

Effects and Mechanisms of Mechanical Activation on Hydrogen Sorption/Desorption of Nanoscale Lithium Nitrides

Leon L. Shaw, Tippawan Markmaitree, William Osborn,
Xuefei Wan, Kyle Crosby
University of Connecticut

Z. Gary Yang, Jianzhi Hu, Ja Hu Kwak
Pacific Northwest National Laboratory

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Project ID: ST14

Overview

Timeline:

- Project start date: December 2004
- Project end date: December 2009
- Percent complete: 55%

Budget:

- Total project funding:
 - DOE share: \$1.6 mil
 - Contractor share: \$0.4 mil
 - Funding received in FY07: \$200,000 for UConn; \$90,000 for PNNL
- Funding for FY08: \$250,000 for UConn; \$80,000 for PNNL

Partners/Collaborators:

- Pacific Northwest National Laboratory – NMR analysis
- Sandia National Laboratory – Information exchange
- Universidad de Extremadura, Badajoz, Spain – X-ray analysis
- HRL Laboratories – Information exchange
- University of Pittsburgh – Information exchange

Barriers

- A. System weight and volume:
2 kWh/kg & 1.5 kWh/L
- E. Charging/discharging rates:
3 min for 5 kg

Objectives

Objective in FY 07:

- Identify hydriding/dehydriding reaction mechanisms and rate-limiting steps of (LiNH₂ + LiH) systems
- Enhance hydriding/dehydriding rates via nano-engineering and mechanical activation
- Improve hydriding/dehydriding properties via thermodynamic destabilization

Objective in FY 08:

- Further improvement in hydriding/dehydriding properties of (LiNH₂ + LiH) systems via nano-engineering, mechanical activation, and thermodynamic destabilization
- Establishment of the atomic level understanding of the reaction mechanism and kinetics of mechanically activated, nano-engineered (LiNH₂ + LiH) systems
- Nano-engineering and mechanical activation of LiBH₄-based materials
- Demonstration of hydrogen uptake and release of (LiBH₄ + MgH₂) systems with a storage capacity of ~ 10 wt% H₂ at 200°C

Milestones

Month/Year	Milestone or Go/No-Go Decision
Nov-07	<p><u>Milestone:</u> Identify the hydriding/dehydriding mechanisms and rate-limiting steps of (LiNH₂ + LiH) systems. Establish the effect of mechanical activation. Enhance the reaction kinetics of mechanically activated, nano-engineered (LiNH₂ + LiH) systems.</p>
Dec-07	<p><u>Go/No-Go Decision:</u> Demonstrate mechanically activated Li₃N-based materials with ~ 7.5 wt% reversible hydrogen storage capacity and uptake/release at temperatures below 130°C and a few bars of hydrogen pressure.</p>
Nov-08	<p><u>Milestone:</u> Establish the atomic level understanding of the reaction mechanism and kinetics of hydriding/dehydriding of mechanically activated, nano-engineered (LiNH₂ + LiH) systems. Demonstrate hydriding and dehydriding reactions of (LiBH₄ + MgH₂) systems at the solid state, i.e., below the melting point of LiBH₄ (T_m = 280°C). Demonstrate hydrogen uptake and release of (LiBH₄ + MgH₂) systems with a storage capacity of ~ 10 wt% H₂ at 200°C.</p>
Dec-08	<p><u>Go/No-Go Decision:</u> Demonstrate hydrogen uptake and release of (LiBH₄ + MgH₂) systems with a storage capacity of ~ 10 wt% H₂ at 200°C.</p>

Approaches

- **Identifying the mechanism and rate-controlling step of hydriding and dehydriding reactions of (LiNH₂ + LiH) systems and LiBH₄-based materials.**
- **Developing the understanding of the effect of mechanical activation and nano-engineering on hydriding and dehydriding properties**
- **Applying the understanding of mechanical activation and the established reaction mechanism and rate-controlling step to enhancing hydriding and dehydriding properties and long-term cyclical stabilities of hydrogen storage materials.**

Identification of Reaction Mechanism



Reversible storage capacity = 6.5 wt% H₂ [1]

ΔH (dehydrating) = 65.6 kJ/mol H₂ [2]

- The current operating temperatures for hydriding and dehydrating are typically at ~ 280°C, higher than the thermodynamic prediction [1-3].
- Why is hydriding very fast, whereas dehydrating is very slow [4]?
- Why is the formation of Li₂NH and NH₃ from LiNH₂ slow [5], whereas the reaction between NH₃ and LiH is very fast [6]?
- There is NH₃ emission associated with this storage system [3,7].

[1] P. Chen, et al., *Nature*, 420, 302 (2002).

[2] Y. Kojima, Y. Kawai, *J. Alloys Comp.*, 395, 236 (2005).

[3] L. Shaw, et al., *J. Alloys Compd.*, 448, 263 (2008).

[4] L. Shaw, et al., *J. Power Sources*, 177, 500 (2008).

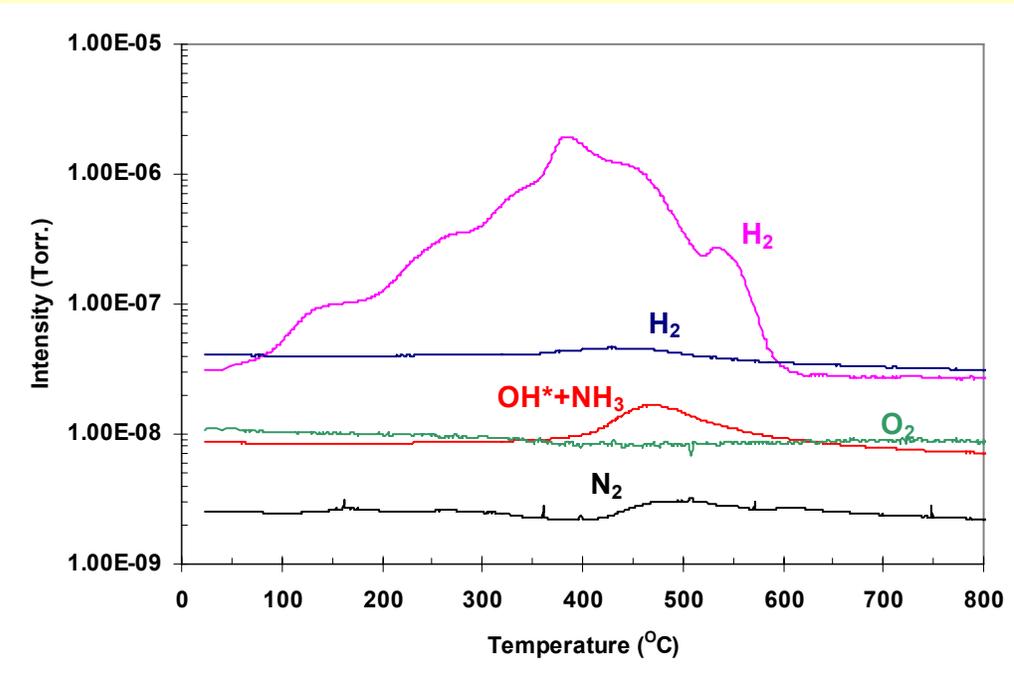
[5] T. Markmaitree, R. Ren, L. Shaw, *J. Phys. Chem. B.*, 110, 20710 (2006).

[6] H. Y. Hu, E. Ruckenstein, *J. Phys. Chem. A*, 107, 9737 (2003).

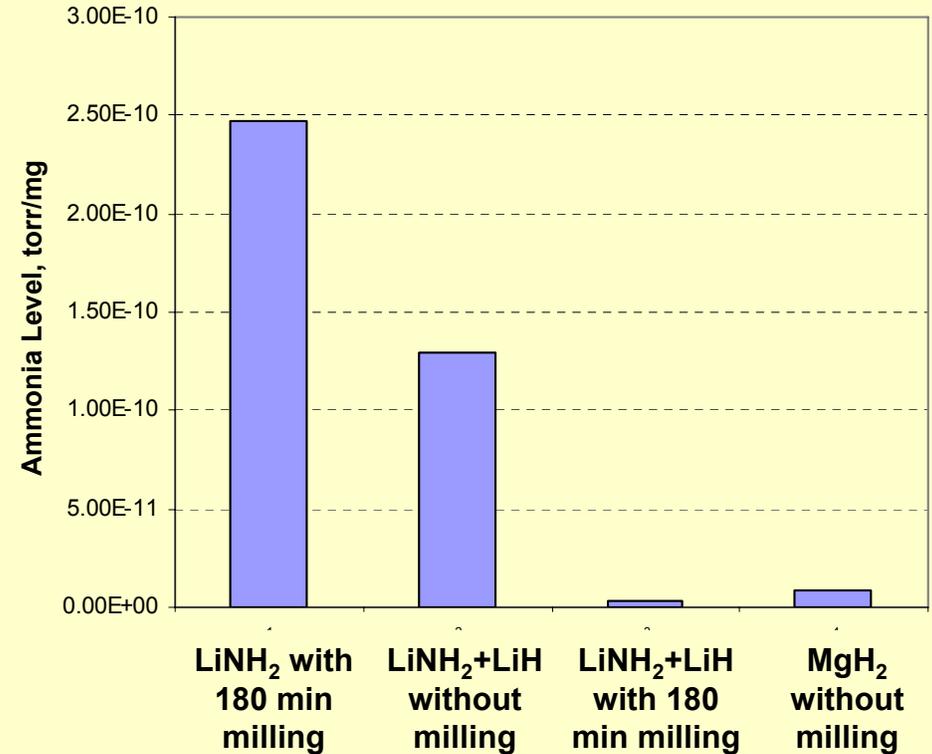
[7] T. Ichikawa, et al., *J. Phys. Chem. B*, 108, 7887 (2004).

