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

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Project ID: STP 2

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Overview

Timeline:
• Project start date: December 2004
• Project end date: December 2008
• Percent complete: 30%

Budget:
• Total project funding
  – DOE share: $1.6 mil
  – Contractor share: $0.4 mil
• Funding received in FY05: $168,000
• Funding received in FY06: $240,000

Partners:
• Sandia National Laboratory
• Pacific Northwest National Laboratory
• Universidad de Extremadura, Badajoz, Spain

Barriers
Sorption/desorption temperatures are too high for the following two reactions:
\[ \text{Li}_3\text{N} + \text{H}_2 \leftrightarrow \text{Li}_2\text{NH} + \text{LiH} \]
\[ \text{Li}_2\text{NH} + \text{H}_2 \leftrightarrow \text{LiNH}_2 + \text{LiH} \]
Need to reduce these sorption/desorption temperatures to near ambient.
Objectives

Overall Objective in 4 Years:

- Investigate, model and develop a novel, mechanically activated, nanoscale Li$_3$N-based material that is able to store and release ~ 10 wt% hydrogen at temperatures below 100$^\circ$C with a plateau hydrogen pressure of less than 10 bar

Objective in FY 05:

- Mechanical activation on LiNH$_2$ to Li$_2$NH transition
- Mechanical activation on hydrogen sorption/desorption kinetics of the LiNH$_2$ and LiH mixture

Objective in FY 06:

- Mechanical activation on hydrogen sorption/desorption kinetics of the LiNH$_2$ and LiH mixture (cont. from FY 05)
- Stability of LiH in different environments
- Dehydrogenation behavior of the MgH$_2$ and LiNH$_2$ mixture
- Advanced catalysts for the LiNH$_2$ and LiH mixture
Approaches

- **Mechanical Activation** to reduce hydrogen sorption/desorption temperatures and increase the hydrogen storage capacity.

- **Chemical Modification** of lithium amide/imide to destabilize the compounds thermodynamically and thus further reduce hydrogen sorption/desorption temperatures.

- **Advanced Catalysts** to catalyze the reactions and thus further enhance hydrogen sorption/desorption processes.

- **Quantum-Chemical Modeling** to identify advanced catalysts and to develop fundamental understanding and guide the efforts of mechanical activation and chemical modification.
Technical Accomplishments, Progress and Results

(May 22, 2005 – May 15, 2006)

I. Enhancement of LiNH₂ to Li₂NH Transition via Mechanical Activation

II. Enhancement of Hydrogen Sorption/Desorption of the LiNH₂ + LiH System via Mechanical Activation

III. Studies of the Stability of LiH in Different Environments

IV. Dehydrogenation Behavior of the LiNH₂ + MgH₂ Systems

V. Initiation of the Investigation of Catalysts for the LiNH₂ + LiH Systems
I. Enhancement of LiNH$_2$ to Li$_2$NH Transition via Mechanical Activation

\[ \text{LiNH}_2 = \frac{1}{2} \text{Li}_2\text{NH} + \frac{1}{2} \text{NH}_3 \]

- Enhancement of LiNH$_2$ to Li$_2$NH transition is necessary because this is the first step for the following dehydrogenation reaction:

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

- NH$_3$ generated from the decomposition of LiNH$_2$ will react with LiH to form LiNH$_2$ and H$_2$:

\[ \frac{1}{2} \text{NH}_3 + \frac{1}{2} \text{LiH} \leftrightarrow \frac{1}{2} \text{LiNH}_2 + \frac{1}{2} \text{LiH} \]

- Complete decomposition of LiNH$_2$ results in the formation of 37 wt% NH$_3$. It is important to capture all of these NH$_3$. 
SEM Images of LiNH$_2$ Powder with and without Ball Milling

Before milling

Milled for 45 min at RT

Milled for 180 min at RT
Specific Surface Area (SSA) and Crystallite Size as a Function of Mechanical Activation

