

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

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2007 DOE Hydrogen Program Review

Project ID: STP34

This presentation does not contain any proprietary or confidential information

Overview

Timeline:

- Project start date: December 2004
- Project end date: December 2008
- Percent complete: 50%

Budget:

- Total project funding
 - DOE share: \$1.6 mil
 - Contractor share: \$0.4 mil
- Funding received (FY05-07):
 - \$529,000 for UConn
 - \$210,000 for PNNL

Partners/Collaborators:

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

Barriers

System gravimetric capacity:
2 kWh/kg
System volumetric capacity:
1.5 kWh/L
Charging/discharging rates:
3 min for 5 kg

Objectives

Overall Objective in 4 Years:

- Investigate and develop novel, mechanically activated, nanoscale Li_3N -based and LiBH_4 -based materials that are able to store and release ~ 10 wt% hydrogen at temperatures below 100°C with a plateau hydrogen pressure of less than 10 bar

Objective in FY 06:

- Mechanical activation on LiNH_2 to Li_2NH transition
- Mechanical activation on hydrogen sorption/desorption kinetics of the LiNH_2 and LiH mixture

Objective in FY 07:

- Understanding of Mechanical activation on hydrogen sorption/desorption kinetics of the $\text{LiNH}_2 + \text{LiH}$ mixture
- Mitigation of NH_3 emission during ball milling and under sorption/desorption conditions
- Understanding of the long-term sorption/desorption cycling stability
- Improvement in sorption/desorption rates and long-term cycling stability

Approaches

- **Establishing the mechanism and rate-controlling step of hydriding and dehydriding reactions of $\text{LiNH}_2 + \text{LiH}$ systems and LiBH_4 -based materials.**
- **Developing fundamental understandings of the effect of mechanical activation on hydriding and dehydriding properties of hydrogen storage materials.**
- **Investigating combined effects of mechanical activation, advanced catalysts, and thermodynamic destabilization on hydriding and dehydriding properties and their long-term stabilities.**
- **Applying the understanding of mechanical activation and the established reaction mechanism and rate-controlling step to enhancing hydriding and dehydriding properties and long-term stabilities of hydrogen storage materials.**

Technical Accomplishments, Progress and Results

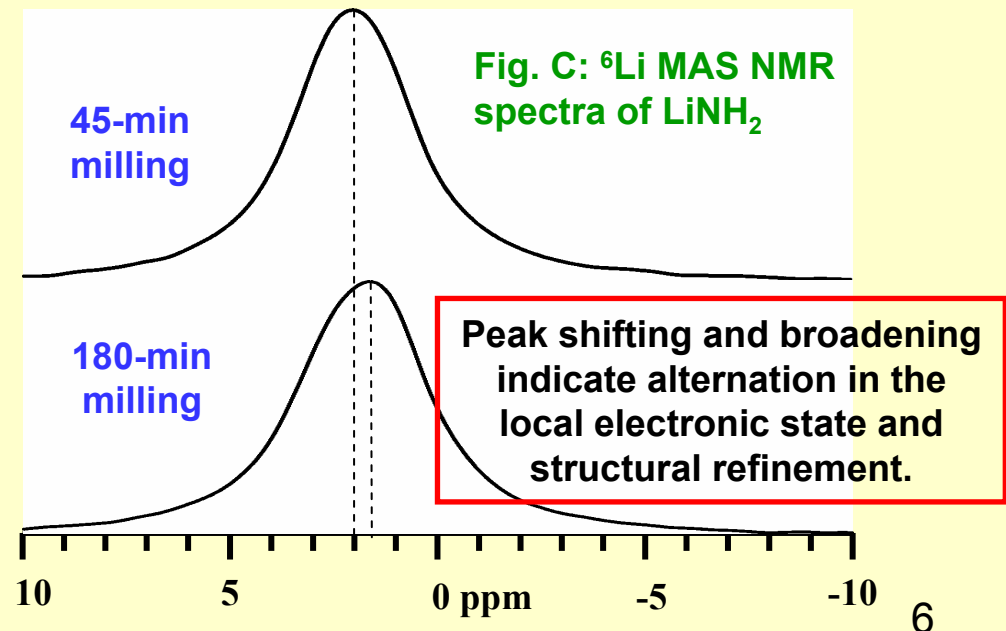
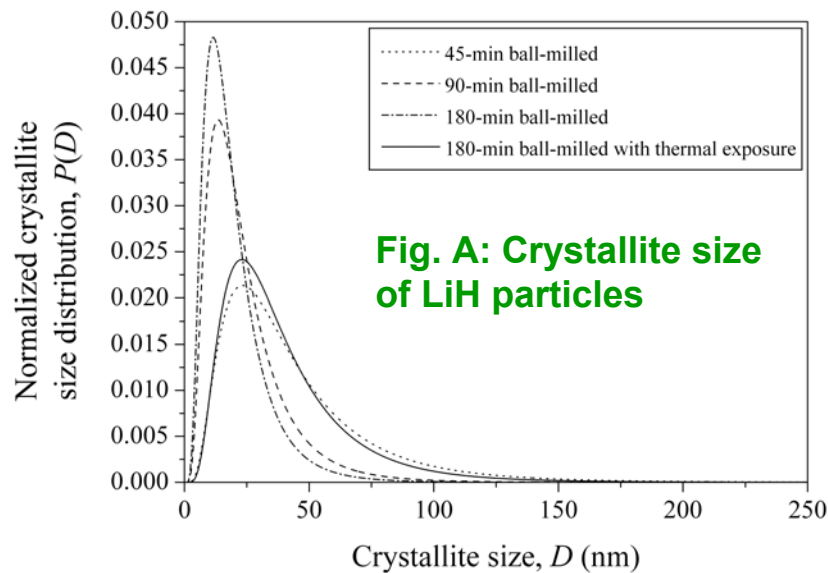
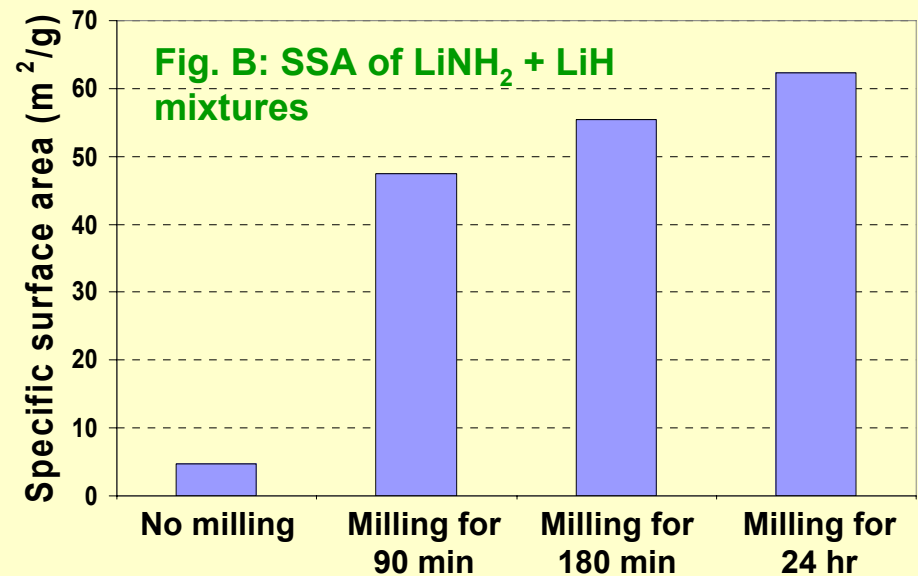
(May 1, 2006 – April 30, 2007)

- I. Evidence of Nano-Engineering and Mechanical Activation Obtained via High-Energy Ball Milling (UConn & PNNL)**
- II. Reaction Mechanism, Kinetics, and Enhancement of LiNH_2 to Li_2NH Transition via Mechanical Activation (UConn)**
- III. Reaction Mechanism, Kinetics, and Enhancement of Hydrogen Sorption/Desorption of $\text{LiNH}_2 + \text{LiH}$ Systems via Mechanical Activation (UConn)**
- IV. Atomic Level Understanding of Reaction Mechanism and Effects of Mechanical Activation via NMR (PNNL)**
- V. Enhancement of Reaction Kinetics and Stability of Mechanically Activated $\text{LiNH}_2 + \text{LiH}$ Systems (UConn)**

I. Evidence of Nano-Engineering and Mechanical Activation Achieved via High-Energy Ball Milling

High-energy ball milling leads to changes in powder characteristics including:

- formation of nano-particles (Fig. A);
- increases in specific surface area, SSA (Fig. B); and
- introduction of internal strains and alternation in the local electronic state (Fig. C).



II. Reaction Mechanism, Kinetics, and Enhancement of LiNH₂ to Li₂NH Transition via Mechanical Activation

Dehydrogenation of the LiNH₂ + LiH mixture:



proceeds with two elementary reactions*:



LiNH₂ produced from (3) will repeat (2) and (3) until exhaust of LiNH₂.

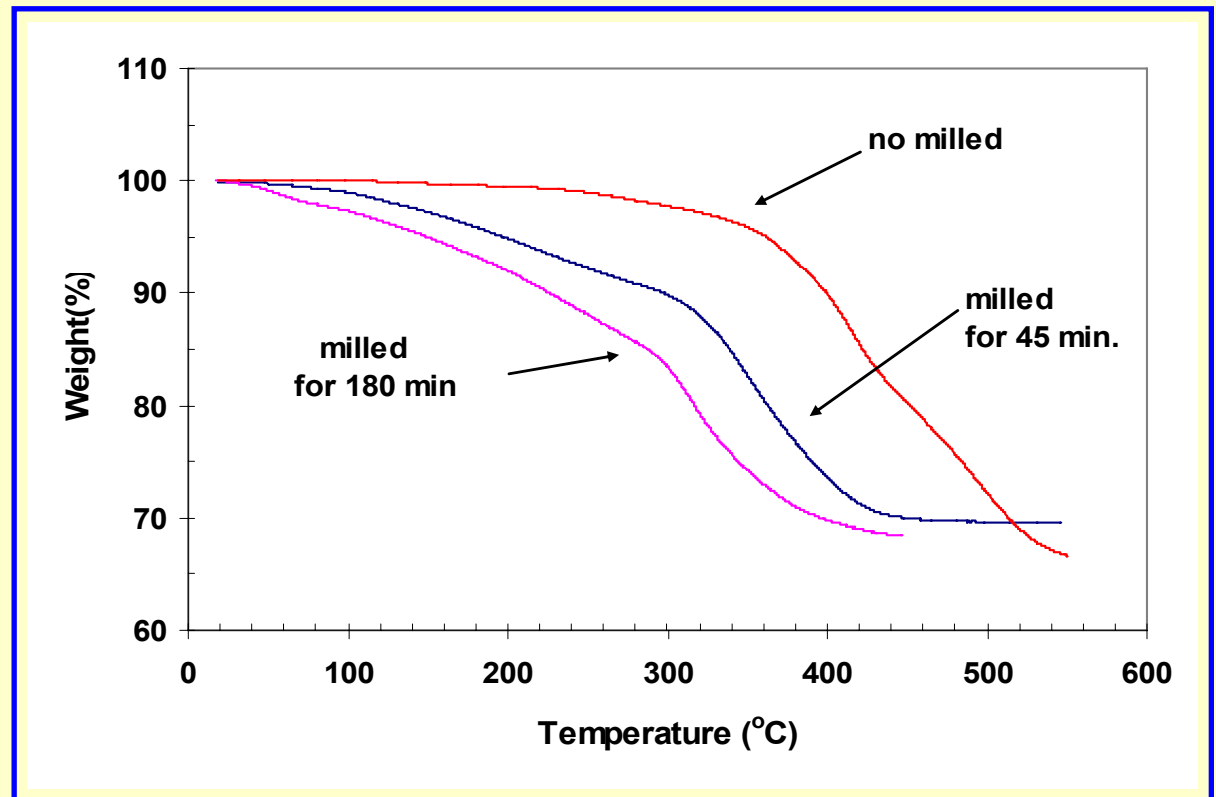
- Enhancement of LiNH₂ to Li₂NH transition via Eq. (2) is necessary because this is the first step for dehydrogenation of the LiNH₂ + LiH mixture.
- NH₃ generated from decomposition of LiNH₂ should be captured by LiH. Otherwise, H₂ fuel will be contaminated and the storage capacity will decrease with sorption/desorption cycles.

* T. Ichikawa, N. Hanada, S. Isobe, H. Leng, H. Fujii, J. Phys. Chem. B, Vol. 108, 7887 (2004).

Enhancement of LiNH_2 to Li_2NH Transition via Mechanical Activation

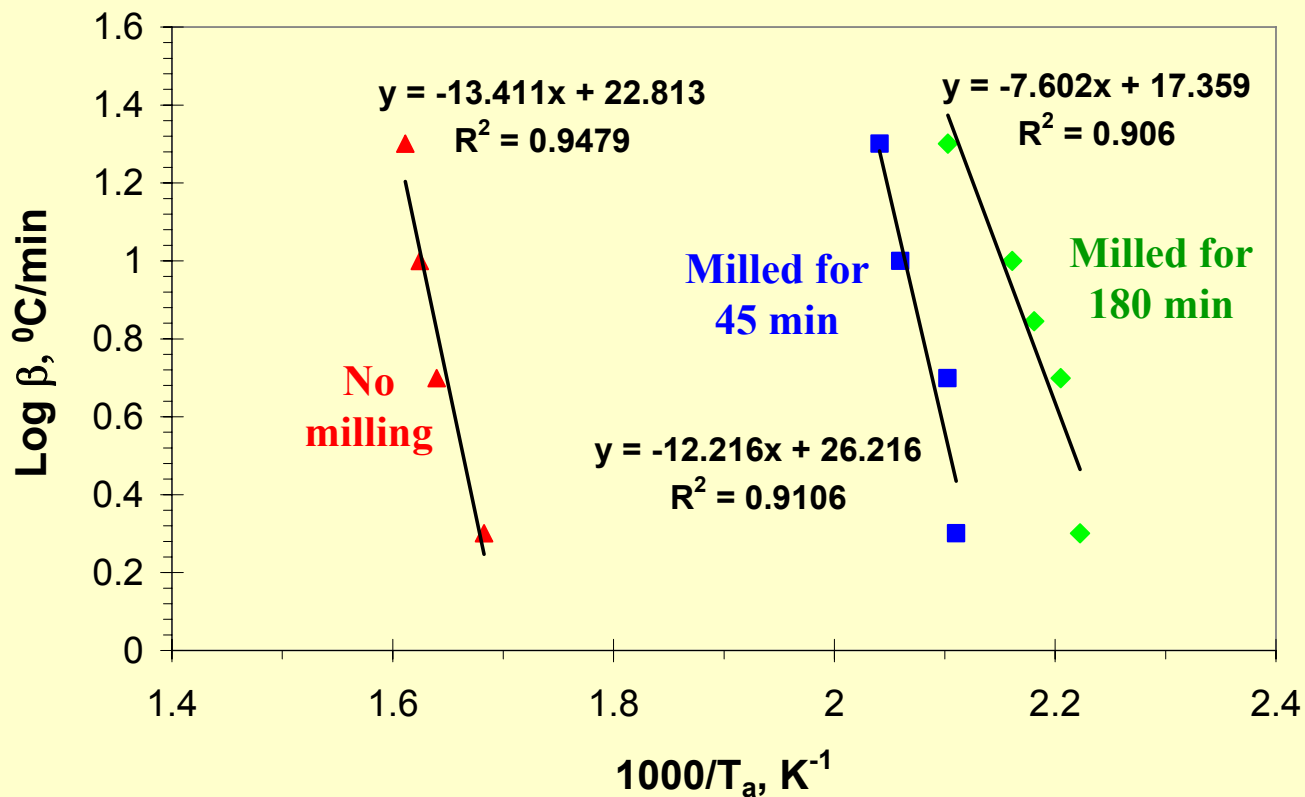
TGA Results of LiNH_2 with and without ball milling

- The onset temperature for weight loss of LiNH_2 without milling is 120°C , whereas the corresponding value for LiNH_2 with ball milling is room temperature.
- The transition rate from LiNH_2 to Li_2NH and NH_3 increases with the ball milling time, i.e., the more mechanical activation, the higher the transition rate.



