Amide and Combined Amide/Borohydride Investigations

Donald Anton, Charles James, Christine Erdy, Long Dinh, and Rob Lascola

Savannah River National Laboratory

June 9, 2010

Project ID #: ST070

SRNL

This presentation does not contain proprietary, confidential, or otherwise restricted information

METAL HYDRIDE CENTER OF EXCELLENCE

Overview

Timeline

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

Barriers Addressed

A. System Weight and Volume

E. Charging/Discharging Rate

P. Understanding Chemisorption

Budget

- Funding for FY09
  - $400K
- Funding for FY10
  - $350K

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

Relevance – Objectives and Motivation

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 - $M_1M_2(BH_4)_x(NH_2)_y$

- Perform an empirical study of **high hydrogen content** bimetallic **mixed borohydride/amide** systems of the form: $M_1M_2(BH_4)_x(NH_2)_y$. These systems include $Mg(BH_4)_2/LiNH_2$, $Mg(NH_2)_2/LiBH_4$, and $Ca(NH_2)_2/LiBH_4$.
- Investigate the **addition of NH_3BH_3 to $Ca(BH_4)_2$ and $LiNH_2$** as a potential high hydrogen containing mixture.

Relevance – LiMgN as a Hydrogen Storage Material

$$LiNH_2 + MgH_2 \rightarrow LiMgN + 2H_2 \qquad \Delta H_{rxn} = 32\ kJ/molH_2$$

- Identified using DFT calculations as potentially reversible with a theoretical H_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

$$LiMgN + 2H_2 \leftrightarrow \tfrac{1}{2}\, Mg(NH_2)_2 + \tfrac{1}{2}\, MgH_2 + LiH$$

  - 8 wt% observed experimentally at 160°C and 140 bar in pressure vessel
- Dehydrogenation is proposed to proceed through an intermediate step

$$\tfrac{1}{2}\, Mg(NH_2)_2 + \tfrac{1}{2}\, MgH_2 + LiH \rightarrow Li_{2x}Mg_{1-x}(NH)_2 + MgH_2 + H_2 \rightarrow LiMgN + H_2$$

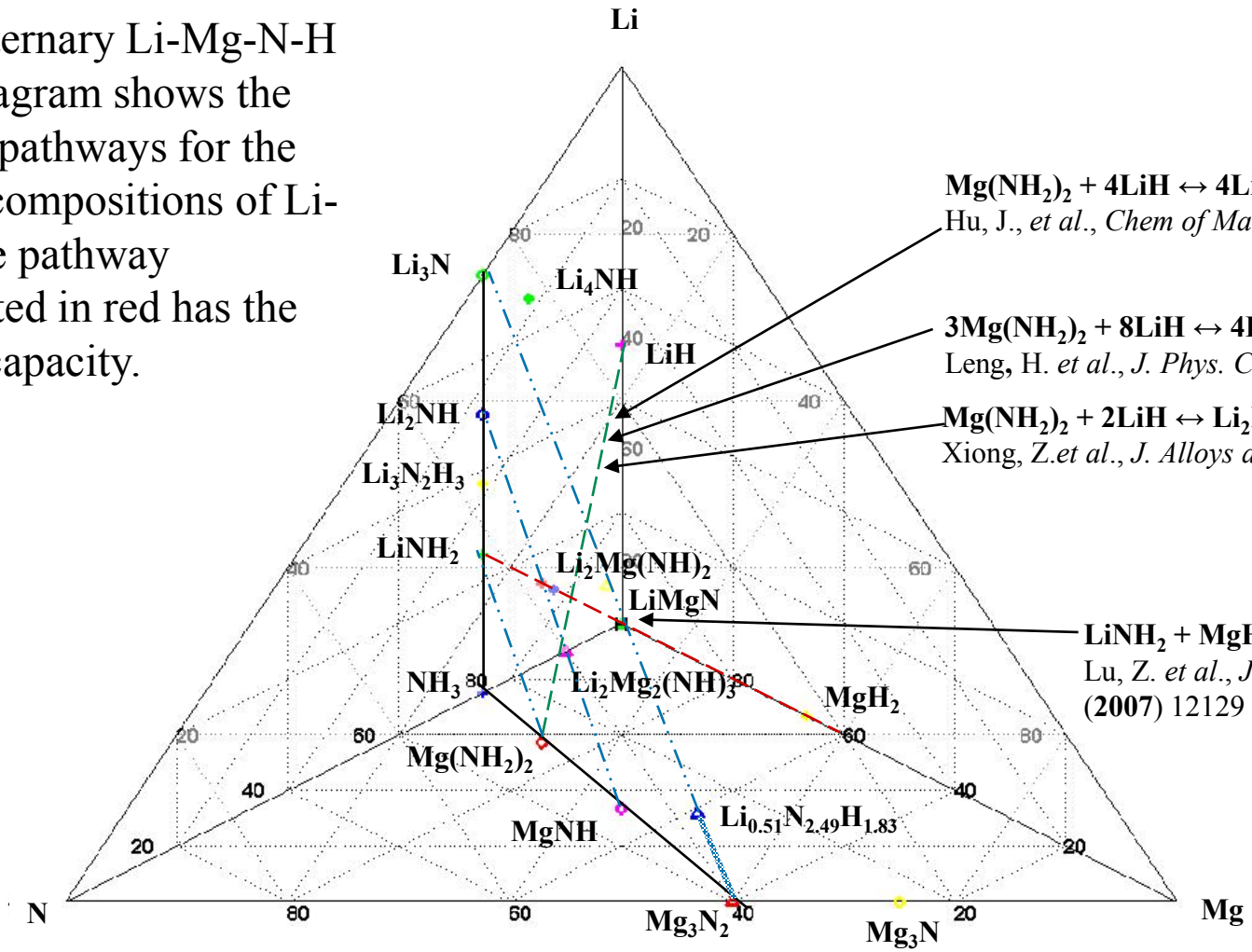
- Accelerated reversibility has been observed using 4 wt% $TiCl_3$ dopant (Lu *et al.*, *J. Phys. Chem. C* 111 (**2007**) 12129)
- Planetary milling for 36 hours resulted in 6.1 wt% lost by 390°C, the formation of $Li_2MgN_2H_2$, a ΔH_{rxn} = 45.9 $kJ/molH_2$ and a reversible capacity of 2.5 wt% at 210°C/101 bar pressure (Liu *et al.*, *Chem. Mater.* 20 (**2008**) 3521)

SRNL

METAL HYDRIDE CENTER OF EXCELLENCE

Approach – Li-Mg-N-H Quaternary Phase Diagram

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.



$Mg(NH_2)_2 + 4LiH \leftrightarrow 4Li_3N + Mg_3N_2 + 12H_2$
Hu, J., *et al.*, *Chem of Materials* 21 (**2009**) 3485

$3Mg(NH_2)_2 + 8LiH \leftrightarrow 4Li_2NH + Mg_3N_2 + 8H_2$
Leng, H. *et al.*, *J. Phys. Chem. B* 108 (**2004**) 8763

$Mg(NH_2)_2 + 2LiH \leftrightarrow Li_2Mg(NH)_2 + 2H_2$
Xiong, Z.*et al.*, *J. Alloys and Comp* 398 (**2004**) 235

$LiNH_2 + MgH_2 \leftrightarrow LiMgN + 2H_2$
Lu, Z. *et al.*, *J. Phys. Chem. C* 111 (**2007**) 12129

