content, but at higher concentrations there is no absorption of hydrogen. It should be noted that in the case of heavy classical metal hydrides these difference in the calculation methods do not result in changes of the isotherm profile. Also, we have new high resolution very low pressure isotherms from UNR, obtained recently which gives more details.

In situ differential scanning calorimetry performed on the Li-N-H system showed that there were two possible melts during heating with hydrogen gas. Starting with Li₃N in hydrogen atmosphere we obtained data that suggests two possible melts around ~50° and ~325°C (endotherms) during heating. In the same experiment a cooling curve was also obtained. There is a large exothermic region (between 180° and 330°C) which does not correspond to Li₂NH to LiNH₂ transformation. More detailed studies are in progress in Reno, using industrial hydrogen gas environment in the differential scanning calorimeter.

Although detailed analyses are in progress, we show a section of the X-diffraction pattern that relates to the presence of Li₄NH and a new solid solution cubic phase in addition to Li₂NH (cubic phase). We determined details of phase transformations during hydriding of Li₃N by intentional termination of the hydrogenation at pre-determined compositions in a Sievert's apparatus. Crystal structure evaluation was performed by using X-ray diffractometry at room temperature on a series of samples. X-ray diffraction data (inset) shows details of phase transformations (Figure 2). We discuss only the formation of Li_{2-x}NH_{1+x} phase here. Between 0.52 and 3.2 wt% H we found presence of Li₂NH phase. At higher H-concentration we found the Bragg peaks of a new solid solution phase Li_{2-x}NH_{1+x} up to 8.1 wt%. At 9.5 wt% H, we found Bragg peaks corresponding to LiNH₂. We also found the compositions at which

Li₄NH is stable; up to 3.2 wt% H. The LiH phase begins to form at slightly higher pressures when hydrogen contents reach ~4.8 wt% H.

In another study, we confirmed the formation of hydride phases using quantitative X-ray diffraction analyses on two partially hydrogenated samples at ~1 and ~8 wt% H. At 1 wt% H we found 19 wt% Li₄NH phase, with 33 wt% Li₃N and other phases (Table 1). At 8 wt% there is a large amount of LiH (42.5 wt%). It is interesting to note that there small amount of LiNH₂ (8.5 wt% H) although this phase should form at ~8.78 wt% H; this is possibly due to a start of two phase region in the binary Li₃N-H₂ phase diagram.

TABLE 1. Quantitative Analysis of Phases Present after Loading of Li₃N to 1 and 8 wt%

Phase	wt% @ 1 wt% overall H ₂	wt% @ 8 wt% overall H ₂
LiNH ₂	0	8.5
Li ₂ NH	43	41.5
Li ₃ N	33	2.5
Li ₂ O	2.5	5
LiH	2.5	42.5
Li ₄ NH	19	0

In an effort to characterize the defect structure of the complex hydride precursors, we added impurities to Li₃N. A very brief background is given below of the methodology. In this method we measure elastic energy dissipation coefficient that is given by Q⁻¹=M''/M', where Q⁻¹ is the elastic energy coefficient. A pulse is applied to the sample momentarily, and then turned off, and we measure the logarithmic decrement of the vibration

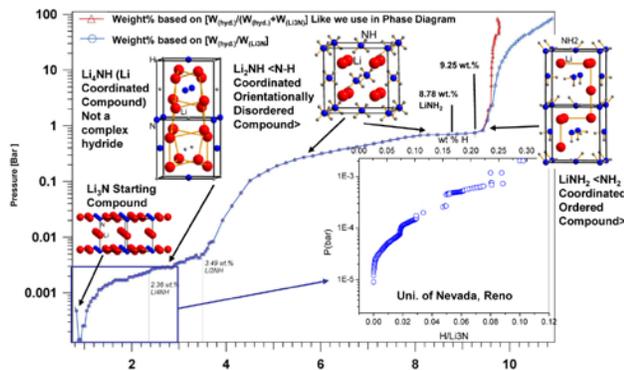


FIGURE 1. A baseline high resolution isotherm for the Li-N-H system, with Li₃N as starting material is shown obtained at University of Genève. The inset shows very low pressure isotherm obtained at University of Nevada, Reno at 255°C.

