

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

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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).

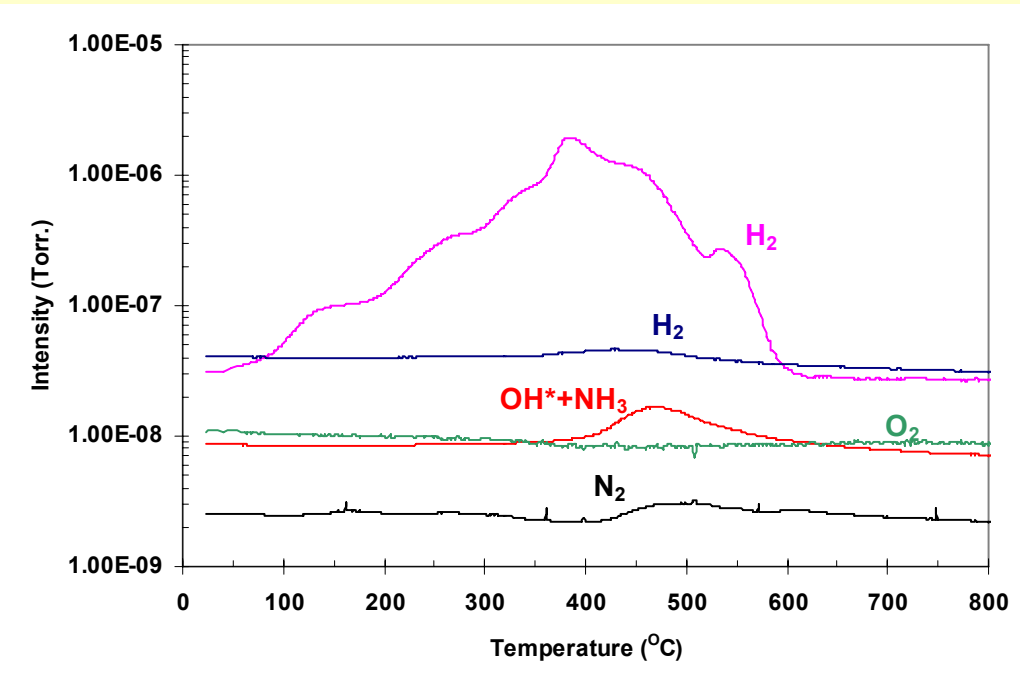
[5] T. Markmaitree, R. Ren, L. Shaw, *J. Phys. Chem. B.*, 110, 20710 (2006).

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

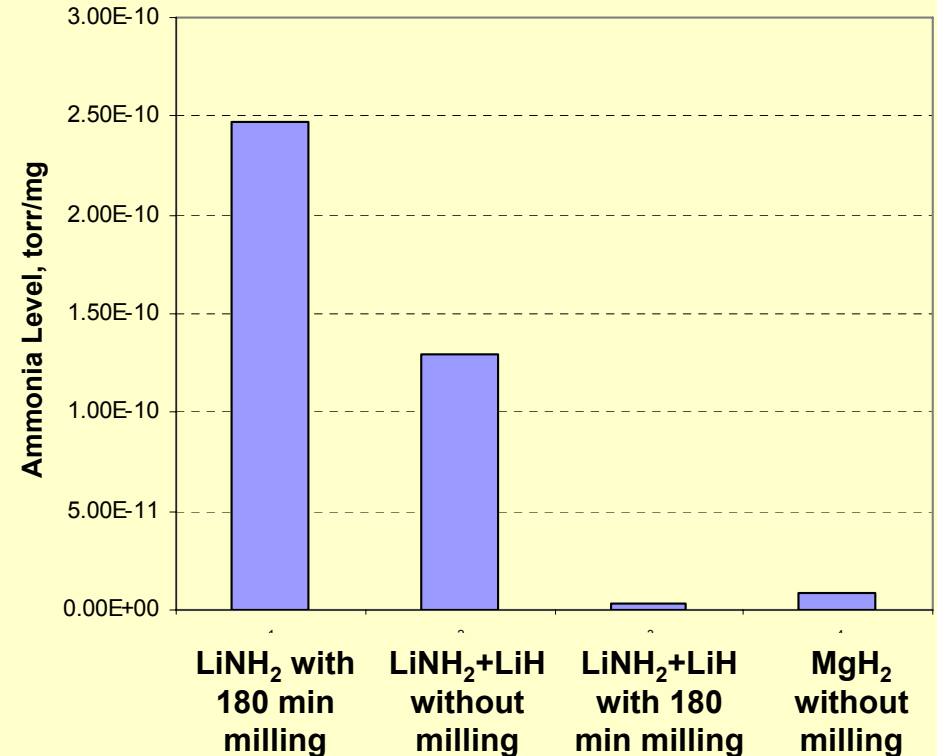
[7] T. Ichikawa, et al., *J. Phys. Chem. B*, 108, 7887 (2004).

Identification of Reaction Mechanism

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



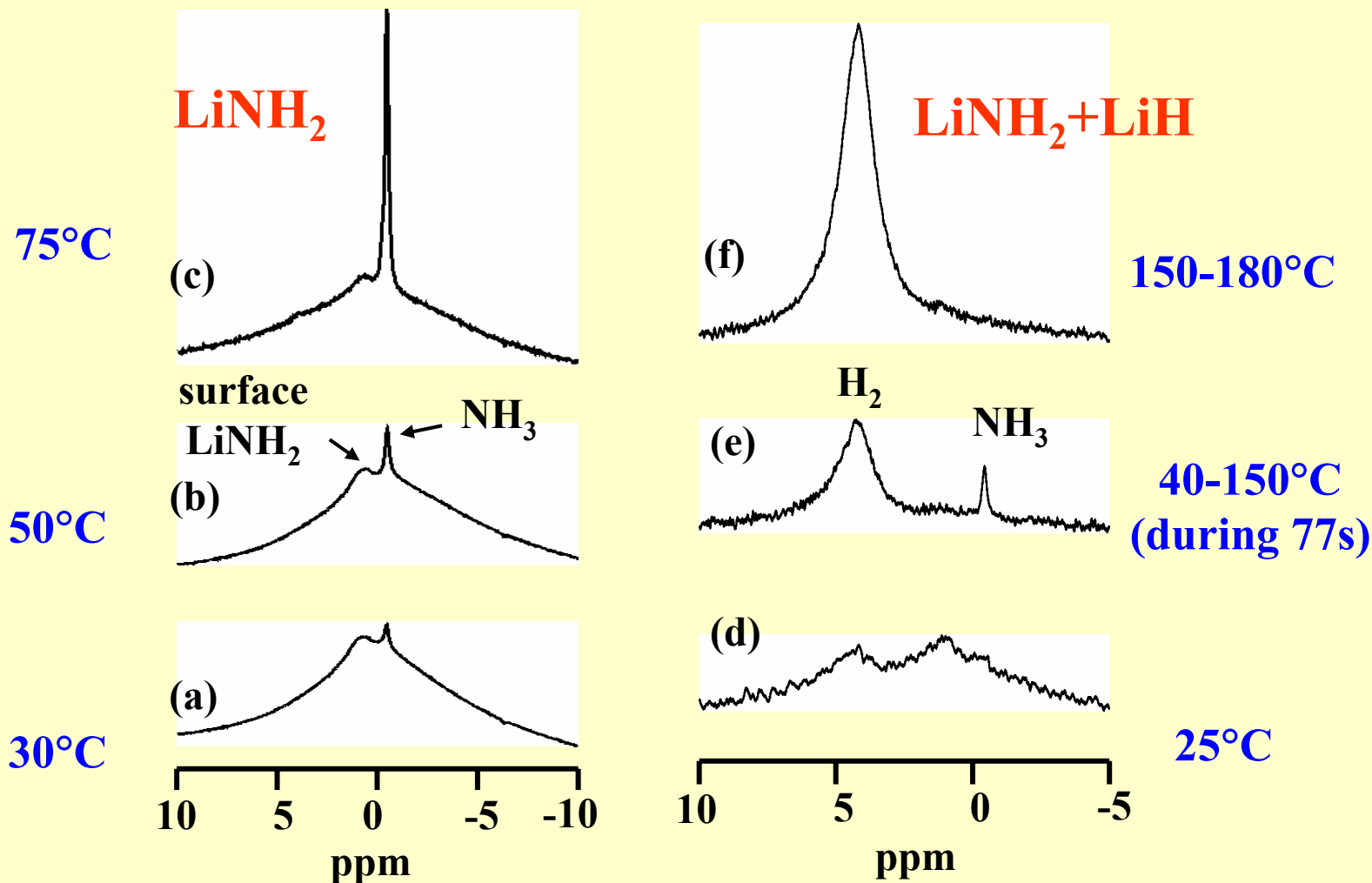
Comparisons in the NH_3 emission from different hydride systems