SRNL

METAL HYDRIDE CENTER OF EXCELLENCE

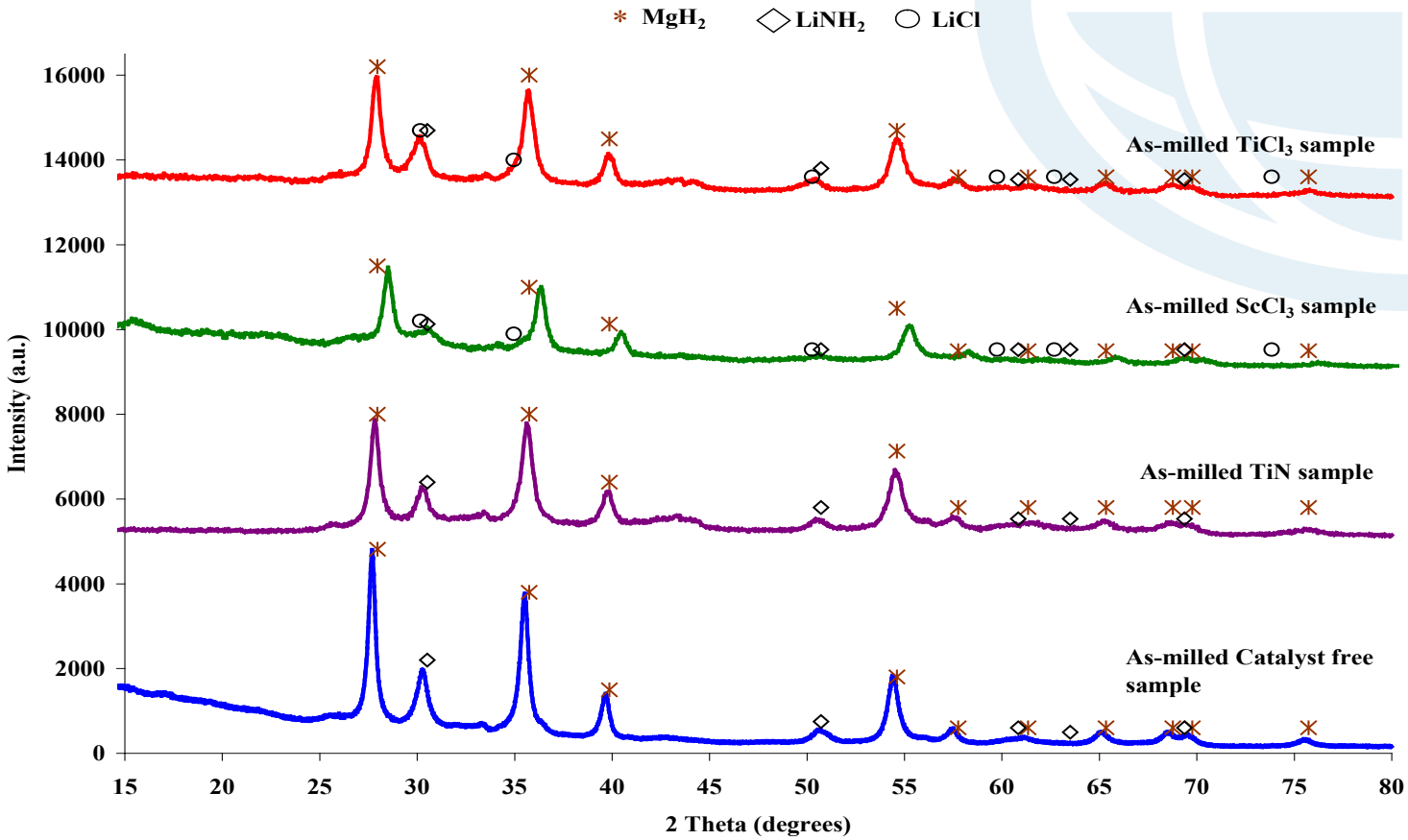
Approach – LiMgN Experimental Plan

- 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 $LiNH_2$ or LiH, MgH_2 and/or $Mg(NH_2)_2$ 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 (H_2), 16 (NH_2^-), 17 (NH_3/OH) and 18 (H_2O) in RGA

Technical Accomplishments and Progress – XRD Analysis of As-milled 1:1 $LiNH_2$:MgH_2 w/w/o catalyst



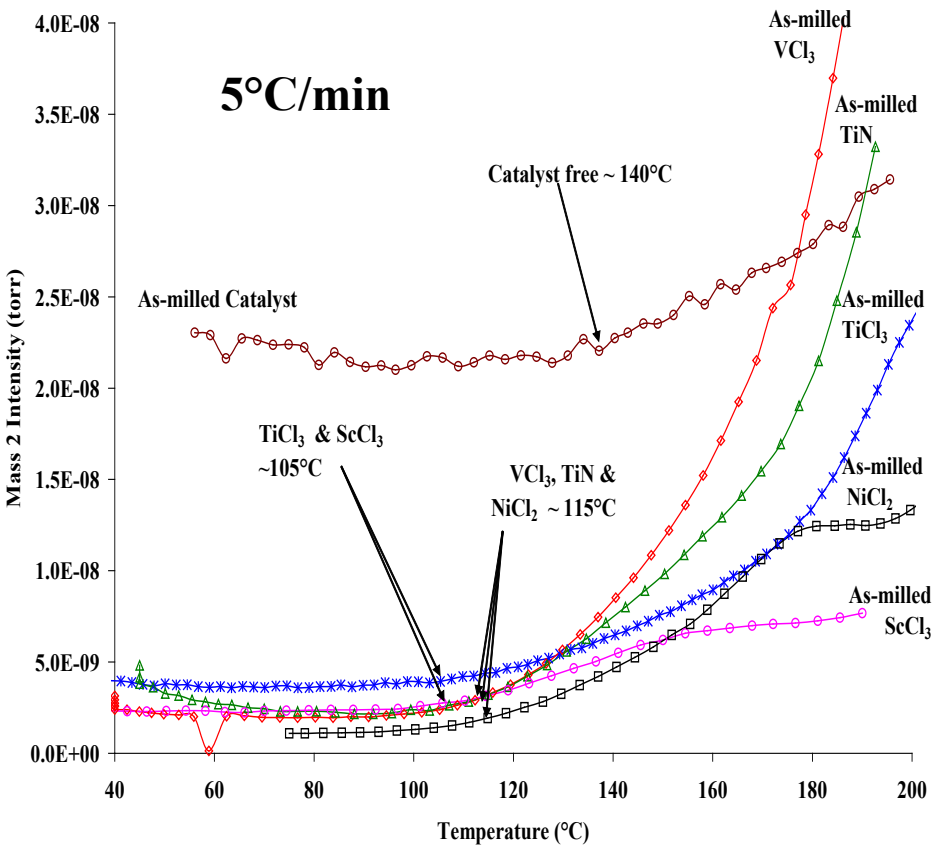
MgH_2 and $LiNH_2$ patterns identified; however, LiCl also identified for halide catalysts

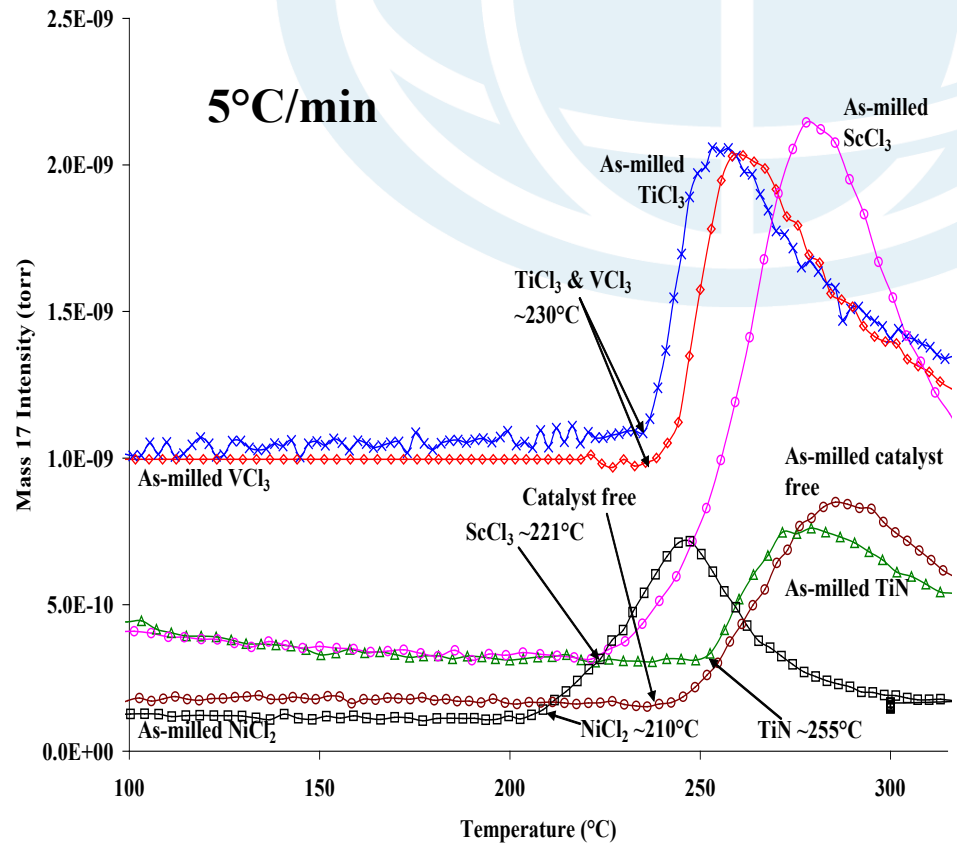
- No indication of decomposition of TiN resulting from milling
- Metathesis reaction going on which produces LiCl in samples (ball-milling may provide enough energy to initiate the reaction) [observed by: Parkin *et al.*, *J. Mater. Chem.* **5**, (**1995**) 909.]

