Effect of Gaseous Impurities on Long-Term Thermal Cycling and Aging Properties of Complex 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, including effects of long-term cycling.
- Evaluate the long term durability of light weight Li-N based compounds, and methods for improvements of hydrogen capacity after pressure cycling.
- 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 Fuel Cell Technology 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 involved studies on development 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): 1000 Cycles

Executive Summary

Hydrogen is one of the alternate fuels for vehicular applications where the exhaust is mainly water vapor when used with either fuel cells or internal combustion engines. In the transportation sector, a proton exchange membrane (PEM) fuel cell, that electrochemically combines inputs of pure hydrogen and oxygen (from air), may be used to directly generate electricity for an electric motor drive with water vapor and heat produced as byproducts. However, hydrogen fuel cell technologies must be competitive in this venue with the ubiquitous internal combustion engine using gasoline and diesel fuels, both of which offer an established production and distribution infrastructure as well as a familiar and commonly accepted form of high density and stable energy storage. The United States Department of Energy (DOE) is addressing the standards that a hydrogen fuel system would have to meet as part of their FreedomCAR initiative. Conventionally, hydrogen is compressed in high pressure cylinders with obvious safety issues. We believe that hydrogen may be stored in metal hydrides at low pressures. Hydrides may be classified as (a) Classical hydrides (heavy hydrides with low wt.%H), and (b) Complex hydrides (light weight hydrides with high H-wt.%). In this study, our focus was on practical aspects of complex hydrides related to refilling hydrogen in vehicles at “Hydrogen Gas Stations,” where one expects ppm levels of impurities. These gaseous impurities affect the performance of the complex hydrides as a medium for storing hydrogen. The main focus of the project was to understand the effect of trace element gases, mixed with hydrogen, on the long-term cycling and aging properties of complex hydrides of Li₃N-H₂. Another secondary aspect was to test complex hydrides developed by our MHCoe partners, for example, Ca(BH₄)₂, Mg(BH₄)₂, Amide-Alanate(3LiNH₂:Li₃AlH₆) and others. In addition, we also conducted thermodynamic and crystallographic research of these hydrides to understand the reaction pathways.

Gaseous impurities in hydrogen have a great impact on the long-term hydrogen capacity of Li-N compounds. For example, we found that the addition of nitrogen to hydrogen has a noticeable beneficial effect on the cyclic performance of the hydride, yielding 10 wt.%H reversible capacity after many cycles. On the other hand, some impurity gases in hydrogen are detrimental to the cycle life of the Li-N-H compounds and may result in a loss of hydrogen capacity in solid state storage of hydrogen in complex hydrides. To evaluate these effects we performed extrinsic pressure cycling with impure hydrogen; these tests are rather long. We have also performed thermal aging experiments where necessary. These tests are important for understanding how these materials perform relative to achieving DOE’s technical targets for the long-term reliability of metal hydrides as vehicular hydrogen storage materials. In general, ultrahigh purity (UHP) hydrogen is used in the research laboratories for the development of

metal hydrides. However, in practical vehicular applications commercial hydrogen (ppm level impurities) will be used. Commercial hydrogen contains ppm levels of O₂, H₂O, CH₄, N₂, hydrocarbons, and others; the industrial grade hydrogen that we used was labeled: “Hydrogen min % (v/v) 99%, Water~32 ppm, O₂~10ppm, N₂~400 ppm, total hydrocarbons: 10 ppm, CO₂~10 ppm, CO~10 ppm, argon may be present, reads as oxygen.” We also used several special mixtures of gases containing 100 ppm of a specific impurity gas 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. Pressure cycling experiments (with fresh charges of impure hydrogen each cycle) were performed to simulate the long-term performance of complex metal hydrides with ppm levels of impurities in the hydrogen; these parallel contamination studies are essential for using hydride beds for a vehicular application. The degradation of the hydriding properties are generally associated with disproportionation or decomposition of hydride surface or bulk properties during normal periodic charges (with slightly impure) hydrogen. These studies are expected to lead to the understanding of mechanisms that occur after repeated filling of hydrogen gas from a typical “Hydrogen dispensing Gas pump.” New complex hydride materials are being developed by the Metal Hydride Center of Excellence (MHCoe) partners who are using UHP hydrogen to establish their properties. Once the properties are established, extrinsic cycling tests need to be performed to determine which complex hydrides have minimal degradation after many hundred cycles.

The objective of this research project was to investigate the effect of impurities in complex hydrides that will store hydrogen for use in fuel cells and other applications, and aid in the development of materials solutions to potential hydrogen-sorption degradation problems. The relevance to the MHCoe 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 accelerated laboratory tests are extremely useful to understand the reliability of hydrogen fuel. At the University of Nevada, Reno we have automated and semi-automated extrinsic cycling apparatus to perform pressure cycling on Li₃N-H, imide/amide system, due to high hydrogen content ~10.5 wt%H.

Results of cycling/aging of amide-imide, isotherms, and crystal structure analyses are presented. In addition to the above mentioned studies, we also performed research to support the MHCoe partners on alanate-amide (University of Utah), and determination of new phase transitions observed in Ca(BH₄)₂ hydride (Sandia National Laboratories). Crystallographic studies on Li₃N-H to characterize the intermediate phases and correlate with the amount of hydrogen added were performed at University of Geneva. The approach used for these materials was extended to the hydrides that are being developed by MHCoe partners. Structural decomposition reaction of lithium amide studied by anelastic spectroscopy and thermogravimetry (University of Rome), and initiated defect structure studies on Ni and Co doped Li₃N, and DFT calculations on complex hydrides formed from Li₃N were performed in collaboration with University of Paris (CNRS).

Key Accomplishments

- Significant cycle life improvements were achieved by using mixtures of H₂ and N₂ gases; with 80/20 molar mixtures of H₂/N₂; we obtained near initial capacity Li₃N-H₂ reversible capacity of ~10 wt.%H at 255°C after 516 cycles.
- It was determined that there was continuous loss of nitrogen from solid phases during the dehydrogenation cycle under dynamic vacuum, leading to the formation of a rather stable LiH phase which traps the hydrogen at operating temperature of 528K (255°C).
- Critical phase reaction pathways determined using progressive incremental loading of hydrogen in Li₃N, supported by CALPHAD thermodynamic modeling developed Li-N-H phase diagrams.
- Determined the effects of other gaseous impurities in H₂ (100 ppm levels of O₂, CO, H₂O, CH₄, NH₃) by pressure cycling to simulate the charge/discharge behavior of Li-N-H system with fresh charges of H₂ mixed with gaseous impurities.
- The NH₃ gas impurity did not contribute to the loss of hydrogen capacity. These experiments were performed by isobaric aging at 6.2 bar H₂ at 255°C using 100ppm NH₃ in H₂. (Pressure cycling could not be performed due to damage to vacuum pumps).
- Determined the 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.
- Determined details of the amount of LiH phase formed under equilibrium loading of hydrogen.
- New higher capacity cubic phase of Li_{2-x}NH_{1+x} (x=1/2) type, as compared to Li₂NH (x=0) was found.
- DFT calculations were made to determine the structure of Li_{2-x}NH_{1+x} (x=1/2) and compared with Li₂NH.

- Improved kinetics observed at higher than equilibrium pressures during hydriding of Li_3N .
- Showed feasibility of making Ni and Co substituted Li_3N by spark plasma synthesis method.

E. Summary of Gaseous Impurities Effects

- We tested hydriding of Li_3N with commercially available inexpensive hydrogen (not UHP grade). The initial capacity was ~ 10 wt.% H_{mb} (maximum basis-mb) during the very first hydrogen loading (called 0th cycle). Then it is reduced to 4.5 wt.% H_{pb} (plateau pressure basis-pb) and 5.8 wt.% H_{mb} , after the first cycle. The overall storage capacity was reduced from 5.8 wt.% H_{mb} to 3 wt.% H_{mb} after 500 cycles, with ppm levels of O_2 and H_2O as major impurities. Further increase in number of cycles from 500 to 1100 did not show significant weight loss, indicating some capacity is still maintained after a significant number of cycles. The loss of capacity is attributed to the formation of ~ 55 wt% LiH and $\sim 30\%$ Li_2O , as major contaminant phases, along with the hydride Li_2NH phase. There is little increase in the amount of LiOH after many cycles even with the presence of water vapor as an impurity. It is concluded that either none of the gas impurities present form LiOH in measurable quantities, or that LiOH is further reacting to form Li_2O . The kinetics of Li_3N as a function of cycling showed a dramatic reduction in reaction rates after 1100 cycles ($k_1 = 0.0075$, $k_{1100} = 0.00075$). A summary is shown Figure ES1.
- During initial cycling experiments with hydrogen gas, we observed ~ 5.8 wt.%H (maximum) reversible. We observed the formation of cubic phase Li_2NH , and tetragonal LiNH_2 phases, but the complete reversal of the reactions $\text{Li}_3\text{N} \rightarrow \text{Li}_2\text{NH} \rightarrow \text{LiNH}_2$ was not possible. Only cycling between $\text{Li}_2\text{NH} \leftrightarrow \text{LiNH}_2$ appeared reversible, with the formation of LiH additional phase.
- The effect of 100 ppm water vapor as a specific impurity in UHP H_2 showed a reduction of 2.5 wt.% out of 4.5 wt.% hydrogen after 560 cycles. Surprisingly, more pronounced effects were observed using 100ppm oxygen as an impurity in UHP hydrogen in a similar experiment; a loss of 4.1 wt% out of 4.5 wt% was observed. The following capacity losses were seen using other impurity gases: H_2O (~ 3 wt.%H loss after 560 cycles), CH_4 (~ 2 wt.%H loss after 100 cycles), $\text{H}_2\text{O} + \text{O}_2$ (~ 3 wt.%H loss after 501 cycles). A summary of the results is shown Figure ES2. Note the very first cycle is not shown here.
- Additions of N_2 to H_2 gas showed beneficial effect and that the original ~ 10 wt.%H hydrogen capacity was maintained after 560 pressure cycles of the mixed gas. Isotherms taken after cycling (with pure hydrogen) are shown in the summary Figure ES3.
- The effect of 100 ppm ammonia as an impurity gas was tested with a thermal aging system; and showed no significant losses in capacity. (We could not test this mixture with our pressure cycling apparatus as the initial experiments damaged both the turbo and mechanical pump of the cycling system.)
- Methane impurity (100 ppm, 100cycles) showed a very small capacity loss of 0.9 wt% out of 4.5 wt% under similar conditions.
- Pressure cycling of Li-N-H compounds with N_2/H_2 mixtures that showed significant improvement of the H-capacity was explained by using CALPHAD modeling. It was found that small amounts of pure liquid lithium phase were formed during cycling. This Li (l) reacts with N_2 to form Li_3N and then forms Li_2NH rather quickly. Therefore there is an accumulation of Li_2NH phase during cycling. The presence of N_2/H_2 in a closed system generates Li_2NH rather than LiH .

F. Summary of DFT Calculations of New Structures

It was found that there is formation of two new compounds, namely, Li_4NH and $\text{Li}_{1.5}\text{NH}_{1.5}$ during the hydrogenation process of Li_3N . The formation of these compounds could modify the hydrogen absorption and desorption characteristics of Li_3N . We find that the direct hydrogenation reaction of Li_3N to Li_2NH is predominantly favored but the formation of Li_4NH may be possible through the direct formation involving Li_3N and LiH with an enthalpy of reaction much less negative than for the direct formation of Li_2NH . The formation of this compound through the release of ammonia is not possible. This compound readily reacts with H_2 exothermically with an enthalpy of reaction less negative than for the direct process. We also find that the formation of the intermediate phase $\text{Li}_{2-x}\text{NH}_{1+x}$ for $x=0.5$ between imide ($x=0$) and amide ($x=1$) is possible. $\text{Li}_{1.5}\text{NH}_{1.5}$ ($x=0.5$) is found to form in a cubic Li-vacant-type compound. After full relaxations of several structural models, the $\text{Li}_{1.5}\text{NH}_{1.5}$ compound shows coexistence of ordered $[\text{NH}]^{-2}$ and $[\text{NH}_2]^{-}$ anions. The electronic structure and ELF diagrams are shown in Figure ES4.

G. Summary of LiNH_2 - LiAlH_4 Thermodynamics and Structures

Binary $\text{Li}_3\text{AlH}_6\text{-}3\text{LiNH}_2$ (~7.1 wt%) - (4% TiCl_2 - $1/3\text{AlCl}_3$), shows an overall reaction: $\text{Li}_3\text{AlH}_6 + 3\text{LiNH}_2 \leftrightarrow \text{Al} + 3\text{Li}_2\text{NH} + 9/2\text{H}_2$ ~7.1 wt% (Hauback et al.). Mixed alanates ($3\text{LiNH}_2\text{:Li}_3\text{AlH}_6$) showed that 7 wt% hydrogen desorbed under dynamic vacuum (collaboration with Dr. Zak Fang, University of Utah). Equilibrium experiments (maximum 12 bar H_2) showed up to 4wt% hydrogen reversibly stores in the material after the first desorption. Pressure cycling performed at UNR on $\text{Li}_3\text{AlH}_6\text{-}3\text{LiNH}_2$ system after 540 cycles is encouraging. Formation of Li_3AlN_2 is confirmed. However, it may be hydrided at higher pressures (60 bar- Ref: K. Gross). Figure ES5 shows that there is very little loss in hydrogen capacity for this mixed hydride. The activation energy was found to be 51 kJ/mol as compared to 81 kJ/mol for pure lithium alanate.

H. Summary of $\text{Ca}(\text{BH}_4)_2$ Phase Transitions

Phase transitions in $\text{Ca}(\text{BH}_4)_2$ are rather complex. The in-situ synchrotron x-ray diffraction experiments we performed (between 317K and 573K) at ESRF, Grenoble, showed α -to- γ and γ -to- β phase transitions. Projections of the α , γ and β phases of $\text{Ca}(\text{BH}_4)_2$ α -phase at 91K are: F2dd, $Z = 8$, $a = 8.7759(3)$, $b = 13.0234(4)$, $c = 7.4132(2)$ Å. γ -phase at 495K, I-42d, $Z = 4$: $a = 5.8446(3)$, and $c = 13.2279(11)$ Å, and β -phase at 305K: P42nm, $Z = 2$, $a = 6.91885(12)$ and $c = 4.34711(14)$ Å. Figure ES6 shows the in-situ plot and the structures found.

E. Structural Phase Transitions and Adduct Release in Imide, Amide and $\text{Ca}(\text{BH}_4)_2$

“Hydrogen Dynamics, Lattice interactions, and Atomic-scale Structure of Complex/Chemical Hydrides” is a subject of an International Partnership for the Hydrogen Economy research topic. This proposed study is on lattice dynamics of complex hydrides, such as amides, imides, and other hydrides. This collaborative study between Prof. Cantelli at the Univ. of Rome, Italy and Prof. D. Chandra includes spectroscopes that allowed understanding of the H dynamics, such as anelastic properties. In addition, $\text{Ca}(\text{BH}_4)_2$ compounds were investigated above room temperature by anelastic spectroscopy (AS) and concomitant measurements of thermogravimetry and mass spectrometry (TGA/MS). Both AS and TGA/MS indicate that even after a thermal treatment at 125°C for 20 h, a non-negligible residual amount of THF adduct is still present in the sample, which can be removed on a subsequent thermal treatment at temperatures lower than 250°C. Above 250°C dehydrogenation takes place. The two transitions are not detected by differential scanning calorimetry. We also show that both transitions are irreversible and are not accompanied by a latent heat.

F. Summary of Defect Structure Work

This work was initiated to form defect structure of Li_3N with Co and Ni impurities. The purpose was to reduce the temperature of hydriding from 250°C to ~100°C. We were able to synthesize Ni and Co solid solutions of Li_3N by spark sintering method.

G. Vapor Pressure Studies on $\text{Mg}(\text{BH}_4)_2$

We performed vapor pressure studies on $\text{Mg}(\text{BH}_4)_2$ as this material has very high hydrogen capacity (~15 wt%H); in collaboration with Dr. J.C. Zhao (GE) to determine the thermodynamics of vaporization by measuring vapor pressures of this material. Torsion effusion apparatus was available with us and was used for this purpose, with Mo Knudsen cells.

I. Summary of Structures formed during the Hydriding of Li_3N

Figure ES7 shows a summary of the phase formed during hydriding of Li_3N . That LiH formation occurs concurrently when the Li_2NH is formed.

Conclusions

We present the key conclusions from this research:

- At the start of the program we found reversibility between $\text{Li}_2\text{NH} + \text{LiH} \leftrightarrow \text{LiH} + \text{LiNH}_2$ (yielding ~5.8 wt.% H_{mb} capacity on a maximum basis (mb) or ~4.25 wt.% H_{pb} plateau basis(pb), as shown in Figure ES1. The Li_2NH did not revert back to Li_3N .
- Then we tested the effect of impurity in H_2 gas by pressure cycling at 255°C; first with industrial gas containing ppm levels of O_2 and H_2O as major impurities. Both these impurities had a significant impact on the reversibility and decreased the capacity by 2.65 wt.%H, (from ~4.25 to ~1.6 wt.% H_{pb}). Further increase in number of cycles from 500 to 1100 showed only a 0.2 wt%H more weight loss, showing some capacity is still maintained after a significant number of cycles. The loss of capacity is attributed to the formation of

~55 wt% LiH and ~30% Li₂O, as major contaminant phases, along with the hydride Li₂NH phase. The effect of 100 ppm H₂O in H₂ also showed a decrease of 2.5 wt.%H out of 4.5 wt.%H_{pb} (560 cycles), and 100ppm O₂ in H₂; a loss of 4.1 wt.% out of 4.25 wt.%H_{pb} was observed. Methane impurity (100 ppm, 100cycles), showed a very small capacity loss of 0.9 wt.% out of 4.5 wt.%H_{pb} under similar conditions.

- However, when Li₃N was pressure cycled with 100ppmN₂-UHP H₂, there were beneficial effects observed (255°C); the reversible capacity increased by 2.35 wt.%H reaching ~6.7wt.%H_{pb}(8.4wt.%H_{mb}) after 853 cycles. Furthermore, with 20mol.%N₂-H₂ capacity increased by ~4.10wt.%H, to 8.4wt.%H_{pb}(~10 wt.%H_{mb}) after 516 cycles. We attribute this enhancement to the reaction of nitrogen with liquid lithium during cycling as the Gibbs free energy of formation of Li₃N ($\Delta G^\circ = -98.7$ kJ/mol) is more negative than that of LiH ($\Delta G^\circ = -50.3$ kJ/mol). We propose that the mitigation of hydrogen capacity losses is due to the destabilization of the LiH phase that tends to accumulate during cycling.

Figure ES 1. Summary of pressure cycling data showing (Left) Loss of hydrogen capacity from ~10 wt.%H to ~3 wt.% after 1100 cycles using industrial hydrogen that ppm levels of O₂ and H₂O. Note the cycling tests were performed between 2 bar H₂ and vacuum separately at 255°C. After cycling, the isotherms were obtained in a Sieverts apparatus. The very first cycle data is not shown in this Figure. (Right) X-ray diffraction patterns showing increase in the Li₂O and LiH amount and decrease in Li₂NH.

Figure ES2. Summary of Effect of mixing 100 ppm of O₂, H₂O, CH₄ in UHP H₂.

Figure ES3. Pressure-Composition Isotherms (Absorption) collected after cycling in hydrogen containing 20 mol % N_2 mixed with H_2 . This shows ~ 10 wt.%H reversibility with N_2 additions (left). X-ray diffraction data collected after cycling with hydrogen containing N_2 . Diffraction was done after full desorption and shows Li_2NH and LiH as major components. Li_2NH and LiH are expected as reaction products, while Li_2O is present as an impurity in the starting Li_3N test material.

Figure ES4. Summary of the Density of States and splitting of N - NH and NH_2 bonds (Left). Electronic Localization Function (ELF) for the structures showing NH and NH_2 bonds in the $Li_{1.5}NH_{1.5}$ phase (right).

MHCoE-IEA and other Collaborations

- Prof. Klaus Yvon, and Dr. Radovan Cerny, University of Geneva, Switzerland – Crystallographic and Thermodynamic Aspects (IEA)
- Prof. Rosario Cantelli, Uni. of Rome- Hydrogen Lattice Dynamics Studies on Complex Hydrides and IEA/IPHE Proposal participation. (IEA/IPHE)
- Dr. Michel Latroche Uni. of Paris/CNRS Thias, France- Synthesis of defect structure Li_3N complex.(IEA)
- Dr. J.C. Zhao (GE Corp-Now at Ohio State Universit) - Vapor Pressure Studies on $Mg(BH_4)_2$

- Dr. Yaroslav Filinchuk of ESRF (Synchrotron Facility), Grenoble France- Phase Transformations in $\text{Ca}(\text{BH}_4)_2$.
- Dr. Zak Fang, University of Utah- Li amide-LiAlHydrides.
- Dr. Ewa Ronnebro, Pacific National Laboratory- Phase Transformations in $\text{Ca}(\text{BH}_4)_2$.
- Dr. Ashfia Huq, Oak Ridge National Laboratory, Oak Ridge TN-Neutron diffraction.- In-situ Neutron Diffraction on $\text{Li}_3\text{N-H}$ and LiAl Hydrides
- Dr. Darlene Slattery and Dr. Mike Hampton (Florida Solar Energy Center, Cocoa Beach) DSC on $\text{Li}_3\text{N-H}$

Figure ES 5 (top) . TGA desorption of hydrogen of the Binary $\text{Li}_3\text{AlH}_6\text{-}3\text{LiNH}_2$ (~7.1 wt%) - (4% TiCl_2 - $1/3\text{AlCl}_3$), showing overall reaction: $\text{Li}_3\text{AlH}_6 + 3\text{LiNH}_2 \leftrightarrow \text{Al} + 3\text{Li}_2\text{NH} + 9/2\text{H}_2$ ~7.1 wt%. [References](#) C.M Andrei, H.W. Brinks, B.C. Hauback et al. *J. Alloys and compds*, 395 307-312, 2005 and J. Lu, Z. Z. Fang, and H.Y. Sohn, *J. Phys. Chem. B* 110(29), 14236-14241, 2006. (Bottom) The small loss in H_2 (~0.6 wt.% H_2) capacity in $\text{Li}_3\text{AlH}_6\text{-}3\text{LiNH}_2$ system after 540 cycles is encouraging. Formation of Li_3AlN_2 is confirmed however it may be hydrided at higher pressures (60 Bars- Ref: K. Gross).

Figure ES 6. (top) In-situ synchrotron x-ray diffraction data of $\text{Ca}(\text{BH}_4)_2$ taken between 317-573K $\lambda = 0.711385 \text{ \AA}$ showing α -to- γ (Red line) γ -to- β phase transitions (Green line). (Bottom) Projections of the α , γ and β phases of $\text{Ca}(\text{BH}_4)_2$ α -phase at 91K: $F2dd$, $Z = 8$, $a = 8.7759(3)$, $b = 13.0234(4)$ $c = 7.4132(2) \text{ \AA}$ γ -phase at 495K: $I-42d$, $Z = 4$ $a = 5.8446(3)$, and $c = 13.2279(11) \text{ \AA}$, and β -phase at 305K: $P42nm$, $Z = 2$, $a = 6.91885(12)$ and $c = 4.34711(14) \text{ \AA}$.