- ❑ 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

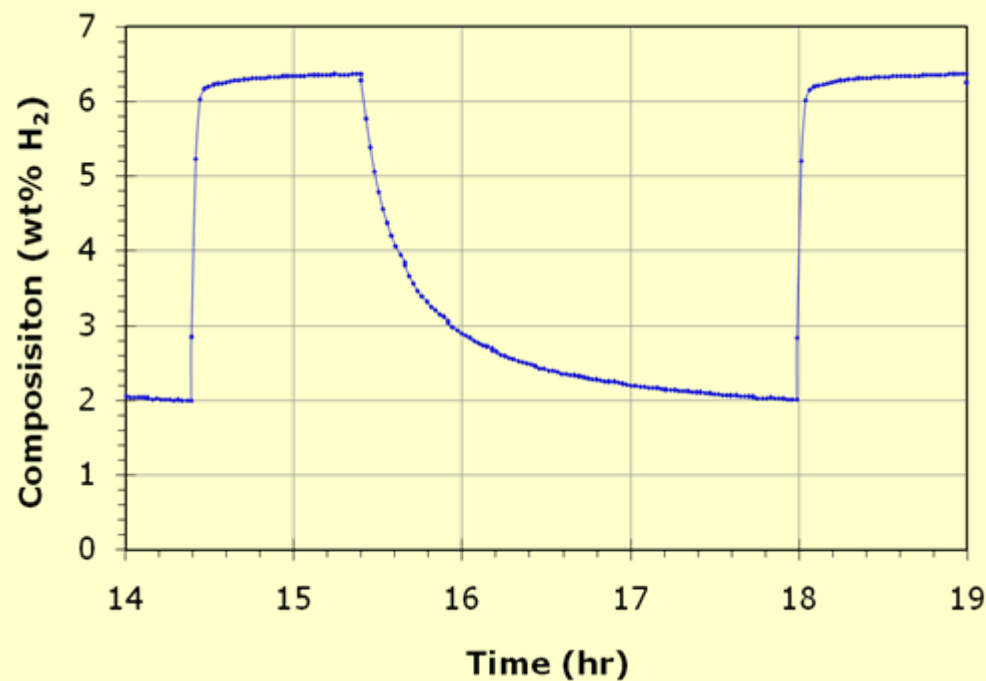
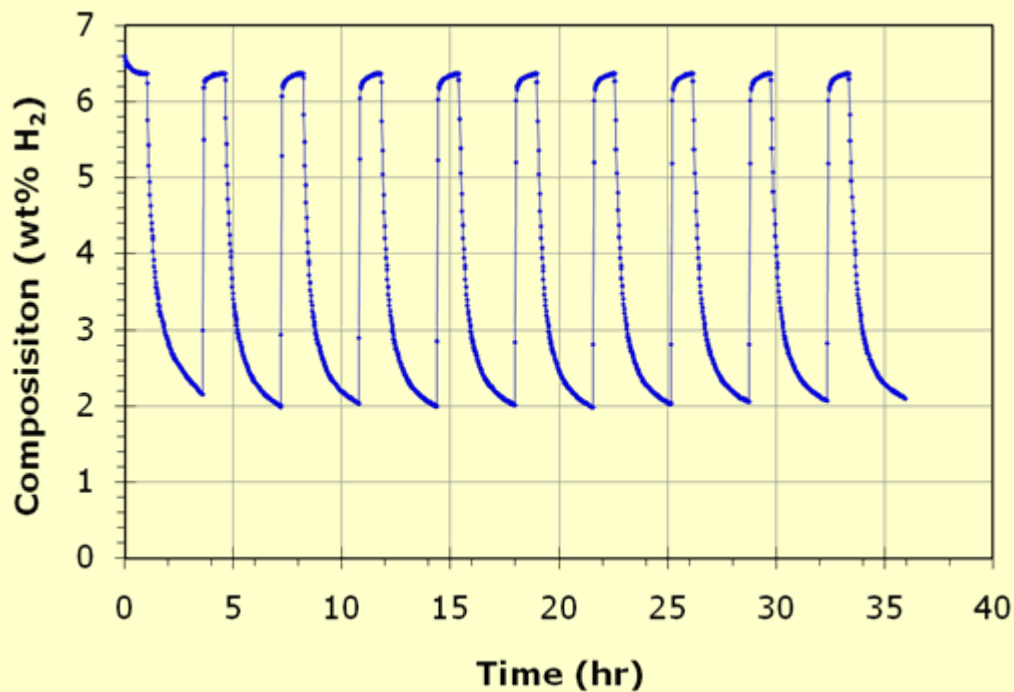
VT 300MHz *in situ* ^1H MAS NMR Spectra



- 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^*

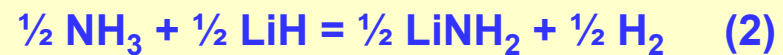
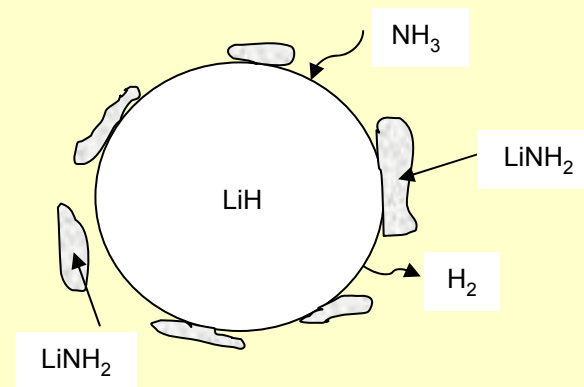
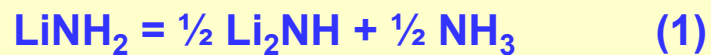
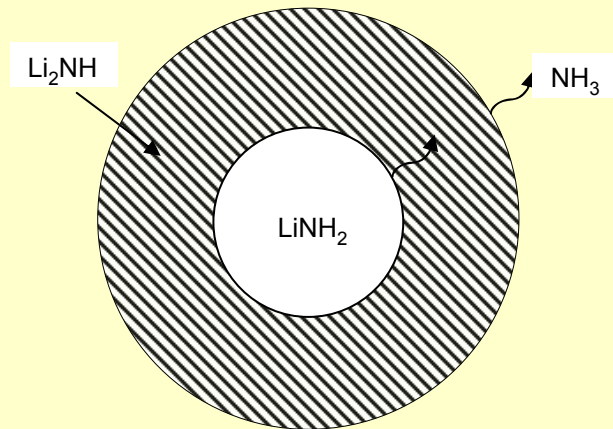


- A rapid hydrogen uptake rate (i.e., approaching the theoretical storage capacity in ~ 5 min)
- A slow release rate (i.e., incomplete release of hydrogen in 2.5 h).
- Modeling of the release kinetics under a constant temperature and constant hydrogen pressure to investigate the rate-limiting step.

* *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].

