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Objectives

• The overall goal of the entire Hydrogen Storage Program is to develop and verify on-board hydrogen storage systems achieving 2 kWh/kg (6 wt%), 1.5 kWh/L, and $4/kWh by 2010.

• The specific goal of this project is to understand long-term effects of gaseous impurities on complex metal hydrides, so as to simulate fuel charging from hydrogen gas pumps in vehicular applications.

Technical Barriers

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

(A) System Weight and Volume

(D) Durability/Operability

Technical Targets

The project is conducting fundamental and pressure cycling studies on Li amide-imide complex hydrides. Insights gained from these studies will be applied towards design and synthesis of new hydrogen materials that meet the following DOE 2010 hydrogen storage targets:

• Cost: $4/kWh net

• Specific energy: 133/kWh/kg

• Energy Density: 2-3 kWh/L

Accomplishments

• Discovered that impurities such as oxygen has greater impact than others such as methane, carbon monoxide or moisture in trace amounts present in hydrogen during pressure cycling of light weight lithium amide-imide complex hydrides (theoretical capacity ~10.5 wt% hydrogen, and ~ 6 wt% reversible at this time).

• Determined two new phase transitions ($\alpha \rightarrow \alpha' \rightarrow \beta$) in Ca(BH$_4$)$_2$ by in situ neutron diffraction method, details will be released after the acceptance of manuscript submitted.

• Determined Mg(BH$_4$)$_2$ does not contaminate the system by vaporization of the complex hydride itself with no observable vapor contamination from Mg(BH$_4$)$_2$, below 233°C. Above 233°C, partial pressures: $P_{H_2} = 8.9 \times 10^{-6}$ bar, and $P_{Mg(BH_4)_2} = 2.05 \times 10^{-7}$ bar at 255°C.

Introduction

Light-weight complex metal hydrides are becoming increasingly important for hydrogen storage in vehicular applications. Modern hydrogen powered vehicles are expected to be regularly fueled at “hydrogen gas stations.” Research performed on the contemporary hydrides in laboratories generally use ultra-high-purity (UHP) gases that may not reflect on the loading/unloading of the hydride beds that use commercial hydrogen gases. In general, there are trace (ppm) levels of gaseous impurities in commercial hydrogen gas. Complex hydrides generally are composed of reactive metal components, such as Na, Li, K and others, that may readily oxidize even with small amounts of oxygen partial pressure. The degradation of the hydriding properties are generally associated with disproportionation or decomposition of hydride 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...
of degradation, if any, that occur due to repetitive charging of hydrogen in hydride beds. Contamination studies are essential for evaluation of impurity effects, before designing any hydride bed for a vehicular application containing complex hydride materials. Our prior research reflected on degradation testing of the amide-imide complex hydrides, using industrial grade hydrogen that contained ppm levels of O\(_2\), H\(_2\)O, N\(_2\), and others which showed oxygen contamination was very predominant.

More recently, Mg and Ca hydrides have been investigated for hydrogen storage due to their large theoretical ~15% hydrogen capacity with reversible storage capacity of 6.1 wt% hydrogen. The importance of these measurements is that the vaporization behavior of the hydride may be evaluated to check if the original molecular species may be potentially disproportionate subliming undesirable vapors in the system during dehydriding processes. The other borohydride of interest is the Ca(BH\(_4\))\(_2\); this material has been prepared by high-pressure methods by Ewa Ronnebro from Sandia National Laboratories using Barkhordarian et al. [1] methodology. Results of cycling/aging of amide-imide, isotherms, and crystal structure analyses are presented. New phase transitions observed in Ca(BH\(_4\))\(_2\) hydride are also reported.

### Approach

The approach taken is to conduct contamination tests by pressure cycling and aging of materials such as amide-imide hydrogen storage materials, as the primary focus, details of approaches taken are shown in prior annual reports. The specific tasks this year were to determine the changes in the pressure-composition isotherm after cycling with impure hydrogen. A reference temperature of 255°C and a hydrogen pressure range from vacuum to 2 bar was chosen based on the pioneering research of Chen et al. [2]. Typical impurities in commercial hydrogen gas are expected to be O\(_2\), CO, H\(_2\)O, CH\(_4\), and others minor constituents. As part of collaboration with our Metal Hydride Center of Excellence (MHCoE) members we also performed studies on Mg(BH\(_4\))\(_2\) to evaluate impurity contamination from the hydride materials itself due to vaporization and disproportionation using the gravimetric torsion effusion apparatus at UNR. Finally, we performed in situ X-ray diffraction (XRD) studies on Ca(BH\(_4\))\(_2\) and observed new phase transformations from the samples synthesized at Sandia National Laboratories; only initial findings are shown in this report with the remainder to be presented later, once the manuscript is accepted. 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. Impurity Effects in Imide – Amide System

