Amide and Combined Amide/Borohydride Investigations

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#Savannah River National Laboratory
*University of South Carolina
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Overview

Timeline
- Start: 10/1/05
- End: 9/30/10
- Percent complete: 50%

Budget
- FY’08 Funding
  - $100K
- Planned FY’09 Funding
  - $400K

Barriers Addressed
- A. System Weight and Volume
- E. Charging/Discharging Rates
- P. Understanding of Hydrogen Chemisorption

Partners
- Z. Fang – University of Utah
- H. zurLoye – University of South Carolina
- E. Ronnebro – SNL (now PNNL)
Relevance: LiMgN as a Hydrogen Storage Material

\[ \text{LiNH}_2 + \text{MgH}_2 \rightarrow \text{LiMgN} + 2\text{H}_2 \]

- Identified with DFT calculations performed by Alapati and colleagues as potentially reversible with reasonable \( \text{H}_2 \) storage content
  
  \[ \text{(Alapati et al, Phys. Chem. Chem. Physics. 9 1438 (2007))} \]

- Theoretical \( \text{H}_2 \) gravimetric storage capacity of system is 8.2 wt%
  - Experimentally, 8.1 wt% was observed by Lu et al. under moderate temperature (160°C – 220°C) using TGA (Lu et al., J. Phys. Chem. C, 111, pp. 12129. (2007))

- Recharge theorized by Lu et. al. to take different pathway
  - Theoretical \( \text{H}_2 \) storage capacity is 8.2 wt%
    
    \[ \text{(8.0 wt% observed experimentally at 160 °C and 140 bar in pressure vessel)} \]

  \[ \text{LiMgN} + \text{H}_2 \leftrightarrow \frac{1}{2} \text{Mg(NH}_2)_2 + \frac{1}{2} \text{MgH}_2 + \text{LiH} \]

- Dehydrogenation is proposed to proceed through an intermediate step

  \[ \frac{1}{2} \text{Mg(NH}_2)_2 + \frac{1}{2} \text{MgH}_2 + \text{LiH} \rightarrow \text{Li}_{2x}\text{Mg}_{1-x}(\text{NH})_2 + \text{MgH}_2 + \text{H}_2 \rightarrow \text{LiMgN} + \text{H}_2 \]

- Accelerated reversibility has been observed using 4 wt.% TiCl\(_3\) dopant by Lu et al.
Li-Mg-N-H Systems Published in Literature

- $\text{Li}_x\text{Mg}_y$-amide materials have been studied by numerous groups which have cited both $\text{NH}_3$ production and high discharge temperatures as limiting their utility.

- Various compositional ratios of these compounds have been investigated to determine experimental hydrogen storage capacities, reaction pathways, reversibility, and rate of hydrogen release:

  - $\text{LiNH}_2 + \text{MgH}_2 \leftrightarrow \text{LiMgN} + 2\text{H}_2$
  
  - $\text{Mg(NH}_2)_2 + 2\text{LiH} \leftrightarrow \text{Li}_2\text{Mg(NH)}_2 + 2\text{H}_2$
    (Xiong et al., Adv. Mater. 16 1522 (2004))
  
  - $3\text{Mg(NH}_2)_2 + 8\text{LiH} \leftrightarrow 4\text{Li}_2\text{NH} + \text{Mg}_3\text{N}_2 + 8\text{H}_2$
  
  - $3\text{Mg(NH}_2)_2 + 12\text{LiH} \leftrightarrow 4\text{Li}_2\text{N}_3 + \text{Mg}_3\text{N}_2 + 12\text{H}_2$
  
  - $2\text{LiNH}_2 + \text{MgH}_2 \leftrightarrow \text{Li}_2\text{Mg(NH)}_2 + 2\text{H}_2$

Primary issues remain hydrogen storage content, discharge and charge temperatures, kinetics, reversibility, and hydrogen purity
Objectives

- Collaborate with University of Utah group - perform complementary experiments to analyze the LiMgN system
- Verify reversibility conditions of TiCl$_3$ doped LiMgN
- Explore the effect of catalyst loading on both charge and discharge reaction pathways and kinetics.
- Outline discharge and charge kinetics under various temperature and pressure conditions to prepare for hydrogen storage system design
Experimental Plan

• Perform isothermal kinetic studies under well-defined, controlled reaction conditions

• Experimental conditions to be explored:
  • Discharge Kinetics
  • Charge Kinetics
  • Effect of Composition – Li:Mg:M_{tr}