SRNL

METAL HYDRIDE CENTER OF EXCELLENCE

Technical Accomplishments and Progress – RGA results of As-milled 1:1 $LiNH_2$:MgH_2 $^{w}/_{w/o}$ catalyst





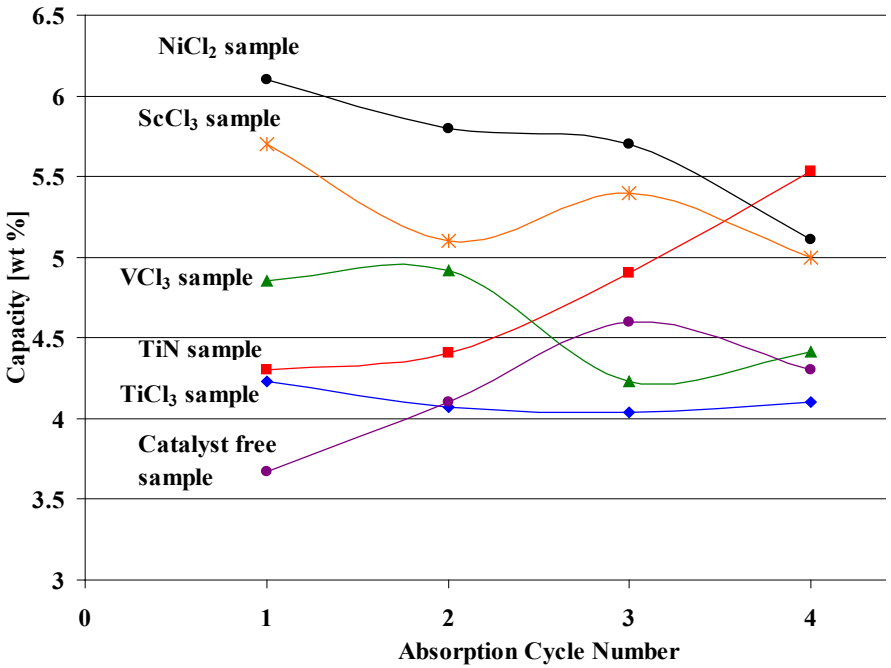
- All catalysts reduce 1st cycle hydrogen desorption temperature by 25 - 35°C
- Metathesis reaction between $LiNH_2$ and $M_{tr}Cl_3$ promotes ammonia release
- Only TiN increased the temperature of initial ammonia release by 15°C

SRNL

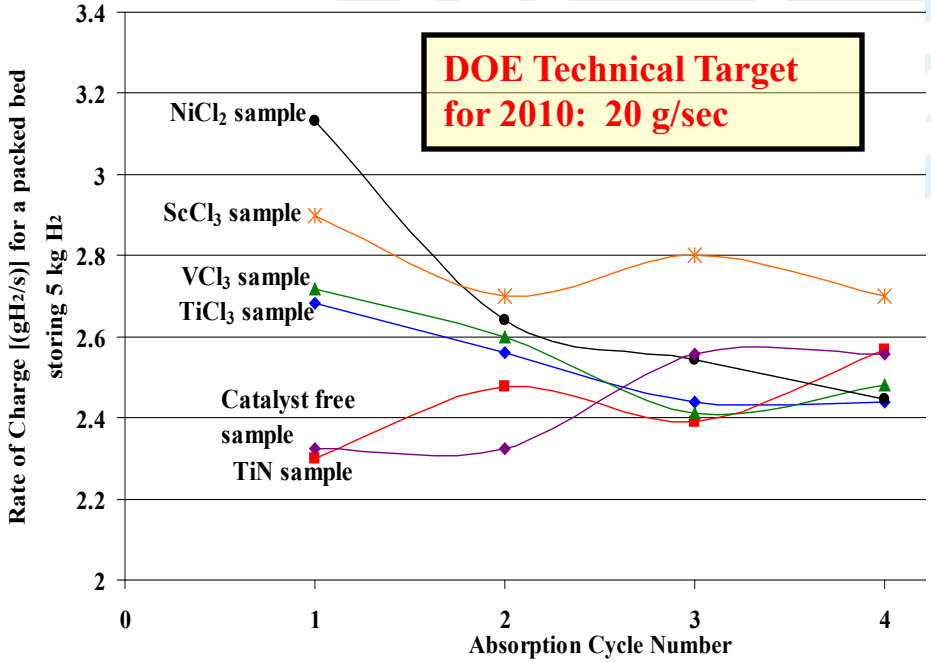
METAL HYDRIDE CENTER OF EXCELLENCE

Technical Accomplishments and Progress – Average Rate of Hydrogen Charge [gH_2/s]

Hydrogen Capacity over four absorption cycles at 180 C under 100 bar for 6 hours



Average Rate of Hydrogen Charge for a packed bed storing 5kg H_2



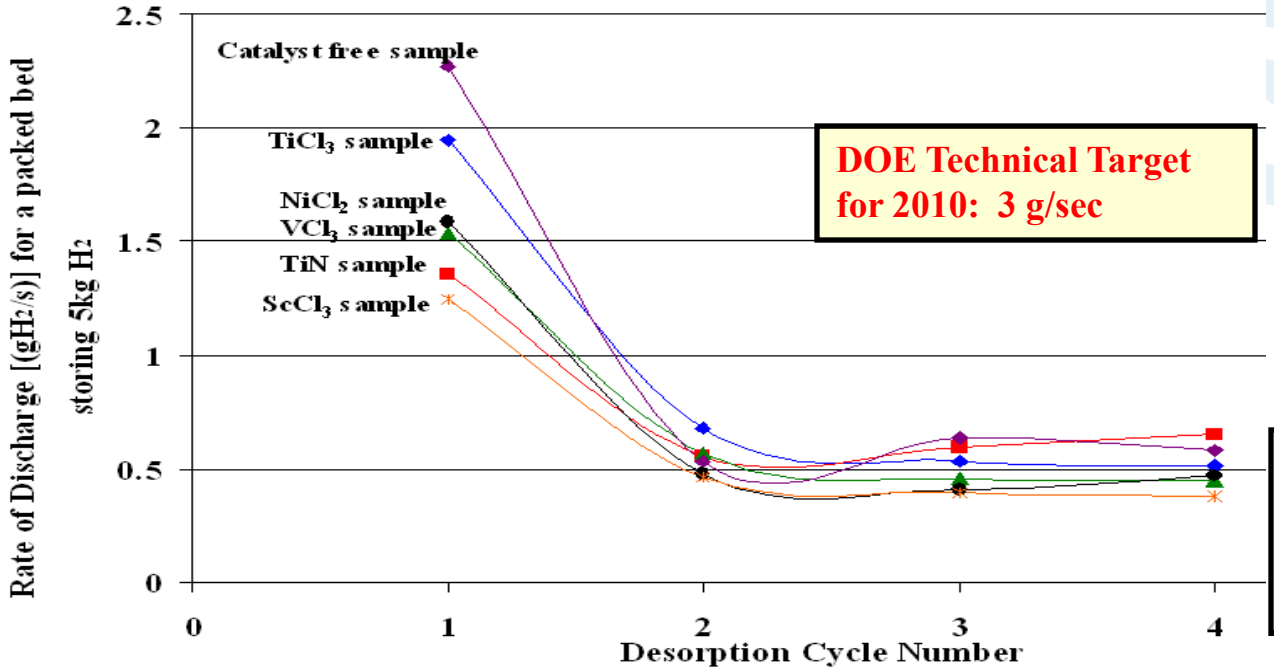
- **Rates of hydrogen charge are an order of magnitude lower than the DoE technical target**
- **TiN continues to significantly increase absorption capacity through four cycles while the halide catalysts continue to decrease**
  - Metathesis reaction between $LiNH_2$ and $M_{tr}Cl_3$ hinders hydrogen absorption through the loss of essential nitrogen

SRNL

METAL HYDRIDE CENTER OF EXCELLENCE

Technical Accomplishments and Progress – Average Rate of Hydrogen Discharge [gH_2/s]