Identification of Reaction Mechanism

Composition analysis of the effluent gas from LiNH_2+LiH mixtures during heating



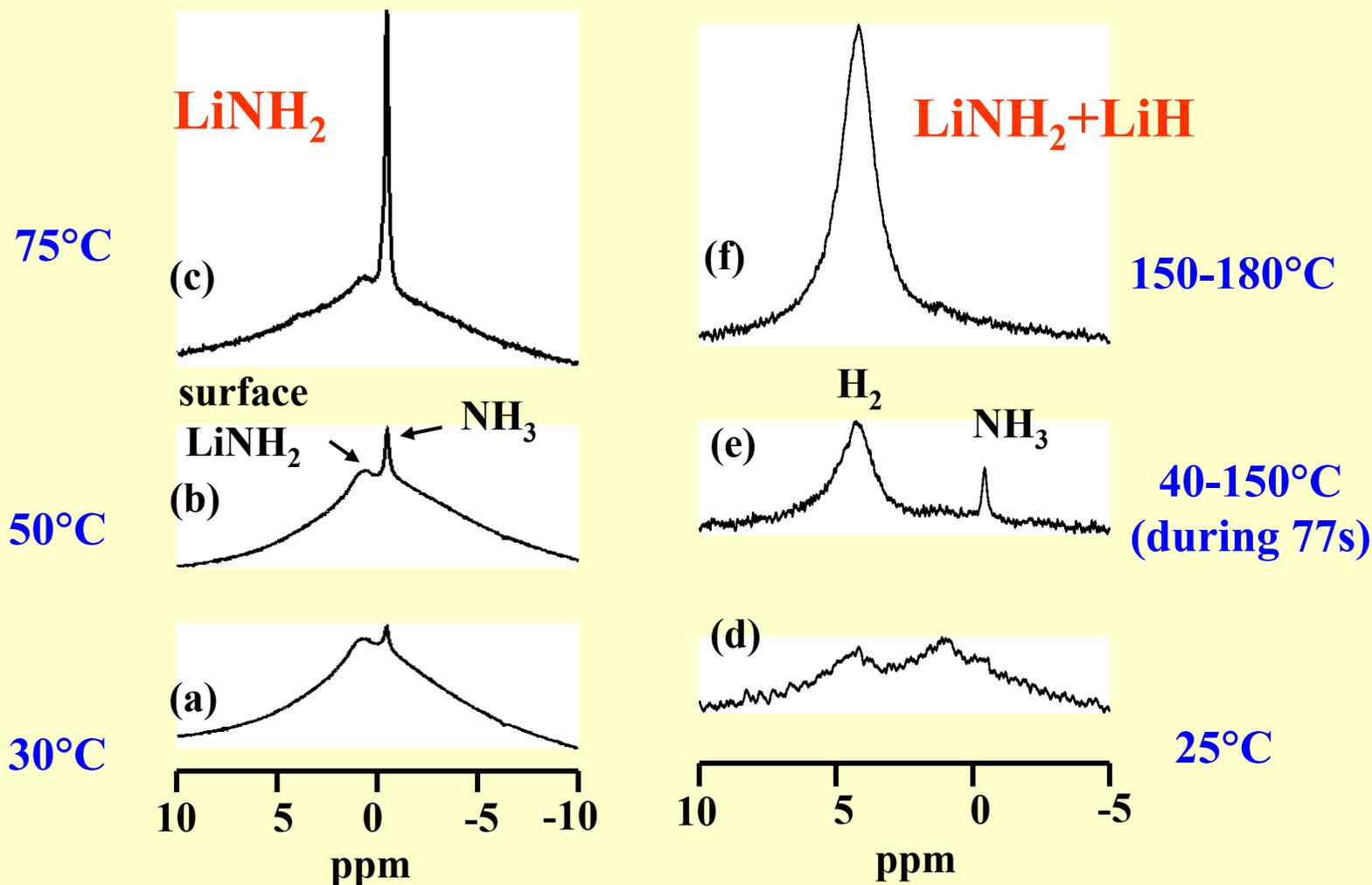
Comparisons in the NH_3 emission from different hydride systems



- ❑ The LiNH_2 -only sample exhibits the highest NH_3 emission.
- ❑ LiNH_2+LiH mixtures display much less NH_3 emission, indicating the “capturing” of NH_3 by LiH and offering the evidence of two elementary steps for dehydrating reaction.
- ❑ Ball milling reduces the NH_3 emission dramatically (by about 36 times); In fact, the NH_3 intensity is so low that it is below the detection limit of the mass spectrometer.

Identification of Reaction Mechanism

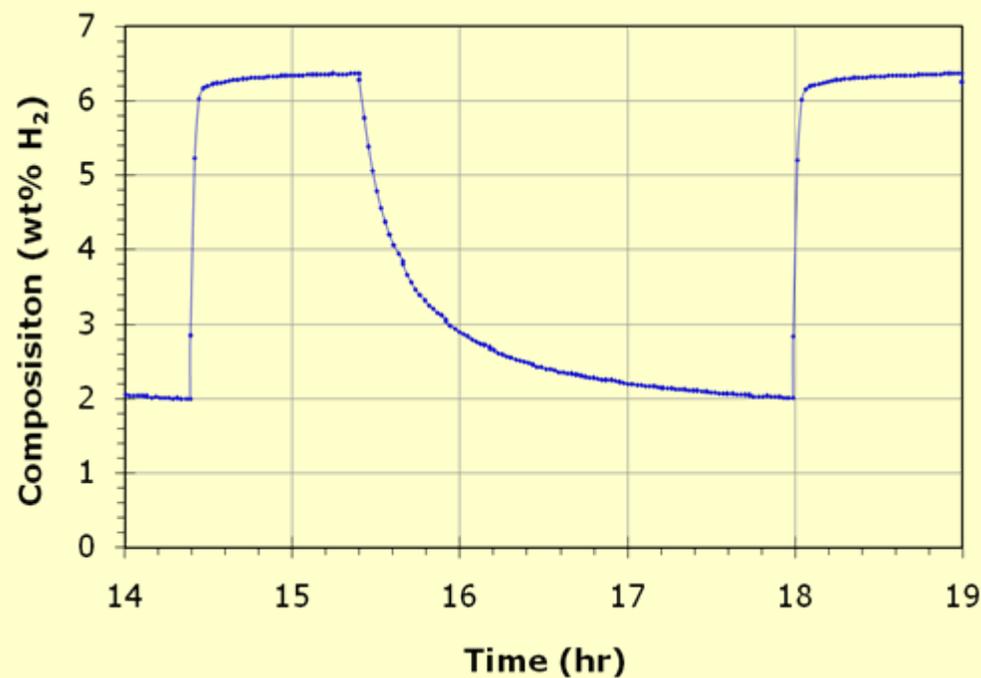
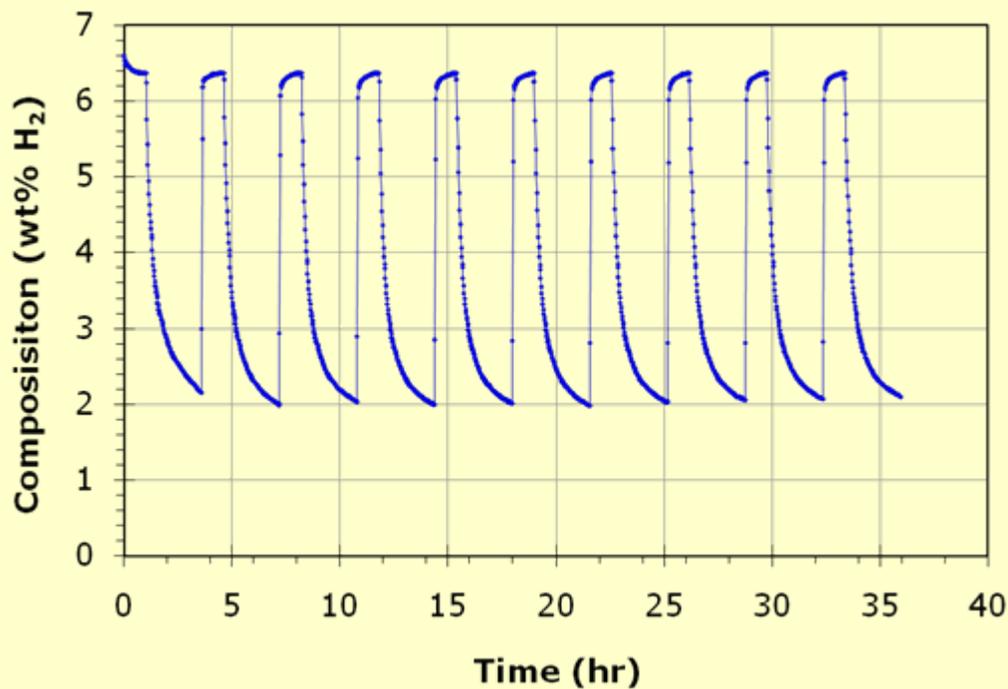
VT 300MHz *in situ* ^1H MAS NMR Spectra



- NH_3 releases from LiNH_2 at temperatures as low as 30°C. The speed of NH_3 release increases dramatically at $\sim 75^\circ\text{C}$.
- LiH reacts with NH_3 at RT; however, the minimum temperature for LiH to capture all the NH_3 molecules is higher than the temperature at which a large quantity of NH_3 is released from LiNH_2 .

