

## IV.A.5g Chemical Vapor Synthesis and Discovery of H<sub>2</sub> Storage Materials: Li-Al-Mg-N-H System

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### Introduction

As an integral part of the overall Metal Hydride Center of Excellence (MHCoe) program, 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 a 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 nanoscaled 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.

We believe the synthesis and discovery are integral parts of the R&D efforts. During the course of this project, an important finding was made which indicated that a 7 wt% hydrogen storage system (on material basis) can be achieved by utilizing a reaction between lithium hexaluminum hydride (Li<sub>3</sub>AlH<sub>6</sub>) and lithium amide (LiNH<sub>2</sub>) or magnesium amide (Mg(NH<sub>2</sub>)<sub>2</sub>).

The reversibility of lithium alanate or hexalanate is made possible by the presence of amide materials. It was also discovered that lithium magnesium binary nitride (LiMgN) can be used for hydrogen storage with a demonstrated reversible capacity of 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

With respect to the scope of our project as outlined in the Introduction, the technical approach is summarized as follows:

#### Discovery of New Materials

During FY 2006, the basic approach that we took for discovery of new materials was based on the fundamentals of inorganic chemistry. We focused on possible reactions involving alanates, amides, and nitrides. We also relied on theoretical modeling results within the MHCoe or in the public literature for ideas and concepts. Once a plausible concept is formed, debated, and prioritized, we will take actions by carrying out experimental research of selected reactions.

#### Synthesis and Processing

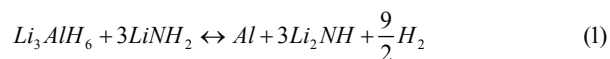
A chemical vapor synthesis (CVS) process is being developed for the synthesis of nanosized metal hydrides precursor powders. The primary advantage of the CVS process is that it yields materials with homogeneity at the atomic level. The CVS process is also very flexible for fine tuning the chemical formula of materials. The Utah team is also currently experimenting with the application of the CVS technique for incorporating metals in a carbon aerogel.

A high energy, high pressure reactive milling process has been developed. It is widely expected that a high pressure H<sub>2</sub> reactive milling method will be very useful 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 the University of Illinois at Urbana-Champaign (UIUC) on the preparation of powder materials for detailed studies.

## Results

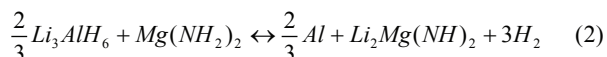
### Reactions of Lithium Hexahydroaluminum Hydride ( $\text{Li}_3\text{AlH}_6$ ) with Amides

In FY 2005, a new material/reaction system that can potentially be used for hydrogen storage was discovered. This material system is based on the reaction between lithium hexaluminum hydride and lithium amide. The overall reaction is shown by the following equation:

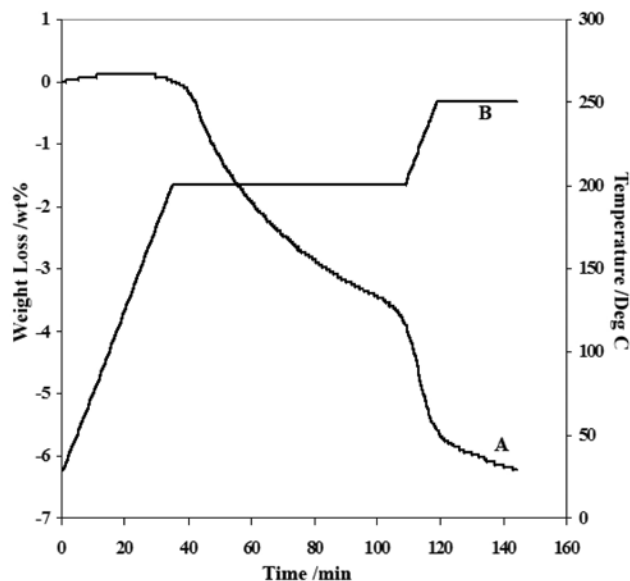


The results indicated that this reaction is reversible, producing approximately ~7 wt%  $\text{H}_2$ .

In FY 2007, we continued on this path of finding potential materials and systems based on the reactions of  $\text{Li}_3\text{AlH}_6$  with amides. Specifically, the reaction of magnesium amide ( $\text{Mg}(\text{NH}_2)_2$ ) with  $\text{Li}_3\text{AlH}_6$  was investigated. Figure 1 shows the thermal gravimetric analysis (TGA) of the samples after three cycles of dehydrogenation and hydrogenation. It shows that the reaction, given as follows, is reversible with a reversible hydrogen storage capacity of approximately 6.0 wt%.