The thermogravimetric analysis (TGA) was conducted under a flowing argon condition, and thus the weight loss was due to NH_3 formation as indicated by Eq. (2) of Slide 7 and its flowing out of the TGA chamber with the flowing argon.

Apparent Activation Energy for LiNH_2 Decomposition Decreases with Increase in the Degree of Mechanical Activation



Activation Energy Determined from Flynn-Wall plot

LiNH_2 without milling:

$$E_a = 243.9 \text{ kJ/mol}$$

LiNH_2 milled for 45 min:

$$E_a = 222.2 \text{ kJ/mol}$$

LiNH_2 milled for 180 min:

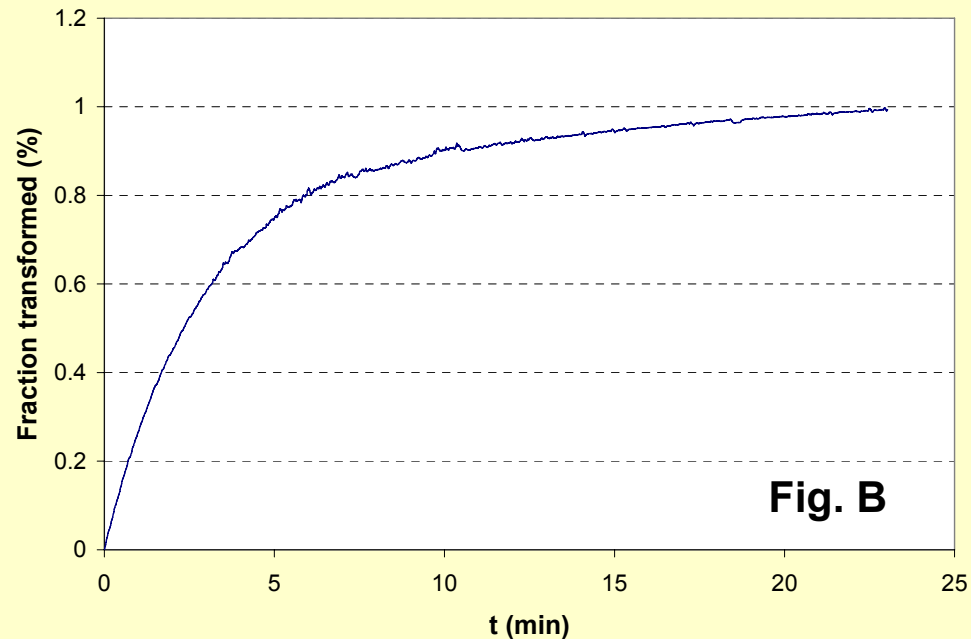
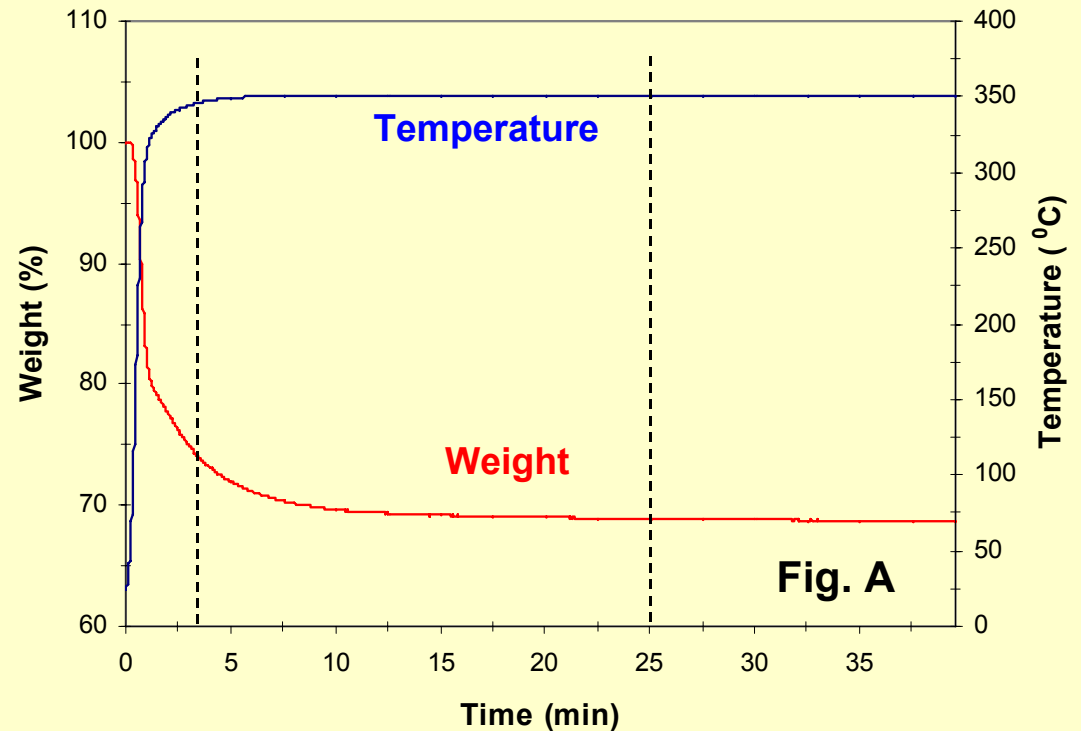
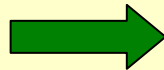
$$E_a = 138.0 \text{ kJ/mol}$$

Flynn-Wall Plot: The constant heating rate, β , during TGA vs the reciprocal of the temperature at which 15% transformation has occurred for the LiNH_2 to Li_2NH transition.

Reaction Kinetics of LiNH_2 Decomposition

The weight change of LiNH_2 under a constant temperature and pressure condition was monitored to determine the decomposition kinetics and rate-limiting mechanism. Fig. A shows such an experiment with rapid heating of LiNH_2 to 350°C in a TGA chamber and holding at 350°C with a flowing argon until the reaction was completed.

There is no linear relationship between the fraction decomposed and the holding time in the isothermal and isobaric experiment.



Analysis of LiNH₂ Decomposition under Isothermal and Isobaric Conditions



$$(1 - f)^{1/3} = 1 - \frac{k_1^{1/2}}{R} t^{1/2}$$

Controlled by diffusion of NH₃, N, or H through the Li₂NH product layer

$$(1 - f)^{1/3} = 1 - \frac{k_2}{R} t$$

Controlled by movement of the LiNH₂/Li₂NH phase boundary

$$f = 1 - \exp(-k_3 t^m)$$

Controlled by nucleation and subsequent growth of Li₂NH

$$f = k_4 t$$

Controlled by desorption of NH₃ from the surface of Li₂NH

Analysis of the reaction kinetics unambiguously indicates that LiNH₂ to Li₂NH transition is controlled by diffusion of NH₃, N, or H through the Li₂NH product layer.

Summary of Enhancement of LiNH_2 to Li_2NH and NH_3 Transition

1. Mechanical activation enhances the transition of LiNH_2 to Li_2NH and NH_3 , and reduces the onset temperature of the transition to room temperature.
2. Mechanical activation also decreases the apparent activation energy for decomposition of LiNH_2 . The more mechanical activation, the more reduction in the apparent activation energy.
3. The decomposition rate of LiNH_2 to Li_2NH and NH_3 is controlled by diffusion of NH_3 , N , or H species through the Li_2NH product layer.

Challenges:

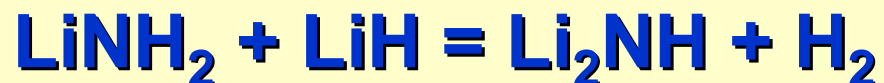
➤ Since decomposition of LiNH_2 is the first step of dehydrogenation of the $\text{LiNH}_2 + \text{LiH}$ mixture, how can we increase a diffusion-controlled decomposition to enhance dehydrogenation of the $\text{LiNH}_2 + \text{LiH}$ mixture? Three possible solutions are:

1. Nano-engineering to decrease the diffusion distance.
2. Increasing the composition gradient to enhance diffusion via advanced catalysts.
3. Increasing the diffusion coefficient to augment the diffusion rate via mechanical activation and doping.

➤ How can NH_3 emission be avoided if the decomposition rate of LiNH_2 has been increased substantially? The solution is:

Nano-engineering and mechanical activation to increase the reaction rate between LiH and NH_3 .

III. Reaction Mechanism, Kinetics, and Enhancement of Hydrogen Sorption/Desorption of the $\text{LiNH}_2 + \text{LiH}$ Systems

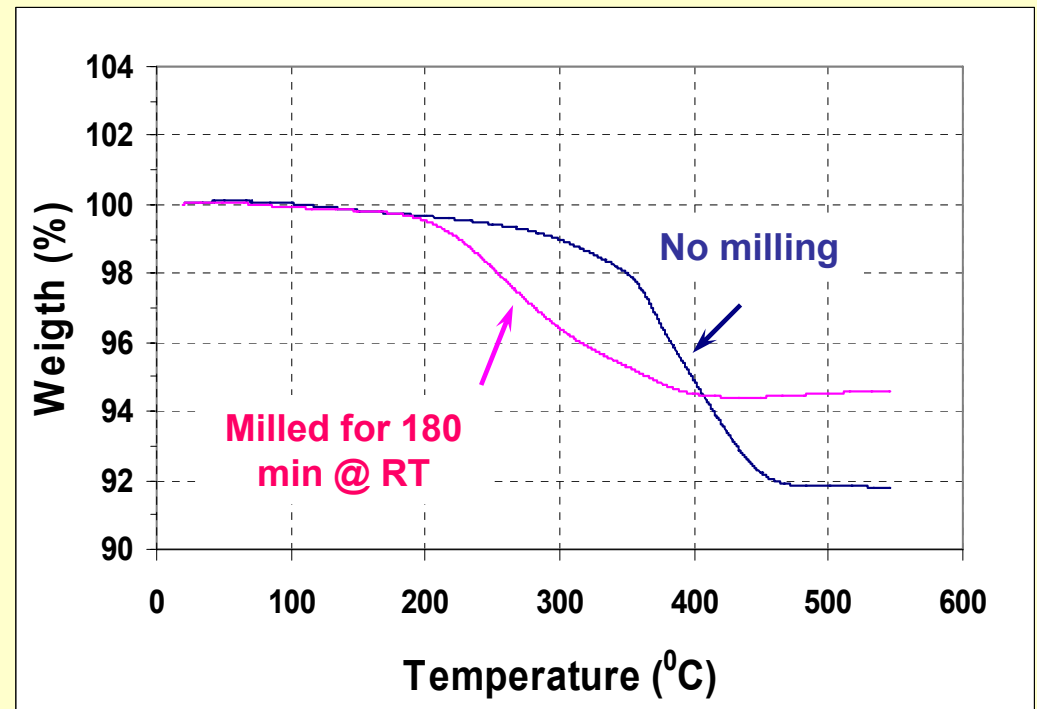


- The key to the success of this system is to reduce its hydrogen sorption/desorption temperatures to near ambient
- How to use mechanical activation to accomplish this goal? Is mechanical activation alone sufficient to achieve this goal? The following issues have been investigated in order to develop fundamental understanding and thus answer these key questions.
 - **Effects of mechanical activation on sorption/desorption behavior of $\text{LiNH}_2 + \text{LiH}$**
 - **Dehydrogenation mechanism and kinetics of the $\text{LiNH}_2 + \text{LiH}$ mixture**
 - **Long-term sorption/desorption cycling stability of mechanically activated $\text{LiNH}_2 + \text{LiH}$ mixtures**
 - **Effects of mechanical activation achieved with high-energy ball milling at liquid nitrogen temperature**
 - **Mitigation of NH_3 emission during ball milling and in subsequent sorption/desorption cycling**

Enhancement of Dehydrogenation of $\text{LiNH}_2 + \text{LiH}$ Mixtures via Mechanical Activation

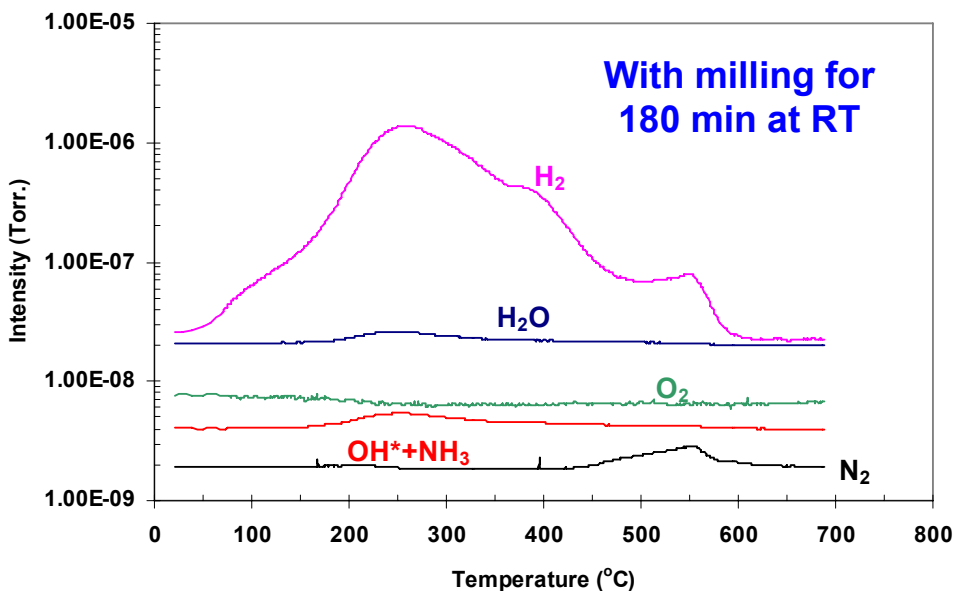
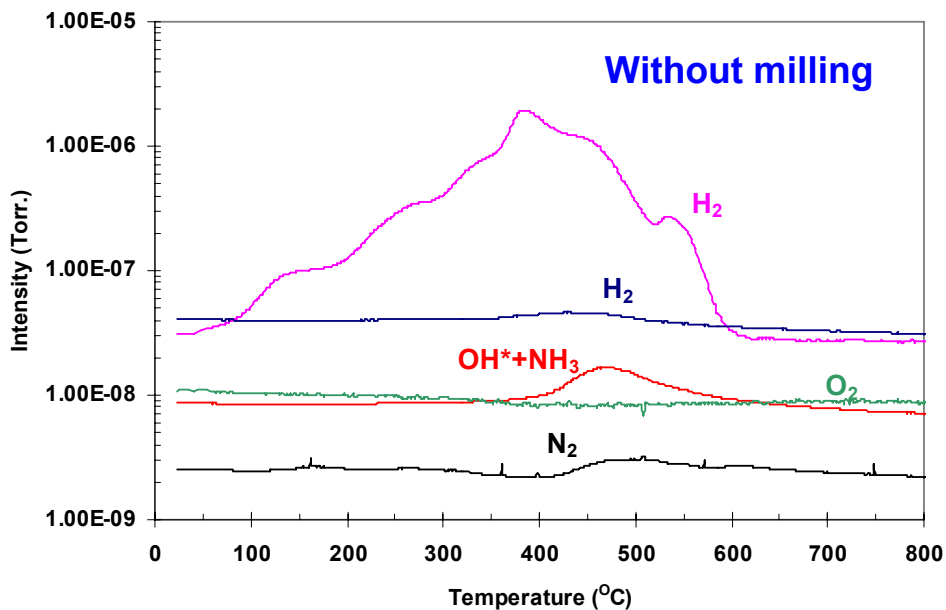
- The onset temperature and the temperature for release of a large amount of H_2 have been reduced substantially via ball milling.
- The weight loss for the milled sample is about 5.5%, which is in excellent agreement with the theoretical prediction of Eq. (1) of Slide 7 if lithium oxides and 10% additional LiH in the starting powder mixture are considered.
- The weight loss for the sample without milling is substantially larger than the theoretical prediction (~ 5.5 wt%). This is due to NH_3 emission because of the incomplete reaction between ammonia and lithium hydride of Eq. (3) on Slide 7.

