

IV.A.1c Chemical Vapor Synthesis and Discovery of H₂ Storage Materials: Li-Al-Mg-N-H System

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Objectives

- To develop advanced high capacity reversible hydrogen storage materials,
- To develop chemical vapor synthesis process for making nano particles for hydrogen storage, and
- To develop mechano-chemical process for synthesis and preparation of solid hydride materials.

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
- (E) Charging/Discharging Rates
- (J) Thermal Management

Technical Targets

As a partner in the Metal Hydride Center of Excellence (MHCoE), the team at the University of Utah is responsible for exploring the potential of materials and reactions related to amide materials. Based on this charter of the team, the following technical targets are set:

- The reversible hydrogen storage capacity should be higher than 5 wt%,

- The temperature of desorption should be below 300°C, preferably between 80 to 150°C, and
- The kinetic rate of dehydrogenation and hydrogenation must be sufficiently rapid to meet the requirements of fuel cells.

Accomplishments

- Using pressure-concentration-temperature (PCT), confirmed that LiMgN is a reversible material with 6.6 wt% or greater capacity, characterized reaction mechanisms with X-ray diffraction (XRD), Fourier transform infrared (FTIR), and nuclear magnetic resonance (NMR).
- Elucidated the cycling mechanism for Li₃AlH₆ + 3LiNH₂.
- Identified the critical dependence of the regeneration of Li₃AlH₆ on the heating rate of hydrogenation process.
- Developed and used pH-ion meter capability to quantify the concentrations of NH₃ during dehydrogenation.
- Identified the role of heating rate in NH₃ release from hydrogenated LiMgN.
- Conducted preliminary measurement of the reaction enthalpy of LiMgN.
- Achieved improved desorption properties of 7MgH₂/TiH system prepared by high-pressure, high-energy milling.
- Made nano-sized Al powder using the chemical vapor synthesis (CVS) method.



Introduction

As an integral part of the overall MHCoE project, the team at the University of Utah focuses on three aspects: the discovery, synthesis, and processing of nanocrystalline metal hydride materials for hydrogen storage applications.

The discovery of new metal hydride is particularly crucial because the properties of materials or material systems available to date do not meet the targets set by DOE. The synthesis of nanocrystalline metal hydride material has two aims: 1) improving the kinetic properties of both dehydrogenation and hydrogenation reactions through use of nano-scaled metal hydride materials, and 2) addressing the issues of mass production of selected metal hydrides that will

be needed in the future. The study on processing of metal hydrides is also necessary because the results have shown that the properties of metal hydrides during cycling have strong dependences on how these materials are processed or prepared.

Built on the accomplishments of Fiscal Year 2007, we focused on two reaction-based material systems: the reaction between lithium hexaluminum hydride (Li_3AlH_6) and lithium amide (LiNH_2) and binary lithium magnesium nitride (LiMgN). The reversibility of lithium hexalanate as a function of processing conditions was studied. The hydrogen storage properties of LiMgN was further explored using differential thermal analysis, PCT, and NMR. The results demonstrate that LiMgN is indeed a reversible hydrogen storage material with a demonstrated reversible capacity between 6.0 to 8.0 wt%. The kinetics of hydrogen storage reactions using LiMgN is currently under investigation. This is a material system closer to meeting DOE targets than many other materials that are under consideration.

Approach

The basic approach that we took for discovery of new materials is select candidate materials for experiments based on fundamentals of inorganic chemistry as well as the predictions of theoretical thermodynamic modeling. We focused on possible reactions involving alanates, amides, and nitrides. Once a candidate material is identified and prioritized, experimental screening of selected reactions will then be carried out.

A CVS process has been developed for the synthesis of nano-sized metal hydrides precursor powders. The primary advantage of the CVS process is that it yields materials with homogeneity at the atomic level. The CVS process is also very flexible for fine tuning chemical formula of materials.

A high-energy high-pressure reactive milling process has been developed for the synthesis of non-equilibrium metal hydride materials that cannot be synthesized otherwise. The Utah team is also assisting other partners in the MHCoE including Sandia National Laboratories, HRL Laboratories, and Brookhaven National Laboratory on the preparation of powder materials for detailed studies.