• XRD analysis at various points in hydrogenation/dehydrogenation cycle

• **Deliverable:** Experimental data required to determine isothermal kinetics and characterize the proposed reaction for hydrogenation and dehydrogenation of LiMgN

\[ M_{tr} = \text{Ti, V, Cr, Ni} \ldots \]
\[ \text{composition} = [0.5 \text{ mol\%} - 6 \text{ mol\%}] \]
Material Synthesis and Experimental Procedure

• **Synthesis**
  - All materials prepared using Frisch mill rotational milling technique
  - FM for 3 hrs at 500 rpm, with rotational direction reversed every 3 min
  - All reactors are loaded in an inert Ar glove box
  - Standard discharge condition: 280°C/1 bar/6 hr
  - Standard charge condition: 180°C/150 bar/6 hr

• **Discharge Procedure**
  - Reactor is placed under high pressure (~150 bar) and heated to desired temperature
  - Manifold is controlled so that when the reactor is released to the reservoir, the nominal backpressure is equal to 1 bar
  - Temperature Programmed Desorption (TPD) performed at 2°C/min into 1 bar reservoir pressure

• **Charge Procedure**
  - Reactor is placed under active vacuum and heated to desired temperature
  - Reservoir is pressurized to the desired pressure and released to the reactor
Discharge products are comprised of LiCl, Mg₃N₂, LiMgN and a minor amount of an unidentified phase (< 5%). Mg₃N₂ and LiMgN nearly iso-structural with a cation disordered anti fluorite structure type.

\[ (\text{Li},\text{Mg}_{1-x})_3\text{N}_{2-x} \quad 0.0 < x < 0.20 \]
\[ (\text{Li},\text{Mg}_{1-x})_2\text{N}_{(2-x)2/3} \quad 0.5 < x < 0.60 \]

- 180°C selected as optimal charging condition
- Time to 80% charge \((\tau_{80}) = 37\) min
  - DOE target = 3 min
Temperature Programmed Desorption Data – 4 mol% TiCl$_3$

Evidence of three reaction steps observed at 100, 200 & 260°C

dT/dt = 2°C/min 25°C to 28°C
Isothermal Recharging Data – 4 mol% TiCl₃

Charges performed between 160⁰C-200⁰C/150 bar/10 hr

• Discharge products are similar to those obtained at 1 bar and comprised of LiCl, Mg₃N₂, LiMgN and a minor amount of an unidentified phase (< 5%).
• Time to 80% Charge ($\tau_{80}$) = 30 min.
• DOE target = 3 min.
The quaternary Li-Mg-N-H phase diagram is given showing the relative regions of stability for the various possible components and the proposed closed cyclic compositions (in blue).
Discharge Kinetic Analysis of Li-Mg-N System

• Traditional kinetic analysis follows from Arrhenius equation

• Linear kinetics gives activation energy of 60 kJ/mol H\(_2\) for discharge reaction
Discharge Kinetic Analysis
Johnson-Mehl-Avrami Approximation

- \( \alpha(t) = 1 - \exp(-kt^n) \)
- \( \frac{d\alpha}{dt} = k\times nt^{(n-1)}\times \exp(-kt^n) \)
- \( \ln(-\ln(1-\alpha)) = n\ln(t) + \ln(k) \)

- Transformations between different linear segments indicative of changes in reaction mechanism

Evidence of multi-step reaction mechanism observed
Li-Mg-N Discharge Kinetics

Bed calculation assumes 7 wt% with 5 kg H₂ stored
Discharge at 280°C/1bar/6hours

- Catalyst loading has significant effect on discharge rate
- Fastest kinetics observed in the literature for LiMgN

DOE 2015 goal for 80 KW PEMFC
Li-Mg-N Charge Kinetics

Charging rate strongly affected by pressure

Catalyst loading has little effect on charging rates
4 mol% material discharge rate is 57% of DOE technical target at 280°C
0.667 mol% material discharge rate is 24% of target at 280°C