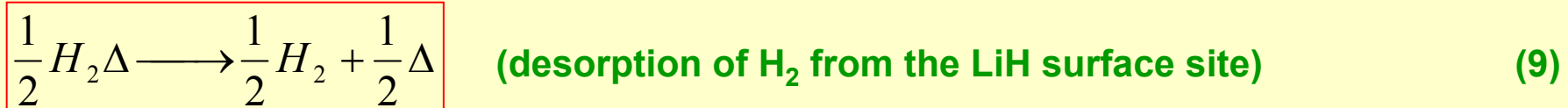
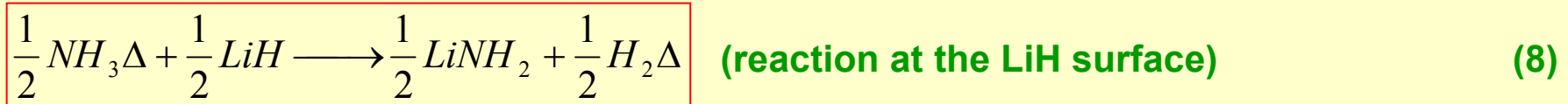
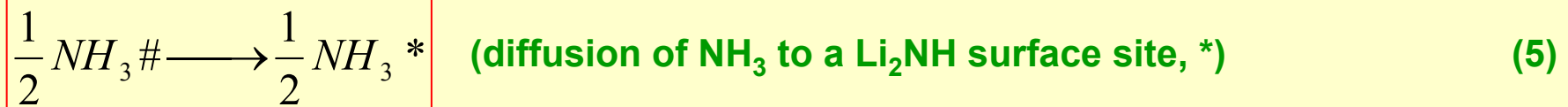
[1] T. Markmaitree, R. Ren, L. Shaw, *J. Phys. Chem. B.*, 110, 20710 (2006).

[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

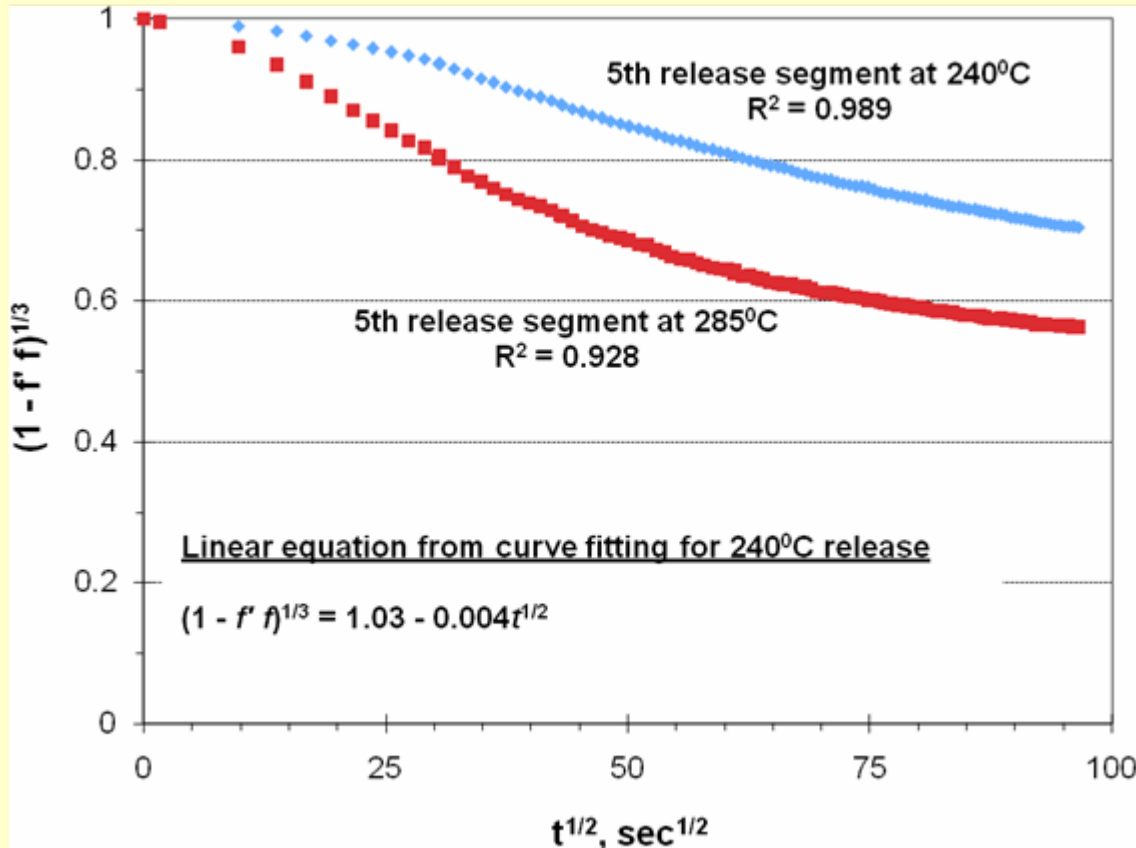
Based on the reaction pathway proposed, the hydrogen release of the $\text{LiNH}_2 + \text{LiH}$ system can be described at least with the following 6 steps.



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.

$$x^2 \propto Dt$$

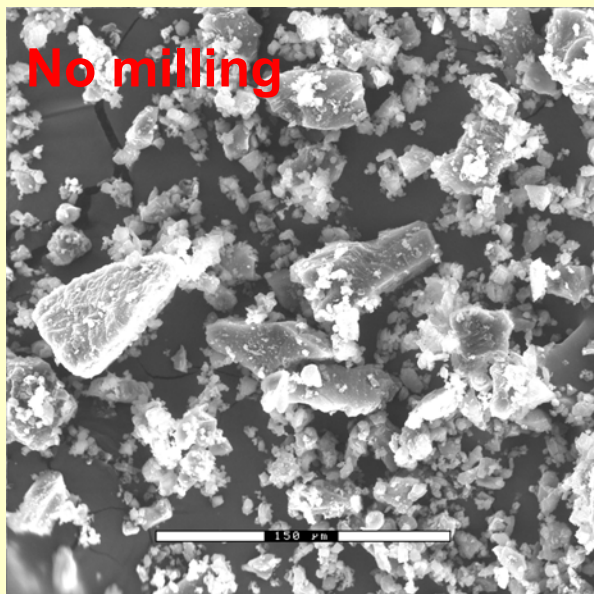
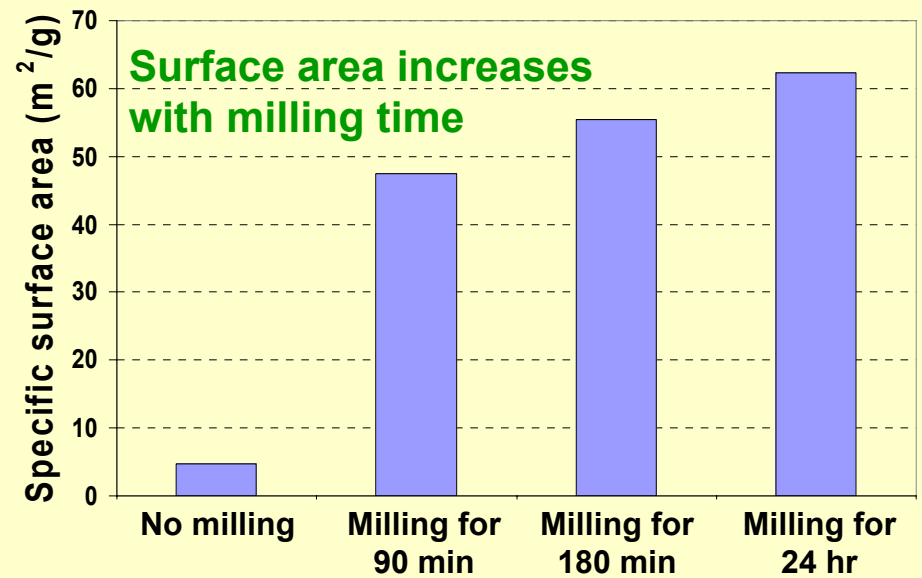
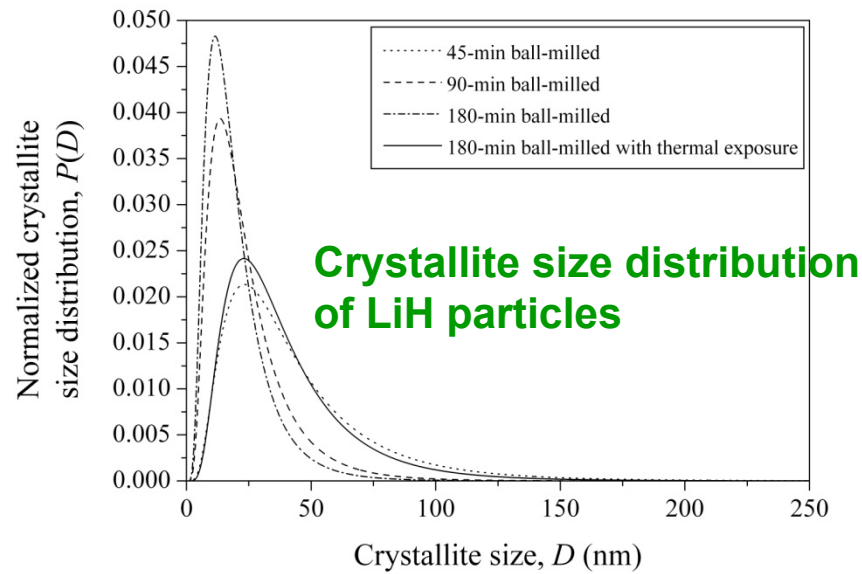
2. Increasing the composition gradient to enhance diffusion via advanced catalysts.