Identification of Rate-Limiting Steps

Isothermal hydrogen uptake/release cycles of the $\text{LiNH}_2 + \text{LiH}$ mixture at 285°C^*

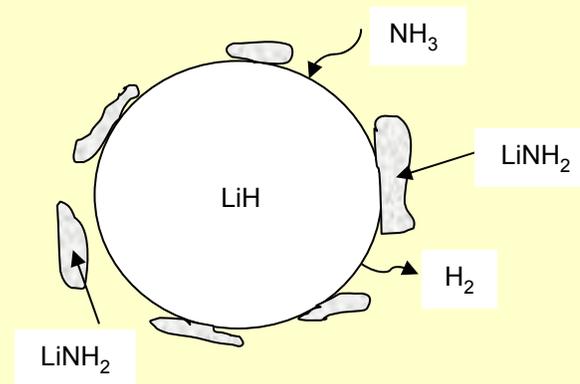
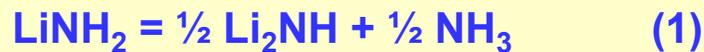
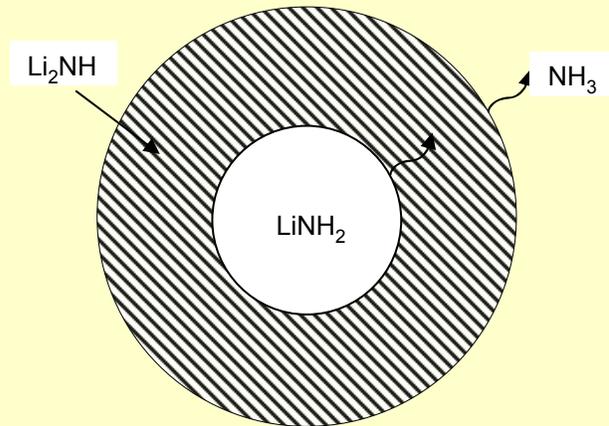


- A rapid hydrogen uptake rate (i.e., approaching the theoretical storage capacity in ~ 5 min)
- A slow release rate (i.e., incomplete release of hydrogen in 2.5 h).
- Modeling of the release kinetics under a constant temperature and constant hydrogen pressure to investigate the rate-limiting step.

* *L. Shaw, W. Osborn, T. Markmaitree, X. Wan, J. Power Sources, 177, 500 (2008).*

Identification of Rate-Limiting Steps

Dehydriding of $\text{LiNH}_2 + \text{LiH}$ proceeds with two elementary reactions:



- ❑ Both reactions produce solid products. However, Reaction (1) occurs very slow because of the diffusion-controlled reaction [1], whereas Reaction (2) takes place in microseconds [2] because of cracking and flaking off of the LiNH_2 product [3].
- ❑ The cracking and flaking off of the LiNH_2 product is due to the fact that the volume of the solid product from Reaction (2) is substantially larger than that of the solid reactant (2 times larger) [3].

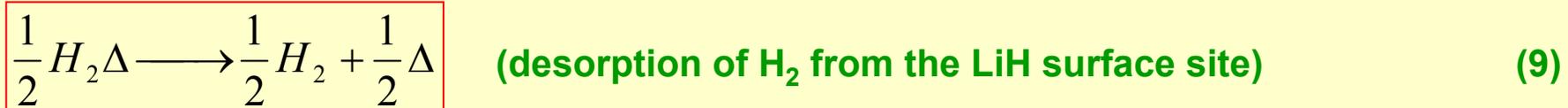
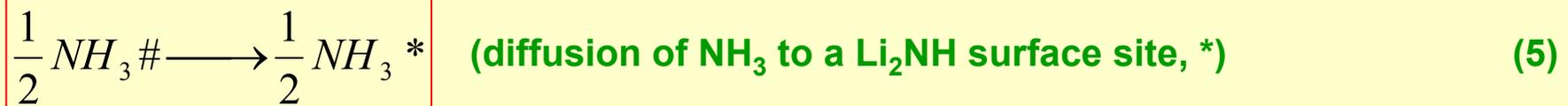
[1] T. Markmaitree, R. Ren, L. Shaw, *J. Phys. Chem. B.*, 110, 20710 (2006).

[2] H. Y. Hu, E. Ruckenstein, *J. Phys. Chem. A*, 107, 9737 (2003).

[3] L. Shaw, et al., *J. Power Sources*, 177, 500 (2008).

Identification of Rate-Limiting Steps

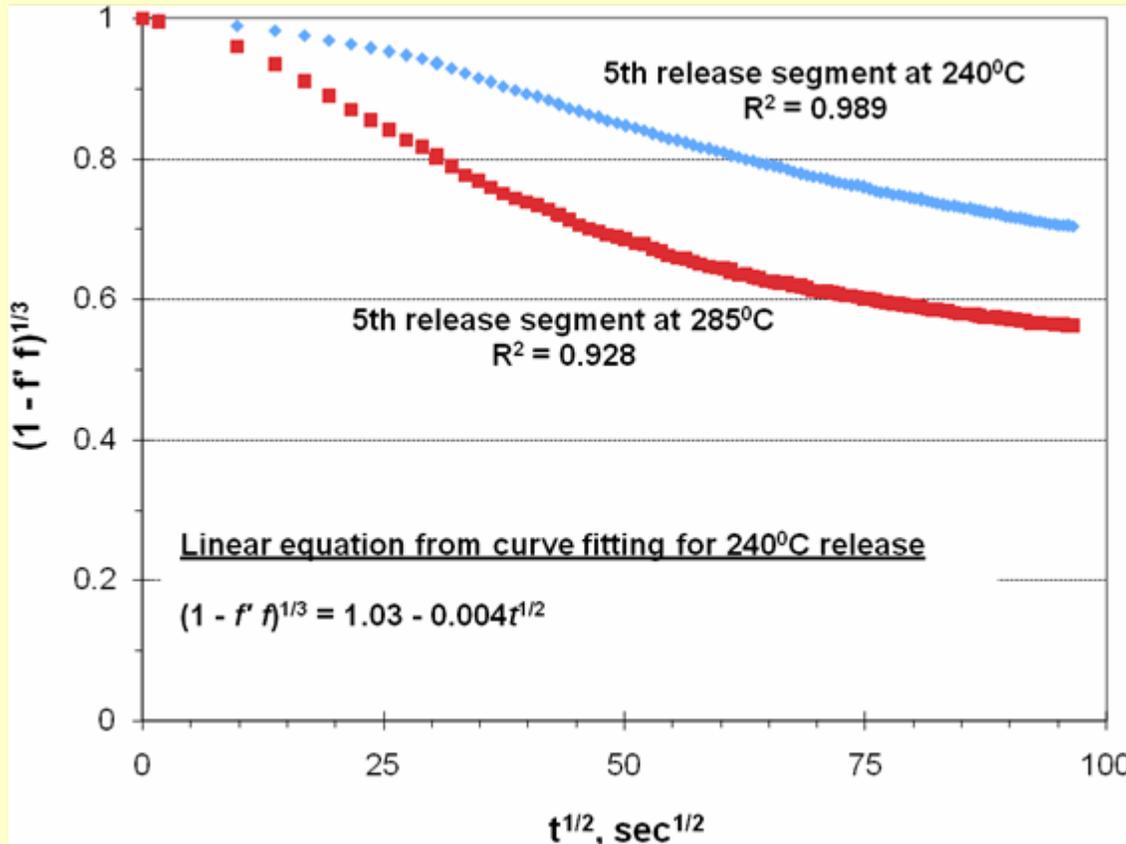
Based on the reaction pathway proposed, the hydrogen release of the $\text{LiNH}_2 + \text{LiH}$ system can be described at least with the following 6 steps.



The rate of dehydriding will be controlled by the slowest step.

Identification of Rate-Limiting Steps

Curve Fitting of the Amount of H₂ Released at 285°C



$$(1 - f' f)^{1/3} = 1 - \frac{5.6D^{1/2}}{R} t^{1/2}$$

The shrinking-core model with the moving speed of the LiNH₂/Li₂NH interface controlled by a diffusing specie (e.g., N or NH₃)

Conclusions*: Dehydrating of the LiNH₂ + LiH system is controlled by the slowest step of the decomposition of LiNH₂ which is a diffusion controlled reaction.

* L. Shaw, W. Osborn, T. Markmaitree, X. Wan, *J. Power Sources*, 177, 500 (2008).

Challenges for Improving Hydriding and Dehydriding Properties

We have established that dehydrogenation of the $\text{LiNH}_2 + \text{LiH}$ system is a diffusion-controlled process and thus takes place very slowly.

How can we increase the rate of a diffusion-controlled reaction?

