IV.A.4 Effects and Mechanisms of Mechanical Activation on Hydrogen Sorption/Desorption of Nanoscale Lithium Nitrides and Lithium Borohydrides

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Objectives

- Investigate the effects and mechanisms of mechanical activation on hydrogen sorption/desorption behavior of Li_3N- and $LiBH_4$-based materials.
- Develop a novel, mechanically activated, nanoscale Li_3N- or $LiBH_4$-based material that is able to store and release ~10 wt% hydrogen at temperatures below 100°C with a plateau hydrogen pressure of less than 10 bar.

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

Technical Targets

This project is to develop a fundamental understanding of effects and mechanisms of mechanical activation on hydrogen storage capacity and sorption/desorption kinetics of nanoscale Li_3N- and $LiBH_4$-based materials. Insights gained from these studies will be applied to producing a novel, mechanically activated, nanoscale Li_3N- or $LiBH_4$-based material that meets the following DOE 2010 hydrogen storage targets:

- Cost: $4/kWh net
- System gravimetric capacity: 2 kWh/kg
- System volumetric capacity: 1.5 kWh/L
- Charging/discharging rates: 3 min for 5 kg

Progress towards meeting the DOE on-board hydrogen storage targets made up to Fiscal Year 2008 is summarized in the following table.

Storage Parameter	Units	2010 System Target	FY 2008 Material Status
Specific Energy	kWh/kg	2.0	2.0 at 200°C
Energy Density	kWh/L	1.5	2.6 at 200°C
Charging/Discharging Rate (system fill time for 5 kg)	min	3.0	3.0 at 200°C

Accomplishments

- Reduced the onset and peak temperature for hydrogen release of the $LiNH_2$ + LiH system from 50°C to room temperature and from 308°C to 200°C, respectively.
- Identified the reaction pathway and rate-limiting step in hydrogen uptake and release of the $LiNH_2$ + LiH system.
- Developed the fundamental understanding of mechanical activation effects via high-energy ball milling at liquid nitrogen temperature.
- Synthesized, for the very first time, the $LiBH_4$ + MgH_2 mixture that exhibits 8.3 wt% hydrogen uptake in the solid state (i.e., below the melting point of $LiBH_4$ which is about 280°C) without any catalysts.
- Demonstrated that the solid-state hydrogenation and dehydrogenation of the $LiBH_4$ + MgH_2 mixture are reversible and emit no borane.
- Established the method of the unique ultra-high magnetic field nuclear magnetic resonance (NMR) experiments at PNNL for studying $LiBH_4$-based materials.

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Introduction

A key component for the hydrogen economy is fuel cell-powered vehicles which, in turn, depend critically upon advanced hydrogen storage materials. The challenge is to develop a storage material that simultaneously satisfies three competitive requirements: (i) high hydrogen density, (ii) reversibility of hydrogen release/uptake cycle near the ambient temperature and pressure, and (iii) fast release/uptake kinetics. This project is aimed at investigation and development of such hydrogen storage materials with capabilities to reversibly uptake and release hydrogen near the ambient temperature and pressure.

Approach

To achieve the project objectives, we have employed nano-engineering and mechanical activation approaches to develop hydrogen storage materials that simultaneously satisfy the three requirements mentioned above. ($LiNH_2$+LiH)-based systems, which have a theoretical storage capacity of 6.5 wt% H_2 [1], have been studied as a model system to develop the fundamental understanding of the reaction mechanisms and rate-limiting steps in hydriding and dehydriding processes. Once sufficient understanding was gained on the model system, the effort was expanded to ($LiBH_4$+MgH_2)-based systems, which have a theoretical storage capacity of 11.5 wt% H_2 [2]. Nano-engineering and mechanical activation approaches are pursued to reduce the hydride particle sizes, increase their surface areas, and mix the reactants at the nanoscale – all of which will enable rapid sorption and desorption of hydrogen molecules on the solid surface, provide large interfacial area for reactions between solid hydrides, and reduce the diffusion distance of hydrogen within the solids.

