IV.A.4o Effect of Gaseous Impurities on Long-Term Thermal Cycling and Aging Properties of Complex Hydrides for Hydrogen Storage

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Introduction

The effect of *extrinsic thermal cycling and aging* are important for long-term reliability of metal hydrides that is important for working towards achieving DOE technical targets for a hydrogen economy. It should be noted that all the laboratory experiments for the development of metal hydride materials are performed using ultra-high purity (UHP) hydrogen. However, the hydrogen that one may fill from a *"commercial hydrogen gas station"* will always have some very low level impurities (ppm levels). Hydrogen gas typically has ppm level impurities, such as, O_2, CH_4, H_2O, N_2, hydrocarbons, and others introduced along with the hydrogen. The supplier of industrial hydrogen gas in Reno has sent us the following specification for the industrial grade hydrogen, as follows: "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." During long-term use, these low level impurities will affect the performance of hydrogen storage materials in the hydride beds that are installed in automobiles. The purpose of the extrinsic pressure/thermal cycling experiments is to simulate what may happen to the performance of metal hydrides if there are trace amounts of impurities in the hydrogen. The evaluation of this effect is essential, before any major engineering deployment of the *hydride bed* of an automobile containing "newly developed hydride" materials. When hydride performance degraded by external impurities it is called "extrinsic disproportionation" of hydrides. This may affect surface or bulk properties of the material during numerous recharges. One can think of this as the effect of filling a new volume of hydrogen gas in the gas tank (just like one fills gasoline in a car gas tank, every time we run out of gas) and then removing most of the hydrogen from the hydride (in a cycle) to observe the long term effects. 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 an *Thermal Aging*; usually we perform these experiments at elevated temperatures and pressures to complete the experiment in a few weeks, rather 6 to 12 months. In the Metal Hydride Center of Excellence (MHCoE), the center partners are developing new hydride materials using UHP hydrogen that will be subjected these above mentioned extrinsic tests; the importance is that there should be minimal degradation after many hundred cycles.

The objective of this research is to investigate the effect of trace impurities (as described) in complex hydrides, 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 DOE MHCoE program is that, in practical applications, trace impurities in hydrogen gas will have an impact on the hydrogen loading capacities during periodic recharging with fresh hydrogen. Prolonged charge/discharge of hydrides in actual use may be performed by accelerated laboratory tests which are extremely useful to understand the reliable use of hydrogen fuel. UNR has constructed a semi-automated extrinsic cycling apparatus and as baseline tests we have performed pressure cycling on Li_3N based imide/amide system (this system is of interest due to high theoretical hydrogen content ~10.5 wt%). We found that there is a decrease in hydrogen capacity after more than 1,000 cycles. We also performed characterization tests using x-ray/neutron diffraction and calorimetry to identify the intermediate species and determine their effects on hydrogen capacity. The approach used for the baseline material will be extended to the hydrides that are being developed by MHCoE partners.

Approach

The primary objective of the current research is to conduct extensive extrinsic thermal cycling and aging

test for "new metal hydrides" that are being developed by MHCoE center partners. Towards this goal, a non-equilibrium (extrinsic) isothermal pressure cycling apparatus was constructed at UNR for hydrogen loading and unloading. The overall approach for the conducting this extrinsic impurity research is to identify key steps for conducting the experiments using a baseline material. The baseline material for the current year was the imide/amide system (using Li_3N as precursor) that has theoretical hydrogen capacity of ~10.5 wt%. The task was to determine the changes in the pressure-composition isotherm (PCI) after pressure cycling with impure hydrogen. A reference temperature of 255°C and a hydrogen pressure range from vacuum to 2 atm. was chosen, based on pioneering research of Prof. Ping Chen [1]. A reference PCI was determined using UHP hydrogen at the operating temperature and was in good agreement with that of Chen et al. [1]. The next step was to use industrial grade hydrogen to perform more than 1,000 cycles at 255°C with the duration of each cycle being one hour. After this, gaseous impurities (O_2, CO, H_2O, and others) in 100 ppm levels (determined in consultation with the Hydrogen Codes and Standards group at NREL) were separately mixed with the UHP hydrogen to determine any deleterious effects of these gases. Structural characterization of the phases before and after these cycling tests was performed using both static and dynamic (*in situ*) x-ray diffraction and neutron diffraction to reveal the phase transformation dynamics as a function of temperature and pressure. *In situ* thermal characterization using differential scanning calorimetry was also performed on the baseline materials. In addition to this, sublimation experiments of the baseline materials (using the gravimetric torsion effusion apparatus at UNR) were performed to identify any potential issues (that can be of importance in the desorption mode) regarding disproportionation in the vapor phase. In summary, the above mentioned experiments and characterization will be performed on new metal hydrides that are being developed by MHCoE center partners.

