Amide and Combined Amide/Borohydride Investigations

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Savannah River National Laboratory

May 11, 2011

Project ID #: ST070

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Overview

Timeline

- Start: 06/10
- End: 09/11
- Percent Complete: 63%

Barriers Addressed

- A. Charge/Discharge Rates
- E. System Weight & Volume
- P. Understanding Chemisorption

Budget

- Funding received in FY10:
  - $350K
- Funding received in FY 11:
  - $100K

Partners

- H. zur Loye – University of South Carolina
- Hydrogen Storage Engineering CoE Partners

Relevance – Objectives and Motivation

- 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.
- Modification of LiMgN system through the addition of alkali earth metals in the form of $LiMg(NH_2)_x(BH_4)_y$, for the possible formation of **high hydrogen content** bimetallic hydrogen storage systems.
- Prepare a **database** for use by the Hydrogen Storage Engineering Center of Excellence (**HSECoE**) to assess the utility of LiMgN in a **prototype system**.

Relevance – LiMgN as a Hydrogen Storage Material

Overall rxn: $LiNH_2 + MgH_2 \rightarrow LiMgN + 2H_2$ $\Delta H_{rxn} = 32\ kJ/molH_2$[1]

- Identified using DFT calculations as potentially reversible with a theoretical H_2 gravimetric storage capacity of **8.2 wt%**[1]
- 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[2]
- The reversible hydrogen absorption reaction involved:
  - **8 wt%** observed experimentally at 160°C and 140 bar

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

- Dehydrogenation is proposed to proceed through an intermediate step

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

- Accelerated reversibility has been observed using 4 wt% $TiCl_3$ dopant[2]

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[1] Alapati *et al.*, *Phys. Chem. Chem. Physics.* 9 (2007) 1438
[2] Lu *et al.*, *J. Phys. Chem. C* 111 (2007) 12129

Approach – LiMgN Experimental Plan

- Perform isothermal and isobaric kinetic studies under controlled reaction conditions
- Explore effect of milling technique and modifier composition
  - V_2O_5 and Fe_2O_3 with composition = 1.5 mol%
  - More current modifiers explored include KH (4 mol%) and $LiBH_4$ (1.5 mol%)
- XRD analysis performed on as-milled material and after hydrogenation/dehydrogenation cycles
- TGA-RGA to determine gas composition during dehydrogenation
- DSC performed on as-milled and cycled material to determine enthalpy of 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 Spex milling techniques
- Fritsch milled for 2 hours at 500 rpm with rotational direction reversed every 30 minutes, Spex milled for 2 hours with a period of rest every 30 minutes

Starting Discharge Procedure

- Reactor placed under high pressure (~ 110 bar) and heated to desired temperature
- Manifold controlled so that the nominal backpressure is equal to 1 bar between the reactor and reservoir.
- Standard discharge condition: 200°C/1 bar/ 6 hrs

Recharge Procedure

- Reactor placed under active vacuum and heated to desired temperature
- Reservoir is pressurized to desired pressure and the reactor is opened.
- Standard charge condition: 180°C/ 100 bar/ 6 hrs

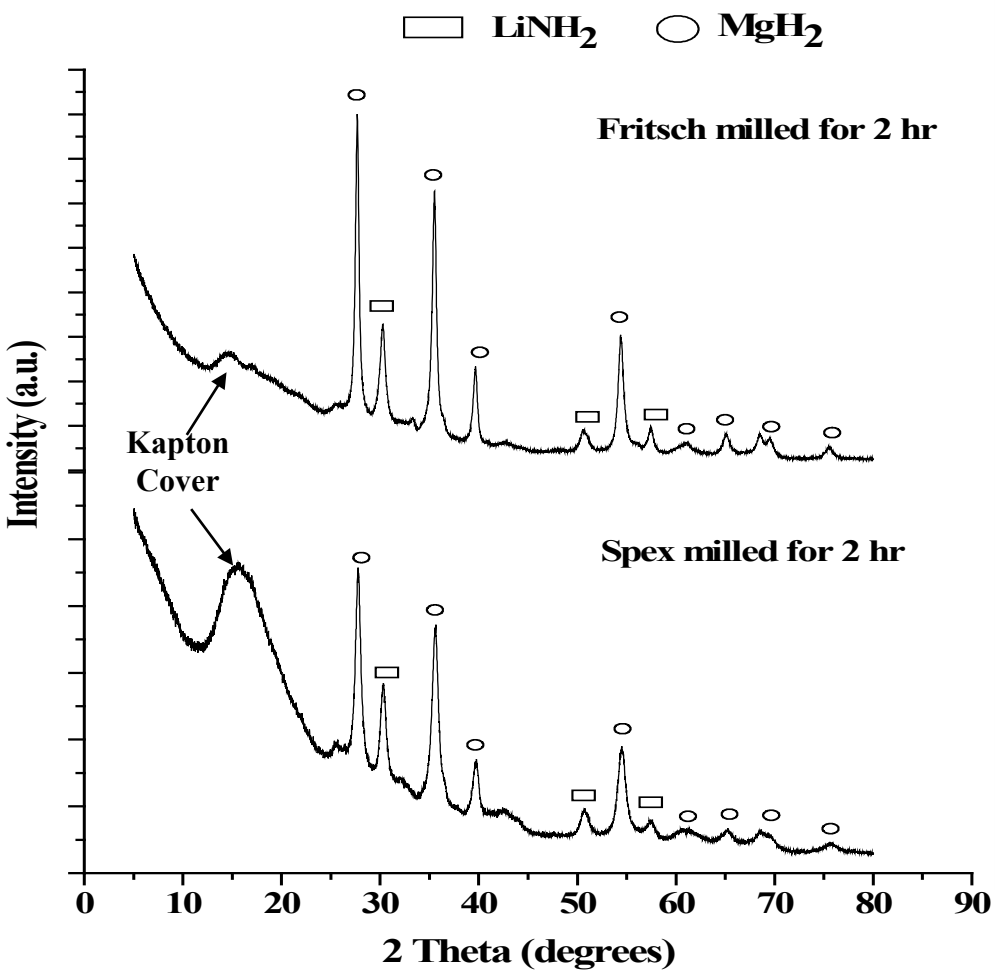
TGA-RGA Procedure

- Heating rate at 5°C/min from RT to 400°C
- Looked at mass 2 (H_2), 16 (NH_2^-), 17 (NH_3/OH) and 18 (H_2O) in RGA

DSC Procedure

- Heating rate at 2°C/min from RT to 400°C

Technical Accomplishment and Progress –
XRD Analysis as function of milling technique w/o modifiers

