IV.A.1 Amide and Combined Amide/Borohydride Investigations

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Fiscal Year (FY) 2011 Objectives

- Determine the sorption kinetics for the transition metal catalyzed $2LiH+Mg(NH_2)_2+MgH_2$ system under the full spectrum of temperatures and pressures required for hydrogen storage system design.
- Explore the effect of catalyst loading on both charge and discharge reaction pathways and kinetics as well as ammonia release.
- Identify reversible hydrogen storage compounds in the mixed metal/mix amide-borohydride system.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan in descending order of impact:

(A) System Weight and Volume
(E) Charging/Discharging Rates
(P) Understanding Chemisorption

Technical Targets

This project includes both fundamental studies of the sorption kinetics in the mixed metal amide, $LiH/Mg(NH_2)_2$ system, as well as new materials discovery in the mixed amide/borohydride system. Insights gained from these studies will be applied toward the design of storage systems that meet the following DOE 2010 and 2015 hydrogen storage targets (see Table 1 for values):

- System Gravimetric Capacity and Volumetric Density
- Charging/Discharging Rates
- Fuel Purity
- System Fill Time
- Minimum Hydrogen Delivery Rate

FY 2011 Accomplishments

- Majority of desorption products appear to be comprised of a mixture Mg_3N_2 and LiMgN while absorption products

TABLE 1. Technical Targets for Onboard Hydrogen Storage Systems for Light-Duty Vehicle Applications using LiMgN System[1]

Technical Target	Units	2010	2015	Ultimate	Spex milled	Fritsch milled	V_2O_5	Fe_2O_3	KH
Gravimetric Density	kg_{H_2}/kg_{system}	0.045	0.055	0.075	4.2	4.6	3.8	3.5	3.9
Volumetric Density	kgH_2/L	0.028	0.04	0.07	0.023	0.025	0.021	0.019	0.023
Fill Time[2]	Min	4.2	3.3	2.5	30	30	30	30	30
Min. Full Flow Rate[3]	$(gH_2/s)/kW$	0.02	0.02	0.02	0.024	0.016	0.019	0.022	0.024
Min./Max Delivery Temp.	°C	-40/85	-40/85	-40/85	180/200	180/200	180/200	180/200	180/200
Min./Max Delivery Pressure	Bar	5/12	5/12	3/12	1/100	1/100	1/100	1/100	1/100
Fuel Purity	%	99.97	99.97	99.97	TBD	TBD	TBD	TBD	TBD

[1] Values were determined from the average between the 2nd, 3rd and 4th isothermal absorption cycles for each system with the 1st cycle was excluded.
[2] Long fill times account for 2-step reaction, which accounts for approximately 60–80% H_2 absorbed.
[3] Assumed 80 kW fuel cell for reported data,
TBD – to be determined

are comprised of MgH_2, LiH, $Mg(NH_2)_2$ (confirmed by Raman spectroscopy) and unreacted Mg_3N_2.

- All chemical dopants tested thus far, while significantly increasing desorption rate in the first cycle, have been shown to have no effect on sorption kinetics after the third cycle.

- A characteristic charging time ($\tau 80$) of 30 minutes, calculated for the isothermal charging results, is faster than those presented for this material elsewhere in the literature.

- Processing methods have been shown to greatly affect sorption kinetics and capacity with high energy processing leading to formation of NH_3 and loss of capacity (6.66 wt%) while lower energy processes minimizing NH_3 release and resulting in higher capacities (8.0 wt%) and sorption kinetics.

