

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

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Objectives

- To discover and develop advanced high capacity reversible hydrogen storage materials.
- To develop chemical vapor synthesis process for making nano particles for hydrogen storage.
- To develop reactive 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 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 dehydrogenation 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

- Systemically investigated the effects of ball milling variables on reaction pathways of the LiNH₂-MgH₂ system. An optimized milling method for synthesizing pure LiMgN was developed.
- Conducted pressure-concentration-temperature (PCT) studies on hydrogenation properties of LiMgN and demonstrated that the hydrogenation of LiMgN is pressure sensitive.
- Systemically investigated the effect TiH₂ content on the dehydrogenation properties of the Mg-Ti-H system.
- Investigated the kinetics and thermodynamics of hydrogen storage reactions of nanostructured MgH₂-0.1TiH₂ by using PCT.
- Conducted exploratory studies on a new Li-B-Al-H system, which consists of Li₃AlH₆/LiBH₄ or Al/LiBH₄, as a potential reversible hydrogen storage material.
- Made Ti-doped nanosized Al powder using the chemical vapor synthesis (CVS) method, and tested the hydrogenation properties of NaH-Al (NaAlH₄) system using the CVS-prepared nanosized Al powder.



Introduction

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

The discovery of new metal hydrides 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 materials 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 of 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 2008, we focused on two material systems: ternary lithium magnesium nitride (LiMgN) and nano-structured Mg-Ti-H systems.

1. The effect of mechanical milling technique on the synthesis of pure LiMgN from the mixture of LiNH_2 - MgH_2 was studied. An optimized condition for synthesizing pure LiMgN is proposed based on the results obtained. The hydrogenation properties of as-prepared LiMgN were further explored using PCT, X-ray diffraction (XRD) and nuclear magnetic resonance (NMR). The results demonstrated that the hydrogenation of LiMgN is pressure sensitive and a full charge of the samples (8 wt%) can be achieved only when the applied hydrogen pressure is higher than 140 bar at 180°C.
2. The effect of milling parameters and TiH_2 content on the dehydrogenation properties of Mg-Ti-H system was investigated. The results showed that dehydrogenation characteristics were significantly improved, releasing a large amount of hydrogen (~6.0 wt%) starting at 101°C, when 9.1 mol% TiH_2 was added and the samples were milled for 4 hours using a ultrahigh energy planetary mill under H_2 pressure. The isothermal desorption and absorption measurements on this sample demonstrated that the dehydrogenation and hydrogenation kinetics were rapid at 290°C measured by a PCT apparatus. This sample also showed an excellent cyclic stability upon hydrogenation/dehydrogenation tests.

In addition, a new Li-B-Al-H system, which consists of $\text{Li}_3\text{AlH}_6/\text{LiBH}_4$ or Al/LiBH_4 , is explored as a potential reversible hydrogen storage material. The results demonstrated that the presence of Al had a positive effect on the rehydrogenation of LiBH_4 at a much lower temperature than without aluminum addition.

Approach

The basic approach that we took for discovery of new materials is to 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, nitrides and borohydrides. 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 nanosized metal hydride 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.

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

1. Investigation of the Li-Mg-N-H (LiMgN) System

In FY 2008, experimental studies were carried out to 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. In FY 2009, we continued research on finding an optimized condition for synthesizing pure LiMgN from the mixture of LiNH_2 and MgH_2 , and PCT characterization of the hydrogenation properties of LiMgN.

a. Effects of Mechanical Ball Milling on Synthesis of Pure LiMgN from LiNH_2 - MgH_2

To optimize the condition for preparing pure LiMgN, the effect of the mechanical milling technique on the dehydrogenation reactions of the mixture of $\text{LiNH}_2/\text{MgH}_2/4\text{wt}\%\text{TiCl}_3$ was investigated. Two different types of ball milling methods, namely low-energy ball milling (Jar-rolling) and high-energy ball milling (Spex Mill), were used in this study. The results are presented in the following.