1. Nano-engineering to decrease the diffusion distance.

$$x^2 \propto Dt$$

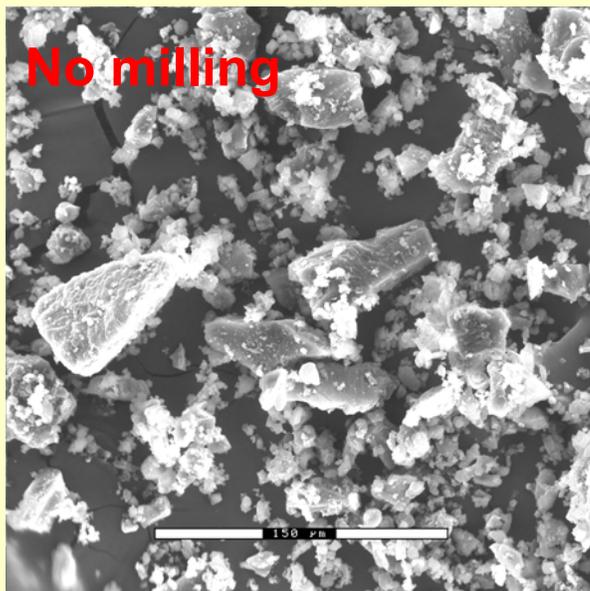
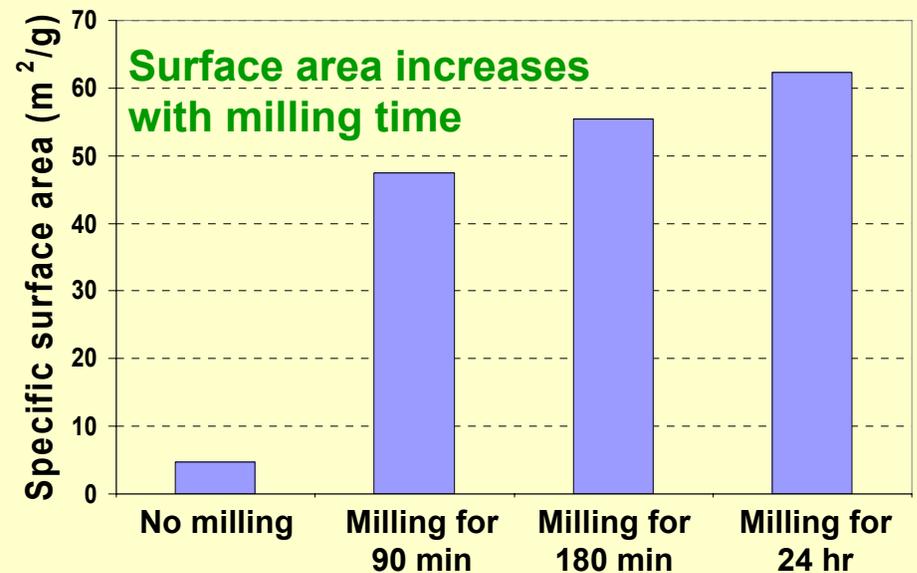
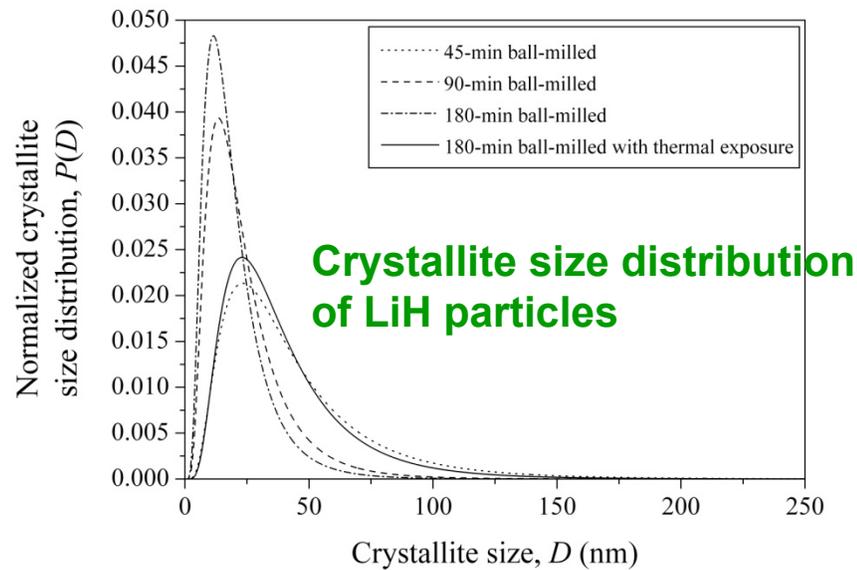
2. Increasing the composition gradient to enhance diffusion via advanced catalysts.

$$J = -D \frac{dC}{dx}$$

3. Increasing the diffusion coefficient to augment the diffusion rate via mechanical activation and doping.

$$D = D_0 \exp\left(-\frac{Q}{RT}\right)$$

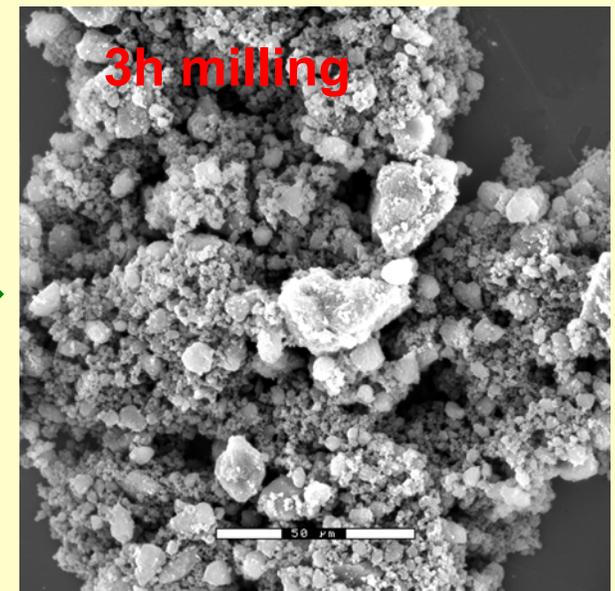
Nano-Engineering and Mechanical Activation through High-Energy Ball Milling