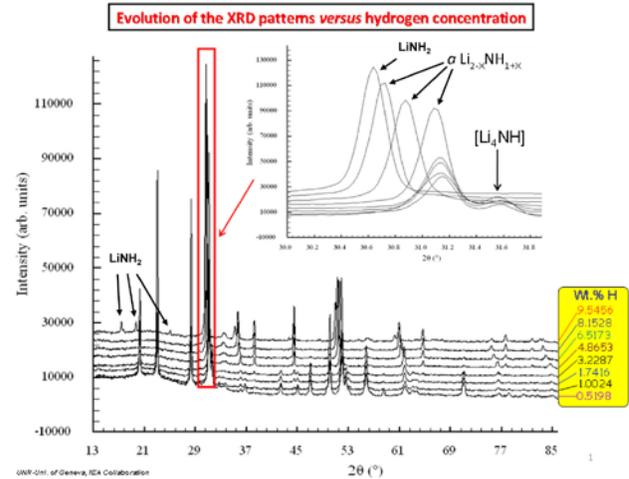


FIGURE 2. X-ray diffraction pattern from several experiments showing evolution of the Li_{2-x}NH_{1+x} phase above ~5 wt% H for hydrogen loading at 255°C. However, the patterns were taken at room temperature.

amplitude, through the width of the resonance curve as shown in the equations:

$$Q^{-1} = \frac{1}{\pi} \ln \left(\frac{A(t)}{A(t+T)} \right) \quad \text{and} \quad A = \frac{\text{const.}}{(\omega^2 - \omega_0^2)^2 + (\omega_0^2 Q^{-1})^2}$$

$$\text{where, } \omega = 2\pi f$$

$$M' = 0.95 \times \rho \times \left(\frac{l^2}{t} \right) \times f_0^2 \quad \text{where, } \rho \text{ is the density.}$$

Details can be found in the papers of O. Palumbo et al. [2] listed in this report. These studies in progress at Università di Roma “La Sapienza” (International Energy Agency [IEA] collaboration with Dr. Rosario Cantelli and co-workers); data will be reported later.

A detailed room temperature X-ray diffraction study of phase evolution was conducted in which the hydrogen loading experiments were performed at 255°C, and the samples were cooled to room temperature (at University of Geneva under IEA collaboration). The X-ray diffraction data was taken from samples at 0.52, 1.0, 1.7, 3.2, 4.9, 6.5, 8.1, and 9.5 wt% H. Care was taken to ensure that the pressure in the system did not rise above ~1 to 1.2 bar at each loading. First we will discuss the stability of the Li₄NH phase as a function of hydrogen concentration. It can be noted in Figure 3 that the Li₄NH concentration increases up to ~1.7 wt% then begins decreasing and finally disappears at slightly >~4.9 wt%. The presence of this phase was first reported by Weidner et al. [3] by performing low pressure studies on amide-imide studies. We confirmed that this Li₄NH phase forms peritectically at lower temperatures up to about ~5 wt% H. Marx [4] synthesized single crystals of this phase at low temperatures and determined the structure. Also, once the Li₄NH concentration decreases, the Li₂NH concentration rapidly increases. Next we discuss the termination of Li₂NH at ~5 wt% H and start of Li_{2-x}NH_{1+x} phase (see Figure 3); the X-ray data for Figure 3 is shown in Figure 2. The LiNH₂ phase evolves around 8 wt% H. The concentration of LiH phase continues to increase up to ~8 wt% H. A small amount of Li₂O phase is present at all concentrations.

In the imide-amide system there is always concern that NH₃ emission may occur during loading/unloading of hydrogen, that may have an impact on stability of these hydride phase. Therefore, experiments were performed on the Li₃N-H₂ system by thermal aging with 100 ppm NH₃ in H₂ at 255°C at 6.3 bar. Isotherms were taken before and after aging for 3 and 23 days, as shown in Figure 4(a). It can be concluded that 100 ppm levels of NH₃ in H₂ are not detrimental to this Li-N-H system at 225°C. X-ray diffraction patterns taken with and without NH₃ aging are shown in Figure 4(b). X-ray diffraction patterns (blue) obtained from the hydrides obtained *before aging at low pressure* (<<1.3 bar)