**Extrinsic Pressure Cycling on Li\(_2\)NH-LiNH\(_2\) with 100 ppm O\(_2\) and H\(_2\)O in UHP Hydrogen:** We present our extrinsic impurity gas test results after cycling on imide-amide hydrogen storage materials. In addition, we show potential contamination or disproportionation effects due to vaporization magnesium borohydrides.

The hydrogen storage capacity of the Li\(_2\)N-Li\(_2\)NH-LiNH\(_2\) was obtained by volumetric methods. Using Li\(_3\)N as starting a material and when we load hydrogen for the time, 10.05 wt% hydrogen is absorbed and forms LiNH\(_2\). We show the full spectrum of the isotherm in Figure 1. The crystal structures of these compounds have been described in references [3-7]. Next we show results from cycling experiments in which the starting point of the isotherm is Li\(_2\)NH and reversibility is shown between Li\(_2\)NH ↔ LiNH\(_2\) absorbing/desorbing approximately 5.6 wt% hydrogen. Details of the cycling procedures have already been presented in other reports. It should be noted that computer program ensures that equilibrium is reached during absorption/desorption cycles until system reaches a prescribed (dp/dt). The absorption kinetics shows very little change from cycle to cycle, indicating that the capacity losses seen stems largely from a loss in hydrogen capacity of the material.

![FIGURE 1. Isotherm obtained from hydriding of the precursor α-Li\(_2\)N compound is shown indicating theoretical compositions of various compounds. Ideally, the Li\(_2\)NH phase absorbs hydrogen from 3.49 to ~10.05 wt% hydrogen. The crystal structures are of each of the phases are listed as follows: 1. α-Li\(_2\)N – Hexagonal, P6/mmm - Z = 1 a = 3.6587 Å, c = 3.876 Å, Vol. = 44.933 Å\(^3\) [3]. 2. Li\(_4\)NH, Tetragonal, I41/a, a = 4.8769(3) Å, c = 9.8769(9) Å, V = 234.9 Å\(^3\), Z = 4, Rgt(F)/ = 0.052, wRef(F2Y) = 0.121, T = 293 [4,5]. 3. Li\(_2\)NO, Cubic – Fm 3m - Z = 4; a = 5.0476 Å, Vol = 128.602 Å\(^3\) [6]. 4. LiNH, – BCT, I-4 - Z = 8: a = 5.0895 Å, c = 10.2599 Å, volume = 263.68 Å\(^3\) [7] (See page 492 for more details.)](attachment:image-url)
A summary of the key impurity effect results obtained from pressure cycling of Li$_2$NH→LiNH$_2$ are shown in the isotherms obtained at 255°C in Figure 2. Although desorption isotherms for these were obtained, but these are not included for clarity. It should be noted that the isotherms were taken up to 10 bar hydrogen pressure, rather than 20 bar (cycling pressure), for comparison with other data sets that were already obtained. Superscripts on the impurity gas designation on left represent the number of pressure cycles. For example $^{100}$CH$_4$ showed a capacity of 4.2 wt% hydrogen as compared to $^{1}$H$_2$, $^{16}$H$_2$$_{2indus}$ of 6.0 wt% and 4.2 wt% hydrogen, respectively. The original capacity is ~6.0 wt% hydrogen at 10 bar. For higher number of cycles, as in the case of $^{501}$O$_2$, the capacity reduced to ~1.5 wt% hydrogen at ~10 bar for $^{501}$H$_2$O the capacity reduced to 2.7 wt%, as compared to $^{501}$H$_2$$_{2indus}$ of 3.01 wt% hydrogen. Experiments with carbon monoxide did not show any measurable loss of hydrogen capacity, data are not shown here. XRD results of the powder obtained in desorbed condition after cycling 100 ppm H$_2$O added to hydrogen showed the major phases (after desorption) Li$_2$O, Li$_2$NH, Li(OH)$_2$, and LiH phase. Oxygen, on the other hand, showed a significantly larger capacity loss from cycling compared to similarly cycled impurity gases. We have also performed impurity testing on mixed hydrides, 3LiNH$_2$-Li$_2$AlH$_4$ for 540 cycles in 100 ppm O$_2$ in hydrogen at 325°C, and found only approximately 0.5 wt% loss; performance appeared better than Li$_2$NH-LiNH$_2$ and these data were reported previously. Along with this, it is worth noting that in all cases increased formation of LiH was seen with more cycles observed from XRD results. A portion of the loss in capacity is due to LiH that does not fully transform to Li$_2$NH each cycle. Table 1 shows the hydrogen capacity with first hydriding from Li$_2$N phase to LiNH$_2$. Table 2 gives a summary of the capacities with different gaseous impurity.