LiNH₂ + LiH mixtures with particles of 6 to 120 μm before milling

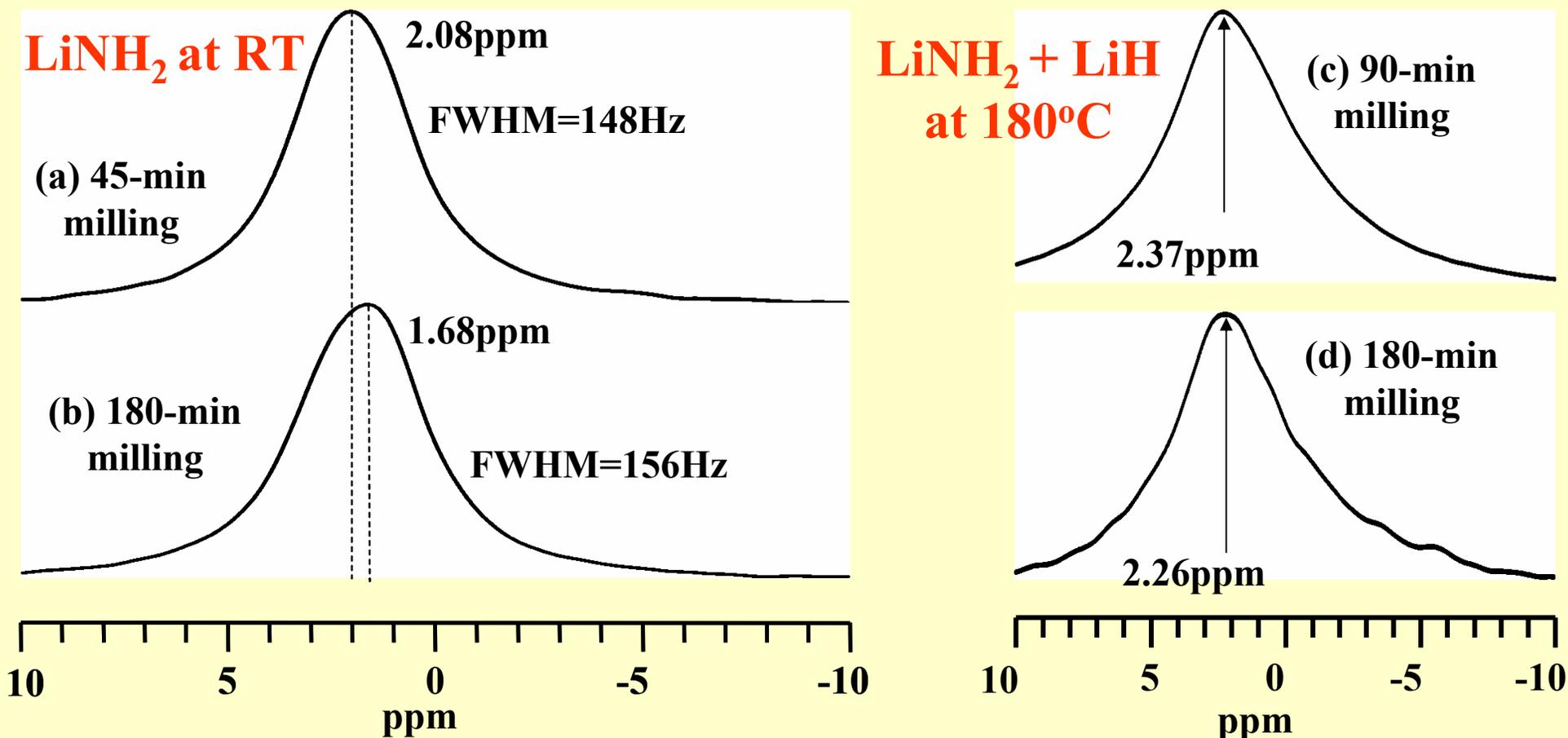


Particle sizes reduced to 0.5 to 6 μm after 3h milling



Nano-Engineering and Mechanical Activation through High-Energy Ball Milling

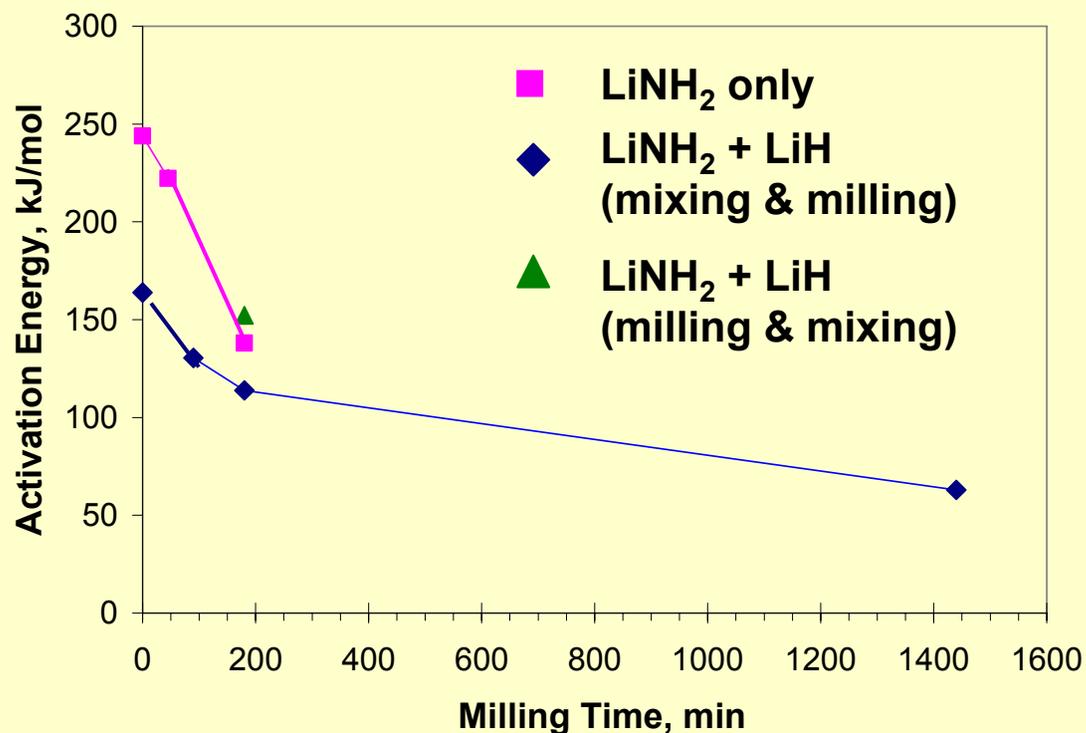
300MHz ^6Li MAS NMR Spectra*



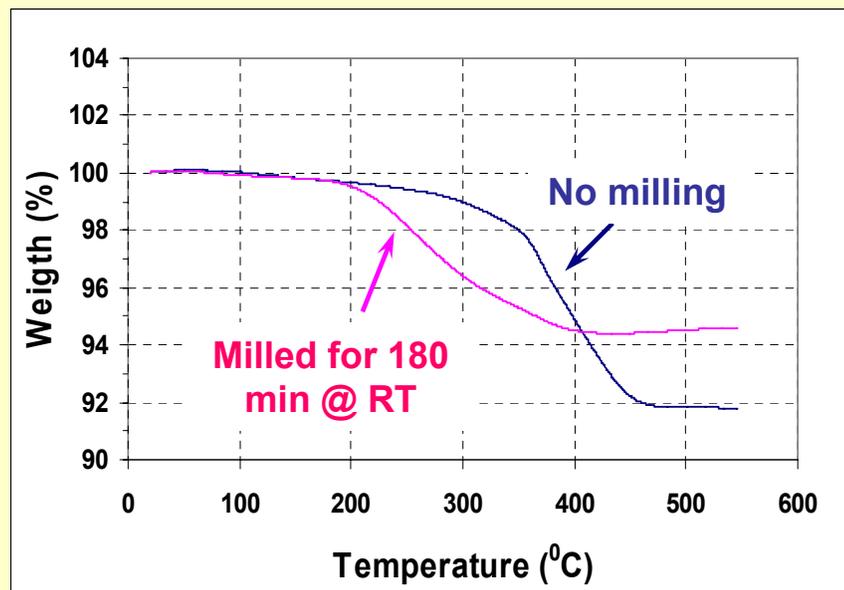
Broadening and up-field shifting of ^6Li peaks indicate that ball milling has not only resulted in structural refinement, but also led to the alternation in the local electronic state around Li nuclei.

* C. Lu, et al., *J. Power Sources*, 170, 419 (2007).

Enhancing Dehydrogenation of $\text{LiNH}_2 + \text{LiH}$ Mixtures via Nano-Engineering & Mechanical Activation

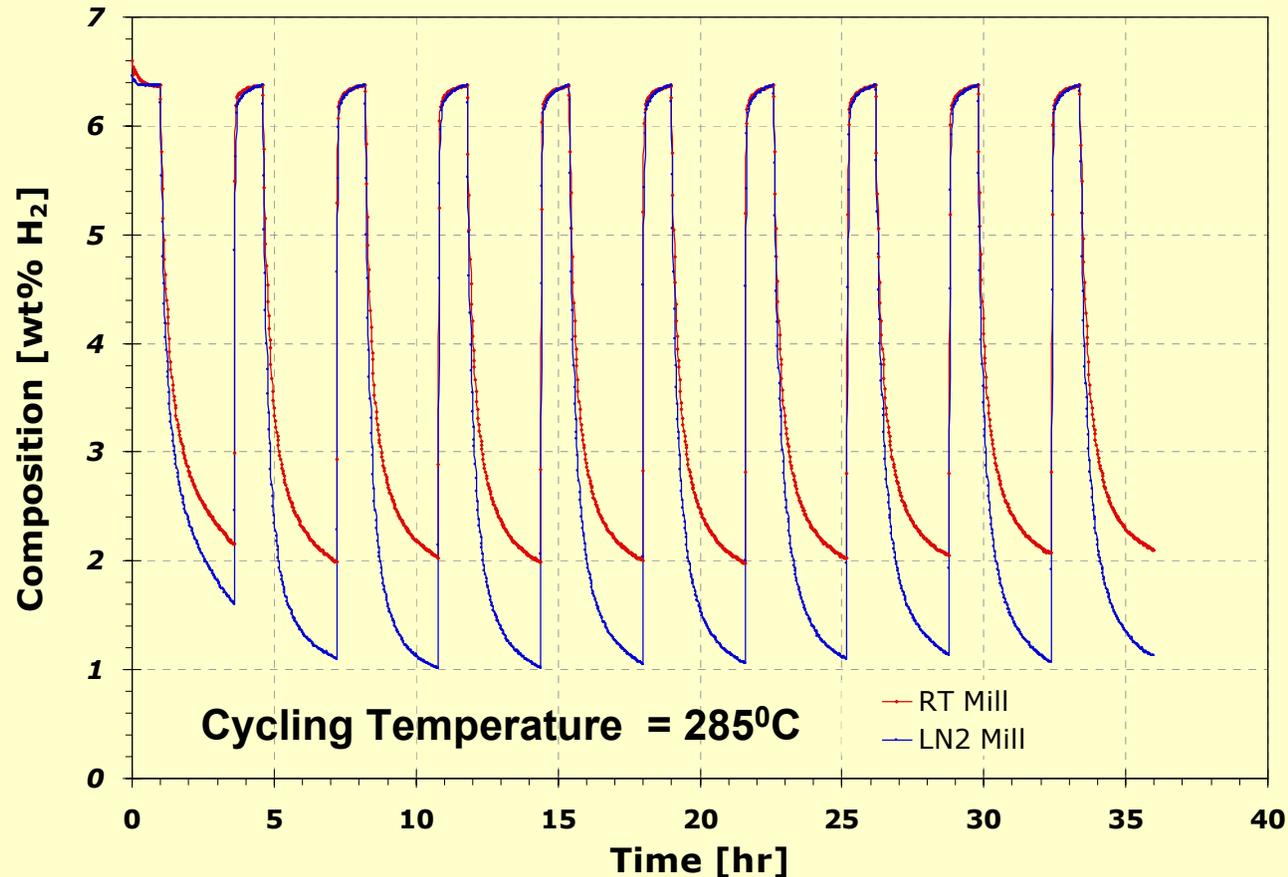


TGA Traces of $\text{LiNH}_2 + \text{LiH}$



- The peak temperature for hydrogen release has been reduced by $\sim 100^\circ\text{C}$ via ball milling.
- The weight loss for the sample without milling is substantially larger than the theoretical prediction ($\sim 5.5 \text{ wt}\%$) because of the NH_3 emission. In contrast, the milled sample is in excellent agreement with the theoretical prediction.
- The activation energy for dehydrogenation decreases with an increase in the milling time, indicating the effect of mechanical activation.
- The activation energy is also affected by the milling and mixing sequence, suggesting that LiH has the catalytic effect on the decomposition of LiNH_2 .

