

IV.A.5 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 -based material.
- Develop a novel, mechanically activated, nanoscale Li_3N -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 (3.3.4.2) 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 -based materials. Insights gained from these studies will be applied to producing a novel, mechanically activated, nanoscale Li_3N -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 2006 is summarized in the following table.

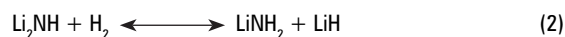
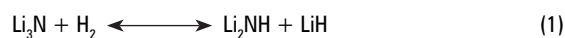
Storage Parameter	Units	2010 System Target	FY06 Material Status
Specific Energy	kWh/kg	2.0	2.0 at 200°C
Energy Density	kWh/L	1.5	2.6 at 200°C
Charging/Discharging Rate (system fill time for 5 kg)	min	3.0	3.0 at 200°C

Accomplishments

- Reduced the temperature for the LiNH_2 to Li_2NH transition from 120°C to 50°C via mechanical activation. This reduction paves the way for near-room-temperature hydrogen sorption and desorption of the $\text{LiNH}_2 + \text{LiH}$ system.
- Enhanced hydrogen sorption and desorption rates of the $\text{LiNH}_2 + \text{LiH}$ system at and below 200°C via mechanical activation.
- Identified the dehydrating behavior and issues associated with the $\text{LiNH}_2 + \text{MgH}_2$ system.

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]:



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°C) 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

The goal of increasing the hydrogen storage capacity and reducing hydrogen sorption/desorption temperatures and the specific technical targets set forth above will be achieved through three major approaches:

1. **Mechanical Activation** to reduce hydrogen sorption/desorption temperatures and increase the on-board reversible hydrogen storage capacity.
2. **Chemical Modification** of lithium amide/imide to destabilize the compounds thermodynamically and thus further reduce hydrogen sorption/desorption temperatures.
3. **Advanced Catalysts** to catalyze the reactions and thus further enhance hydrogen sorption/desorption processes.

Approach 1 will be the focus of this project because the fundamental understanding developed from this approach will not only be applied to producing Li_3N -based hydrogen storage materials to be developed in this project, but also can be utilized by other DOE hydrogen storage research teams in developing their respective hydrogen storage materials. Accomplishment of Approaches 2 and 3 will be achieved by collaborating with other DOE hydrogen storage research teams (e.g., those in the Metal Hydrides Hydrogen Storage Center of Excellence). Progress made by other DOE hydrogen storage teams in Approaches 2 and 3 will be integrated into this project so that we can make the promising lithium amide/imide/hydride materials a viable system for the on-board hydrogen storage application.

Results

It has been established that the reverse process of Reaction (2) proceeds with two elementary reactions [2,3]:

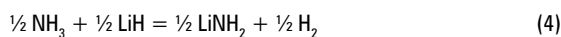


Figure 1 shows that the decomposition of LiNH_2 to Li_2NH and NH_3 , i.e., Reaction (3), can be greatly enhanced by mechanical activation through high-energy ball milling at room temperature (RT) using an attritor with a charge ratio of 60:1 and an argon atmosphere.

The decomposition of LiNH_2 without ball milling starts at 120°C which is reduced to 50°C for LiNH_2 ball milled for 45 min. After ball milling for 180 min, the onset temperature for the decomposition of LiNH_2 is further reduced to room temperature. The enhanced decomposition of LiNH_2 is due to the formation of nanostructured particles and the introduction of defects in the particles. The latter, in turn, has resulted in a decreased apparent activation energy for the decomposition of LiNH_2 , as shown in Figure 2.

Mechanical activation through high-energy ball milling at RT has also led to the enhancement of Reaction (2), i.e., combination of Reactions (3) and (4). As shown in Figure 3, the endothermic peak of Reaction (2) has been reduced from 308°C to 215°C by ball milling for 90 min. This peak is further reduced to 200°C if the ball milling time is increased to 180 min. If the temperature at which the heat flow curve starts to deviate from the horizontal line is taken as the onset temperature for Reaction (2), then the LiNH_2 and LiH

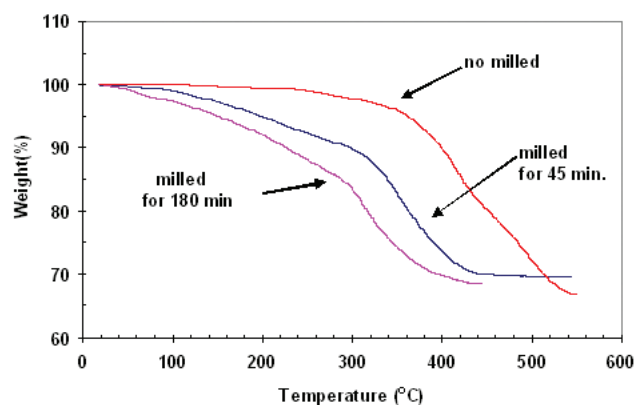


FIGURE 1. TGA curves of lithium amide without and with ball milling for different times. The heating rate in the analysis is 10°C/min, and a flowing argon atmosphere is employed.

