Lithium Nitride-Based Materials for Hydrogen Storage

Leon L. Shaw[1], Marcel Utz[2], Z. Gary Yang[3]
Ruiming Ren[1], Tippawan Markmaitree[1], and Hong Luo[1]
[1] Department of Materials Science and Engineering
University of Connecticut
[2] Department of Physics
University of Connecticut
[3] Materials Science Division
Pacific Northwest National Laboratory

May 23, 2005
2005 DOE Hydrogen Program Review

Project ID: STP51

Overview

Timeline:

- Project start date: December 2004
- Project end date: December 2008
- Percent complete: < 8%

Budget:

- Total project funding
  - DOE share: $1.6 mil
  - Contractor share: $0.4 mil
- Funding received in FY05: $160,000

Partners (interactions/collaborations):

- Sandia National Laboratory (Drs. J. Wang & W. Luo)
- United Technology Research Center (Dr. D. Anton)
- National University of Singapor (Dr. P. Chen)

Objectives

Overall Program Objective in 4 Years:

- **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 100^0C with a plateau hydrogen pressure of less than 10 bar.**

Objective in FY 05:

- **Duplicate the 5.5 wt% reversible storage capacity cited by Dr. Wang's group at Sandia National Lab and Dr. Chen's group at National University of Singapore.**
- **Investigate the effects of the degree of mechanical activation on hydrogen sorption/desorption kinetics.**
- **Demonstrate improvements in hydrogen sorption/desorption kinetics of Li_3N-based materials induced by mechanical activation.**

Background for Li_3N-Based Materials*

The reaction path for the hydrogen storage in Li_3N can be divided into two steps:

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

$$Li_2NH + H_2 \longleftrightarrow LiNH_2 + LiH \qquad (2)$$

Reaction (1) is not easily accessible because of the high reversible hydrogen uptake and release temperatures (~ 430^0C), and thus our efforts will focus on Reaction (2) at this stage. Reaction (2) has the following characteristics:

- **an enthalpy of absorption of - 45 kJ/mol,**
- **6.5 wt% of hydrogen storage capacity, and**
- **reversible hydrogen uptake and release at about 250^0C under a hydrogen pressure of 15 bar.**

** P. Chen, et al., Nature, Vol. 420, 302 (2002).*

Technical Barriers and Approaches

Barriers:

- How to reduce hydrogen sorption/desorption temperatures of Reaction (2)?
- How to increase hydrogen storage capacity based on Reaction (2)?

$$Li_2NH + H_2 \longleftrightarrow LiNH_2 + LiH \qquad (2)$$

Approaches:

- *Mechanical Activation* to reduce hydrogen sorption/desorption temperatures and increase the hydrogen storage capacity.
- *Chemical Modification* of lithium amide/imide to destabilize the compound and thus further reduce hydrogen sorption/desorption temperatures.
- *Quantum-Chemical Modeling* to develop fundamental understanding and guide the effort of mechanical activation and chemical modification.

Key Aspects of Technical Approaches

➢ *Mechanical Activation (UConn)*:*

- **The degree of mechanical activation on the sorption/desorption temperatures will be achieved by controlling the ball milling time, milling temperature, and milled compounds.**
- **5 different milling times: 45 min, 90 min, 180 min, 1,440 min, and 6,000 min.**
- **3 different milling temperatures: (i) water-cooled (20^{0}C), (ii) dry-ice-chilled-ethanol-cooled (- 50^{0}C), and (iii) liquid-nitrogen-cooled (- 196^{0}C).**
- **5 different milled compound systems: (a) $LiNH_2$, (b) LiH, (c) Li_2NH, (d) $LiNH_2$ + LiH, and (e) $LiNH_2$ + TiH**

** Started in FY 05.*

Key Aspects of Technical Approaches (Cont.)

➢ *Quantum-Chemical Modeling (UConn)*:*

- **Simulation of hydrogen absorption at the solid/gas interface.**
- **Simulation of solid state reactions to form lithium amide ($LiNH_2$) and lithium imide (Li_2NH)**
- **Simulation of the interaction of crystal lattice defects with the sorption/desorption and diffusion of hydrogen in lithium amide and imide.**
- **Simulation of the effects of the degree of mechanical activation on the hydrogen sorption/desorption and hydrogen storage capacity.**
- **Simulation of the influence of dopants on the thermodynamics and kinetics of hydrogen sorption/desorption as well as hydrogen storage capacity.**

** To be pursued in FY 06.*

Key Aspects of Technical Approaches (Cont.)

➢ *Advanced NMR Studies (PNNL)*:*

- **A range of advanced NMR measurements including the wideline NMR, the combined magic angle spinning and multiple pulse (CRAMPS), multiple-quantum NMR combined with magic angle spinning (MQ-MAS) and chemical shift tensor measurements.**
- **Determination of ordering/disordering, phase transformation, bond length and angle changes induced by mechanical activation with the help of quantum chemistry calculations at the density function level.**
- **Establishment of the strength of the hydrogen bond between the host material and the stored H_2 as a function of mechanical activation.**
- **Determination of diffusivity, activation energy, diffusion paths, and possibly the volume fraction of mobile hydrogen.**

** To be started in the second quarter of FY 05.*

Technical Accomplishments and Progress

(December 9, 2004 – March 30, 2005)

- ***Equipment Setup:***

  Ball milling system; Thermal analysis instrument; Powder analysis equipment; Crystal structure/grain size measurement equipment; Gas composition analysis instrument; Pressure-composition-isotherm unit.