Average Rate of Hydrogen Discharge for a packed bed storing 5kg H_2



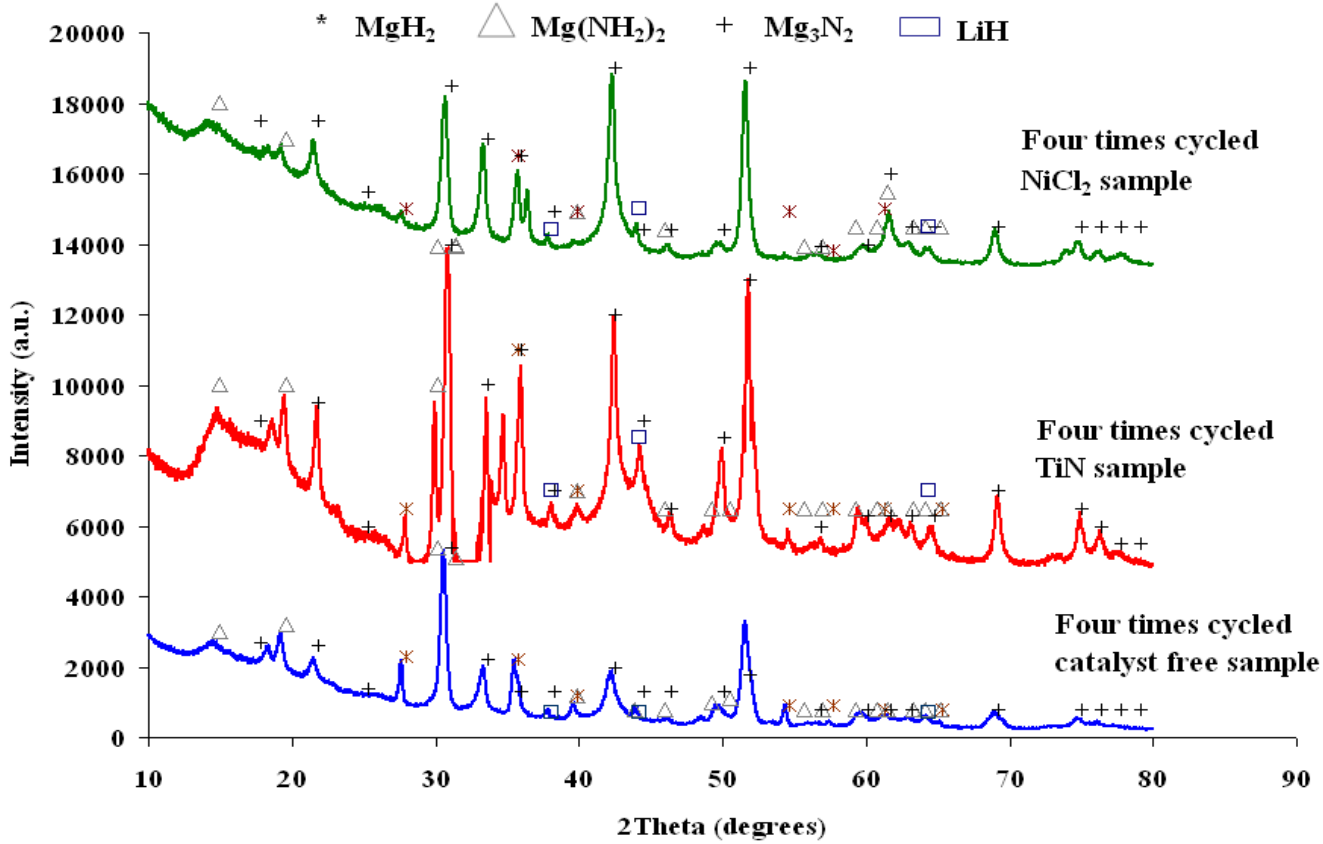
Discharge conditions: 260°C into 1 bar for 6 hours

- **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 $LiNH_2$ and $M_{tr}Cl_3$: $LiNH_2 + TiCl_3 \rightarrow LiCl + Ti(\text{unknown state}) + NH_2$

SRNL

METAL HYDRIDE CENTER OF EXCELLENCE

Technical Accomplishments and Progress – XRD Analysis of four cycled 1:1 $LiNH_2$:MgH_2 $^{w}/_{w/o}$ catalyst

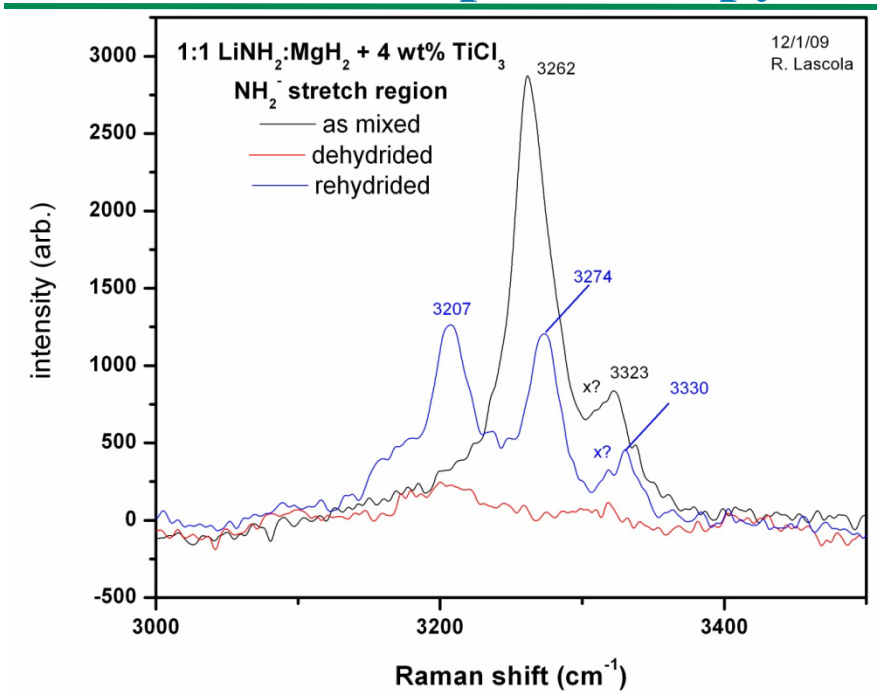


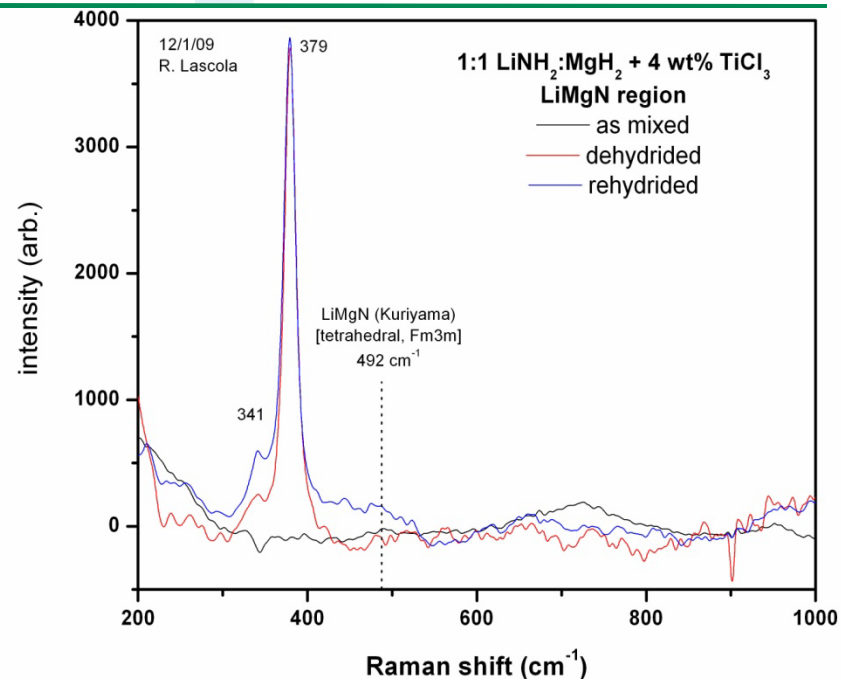
- $Mg(NH_2)_2$, MgH_2 and LiH identified showing LiMgN ↔ LiH + ½ MgH_2 + ½ $Mg(NH_2)_2$
- Mg_3N_2 also identified, possibly forming from $Mg(NH_2)_2 + 2MgH_2 \rightarrow Mg_3N_2 + 4H_2$ [ΔH = 15 kJ/mol H_2 at 500K, Akbarzadeh, *et al., Adv Mat.* **19 (2007)** 3233] or $LiMgN + H_2 \rightarrow LiH + Mg_3N_2$

SRNL

METAL HYDRIDE CENTER OF EXCELLENCE

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_3N_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 ($I2_13$) 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 $Mg(NH_2)_2$**