Figure ES7. Summary of the phase formed during hydriding of Li_3N . That LiH formation occurs concurrently when the Li_2NH is formed (UNR).

Figure ES8. Phase diagrams of Li-N-H plotted for using CALPHAD modeling @ (1) 255°C and 9 atm (under H₂ loading conditions) (2) 25°C and 9 atm, and (3) 25°C and vacuum (unloading condition) showing phase under different pressure and temperature conditions (UNR).

I. Introduction

Objectives of Research

The environmental effects of greenhouse gas emissions and other pollutants caused by automobile exhaust have led to a drive to develop alternative fuels which will lead to reduction of pollution and improve energy efficiency. More recently, research on hydrogen as a fuel source has been emphasized as the exhaust is mainly water vapor. Two possible systems may be adapted for hydrogen use, (1) Among the most well known solutions for vehicular application is the use of hydrogen as a fuel source, which can be combusted with oxygen producing water as a byproduct. In a classical approach, internal combustion (IC) engines may be used to achieve this, but by far the most popular method is the direct generation of electricity using a proton exchange membrane (PEM) fuel cell. PEM fuel cells electrochemically combine pure hydrogen fuel with oxygen from intake air and are able to generate energy much more efficiently than an IC engine, and hydrogen based PEM fuel cells produce water vapor and heat as byproducts. However, hydrogen fuel technologies must be competitive with gasoline and diesel fuel, which offer both established infrastructure as well as high density, stable energy storage. The United States Department of Energy (DOE) is addressing the standards that a hydrogen fuel system would have to meet as part of their FreedomCAR initiative [1]. Table 1.1 details the goals set forth by DOE for the storage system of a hydrogen based vehicle.

Most hydrogen used in research and industry is stored in compressed gas cylinders at ~150 bar (~2200 psi) which contains, on a system basis, approximately 1 wt% of hydrogen based on the average mass of the cylinder. While not so desirable for vehicular applications, new technologies for the construction of gas cylinders have allowed pressures of up to 700 bar (~10150 psi) and storage just under 5 wt% on a system basis[2, 3]. High-pressure gas cylinders, however, present several challenges. First, high-pressure cylinders operate at pressures where hydrogen no longer closely follows the ideal gas law, for example increasing the pressure from 10,000 psi to 20,000 psi would only increase the gas density by about half. Furthermore, gas cylinders need to be cylindrical or near cylindrical in shape, limiting options for placement on a vehicle. Finally, there are concerns about the potential for accidents when equipping the general public with compressed gas cylinders pressurized to these extreme levels.

Table 1.1 DOE FreedomCAR Objectives [1].

Subject	Goal
Gravimetric Energy Density	2 kWh/kg
Volumetric Energy Density	1.5 kWh/l
H ₂ Storage Capacity (system basis)	6 wt%
Operating Temperature Range	-30 to +50°C
Refueling Time	<5 min
Hydrogen Release Rate (60 kW basis)	1.5 g/s
Hydrogen Release Temperature	< 80°C
Energy Loss During H ₂ Release	<5%
Range While Maintaining <80% Capacity	150,000 miles

Liquid hydrogen is another storage medium where the technology is application-ready, and has been demonstrated by a series of BMW vehicles; although in their case a hydrogen powered IC

engine was used [4]. Liquid hydrogen has a gravimetric storage on a materials basis of 100 wt% and working storage systems have exceeded 6 wt% on a system basis. However, liquid hydrogen evaporates at about 20 K, which requires bulky insulated cryogenic storage tanks that must be placed somewhere on the vehicle. Further, even the best storage tanks may lose greater than 1% hydrogen per day due to boil-off. There is also a significant energy cost involved in liquefying hydrogen to the tune of about 30% of the energy of the hydrogen stored [5]. It should be noted, however, that this energy loss is not seen by the storage system itself and is more an overall concern rather than a specific concern for a vehicular application.

Although compressed gas cylinders and liquid hydrogen are application-ready technologies, their significant engineering concerns have prompted much recent work in alternative methods of hydrogen storage, specifically in the form of solid state hydrogen storage, or hydrides. Modern hydrides are classified as follows:

(1) Classical Hydrides (Example Metallic Hydrides AB_2 , AB_5 , A_2B and other Hydrides)

Classical hydrides are (most commonly) transition or rare earth metal based hydrides where hydrogen is stored interstitially in the crystal lattice of a pure metal or an intermetallic alloy. The properties of binary and intermetallic metal hydrides are well documented, where a hydrogen atom can partially donate its electron to the conduction band of a transition metal or rare earth metal, allowing the proton (hydrogen ion) to move relatively freely through the metal. However, the resulting intermetallic hydrides are very heavy and have low gravimetric capacity for vehicular applications. There are a few well known metal hydrides that have an equilibrium hydride phase at close to room temperature, with intermetallic hydrides typically taking the form of AB_2H_x or AB_5H_x , where A is generally a group of IVA metal for AB_2 or lanthanide or actinide for AB_5 alloys and B is a transition metal. The most well known of these hydrides by far is the AB_5H_x hydride $LaNi_5H_6$ first investigated by Buschow and Miedema [6]. The $LaNi_5$ based alloys have been successfully used in battery and space applications; however this and other classical metal hydrides are generally considered unsuitable for vehicular applications due to their low gravimetric hydrogen density creating a need for new lightweight complex hydrides.

(2) Complex Hydrides (Alanates, Imide-Amide complexes, Borohydrides, and others)

The storage of hydrogen in modern complex hydrides has shown great potential with theoretical gravimetric capacities of up to 10-11 wt%. Complex hydrides are stoichiometric compounds that generate hydrogen through reversible gas-solid reactions. These compounds, however, were generally thought to react at a temperature too high to be useful until Bogdanovic and Schwickardi [7-9] found that sodium alanate ($NaAlH_4$) would reversibly dehydride at moderate temperatures when catalyzed using transition metals. This has led to extensive research on materials including Alanates ($NaAlH_4$, $LiAlH_4$), [2, 7, 10-51] borohydrides ($NaBH_4$, KBH_4 , $Ca[BH_4]_2$) [2, 31, 52-56], Li-N-H based hydrides such as Li_3N and $LiNH_2$ [2, 22, 29-31, 33, 37, 53-55, 57-89] and MgH_x based hydrides [2, 28, 53, 54, 65, 88, 90-96]. Current effort on these materials includes the use of catalysts to improve the kinetics of the materials and further reduce the temperature to meet the requirements for a commercially viable hydride bed.

(3) Chemical Hydrides (CH_4 , NH_3 , CH_3OH , and others)

Further research into solid state hydrogen storage has led to the development of chemical hydrides. Chemical hydrides are stoichiometric compounds that produce hydrogen through a

chemical reaction and generally have good volumetric and gravimetric densities. The primary concern with chemical hydrides is that the materials generally cannot be recharged at a filling station and must be returned to a factory for regeneration. The reactions involved are not readily reversible, generally involving the one-way reaction of a compound to produce hydrogen gas.

This category also includes complex hydrides that are used to generate hydrogen through hydrolysis reactions. Sodium borohydride (NaBH_4), for example, has been used in commercial generators producing hydrogen gas through the following reaction [97,98, 99]:

Sodium borohydride has garnered attention largely due to its theoretical gravimetric density of 10.9 wt% [100]; it is also more easily handled and stable at room temperature when compared to other chemical and complex hydrides. In practice, however, only a fraction of the theoretical hydrogen density is normally seen. Because of this, much of the work concerning this material has gone toward the development of catalysts to improve reaction behavior [99, 101-107]. This material has become very popular for one time use hydrogen generators; however the resulting materials, particularly the H_3BO_3 salt, are very stable, making this reaction not readily reversible.

(4) Nanostructured molecular hydrogen sorption material (carbon nanotubes)

Work on nanostructured carbon materials has produced a wide range of claims in hydrogen storage capacity, with differing researchers claiming values from 3 wt% all the way up to 67 wt% storage capacity at room temperature. Most researchers report needing to apply upwards of 100 bar of hydrogen pressure to obtain this level of storage; however some have claimed high capacity at close to atmospheric pressure. It is largely accepted that carbon can hold a significant amount of hydrogen at low temperatures ($<77\text{K}$) and hydrogen pressures in the range of 20 to 65 bar through physical adsorption; however greater total capacities may continue to be realized due to higher densities in the void volumes at higher pressures. Because of the wide range of values cited as well as disputes over experimental techniques used the use of nanostructured carbon as a hydrogen storage medium remains a highly debated topic.

(5) Current Hydrogen Storage Technology

The requirements set by the DOE present significant technical challenges to be met in the near future. The most technically significant of these are (a) a storage capacity of 6 wt% (b) a release temperature under 80°C , and (c) a refueling time of less than five minutes. This will require a storage medium that is both high capacity and has decent refueling rates at moderate temperatures. Several existing technologies are detailed in Figure 1.1 [108].

Figure 1.1. Current hydrogen storage media detailing volumetric and gravimetric capacities [108]. Note: The targets are for complete systems and not just for materials.

Current compressed gas technologies and liquid hydrogen storage are shown in Figure 1.1 for comparison and are well outside the desired volumetric and gravimetric densities. The leftmost rectangular area highlights several known classical hydrides. These materials, as shown, can have very high volumetric densities, but because of the high density of the elements involved the gravimetric densities are much lower than desired. The middle highlighted area details several known complex hydrides. The theoretical capacities of the materials shown approach and in some cases exceed the systems goals. Chemical hydrides have the highest gravimetric capacities of the materials shown and are highlighted in the rightmost area. The materials that fall within 6 wt% and 9 wt% are those materials that have theoretical capacities that meet the desired goals for a hydrogen storage material, and are therefore of value to study.

(6) Hydrogen Storage System Engineering Concerns

Aside from capacity and reversibility problems, a storage medium must also be durable and reliable. Table 1.1 above notes that the DOE expects a durable range of 150,000 miles with the storage medium maintaining 80% of its original capacity [1]. Many hydrides, most notably complex and chemical hydrides, may be sensitive to impurities such as air and water. This problem is solved in laboratories by using high purity hydrogen and clean high vacuum systems to keep the reacting materials safe from any impurities. The fuel cell quality hydrogen for vehicles is expected to meet the SAE and ISO standards which have very stringent allowable levels of most key poisons and impurities. Therefore, it is important to understand how varying impurities will affect a hydrogen storage material's performance or its long-term stability.

II. Background

1. Li-N-H Complex Hydrides

Development and research into Li-N-H based compounds began when Chen et al. [57] reported a total absorption of 11.5 wt% of hydrogen by Li_3N . Their studies found that Li_3N was able to store hydrogen in the lithium amide form following the multi-step reaction shown in Equation 2.1, and Figure 2.1 shows the structural transition from α Li_3N to Li_2NH .

Lithium nitride in the temperature ranges that are useful for this work has an α and β phase. The material itself has long been known as an ionic conductor, and the currently accepted structures of these phases were originally determined by Rabenau and Schulz [109]. The α phase is a hexagonal structure in the space group P6/mmm. There are two sites for the lithium atoms, the first being the $(0, 0, \frac{1}{2})$ site and the second at $(\frac{1}{3}, \frac{2}{3}, 0)$. The nitrogen atom sits at $(0, 0, 0)$ and is coordinated to both lithium atoms. This structure can be seen in Figure 2.2. The β structure is hexagonal, but in the space group P63/mmc. The first lithium atom sits at $(0, 0, \frac{1}{2})$ and the second at $(\frac{1}{3}, \frac{2}{3}, 0.583)$. The nitrogen atom sits at $(0, 0, 0.25)$. This structure can be seen in Figure 2.3.

Figure 2.1. Hexagonal structure P6/mmm (191) of Li_3N (left), and transformation to cubic Li_2NH ($F43m$), (right) [80, 108].

The defect structure of $\alpha\text{Li}_3\text{N}$ over a temperature range of 153K to 678K was studied by Schulz and Thiemann. [110] This work found that the first lithium atom $(0,0,1/2)$ and the nitrogen atom both sat in fully occupied sites and remained fully ordered over the temperature range. The second lithium atom $(1/3, 2/3, 0)$ was shown to have a vacancy concentration of approximately 1-2%, and it was found that the vacancy concentration did not increase significantly over this temperature range.

Different possibilities have been reported for the crystal structure of Li_2NH , with the topic of the precise structure of Li_2NH still debated. The earliest work attempting to identify the structure of Li_2NH was done by Juza and Opp [71] determined the crystal structure to be an anti-fluorite type structure ($Fm\bar{3}m$) that consists of Li^+ and NH^{2-} , with the NH^{2-} groups rotating randomly giving them spherical symmetry. This determination specifically proposes a cubic structure with NH^{2-} at the 4a $(0,0,0)$ site and Li^+ at the 8c $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ site.

Figure 2.2. Structure of α Li_3N (left) and β Li_3N (right) [109]

A later refinement by Ohoyama et al. [80] using neutron powder diffraction proposed a face centered cubic structure in the space group $F\bar{4}3m$. This refinement proposed that the hydrogen sits randomly on the 16e sites surrounding the nitrogen atom, sitting at a distance of 0.82 Å from nitrogen. Noritake et al. [79] attempted to further refine the system using synchrotron X-ray diffraction and charge density analysis. This research proposed an fcc structure similar to that of Ohoyama [80], but in the space group $Fm\bar{3}m$ similar to that of Juza and Opp [71]. Their work suggested that the hydrogen atom is located around the nitrogen atom, randomly occupying the 48h sites in the lattice at a distance of 0.80 Å from the nitrogen atom. The charge densities studied found that the minimum density in the interstitial sites is $0.004\text{e}/\text{\AA}^3$, which would indicate no metallic bonding within the Li_2NH lattice. All three structures are statistically similar and essentially propose that the lithium and nitrogen atoms form an ordered lattice with the Li and N sites all filled and the hydrogen atoms randomly occupying available sites.

Figure 2.3. Li_2NH Structure as determined by Ohoyama et al. [80]

Most recently Balogh et al. [111] proposed a refined crystal structure using neutron powder diffraction of deuterated lithium imide (Li_2ND). This research, unlike that discussed above, proposes that the crystal goes through an order-disorder transition at 358 K. Above this temperature, their findings agree with that of Noritake et al. [79] proposing the anti-fluorite type $Fm\bar{3}m$ space group. Below that temperature, it was proposed that the structure took on the $Fd\bar{3}m$ space group with the NH^{2-} anions in a close packed configuration. This proposes that the N and H atoms sit at fully occupied 32e sites with the H atoms coordinated to empty 8b sites and N atoms coordinated to Li atoms that sit at the 8a and 48f sites. This leaves Li atoms that randomly occupy available 32e sites. The primary difference between this model and those proposed earlier is that this model proposes that the hydrogen atoms sit at fully occupied sites with random arrangement of lithium atoms.

Although initial hydriding of this material provides relatively high values, the reversible content of this material is typically only 6 to 7 wt% at 285°C. [80] The reduction in overall capacity comes primarily from the irreversibility of the conversion of $\text{Li}_3\text{N} \rightarrow \text{Li}_2\text{NH}$, shown in Equation 2.2 [57, 80].

Because of this irreversibility the bulk of the reversible capacity of this material comes from the second half of the reaction, detailed in Equation 2.3.

Work by Nakamori and Orimo [34] found dehydrogenation of Li_2NH starting at approximately 427°C, verifying the presence of Li_3N through Raman spectroscopy. Unfortunately this is too high of a temperature to be generally useful for an on-board system.

Uncertainty in the structure of Li_2NH has also led to uncertainty in the mechanisms by which the reversible reaction seen in Equation 2.3 is able to occur, specifically the mechanism by which $\text{LiNH}_2 + \text{LiH}$ is able to decompose into $\text{Li}_2\text{NH} + \text{H}_2$ is still debated. Chen et al. [60] originally proposed a redox reaction between the positively charged hydrogen in LiNH_2 and the negatively charged hydrogen in LiH . This theory was tested by observing the dehydrogenation product of the decomposition of lithium amide and deuterated lithium hydride, $\text{LiNH}_2 + \text{LiD}$. If the predominant mechanism is the proposed redox reaction, then it would be expected that the product would be primarily HD gas. Their experiments found, however, that the gas was instead a mixture of H_2 , HD and D_2 and that the L-N-H remaining still retained a significant amount of deuterium, with Li_2ND likely present [60].

More recent studies, particularly those by Ichikawa et al. [22, 67], have proposed that the decomposition is mediated by ammonia that forms as part of the initial decomposition of LiNH_2 . [22, 67, 112, 113] It is well known that LiNH_2 , upon heating, can decompose to ammonia following reaction 2.4. Hu and Ruckenstein [112] proposed that the ammonia then is able to quickly react with the LiH present, forming LiNH_2 and hydrogen, as seen in Equation 2.5.

So far, however, evidence supporting this reaction mechanism has been indirect. Hu and Ruckenstein [112] showed that NH_3 would react quickly with LiH to form LiNH_2 and H_2 . Ichikawa et al. [22] found evidence that supported a two-step reaction during the decomposition reaction. Isobe et al. [113] proposed that the decomposition occurred through this mechanism by

LiH and NH₃ reacting to form a theoretical LiNH₄ intermediary compound, which then decomposes to form LiNH₂ and H₂. They supported this theory with thermogravimetric analysis as well as desorption spectroscopy. These proposed mechanisms all share the common feature that NH₃ gas forms and then reacts with LiH so quickly that it is not practically detectable, leading to little in the way of direct evidence for this mechanism.

Most recently Weidner et al. [114] have proposed that the reaction proceeds through the formation of the intermediate compound Li₄NH. Li₄NH is a known compound and has been previously synthesized by Marx [115] from the direct synthesis of Li₃N and LiH as shown in Equation 2.6.

The work by Weidner et al. [114] used neutron diffraction on the products of reaction between Li₃N and D₂ over a molar ratio (D₂/Li₃N) range of 0 to 2. The patterns showed the formation of Li₄ND starting at a molar ratio of approximately 0.2, and the maximum formation was seen at a ratio of approximately 0.6 where LiD began to form. They also reported the presence of a non-stoichiometric imide phase: Li_{2+y}ND. This compound was proposed to be an anti-fluorite type structure with Li⁺ occupying the tetrahedral (1/4, 1/4, 1/4) sites and (NH)²⁻ anions at the fcc positions. Li₄NH, meanwhile, is a tetragonal structure where the Li⁺ cations are coordinated to N³⁻ and H⁻ anions. This model provides a potential mechanism for the formation of mixed H₂, HD and D₂ from the desorption of LiNH₂ + LiD as seen by Chen et al [60], as solid-solid reactions between the non-stoichiometric imide and Li₄NH that form during the desorption could account for the formation of HD in particular.

Work by Crivello et al. [116] and David et al. [63] has suggested that the progression of Li₂NH to LiNH₂ does not follow a stoichiometric path according to Equation 2.1, but rather progresses through a series of non-stoichiometric phases with the general composition of Li_{2-x}NH_{1+x}. In particular, Crivello et al. [116] have observed the formation of compound Li_{1.5}NH_{1.5} and modeled the crystal structure showing the existence of both [NH]²⁻ and [NH₂]⁻ anions at the same time.

Lu and Fang [26] have attempted to improve the system by using a mixture of LiNH₂:2LiAlH₄. This decomposes to form hydrogen under the proposed reaction, 2LiAlH₄ + LiNH₂ → 2Al + Li₂NH + LiH + 4H₂. This work claimed a total desorption of 6.6 wt% hydrogen over two steps. The first step evolved 4.4 wt% hydrogen at ~170°C and the second step evolved a further 2.2 wt% hydrogen at ~125°C. The same material was doped with TiCl₃ to provide a total desorption of 8.1 wt% at a final temperature of approximately 315°C.

Further work has been done by Meisner et al. [31] attempting to improve the Li-N-H system by mixing lithium amide with lithium borohydride. The composition studied, LiB_{0.33}N_{0.67}H_{2.67}, has a theoretical hydrogen capacity of 11.9 wt%. The actual material released approximately 10 wt% when heated to up to 250°C. It was also found that a small portion of the gas released, about 2-3 mol%, was in the form of ammonia. A non-equilibrium phase diagram was also constructed, as seen in Figure 2.4, showing that at higher temperatures the hydrogen desorption occurred with the material in a liquid form.

Figure 2.4. Non-equilibrium phase diagram of the LiBH_4 - LiNH_2 system as determined by Meisner, Scullin, Balogh, Pinkerton and Meyer. [31]

Further research has been done by Pinkerton et al. [117] on this $\text{LiB}_{0.33}\text{N}_{0.67}\text{H}_{2.67}$ system. Their research focusing on Ni, Fe and Zn additives found significant reduction of the desorption temperature when using NiCl_2 and FeCl_2 as additives. A temperature reduction of 36°C was achieved with 5 wt% FeCl_2 as a catalyst. NiCl_2 gave the best results with a temperature reduction of 90°C with 5 wt% added and 112°C with 11 wt% added. Additionally, it was noted that when using NiCl_2 as an additive, hydrogen could be released with only partial melting, whereas the additive-free material only released hydrogen in the liquid phase.

2. Other Complex Hydrides

Bogdanovic and Schwickardi [8, 118] provided the first work that demonstrated the potential for Alanes, specifically NaAlH_4 and LiAlH_4 , to become practical hydrogen storage materials. Their work showed that the use of titanium and other transition metals as a catalyst allowed as much as 3.7 wt% reversible hydrogen storage for NaAlH_4 under reasonable pressures and temperatures. Further work spurred on from these results found that the hydrogen release likely occurred in two steps [16, 18, 19, 39, 43, 119]. The first, higher pressure step is the dehydrogenation of NaAlH_4 to Na_3AlH_6 as seen in Equation 2.7. The next, lower pressure step, is the decomposition of Na_3AlH_6 to NaH as seen in Equation 2.8. Reversible decomposition of NaH occurs at too high of a temperature to be considered useful.

Further important developments were seen by Jensen et al. [119], Zaluska et al. [49, 120], and Zidan et al. [121] where it was found that the catalysts could be added through high-energy ball milling. This effectively reduced the temperatures at which desorption of hydrogen would occur.

Researchers studying LiAlH_4 have found that it has a higher storage than NaAlH_4 , with a theoretical capacity of 10.5 wt%, and undergoes a two-step decomposition similar to that noted in equations 2.7 and 2.8 above [10, 122]. Studies on the material have shown that the decomposition of LiAlH_4 to Li_3AlH_6 yields 5.3 wt% H_2 at 150 - 175°C and that of Li_3AlH_6 to LiH

yields 2.6 wt% at 180-220°C [122]. Like sodium hydride, LiH is generally not pursued due to the high temperatures required to obtain any meaningful amount of hydrogen. Further developments have focused on improving kinetics and reducing the temperature required for hydrogen desorption. Work by Chen et al. [123] showed that using $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$ as a catalyst promoted reversibility of the reaction, while further work by Blanchard et al. [12] used TiCl_3 and VCl_3 as catalysts to reduce the dehydriding temperature by over 50 K. Further research by Resan et al. [38] used Ti_xAl_y compounds as catalysts and realized a reduction of approximately 30 K, however with a measurable loss in hydrogen content.