Results

Reactions of Lithium Hexahydroaluminum Hydride (Li_3AlH_6) with Amides

In FY 2008, we continued research on the reaction of $\text{Li}_3\text{AlH}_6 + 3\text{LiNH}_2$, specifically focusing on understanding reaction mechanisms and the dependence of the reaction pathway on material processing parameters. The effect of heating rate on the hydrogenation reactions of the mixture of $3\text{Li}_2\text{NH}/\text{Al}/4\text{wt}\%\text{TiCl}_3$ was investigated. The hydrogenated products were characterized by thermogravimetric analysis (TGA), XRD and solid-state NMR. Using the weight loss as an indicator of the reformation of Li_3AlH_6 from Li_2NH and Al, Figure 1 shows that the mixture can

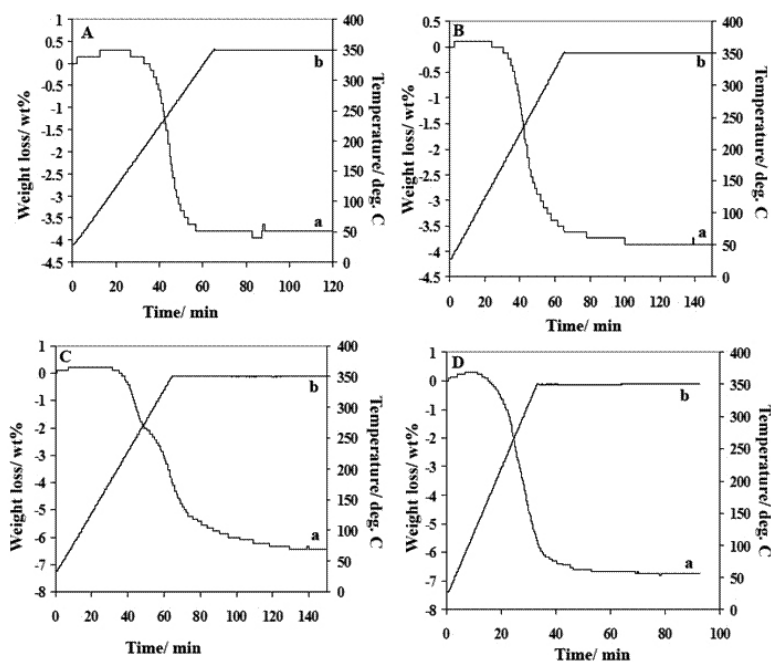
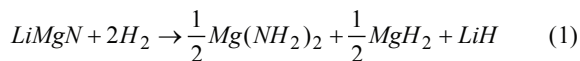


FIGURE 1. TGA Weight Loss of Hydrogenated $\text{Li}_2\text{NH} + \text{Al}$ Mixture using Different Heating Rates

be hydrogenated, resulting in Li_3AlH_6 formation, under 172 bar hydrogen pressure and 300°C with a heating rate faster than $5^\circ/\text{min}$. Only partial hydrogenation ($\text{Li}_2\text{NH} \leftrightarrow \text{LiNH}_2 + \text{LiH}$) is achieved when the heating rate is slower than $2^\circ/\text{min}$. The formation of the Li_3AlH_6 phase dominates when faster heating rates are used, while the formation of nitride species occurs when slow heating rates were used. The dehydrogenation and rehydrogenation reaction pathways and possible mechanisms of the combined system are, however, still under investigation.

Potential of Lithium Magnesium Binary Nitride for Hydrogen Storage

LiMgN was discovered in FY 2007 as a candidate material for reversible hydrogen storage by both MHCoe theoretical modeling group (Dave Sholl and Karl Johnson) and the experimental team of the University of Utah. In FY 2008, experimental studies were carried out to further characterize and explore the potentials of LiMgN . We were able to demonstrate that TiCl_3 -doped LiMgN can reversibly store up to 8 wt% H_2 by hydrogenating it in a custom-made autoclave. Based on the data of XRD, FTIR, and NMR, the following reaction is proposed as the most likely overall reversible reaction:



Preliminary study of LiMgN using PCT measurement was also carried out. The plateau pressure of 1st adsorption for this material has been shown at about 1 and 20 bar at the temperature of 240°C with 6.6 wt% H_2 adsorption. Figure 2 shows a temperature-programmed adsorption (TPA) curve for the TiCl_3 -doped LiMgN , which is obtained from the PCT apparatus under 140 bar H_2 pressure. It shows that 6.8 wt% H_2 was recharged under the current conditions. However, several aspects of the preliminary PCT results are indeed “preliminary.” For example, only partial

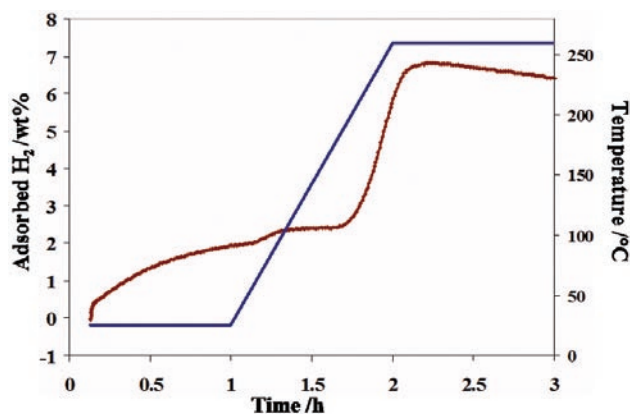


FIGURE 2. TPA Analysis of LiMgN

rehydrogenation was achieved using PCT. Possible explanations are that the H_2 back pressure might hinder the further dehydrogenation.