Results

Condensed Summary

Pressure cycling experiments were initiated to determine loss of capacity by fabricating an extrinsic cycling apparatus After subjecting the hydride for 1,101 cycles in industrial grade hydride, we determined the isotherms and found ~2.3 wt% hydrogen loss between $Li_2NH \Leftrightarrow LiNH_2$. It should be noted that after the very first cycle Li_2NH and LiH were formed, and subsequent cycles were expected to be between $Li_2NH \Leftrightarrow LiNH_2$ phases at 255°C. X-ray diffraction characterization after cycling showed formation of Li_2O (~30%) besides other phases. We also studied the commercial precursor Li_3N

from three different companies, and they have retained β phase [2] Li_3N along with α-phase [3]. *In situ* non-equilibrium deuteriding (neutron diffraction) showed $LiNH_2$ was the predominant phase formed. Lower concentrations of LiH and Li_2NH were formed between 200° and 250°C. During dehydriding at 250°C, we observed expected decrease in the $LiNH_2$ and increase in Li_2NH with the LiH phase amount remaining nearly unchanged. Vapor pressure studies were performed to study the release of Li or Li_3N and other vapors in the system that are detrimental to plumbing of the engineered system in long term use of fuel cell and other components; such as reactivity of Li with fuel cell's catalyst Pt interfaces. We found release of Li gas along with Li_3N gas during heating due to disproportionation of the precursor Li_3N.

A. Thermodynamic Studies

A1. Pressure Cycling Studies on Imide/Amide System

The results of long-term isothermal pressure cycling, between ~2 atmospheres and vacuum, showed that there was loss of ~2.3 wt% hydrogen at 255°C between $Li_2NH \Leftrightarrow LiNH_2$, using industrial hydrogen. A baseline isotherm was obtained starting with α-Li_3N that is shown in Figure 1. After the first cycle, Li_2NH and LiH were formed, and subsequent pressure cycling was performed between $Li_2NH \Leftrightarrow LiNH_2$. The very next isotherm taken after the baseline isotherm, before cycling, was denoted as the 1st cycle (middle isotherm in Figure 1).

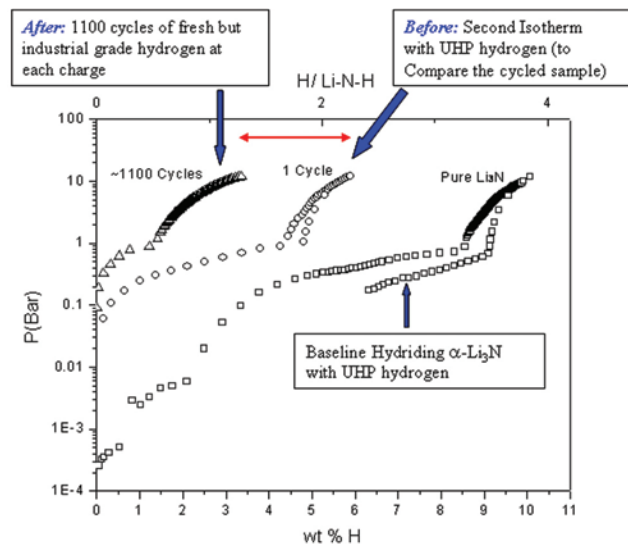**FIGURE 1.** Isotherms obtained from the *baseline* Li_3N sample, the 1st cycle with UHP hydrogen, and a 1,101 cycled sample using industrial grade hydrogen whose composition is given in the text. The starting point of 1st cycle and 1,101 cycled materials have been normalized to H/M =0; i.e the 1st cycle should overlap with baseline isotherm.