Sodium borohydride (NaBH_4) and lithium borohydride (LiBH_4) both have fairly high theoretical capacities, with NaBH_4 containing 10.9 wt% H_2 and LiBH_4 containing 18.5 wt% H_2 . Recent research has explored using these materials as a liquid storage medium, obtaining hydrogen through decomposition with water as described in Equation 2.9 [124]. The major drawback to this method would be that rehydriding of the storage material could not be performed in an on-board storage system, presenting further infrastructure and engineering challenges.

Other research has been performed using borohydrides in a mixture with other complex hydrides to try and improve the kinetic properties and obtain a consistently reversible reaction [125].

The most commonly studied material in this category is magnesium hydride (MgH_2) which has a fairly high density of hydrogen of 7.6 wt%. Unfortunately, it is a very stable compound and does not readily decompose (into Mg metal and H_2 gas) until approximately 400°C [126]. Work attempting to reduce this decomposition temperature has included ball milling with Ni and transition metal oxides [127, 128] to reach 6.5 wt% desorption at 300°C. Varin et al. [129] also obtained 3.8 wt% decomposition using a nanocrystalline composite of $\text{MgH}_2 + \text{Mg-Fe}$ at 306°C. There have been promising improvements in these materials, but they are still well short of DOE goals.

3. Kinetics of Complex Hydrides

The kinetics of complex hydrides are an important engineering concern, especially for use in on-board applications. Kinetic data for varying systems are generally described using the Arrhenius relationship, shown in Equation 2.10.

$$k = k_0 \exp (-Q/RT) \quad 2.10$$

Where k is the rate constant at the given temperature T (in absolute scale), k_0 is a constant pre-exponential factor, R is the ideal gas constant and Q is the activation energy. Typically, data is evaluated by plotting the natural logarithm of k versus $1/T$. Assuming Q does not vary with temperature, the plot should be linear with the slope being equivalent to $-Q/R$. It is important to note, however, that the activation energy does not suggest fast or slow kinetics in and of itself; it merely quantifies the thermal dependency of the reaction occurring. It is useful, however, in comparing the effect of catalysts on materials that are thermally activated.

The reaction constants can be easily determined if it is assumed to follow a first order rate law, as given in Equation 2.11.

$$dC/dt = -kC \quad 2.11$$

The reaction is studied with respect to the depletion of hydrogen, making the partial pressure of hydrogen equivalent to the calculation for the first order rate law. As all gas within the reactor is hydrogen the equation is re-written as Equation 2.12.

$$dP/dt = -kP \quad 2.12$$

Fogler [130] outlines a method for finding the rate constant “k” using experimental data. Equation 2.11 is solved assuming an initial condition of $P = P_0$ at $t = 0$. The solution gives Equation 2.13.

$$\ln (P_0/P) = kt \quad 2.13$$

The natural log of P_0/P is plotted versus t , with the slope being k . This also provides a method for checking the assumption of first order behavior, as if the reaction can be approximated using a first order rate law. The plot of the data generated will be linear.

The kinetic mechanisms of classical interstitial hydrides have been well studied [131-134] and generally follow the steps of (1) gas phase hydrogen transport, (2) hydrogen adsorption and diffusion on the surface, dissociation of H_2 into H^+ ions, (3) absorption and diffusion of hydrogen into the solid and finally (4) hydride formation, with kinetic models being determined based on the rate which of these is the rate limiting step for the system in question. Complex hydrides, however, are stoichiometric compounds and do not generally exhibit the solid solution behavior seen in interstitial hydrides. Further, different phases observed in a complex hydride system tend to have noticeably discrete equilibrium pressures [8]. A final complication is that the dehydrided material can often be composed of multiple solid phases, requiring the long range diffusion of metal atoms.

After the discovery of metal doped sodium alanate as a potential storage material, work was done by Sandrock et al. [39] on the desorption kinetics of $NaAlH_4$ and Na_3AlH_6 catalyzed with 2 mol% $TiCl_3$. Activation energies of 79.5 and 96.9 kJ/mol were reported for $NaAlH_4$ and Na_3AlH_6 , respectively. Rates reported at 150°C were 10 wt%/hr for $NaAlH_4$ and 0.6 wt%/hr for Na_3AlH_6 . Further work by Gross et al. [19] detailed the effect of varying amounts of $TiCl_3$ catalyst on the desorption kinetics of the material. It was found that as little as 0.9 mol% $TiCl_3$ reduced the activation energy, in the case of $NaAlH_4$, from 118.1 kJ/mol to 72.8 kJ/mol, and that little measurable change was observed by further addition of catalyst. Significant increase in the rate constant, however, was seen by increasing the catalyst content by up to 6 mol%, although it was met with significant reduction in the true hydrogen capacity. Luo and Gross [27] built further upon this work by attempting to further explore the rate mechanisms of $NaAlH_4$ and Na_3AlH_6 reactions. A semi-empirical rate model was developed and activation energies for the desorption reaction of 80.0 and 97.5 kJ/mol were found for $NaAlH_4$ and Na_3AlH_6 , respectively, while the absorption reaction had respective activation energies of 61.6 and 56.2 kJ/mol.

McCarthy et al. [135] performed studies on the un-catalyzed decomposition of $LiAlH_4$ and found an activation energy of 100 kJ/mol, although it should be noted that the work did not make a distinction between the decomposition of $LiAlH_4$ and Li_3AlH_6 , making it uncertain to the influence of further material decomposition. More recent work, however, by Blanchard et al. [13] found an activation energy in close agreement with these results of 102 kJ/mol. Research on the effect of catalysts on the kinetics of the lithium-aluminum-hydrogen system has been done by Blanchard et al., Andreason and Chen et al. [13, 123, 136]. Blanchard et al. [13] studied the effects of $TiCl_3 \cdot 1/3 AlCl_3$ and VCl_3 and found a reduction of 5-10 kJ/mol with little difference in

the effectiveness of the two catalysts. Andreason [136] also studied $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$ as well as TiCl_3 and found a similar reduction of 5-10 kJ/mol. The reduction found by these studies is not significant enough to assume there is any effect on the decomposition of LiAlH_4 when using Ti as a catalyst. Chen et al.[123], however, did report results contradicting the other two studies. The research found catalysis by $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$ reduced the activation energies to 43 and 55 kJ/mol for the decomposition of LiAlH_4 and Li_3AlH_6 , respectively.

The magnesium hydride system has been studied extensively due to the relatively high gravimetric hydrogen density of MgH_2 of approximately 7.6 wt%. The system faces significant engineering problems, however, due to the relatively high temperatures at which desorption occurs, approximately 280°C and higher, and relatively slow kinetics of the system [1, 137]. A considerable amount of effort has gone into improving the kinetics and significant improvements have been made by ball milling and by the addition of various catalysts to reduce the particle size [2, 28, 53, 54, 65, 88, 90-96, 138-140].

III. Research and Development

1. Approach

In this research, we conducted experiments on cycling and aging tests of materials (as described in the above section) developed by the MHCoe Center partners. Pressure cycling apparatus was constructed at UNR for hydrogen loading and unloading. The overall approach was 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 (PCI) 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 Nature paper [57].

We have studied the Li-N-H system in which an unusual improvement of hydrogen capacity was observed during pressure cycling at 528 K using mixed nitrogen/hydrogen gases. Without mixing in nitrogen, we observed a loss in hydrogen capacity, from ~10.2 to 3.1 wt.%H after 501 cycles, during cycling due to the formation of a small amount of liquid lithium metal which formed a stable LiH phase during each cycle. This leads to a loss of nitrogen that significantly degrades the reversible hydrogen capacity of the Li_3N -H system. Here we report results from data obtained by prolonged pressure cycling of Li_3N with H_2 -100ppm N_2 and 80/20 H_2/N_2 mixed gases. We observed a significantly enhanced reversible capacity of up to ~ 10 wt.%H after 516 cycles with 80/20 H_2/N_2 mixtures, an improvement of ~7.1 wt.%H as compared to using hydrogen with nitrogen additives. We attribute this enhancement to the reaction of nitrogen with liquid lithium during cycling as the Gibbs energies of formation of Li_3N ($\Delta G^\circ = -100.16$ kJ/mol) are more negative than that of LiH phase ($\Delta G^\circ = -50.74$ kJ/mol). We propose that there is continuous accumulation of the Li_2NH phase and minimizations of LiH formation as these materials are subjected to many cycles. The cyclic behavior mechanism of Li_3N with H_2/N_2 gas mixtures is quite a different phenomenon as compared to mechanisms occurring in classical hydrides.

2. Systems Investigated

- Li_3N - Li_2NH - LiNH_2

- LiAlH_4
- $\text{LiNH}_2\text{-Li}_3\text{AlH}_6$
- $\text{Ca}(\text{BH}_4)_2$

3. Research Methodology

Method 1: Equilibrium and Cycling data.

Gas phase data was collected on a Sievert's reactor. This equipment at the University of Nevada, Reno (UNR) is shown in Figure 3.1.

Figure 3.1. Sievert's reactor at UNR. This reactor can be operated at pressures of up to 10,000 torr and also uses a MKS Baratron transducer to collect data at pressures under 1 torr, with a resolution of ~ 0.0001 torr.

The apparatus at UNR is built off of a cylinder manifold with 10 ports extending from the body of the cylinder. The reactor is constructed of 316 stainless steel. VCR fittings are used to create a high vacuum system. The system is automated using National Instruments automation equipment and Lab View software. The equipment attached to the ports includes the sample chamber itself, an inlet for hydrogen gas, an inlet for helium, a vacuum connection, various pressure transducers for use at different temperature ranges, and two known volumes (50cc and 25cc) used for calibration. The vacuum is maintained by a Varian V70 turbo pump. The primary pressure transducers used for experiments are a 10,000 torr Datametric transducer and a MKS Baratron 1 torr transducer. This allows for collection of pressure data between 0.0001 torr and 10000 torr. The temperature of the manifold and the reaction chamber are also continuously monitored using thermocouples, and the temperature of the sample chamber is controlled with a Watlow furnace and temperature controller.

Before operation, the volume of the reactor is determined. This is done using helium and the two calibrated volumes. The entire system is first evacuated. Next helium is added to approximately 1500 torr and the exact pressure is recorded by a transducer. The two volumes are then closed and the remainder of the system is evacuated. The 50cc volume is then opened to various parts of the system. The use of helium allows the volume to be easily calculated using the ideal gas law,

specifically as per Equation 3.1. This procedure is then repeated using the 25cc volume and the two resulting values averaged to determine the working volume for the reactor.

$$P_1V_1 = P_2V_2 \quad 3.1$$

The experiment is then run by the Lab View software. Fixed pressure steps of hydrogen are set at the beginning of the experiment. The forward (adsorption) PCI diagram is then collected. First, the reaction chamber is closed off and the manifold is opened to hydrogen gas, where the pressure is allowed to increase an amount equal to the fixed pressure step. The pressure is then measured and the reaction chamber opened to the manifold. Pressure versus time data is collected by the program and the reaction is allowed to continue until $dP/dt \approx 0$. The pressure is then recorded and the moles of hydrogen adsorbed by the material are calculated. As the temperature has been monitored, and the starting and final volumes and pressures are known, this can be easily accomplished using the ideal gas law, which is generally accurate over a large range of pressures and temperatures for hydrogen gas. However, if the investigator feels that the pressure has become large enough to have a significant effect; other equations of state may be used. The PCI diagram is constructed using several of these steps plotting the equilibrium pressure at each point versus the total amount of hydrogen adsorbed using $PV=nRT$ equation.

After collecting the forward PCI data, a reverse (desorption) curve is collected. The reaction chamber is closed and the manifold is evacuated. The manifold is then opened and the pressure allowed to equilibrate similarly to the forward run. The amount of hydrogen desorbed from the sample is determined and the pressure recorded. The reverse diagram is then drawn by plotting the equilibrium pressure versus the amount of hydrogen remaining in the sample. Note that this means some knowledge of the amount of hydrogen currently stored in a material is generally required, usually through first completing a forward diagram.

During these experiments, the pressure versus time data as well as the PCI points are recorded. The pressure versus time data can be used to determine kinetic information. The rate of pressure drop is equivalent to the rate of hydriding, as long as the gas environment contains only hydrogen. So, assuming the reaction follows a first order rate law the kinetic constant at a given temperature can be determined using Equation 3.2, where k is the kinetic constant.

$$dP/dt = kt \quad 3.2$$

Cycling is performed on both a high pressure equilibrium cycling Sievert's and a mechanical long term cycling apparatus, which can both be seen in Figure 3.2. The high pressure equilibrium Sievert's reactor pressurizes the manifold volume to a preset point. Afterwards the sample is exposed to the gas and allowed to reach equilibrium. The sample is then desorbed by applying vacuum for a predetermined amount of time, after which the sample is checked by closing the vacuum line and allowing the sample to off-gas. If the pressure rises too high, vacuum is reapplied for another preset amount of time. These processes are detailed in Figures 3.4 and 3.5.

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

120 bar H_2 Pressure Cycling apparatus -2 bar

Pressure Cycling apparatus -2 bar H_2

Figure 3.2. Equilibrium high pressure cycling apparatus viewed from the front (Top) and rear (Bottom Left). Also shown is the long-term cycling apparatus used to test materials under long-term cycling conditions. (Bottom Right).

Figure 3.3. Example raw cycling data collected from the high pressure cycling apparatus shown in Figure 2.2. The left figure shows data collected for cycles 3-8 while the right figure shows data collected for cycles 22-24. Both figures show data collected over a 25-hour time period.

Figure 3.4. This figure shows a single equilibrium absorption collected during a cycle. The reaching of a stable minimum pressure is used to determine the equilibrium.

Figure 3.5. This shows the method of performing desorption on the sample during cycling. Vacuum is applied for a predetermined amount of time. Afterwards the sample is checked by turning off the vacuum and allowing the sample to off-gas. This pressure must remain below a predetermined level or vacuum is reapplied.

The long-term mechanical cycling operates by applying a constant 2 bar of hydrogen followed by vacuum for 30-minute increments each. This process continues while a counter keeps track of the number of cycles the material has been exposed to. This attempts to simulate the effect of repeated exposure to charging gas and vacuum desorption.

Method 2: X-ray Diffraction

X-ray diffraction was performed on a PANalytical X'Pert diffractometer with an available environmental sample stage on as-made powder samples. The as-made materials were tested in an inert environment to determine the initial structure. The materials were then cycled, either using the Sievert's reactor or within the environmental stage itself. Figure 3.6 shows the diffractometer available at UNR. The environmental chamber can also be used to determine the changes in structure as the material approaches hydrogen equilibrium by using varying pressures of hydrogen within the chamber.

Figure 3.6. Environmental sample stage on the PANalytical X'Pert X-ray diffractometer. This stage allows in-situ diffraction experiments to be conducted under heating and pressurized conditions, as well as under vacuum.

Methods 3: General Purpose Neutron Powder Diffraction

Neutron powder diffraction is a powerful tool that is available to help determine the location of hydrogen atoms within a metal hydride. A schematic of the general purpose neutron powder diffractometer available at Argonne National Laboratory is given in Figure 3.7 [141].

Figure 3.7. General Purpose Powder Diffractometer at Argonne National Laboratory. This schematic shows the general orientation of the beam and detector equipment used to generate neutron diffraction patterns[141].

The mathematics of operation of this instrument were described by Jorgensen et al. [142]. As neutron diffraction is the diffraction of uncharged particles by the crystal lattice, the diffraction can be described by Bragg's Law similarly to the diffraction of photons.

$$\lambda = 2d \sin \theta \quad 3.3$$

However, because neutrons are diffracted rather than photons, the wavelength can be described by the neutrons' de Broglie wavelengths.

$$\lambda = \frac{h}{mv} = \frac{ht}{ml} \quad 3.4$$

Where h is Planck's constant, m is the mass of a neutron, t is the time of flight from the sample to the detector and l is the path length to the detector. This allows Bragg's Law to be rewritten as in Equation 3.5.

$$d = \frac{ht}{2ml \sin \theta} \quad 3.5$$

In practice, detection is done using an array of detectors. Each detector sits at a set length and angle from the sample, l_i and θ_i . The neutrons diffracted from planes of a particular d spacing arrive at the detector at time t_i .

$$t_i = \frac{2md}{h} l_i \sin \theta \quad 3.6$$

This equation allows the resolution of the d -spacings of the material studied based on the neutron time of flight and diffraction angle.

Samples that are tested using the GPPD are generally charged with deuterium to enhance the resolution of the diffraction patterns obtained. This is done with the apparatus detailed by the schematic in Figure 3.10. This figure also details the heating apparatus for the sample, where the sample is heated by applying two band heaters (at the top and bottom of the sample chamber). These are each set to the desired temperature to bring the sample chamber to the temperature at which the sample will be analyzed.

Figure 3.8. (Left) General Purpose Powder Diffraction (GPPD) facility at the Intense Pulsed Neutron Source: (IPNS); Argonne National Laboratory.

Figure 3.9. (Right) Sample holders used in neutron diffraction. The sample holders are constructed using an Inconel alloy and can be loaded inside a glove box then sealed to ensure a clean environment before hydriding.

Figure 3.10. Heating and deuterium charging pressurized sample holder used for neutron diffraction measurements.

Figure 3.11. Neutron diffraction pattern of LiAlD₄ showing the raw data collected using neutron diffraction

4. Milestones

Milestone Status Table:

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
B.	Complex Anionic Materials (Borohydrides and Alanates)			
1	Modified Complex Hydrides h			
1.2.10	Diffraction measurements of LiAl hydrides	4/30/06	4/30/08	
2	New Hydrogen Storage materials Impurity Tests	10/15/07		
2..2.3	In-situ diffraction measurements of new hydrogen storage materials	4/10/07	10/20/08	
C.	Amides/Imides (M-N-H Systems)			
2	Understand reaction mechanisms	10/30/08	10/30/10	
3.3	Defect Effects on Sorption properties 1. (Uni. of Rome and UNR) 2. UNR-IPNS-ANL, and ORNL	4/30/07	5/10/09	
5	Cycle Stability and Contamination tests	4/30/06	10/30/09	
5.4	Extrinsic Cycling tests Effect of Impurities and cyclic tests on Li-Mg-N-H system	10/30/08	10/30/08	

IV. Results and Discussion

4.1. The Li-N-H System

Pressure composition isotherms of lithium nitrogen hydrides are plotted in Figures 4.1 and 4.2 (a). Specifically, Figure 4.1 shows the absorption isotherm for the reaction $\text{Li}_3\text{N} + 2\text{H}_2 = \text{LiNH}_2 + 2\text{LiH}$ and Figure 4.2(a) shows the absorption isotherm for the reaction $\text{Li}_2\text{NH} + \text{H}_2 = \text{LiNH}_2 + \text{LiH}$. Figure 4.2(a) also shows the effects of multiple cycles of industrial grade hydrogen on the absorption isotherm. These plots show that the plateau of the first system contains 8.6 wt% hydrogen and a total of 10.1 wt% hydrogen at 11 bar. The second system contains 4.3 wt% in the plateau and a total of 5.8wt% at 11 bar. These values correspond fairly well to similar data collected by Chen et al. [57, 60]. The material shows only partial reversibility, as once all Li_3N has been converted to $\text{Li}_2\text{NH} + \text{LiH}$, the reverse reaction will not progress back to pure Li_3N at this temperature. The data shows a small plateau increasing to ~2.2 wt%, after which the curve slopes upward entering a new plateau at ~3.5 wt%. This corresponds well with the theoretical wt% values of Li_4NH (2.36 wt%) and Li_2NH (3.49 wt%), lending support to the hypothesis of Weidner et al. [114] that the material first converts to Li_4NH followed by the formation of a non-stoichiometric imide phase.

As the Li_3N in Figure 4.1 begins absorbing hydrogen, it first enters a small plateau absorbing up to ~2.3 wt% hydrogen. After this plateau has completed the data begins to slope up toward a higher plateau. This sloping behavior is typically interpreted in classical metal hydrides such as the vanadium-hydride system, as hydrogen entering into solid solution with the α phase of the

metal. (The basic form of this can also be seen in Figures 4.1 and 4.3.) However, complex hydrides such as LiNH_2 are generally thought to be stoichiometric compounds and are not expected to demonstrate similar behavior. The work by Weidner et al. [114] does propose a potential mechanism by which this could occur. This interpretation proposes that when Li_3N is first exposed to hydrogen it begins to form Li_4NH as per the reaction: $2\text{Li}_3\text{N} + \text{H}_2 \rightarrow \text{Li}_4\text{NH} + \text{Li}_2\text{NH}$. The plateau ends as the storage approaches 2.3 wt%. Marx [115] and Weidner et al. [114] both identify the formation of a non-stoichiometric compound based on lithium imide (Li_2NH) that can form by the reaction of Li_4NH and Li_2NH , which Weidner et al. propose takes the form of the reaction $(1-y)\text{Li}_4\text{NH} + y\text{Li}_2\text{NH} \rightarrow \text{Li}_{4-2y}\text{N}_{1-y}\text{H}_{1-y}(\text{NH})_y$. This may help to explain the behavior seen in Figure 4.6 between 2.3 wt% and 3.5 wt%, where, as more hydrogen is added, we see a non-stoichiometric compound forming. These capacities also correspond relatively well to the theoretical capacity of Li_4NH and Li_2NH , which are 2.36 wt% and 3.49 wt% respectively.

Figure 4.1. Forward pressure-composition isotherm showing full conversion of Li_3N to the $\text{LiNH}_2 + 2\text{LiH}$ hydride phase. Inset shows Li_4NH structure with H^+ dissociated from the NH^{2-} ions as given by Weidner et al. [114]. Other structures displayed are Li_3N structure as given by Rabenau and Schulz [109], Li_2NH as given by Noritake et al. [79] and LiNH_2 as given by Miwa et al. [76].

After the material has absorbed ~3.5 wt% hydrogen it enters the plateau that forms the dominant feature seen in Figure 4.1. This plateau increases as seen until ~8.5 wt% hydrogen has been absorbed by the material. This corresponds well with the theoretical capacity of LiNH_2 of 8.78

wt% hydrogen. At this point the reaction occurring is likely that given by Chen et al. [57, 60-62], where Li_2NH converts to the amide LiNH_2 by the reaction $\text{Li}_2\text{NH} + \text{H}_2 \rightarrow \text{LiNH}_2 + \text{LiH}$. This region between 3.5 wt% and 8.5 wt% also comprises the reversible portion of the plateau, where hydrogen is reversibly stored by the aforementioned reaction. The behavior of this material after this initial hydrogen absorption can be seen in Figure 4.2(a) and 4.4 (left).

To summarize this proposed behavior, Li_3N , upon first exposure to hydrogen in small quantities, begins to first form Li_4NH until the maximum capacity of the material to form this compound has been reached, shown at $x=2.36$ wt% hydrogen on Figure 4.1. At this point the material begins to convert to Li_2NH until $x=3.49$ wt%, where all of the material has been converted to Li_2NH . The reaction up to this point has so far not proven reversible. Finally, the material begins the reversible conversion of Li_2NH to LiNH_2 . This portion of the reaction is the region in which all reversible cycling experiments were performed.