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

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

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

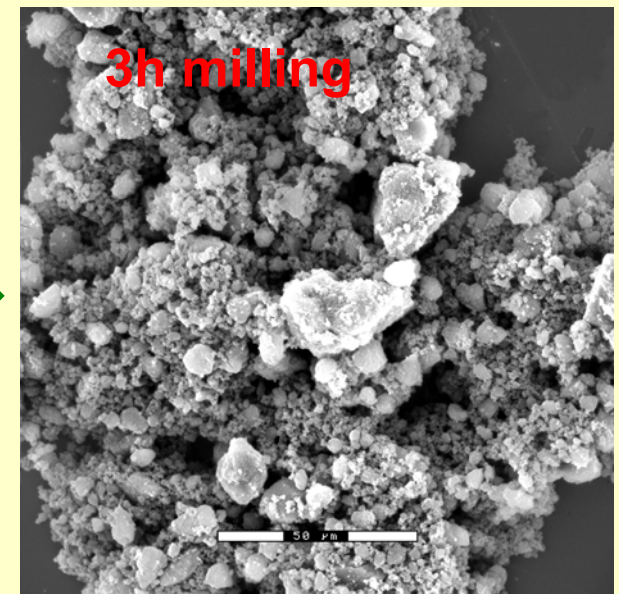
Nano-Engineering and Mechanical Activation through High-Energy Ball Milling