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



The TG analysis was conducted under a flowing argon condition with a heat rate of $10^\circ\text{C}/\text{min}$.

Composition Analysis of the Effluent Gas from $\text{LiNH}_2 + \text{LiH}$ Mixtures during TG analysis



The composition analysis of the effluent gas confirms that:

- (i) the weight loss observed in the TGA trace of $\text{LiNH}_2 + \text{LiH}$ ball milled at RT for 180 min is due to hydrogen release;
- (ii) there exists a small amount of NH_3 in the effluent gas of $\text{LiNH}_2 + \text{LiH}$ without milling; this is especially true at temperatures between 400 and 600 $^{\circ}\text{C}$;
- (iii) ball milling reduces the peak temperature for releasing H_2 from 388 to 250 $^{\circ}\text{C}$; and
- (iv) NH_3 emission is a kinetic issue. Fast reaction between NH_3 and LiH or slow generation of NH_3 can all eliminate NH_3 emission. See the next slide for more details.

Comparisons in the Ammonia Level of the Effluent Gas Among Different LiNH₂+LiH Mixtures during TG analysis

Quantification of the NH₃ concentration in the effluent gas is based on analysis of the intensity of the signal at the mass-to-charge ratio of 17 from a mass spectrometer. The intensity of Mass 17, $I_{Mass\ 17}$, constitutes two components: the intensity of NH₃⁺ and the intensity of OH⁺:

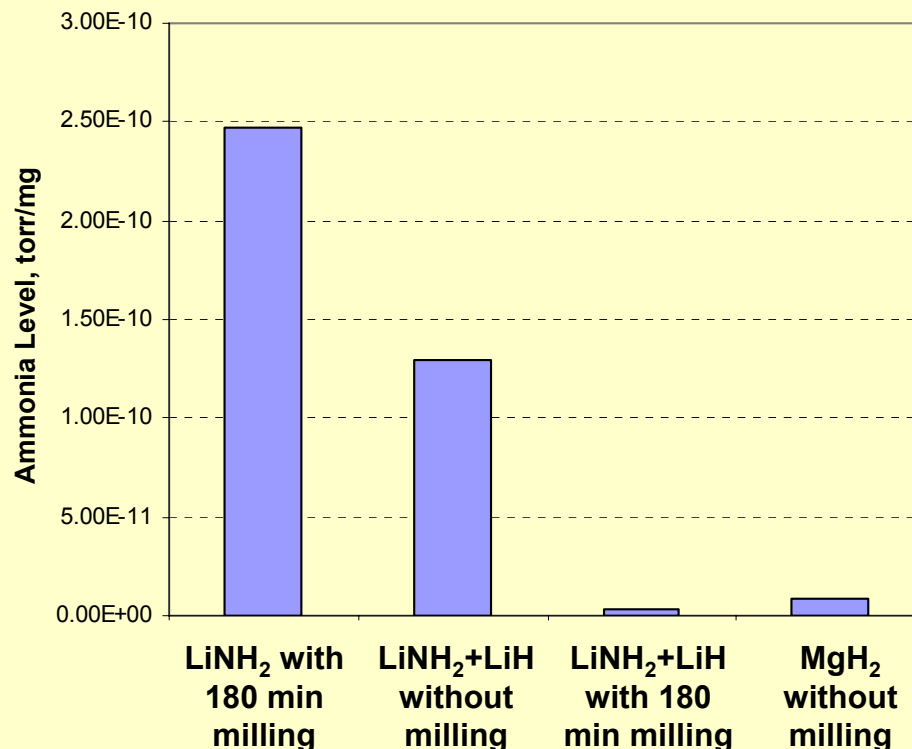
$$I_{Mass17} = I_{Mass17}^{NH3} + I_{Mass17}^{OH}$$

The intensity of OH⁺ is also related to the intensity of H₂O⁺ species:

$$I_{Mass17} = I_{Mass17}^{NH3} + 0.212I_{Mass18}$$

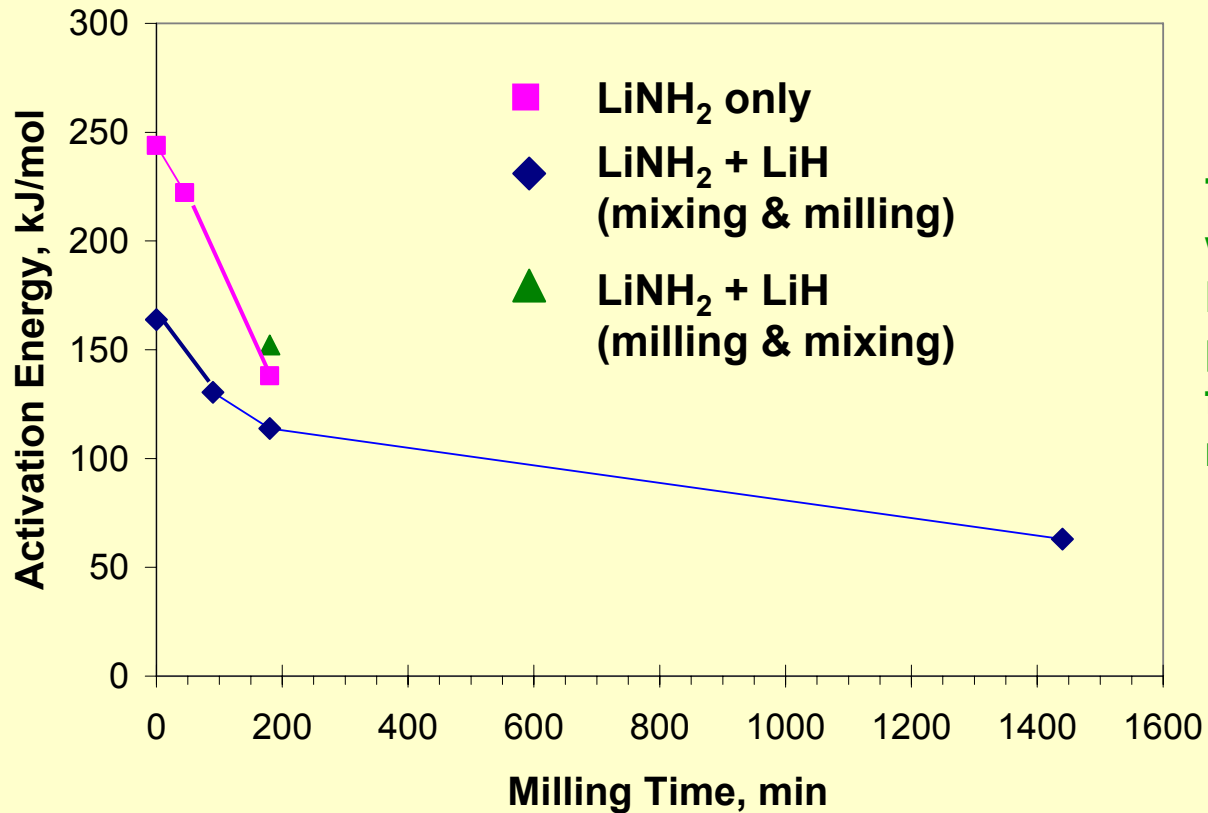
Thus, the intensity of NH₃⁺ species can be calculated from

$$I_{Mass17}^{NH3} = I_{Mass17} - 0.212I_{Mass18}$$



The data above shows that (i) the LiNH₂-only sample exhibits the highest NH₃ intensity because there is no LiH to “capture” NH₃; (ii) the LiNH₂+LiH mixture without ball milling displays the second highest NH₃ intensity because of slow reaction between LiH and NH₃; and (iii) the NH₃ intensity for the LiNH₂+LiH mixture with ball milling drops dramatically (by about 36 times); As a result, this intensity becomes lower than the detection limit of the mass spectrometer because MgH₂ does not have NH₃, but exhibits an NH₃ intensity of 8.4 x 10⁻¹² Torr/mg MgH₂.

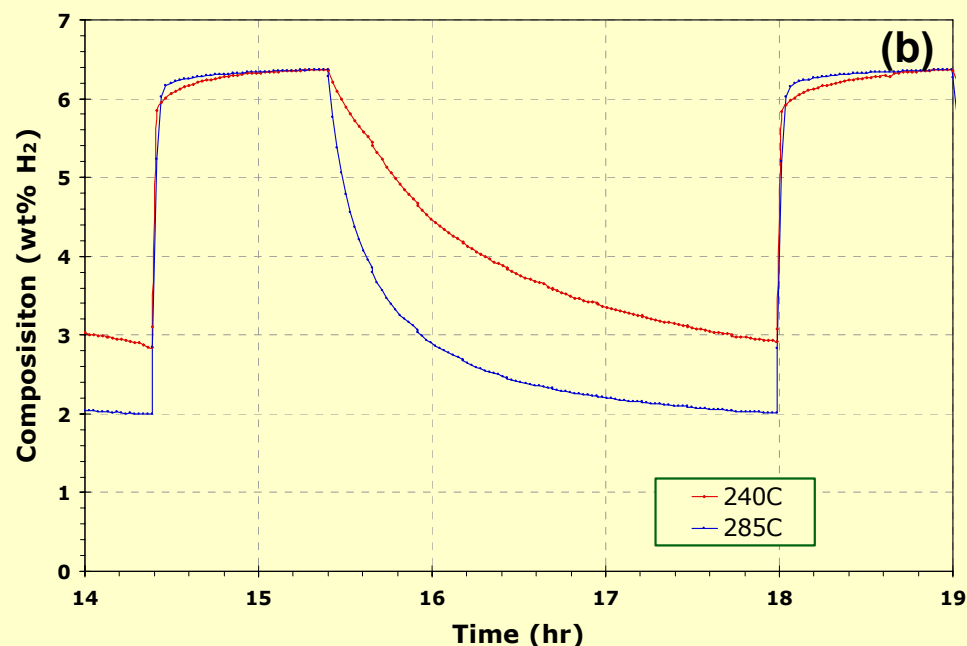
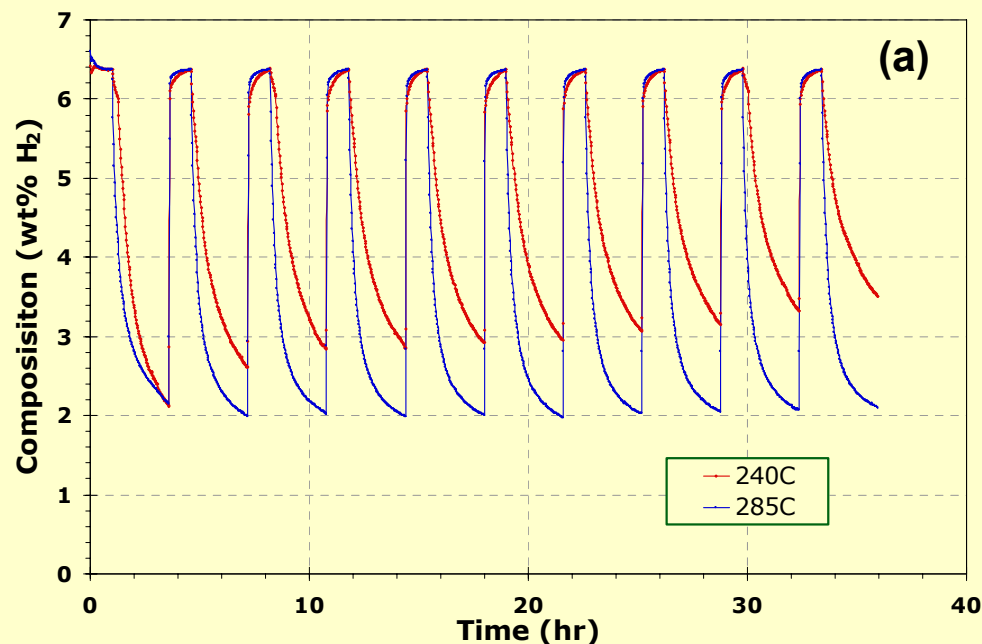
Mechanical Activation Decreases Apparent Activation Energies of Various Reactions



The apparent activation energies were determined using the Kissinger method based on the peak position of the reaction as a function of the heating rate measured from DSC traces.

- The activation energy decreases with increase in the milling time for all reactions.
- Reaction 2 of Slide 7 is the first step of Reaction 1. However, the apparent activation energy of Reaction 1 is lower than that of Reaction 2, suggesting that the presence of LiH can reduce the activation energy of Reaction 2.
- The activation energy is also affected by the milling and mixing sequence, supporting the notion that LiH does have the catalytic effect on Reaction 2.

Identification of Reaction Mechanisms and Quantification of Reaction Kinetics of $\text{LiNH}_2 + \text{LiH}$ Systems

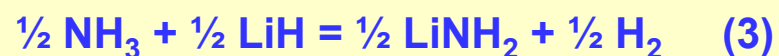
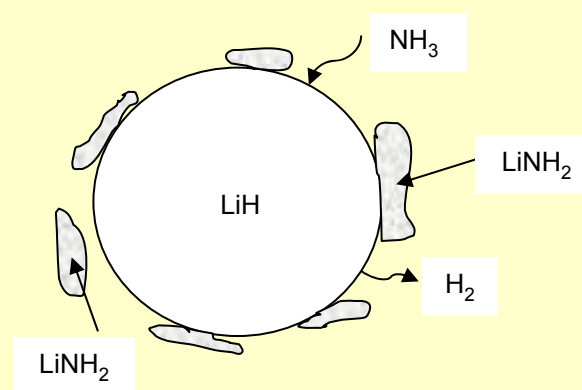
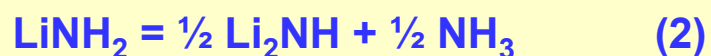
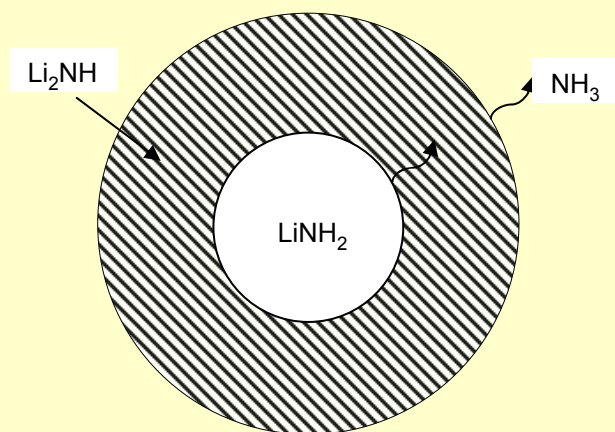


The isothermal sorption/desorption cycles, consisting of a one-hour sorption at 10 atm and a subsequent 2.5-hour desorption under an evacuated condition, were performed using a pressure-composition-isotherm (PCI) unit: (a) an overview of the 10 cycles, and (b) a close view of the 5th cycle.

