

## IV.A.4p Synthesis and Discovery of Nanocrystalline Reversible Hydrides by Vapor Phase Reactions

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### Introduction

As an integral part of the Metal Hydride Center of Excellence (MHCoE), the team at the University of Utah focuses on three aspects: the synthesis, discovery, and processing of nanocrystalline metal hydride materials for hydrogen storage applications. The synthesis of nanocrystalline metal hydride material has two aims: 1) nanoscaled metal hydride materials have potential to improve kinetic properties of both dehydrogenation and hydrogenation reactions 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 dependence on how these materials are processed or prepared.

The discovery of new metal hydrides are particularly crucial because the properties of material or material systems available to date do not meet the targets set by DOE. 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 indicates that a 7 wt% hydrogen storage system (on a material basis) can be achieved by utilizing a reaction between lithium hex aluminum hydride and lithium amide. 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 2005, the approach for discovery of new materials was based on reactions involving amides. The positive effects of lithium amides on the dehydrogenation of LiH, which was shown in the literature, suggested that there are a wide range of opportunities for discovering new material systems involving similar reactions. The hypothesis was that by taking advantage of the effects of lithium amides on LiH, a range of reactions that have higher hydrogen content should be explored.

#### Synthesis and Processing

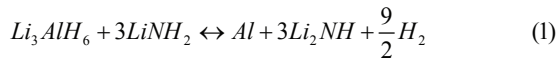
1. A chemical vapor synthesis (CVS) process has been developed for the synthesis of nanosized metal hydrides precursor powders. The primary advantage of the CVS process is that it yields materials with homogeneity at the atomic level. The CVS process is also very flexible for fine tuning chemical formula of materials.
2. 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 may be very useful for the synthesis of non-equilibrium metal hydride materials that cannot be synthesized otherwise. The Utah team is assisting other partners in the MHCoE including HRL and Sandia National Laboratory on rehydrogenation of Mg<sub>2</sub>Si and the synthesis of complex anionic hydride materials including the ternary metal hydrides of NaH and Si.
3. Milling is a method widely used in the preparation of metal hydrides for research. Many methods used in the community, however, are not consistent and are not the best approach. We investigated several different milling methods and milling procedures that produced different results.

### Results

#### Discovery of New Materials

A new material/reaction system that could potentially be used for hydrogen storage was discovered. This material system is based on the reaction between

lithium hex aluminum hydride and lithium amide. The overall reaction is shown in the following equation:



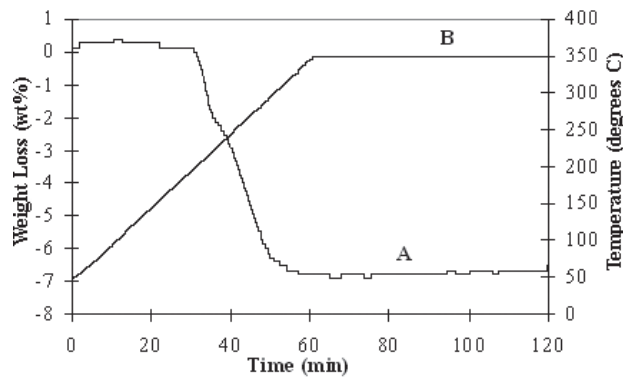
The results showed that this reaction produces reversibly approximately ~7 wt% H<sub>2</sub>.

Figure 1 shows the thermal gravimetric analysis (TGA) result of the Li<sub>3</sub>AlH<sub>6</sub>/3LiNH<sub>2</sub>/4 wt% TiCl<sub>3</sub>- AlCl<sub>3</sub> (Sample 1). The experiment was run under argon atmosphere with a heating rate of 5°C/min. Each reaction step is identified by the changes in the weight loss rate. It can be seen that a total of 7.1 wt% hydrogen was released within the temperature range tested. The dehydrogenation process appears to consist of two steps: the first step is in the temperature range of 160 to 200°C. A total of 2.4 wt% of hydrogen was released by this step. The second step occurs at above 210°C. Another 4.7 wt% of hydrogen was released during the second step. The overall dehydrogenation reaction, which is a combination of these two steps as given by R(1). The total 7.1 wt% weight loss as shown in Figure 1 indicates

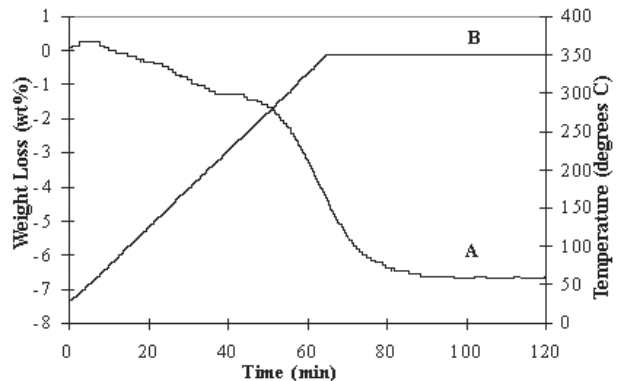
that the dehydrogenation is complete, according to reaction (1).