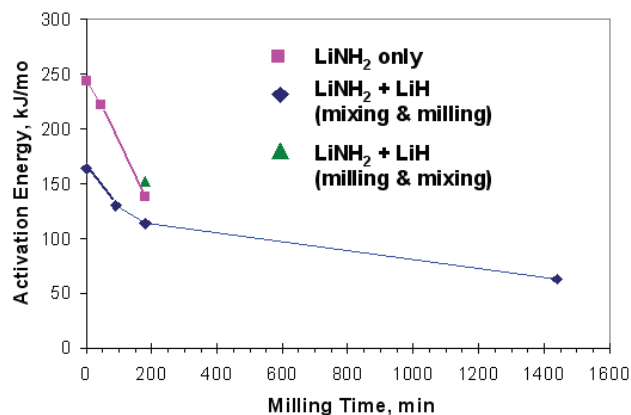


FIGURE 2. A comparison of the activation energies for Reactions (2) and (3) as a function of the ball milling time.

mixture without ball milling has an onset temperature of $\sim 100^\circ\text{C}$. This temperature decreases to $\sim 85^\circ\text{C}$ and $\sim 50^\circ\text{C}$ after ball milling for 90 and 180 min, respectively. In addition, the completion temperature for dehydriding has also been reduced by ball milling. As shown in Figure 3, the powder mixture without ball milling exhibits an endothermic peak at 360°C , corresponding to melting of the unreacted LiNH_2 present at that temperature. However, such a melting peak is absent for the powder mixture with ball milling for either 90 or 180 min, indicating that all LiNH_2 has reacted with LiH below 360°C .

Similar to the case for the decomposition of LiNH_2 , mechanical activation at RT also has immense impact on the activation energy of Reaction (2). As shown in Figure 2, the apparent activation energy for Reaction (2) decreases with increasing the ball milling time. Indeed, the apparent activation energy can be reduced to as low as 63 kJ/mol after ball milling for 1,440 min (24 hours). This activation energy is the lowest one for Reaction (2) ever reported in the literature.

Ball milling not only enhances the dehydriding process, but also mitigates or eliminates the NH_3 escaping issue from the LiNH_2 and LiH system. According to Reactions (3) and (4), the escaping of NH_3 can be minimized or eliminated by enhancing Reaction (4). This can be achieved by adding additional LiH to the hydrogen storage system, as demonstrated in Ref. 4. However, this approach will lower the hydrogen storage capacity of the system. An alternative approach would be to enhance the rate of Reaction (4) through mechanical activation. As shown in Figure 4, the NH_3 level in the effluent gas is highest when the thermogravimetric (TG) chamber only contains the LiNH_2 sample. This is not surprising because there is no

LiH to capture NH_3 (see Reaction 3). With the addition of LiH , the level of NH_3 in the effluent gas during the TG analysis is reduced, but is still very high. High-energy ball milling for 180 min at RT for the LiNH_2 and LiH mixture (at 1-to-1.1 molar ratio), however, can reduce the level of NH_3 in the effluent gas to below the detection limit of the quadrupole residual gas analyzer (RGA). For comparison, the NH_3 level in the effluent gas during the TG analysis of a MgH_2 sample is also included in Figure 4. The NH_3 level detected from the MgH_2 sample represents the detection limit of the RGA because there is no NH_3 release in the MgH_2 sample. Note that the NH_3 level in the effluent gas from the LiNH_2 and LiH mixture with 180 min milling is lower than the NH_3 level exhibited by the MgH_2 sample. This clearly demonstrates that mechanical activation can greatly enhance Reaction (4) and eliminate the escaping of NH_3 from the LiNH_2 and LiH mixture, thereby providing clean H_2 to fuel cells.