- (1) The hydriding rate is much faster than the dehydriding rate. As a result, hydriding is almost complete in 5-min holding, whereas 2.5 hours are not sufficient for dehydriding, This leads to incomplete dehydriding and utilization of ~ 80% storage capacity.
- (2) As expected, the hydriding/dehydriding kinetics at 240°C is slower than that at 285°C.

Mechanisms of the Dehydrating Reaction of $\text{LiNH}_2 + \text{LiH}$ Systems

Dehydrating of $\text{LiNH}_2 + \text{LiH}$ proceeds with two elementary reactions, (2) and (3). However, Reaction (3) takes place in microseconds*, whereas Reaction (2) occurs in minutes because of the diffusion-controlled reaction. Both reactions produce solid products, why does one proceed so fast and the other is diffusion-controlled?

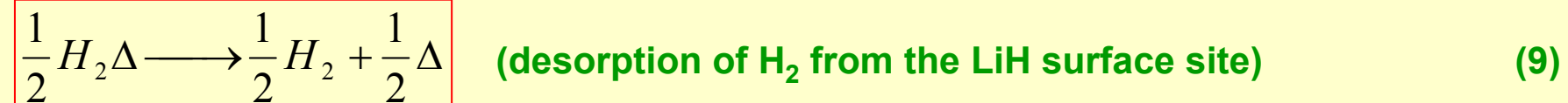
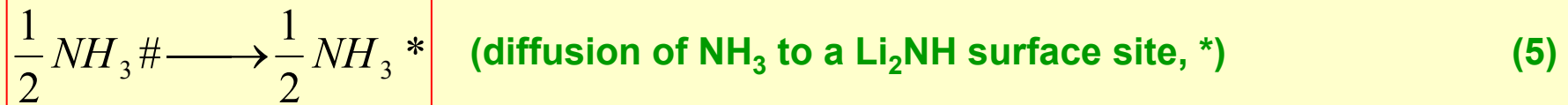


The volume of the solid product Li_2NH from Reaction (2) is smaller than that of the reactant LiNH_2 . As a result, a continuous yet porous Li_2NH layer forms on the surface of the LiNH_2 core. In contrast, the volume of the product LiNH_2 from (3) is 2 times that of the reactant LiH . Thus, flaking off of the product LiNH_2 layer takes place constantly, thereby continuously providing new LiH surface for reaction with NH_3 . As a result, Reaction (3) is not diffusion-controlled and can occur very fast.

* H. Y. Hu and E. Ruckenstein, J. Phys. Chem. A, Vol. 107, 9737 (2003).

Reaction Pathway of Dehydrating of $\text{LiNH}_2 + \text{LiH}$ Systems

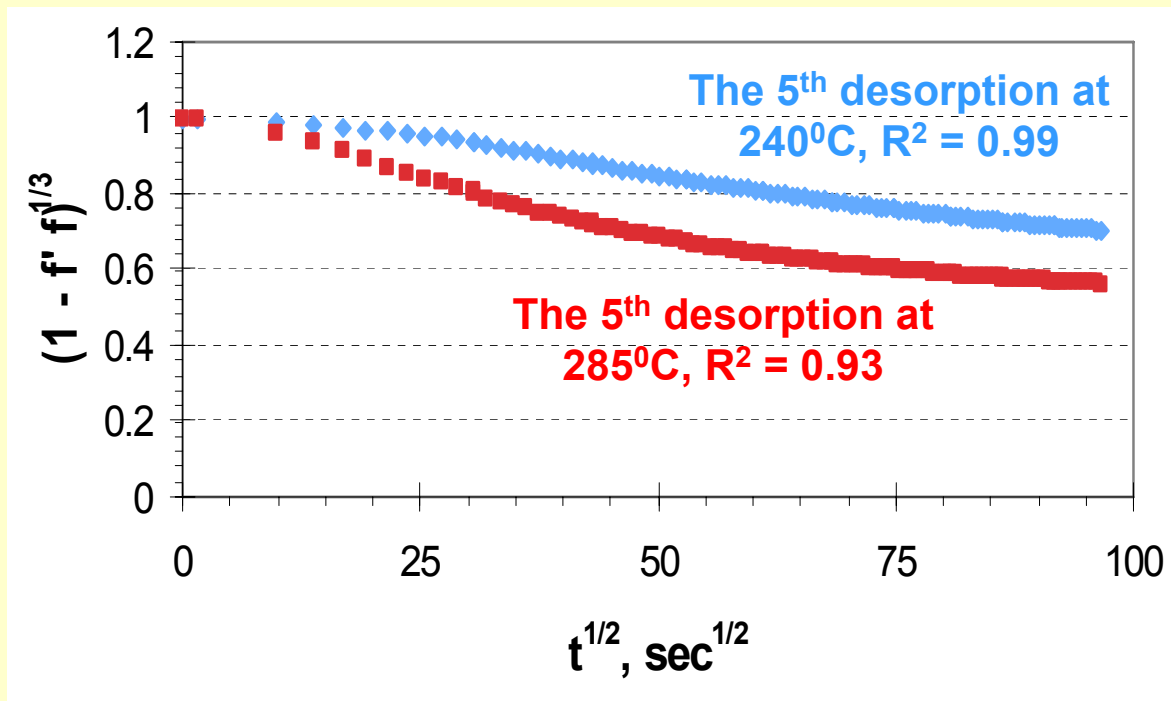
Based on the reaction mechanism proposed on Slide 19, the reaction pathway of dehydrating of $\text{LiNH}_2 + \text{LiH}$ can be described at least with the following 6 steps.



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

Reaction Kinetics of Dehydrating of $\text{LiNH}_2 + \text{LiH}$ Systems

Reactions (7), (8) and (9) should proceed very fast because they are elementary steps of Reaction (3). Thus, the desorption rate shown on Slide 18 has been analyzed for 4 possible rate-limiting steps: (i) movement of the $\text{LiNH}_2/\text{Li}_2\text{NH}$ phase boundary, (ii) diffusion of NH_3 , N, or H through the Li_2NH layer, (iii) nucleation and growth of Li_2NH into the LiNH_2 core, and (iv) desorption of NH_3 from the Li_2NH surface.



Conclusions:

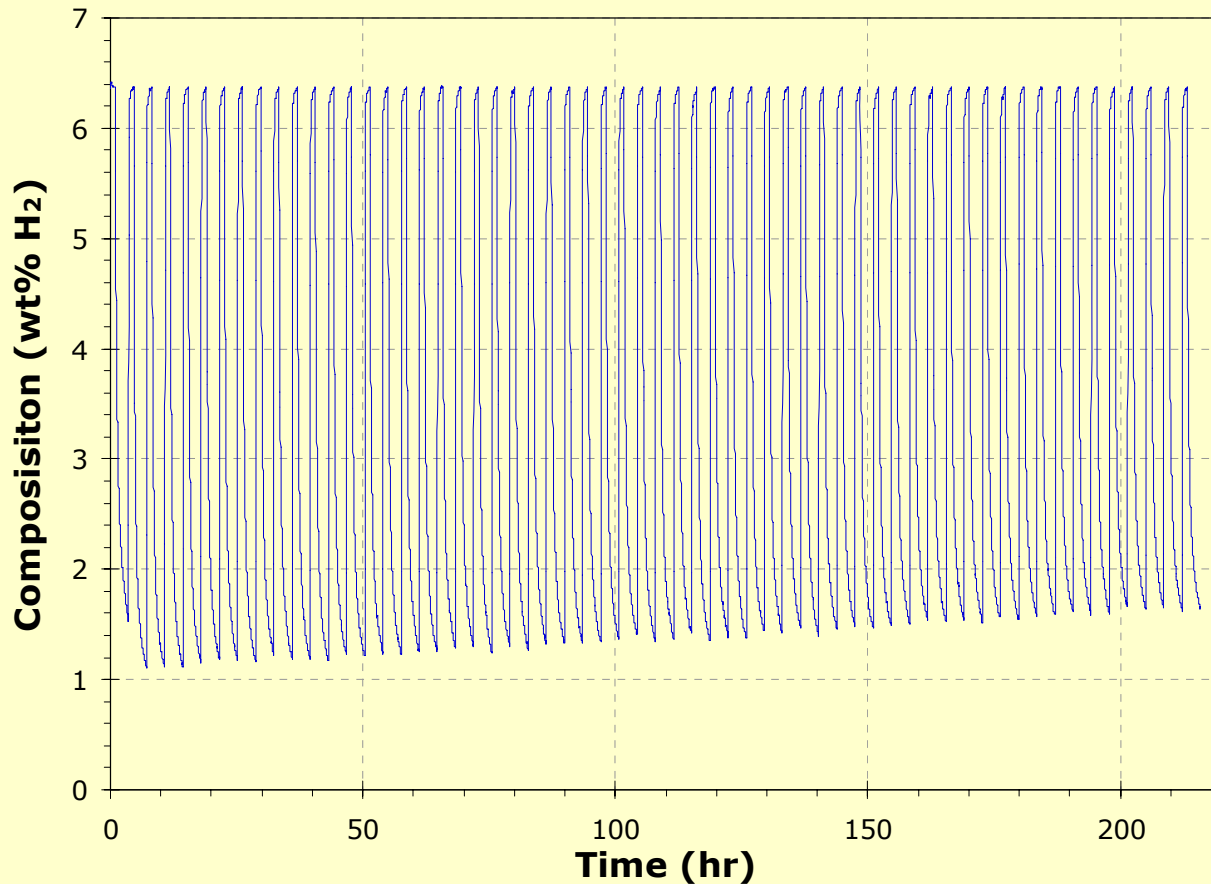
1. The rate-limiting step for dehydrating of $\text{LiNH}_2 + \text{LiH}$ is diffusion of NH_3 , N, or H through the Li_2NH product layer.
2. The activation energy for diffusion is very low (only 19.3 kJ/mol).

The analysis reveals that the fraction of H_2 released, f , as a function of time, t , can be described well by a parabolic-rate law derived from Fick's second law:

where f' is the fraction of H_2 released at the end of the desorption cycle, R the average radius of LiNH_2 particles, and k_5 a constant related to the diffusion coefficient, D .

$$(1 - f' \cdot f)^{1/3} = 1 - \frac{k_5}{R} \cdot t^{1/2}$$

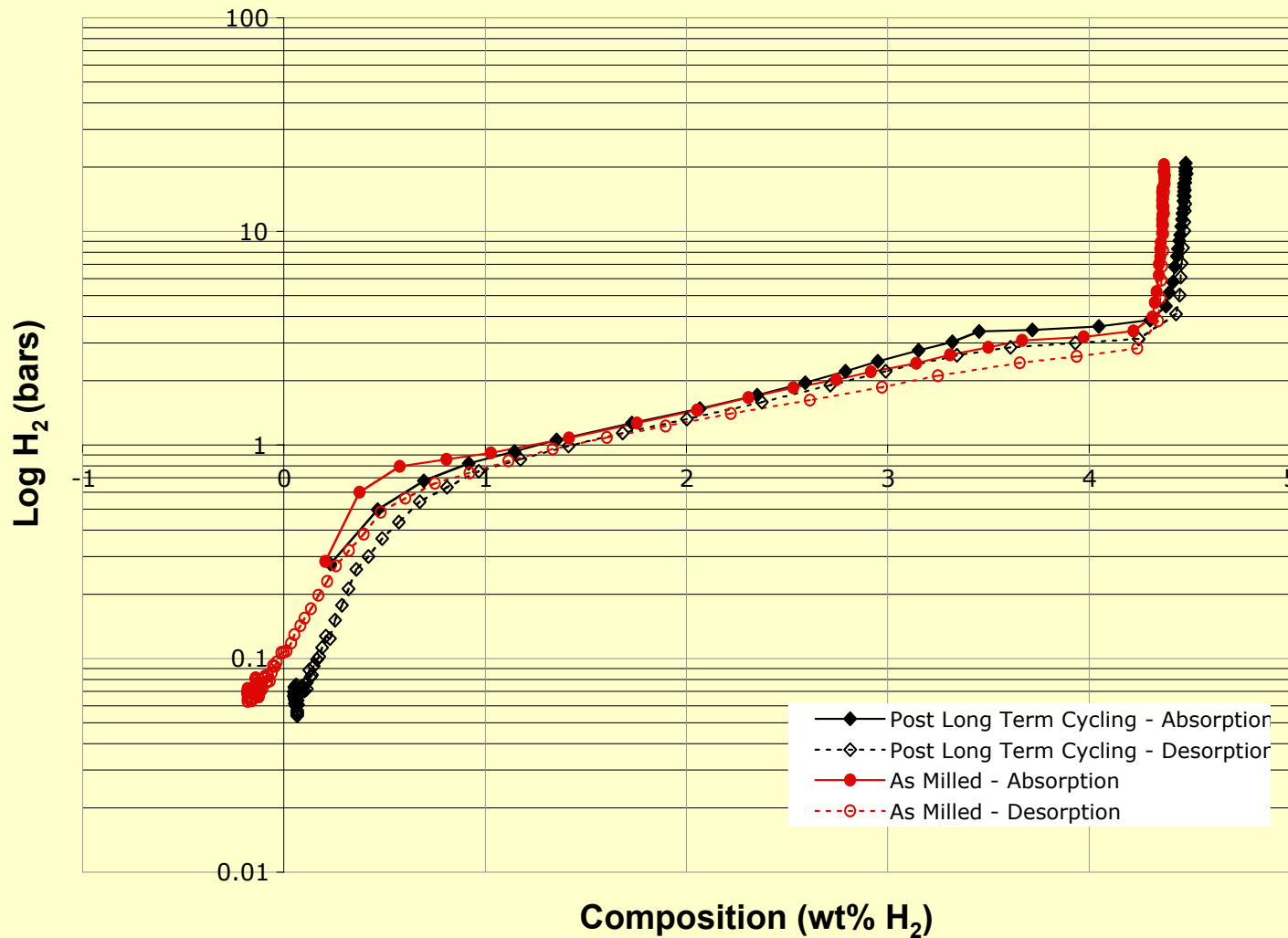
Long-Term Cycling Stability of Mechanically Activated $\text{LiNH}_2 + \text{LiH}$



The long-term cycling stability was studied using a PCI unit with 60 isothermal sorption/desorption cycles at 285°C for 210 hr.