✧   ✧   ✧   ✧   ✧

Introduction

In an effort to identify and synthesize a reversible metal hydride material capable of meeting the 2015 hydrogen storage technical targets, researchers are investigating various metal hydrides/catalyst combinations. To date, the most promising in situ reversible compound stemming from the Metal Hydride Center of Excellence is $2LiH/MgH_2/Mg(NH_2)_2$ [1,2]. This compound resides among a series of similar compound stoichiometries ranging from Li:Mg ratios of 1:1 through 4:1 [1-7]. It has been found that the greatest hydrogen absorbing material is $2LiH+Mg(NH_2)_2+MgH_2$ which decomposes to LiMgN plus 8.1 wt% H_2 [1] with a calculated enthalpy of desorption of 32 kJ/mole H_2. This composition has been reported to be reversible under fairly moderate conditions (160°C – 220°C for dehydriding, 160°C and 2,000 psi for rehydriding) [1]. This study of the LiMgN system used an autoclave-type high pressure charging apparatus and thermo-gravimetric analysis (TGA) measurements to confirm hydrogen storage capacities. The work reported in this investigation was designed to compliment the work of Lu *et al.* [1], by thoroughly measuring the isothermal kinetic hydrogen charge and discharge rates and further optimizing the kinetics through compositional adjustments.

Approach

LiH/Mg(NH$_2$)$_2$

The previously identified LiMgN material was studied by ball milling the precursor $LiNH_2$ and MgH_2 materials with the various modifiers to ensure a well-mixed and controlled initial state in terms of particle size. Material for this study was Frisch milled with a ball mass to material mass ratio of 30:1, following the work of Lu [1]. A Seivert's apparatus was used to measure the isothermal kinetics of

hydrogen charge and discharge. The hydrogen uptake was monitored by the drop in the hydrogen pressure in the system while hydrogen release is monitored by the rise in hydrogen pressure. The present studies are intended to provide a detailed understanding of the isothermal kinetics of charging and discharging of the material, and the effects of materials synthesis and chemical modifications to these rates. The parameters that are explored in the current study are charge and discharge temperature, charge pressure, and the composition of the modifiers used to activate the material.

The gravimetric capacities were determined from the average of the lowest and highest weight percent of hydrogen absorbed into the 1:1 $LiNH_2$:MgH_2 mixtures. The desorption weight percents were not included due to the lack of composition data for the off-gas stream. The following equation shows the calculations used to convert weight percent to kg_{H2}/kg_{media}:

$$wt\% \rightarrow {gH_2}/{g_{media}} \rightarrow {kgH_2}/{kg_{media}}$$

where g_{H2} is the average weight of hydrogen absorbed during recharge and g_{media} is the weight of the loaded sample prior to discharge. The volumetric capacity of the metal hydrides was calculated from the gravimetric capacity and the powder packing density of the hydrogen storage materials. The following equation shows the series of calculation used to convert weight percent hydrogen to volumetric capacity in kWh/L.

$$wt\% \rightarrow {gH_2}/{g_{media}} \times \rho_{media} \rightarrow {gH_2}/{mL} \rightarrow {kgH_2}/{L}$$

where ρ_{media} is the packing density of the powder. The material used in the determination of the density for the $LiNH_2$:MgH_2 mixture was a three gram sample of 1:1 $LiNH_2$:MgH_2 milled for 2 hours using a planetary mill with a ball mill ball mass to sample mass ratio of 30:1 (for every one gram of sample, 30 grams of ball mill balls were added to the vial prior to milling). A 10 mL graduated cylinder was then gradually packed with small quantities of the milled powder with the mass and volume occupied of the powder recorded at each interval. The powder was packed via tapping the bottom of the cylinder and by inserting a plunger to pack the top of the powder. This reduced the number of layers within the powder. The average powder packing density was determined to be 0.554 g_{media}/mL.

Mixed Amide/Borohydrides

The synthesis of materials was accomplished by ball milling one component metal borohydride ($Ca(BH_4)_2$, $Mg(BH_4)_2$) with another metal amide ($LiNH_2$). This is also extended for metal amides ($Ca(NH_2)_2$, $Mg(NH_2)_2$) with lithium borohydride ($LiBH_4$). These precursors such as $LiNH_2$, $LiBH_4$, and $Mg(BH_4)_2$ are available commercially

through Aldrich, with others such as $Mg(NH_2)_2$ and $Ca(NH_2)_2$ prepared by the ammoniation of Mg and Ca inside a high pressure reactor. Once the desired metal hydrides are ball milled, powder X-ray diffraction (XRD) was used as the initial screening tool. Furthermore, thermo-gravimetric analysis, in conjunction with mass spectroscopy, was used to verify mass loss vs. temperature and identify the gas decomposition products as a function of temperature. Fourier transform infrared, Raman and nuclear magnetic resonance were used to verify investigate the characteristics of new formed compounds.