Figure 5 shows the TGA curve of the LiNH_2 and MgH_2 powder system mixed in a 2-to-1.1 ratio. For comparison, the TGA curve of the LiNH_2 and LiH powder system mixed in a 1-to-1.1 ratio is also included. Three important phenomena are noted from this figure. First, as for the LiNH_2 and LiH mixture, ball milling at RT reduces the dehydriding temperature of the LiNH_2 and MgH_2 mixture. Second, the MgH_2 -containing system exhibits a lower dehydriding temperature than the LiH -containing system when both systems are ball milled under the same condition. This trend is consistent with the thermodynamic analysis, which indicates that Reaction (2) has an enthalpy of desorption of 45 kJ/mol [1], whereas it is 34 kJ/mol for Reaction (5) [5]. Thus, for Reaction (5) to take place, it requires a lower temperature than Reaction (2) if kinetic factors are equal.

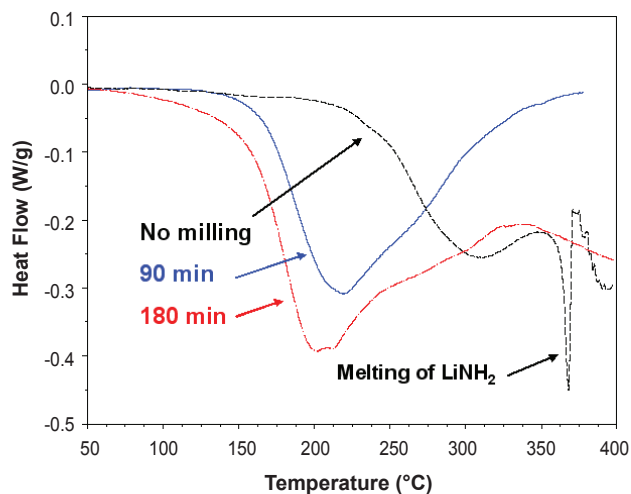
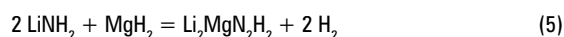


FIGURE 3. Differential Scanning Calorimetry (DSC) traces of the LiNH_2 and LiH mixture with and without ball milling at room temperature. The heating rate during the DSC analysis was 10°C/min .

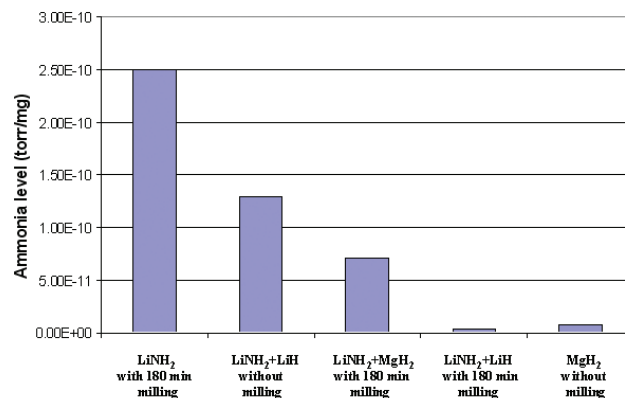


FIGURE 4. Comparisons in the ammonia level among various systems with or without ball milling as indicated.

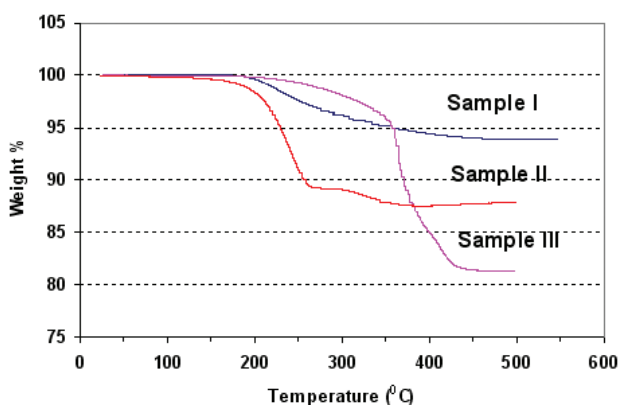


FIGURE 5. Thermogravimetric analysis of (i) LiNH_2 and LiH mixture (in a 1-to-1.1 ratio) ball milled at RT for 180 min, (ii) LiNH_2 and MgH_2 mixture (in a 2-to-1.1 ratio) ball milled at RT for 180 min, and (iii) LiNH_2 and MgH_2 mixture (in a 2-to-1.1 ratio) without milling.

