VI.A.6 Effects and Mechanisms of Mechanical Activation on Hydrogen Sorption/Desorption of Nanoscale Lithium Nitrides

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Contract Number: DE-FC36-05GO15008

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Start Date: December 9, 2004
Projected End Date: December 8, 2008

Objectives

Investigate, model and 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 Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- M. Hydrogen Capacity and Reversibility

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 is able to store and release ~10 wt% hydrogen at temperatures below 100°C with a plateau hydrogen pressure of a few bars. If successful, this storage material has the potential to meet the DOE 2010 system-level hydrogen storage targets.

Approach

The technical targets will be achieved by implementing the following 6 major tasks. These 6 major tasks represent our systematic and comprehensive approach of integrating experiments and quantum-chemical simulation to develop fundamental understanding and mechanically activated, nanoscale Li_3N-based materials for hydrogen storage applications.

- *Task 1*
  Investigate how mechanical activation affects hydrogen sorption and desorption of nanoscale Li_3N and its derivatives (Li_2NH, $LiNH_2$ and LiH).
- *Task 2*
  Determine the nature of interactions of H_2 with Li_3N, Li_2NH, $LiNH_2$ and LiH surfaces as a function of mechanical activation.
- *Task 3*
  Develop mechanistic understanding of the hydrogen storage capacity, including both reversible and maximum, as a function of temperature, pressure, and mechanical activation.
- *Task 4:* Study the cycling life and resistance of mechanically-activated Li_3N-based materials to gaseous impurities.
- *Task 5*
  Perform quantum chemical calculation and molecular dynamic simulation of the surface adsorption and solid-state reactions to form lithium imides and amides, and the effects of crystal lattice defects on the thermodynamics and kinetics of hydrogen sorption in lithium nitrides.
- *Task 6*
  Optimize mechanical activation and perform doping activities for further improvements in both hydrogen storage capacity and kinetics of hydrogen uptake and release.

Accomplishments

The work performed last year (from December 2004 to June 2005) has led to the following three major findings.

- Ball milling can greatly increase the hydrogen release kinetics of the mixture of lithium amide ($LiNH_2$) and lithium hydride (LiH). The onset temperature for releasing hydrogen has been reduced from 90 to 50°C after ball milling for 3 hours at ambient temperature, and the peak temperature, T_p, at which the maximum hydrogen release rate occurs, has been reduced from 390 to 260°C under a constant heating rate of 10°C/min (Figures 1 and 2).

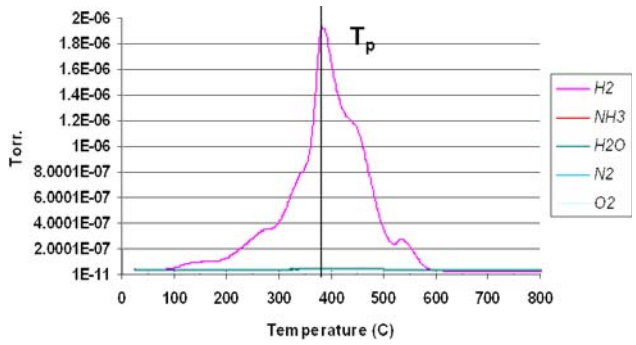

Figure 1. Gas composition of the $LiNH_2$ and LiH mixture *without* ball milling as a function of temperature; measured using a residual gas analyzer connected to a thermogravimetric analyzer (TGA) with a constant heating rate of 10°C/min under a flowing argon atmosphere.

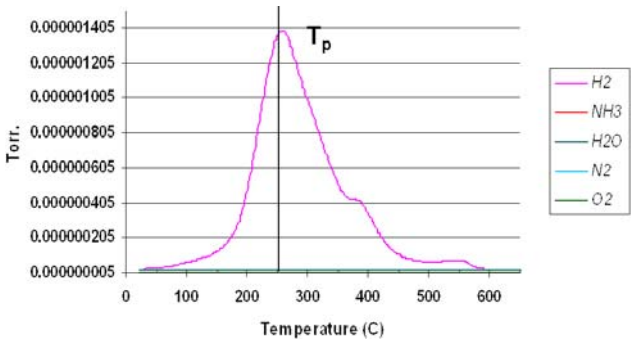

Figure 2. Gas composition of the $LiNH_2$ and LiH mixture *with* ball milling as a function of temperature, measured using a residual gas analyzer connected to a TGA with a constant heating rate of 10°C/min under a flowing argon atmosphere.