SRNL

METAL HYDRIDE CENTER OF EXCELLENCE

Conclusions for Task I - LiMgN

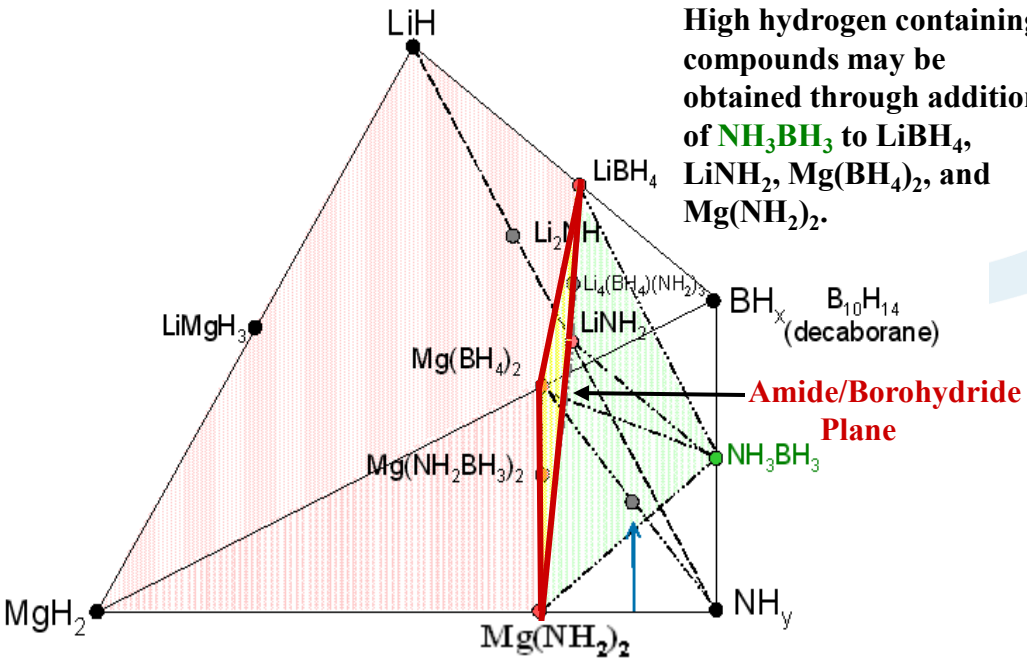
- **Catalyst composition has a significant effect on H_2 and NH_3 discharge temperatures, cyclic capacity and sorption rates**
  - **Uncatalyzed**
    - Showed a decrease in hydrogen discharge rate over four desorption cycles
      - Rate of conversion from $LiNH_2 + MgH_2 \rightarrow LiMgN > LiH + ½\ MgH_2 + ½\ Mg(NH_2)_2 \rightarrow LiMgN$
  - **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 $LiNH_2$ and $M_{tr}Cl_3$
- **Sorption rates are an order of magnitude less than the 2010 DOE goals.**

SRNL

METAL HYDRIDE CENTER OF EXCELLENCE

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 $M(BH_4)$ 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

SRNL

METAL HYDRIDE CENTER OF EXCELLENCE

Relevance –

Competing Systems of Mixed Amide/Borohydride

Di-Anionic Complexes: $M(BH_4)^-(NH_2)^-$

- Synthesis of $Li_4(BH_4)(NH_2)_3$ and desorption >10wt% H_2 at 250-350 ^oC, *Pinkerton et al., 2006*
- Synthesis of new $Li_4(BH_4)(NH_2)_3$ [$Li_4BN_3H_{10}$], by mechanco-chemical milling of $LiNH_2$ and $LiBH_4$, *Chater 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 ΔH ~13 kJ/mol H_2, *Siegel et al., 2007*
- Evidence of B-H and N-H bond destabilization as compared to the parent $LiBH_4$ and $LiNH_2$ structures, *Yang et al., 2007*
- Impact of Stoichiometry on Hydrogen Storage Properties of $LiNH_2 + LiBH_4 + MgH_2$ Composites,

  Sudik et al., 2009 (Optimal Ratio 3:1:1.5 for H_2 Desorption and Reversible at Ratio 2:1:1 and 2:0.5:1)

Ammoniated Borohydride Complexes: $M(BH_4)^-\cdot NH_3$

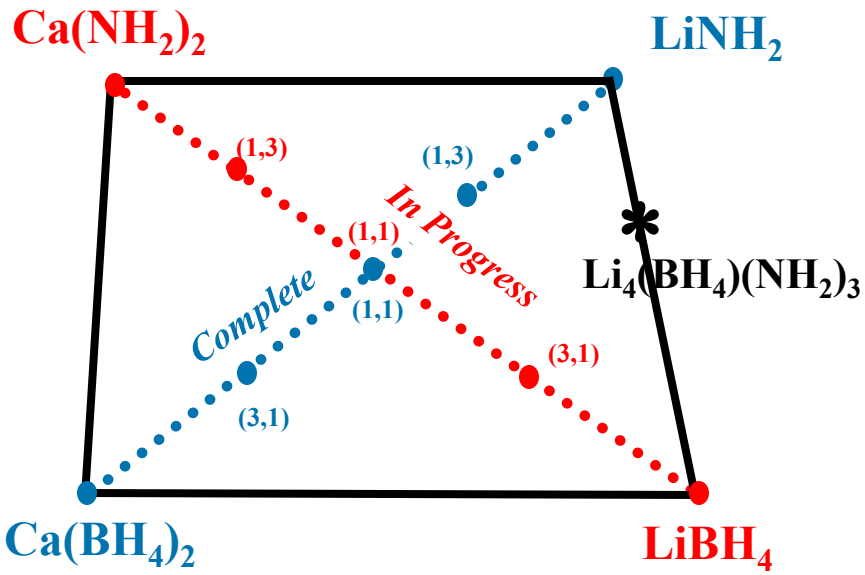
- Ammonia complex of magnesium borohydride, *Soloveichik et al., 2008*

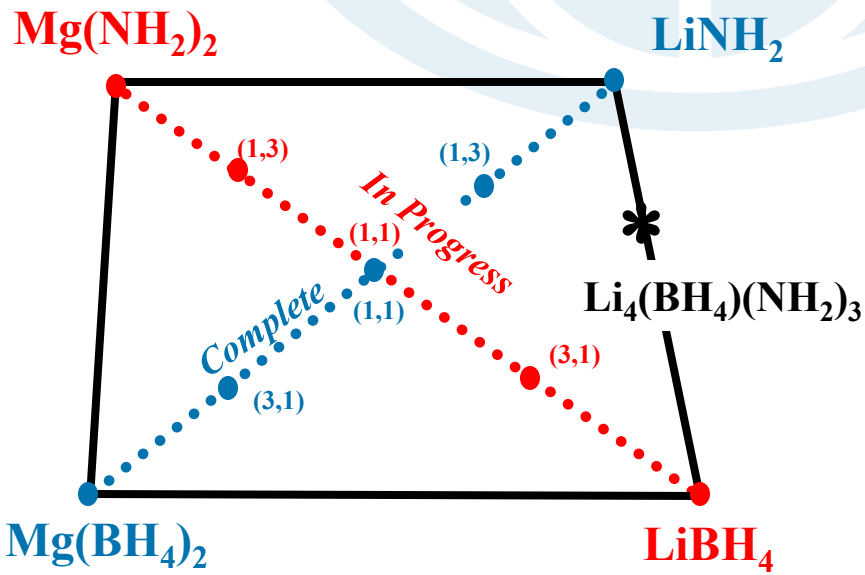
Amidoborane Complexes: $M(NH_2)^-\cdot BH_3$

- Calcium amidotrihydroborate as hydrogen storage material, *Burrell et al., 2007*

Approach – Experimental Plan

Amide/Borohydride Plane of Quaternary Phase Diagram





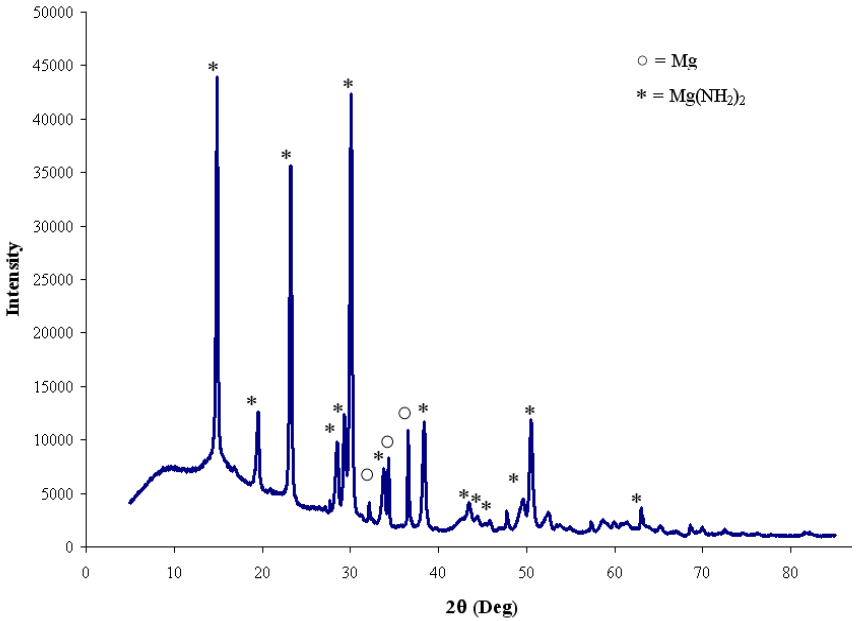
- Mixtures are formed using planetary ball-milling techniques.
- Identify isothermal/isobaric sorption properties of mixed phases using Sievert's apparatus.
- XRD analysis after ball milling process and after hydrogenation and dehydrogenation.
- TGA-RGA to determine composition of hydrogen during dehydrogenation.