- ***Ball Milling of $LiNH_2$ and $LiNH_2$ + LiH Systems:***

  Ball milling time: 45 min, 90 min, and 180 min
  Ball milling temperature: 25^0C

- ***Characterization of Ball Milling Effects:***

  Particle size; Grain size; Specific surface area; Sorption/desorption temperatures; Weight changes during reactions; Gas composition analysis

Technical Accomplishments and Progress

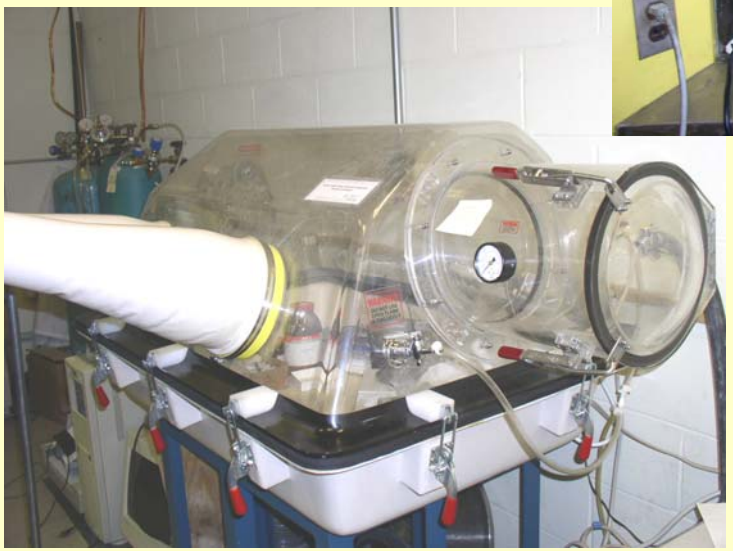
I. Equipment Setup

Mechanical activation equipment with temperature capabilities ranging from 80^0C to – 196^0C.

Technical Accomplishments and Progress (Cont.)

I. Equipment Setup (Cont.)

Tube furnace with controlled atmosphere for sample synthesis

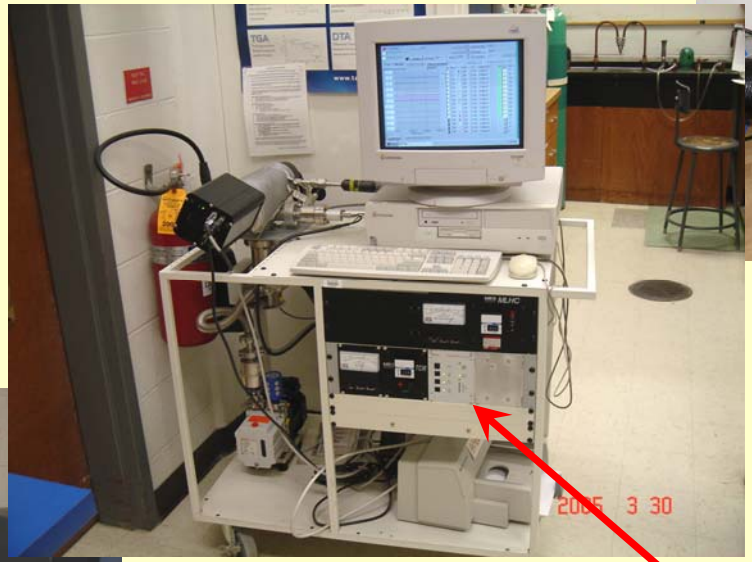


Glove boxes with inert or hydrogen atmosphere for sample handling

Technical Accomplishments and Progress (Cont.)

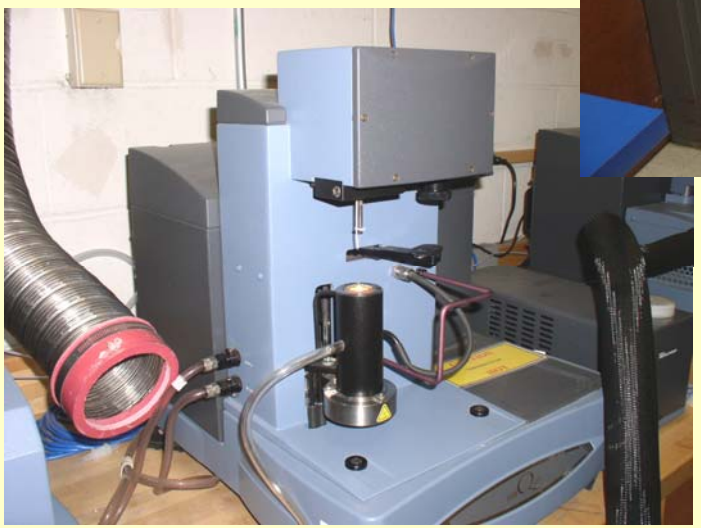
I. Equipment Setup (Cont.)

