Amide and Combined Amide/Borohydride Investigations

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June 9, 2010

Project ID #: ST070

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Overview

Timeline
• Start: 10/1/05
• End: 9/30/10
• Percent complete: 83%

Budget
• Funding for FY09
  • $400K
• Funding for FY10
  • $350K

Barriers Addressed
A. System Weight and Volume
E. Charging/Discharging Rate
P. Understanding Chemisorption

Partners
• Z. Fang – U. of Utah
• H. zurLoye – U. of South Carolina
  D. Bugaris – U. of South Carolina
• E. Ronnebro – PNNL
  T. Autrey – PNNL
• Hydrogen Storage Engineering CoE
• D. Chandra – U. of Nevada-Reno
Task I - LiMgN

- Perform isothermal/isobaric hydrogenation and dehydrogenation experiments to analyze the effect of composition on the kinetics of the LiMgN system.

- Formulate an outline of discharge and charge conditions to prepare a hydrogen storage system based on the kinetics.

- Prepare a database for use by the Hydrogen Storage Engineering Center of Excellence (HSECoE) to assess the utility of LiMgN in a prototype system.

Task II - M₁M₂(BH₄)ₓ(NH₂)ᵧ

- Perform an empirical study of high hydrogen content bimetallic mixed borohydride/amide systems of the form: M₁M₂(BH₄)ₓ(NH₂)ᵧ. These systems include Mg(BH₄)₂/LiNH₂, Mg(NH₂)₂/LiBH₄, and Ca(NH₂)₂/LiBH₄.

- Investigate the addition of NH₃BH₃ to Ca(BH₄)₂ and LiNH₂ as a potential high hydrogen containing mixture.
Relevance –

**LiMgN as a Hydrogen Storage Material**

\[ \text{LiNH}_2 + \text{MgH}_2 \rightarrow \text{LiMgN} + 2\text{H}_2 \quad \Delta H_{\text{rxn}} = 32 \text{ kJ/molH}_2 \]

- Identified using DFT calculations as potentially reversible with a theoretical H\textsubscript{2} gravimetric storage capacity of 8.2 wt% (Alapati et al., *Phys. Chem. Chem. Physics.* 9 (2007) 1438)
  - Experimentally 8.1 wt% was observed by Lu et al. under moderate temperature (160°C to 220°C) using TGA after jar rolling for 12 to 24 hours (Lu et al., *J. Phys. Chem. C* 111 (2007) 12129)

- The reversible hydrogen absorption reaction involved
  \[ \text{LiMgN} + 2\text{H}_2 \leftrightarrow \frac{1}{2} \text{Mg(NH}_2)_2 + \frac{1}{2} \text{MgH}_2 + \text{LiH} \]
  - 8 wt% observed experimentally at 160°C and 140 bar in pressure vessel

- 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\textsubscript{3} dopant (Lu et al., *J. Phys. Chem. C* 111 (2007) 12129)

- Planetary milling for 36 hours resulted in 6.1 wt% lost by 390°C, the formation of Li\textsubscript{2}MgN\textsubscript{2}H\textsubscript{2}, a \( \Delta H_{\text{rxn}} = 45.9 \text{ kJ/molH}_2 \) and a reversible capacity of 2.5 wt% at 210°C/101 bar pressure (Liu et al., *Chem. Mater.* 20 (2008) 3521)
The quaternary Li-Mg-N-H phase diagram shows the reaction pathways for the various compositions of Li-Mg. The pathway highlighted in red has the highest capacity.
**Approach – LiMgN Experimental Plan**

- Perform isothermal and isobaric kinetic studies under controlled reaction conditions
  - Explore effect of catalysts composition – Li:Mg:M_{tr}
    - $M_{tr} = TiCl_3, VCl_3, TiN, NiCl_2$ and $ScCl_3$ with composition = 1.5 mol%
- XRD analysis performed on as-milled material and after hydrogenation/dehydrogenation cycles
- TGA-RGA to determine gas composition during dehydrogenation
- **Deliverable**: Experimental data necessary to determine isothermal kinetics, characterize the proposed reaction for hydrogenation and dehydrogenation and database for use by HSECoE to assess the utility of LiMgN in a prototype system
Approach –