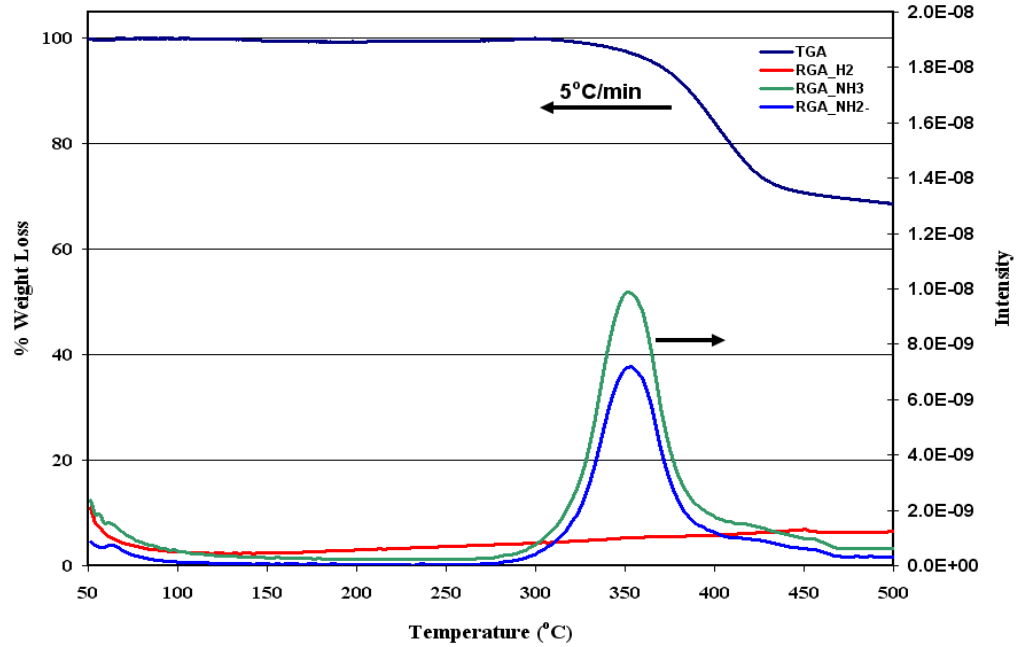
SRNL

METAL HYDRIDE CENTER OF EXCELLENCE

Technical Accomplishments and Progress – Synthesis of $Mg(NH_2)_2$

$$Mg\ (powder) \xrightarrow[110^{o}C,\ 120\ hr]{2NH_{3(g)}\ (120\ psi)} Mg(NH_2)_2 + H_2$$





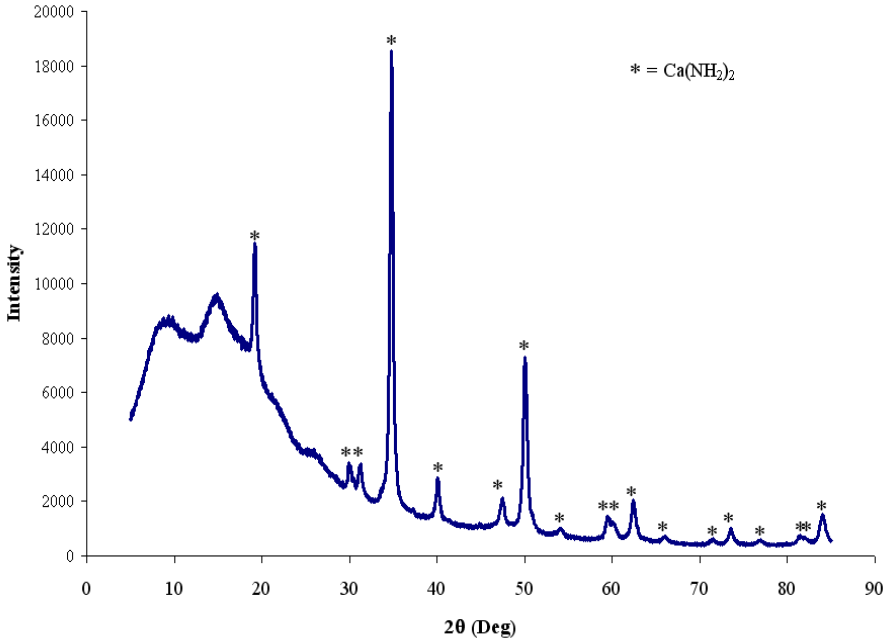
- XRD confirmed ~ 95% pure $Mg(NH_2)_2$ by simple addition of ammonia to magnesium powder and heat in a high pressure reactor vessel.
- Theoretical H_2 capacity is ~ 7.1 wt%
- TGA shows a total weight loss of more than 30%.
- RGA shows a disproportionate amount of NH_3, NH_2^- to H_2.

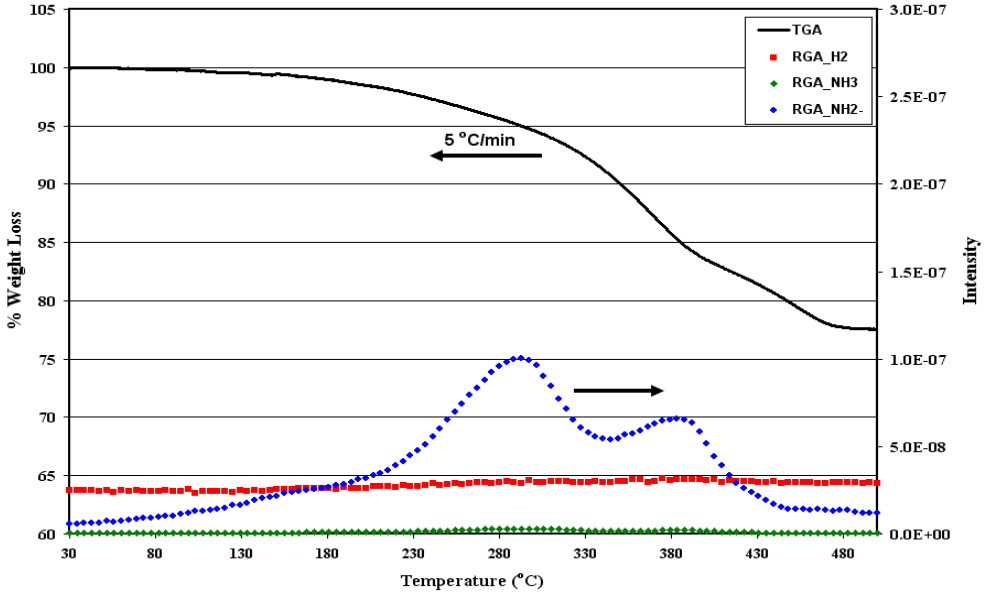
SRNL

METAL HYDRIDE CENTER OF EXCELLENCE

Technical Accomplishments and Progress – Synthesis of $Ca(NH_2)_2$

$$\text{Ca (granule)} \xrightarrow[25^{o}C,\ 48\ hr]{2NH_{3(g)},\ (120\ psi)} Ca(NH_2)_2 + H_2$$