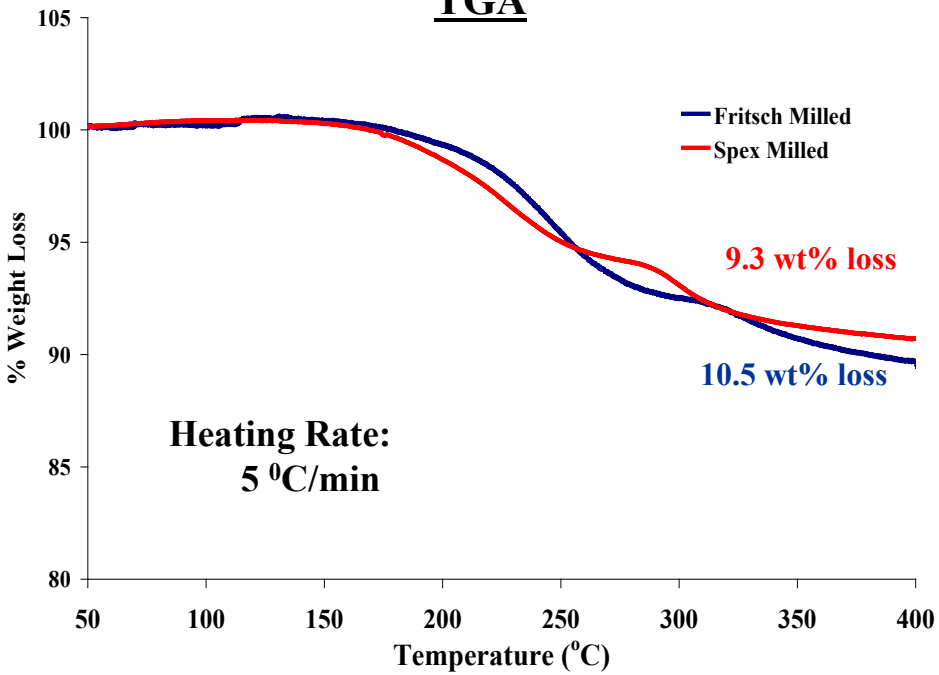


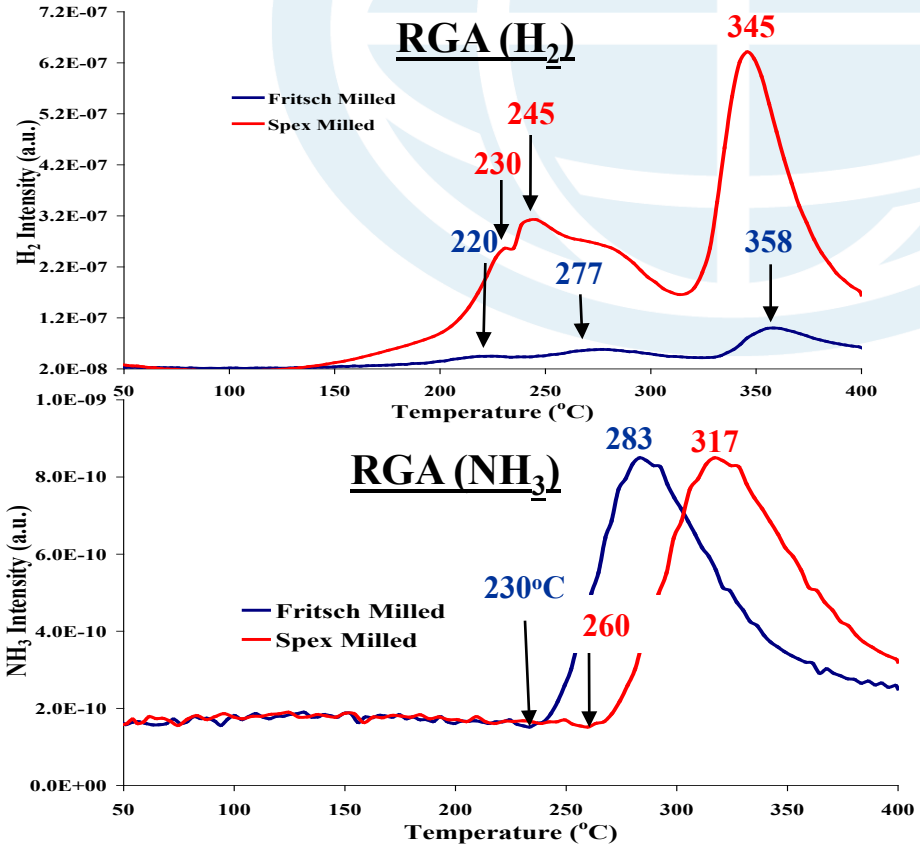
MgH_2 and $LiNH_2$ patterns identified

- No indication of reaction or decomposition of starting materials resulting from milling
- The pattern of the Spex milled sample did reveal peak broadening and lower intensity indicating a decrease in particle size and an increase in defects
- The particle size was calculated from XRD patterns, the average MgH_2 particle was reduced from 35.3 nm to 23.6 nm (33% reduction).
- These results are similar to those observed by Liu *et al.* after milling for 2 hours at 500 rpm on the Fritsch mill and Lu *et al.* after milling for 30 minutes on the Spex mill

Technical Accomplishment and Progress –

TGA/RGA results as a function of milling technique w/o modifiers





- Hydrogen desorption for the Fritsch-milled sample started at approximately 135°C; Spex-milled material started at 120°C. Reduction in temperature is attributed to the smaller particle size which resulted in increased surface area and lower surface activation energy
- Difference in max ammonia release attributed to the slow reaction kinetics between MgH_2 and NH_3 from decomposing $LiNH_2$, the decomposition of unreacted $LiNH_2$ and/or the self-decomposition of $Mg(NH_2)_2$

- Spex milling increased the ammonia release temperature. It also reduced the amount of ammonia released, further indicating the importance of particle size on desorption kinetics.

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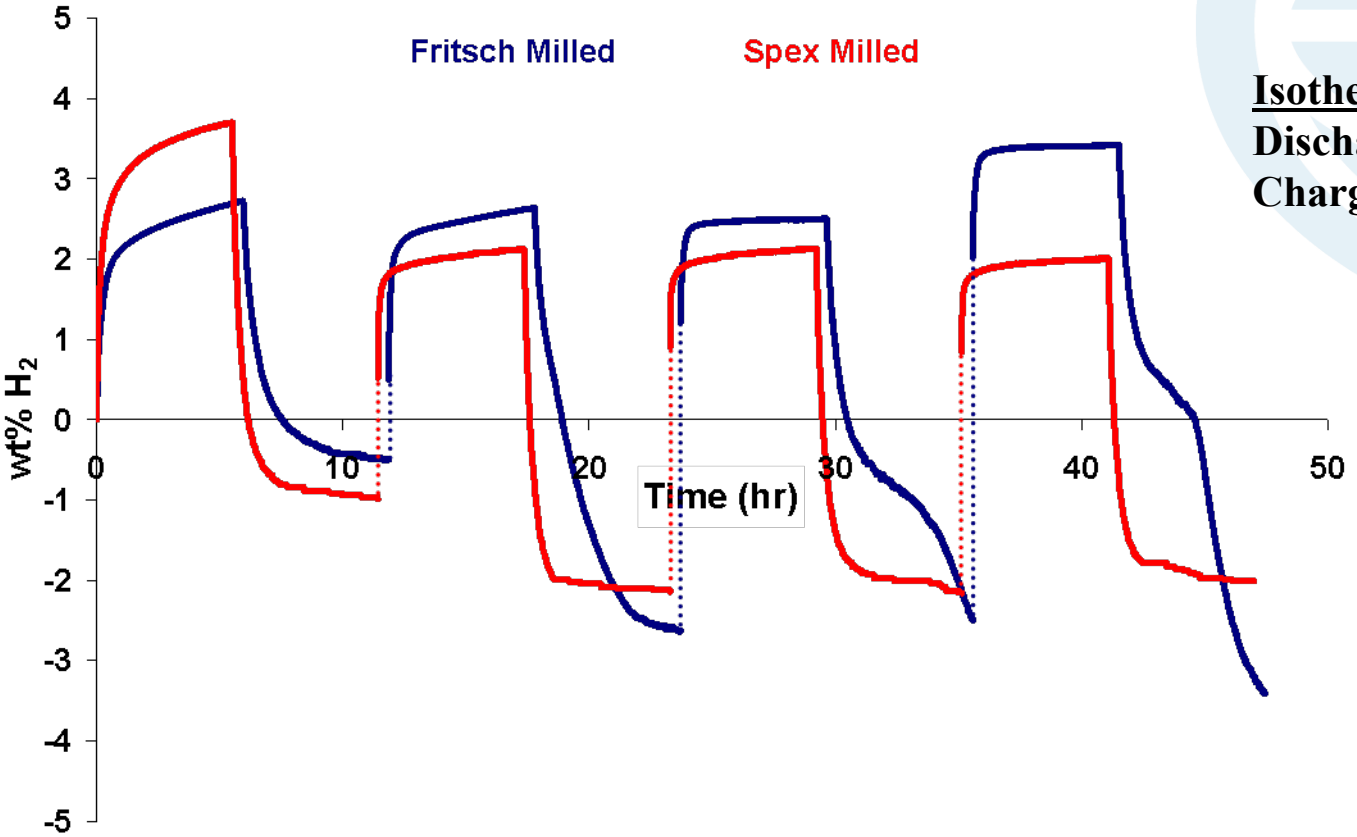
Technical Accomplishments and Progress –
Milling technique dependence on H_2 Capacity over 4 cycles



Isothermal Cycling Conditions
Discharged: 200°C/1 bar/6 hr
Charged: 180°C/100 bar/6 hr

- **Spex milling provided a more constant H_2 capacity over 4 cycles and a faster charging rate, which is due to the homogeneity of the material formed during milling supported by XRD analysis that revealed finer crystal size.**
- **Fritsch milling promotes an increase in H_2 capacity starting with the 4th cycle.**

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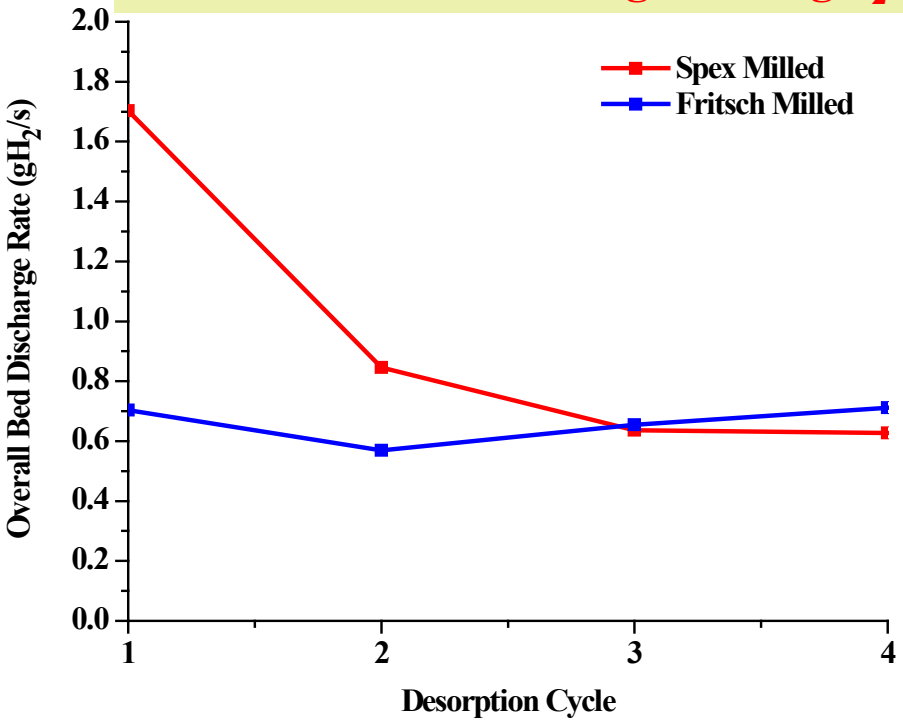
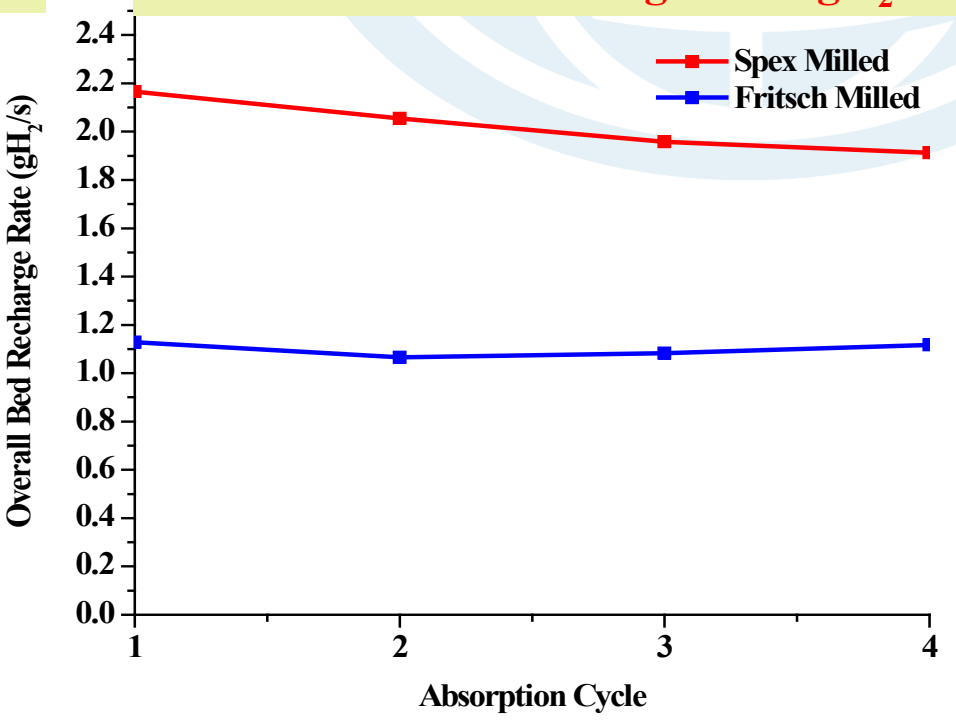
Technical Accomplishment and Progress – Discharge/Recharge Rate Dependence on Milling Technique

