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

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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 Li₃N-based and LiBH₄-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 LiNH₂ to Li₂NH transition
- Mechanical activation on hydrogen sorption/desorption kinetics of the LiNH₂ and LiH mixture

Objective in FY 07:

- Understanding of Mechanical activation on hydrogen sorption/desorption kinetics of the LiNH₂ + LiH mixture
- Mitigation of NH₃ 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 LiNH$_2$ + 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$_2$NH Transition via Mechanical Activation (UConn)

III. Reaction Mechanism, Kinetics, and Enhancement of Hydrogen Sorption/Desorption of LiNH$_2$ + 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 LiNH$_2$ + LiH Systems (UConn)
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 alteration in the local electronic state (Fig. C).

**Fig. A: Crystallite size of LiH particles**

**Fig. B: SSA of LiNH₂ + LiH mixtures**

**Fig. C: ⁶Li MAS NMR spectra of LiNH₂**

Peak shifting and broadening indicate alternation in the local electronic state and structural refinement.
II. Reaction Mechanism, Kinetics, and Enhancement of LiNH\(_2\) to Li\(_2\)NH Transition via Mechanical Activation

Dehydrogenation of the LiNH\(_2\) + LiH mixture:

\[
\text{LiNH}_2 + \text{LiH} \leftrightarrow \text{Li}_2\text{NH} + \text{H}_2 \quad (1)
\]

proceeds with two elementary reactions*:

\[
\begin{align*}
\text{LiNH}_2 & \leftrightarrow \frac{1}{2} \text{Li}_2\text{NH} + \frac{1}{2} \text{NH}_3 \quad (2) \\
\frac{1}{2} \text{NH}_3 + \frac{1}{2} \text{LiH} & \leftrightarrow \frac{1}{2} \text{LiNH}_2 + \frac{1}{2} \text{H}_2 \quad (3)
\end{align*}
\]

LiNH\(_2\) produced from (3) will repeat (2) and (3) until exhaust of LiNH\(_2\).

* Enhancement of LiNH\(_2\) to Li\(_2\)NH transition via Eq. (2) is necessary because this is the first step for dehydrogenation of the LiNH\(_2\) + LiH mixture.

* NH\(_3\) generated from decomposition of LiNH\(_2\) should be captured by LiH. Otherwise, H\(_2\) fuel will be contaminated and the storage capacity will decrease with sorption/desorption cycles.

The onset temperature for weight loss of LiNH₂ without milling is 120°C, whereas the corresponding value for LiNH₂ with ball milling is room temperature.

The transition rate from LiNH₂ to Li₂NH and NH₃ 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 NH₃ 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 LiNH₂ Decomposition Decreases with Increase in the Degree of Mechanical Activation

Flynn-Wall Plot: The constant heating rate, $\beta$, during TGA vs the reciprocal of the temperature at which 15% transformation has occurred for the LiNH₂ to Li₂NH transition.

- **LiNH₂ without milling:**
  - $E_a = 243.9$ kJ/mol

- **LiNH₂ milled for 45 min:**
  - $E_a = 222.2$ kJ/mol

- **LiNH₂ milled for 180 min:**
  - $E_a = 138.0$ kJ/mol
Reaction Kinetics of LiNH₂ Decomposition

The weight change of LiNH₂ 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 LiNH₂ 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

LiNH₂ = ½ Li₂NH + ½ NH₃

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

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

\[ f = 1 - \exp\left(-k_3 t^m\right) \]

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$_2$NH and NH$_3$ Transition

1. Mechanical activation enhances the transition of LiNH$_2$ to Li$_2$NH 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$_2$NH and NH$_3$ is controlled by diffusion of NH$_3$, N, or H species through the Li$_2$NH product layer.

Challenges:

- Since decomposition of LiNH$_2$ is the first step of dehydrogenation of the LiNH$_2$ + LiH mixture, how can we increase a diffusion-controlled decomposition to enhance dehydrogenation of the LiNH$_2$ + 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 LiNH$_2$ + LiH Systems

\[ \text{LiNH}_2 + \text{LiH} = \text{Li}_2\text{NH} + \text{H}_2 \]

- 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 LiNH$_2$ + LiH
  - Dehydrogenation mechanism and kinetics of the LiNH$_2$ + LiH mixture
  - Long-term sorption/desorption cycling stability of mechanically activated LiNH$_2$ + 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 LiNH$_2$ + 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.

The TG analysis was conducted under a flowing argon condition with a heat rate of 10$^\circ$C/min.
The composition analysis of the effluent gas confirms that:

(i) the weight loss observed in the TGA trace of LiNH₂ + LiH ball milled at RT for 180 min is due to hydrogen release;

(ii) there exists a small amount of NH₃ in the effluent gas of LiNH₂ + LiH without milling; this is especially true at temperatures between 400 and 600°C;

(iii) ball milling reduces the peak temperature for releasing H₂ from 388 to 250°C; and

(iv) NH₃ emission is a kinetic issue. Fast reaction between NH₃ and LiH or slow generation of NH₃ can all eliminate NH₃ 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, $I_{\text{Mass} 17}$, constitutes two components: the intensity of NH₃⁺ and the intensity of OH⁺:

$$I_{\text{Mass} 17} = I_{\text{Mass} 17}^{\text{NH₃⁺}} + I_{\text{Mass} 17}^{\text{OH⁺}}$$

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

$$I_{\text{Mass} 17} = I_{\text{Mass} 17}^{\text{NH₃⁺}} + 0.212I_{\text{Mass} 18}$$

