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

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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 FY 2007 is summarized in the following table:

| Storage Parameter	Units	2010 System Target	FY 06 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 temperature for the $LiNH_2$ to Li_2NH transition from 120°C to room temperature via mechanical activation. This reduction paves the way for near-room-temperature hydrogen uptake and release of the $LiNH_2$ + LiH system.
- 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.
- Demonstrated the unusual long-term stability of hydrogen uptake/release cycles of the $LiNH_2$ + LiH system at temperatures ~86% of the melting temperature of $LiNH_2$.
- Identified the reaction pathway and rate-limiting step in hydrogen release of the $LiNH_2$ + LiH system. This paves the way for future enhancement in the hydrogen release rate of the $LiNH_2$ + LiH system.
- Developed the fundamental understanding of mechanical activation effects via high-energy ball milling at liquid nitrogen temperature and newly established *in situ* nuclear magnetic resonance (NMR) facilities at PNNL.
- Minimized NH_3 emission from the $LiNH_2$ + LiH system to below the detection limit of mass spectrometry, and demonstrated that NH_3 emission

is a kinetic issue and can be minimized via mechanical activation.

✧   ✧   ✧   ✧   ✧

Introduction

Recent studies have shown that Li_3N is a promising hydrogen storage material, and the reaction path for hydrogen storage in Li_3N consists of two steps [1]:

$$Li_3N + H_2 \longleftrightarrow Li_2NH + LiH \qquad (1)$$

$$Li_2NH + H_2 \longleftrightarrow LiNH_2 + LiH \qquad (2)$$
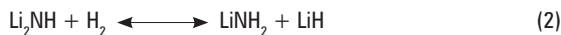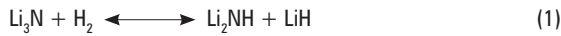
Reaction (1) can store and release 5.0 wt% H_2, whereas the corresponding value for Reaction (2) is 6.5 wt% H_2 [1]. However, the temperature required to release the hydrogen at the usable pressure is too high (about 250^0C) for practical applications. Furthermore, the reversible hydrogen is only ~6 wt%, still lower than DOE's FreedomCAR requirements. Clearly, to make Li_3N a viable hydrogen storage material for on-board applications, the reversible hydrogen storage capacity and the hydrogen sorption/desorption kinetics at ambient temperature and usable pressures need to be improved substantially.

Approach

This project focuses on investigation of the fundamental mechanism of mechanical activation and applies the understanding to reducing hydrogen sorption/desorption temperatures to near ambient.

Results

Figure 1 shows the ^6Li magic angle spinning (MAS) NMR peak shifting and broadening as the high-energy ball milling time increases, indicating that mechanical activation leads to not only structural refinement of $LiNH_2$, but also changes in the local electronic state around Li nuclei in $LiNH_2$. Combining this finding with our previous studies [2-4], it can be concluded that high-energy ball milling can result in (i) formation of nano-particles, (ii) increases in specific surface area, (iii) introduction of lattice strains, and (iv) changes in the local electronic state around Li nuclei. Mechanical activation derived from high-energy ball milling have 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 [3]. Mechanical activation also leads to the reduced activation energy for the dehydriding reaction as well as minimization of NH_3 emission to below the detection limit of mass spectrometry [3].