Modulated DSC



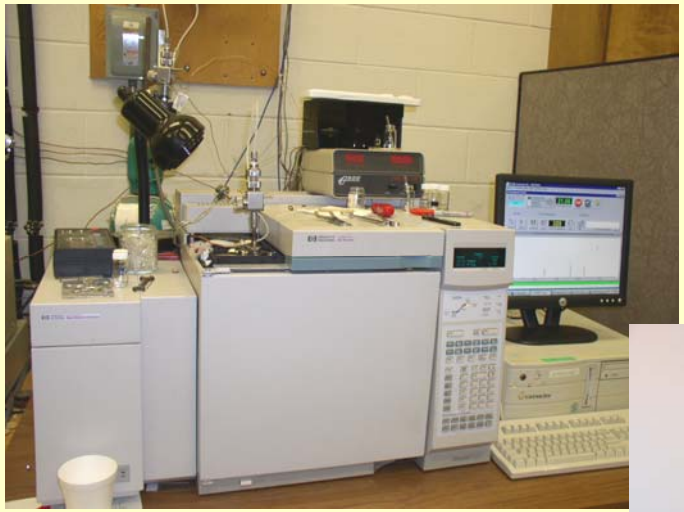
Residual gas analyzer (RGA) for composition analysis of the outlet gas from TGA or DSC

TGA



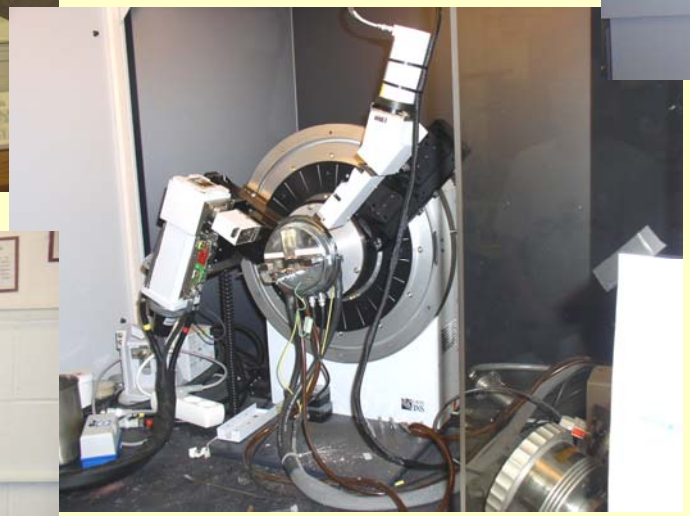
Technical Accomplishments and Progress (Cont.)

I. Equipment Setup (Cont.)



GC/MS

Environmental SEM



X-ray diffractometer with a heating stage

Specific surface area analyzer

Technical Accomplishments and Progress (Cont.)

I. Equipment Setup (Cont.)

Pressure-Composition Isotherm (PCI) instrument to be installed in June 2005

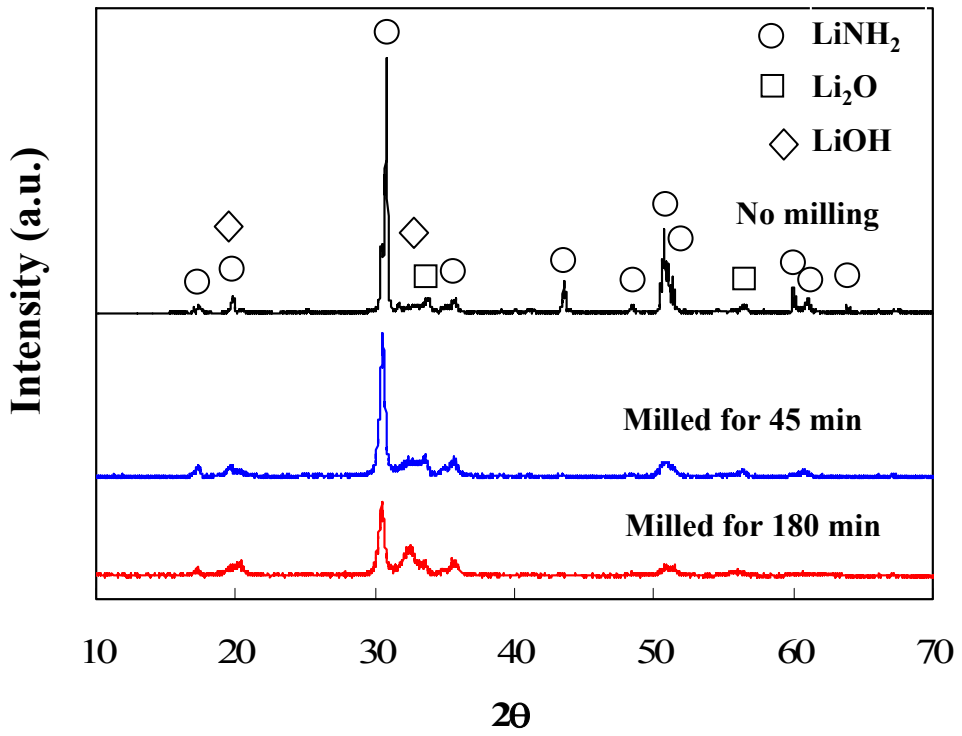
FTIR

NMR

Technical Accomplishments and Progress (Cont.)