The starting point of 1st cycle isotherm is designated as H/M=0, to compare the changes in hydrogen capacities with long term cycled material. From the isotherm taken after 1,101 loading and unloading cycles of industrial hydrogen (far left, Figure 1) it can be seen there is a loss of 2.3 wt% hydrogen. The reason for this loss in capacity after cycling is attributed mainly due to the formation of Li_2O. Semi-quantitative x-ray diffraction analyses showed presence of LiH (~15.2%), Li_2O (30.5%), Li_2NH (~54.3%) after 1,101 cycles. Besides the presence of LiH, the increased amount of Li_2O phase formation is detrimental to amide/imide systems. Nominal gas analyses from supplier of industrial hydrogen gas are as follows: Hydrogen min % (v/v) 99%, Water~32 ppm, O_2~10 ppm, N_2~400 ppm, Total Hydrocarbons: 10 ppm, CO2~10 ppm, CO~10 ppm, Argon may be present.

A2. Vapor Pressures Measurement of α-Li3N

The vapor pressure of α-Li₃N was measured and found to be very low, 1.01×10^{-6} atm (~0.1 Pa) at 410°C increasing to 9.94×10^{-6} atm (~1 Pa) at 470°C during vaporization (Figure 2). A torsion effusion gravimetric apparatus was used at UNR to obtain these results [4]. The vaporization behavior is shown in Figure 3, and the equilibrium total pressure equation for vaporization is obtained as follows:

$$\ln P(Pa) = -9318 + \frac{12.24}{T(K)} \qquad (1)$$

The UNR data taken between 400-470°C is circled in Figure 4. Also superimposed is the literature data of Kimura et al. [5], who reported data between 466 and 586°C, but their pressures, are lower than ours. In general, the total vapor pressure (all gaseous
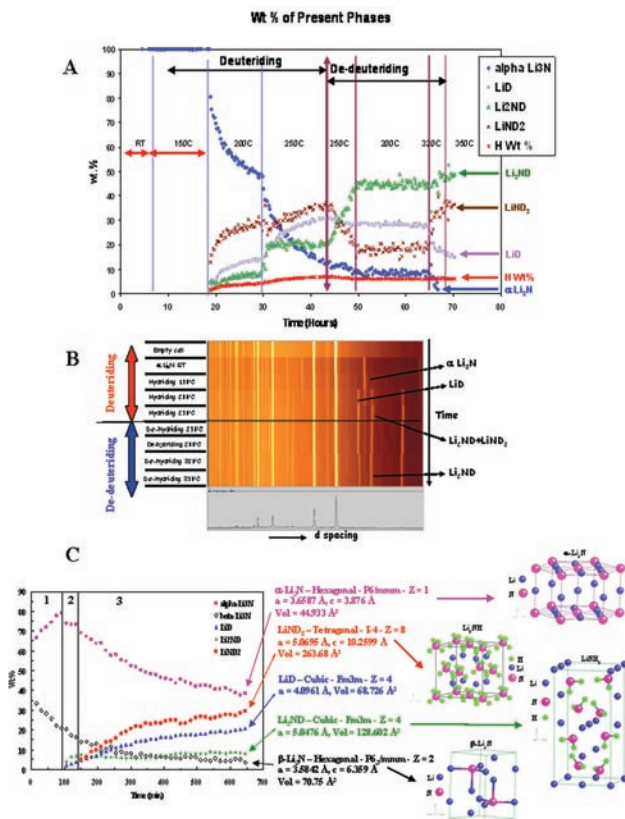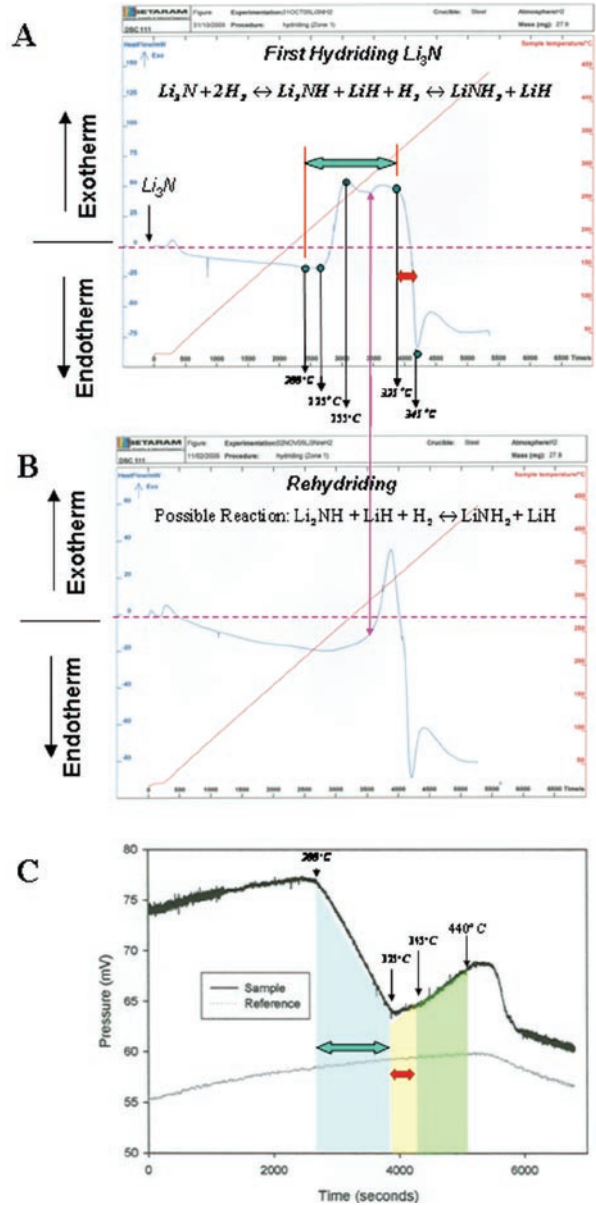
FIGURE 3. (A) Differential scanning calorimetric results with the starting materials as Li₃N showing the exothermic formation of hydride phases, and endothermic event possibly due to hydrogen release or ammonia formation. (B) A DSC scan was made with same material (as in Figure 3A) the second time which the exotherm appears at a higher temperature but the endotherm appear at approximately the same position suggesting that there no or very Li₃N phase present during the second trace. (C) A pressure vs. time plot for the first (Figure 3A) DSC trace.
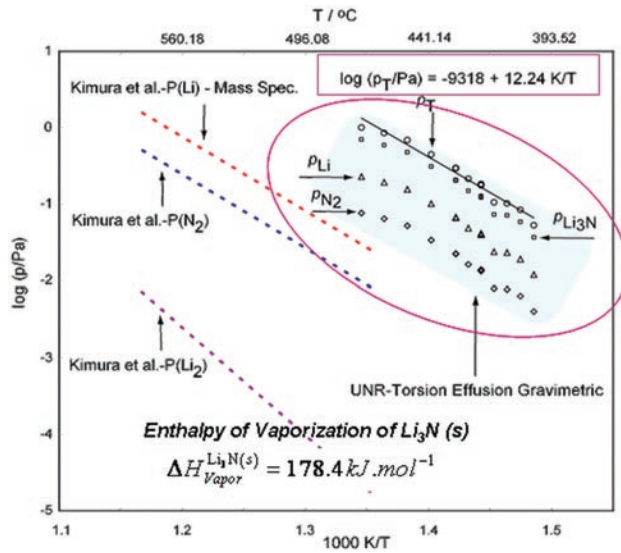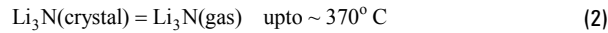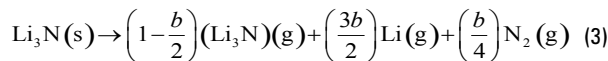
FIGURE 2. Vapor pressure data of the Li₃N obtained from torsion effusion gravimetric method at UNR.