The milled samples were characterized using thermal gravimetric analysis (TGA), XRD and Fourier transform infrared (FTIR). The results showed that there is no phase change during the whole low-energy ball milling process, and a relatively pure LiMgN is obtained after the sample was milled for 96 hours and then dehydrogenated. However, the high-energy ball milling technique initiates some reactions including the metathesis reaction between LiNH_2 and MgH_2 and release of H_2 and/or NH_3 during the milling process, which makes the subsequent dehydrogenation reactions more complicated and unexpected. Figure 1 shows the XRD patterns of a series of samples after Spex milling. It can be seen that the samples milled after first 0.5 hour (SP-0.25 and SP-0.5) only consist of the original LiNH_2 and MgH_2 phase, which indicates that following reaction does not take place at the earlier stage of high-energy ball milling, although the components on the right side

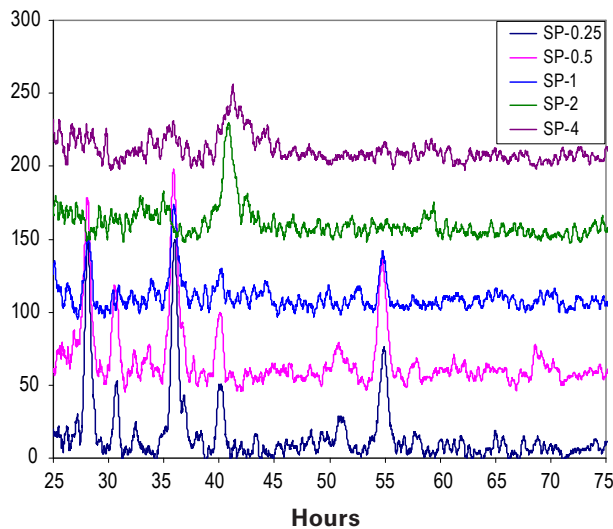
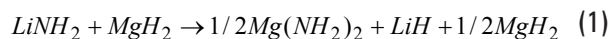


FIGURE 1. XRD patterns of a series samples for the mixture of LiNH_2 - MgH_2 -4wt% TiCl_3 after Spex mill treatments, where SP represents the Spex milling method and Hours represents the milling time.

of this reaction are predicted to be thermodynamically more stable than those on the left side.



After 1 hour Spex milling, although the MgH_2 phase is still dominating the XRD profile, the diffraction peaks of LiNH_2 become invisible. Two small peaks at 38° and 44° (2θ) are observed which can be assigned to the LiH phase based on the JCPDS database. This result indicates the presence of a new chemical reaction (reaction 1) between LiNH_2 and MgH_2 during the high-energy ball milling. However, the diffraction peaks of $\text{Mg}(\text{NH}_2)_2$, one of the expected products according to reaction 1, is undetectable by XRD, which can be attributed to the fact that the compound is easily deformed into an amorphous state under high-energy ball milling process. When the milling time is further prolonged to 2 or 4 hours, the diffraction peaks of MgH_2 also disappears completely, suggesting that MgH_2 is either consumed by the newly-formed $\text{Mg}(\text{NH}_2)_2$ or turned into an amorphous state due to the high-energy ball milling. At the same time, one broader peak at 41.5° is observed in the XRD profiles of samples SP-2 and SP-4, which can be assigned to MgNH phase according to the previous work.

The dehydrogenated SP-H samples are also rather complex due to the multi-steps reactions during the high-energy ball milling and subsequent dehydrogenation processes. The dehydrogenated products from the high-energy ball milled samples consist of multiphase structures, which were confirmed by the XRD and FTIR analysis. The results showed that pure LiMgN could not be made by using the high-energy ball milling technique. It is also worthwhile to

point out that the temperature and heating rate during the dehydrogenation process have critical effects on the components of the final products, which are under further investigation.

b. PCT Studies of the Hydrogenation Properties of LiMgN

Based on the above results, relatively pure LiMgN was prepared for further studies using PCT instrument and cyclic measurements. The isothermal adsorption experiments at 180°C for the as-prepared LiMgN under different hydrogen pressure were conducted in the Sieverts' type PCT instrument. The results showed that the hydrogenation of as-prepared LiMgN is pressure sensitive. To achieve a full charge of the sample, a hydrogen pressure higher than 140 bar is required. The hydrogenated sample contained $\text{Mg}(\text{NH}_2)_2$ rather than LiNH_2 confirmed by FTIR analysis, which is in agreement with our previous results.