II. Results for lithium amide ($LiNH_2$)

- **Ball milling at room temperature induces the XRD peak broadening, suggesting grain refinement and/or introduction of crystal defects.**
- **Peak broadening increases as the milling time increases.**
- **A small amount of Li_2O and LiOH are present at the as-purchased $LiNH_2$.**

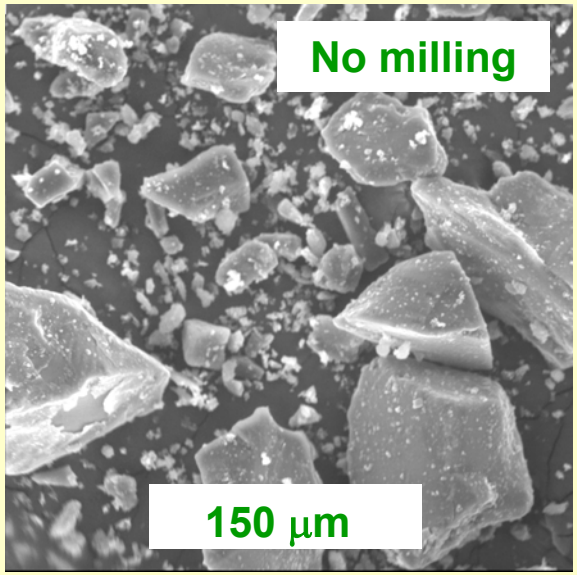


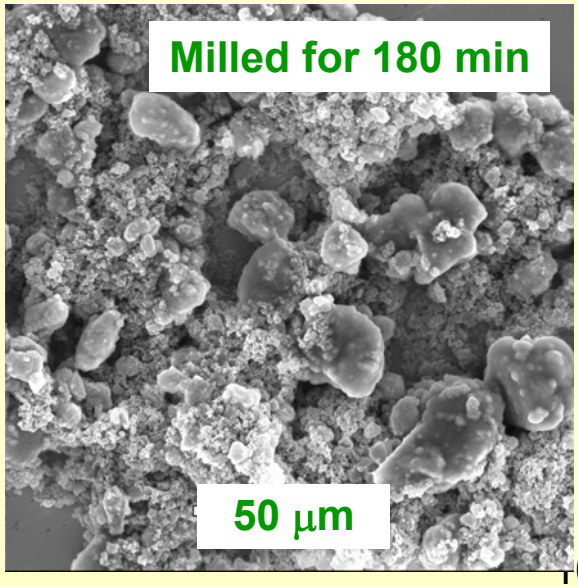
Technical Accomplishments and Progress (Cont.)

II. Results for lithium amide ($LiNH_2$)

- Specific surface area (SSA) increases with the milling time.
- The crystallite size determined from XRD peak broadening decreases with the increase in the milling time.
- The equivalent particle size calculated from SSA exhibits the same trend as the SEM analysis, i.e., particle sizes decrease with the increase in the milling time.
- All these changes will affect the $LiNH_2$-to-Li_2NH reaction.

Milling time (min)	SSA (m^2/g)	Crystallite size (nm)	Equivalent particle size (μm)
0	3.72	> 100	1.37
45	40.71	5.9	0.13
180	46.65	5.5	0.11





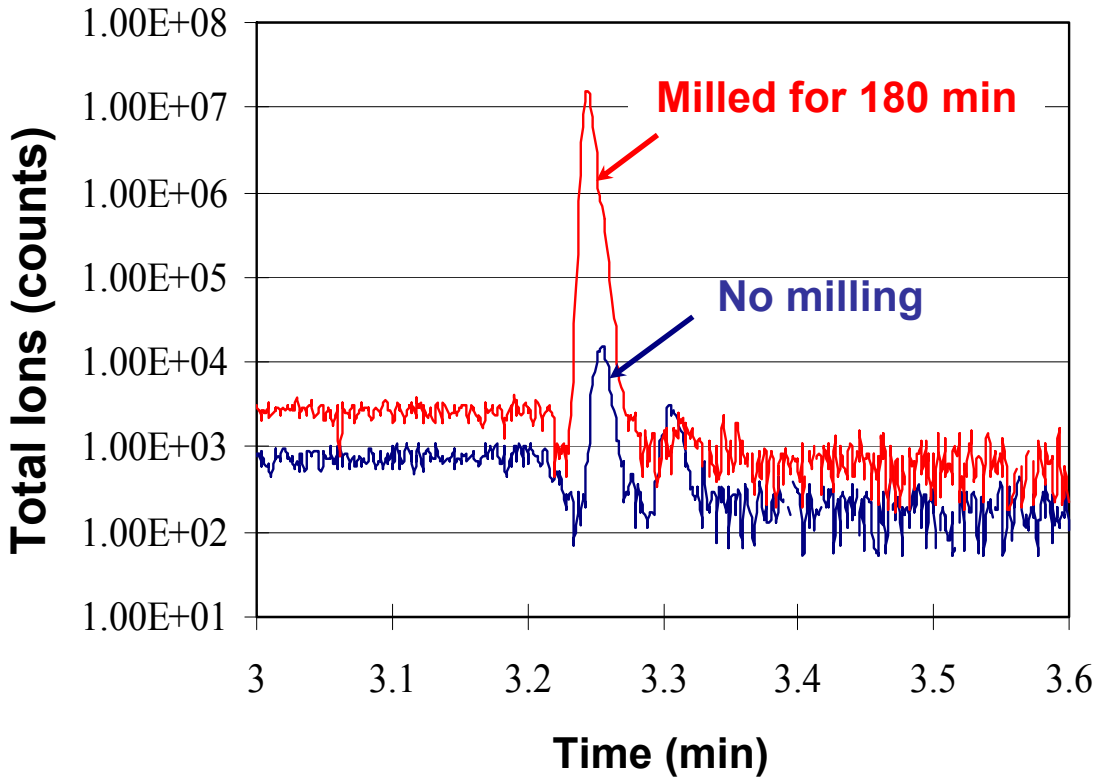
Technical Accomplishments and Progress (Cont.)