<table>
<thead>
<tr>
<th>Composition</th>
<th>Milling time (min)</th>
<th>SSA (m²/g)</th>
<th>Crystallite Size (nm)</th>
<th>Equivalent Particle size (μm)**</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNH₂</td>
<td>0</td>
<td>3.72</td>
<td>&gt; 100</td>
<td>1.37</td>
</tr>
<tr>
<td>LiNH₂</td>
<td>45</td>
<td>40.71</td>
<td>5.9</td>
<td>0.13</td>
</tr>
<tr>
<td>LiNH₂</td>
<td>180</td>
<td>46.65</td>
<td>5.5</td>
<td>0.11</td>
</tr>
</tbody>
</table>

** Estimated according to the SSA.
Decomposition of LiNH$_2$ at Ambient Temperature

- LiNH$_2$ can decompose to NH$_3$ and Li$_2$NH according to the following reaction:

$$2 \text{LiNH}_2 = \text{Li}_2\text{NH} + \text{NH}_3$$

- Ball milling has decreased the decomposition temperature dramatically.

- The gas chromatograph (GC)/mass spectrometry (MS) analysis shows that NH$_3$ released by the ball milled LiNH$_2$ at 50$^\circ$C is 820 times higher than that from the LiNH$_2$ without milling.
TGA Analysis of LiNH$_2$ with and without Mechanical Activation

- The onset temperature for weight loss of the LiNH$_2$ without milling is 120$^\circ$C, whereas the corresponding value for the LiNH$_2$ with ball milling is room temperature.
- The transition rate from LiNH$_2$ to Li$_2$NH and NH$_3$ increases with the ball milling time, i.e., the more mechanical activation, the higher the transition rate.

![TGA Results](image)
Calculation of the Activation Energy for LiNH$_2$ Decomposition via the Flynn-Wall Method

**Flynn-Wall-Ozawa Equation:**

\[
\log \beta = \log \left( \frac{AE_a}{g(\alpha)R} \right) - 2.315 - \frac{0.457E_a}{RT}
\]

where

- $\beta$ = heating rate
- $E_a$ = activation energy
- $\alpha$ = fraction of transformation
- $g(\alpha)$ = the kinetic function
- $A$ = the pre-exponential factor of the Arrhenius equation

**TGA Curves vs Heating Rate**

- 20°C/min
- 15°C/min
- 5°C/min
- 2°C/min
Activation Energy for LiNH₂ Decomposition via the Flynn-Wall Method

The activation energy decreases as the ball milling time increases!
Summary for Enhancement of LiNH$_2$ to Li$_2$NH and NH$_3$ Transition

1. Ball milling reduces particle size, increases specific surface area, and introduces nanograins as well as a large amount of defects to LiNH$_2$ crystals.

2. All of these enhance the transition of LiNH$_2$ to Li$_2$NH and NH$_3$. The activation energy for the transition decreases as the ball milling time increases.

3. The onset temperature for the decomposition of LiNH$_2$ without ball milling is 120$^0$C, while the corresponding value for the LiNH$_2$ with ball milling is room temperature.

4. The transition rate from LiNH$_2$ to Li$_2$NH and NH$_3$ increases with the ball milling time, i.e., the more mechanical activation, the higher the transition rate.

5. The decomposition of LiNH$_2$ without ball milling does not complete even above 550$^0$C, while this temperature is reduced to 450$^0$C for LiNH$_2$ with ball milling.
II. Enhancement of Hydrogen Sorption/Desorption of the LiNH\textsubscript{2} plus 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
- Complete dehydriding of the LiNH\textsubscript{2} + LiH mixture releases 6.5 wt\% H\textsubscript{2}
SEM Images of LiNH₂+LiH Powders

(a) Before milling
(b) Milled for 90 min
(c) Milled for 180 min
(d) Milled for 1,440 min

• Particle sizes decrease with increasing the milling time.
• The reduction rate of particle sizes becomes smaller as the milling time becomes larger.
## Specific Surface Area (SSA) and Crystallite Size as a Function of Mechanical Activation