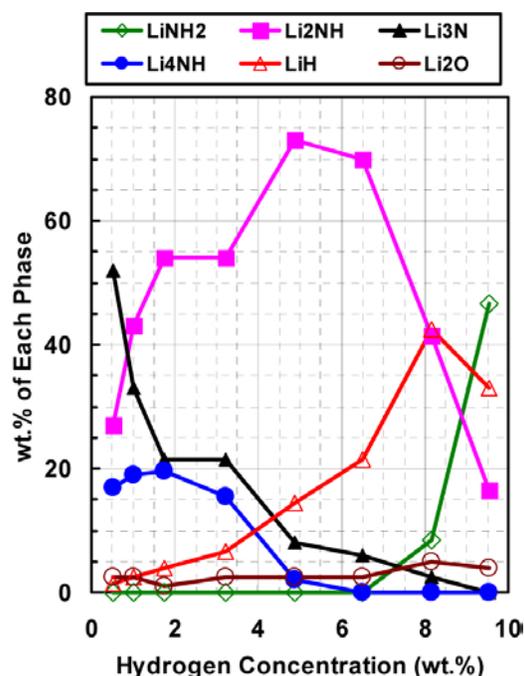


FIGURE 3. The amount of phase evolved (y-axis) after various amount of hydrogen loading (x-axis). Note the growth and decrease of Li₄NH and LiH phases.

showed predominantly Li₂NH phase, and some impurity phase Li₂O, as expected. After aging with 100 ppm NH₃ @ 6.3 bar, the X-ray diffraction pattern (red) showed mainly LiNH₂, LiH, and small amount of Li₂O phase. These are also expected phases under the pressure conditions.

Thermodynamic CALPHAD modeling is in progress. We have developed Li-N-H ternary phase diagrams at (1) 255°C and 9 atm (under H₂ loading condition), (2) 25°C and 9 atm, and (3) 25°C and vacuum (unloading condition). The ternary Li-N-H phase diagrams, not shown here, indicate the reaction pathways for the composition of ~2.5 wt% H:

- (1) Li₂NH(s) + Li₃N + Li (liq.) – (small amount @ 225°C, 9 atm.)
- (2) Li₃N(s) + Li₂NH(s) + LiH(s) – (cooled to 25°C, 9 atm.)
- (3) Li₂NH(s) + Li₄NH + LiH (s) – (25°C, with all gaseous H₂ removed)

Conclusions and Future Directions

- In support of the DOE 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

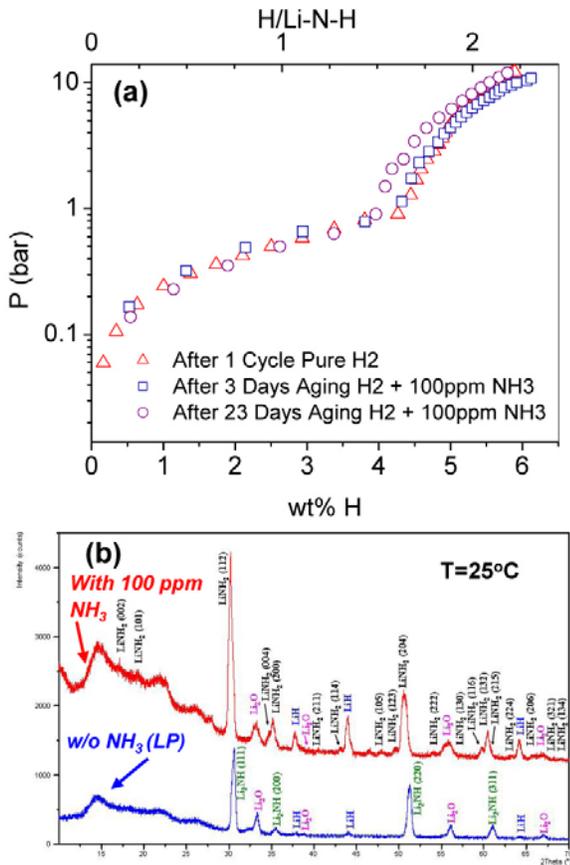


FIGURE 4. (a) Isotherms obtained before and after ammonia aging at 255°C at 6.3 bar with 100 NH₃/H₂ for 3 and 23 days, showing very little loss of capacity after 23 days. (b) X-ray diffraction pattern of sample taken before and after loading hydrogen with expected phases formed. At higher pressures, LiNH₂ phase is stable; but it is not a result of ammonia aging, just the experimental conditions.

during periodic filling at a commercial hydrogen gas station for future H₂ vehicles. Much of the data has been reported in previous years.