The data in Figure 4.2(a) shows the PCI data after long-term pressure cycling (1, 56, 163, 501 and 1100 cycles) for the Li-N-H system, specifically for the reaction of Li_2NH to LiNH_2 . This data shows storage of ~6 wt% hydrogen for LiNH_2 , and there was ~2.53wt% hydrogen loss after 1100 pressure cycles. The material was subjected to 1-hour hydriding-dehydriding cycles holding at 2 bar for 30 minutes then holding at vacuum for 30 minutes to constitute one cycle using industrial grade hydrogen as the cycling gas. Figure 4.2(b) details the effect of cycling on the capacity at the end of the plateau region of each equilibrium curve from Figure 4.2(a). Figure 4.2(b) shows that the capacity drops quite rapidly after several hundred cycles, dropping to almost 25% of its initial capacity after the first 500 cycles, but then only losing minimal capacity after several hundred further cycles.

Figure 4.2. (a). Absorption isotherms obtained after non-equilibrium pressure cycling for 1, 56, 163, 501, 1100 times with impure hydrogen (ppm levels of O_2 , H_2O and others). 1(b): Hydrogen storage of Li_2NH after pressure cycling.

Figure 4.3. Differential Scanning Calorimetric scans showing the first desorption (top) and a second desorption (bottom) of Li_3N starting material. This data shows that there is an initial reaction, starting at approximately 200°C that is not present after the first desorption. The second reaction occurring at approximately 290°C occurs in both. This data was collected in collaboration with Dr. Darlene Slattery and Dr. Mike Hampton (Florida Solar Energy Center, Cocoa Beach).

The Differential Scanning Calorimetry data in Figure 4.3 shows that the first hydriding has two separate reactions, which can be interpreted as first the formation of Li_2NH from Li_3N followed by the formation of LiNH_2 from Li_2NH , as has been previously reported by Chen et al. [57, 60]. The subsequent hydriding seen in the bottom half of the figure confirmed both the irreversibility of the first reaction as well as the reversibility of the final reaction.

The first cycle equilibrium PCI isotherm and X-ray diffraction pattern of the products after 1 cycle with impure hydrogen gases are shown in Figure 4.4. The PCI isotherm shows that the 4.3wt% hydrogen was stored at the maximum isotherm plateau (~0.86 bar) and 5.9wt% at the maximum capacity (~10.25 bar). The phase in desorbed condition showed mainly Li_2NH , LiH , and Li_2O phases. XRD pattern showed nearly complete reversal from $\text{LiNH}_2 \rightarrow \text{Li}_2\text{NH}$ after cycling with expected LiH phase and impurity phase (Li_2O).

Figure 4.4. The 1st cycle equilibrium PCI isotherm of Li₂NH and X-ray diffraction pattern of the products after 1 cycle with hydrogen gases.

Figure 4.5. Absorption pressure isotherms of 1, 56, 163, 501 and 1100 cycles show loss of ~2.53 wt.% hydrogen at ~10.25 bar gas pressure after 1100 cycles for imide/amide system.

Figure 4.6. Qualitative phase analyses showing increases in the impurity phases and decrease in the Li_2NH phase. Note the expected increase in LiH phase.

X-ray diffraction analyses of the products after cycling with impure hydrogen gases, and subsequently obtaining the equilibrium isotherms are shown in Figure 4.5. The 1-cycle diffraction pattern indicates formation of imide and other products. Similarly, the cycled products after 56, 163, 501 and 1100 are shown in the Figure 4.6. The observed phase in desorbed condition was mainly Li_2NH , LiH, and Li_2O phases. XRD pattern shows nearly complete reversal from $\text{LiNH}_2 \rightarrow \text{Li}_2\text{NH}$ after cycling with expected LiH phase and impurity phase (Li_2O). After 1100 pressure cycles, the LiH phase increased from 11 wt% to 58 wt%, and the Li_2NH phase decreased from 82 wt% to 13 wt%. The decrease in amount of Li_2NH can be observed in the Bragg peak at 30.5° of the XRD patterns in Figure 4.4. The impurity Li_2O phase increased from 7 wt% to 29 wt% after 1100 cycles; as indicated by the increase in Bragg peak intensity at 56° of the XRD patterns. A very small amount of LiOH phase was also found in the XRD results. In Figure 4.5, the preliminary qualitative phase analyses show the increase in the impurity phase (Li_2O) and decrease in the Li_2NH phase. Note the expected increase in LiH phase. The inference from this graph (Figure 4.6) was that the nitrogen levels are lowered in the system resulting in formation of LiH, indicating that nitrogen may be evolving as a gas and needed to be replenished.

Lithium nitride starting material was aged in hydrogen containing 100 ppm CO for approximately 240 hours at 12 bar and 325°C . The pressure versus time data collected during aging can be seen in Figure 4.7. After aging was complete, PCI data was collected at 325°C and is shown in Figure 4.8. The PCI data collected shows a capacity similar to that of pure Li_2NH , indicating that ppm levels of CO (as may be found in industrial grade hydrogen) had little effect on the storage properties of the material.

The effect of high-pressure equilibrium cycling of hydrogen with 100 ppm methane impurity has been studied. The results of this can be seen in Figure 4.9 below. This is plotted with material that was cycled a similar number of times in industrial grade hydrogen for comparison. The plot

shows only minimal differences between the material cycled with methane impurity and that cycled with industrial grade hydrogen.

Figure 4.7. Pressure versus time data collected during aging of Li_2NH in CO. The data shows little change in the overall pressure, with short-term fluctuations matching fluctuations in room temperature.

Figure 4.8. PCI data of Li_2NH collected after aging for ~ 240 hours in H_2 with 100 ppm CO at 325°C .

Figure 4.9. PCI comparing the effect of Li-N-H cycling in industrial grade hydrogen to hydrogen with 100 ppm methane impurity.

Figure 4.10 shows the uptake of hydrogen by the sample in wt%, determined from the pressure drop of the equilibrium cycle, as a function of the number of cycles. Although not without outliers, this data shows a trend of capacity loss as the material is cycled. The overall difference between the maximum and minimum points (ignoring cycles 1 and 25 as outliers) is 0.2 wt %. The pressure versus time data collected can be seen in Figure 4.11. This data shows that there is little loss in kinetics due to cycling, while the capacity is dropping, as seen in Figure 4.10. This provides evidence that the capacity loss in this case is primarily due to bulk composition changes, rather than reduced kinetics, making it impractical to reach the true equilibrium temperature.

This data also shows the degree to which the material was loaded during cycling. The PCI diagram taken after cycling, as seen in Figure 4.9, shows that after cycling the material was able to absorb a total of 4.8 wt% hydrogen and the plateau showing a maximum capacity of ~3.8% hydrogen. This compares to uncycled Li_2NH which was able to store 5.9 wt% hydrogen with a plateau having a capacity of 4.3 wt% hydrogen. This shows a loss of 0.5 wt% stored in the equilibrium plateau, compared to a loss of ~0.2 wt% from the first cycle to the 50th (Figure 4.10).

Figure 4.10. Hydrogen absorption in wt% H₂ as a function of Li₂NH-LiNH₂ cycles using 100 ppm CH₄ impurity.

The figure below shows pressure versus time cycling data for Li₂NH-LiNH₂ cycling performed with hydrogen containing 100 ppm CH₄ impurity. Figure 4.11 (top) shows the overall pressure versus time data collected during cycling. This data shows that the equilibrium pressure reached during each cycle is rising slightly on average with each cycle, indicating a small loss of capacity with each cycle. Figure 4.11 (bottom left) shows the behavior for a selected individual cycle showing absorption kinetics, while Figure 4.11 (bottom right) shows the desorption process where the material is allowed to off-gas briefly followed by further exposure to vacuum if the material continues to off-gas beyond a certain point. Qualitative examination of the absorption kinetics shows little change from cycle to cycle, seeming to indicate that the capacity losses seen stem largely from a loss in bulk capacity of the material.

Figure 4.11. Pressure versus time data for $\text{Li}_2\text{NH-LiNH}_2$ cycling performed with hydrogen containing 100ppm CH_4 impurity. This shows the overall data (top) data for individual cycles (bottom left) and the desorption processes (bottom right).

The figure below shows the pressure versus time cycling data for $\text{Li}_2\text{NH-LiNH}_2$ cycling performed with hydrogen containing 100 ppm NH_3 impurity. Figure 4.12 (top) shows the overall pressure versus time data collected during cycling. This data shows a fairly distinct increase in the equilibrium pressure over several cycles indicating a fairly dramatic loss of capacity. Figure 4.12 (bottom left) shows the behavior for a selected individual cycle showing absorption kinetics, while Figure 4.12 (bottom right) shows the desorption process where the material is allowed to off-gas briefly followed by further exposure to vacuum if the material continues to off-gas beyond a certain point. The total capacity loss after cycling is detailed and compared to similar length cycling in Figure 4.14, showing an overall capacity loss of ~3.9 wt% hydrogen at 10 bar. This shows over three times the capacity loss when compared to methane impurity or industrial hydrogen.

Figure 4.12. Pressure versus time data for $\text{Li}_2\text{NH-LiNH}_2$ cycling performed with hydrogen containing 100ppm NH_3 impurity. This shows the overall data (top) data for individual cycles (bottom left) and the desorption process (bottom right).

Figure 4.13. The pressure versus time data collected during cycling of Li-N-H with $\text{H}_2 + 100$ ppm CH_4 , with both the left and right showing data over a 20-hour interval. While there was capacity as seen in the previous figure, a qualitative analysis of these figures shows little loss in kinetics. This would indicate that the capacity loss came primarily from new bulk compounds forming.

Figure 4.14 shows the PCI data collected after exposing the material to 560 cycles of hydrogen containing 100 ppm H₂O impurity. This cycling was performed by exposing the material to 2 bar hydrogen for 30 minutes followed by vacuum for 30 minutes to comprise a complete cycle. The data is plotted with material that was cycled similarly in industrial grade hydrogen for comparison. This data shows similar results in the final capacity of the material, with a difference at the highest pressure of 0.3 wt% hydrogen.

Figure 4.14. Pressure-composition isotherm comparing Li-N-H after 560 cycles in hydrogen containing 100ppm H₂O to that cycled 501 times in industrial hydrogen.

This material was also analyzed using X-ray diffraction with the results shown below (Figure 4.15). Most interestingly the material shows no noticeable formation of any hydroxide phases that may occur if the material is exposed to water. This seems to indicate that either lithium oxide simply has a more favorable chance to form in these conditions, or any hydroxide compounds that form are quickly reacting to form the oxide after their initial formation.

Figure 4.15. The X-ray diffraction data collected after 560 cycles in $H_2 + 100\text{ppm } H_2O$ shows strong Li_2O peaks, but only weak $LiOH$ peaks.

Figure 4.16 shows forward PCI data collected after various cycling tests, allowing comparison of varying potential impurities. CH_4 impurity showed slightly less capacity loss than industrial hydrogen with a similar number of cycles. It is, therefore, unlikely that methane gas in particular is not very reactive with the lithium imide-amide system, with the observed capacity losses more likely long-term losses due to the material itself. Along with this, it is worth noting that in all cases increased formation of LiH was seen with more cycles as can be seen in the previous X-ray patterns. A portion of the loss in capacity appears to be from LiH that does not fully reform to Li_2NH each cycle.

The loss due to water vapor is not significantly different from that seen due to a similar number of hydrogen cycles. Coupled with the fact that the X-ray pattern showed no noticeable $LiOH$ formation it would appear that this material is relatively durable with regards to water vapor. Oxygen, on the other hand, showed a significantly larger capacity loss from cycling compared to similarly cycled impurity gasses. This shows that a working system would need to be fairly free of oxygen impurity to maintain long-term operability.

Ammonia impurity caused a surprisingly large capacity loss. This is in particular noteworthy because of the current thought that the mechanism of the reverse reaction is the decomposition of $LiNH_2$ to ammonia gas, which then reacts with LiH as originally proposed by Ichikawa et al. [22]. This lends credence to recent work by Weidner et al. [114] and David et al. [63] that propose alternate methods of reaction, as the ammonia present in the system appears to, if anything, poison the reversibility of the reaction.

Figure 4.16. Collected impurity cycling data on Li-N-H. This data shows that O₂ and NH₃ gaseous impurities cause the largest capacity loss out of those tested.

4.1.1 Neutron Diffraction Studies of Li-N-H

In-situ neutron diffraction analyses have been used to observe the phase transformations occurring during the hydriding of α -Li₃N as a function of time and temperature. Figure 4.17(a) shows the time resolved phase formations at different temperatures during both the addition of deuterium and the removal. Diffraction patterns were collected every 15 minutes and the temperature of the isothermal regions is noted on the figure. This data shows the formation of LiND₂, and also shows small amounts of LiD and Li₂ND, but these phases are never substantial during the deuteriding stage, suggesting that LiND₂ is forming rapidly from these compounds in the presence of deuterium gas. Desorption at 250°C caused the LiND₂ phase to disappear as it transformed to Li₂ND. Reducing the temperature showed no notable change in the phase concentrations, while increasing the temperature to 320°C significantly increased the rate of desorption, resulting in a decrease in LiD and an increase in both Li₂ND and LiND₂. It has been shown by Chen et al. that complete reversal to Li₃N is possible at 450°C. The image plate neutron diffraction data showing the changes in the d-spacings are shown in Figure 4.17(b).

Figure 4.17(c) shows the phase changes in mixed α + β Li₃N over time while under 2 bar deuterium pressure at 200°C. At first, the only observable reaction is the conversion of the beta Li₃N to the alpha phase. As the reaction progresses, both the alpha and beta phases begin to decrease as the LiND₂, LiD and Li₂ND phases begin to form. Although not calculated in detail from this data, the conversion of Li₃N to hydride phases is qualitatively much slower than the conversion of Li₂ND to LiND₂.

Figure 4.17. Neutron diffraction studies of the lithium nitride system showing: A) Quantitative evolution of phases from α Li_3N upon exposure and removal of deuterium, B) Image plate neutron diffraction data showing changes in d-spacing, and C) Isothermal in situ showing phase change over time under 2 bar deuterium pressure. Collected in collaboration with A. Huq, Richardson and Maxey at Argonne National Laboratory [143, 144].

Volumes of Different Phases as a Function of Temperature - No Deuterium Gas Flow

	Volume	Volume	Volume
Temp	α - Li_3N	LiD	LiND_2
	Z=1	Z=4	Z=8
100°C	44.59	67.763	260.79
150°C	44.71	68.2147	262.314
200°C	44.84	68.6732	263.871
250°C	44.83	69.1286	265.471
300°C	45.2	69.5847	266.845

Figure 4.18. Volume expansions of Li_3N , LiND_2 and LiD determined by neutron diffraction. Collected in collaboration with Huq, Richardson and Maxey at Argonne National Laboratory [143, 144].

4.2 Studies on 3LiNH₂:Li₃AlH₆

Studies were conducted on 3LiNH₂:Li₃AlH₆ material synthesized and provided by Zak Fang at the University of Utah [26]. PCI data for this material is shown in Figures 4.19 and 4.20. Prior to collecting the PCI data, the material was dehydrided in vacuum to determine the amount of hydrogen released by the material. The material was placed in the Sievert's reactor used at UNR and the volume available was evacuated at room temperature. The material was then heated to 350°C and allowed to desorb into the available volume. The material was given sufficient time to reach equilibrium. The pressure was noted and the sample chamber closed, while the manifold volume was re-evacuated. The sample chamber was then opened so further desorption could take place. A total of six such cycles were performed to reasonably assure that the material was fully desorbed. The result of the calculations determined that approximately 7.0 wt% of hydrogen was stored. This is approximately 1.1% less than that seen by Lu and Fang [26], whose results can be seen in Figure 4.22 where they obtained approximately 8.1 wt% desorption through TGA analysis. However, the reversible capacity shown by the PCI data in Figures 4.19 and 4.20 was significantly smaller. This would indicate that only a portion of the material remains active at moderate temperatures and pressures following the initial desorption of the material. The desorption and desired reversibility of this material rely on the beneficial interactions between LiNH₂, Li₂NH and Li₃AlH₆ when present in the system. The structural parameters of these compounds are given in Figure 4.23 for reference.

Figure 4.19. Full cycle PCI data collected on 3LiNH₂:Li₃AlH₆.

Figure 4.20. PCI data collected on $3\text{LiNH}_2:\text{Li}_3\text{AlH}_6$ separated into forward (left) and reverse (right) data.

Figure 4.21. van't Hoff plot determined from the desorption isotherms in Figure 4.18.

Figure 4.22. TGA data collected by Lu and Fang showing the two-step desorption of the mixed alanate/amide material [26].

Li₂NH Phase
Cubic – F-43m

a = 5.0769 Å

Li1	1/4	1/4	1/4
Li2	3/4	3/4	3/4
N	0	0	0
H	0.093	0.093	0.093

T. Noritake, H. Nozaki, M. Aoki, S. Towata, G. Kitahara, Y. Nakamori and S. Orimo,

LiNH₂ Phase
Tetragonal – I-4

a = 5.079 Å c = 10.113 Å

Li1	0	0	0
Li2	0	1/2	1/4
Li3	0	1/2	0.0018
N	0.2253	0.2480	0.1155
H1	0.2392	0.1337	0.1999
H2	0.3949	0.3603	0.1198

K. Miwa, N. Ohba, S. Towata, Y. Nakamori, and S. Orimo

Physical Review, B71(2005), 195109.

Li₃AlD₆ Phase
R-3

a = 8.07117 Å c = 9.51302 Å

Li	0.9576	0.2260	0.2911
Al1	0	0	0
Al2	0	0	1/2
D1	0.8333	0.8057	0.1007
D2	0.1582	0.1820	0.3900

H.W. Brinks and B.C. Hauback

J. Alloy and Compounds, 354 (2003), 143-147.

Figure 4.23. Structural parameters of Li₂NH, LiNH₂ and Li₃Al H₆ found in the mixed alanate sample [76, 79, 145].

The data in Figure 4.22 shows that the material at 165°C has much smaller capacity than that at higher temperatures. This would seem to indicate that the material has little active capacity at that temperature, possibly due to a phase change somewhere between 165°C and 200°C. Also, the X-ray diffraction data collected in Figures 4.21, 4.22 and 4.25 show little reformation of Li_3AlH_6 at the rehydriding pressures used, instead showing formation of Li_3AlN_2 . Lu and Fang [26] have reported success rehydriding this material at elevated pressures.

Figure 4.24. In-situ dehydriding of $\text{Li}_3\text{AlH}_6 + 3\text{LiNH}_2$. This shows that the mixed sample decomposes primarily to Al, LiH and Li_2NH .

Figure 4.25. In-situ rehydriding of the decomposed sample performed under 2 bar of hydrogen pressure at 325°C. This shows that during re-hydriding Li_3AlN_2 begins to form.

In-situ desorption and rehydriding X-ray diffraction patterns were collected for the mixed amide-alanate system and are seen in Figures 4.24 and 4.25. This shows fairly complete desorption from the initial material; however, the material does not return to the initial mixed alanate-amide form during rehydriding. Instead, the data shows the formation of Li_3AlN_2 as the re-hydriding proceeds. This may be creating the barrier to reversibility at moderate pressures that is seen in the isotherm data above. Some researchers have reported some success, however, using catalytically enhanced Li_3AlN_2 as a hydrogen storage material. [55, 146]

Figure 4.26. PCI diagram of $3\text{LiNH}_2:\text{Li}_3\text{AlH}_6$ material collected at 325°C after 540 1-hour cycles at 325°C in H_2 with 100 ppm O_2 .

Figure 4.27. PCI diagram of $3\text{LiNH}_2:\text{Li}_3\text{AlH}_6$ material collected at 250°C after 540 1-hour cycles at 325°C in H_2 with 100 ppm O_2 .

Figure 4.28. Phases present after 540 cycles in $\text{H}_2 + 100 \text{ ppm O}_2$. Notable phases that form are Li_2O forming due to the oxygen impurity and Li_3AlN_2 formation.

The Li-N-Al-H material examined in Figure 4.19 was also subjected to oxygen impurities to determine the effect of exposure of trace amounts of oxygen on its capacity. This was done by exposing the material in 1-hour cycles to hydrogen containing 100 ppm of oxygen for 540 cycles at 325°C . After cycling PCI data was collected at 325°C (Figure 4.26) and 250°C (Figure 4.27) and compared to PCI data of material that had not undergone the cycling test. In each case the material lost approximately 0.5 wt% of capacity, a significant amount, but the material still retained the majority of its capacity after 540 cycles with oxygen present with the hydrogen, showing a reasonable amount of durability with respect to oxygen. The X-ray diffraction data collected before and after cycling can also be seen in Figure 4.28 above. This shows the formation of Li_2O due to the oxygen impurity, as well as the Li_3AlN_2 phases that has been previously seen in Figure 4.18.

4.3 Effect of Cycling on Kinetics

The data in Figure 4.29 and Table 4.1 show the effects of cycling on the kinetics of the hydriding reaction of the lithium amide/imide system at 255°C . The reaction being studied is shown in Equation 4.1.

The plots shown in Figure 4.29 are approximately linear, helping to verify the first order assumption, and the rate constants found are given in Table 4.1. The rate constants show a small decay in kinetics at first, with only 15% reduction in the rate constant after 163 cycles. However, with multiple cycles there was a dramatic loss in kinetics, with an entire order of magnitude lost after 1100 cycles.

Table 4.1 Estimated first order kinetic constants from Figure 4.29 below.

Cycles	K (1/s)
1	0.0075
163	0.0064
502	0.0035
1100	0.00075

Figure 4.29. Effect of cycling on hydrogen absorption kinetics.

4.4 Kinetic Properties of Lithium Amide/Imide Reaction

Kinetic behavior was explored for a sample comprised of a mixture of lithium amide and lithium aluminum hydride. The specific stoichiometry of the mixture prepared was $3\text{LiNH}_2:\text{Li}_3\text{AlH}_6$. The kinetics were observed for activity occurring during initial hydriding with a partial pressure of approximately 500 torr. The kinetic constants were determined from pressure versus time data, and the activation energy was determined using the Arrhenius equation, specifically from a plot of $-\ln k(T)$ versus $1/T$, multiplying the slope by the ideal gas constant to determine the activation energy. This is plotted in Figure 4.30.

The material studied yielded an activation energy of 51 kJ/mol. This is compared in Table 4.2 with other hydride materials from other studies.

Figure 4.30 Arrhenius plot of the kinetic behavior of the 3LiNH₂:Li₃AlH₆ system.

Table 4.2 Comparison of the Activation Energy determined for 3LiNH₂:Li₃AlH₆ compared to materials from other studies.

Material	Activation Energy	Source
3LiNH ₂ :Li ₃ AlH ₆	51 kJ/mol	This study
MgH ₂	241 kJ/mol	[93]
Mg(Ni)H ₂	216 kJ/mol	[93]
LiAlH ₄	81 kJ/mol	[136]
Ti Catalyzed LiAlH ₄	89 kJ/mol	[136]
NaAlH ₄ to Na ₃ AlH ₆	73-100 kJ/mol	[24, 27, 39, 40]
Na ₃ AlH ₆	97-100 kJ/mol	[24, 27, 39, 40]

4.5 Effect of Nitrogen in Cycling Gas on Hydriding Stability

Lithium nitride was exposed to 2 bar pressure of hydrogen containing 100 ppm N₂, followed by vacuum, in one hour cycles. The hydrogen storage capability of the sample was checked using a Sievert's reactor after 345, 853 and 1359 cycles. The absorption data is shown in Figure 4.31 with the desorption data shown in Figure 4.32. The data shows an ultimate reduction in the equilibrium plateau pressure. There was an increase in capacity seen in up to 853 cycles, after which a reduction in the capacity was seen after 1359 cycles.