Results

LiNH$_2$/MgH$_2$ Kinetics

Previously, we reported the charge and discharge profiles for precursor materials $LiNH_2$ and MgH_2 in a 1:1 mole ratio with 1.5 mol% $TiCl_3$, VCl_3, $ScCl_3$, $NiCl_2$, or TiN added dopant. From TGA-residual gas analysis (RGA) data, the initial hydrogen desorption temperature began between 105°C and 120°C, depending on the dopant composition, which is lower than the 135°C release temperature for the unmodified material. Compositional additions also greatly affect ammonia release. Mixtures with $TiCl_3$, VCl_3, $ScCl_3$ and $NiCl_2$ released ammonia at temperatures lower or equal to the unmodified material, approximately 230°C. The sorption profiles were measured using a Sievert's apparatus under isothermal conditions. A standard discharge condition of 260°C into a nominal 1 bar back pressure for ~6 hours was selected, along with a standard charge condition of 180°C under a nominal 100 bar pressure for 6 hrs. These conditions were selected to reach maximum charge and discharge capacities in a single work day and were used to compare differing compositions, dopants etc.

Previous MHCoE work [1,2] on this material indicated the presence of a LiMgN phase which was not definitively confirmed in this study. Instead, a Mg_3N_2 or partially substituted $(Li,Mg)_3N_2$ phase was detected using powder XRD analysis. Other researchers have observed the presence of alternate discharge products in this system as well [3]. After cycling, no discernable kinetic affect remained from the additions. It is concluded that once the metathesis reaction between $LiNH_2$ and the halide modifiers is complete, the added metallic species are no longer active in the sorption cycle. This work has highlighted the requirement of cycling these materials to reach a steady-state operating chemistry to evaluate the effectiveness of potential additives as kinetic aids.

In order to investigate the effect of various modifiers, material was prepared to the stoichiometric composition of $LiNH_2$:MgH_2 (1:1) with 1.5 mol% vanadium oxide (V_2O_5) or iron oxide (Fe_2O_3) via Spex milling. A mixture containing 4 mol% potassium hydride (KH) was also investigated based on literature reporting an increase in kinetics of the 2:1 $LiNH_2$:MgH_2 system with the addition of KH [4]. To

determine the onset of hydrogen and ammonia release, the samples were heated in the TGA at a rate of 5°C/min from 30°C to 400°C while the off-gas composition was determined from a connected RGA (Table 2).

TABLE 2. Summary of TGA/RGA Decomposition Data of the As-Milled Samples Without and Without and With Modifiers

No Modification	8.2	9.3	240	345	285°C
1.5 mol% Fe_2O_3	7.45	6.9	225	330	270°C
1.5 mol% V_2O_5	7.36	7.2	220	325	270°C
4 mol% KH	7.82	11.2	230	290	No ammonia detected

With the addition of oxide modifiers, the theoretical hydrogen capacity drops from 8.14 wt% to 7.45 wt% and 7.36 wt% for Fe_2O_3 and V_2O_5 respectively. The measured weight loss of the Fe_2O_3 modified sample was 6.9 wt% and 7.2 wt% for the V_2O_5 modified sample, which are both reasonably close to their respective theoretical capacities, indicating that the dehydrogenation process was complete without significant NH_3 release. The differences from theoretical weight capacity is attributed to the possible releasing hydrogen during the milling process. However, the KH-modified sample lost a total of 11.2 wt%, which is significantly more than the system's theoretical hydrogen content. Unlike the oxide modified samples, during the decomposition of the KH-modified sample there was no detectable release of ammonia. The addition weight loss can be attributed to the release of nitrogen gas. Desorption mechanisms for these systems are not well understood at this time.

The impact of the transition metal oxides and potassium hydride additions on average bed dis(re)charging rates were investigated with a discharge condition of 200°C into a nominal 1 bar back pressure for ~6 hours followed with a standard charge condition of 180°C under a nominal 100 bar pressure for 6 hrs.   The bed recharge rates were calculated on a mass-specific basis, determining from data the quantity of hydride bed that would be required to store 5 kg of hydrogen. The bed discharge rates are not included in the values reported in Table 2 due to the lack of information on the off-gas composition, especially the concentration of ammonia and nitrogen.