The reactants and products of the hydrogenation and dehydrogenation reactions were characterized using nuclear magnetic resonance (NMR). The results, as shown in Figure 2, clearly confirm the rehydrogenation of  $\text{Li}_3\text{AlH}_6$  from  $\text{LiH} + \text{Al} + \text{H}_2$ . The

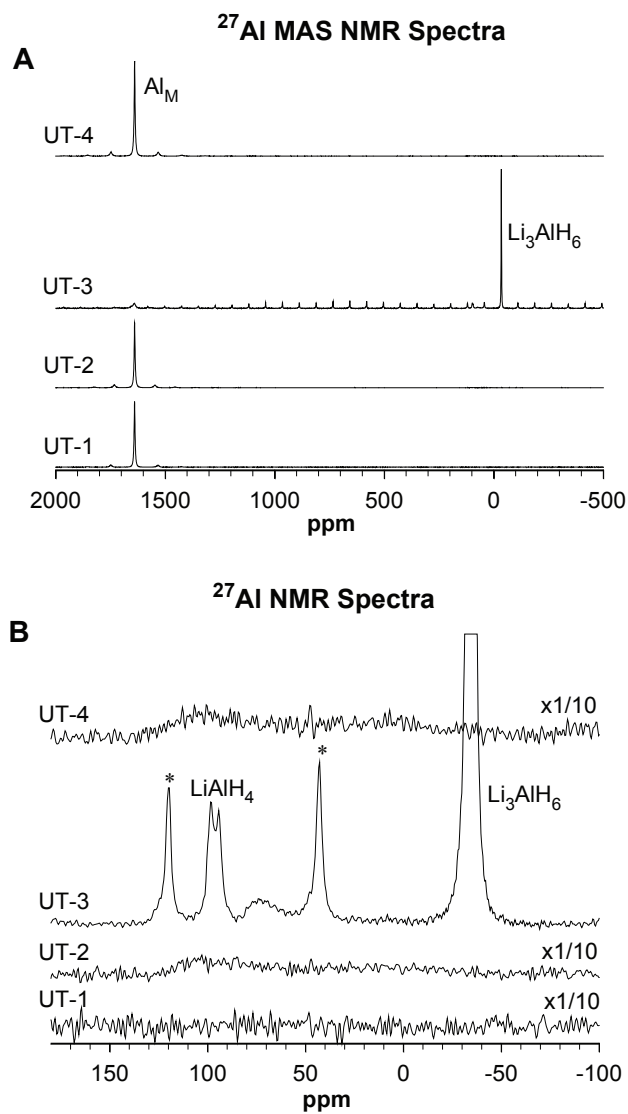


**FIGURE 1.** TGA Analysis of the Dehydrogenation of  $2\text{Li}_3\text{AlH}_6 + 3\text{Mg}(\text{NH}_2)_2$  Reaction

rehydrogenation of  $\text{Li}_3\text{AlH}_6$  is a very important result because rehydrogenation of lithium alanates, including  $\text{Li}_3\text{AlH}_6$  and  $\text{LiAlH}_4$ , has been extensively studied and is well known to be very difficult. We believe that the rehydrogenation of  $\text{Li}_3\text{AlH}_6$  is at least partially due to the presence of amides. The “destabilization” effect of lithium and magnesium amide is an important scientific issue that we will further study in FY 2007 and 2008.

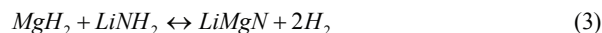
### Potential of Lithium Magnesium Binary Nitride for Hydrogen Storage

During the course of searching for new materials, we analyzed some of the published reactions involving  $\text{MgH}_2$  and  $\text{LiNH}_2$ . We found that by varying the molar ratio, the reaction between  $\text{MgH}_2$  and  $\text{LiNH}_2$  yields different results, which is supported by published work