<table>
<thead>
<tr>
<th>Composition</th>
<th>Milling time (min)</th>
<th>SSA* (m²/g)</th>
<th>Crystallite Size LiNH₂ / LiH (nm)</th>
<th>Equivalent Particle size (μm)**</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNH₂+LiH</td>
<td>0</td>
<td>4.65</td>
<td>&gt; 100 / &gt; 100</td>
<td>-</td>
</tr>
<tr>
<td>LiNH₂+LiH</td>
<td>90</td>
<td>47.36</td>
<td>7.2 / 13.6</td>
<td>0.120</td>
</tr>
<tr>
<td>LiNH₂+LiH</td>
<td>180</td>
<td>51.32</td>
<td>4.1 / 32.4</td>
<td>0.111</td>
</tr>
<tr>
<td>LiNH₂+LiH</td>
<td>1,440</td>
<td>62.35</td>
<td>-</td>
<td>0.091</td>
</tr>
</tbody>
</table>

* Based on the SSA using the average density (1.05 g/cm³) of the mixture.

** Estimated from the SSA.
The onset temperatures for hydrogen release from the LiNH₂ + LiH mixtures with and without ball milling are 25 and 50°C, respectively.

The temperature for release of a large amount of H₂ (e.g., 2 wt%) is decreased from about 350°C to 255°C after ball milling.

The weight loss for the milled sample is about 5.5% which is slightly smaller than 6.5% if the mixture were 100% LiNH₂ + LiH.

The weight loss for the sample without milling is substantially larger than 6.5% because of the NH₃ escape due to the incomplete reaction between ammonia and lithium hydride.

\[
\text{LiNH}_2 + \text{LiH} = \text{Li}_2\text{NH} + \text{H}_2 \quad \text{6.5 wt\% H}_2
\]
Composition Analysis of the Effluent Gas from LiNH₂+LiH Mixture with Mechanical Activation (90 min ball milling at RT)

Lower NH₃ concentration when compared with the LiNH₂ + LiH mixture without ball milling.
DSC Curves of LiNH$_2$+LiH Mixtures with Different Degrees of Mechanical Activation

(heating rate = 1°C/min)

- The dehydrogenation rate of LiNH$_2$ + LiH mixture increases with the ball milling time.
- Dehydrogenation occurs at ambient temperature when the ball milling time is 180 min.
- The mixture without ball milling exhibits melting of LiNH$_2$ at ~ 360°C because of the slow reaction rate at low temperatures.

As received
90 min
180 min

Melting of LiNH$_2$
Calculation of the Activation Energy for Dehydriding Reaction via the Kissinger Method

- Reaction: \( \text{LiNH}_2 + \text{LiH} = \text{Li}_2\text{NH} + \text{H}_2 \)

- Kissinger Method:

\[
\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E_a}{RT_p} + F_{KAS}(\alpha)
\]

where \( T_p \) is the endothermic peak temperature measured for the heating rate, \( \beta \), during DSC. \( F_{KAS}(\alpha) \) is a parameter that is a function of the fraction of transformation, \( \alpha \).

- The activation energy decreases with increasing the milling time.
- The activation energy is affected by the milling and mixing sequence.

![Graph showing the relationship between milling time and activation energy](image-url)
• The activation energy decreases with increasing of the milling time for all reactions.

• Reaction 1 is the first step of Reaction 2. However, the “apparent” activation energy of Reaction 2 is lower than that of Reaction 1, suggesting that the presence of LiH can reduce the activation energy of Reaction 1.

• The activation energy is also affected by the milling and mixing sequence, supporting the notion that LiH does have the catalytic effect on Reaction 1.

LiNH₂ only: \[ \text{LiNH}_2 = \frac{1}{2} \text{Li}_2\text{NH} + \frac{1}{2} \text{NH}_3 \] (1)

LiNH₂ + LiH: \[ \text{LiNH}_2 + \text{LiH} = \text{Li}_2\text{NH} + \text{H}_2 \] (2)
Summary for Enhancement of Hydrogen Sorption/Desorption of LiNH$_2$ + LiH Systems

1. Mechanical activation through ball milling reduces particle size, increases specific surface area, and introduces nanograins as well as a large amount of defects to LiNH$_2$ and LiH crystals.

