IV.A.5m Effect of Gaseous Impurities on Long-Term Thermal Cycling and Aging Properties of Complex Hydrides for Hydrogen Storage

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Introduction

Trace amount (ppm levels) of gaseous impurities in ultra-high purity (UHP) hydrogen may cause loss in hydrogen capacity in solid-state storage of hydrogen in complex hydrides. To evaluate these effects we performed extrinsic thermal cycling with impure hydrogen; these tests are rather long. We also performed thermal aging where necessary. These tests are important for long-term reliability of metal hydrides, which is important for work towards achieving DOE technical targets for a hydrogen economy. In general, UHP hydrogen is used in research laboratories for the development of metal hydrides. However, the commercial hydrogen will always have some very low level impurities (ppm levels), typically O_2, H_2O, CH_4, N_2, hydrocarbons, and others. Typical industrial grade hydrogen that we used showed: "Hydrogen min % (v/v) 99%, Water~32 ppm, O_2~10ppm, N_2~400 ppm, Total Hydrocarbons: 10 ppm, CO_2~10 ppm, CO~10 ppm, argon may be present, reads as oxygen." We also used special 100 ppm O_2 mixed with UHP hydrogen in this study. These low level impurities affect the performance of hydrogen storage materials in the hydride beds that are installed in automobiles. The purpose of the pressure cycling experiments (with fresh charges of impure hydrogen) is to simulate the long-term performance of metal hydrides with trace amounts of impurities in the hydrogen. Parallel contamination studies are essential for evaluation of impurity effects, before design of any hydride bed for a vehicular application containing complex hydride materials. The degradation of the hydriding properties are generally associated with disproportionation or decomposition of hydrides surface or bulk properties of the material during normal periodic charges of impure hydrogen. These studies are expected to lead to the understanding of mechanisms that occur after multiple hydrogen filling of tanks. In another situation, for example, a hydride bed is left unused for a prolonged period of time, i.e., hydrogen is fully loaded in a hydride bed from a gas station; this type of test is called thermal aging performed at elevated pressures and temperatures. New complex hydride materials are being developed by the Metal Hydride Center of Excellence (MHCoE) partners using UHP hydrogen that will be subjected to these impurity tests to determine which ones have minimal degradation after many hundred cycles.

The objective of this research is to investigate the effect of trace impurities in complex hydrides, which can be potentially used for fuel cell and other applications and aid in the development of materials solutions to potential hydrogen sorption degradation problems by the principal investigator's group as well as MHCoE partners. 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. This accelerated laboratory testing will be extremely useful to understanding the reliable use of hydrogen fuel. At the University of Nevada, Reno we have automated extrinsic cycling apparatus to perform pressure cycling on Li_3N-H-imide/amide and other systems (this system is of interest due to high theoretical hydrogen content ~10.5 wt%). Results of cycling/aging of amide-imide, isotherms, and crystal structure analyses are presented. We also performed thermodynamic structural analyses of two component alanate-amides (in collaboration with Dr. Zak Fang, University of Utah). New phase transitions observed in $Ca(BH_4)_2$ hydride (in collaboration with Ewa Ronnebro of Sandia National Laboratories) are also reported. The approach used for these materials will be extended to the hydrides that are being developed by MHCoE partners.

Approach

In this research, we are conducting experiments on cycling and aging tests of materials (as described in the above section) developed by the MHCoE partners.

Pressure cycling apparatuses were constructed at UNR for hydrogen loading and unloading. The overall approach to performing cycling on currently reversible complex hydrides such as imide/amide systems (using Li_3N as precursor), including Li amide-alanate, which has a 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 255ºC and a hydrogen pressure range from vacuum to 2 bar was chosen based on the pioneering research of Prof. Ping Chen's *Nature* paper [1].

We have expanded on the initial results obtained last year by performing crystal structure analyses after cycling steps, by obtaining isotherms with UHP hydrogen (after cycling with impure hydrogen). Tests were also performed using industrial grade hydrogen by subjecting these materials to 1,100 cycles at 255ºC with gaseous impurities (O_2, CO, H_2O, and others). Kinetic analyses were also performed on the cycled samples. The rate constant $k(s^{-1})$ varied by an order of magnitude as the sample was cycled from 1 to 1,100 cycles. We had synthesized alanate-amide samples from the University of Utah on which we performed impurity gas tests that revealed small changes in properties after 500 cycles. Crystal structure analyses were performed as well, which revealed new phase formation yet showed hydrogen storage properties. Characterization of the phases before and after these cycling tests was performed using both static and dynamic X-ray diffraction (XRD) revealed the impurity related and intrinsic impurity phases after cycling. In addition to this, vaporization experiments were performed on Mg borohydrides (from J.C. Zhao, GE) with results that will be presented after completion of these experiments (using the gravimetric torsion effusion apparatus at UNR); these have importance in desorption cycles where impurities from the solid materials may sublime. Finally, we performed *in situ* XRD studies on $Ca(BH_4)_2$ and observed new phase transformations from the samples synthesized by Dr. Ewa Ronnebro at Sandia National Laboratories; only initial findings are shown in this report with the remainder to be presented later. The methodologies developed during this year will be used in the future for new metal hydrides that are being developed by MHCoE partners.