<table>
<thead>
<tr>
<th>Temp</th>
<th>0.667 mol% TiCl₃ (4 wt%)</th>
<th>Rate [g H₂ / (s·g₂)]</th>
<th>Rate 72 kg bed*</th>
</tr>
</thead>
<tbody>
<tr>
<td>160°C</td>
<td>2.0 x 10⁻⁵</td>
<td>1.43</td>
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</tr>
<tr>
<td>180°C</td>
<td>2.4 x 10⁻⁵</td>
<td>1.73</td>
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</tr>
<tr>
<td>200°C</td>
<td>1.9 x 10⁻⁵</td>
<td>1.38</td>
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</tr>
<tr>
<td>220°C</td>
<td>1.7 x 10⁻⁵</td>
<td>1.26</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Temp</th>
<th>4 mol% TiCl₃ (13.7 wt%)</th>
<th>Rate [g H₂ / (s·g₂)]</th>
<th>Rate 72 kg bed*</th>
</tr>
</thead>
<tbody>
<tr>
<td>160°C</td>
<td>1.9 x 10⁻⁵</td>
<td>1.40</td>
<td></td>
</tr>
<tr>
<td>180°C</td>
<td>2.5 x 10⁻⁵</td>
<td>1.80</td>
<td></td>
</tr>
<tr>
<td>200°C</td>
<td>2.3 x 10⁻⁵</td>
<td>1.68</td>
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<table>
<thead>
<tr>
<th>P</th>
<th>Charge</th>
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</thead>
<tbody>
<tr>
<td>150 bar</td>
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</tr>
<tr>
<td>70 bar</td>
<td>4.6 x 10⁻⁶</td>
</tr>
<tr>
<td>100 bar</td>
<td>1.2 x 10⁻⁵</td>
</tr>
<tr>
<td>150 bar</td>
<td>2.0 x 10⁻⁵</td>
</tr>
</tbody>
</table>

<table>
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<th>Charge</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
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</tr>
<tr>
<td>180°C</td>
<td>2.5 x 10⁻⁵</td>
</tr>
<tr>
<td>200°C</td>
<td>2.3 x 10⁻⁵</td>
</tr>
</tbody>
</table>

Discharge temperature of 280°C needs to be decreased while maintaining current rates

*Assumes 7 wt% with 5 kg H₂ stored
Conclusions

• Desorption products at both ambient and higher pressures (1, 150 & 180 bar) appear to be the same (mixture of \( \text{LiCl}, \text{Mg}_3\text{N}_2 \) and \( \text{LiMgN} \) a minor amount of an unidentified phase (< 5%)).

• Increased catalyst loading has significant effect on \( \text{H}_2 \) discharge rate

• Different kinetic modeling approaches are being applied to characterize and understand reaction kinetics to enable prediction of charge/discharge rates under varying engineering conditions
Future Directions

• Resolve \( \text{Li}_{0.51}\text{Mg}_{2.49}\text{N}_{1.83} \) vs. \( \text{LiMgN} \) characterization issue (IR, NMR…)
  • Further characterization of the unidentified discharge product

• Test other catalysts to render faster kinetics, lower temperatures of operation (e.g. \( \text{VCl}_3, \text{NiCl}_3, \text{FeCl}_3 \)…)

• Analyze the purity of the discharged \( \text{H}_2 \) as a function of temperature using RGA and FTIR

• Conduct a study to determine the effect of milling time on isothermal kinetics
Amide-Borohydride Systems

\[ M(BH_4)_i(NH_2)_j \]

- Tailoring the electronegativity of the metal ion \( M^+ \) in the borohydride \( BH_4^- \) complex, \( Nakamori \textit{et al.}, 2006 \)
- Adding secondary reactant to form a stable boron containing product, \( 2LiBH_4 + MgH_2 \rightarrow MgB_2 + 2LiH + 4H_2 \), \( Vajo \textit{& Olsen}, 2007 \)
- Synthesis of new \( Li_4(BH_4)(NH_2)_3 \) \([Li_4BN_3H_{10}]\), by mechanico-chemical milling of \( LiNH_2 \) and \( LiBH_4 \), \( Chater \textit{et al.}, 2006 \)
- Confirmation that \( Li_4(BH_4)(NH_2)_3 \) desorbs >10wt\% \( H_2 \) at 250 \( ^\circ \text{C} \), \( Pinkerton \textit{et al.}, 2006 \)
- Theoretical calculations revealed that \( Li_4BN_3H_{10} \rightarrow Li_3BN_2 + LiNH_2 + H_2 \) is only weakly endothermic, with a \( \Delta H \sim 13 \text{ kJ/mol } H_2 \), \( Siegel \textit{et al.}, 2007 \)
- Evidence of B-H and N-H bond destabilization as compared to the parent \( LiBH_4 \) and \( LiNH_2 \) structures, \( Yang \textit{et al.}, 2007 \)

\[ M(BH_4)_i \cdot xNH_3 \]