Reverse isotherms are shown in Figure 4.32 and show full or near full desorption of the material in most cases. After 853 cycles the material only desorbed to ~2.5 wt% down to a pressure of 0.01 bar. This may show a reduction in the reversible capacity that accounts for the losses that are seen after subsequent cycling. Also, by the collection of data at 1359 cycles very little hysteresis was observed between the absorption and desorption curves.

X-ray diffraction data was collected on the desorbed sample after the completion of 1359 cycles and is shown in Figure 4.33. Three primary phases were observed: Li_2NH , LiH and Li_2O . Li_2NH and LiH are the primary reaction products in the desorbed state of the hydriding reactions detailed earlier. Li_2O is present as an impurity in the starting Li_3N precursor, and is largely inert to the reacting gases present.

Data was also collected using 20 mol% nitrogen mixed in hydrogen cycling gas for up to 850 cycles. This data showed that the material was able to maintain its original capacity for up to 516 cycles, although a significant decrease was seen after 850 cycles (Figure 4.34). X-ray diffraction data was collected after 850 cycles showing a significant increase in the amount of Li_2O along with the expected Li_2NH and LiH phases (Figure 4.35).

Figure 4.36 shows further isotherms collected at University of Geneva using hydrogen with 20 mol% nitrogen and is compared to the isotherm collected in pure hydrogen. This shows an elevated, and more flat, lower pressure plateau with the final hydrogen stored being similar to that done with pure hydrogen. X-Ray diffraction patterns were collected at different points of the hydrogenation process and are shown in Figures 4.37 and 4.38. Phase analysis of this data (Table 4.2) shows the existence of the non-stoichiometric compound $\text{Li}_{2-x}\text{NH}_{1+x}$ present at Point 1 (Figure 4.37) where full hydrogenation has not yet occurred. Diffraction data at Point 2 (Figure 4.38) shows near full conversion to LiNH_2 .

The data given shows surprising results in that the addition of a very small amount of nitrogen is able to both improve cycling stability compared for example, to the data presented above in Figures 4.2-4.6. Using the higher nitrogen content of 20 mol% further increased the cycling stability, only appearing to lose capacity well over 500 cycles. Further, the high Li_2O content seen by XRD (Figure 4.35) would seem to indicate that the loss in capacity was due to the presence of oxygen impurity in the gases used having a strong effect after a large number of cycles. The data in Figures 4.2-4.6 show that these compounds are very sensitive to oxygen impurities in gas over a large number of cycles. Comparatively, the material cycled here shows both: better cycling stability as well partially improved capacity, with an ultimate goal of reaching the theoretical capacity of Li_3N of 10.4 wt%.

The X-ray diffraction patterns in Figure 4.39 show that cycling had a declining effect on the amount of Li_2NH present in the material, while the fraction of LiH continually increases. Because no nitrogen containing compounds are observed in the patterns, it is likely that the nitrogen was lost as a gaseous compound. It has been proposed, for example, that ammonia gas is formed as part of an intermediate reaction, but is quickly

consumed [21, 22, 82, 112, 135]. This may simply be causing a loss of nitrogen from the system making it impossible to form the fully hydrided LiNH_2 .

The LiH phase forms during hydriding and is more stable than the other compounds involved at the temperature that we were performing the experiments (at 255°C); however it would decompose at higher temperatures[147, 148] also see Figure 4.17 above. The addition of nitrogen during hydriding facilitates the suppression of LiH formation.

Nitrogen, however, is a largely inert gas, reacting with very few materials. Ternary phase diagrams were constructed using the CALPHAD method, specifically with FactSage software, to help determine these mechanisms and are shown in Figure 4.40. These show that there are regions of the phase diagram where it is possible to form pure lithium. Pure lithium is known to react with nitrogen to produce Li_3N [71, 135]. This creates a mechanism by which lithium nitride may be regenerated in the hydride while in the presence of nitrogen gas. Assuming the only other gas present for any length of time would be hydrogen, pure lithium that formed in this way would likely react with hydrogen present, forming LiH and degrading the hydrogen capacity over a large number of cycles.

The data collected on the phase compositions at various stages of hydriding support results by other researchers [63, 116] that indicate the progression from Li_3N to Li_2NH to LiNH_2 is not as simple as first believed. The phase composition analysis as a function of hydrogen content is plotted in Figure 4.41.

Figure 4.31. Pressure-Composition Isotherms (Absorption) collected after cycling in hydrogen containing 100ppm N_2 . The data is compared to Li_3N before cycling and after cycling with pure hydrogen. The cycling with the nitrogenated gas has partially mitigated the loss due to cycling.

Figure 4.32. Pressure-Composition Isotherms (Absorption) collected after cycling in hydrogen containing 20 mol % N₂. This was able to further mitigate losses due to cycling

Figure 4.33. X-ray diffraction data collected after cycling with hydrogen containing N₂. Diffraction was done after full desorption and shows Li₂NH and LiH as major components. Li₂NH and LiH are expected as reaction products, while Li₂O is present as an impurity in the starting Li₃N test material.

Figure 4.34. Pressure composition isotherms (absorption) at 528 K of $\text{Li}_3\text{N-H}_2(\text{N}_2)$ systems (1a) Li_3N hydrided with pure H_2 (0th cycle), 1 cycle with pure H_2 , and 501 cycles with industrial hydrogen. (1b) We compare the isotherms of the 345 and 853 pressure cycles (with 100 ppm N_2 in H_2) with 1 cycle H_2 isotherm, showing a trend of increasing capacity with pressure cycling.

Figure 4.35 Pressure composition isotherms (absorption) at 528 K of $\text{Li}_3\text{N-H}_2$ systems which were previously cycled in 20 mol% N_2 in H_2 up to 516 cycles.

Figure 4.36. Pressure-composition isotherms collected using both hydrogen and hydrogen in 80-20 $\text{H}_2\text{-N}_2$ mixed gas (molar ratio). This shows an increase in the pressure of the low pressure part of the plateau.

4.6 DFT Calculations of New Structures

Two new compounds, namely, Li_4NH and $\text{Li}_{1.5}\text{NH}_{1.5}$ were detected during the hydrogenation process of Li_3N . The formation of these compounds changes hydrogen absorption and desorption sequence of hydrogenation of Li_3N . In general, hydrogenation reaction of Li_3N to Li_2NH is predominantly favored during large of aliquots of hydrogen addition, but the formation of Li_4NH is possible when small aliquots of hydrogen are used with an enthalpy of reaction much less negative than for the direct formation of Li_2NH . The formation of this compound through the release of ammonia is not possible. This compound readily reacts with H_2 exothermically with an enthalpy of reaction less negative than for the direct process. We also find that the formation of the intermediate phase $\text{Li}_{2-x}\text{NH}_{1+x}$ for $x=0.5$ between imide ($x=0$) and amide ($x=1$) is possible. $\text{Li}_{1.5}\text{NH}_{1.5}$ ($x=0.5$) is found to form in a cubic Li-vacant-type compound. After full relaxations of several structural models, the $\text{Li}_{1.5}\text{NH}_{1.5}$ compound shows coexistence of ordered $[\text{NH}]^{-2}$ and $[\text{NH}_2]^{-}$ anions. The electronic structure and ELF diagrams are shown in Figure 4.42.

Figure 4.37. X-ray diffraction collected after partial hydrogenation with the 80-20 H_2 - N_2 gas. The diffraction data shows a large amount of $\text{Li}_{2-x}\text{NH}_{1+x}$ and a small amount of Li_4NH at this stage of hydrogenation.

Figure 4.38. X-ray diffraction data collected after full hydrogenation with the 80-20 H_2 - N_2 gas. This shows essentially full conversion of the material to $\text{LiNH}_2 + \text{LiH}$.

Figure 4.39. Phase diagrams of Li-N-H plotted for using CALPHAD modeling @ (1) 255°C and 9 atm (under H₂ loading conditions) (2) 25°C and 9 atm, and (3) 25°C and vacuum (unloading condition) showing phase under different pressure and temperature conditions.

Figure 4.40. Phase analysis of composition as a function of the hydrogenation of Li_3N . This shows Li_4NH present in varying amounts during the intermediate stages of the hydrogenation process.

Table 4.3. Phase composition analysis of XRD data seen in Figures 7 and 8, showing the presence of $\text{Li}_{2-x}\text{NH}_{1+x}$

	wt.% LiNH_2	wt.% Li_2NH	wt.% $\text{Li}_{2-x}\text{NH}_{1+x}$	wt.% Li_3N	wt.% Li_2O	wt.% LiH	wt.% Li_4NH	$\text{Li}_{2-x}\text{NH}_{1+x}$ ($\text{\AA}$)	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

Figure 4.41. X-ray diffraction pattern from several experiments showing evolution of the $\text{Li}_{2-x}\text{NH}_{1+x}$ phase above ~ 5 wt.%H for hydrogen loading at 255°C . However, the patterns were taken at room temperature (Uni. of Geneva).

Figure 4.42. Summary of the Density of States and splitting of N - NH and NH_2 bonds (Left). Electronic Localization Function (ELF) for the structures showing NH and NH_2 bonds in the $\text{Li}_{1.5}\text{NH}_{1.5}$ phase (right).

Figure 4.43. Density of states collected on LiNH₂ (in collaboration with University of Geneva) showing the presence of N-H₂ bonds.

4.7 Ca(BH₄)₂ Phase Transitions

Phase transitions in Ca(BH₄)₂ are rather complex. We performed in-situ synchrotron x-ray diffraction experiments we performed (between 317K and 573K) at ESRF, Grenoble, showed α -to- γ and γ -to- β phase transitions (in collaboration with Dr. Filinchuk and Dr. Ronnebro). Projections of the α , γ and β phases of Ca(BH₄)₂ α -phase at 91K are: F2dd, Z = 8, a = 8.7759(3), b = 13.0234(4) c = 7.4132(2) Å γ -phase at 495K, I-42d, Z = 4: a = 5.8446(3), and c = 13.2279(11) Å, and β -phase at 305K: P42nm, Z = 2, a = 6.91885(12) and c = 4.34711(14) Å. Figure 4.44 shows the in-situ plot and the structures. More details are in the publication by Filinchuk et al. 2009.

4.8 Neutron Diffraction Studies on LiAlD₄

Neutron diffraction data of LiAlD₄ was collected in collaboration with A. Huq, E. Maxey and J. Richardson at Argonne National Laboratory and is shown in Figures 4.45-4.47. Neutron diffraction data of LiAlD₄ sample shows the monoclinic structure with P2₁/c space group for 10 K to 300 K. (Figure 4.45 shows room temperature pattern).

Figure 4.44 (top) In-situ synchrotron x-ray diffraction data of $\text{Ca}(\text{BH}_4)_2$ taken between 317-573K $\lambda = 0.711385 \text{ \AA}$ showing α -to- γ (Red line) γ -to- β phase transitions (Green line). (Bottom) Projections of the α , γ and β phases of $\text{Ca}(\text{BH}_4)_2$ α -phase at 91K: $F2dd$, $Z = 8$, $a = 8.7759(3)$, $b = 13.0234(4)$ $c = 7.4132(2) \text{ \AA}$ γ -phase at 495K: $I-42d$, $Z = 4$ $a = 5.8446(3)$, and $c = 13.2279(11) \text{ \AA}$, and β -phase at 305K: $P42nm$, $Z = 2$, $a = 6.91885(12)$ and $c = 4.34711(14) \text{ \AA}$.

Figure 4.45. Neutron diffraction patterns of LiAlD_4 at 300 K show monoclinic ($P2_1/c$) structure.

Lattice expansion of LiAlD₄ from 10 K to 300 K show anisotropic expansions in lattice parameters (Figures 4.46(a)-(c)); the Bragg peaks of 200, 21-2 and 130 reflections do not show appreciable change in position, where as the 013 Bragg peaks of LiAlD₄ are shifted significantly with the change in temperature from 10 K to 300 K (Figures 4.47(a) and (b)). This anisotropy is also true for volume expansions as shown in Figures 4.46(d). The fractional changes in lattice parameters and volumes are shown in Figure 4.46(e).

Figure 4.46. (a)-(d) Lattice parameter and volume change as a function of temperature plots of LiAlD₄ from 10 K to 300 K. (e) The lattice and volume expansion plots show that (1) 10-70 K lattice expansion in *c* direction decreases, *b* increases, *a* remains virtually the same. (2) 70-150 K lattice expansion in *c* direction increases, *b* decreases, *a* remains virtually the same. (3) 150-300K: There is increase in lattice dimensions in all direction: with *c* being more than *a* and *b*.

Figure 4.47. (a) Neutron diffraction patterns of LiAlD₄ showing significant anisotropy that the (200), (21-2) and (130) as compared to 013 crystal plane. (b) The 013 Bragg peaks shift significant due to increase in temperature from 10 K to 300 K.

4.9 Pressure measurements and Disproportionation of Li_3N

Summary

It is important to understand the vaporization behavior of Li_3N (s) by determining the decomposition pressures of the various species that could form over Li_3N (s) in the range of 200° to 470°C. The disproportionation behavior of a molecule, i.e., the disassociation of the molecule into various sub-species in the vapor phase, provides fundamental insights into the strength of the molecular bonding of that molecule. These have significance in amides, imides research.

Introduction

Vapor pressure studies were conducted on Li_3N using a new automated torsion-effusion gravimetric apparatus fabricated at University of Nevada, Reno. This apparatus enables the determination of the total equilibrium pressure over the substance of interest through the well known torsion-effusion method as well as simultaneous determination of the average molecular weight of the effusion species.

Although, Li_3N has been the focus of numerous thermodynamic, electrochemical, and crystallographic studies in the past, it is rather surprising that there have been very few studies (two that we could find) to understanding the vaporization behavior of Li_3N . In fact, only Kimura et al. [1] determined the composition of the vaporizing species (by mass spectrometry) and concluded that the dissociation of Li_3N (s) occurs by the following reaction:

with the following equations for the partial pressures of the vapor species,

$$\log p_{\text{Li}}(\text{Pa}) = -(9.670 \pm 0.081)10^3 / T + (11.487 \pm 0.102) \quad (2)$$

$$\log p_{\text{Li}_2}(\text{Pa}) = -(14.090 \pm 0.166)10^3 / T + (14.306 \pm 0.209)$$

(3)

$$\log p_{\text{N}_2}(\text{Pa}) = -(9.638 \pm 0.124)10^3 / T + (10.959 \pm 0.157) \quad (4)$$

in the temperature range 739-859 K.

However, in a recent study, Yokoyama et al. [2] predicted from their ab-initio calculations that the energetically favorable vaporization model for Li_3N is:

They also predicted another vaporization model with lesser feasibility,

The main goal of the current study was to determine possible reaction routes to establish the disproportionation reactions during the vaporization of Li_3N .

Experimental

The basic design of the torsion-effusion gravimetric apparatus is described by Chandra et al. [2], however some major modifications were done in the current set-up. They include replacing the viewing telescope by a CCD camera which is connected to a TV for real-time viewing of the torsion assembly. The temperature recording is also automated by the use of an Omega data logger. The major consideration in the experiments conducted was the use of a Pt/Rh Knudsen cell since it is known that molten Li has a propensity to react vigorously with Pt. However the partial pressure of Li (g) over Li_3N (s) reported by Kimura et al. [3] at 465.85 °C (739 K) was only $p_{\text{Li}} = 1.89 \times 10^{-4}$ torr (2.5×10^{-2} Pa), experiments were conducted at lower temperatures from 400 to 470 °C (673-743K). The catastrophic reaction of effused Li (g) with our Knudsen cell at temperatures greater than 460 °C is further discussed in the results section.

Results

The total equilibrium vapor pressure determined in this study is shown in Figures 4.48 (a) and (b). The table of equilibrium vapor pressures determined is given in Table 4.8. From the slope of $\log (P/\text{Pa})$ versus $1/T$ it can be seen that there is agreement between the total equilibrium pressure determined in this study to

that reported by Kimura et al. [*] using mass spectrometry. The following two reactions were considered with regards to understanding the nature of disproportionation of Li_3N (s):

Although, there is evidence that $\text{Li}(\text{g})$ and $\text{N}_2(\text{g})$ are the gaseous species that are present over Li_3N (s), it has not been conclusively established that $\text{Li}_3\text{N}(\text{g})$ cannot exist in the gaseous phase. Therefore, a small of the total equilibrium pressure over Li_3N could be due to the presence of $\text{Li}_3\text{N}(\text{g})$. Also, since the average molecular weight has also been determined in this study, any discrepancy will be revealed by following a disproportionation analysis presented below. In case of Reaction #2, as mentioned in “Introduction”, the presence of dimer of Li_3N in the gas phase is unlikely and hence there is no $(\text{Li}_3\text{N})_2$ in the product side.

Disproportionation of Li_3N via Reaction #1

The disproportionation analysis is determining the value of ‘b’ from equating the predicted average molecular weight and the experimentally determined molecular weight. The weighted average molecular weight is given by:

$$M_{\text{avg}} = \left[\sum_{i=1}^N m_i M_i^{1/2} \right]^{-2} \quad (9)$$

Where, m_i is the mass fraction of i^{th} species in the vapor and M_i is the corresponding molecular weight. Therefore, for reaction #1,

$$M_{\text{avg}} = \left[\frac{(1-b)M_{\text{Li}_3\text{N}}^{1/2} + (3b)M_{\text{Li}}^{1/2} + \left(\frac{b}{2}\right)M_{\text{N}_2}^{1/2}}{(1-b)M_{\text{Li}_3\text{N}} + (3b)M_{\text{Li}} + \left(\frac{b}{2}\right)M_{\text{N}_2}} \right]^{-2} \quad (10)$$

We now equate this molecular weight to the experimentally determined average molecular weight (26.15) and get $b=0.196$. We can now determine partial pressure of the effusing species by the following expressions:

$$\frac{p_{\text{Li}_3\text{N}}}{P_T} = \frac{(1-b)M_{\text{Li}_3\text{N}}^{1/2}}{(1-b)M_{\text{Li}_3\text{N}}^{1/2} + (3b)M_{\text{Li}}^{1/2} + \left(\frac{b}{2}\right)M_{\text{N}_2}^{1/2}} \quad p_{\text{Li}_3\text{N}} = 0.059P_T \quad (11)$$

$$\frac{p_{\text{Li}}}{P_T} = \frac{(3b)M_{\text{Li}}^{1/2}}{(1-b)M_{\text{Li}_3\text{N}}^{1/2} + (3b)M_{\text{Li}}^{1/2} + \left(\frac{b}{2}\right)M_{\text{N}_2}^{1/2}} \quad p_{\text{Li}} = 0.705P_T \quad (12)$$

$$\frac{p_{\text{N}_2}}{P_T} = \frac{\left(\frac{b}{2}\right)M_{\text{N}_2}^{1/2}}{(1-b)M_{\text{Li}_3\text{N}}^{1/2} + (3b)M_{\text{Li}}^{1/2} + \left(\frac{b}{2}\right)M_{\text{N}_2}^{1/2}} \quad p_{\text{N}_2} = 0.236P_T \quad (13)$$

The plots corresponding to these partial pressures are given in Figure 4.48 (a). The enthalpy of vaporization determined in this study is $178.396 \text{ kJ mol}^{-1}$ which is close to that reported by Kimura et al. [1] of $185 \pm 1.5 \text{ kJ mol}^{-1}$.

Disproportionation of Li_3N via Reaction #2

The average molecular weight if the disproportionation proceeds via reaction #2 is given by:

$$M_{avg} = \left[\frac{(2-b)M_{Li_3N}^{1/2} + (3b)M_{Li}^{1/2} + \left(\frac{b}{2}\right)M_{N_2}^{1/2}}{(2-b)M_{Li_3N} + (3b)M_{Li} + \left(\frac{b}{2}\right)M_{N_2}} \right]^{-2} \quad (14)$$

The value of 'b' determined from equating the above expression to the experimentally determined molecular weight (26.15)

$$\frac{p_{Li_3N}}{P_T} = \frac{(2-b)M_{Li_3N}^{1/2}}{(2-b)M_{Li_3N}^{1/2} + (3b)M_{Li}^{1/2} + \left(\frac{b}{2}\right)M_{N_2}^{1/2}} \quad p_{Li_3N} = 0.406P_T \quad (15)$$

$$\frac{p_{Li}}{P_T} = \frac{(3b)M_{Li}^{1/2}}{(2-b)M_{Li_3N}^{1/2} + (3b)M_{Li}^{1/2} + \left(\frac{b}{2}\right)M_{N_2}^{1/2}} \quad p_{Li} = 0.445P_T \quad (16)$$

$$\frac{p_{N_2}}{P_T} = \frac{\left(\frac{b}{2}\right)M_{N_2}^{1/2}}{(2-b)M_{Li_3N}^{1/2} + (3b)M_{Li}^{1/2} + \left(\frac{b}{2}\right)M_{N_2}^{1/2}} \quad p_{N_2} = 0.149P_T \quad (17)$$

The plots corresponding to these partial pressures are given in Figure 4.49. It can be seen that the partial pressure of Li is lowered significantly if the vaporization model assumes a disproportionation of the dimer.

It is pointed out that reaction #2 does not seem to be plausible due to physical evidence of deterioration of the Knudsen cell due to likely deposition of Li on the walls of the Knudsen cell that may have melted reacted with Pt. Furthermore, there is significant deposition of Li on the copper foils (to allow condensation of vapor) evident by the white color of Li₂O after air was let in at the end of the experiment. It is also mentioned that prolonged heating at 470 °C may have caused Knudsen cell to develop cracks and spall. Due to these reasons, future experiments will be conducted using a Molybdenum Knudsen cell which is known to be resistant to alkali metals.

References for Figure 4.48 a:

1. H. Kimura, M. Asano, K. Kubo, J. Nucl. Mater. 91 (1980) 200-204.
2. K. Yokoyama, N. Haketa, M. Hashimoto, F. Furukawa, H. Tanaka, H. Kudo, Chem. Phys. Lett. 320 (2000) 645-650.
3. D. Chandra, M.L. Garner, K.H. Lau, J. Phase Equil. 20(6) 1999 565-571.

Figure 4.48a. Vapor pressure Li₃N and comparison with other published

Figure 4.48 b. Total equilibrium pressure ($\log (P/\text{Pa})$ and $\ln (P/\text{Pa})$) over Li₃N (s) from 400-470°C.