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

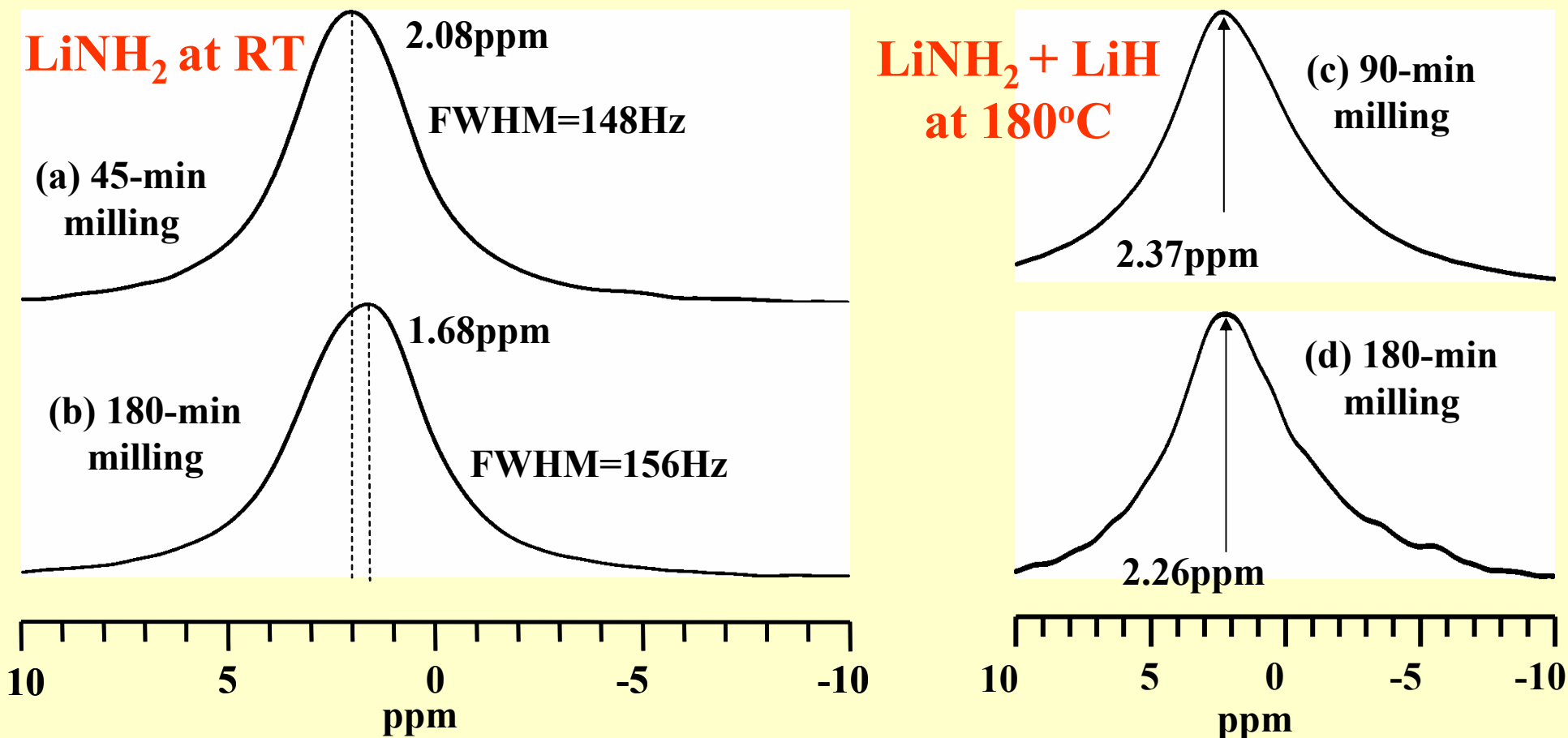


Particle sizes reduced to 0.5 to 6 μm after 3h milling



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

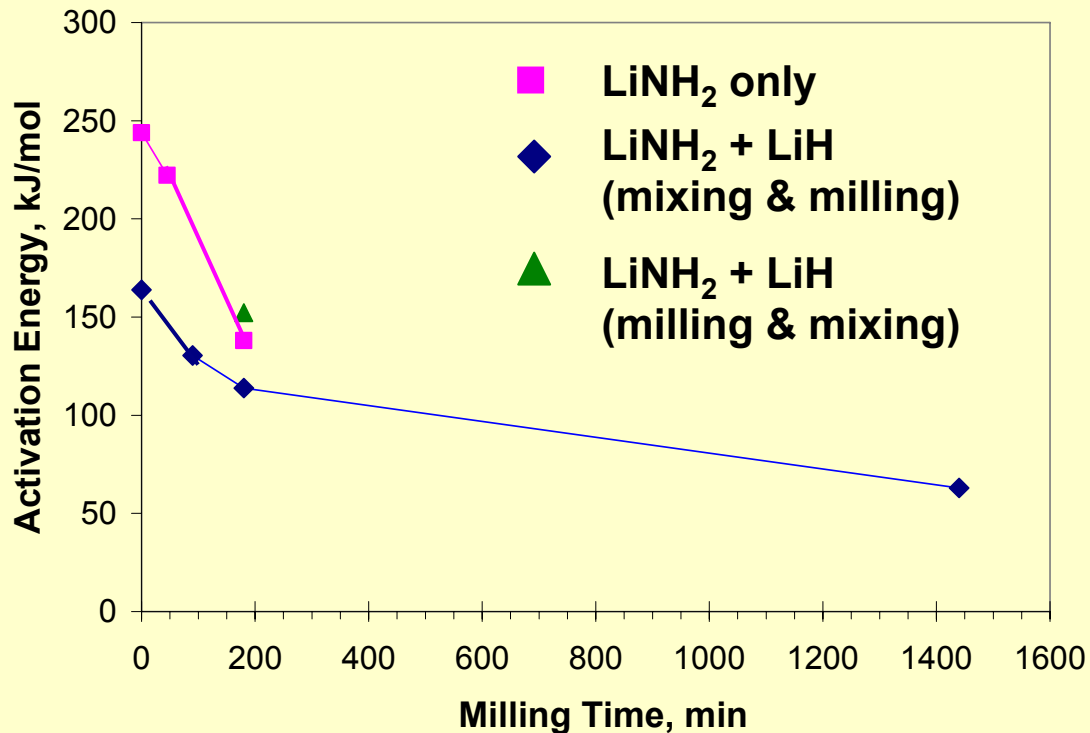
300MHz ^6Li MAS NMR Spectra*



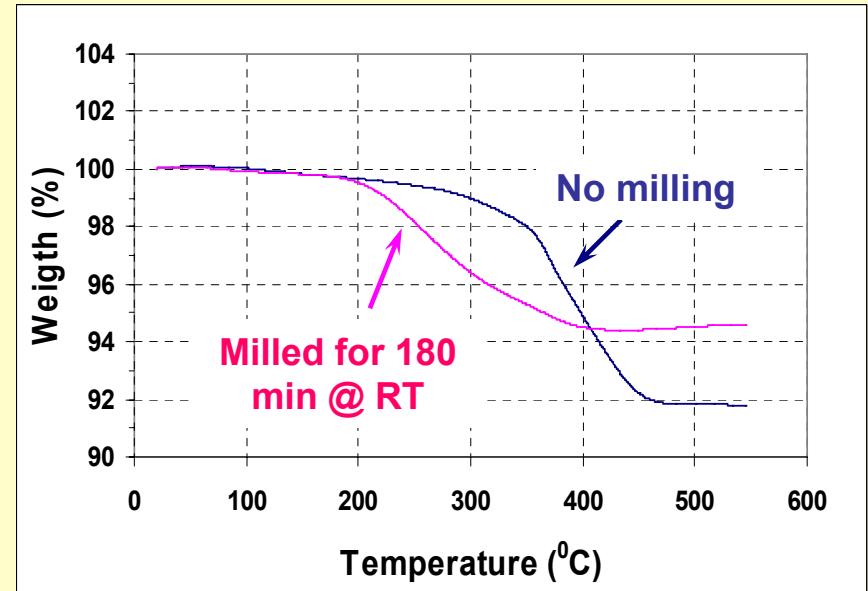
Broadening and up-field shifting of ^6Li peaks indicate that ball milling has not only resulted in structural refinement, but also led to the alternation in the local electronic state around Li nuclei.

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

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

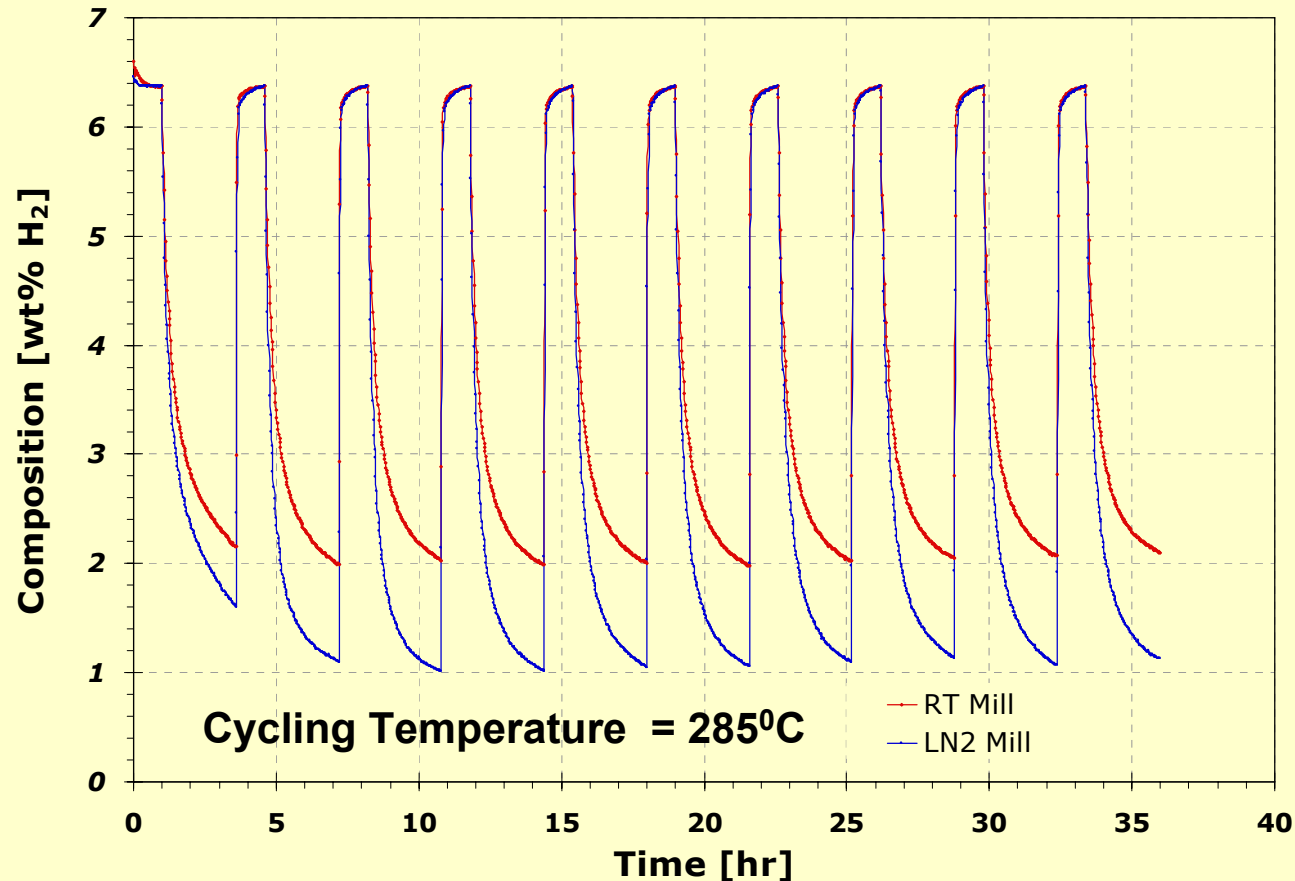


TGA Traces of $\text{LiNH}_2 + \text{LiH}$



- 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 .