Results

In the past year, the effort was focused on (1) identification of the reaction mechanisms of and the rate-limiting steps in hydriding and dehydriding processes of the ($LiNH_2$+LiH) model system, (2) development of the fundamental understanding of the effects of mechanical activation and nano-engineering on hydriding and dehydriding processes of the ($LiNH_2$+LiH) model system, and (3) transition to investigation and development of ($LiBH_4$+MgH_2)-based systems, which have the potential to meet the DOE 2010 hydrogen storage target.

With the aid of a wide range of analytical instruments, it was demonstrated that dehydrogenation of the $LiNH_2$ + LiH mixture is an NH_3-mediated reaction and the rate-limiting step is diffusion of reaction product(s) through the solid [3]. Thus, nano-engineering is critical in enhancing hydrogen uptake and release for this type of reactions because a factor of 100 decrease in the diffusion distance can result in a factor of 10,000 decrease in the reaction time. Mechanical activation, which can introduce high concentrations of defects into solids, can also enhance hydrogen uptake and release rates because of the augment in the diffusion coefficients due to the presence of a large amount of defects. Proper catalysts, which can increase the composition gradient for diffusion via rapid removal of the gaseous phases (e.g, NH_3) from the solid surface, can also enhance hydrogen uptake and release of these diffusion-controlled reactions. All of these expectations were demonstrated in the past year.

Figure 1 shows the ^{1}H MAS NMR spectra of $LiNH_2$ + LiH ball milled at liquid nitrogen (LN_2) and room temperature as a function of temperature [4]. In general, each spectrum consists of two major peaks, i.e., one narrow peak located at about 4.1 ppm and a very broad peak underneath the narrow peak. The narrow peak at 4.1 ppm corresponds to both gaseous and chemical and physical adsorbed H_2 molecules, whereas the broad peak beneath the narrow peak is due to the rigid lattice protons. Note that gaseous H_2 is observed below 100°C for LN_2-milled samples, but not for room temperature (RT)-milled samples. Furthermore, at 180°C, the amount of H_2 released from LN_2-milled samples is four times more than that from RT-milled samples. These results clearly indicate that LN_2-milled samples have much higher dehydriding rates than RT-milled samples. Detailed X-ray diffraction, specific surface area measurement, and NMR analysis [5] revealed that the crystallite sizes and specific surface areas for LN_2-milled and RT-milled samples are similar and thus cannot account for the observed enhancement of LN_2-milled samples. Instead, NMR analysis indicates that the enhancement is due to more efficient defect generation with milling at liquid nitrogen temperature, which in turn increases the diffusion rate.

Figure 2 compares hydriding and dehydriding cycling stabilities of mechanically activated, nano-engineered $LiNH_2$ + LiH mixtures with and without 1 mol% catalyst in isothermal hydrogen uptake/release cycle tests at 240°C. Note that both mixtures have a rapid hydrogen uptake rate and slow release rate. Because of their slow release rates, the mixtures desorb less H_2 in each release segment (2.5-hr duration) than that absorbed in each uptake segment (only 1-hr duration). Because of the presence of the un-released hydrogen at the end of each release segment, the amount of the absorbed hydrogen decreases as the number of cycles increases. Such degradation in the kinetic performance is much more severe for the sample without the catalyst than the sample with the catalyst. This phenomenon is attributed to the role of the catalyst in rapidly removing the gaseous phase from the solid