FIGURE 4. (A) *In situ* neutron diffraction (quantitative) showing the evolution of different phases during deuteration and removal of deuterium gas (dehydriding). The starting material is α-Li$_3$N. (B) The image plate neutron diffraction data showing the changes in the d-spacings. (C) Isothermal (200°C) *in situ* deuteration studies, with the starting materials α+β Li$_3$N, were performed using neutron diffraction in which data was taken every 15 minutes, at 2 bar deuterium pressure. The Li$_2$ND and LiD phase are observed in region 2.

species) of Li$_3$N is low. We found that there is partial disproportionation of Li3N vapors to Li (gas) and N$_2$ (gas) at elevated temperatures ~470°C. Further, Li vapor then equilibrates to liquid Li in very small amounts. Also note that at room temperature the pressures are extremely low, so we could not obtain data. The following are the results from this study. The details of vapor pressure measurements and calculations are shown in Chandra et al. [6], the following relevant equations are shown for Li$_3$N:

Normal Vaporization:

$$\mathrm{Li_3N(crystal)=Li_3N(gas)}\quad \mathrm{upto}\sim 370^o\ \mathrm{C}\qquad(2)$$

Disproportionation:

$$\mathrm{Li_3N}(s)\rightarrow\left(1-\frac{b}{2}\right)(\mathrm{Li_3N})(g)+\left(\frac{3b}{2}\right)\mathrm{Li}(g)+\left(\frac{b}{4}\right)\mathrm{N_2}(g)\quad(3)$$

General Molecular weight equation:
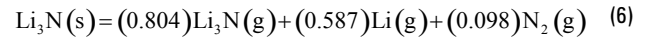
$$M_{\mathrm{AVG}}=\frac{2\pi RT}{(2K)^2}\cdot\left(\frac{(dw/dt)}{\theta}\right)^2\left[\frac{(a_1f_1d_1)+(a_2f_2d_2)}{(a_1c_1)+(a_2c_2)}\right]^2=\sum_{i=1}^{n}\left[m_iM_i^{1/2}\right]^{-2}\ (4)$$
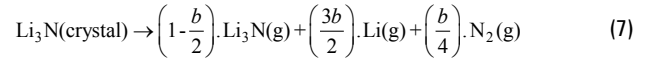
Projected molecular weight equation for Li$_3$N:

$$M_{AVG}^{CALC}=\left[\frac{\left(1-\frac{b}{2}\right)(M_{Li_3N})^{0.5}+\frac{3b}{2}(M_{Li})^{0.5}+\left(\frac{b}{4}\right)(M_{N_2})^{0.5}}{\left(1-\frac{b}{2}\right)(M_{Li_3N})+\left(\frac{3b}{2}\right)(M_{Li})+\left(\frac{b}{4}\right)(M_{N_2})}\right]^{-2}\quad(5)$$

The measured molecular weight is 26.15 g/mol for Li$_3$N in this study, which is 25% less than that of pure Li$_3$N of 34.83 g/mol; indicating disproportionation. The value of b = 0.391from equation (5).

This gives the following equation (Equation 6):

$$\mathrm{Li_3N}(s)=(0.804)\mathrm{Li_3N}(g)+(0.587)\mathrm{Li}(g)+(0.098)\mathrm{N_2}(g)\quad(6)$$

By substituting the value of 'b',

$$\mathrm{Li_3N(crystal)}\rightarrow\left(1-\frac{b}{2}\right).\mathrm{Li_3N(g)}+\left(\frac{3b}{2}\right).\mathrm{Li(g)}+\left(\frac{b}{4}\right).\mathrm{N_2(g)}\qquad(7)$$

Although details will be presented in a forthcoming manuscript, the partial pressures were calculated for each of these gases; which are given as follows:

$$p_{Li_3N}=0.406\ P_T,\ p_{N_2}=0.149\ P_T,\ and\ p_{Li}=0.445\ P_T$$

where, P_T is given by the equation 1 determined in this study.