Results

A. Thermodynamic and Crystal Structure Studies Related Gas Contamination Effects

A1. Pressure Cycling and Thermal Aging Studies Li Amide-Imides with Li_3N as the Precursor Material-UNR Sample

Pressure cycling gas contamination studies were performed on the UNR sample, between $Li_2NH \leftrightarrow LiNH_2$ phases to observe long-term effects on hydrogen capacity changes using industrial grade hydrogen that contains ppm levels of oxygen, water vapor, and other gases. The material was subjected to a 1 hour cycle consisting of hydriding at 2 bar for 30 minutes then evacuating for 30 minutes. Figure 1(a) shows isotherms taken after 1, 56, 163, 501, and 1,100 non-equilibrium cycles showing hydrogen capacity loss due to the effect of cycling with
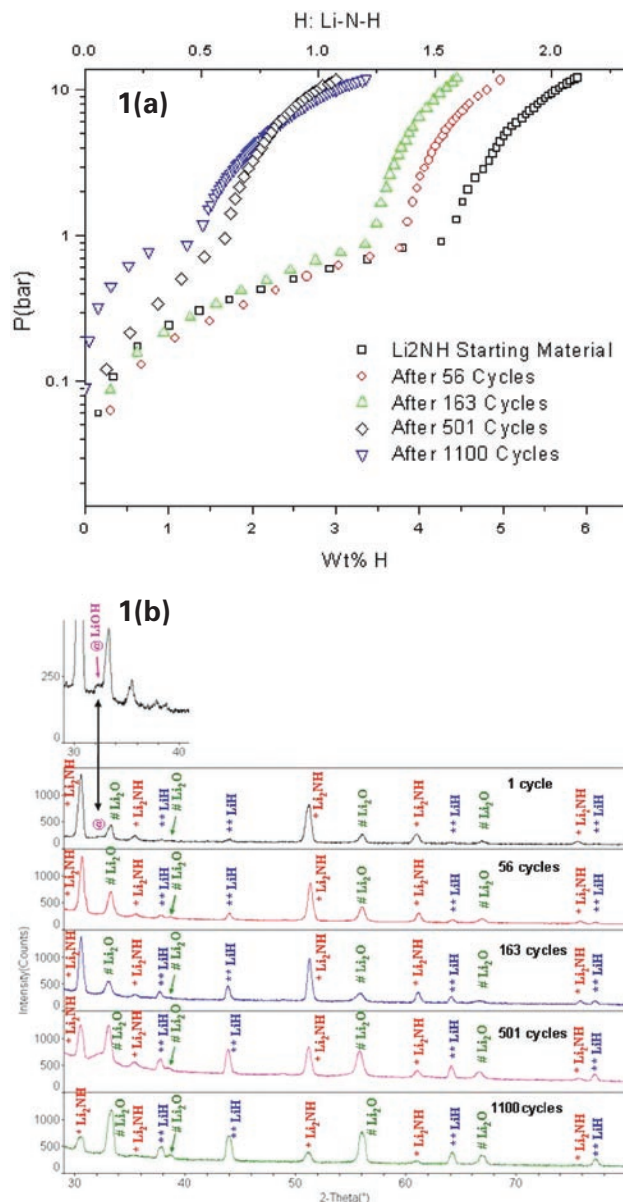
FIGURE 1. (a) Absorption pressure isotherms of 1, 56, 163, 501 and 1,100 cycles show loss of ~2.53 wt% hydrogen at ~10.25 bar gas pressure after 1,100 cycles for imide/amide system. (b) XRD patterns after each cycling event taken after a Sievert's experiment was performed after desorption show loss of Li_2NH and formation of LiH and impurity related phase of Li_2O.

impure gas. These data show ~5.6 wt% hydrogen (between Li$_2$NH↔LiNH$_2$), out of ~10.5 wt% total, starting with Li$_3$N. After 1,100 cycles, we lost ~2.3 wt% capacity between amide-imide transformations, indicated an overall 42% reduction in hydrogen capacity.