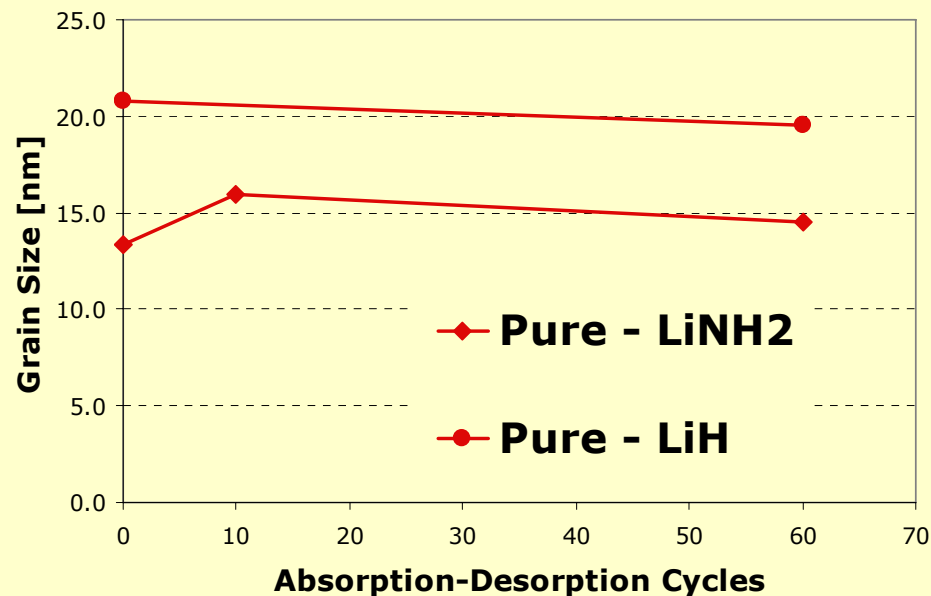
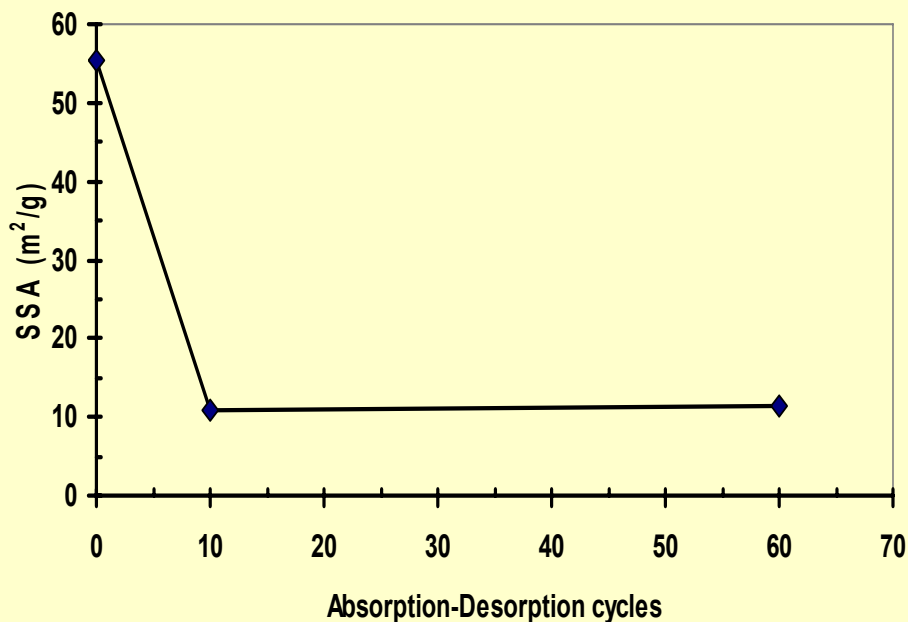
- The kinetic performance decreases gradually as the number of cycles increases.
- Slow dehydriding rates lead to incomplete release of hydrogen and utilization of ~ 96% of the theoretical storage capacity at the beginning of the cycles, which decreases to ~ 87% of the theoretical after 60 cycles.
- Although degraded, the mechanically activated $\text{LiNH}_2 + \text{LiH}$ mixture displays incredible stability, considering that 285°C is 86% of LiNH_2 's melting temperature and 58% of LiH 's melting temperature.

Pressure-Composition-Isotherms before and after 60 Sorption/Desorption Cycles of Mechanically Activated (LiNH₂+LiH+5vol% graphite) Systems



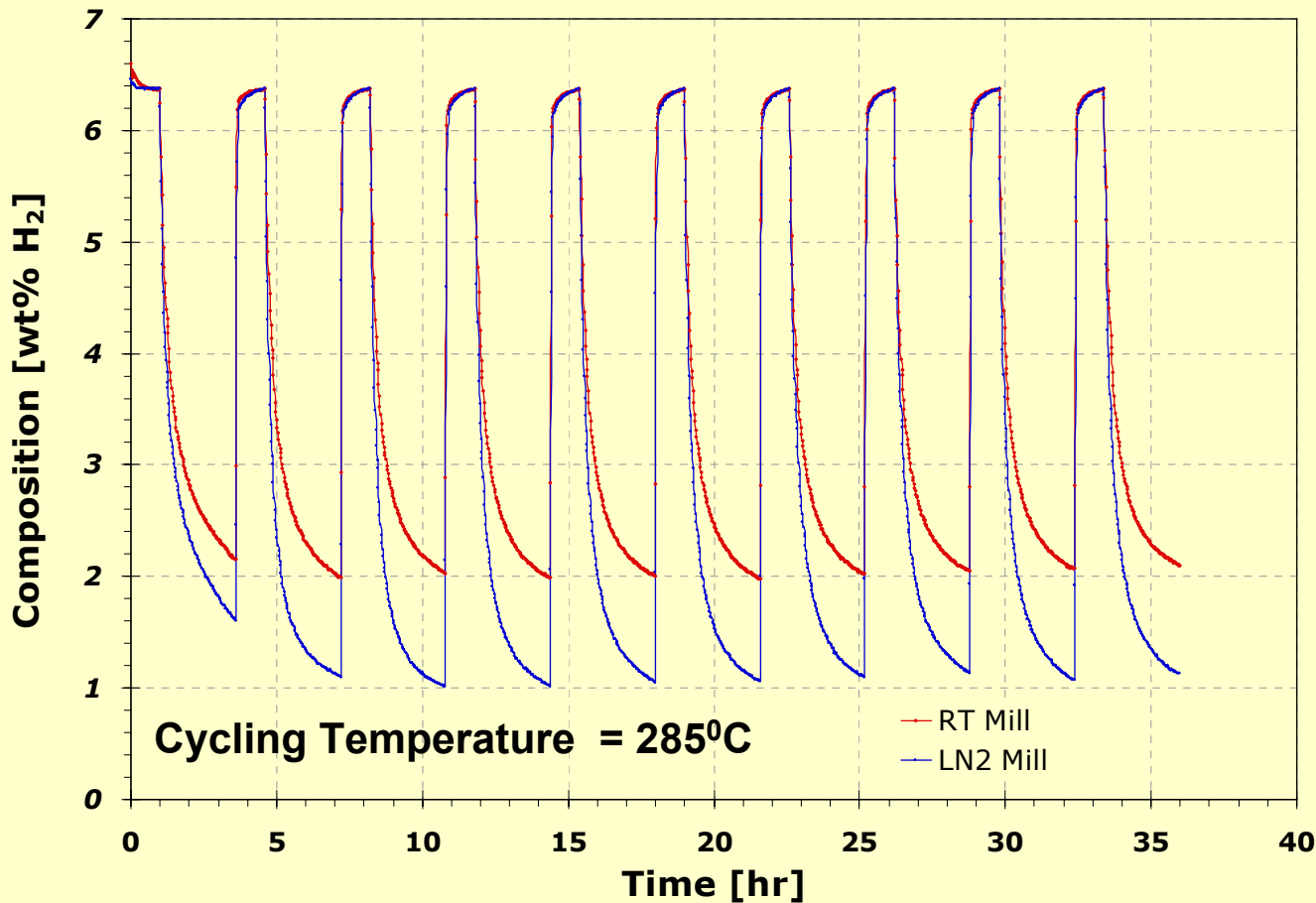
- The thermodynamic storage capacities before and after the long-term cyclic stability test are identical.
- This unequivocally confirms that the loss in the utilization of the theoretical storage capacity in long-term cycling is due to the loss of kinetic performance.
- This also proves that there is no NH₃ escaping from the system during cycling; otherwise, the thermodynamic storage capacity will decrease.

Mechanisms of Long-Term Cycling Stability of Mechanically Activated $\text{LiNH}_2 + \text{LiH}$



- The long-term stability is a significant concern for the viability of mechanically activated storage systems. These systems comprise nano-particles with high concentration defects. Long-term exposure to elevated temperatures could potentially cause annealing, grain growth, and even sintering.
- The data above shows the substantial reduction in specific surface area (SSA) in the first 10 cycles after which SSA has little change.
- The crystallite sizes of nano- LiNH_2 and LiH change little in the entire period of cycling. The stability of nano-grains is likely due to repeated phase transformation, flaking off of the LiNH_2 layer from LiH particles, and presence of the gaseous phase which effectively prevents sintering from taking place.
- The loss of kinetic performance in the long-term cycling test (Slide 22) is due to reduction in both SSA of and defects inside nano-particles.

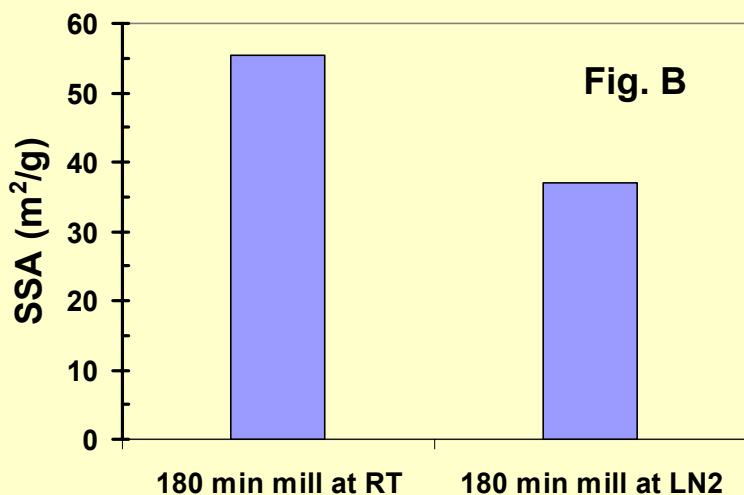
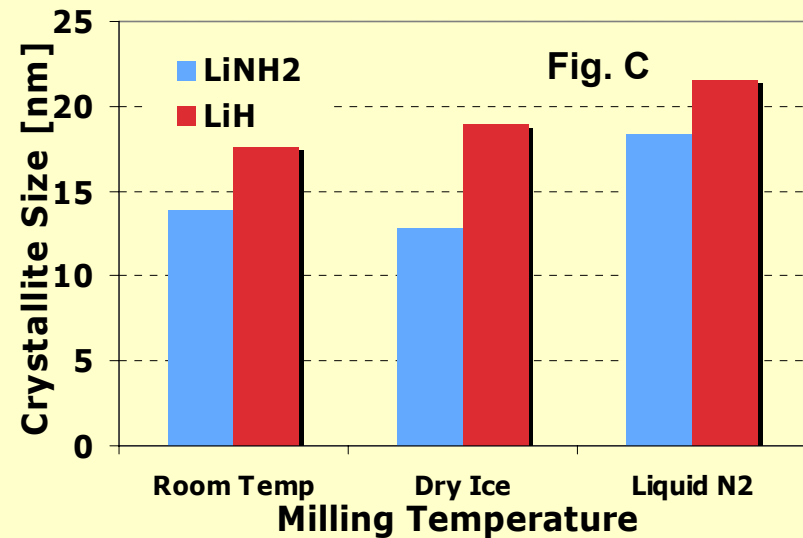
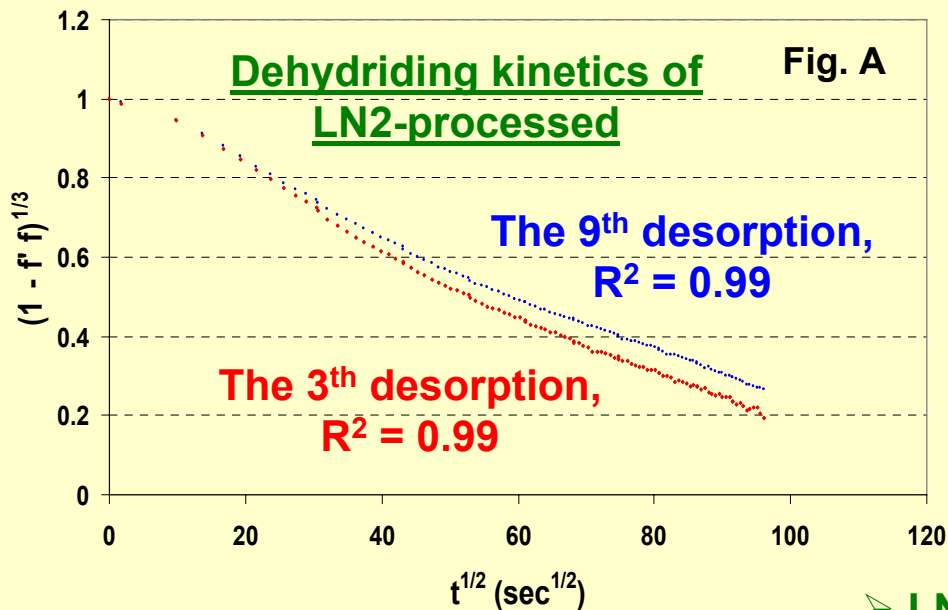
Enhancement of Hydrogen Sorption/Desorption of $\text{LiNH}_2 + \text{LiH}$ Systems through Mechanical Activation at Liquid Nitrogen Temperature



$\text{LiNH}_2 + \text{LiH}$ mechanically activated at liquid nitrogen temperature (LN2) displays much faster hydriding/dehydriding kinetics than that mechanically activated at RT. As a result, LN2-processed $\text{LiNH}_2 + \text{LiH}$ has improved the utilization of the theoretical storage capacity by 22%.

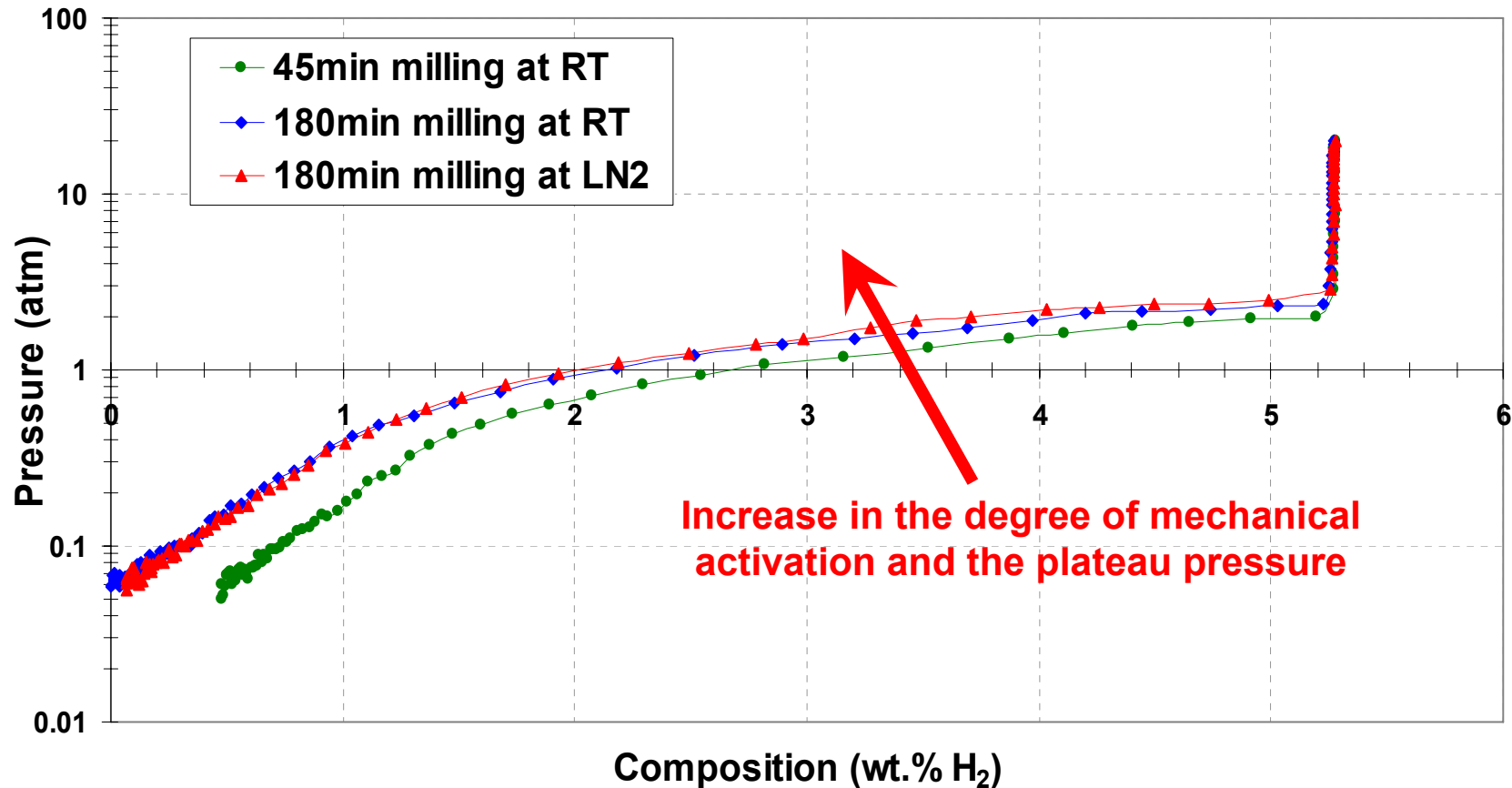
LN2 temperature is 12% of LiNH_2 's melting temperature and 8% of LiH's melting temperature. Thus, ball milling at LN2 can potentially make finer nano-particles with larger SSA and introduce more defects to nano-particles than ball milling at RT.