**Material Synthesis and Experimental Procedure**

- **Synthesis**
  - Starting materials include LiNH₂ or LiH, MgH₂ and/or Mg(NH₂)₂ and catalysts
  - All materials prepared using Fritsch mill rotational or jar roll milling techniques
  - FM for 2.5 hours at 500 rpm with rotational direction reversed every 30 minutes
  - Standard discharge condition: 260°C/1 bar/6 hrs
  - Standard charge condition: 180°C/100 bar/6 hrs

- **Discharge Procedure**
  - Reactor placed under high pressure (~110 bar) and heated to desired temperature
  - Manifold controlled so that when the reactor is released to the reservoir, the nominal backpressure is equal to 1 bar

- **Charge Procedure**
  - Reactor placed under active vacuum and heated to desired temperature
  - Reservoir is pressurized to desired pressure and released to the reactor

- **TGA-RGA Procedure**
  - Heating rate at 5°C/min from RT to 315°C
  - Looked at mass 2 (H₂), 16 (NH₂⁻), 17 (NH₃/OH) and 18 (H₂O) in RGA
Technical Accomplishments and Progress –
XRD Analysis of As-milled 1:1 LiNH₂:MgH₂ w/w/o catalyst

MgH₂ and LiNH₂ patterns identified; however, LiCl also identified for halide catalysts

- No indication of decomposition of TiN resulting from milling
- Metathesis reaction going on which produces LiCl in samples (ball-milling may provide enough energy to initiate the reaction) [observed by: Parkin et al., J. Mater. Chem. 5, (1995) 909.]
Technical Accomplishments and Progress – RGA results of As-milled 1:1 LiNH$_2$:MgH$_2$ w/ w/o catalyst

- All catalysts reduce 1st cycle hydrogen desorption temperature by 25 - 35°C
- Metathesis reaction between LiNH$_2$ and M$_{tr}$Cl$_3$ promotes ammonia release
- Only TiN increased the temperature of initial ammonia release by 15°C
Technical Accomplishments and Progress –
Average Rate of Hydrogen Charge [gH₂/s]

- Rates of hydrogen charge are an order of magnitude lower than the DoE technical target
- TiN continues to significantly increase absorption capacity through four cycles while the halide catalysts continue to decrease
  - Metathesis reaction between LiNH₂ and M₄Cl₃ hinders hydrogen absorption through the loss of essential nitrogen
Technical Accomplishments and Progress – Average Rate of Hydrogen Discharge [gH₂/s]

Average Rate of Hydrogen Discharge for a packed bed storing 5kg H₂

- Hydrogen discharge rate for TiN continues to increase through four cycles due to:
  - The cycled material not being completely homogenized after four cycles resulting in the loss of available surface area for the reaction to occur
- The hydrogen discharge rate decreased drastically for the halide catalysts after the first cycled due to:
  - Metathesis reaction between LiNH₂ and MₓCl₃: LiNH₂ + TiCl₃ → LiCl + Ti(unknown state) + NH₂

DOE Technical Target for 2010: 3 g/sec

Discharge conditions: 260°C into 1 bar for 6 hours
Technical Accomplishments and Progress –
XRD Analysis of four cycled 1:1 LiNH\textsubscript{2}:MgH\textsubscript{2} with/without catalyst

- Mg(NH\textsubscript{2})\textsubscript{2}, MgH\textsubscript{2} and LiH identified showing LiMgN $\leftrightarrow$ LiH + $\frac{1}{2}$ MgH\textsubscript{2} + $\frac{1}{2}$ Mg(NH\textsubscript{2})\textsubscript{2}