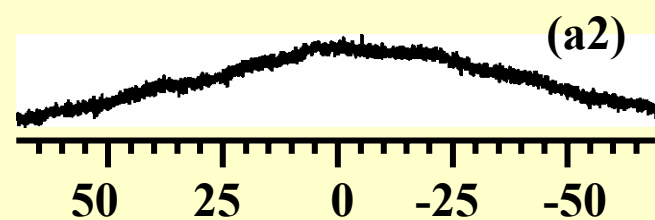
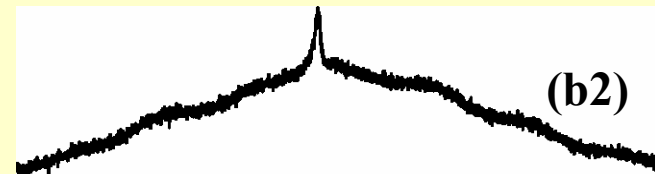
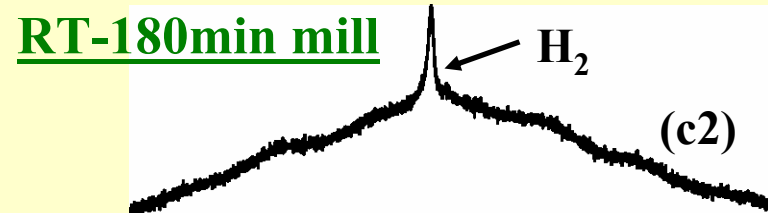
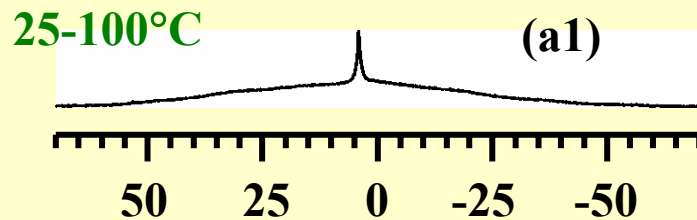
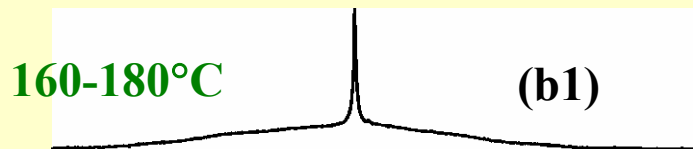
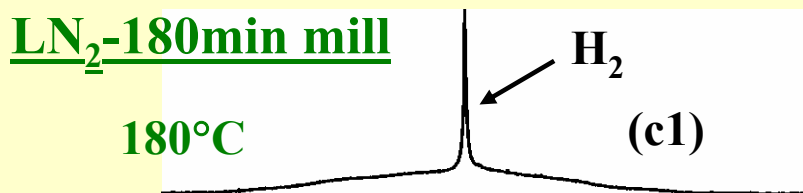
Enhancing Hydrogenation/Dehydrogenation through Mechanical Activation at Liquid Nitrogen Temperature



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%.

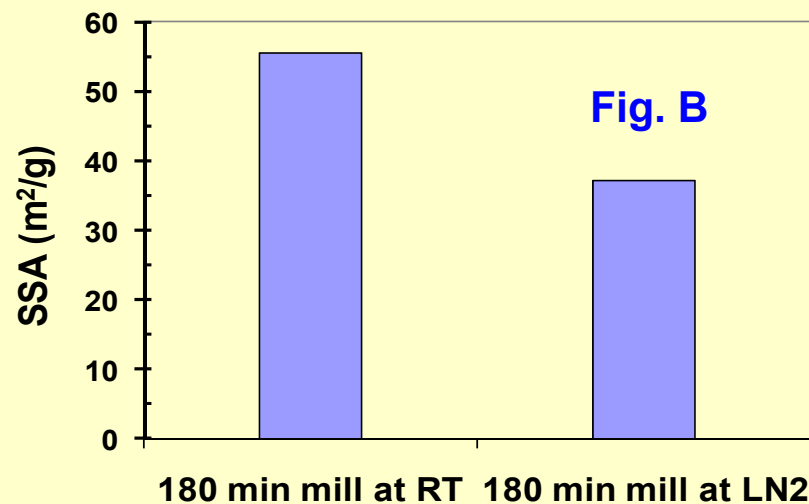
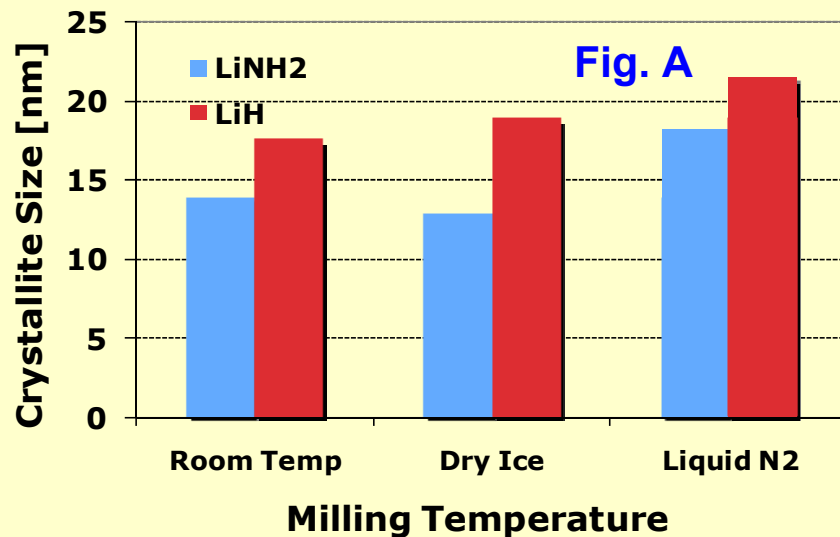
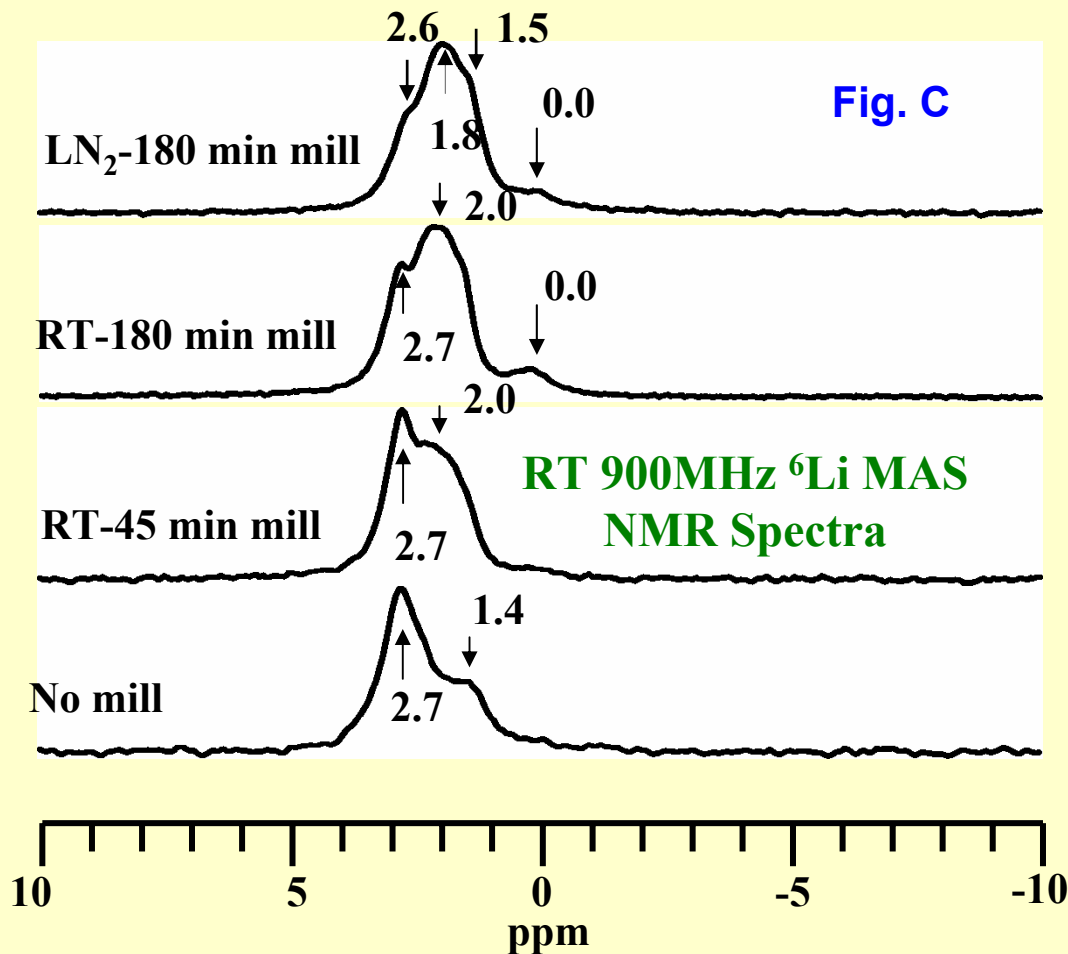
Enhancing Hydrogenation/Dehydrogenation through Mechanical Activation at Liquid Nitrogen Temperature

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.