A3. Calorimetric Studies of Li$_3$N

In situ differential scanning calorimetry (DSC) was performed to observe the phase transitions. These studies were performed at Florida Central University in collaboration with Dr. Darleen Slattery and Dr. Mike Hampton using a modified *Setaram DSC*. In Figure 3, it can be seen that there is the onset of an exothermic peak starting at ~225°C continuing to ~325°C, suggesting hydrogen absorption in Figure 3a where there is a reading of the pressure transducer (mV) vs time for this scan. Although we do not have an accurate conversion of mV to pressure (Pa) at this time, there is a general trend showing a decrease in pressure between 200° to 325°C, and subsequent increase at 325°C. Further increase in temperature, shows an interesting endothermic event that takes place starting at 325° to 345°C exhibiting changes from exothermic to endothermic regions. Thus, we believe that there is a hydrogen release, or even release of ammonia, perhaps with a concurrent phase transformation in presence of hydrogen. The same sample was cooled in the DSC and rescanned and we did not observe the exothermic peak from 225 to 265°C. However, it appeared around 250°C and traced a similar endothermic as in the first scan. This research is in progress.

B. Crystal Structure and *In Situ* Studies on Li$_3$N

B1. Characterization of Precursor Li$_3$N Phase

It was found that the commercial Li$_3$N contained two phases α [3] and β [4], where latter has been suggested to be a high pressure phase. So, experiments were performed to characterize commercial Li$_3$N from different vendors. Quantitative synchrotron x-ray diffraction as well as neutron diffraction analyses of Li$_3$N in as-received condition showed that the average

composition was ~47.5 wt% β phase, and the rest the desired α phase (*neutron diffraction: ~49 w % β phase and synchrotron x-rays: ~45 w % β phase*). The β-Li$_3$N phase starts to transform to the α phase at ~473K and completes at ~690K; this process is irreversible. A manuscript is in review with *Journal of Alloys and Compounds* [7], where we report lattice parameters, volume changes, c/a changes, and other dynamic changes.

B2. Dynamics of Phase Transitions - An *In Situ* Neutron Diffraction Study

B2.1. Effect of Temperature

Phase transformations occurring during hydriding (deuteration) of α-Li$_3$N as a function of temperature and time were obtained from in-situ neutron diffraction analyses. Figure 4A shows non-equilibrium situation of adding deuterium to α-Li$_3$N; the sections shown are isothermal regions of (a) deuteriding and (b) removal of deuterium; data taken every 15 minutes. The amount of deuterium absorbed in the solids was deduced from back calculations. Initial loading of deuterium at 200ºC showed that the amount of LiND$_2$ phase formed is higher in concentration than that of Li$_2$ND. Also, once Li$_2$ND forms, it immediately transforms to LiND$_2$ in presence of deuterium gas. An intermediate LiD phase forms and the amount of this phase does not change substantially as a function at 250ºC. Although detailed kinetic evaluations were not performed, the rate of formation of Li$_2$ND and LiD increased substantially as the temperature was increased from 200º to 250ºC. Isothermal desorption at 250ºC showed the LiND$_2$ phase transforming to Li$_2$ND, but the amount of LiD phase did not change significantly shown in mid-section where the concentration curves cross each other in Figure 4A. To check if there is further desorption at lower temperatures, the temperature was lowered from 250º to 200ºC during desorption that showed virtually no change in concentration of any phase. Further increase from 200º to 320ºC showed a significant effect showing a decrease in LiD phase and increase in LiND$_2$. Chen et al. [1] showed that complete dehydrogenation reverting to Li$_3$N phase at 450ºC is possible. It should be noted that the decrease in amount of LiD phase occurs as the temperature is increased to 320ºC with no deuterium additions (and under vacuum) suggesting inter-phase reactions. Also note the rapid decrease in the residual amount of α-Li$_3$N at higher temperature (320ºC) in the desorption region. The image plate neutron diffraction data showing the changes in the d-spacings are shown in Figure 4B.