- Mg\textsubscript{3}N\textsubscript{2} also identified, possibly forming from Mg(NH\textsubscript{2})\textsubscript{2} + 2MgH\textsubscript{2} $\rightarrow$ Mg\textsubscript{3}N\textsubscript{2} + 4H\textsubscript{2}
  \[\Delta H = 15 \text{ kJ/mol H}_2 \text{ at 500K}, \text{ Akbarzadeh, et al., Adv Mat. 19 (2007) 3233}\] or
  LiMgN + H\textsubscript{2} $\rightarrow$ LiH + Mg\textsubscript{3}N\textsubscript{2}
Technical Accomplishments and Progress – Raman Spectroscopy Analysis

- **As-milled:** High-shift region shows spectrum consistent with LiNH$_2$ amide stretches

- **Discharged:** Doublet at 379 (strong) and 341 (weak) cm$^{-1}$ which closely resembles that of Mg$_3$N$_2$; LiMgN reported in literature [Kuriyama, *et al.*, *Phys Rev B* 75 (2005) 233204] not observed due to different crystal structure
  - Kuriyama observed a cubic disordered antifluorite structure (Fm3m),
  - Instead a nitrogen-vacancy model for antibixbyite-structure (I2$_1$3) was observed similar to that observed by Yamane, *et al.*, *J of Alloys and Comp* 319 (2009) 124

- **Recharged:** The bands at 3274 and 3330 cm$^{-1}$ are consistent with the formation of Mg(NH$_2$)$_2$
Conclusions for Task I - LiMgN

• Catalyst composition has a significant effect on H₂ and NH₃ discharge temperatures, cyclic capacity and sorption rates

  • Uncatalyzed
    • Showed a decrease in hydrogen discharge rate over four desorption cycles
      • Rate of conversion from LiNH₂ + MgH₂ → LiMgN > LiH + ½ MgH₂ + ½ Mg(NH₂)₂ → LiMgN

  • TiN
    • Only catalyst to increases temperature of ammonia release
    • Showed a significant increase in hydrogen capacity and rate over four absorption cycles
    • Showed an increase in hydrogen discharge rate over four desorption cycles
      • Indicates cycled material not being completely homogenized after four cycles resulting in the loss of available surface area for the reaction to occur

  • Other catalyst
    • Reduced the temperature of ammonia release
    • Showed decrease in sorption rates and absorption capacities over four cycles due to metathesis reaction between LiNH₂ and M₄Cl₃

• Sorption rates are an order of magnitude less than the 2010 DOE goals.
Relevance –

Introduction of Mixed Borohydride/Amide Systems

- New set of binary anion complex compounds $M(BH_4)_x(NH_2)_y$ exists with high wt% H$_2$
- Relatively unexplored area with good potential for low temperature high capacity media
- The addition of mixed metal cations to the borohydride/amide compounds may decrease the strength of the B-H and N-H bonds as compared to their parent $M(BH_4)_x$ chemical compounds leading to the possibility of
  - amorphous compounds with significantly reduced entropy associated with dehydrogenation reaction
  - provide lower heats of reaction for hydrogenation

High hydrogen containing compounds may be obtained through additions of $NH_3BH_3$ to LiBH$_4$, LiNH$_2$, Mg(BH$_4$)$_2$, and Mg(NH$_2$)$_2$.