Table 4.4. Measured total vapor pressure Li₃N (s) (orifice diameter 0.6 mm)

T (deg C)	T (K)	1/T	P (atm)	P (Pa)	log (P/Pa)	ln (P/Pa)	Calc MW
400	673.15	0.00148553	5.2329E-07	0.053022035	-	-	-
405	678.15	0.00147460	8.3180E-07	0.08428235	1.275543605	-2.93704769	17.640515
410	683.15	0.001463807	1.01166E-06	0.102506738	1.074263363	2.473582807	13.3158936
415	688.15	0.001453172	1.0420E-06	0.105577568	0.989247586	2.277826745	28.827845
420	693.15	0.001442689	1.7364E-06	0.175936307	0.976428347	2.248309355	24.798203
425	698.15	0.001432357	2.1231E-06	0.215120351	0.754644527	1.737633239	25.071644
420	693.15	0.001442689	1.7685E-06	0.179195094	0.667318501	1.536557633	23.793449
430	703.15	0.001422172	2.9040E-06	0.294244341	0.746673886	1.719280158	35.575725
430	703.15	0.001422172	2.9330E-06	0.297187104	0.531291881	1.223344764	29.156730
440	713.15	0.001402230	4.4071E-06	0.446546013	-0.52697004	1.213393358	32.034399
450	723.15	0.001382839	6.7866E-06	0.68765502	0.350133784	0.806212832	30.866666
460	733.15	0.001363977	8.4036E-06	0.851493032	0.162629382	0.374467991	36.541291
470	743.15	0.001345623	9.9396E-06	1.007126481	0.069818901	0.160763962	23.235709
Average MW (420-470 °C)							26.15
MW (Li ₃ N)							34.83

Note: The average molecular weight was calculated for the values determined from 420 to 470 °C.

Figure 4.49 Partial pressures of Li, Li₃N, and N₂

Vapor Pressure measurements of MgBH₄)₂ A pair of Knudsen Cells with opposed orifices are suspended by a Pt-10%Ni torsion wire with known stiffness. A mirror placed in this assembly that records the torque induced by vapors jetting out of the cell orifices. From the distances recorded from the mirror reflection of the meter scale, we can determine the angular displacement 'θ'

To determine total equilibrium pressure we use the following Eq.:

$$P_r = \frac{K(2\theta)}{(a_1 f_1 d_1) + (a_2 f_2 d_2)}$$

Molecular Weight Measurements of Vapors:

Measure the rate of weight loss using Cahn digital balance. The slope of the rate of weight loss curve as function of time give the molecular weight of the effusing species. Disproportionation equations (below) in the vapor phase can be determined equating the experimental M_{AVG} to the theoretical Mol. Wt. of the effusing gas species:

$$M_{AVG} = \frac{2\pi RT}{(2K)^2} \cdot \left(\frac{dw/dt}{\theta} \right)^2 \left[\frac{(a_1 f_1 d_1) + (a_2 f_2 d_2)}{(a_1 c_1) + (a_2 c_2)} \right]^2 = \sum_{i=1}^n [m_i M_i^{1/2}]^{-2}$$

The average molecular weight determined from our experiments is 2.42 g/mol. This implies that the vapor phase is predominantly hydrogen. The XRD pattern of the residual powder (dark brown) shows evidence of pure Magnesium. Although, we did not detect Boron, we suspect that it exists in amorphous phase. Assuming that a small amount of Mg(BH₄)₂ exists in the vapor just above the solid:

Equations for MW of individual vapor species and average molecular weight

$$m_{\text{H}_2} = \left[\frac{(4b)M_{\text{H}_2}^{1/2}}{(1-b)M_{\text{Mg}(\text{BH}_4)_2} + (4b)M_{\text{H}_2}} \right]^{-2} \quad m_{\text{Mg}(\text{BH}_4)_2} = \left[\frac{(1-b)M_{\text{Mg}(\text{BH}_4)_2}^{1/2}}{(1-b)M_{\text{Mg}(\text{BH}_4)_2} + (4b)M_{\text{H}_2}} \right]^{-2}$$

$$M_{\text{avg}} = \left[\frac{(1-b)M_{\text{Mg}(\text{BH}_4)_2}^{1/2} + (4b)M_{\text{H}_2}^{1/2}}{(1-b)M_{\text{Mg}(\text{BH}_4)_2} + (4b)M_{\text{H}_2}} \right]^{-2} \quad \boxed{b=0.982}$$

Partial Pressure

$$\frac{p_{\text{Mg}(\text{BH}_4)_2}}{p_{\text{TOTAL}}} = \left[\frac{(1-b)M_{\text{Mg}(\text{BH}_4)_2}^{1/2}}{(1-b)M_{\text{Mg}(\text{BH}_4)_2}^{1/2} + (4b)M_{\text{H}_2}^{1/2}} \right] = 0.023 \quad \frac{p_{\text{H}_2}}{p_{\text{TOTAL}}} = \left[\frac{(4b)M_{\text{H}_2}^{1/2}}{(1-b)M_{\text{Mg}(\text{BH}_4)_2}^{1/2} + (4b)M_{\text{H}_2}^{1/2}} \right] = 0.977$$

Complete disproportionation of $\text{Mg}(\text{BH}_4)_2$ cannot be ruled out as the measured molecular weight of the effusing species is within acceptable uncertainty.

The Figure 4.50 shows vapor pressures of $\text{Mg}(\text{BH}_4)_2$ and pure H_2 . Figure 4.51 shows the XRD pattern of the residue from the sample taken from the Knudsen cell after the experiment.

Figure 4.50. Vapor pressure plots of $\text{Mg}(\text{BH}_4)_2$ and decomposed Hydrogen.

Figure 4.51. XRD Pattern of Residual Powder After Vapor Pressure Measurements showing Pure Mg phase.

4.10 Mechanical Spectroscopy

Measurement of Elastic energy dissipation coefficient

In an effort to characterize the defect structure of the complex hydride precursors, we added impurities to Li_3N . 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} . A voltage is applied to the sample and then turned off, and we measure the logarithmic decrement of the vibration amplitude, through the width of the resonance curve shown in Figures 4.52 (a) and (b) (courtesy of Rosario Cantelli, and associates at Uni. of Rome):

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

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

Details can be found in the papers of O. Palumbo et al. [3] listed in this report. The Q^{-1} elastic energy coefficient is presented in Figure 4.53. It can be seen that a lot of scatter is observed in the data of $\text{Li}_3\text{N-Fe}$ (blue) as compared to the pure Li_3N (shown below in red). These experiments have to be repeated with a new sample.

Figure 4.52 a (left) shows the logarithmic damping of vibration that is measured by the width of the curve shown (Fig. b) right.

Figure 4.53 Comparison of vibrational spectra of Li_3N -Fe defect structure sample as compared to pure Li_3N sample; data taken at University of Rome.

V. Recommendations

The following are key recommendations:

- We have shown that we store reversibly up to ~10 wt.%H in the $\text{Li}_3\text{N-H}$ system using H_2/N_2 mixtures. Further studies should be performed in order to reduce the operating temperatures, and improve kinetics. This requires thermodynamic modeling and use of alloying elements with Li_3N to create defect structures.
- The kinetics are rather slow and decay occurs particularly after many cycles. So it is recommended appropriate catalysts be developed to improve kinetics.
- Oxygen and water in ppm levels were found to be detrimental to cycle life for the $\text{Li}_3\text{N-H}$ system; so it is recommended that appropriate gettering of gases be used maintain long term operability of the hydride beds.
- Nitrogen gas mixtures with hydrogen were found to be beneficial for the long-term cycle life. It is recommended that appropriate N_2/H_2 mixtures be used for the applications, and kinetics be evaluated.
- There are two cubic phases Li_2NH and $\text{Li}_{1.5}\text{NH}_{1.5}$ present in the system. We recommend further work be done on the non-stoichiometric phase $\text{Li}_{2-x}\text{NH}_{1+x}$.
- In conducting cycling experiments with mixtures of $\text{H}_2/100$ ppm NH_3 , we found that the exhaust gases damaged the turbo pump as well the mechanical pump seals. We lost two sets of vacuum systems during these experiments. It is recommend that special pumps, inert to NH_3 , be used or methods for aging the samples with these mixtures be developed.
- It is suggested that Pt cells not be used in measurement of vapor pressure of Li_3N and $\text{Li}_3\text{N-H}$ systems, as Pt forms eutectics with Li at relatively low temperatures. We found that Mo cells work better with $\text{Li}_3\text{N-H}$ system.

VI. Lessons Learned from the Center Approach

- This Center Approach seemed to work out well to facilitate collaborations and communications seamlessly between various diverse research groups.
- We felt that face-to-face meetings held at various laboratories were much better than the teleconferences that were occasionally held.
- It may be better to align the face-to-face meetings with some major Hydrogen meetings.

VII. Conclusions

- At the start of the program we found reversibility between $\text{Li}_2\text{NH}+\text{LiH} \rightleftharpoons \text{LiH}+\text{LiNH}_2$ (yielding ~5.8 wt.% H_{mb} capacity on a maximum basis (mb) or ~4.25 wt.% H_{pb} plateau basis(pb), as shown in Figure ES1. The Li_2NH did not revert back to Li_3N .
- Then we tested the effect of impurity in H_2 gas by pressure cycling at 255°C; first with industrial gas containing ppm levels of O_2 and H_2O as major impurities. Both these impurities had a significant impact on the reversibility and decreased the capacity by 2.65 wt.%H, (from ~4.25 to ~1.6 wt.% H_{pb}). Further increase in number of cycles from 500 to 1100 showed only a 0.2 wt%H more weight loss, showing some capacity is still maintained after a significant number of cycles.

The loss of capacity is attributed to the formation of ~55 wt% LiH and ~30% Li₂O, as major contaminant phases, along with the hydride Li₂NH phase; suggesting loss of nitrogen during cycling. The effect of 100 ppm H₂O in H₂ also showed a decrease of 2.5 wt.%H out of 4.5 wt.%H_{pb} (560 cycles), and 100ppm O₂ in H₂; a loss of 4.1 wt.% out of 4.25 wt.%H_{pb} was observed. Methane impurity (100 ppm, 100cycles), showed a very small capacity loss of 0.9 wt.% out of 4.5 wt.%H_{pb} under similar conditions.

- However, when Li₃N was pressure cycled with 100ppmN₂-H₂ there were beneficial effects were observed (255°C); the reversible capacity increased by 2.35 wt.%H reaching ~6.7wt.%H_{pb}(8.4wt.%H_{mb}) after 853 cycles. Furthermore, with 20 mol.%N₂-H₂ capacity increased by ~4.10wt.%H, to 8.4wt.%H_{pb}(~10 wt.%H_{mb}) after 516 cycles. We attribute this enhancement to the reaction of nitrogen with liquid lithium during cycling as the Gibbs free energy of formation of Li₃N ($\Delta G^\circ = -98.7$ kJ/mol) is more negative than that of LiH ($\Delta G^\circ = -50.3$ kJ/mol). We propose that the mitigation of hydrogen capacity losses is due to the destabilization of the LiH phase that tends to accumulate during cycling. Also more Li₂NH phase was found in the cycled product.
- Mixed Alanates (3LiNH₂:Li₃AlH₆) showed that 7 wt% hydrogen desorbed under dynamic vacuum. Equilibrium experiments (maximum 12 bar H₂) showed up to 4wt% hydrogen reversibly stored in the material after the first desorption. The activation energy was found to be 51 kJ/mol as compared to 81 kJ/mol for pure lithium alanate.
- It is proposed that based on the data obtained and CALPHAD modeling that the improvement in cycling is due to the formation of pure lithium (liquid at 255°C), which is able to react with nitrogen specifically forming Li₃N. The presence of nitrogen in the 80/20 molar mixtures in a hydride bed along with hydrogen causes Li to form Li₃N rather than LiH, and subsequently regenerates the Li₂NH phase and yields a ~10 wt.%H reversibly.

VIII. Appendix

VIIIA. Publications and Major Presentations

PUBLICATIONS (includes Peer Reviewed/Proceeding Articles)

1. J.-C. Crivello, M. Gupta, R. Černý, M. Latroche, and D. Chandra,” Density functional study of Li₄NH and Li_{1.5}NH_{1.5} as intermediary compounds during hydrogenation of Li₃N” PHYSICAL REVIEW B 81, 104113, 2010
2. Joshua Lamb, Dhanesh Chandra, Michael Coleman, Archana Sharma, William N. Cathey, Stephen N. Paglieri, Joseph R. Wermer, Robert C. Bowman Jr., Franklin E. Lynch,” Low and high-pressure hydriding of V–0.5at.%C” Journal of Nuclear Materials 399 (2010) 55–61.

3. A. Paolone, O. Palumbo, P. Rispoli, A. Miriametro, R. Cantelli, E. Rönnebro, D. Chandra, "Structural phase transitions and adduct release in calcium borohydride," *Journal of Alloys and Compounds*, MHCoe 2010, Moscow, Conf. Paper 2010, In print.
4. J. Zhang, R. Cerny, B. Villeroy, C. Godart, D. Chandra, M. Latroche. "Li_{3-x}M_xN (M = Co, Ni) synthesized by Spark Plasma Sintering for hydrogen storage," *Journal of Alloys and Compounds*, MHCoe 2010, Moscow, Conf. Paper 2010, DOI: doi:10.1016/j.jallcom.2010.09.160, In Print.
5. Y. Filinchuk, E. Ronnebro, D. Chandra, *Crystal Structures and Phase Transformations in Ca(BH₄)₂*, In Print, Acta Materialia, 57, 3, 2009, 732-738.
6. W. Chien, J. H. Lamb and D. Chandra "Phase Transformation and X-ray Diffraction Studies of Li-Based Complex Hydrides After Pressure Cycling," *Proceedings of Materials Science and Technology (MS&T) 2009*, P. 435-441.
7. D. Chandra, A. Sharma, R. Chellappa, W.N. Cathy, F.E. Lynch, R.C. Bowman Jr., J.R. Wermer, S.N. Paglieri, "Hydriding and structural characteristics of thermally cycled and cold work V-0.5at.% C alloy," *J. Alloys and Compounds*, V. 452, 312-324. (2008).
8. 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*, Volume **99**, May **2008**, Pages 487-490..
9. O. Palumbo, A. Paolone, R. Cantelli, and D. Chandra, "Lithium nitride as hydrogen storage material," *International Journal of Hydrogen Energy*, 33 (2008), pp.3107-3110.
10. R. Chellappa, D. Chandra, M. Somayazulu, S.A. Gramsch, R.J. Hemley, "Pressure-Induced Phase Transitions in LiNH₂," *J. Phys. Chem. B* 2007,111, 10785-10789.
11. A. Huq, J.W. Richardson Jr., E. Maxey, D. Chandra, W. Chien, "Structural Studies of Li₃N Using Neutron Powder Diffraction," *Journal of Alloys and Compounds*, 436, pp. 256-260 (2007).
12. A. Huq, J.W. Richardson Jr., E. Maxey, D. Chandra, W. Chien, "Structural Studies of Deuteration and Dedeuteration of Li₃N by Use of In Situ Neutron Diffraction," *Journal of Physical Chemistry C* 2007, 111 (28), pp. 10712-10717.
13. 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 (2007).
14. Wen-Ming Chien, Joshua Lamb, Dhanesh Chandra, Ashfia Huq, James Richardson Jr. and Evan Maxey, "Phase evolution of Li₂ND, LiD and LiND₂ in hydriding/dehydriding of Li₃N," *Journal of Alloys and Compounds*, Volumes 446-447, 31, Pages 363-367.
15. R. Chellappa, D. Chandra, S.A. Gramsch, R.J. Hemley, J-F. Lin, Y. Song, "Pressure Induced Phase Transformations in LiAlH₄," *J. Phys. Chem. B* 2006, 110, 11088-11097.
16. D. Chandra, J.J. Reilly, R. Chellappa, "Metal Hydrides for Vehicular Applications: The State of the Art," *Journal of Metals*, 58, (2006) 26-32.- A Review Paper.
17. R. Chellappa, D. Chandra, S.A. Gramsch, M. Somayazulu, R.J. Hemley, "Pressure-induced Transformations Li-based Complex Hydrides," *Proceedings of Materials Research at High Pressure Symposium, MRS Annual Meeting, 2006, Submission # 0987*.

18. "Overview of the Advanced Materials for Energy Conversion – III, Symposium in Honor of Drs. Gary Sandrock, Louis Schlapbach, and Seijirau Suda For Lifetime Achievements in Metal Hydride Research and Development, D. Chandra, J. Petrovic, R. Bautista, and A. Imam. "Advanced Materials for Energy Conversion III, Proceeding of the TMS Annual Symposium in San Antonio, TX, ISBN: 978-0-87339-610-3, TMS Press, 383pages, March, 2006; vol III, pp. 3.
19. W. Chien, J. Lamb and D. Chandra, "Structural Behavior and Pressure Cycling Effect Studies of Li-Based Complex Hydrides," TMS2007 Extraction, Processing, Structure and Properties Proceedings, General Abstracts: Structure Materials Division, pp 143-149, 2007
20. Wen-Ming Chien, Dhanesh Chandra, Ashfia Huq, James W. Richardson, Jr., Evan Maxey, Sirine Fakra and Martin Kunz, "Deuteriding and Low Temperature Structural Studies of Li-Based Complex Hydrides," Materials Science & Technology (MS&T) 2006: FUNDAMENTAL AND CHARACTERIZATION, Volume 1, 501-507, 2006.
21. D. Chandra, R.G. Bautista, and L. Schlapbach "Overview of Advanced Materials for Energy Conversion II" TMS Conference Proceedings, Edited by D. Chandra, R.G. Bautista, L. Schlapbach, (2004) pp7-13.

Major Reports:

Dhanesh Chandra, Joshua Lamb, Wen-Ming Chien, Klaus Yvon, Delphine Phanon, Radovan Cerny, and Nicolas Penin, "Effect of Gaseous Impurities on Long-Term Thermal Cycling and Aging Properties of Complex Hydrides for Hydrogen Storage, Final report to DOE Center of Excellence 9-15-10. (Five Major reports submitted for each year, and several quarterly reports)

Conferences and other Presentations:

1. Wen-Ming Chien, Joshua H. Lamb and Dhanesh Chandra, "Hydrogen Storage and Effects of Cycling On Li-Based Hydrides," T8011: Hydrogen Storage System Engineering and Applications, 2010 AIChE Annual Meeting, November 7-12, 2010, Salt Lake City, UT.
2. Wen-Ming Chien, Joshua H. Lamb, Narendra K. Pal and Dhanesh Chandra, "Pressure Cycling and Structural Behavior Studies on Hydrogen Storage Materials" 2010 NHA - Hydrogen Conference & Expo, May 3-6, 2010, Long Beach, CA, USA.
3. J. Zhang, R. Cerny, B. Villeroy, C. Godart, D.Chandra, M. Latroche. "Li₃-xM_xN (M = Co, Ni) synthesized by Spark Plasma Sintering for hydrogen storage," Journal of Alloys and Compounds, MH 2010, Moscow, Conf. Paper 2010. Paper given by Dr. Zhang.
4. Paolone, O. Palumbo, P. Rispoli, A. Miriametro, R. Cantelli, E. Rönnebro, D. Chandra, "Structural phase transitions and adduct release in calcium borohydride," Journal of Alloys and Compounds, MH 2010, Moscow, Paper given by Dr. Prof. Cantelli.
5. Wen-Ming Chien, Joshua H. Lamb, Narendra K. Pal, Dhanesh Chandra, "Effects of Cycling Hydrogen and Nitrogen Mixed Gases on Lithium Nitride Based Hydrogen Storage Materials" 2010 Denver X-ray Conference, August 2-8, 2010, Denver, CO, USA
6. Dhanesh Chandra, "Extrinsic Effects of Impurities on Long-Term Behavior of Complex Hydrides and Phase Equilibria Studies" International Energy association Meeting , International Energy Agency Task 22 – Workshop, IEA Task-22 Death Valley California April 11-15, 2010. – Topic No.1.
7. Dhanesh Chandra, J. Lamb, W-M Chien, N. Pal, K. Yvon, R. Cerny*, D. Phanon*, and N. Penin*J-C Crivello, M. Latroche."Effect of Trace Elements on Long-Term Cycling/Aging Properties and Thermodynamic Studies of Complex Hydrides for Hydrogen Storage"2010 U.S. Department of Energy Hydrogen Program Annual Merit Review and Peer Evaluation Meeting, Washington DC, May 30th 2010.

8. Wen-Ming Chien, Joshua H. Lamb, Narendra K. Pal, Dhanesh Chandra, "Effects of Cycling Hydrogen and Nitrogen Mixed Gases on Lithium Nitride Based Hydrogen Storage Materials" 2010 Denver X-ray Conference, August 2-8, 2010, Denver, CO, USA
9. Wen-Ming Chien, Joshua H. Lamb, Narendra K. Pal and Dhanesh Chandra, "Pressure Cycling and Structural Behavior Studies on Hydrogen Storage Materials" 2010 NHA - Hydrogen Conference & Expo, May 3-6, 2010, Long Beach, CA, USA
10. W. Chien, J. H. Lamb and D. Chandra, "Phase Transformation and X-ray Diffraction Studies of Li-Based Complex Hydrides After Pressure Cycling," Presentation at MS&T'09 Materials Science & Technology 2009 Conference, Pittsburgh, Pennsylvania, U.S.A, Oct. 25-29, 2009.
11. W. Chien, J. H. Lamb and D. Chandra, "X-RAY DIFFRACTION AND STRUCTURAL BEHAVIOR STUDIES OF Li-BASED HYDRIDES," Presentation at 58th Annual Denver X-ray Conference, Colorado Springs, Colorado, U.S.A, July 27-31, 2009.
12. W. Chien, J. H. Lamb and D. Chandra, "Effects of Impurity Gases and Pressure Cycling on Li-Based Complex Hydrides," Presentation at EIGHTEENTH International Symposium on "PROCESSING AND FABRICATION OF ADVANCED MATERIALS: XVIII", Sendai, Japan, December 12-14, 2009
13. D. Chandra and M. Latroche, "Extrinsic Effects of Impurities on Long-Term Behavior of Complex Hydrides and Phase Equilibria Studies International Energy Agency Task 22 – Workshop IEA Task-22 Jeju Island Meeting April, 16-18 2009" Organizers: B. Hauback (Norway), Young Whan Cho (Korea), Dhanesh Chandra University of Nevada, Reno, MS 388 Metallurgical and Materials Engineering 1664 N Virginia Street Reno, NV 89557-0136 Presented by Michel Latroche, Uni.of Paris/CNRS Paris.
14. 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.
15. D. Chandra, "Hydrogen Storage in Li-N Complex Hydrides," Invited Talk given at the University of Goettingen, Germany, Nov. 12, 2008.
16. Dhanesh Chandra "Effect of Trace Elements on Long-Term Cycling and Aging Properties of Complex Metal Hydrides Dhanesh Chandra, University of Nevada, Reno (UNR)" 2008 U.S. Department of Energy Hydrogen Program Annual Merit Review and Peer Evaluation Meeting Registration, Crystal Gateway Marriott, Arlington, VA. (presentation DOE on June 12, 2008).
17. 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
18. R. Cantelli, O. Palumbo, b, A. Paolonea, c, P. Rispolia and D. Chandra, "The Li-N-H system studied by anelastic spectroscopy and Thermogravimetry" June, 24^h. 2008, Poster session, Thermodynamics, phase diagrams session F5. 2, International Symposium on Metal-Hydrogen systems MH2008, Reykjavik, Iceland June 24-28, 2008.
19. E.D. Emmons, J.C. Fallas, V.K. Kamiseti, W. Chien, A.M. Covington, R.S. Chellappa, Stephan Gramsch, Russell Hemley, M. Somayazulu, M. Kunz, S. Clark, and D. Chandra, Carnegie Annual Review (SSAA) Program Symposium, "High Pressure Research on Complex Hydrides and Energy Storage Materials," Washington, DC, February 5-7, 2008.