- Assumed 5 kg H_2 Capacity and average rate over 30 mins
  - Desorption: 200°C/1 bar/ 6hr
  - Absorption: 180°C/100 bar/ 6hr

DOE 2015 Technical target = 1.6 gH_2/s



DOE 2015 Technical target = 25 gH_2/s



- Discharge rate is initially 2x faster for Spex milled material due to smaller particle size, but reduces to the discharge rate of Fritsch milled material by the 3rd cycle.
- Average bed recharge rates over 4 isothermal cycles showed strong dependence on milling technique w/the bed recharge rate being 2x greater for Spex milling.

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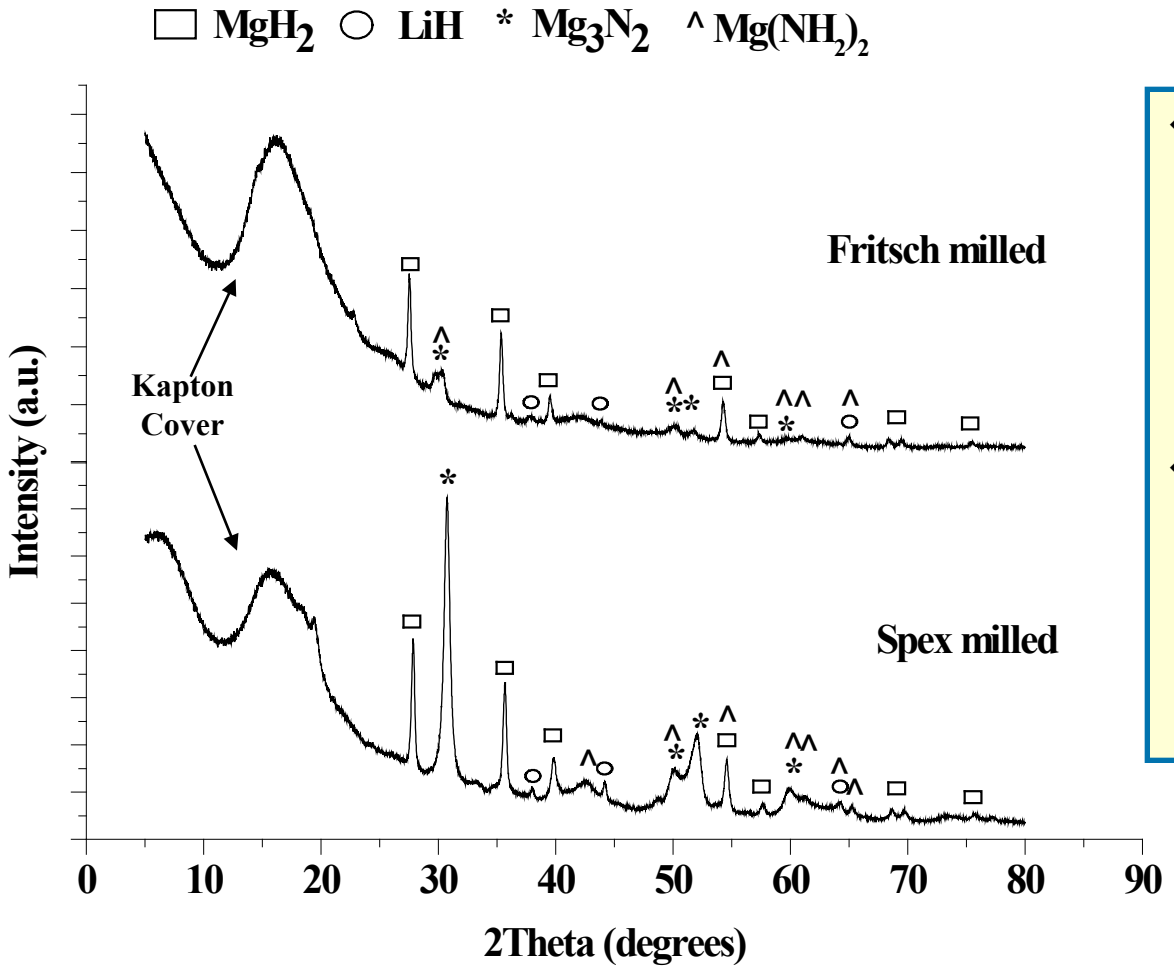
Technical Accomplishment and Progress – XRD as a function of milling technique (4th cycle)

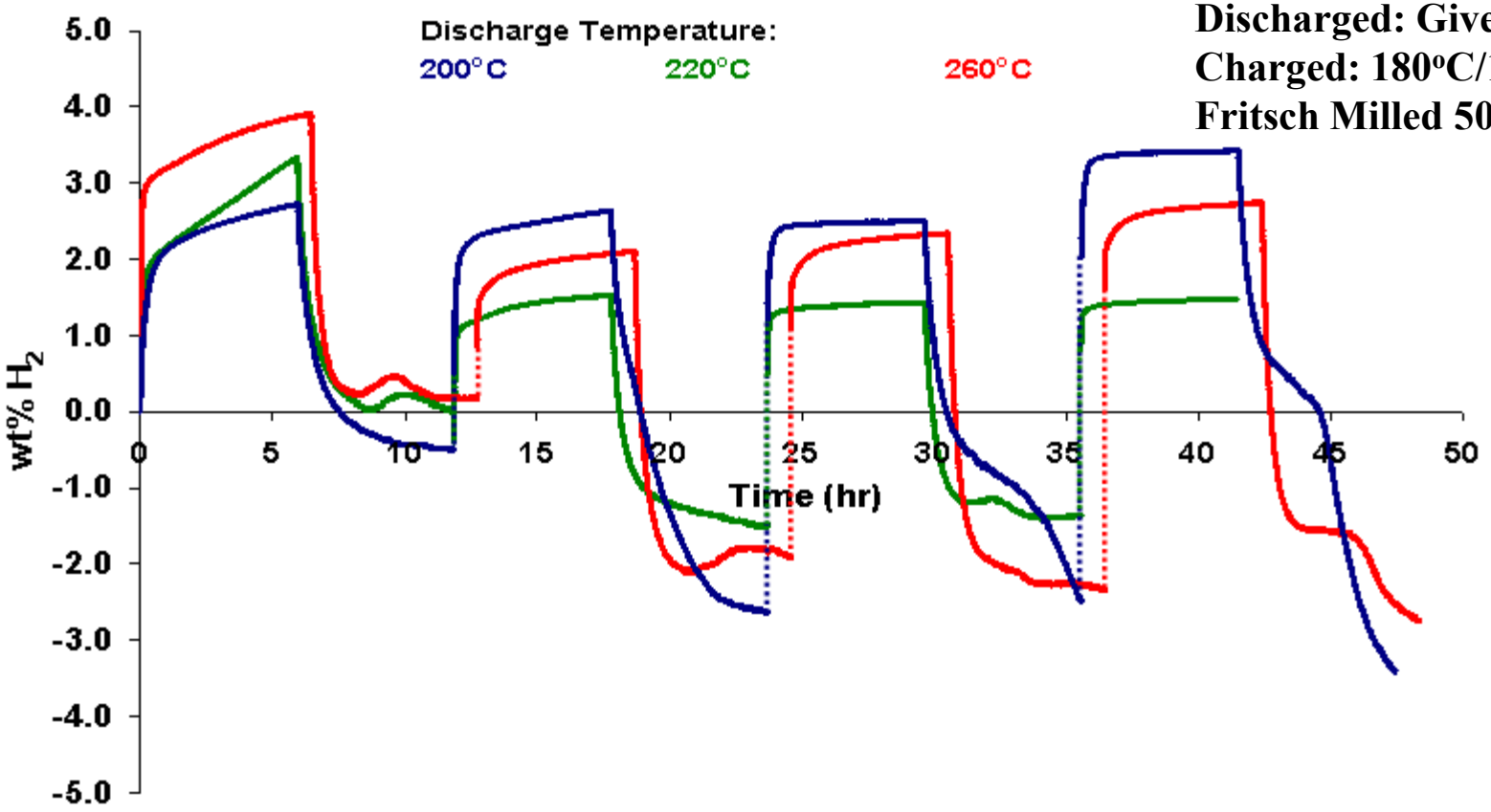
Charged State XRD:



- Shows that Mg_3N_2 and MgH_2 were the predominate products accompanied by LiH formation.
  - Presence of Mg_3N_2 could indicate incomplete rehydrogenation under 100 bar at 180°C.
- $Mg(NH_2)_2$ not differentiated from Mg_3N_2
  - Raman: N-H stretching bands at 3273 $cm^{-1}$and 3326 cm^{-1} were observed, which are consistent with $Mg(NH_2)_2$ formation