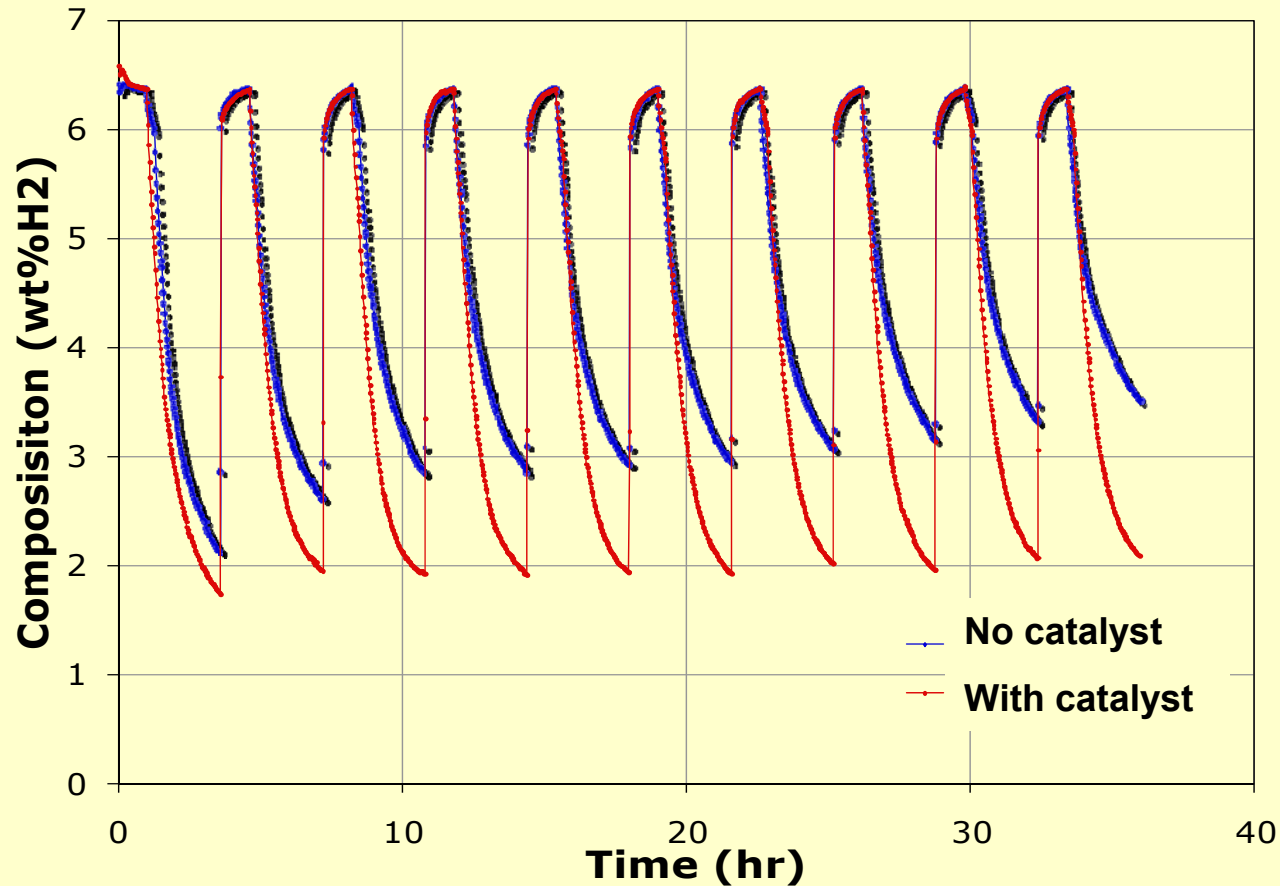
Enhancing Hydrogenation/Dehydrogenation through Mechanical Activation at Liquid Nitrogen Temperature



➤ 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.

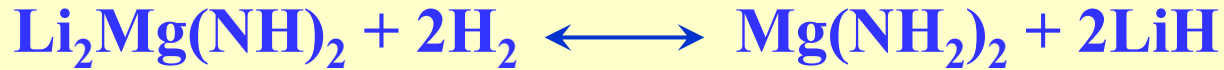
➤ NMR analysis (Fig. C) reveals an up-field shift of the ⁶Li peak and a stronger surface defect peak (1.8ppm peak) for the LN₂-ball-milled sample.

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.

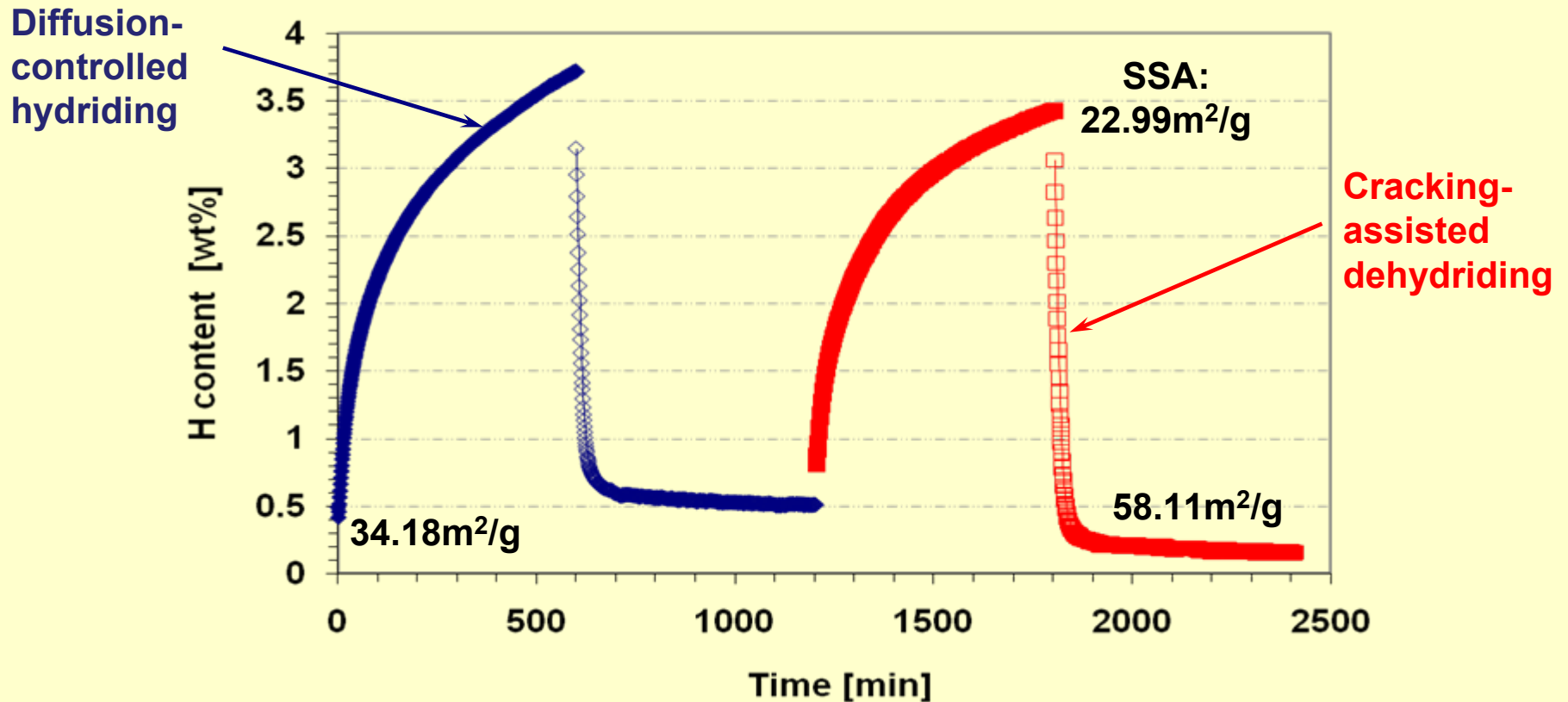
Improving Hydriding/Dehydriding Properties via Thermodynamic Destabilization