A short cyclic measurement on the as-prepared LiMgN was also conducted using the PCT instrument. Figure 2 plotted the amount of hydrogen release/uptake versus cyclic number. It can be seen that a significant loss of the hydrogen capacity occurs during the cyclic experiments. It should be noted that the amount of the absorbed hydrogen is always higher than that of desorbed hydrogen at the same cycle which is a misleading result that will be further studied. More detailed dehydrogenation/rehydrogenation properties including reaction mechanisms will be also be studied further by the use of XRD, FTIR and solid-state NMR.

2. Investigation of the Nano-Scale Mg-Ti-H System

In FY 2008, we investigated the nano-scaled Mg-Ti-H mixtures prepared by high-energy-high-pressure milling. The analyses of TGA data indicated that the hydrogen

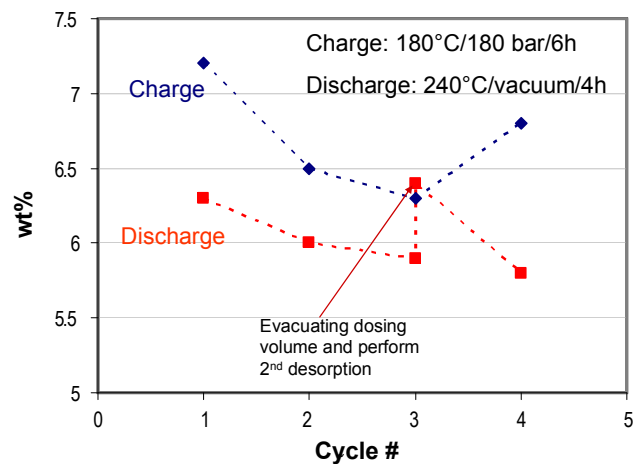


FIGURE 2. Cyclic Measurements of the As-Prepared LiMgN

release temperature for the $7\text{MgH}_2/\text{TiH}_2$ mixture was lower by about 255°C than that of as-received MgH_2 and fast dehydrogenation kinetics was achieved within 60 minutes. In FY 2009, we continued research on 1) effect of milling parameters on the dehydrogenation properties of Mg-Ti-H system, and 2) thermodynamics and kinetics of the hydrogen storage reactions of selected $\text{MgH}_2\text{-TiH}_2$ system (10:1) by a comprehensive PCT analysis.

a. Effect of Milling Parameters on the Dehydrogenation Properties of Mg-Ti-H System

The effects of milling parameters and TiH_2 content on the dehydrogenation properties of the Mg-Ti-H system were investigated by TGA and differential thermal analysis. The mixtures of MgH_2 and TiH_2 in various molar ratios were prepared using low energy and high energy ball-milling methods under an argon or hydrogen atmosphere. The results showed that dehydrogenation characteristics were significantly improved, releasing a large amount of hydrogen (~ 6.0 wt%) starting at 101°C , when 9.1 mol% TiH_2 was added and the samples were milled for 4 hours by ultrahigh energy planetary mill under 13.8 MPa hydrogen pressure. Figure 3 presented the activation energy (E_a) for the dehydrogenation of the milled Mg-Ti-H mixtures with various TiH_2 contents using the Ozawa-Flynn-Wall method. The most noticeable result is that the activation energy is reduced significantly when only 2 mol% of TiH_2 is added, and decreases gradually as the TiH_2 content is increased, which is similar to the plot of on-set temperature (at $5^\circ\text{C}/\text{min}$ heating rate) vs. TiH_2 content. In addition, the activation energy is further reduced from 81 to 68 kJ/mol when the molar ratio Mg:Ti was decreased from 50:1 to 4:1 (corresponding to 2 and 20 mol% of TiH_2 , respectively), although this lowers the hydrogen storage capacity to below 5 wt%. Thus, it can be concluded that the kinetics of dehydrogenation of Mg-Ti-H mixtures is improved as more TiH_2 is added.