The long-term stability of mechanically activated $(LiNH_2 + LiH)$ is a significant concern because these powders are highly activated with nanostructures. Shown in Figure 2 is the result from an isothermal hydrogen uptake/release cycle test at 285°C of a mechanically activated $LiNH_2 + LiH$ mixture. Note that the mixture has a rapid hydrogen uptake rate (i.e., approaching the theoretical storage capacity in ~5 min) and slow release rate (i.e., incomplete release of hydrogen in 2.5 h). Because of its slow desorption rate, the mixture can only desorb ~4.4 wt% H_2 in each release segment. This number is clearly lower than its theoretical storage capacity which is estimated to be about 5.7 wt% H_2 if the extra 10 mol% LiH addition and the presence of the oxides in the starting materials
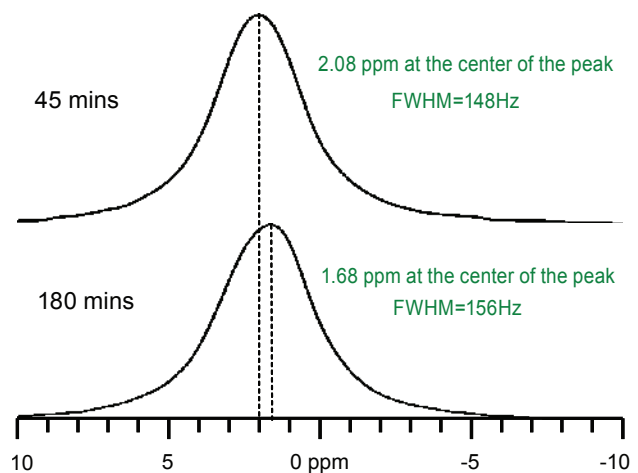
FIGURE 1. ^6Li MAS NMR spectra of $LiNH_2$ ball milled at room temperature for different times as indicated, showing the ^6Li peak shifting and broadening as the milling time increases.
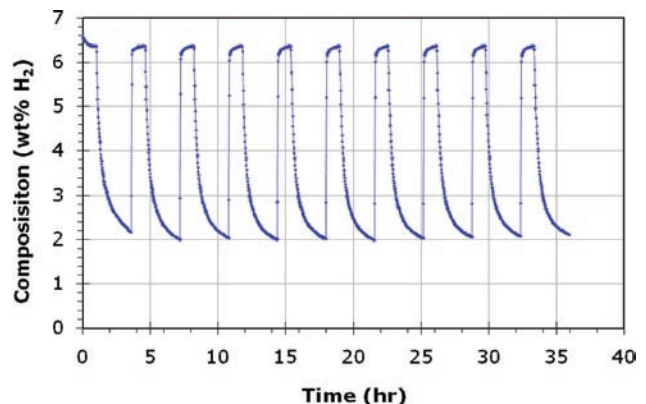

FIGURE 2. Isothermal hydrogen uptake/release cycles of the $LiNH_2 +$ LiH mixture ball milled at room temperature for 3 h, determined using a Sieverts'-type pressure-composition-isotherm (PCI) device. The isothermal cycle entailed a 1-h uptake at a hydrogen pressure of 10 atm and a subsequent 2.5-h release under an evacuated condition, all at 285°C and repeated for 10 times.

are considered. As a result of the un-released hydrogen at the end of each release segment, the amount of the absorbed hydrogen can only be 4.4 wt% in each soak segment. It is also noted that little degradation in the kinetic performance occurs over the 10 uptake/release cycles. This is remarkable, considering that the cyclic temperature (285°C) is 86% of LiNH$_2$'s melting temperature and 58% of LiH's melting temperature, and that the holding time is 35 h. The remarkable stability is believed to be due to the reaction mechanism of the LiNH$_2$ + LiH system, the presence of H$_2$, and repeated nucleation of solid phases due to the hydriding and dehydriding reactions.
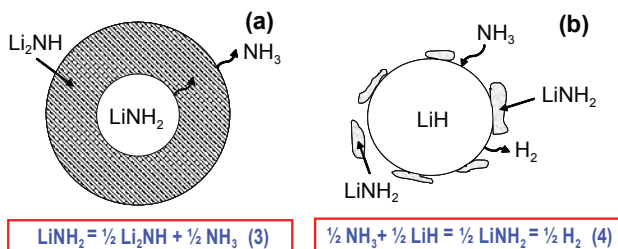
Detailed modeling of the hydrogen release kinetics in the isothermal cycles has revealed that hydrogen release is diffusion controlled, and the rate-limiting step is diffusion of NH$_3$ through the Li$_2$NH product layer during the decomposition of LiNH$_2$ particles. Figure 3 shows schematically the reaction pathway identified in this study. The dehydriding reaction of the LiNH$_2$ + LiH mixture proceeds with two elementary reactions [2,3,5]. First, LiNH$_2$ decomposes, as shown in Reaction (3).

$$\text{LiNH}_2 \;=\; \tfrac{1}{2}\,\text{Li}_2\text{NH} + \tfrac{1}{2}\,\text{NH}_3 \qquad (3)$$

The NH$_3$ from Reaction (3) then reacts with LiH to form LiNH$_2$ again and liberate H$_2$, as shown in Reaction (4).