After cycling with impure hydrogen gas, and subsequently obtaining equilibrium isotherms, the products after each test cycle were examined using XRD patterns in desorbed condition as shown in Figure 1(b). XRD patterns showed nearly complete reversal from LiNH$_2$ → Li$_2$NH after cycling with expected LiH phase and impurity (Li$_2$O) phase; the starting material was Li$_3$N. After 1,100 pressure cycles, the LiH phase increases from 11 wt% to 58 wt%, and the Li$_2$NH phase decreases from 82 wt% to 13 wt%. The decrease in amount of Li$_2$NH can be observed in the Bragg peak at 30.5° of the XRD patterns. The impurity Li$_2$O phase content increased from 7 wt% to 29 wt% after 1,100 cycles indicated by the increase in Bragg peak intensity at 56° of the XRD pattern. We believe that these decreases are due to impurities present in the industrial hydrogen gases; even the low ppm level impurity gases present in hydrogen have significant impact on the performance of the hydrides. A very small amount of LiOH phase was also found in the synchrotron X-ray analyses although more was expected.

Thermal aging contamination experiments were also performed on amide-imide material (starting material-Li$_3$N) by aging in hydrogen containing 100 ppm CO for approximately 240 hours at 12 bar and 325°C. After aging, PCI data was obtained at 325°C. The PCI data obtained showed a capacity similar to that of pure Li$_2$NH, indicating that ppm levels of CO (as may be found in industrial grade hydrogen) had little effect on the storage properties of the material (isotherms not shown, but available upon request).

A2. Isothermal and Pressure Cycling/ Thermal Aging Studies on Two Phase 3LiNH$_2$:Li$_3$AlH$_6$ (Utah Sample)

Pressure composition isotherms were obtained from 3LiNH$_2$:Li$_3$AlH$_6$ binaries synthesized by Dr. Zak Fang of the University of Utah. Absorption and desorption isotherms for this material are shown in Figures 2a and 2b, at different temperatures. Prior to collecting the PCI data, the material was dehydrided in vacuum to estimate the amount of hydrogen released - estimated to be ~7 wt% hydrogen. However, the reversible capacity is significantly lower in value, as shown in the PCI data in Figure 2b. This indicates either that only a portion of the material remains active at moderate temperatures and pressures following the initial desorption of the material or that some new compounds are formed. A rather peculiar 165°C isotherm that has a higher isotherm pressure than the ones taken at higher temperatures is also apparent. It appears that the material has little active capacity at this temperature, possibly due to a
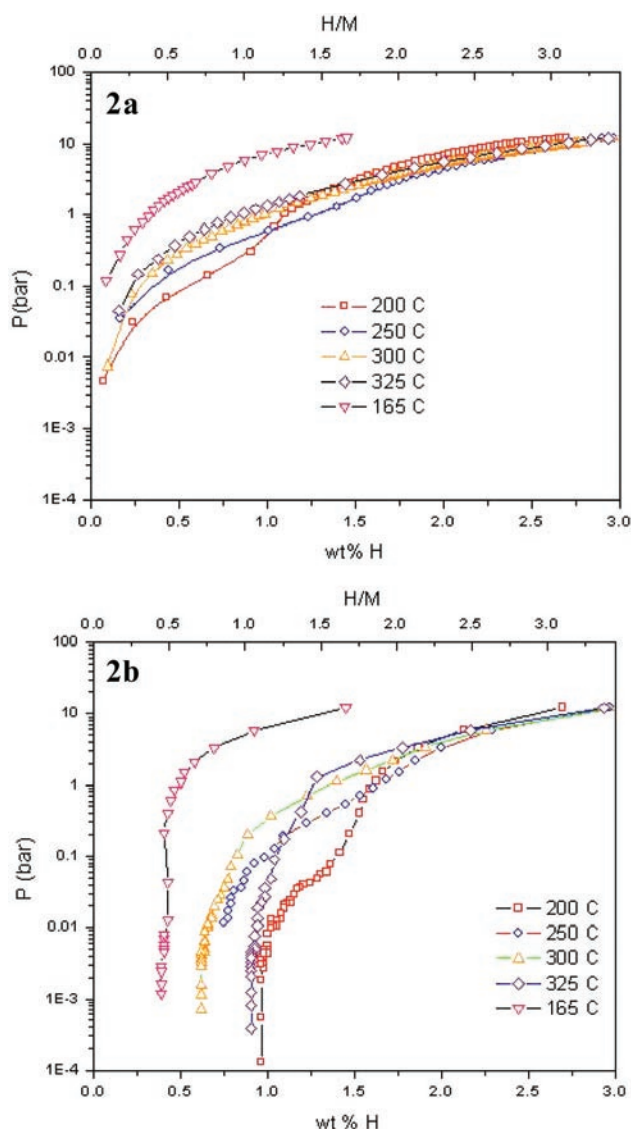

FIGURE 2A AND 2B. Isotherms Obtained from 3LiNH$_2$:Li$_3$AlH$_6$ in UHP Hydrogen at Different Temperatures

phase changes/decomposition somewhere between 165°C and 200°C.