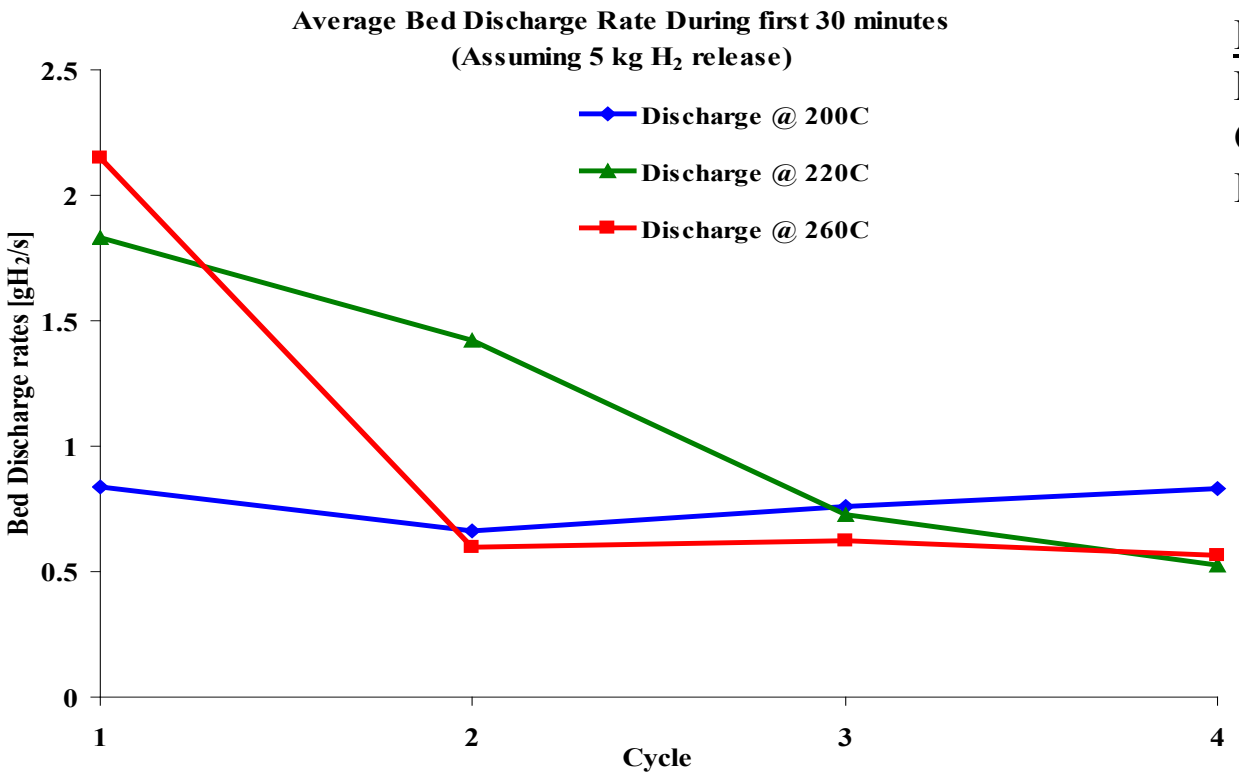
Technical Accomplishments and Progress – Temperature dependence on H_2 Capacity (4 cycles)

Isothermal Cycling Conditions
Discharged: Given T/1 bar/6 hr
Charged: 180°C/100 bar/6 hr
Fritsch Milled 500 rpm, 2 hrs



- **The differences in desorption/absorption capacity at 200°C and 260°C may be due to differences in sorption pathways at low and high temperatures such as the formation LiMgN versus Mg_3N_2+Li_3N.**

Technical Accomplishment and Progress – Discharge Rate Temperature Dependence



Isothermal Cycling Conditions
Discharged: Given T/1 bar/6 hr
Charged: 180°C/100 bar/6 hr
Fritsch Milled at 500 rpm, 2 hrs

- **Average bed discharge rate over 4 isothermal cycles showed strong dependence on discharge temperature**
  - Cycle at a 200 C discharge temperature resulted in relatively constant discharge rate over 4 cycles
  - Cycling at 220°C and 260°C resulted in significant reduction in bed discharge rate after the first discharge, which was attributed to formation of Mg_3N_2 due to loss of ammonia at high temperatures

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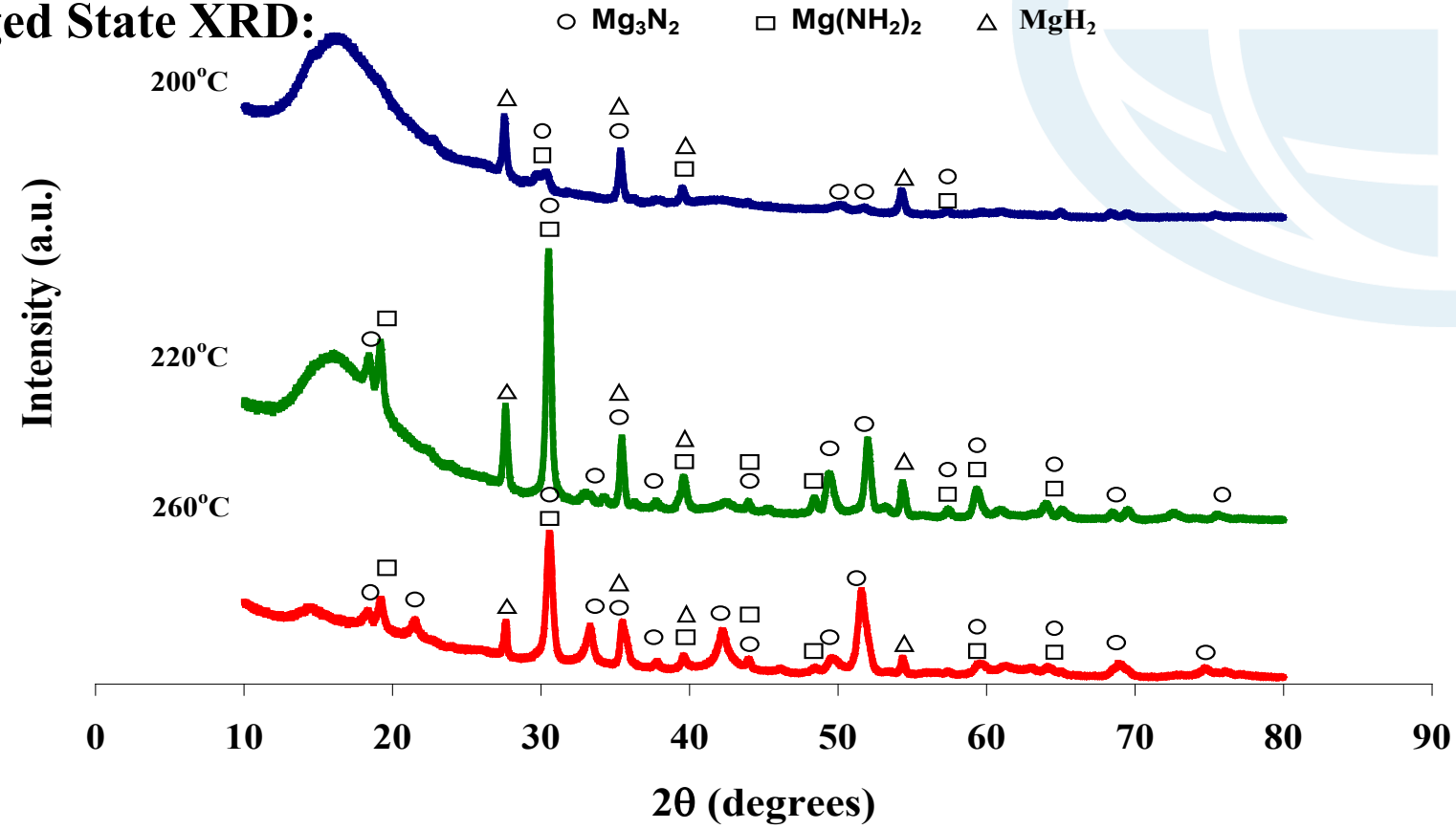
Technical Accomplishment and Progress –

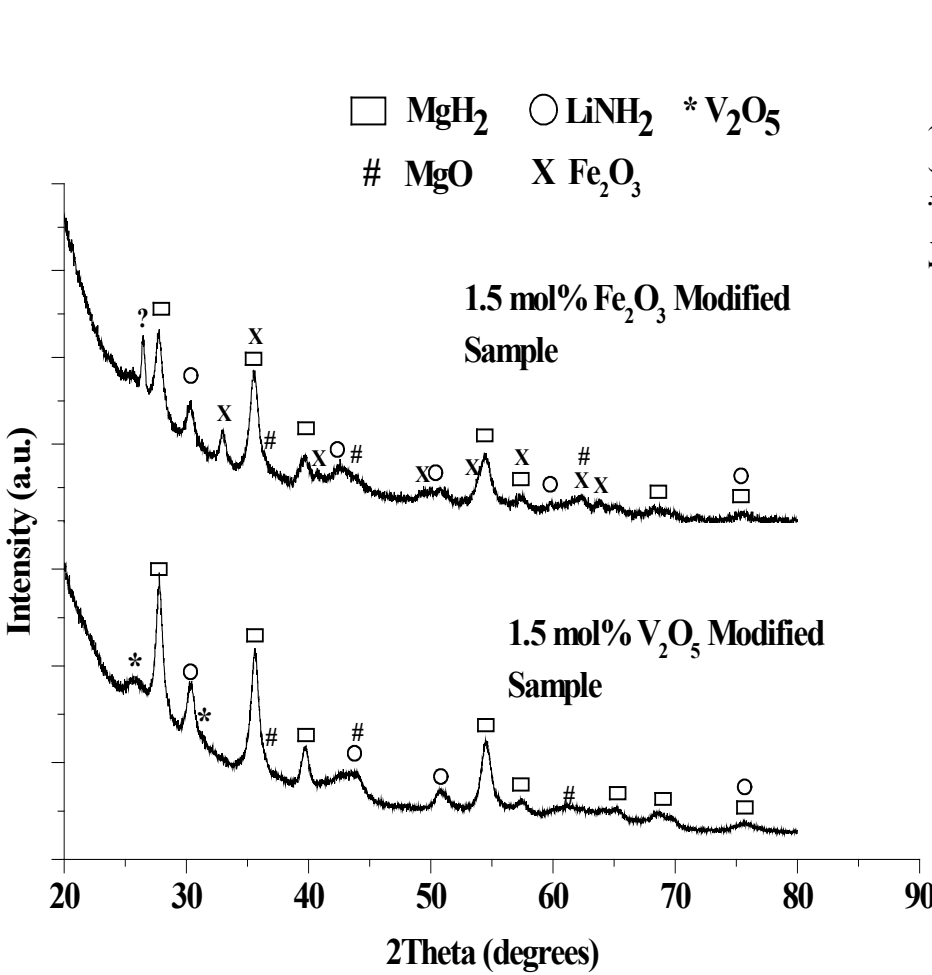
XRD analysis as a function of milling technique for 4th cycle