To demonstrate the reversibility of the combined Li<sub>3</sub>AlH<sub>6</sub>/3LiNH<sub>2</sub> system, the re-hydrogenation of the product of reaction (1) (Al/3Li<sub>2</sub>NH/4 wt% TiCl<sub>3</sub>- 1/3AlCl<sub>3</sub>), was carried out by using a custom-made autoclave under 2,000 psi H<sub>2</sub> pressure and 300°C. Figure 2 shows TGA curves of the hydrogenated Sample 2. It shows that Sample 2 gained about 7.0 wt% hydrogen from the re-hydrogenation process. The TGA curve shows two dehydrogenation steps of the hydrogenated Sample 2, which is nearly identical to the original dehydrogenation curve of Sample 1. This demonstrates that the hydrogenation of Sample 2 is complete. In other words, the dehydrogenation of Li<sub>3</sub>AlH<sub>6</sub>/3LiNH<sub>2</sub> is reversed.

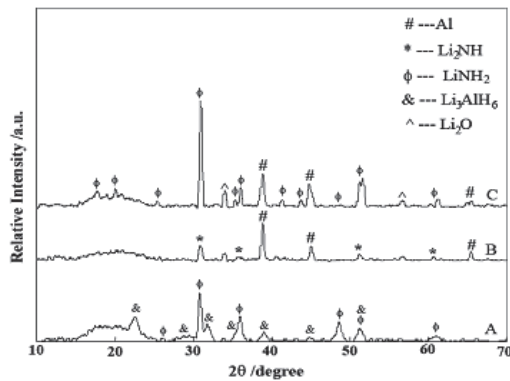
Compared to other candidate materials, considering all factors including the kinetics of dehydrogenation, the temperature range of the dehydrogenation/hydrogenation reactions, and the reversible hydrogen storage capacity, we believe that the Li<sub>3</sub>AlH<sub>6</sub>+3LiNH<sub>2</sub> reaction system is a very promising one. Assuming a



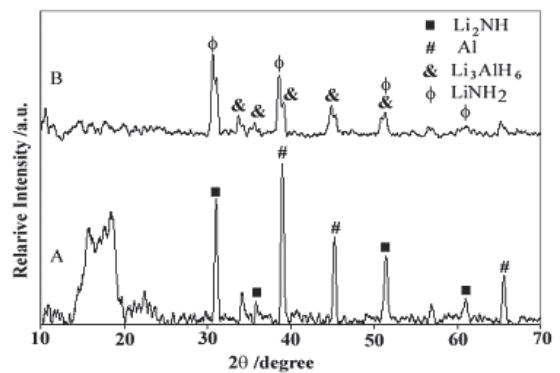
TGA curves for sample 1 (Li<sub>3</sub>AlH<sub>6</sub>/3LiNH<sub>2</sub>/4 wt% TiCl<sub>3</sub>- AlCl<sub>3</sub>) system



TGA curves for Sample 2 (Al/3Li<sub>2</sub>NH/4 wt% TiCl<sub>3</sub>- AlCl<sub>3</sub>) after hydrogenation.



XRD patterns of A) Sample 1 after ball milling, B) Sample 1 after being heated up to 300 °C. C) Sample 1 after being heated up to 200 °C.



XRD patterns of A) Sample 2 after ball milling, B) Sample 2 after re-hydrogenation.

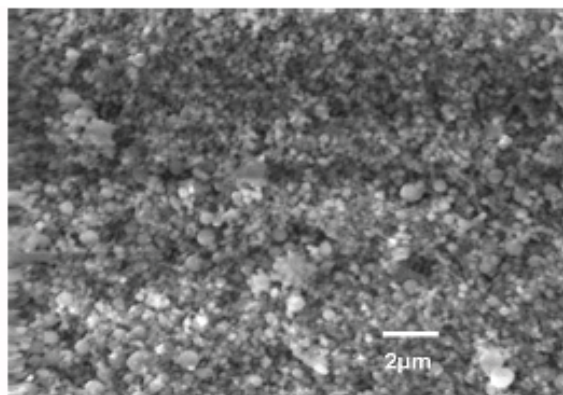
FIGURE 1. TGA of the Dehydrogenation of Li<sub>3</sub>AlH<sub>6</sub>+3LiNH<sub>2</sub> Reaction

FIGURE 2. TGA of the Dehydrogenated and then Rehydrogenated Li<sub>3</sub>AlH<sub>6</sub>+3LiNH<sub>2</sub> Mixture

fixed temperature range of below 300°C and adequate kinetics of dehydrogenation reaction, this material system has the highest reversible hydrogen storage capacity that are reported to date. Certainly, more research work is needed to characterize the isothermal pressure-composition-temperature (PCT) behavior of this material system and lower its dehydrogenation temperature.