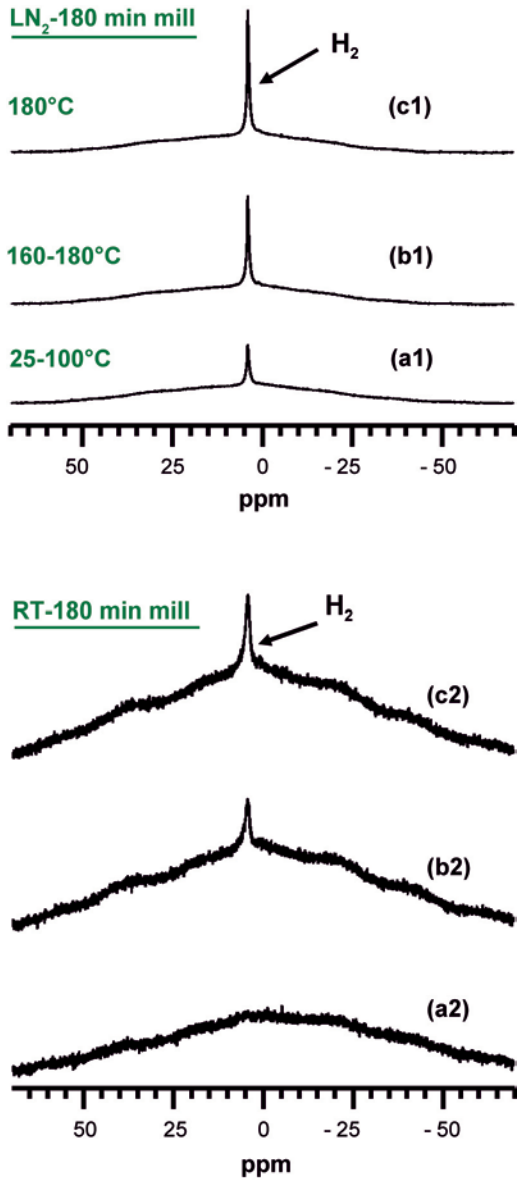

FIGURE 1. ^{1}H MAS (5 kHz) NMR spectra of $LiNH_2$ + LiH mixtures ball milled at liquid nitrogen (LN_2) and room temperature, as a function of temperature during the temperature ramp from RT to 180°C. These spectra were acquired at a magnetic field of 7.05 tesla (300 MHz spectrometer). Each spectrum was acquired using 32 accumulation numbers and a total acquisition time of 64 s.

surface so that the diffusion-controlled reactions can proceed quickly because of the large composition gradient.

Enhancement in hydriding and dehydriding rates through nano-engineering has also been demonstrated [6]. It was shown that the onset and peak temperature for hydrogen release of the $LiNH_2$ + LiH system can be decreased from 50°C to room temperature and from 308°C to 200°C, respectively, by reducing the crystallite size from micrometers to nanometers [6]. The substantially increased surface area of LiH particles

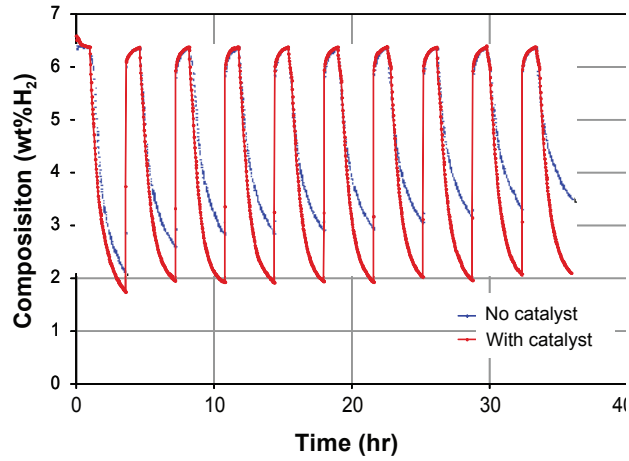

FIGURE 2. Isothermal hydrogen uptake/release cycles of the $LiNH_2$ + LiH mixtures ball milled at RT for 3 hours with and without 1 mol% catalyst. The cycling was conducted using a Sieverts'-type PCI device. The isothermal cycle entailed a 1-hr uptake at a hydrogen pressure of 10 atm and a subsequent 2.5-hr release under an evacuated condition, all at 240°C and repeated for 10 times.

through nano-engineering has also reduced NH_3 emission from the $LiNH_2$ + LiH system to below the detection limit of mass spectrometry because of the large reaction area of LiH particles with NH_3 [6].

The understanding of the effects of nano-engineering and mechanical activation developed from the $LiNH_2$ + LiH system has been expanded to develop the $LiBH_4$ + MgH_2 system that, for the very first time, exhibits 8.3 wt% H_2 uptake in the solid state (i.e., below the melting point of $LiBH_4$ which is about 280°C) without any catalysts [7]. Figure 3 shows hydrogenation and dehydrogenation behavior of the LiH + MgB_2 mixture after ball milling under an argon atmosphere for 3, 24, and 120 hrs. As shown, the total hydrogen absorbed after holding at 265°C under a hydrogen pressure of 90 bars for 5 hrs is 8.3 wt% for the 120-hr ball-milled mixture, which is much higher than that for the 24-hr and 3-hr ball-milled mixtures (i.e., 8.3 wt% vs 5.9 wt% and 3.2 wt%). Analysis of the reaction kinetics of hydrogenation and dehydrogenation reveals that both reactions are controlled by diffusion [7]. The much higher reaction rates displayed by the 120-hr ball-milled mixture is due to its high diffusion coefficient, about 400% and 1,800% higher than that of the 24-hr and 3-hr ball-milled counterparts, respectively [7]. Furthermore, the high diffusion coefficient of the 120-hr ball-milled mixture results from its smaller crystallite size and higher defect concentration induced by its longer ball milling time [7].