Third, the LiNH_2 and LiH mixture exhibits ~6 wt% loss, very close to the theoretical value (6.5 wt%) if the LiOH impurity in the sample is considered. However, for the LiNH_2 and MgH_2 powder mixture without ball milling the weight loss is about 18%, which is substantially larger than the theoretical value (5.35 wt%) calculated from Reaction (5) for a 2-to-1.1 powder mixture. After ball milling at room temperature for 180 min, the weight loss of the LiNH_2 and MgH_2 mixture is reduced to about 14%, which is still larger than the theoretical value. The larger weight loss than the theoretical prediction is caused by escaping of NH_3 from the system, as detected from the effluent gas using RGA (Figure 4). Based on these studies, it is concluded that the $\text{LiNH}_2 + \text{MgH}_2$ system has a larger driving force for hydriding and dehydriding than the $\text{LiNH}_2 + \text{LiH}$ system. However, the reaction rate between MgH_2 and NH_3 is slower than that between LiH and NH_3 .

Conclusions and Future Directions

- Established the effect of mechanical activation at RT. Effects of mechanical activation below RT will be investigated in FY 2007.
- Demonstrated the dehydrogenation at room temperature for both $\text{LiNH}_2 + \text{LiH}$ and $\text{LiNH}_2 + \text{MgH}_2$ systems, but the peak temperature for dehydrogenation was still high (~200°C). Further reduction of the peak temperature is needed, which will be achieved by mechanical activation below RT in FY 2007.
- Mitigated the NH_3 issue in the $\text{LiNH}_2 + \text{LiH}$ system. However, the efficiency of mechanical activation in multiple cycles remains to be investigated, which will be conducted in FY 2007.
- Identified the NH_3 escaping issue in the $\text{LiNH}_2 + \text{MgH}_2$ system. Solutions to this problem will be

pursued in FY 2007 by using the starting materials containing LiH and $\text{Mg}(\text{NH}_2)_2$ because LiH reacts with NH_3 much faster than MgH_2 .

- Mechanisms of mechanical activation in the $\text{LiH} + \text{LiNH}_2$ system will be investigated in FY 2007 to develop fundamental understandings and guide the utilization of mechanical activation. The major tool for developing such a understanding is nuclear magnetic resonance.

FY 2006 Publications/Presentations

1. R. Ren, T. Markmaitree, L. Shaw, and Z. G. Yang, "Effects of Mechanical Activation on Lithium Amide/Imide Transition and Hydrogen Sorption/Desorption," presented at the Symposium on "Materials for the Hydrogen Economy" in the MS&T '05, Pittsburgh, PA, September 2005.
2. T. Markmaitree, R. Ren, and L. Shaw, "Enhancement of Lithium Amide to Lithium Imide Transition via Mechanical Activation," submitted to *J. Phys. Chem. B*.
3. R. Ren, A. L. Ortiz, T. Markmaitree, W. Osborn, and L. Shaw, "Stability of Lithium Amide and Lithium Hydride in Ambient Atmosphere," *J. Phys. Chem. B*, 110, 10567-10575 (2006).
4. R. Ren, T. Markmaitree, L. Shaw, Z. G. Yang, and J. Hu, "Effects of Mechanical Activation on Dehydrogenation of the Lithium Amide and Lithium Hydride System," submitted to *J. Alloys Compd.*
5. L. Shaw, "Nanostructured Lithium Hydrides, Amides, Imides, and Nitrides for Hydrogen Storage Applications," an Invited Chapter for a book on "Nanomaterials for Energy Storage Applications," H. S. Nalwa, Eds., American Scientific Publishers, December 2006.
6. L. Shaw, "Hydrogen Economy and Materials Issues," Invited Presentation at the ASM Hartford Chapter meeting, Hartford, CT, January 2006.

References

1. Chen, P.; Xiong, Z.; Luo, J. Z.; Lin, J.Y.; Tan, K. L.; "Interaction of hydrogen with metal nitrides and imides," *Nature*, 2002, 420, 302.
2. Hu, Y. H.; Ruckenstein, E.; "Ultrafast reaction between LiH and NH_3 during H_2 storage in Li_3N ," *J. Phys. Chem. A*, 2003, 107, 9737.
3. 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.
4. Luo, W.; "(LiNH_2 - MgH_2): a viable hydrogen storage system," *J. Alloys Compd.*, 2004, 381, 284.
5. Chen, P.; Xiong, Z.; Luo, J. Z.; Lin, J.Y.; Tan, K. L.; "Interaction between lithium amide and lithium hydride," *J. Phys. Chem.*, 2003, 107, 10967.