Mechanisms of Enhanced Hydrogen Sorption/Desorption through Mechanical Activation at Liquid Nitrogen Temperature



- LN₂-processed LiNH₂+LiH still exhibits diffusion-controlled dehydrating reactions, i.e. LN₂ ball milling does not change the reaction mechanism (Fig. A).
- LN₂-processed LiNH₂+LiH has a lower SSA (Fig. B) and larger crystallite sizes (Fig. C) than that processed at RT.
- Therefore, the enhanced dehydrating rate of LN₂-processed LiNH₂+LiH observed in isothermal sorption/desorption cycling is due to the increased defect concentration in nano-particles.

Effects of the Degree of Mechanical Activation on Sorption/Desorption Properties

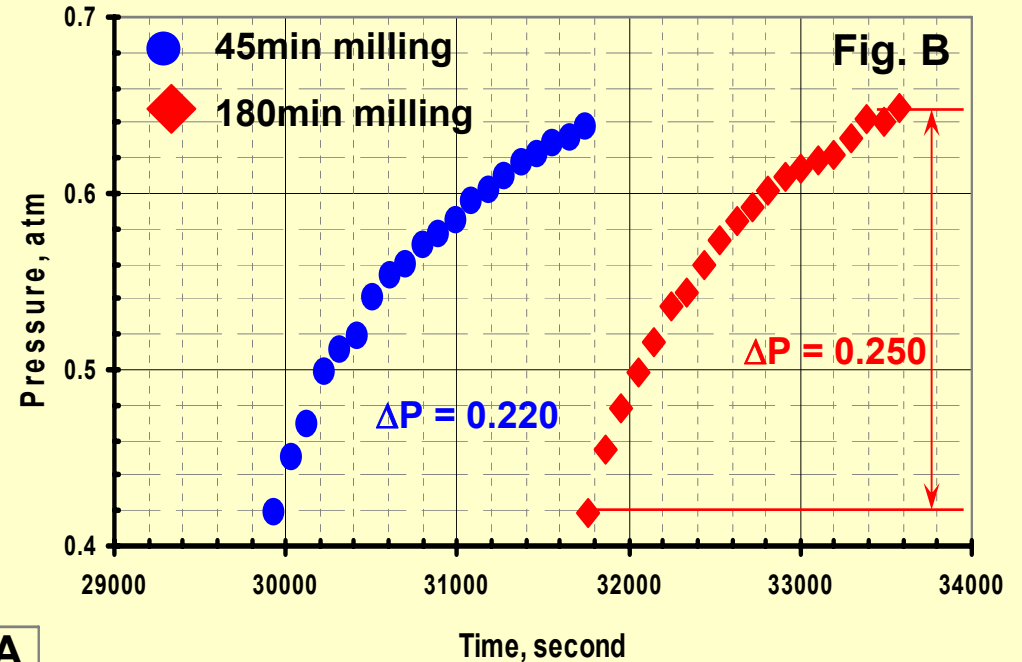
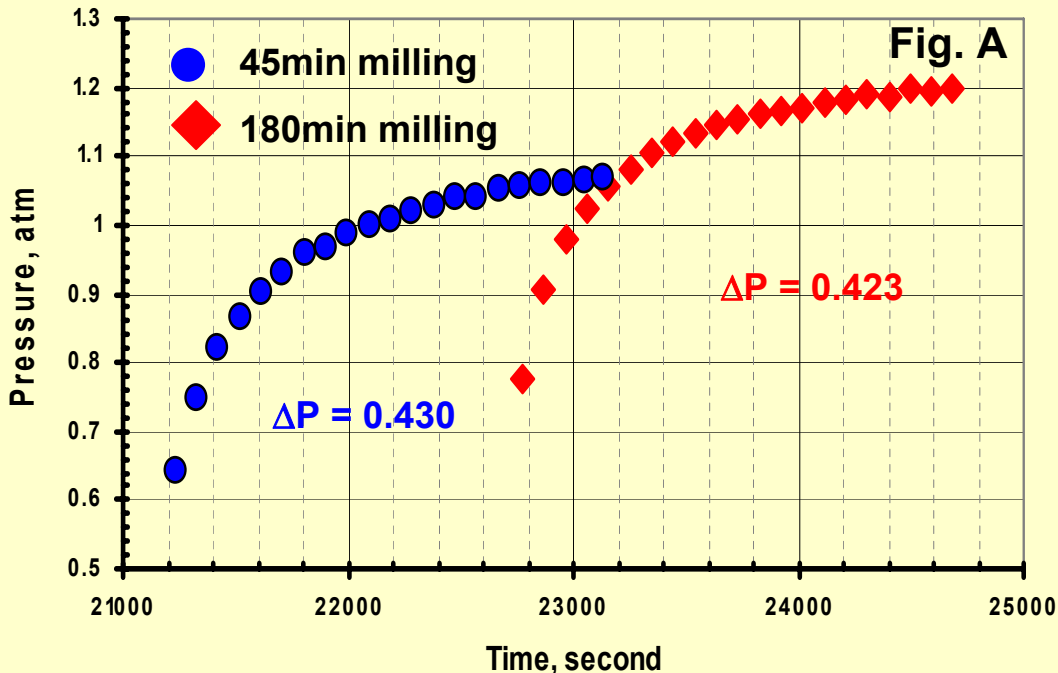


The plateau pressure of the pressure-composition-isotherm curve at 285^oC (desorption curves are shown here) increases with the degree of mechanical activation.

The lower storage capacity of the 45-min milled sample is due to its slower dehydriding rate. See Slide 28 for more details.

Effects of Desorption Kinetics on the Desorption Isotherm

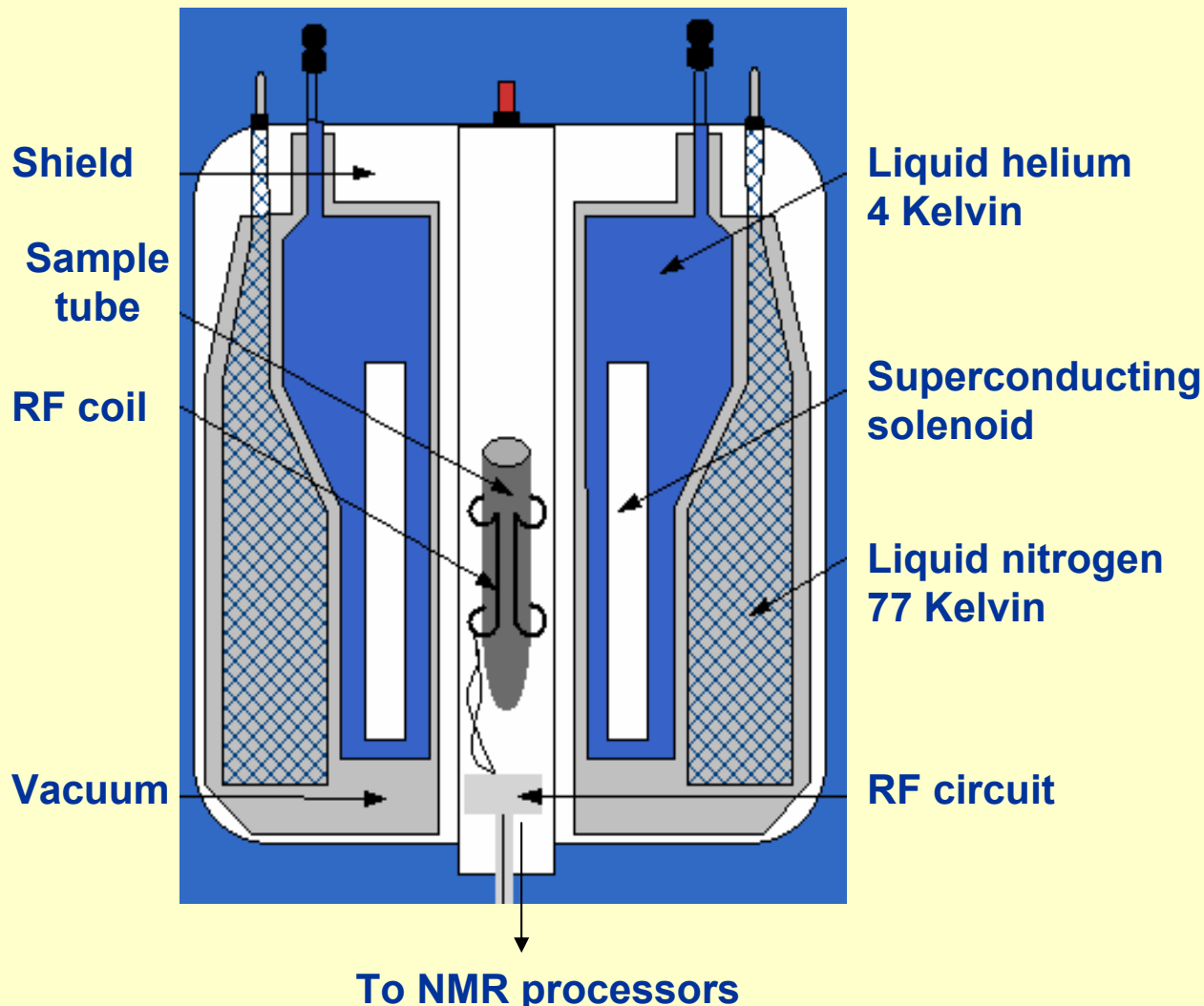
Desorption isotherms are measured by decreasing pressure step by step and letting pressure approach equilibrium in each step. 100% equilibrium will never be reached because it takes extremely long time to accomplish that for each step. As a result, the measurement condition and the desorption rate of the material will determine the percentage of equilibrium being reached, and ΔP in each pressure change step will determine how much H_2 has been released in each step. Summation of all the steps gives the hydrogen storage capacity.



The analysis of ΔP in each pressure change step indicates that when pressure is at or above 1 atm (Fig. A), hydrogen released in each step is similar for 45min and 180min milled samples. However, when pressure is below 1 atm (Fig. B) the 45min milled sample releases less hydrogen in each step than the 180min milled sample (Fig. B). As a result, 45min milled sample shows less storage capacity (Slide 27).

III. Atomic Level Understanding of Effects of Mechanical Activation via NMR

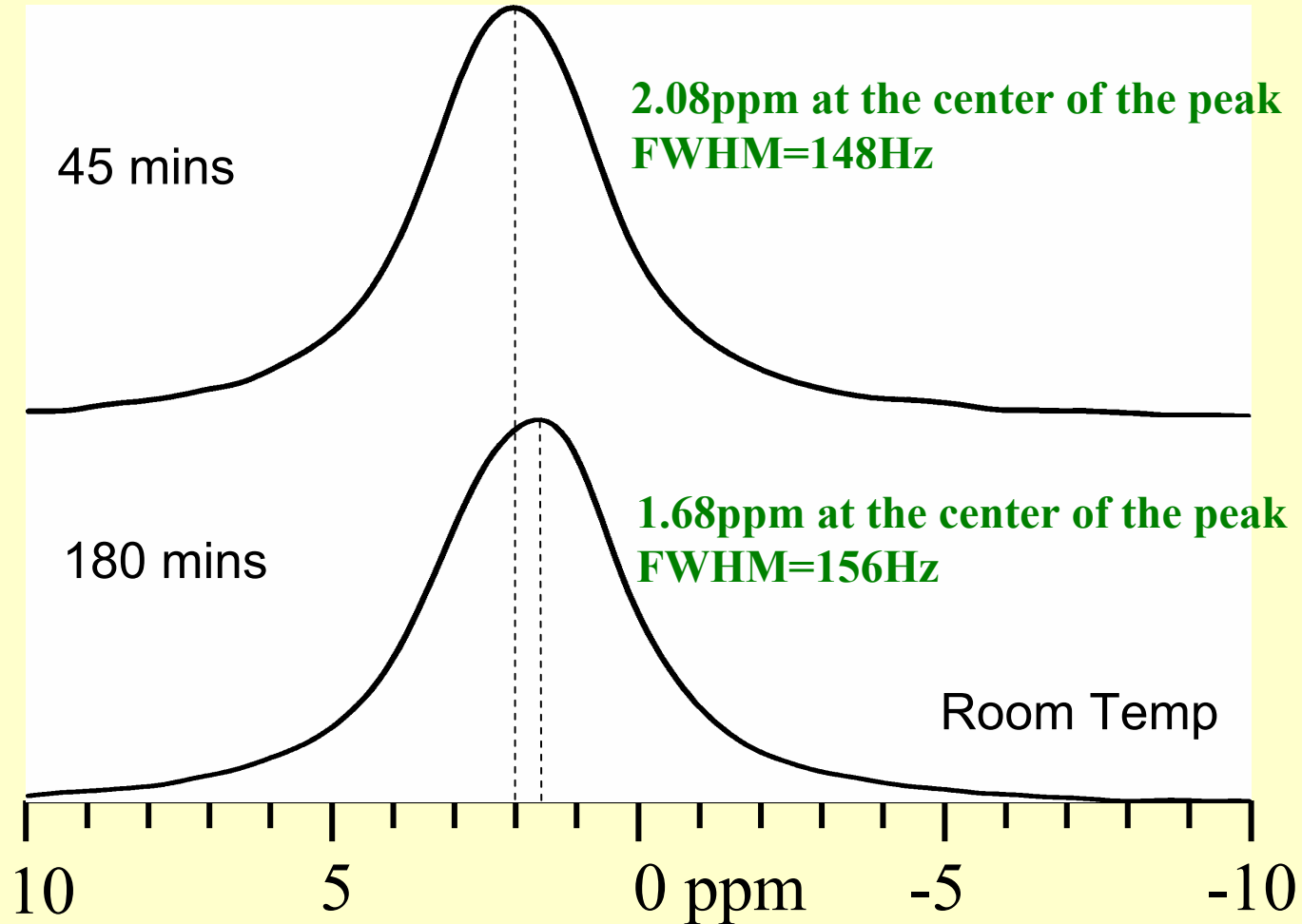
In this past year, researchers at PNNL have designed and developed a sealed sample stage that allows for *in situ* MAS NMR study of hydrogen storage materials at elevated temperatures up to 200°C.