2. All of these changes induced by ball milling enhance the hydrogen sorption/desorption of LiNH$_2$ + LiH systems. The activation energy decreases as the ball milling time increases.

3. LiH has a catalytic effect on the transition of LiNH$_2$ to Li$_2$NH and NH$_3$. This is manifested in that (a) the activation energy for the reaction between LiNH$_2$ and LiH is lower than that for the transition of LiNH$_2$ to Li$_2$NH and NH$_3$, and (b) the activation energy for the reaction between LiNH$_2$ and LiH depends on the mixing and milling sequence.

4. Although the onset temperature for dehydrogenation of the mechanically activated LiNH$_3$ + LiH system is improved to ambient, the peak temperature for releasing the largest amount of H$_2$ is still very high (260$^0$C). Other approaches (e.g., advanced catalysts and modification of the composition) are needed to reduce the peak temperature to near ambient.
III. Stabilities of LiH in Different Environments

- The cyclic stability of LiNH$_2$ + LiH systems in hydrogen uptake and release cycles depends on the sensitivity of these lithium hydrides, amides, and imides to impurities in the hydrogen source. This is an especially important issue if impurities enter the hydrogen storage tank with each refueling.

- The present study investigates the stability of LiH under (i) a high purity argon atmosphere, (ii) an argon atmosphere with some O$_2$ and H$_2$O impurities, and (iii) ambient air at both room and high temperatures.
XRD Patterns of LiH Exposing to Ambient Air as a Function of Time

- The oxidation product of LiH in ambient air is LiOH.
- The oxidation rate of the milled LiH is faster than that of the un-milled LiH.
- The oxidation of LiH in ambient air proceeds with the following two reactions:
  \[ \text{LiH} + \text{H}_2\text{O} = \text{LiOH} + \text{H}_2 \]
  \[ \text{LiH} + \frac{1}{2} \text{O}_2 = \text{LiOH} \]
Rate-Controlling Mechanisms for Oxidation of LiH in Ambient Air

The oxidation rate of LiH in ambient air is controlled by the nucleation and growth of the LiOH shell, and can be described by Johnson-Mehl-Avrami (JMA) equation.

**JMA Equation for LiH without milling:**

\[ f = 1 - \exp\left(-0.018t^{1.01}\right) \]

**JMA Equation for LiH with milling:**

\[ f = 1 - \exp\left(-0.028t^{1.01}\right) \]

Ball milling increases the oxidation rate of LiH in ambient air.
Oxidation of LiH in Argon with $O_2$ and $H_2O$ Impurities during TGA Analysis

With 515 ppm $O_2$ and 5,692 ppm $H_2$ in argon, the oxidation of LiH proceeds with the following reactions:

LiH + $H_2O$ = LiOH + $H_2$  (at RT)
LiH + $\frac{1}{2} O_2$ = LiOH  (at RT)
LiH + $\frac{1}{4} O_2$ = $\frac{1}{2} Li_2O$ + $1/2 H_2$  (at $T > 60^0C$)
Summary for Stabilities of LiH in Different Environments

1. No oxidation of LiH occurs under an argon atmosphere of 99.999% purity with $\text{H}_2\text{O} < 1$ ppm, $\text{O}_2 < 1$ ppm, $\text{H}_2 < 3$ ppm, $\text{N}_2 < 5$ ppm, and THC < 0.5 ppm.

2. The oxidation product of LiH in ambient air with a relative humidity of 27% at room temperature is LiOH.

3. The oxidation kinetics of LiH in ambient air at room temperature can be described very well by the Johnson-Mehl-Avrami equation.

4. Oxidation of LiH occurs under an argon atmosphere containing 5,692 ppm $\text{H}_2\text{O}$, 515 ppm $\text{O}_2$, 585 ppm $\text{H}_2$, 88 ppm $\text{N}_2$, and 1.3 ppm NH$_3$. At temperatures ranging from $\sim$ 55 to 600$^\circ$C, oxidation of LiH proceeds via the equation of $\text{LiH} + \frac{1}{4} \text{O}_2 = \frac{1}{2} \text{Li}_2\text{O} + \frac{1}{2} \text{H}_2$.