**TABLE 1.** Overall Hydrogen Capacity of the Li$_2$N-Li$_2$NH-LiNH$_2$ Starting from Li$_2$N Compound

<table>
<thead>
<tr>
<th>Material</th>
<th>Gas Used</th>
<th>wt% Hydrogen without any cycling from Li$_2$N precursor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$NH-LiNH$_2$</td>
<td>UHP H$_2$</td>
<td>10.05</td>
</tr>
</tbody>
</table>

**TABLE 2.** Summary of effects of impurity upon extrinsic pressure cycling. This table includes some of the previous results for comparison. The number in parenthesis represents the number of cycles.

<table>
<thead>
<tr>
<th>Material</th>
<th>Gas Used</th>
<th>Number of Cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$NH-LiNH$_2$</td>
<td>Industrial H$_2$</td>
<td>255 10 1 50-56 100 to 163 500 to 560 1,100</td>
</tr>
<tr>
<td>Li$_2$NH-LiNH$_2$</td>
<td>100 ppm O$_2$ in H$_2$</td>
<td>255 10 5.8 (1) 4.85 (56) 4.25 (101) 3.05 (501) 3.1 (1,100)</td>
</tr>
<tr>
<td>Li$_2$NH-LiNH$_2$</td>
<td>100 ppm H$_2$O in H$_2$</td>
<td>255 10 5.8 (1) - - 1.45 (560) -</td>
</tr>
<tr>
<td>Li$_2$NH-LiNH$_2$</td>
<td>100 ppm CH$_4$ in H$_2$</td>
<td>255 10 5.8 (1) - - 2.75 (560) -</td>
</tr>
<tr>
<td>Li$_2$NH-LiNH$_2$</td>
<td>100 ppm CO in H$_2$</td>
<td>325 12 6.3 (1)</td>
</tr>
</tbody>
</table>

* Approximate maximum pressure (bar) of isotherm at which the wt% values are reported.
** The hydrogen absorption capacities are reported after the first cycle by normalizing the data to Li$_2$NH as starting point. The maximum observed reversible capacity is approximately 5.6 wt% between Li$_2$NH→LiNH$_2$, although 6.3 wt% is observed during absorption of the very first loading. Note that the Li$_2$NH does not completely reverse to Li$_2$NH or Li$_2$N which yield a hydrogen capacity of 10.07 wt%.
Vapor pressure Eq.: $\log P \text{(bar)} = 2.216 - \frac{4485}{T}$, and
Mg(BH$_4$)$_2$ magnesium borohydride, and presented in Figure 3:

Above 235°C (508 K) the Mg(BH$_4$)$_2$ powder sample shows complete decomposition according to the reaction:

$$\text{Mg(BH}_4\text{)}_2(s) = \text{Mg} (s) + \text{B(s)} + 4\text{H}_2(g)$$

The presence of Mg metal in the residual sample was confirmed by XRD analyses. We did not observe Boron metal Bragg peaks in the XRD pattern, but it is most likely amorphous. Thus information from the torsion effusion experiments is useful to determine the stability of the borohydrides. There are always valid questions regarding borane or other toxic gases evolving during decomposition of Mg(BH$_4$)$_2$. Using our data we calculated the average molecular weight (MW) of effusing gases which in this case the MW = 2.42 g/mol that suggests that the majority of the gas was hydrogen. Also, thermodynamic analyses revealed that B$_2$H$_6$, if formed, may decompose to boron (metal) and hydrogen according to the equation:

$$\text{B}_2\text{H}_6(g) + 2\text{B} (\text{solid}) + 3\text{H}_2 (g)$$

To summarize, the vapor pressures of Mg(BH$_4$)$_2$ below 235°C are quite low and there hydrogen gas release. The vapor pressure of Mg(BH$_4$)$_2$ at 298.15 K, 1 bar is $\Delta G_{vap} = 87.6 \text{kJ/mol}$ (unlikely) and at 255°C is $\Delta G_{vap} = 8.7 \times 10^{-4} \text{bar}$. The presence of Mg metal in the residual sample was confirmed by XRD analyses. We did not observe Boron metal Bragg peaks in the XRD pattern, but it is most likely amorphous. Thus information from the torsion effusion experiments is useful to determine the stability of the borohydrides. There are always valid questions regarding borane or other toxic gases evolving during decomposition of Mg(BH$_4$)$_2$. Using our data we calculated the average molecular weight (MW) of effusing gases which in this case the MW = 2.42 g/mol that suggests that the majority of the gas was hydrogen. Also, thermodynamic analyses revealed that B$_2$H$_6$, if formed, may decompose to boron (metal) and hydrogen according to the equation:

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(C) Phase Transformations in Ca(BH$_4$)$_2$

Calcium borohydride studies were performed in collaboration with Ewa Ronnebro of Sandia National Laboratories and Yaroslav Filinchuk of ESRF, Grenoble, France using high resolution synchrotron SRD at ESRF. In this, we used commercial Ca(BH$_4$)$_2$-2-tetrahydrofuran from Aldrich corporation that was desolvated according to reference [8]. The crystal structure details, although determined, are left out in this report as the manuscript for publication is in reviews process. Other researchers, such as, Konoplev et al. [9], Miwa et al. [10], and Kim et al. [11] were also working on this problem around that time. A recent thermal-gravimetric study by Kim et al [11] indicated partial reversibility (90 bar) based on thermogravimetric results.

IV.A Hydrogen Storage / Metal Hydride CoE

(b) Thermodynamics of Vaporization of Mg(BH$_4$)$_2$

Contamination of a hydrogen storage system is also possible due to release of vapors from the hydride compounds themselves. In some cases the hydrides decompose and release elemental or molecular compounds during desorption processes in hydriding bed, especially under vacuum testing. This behavior of the complex hydride materials was evaluated by using a torsion effusion Knudsen cell method at UNR. In this method, we can obtain the vapor pressure as well as the molecular weight of the effusing species which yields the disproportionation aspects of the systems under consideration. The details of the experimental methods used were presented in the earlier reports. This report gives thermodynamic analyses of vaporization of Mg (BH$_4$)$_2$. Vapor pressures of Mg (s) →Mg (g) and decomposition of MgH$_2$ → Mg (s) and H$_2$ are included for comparison purposes. At 225°C, $P_{\text{H}_2} = 8.8 \times 10^6$ atm, $P_{\text{Mg(BH}_4\text{)}_2} = 2.03 \times 10^7$ atm. There is no indication that Mg vaporization occurs (up to 233°C). There is some amount of expected Mg(BH$_4$)$_2$ (~2%) vaporized and the rest (~98%) is hydrogen, i.e. there is decomposition of the borohydride. Above 226°C (509 K) the $\Delta G^\circ$ becomes negative and vigorous vaporization (hydrogen gas) starts. We propose two principal reactions for which the thermodynamic parameters are determined for magnesium borohydride, and presented in Figure 3:

$$\text{Mg(BH}_4\text{)}_2(s) \rightarrow \text{Mg(BH}_4\text{)}_2(g) \text{ (congruently vaporized)}$$

Vapor pressure Eq.: $\log P \text{(bar)} = 2.216 - \frac{4485}{T}$, and $\Delta G^\circ (J/mol)$

$$= 93366-152.85 \text{T (Eq. at 610 K)}$$

Mg(BH$_4$)$_2$ magnesium borohydride, and presented in Figure 3:

Figure 3. Gibbs energy ($\Delta G^\circ$) for the reactions for Mg(BH$_4$)$_2$ showing the two different pathways for the Li-N-H system.
In situ XRD data showed that there were three phase transitions, $\alpha \rightarrow \alpha' \rightarrow \beta$ phases a small amount of $\beta$ phase was present in the sample when we desolvated the tetrahydrofuran, so the samples were mixtures of $\alpha$- and $\beta$-phases. Upon heating, the $\alpha$-phase Ca(BH)$_4$ cell parameter $a$ increased, whereas the $c$-parameter decreased up to phase transition to the tetragonal $\alpha'$-phase at 222°C. In situ synchrotron diffraction data taken between 44-382°C show all the three Ca(BH)$_4$ phases in the expanded X-axis, 20 scale, 10-22°, in the Figure 4. The changes in unit cell parameters and volume/ $\alpha$ of the unit cell, as a function of temperature, have been calculated form the data for the orthorhombic and tetragonal cells. The $\beta$-phase is 3.7-5.6% denser than the $\alpha$- and $\alpha'$-phases, depending on the temperature, the latter polymorphs transform into the stable $\beta$-phase in the temperature range of 177°C to 297°C. The unit cell parameters $a$ and $c$ (Å) and volume (Å$^3$) of the stable $\beta$-Ca(BH)$_4$, increase linearly with temperature (K): $a = 6.9187(1) + 2.821(7) \cdot 10^{-4} T$, $c = 4.54459(9) + 2.062(5) \cdot 10^{-4} T$, $V = 207.938(5) + 2.725(3) \cdot 10^{-2} T$. Further, $\beta$-Ca(BH)$_4$ completely decomposes between 382°C and 387°C. The phase transformations observed in the in situ synchrotron experiments are supported by thermogravimetric analysis (TGA) and difference scanning calorimetric experiments performed at the Sandia National Laboratories (not shown here). This study suggests that the decomposition products from a desolvated sample of Ca(BH)$_4$ and a solid-state prepared catalyzed sample of Ca(BH)$_4$ may be different from the high pressure synthesized sample.

Conclusions

1. Imide-Amide (Li,NH-LiNH$_2$) Impurity Effects (UNR Sample):
   - Studies on trace amounts of impurity gases (100 ppm) such as O$_2$, CO, H$_2$O, and CH$_4$ in H$_2$ and industrial hydrogen, up to ~1,100 cycles showed that the O$_2$ impurity was most detrimental to the cycling behavior of amide-imide hydrides. The H$_2$O (100 ppm) impurity surprisingly showed lower loss as compared with oxygen (100 ppm) impurity.
   - Carbon monoxide was the least reactive and did not show significant loss in capacity.
   - Cycling with methane showed a little loss in hydrogen capacity. Aging results also showed no significant loss in capacity.

2. Vapor Pressure Measurement of Mg(BH$_4$)$_2$ (Sample from GE):
   - No significant vaporization of Mg(BH$_4$)$_2$. Below 233°C it is not possible to record any vapor pressure data. However, above 233°C the $\Delta G^\circ$ becomes negative and vaporization starts. The $\Delta G^\circ$ of Mg(BH$_4$)$_2$ was determined. Mg(BH$_4$)$_2$ (s) $\rightarrow$ Mg(BH$_4$)$_2$ (g) ($\Delta H = 93.4$ kJ/mol) only ~2% of the vaporization. The majority of the vaporization was due to disproportionation of Mg(BH$_4$)$_2$ $\rightarrow$ Mg(s)+B(s)+4H$_2$(g), $\Delta H = 44.82$ kJ/mol (~98% majority hydrogen).

3. Structure and Phase Transformations in Ca(BH)$_4$ (UNR-SNL Sample):
   - In situ synchrotron data showed two polymorphs of $\alpha$-Ca(BH)$_4$, and a small amount of $\beta$-phase. A second order $\alpha \rightarrow \alpha'$ phase transition occurred at 222°C (confirmed by differential scanning calorimetry). Another phase transition, $\alpha' \rightarrow \beta$ phase upon heating above 297°C and decomposes at 382°C into unknown products which according to TGA is associated with a weight loss, likely due to release of hydrogen.

Future Directions

1. Continue Work on Effect of Impurities on Specific Contaminants: (a) Pressure cycling on mixed -Li based complex hydrides, (b) testing of hydrides developed by MHCoE partners.

2. Vapor Pressure Studies on LiBH$_4$ and other Borohydrides: Thermodynamics of vaporization of LiBH$_4$ and others.


5. Lattice Dynamics of Imide-amides (a) Hydrogen Lattice Dynamics Studies on Complex Hydrides, University of Rome – International Energy Agency/ International Partnership for the Hydrogen

6. Effect of Solid State impurities in complex Hydrides and Phase Equilibria: (a) Collaboration between Cantelli (Rome, Italy) and Chandra-Jensen, (USA), (b) IEA/IPHE Collaborative Studies at University of Geneva and CRNS (France) on defect structure thermodynamics and crystallography. Collaborative program between Chandra (USA)-Yvon (Switzerland)-Latroche (France).

FY 2008 Publications/Presentations


References