- Ammonia complex of magnesium borohydride, \( Soloveichik \textit{et al.}, 2008 \)

\[ M(NH_2)_j \cdot x(BH_3) \]

- Calcium amidotrihydroborate as hydrogen storage material, \( Burrell \textit{et al.}, 2007 \)
Literature Conclusions

- Competing but related $M(BH_4)_i(NH_2)_j$, $M(BH_4)_i\cdot xNH_3$ and $M(NH_2)_j\cdot x(BH_3)$ phases have been identified.
- New set of **binary anion complex compounds** $M(BH_4)_i(NH_2)_j$ exists with high wt% $H_2$
- Interaction between $(BH_4)^-$ and $(NH_2)^-$ reduces $\Delta H$ of sorption
- Relatively unexplored area with good potential for low temperature high capacity media

**Objective**

Perform an in-depth empirical study of the bimetallic borohydride/amide phase space formed in $M^1M^2(BH_4)_i(NH_2)_j$

where:
$M^1$= Li, Na, K and
$M^2$=Mg, Ca, Ti and/or other transition metals.
# Existing Borohydride and Amide Compounds Opportunities for Materials Discovery

<table>
<thead>
<tr>
<th>Precursor 1</th>
<th>Precursor 2</th>
<th>Mixed Borohydride/Amides</th>
<th>$\Delta H_{\text{mix}}$ (kJ/mol H$_2$) Dehydriding</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiH</td>
<td>NH$_3$BH$_3$</td>
<td>LiNH$_2$BH$_3$ [Xiong et.al. 2008]</td>
<td>-5</td>
</tr>
<tr>
<td>LiBH$_4$</td>
<td>LiNH$_2$</td>
<td>Li$_4$BN$<em>3$H$</em>{10}$ [Chater et.al. 2006]</td>
<td>13</td>
</tr>
<tr>
<td>NaBH$_4$</td>
<td>NaNH$_2$</td>
<td>Na$_2$BNH$_6$ [Chater et.al. 2006]</td>
<td></td>
</tr>
<tr>
<td>KBH$_4$</td>
<td>KNH$_2$</td>
<td>opportunities for novel materials discovery</td>
<td></td>
</tr>
<tr>
<td>Mg(BH$_4$)$_2$</td>
<td>Mg(NH$_2$)$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca(BH$_4$)$_2$</td>
<td>Ca(NH$_2$)$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M$_1$ BH$_4$</td>
<td>M$_2$NH$_2$</td>
<td>M$_2$=Li, Na, K, Mg, Ca</td>
<td></td>
</tr>
</tbody>
</table>

opportunities for novel materials discovery
## Borohydride and Amide Precursors Used

<table>
<thead>
<tr>
<th><strong>BOROHYDRIDE</strong></th>
<th><strong>COMMERCIALY AVAILABLE</strong></th>
<th><strong>AMIDE</strong></th>
<th><strong>COMMERCIALY AVAILABLE</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>LiBH₄</td>
<td>Yes</td>
<td>LiNH₂</td>
<td>Yes</td>
</tr>
<tr>
<td>NaBH₄</td>
<td>Yes</td>
<td>NaNH₂</td>
<td>Yes</td>
</tr>
<tr>
<td>KBH₄</td>
<td>Yes</td>
<td>KNH₂</td>
<td>Yes</td>
</tr>
<tr>
<td>NH₃BH₃</td>
<td>Yes</td>
<td>Ca(NH₂)₂</td>
<td>Synthesis via</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[Hino et al., 2005]</td>
</tr>
<tr>
<td>Ca(BH₄)₂</td>
<td>Yes</td>
<td>Mg(NH₂)₂</td>
<td>Synthesis via</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[Nakamori et al., 2004] or Ball milling MgH₂ under P_NH₃ = 7 bar</td>
</tr>
</tbody>
</table>

*Synthesized via [Zanella et al., 2007]*
High hydrogen containing compounds may be obtained through additions of \( \text{NH}_3 \) to \( \text{LiBH}_4 \), \( \text{LiNH}_2 \), \( \text{Mg(BH}_4\text{)}_2 \) and \( \text{Mg(NH}_2\text{)}_2 \).
LiH-MgH₂-BHₓ-NHᵧ Phase Diagram: Map of Identified Compounds