#### Chemical Vapor Synthesis Metal Hydride Precursor Materials

One of the objectives of our project for FY 2005 was to demonstrate the feasibility of making nanosized metal hydride precursor materials using the CVS method. This objective has been achieved. Several nanosized metal powders have been made using the CVS methods including Li, LiN, Li/Mg, Al, and Mg<sub>2</sub>Si. For example, Figure 3 is the SEM micrograph of the nanosized Al powder that was made by the CVS method. The nanosized CVS Al powder has been sent to partners for evaluations as a precursor for forming AlH<sub>3</sub>. Nanograined Mg<sub>2</sub>Si was also synthesized and sent to Center partners for evaluation.



SEM micrograph

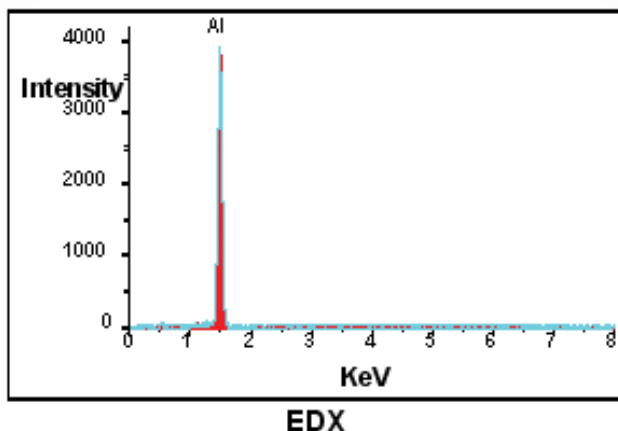


FIGURE 3. Nanosized Aluminum Powder Synthesized by the Chemical Vapor Synthesis Method

#### Processing - Milling Method of Metal Hydrides

As mentioned earlier, milling is a popular material preparation method by researchers of hydrogen storage materials. Specifically, the Spex vibratory mill is most often used. There are, however, many issues with using the Spex mill. Although it is high energy and high efficiency, it is not the most consistent method of mixing materials. Further, when milling materials involving amides, the reactions during milling often lead to degassing, and hence loss of H<sub>2</sub> and even NH<sub>3</sub>.

We investigated different methods of ball milling for preparing hydride materials for experiments and obtained some useful results. For example, a new procedure for preparing MgH+2LiNH<sub>2</sub> mixtures is experimented and proved to be useful. It is recommended that instead of milling MgH+2LiNH<sub>2</sub> mixtures, the dehydrogenation products of MgH+2LiNH<sub>2</sub> should be milled and hydrogenated. By following this procedure, there is no possibility for any reaction during milling, and therefore, there is no H<sub>2</sub> or NH<sub>3</sub> loss after milling. As the result, the actual hydrogen storage capacity of the MgH+2LiNH<sub>2</sub> system is increased from ~4.5% to above 5%.

#### Conclusions and Future Directions

##### Conclusions

1. The combination and reaction of lithium hex-aluminum hydride and lithium amide is a potentially useful hydrogen storage material system with a 7 wt% reversible hydrogen storage capacity.
2. The CVS method can be used to produce precursor powders for the synthesis of metal hydrides.
3. New milling methods and procedures should be adopted to improve the quality and repeatability of the data on hydrogen storage materials.

##### Future Directions

1. Continue to explore potential novel reactions of the Li-Al-N-H material system.
2. Synthesize and evaluate the properties of metal hydrides produced using the CVS method.
3. Synthesize and evaluate complex anionic metal hydrides using the high-energy, high-pressure reactive milling process.

#### Special Recognitions & Awards/Patents Issued

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

**FY 2006 Publications/Presentations**

1. Jun Lu, Zhigang Zak Fang, and H. Y. Sohn, "A New Li-Al-N-H System for Reversible Hydrogen Storage", *J. Physical Chemistry B* 2006, 110, 14236-14239.
2. Jun Lu and Zhigang Zak Fang, "Dehydrogenation of a combined LiAlH<sub>4</sub>/LiNH<sub>2</sub> system", *The Journal of Physical Chemistry B*, 109(44), 20830-20834, 2005.
3. Jun Lu, Zhigang Zak Fang, and H. Y. Sohn, "Destabilization of Metal Hydrides Based on Negatively Charged Hydrogen (H<sup>-</sup>) and Positively Charged Hydrogen (H<sup>δ+</sup>) Interactions", *Inorganic Chemistry*, in press, available online September 5, 2006.
4. Jun Lu, Zhigang Zak Fang, and H. Y. Sohn, "A New Li-Al-N-H System for Reversible Hydrogen Storage", presented during MRS Spring Meeting, San Francisco, April 20, 2006.