- The enhancement in the hydrogen release rate by ball milling is achieved via increases in the rate of lithium amide decomposition to lithium imide and ammonia [Eq. (1)] as well as the reaction rate between ammonia and lithium hydride [Eq. (2)]. (See Figures 3 and 4).

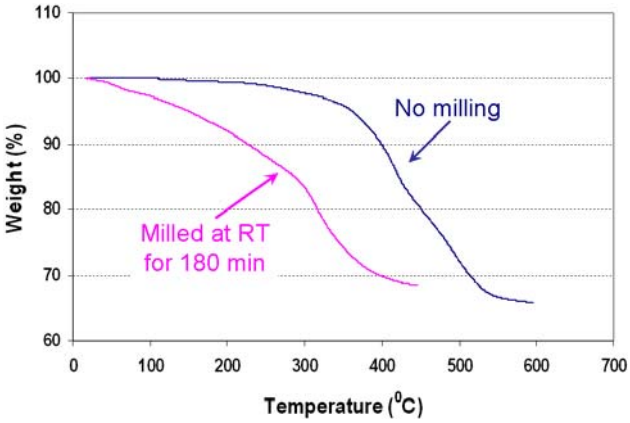

Figure 3. TGA curves of lithium amide before and after ball milling, indicating the enhanced decomposition of lithium amide by ball milling [Eq. (1)]. The analysis is performed with a heating rate of 10°C/min under a flowing argon atmosphere.

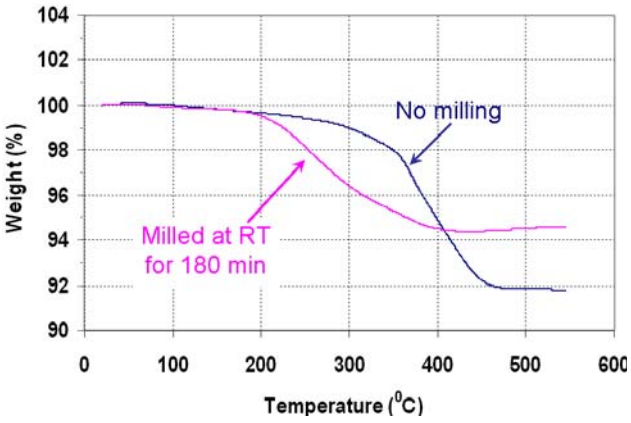

Figure 4. TGA curves of the mixture of lithium amide and lithium hydride with and without ball milling. The hydrogen release rate of the ball-milled mixture is higher than the mixture without ball milling. Further, the weight loss of the ball-milled mixture is consistent with the prediction of Eq. (3), whereas the weight loss of the mixture without ball milling is larger than the prediction of Eq. (3).

$$LiNH_2 = \tfrac{1}{2}\, Li_2NH + \tfrac{1}{2}\, NH_3 \qquad (1)$$

$$\tfrac{1}{2}\, NH_3 + \tfrac{1}{2}\, LiH = \tfrac{1}{2}\, LiNH_2 + \tfrac{1}{2}\, H_2 \qquad (2)$$

Repeated reactions (1) and (2) lead to the overall hydrogen release reaction of the $LiNH_2$ plus LiH mixture:

$$LiNH_2 + LiH = Li_2NH + H_2 \qquad (3)$$

The complete release of H_2 according to Eq. (3) will result in 6.5% weight loss.

- Without ball milling the reaction rate of Eq. (2) is very low. As a result, a substantial amount of ammonia generated from Eq. (1) escapes from the powder mixture, leading to larger weight loss than 6.5% predicted from Eq. (3). In contrast, with ball milling the enhancement in Eq. (2) nearly eliminates the escape of ammonia (Figure 4) and the weight loss observed becomes consistent with the prediction of Eq. (3).