Reversible storage capacity = 5.5 wt% H₂

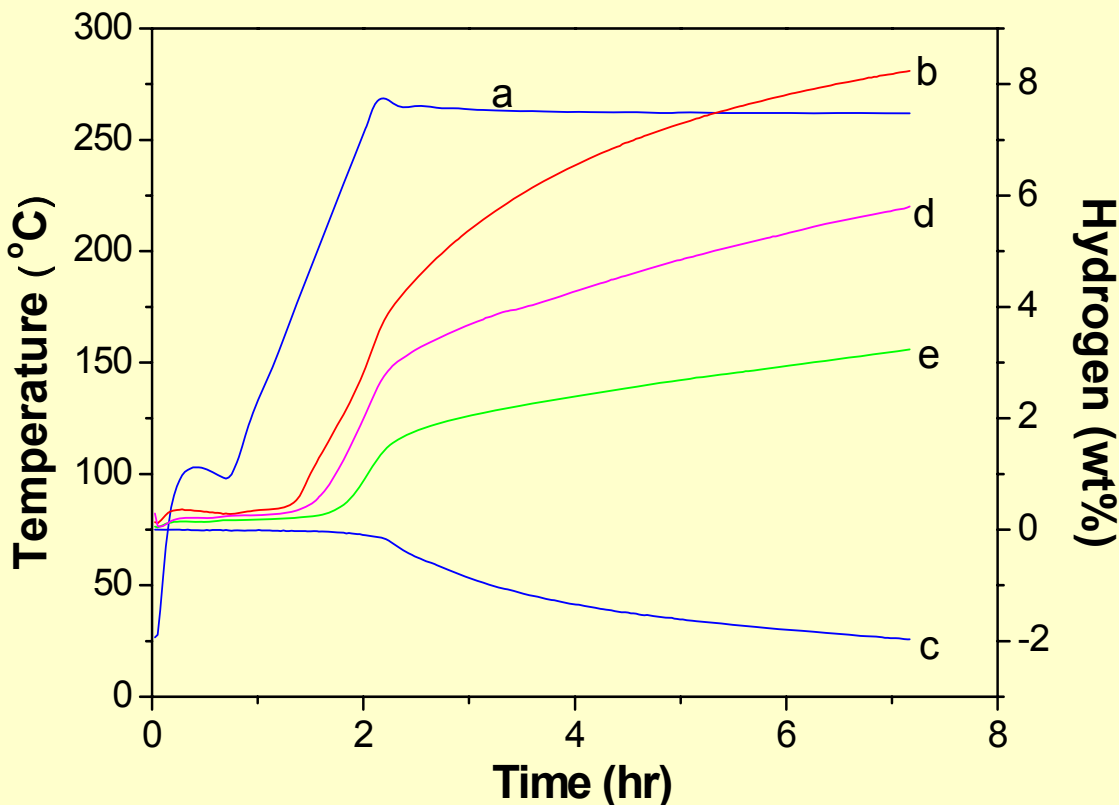
ΔH (dehydriding) = 44 kJ/mol H₂

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.

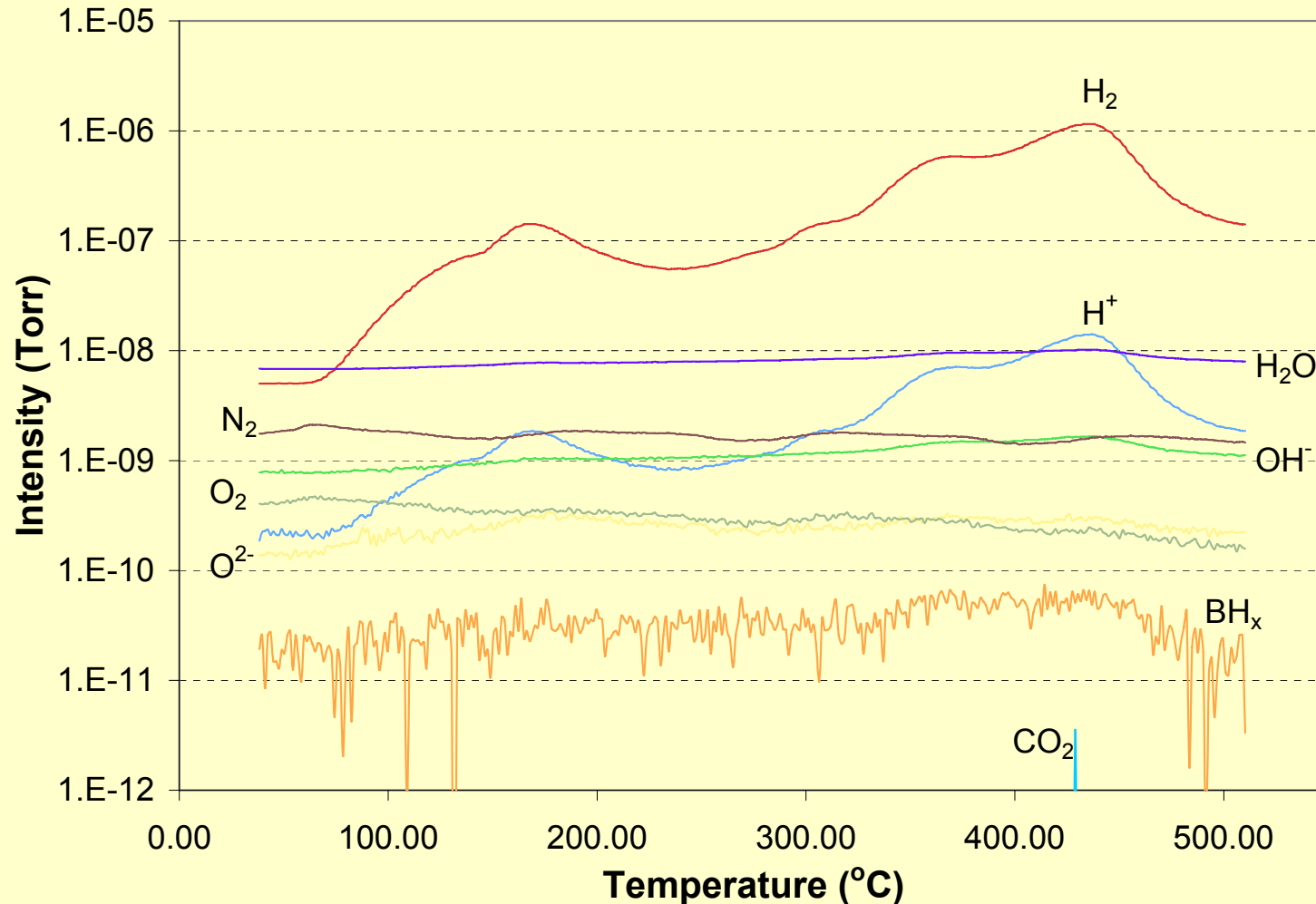
Solid-State Hydrogenation/Dehydrogenation of $\text{LiBH}_4 + \text{MgH}_2$ Enabled via Nano-Engineering and Mechanical Activation



	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 (LiNH₂ + 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 (LiNH₂ + LiH) systems (PNNL and UConn)
- Demonstration of hydrogen uptake and release of (LiBH₄ + MgH₂) systems with a storage capacity of ~ 10 wt% H₂ at 200°C (UConn)

- **FY 2009:**

- Develop the atomic level understanding of the reaction mechanism and rate-limiting steps of mechanically activated, nano-engineered (LiBH₄ + MgH₂) systems (PNNL and UConn)
- Further enhance hydriding/dehydriding rates of (LiBH₄ + MgH₂) systems (UConn)
- Improve the hydriding/dehydriding cyclic stability of (LiBH₄ + MgH₂) 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.