Figure 4 shows the composition profile of the effluent gas from the 120-hr ball-milled mixture during a thermogravimetric analysis. It is obvious that the only intensive change of the gaseous species during heating

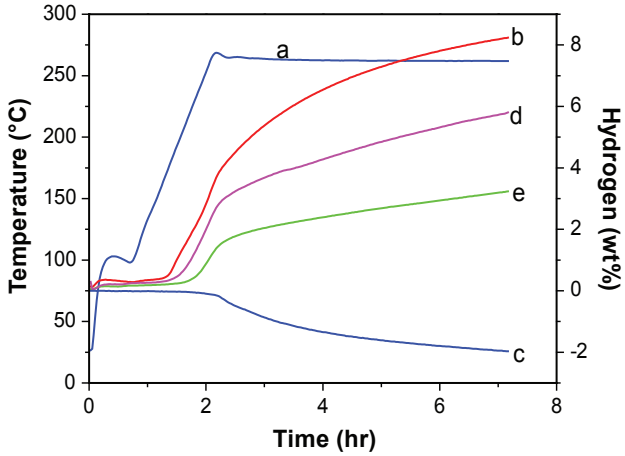

FIGURE 3. Hydrogenation and dehydrogenation behavior of ball-milled LiH + MgB_2 mixtures: (a) the temperature ramp as a function of time, (b) the hydrogenation curve of the 120-hr ball-milled mixture, (c) the dehydrogenation curve of the 120-hr ball-milled mixture after hydrogenation under the condition of (b), (d) the hydrogenation curve of the 24-hr ball-milled mixture, and (e) the hydrogenation curve of the 3-hr ball-milled mixture. The hydrogenation was conducted under a hydrogen pressure of 90 bars, whereas the dehydrogenation was performed with a hydrogen pressure of approximately 0.01 bars.

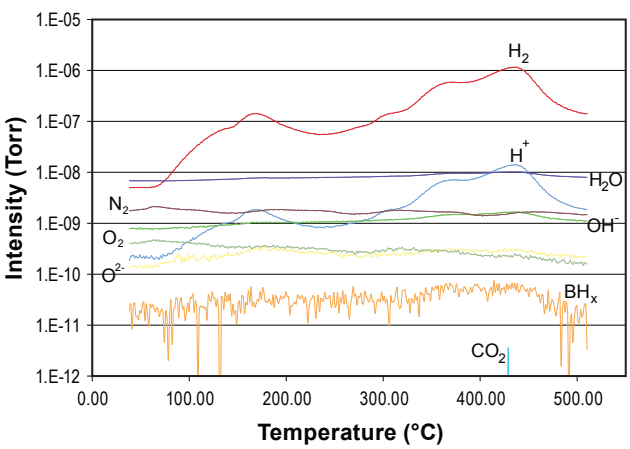

FIGURE 4. The composition profile of the effluent gas of the 120-hr ball-milled LiH + MgB_2 mixture after hydrogenation under the condition of (b) in Figure 3, as a function of temperature. The heating rate was 10°C/min and an argon flow was maintained at 60 ml/min in the entire heating process.

from room temperature to 500°C is hydrogen gas. This result, combining with the X-ray diffraction analysis, confirms that the hydriding and dehydriding processes of ball-milled LiH + MgB_2 mixtures follow the following reversible reactions [7]

$$LiBH_4 + \tfrac{1}{2} MgH_2 \leftrightarrow LiH + \tfrac{1}{2} MgB_2 + 2 H_2 \quad (1)$$

Furthermore, it is noted that the intensity of borane (BH_x) is always lower than 10^{-10} Torr in the entire heating process, which is clearly lower than the intensity of borane, if any, in air.