As seen from Figure 1, the discharge rate was dependent on the dopant composition and cycle. Initially, the oxide modified samples showed a slight improvement over the unmodified system during the first two desorption cycles. However, after the third desorption, both samples demonstrated a continual decrease in desorption rate while the unmodified sample began to increase its rate. The reduction in discharge kinetics over four cycles can potentially be attributed to exposure to high temperatures which led to significant coarsening of the particles resulting in lowered kinetics [5]. The potassium hydride modified sample showed significantly worse discharge rates than the other samples. This indicates potential interference
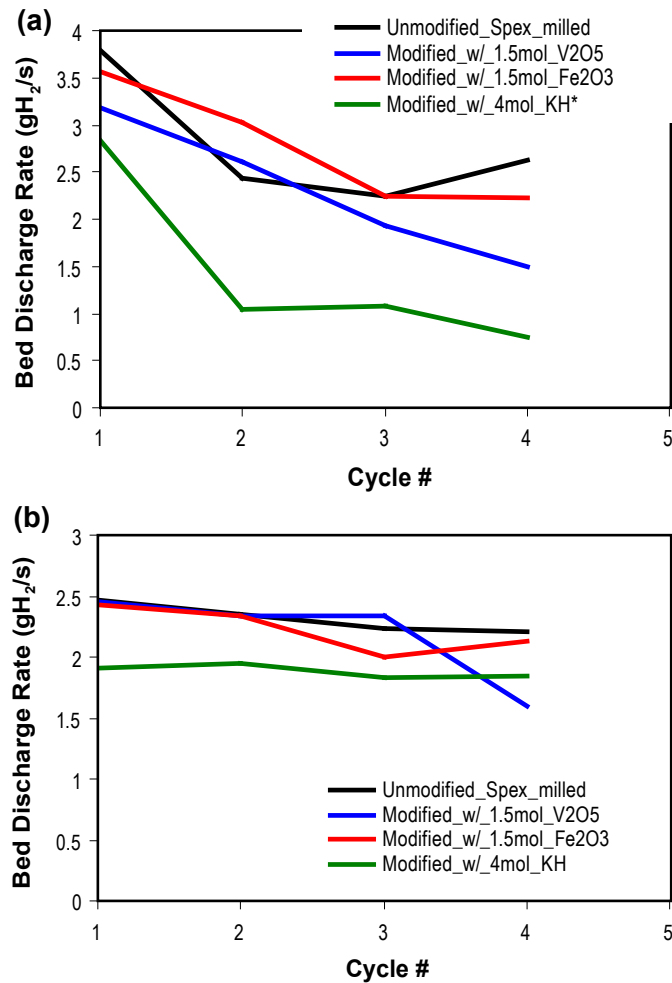
(a)

(b)

FIGURE 1. (a) Bed discharge (top) and (b) recharge (bottom) rate for unmodified (black), Fe_2O_3 (red), V_2O_5 (blue), and KH (green) modified samples. The cycling conditions are listed in the previous paragraph. (*Note: The KH sample was discharged into a smaller volume [1,030 mL] than the oxide and unmodified samples [1,190 mL] due to the use of a different pressure-concentration-temperature.)

of the modifier in the discharge reaction pathway, thus hindering the release of hydrogen from the system. An in situ diffraction study is needed to fully understand the interactions between the modifiers and the LiMgN system.

Unlike the discharge rates, the rate of recharging was not as dependent on composition of the modifier. However, the potassium hydride modified samples showed the slowest recharging rate, further indicating possible interference in the complex reaction pathway of the LiMgN system.