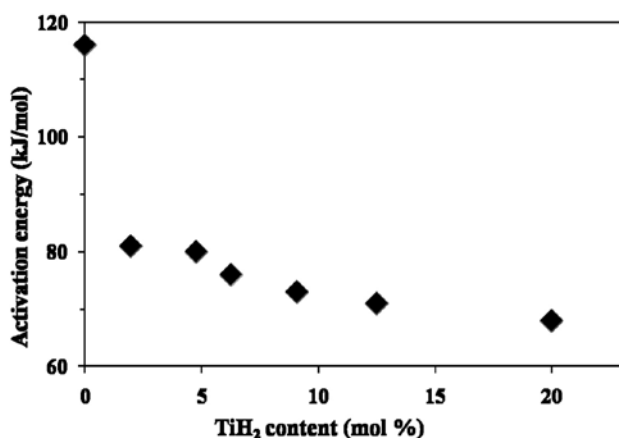


FIGURE 3. Activation energy (E_a) for the dehydrogenation of milled Mg-Ti-H mixtures with various TiH_2 contents.

The $10\text{MgH}_2/\text{TiH}_2$ was selected for further investigation because it showed the lowest on-set temperature (at $5^\circ\text{C}/\text{min}$ heating rate) at around 101°C and a reasonable reaction rate with over 6 wt% theoretical H_2 capacity. The effects of milling technique (low-energy or high-energy milling) and milling time on the dehydrogenation behavior of the Mg-Ti-H systems are also investigated.

b. PCT Studies on the Hydrogen Storage Properties of the Nano-Scaled $\text{MgH}_2\text{-0.1TiH}_2$ System

To improve the kinetics and thermodynamic properties of MgH_2 during dehydrogenation-rehydrogenation cycles, a nano-structured $\text{MgH}_2\text{-0.1TiH}_2$ material system prepared by ultrahigh-energy-high-pressure (UHEHP) mechanical milling was investigated. The mixtures of MgH_2 and TiH_2 in molar ratio of 10:1 were milled using a UHEHP ball milling device under 13.8 MPa hydrogen pressure for 4 hours at room temperature. High-resolution transmission electron microscopy and scanning transmission electron microscopy analysis showed that the grain size of the milled $\text{MgH}_2\text{-0.1TiH}_2$ powder is approximately 5-10 nm with TiH_2 distributed uniformly among the MgH_2 particles.

The isothermal desorption and absorption measurements by a PCT apparatus demonstrated that the dehydrogenation and hydrogenation kinetics of the milled $\text{MgH}_2\text{-0.1TiH}_2$ powder are rapid at 290°C . More importantly, the milled $\text{MgH}_2\text{-0.1TiH}_2$ material shows an excellent cyclic stability upon hydrogenation/dehydrogenation tests. A total of 80 cycles were performed and the results are presented in Figure 4A, showing that there was little loss in hydrogen storage capacity after 80 cycles. The kinetic data of the first and last cycles from the cyclic measurements were extracted and plotted as shown in Figures 4B and 4C. It is obvious that the kinetic of both hydrogenation and dehydrogenation remained intact from the first to the last cycle. Thus, in this respect, $\text{MgH}_2\text{-0.1TiH}_2$ is superior to un-doped nano- or micro-scaled MgH_2 , which loses its hydrogen storage capacity during cycling. The above results demonstrate that both the nanosize and the addition of TiH_2 contribute to the improvement of the kinetics of dehydrogenation and hydrogenation of MgH_2 .

In addition to the kinetic aspect, the pressure-composition-isothermal results showed that the ΔH value of the dehydrogenation of the milled $\text{MgH}_2\text{-0.1TiH}_2$ is lower than that of MgH_2 . The ΔS value is, however, also lower than that of commercial pure MgH_2 . Therefore, the net effect of the use of nanosized particles and the addition of TiH_2 had minimum effect on P_{eq} – the equilibrium pressure of dehydrogenation in the temperature range tested.