II. Results for lithium amide ($LiNH_2$)

- $LiNH_2$ can decompose to NH_3 and Li_2NH according to the following reaction

$2\ LiNH_2 = Li_2NH + NH_3$

- Ball milling has decreased the decomposition temperature dramatically.
- The gas chromatograph (GC)/mass spectrometry (MS) analysis shows that NH_3 released by the ball milled $LiNH_2$ at 50^0C is 820 times higher than that from the $LiNH_2$ without milling.

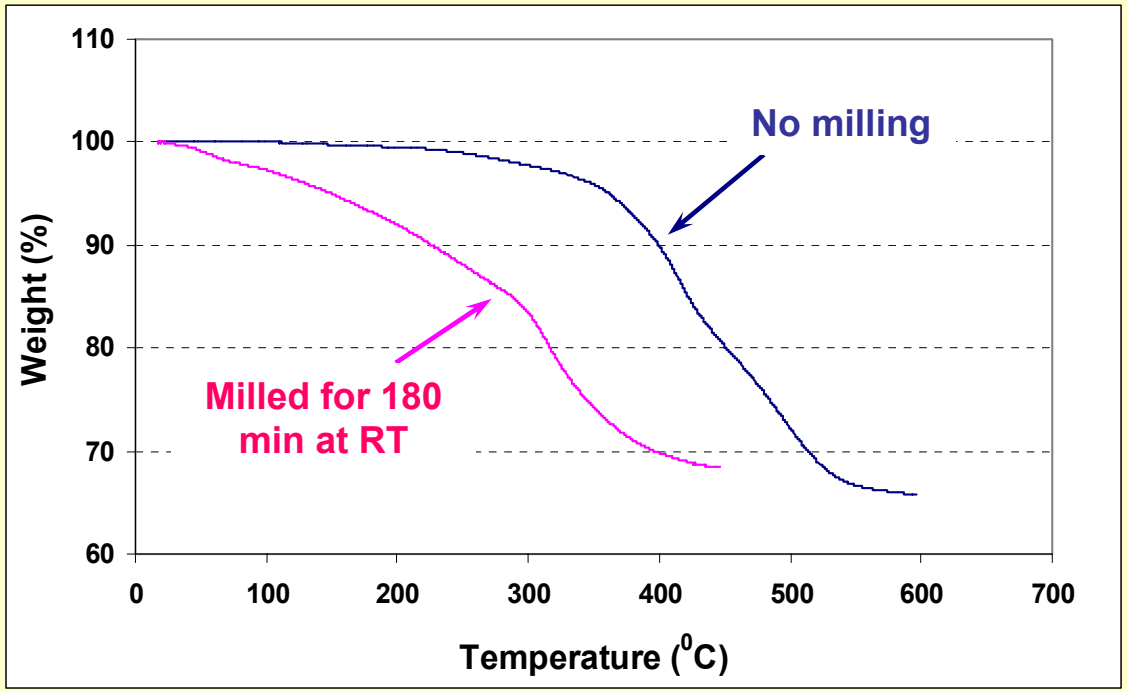


Technical Accomplishments and Progress (Cont.)

II. Results for lithium amide ($LiNH_2$)

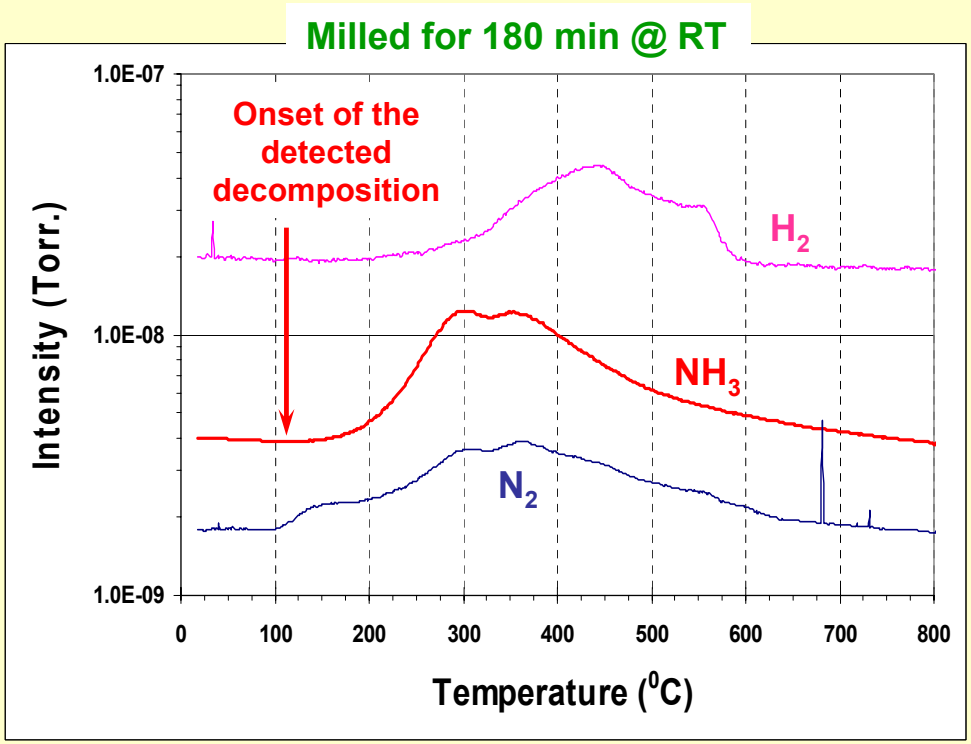
- TGA analysis indicates that the onset temperature for the decomposition of the $LiNH_2$ without milling is about 120^0C.
- After ball milling, $LiNH_2$ decomposes to NH_3 and Li_2NH at room temperature, a result consistent with the GC/MS analysis.
- Weight loss of about 33% is slightly lower than 37%, the theoretical weight loss for decomposition of 100% $LiNH_2$ starting powder.