Regarding the NH_3 issue, an experimental set up connecting a pH-ion meter to the TGA gas outlet allowed us to measure quantitatively in situ the concentration of NH_3 in the gas flow. It was determined that during the dehydrogenation of hydrogenated LiMgN the concentration of NH_3 reaches as high as 15-20 ppm at approximately $150\text{-}200^\circ\text{C}$. However, during continuous dehydrogenation, NH_3 concentration drops to minimum (<1 ppm). We also found that the NH_3 co-production from the hydrogenated LiMgN depends strongly on the heating rate. When fast heating rates ($>10^\circ\text{C}/\text{min}$) are used, significant higher concentration of NH_3 ($>5,000$ ppm) is detected.

Investigation of the $\text{MgH}_2 + \text{TiH}_2$

Nano-scaled Mg-Ti-H mixtures prepared by high-energy, high-pressure reactive milling were investigated. The TGA and XRD data indicate that the $7\text{MgH}_2/\text{TiH}_2$ mixture decomposes into metallic Mg and TiH_2 , releasing a large amount of hydrogen (5.91 wt%) between 126 and 313°C . This hydrogen release temperature was lower by about 255°C than that of as-received MgH_2 and fast dehydrogenation kinetics was achieved within 60 minutes at a heating rate of $5^\circ\text{C}/\text{min}$. The activation energy (E_a) for the dehydrogenation of the milled $7\text{MgH}_2/\text{TiH}_2$ was measured to be 71 kJ/mol, which is significantly lower than that determined for the as-received MgH_2 or milled MgH_2 by 153 and 96 kJ/mol, respectively. The activation energy is further reduced to 68 kJ/mol when the molar ratio of Mg:Ti was decreased from 7:1 to 4:1, which causes a decrease in the hydrogen storage capacity from 5.91 to 4.82 wt%. Thus, MgH_2 combined with TiH_2 significantly reduces the activation energy of MgH_2 dehydrogenation.

In order to further confirm the role of TiH_2 , different Ti species including Ti and TiCl_3 instead of TiH_2 were milled under the same condition as that of $7\text{MgH}_2/\text{TiH}_2$. TGA results indicate that the onset temperature of the dehydrogenation is increased when TiH_2 is replaced by Ti or TiCl_3 . The hydrogenation experiment of the dehydrogenated sample proved that the properties of dehydrogenation reaction of the Mg-Ti-H system remained nearly unchanged after five cycles of dehydrogenation and rehydrogenation.

Chemical Vapor Synthesis of Metal Hydride Precursor Materials

One of the objectives of our project is to demonstrate the feasibility of making nano-sized metal hydride precursor materials using the CVS method. Nano-sized aluminum powder with size range of ~ 50 nm was synthesized using a modified CVS

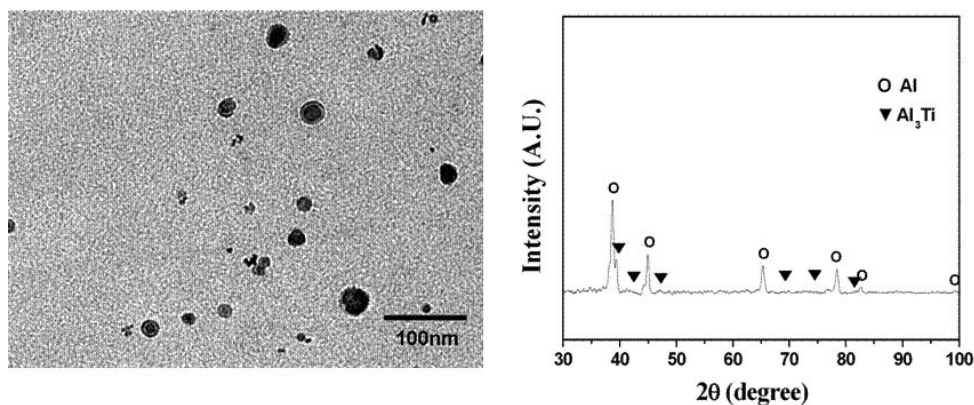


FIGURE 3. Transmission Electron Microscopy Image of CVS Al Powder and XRD Pattern of the Ti-doped Al Powder

system. The size of the product powder was much smaller in comparison to the previous results. Ti-doped aluminum powder was successfully synthesized using the premixed 4 mol% $\text{TiCl}_3\text{-AlCl}_3$ precursor. Energy dispersive spectrum and XRD results showed that Ti was distributed uniformly in the nano-sized aluminum powder and small amount of Al_3Ti intermetallic compound was formed in the product powder (Figure 3).