$$\tfrac{1}{2}\,\text{NH}_3 + \tfrac{1}{2}\,\text{LiH} \;=\; \tfrac{1}{2}\,\text{LiNH}_2 + \tfrac{1}{2}\,\text{H}_2 \qquad (4)$$
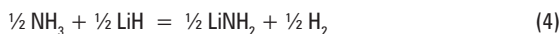
For a mixture of LiNH$_2$ + LiH (with a molar ratio of 1:1), the reaction would continue to repeat the cycle of Reactions (3) and (4) until all LiNH$_2$ and LiH transform to Li$_2$NH and H$_2$ completely. Although both reactions (3) and (4) produce solid products, there is a huge difference between them. The Li$_2$NH product forms a continuous shell outside the LiNH$_2$ shrinking core (Figure 3a), whereas the LiNH$_2$ product continues
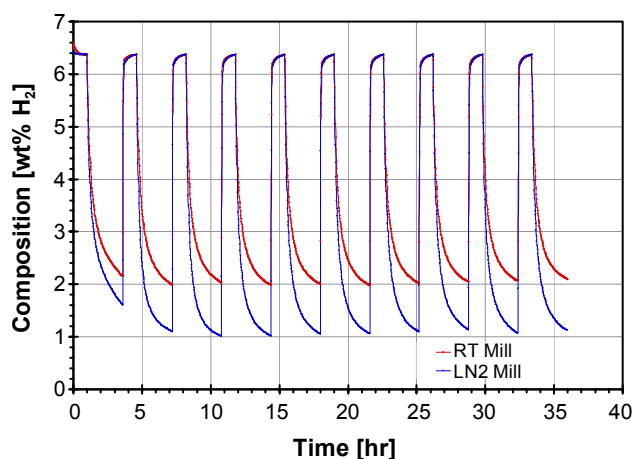
to flake off (Figure 3b). As a result, Reaction (3) takes place very slowly and is diffusion controlled [3], while Reaction (4) is ultrafast and proceeds in the order of microseconds [6].

Once the mechanism of hydrogen release of the LiNH$_2$ + LiH mixture is identified, the strategy to enhance the hydrogen release rate can then be formulated. To increase a reaction rate controlled by diffusion, the first strategy should be to change the diffusion-controlled reaction to a non-diffusion controlled reaction (i.e., changes from Figure 3a to Figure 3b via chemical modification). If this is not feasible, then the strategy should be focused on (i) nano-engineering to decrease the diffusion distance, (ii) increasing the composition gradient to enhance diffusion, and (iii) augmenting the diffusion coefficient to enhance the diffusion rate. Figure 4 shows a 22% improvement in the hydrogen release rate achieved by liquid-nitrogen-temperature ball milling which introduces more defects into nano-particles than room-temperature ball milling and thus increases diffusion rates.

Conclusions and Future Directions

- The understanding developed from the LiNH$_2$ + LiH system can be applied to many other reversible hydrogen storage materials that have solid phases as hydriding and dehydriding products. One example of this kind would be the well-known thermodynamically destabilized LiBH$_4$ reaction [7]: $2\text{LiBH}_4 + \text{MgH}_2 = 2\text{LiH} + \text{MgB}_2 + 4\text{H}_2$. Because of the presence of solid phases in both sides of the reaction, hydriding and/or dehydriding reactions

FIGURE 3. Schematic of the hydrogen release pathway of the LiNH$_2$ + LiH mixture: (a) the Li$_2$NH product from the decomposition of LiNH$_2$ forms a continuous shell outside the LiNH$_2$ shrinking core because the volume of the Li$_2$NH product is smaller than that of the LiNH$_2$ reactant, and (b) the LiNH$_2$ product from the reaction between NH$_3$ and LiH flakes off continuously because the volume of the LiNH$_2$ product is substantially larger than that of the LiH reactant.

FIGURE 4. Enhancement in the hydrogen release rate during isothermal hydrogen uptake/release cycles at 285°C via liquid-nitrogen-temperature (LN$_2$) ball milling. The milling time is 3 h for both LiNH$_2$ + LiH mixtures; however, the LN$_2$-processed mixture has a faster hydrogen release rate and improved the utilization of the theoretical storage capacity by 22%.

are likely to be controlled by diffusion. The multiple strategies identified in this study can be investigated for these systems to improve their reaction kinetics.