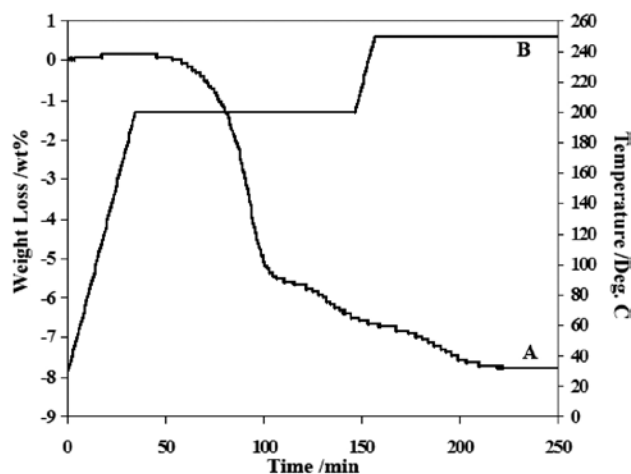
**FIGURE 2.**  $^{27}\text{Al}$  NMR Spectra that Provide Evidence for the Rehydrogenation of  $\text{Li}_3\text{AlH}_6$

in the literature by various labs. The reaction of  $MgH_2$  with  $LiNH_2$  in a 1:1 molar ratio was of particular interest to us. The reaction equation is



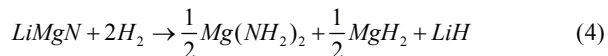
The modeling group at Carnegie Mellon University (CMU) and the University of Pittsburgh calculated the heat of reaction (3), showing that it appears to be an attractive reaction for hydrogen storage.

An experimental study was carried out to explore the potentials of  $LiMgN$ . Figure 3 shows the TGA of hydrogenated  $LiMgN$  after five cycles of hydrogenation and dehydrogenation. It demonstrates that  $LiMgN$  can reversibly store up to 8 wt%  $H_2$ . This is a remarkable



**FIGURE 3.** TGA Curves for  $TiCl_3$ -doped  $LiMgN$  after Five Hydrogenation/Dehydrogenation Cycles at Hydrogenated State

result. X-ray diffraction (XRD), Fourier transform infrared (FTIR), and NMR analysis showed that the reversible reaction, however, does not follow that of reaction 3. Based on the information that we have been able to collect to date, the following reaction is proposed as a likely scenario of the reversible reaction pathways.



It is noted that the total mass of the products of reaction (4) is the same as that of the starting mixture  $MgH_2 + LiNH_2$ .

Further detailed characterizations of the thermodynamic and kinetic properties of the reversible  $H_2$  storage reactions using  $LiMgN$  will be a focus of our work in FY 2007-2008.

### Chemical Vapor Synthesis of Metal Hydride Precursor Materials

One of the objectives of our project is to demonstrate the feasibility of making nanosized metal hydride precursor materials using the CVS method. This objective has been achieved and the work is continuing on making precursor materials using the CVS technique. Several nanosized metal powders have been made using the CVS methods including Li,  $Li_3N$ , Li/Mg, Al, and  $Mg_2Si$ . Current efforts are focused on making nanosized Al and catalyzed/doped Al as raw materials for hydrogenation experiments at Brookhaven National Laboratory and Savannah River National Laboratory, and nano  $MgB_2$  powders to support work at HRL and UIUC.

Table 1 lists the performance of the metal hydrides of this project.

**TABLE 1.** Selected Reversible Hydrogen Storage Material Systems

Properties	$MgH_2/Ni^{nano}$	$NaAlH_4$	$2LiH/LiNH_2$	$MgH_2/2LiNH_2$	$LiBH_4/1/2MgH_2$	$Li_3AlH_6/3LiNH_2$	$2/3Li_3AlH_6/Mg(NH_2)_2$
Theoretical reversible wt% $H_2$	7.6	6.5	10.4	5.6	11.4	7.3	6.5
Demonstrated reversible wt% $H_2$	6.5	5.5~6.0	9.3	5.2	8-10	7.1	6.1
Desorp. Temp (°C)	150-250	150~250	200~450 vacuum	100~250	315-400	160-300	100~240
Adsorp. Temp (°C)	150	180	170-255	100~200	315-400	200-300	200-300
Isothermal Plateau Pressure	<1 (250)	~10 (180) ~130 (180)	0.2 (230°C) 1.0 (255°C)	46 (200°C)	1 (255)	1 (255°C) 60 (375°C)	TBD
Kinetics	Slow	Good	Good	Good	Very Slow	TBD	TBD

## Conclusions and Future Directions

### Conclusions

- The reaction of lithium hex-aluminum hydride and magnesium amide is a potentially useful hydrogen storage material system with a 6 wt% reversible hydrogen storage capacity.
- LiMgN is a very promising material that can reversibly store 8.0 wt% hydrogen.
- The CVS method can be used to produce precursor powders for the synthesis of metal hydrides.