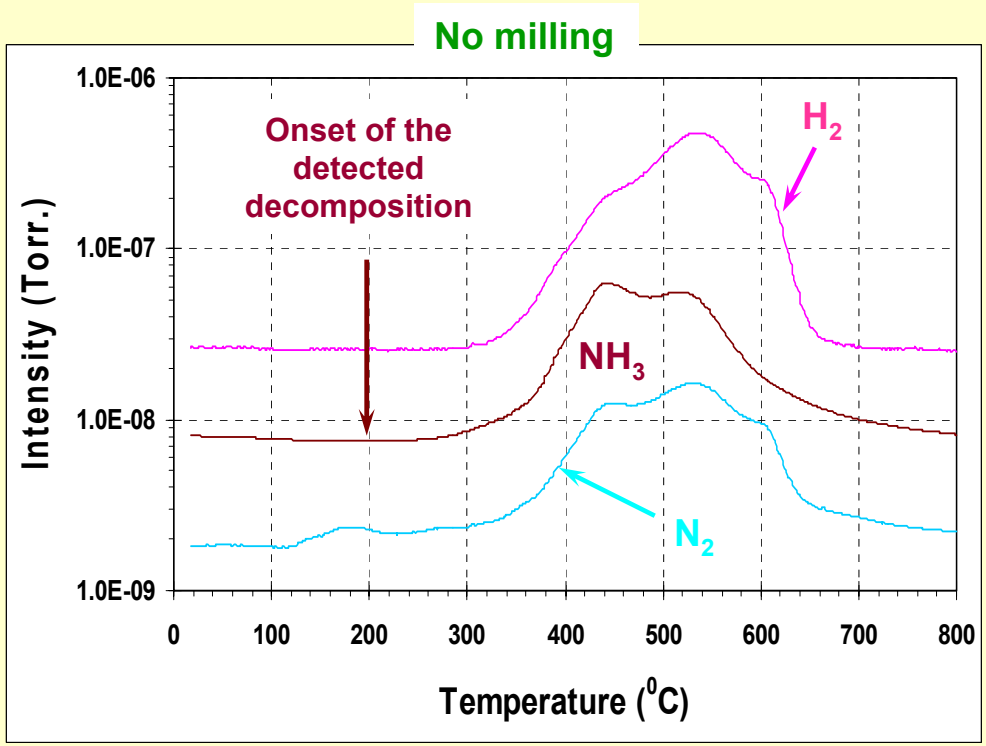
TGA Results



Technical Accomplishments and Progress (Cont.)

II. Results for lithium amide ($LiNH_2$)



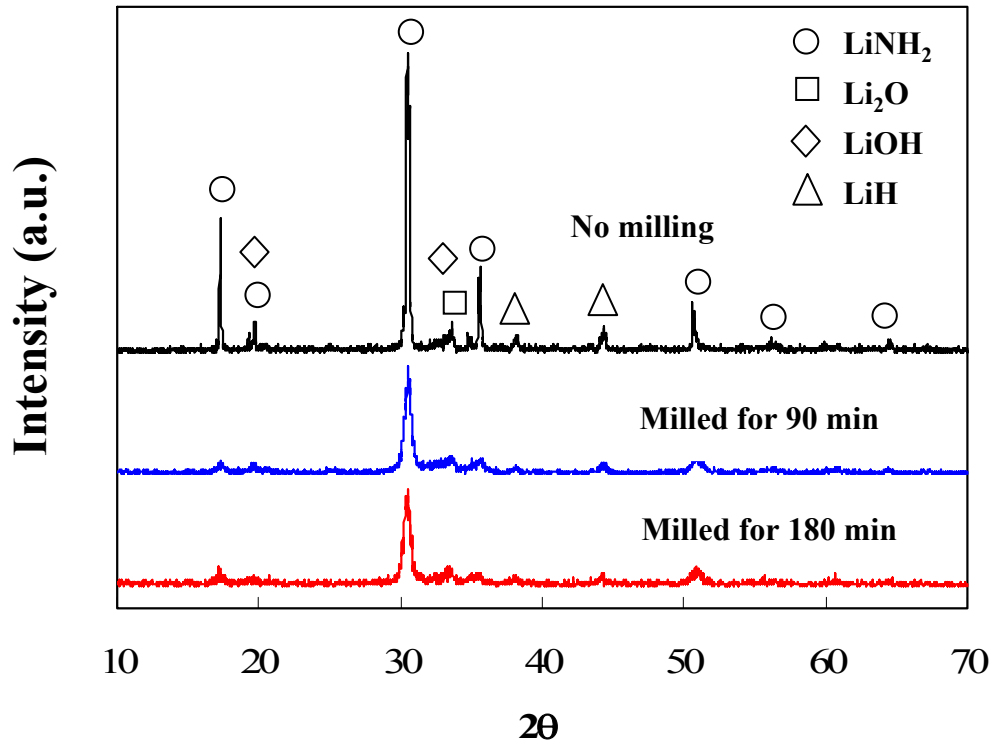


- **RGA analysis indicates that the onset temperature for the $LiNH_2$ without milling is about 200^0C, which decreases to about 110^0C after ball milling for 180 min at RT.**
- **The presence of H_2 and N_2 are likely related to the decomposition of NH_3 which comes from the reaction: $2\ LiNH_2 = Li_2NH + NH_3$**

Technical Accomplishments and Progress (Cont.)