- In the remainder of FY 2007, the effort will be in integrating mechanical activation with chemical modification to further increase the diffusion coefficient and to thermodynamically destabilize the $LiNH_2$ + LiH system, both of which will further reduce the hydrogen uptake and release temperature and enhance their reaction rates.

- In FY 2008 and beyond, the focus will be to apply the fundamental understanding developed from the $LiNH_2$ + LiH system to $LiBH_4$-based materials and to provide good support to meet DOE objectives on new high-potential storage materials.

FY 2006 Publications/Presentations

1. *Enhancement of Lithium Amide to Lithium Imide Transition via Mechanical Activation*, T. Markmaitree, R. Ren, and L. Shaw, *J. Phys. Chem. B*., 110, 20710-20718 (2006).

2. *Stability of Lithium Amide and Lithium Hydride in Ambient Atmosphere*, R. Ren, A. Ortiz, T. Markmaitree, W. Osborn, and L. Shaw, *J. Phys. Chem. B*, 110, 10567-10575 (2006).

3. *Effects of Mechanical Activation on Dehydrogeneation of the Lithium Amide and Hydride System*, L. Shaw, R. Ren, T. Markmaitree, and W. Osborn, *J. Alloys Compd.,* in press.

4. *Crystallite Sizes of LiH before and after Ball Milling and Thermal Exposure*, A. Ortiz, W. Osborn, T. Markmaitree, and L. Shaw, *J. Alloys Compd.,* in press.

5. *Study the Effects of Mechanical Activation on Li-N-H Systems with ^1H and ^6Li Solid-State NMR*, C. Lu, J. Hu, J. H. Kwak, Z. G. Yang, R. Ren, T. Markmaitree, and L. Shaw, *J. Alloys Compd*., in press.

6. *Effects of Mechanical Activation on Lithium Amide/ Imide Transition and Hydrogen Sorption/Desorption*, R. Ren, T. Markmaitree, L. Shaw, and Z. G. Yang, Symposium on "Materials for the Hydrogen Economy" in the MS&T '05, Pittsburgh, PA, September 2005.

7. *Hydrogen Economy and Materials Issues*, L. Shaw, <u>Invited Presentation</u> at the ASM Hartford Chapter meeting, Hartford, CT, January 2006.

8. Study of Mechanically Activated Lithium Amide and Hydride with Nuclear Magnetic Resonance (NMR), C. Lu, J. Hu, K. J. Hun, J. Y. Kim, Z. Yang, and L. Shaw, Symposium on "Materials and Devices for Energy Harvesting, Generation and Storage Systems" in MS&T '06, Cincinnati, Ohio, October 15–18, 2006.

9. Nanostructured Lithium Amide and Lithium Hydride for Reversible Hydrogen Storage Applications, L. Shaw, <u>Invited Presentation</u> at WPI, March 28, 2007.

10. Effects of Mechanical Activation on Dehydrogeneation of the Lithium Amide and Lithium Hydride System, R. Ren, T. Markmaitree, W. Osborn, L. Shaw, and Z. Yang, <u>Invited Presentation</u> at the Symposium on "Materials in Clean Powder System II: Fuel Cells, Solar, and Hydrogen Based Technologies" in the TMS 2007 Annual Meeting, Orlando, FL, February 25 – March 1, 2007.

11. NMR Study of Mechanically Activated Li-N-H System, C. Lu, J. Hu, Z. Yang, and L. Shaw, Symposium on "Materials in Clean Powder System II: Fuel Cells, Solar, and Hydrogen Based Technologies" in the TMS 2007 Annual Meeting, Orlando, FL, February 25 – March 1, 2007.

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3. Shaw, L.; Ren, R.; Markmaitree, T.; Osborn, W.; "Effects of Mechanical Activation on Dehydrogeneation of the Lithium Amide and Hydride System," *J. Alloys Compd.,* in press.

4. Ortiz, A.; Osborn, W.; Markmaitree, T.; Shaw, L.; "Crystallite Sizes of LiH before and after Ball Milling and Thermal Exposure," *J. Alloys Compd.,* in press.

5. Ichikawa, T.; Hanada, N.; Isobe, S.; Leng, H.; Fujii, H.; "Mechanism of novel reaction from $LiNH_2$ and LiH to Li_2NH and H_2 as a promising hydrogen storage system," *J. Phys. Chem. B*, 2004, 108, 7887.

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