The potentials of the materials as discussed in this report can also be summarized in the following table in comparison with other categories of candidate hydrogen storage materials:

### Future Directions

- Characterize the thermodynamic equilibrium plateau pressure of the material systems described in this report.
- Characterize the kinetic properties of the hydrogen storage reactions using LiMgN.
- Conduct in-depth study of the effects of amide on the reversibility of  $\text{Li}_3\text{AlH}_6$ .
- Synthesize and evaluate the properties of metal hydrides produced using the CVS method.
- Synthesize and evaluate complex anionic metal hydrides using the high energy high pressure reactive milling process.

## Special Recognitions & Awards/Patents Issued

Three provisional patent applications were filed by the University of Utah.

1. Zhigang Zak Fang, Jun Lu, and H. Y. Sohn, "A Light Metal Based Material System for Hydrogen Storage," Docket No. 00846-32676, provisional (U-4112), November 2006.
2. Jun Lu, Zhigang Zak Fang, and H. Y. Sohn, "Hydrogen Storage on a Combined  $\text{M}_x\text{AlH}_6/\text{M}'_y(\text{NH}_2)_z$  System and Methods of Making and Using the Same," Docket No. 25763, provisional, April 2006.
3. Jun Lu, Zhigang Zak Fang, and H. Y. Sohn, "New Indirect Method to Generate Hydrogen from Water for Reversible Hydrogen Storage Application," Docket No. xxx, provisional, April 2006.

## FY 2007 Publications/Presentations

1. 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", submitted to *J. Phys. Chem. C*, June 2007.
2. Jun Lu, Zhigang Zak Fang\*, Young Joon Choi, and Hong Yong Sohn, "Effect of Mechanical Milling of N-Containing Hydrogen Storage Materials," in preparation.
3. 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*, in press, June, 2007.
4. Jun Lu, Zhigang Zak Fang\* and Hong Yong Sohn, "A Hybrid Method for Hydrogen Storage and Generation from Water," *J. Power Sources*, ASAP paper online, May 18, 2007. (doi:10.1016/j.jpowsour.2007.05.021.)
5. Jun Lu, Zhigang Zak Fang\* and Hong Yong Sohn, "Destabilization of Metal Hydrides Based on Negatively Charged Hydrogen ( $\text{H}^-$ ) and Positively Charged Hydrogen ( $\text{H}^{\delta+}$ ) Interactions" *Inorg. Chem.*, 45, 8749-8754, 2006.
6. Jun Lu, Zhigang Zak Fang\* and Hong Yong Sohn, "A New Li-Al-N-H System for Reversible Hydrogen Storage" *J. Phys. Chem. B*, 110(29), 14236-14239, 2006.
7. Jun Lu, Zhigang Zak Fang, Young Joon Choi, and H. Y. Sohn, "Effect of Mechanical Milling on Light Metal Based Hydrogen Storage," oral presentation, The Minerals, Metals and Materials Society 2007 annual meeting, Orlando, FL, February 25 – March 1, 2007.
8. Jun Lu, Zhigang Zak Fang, and H. Y. Sohn, "A New Li-Al-N-H System for Reversible Hydrogen Storage," oral presentation during Materials Research Society spring meeting, San Francisco, CA, April 20, 2006.
9. Jun Lu, Zhigang Zak Fang, H. Y. Sohn, and Karl Gross, "A New Li-Al-N-H System for Reversible Hydrogen Storage," Santa Barbara, CA, October 26, 2006.
10. Brady G. Butler, Jun Lu, Zhigang Zak Fang, and Hong Yong Sohn, "Enhanced Properties of High Capacity Nanostructured Metal Hydrides," Sohn International Symposium, Advanced Processing of Metal and Materials, The Minerals, Metals and Materials Society meeting, August 27-31, 2006, San Diego, CA.
11. Jin Won Choi, Hong Yong Sohn, Young Joon Choi, Jun Lu, Gilsoo Han, and Zhigang Zak Fang, "Aluminum Nanopowder as a Precursor of Hydrogen Storage Materials," *Proceedings of The Minerals, Metals and Materials Society Annual Meeting*, Orlando, FL, Feb. 2007, pages 1-8.