Isothermal contamination studies using pressure cycling were performed on 3LiNH$_2$:Li$_3$AlH$_6$ binary sample using 100 ppm O$_2$ in H$_2$. The sample was exposed to 1 hour cycles of (non-equilibrium) hydrogen absorption/desorption for 540 cycles at 325°C, similar to the ones discussed for amide-imide sample. After cycling, PCI data was collected at 325°C and compared to PCI data for material that had not undergone the cycling test (see Figure 2c). The material lost only ~0.5 wt% of the capacity, showing a reasonable amount of durability with respect to oxygen impurity.
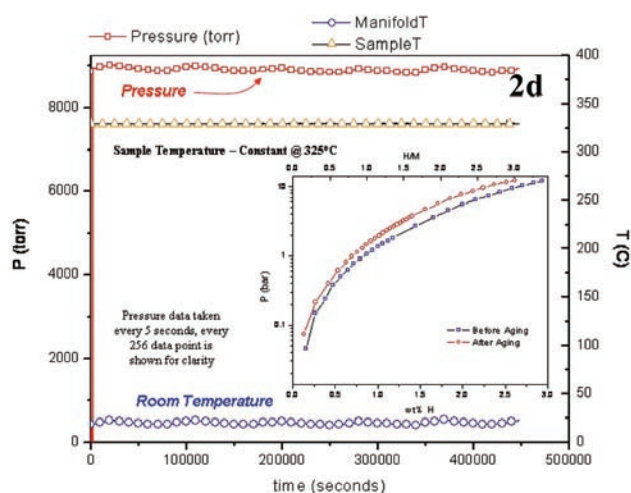
More contamination studies (using thermal aging method at constant pressure of ~9.5 bar pressure) were
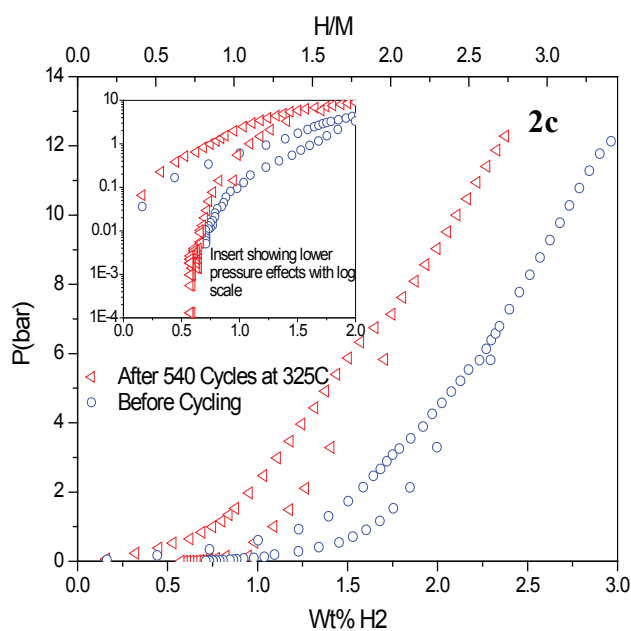
FIGURE 2C. Oxygen Contamination Effects Determined by Pressure Cycling of $3LiNH_2:Li_3AlH_6$ in 100 ppm O_2 in UHP H_2 (Eqilibrium isotherms were taken before and after non-equilibrium pressure cycles at 325°C; 1 hour cycle at 325°C in H_2 with 100 ppm O_2. Cycling showed a loss of only ~0.5 wt% hydrogen.)

