

IV.A.1k Li-Mg-N Hydrogen Storage Materials

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Objectives

- Determine the sorption kinetics for the transition metal-catalyzed $2\text{LiH}+\text{Mg}(\text{NH}_2)_2+\text{MgH}_2$ 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) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

This project includes both fundamental studies of the sorption kinetics in the mixed metal amide, $\text{LiH}/\text{Mg}(\text{NH}_2)_2$ 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 target:

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

Accomplishments

- Desorption products in all cases considered appear to be the same (mixture of LiCl , Mg_3N_2 , LiMgN and a minor amount of an unidentified phase [$<5\%$]).
- All chemical modifications 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 (τ_{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.
- Additions of TiN have been shown to increase the release temperature of NH_3 from 220 to 250°C.
- The formation of mixed bi-metallic amides/borohydrides have resulted in lower dehydrogenation temperatures and reduced ammonia release compared to the individual amide or borohydride materials.



Introduction

In an effort to identify and synthesize a reversible metal hydride material capable of meeting the 2010 and 2015 DOE FreedomCar 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 (MHCoe) is $2\text{LiH}/\text{MgH}_2/\text{Mg}(\text{NH}_2)_2$ [1,2]. This compound resides among a series of similar compound stoichiometries ranging from $\text{Li}:\text{Mg}$ ratios of 1:1 through 4:1 [1-7]. It has been found that the greatest hydrogen absorbing material is $2\text{LiH}+\text{Mg}(\text{NH}_2)_2+\text{MgH}_2$ 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 used an autoclave-type high-pressure charging apparatus and transient thermogravimetric analysis (TGA) measurements to confirm hydrogen storage capacities. The work reported here 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.

Additionally, materials of the form $M^1M^2(BH_4)_x(NH_2)_y$, where $M^1 = Li, Na, K$ and $M^2 = Mg, Ca, Ti$ and/or other transition metals are of interest for their high hydrogen storage as well as potential novel phase properties. New materials of these di-anionic species such as $Li_4BH_4(NH_2)_3$ have been identified, which have been found to discharge initial hydrogen from the amide complex at lower temperatures with the borohydride present.

Approach

LiH/Mg(NH₂)₂

The previously identified LiMgN material was studied by ball milling the precursor LiNH₂ and MgH₂ 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 Sievert's apparatus was used to measure the isothermal kinetic rates of hydrogen charge and discharge. The present studies are intended to provide a detailed understanding of the isothermal kinetics of charging and discharging of the material, in addition to tabulations of the weight percent of hydrogen stored under specified conditions. 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.

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 (LiNH₂). This is also extended for metal amides ($Ca(NH_2)_2$, $Mg(NH_2)_2$) with lithium borohydride (LiBH₄). These precursors such as LiNH₂, LiBH₄, 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 analyses, 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 (FTIR), Raman scattering and nuclear magnetic resonance were used to verify investigate the characteristics of new formed compounds.

Results

LiNH₂/MgH₂ Kinetics

Previously, this study reported the charge and discharge profiles for precursor materials LiNH₂ and MgH₂ in a 1:1 mole ratio with 0.67 m% TiCl₃ catalyst loading. These profiles were measured using a Sievert's apparatus under isothermal conditions. Previous MHCoe work [1,2] on this material indicated the presence of a LiMgN phase which was not confirmed in this work. Instead, a Mg₃N₂ or partially substituted (Li,Mg)₃N₂ phase was detected using powder XRD. Other researchers have observed the presence of alternate discharge products in this system as well [8]. A standard discharge condition of 280°C into a nominal 1 bar back pressure for ~8 hours was selected (D-280°C/1 bar/8 hrs), along with a standard charge condition of 180°C under a nominal 150 bar pressure for 6 hrs (D-180°C/150 bar/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, catalysts etc. A traditional kinetic analysis on the 0.67 m% TiCl₃ doped material yielded an activation energy for hydrogen discharge of ~60 kJ/mol. A Johnson-Mehl-Avrami approximation was performed that indicated the reaction mechanism changes at least once during discharge cycle. Preliminary isoconversional kinetic analysis is consistent with the Johnson-Mehl-Avrami analysis, indicating that the discharge reaction occurs via a multi-step mechanism.