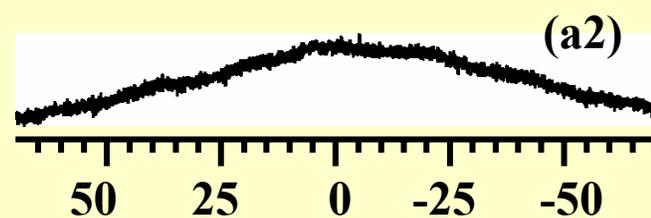
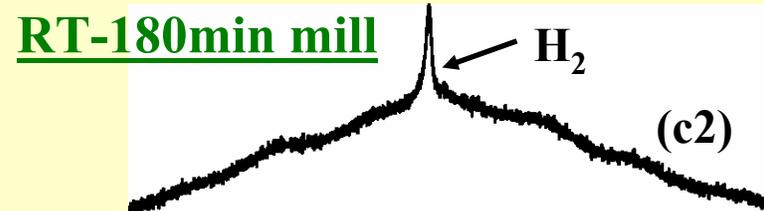
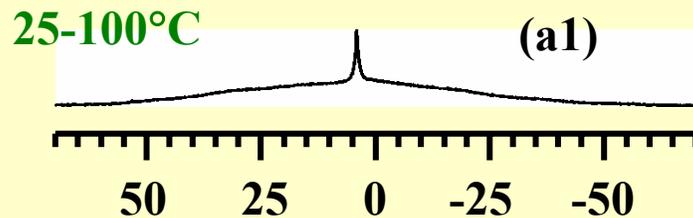
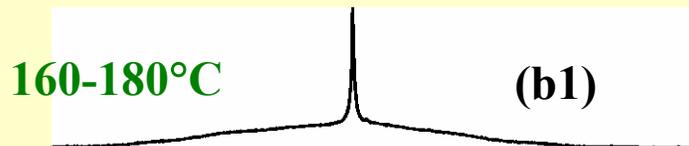
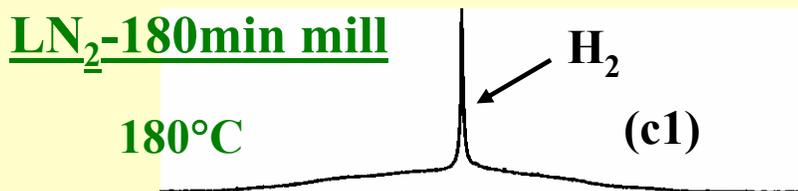
Enhancing Hydrogenation/Dehydrogenation through Mechanical Activation at Liquid Nitrogen Temperature



LiNH₂+LiH ball milled at liquid nitrogen temperature (LN₂) displays much faster hydriding/dehydriding kinetics than that ball milled at RT. As a result, LN₂-processed LiNH₂+LiH has improved the utilization of the theoretical storage capacity by 22%.

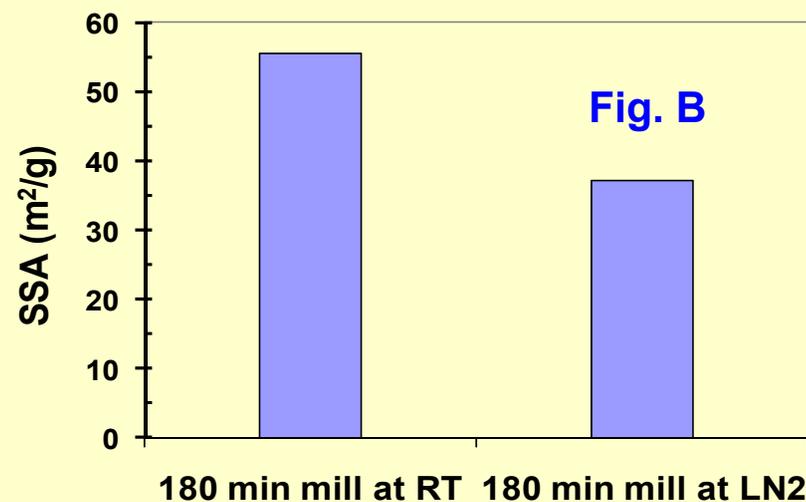
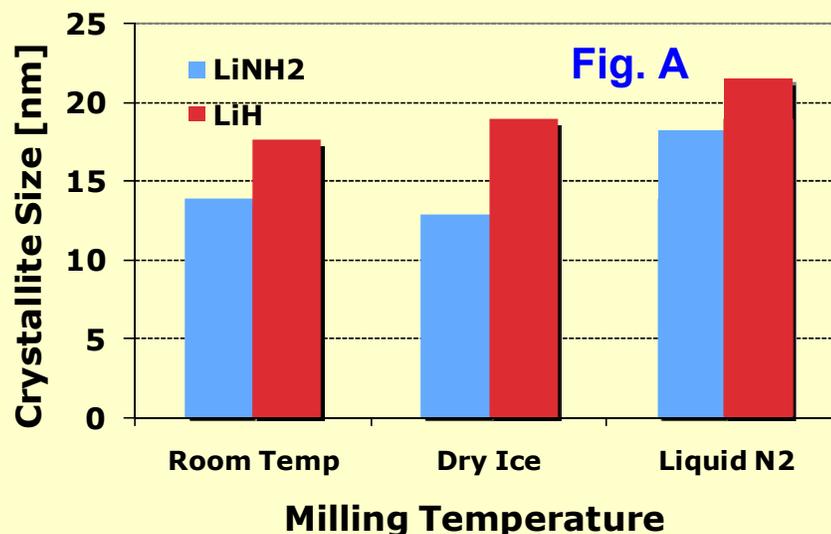
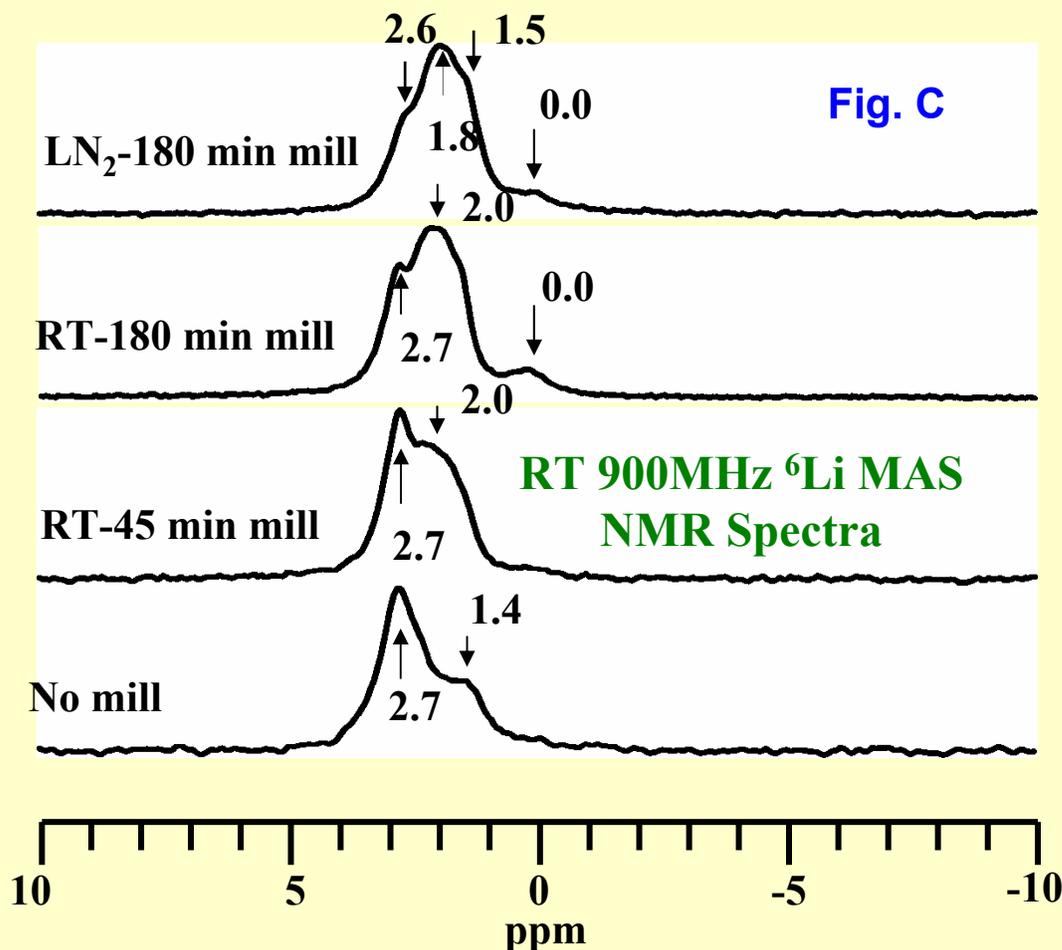
Enhancing Hydrogenation/Dehydrogenation through Mechanical Activation at Liquid Nitrogen Temperature

VT 300MHz *in situ* ^1H MAS NMR Spectra



- The narrow peak at 4.1ppm corresponds to both gaseous and chemical and physical adsorbed H₂ molecules, whereas the broad peak beneath the narrow peak is due to the rigid lattice protons.
- Gaseous H₂ is observed below 100°C for LN₂-milled samples, but not for RT-milled samples.
- At 180°C, the amount of H₂ released from LN₂-milled samples is 4 times more than that from RT-milled samples.