Conclusions and Future Directions

- The understanding developed from the $LiNH_2$ + LiH system is applicable to many other reversible hydrogen storage materials that have solid phases as hydriding and dehydriding products. One example of this kind is the well-known thermodynamically destabilized $LiBH_4$ reaction shown in Eq. (1). Because of the presence of solid phases in both sides of the reaction, hydriding and/or dehydriding reactions are likely to be controlled by diffusion. The multiple strategies successfully demonstrated in the $LiNH_2$ + LiH system can be utilized for these diffusion-controlled systems to improve their reaction kinetics.
- The successful demonstration of hydriding and dehydriding of $LiBH_4$ + MgH_2 systems in the solid state without any catalysts indicates that nano-engineering and mechanical activation are effective methods in enhancing diffusion-controlled reactions. Based on the Fick's second law of diffusion, it is expected that further reduction of particle sizes to a few nanometers can further enhance the hydriding and dehydriding kinetics of $LiBH_4$ + MgH_2 systems. Therefore, in the remainder of FY 2008, efforts will be focused on exploring a wide range of nano-engineering approaches to reduce the hydrogen uptake and release temperature and enhance the reaction rate of $LiBH_4$ + MgH_2 systems.
- In FY 2009 and beyond, the effort of exploring effective nano-engineering approaches will be continued. In addition, the long-term hydriding and dehydriding cycling stability of nano-engineered, mechanically activated $LiBH_4$ + MgH_2 systems will be investigated and the method(s) to achieve the long-term stability will be established in order to meet the DOE objectives of new high-potential hydrogen storage materials.

FY 2008 Publications/Presentations

1. T. Markmaitree, W. Osborn and L. Shaw, "Comparison between MgH_2- and LiH-Containing Systems for Hydrogen Storage Applications," *Int. J. Hydrogen Energy,* 33, 3915-3924 (2008).

2. J. Z. Hu, J. H. Kwak, Z. G. Yang, W. Osborn, T. Markmaitree, and L. Shaw, "Investigation of Mechanical Activation on Li-N-H Systems using ^{6}Li MAS NMR at Ultrahigh Field," *J. Power Sources,* 182, 278-283 (2008).

3. J. Z. Hu, J. H. Kwak, Z. G. Yang, W. Osborn, T. Markmaitree, and L. Shaw, "Probing the Reaction Pathway of Dehydrogenation of the $LiNH_2$ + LiH Mixture

using In-Situ 1H NMR Spectroscopy," *J. Power Sources,* 181, 116-119 (2008).

4. T. Markmaitree, W. Osborn, and L. Shaw, "Comparative Studies of Reaction Rates of NH_3 with LiH and MgH_2," *J. Power Sources,* 180, 535-538 (2008).

5. A. Ortiz, W. Osborn, T. Markmaitree and L. Shaw, "Crystallite Sizes of LiH before and after Ball Milling and Thermal Exposure," *J. Alloys Compd.,* 454 [1-2] 297-305 (2008).

6. L. Shaw, W. Osborn, T. Markmaitree, and X. Wan, "The Reaction Pathway and Rate-Limiting Step of Dehydrogenation of $LiHN_2$ + LiH Mixture," *J. Power Sources*, 177, 500-505 (2008).

7. L. Shaw, R. Ren, T. Markmaitree, and W. Osborn, "Effects of Mechanical Activation on Dehydrogeneation of the Lithium Amide and Hydride System," *J. Alloys Compd.,* 448, 263-271 (2008).

8. C. Lu, J. Hu, J. H. Kwak, Z. G. Yang, R. Ren, T. Markmaitree, and L. Shaw, "Study the Effects of Mechanical Activation on Li-N-H Systems with ^{1}H and ^{6}Li Solid-State NMR," *J. Power Sources*, 170, 419-424 (2007).

9. W. Osborn, T. Markmaitree and L. Shaw, "Evaluation of the Hydrogen Storage Behavior of a $LiNH_2$-MgH_2 System with a 1:1 Ratio," *J. Power Sources,* 172, 376-378 (2007).

10. W. Osborn, T. Markmaitree, X. Wan, L. Shaw, and Z. Gary Yang, "Hydrogen Uptake and Release Behavior of Lithium Amide and Hydride Systems for Hydrogen Storage Applications," presented at the TMS 2008 Annual Meeting, New Orleans, Louisiana, March 9 – 13, 2008.