5. At room temperature, oxidation of LiH in ambient air and in an argon atmosphere containing 5,692 ppm $\text{H}_2\text{O}$, 515 ppm $\text{O}_2$, 585 ppm $\text{H}_2$, 88 ppm $\text{N}_2$, and 1.3 ppm NH$_3$ is due to two reactions: $\text{LiH} + \text{H}_2\text{O} = \text{LiOH} + \text{H}_2$ and $\text{LiH} + \frac{1}{2} \text{O}_2 = \text{LiOH}$. 
IV. Dehydrogenation Behavior of the LiNH$_2$ + MgH$_2$ Systems

- Partial substitution of Li by Mg in LiNH$_2$ can destabilize the compound and thus reduce the hydrogenation and dehydrogenation temperatures.

- The present study investigates dehydrogenation behavior of the LiNH$_2$ plus MgH$_2$ system and compares this behavior to that of the LiNH$_2$ plus LiH system with particular attention to the reaction kinetics.
TGA Analysis of LiNH₂ and MgH₂ Mixtures
(In a 2-to-1.1 ratio)

Sample I = LiNH₂ + LiH (3hr milling)
Sample II = 2LiNH₂ + MgH₂ (3hr milling)
Sample III = 2LiNH₂ + MgH₂ (no milling)

• Ball milling reduces the dehydriding temperature.
• The MgH₂-containing system exhibits lower dehydriding temperatures than the LiH-containing system when both systems are ball milled.
• The weight loss of the MgH₂-containing systems with and without ball milling is substantially larger than the theoretical prediction.

Sample I
Sample II
Sample III

Heating rate = 5°C/min
Argon atmosphere

Ball milling time is indicated

2 LiNH₂ + MgH₂
Argon atmosphere
Heating rate = 5°C/min

• The weight loss decreases as the ball milling time increases.
• However, after 3-hr of ball milling the weight loss is still larger than the theoretical prediction based on the following reaction:
  \[ 2 \text{LiNH}_2 + \text{MgH}_2 = \text{Li}_2\text{MgN}_2\text{H}_2 + 2 \text{H}_2 \]
• The large weight loss results from the NH₃ escape owing to the slow reaction between MgH₂ and NH₃, as confirmed by the composition analysis of the effluent gases.
Analysis of NH$_3$ Concentration in the Effluent Gases using Residual Gas Analyzer

- Detection of NH$_3$ in the outlet gas during TGA analysis using a quadrupole residual gas analyzer (RGA) is difficult because NH$_3$ signal is interfered by OH species which also has a mass of 17.

- Monitoring the signal of Mass 16, however, provides a satisfactory result for semi-quantification of the NH$_3$ concentration in the outlet gas. Mass 16 contains both NH$_2$ and O species; however, the intensity of NH$_2$ species is 80% of the NH$_3$ intensity, whereas the intensity of O is only 1% of the H$_2$O intensity. As a result, the intensity of Mass 16 is very sensitive to the alternation of the NH$_3$ concentration. In contrast, the change in the H$_2$O concentration only induces negligible alternation in the intensity of Mass 16, as shown in the MgH$_2$ only sample above.
Analysis of NH₃ Concentration in the Effluent Gases using Residual Gas Analyzer

- **Milled 2 LiNH₂ + MgH₂ in TGA**
  - Mass 18 = H₂O
  - Mass 17 = NH₃ + OH
  - Mass 16 = NH₂ + O

- **Milled LiNH₂ in TGA**
  - Mass 18 = H₂O
  - Mass 17 = NH₃ + OH
  - Mass 16 = NH₂ + O

- **Milled LiNH₂ + LiH₂ in TGA**
  - Mass 18 = H₂O
  - Mass 17 = NH₃ + OH
  - Mass 16 = NH₂ + O

- The LiNH₂ + MgH₂ mixture releases NH₃, whereas the LiNH₂ + LiH system does not, as indicated by the change in the signal of Mass 16.