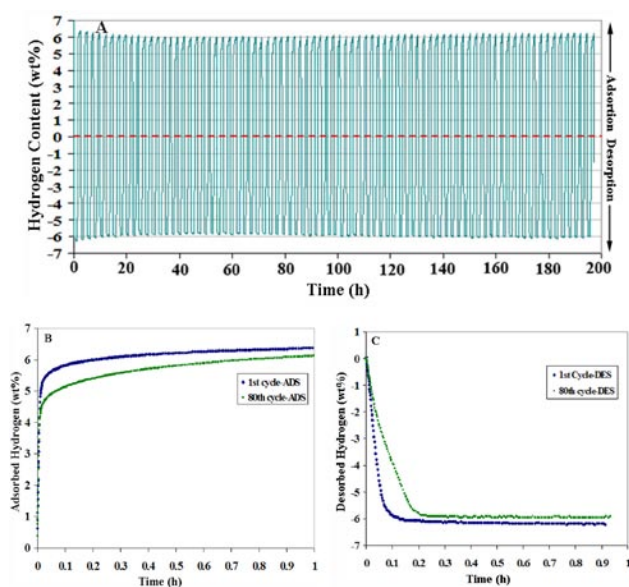


FIGURE 4. A) Cyclic measurements of the milled $\text{MgH}_2/0.1\text{TiH}_2$; B) Isothermal desorption curves for the milled $\text{MgH}_2/0.1\text{TiH}_2$ under 1kPa hydrogen pressure at 300°C during the 1st and 80th cyclic measurements, respectively; C) Isothermal hydrogenation curves for the dehydrogenated $\text{MgH}_2/0.1\text{TiH}_2$ under 2 MPa hydrogen pressure at 300°C during the 1st and 80th cyclic measurements, respectively.

3. Investigation of Li-B-Al-H System for Reversible Hydrogen Storage

In FY 2009, a new Li-B-Al-H system, which consists of $\text{Li}_3\text{AlH}_6/\text{LiBH}_4$ or Al/LiBH_4 , was explored as a potential reversible hydrogen storage material. LiBH_4 and $\text{Li}_3\text{AlH}_6/\text{Al}$ were mechanically milled to form Li-Al-B-H systems by low-energy milling. The dehydrogenation and rehydrogenation properties were investigated by the use of XRD, TGA and solid-state NMR. The analysis of TGA data showed that the TiCl_3 -doped $\text{Li}_3\text{AlH}_6/2\text{LiBH}_4$ and $0.5\text{Al}/\text{LiBH}_4$ can release ~ 8.8 and ~ 8.4 wt% H_2 up to 450 and 380°C , with ~ 3.8 and ~ 5.8 wt% of hydrogen recovery, respectively. The XRD and solid-state NMR results showed that the dehydrogenated products are composed of LiH and AlB_2 . It has been determined by the NMR that the addition of Al has resulted in a remarkable improvement of the reversible dehydrogenation of LiBH_4 , and its reactivity has been substantially changed when smaller amount of aluminum (0.5 vs. 0.05 mol% Al) was added under the same H_2 release/uptake conditions. Although some unknown species has been found in the dehydrogenation process and the hydrogenation was only partially occurred in the limited temperature and pressure ranges, we believed that the presence of Al could be an important factor to make the rehydrogenation happen for LiBH_4 at a much lower temperature, at which dehydrogenation product from LiBH_4 alone does not show any degree of rehydrogenation.

4. Chemical Vapor Synthesis of Ti-doped Al Nanopowders and its Hydrogenation Properties in NaH-Al-H_2 (NaAlH_4) System

One of the objectives of our project is to demonstrate the feasibility of making nanosized metal or metal hydride precursor materials using the CVS method. In FY 2008, Ti-doped nano aluminum powder was successfully synthesized using the premixed 4 mol% TiCl_3 - AlCl_3 precursor. Energy dispersive X-ray spectroscopy 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. In FY 2009, the hydrogenation properties of NaAlH_4 system using the CVS-prepared nano Al powders were tested. The results indeed showed that a better dehydrogenation/hydrogenation kinetics is achieved compared to that of using commercial Al or NaAlH_4 powders.

Conclusions and Future Directions

Summary and Conclusions

- The mechanical milling processing variables have critical effects on synthesis of LiMgN from the mixture of LiNH_2 and MgH_2 . The likely reaction pathways during the high-energy ball milling were identified based on the XRD and FTIR results.
- The PCT results showed that the hydrogenation of LiMgN is pressure sensitive. Hydrogen pressure higher than 140 bar is required to fully charge LiMgN ($\sim 8\text{wt}\%$).
- The isothermal desorption and absorption measurements of nanostructured MgH_2 - 0.1TiH_2 demonstrated that the dehydrogenation and hydrogenation rates are very rapid at 290°C . This material also showed an excellent cyclic stability upon hydrogenation/dehydrogenation tests.
- A new Li-B-Al-H system, which consists of $\text{Li}_3\text{AlH}_6/\text{LiBH}_4$ or Al/LiBH_4 , is explored and investigated as a potential reversible hydrogen storage material.
- The CVS method is used to produce Ti doped nano Al powders, and the hydrogenation properties of NaAlH_4 system using the CVS-prepared nano Al powders were tested.