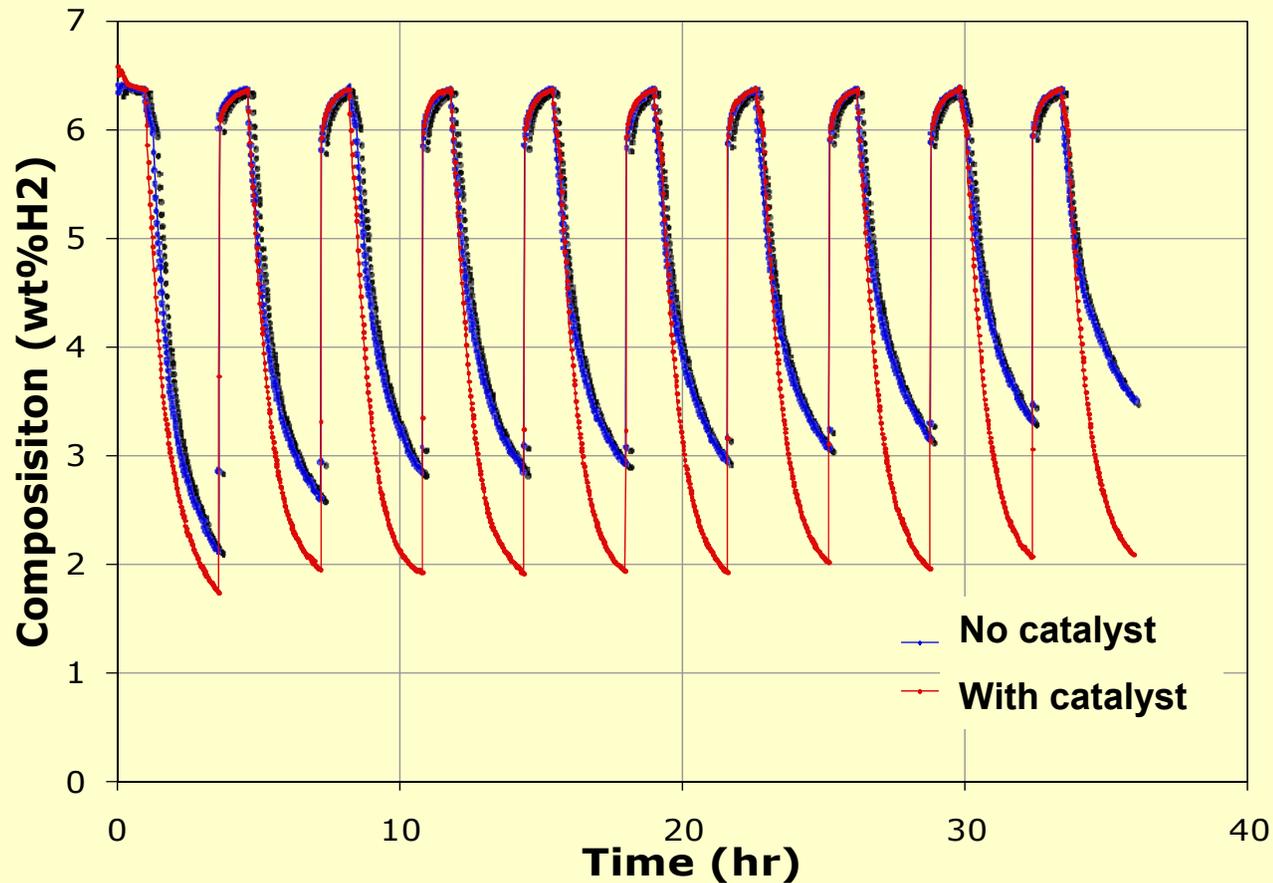
Enhancing Hydrogenation/Dehydrogenation through Mechanical Activation at Liquid Nitrogen Temperature



➤ LN₂-processed LiNH₂+LiH has larger crystallite sizes (Fig. A) and a lower specific surface area (Fig. B) than the LiNH₂+LiH processed at RT.

➤ NMR analysis (Fig. C) reveals an up-field shift of the ⁶Li peak and a stronger surface defect peak (1.8ppm peak) for the LN₂-ball-milled sample.

Enhancing the Reaction Kinetics of Mechanically Activated, Nano-Engineered LiNH_2+LiH via Advanced Catalysts



- Addition of 1 mol% nano-catalyst particles increases the hydriding/dehydriding kinetics.
- Analysis of the dehydriding kinetics indicates that the dehydriding reaction of the catalyzed system is still diffusion-controlled. Thus, it is hypothesized that the added catalyst enhances desorption of NH_3 from the Li_2NH surface and thus creates a large composition gradient for diffusion within the Li_2NH solid.

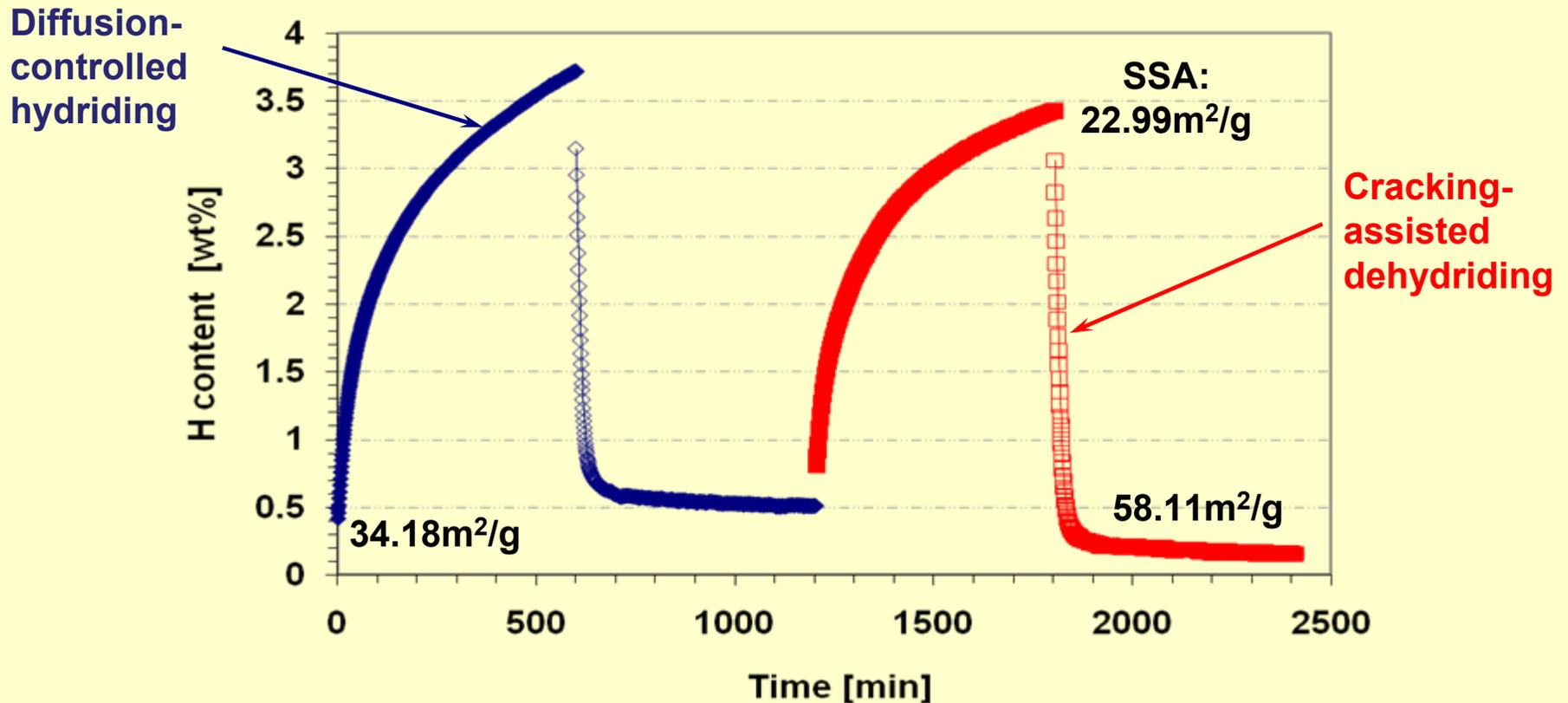
Improving Hydriding/Dehydriding Properties via Thermodynamic Destabilization