With the newly established capability, we have:

- Obtained high resolution ${}^6\text{Li}$ and ${}^1\text{H}$ spectra from varied hydrides, providing useful information for mechanistic understanding.
- Carried out dynamic NMR that further mechanistic understanding on hydrogen desorption over time.
- Planned to measure proton transport properties in hydrides, with combination of software capabilities.

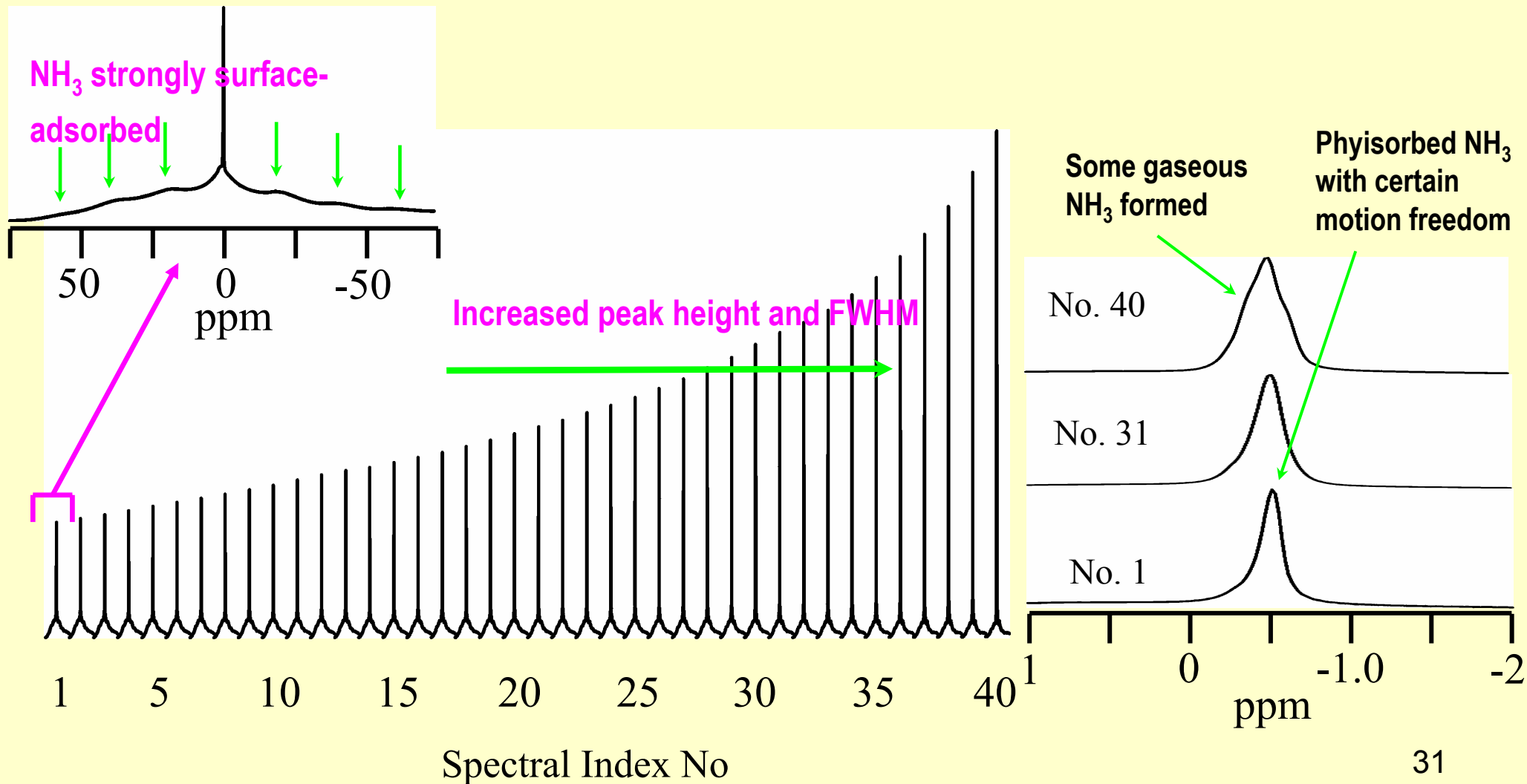
Effects of Mechanical Activation on ${}^6\text{Li}$ MAS NMR spectra of LiNH_2



The ${}^6\text{Li}$ peak shift and broadening indicate that mechanical activation leads to not only structural refinement of the hydride, but also changes in the local electronic state around Li nuclei.

Dynamic In Situ ^1H MAS NMR

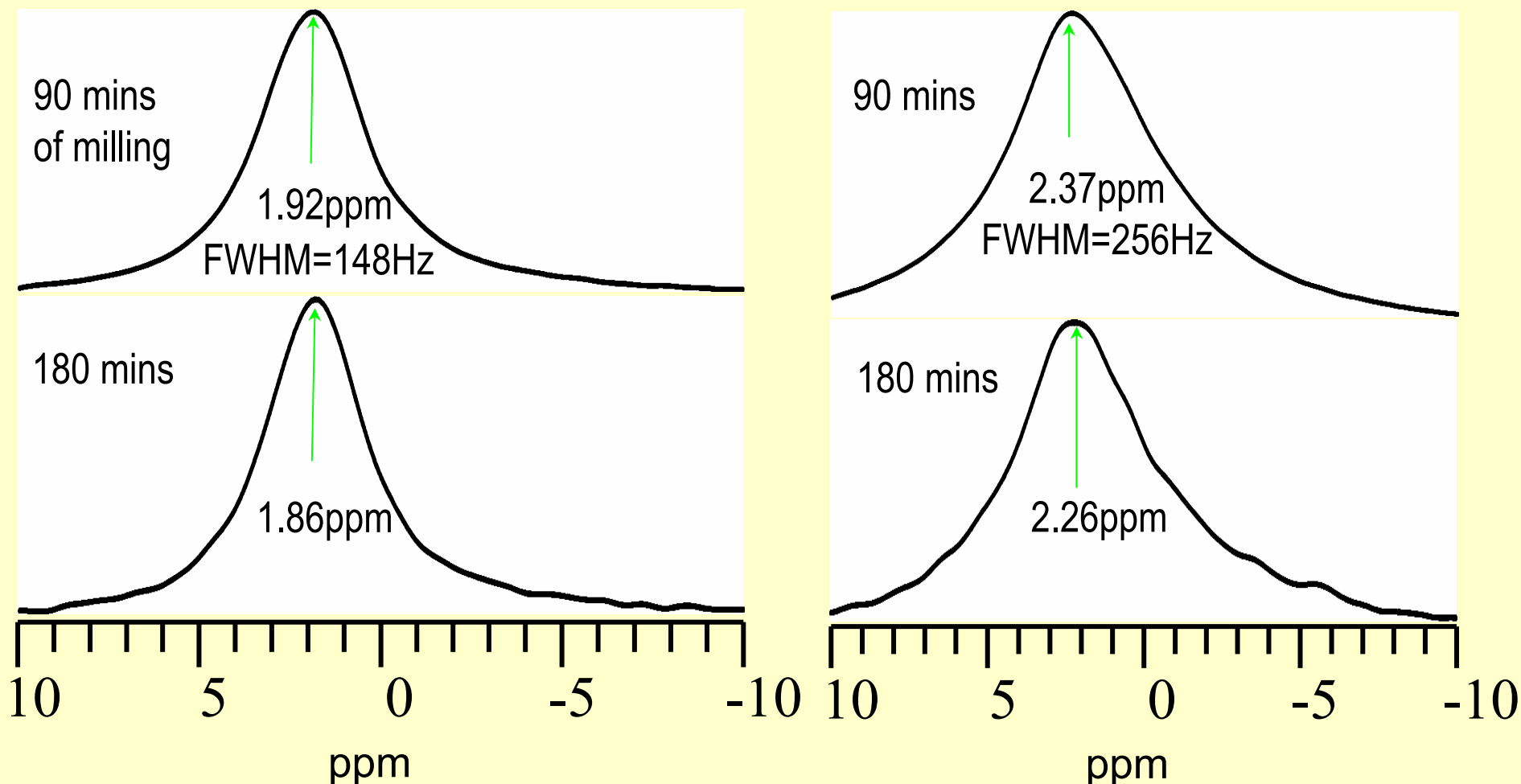
Dynamic in situ ^1H NMR was carried out in a closed sample tube at 50°C as a function of holding time with an acquiring time of 0.5 hour for each spectrum on LiNH_2 milled at RT for 180 minutes. The study indicates the ammonia formed and strongly physisorbed on the surface first, then accumulated and gained motion freedom to become a gas phase.



^6Li MAS NMR of Mechanically Activated LiNH_2+LiH

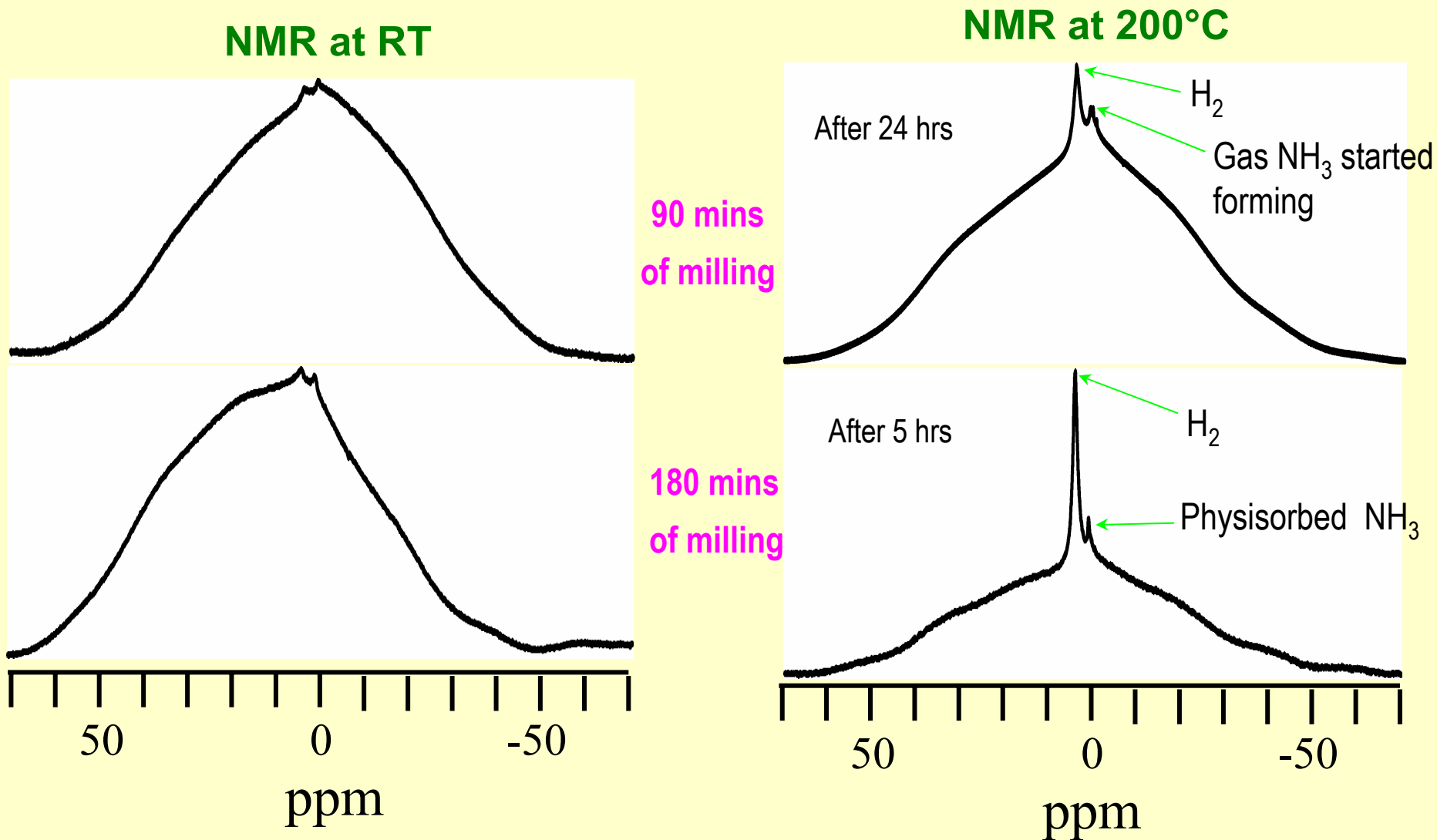
NMR at RT

NMR at 200°C



Like the amide, MAed (LiNH_2+LiH) also displays the ^6Li peak shift and broadening that increase with milling time. Thus, mechanical activation leads to not only structural refinement of the hydride mixture, but also changes in the local electronic state around Li nuclei.

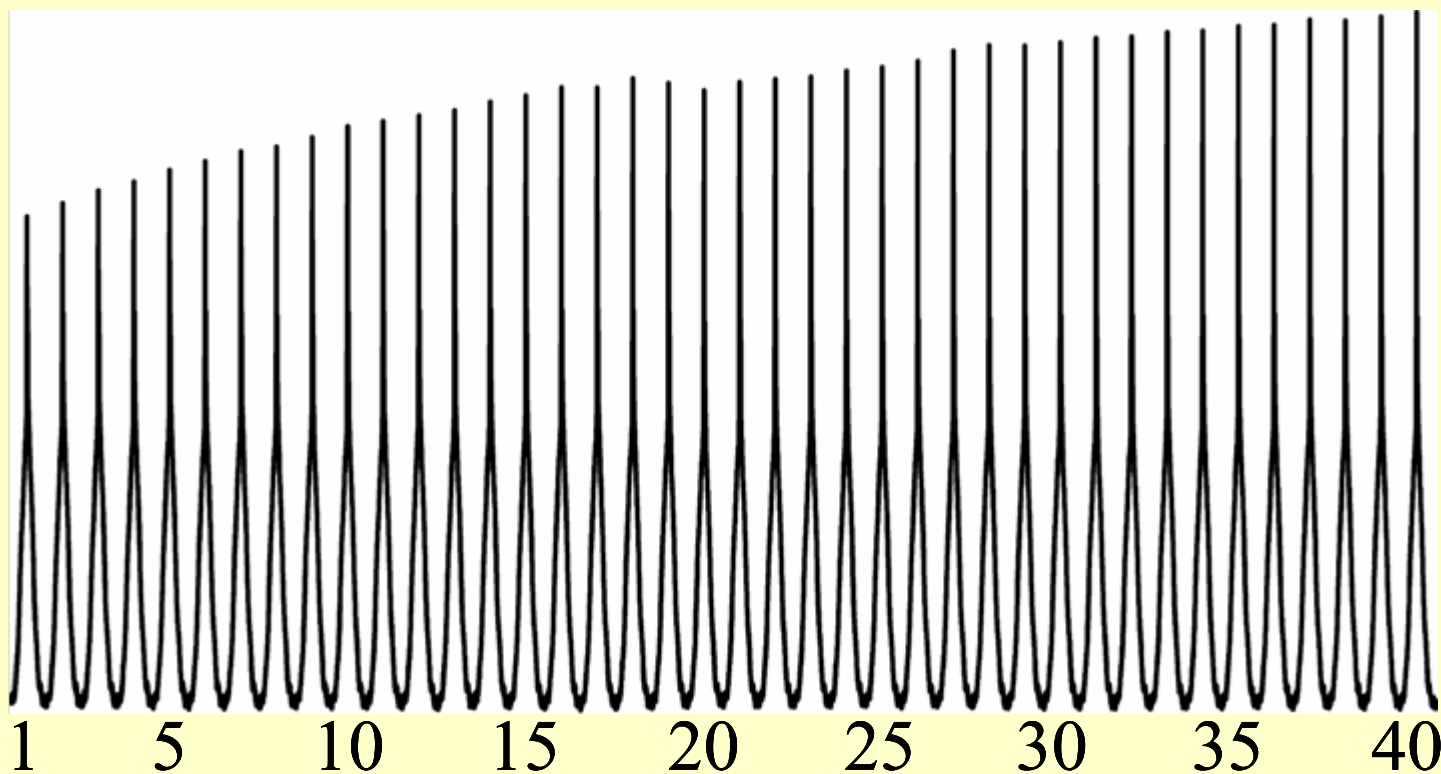
^1H MAS NMR of Mechanically Activated (LiNH_2+LiH)



