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

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Objectives

- Determine the sorption kinetics for the transition metal catalyzed $LiH/Mg(NH_2)_2$ system.
- Verify reversibility conditions of $TiCl_3$ doped LiMgN.
- Explore the effect of catalyst loading on both charge and discharge reaction pathways and kinetics.
- 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 Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan in descending order of impact:

(A) System Weight and Volume
(B) Charging/Discharging Rates

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:

- 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%]).
- Ti is a catalyst for desorption but has minimal effect in absorption.
- Increased catalyst loading significantly affects H_2 discharge rate.
- Different kinetic modeling approaches are being applied to characterize and understand reaction mechanisms and to enable prediction of charge/ discharge rates under varying conditions.
- A characteristic charging time (τ80) of 30 minutes, calculated for the isothermal charging results, is faster than those presented for this material elsewhere in the literature.
- Reversible gravimetric storage density for the isothermal measurements is lower than that reported by Lu et al. [1] for the same material (~6.66 wt% versus ~8.0 wt%).
- The amorphous phase $Li_xCa(BH_4)_x(NH_2)_y$ resulted in a dehydriding temperature 100°C lower than $Ca(BH_4)_2$.

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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 $LiH/Mg(NH_2)_2$ [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 LiMgN, which was reported to be reversible under fairly moderate conditions (160°C–220°C for dehydriding, 160°C and 2,000 psi for rehydriding) [1]. Furthermore, the material has been reported to have a hydrogen storage capacity of (8.0–8.1) wt% [1], where the starting materials are $LiNH_2$ and MgH_2 combined in a (1:1) molar ratio with a small amount of $TiCl_3$ dopant. This study of the LiMgN used an autoclave-type high pressure charging apparatus and transient thermodynamic gravimetric 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.

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 TiCl$_3$ catalyst 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 35:1, following the work of Lu [1]. A Seivert'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 and discharge pressure, and the catalyst loading used to activate the material.

Mixed Amide/Borohydrides

The synthesis of materials was accomplished by ball milling one component metal borohydride (e.g. Ca(BH$_4$)$_2$) with another metal amide (e.g. LiNH$_2$). These precursors are available commercially through Aldrich, with others such as Mg(BH$_4$)$_2$, Mg(NH$_2$)$_2$ and Ca(NH$_2$)$_2$ prepared by established procedures [4-6, respectively]. Once the components metal hydrides are ball milled, powder X-ray diffraction (XRD) was used as the initial screening tool. Fourier transform infrared spectroscopy (FTIR), Raman and nuclear magnetic resonance will also be used to verify the formation of new compounds. Where ball milling does not yield suitable materials, wet chemical synthesis techniques will also be employed in which the metal hydrides are mixed within a suitable solvent under inert atmosphere. Subsequent procedures will be established to first purify the materials and to characterize their structures. TGA, in conjunction with mass spectroscopy, will be used to verify mass loss vs. temperature as well as to identify the gas decomposition products as a function of temperature.

Results

LiNH$_2$/MgH$_2$ Kinetics

Previously, this study reported the charge and discharge profiles for precursor materials LiNH$_2$ and MgH$_2$ in a 1:1 mole ratio with 0.67 mol% TiCl$_3$

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 Mg$_3$N$_2$ or partially substituted (Li,Mg)$_3$N$_2$ phase was detected using powder XRD. Other researchers have observed the presence of alternate discharge products in this system [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 will be used to compare differing compositions, catalysts etc.

A traditional kinetic analysis on the 0.67 mol% TiCl$_3$ 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 higher catalyst loading, material was prepared at the stoichiometric ratio of LiNH$_2$:MgH$_2$ (1:1) with 4 mol% TiCl$_3$ added. The data for the two catalyst loadings are shown in Table 1. The charge and discharge rates are calculated on a mass-specific basis and an extrapolated system basis, assuming a 72 kg hydride bed would be required to store 5 kg of hydrogen for an automotive application. From these data, it is observed that the catalyst loading has little effect on the charging rate and temperature has only a moderate effect on the charging rate. A maximum in charging rate is observed at approximately 180°C. A strong effect of charging pressure on the charge rate is observed, with a 500% increase in charging rate between 70 bar and 150 bar. The charging times associated with these rates required to reach 80% of the full charging capacity for a given experiment are ~30 min, which is within an order of magnitude of the DOE technical target for a charging time of 3 minutes.

The effect of catalyst loading on discharge time was also examined. The catalyst loading has a significant effect on the discharge rate of the material, with a 2.5x charging rate increase with a 2.5x increase in catalyst loading. This suggests that while catalyst loading may not be a significant parameter for the charging rates, it is very important to understand and optimize the catalyst for the discharge rate. The projected rate of discharge for the scaled-up bed approximation is ~1.8 gH$_2$/sec, which is the same order of magnitude as the requirement of a 80-100 kW fuel cell.

TABLE 1. Summary of charge and discharge data for $LiNH_2:MgH_2$ (1:1) as a function of $TiCl_3$ loading, temperature and pressure.