B2.2. Isothermal Phase Transformations During Hydriding at 200ºC

In situ deuteration studies with the starting materials α+β Li$_3$N were performed using neutron diffraction in which data was taken every 15 minutes at 200ºC, at 2 bar deuterium pressure. Initially, as the experiment progressed (in the region 1), only the β-Li$_3$N transforms to α-Li$_3$N (Figure 2C). In the region 2, the hydride phases begin to appear; only Li$_2$ND and LiD form. The LiND$_2$ formation can be seen in region 3 and the amount of LiD and LiND$_2$ increased with time. Note the decrease in the amount of α- as well as β-Li$_3$N during hydriding; these processes are kinetically slow as seen in the plot.

Conclusions and Future Directions

Conclusions

1. Extrinsic pressure cycling using industrial grade hydrogen was conducted on an amide/imide system (baseline material) and a comparison between the 1st and 1,101 cycle shows a 2.3 wt% hydrogen loss.

2. The characterization tests show that the hydrogen loss can be attributed to formation Li$_2$O and other undesirable phases due to cycling.

3. The formation of LiH and NH$_3$ evolution is still an issue that has been pointed out by other researchers as well [8-10].

4. *In situ* DSC hydrogenation studies on Li$_3$N reveal that there is an endothermic event at ~325º to 345ºC, suggesting either phase transformation or hydrogen release concurrent with NH$_3$.

5. *In situ* non-equilibrium neutron diffraction during deuteriding shows the predominant formation of LiNH$_2$, followed by LiH and then Li$_2$NH between 200º and 250ºC. During dehydriding at 250ºC, we observe the expected decrease in the LiNH$_2$ and increase in Li$_2$NH; the LiH phase concentration remains relatively unchanged.

6. The Li$_3$N obtained from three commercial vendors showed a two phase mixtures (α+β) phases. The retention of high pressure β-phase was observed in all the three samples. The average composition of the b phase was ~47.5 wt% at ambient pressure. Crystal structure studies show transformation of β→α Li$_3$N transformation completes at 460K.

7. Vapor pressure of Li3N is very low on the order of 0.1 to 1 Pa, however, there is disproportionation of Li$_3$N at higher temperatures (> 410 ºC). Total pressure, as well as partial pressure of disproportionated species, such as Li (vapor), N$_2$, and Li$_3$N (gas) has been determined.

Future Directions

We would like the DOE MHCoE in the future to focus on the contemporary issues. We propose the following:

1. **Continue research on the effect of specific impurities on Complex Hydrides**
   We propose to continue work on our imide/amide research on the effect of low level impurities on pressure cycling of hydrides to complete the extrinsic cycling studies on this system. The effect of individual impurities in ppm levels in O_2, CO, CO_2, CH_4, and H_2O in UHP hydrogen will be determined. In FY 2007, we will begin high pressure (120 bar) cycling work on MgH_2/Li_2NH (with Sandia National Laboratory); the apparatus is being constructed and will be functional by late FY 2006. The experience and apparatus developed for the Li_3N cycling experiments will be useful for high-pressure cycling of Mg-Li-N-H and other complex hydrides. This apparatus will be available to the MHCoE team.

2. **In Situ Hydriding/dehydriding X-ray and Neutron Diffraction Studies at UNR, NIST, and IPNS**
   In situ hydriding/dehydriding using UNR's x-ray diffraction system: start Ca borohydride in situ hydriding-x-ray diffraction work (Sandia National Laboratory - Mechanistic Studies) in FY 2006. PANalytical x-ray diffraction system - hydrogen and high temperature Anton Paar stage (with maximum 10 bar pressure and 900°C) will be used for this purpose. Mechanistic studies on new formulation of Ca borohydride that is prepared at the Sandia National Laboratories will be performed in the near future. We will also continue *in situ* neutron studies at IPNS-ANL, and NIST-Maryland on deuteration of catalyzed complex hydrides furnished by team members.

3. **Vapor Pressure Studies on $Mg(BH_4)_2$ - GE Collaboration**
   It has been proposed that UNR perform vapor pressure studies on $Mg(BH4)_2$ as this material has very high hydrogen capacity (~15 wt%); in collaboration with Dr. J.C. Zhao (GE) to determine the thermodynamics of vaporization by measuring vapor pressures of this material. Torsion effusion apparatus available and will be used for this purpose, except for new Mo Knudsen cells that will have to be fabricated.