In order to investigate the effect of various modifiers, material was prepared at the stoichiometric ratio of LiNH₂:MgH₂ (1:1) with 1.5 mol% TiCl₃, VCl₃, ScCl₃, NiCl₂, or TiN added. The initial decomposition data for the modified material are shown in Table 1. By adding a modifier, the initial hydrogen desorption temperature of the began between 105°C and 120°C, lower than the 135°C release temperature for the unmodified material. Compositional additions also greatly affect ammonia release. As seen in Table 1, the mixtures with TiCl₃, VCl₃, ScCl₃ and NiCl₂ released ammonia at temperatures lower or equal to the unmodified material, approximately 230°C. Through a metathesis reaction between LiNH₂ and transition metal chlorides, modification resulted in the formation of LiCl and a transition metal through the release of NH₃. For all additions other than TiN, the H₂ and NH₃ peaks were coincidental. TiN additions decoupled the these two peaks, substantially increasing the NH₃ peak by

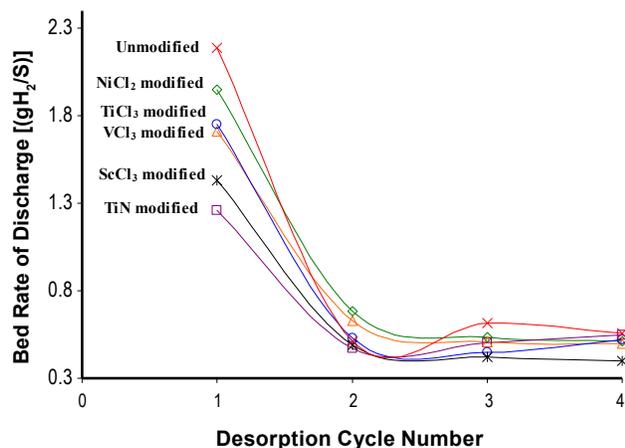
TABLE 1. Summary of TGA/residual gas analysis decomposition data of the as-milled 1:1 $\text{LiNH}_2:\text{MgH}_2$ samples without and with various additions while heating from 30°C to 400°C at 5°C/min.

Compositional Modification	Theoretical H_2 Weight%	Total Weight% Released	Initial Hydrogen Release Temperature (°C)	H ¹ (°C)	H ² (°C)	H ³ (°C)	Initial Ammonia Release Temperature (°C)	Ammonia Peak (°C)
No Modification	8.14	10.5	135	204	260	340	220	265
1.5 mol% TiCl_3	7.85	7.87	105	201	240	285	225	245
1.5 mol% VCl_3	7.46	6.5	115	190	245	290	225	250
1.5 mol% TiN	7.94	7.19	120	210	255	325	247	277
1.5 mol% ScCl_3	7.48	10.32	105	270	335	-	220	277
1.5 mol% NiCl_2	7.57	7.59 (by 300°C)	120	230	290	-	186	230

20°C while maintaining the H² peak at 270°C. Lai-Peng Ma, et al. have reported that for the 2:1 $\text{LiNH}_2:\text{MgH}_2$, the defective metal-N pairs in transition metal nitrides (specifically TaN and TiN) act as active sites in favor of dissociating the N-H bond of the amide in the system, which then promotes the generation of reactant species [9]. This suggests that TiN is not only effective at reducing the temperature of hydrogen release but also as acting as an ammonia mitigant.

The bed discharge 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. From these data, it was observed that after two sorption cycles (see Figure 1), the modifier composition has little effect on the discharging rate. This was determined to be due to the metathesis reaction between the metal chlorides and LiNH_2 .

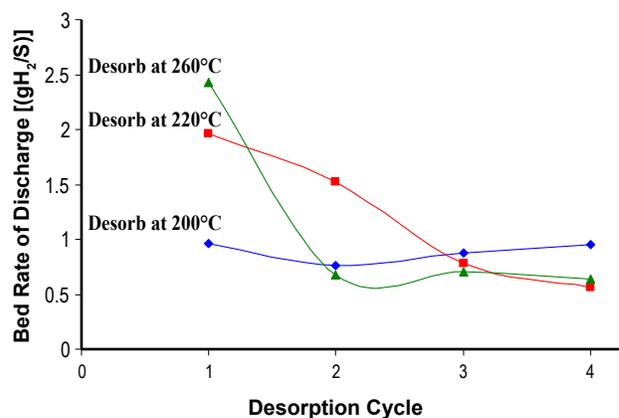
To optimize the cycling conditions, a desorption temperature study was conducted on the unmodified $\text{LiNH}_2:\text{MgH}_2$ mixture, as seen in Figure 2.

**FIGURE 1.** Rates of hydrogen discharge at 260°C into 1 bar of pressure during the first 30 minutes of each cycle for the unmodified (crosses), TiCl_3 (diamonds), VCl_3 (triangles), NiCl_2 (circles), ScCl_3 (asterisk), and TiN (squares) systems.

A strong effect of discharging temperature on the discharge rate is observed, with a more linear rate observed for the 200°C. The discharge rate associated with 200°C is a third of the 2010 DOE technical target of 3 gH_2/s .