II. Results for the mixture of lithium amide/hydride ($LiNH_2$+ LiH)

- Similar to the case of $LiNH_2$, ball milling at room temperature also induces the peak broadening to the $LiNH_2$ and LiH mixture.
- Peak broadening for both $LiNH_2$ and LiH increases as the milling time increases, suggesting grain refinement and/or introduction of crystal defects.

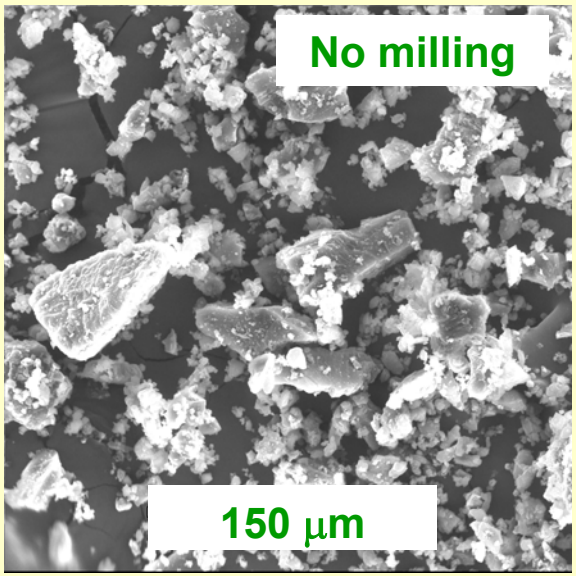


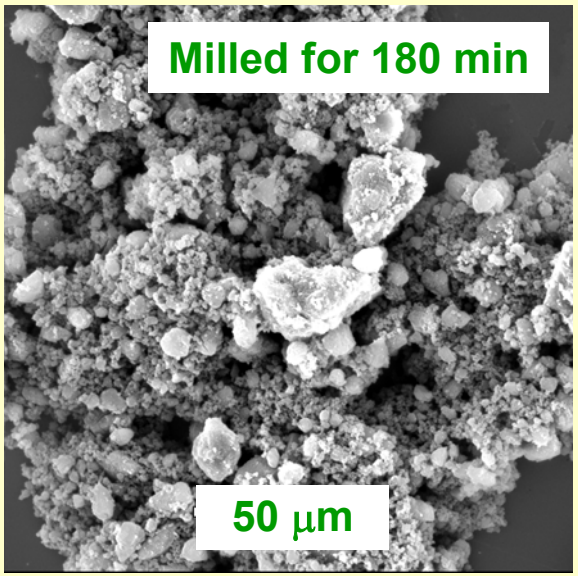
Technical Accomplishments and Progress (Cont.)

II. Results for the mixture of lithium amide/hydride ($LiNH_2$+ LiH)

- Specific surface area (SSA) increases with ball milling.
- The crystallite size determined from XRD peak broadening decreases with the increase in the milling time.
- The equivalent particle size calculated from SSA exhibits the same trend as the SEM analysis, i.e., particle sizes decrease with the increase in the milling time.
- All SSA and crystallite size changes affect the hydrogen desorption temperature.

Milling time (min)	SSA (m^2/g)	Crystallite size $LiNH_2$/LiH (nm)	Equivalent particle size (μm)
0	4.65	> 100 / > 100	1.23
90	56.82	7.2 / 13.6	0.10
180	54.86	4.1 / 32.4	0.10