4. **Hydrogen Lattice Dynamics Studies on Complex Hydrides - Prof. Cantelli, Uni. of Rome - IEA Proposal**
   "Hydrogen Dynamics, Lattice interactions, and Atomic-scale Structure of Complex/Chemical Hydrides" will be a subject of International Partnership for the Hydrogen Economy research topic for mid-2007. This proposed study is on lattice dynamics of complex hydrides, such as amides, imides, and other hydrides. This collaborative study between Cantelli-Rome, Italy and Chandra, Jensen-USA includes spectroscopes that will allow understanding of the H dynamics, like muons (an Italian group), neutrons (Italy and perhaps Denmark), anelasticity (Prof. Cantelli's group), and the local structure like positrons (Italy and Japan).

FY 2006 Publications/Presentations

1. D. Chandra, J.J. Reilly, R. Chellappa, "Metal Hydrides for Vehicular Applications: The State of the Art," *Journal of Metals*, 58(2) 2006, 26-32. (Review Paper).

2. *Symposium proceedings edited* "Advanced Materials for Energy Conversion III" *A Symposium in Honor of Drs. Gary Sandrock, Louis Schlapbach and Seijirau Suda* Editors: D. Chandra, J. Petrovic, R. Bautista and A. Imam, 2006 TMS Annual Meeting, ISBN: 978-0-87339-610-3.

3. A. Huq, J. Richardson, E. Maxey, D. Chandra, W-M. Chien, "Structural studies of Li_3N using Neutron Powder Diffraction," *Journal of Alloys and Compounds*, *in review, Manuscript Number: JALCOM-D-05-00350R1*.

4. W-M. Chien, D. Chandra, A. Huq, J. Richardson, Jr., E. Maxey, S. Fakra, and M. Kunz "Neutron and Synchrotron Studies on Li-Based Nitride and Hydride", Presented in *2006 TMS Annual Meeting*, San Antonio, Texas, USA, March 12-16, 2006.

5. A. Huq, J. Richardson, E. Maxey, D. Chandra, W-M. Chien "Time Resolved Neutron Diffraction Studies of the Hydrogen Storage Material Li_3N," Presented in *APS (American Physical Societies) March Meeting 2006*, Baltimore, MD, USA, March 13-17, 2006.

6. D. Chandra, "Effect of Trace Elements on Long-Term Cycling and Aging Properties of Complex Hydrides for Hydrogen Storage," Presentation at the MRS MHCoE Meeting, Boston, MA, November 11, 2005.

7. D. Chandra, "Extrinsic Effects of Impurities on Hydrogen Cycling on Li based Hydrides and In-situ Neutron Diffraction Studies on Hydriding/Dehydriding Li_3N," Presentation at the IEA Hydrogen Implementing Agreement Task 17/22, Joint IEA HIA-IPHE Workshop, Windermere, UK, April, 30-May 4, 2006.

8. D. Chandra, R. Chellappa, W-M Chien, Y. Song, J.F. Lin, S. Gramsch, R. Hemley, J.W. Richardson, Jr., A. Huq, E. Maxey, J.N. Wermer, S.N. Paglieri, "Baseline Studies on the Effect of Gaseous Impurities on Long-Term Thermal Cycling and Aging Properties of Complex Hydrides for Hydrogen Storage," IPHE International Hydrogen Storage Technology Conference, Lucca, Italy, June 19-23, 2005.

9. D. Chandra, "Effect of Trace Elements on Long-Term Cycling and Aging Properties of Complex Hydrides for Hydrogen Storage," Presentation at DOE 2006 Hydrogen Program Annual Review, Washington D.C. held in Crystal Gateway Marriot, Arlington, VA, May 16-19, 2006.

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6. D. Chandra, M.L. Garner, K.H. Lau, *J. Phase Equilib.* 20(6) (1999) 565-572.

7. A. Huq, J. Richardson, E. Maxey, D. Chandra, W-M. Chien, "Structural studies of Li_3N use Neutron Powder Diffraction," *J. Alloys and Compd.*, in review, Manuscript Number: JALCOM-D-05-00350R1.

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