FIGURE 2D. Carbon monoxide contamination effects were evaluated on $3LiNH_2:Li_3AlH_6$ using 100 ppm CO mixed with UHP hydrogen at 325°C using thermal aging method; showed minor changes in pressure due to room temperature fluctuations over the period of time. Isotherms taken before and after are also shown in the inset, showing small changes in hydrogen capacity.
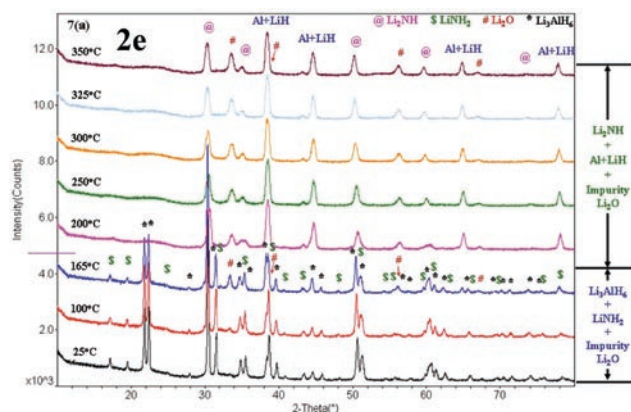
FIGURE 2E. XRD Patterns of $3LiNH_2:Li_3AlH_6$ Sample Obtained from *In Situ* Experiments by Heating from Room Temperature to 350°C under Vacuum. (There is decomposition of the mixture that leads to the formation of a new phases Li_2NH and Li_3AlN_2, along with formation of LiH and apparently Al. [Bragg peaks match Al, but it could interpreted as AlN].)

performed with 100 ppm of carbon monoxide in H_2 on the Utah sample, which showed good resistance. Figure 2d shows the pressure vs. time data. Minor variation of pressure is due to the room temperature fluctuations, as seen in the room temperature pressure versus time plot. Capacity loss would be expected if there is an increase in the pressure, as the material gives up hydrogen as its capacity drops. These materials appears to be fairly resistant to CO with little capacity loss (under these conditions) as determined by the isotherms (shown in the inset) taken before and after aging.

We also performed an *in situ* XRD study on $3LiNH_2:Li_3AlH_6$ sample from room temperature to 350°C under vacuum shown in Figure 2(e). The XRD patterns in Figure 2(e) show that between 25°C and 165°C, the Li_3AlH_6 and $LiNH_2$ mixtures are stable, with a small amount of Li_2O phase. Above 165°C, new phases, Li_2NH, Li_3AlN_2, LiH and Al (or possibly AlN) phases form, and are stable up to 350°C. The sample was re-hydriding at 325°C under 2 atm H_2 for 20 hours, but the hydride phases ($LiNH_2$ and Li_3AlH_6) did not appear (X-ray patterns not shown here). In yet another experiment, we aged this binary sample at 20-hours aging under hydrogen atmosphere, the Li_3AlN_2 phase was formed.

B. Kinetics Study of Li-N-H Systems

B1. Background

The kinetics of complex hydrides have been 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 1:

$$k = k_0 \exp(-Q/RT) \qquad (1)$$

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 kinetic mechanisms of classical interstitial hydrides have been well studied [2-5] and generally follow the steps of gas phase hydrogen transport, hydrogen adsorption and diffusion on the surface, dissociation of H_2 into H^+ ions, absorption and diffusion of hydrogen into the solid, and, finally, hydrogen formation, with kinetic models being determined based on 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 [6]. A final complication is that the dehydrided material can oftentimes 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 [7] 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 [8] 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 [9] 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 [10] 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, leaving

some uncertainty regarding the influence of further material decomposition. More recent work, however, by Blanchard et al [11] 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 and by Andreasen and Chen et al [12-14]. Blanchard et al [12] studied the effects of $TiCl_3·1/3AlCl_3$ and VCl_3 and found a reduction of 5-10 kJ/mol with little difference in the effectiveness of the two catalysts. Andreasen [13] also studied $TiCl_3·1/3AlCl_3$ 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 create an assumption that there is any effect on the decomposition of $LiAlH_4$ when using Ti as a catalyst. Chen et al [14], however, did report results contradicting the other two studies. The research found catalysis by $TiCl_3·1/3AlCl_3$ 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 intensively 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 [15,16]. A considerable amount of effort has gone into improving the kinetics and significant improvements have been made by ball milling to reduce the particle size and by the addition of various catalysts [17-20].

B2. Kinetics Effects of Cycling on Imide-Amide System-UNR Sample

Kinetic analyses of the cycled amide–imide samples (see isotherms in Figure 1) were performed, the results of which are shown in Figure 3A. There is a clear effect 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 2:
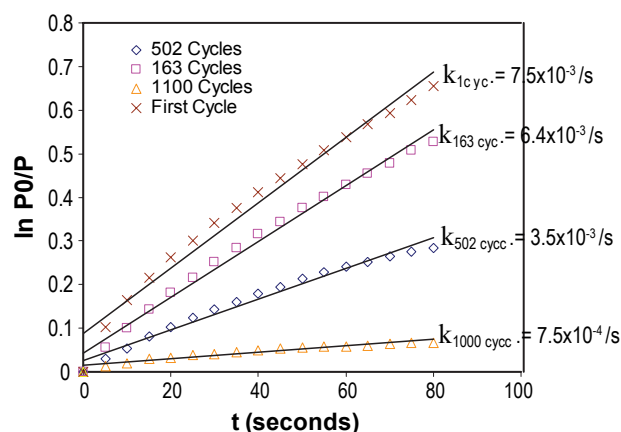
$$Li_2NH + H_2 = LiNH_2 + LiH \qquad (2)$$
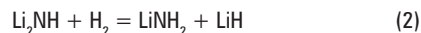
This reaction is assumed to follow a first order rate law, as given in Equation 3:

$$dC/dt = -kC \qquad (3)$$

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 4:

$$dP/dt = -kP \qquad (4)$$

FIGURE 3A. Effect of Cycling of L_2NH-$LiNH_2$ (UNR sample) with Contaminated Gases on Kinetic Rates (See Figure 1 for Isotherms. These experiments were performed at 255°C. Greater slope translates to greater rate. First order rate constants are shown for these experiments along the plot.)

Fogler [21] outlines a method for finding the rate constant **k** using experimental data. Equation 3 is solved assuming an initial condition of $P = P_0$ at $t = 0$. The solution gives Equation 5.

$$\ln (P_0/P) = kt \qquad (5)$$

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 does follow a first order rate law, the plot of the data generated will be linear. The plots shown in Figure 3a are approximately linear, leading to first order assumption, and the rate constants found are shown along with the plots. 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 1,100 cycles.

B3. Kinetic Properties of Binary Lithium Amide-Alanate (Utah Sample)

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 $3LiNH_2$:Li_3AlH_6. The kinetic constants and activation energies were determined from a plot of $-\ln k(T)$ versus $1/T$; we determined the activation energy of $E_{act}.\sim 51$ kJ/mol for this Utah sample (see Figure 3b). In Table 1, we compare the activation energies of other hydrides.
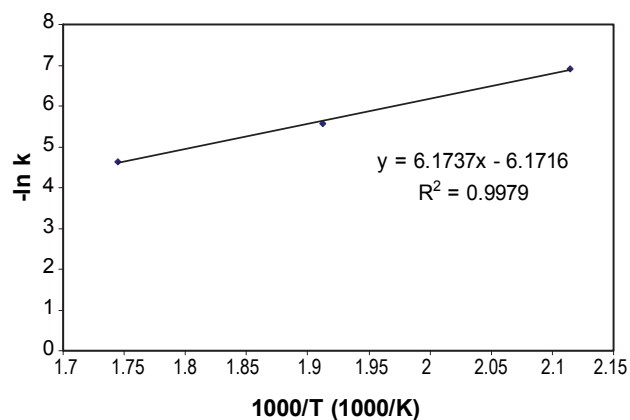
FIGURE 3B. Arrhenius Plot from the Kinetic Data Collected for Binary $3LiNH_2$: Li_3AlH_6 (Utah Sample)

## C. Characterization of a New β-High Temperature Phase of $Ca(BH_4)_2$

High pressure calcium borohydride samples synthesized at the Sandia National Laboratories were

**TABLE 1.** Activation Energies Obtained from Various Sources for Several Complex Hydrides

Material	Activation Energy	References
$3LiNH_2$:Li_3AlH_6	51 kJ/mol	This study
MgH_2	241 kJ/mol	[16]
$Mg(Ni)H_2$	216 kJ/mol	[12]
$LiAlH_4$	81 kJ/mol	[22]
Ti Catalyzed $LiAlH_4$	89 kJ/mol	[22]
$NaAlH_4$ to Na_3AlH_6	73-100 kJ/mol	[7-9]
Na_3AlH_6	97-100 kJ/mol	[7-9]

studied at UNR. Room temperature XRD pattern (Figure 4a) showed presence of α-$Ca(BH_4)_2$, CaB_6, and CaO phases obtained, indicating that high pressure gas synthesis method is successful using proprietary catalysts. We did not find CaH_2 phase in this button that was sent.