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

$$I_{\text{Mass} 17}^{\text{NH₃⁺}} = I_{\text{Mass} 17} - 0.212I_{\text{Mass} 18}$$

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 $8.4 \times 10^{-12}$ Torr/mg MgH₂.
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 LiNH₂ + 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 Dehydriding Reaction of LiNH$_2$ + LiH Systems

Dehydriding of LiNH$_2$ + 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?

\[
\text{LiNH}_2 = \frac{1}{2} \text{Li}_2\text{NH} + \frac{1}{2} \text{NH}_3 \quad (2) \\
\frac{1}{2} \text{NH}_3 + \frac{1}{2} \text{LiH} = \frac{1}{2} \text{LiNH}_2 + \frac{1}{2} \text{H}_2 \quad (3)
\]

The volume of the solid product Li$_2$NH from Reaction (2) is smaller than that of the reactant LiNH$_2$. As a result, a continuous yet porous Li$_2$NH 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.

Based on the reaction mechanism proposed on Slide 19, the reaction pathway of dehydriding of LiNH₂ + LiH can be described at least with the following 6 steps.

- (decomposition at the LiNH₂/Li₂NH interface) (4)

- (diffusion of NH₃ to a Li₂NH surface site, *) (5)

- (desorption of NH₃ from the Li₂NH surface site) (6)

- (adsorption of NH₃ on a LiH surface site, Δ) (7)

- (reaction at the LiH surface) (8)

- (desorption of H₂ from the LiH surface site) (9)

The rate of dehydriding will be controlled by the slowest step.
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 LiNH₂/Li₂NH phase boundary, (ii) diffusion of NH₃, N, or H through the Li₂NH layer, (iii) nucleation and growth of Li₂NH into the LiNH₂ core, and (iv) desorption of NH₃ from the Li₂NH surface.

The analysis reveals that the fraction of H₂ released, f, as a function of time, t, can be described well by a parabolic-rate law derived from Fick’s second law:

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

where \( f' \) is the fraction of H₂ released at the end of the desorption cycle, R the average radius of LiNH₂ particles, and \( k_5 \) a constant related to the diffusion coefficient, D.

Conclusions:

1. The rate-limiting step for dehydriding of LiNH₂ + LiH is diffusion of NH₃, N, or H through the Li₂NH product layer.
2. The activation energy for diffusion is very low (only 19.3 kJ/mol).
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 LiNH$_2$+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 (LiNH$_2$+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 NH$_3$ escaping from the system during cycling; otherwise, the thermodynamic storage capacity will decrease.
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-LiNH₂ 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 LiNH₂ 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 LiNH$_2$ + LiH Systems through Mechanical Activation at Liquid Nitrogen Temperature

LiNH$_2$+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 LiNH$_2$+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

Fig. A

Dehydriding kinetics of LN2-processed

The 9th desorption, $R^2 = 0.99$

The 3th desorption, $R^2 = 0.99$

Fig. B

SSA (m$^2$/g)

180 min mill at RT 180 min mill at LN2

Fig. C

Crystallite Size [nm]

LiNH$_2$ LiH

Room Temp Dry Ice Liquid N2

- LN2-processed LiNH$_2$+LiH still exhibits diffusion-controlled dehydriding reactions, i.e. LN2 ball milling does not change the reaction mechanism (Fig. A).
- LN2-processed LiNH$_2$+LiH has a lower SSA (Fig. B) and larger crystallite sizes (Fig. C) than that processed at RT.
- Therefore, the enhanced dehydriding rate of LN2-processed LiNH$_2$+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°C (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 $\Delta P$ 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 $\Delta P$ 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).
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.
- Planed to measure proton transport properties in hydrides, with combination of software capabilities.
Effects of Mechanical Activation on $^6$Li MAS NMR spectra of LiNH$_2$

![Graph showing NMR spectra of LiNH$_2$]

The $^6$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 $^1$H MAS NMR

Dynamic in situ $^1$H 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.
Like the amide, MAed (LiNH$_2$+LiH) also displays the $^6$Li 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.
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 $^1$H MAS NMR on Mechanically Activated (LiNH$_2$+LiH)

The dynamic $^1$H 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.
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 LiHN₂+LiH (Slide 7) and the high reaction rate between NH₃ and LiH even at 50°C (Slide 19).
IV. Enhancement of Reaction Kinetics of Mechanically Activated LiNH₂+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 NH₃ from the Li₂NH surface and thus creates a large composition gradient for diffusion within the Li₂NH solid.
Future Work

• **Remainder of FY 2007:**
  - Develop understanding of the mechanism responsible for the enhanced performance of LiH + LiNH₂ mechanically activated at LN temperature (UConn)
  - Extend the NMR analysis of mechanically activated LiH + LiNH₂ 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 LiH + LiNH₂ by integrating mechanical activation, thermodynamic destabilization, and ceria-addition (UConn)

• **FY 2008:**
  - Shift the material system from LiNH₂+LiH to LiBH₄-based materials (UConn & PNNL)
  - Apply the understanding learned from LiNH₂+LiH to LiBH₄-based materials (UConn & PNNL)
  - Work with HRL Laboratories to enhance hydriding/dehydriding rates of LiBH₄-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 285°C), (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
Technical Accomplishments (cont.): and dehydriding reactions even though particle sizes are larger and surface areas are smaller, and (vi) Enhanced hydriding/dehydriding performance of LiNH$_2$+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 LiNH$_2$ + LiH system to LiBH$_4$-based systems.