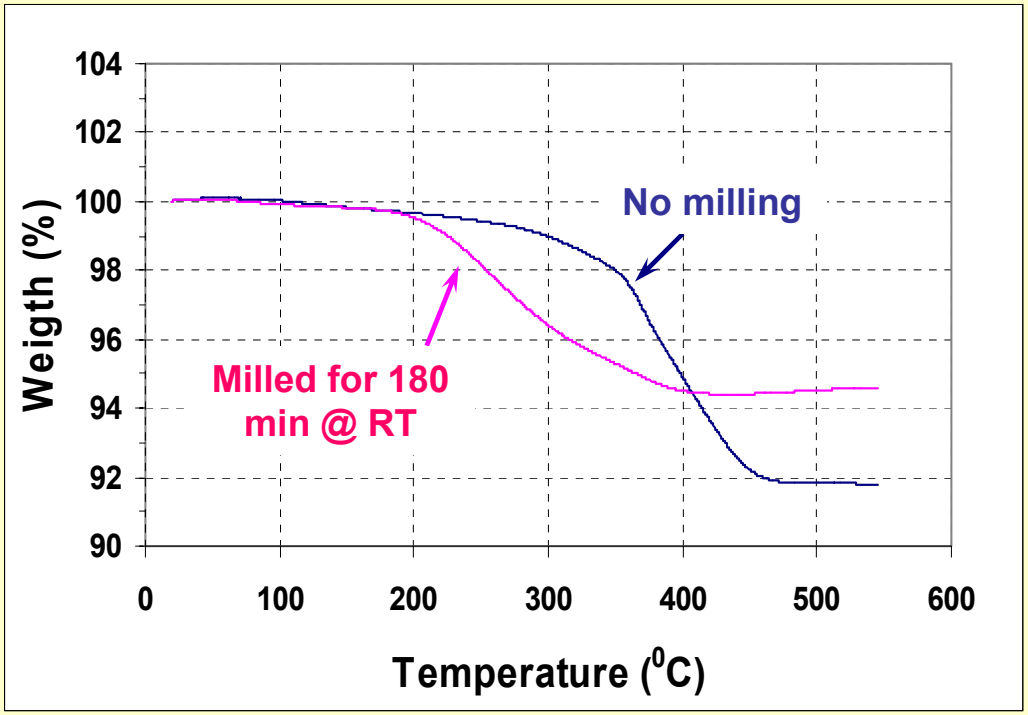


Technical Accomplishments and Progress (Cont.)

II. Results for the mixture of lithium amide/hydride ($LiNH_2$+ LiH)

- **TGA analysis indicates that the onset temperature of hydrogen release for the $LiNH_2$ + LiH mixture with and without ball milling is about the same, all around 75^0C.**
- **However, the temperature for release of a large amount of H_2 (1 wt%) is decreased from about 300^0C to 230^0C after ball milling.**
- **The weight loss for the milled sample is about 5.5% which is slightly smaller than 6.5% if the mixture is 100% $LiNH_2$ + LiH.**
- **The weight loss for the sample without milling is larger than 6.5% because of NH_3 release due to the incomplete reaction between ammonia and hydride.**

TGA Results



Summary of Technical Accomplishments and Progress

- The theoretical hydrogen storage capacity based on Rx (2) is 6.5 wt% H_2. The ball milled sample has indeed shown 5.5 wt% H_2 release [slice 22], which is slightly lower than 6.5 wt% because of the presence of Li_2O and LiOH in the as-purchased $LiNH_2$.

$$LiNH_2 + LiH \longleftrightarrow Li_2NH + H_2 \qquad (2)$$

- Rx (2) is proposed to proceed with two elementary reactions as shown below*:

$$LiNH_2 \longleftrightarrow \tfrac{1}{2}\, Li_2NH + \tfrac{1}{2}\, NH_3 \qquad (3)$$

$$\tfrac{1}{2}\, NH_3 + \tfrac{1}{2}\, LiH \longleftrightarrow \tfrac{1}{2}\, LiNH_2 + \tfrac{1}{2}\, H_2 \qquad (4)$$

The newly formed ½ $LiNH_2$ from Rx (4) will decompose to ¼ Li_2NH and ¼ NH_3 as indicated by Rx (3), and the ¼ NH_3 formed from Rx (3) will be captured by ¼ LiH as shown by Rx (4). These two elementary reactions continue until exhaustion of $LiNH_2$.

- Ball milling has substantially reduced the reaction temperature of Rx (3) [slices 17 – 19], and thus decreased the hydrogen desorption temperature of Rx (2) [slice 22].

- The NH_3 produced from Rx (3) is captured by LiH as shown by Rx (4) and thus there is no NH_3 contamination to PEM fuel cells. Therefore, Rx (4) is critical in preventing the NH_3 contamination. Without ball milling, escaping of NH_3 is present. In contrast, with ball milling, Rx (4) is enhanced and escaping of NH_3 is eliminated [slice 22].

* T. Ichikawa, et al., J. Phys. Chem. B, Vol. 108, 7887-7892 (2004).

Future Work

- **Remainder of FY 2005:**

  - **Investigate effects of long milling time (1,440 min & 6,000 min) and low-temperature milling (-50^{0}C and –196^{0}C) on the sorption/desorption temperatures, activation energy for reactions, enthalpies of reactions, and hydrogen storage capacities. (UConn)**

  - **Determine ordering/disordering, phase transformation, bond length and angle changes induced by mechanical activation with the help of quantum chemistry calculations at the density function level. (PNNL & UConn)**

- **FY 2006:**

  - **Integration of mechanical activation and chemical modification of lithium amide/imide. (UConn)**

  - **Determination of the strength of the hydrogen bond between the host material and the stored H_2, diffusivity, diffusion paths, and possibly the volume fraction of mobile hydrogen as a function of mechanical activation. (PNNL & UConn)**

  - **Quantum-chemical modeling for fundamental understanding to guide the effort of mechanical activation and chemical modification. (UConn)**

Publications and Presentations

- R. Ren, T. Markmaitree, L. Shaw and Z. G. Yang, "Effects of Mechanical Activation on Lithium Amide/Imide Transition and Hydrogen Sorption/ Desorption," to be presented at the Symposium on "Materials for the Hydrogen Economy" in the MS&T '05, Pittsburgh, PA, Sept. 2005.
- T. Markmaitree, R. Ren and L. Shaw, "Effects of Mechanical Activation on the Lithium Amide-to-Lithium Imide Reaction," to be submitted to J. Phys. Chem. B.
- R. Ren, T. Markmaitree and L. Shaw, "Stability of Lithium Amide and Lithium Hydride in Ambient Atmosphere," to be submitted to J. Phys. Chem. A.
- R. Ren, T. Markmaitree, L. Shaw, Z. G. Yang and J. Hu, "Enhanced Hydrogen Sorption/Desorption of Lithium Amide and Imide via Mechanical Activation," to be submitted to J. Phys. Chem. B.