20. W. Chien, D. Chandra, and J. Lamb and “Effect of Low Level Impurity Gases in Hydrogen on Li-based complex hydrides,” Poster Presentation at MH 2008, Metal Hydrides International Conference, No. 24, F2. Catalyses and reaction kinetics, Jan. 27th. 2008. International Symposium on Metal – Hydrogen systems MH2008, Reykjavik, Iceland June 24-28, 2008.
21. W. Chien, J. Lamb and D. Chandra, “Contamination Effect Studies in Li-Based Complex Hydrides,” Poster Presentation at Denver X-ray Conference, Colorado Springs, CO, July 31 – Aug. 4, 2007.
22. Dhanesh Chandra, “Extrinsic Effects of Impurities on Long-Term Behavior of Complex Hydrides” Session 5: H-18, Thursday, Sept. 6th 2007. Presented at the International Energy Agency Task 22 – Workshop Hosted by European Union, JRC-Institute, Petten September 3rd to 7th, 2007 Hotel Zuiderduin, Zeeweg 52, 1931 VL Egmond aan Zee, The Netherlands.
23. Dhanesh Chandra “Effect of Trace Elements on Long-Term Cycling and Aging Properties of Complex Hydrides for Hydrogen Storage” 2007 U.S. Department of Energy Hydrogen Program Annual Merit Review and Peer Evaluation Meeting Registration, Crystal Gateway Marriott, Arlington, VA. May 15-18, 2007 (presentation sent to DOE on April 22, 2007).
24. 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 Review Meeting, December 10 and 11th, 2007, Livermore CA.
25. W. Chien, J. Lamb and D. Chandra, “Structural Behavior and Pressure Cycling Effect Studies of Li-Based Complex Hydrides,” Presentation at TMS 2007 Annual Meeting & Exhibition, Orlando, Florida, USA, February 25-March 1, 2007.
26. W. Chien, J. Lamb and D. Chandra, “Contamination Effect Studies in Li-Based Complex Hydrides,” Presentation at Denver X-ray Conference, July 31 – Aug. 4, 2007, Colorado Springs, CO (poster).
27. W. Chien, J. Lamb and D. Chandra, “Structural Behavior and Pressure Cycling Effect Studies of Li-Based Complex Hydrides,” Presentation at TMS 2007 Annual Meeting & Exhibition, Orlando, Florida, USA, February 25-March 1, 2007.
28. D. Chandra, W. Chien, J. Lamb, “Extrinsic Effects of Impurities on Long-Term Behavior of Complex Hydrides,” International Energy Agency Task 22 - January 2007 Experts Meeting Hosted by Sandia National Laboratory, January 28 to Feb 1st, 2007, Monterey Plaza Hotel, Monterey California, Session F: H-18 Wednesday Jan. 31st. 2007.
29. D. Chandra, W. Chien, and J. Lamb: “Pressure Cycling Effect Studies of Li-Based Complex Hydrides,” Presentation at 2006 MRS Fall Meeting, Boston, MA, USA, November 27-December 1, 2006.
30. W. Chien, D. Chandra, A. Huq, J.W. Richardson, Jr., E. Maxey, S. Fakra, and M. Kunz, “Deuteriding and Low Temperature Structural Studies of Li-Based Complex Hydrides,” Materials Science and Technology (MS&T) 2006 Conference, Cincinnati, Ohio, USA, October 15-19, 2006.
31. W. Chien, D. Chandra, A. Huq, J.W. Richardson Jr., E. Maxey, M. Kunz, and S. Fakra, “Phase Evolution of Li_2ND , LiD and LiND_2 in Hydriding/Dehydriding of Li_3N ,” Presentation at MH2006 International Symposium on Metal-Hydrogen Systems: Fundamentals and Applications, Lahaina, Maui, Hawaii, U.S.A., October 1-6, 2006.
32. D. Chandra, W. Chien, R. Chellappa, J. Lamb, A. Oxner, “Trace Element Effects on Long-Term Cycling and Aging Properties of Complex Hydrides for Hydrogen Storage” Final Report to IEA to the Chief Operating Officer Task 17-2006, August 28th. 2006.

33. W. Chien, D. Chandra, A. Huq, J.W. Richardson Jr., E. Maxey, M. Kunz, and S. Fakra, "Neutron and Synchrotron Structure Evaluation of Li_3N during Hydriding and Dehydriding," 55th Annual Denver X-ray Conference, Denver, Colorado, U.S.A, August 7-11, 2006.
34. W. Chien, D. Chandra, A. Huq, J.W. Richardson, Jr., E. Maxey, S. Fakra, and M. Kunz, "Structural and Hydriding Behaviors Neutron Studies on Li-Based Hydrogen Storage Materials," 2006 American Conference on Neutron Scattering (ACNS), St. Charles, IL, USA, June 18-22, 2006.
35. Dhanesh Chandra, Wen-Ming Chien, Josh Lamb " Pressure Cycling Effect Studies of Li-Based Complex Hydrides" MRS Annual Meeting, November 27-December 1, 2006, Boston MA. (Abstract, pp.278).
36. Dhanesh Chandra, "Effect of Trace Elements on Long-Term Cycling of Complex Hydrides for Hydrogen Storage" IEA Meeting on Hydrogen Storage, Windermere (Birmingham, UK), May-2-6-2006.
37. Dhanesh Chandra, "Effect of Trace Elements on Long-Term Cycling and Aging Properties of Complex Hydrides for Hydrogen Storage," DOE 2006 Hydrogen Program Annual Review, Washington D.C. Crystal Gateway Marriot, Arlington, VA, May 16-19,2006.
38. W.-M. Chien, D. Chandra, A. Huq, J.W. Richardson, Jr., E. Maxey, M. Kunz, and S. Fakra, "Neutron and Synchrotron Studies on Li-Based Nitride and Hydride," Advanced Materials for Energy Conversion III, Proceeding of the TMS Annual Symposium in San Antonio, TX, ISBN: 978-0-87339-610-3, TMS Press, 383pages, March, 2006; Vol III, (Abstract, pp.311).
39. Wen-Ming Chien, Dhanesh Chandra, Ashfia Huq, James W. Richardson, Jr., Evan Maxey, Sirine Fakra, and Martin Kunz, "Structural and Hydriding Behaviors Neutron Studies on Li-Based Hydrogen Storage Materials," Poster Presentation, 2006 American Conference on Neutron Scattering - St. Charles, IL, June 18-22, 2006. (Abstract, pp. 88).
40. Wen-Ming Chien, Dhanesh Chandra, Joshua H. Lamb, Ashfia Huq, James W. Richardson, Jr., Evan Maxey, Martin Kunz and Sirine Fakra, "Neutron and Synchrotron Structure Evaluation of Li_3N During Hydriding and Dehydriding" Poster Presentation, 2006 Denver X-ray Conference - Denver, Colorado, August 7-11, 2006. (Abstract, pp. 5).
41. Wen-Ming Chien, Dhanesh Chandra, Ashfia Huq, James W. Richardson, Jr., Evan Maxey, Sirine Fakra and Martin Kunz, "Deuteriding and Low Temperature Structural Studies of Li-Based Complex Hydrides" Poster Presentation, Materials Science &Technology 2006 Conference and Exhibition – October 15-19, 2006 – Duke Energy Center – Cincinnati, OH, USA. (Abstract, pp. 39).
42. W.M.Chien, D.Chandra, A. Huq, J. Richardson,Jr, E. Maxey, M. Kunz, S. Fakra, "Phase Evolution of Li_2ND LiD and LiND_2 in Hydriding/Dehydriding of Li_3N ," MH2006-International Symposium on Metal-Hydrogen Systems-Fundamentals and Applications, Lahaina, Maui, Hawaii, October 1-6, 2006. Paper#373. (Abstract, pp.97).

VIIIB. References

1. USDOE. Hydrogen, Fuel Cells and Infrastructure Tehcnologies Program. [cited; Available from: <http://www1.eere.energy.gov/hydrogenandfuelcells/>].

2. Ross, D.K., Hydrogen Storage: The Major Technological Barrier to the Development. Of Hydrogen Fuel Cell Cars. Vacuum, 2006. **80**(10): p. 1084-1089.
3. Pinkerton, F.E. and B.G. Wicke, Bottling the Hydrogen Genie. Industrial Physicist, 2004. **10**(1): p. 22-25.
4. BMW. Bmw World - Bmw 750 Hl. [cited; Available from: <http://www.bmwworld.com/models/750hl.htm>.
5. Bossel, U., B. Eliason, and G. Taylor. The Future of the Hydrogen Economy, Bright or Bleak? 2003 [cited; Available from: <http://www.evworld.com/library/h2economyFinalReport.pdf>.
6. Buschow, K.H.J. and A.R. Miedema, in Hydrides for Energy Storage, A.F. Andreasen and A.J. Maeland, Editors. 1978, Pergamon: Oxford.
7. Bogdanovic, B., U. Eberle, M. Felderhoff, and F. Schuth, Complex Aluminum Hydrides. Scripta Materialia, 2007. **56**(10): p. 813-816.
8. Bogdanovic, B. and M. Schwickardi, Ti-Doped Alkali Metal Aluminium Hydrides as Potential Novel Reversible Hydrogen Storage Materials. Journal of Alloys and Compounds, 1997. **253**: p. 1-9.
9. Bogdanovic, B. and M. Schwickardi, Ti-Doped NaAlH₄ as a Hydrogen-Storage Material - Preparation by Ti-Catalyzed Hydrogenation of Aluminum Powder in Conjunction with Sodium Hydride. Applied Physics a-Materials Science & Processing, 2001. **72**(2): p. 221-223.
10. Balema, V.P. and L. Balema, Missing Pieces of the Puzzle or About Some Unresolved Issues in Solid State Chemistry of Alkali Metal Aluminohydrides. Physical Chemistry Chemical Physics, 2005. **7**(6): p. 1310-1314.
11. Balogh, M.P., G.G. Tibbetts, F.E. Pinkerton, G.P. Meisner, and C.H. Olk, Phase Changes and Hydrogen Release During Decomposition of Sodium Alanates. Journal of Alloys and Compounds, 2003. **350**(1-2): p. 136-144.
12. Blanchard, D., H.W. Brinks, B.C. Hauback, and P. Norby, Desorption of LiAlH₄ with Ti- and V-Based Additives. Materials Science and Engineering B, 2004. **108**(1-2): p. 54-59.
13. Blanchard, D., H.W. Brinks, B.C. Hauback, P. Norby, and J. Muller, Isothermal Decomposition of LiAlH₄ with and without Additives. Journal of Alloys and Compounds, 2005. **404-406**: p. 743-747.
14. Bogdanovic, B., M. Felderhoff, S. Kaskel, A. Pommerin, K. Schlichte, and F. Schuth, Improved Hydrogen Storage Properties of Ti-Doped Sodium Alanate Using Titanium Nanoparticles as Doping Agents. Advanced Materials, 2003. **15**(12): p. 1012-+.
15. Brinks, H.W., B.C. Hauback, C.M. Jensen, and R. Zidan, Synthesis and Crystal Structure of Na₂LiAlD₆. Journal of Alloys and Compounds, 2005. **392**(1-2): p. 27-30.
16. Brinks, H.W., C.M. Jensen, S.S. Srinivasan, B.C. Hauback, D. Blanchard, and K. Murphy, Synchrotron X-Ray and Neutron Diffraction Studies of NaAlH₄ Containing Ti Additives. Journal of Alloys and Compounds, 2004. **376**(1-2): p. 215-221.
17. Gross, K.J., S. Guthrie, S. Takara, and G. Thomas, In-Situ X-Ray Diffraction Study of the Decomposition of NaAlH₄. Journal of Alloys and Compounds, 2000. **297**(1-2): p. 270-281.

18. Gross, K.J., G. Sandrock, and G.J. Thomas, Dynamic in Situ X-Ray Diffraction of Catalyzed Alanates. *Journal of Alloys and Compounds*, 2002. **330-332**: p. 691-695.
19. Gross, K.J., G.J. Thomas, and C.M. Jensen, Catalyzed Alanates for Hydrogen Storage. *Journal of Alloys and Compounds*, 2002. **330-332**: p. 683-690.
20. Hou, Z.F., First-Principles Investigation of $\text{Mg}(\text{AlH}_4)_2$ Complex Hydride. *Journal of Power Sources*, 2006. **159**(1): p. 111-115.
21. Hu, Y.H. and E. Ruckenstein, Hydrogen Storage of Li_2NH Prepared by Reacting Li with NH_3 . *Industrial & Engineering Chemistry Research*, 2006. **45**(1): p. 182-186.
22. Ichikawa, T., N. Hanada, S. Isobe, H.Y. Leng, and H. Fujii, Mechanism of Novel Reaction from LiNH_2 and LiH to Li_2NH and H_2 as a Promising Hydrogen Storage System. *Journal of Physical Chemistry B*, 2004. **108**(23): p. 7887-7892.
23. Kircher, O. and A. Fichtner, Kinetic Studies of the Decomposition of NaAlH_4 Doped with a Ti-Based Catalyst. *Journal of Alloys and Compounds*, 2005. **404**: p. 339-342.
24. Kiyobayashi, T., S.S. Srinivasan, D. Sun, and C.M. Jensen, Kinetic Study and Determination of the Enthalpies of Activation of the Dehydrogenation of Titanium- and Zirconium-Doped NaAlH_4 and Na_3AlH_6 . *Journal of Physical Chemistry A*, 2003. **107**(39): p. 7671-7674.
25. Kumar, R.S., E. Kim, O. Tschauner, A.L. Cornelius, M.P. Sulic, and C.M. Jensen, Pressure-Induced Structural Phase Transition in NaAlH_4 . *Physical Review B*, 2007. **75**(17): p. 7.
26. Lu, J. and Z.G.Z. Fang, Dehydrogenation of a Combined $\text{LiAlH}_4/\text{LiNH}_2$ System. *Journal of Physical Chemistry B*, 2005. **109**(44): p. 20830-20834.
27. Luo, W. and K.J. Gross, A Kinetics Model of Hydrogen Absorption and Desorption in Ti-Doped NaAlH_4 . *Journal of Alloys and Compounds*, 2004. **385**(1-2): p. 224-231.
28. Luo, W. and E. Ronnebro, Towards a Viable Hydrogen Storage System for Transportation Application. *Journal of Alloys and Compounds*, 2005. **404**: p. 392-395.
29. Luo, W.F. and S. Sickafoose, Thermodynamic and Structural Characterization of the Mg-Li-N-H Hydrogen Storage System. *Journal of Alloys and Compounds*, 2006. **407**(1-2): p. 274-281.
30. Meisner, G.P., F.E. Pinkerton, M.S. Meyer, M.P. Balogh, and M.D. Kundrat, Study of the Lithium-Nitrogen-Hydrogen System. *Journal of Alloys and Compounds*, 2005. **404**: p. 24-26.
31. Meisner, G.P., M.L. Scullin, M.P. Balogh, F.E. Pinkerton, and M.S. Meyer, Hydrogen Release from Mixtures of Lithium Borohydride and Lithium Amide: A Phase Diagram Study. *Journal of Physical Chemistry B*, 2006. **110**(9): p. 4186-4192.
32. Meisner, G.P., G.G. Tibbetts, F.E. Pinkerton, C.H. Olk, and M.P. Balogh, Enhancing Low Pressure Hydrogen Storage in Sodium Alanates. *Journal of Alloys and Compounds*, 2002. **337**: p. 254-263.

33. Nakamori, Y., G. Kitahara, and S. Orimo, Synthesis and Dehydrogenating Studies of Mg-N-H Systems. *Journal of Power Sources*, 2004. **138**(1-2): p. 309-312.
34. Nakamori, Y. and S. Orimo, Destabilization of Li-Based Complex Hydrides. *Journal of Alloys and Compounds*, 2004. **370**(1-2): p. 271-275.
35. Opalka, S.M., O.M. Lovvik, H.W. Brinks, P.W. Saxe, and B.C. Hauback, Integrated Experimental-Theoretical Investigation of the Na-Li-Al-H System. *Inorganic Chemistry*, 2007. **46**(4): p. 1401-1409.
36. Pinkerton, F.E., G.P. Meisner, M.S. Meyer, M.P. Balogh, and M.D. Kundrat, Hydrogen Desorption Exceeding Ten Weight Percent from the New Quaternary Hydride $\text{Li}_3\text{Bn}_2\text{H}_8$. *Journal of Physical Chemistry B*, 2005. **109**(1): p. 6-8.
37. Pinkerton, F.E., M.S. Meyer, G.P. Meisner, and M.P. Balogh, Improved Hydrogen Release from $\text{LiB}_{0.33}\text{N}_{0.67}\text{H}_{2.67}$ with Noble Metal Additions. *Journal of Physical Chemistry B*, 2006. **110**(15): p. 7967-7974.
38. Resan, M., M.D. Hampton, J.K. Lomness, and D.K. Slattey, Effect of Tixaly Catalysts on Hydrogen Storage Properties of LiAlH_4 and NaAlH_4 . *International Journal of Hydrogen Energy*, 2005. **30**(13-14): p. 1417-1421.
39. Sandrock, G., K. Gross, and G. Thomas, Effect of Ti-Catalyst Content on the Reversible Hydrogen Storage Properties of the Sodium Alanes. *Journal of Alloys and Compounds*, 2002. **339**(1-2): p. 299-308.
40. Sandrock, G., K. Gross, G. Thomas, C. Jensen, D. Meeker, and S. Takara, Engineering Considerations in the Use of Catalyzed Sodium Alanes for Hydrogen Storage. *Journal of Alloys and Compounds*, 2002. **330**: p. 696-701.
41. Seayad, A.M. and D.M. Antonelli, Recent Advances in Hydrogen Storage in Metal-Containing Inorganic Nanostructures and Related Materials. *Advanced Materials*, 2004. **16**(9-10): p. 765-777.
42. Sun, D.L., S.S. Srinivasan, T. Kiyobayashi, N. Kuriyama, and C.M. Jensen, Rehydrogenation of Dehydrogenated NaAlH_4 at Low Temperature and Pressure 10.1021/jp030637f. *Journal of Physical Chemistry B*, 2003. **107**(37): p. 10176-10179.
43. Thomas, G.J., K.J. Gross, N.Y.C. Yang, and C. Jensen, Microstructural Characterization of Catalyzed NaAlH_4 . *Journal of Alloys and Compounds*, 2002. **330**: p. 702-707.
44. Voss, J., Q. Shi, H.S. Jacobsen, M. Zamponi, K. Lefmann, and T. Vegge, Hydrogen Dynamics in Na_3AlH_6 : A Combined Density Functional Theory and Quasielastic Neutron Scattering Study. *Journal of Physical Chemistry B*, 2007. **111**(15): p. 3886-3892.
45. Walters, R.T. and J.H. Scogin, A General Initial Decomposition Reaction for Complex Metal Hydrides. *Journal of Alloys and Compounds*, 2006. **421**(1-2): p. 54-56.
46. Wang, J., A.D. Ebner, and J.A. Ritter, On the Reversibility of Hydrogen Storage in Novel Complex Hydrides. *Adsorption-Journal of the International Adsorption Society*, 2005. **11**: p. 811-816.
47. Xiao, X.Z., L.X. Chen, X.H. Wang, S.Q. Li, and C.P. Chen, Preparation and Hydrogen Storage Characteristics of Ti-NaAlH_4 Complex Hydride. *Acta Physico-Chimica Sinica*, 2006. **22**(12): p. 1511-1515.

48. Zaluska, A. and L. Zaluski, New Catalytic Complexes for Metal Hydride Systems. *Journal of Alloys and Compounds*, 2005. **404**: p. 706-711.
49. Zaluska, A., L. Zaluski, and J.O. Strom-Olsen, Sodium Alanates for Reversible Hydrogen Storage. *Journal of Alloys and Compounds*, 2000. **298**(1-2): p. 125-134.
50. Zhang, S., A. Taniguchi, Q. Xu, N. Takeichi, H.T. Takeshita, N. Kuriyama, and T. Kiyobayashi, Understanding the Effect of Titanium Species on the Decomposition of Alanates in Homogeneous Solution. *Journal of Alloys and Compounds*, 2006. **413**(1-2): p. 218-221.
51. Zhou, L., Progress and Problems in Hydrogen Storage Methods. *Renewable & Sustainable Energy Reviews*, 2005. **9**(4): p. 395-408.
52. Barkhordarian, G., T. Klassen, M. Dornheim, and R. Bormann, Unexpected Kinetic Effect of MgB₂ in Reactive Hydride Composites Containing Complex Borohydrides. *Journal of Alloys and Compounds*, 2007. **440**(1-2): p. L18-L21.
53. Kojima, Y., Y. Kawai, and N. Ohba, Hydrogen Storage of Metal Nitrides by a Mechanochemical Reaction. *Journal of Power Sources*, 2006. **159**(1): p. 81-87.
54. Kojima, Y., M. Matsumoto, Y. Kawai, T. Haga, N. Ohba, K. Miwa, S.I. Towata, Y. Nakamori, and S. Orimo, Hydrogen Absorption and Desorption by the Li-Al-N-H System. *Journal of Physical Chemistry B*, 2006. **110**(19): p. 9632-9636.
55. Nakamori, Y., A. Ninomiya, G. Kitahara, M. Aoki, T. Noritake, K. Miwa, Y. Kojima, and S. Orimo, Dehydriding Reactions of Mixed Complex Hydrides. *Journal of Power Sources*, 2006. **155**(2): p. 447-455.
56. Zuttel, A., A. Borgschulte, and S.I. Orimo, Tetrahydroborates as New Hydrogen Storage Materials. *Scripta Materialia*, 2007. **56**(10): p. 823-828.
57. Chen, P., Z.T. Xiong, J.Z. Luo, J.Y. Lin, and K.L. Tan, Interaction of Hydrogen with Metal Nitrides and Imides. *Nature*, 2002. **420**(6913): p. 302-304.
58. Aoki, M., T. Noritake, G. Kitahara, Y. Nakamori, S. Towata, and S. Orimo, Dehydriding Reaction of Mg(NH₂)₂-LiH System under Hydrogen Pressure. *Journal of Alloys and Compounds*, 2007. **428**(1-2): p. 307-311.
59. Bohger, J.P.O., R.R. Essmann, and H. Jacobs, Infrared and Raman Studies on the Internal-Modes of Lithium Amide. *Journal of Molecular Structure*, 1995. **348**: p. 325-328.
60. Chen, P., Z.T. Xiong, J.Z. Luo, J.Y. Lin, and K.L. Tan, Interaction between Lithium Amide and Lithium Hydride. *Journal of Physical Chemistry B*, 2003. **107**(39): p. 10967-10970.
61. Chen, P., Z.T. Xiong, G.T. Wu, Y.F. Liu, J.J. Hu, and W.F. Luo, Metal-N-H Systems for the Hydrogen Storage. *Scripta Materialia*, 2007. **56**(10): p. 817-822.
62. Chen, P., Z.T. Xiong, L.F. Yang, G.T. Wu, and W.F. Luo, Mechanistic Investigations on the Heterogeneous Solid-State Reaction of Magnesium Amides and Lithium Hydrides. *Journal of Physical Chemistry B*, 2006. **110**(29): p. 14221-14225.
63. David, W.I.F., M.O. Jones, D.H. Gregory, C.M. Jewell, S.R. Johnson, A. Walton, and P.P. Edwards, A Mechanism for Non-Stoichiometry in the Lithium Amide/Lithium Imide Hydrogen Storage Reaction. *Journal of the American Chemical Society*, 2007. **129**(6): p. 1594-1601.