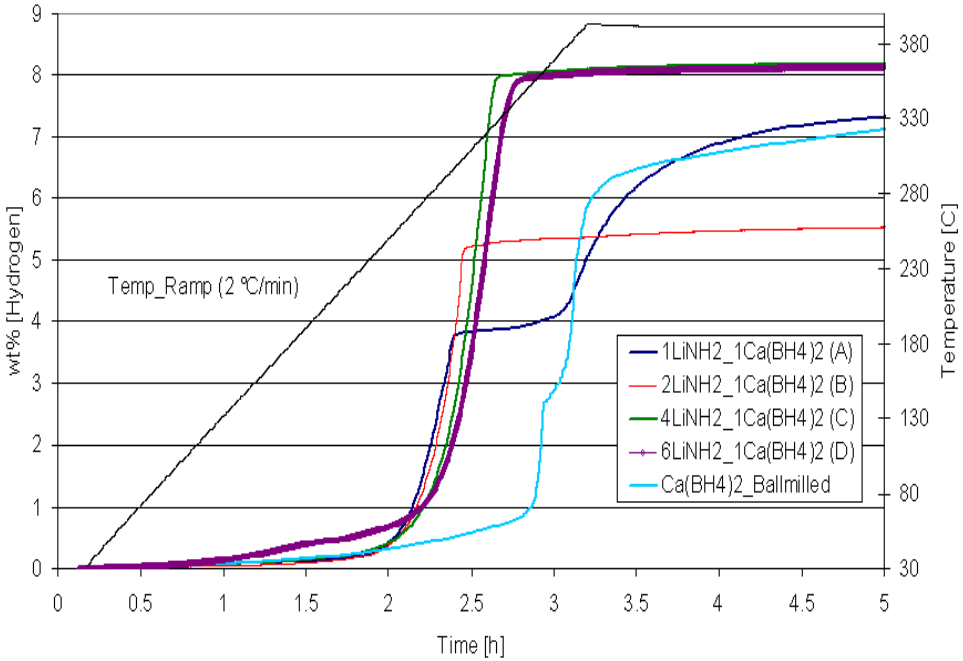
- XRD confirmed ~ 99% pure $Ca(NH_2)_2$ by simple addition of ammonia to calcium granules in a high pressure reactor vessel.
- Theoretical H_2 capacity is ~ 5.5 wt%
- Total weight loss from TGA is near 23%.
- RGA shows an immediate release of NH_2^- near RT followed by a release of hydrogen at around 130°C, and an ammonia release at 230°C.

SRNL

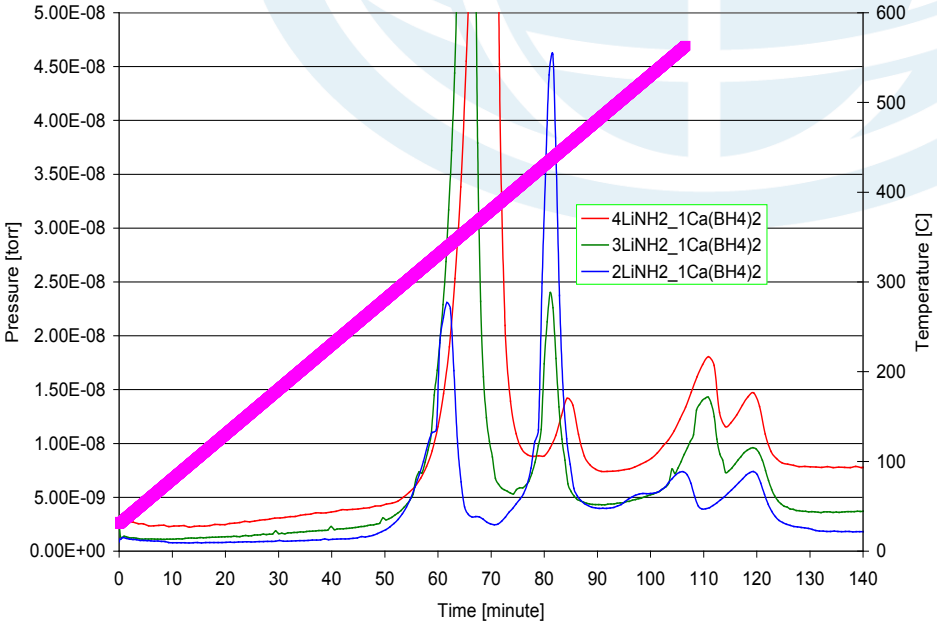
METAL HYDRIDE CENTER OF EXCELLENCE

Technical Accomplishments and Progress – $Ca(BH_4)_2$+$LiNH_2$

Sievert's TPD:



RGA:



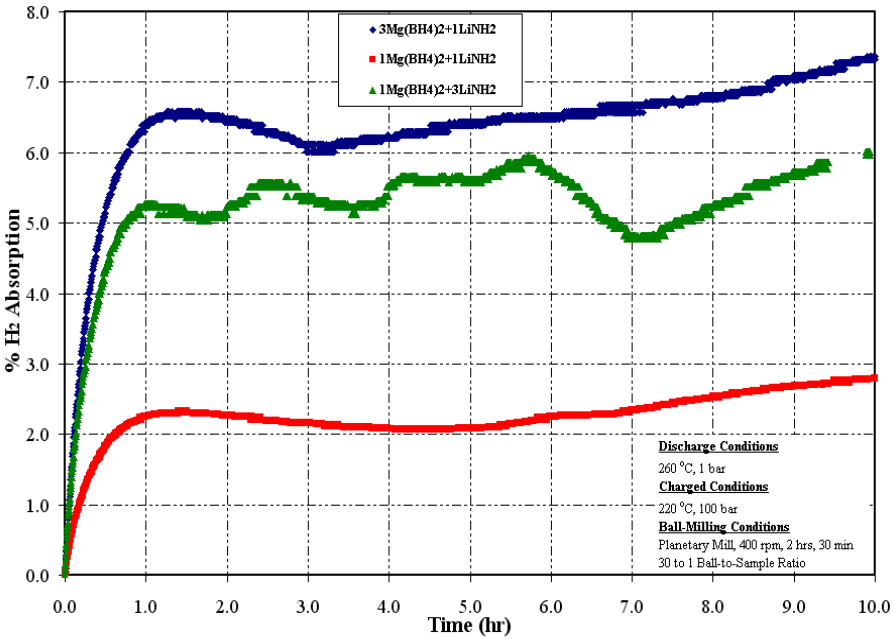
- 4 $LiNH_2$: 1 $Ca(BH_4)_2$ ratio is most effective for dehydrogenation.
- Mixtures of $Ca(BH_4)_2$ and $LiNH_2$ leads to predominately H_2 release at 150-300°C vs NH_3.
- $Li_4(BH_4)(NH_2)_3$ is the major phase for the 4$LiNH_2$:1$Ca(BH_4)_2$ mixture.

SRNL

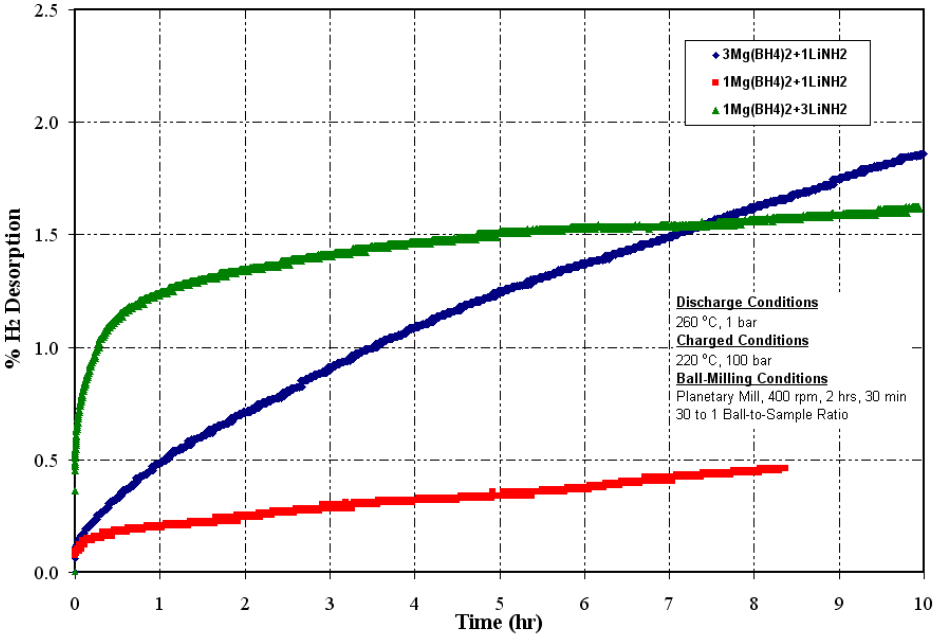
METAL HYDRIDE CENTER OF EXCELLENCE

Technical Accomplishments and Progress – $Mg(BH_4)_2$+$LiNH_2$: Isothermal Sievert's Measurements

2nd Cycle Absorption:



2nd Cycle Desorption:



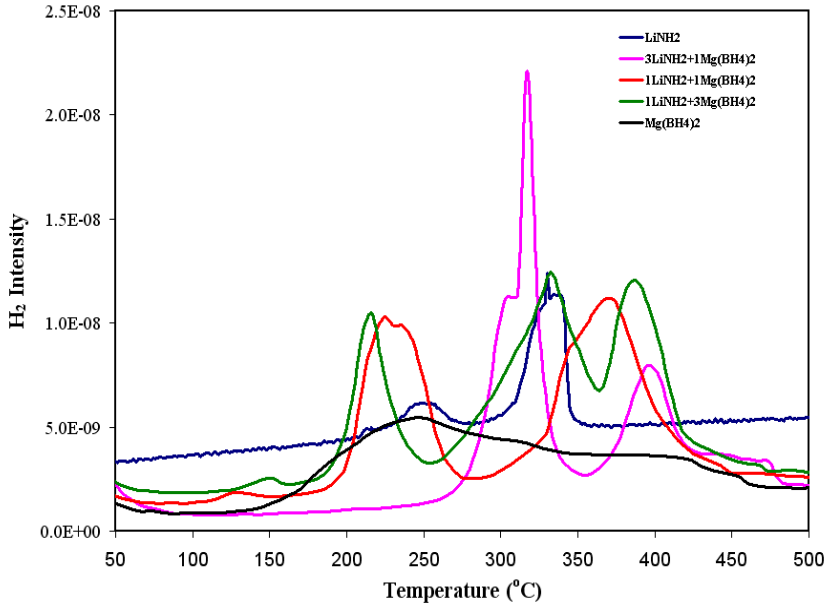
- H_2 absorption fluctuations occur due to competing desorption/absorption processes in the heterogeneous material.
- Absorption of the $3Mg(BH_4)_2 + LiNH_2$ has the maximum absorption of 7.5 wt%.
- Desorption of the $3Mg(BH_4)_2 + LiNH_2$ is incomplete at 2 wt% due to initial time constraints on the experiment for the mixture to reach steady state.
- Large H_2 absorption indicates a reversible system.

SRNL

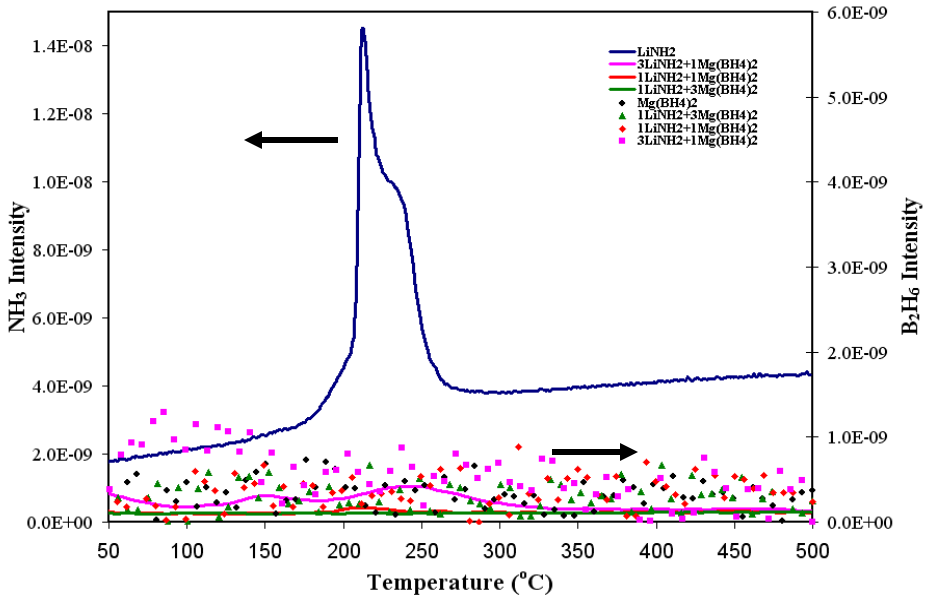
METAL HYDRIDE CENTER OF EXCELLENCE

Technical Accomplishments and Progress – $Mg(BH_4)_2$+$LiNH_2$: RGA

H_2 RGA Analysis at 5°C/min



NH_3 and B_2H_6 RGA Analysis at 5°C/min



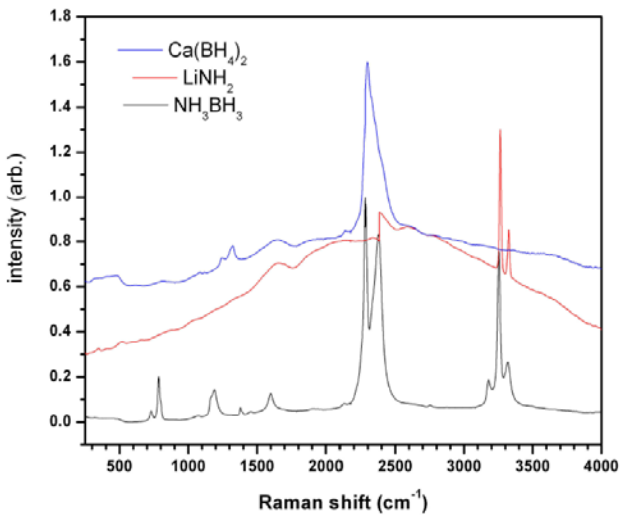
- The $Mg(BH_4)_2$ and $LiNH_2$ mixtures produce multiple H_2 releases over the temperature range shown. Initial hydrogen release (~200°C) is at lower temperature compared to $LiNH_2$ (230°C).
- Multiple H_2 releases are broad which indicates more H_2 and less NH_3 (shown on the right).
- The mixtures showed a significant reduction in ammonia release compared to $LiNH_2$. Diborane release is negligible.

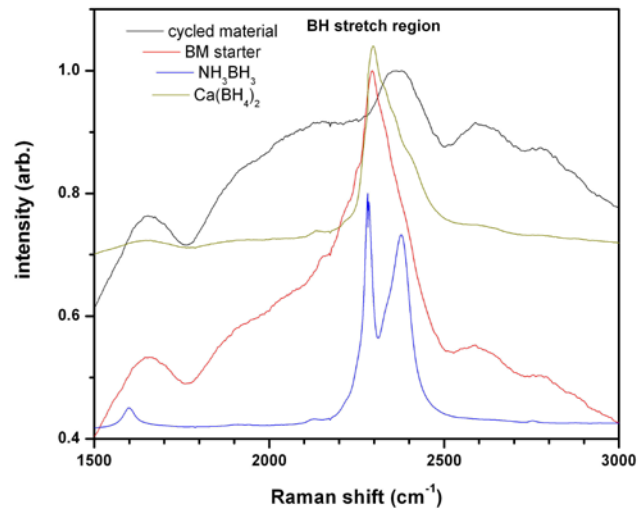
SRNL

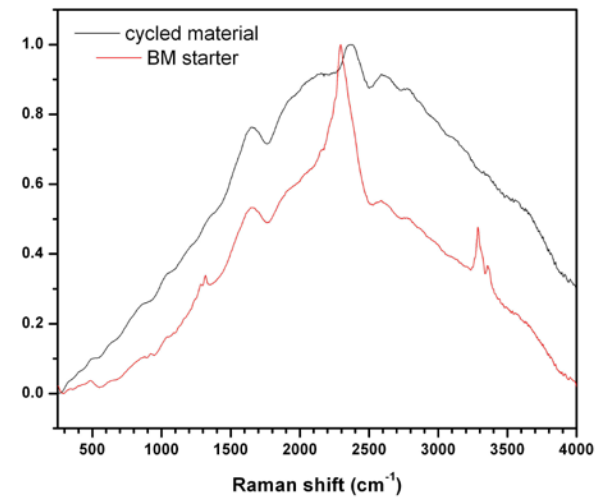
METAL HYDRIDE CENTER OF EXCELLENCE

Technical Accomplishments and Progress – Raman Spectroscopy: $Ca(BH_4)_2$+$LiNH_2$+NH_3BH_3

$$Ca(BH_4)_2 + LiNH_2 + NH_3BH_3 \xrightarrow[\text{3 hr}]{\text{BM, 200 rpm}} ?$$







* Cycle Conditions: (d) 260°C, 1bar, 12 hr
(c) 220°C, 100 bar, 12 hr

- **spectra of the 3 starting materials look pretty much like the literature/reference spectra**
- **spectra of the ball-milled starting materials suggests 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 $Ca(BH_4)_2$ (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**

SRNL

METAL HYDRIDE CENTER OF EXCELLENCE

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_3BH_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 $150^{O}C$ for the mixture of $Ca(BH_4)_2$:$LiNH_2$:NH_3BH_3.

SRNL

METAL HYDRIDE CENTER OF EXCELLENCE

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, $LiBH_4$, KH,.…)
  - Analyze the purity of the discharged H_2 as a function of temperature using FTIR
- **Task II**
  - Complete a study of $Ca(NH_2)_2$ and $Mg(NH_2)_2$ ball-milled with $LiBH_4$ 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.