Reversible storage capacity = 5.5 wt% H₂

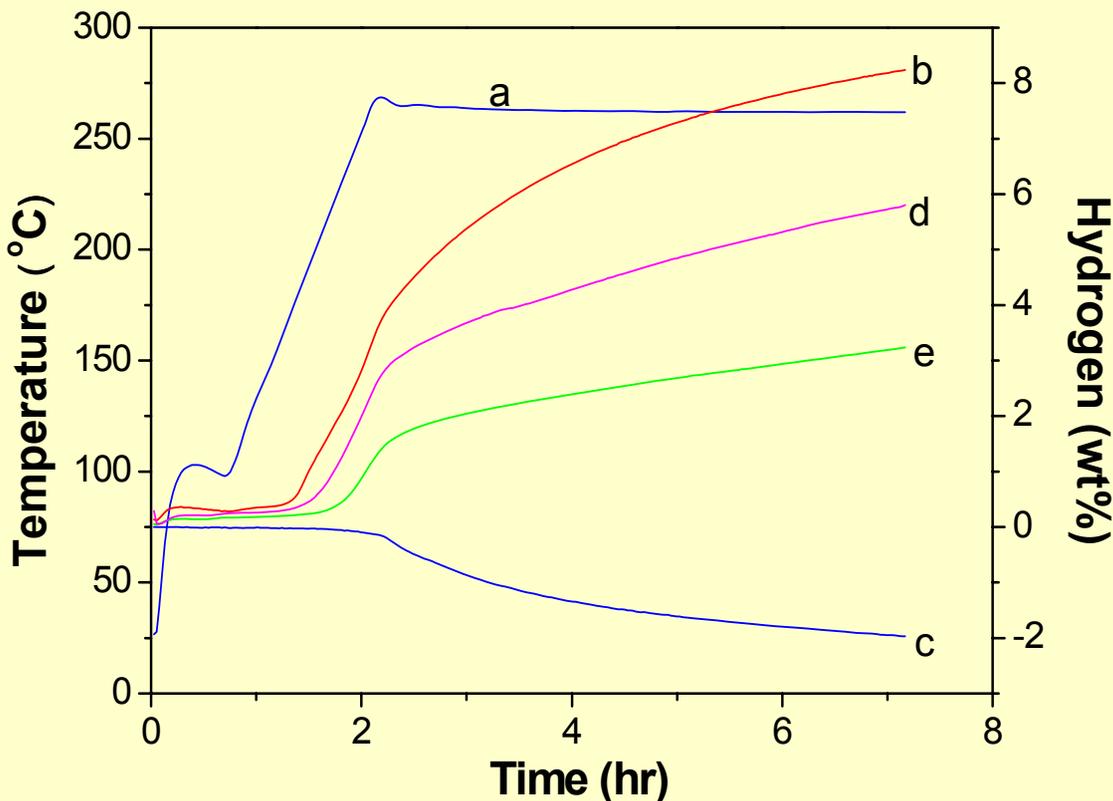
ΔH (dehydriding) = 44 kJ/mol H₂

Cycling at 200°C between H₂ pressures of 68 and 0.01 bars



The slow hydriding process needs to be solved to make this material a viable storage system.

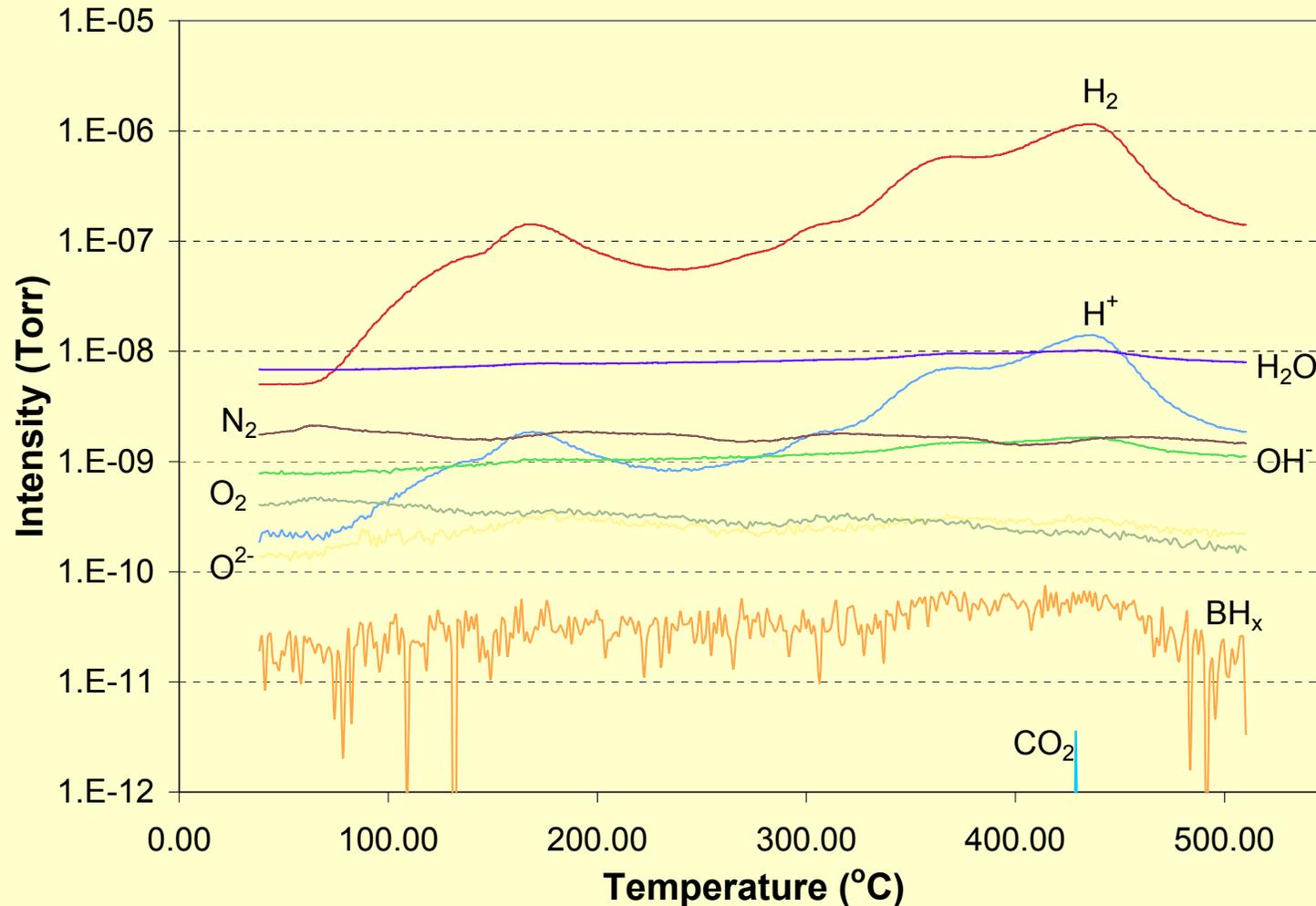
Solid-State Hydrogenation/Dehydrogenation of $\text{LiBH}_4 + \text{MgH}_2$ Enabled via Nano-Engineering and Mechanical Activation



	Curve b	Curve d	Curve e
Crystallite size of LiH (nm)	6.9	7.9	29.0
Crystallite size of MgB_2 (nm)	6.1	9.9	18.1
Equivalent particle diameter (nm)	258	230	217
Lattice microstrain of MgB_2	2.87%	1.94%	1.65%

- 1) Hydrogenation below the melting temperature of LiBH_4 is a strong function of the crystallite size and lattice microstrain.
- 2) The largest hydrogen uptake of 8.3 wt.% in the solid state is achieved using the particles with the smallest crystallites and largest lattice microstrain.

Solid-State Hydrogenation/Dehydrogenation of $\text{LiBH}_4 + \text{MgH}_2$ Enabled via Nano-Engineering and Mechanical Activation



The gas released during dehydrogenation of $\text{LiBH}_4 + \text{MgH}_2$ in the solid state is H_2 . Borane, if present, is below the detection limit of the mass spectrometer.

Future Work

- **Remainder of FY 2008:**

- Further improve hydriding/dehydriding properties of ($\text{LiNH}_2 + \text{LiH}$) systems via nano-engineering, mechanical activation, and thermodynamic destabilization (UConn)
- Establish the atomic level understanding of the reaction mechanism and kinetics of mechanically activated, nano-engineered ($\text{LiNH}_2 + \text{LiH}$) systems (PNNL and UConn)
- Demonstration of hydrogen uptake and release of ($\text{LiBH}_4 + \text{MgH}_2$) systems with a storage capacity of $\sim 10 \text{ wt}\% \text{ H}_2$ at 200°C (UConn)

- **FY 2009:**

- Develop the atomic level understanding of the reaction mechanism and rate-limiting steps of mechanically activated, nano-engineered ($\text{LiBH}_4 + \text{MgH}_2$) systems (PNNL and UConn)
- Further enhance hydriding/dehydriding rates of ($\text{LiBH}_4 + \text{MgH}_2$) systems (UConn)
- Improve the hydriding/dehydriding cyclic stability of ($\text{LiBH}_4 + \text{MgH}_2$) systems by integrating mechanical activation, nano-engineering, and thermodynamic destabilization (UConn)

Project Summary

- Relevance:** Explore fundamental mechanisms related to mechanical activation and nano-engineering necessary for improving kinetics of reversible hydrogen storage materials.
- Approach:** Investigate hydriding/dehydriding properties of (LiNH₂+LiH) and LiBH₄-based materials with different degrees of mechanical activation and nano-engineering; Enhance the storage performance based on the understanding developed.
- Technical Accomplishments:** (i) Identified the reaction mechanism and rate-limiting step in the dehydriding process of the LiNH₂ + LiH systems; (ii) Established the effect of mechanical activation on hydride particles and their hydriding/dehydriding properties; (iii) Proved low temperature milling can introduce a large amount of defects to nano-particles, which can in turn enhance hydriding and dehydriding reactions, (iv) Demonstrated the improved hydriding/dehydriding rates via nano-engineering, mechanical activation, and advanced catalysts even through the reaction rate is controlled by diffusion; and (v) Demonstrated hydriding and dehydriding reactions of (LiBH₄ + MgH₂) systems at the solid state, i.e., below the melting point of LiBH₄ ($T_m = 280^{\circ}\text{C}$) with 8.3 wt% H₂ uptake.