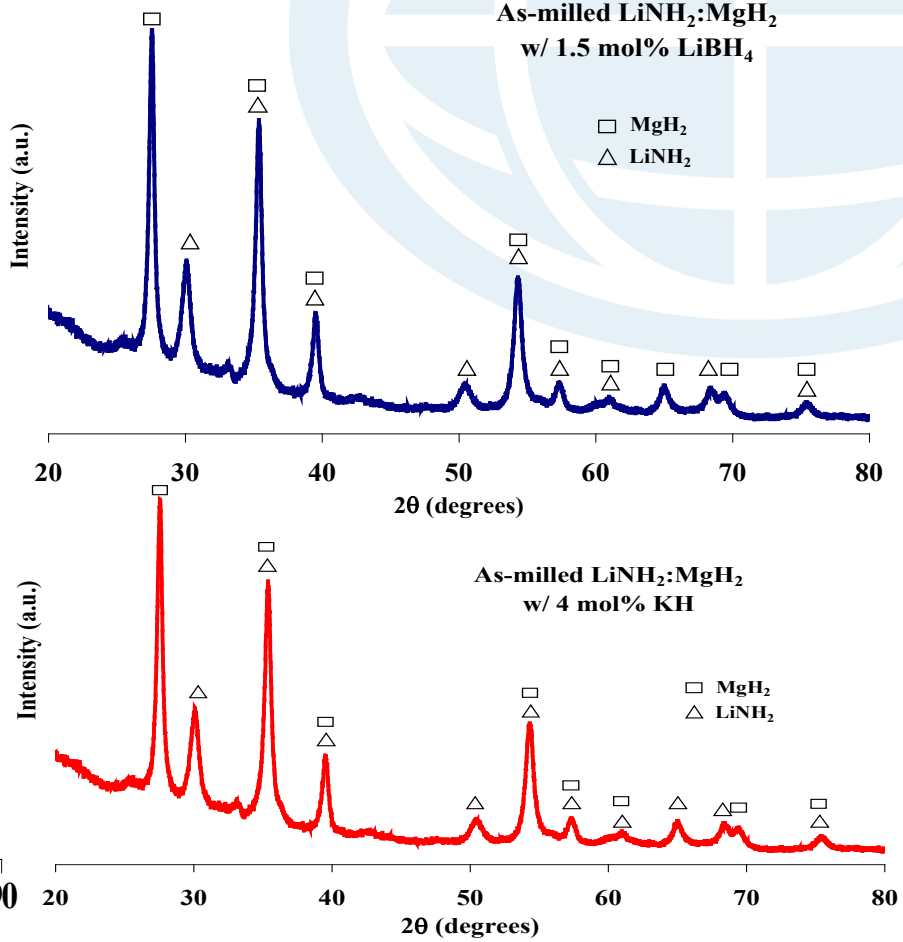
Charged State XRD:



- At 200°C, XRD results show the formation of MgH_2 and minimal Mg_3N_2 formation.
- At 220°C and 260°C, the decrease in H_2 capacity is due to enhanced Mg_3N_2 formation. The amount of $Mg(NH_2)_2$ is difficult to differentiate from Mg_3N_2 because of similar XRD patterns.

Technical Accomplishment and Progress – XRD Analysis of As-milled $LiNH_2$:MgH_2 w/modifiers





- XRD analysis shows that $LiNH_2$ and MgH_2 were the predominate products and no further decomposition was found during milling with the addition of various modifiers.

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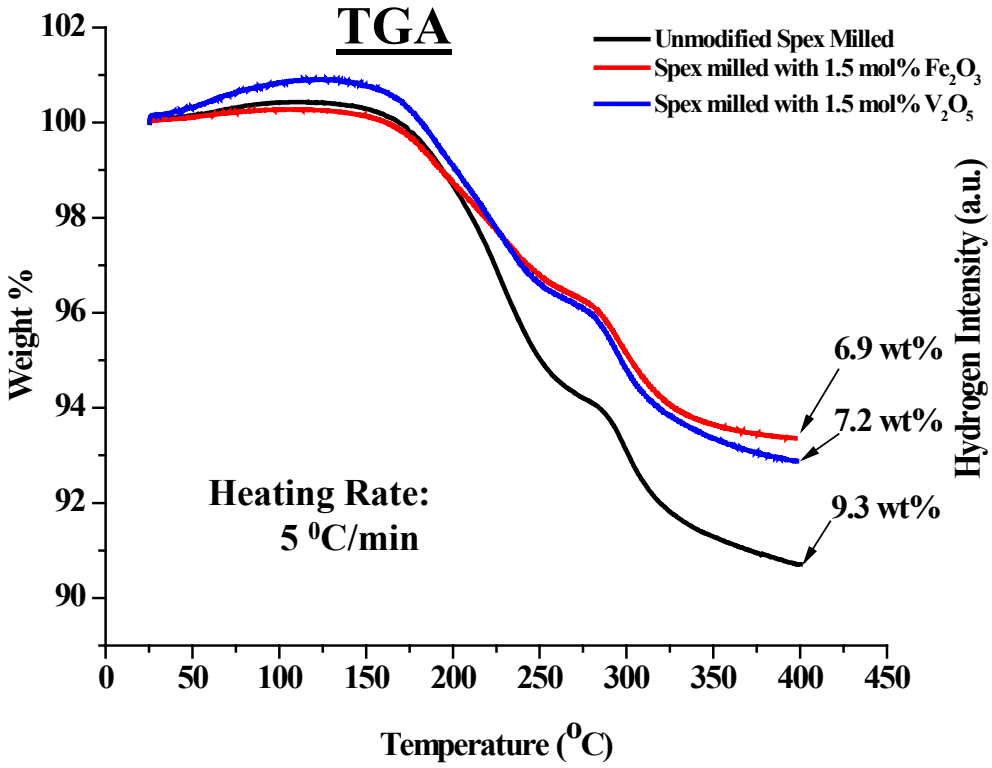
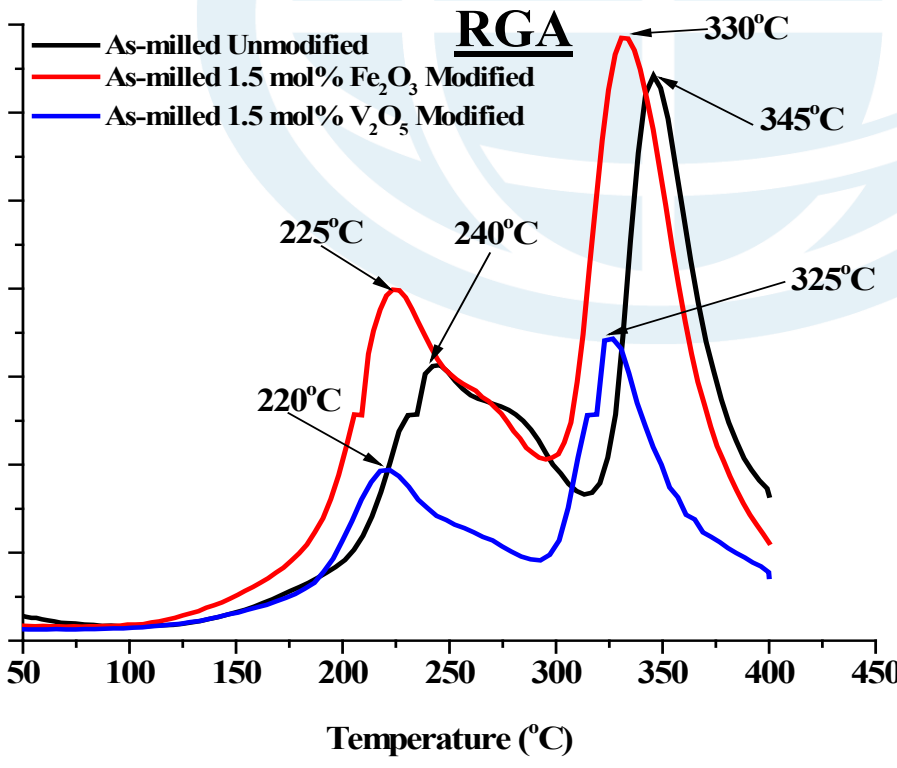
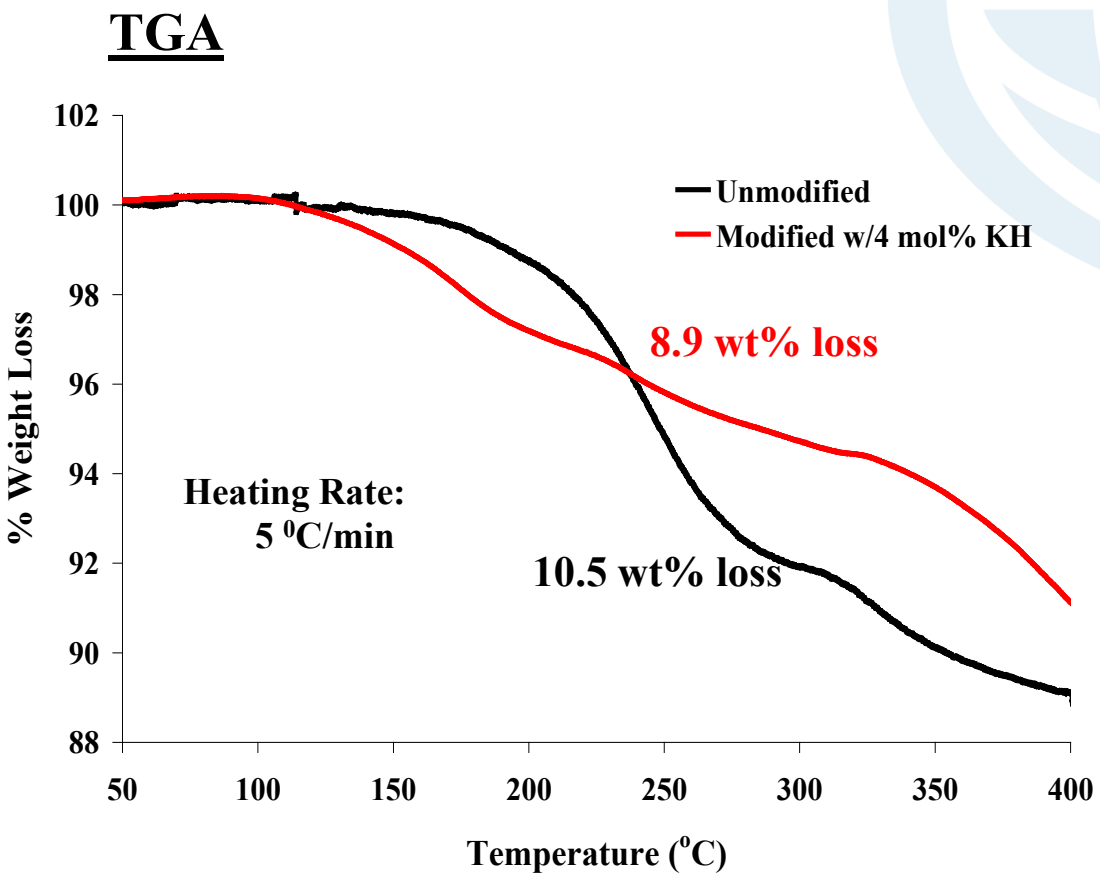
Technical Accomplishment and Progress –
TGA/RGA results of as-milled $LiNH_2$:MgH_2 w/oxide modifiers