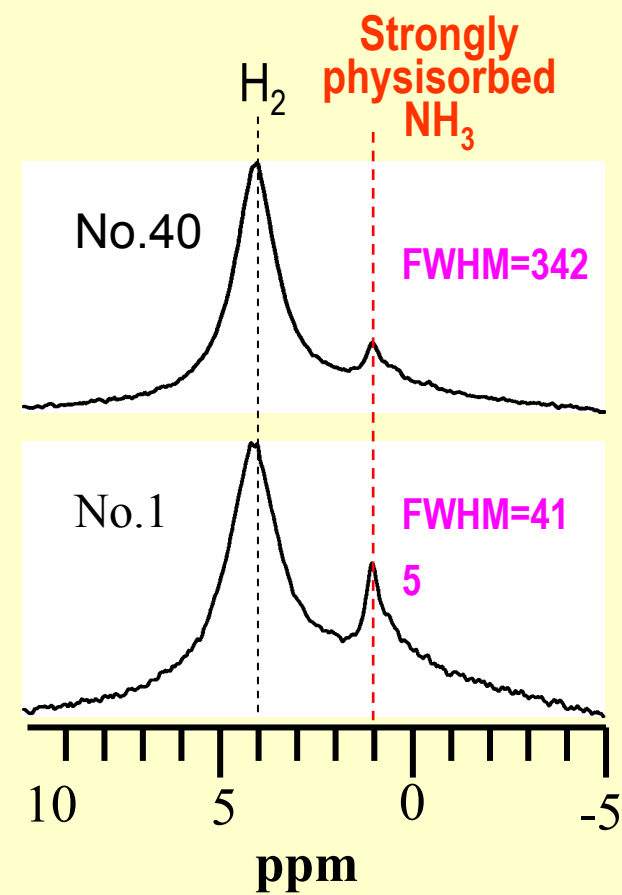
At RT, hydrogen is less mobile (broad peak) and strongly surface-adsorbed; when heated to 200°C, hydrogen gains mobility (sharp peak) and evolves into a gaseous phase, so does a small amount of ammonia. Further mechanical activation enhances hydrogen desorption kinetics.

Dynamic In Situ ^1H MAS NMR on Mechanically Activated (LiNH_2+LiH)

The dynamic ^1H MAS (5.5 KHz) NMR was carried out at 180°C in a closed sample tube with an acquiring time of 0.6 hr for each spectrum. The study indicated that hydrogen gas formed at the very beginning and the desorption appeared to level off over the time; a small amount of NH_3 formed and strongly physisorbed on the surface at early stages and its release decreased over the time because of its reaction with LiH .

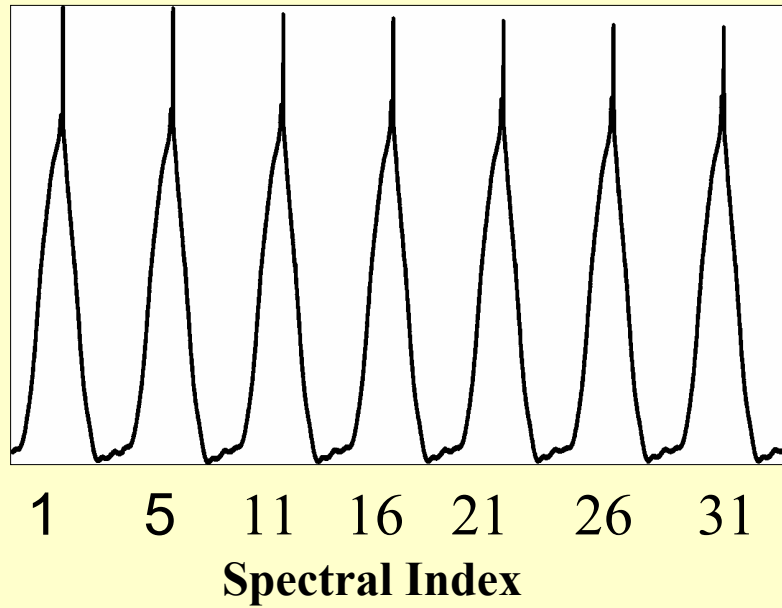


Spectral Index No.

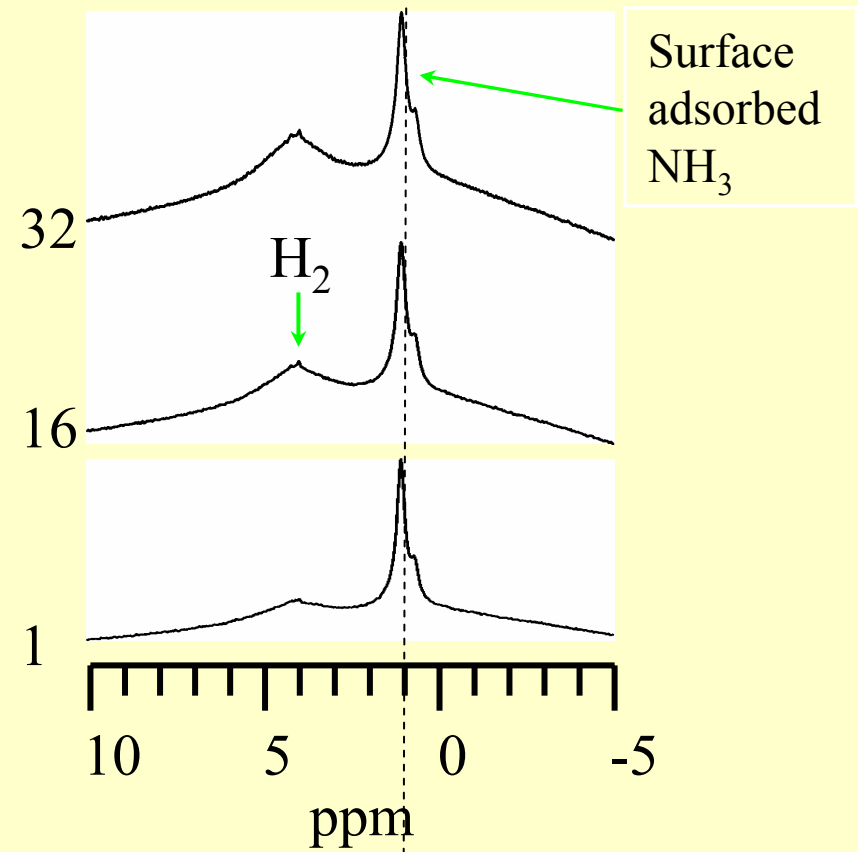


Mechanism of Hydrogen Desorption Determined via NMR

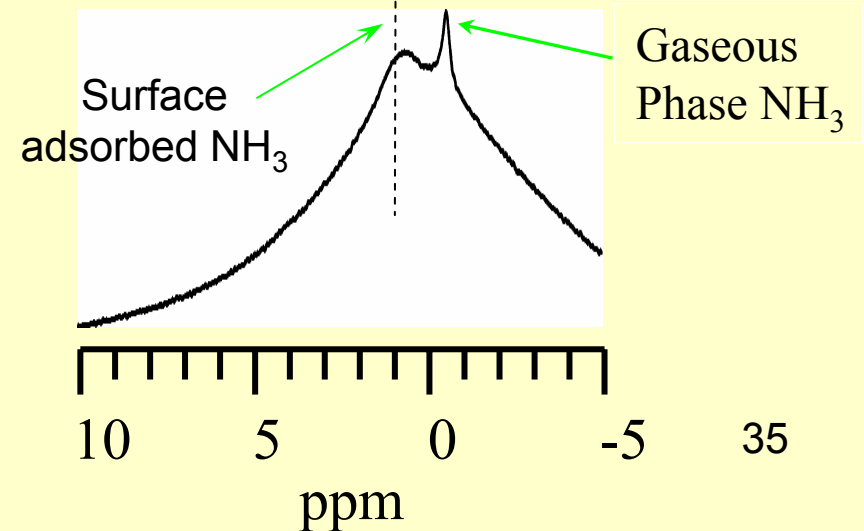
(LiNH₂+LiH), 180min milling at RT, NMR at 50°C, 2000 scans



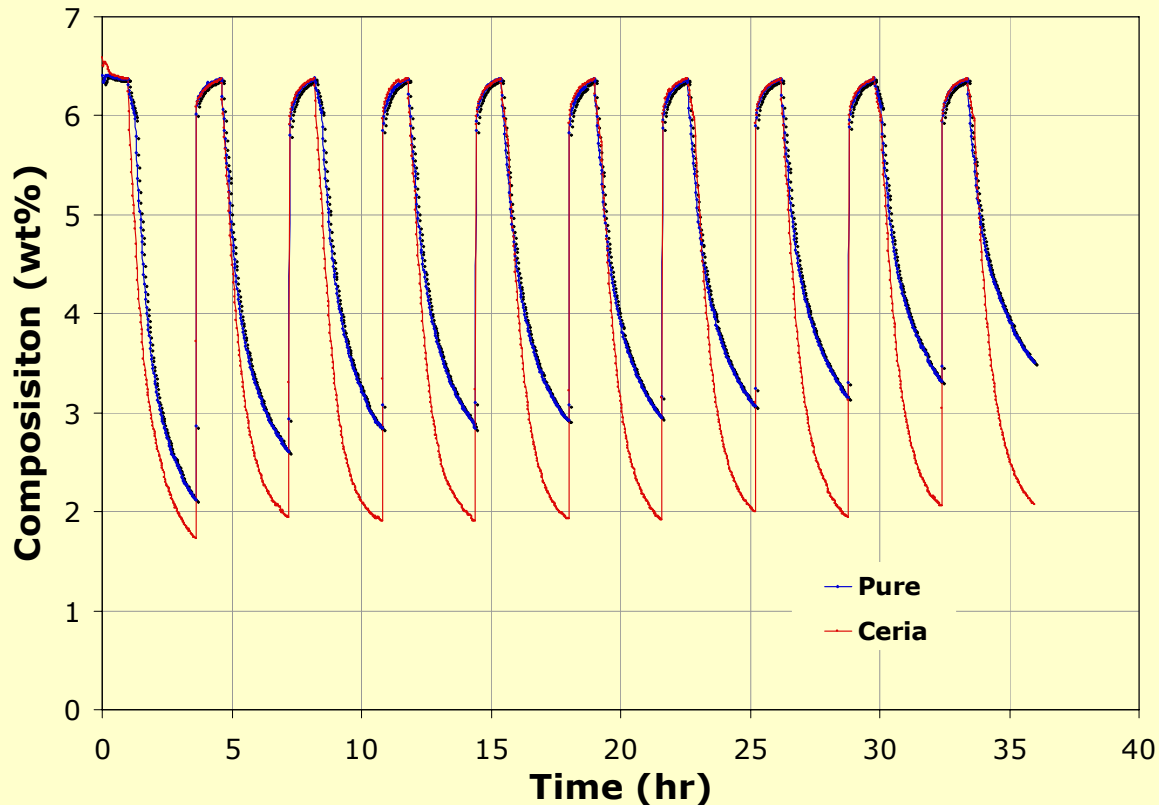
NMR of LiNH₂ at 30°C proves the presence of surface-adsorbed and gaseous NH₃. NMR of LiNH₂+LiH at 50°C shows less surface-adsorbed NH₃ and little gaseous NH₃, suggesting rapid reaction between LiH and gaseous NH₃. The NMR result confirms the presence of two elementary reactions for dehydriding of LiNH₂+LiH (Slide 7) and the high reaction rate between NH₃ and LiH even at 50°C (Slide 19).



LiNH₂, 45 min milling, 30°C, 1500 scans



IV. Enhancement of Reaction Kinetics of Mechanically Activated LiNH_2+LiH via Nano-Ceria



- Addition of 1 mol% nano-ceria particles increases the hydriding/dehydriding rates.
- Performance stability is improved too with the addition of nano-ceria because of the increased hydriding/dehydriding rates.
- Analysis of the dehydriding kinetics indicates that the dehydriding reaction of the ceria-containing system is still diffusion-controlled. Thus, it is hypothesized that ceria is a catalyst that enhances desorption of NH_3 from the Li_2NH surface and thus creates a large composition gradient for diffusion within the Li_2NH solid.

Future Work

- **Remainder of FY 2007:**

- Develop understanding of the mechanism responsible for the enhanced performance of $\text{LiH} + \text{LiNH}_2$ mechanically activated at LN temperature (UConn)
- Extend the NMR analysis of mechanically activated $\text{LiH} + \text{LiNH}_2$ to cycled samples to obtain atomic level understanding of the change due to isothermal cycling (PNNL)
- Study proton transport properties in hydrides with different degrees of mechanical activation via NMR (PNNL)
- Further enhance hydriding/dehydriding rates and improve performance stability of $\text{LiH} + \text{LiNH}_2$ by integrating mechanical activation, thermodynamic destabilization, and ceria-addition (UConn)

- **FY 2008:**

- Shift the material system from $\text{LiNH}_2 + \text{LiH}$ to LiBH_4 -based materials (UConn & PNNL)
- Apply the understanding learned from $\text{LiNH}_2 + \text{LiH}$ to LiBH_4 -based materials (UConn & PNNL)
- Work with HRL Laboratories to enhance hydriding/dehydriding rates of LiBH_4 -based materials by integrating thermodynamically destabilization and mechanical activation (UConn & PNNL)

Project Summary

- Relevance:** Explore fundamental mechanisms related to mechanical activation necessary for improving kinetics of reversible hydrogen storage materials.
- Approach:** Investigate hydriding/dehydriding properties of LiNH_2+LiH materials with different degrees of mechanical activation; Enhance storage performance based on the understanding developed.
- Technical Accomplishments:** (i) Established the effect of mechanical activation, including (a) reducing the onset temperature for dehydriding to room temperature, (b) enhancing hydriding/dehydriding rates at high temperatures (240 and 285⁰C), (c) increasing the plateau pressure of the sorption/desorption isotherm, (d) enhancing reaction between LiH and NH_3 and thus alleviating NH_3 emission issue; (ii) Identified the reaction mechanism and rate-controlling step in the dehydriding process; (iii) Demonstrated the unusual long-term sorption/desorption cycling stability of mechanically activated hydrogen storage materials; (iv) Developed atomic level understanding of the effect of mechanical activation; (v) Proved low temperature milling can introduce a large amount of defects to nano-particles, which in turn can dramatically enhance hydriding

Project Summary (Cont.)

Technical Accomplishments (cont.): and dehydriding reactions even though particle sizes are larger and surface areas are smaller, and
(vi) Enhanced hydriding/dehydriding performance of $\text{LiNH}_2 + \text{LiH}$ systems via integration of mechanical activation and advanced catalysts to solve the rate-limiting step problem.

Future Research: (i) Further development of fundamental understanding of mechanisms of mechanical activation;
(ii) Further enhancement of hydriding/dehydriding properties via integration of mechanical activation, advanced catalysts, and thermodynamic destabilization;
(iii) Application of the understanding developed from the $\text{LiNH}_2 + \text{LiH}$ system to LiBH_4 -based systems.