11. T. Markmaitree, W. Osborn, and L. Shaw, "Comparisons between MgH_2– and LiH-Containing Systems for Hydrogen Storage Applications," presented at MRS 2007 Fall Meeting, Boston, MA, November 26 - 30, 2007.

12. W. Osborn, T. Markmaitree, L. Shaw, J. Hu, Z. Gary Yang, "Low Temperature Milling of the Lithium Hydride and Amide Hydrogen Storage System," presented at MRS 2007 Fall Meeting, Boston, MA, November 26 - 30, 2007.

13. L. Shaw, W. Osborn, T. Markmaitree, and X. Wan, "The Reaction Pathway and Rate-Limiting Step of Dehydrogenation of the $LiHN_2$ + LiH Mixture," presented at MRS 2007 Fall Meeting, Boston, MA, November 26 - 30, 2007.

14. W. Osborn, T. Markmaitree, L. Shaw, and Z. Gary Yang, "Long-Term Cyclic Stability of Lithium Amide and Hydride Systems for Hydrogen Storage Applications," presented at the MS&T 2007 Conference in Detroit, Michigan, September 16 – 20, 2007.

15. L. Shaw, T. Markmaitree, W. Osborn, X. Wan, Z.G. Yang, J. Hu, C. Lu, and J. Liu, "Effect and Mechanisms of Mechanical Activation on Hydrogen Sorption/Desorption of Nanoscale Lithium Nitrides," presented at the 2007 DOE Hydrogen Program Review, Arlington, VA, May 15 – 18, 2007.

16. L. Shaw, "Nanostructured Lithium Amide and Lithium Hydride for Reversible Hydrogen Storage Applications," Presentation at WPI, March 28, 2007. (Invited)

17. R. Ren, T. Markmaitree, W. Osborn, L. Shaw, and Z. Yang, "Effects of Mechanical Activation on Dehydrogeneation of the Lithium Amide and Lithium Hydride System," presented at the TMS 2007 Annual Meeting, Orlando, FL, Feb 25 – March 1, 2007. (Invited)

18. C. Lu, J. Hu, Z. Yang, and L. Shaw, "NMR Study of Mechanically Activated Li-N-H System," presented at the TMS 2007 Annual Meeting, Orlando, FL, Feb 25 – March 1, 2007.

19. C. Lu, J. Kim, Z. Yang, and L. Shaw, "Modification of Light Metal Complex Hydrides for Improved Storage Properties," presented at the TMS 2007 Annual Meeting, Orlando, FL, Feb 25 – March 1, 2007.

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2. J. Vajo, S. Skeith, and F. Mertens, "Reversible storage of hydrogen in destabilized $LiBH_4$," *J. Phys. Chem. B: Lett.,* 109, 3719 (2005).

3. L. Shaw, W. Osborn, T. Markmaitree, and X. Wan, "The Reaction Pathway and Rate-Limiting Step of Dehydrogenation of $LiHN_2$ + LiH Mixture," *J. Power Sources*, 177, 500-505 (2008).

4. J. Z. Hu, J. H. Kwak, Z. G. Yang, W. Osborn, T. Markmaitree, and L. Shaw, "Investigation of Mechanical Activation on Li-N-H Systems using ^{6}Li MAS NMR at Ultrahigh Field," *J. Power Sources,* 182, 278-283 (2008).

5. W. Osborn, T. Markmaitree, L. Shaw, J.Z. Hu, J.H. Kwak, and Z.G. Yang, "Low Temperature Milling of the $LiNH_2$ + LiH Hydrogen Storage System," *Int. J. Hydrogen Energy*, submitted.

6. L. Shaw, R. Ren, T. Markmaitree, and W. Osborn, "Effects of Mechanical Activation on Dehydrogeneation of the Lithium Amide and Hydride System," *J. Alloys Compd.,* 448, 263-271 (2008).

7. X. Wan, T. Markmaitree, W. Osborn, and L. Shaw, "Nano-Engineering-Enabled Solid-State Hydrogen Uptake and Release in the $LiBH_4$ plus MgH_2 System," *J. Phys. Chem. C,* submitted.