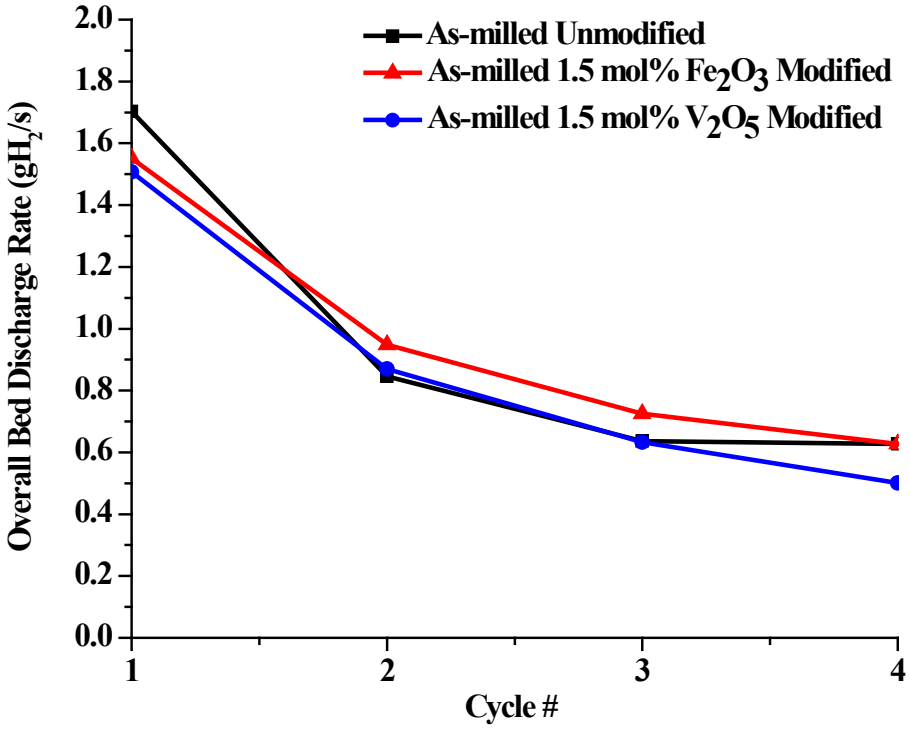
- Modifiers reduced the temperature of the two hydrogen release by 15 to 20°C

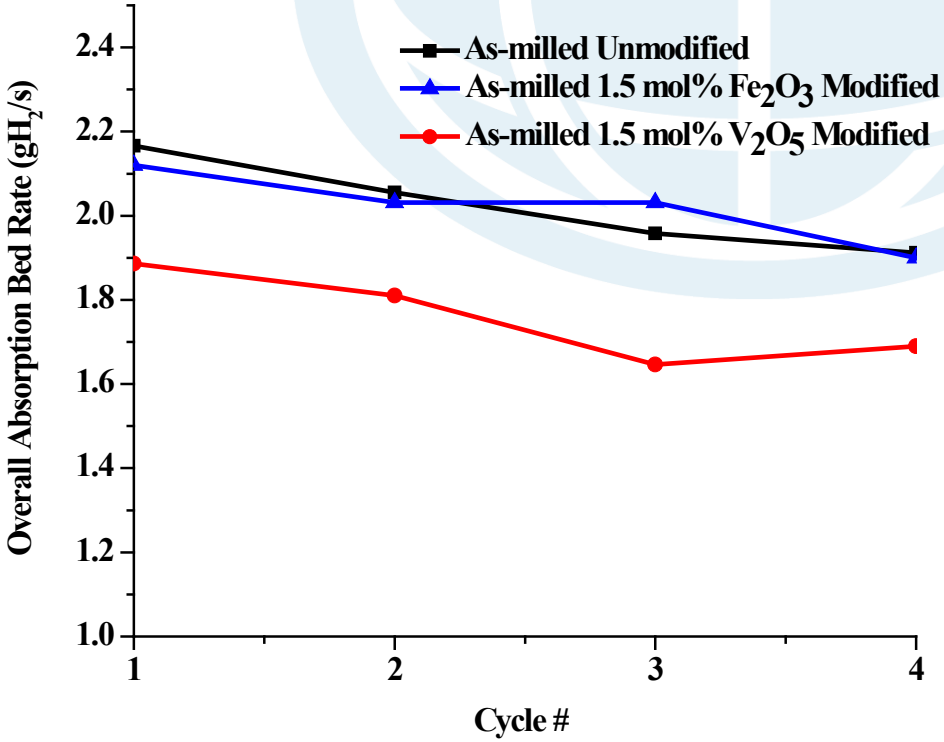
Technical Accomplishment and Progress – TGA/RGA results of as-milled $LiNH_2$:MgH_2 w/KH



- Addition of 4 mol% KH decreases the overall weight loss of the material, but decreased the onset temperature of hydrogen release.

Technical Accomplishment and Progress –
Effect of Modifiers on Average Discharge/Recharge Rate [gH_2/s]





- Modifiers have no effect on the discharge rate compared to the as-milled unmodified material.
- Fe_2O_3 has no effect on the recharge rate, but the addition of V_2O_5 decreased the recharge rate by 11.6%.

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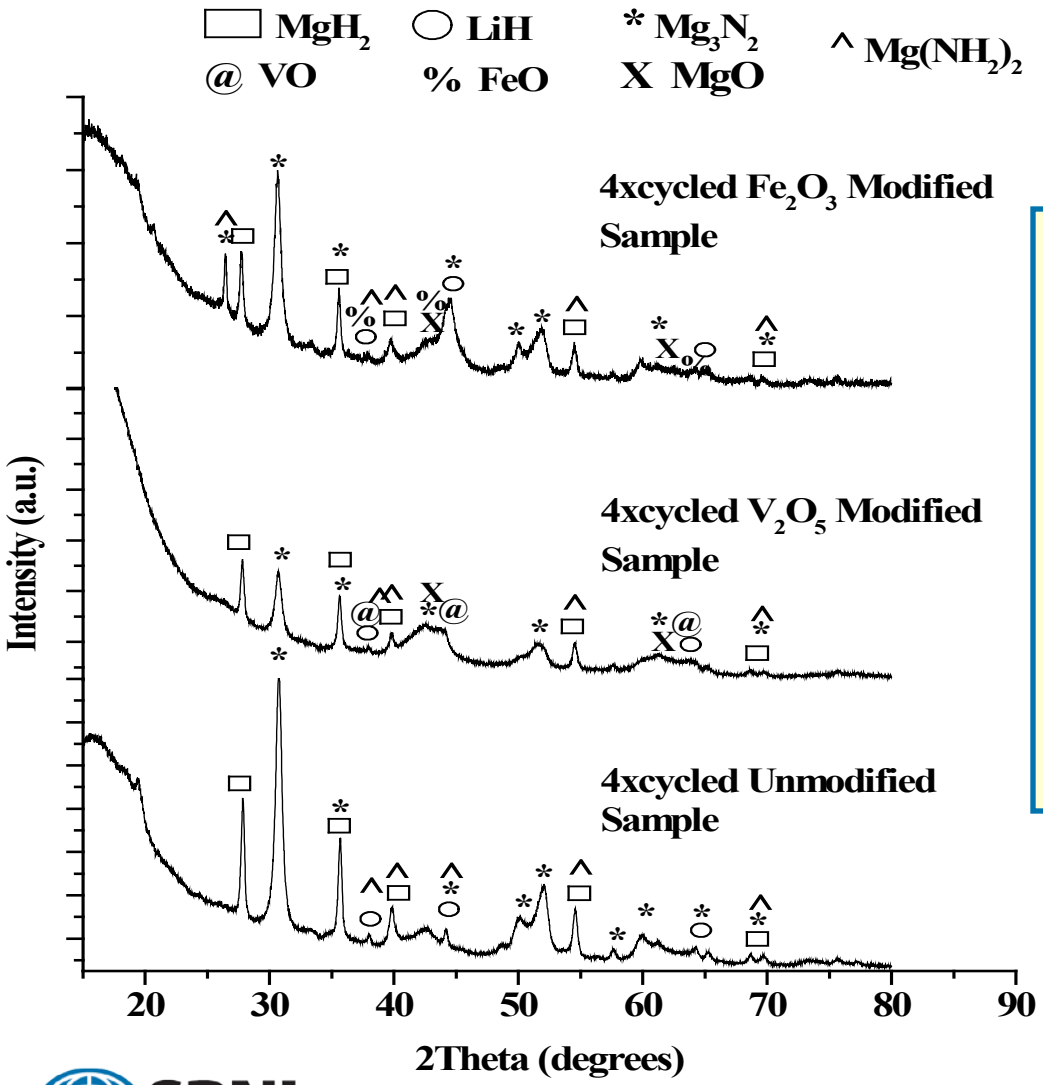
Technical Accomplishment and Progress –
XRD Analysis of Cycled $LiNH_2$:MgH_2 w/oxide modifiers

Charged State XRD:



- XRD shows that LiH and MgH_2 were the predominate products accompanied by Mg_3N_2 and Metal Oxide formation.
  - Presence of Mg_3N_2 could indicate incomplete rehydrogenation under 100 bar at 180°C.
  - Oxide Reduction was observed with the formation of VO and FeO peaks, but is not fully differentiable from other peaks.