CVS of nano- MgB_2 powder was carried out with BCl_3 precursor and Mg. Unfortunately, unwanted phases instead of MgB_2 were found due to the reaction of the precursor with the alumina reactor.

The feasibility of producing hydrogen storage precursor materials has been proven particularly for the Li-Mg-N system. The most recent advancements with this include the PCT and temperature-programmed

desorption/TPA measurements using the Sievert-type analysis for determination of hydrogen release pressure and confirmation of hydrogen storage capacities. The CVS storage materials have shown strong similarities to the ball milled equivalent, with respect to hydrogen storage capacity, dehydrogenation pressures and uptake/release kinetics. A PCT curve for desorption of the ball milled and CVS powders is shown below in Figure 4. The main concerns for the CVS process are contamination of reagents and forming the desired product phase, however, these problems can be minimized through careful control of the experimental procedure. The main impurities in the CVS system include metal oxides (LiO_2 and MgO), lithium cyanamide (Li_2NCN) and alternate metal nitrides (Mg_3N_2 , Li_3N) as a by-product of the reaction. The oxide phases can

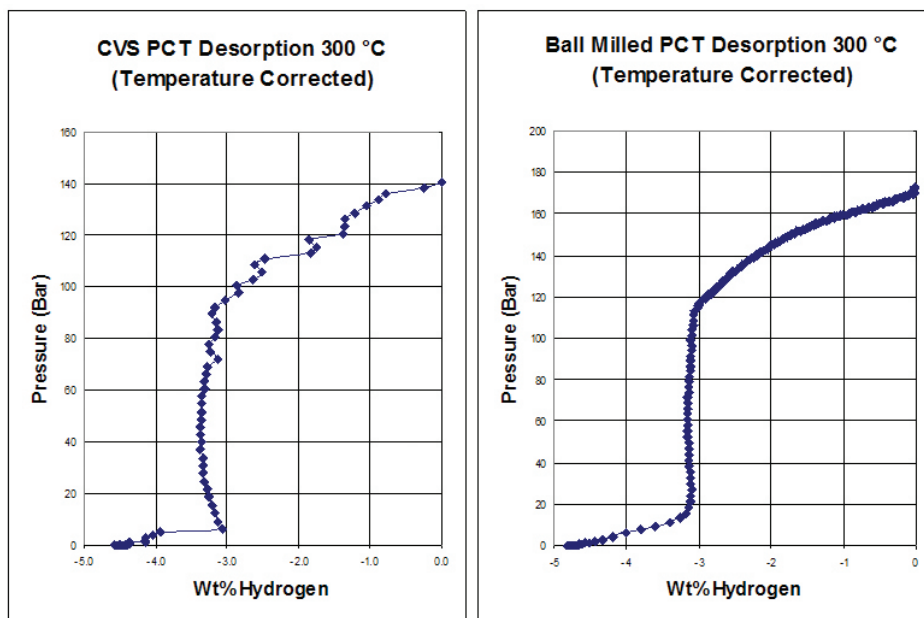


FIGURE 4. PCT desorption curves for CVS and ball milled hydrogen storage materials in the Li-Mg-N-H system. Although the curves are very similar, the CVS powders show a slightly lower set of plateau pressures.

be minimized by purging the reactor system extensively and using ultra-high purity gases, the cyanamide phase is likely a result of leaching carbon from stainless steel components and can be minimized by proper material selection and the nitrides can be removed.

Conclusions and Future Directions

Conclusions

- It is confirmed that LiMgN can be recharged with hydrogen with a reversible capacity between 6 to 8 wt%. The likely reaction pathways were identified. However, details of the reaction mechanisms are yet to be fully understood.
- The reverse formation of Li_3AlH_6 was shown to depend on the heating rate of hydrogenating processes. Kinetics controlled limited multiple reaction pathways are possible in the temperature range from 100 to 300°C.
- A simple but reliable method is established for quantitative measurement of the concentration of NH_3 in the gas stream during dehydrogenation. It was determined that the NH_3 concentration during dehydrogenation of the hydrogenated LiMgN material is primarily in the range of less than 1 ppm. The concentration could however peak as high as 15 to 20 ppm.
- The CVS method is used to produce Ti doped nano Al powders. CVS is also demonstrated as a tool for synthesizing LiMgN powders.