Mixed Amide/Borohydrides

Figure 3 shows the TGA results of $\text{Ca}(\text{NH}_2)_2$, LiBH_4 , and various mixtures of $\text{Ca}(\text{NH}_2)_2/\text{LiBH}_4$. The unmodified samples show a much higher onset of decomposition with respect to the mixtures. The addition of more $\text{Ca}(\text{NH}_2)_2$ resulted in a single decomposition similar to the starting amide material. This was also true for $3\text{LiBH}_4:\text{Ca}(\text{NH}_2)_2$, 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 addition of $\text{Mg}(\text{NH}_2)_2$, but the initial decomposition of

**FIGURE 2.** Rates of hydrogen discharge at 200, 220, and 260°C into 1 bar of pressure during the first 30 minutes of each cycle for the unmodified system.

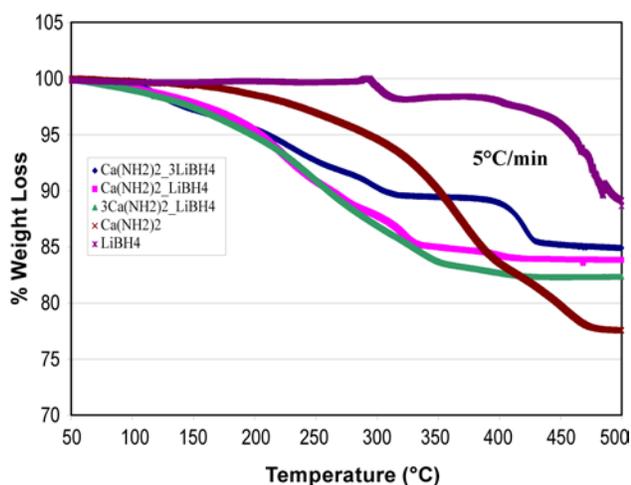


FIGURE 3. TGA results of various mixtures of $\text{Ca}(\text{NH}_2)_2$ and 2LiBH_4

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

LiMgN

- Desorption of LiMgN at 200°C resulted in a constant discharge rate over four isothermal cycles.
- Discharge rate of a hydride bed at 200°C is a third of the 2010 DOE technical target of $3 \text{ gH}_2/\text{s}$.
- Desorption at 260°C and above leads to the loss of essential nitrogen.
- Metathesis reaction between LiNH_2 and metal chlorides resulted in the loss of nitrogen through ammonia release and the loss of capacity with the formation of LiCl.
- Desorption products were identified as a mixture of LiCl, Mg_3N_2 , LiMgN with a minor amount, $<5\%$ of an unidentified phase.
- TiN shows promise as a modifier by increasing the temperature of ammonia release.

Mixed Amide/Borohydrides

- $\text{Ca}(\text{NH}_2)_2$ and $\text{Mg}(\text{NH}_2)_2$ have been successfully synthesized with $>95\%$ purity through direct ammoniation.
- Mixtures of $\text{Mg}(\text{BH}_4)_2$ and LiNH_2 have shown good absorption capabilities but limited kinetically on desorption through two cycles.

- Mixtures of $\text{Mg}(\text{BH}_4)_2$ and LiNH_2 contain multiple H_2 releases, with reduced release of NH_3 .
- Raman has confirmed that a new compound is formed in mixtures of NH_3BH_3 to $\text{Ca}(\text{BH}_4)_2$ and LiNH_2 .
- Initial results show desorption of H_2 as low as 150°C for the mixture of $\text{Ca}(\text{BH}_4)_2:\text{LiNH}_2:\text{NH}_3\text{BH}_3$.

Future Directions

- Complete temperature and pressure dependence on absorption rates.
- Test other catalysts to render faster kinetics, lower temperatures of operation (e.g. KH, LiH, LiBH_4 , nano-Ti, etc...).
- Analyze the purity of the discharged H_2 as a function of temperature using FTIR.
- Identify structures and compositions of $\text{Li}_x\text{Ca}(\text{BH}_4)_x(\text{NH}_2)_y$.
- Synthesize and characterize $\text{LiMg}(\text{BH}_4)_x(\text{NH}_2)_y$ and $\text{LiCa}(\text{BH}_4)_x(\text{NH}_2)_y$.
- Continue characterization of synthesized $\text{Mg}(\text{NH}_2)_2$ and $\text{Ca}(\text{NH}_2)_2$ with LiBH_4 as precursors for synthesis of $\text{LiMg}(\text{BH}_4)_x(\text{NH}_2)_y$ and $\text{LiCa}(\text{BH}_4)_x(\text{NH}_2)_y$.

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