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Relevance –
Modified LiMgN systems of the form $LiMg(NH_2)_x(BH_4)_y$

Overall

Modified LiMgN systems through additions of alkali earth metals in the form of $LiMg(NH_2)_x(BH_4)_y$ have the potential for the formation of high hydrogen content storage materials.

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 °C, *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: $M(BH_4)^-{\cdot}NH_3$

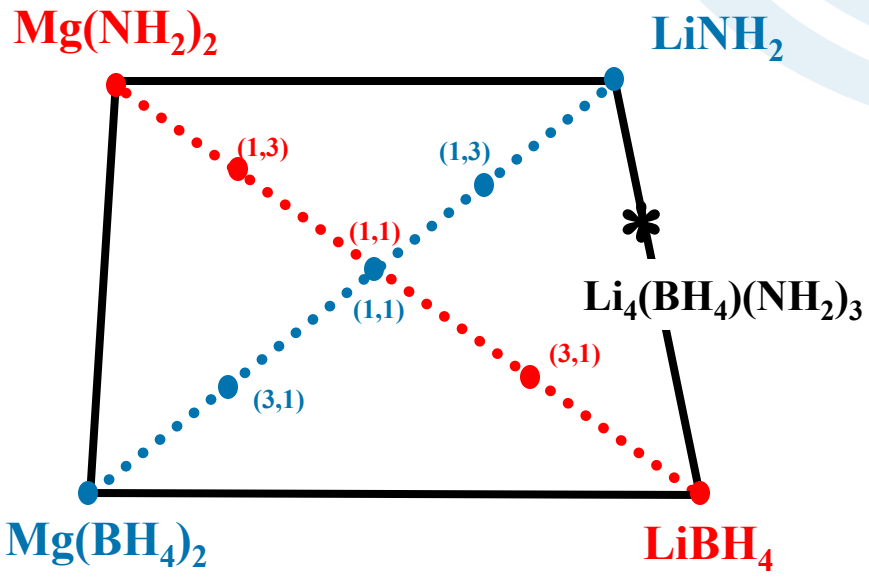
- Ammonia complex of magnesium borohydride, *Soloveichik et al., 2008*

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

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

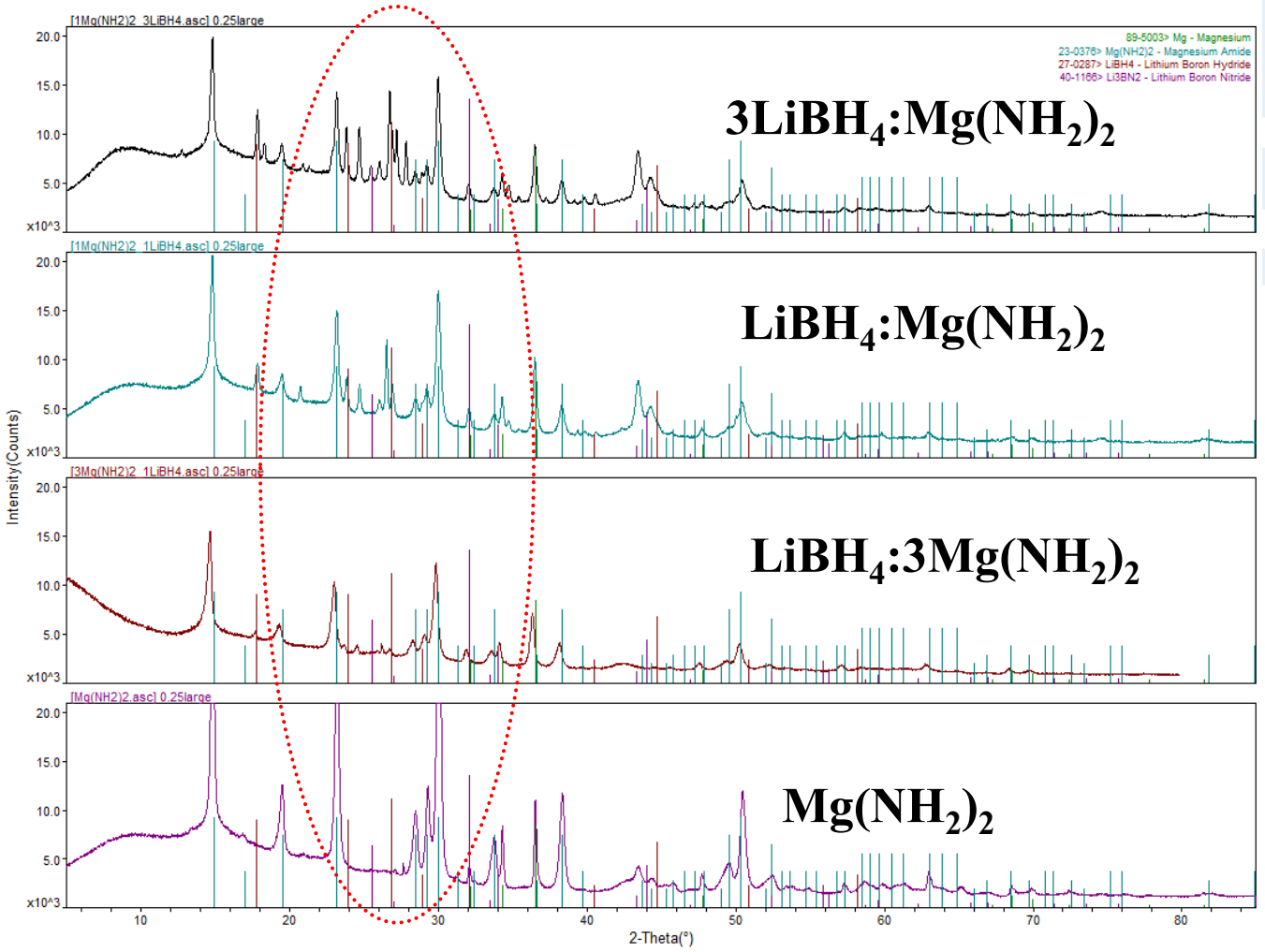
Approach –
Target system $Mg(NH_2)_2$ w/large additions of $LiBH_4$

Amide/Borohydride Plane of Quaternary Phase Diagram



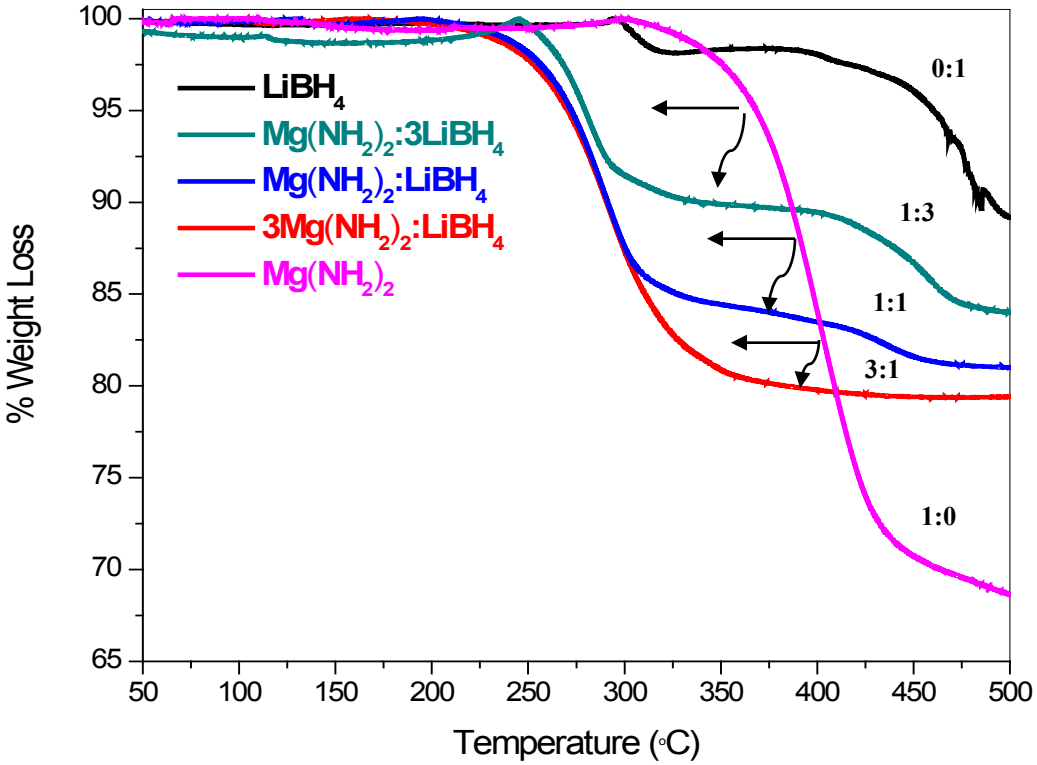
- Mixtures are formed using planetary ball-milling techniques.
- Identify isothermal/isobaric sorption properties of mixed phases using Sievert's apparatus.
- XRD analysis after ball milling process and after cycling.
- TGA-RGA to determine composition of hydrogen during dehydrogenation.