Future Directions

- Fully understand the reaction mechanisms of LiMgN during cyclic hydrogenation and dehydrogenation reactions.
- Study the different catalysts on improving the kinetic properties of the hydrogen storage reactions using LiMgN .

- Further explore means to reduce the temperature of dehydrogenation of $\text{MgH}_2\text{-TiH}_2$ systems.
- Produce sufficient quantities of Ti-doped nano Al powders as precursors for regeneration of AlH_3 .

Special Recognitions & Awards/Patents Issued

1. Dr. Jun Lu, a Postdoc fellow of Professor Zak Fang, was selected for “Garr Cutler Energy Prize” at the University of Utah, 2008 for his research work on reversible hydrogen storage materials.

FY 2009 Publications/Presentations

1. Jun Lu, Young Joon Choi, Zhigang Zak Fang, Hong Yong Sohn and Ewa Ronnebro, “Hydrogen Storage Thermodynamic and Kinetic Properties of Nanosized $\text{MgH}_2\text{-0.1TiH}_2$ Prepared by Reactive Mechanical Milling”, To be submitted to *J. Am. Chem. Soc.*
2. Young Joon Choi, Jun Lu, Hong Yong Sohn, Zhigang Zak Fang and Ewa Ronnebro, “Effect of Milling Parameters on the Dehydrogenation Properties of the Mg-Ti-H system”, To be submitted to *J. Phys. Chem. C.*
3. Young Joon Choi, Jun Lu, Hong Yong Sohn, Zhigang Zak Fang, Chul Kim, Robert C. Bowman Jr., and Son-Jong Hwang, “Hydrogen Storage Properties of a Li-Al-B-H System”, *In preparation.*
4. Jun Lu, Young Joon Choi, Vineet Kumar, Zhigang Zak Fang, and Hong Yong Sohn, “Study of Phase Transformation of MgH_2 during High-pressure-high-energy Mechanical Milling”, *In preparation.*
5. Jun Lu, Young Joon Choi, Zhigang Zak Fang, and Hong Yong Sohn, “Effect of Mechanical Milling on the synthesis of Pure LiMgN and its Hydrogen Storage Properties”, *In preparation.*
6. 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”, *J. Power Sources*, 185, 1354-1358, 2008.
7. 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.
8. Y. J. Choi, Jun Lu, H. Y. Sohn, and Zhigang Zak Fang, “Hydrogen Storage Properties of a Combined $\text{Li}_3\text{AlH}_6\text{-LiBH}_4$ System”, in *The Hydrogen Economy*, edited by B. Choudhury, A. Dillon, J. Keller and C. Moen, *Mater. Res. Soc. Symp. Proc. Volume 1042E*, Warrendale, PA, 2008, 1098-HH03-36. (2008 MRS Spring meeting, San Francisco, CA.)
9. Jun Lu, Zhigang Zak Fang, Young Joon Choi, and H. Y. Sohn, “The Potential of Binary Lithium Magnesium Nitride - LiMgN for Hydrogen Storage Application”, in *Materials and Technology for Hydrogen Storage*, edited by G-A. Nazri, C. Ping, A. Rougier, and A. Hosseinmardi, *Mater. Res. Soc. Symp. Proc. Volume 1042E*, Warrendale, PA, 2008, 1042-S05-03. (2007 MRS Fall meeting, Boston, MA)
10. Jun Lu, Zhigang Zak Fang, Young Joon Choi, H. Y. Sohn, and Eva Ronnebro, “Hydrogen Storage Properties of Mg-Ti-H System Prepared by Mechanical Milling”, presented during 2009 MRS Spring Meeting, San Francisco, CA, April 15, 2009.
11. Zhigang Z. Fang, Jun Lu, Brady Butler, and Hong Yong Sohn, “Hydrogen Storage Materials Based on Li-Al-Mg-N Systems”, International Symposium on Metal-Hydrogen Systems, MH2008, Reykavik, Iceland, June 24-28, 2008.
12. Zhigang Zak Fang et al “Hydrogen Storage Properties of Li-Mg-N-Al-H System”. AsiaNano 2008. Biopolis, Singapore. November 3-7, 2008. (Invited talk).