Ammoniation High Pressure Reactor Set-up
Relevance —

### Competing Systems of Mixed Amide/Borohydride

#### Di-Anionic Complexes: \( \text{M(BH}_4\text{)}^{-}\cdot(\text{NH}_2\text{)}^{-} \)

- Synthesis of \( \text{Li}_4(\text{BH}_4)(\text{NH}_2)_3 \) and desorption >10wt% \( \text{H}_2 \) at 250-350 °C, *Pinkerton et al.*, 2006
- Synthesis of new \( \text{Li}_4(\text{BH}_4)(\text{NH}_2)_3 [\text{Li}_4\text{BN}_3\text{H}_{10}] \), by mechano-chemical milling of \( \text{LiNH}_2 \) and \( \text{LiBH}_4 \), *Chater et al.*, 2006
- Theoretical calculations revealed that \( \text{Li}_4\text{BN}_3\text{H}_{10} \rightarrow \text{Li}_3\text{BN}_2 + \text{LiNH}_2 + \text{H}_2 \) is only weakly endothermic, with a \( \Delta H \sim 13 \text{ kJ/mol H}_2 \), *Siegel et al.*, 2007
- Evidence of B-H and N-H bond destabilization as compared to the parent \( \text{LiBH}_4 \) and \( \text{LiNH}_2 \) structures, *Yang et al.*, 2007
- Impact of Stoichiometry on Hydrogen Storage Properties of \( \text{LiNH}_2 + \text{LiBH}_4 + \text{MgH}_2 \) Composites, *Sudik et al.*, 2009 (Optimal Ratio 3:1:1.5 for \( \text{H}_2 \) Desorption and Reversible at Ratio 2:1:1 and 2:0.5:1)

#### Ammoniated Borohydride Complexes: \( \text{M(BH}_4\text{)}^{-}\cdot\text{NH}_3 \)


#### Amidoborane Complexes: \( \text{M(NH}_2\text{)}^{-}\cdot\text{BH}_3 \)

- Calcium amidotrihydroborate as hydrogen storage material, *Burrell et al.*, 2007
Approach –
Experimental Plan

- Mixtures are formed using planetary ball-milling techniques.
- Identify isothermal/isobaric sorption properties of mixed phases using Sievert’s apparatus.
- XRD analysis after ball milling process and after hydrogenation and dehydrogenation.
- TGA-RGA to determine composition of hydrogen during dehydrogenation.
Technical Accomplishments and Progress – Synthesis of Mg(NH$_2$)$_2$

Mg (powder) $\xrightarrow{2\text{NH}_3(g) \text{(120 psi)} \atop 110^\circ \text{C}, 120 \text{ hr}}$ Mg(NH$_2$)$_2$ + H$_2$

- XRD confirmed ~ 95% pure Mg(NH$_2$)$_2$ by simple addition of ammonia to magnesium powder and heat in a high pressure reactor vessel.
- Theoretical H$_2$ capacity is ~ 7.1 wt%
- TGA shows a total weight loss of more than 30%.
- RGA shows a disproportionate amount of NH$_3$, NH$_2^-$ to H$_2$. 
Technical Accomplishments and Progress – Synthesis of Ca(NH$_2$)$_2$

$\text{Ca (granule)} \xrightarrow{2\text{NH}_3(g); (120 \text{ psi})} 25^\circ\text{C}, 48 \text{ hr} \quad \text{Ca(NH}_2)_2 \xrightarrow{+ \text{ H}_2}$

- XRD confirmed $\approx 99\%$ pure Ca(NH$_2$)$_2$ by simple addition of ammonia to calcium granules in a high pressure reactor vessel.
- Theoretical H$_2$ capacity is $\approx 5.5$ wt%
- Total weight loss from TGA is near 23%.
- RGA shows an immediate release of NH$_2^-$ near RT followed by a release of hydrogen at around 130$^\circ$C, and an ammonia release at 230$^\circ$C.
Technical Accomplishments and Progress – Ca(BH$_4$)$_2$+LiNH$_2$

Sievert’s TPD: 

RGA:

- 4 LiNH$_2$ : 1 Ca(BH$_4$)$_2$ ratio is most effective for dehydrogenation.
- Mixtures of Ca(BH$_4$)$_2$ and LiNH$_2$ leads to predominately H$_2$ release at 150-300°C vs NH$_3$.
- Li$_4$(BH$_4$)(NH$_2$)$_3$ is the major phase for the 4LiNH$_2$:1Ca(BH$_4$)$_2$ mixture.
Technical Accomplishments and Progress – Mg(BH₄)₂+LiNH₂: Isothermal Sievert's Measurements