- LiNH₂ only releases NH₃, and this is reflected in the substantial change of the Mass 16 signal.
The NH$_3$ escape issue in the LiNH$_2$ + MgH$_2$ system can be alleviated by ball milling, but cannot be eliminated because of the slow reaction between NH$_3$ and MgH$_2$.

- LiNH$_2$ releases the largest amount of NH$_3$ per unit weight, which is followed by the LiNH$_2$ + MgH$_2$ system.
- The LiNH$_2$ + LiH system has almost no NH$_3$ escape problem because the reaction between NH$_3$ and LiH is very fast after mechanical activation.
XRD Analysis of the LiNH₂ and MgH₂ Mixture after Dehydrogenation at 210°C

XRD patterns indicate that the following reaction has taken place in the dehydrogenation process of the LiNH₂ and MgH₂ mixture:

\[ 2 \text{LiNH}_2 + \text{MgH}_2 = \text{Li}_2\text{MgN}_2\text{H}_2 + 2 \text{H}_2 \]

Based on TGA, RGA, and XRD analyses, it is proposed that the overall reaction above proceeds with the following steps:

1. \[ 2 \text{LiNH}_2 = \text{Li}_2\text{NH} + \text{NH}_3 \]  
2. \[ \text{NH}_3 + \frac{1}{2} \text{MgH}_2 = \frac{1}{2} \text{Mg(NH)}_2 + \text{H}_2 \]  
3. \[ \frac{1}{2} \text{Mg(NH)}_2 = \frac{1}{2} \text{MgNH} + \text{NH}_3 \]  
(Repeating Reactions (2) and (3) until all \text{NH}_3 and \text{MgH}_2 are converted to \text{H}_2 and \text{MgNH})

4. \[ \text{MgNH} + \text{Li}_2\text{NH} = \text{Li}_2\text{MgN}_2\text{H}_2 \]
Activation Energy Comparison between the LiNH₂ and MgH₂ and the LiNH₂ and LiH Systems

The activation energies of dehydrogenation for LiNH₂ + MgH₂ and LiNH₂ + LiH systems were determined using the Kissinger method (DSC data) and Flynn-Wall method (TGA data), as indicated in the table below.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Processing Conditions</th>
<th>Activation Energy (kJ/mol)</th>
<th>Measurement Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgH₂ + 2 LiNH₂</td>
<td>No milling</td>
<td>182</td>
<td>4 wt.% loss of TGA</td>
</tr>
<tr>
<td>MgH₂ + 2 LiNH₂</td>
<td>Milling for 180 min</td>
<td>133</td>
<td>4 wt.% loss of TGA</td>
</tr>
<tr>
<td>LiH + LiNH₂</td>
<td>Milling for 180 min</td>
<td>118</td>
<td>4 wt.% loss of TGA</td>
</tr>
<tr>
<td>LiH + LiNH₂</td>
<td>Milling for 180 min</td>
<td>113</td>
<td>Peak temperature of DSC</td>
</tr>
<tr>
<td>LiH + LiNH₂</td>
<td>No Milling</td>
<td>164</td>
<td>Peak temperature of DSC</td>
</tr>
</tbody>
</table>

- The activation energy decreases with ball milling.
- LiNH₂ + MgH₂ system has higher activation energies than LiNH₂ + LiH system under the same processing conditions.
Summary for Dehydrogenation Behavior of the LiNH₂ and MgH₂ System

1. The LiNH₂ and MgH₂ system has lower dehydrogenation temperatures than the LiNH₂ and LiH system. This result is consistent with the thermodynamic analysis, i.e., the MgH₂-containing system has a higher thermodynamic driving force for dehydrogenation and thus lower dehydrogenation temperatures.

2. The reaction rate between MgH₂ and NH₃ is lower than that between LiH and NH₃. As a result, the escape of NH₃ occurs in the LiNH₂ and MgH₂ system, leading to a substantial weight loss.