Future Directions

- Comprehensive characterization of thermodynamic properties of hydrogenation and dehydrogenation reactions of LiMgN.
- Characterize the kinetic properties of the hydrogen storage reactions using LiMgN.
- Study methods to improve the kinetics of the hydrogen storage reactions using LiMgN.
- Complete mechanism studies of the reformation of Li_3AlH_6 from Al and Li_2NH mixture.
- Produce sufficient quantities of Ti-doped nano Al powders as precursors for regeneration of AlH_3 .
- Characterize the hydrogen storage properties of the $\text{MgH}_2\text{-TiH}_2$ mixtures prepared by high energy milling process.

Special Recognitions & Awards/Patents Issued

1. Mr. Jun Lu, a Ph.D candidate student of Professor Zak Fang, was selected for “silver award for graduate student” at the MRS Spring meeting in April 2008 at San Francisco for his presentation entitled “Potential Hydrogen Storage Properties of LiMgN”.

FY 2008 Publications/Presentations

1. Jun Lu, Zhigang Zak Fang, Young Joon Choi, Hong Yong Sohn, Robert C. Bowman Jr., Son-Jong Hwang and Chul Kim, “Study of the Reaction Mechanism of Li-Al-N-H System during the Hydrogenation Process”, *Submitted to J. Power Sources*, May, 2008.
2. Jun Lu, Zhigang Zak Fang, Young Joon Choi, and Hong 1. Yong Sohn, “Effect of Mechanical Milling of N-containing Hydrogen Storage Materials” *In preparation*.
3. Young Joon Choi, Jun Lu, Zhigang Zak Fang, and Hong Yong Sohn, “Hydrogen Storage Properties of the Mg-Ti-H System Prepared by High-Energy-High-Pressure Reactive Milling”, *J. Power Sources*, 180(1), 491-497, 2008.
4. Jun Lu, Zhigang Zak Fang, Hong Yong Sohn, Robert C. Bowman Jr. and Son-Jong Hwang “Potential and Mechanism of Li-Mg-Al-N-H system for reversible hydrogen storage”, *J. Phys. Chem. C*, 111(44), 16686-16692, 2007.
5. Jun Lu, Zhigang Zak Fang, Young Joon Choi, and Hong Yong Sohn, “Potential of Ternary Nitride (LiMgN) for Hydrogen Storage Application” *J. Phys. Chem. C*, 111(32), 12129-12134, 2007.
6. Jun Lu, Zhigang Zak Fang and Hong Yong Sohn, “A Hybrid Method for Hydrogen Storage and Generation from Water” *J. Power Sources*, 172(2), 853-858, 2007.
7. Jun Lu, Zhigang Zak Fang, Hong Yong Sohn, Robert C. Bowman Jr., Son-Jong Hwang “Potential and Reaction Mechanism of Li-Mg-Al-N-H System for Reversible Hydrogen Storage”, *MRS Spring Meeting*, 2008-03-26, San Francisco, CA.
8. Z. Zak Fang and H.Y. Sohn, “Understanding and Discovery of H_2 Storage Materials Involving Metal Amides”, *DOE Annual Review Meeting*, Washington, D.C., June 9-13, 2008.
9. Z. Zak Fang, Jun Lu, Brady Butler and H. Y. Sohn, “Hydrogen Storage Materials Based on Li-Al-Mg-N System”, *International Symposium on Metal-hydrogen Systems (MH2008)*, Reykjavik, Iceland, June 24-28, 2008.
10. Zhigang Zak Fang, Jun Lu and H. Y. Song, Hydrogen Storage Materials Based on N-containing material systems, *AICHE Annual meeting*, Salt Lake City, UT, November 4-9, 2007.
11. Jun Lu, Z. Zak Fang*, and H. Y. Sohn “Potential of LiMgN for Reversible Hydrogen Storage,” *MRS Fall Meeting*, 2007-11-26, Boston, MA.
12. Y. J. Choi, Jun Lu, H. Y. Sohn, and Zhigang Zak Fang “Hydrogen Storage Properties of the Mg-Ti-H System Prepared by High-Energy-High-Pressure Reactive Milling,” *2007 AICHE Annual Meeting*, Salt Lake City, Utah, November 4-9, 2007.