After the α-$Ca(BH_4)_2$ phase was identified, we then proceeded to heat the sample in turbo pump vacuum evacuated condition. The samples were heated from room temperature to ~450°C. At 200°C, we found a new phase and assigned β–$Ca(BH_4)_2$ with Catalyst A as shown in Figure 4b. This β-phase is stable up to 300°C, above which it decomposes. The residual pattern at 400°C showed only CaB_6 phase with a minor amount of CaO phase. The presence of CaO phase may be mainly due to the transfer of sample from the sealed environment to the XRD hot stage at UNR.
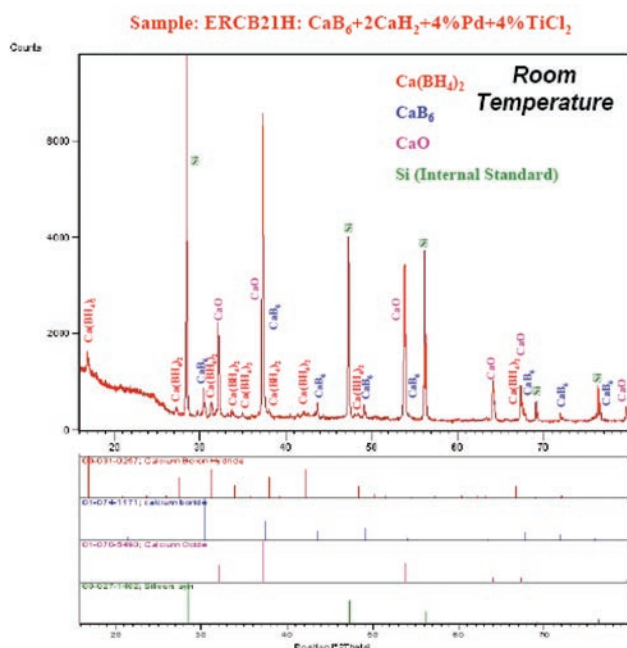
FIGURE 4A. Room Temperature Pattern Showing α-Ca(BH$_4$)$_2$, CaB$_6$, and CaO Phases Showing that High Pressure Gas Synthesis Method Works Using a Proprietary Catalyst (We did not find CaH$_2$ phase in this button.)
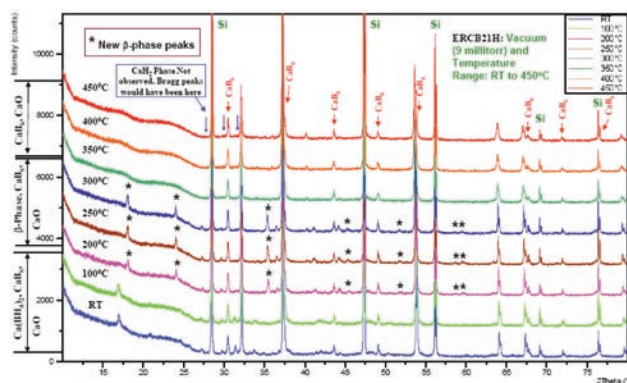
FIGURE 4B. *In Situ* XRD Patterns (in Vacuum) from Catalyzed Samples, Showing Phase Changes as a Function of Temperature (At room temperature and up to ~150°C the α-Ca(BH$_4$)$_2$, CaB$_6$, and CaO phases are present in the product. Further heating to 200°C shows a structural change to new phase assigned as the β–Ca(BH$_4$)$_2$, marked with asterisk*. This beta phase is stable up to ~300°C. Dehydrided sample shows only CaB$_6$ phase; the CaH$_2$ phase was not observed above 350°C.)

In another sample that was also prepared using CaH$_2$ and CaB$_6$ with Catalyst B, the yield of the α-*Ca(BH$_4$)$_2$* was much higher. The $\alpha \rightarrow \beta$ phase boundary was observed at ~150°C; above 300°C, the β–Ca(BH$_4$)$_2$ decomposes to another phase, which is under current investigation. In this case, there was unreacted CaH$_2$ phase present. At present, we are working on the crystal structure determination of the β–Ca(BH$_4$)$_2$.

Conclusions and Future Directions

Conclusions

1. Binary amide-alanate (3LiNH$_2$-Li$_3$AlH$_6$) mixtures appear to be very promising hydrogen storage materials; isotherms show reasonable storage of 3.0 wt% at 10 bar; higher values of hydrogen capacity have been shown by Dr. Zak Fang of University of Utah at elevated pressures based on gravimetric methods.

2. Pressure cycling (540 cycles) of 3LiNH$_2$-Li$_3$AlH$_6$ mixtures, performed at UNR, (under 2 atmosphere H$_2$ mixed with 100 ppm O$_2$) showed only 0.26 wt% loss based on isotherm data.

3. *In situ* (desorption) XRD studies of 3LiNH$_2$-Li$_3$AlH$_6$ at UNR showed that there is a phase transition at ~165°C, in which there is decomposition of the mixture to Li$_2$NH, LiH, and Al. Rehydriding of this decomposed product shows that there is a predominant new compound, Li$_3$AlN$_2$, forming after a period of 20 hours at 325°C.

4. Kinetic parameters of trace contaminants on cycling using impure industrial grade hydrogen was determined to show first order transformation with rate constant, k, ranging 7.5×10^{-3} to 7.5×10^{-4}/sec, from 1 to 1,100 cycles for the amide/imide system (baseline material).