High hydrogen containing compounds may be obtained through additions of NH₃BH₃ to LiBH₄, LiNH₂, Mg(BH₄)₂, and Mg(NH₂)₂.
High hydrogen containing compounds may be obtained through additions of $\text{B}_{10}\text{H}_{14}$ to LiBH$_4$, LiNH$_2$, Mg(BH$_4$)$_2$, Mg(NH$_2$)$_2$. 
High hydrogen containing compounds may be obtained through additions of \( \text{NH}_3\text{BH}_3 \) to \( \text{LiBH}_4 \), \( \text{LiNH}_2 \), \( \text{Ca(BH}_4\text{)}_2 \), and \( \text{Ca(NH}_2\text{)}_2 \).
## Synthetic Plan for Materials $M^1M^2(BH_4)_x(NH_2)_y$

### LiNH$_2$ + Ca(BH$_4$)$_2$

<table>
<thead>
<tr>
<th>Calcium Borohydride Ca(BH$_4$)$_2$</th>
<th>Lithium Amide LiNH$_2$</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 mole</td>
<td>1 mole</td>
<td>in progress</td>
</tr>
<tr>
<td>1 mole</td>
<td>2 mole</td>
<td>Li$_x$Ca(BH$_4$)$_x$(NH$_2$)$_y$ in progress</td>
</tr>
<tr>
<td>2 mole</td>
<td>1 mole</td>
<td>in progress</td>
</tr>
</tbody>
</table>

### LiBH$_4$ + Ca(NH$_2$)$_2$

<table>
<thead>
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</tr>
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<tbody>
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<td>1 mole</td>
<td>in progress</td>
</tr>
<tr>
<td>1 mole</td>
<td>2 mole</td>
<td>in progress</td>
</tr>
<tr>
<td>2 mole</td>
<td>1 mole</td>
<td>in progress</td>
</tr>
</tbody>
</table>

### LiNH$_2$ + Mg(NH$_2$)$_2$

<table>
<thead>
<tr>
<th>Magnesium Amide Mg(NH$_2$)$_2$</th>
<th>Lithium Borohydride LiBH$_4$</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
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<td>2 mole</td>
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</tr>
<tr>
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<td>1 mole</td>
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</tbody>
</table>

### LiBH$_4$ + Mg(BH$_4$)$_2$

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<tbody>
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<td>1 mole</td>
<td>2 mole</td>
<td>in progress</td>
</tr>
<tr>
<td>2 mole</td>
<td>1 mole</td>
<td>in progress</td>
</tr>
</tbody>
</table>
$2\text{LiNH}_2 + \text{Ca(BH}_4\text{)}_2 (\text{Li}_2\text{Ca(BH}_4\text{)}(\text{NH}_2\text{)}_2)_{\text{Fritsch Milled}}$

$2\text{LiNH}_2 + \text{Ca(BH}_4\text{)}_2 \xrightarrow{2\text{h}} \text{Li}_x\text{Ca(BH}_4\text{)}_x(\text{NH}_2\text{)}_y$ (Fritsch)

- The peaks for components Ca(BH$_4$)$_2$ and LiNH$_2$ not present
- Milled mixture gives rise to an amorphous phase.
Ca(BH₄)₂:2LiNH₂
Temperature Programmed Desorption

- Ca(BH₄)₂ dehydrogenates rapidly at ~360°C.
- Ca(BH₄)₂:2LiNH₂ rapid dehydrogenation at ~250 °C completed at ~310 °C.
- Dehydridding temperature of the Ca(BH₄)₂:2LiNH₂ mixture is ~100 °C lower than that of Ca(BH₄)₂. Need to determine reversibility of this compositional ratio.
Summary

- A comprehensive plan has been developed to synthesize mixed metal borohydride/amide compounds of the formula $M^1M^2(BH_4)_x(NH_2)_y$.

- An amorphous phase was achieved by ball milling LiNH$_2$ and Ca(BH$_4$)$_2$ (2:1 mole ratio).

- The amorphous phase $Li_2Ca(BH_4)_1(NH_2)_2$ displayed a dehydriding temperature $\sim$100˚C lower than Ca(BH$_4$)$_2$.

Future Directions

- Identify structures and compositions of Li$_x$Ca(BH$_4$)$_x$(NH$_2$)$_y$.

- Synthesize Mg(NH$_2$)$_2$ and Ca(NH$_2$)$_2$.

- Synthesize and characterize LiMg(BH$_4$)$_x$(NH$_2$)$_y$ and LiCa(BH$_4$)$_x$(NH$_2$)$_y$.

- Elucidate the origin of the reduction in dehydriding temperature.