2nd Cycle Absorption:

2nd Cycle Desorption:

- H₂ absorption fluctuations occur due to competing desorption/absorption processes in the heterogeneous material.
- Absorption of the 3Mg(BH₄)₂ + LiNH₂ has the maximum absorption of 7.5 wt%.
- Desorption of the 3Mg(BH₄)₂ + LiNH₂ is incomplete at 2 wt% due to initial time constraints on the experiment for the mixture to reach steady state.
- Large H₂ absorption indicates a reversible system.
Technical Accomplishments and Progress – Mg(BH₄)₂+LiNH₂: RGA

H₂ RGA Analysis at 5°C/min

NH₃ and B₂H₆ RGA Analysis at 5°C/min

- The Mg(BH₄)₂ and LiNH₂ mixtures produce multiple H₂ releases over the temperature range shown. Initial hydrogen release (~200°C) is at lower temperature compared to LiNH₂ (230°C).
- Multiple H₂ releases are broad which indicates more H₂ and less NH₃ (shown on the right).
- The mixtures showed a significant reduction in ammonia release compared to LiNH₂. Diborane release is negligible.
Technical Accomplishments and Progress –
Raman Spectroscopy: Ca(BH₄)₂+LiNH₂+NH₃BH₃

Ca(BH₄)₂ + LiNH₂ + NH₃BH₃ → BM, 200 rpm

3 hr

- Spectra of the 3 starting materials look pretty much like the literature/reference spectra.
- Spectra of the ball-milled starting materials suggest a new material is formed:
  - BH stretch region looks a lot more like a borohydride than a borane.
  - In the 1240-1350 cm⁻¹ region, there is an extra peak in the BM mixture compared to Ca(BH₄)₂.
  (the peak does not appear in the spectra of the other starting materials)
- Extra peaks suggest possibility of a mixed species, or a mixture of species and broadening of peaks could also be an indication of a mixture of new species.

* Cycle Conditions:  (d) 260°C, 1bar, 12 hr
  (c) 220°C, 100 bar, 12 hr
Conclusions for Task II - $M_1M_2(BH_4)_x(NH_2)_y$

- Ca(NH$_2$)$_2$ and Mg(NH$_2$)$_2$ have been successfully synthesized with > 95% purity.
- Mixtures of Mg(BH$_4$)$_2$ and LiNH$_2$ have shown good absorption capabilities but is limited kinetically on desorption through 2 cycles.
- Mixtures of Mg(BH$_4$)$_2$ and LiNH$_2$ contain multiple H$_2$ releases, with reduced release of NH$_3$.
- Initial work has begun in understanding the effect of adding NH$_3$BH$_3$ to Ca(BH$_4$)$_2$ and LiNH$_2$ as a potential high H$_2$ containing mixture. Raman has confirmed that a new mixture is formed.
- Initial results show desorption of H$_2$ as low as 150$^\circ$C for the mixture of Ca(BH$_4$)$_2$:LiNH$_2$:NH$_3$BH$_3$. 

Future Directions

• **Task I**
  - Carry cycling out further than 4 complete cycles (e.g. 10 – 15 cycles for each material)
  - Continue testing other catalysts to render faster kinetics and lower temperatures of operation (e.g. nano-Ti, LiBH₄, KH, …..)
  - Analyze the purity of the discharged H₂ as a function of temperature using FTIR

• **Task II**
  - Complete a study of Ca(NH₂)₂ and Mg(NH₂)₂ ball-milled with LiBH₄ in various ratios.
  - Continue additions of ammonia borane, decaborane and ammonia to binary compositions to evaluate possible high hydrogen compounds.
  - Further investigate the sorption characteristics of the ball-milled mixtures using each mixture using Sievert's experiments.