5. The hydrogen capacity loss is approximately 50% of the total 5.6 wt% even after 1,100 cycles with industrial hydrogen mainly attributed to extrinsic impurity effects of oxygen due to formation of Li$_2$O and intrinsic formation of LiH.

6. *In situ* XRD studies have revealed phase transformations occurring in Ca(BH$_4$)$_2$. We have observed two distinct structural phase transitions during heating from room temperature to 450°C. Detailed structural studies by using synchrotron radiation will be presented soon.

Future Directions

In the DOE MHCoE program we would like to focus on the contemporary issues. We propose the following:

1. **Contamination Studies on new Complex Hydrides-Continuation Studies**

    We propose to continue imide/amide research on the effect of low level impurities on pressure cycling of hydrides to complete the extrinsic cycling studies on this system. The effect of individual impurities in ppm levels of O$_2$, CO, CO$_2$, CH$_4$, and H$_2$O in UHP hydrogen will be investigated. In FY 2008, we will begin high pressure (120 bar) cycling work on MgH$_2$/Li$_2$NH, the apparatus for which has been constructed. The experience and apparatus

developed for the Li_3N cycling experiments will be useful for high pressure cycling of Mg-Li-N-H and other complex hydrides. This apparatus will be available to the MHCoE team.

2. **Development of New Liquid Phase Eutectic Complex Hydrides at UNR- Phase Diagram Studies Using XRD and Differential Scanning Calorimetric Studies along with CALPHAD Modeling**

   To avoid the kinetic barriers and surface effects of the particles during desorption, it will be interesting to explore the liquid phase complex hydrides. These hydrides may be solid at room temperature or below, but when heated, will form liquid phase hydrides for release of hydrogen. The underlying thermodynamics of this these liquid phase hydrides will be explored in this year's program. We will start with the pseudo binary amide/imide-alanate system, and construct phase diagrams using combined high pressure hydrogen differential scanning calorimetry and *in situ* (above ambient) X-ray diffractometry methods at UNR. *CALPHAD* modeling will also will be applied and we will continue current modeling programs at UNR. (One of the industry stakeholders has already proposed liquid phase hydrogen containing fuel.)

3. *In Situ* **hydriding/dehydriding XRD Studies at UNR complemented by Synchrotron Studies at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory (LBNL)**

   In situ dehydriding will be performed on binary mixtures of complex hydrides using UNR's PANalytical XRD system - hydrogen and high temperature Anton Paar stage (with maximum 10 bar pressure and 900°C) will be used. Additional high resolution studies are proposed on Li-based compounds with the ALS, LBNL at the beam-line 7.3.3; we currently have a collaboration at ALS.

4. **Vapor Pressure Studies on $Mg(BH_4)_2$ – GE Collaboration (Dr. Zhao)**

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

5. **Hydrogen Lattice Dynamics Studies on Complex Hydrides- Prof. Cantelli, Uni. of Rome – International Energy Agency/International Partnership for the Hydrogen Economy (IPHE) Proposal**

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

6. **Phase Transformations in $Ca(BH_4)_2$**

   We have found that new phases are formed during heating of this hydride (synthesized by Dr. Ewa Ronnebro of the Sandia National Laboratories). We are expanding these studies to greater levels of detail in collaboration with Dr. Yaroslav Filinchuk of the European Synchrotron Radiation Facility, Grenoble.

FY 2007 Publications/Presentations

1. A. Huq, J.W. Richardson Jr., E. Maxey, D. Chandra, W. Chien, "Structural Studies of Deuteration and Dedeuteration of Li_3N by Use of *In Situ* Neutron Diffraction," *Journal of Physical Chemistry C*, 111 (28), pp. 10712-10717 (2007).

2. A. Huq, J.W. Richardson Jr., E. Maxey, D. Chandra, W. Chien, "Structural Studies of Li_3N Using Neutron Powder Diffraction," *Journal of Alloys and Compounds*, 436, pp. 256-260 (2007).

3. W. Chien, J. Lamb, D. Chandra, A. Huq, J. Richardson, Jr., E. Maxey, "Phase Evolution of Li_2ND, LiD and $LiND_2$ in Hydriding/Dehydriding of Li_3N," *Journal of Alloys and Compounds* (2007), doi:10.1016/j.jallcom.2007.02.149 – article in press.

4. 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.

5. 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 & Technology (MS&T) 2006: FUNDAMENTAL AND CHARACTERIZATION*, Volume 1, 501-507, 2006.

6. 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.

7. 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 Laboratories, January 28 to Feb 1st, 2007, Monterey Plaza Hotel, Monterey California, Session F: H-18, Jan. 31, 2007.

8. 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.

9. 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.

10. 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.

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