3. The LiNH₂ + MgH₂ system has a higher activation energy than LiNH₂ + LiH system under the same processing condition. This is one of the reasons why the reaction rate between MgH₂ and NH₃ is lower than that between LiH and NH₃.

4. To avoid the escape of NH₃, the LiNH₂ + MgH₂ system should be subjected to a slow reaction treatment. The treatment will permit the complete reaction between NH₃ and MgH₂ and convert the LiNH₂ + MgH₂ mixture to Li₂MgN₂H₂ which will change to Mg(NH₂)₂ + 2 LiH mixture in the subsequent hydrogenation step. After such a treatment, there will be no NH₃ escape issue because the fast reaction rate between LiH and NH₃.
V. Preliminary Studies of Advanced Catalysts for LiNH$_2$ + LiH and LiNH$_2$ + MgH$_2$ Systems

TGA analysis indicates that there are no catalytic effects of TiCl$_3$ and LaNi$_5$ on the LiNH$_2$ + LiH system under the present experimental conditions! Studies with new experimental conditions are currently underway.
Future Work

• Remainder of FY 2006:
  
  - Explore reaction fundamentals of the MgH$_2$ + LiNH$_2$ system: rate-limiting steps, intermediate species, and structure (UConn)
  
  - Investigate the mechanism of mechanical activation in the LiH + LiNH$_2$ system: ordering/disordering, phase transformation, bond length, and angle changes with the help of NMR and quantum chemistry calculations at the density function level (PNNL & UConn)
  
  - Develop advanced catalysts: quantum chemistry calculations coupled with experiments (UConn & PNNL)

• FY 2007:
  
  - Improve kinetics using mechanical activation, nano-engineering, and advanced catalysts: long milling time (1,440 min & 6,000 min), low-temperature milling (-50°C and -196°C), stability of mechanical activation effects, catalytic effects as a function of processing conditions and cyclic life (UConn & PNNL)
  
  - Determine the mechanism of mechanical activation and its stability: the strength of the hydrogen bond between the host material and the stored H$_2$, diffusivity, diffusion paths, and possibly the volume fraction of mobile hydrogen as a function of mechanical activation (PNNL & UConn)
Project Summary

Relevance: Explore fundamental mechanisms related to mechanical activation necessary for improving kinetics of reversible hydrogen storage materials.

Approach: Quantum-chemical modeling and mechanical activation at different temperatures coupled with (i) chemical modification of lithium amide/imide to destabilize the compounds thermodynamically and (ii) advanced catalysts to enhance hydrogen sorption and desorption kinetically.

Technical Accomplishments: (i) Established the effect of mechanical activation; (ii) Demonstrated the dehydrogenation at room temperature for both LiNH₂ + LiH and LiNH₂ + MgH₂ systems; (iii) Identified the NH₃ escaping issue in the LiNH₂ + MgH₂ system; (iv) Alleviated the NH₃ issue in the LiNH₂ + LiH system; (v) Established the sensitivity of LiH to impurities.

Future Research: Improve reaction kinetics using mechanical activation, nano-engineering, and advanced catalysts.
Publications and Presentations


Critical Assumptions and Issues

The present study unambiguously establishes the following two conclusions:

1. Both LiNH₂ + LiH and LiNH₂ + MgH₂ systems exhibit dehydrogenation at room temperature after mechanical activation. This indicates clearly that there is sufficient thermodynamic driving force for hydrogenation and dehydrogenation to occur at room temperature.

2. However, the peak temperature for dehydrogenation is ~ 250°C for both LiNH₂ + LiH and LiNH₂ + MgH₂ systems. Combining with the first observation, it can be concluded that the reaction rate is too slow for both systems even though there is sufficient thermodynamic driving force for the hydrogenation and dehydrogenation to take place at ambient temperature.

Based on these two conclusions, we believe that:

The key to successfully utilizing these two systems for the on-board hydrogen storage application is the development of advanced catalysts and/or high degree of stable mechanical activation so that hydrogenation and dehydrogenation can occur readily at ambient temperature.