- Li-N-based compounds are used to evaluate long-term durability, reaction pathways for both developing new materials with enhanced hydriding properties as well as modifying or controlling reaction pathways for improved performance.
- Reaction pathways to overcome barriers that exist to improve the kinetics, lower hydrogen release temperatures, and extend cycle life are being determined. An example of stepwise incremental hydrogen loading is shown for Li₃N-H that exhibit three primary phase boundaries.
- Determined formation of the Li₄NH phase at room temperature; this phase is stable up to ~5 wt% H.
- Isobaric and isothermal aging at 255°C revealed that 100 ppm levels of NH₃ impurity exhibited virtually no loss of hydrogen capacity, whereas CH₄ impurities have low impact.

- A new non-stoichiometric Li_{2-x}NH_{x+1} cubic phase was found.

As for the future directions, we are continuing studies of cycling/aging with 100 ppm level impurities. We are developing thermal cycling experiment in which hydride samples will be cooled rapidly from 255°C to room temperature and reheated with hydrogen (rather than pressure cycling). In situ X-ray diffraction work will be used on newly developed hydride samples to understand reaction pathways with the goal of developing improved hydrides for vehicular applications.

FY 2009 Publications/Presentations

1. Dhanesh Chandra, Part III - Metal Hydrides, AB₂/AB Intermetallics for Hydrogen Storage, Gavin Walker, editor, Woodhead Publishing, UK, Book Printed 2008.
2. W. Chien, D. Chandra, J.H. Lamb, "X-ray Diffraction Studies of Li-Based Complex Hydrides after Pressure Cycling," *Advances in X-ray Analysis*, vol. 51. p 190-195 (2008).
3. **Book Chapter Printed.** D. Chandra, "Intermetallics for Hydrogen Storage" for the book chapter, Part IV. Chemically Hydrogen Storage, in "Solid State Hydrogen Storage Materials: Materials and Chemistry," Edited by Gavin Walker, Woodhead Publishing, CB21 6AH, England, ISBN 978-1-84569-270-4, 2008.
4. O. Palumbo, A. Paolone, P. Rispoli, A. D'Orazio, R. Cantelli, and D. Chandra, "Decomposition reaction of lithium amide studied by anelastic spectroscopy and thermogravimetry" *International Journal of Materials Research, Zeitschrift fur Metallkunde*, Vol.9, 2008, 487-490. (not reported earlier).
5. O. Palumbo, A. Paolone, R. Cantelli, and D. Chandra, "Lithium nitride as hydrogen storage material," *International Journal of Hydrogen Energy*, 33 (2008), 3107-3110.
6. D. Chandra, "Hydrogen and Nitrogen Interactions in Zr-Fe and Li- Based Hydrides," Seminar at the Chemie Metallurgique des Terres Rares, ICMPE, CNRS, **University of Paris, Oct. 30th, 2008.**
7. D. Chandra, "Hydrogen Storage in Li-N Complex Hydrides," Invited Talk given at the **University of Goettingen, Germany, Nov. 12, 2008.**
8. Dhanesh Chandra, Joshua Lamb, Raja Chellappa, Wen-Ming Chien, "Effect of Gaseous Impurities on Long-Term Thermal Cycling/Aging Properties of Complex Hydrides for Hydrogen Storage" **DOE - Sandia National Laboratory Program 2008 Review Meeting, December 12, 2008 at CalTech, Pasadena CA.**
9. Y. Filinchuk, E. Ronnebro, D. Chandra, Crystal; Structures and Phase Transformations in Ca(BH₄)₂," *Acta Materialia*, 57, 732-738 (2009).

10. **Dhanesh Chandra** and Tom Autrey, “Extrinsic Effects of Impurities on Long-Term Behavior of Complex Hydrides and Phase Equilibria Studies,” presented at International Energy Agency Task 22 – Workshop, IEA Task-22 Jeju Island Meeting April, 16–18 2009, Organizers: B. Hauback (Norway), Young Whan Cho (Korea).

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2. Palumbo, A. Paolone, R. Cantelli, and **D. Chandra**, “Lithium nitride as hydrogen storage material,” *International Journal of Hydrogen Energy*, 33 (2008), pp. 3107-3110.
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