Mixed Amide/Borohydrides

Figure 2 shows the TGA results of $Mg(NH_2)_2$, $LiBH_4$, and various mixtures of $Mg(NH_2)_2/LiBH_4$. The unmodified samples show a much higher onset of decomposition with
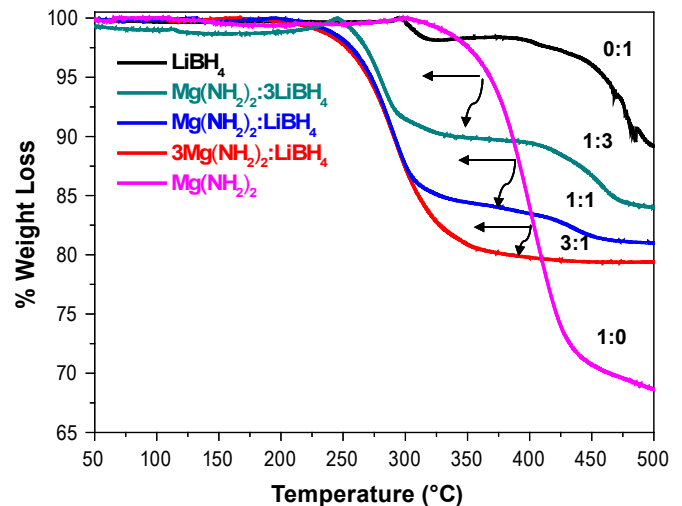

FIGURE 2. TGA Results for Mixed $Mg(NH_2)_2/LiBH_4$ Mixtures

respect to the mixtures. The addition of more $Mg(NH_2)_2$ resulted in a single decomposition similar to the starting amide material. This was also true for $3LiBH_4:Mg(NH_2)_2$, which had a 2-step decomposition reaction, but at a significantly lower temperature than pure $LiBH_4$. These samples were characterized using mass spectroscopy and XRD. From mass spectroscopy, the addition of $LiBH_4$ reduces the release of ammonia and increases the amount of hydrogen released. Similar results were found with the previously reported $Ca(NH_2)_2/LiBH_4$ systems, but the initial decomposition of the mixtures occur at a higher temperature. Isothermal Sievert's measurements were also conducted to evaluate the mixture's cyclic characteristics compared to their respective starting materials.

Conclusions and Future Directions

LiMgN

- Desorption at 260°C and above leads to the loss of essential nitrogen.
- The addition of Fe_2O_3 and V_2O_5 modifiers significantly reduced the amount of ammonia emission during the initial decomposition.
- V_2O_5 modified mixture showed faster sorption kinetics than the Fe_2O_3 mixture.
- Discharge rate of a hydride bed with transition metal oxide dopant at 200°C is a third of the 2010 DOE technical target of 3 g H_2/s.

Mixed Amide/Borohydrides

- Mixtures of $Mg(NH_2)_2$ with $LiBH_4$ have shown an decrease in the dehydrogenation temperature and an increase in the amount of hydrogen released.

The direction for future research is as follows:

- Couple experimental results with *ab-initio* calculations to identify kinetic enhancing mechanisms in complex metal hydride systems.
- Investigate the role of additional additives, which have been identified in other studies, on the kinetics.
- Study the role of ammonia release during cycling of modified $LiNH_2$: MgH_2.
- Determination of the transformation mechanism in $LiNH_2$:MgH_2 using Raman and infrared spectroscopy and neutron diffraction.
- Long-term cyclability studies to determine degradation in hydrogen capacity.
- Regeneration of $LiH/Mg(NH_2)_2$ using mix H_2/N_2 and H_2/NH_3 gas feeds for prolong cyclability.
- Further investigate the sorption characteristics of the $LiBH_4$ modified LiMgN system.

FY 2011 Publications/Presentations

Publications

1. Affects of mechanical milling and metal oxide additives on sorption kinetics of 1:1 $LiNH_2/MgH_2$ mixture, Donald L. Anton, Christine J. Price, and Joshua R. Gray, Energies, Accepted.

2. The Affects of Halide Modifiers on the Sorption Kinetics of the Li-Mg-N-H System, Christine Erdy-Price, Joshua Gray, Robert Lascola Jr, and Donald L. Anton, Special Edition AIChE in IJHE, Submitted.

Presentations

1. The Affects of Halide Modifiers on the Sorption Kinetics of the Li-Mg-N-H System, Christine Price, Joshua Gray, and Donald L. Anton, Fall AIChE Conference 2010, Salt Lake City, Utah.

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