64. Hino, S., T. Ichikawa, H.Y. Leng, and H. Fujii, Hydrogen Desorption Properties of the Ca-N-H System. *Journal of Alloys and Compounds*, 2005. **398**(1-2): p. 62-66.
65. Hu, J.J., G.T. Wu, Y.F. Liu, Z.T. Xiong, P. Chen, K. Murata, K. Sakata, and G. Wolf, Hydrogen Release from $\text{Mg}(\text{NH}_2)_2\text{-MgH}_2$ through Mechanochemical Reaction. *Journal of Physical Chemistry B*, 2006. **110**(30): p. 14688-14692.
66. Ichikawa, T., N. Hanada, S. Isobe, H.Y. Leng, and H. Fujii, Hydrogen Storage Properties in Ti Catalyzed Li-N-H System. *Journal of Alloys and Compounds*, 2005. **404-406**: p. 435-438.
67. Ichikawa, T., S. Isobe, N. Hanada, and H. Fujii, Lithium Nitride for Reversible Hydrogen Storage. *Journal of Alloys and Compounds*, 2004. **365**(1-2): p. 271-276.
68. Ichikawa, T., H.Y. Leng, S. Isobe, N. Hanada, and H. Fujii, Recent Development on Hydrogen Storage Properties in Metal-N-H Systems. *Journal of Power Sources*, 2006. **159**(1): p. 126-131.
69. Janot, R., J.B. Eymery, and J.M. Tarascon, Investigation of the Processes for Reversible Hydrogen Storage in the Li-Mg-N-H System. *Journal of Power Sources*, 2007. **164**(2): p. 496-502.
70. Jin, H.M., J.Z. Luo, and P. Wu, Adsorption and Dissociation of Hydrogen on Li_3N Surface: A First Principles Study. *Applied Physics Letters*, 2007. **90**(8): p. 3.
71. Juza, R. and K. Opp, Metallamide Und Metallnitride .25. Zur Kenntnis Des Lithiumimides. *ZEITSCHRIFT FUR ANORGANISCHE UND ALLGEMEINE CHEMIE*, 1951. **266**: p. 325.
72. Leng, H.Y., T. Ichikawa, S. Hino, N. Hanada, S. Isobe, and H. Fujii, Synthesis and Decomposition Reactions of Metal Amides in Metal-N-H Hydrogen Storage System. *Journal of Power Sources*, 2006. **156**(2): p. 166-170.
73. Leng, H.Y., T. Ichikawa, S. Isobe, S. Hino, N. Hanada, and H. Fujii, Desorption Behaviours from Metal-N-H Systems Synthesized by Ball Milling. *Journal of Alloys and Compounds*, 2005. **404**: p. 443-447.
74. Lu, J., Z.Z.G. Fang, Y.J. Choi, and H.Y. Sohn, Potential of Binary Lithium Magnesium Nitride for Hydrogen Storage Applications. *Journal of Physical Chemistry C*, 2007. **111**(32): p. 12129-12134.
75. Matsumoto, M., T. Haga, Y. Kawai, and Y. Kojima, Hydrogen Desorption Reactions of Li-N-H Hydrogen Storage System: Estimation of Activation Free Energy. *Journal of Alloys and Compounds*, 2007. **439**(1-2): p. 358-362.
76. Miwa, K., N. Ohba, S.-i. Towata, Y. Nakamori, and S.-i. Orimo, First-Principles Study on Lithium Amide for Hydrogen Storage. *Physical Review B (Condensed Matter and Materials Physics)*, 2005. **71**(19): p. 195109-6.
77. Nakamori, Y., G. Kitahara, K. Miwa, N. Ohba, T. Noritake, S. Towata, and S. Orimo, Hydrogen Storage Properties of Li-Mg-N-H Systems. *Journal of Alloys and Compounds*, 2005. **404**: p. 396-398.
78. Nakamori, Y., G. Kitahara, A. Ninomiya, M. Aoki, T. Noritake, S. Towata, and S. Orimo, Guidelines for Developing Amide-Based Hydrogen Storage Materials. *Materials Transactions*, 2005. **46**(9): p. 2093-2097.
79. Noritake, T., H. Nozaki, M. Aoki, S. Towata, G. Kitahara, Y. Nakamori, and S. Orimo, Crystal Structure and Charge Density Analysis of Li_2NH by Synchrotron

- X-Ray Diffraction. *Journal of Alloys and Compounds*, 2005. **393**(1-2): p. 264-268.
80. Ohoyama, K., Y. Nakamori, S. Orimo, and K. Yamada, Revised Crystal Structure Model of Li_2NH by Neutron Powder Diffraction. *Journal of the Physical Society of Japan*, 2005. **74**(1): p. 483-487.
 81. Orimo, S., Y. Nakamori, G. Kitahara, K. Miwa, N. Ohba, T. Noritake, and S. Towata, Destabilization and Enhanced Dehydrogenation Reaction of LiNH_2 : An Electronic Structure Viewpoint. *Applied Physics a-Materials Science & Processing*, 2004. **79**(7): p. 1765-1767.
 82. Pinkerton, F.E., Decomposition Kinetics of Lithium Amide for Hydrogen Storage Materials. *Journal of Alloys and Compounds*, 2005. **400**(1-2): p. 76-82.
 83. Song, Y. and Z.X. Guo, Electronic Structure, Stability and Bonding of the Li-N-H Hydrogen Storage System. *Physical Review B (Condensed Matter and Materials Physics)*, 2006. **74**(19): p. 195120-7.
 84. Wu, G.T., Z.T. Xiong, T. Liu, Y.F. Liu, J.J. Hu, P. Chen, Y.P. Feng, and A.T.S. Wee, Synthesis and Characterization of a New Ternary Imide- $\text{Li}_2\text{Ca}(\text{NH})_2$. *Inorganic Chemistry*, 2007. **46**(2): p. 517-521.
 85. Wurthwein, E.U., K.D. Sen, J.A. Pople, and P.V. Schleyer, Lithiated Ammonia, Amide Anions, and Ammonium-Ions - an Abinitio Study of Structures, Bonding, and Energetic Relationships. *Inorganic Chemistry*, 1983. **22**(3): p. 496-503.
 86. Xiong, Z.T., G.T. Wu, H.J. Hu, and P. Chen, Ternary Imides for Hydrogen Storage. *Advanced Materials*, 2004. **16**(17): p. 1522-+.
 87. Yamane, H., T. Kano, A. Kamegawa, M. Shibata, T. Yamada, M. Okada, and M. Shimada, Reactivity of Hydrogen and Ternary Nitrides Containing Lithium and 13 Group Elements. *Journal of Alloys and Compounds*, 2005. **402**(1-2): p. L1-L3.
 88. Yang, J., A. Sudik, and C. Wolverton, Activation of Hydrogen Storage Materials in the Li-Mg-N-H System: Effect on Storage Properties. *Journal of Alloys and Compounds*, 2007. **430**(1-2): p. 334-338.
 89. Yao, J.H., C. Shang, K.F. Aguey-Zinsou, and Z.X. Guo, Desorption Characteristics of Mechanically and Chemically Modified LiNH_2 and $(\text{LiNH}_2 + \text{LiH})$. *Journal of Alloys and Compounds*, 2007. **432**(1-2): p. 277-282.
 90. Bogdanovic, B., K. Bohmhammel, B. Christ, A. Reiser, K. Schlichte, R. Vehlen, and U. Wolf, Thermodynamic Investigation of the Magnesium-Hydrogen System. *Journal of Alloys and Compounds*, 1999. **282**(1-2): p. 84-92.
 91. Bogdanovic, B., A. Reiser, K. Schlichte, B. Spliethoff, and B. Tesche, Thermodynamics and Dynamics of the Mg-Fe-H System and Its Potential for Thermochemical Thermal Energy Storage. *Journal of Alloys and Compounds*, 2002. **345**(1-2): p. 77-89.
 92. Dehouche, Z., J. Goyette, T.K. Bose, and R. Schulz, Moisture Effect on Hydrogen Storage Properties of Nanostructured MgH_2 -V-Ti Composite. *International Journal of Hydrogen Energy*, 2003. **28**(9): p. 983-988.
 93. Jensen, T.R., A. Andreasen, T. Vegge, J.W. Andreasen, K. Stahl, A.S. Pedersen, M.M. Nielsen, A.M. Molenbroek, and B. Flemming, Dehydrogenation Kinetics of Pure and Nickel-Doped Magnesium Hydride Investigated by in Situ Time-Resolved Powder X-Ray Diffraction. *International Journal of Hydrogen Energy*, 2006. **31**(14): p. 2052-2062.

94. Liang, G., J. Huot, S. Boily, A. Van Neste, and R. Schulz, Catalytic Effect of Transition Metals on Hydrogen Sorption in Nanocrystalline Ball Milled MgH₂-Tm (Tm=Ti, V, Mn, Fe and Ni) Systems. *Journal of Alloys and Compounds*, 1999. **292**(1-2): p. 247-252.
95. Oelerich, W., T. Klassen, and R. Bormann, Metal Oxides as Catalysts for Improved Hydrogen Sorption in Nanocrystalline Mg-Based Materials. *Journal of Alloys and Compounds*, 2001. **315**(1-2): p. 237-242.
96. Zaluska, A., L. Zaluski, and J.O. Strom-Olsen, Synergy of Hydrogen Sorption in Ball-Milled Hydrides of Mg and Mg₂Ni. *Journal of Alloys and Compounds*, 1999. **289**(1-2): p. 197-206.
97. Aiello, R., J.H. Sharp, and M.A. Matthews, Production of Hydrogen from Chemical Hydrides Via Hydrolysis with Steam. *International Journal of Hydrogen Energy*, 1999. **24**(12): p. 1123-1130.
98. Schlesinger, H.I., H.C. Brown, A.E. Finholt, I.R. Gilbreath, H.R. Hoekstra, and E.K. Hyde, Sodium Borohydride Its Hydrolysis and Its Use as a Reducing Agent and in the Generation of Hydrogen. *Journal of the American Chemical Society*, 1953. **75**: p. 215-219.
99. Amendola, S.C., S.L. Sharp-Goldman, M.S. Janjua, M.T. Kelly, P.J. Petillo, and M. Binder, An Ultrasafe Hydrogen Generator: Aqueous, Alkaline Borohydride Solutions and Ru Catalyst. *Journal of Power Sources*, 2000. **85**(2): p. 186-189.
100. Pinto, A.M.F.R., D.S. Falcao, R.A. Silva, and C.M. Rangel, Hydrogen Generation and Storage from Hydrolysis of Sodium Borohydride in Batch Reactors. *International Journal of Hydrogen Energy*, 2006. **31**(10): p. 1341-1347.
101. Amendola, S.C., S.L. Sharp-Goldman, M.S. Janjua, N.C. Spencer, M.T. Kelly, P.J. Petillo, and M. Binder, A Safe, Portable, Hydrogen Gas Generator Using Aqueous Borohydride Solution and Ru Catalyst. *International Journal of Hydrogen Energy*, 2000. **25**(10): p. 969-975.
102. Kojima, Y., K.-i. Suzuki, K. Fukumoto, Y. Kawai, M. Kimbara, H. Nakanishi, and S. Matsumoto, Development of 10 Kw-Scale Hydrogen Generator Using Chemical Hydride. *Journal of Power Sources*, 2004. **125**(1): p. 22-26.
103. Drozd, V., S. Saxena, S.V. Garimella, and A. Durygin, Hydrogen Release from a Mixture of NaBH₄ and Mg(OH)₂. *International Journal of Hydrogen Energy*, 2007. **32**(15): p. 3370-3375.
104. Xu, D.Y., H.M. Zhang, and W. Ye, Hydrogen Production from Sodium Borohydride. *Progress in Chemistry*, 2007. **19**(10): p. 1598-1605.
105. Ma, J.F., J. Wang, and Y.N. Liu, Iron Phthalocyanine as a Cathode Catalyst for a Direct Borohydride Fuel Cell. *Journal of Power Sources*, 2007. **172**(1): p. 220-224.
106. Ersoz, Y., R. Yidirim, and A.N. Akin, Development of an Active Platine-Based Catalyst for the Reaction of H₂ Production from NaBH₄. *Chemical Engineering Journal*, 2007. **134**(1-3): p. 282-287.
107. Hua, D., Y. Hanxi, A. Xinping, and C. Chuansin, Hydrogen Production from Catalytic Hydrolysis of Sodium Borohydride Solution Using Nickel Boride Catalyst. *International Journal of Hydrogen Energy*, 2003. **28**(10): p. 1095-1100.
108. Chandra, D., J.J. Reilly, and R. Chellappa, Metal Hydrides for Vehicular Applications: The State of the Art. *JOM*, 2006. **58**(2).

109. Rabenau, A. and H. Schulz, Re-Evaluation of the Lithium Nitride Structure. *Journal of the Less Common Metals*, 1976. **50**(1): p. 155-159.
110. Schulz, H. and K.H. Thiemann, Defect Structure of the Ionic Conductor Lithium Nitride (Li_3N). *Acta Crystallographica Section A*, 1979. **35**(2): p. 309-314.
111. Balogh, M.P., C.Y. Jones, J.F. Herbst, L.G. Hector, and M. Kundrat, Crystal Structures and Phase Transformation of Deuterated Lithium Imide, Li_2Nd . *Journal of Alloys and Compounds*, 2006. **420**(1-2): p. 326-336.
112. Hu, Y.H. and E. Ruckenstein, Ultrafast Reaction between LiH and NH_3 During H_2 Storage in Li_3N . *Journal of Physical Chemistry A*, 2003. **107**(46): p. 9737-9739.
113. Isobe, S., T. Ichikawa, S. Hino, and H. Fujii, Hydrogen Desorption Mechanism in a Li-N-H System by Means of the Isotopic Exchange Technique. *J. Phys. Chem. B*, 2005. **109**(31): p. 14855-14858.
114. Weidner, E., D.J. Bull, I.L. Shabalin, S.G. Keens, M.T.F. Telling, and D.K. Ross, Observation of Novel Phases During Deuteration of Lithium Nitride from in Situ Neutron Diffraction. *Chemical Physics Letters*, 2007. **444**(1-3): p. 76-79.
115. Marx, R., Preparation and Crystal Structure of Lithium Nitride Hydride, Li_4NH , Li_4Nd . *Zeitschrift Fur Anorganische Und Allgemeine Chemie*, 1997. **623**(12): p. 1912-1916.
116. Crivello, J.-C., M. Gupta, R. Cerny, M. Latroche, and D. Chandra, Density Functional Study of Li_4NH and $\text{Li}_{1.5}\text{NH}_{1.5}$ as Intermediary Compounds During Hydrogenation of Li_3N . *Physical Review B*, 2010. **81**: p. 104113.
117. Pinkerton, F.E., M.S. Meyer, G.P. Meisner, and M.P. Balogh, Improved Hydrogen Release from $\text{Li}_{0.33}\text{N}_{0.67}\text{H}_{2.67}$ with Metal Additives: Ni, Fe, and Zn. *Journal of Alloys and Compounds*, 2007. **433**(1-2): p. 282-291.
118. Bogdanovic, B., R.A. Brand, A. Marjanovic, M. Schwickardi, and J. Tolle, Metal-Doped Sodium Aluminium Hydrides as Potential New Hydrogen Storage Materials. *Journal of Alloys and Compounds*, 2000. **302**(1-2): p. 36-58.
119. Jensen, C.M., R. Zidan, N. Mariels, A. Hee, and C. Hagen, Advanced Titanium Doping of Sodium Aluminum Hydride: Segue to a Practical Hydrogen Storage Material? *International Journal of Hydrogen Energy*, 1999. **24**(5): p. 461-465.
120. Zaluski, L., A. Zaluska, and J.O. Strom-Olsen, Hydrogenation Properties of Complex Alkali Metal Hydrides Fabricated by Mechano-Chemical Synthesis. *Journal of Alloys and Compounds*, 1999. **290**(1-2): p. 71-78.
121. Zidan, R.A., S. Takara, A.G. Hee, and C.M. Jensen, Hydrogen Cycling Behavior of Zirconium and Titanium-Zirconium-Doped Sodium Aluminum Hydride. *Journal of Alloys and Compounds*, 1999. **285**(1-2): p. 119-122.
122. Brinks, H.W., B.C. Hauback, P. Norby, and H. Fjellvag, The Decomposition of LiAlH_4 Studied by in-Situ X-Ray and Neutron Diffraction. *Journal of Alloys and Compounds*, 2003. **351**(1-2): p. 222-227.
123. Chen, J., N. Kuriyama, Q. Xu, H.T. Takeshita, and T. Sakai, Reversible Hydrogen Storage Via Titanium-Catalyzed LiAlH_4 and Li_3AlH_6 . *J. Phys. Chem. B*, 2001. **105**(45): p. 11214-11220.
124. Fakioglu, E., Y. Yurum, and T. Nejat Veziroglu, A Review of Hydrogen Storage Systems Based on Boron and Its Compounds. *International Journal of Hydrogen Energy*, 2004. **29**(13): p. 1371-1376.

125. Read, C., G. Ordaz, and S. Satyapal. We-Heraeus Seminar on Hydrogen Storage with Novel Nanomaterials. 2005 [cited; Available from: <http://www.h-workshop.uni-konstanz.de>.
126. Zidan, R., D.K. Slattery, and J. Burns, Study of Chemically Synthesized Mg---Mgh₂ for Hydrogen Storage. *International Journal of Hydrogen Energy*, 1991. **16**(12): p. 821-827.
127. Chen, Y., C.-Z. Wu, P. Wang, and H.-M. Cheng, Structure and Hydrogen Storage Property of Ball-Milled Linh₂/Mgh₂ Mixture. *International Journal of Hydrogen Energy*, 2006. **31**(9): p. 1236-1240.
128. Shang, C.X., M. Bououdina, Y. Song, and Z.X. Guo, Mechanical Alloying and Electronic Simulations of (Mgh₂+M) Systems (M=Al, Ti, Fe, Ni, Cu and Nb) for Hydrogen Storage. *International Journal of Hydrogen Energy*, 2004. **29**(1): p. 73-80.
129. Varin, R.A., S. Li, A. Calka, and D. Wexler, Formation and Environmental Stability of Nanocrystalline and Amorphous Hydrides in the 2mg-Fe Mixture Processed by Controlled Reactive Mechanical Alloying (Crma). *Journal of Alloys and Compounds*, 2004. **373**(1-2): p. 270-286.
130. Fogler, H.S., *Elements of Chemical Reaction Engineering*. Third ed. Prentice Hall International Series in the Physical and Chemical Engineering Sciences, ed. N.R. Amundson. 1999, Upper Saddle River, NJ: Prentice Hall PTR.
131. Mintz, M.H. and J. Bloch, Evaluation of the Kinetics and Mechanisms of Hybriding Reactions. *Progress in Solid State Chemistry*, 1985. **16**(3): p. 163-194.
132. Andreason, A.F. and A.J. Maeland, eds. *Hydrides for Energy Storage*. 1978, Pergamon: Oxford.
133. Goodell, P.D. and P.S. Rudman, Hydridding and Dehydridding Rates of the Lani5-H System. *Journal of the Less Common Metals*, 1983. **89**(1): p. 117-125.
134. Wang, X.L. and S. Suda, Kinetics of the Hydridding-Dehydridding Reactions of the Hydrogen-Metal Hydride Systems. *International Journal of Hydrogen Energy*, 1992. **17**(2): p. 139-147.
135. McCarty, M., J.N. Maycock, and V.R.P. Verneker, Thermal Decomposition of Lithium Aluminum Hydride. *J. Phys. Chem.*, 1968. **72**(12): p. 4009-4014.
136. Andreasen, A., Effect of Ti-Doping on the Dehydrogenation Kinetic Parameters of Lithium Aluminum Hydride. *Journal of Alloys and Compounds*, 2006. **419**(1-2): p. 40-44.
137. Zaluska, A., L. Zaluski, and J.O. Strom-Olsen, Structure, Catalysis and Atomic Reactions on the Nano-Scale: A Systematic Approach to Metal Hydrides for Hydrogen Storage. *Applied Physics a-Materials Science & Processing*, 2001. **72**(2): p. 157-165.
138. Schlappbach, L., ed. *Hydrogen in Intermetallic Compounds II: Surface and Dynamic Properties, Applictations*. Topics in Applied Physics. 1992, Springer: Berlin.
139. Gross, K.J., P. Spatz, A. Zuttel, and L. Schlappbach, Mg Composites for Hydrogen Storage the Dependence of Hydridding Properties on Composition. *Journal of Alloys and Compounds*, 1997. **261**(1-2): p. 276-280.

140. Reiser, A., B. Bogdanovic, and K. Schlichte, The Application of Mg-Based Metal-Hydrides as Heat Energy Storage Systems. *International Journal of Hydrogen Energy*, 2000. **25**(5): p. 425-430.
141. ANL. Ipns - Instruments - Gppd. 2007 [cited 2007; Available from: <http://www.pns.anl.gov/instruments/gppd/>].
142. Jorgensen, J.D., J. Faber Jr., J.M. Carpenter, R.K. Crawford, J.R. Haumann, R.L. Hitterman, R. Kleb, G.E. Ostrowski, F.J. Rotella, and T.G. Worlton, Electronically Focused Time-of-Flight Powder Diffractometers at the Intense Pulsed Neutron Source. *Journal of Applied Crystallography*, 1989. **22**: p. 321-333.
143. Chien, W.-M., J. Lamb, D. Chandra, A. Huq, J. Richardson Jr, and E. Maxey, Phase Evolution of Li₂nd, Lid and Lind₂ in Hydriding/Dehydriding of Li₃n. *Journal of Alloys and Compounds*, 2007. **446-447**: p. 363-367.
144. Huq, A., J.W. Richardson, E.R. Maxey, D. Chandra, and W.M. Chien, Structural Studies of Li₃n Using Neutron Powder Diffraction. *Journal of Alloys and Compounds*, 2007. **436**(1-2): p. 256-260.
145. Brinks, H.W. and B.C. Hauback, The Structure of Li₃ald₆. *Journal of Alloys and Compounds*, 2003. **354**(1-2): p. 143-147.
146. Xiong, Z.T., G.T. Wu, J.J. Hu, Y.F. Liu, P. Chen, W.F. Luo, and J. Wang, Reversible Hydrogen Storage by a Li-Al-N-H Complex. *Advanced Functional Materials*, 2007. **17**(7): p. 1137-1142.
147. Engbæk, J., G. Nielsen, J.H. Nielsen, and I. Chorkendorff, Decomposition of Lithium Amide and Imide Films on Nickel. *Surface Science*, 2007. **601**(3): p. 830-836.
148. Hu, Y.H. and E. Ruckenstein, H-2 Storage in Li₃n. Temperature-Programmed Hydrogenation and Dehydrogenation. *Industrial & Engineering Chemistry Research*, 2003. **42**(21): p. 5135-5139.

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