0.66 mol% $TiCl_3$ (4 wt%)		Rate [g H_2 / (s·g$_s$)]	Rate 72 kg bed	4 mol% $TiCl_3$ (13.7 wt%)		Rate [g H_2 / (s·g$_s$)]	Rate 72 kg bed
P	**150 bar**	**Charge**		**P**	**150 bar**	**Charge**	
Temp	160°C	2.0×10^{-5}	1.43	**Temp**	160°C	1.9×10^{-5}	1.40
	180°C	2.4×10^{-5}	1.73		180°C	2.5×10^{-5}	1.80
	200°C	1.9×10^{-5}	1.38		200°C	2.3×10^{-5}	1.68
	220°C	1.7×10^{-5}	1.26				
Temp	**160°C**	**Charge**		**Temp**	**180°C**	**Charge**	
P	70 bar	4.6×10^{-6}	0.330	**P**	70 bar	6.0×10^{-6}	0.430
	100 bar	1.2×10^{-5}	0.811		100 bar	1.2×10^{-5}	0.882
	150 bar	2.0×10^{-5}	1.43		150 bar	2.5×10^{-5}	1.80
Discharge				**Discharge**			
T = 280°C	P = 1 bar	1.0×10^{-5}	0.737	**T = 280°C**	P = 1 bar	2.4×10^{-5}	1.72

$Ca(BH_4)_2/LiNH_2$ (1:2 mol) Procedures

Calcium borohydride was purchased from Aldrich as an adduct $Ca(BH_4)_2*2$(tetrahydrofuran). Tetrahydrofuran was evacuated at 180ºC for 8 hrs. $LiNH_2$ (95% purity) was purchased from Aldrich and used as-is. Inside the glove box, $LiNH_2$ (0.329 g, 2.0 mol) was combined with $Ca(BH_4)_2$ (0.500 g, 1.0 mol) into a stainless-steel ball milling vessel along with eight small (0.635 cm diameter) stainless-steel balls. The vessel was put on a Fritsch planetary mill for four 30 min cycles. A white opaque solid was recovered.

Results and Discussion

The ball milled mixture between 2 moles of $LiNH_2$ and 1 mole of the undoped $Ca(BH_4)_2$ showed a main dehydriding event at a more favorable temperature between 250-350ºC. Further TGA analyses of the lone $LiNH_2$ and lone $Ca(BH_4)_2$ will be conducted to see whether or not there is a decrease in dehydriding temperature by mixing $LiNH_2$ and $Ca(BH_4)_2$.

Powder XRD pattern of the mixture between $LiNH_2$ and $Ca(BH_4)_2$ (2:1 mole) revealed that the mixture is largely amorphous. All the attendant peaks of the reactants $LiNH_2$ and $Ca(BH_4)_2$ have disappeared which may indicate that a reaction have taken place. Further characterization by FTIR and Raman spectroscopy will be done to see the extent of the N-H stretching shift which is caused by the rearrangement of the constituent hydrides in a newly formed compound.

Thermally programmed desorption analysis of the mixture (2 $LiNH_2$ + $Ca(BH_4)_2$) by Seivert's apparatus revealed that there is one main dehydriding event which begins at 170°C, accelerates at 250°C and ends at 310°C. The dehydriding temperature is approximately 100°C

less than that of the $Ca(BH_4)_2$ by itself (Figure 1). Mass spectrometry analysis of the discharged gas by residual gas analyzer revealed that hydrogen was the main gas released.

Conclusions

- 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%]).
- Increased catalyst loading significantly affects H_2 discharge rate.
- Ti^{+3} is a powerful catalyst for desorption but has minimal effect in absorption.
- A characteristic charging time (τ_{80}) of 30 minutes, calculated for the isothermal charging results, is faster than those presented elsewhere in the literature.
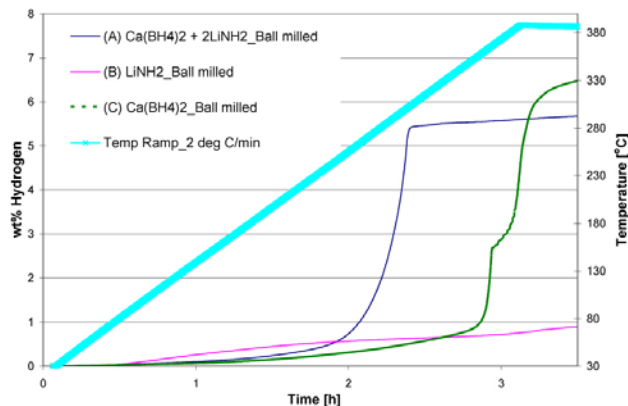

FIGURE 1. Thermally programmed desorption results of (**A**) a mixture between $Ca(BH_4)_2$ + 2$LiNH_2$ (**B**) $LiNH_2$ and (**C**) $Ca(BH_4)_2$.

- Gravimetric storage density for the isothermal measurements is lower than that reported by Lu et al. [1] for the same material (~6.66 wt% versus ~8.0 wt%).
- Ball milling $LiNH_2$ and $Ca(BH_4)_2$ (2:1 mole ratio) gave an amorphous phase. $Li_xCa(BH_4)_x(NH_2)_y$ having a dehydriding temperature at 100°C lower than component $Ca(BH_4)_2$.

Future Directions

- Test other catalysts to render faster kinetics, lower temperatures of operation (e.g. VCl_3, $NiCl_3$, $FeCl_3$…).
- Analyze the purity of the discharged H_2 as a function of temperature using a residual gas analyzer and FTIR.
- Identify structures and compositions of $Li_xCa(BH_4)_x(NH_2)_y$.
- Synthesize and characterize $LiMg(BH_4)_x(NH_2)_y$ and $LiCa(BH_4)_x(NH_2)_y$.
- Elucidate the origin of the reduction in dehydriding temperature.
- Synthesize $Mg(NH_2)_2$ and $Ca(NH_2)_2$ as precursors for synthesis of $LiMg(BH_4)_x(NH_2)_y$ and $LiCa(BH_4)_x(NH_2)_y$.

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