Technical Accomplishments and Progress – XRD analysis of mixed $Mg(NH_2)_2/LiBH_4$



- No chemical reaction observed upon Fritsch milling of $Mg(NH_2)_2$ and $LiBH_4$.

Technical Accomplishments and Progress – TGA analysis of mixed $Mg(NH_2)_2/LiBH_4$



- Pronounced interaction between the $LiBH_4$ and $Mg(NH_2)_2$ results in a 100°C decrease in decomposition temperature.
- Weight loss seen in $Mg(NH_2)_2$ is significantly due to NH_3 loss.
- NH_3 loss decreases significantly with the addition of $LiBH_4$.

Mixture	Theoretical H_2 Capacity (wt%)	Total Weight Loss from TGA (wt%)	Change in Capacity (wt%)
$LiBH_4$	18.4	11.4	7.0
$Mg(NH_2)_2$:3$LiBH_4$	15.6	16.0	0.4
$Mg(NH_2)_2$:$LiBH_4$	12.8	19.0	-6.2
3$Mg(NH_2)_2$:$LiBH_4$	9.9	20.6	-10.7
$Mg(NH_2)_2$	7.1	32.4	-25.3

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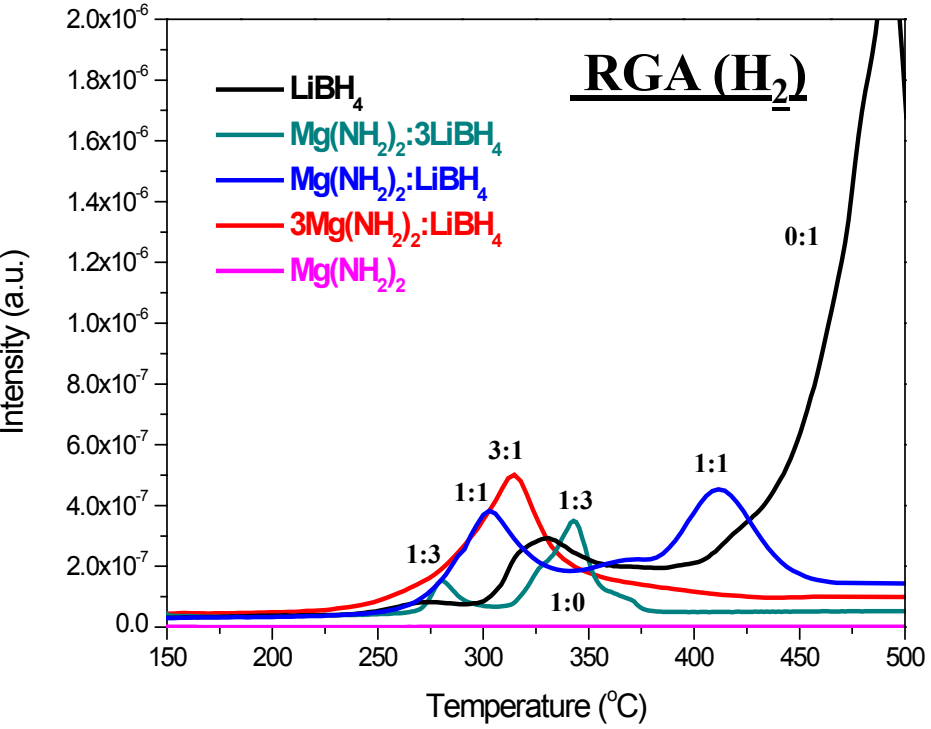
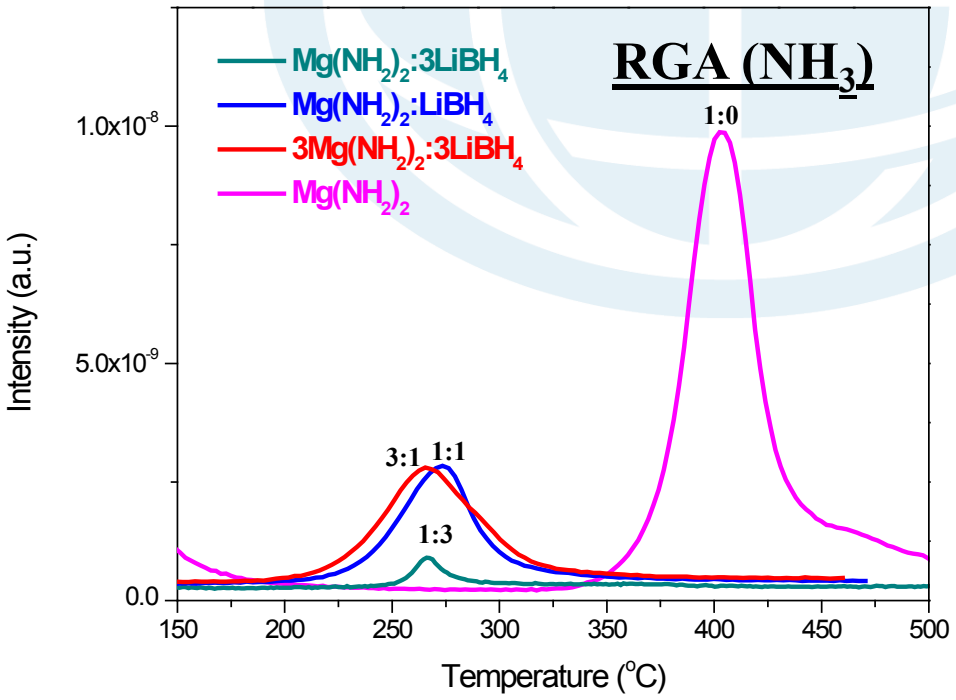
Technical Accomplishments and Progress – RGA analysis of mixed $Mg(NH_2)_2/LiBH_4$

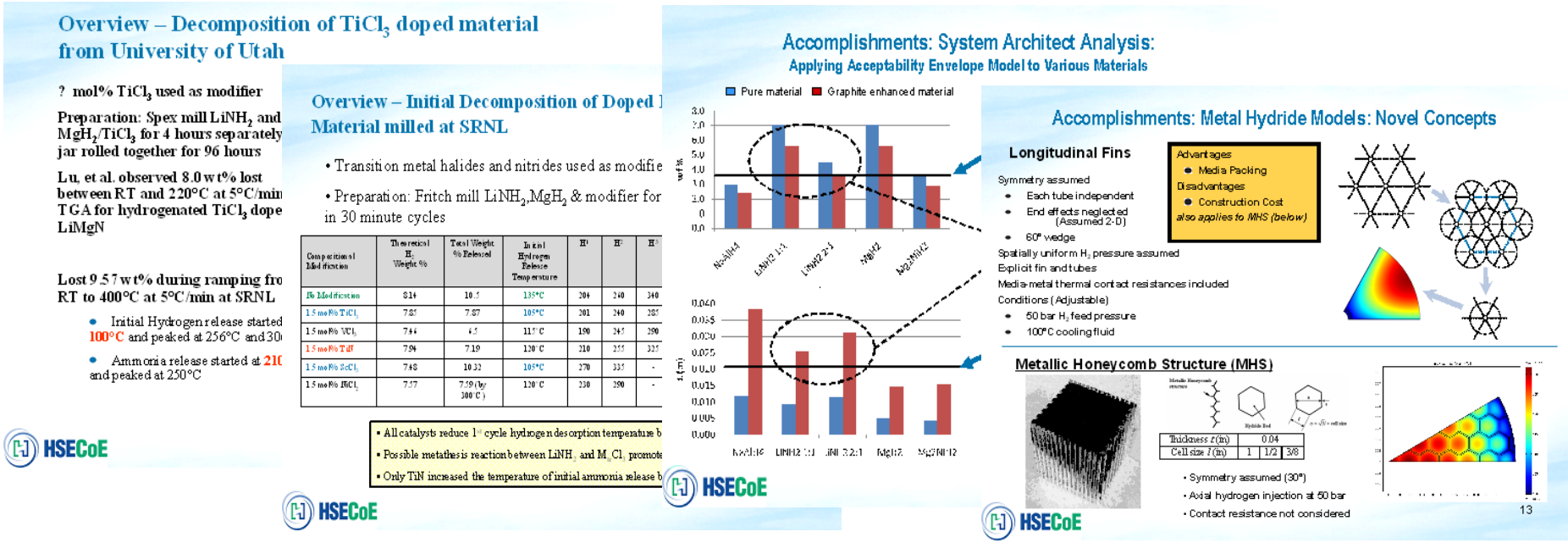




- Pure $Mg(NH_2)_2$ has negligible release of hydrogen and a large NH_3 release at 400°C.
- $3Mg(NH_2)_2$:$LiBH_4$ has a single release of hydrogen close to 225°C.
- $Mg(NH_2)_2$:$LiBH_4$ and $Mg(NH_2)_2$:$3LiBH_4$ contain a 2-step hydrogen release that is broad and affected by concentration ratio.
- The addition of $LiBH_4$ mitigates the release of ammonia and lowers the dehydrogenation temperature by 100°C.

Technical Accomplishment and Progress – HSECoE Database for the LiMgN system

- An objective is to assess the kinetics of LiMgN for a prototype system.
- The required information includes the isothermal kinetics and ammonia expected throughout the temperature and pressure envelope of operation.
- The data identified in this project was used to select LiMgN as a potential candidate for a metal hydride prototype system.



Summary

- Milling technique and modifier composition have a significant effect on initial H_2 and NH_3 discharge temperatures and sorption rates
  - **Unmodified**
    - Spex milling showed improvement from Fritsch milling in recharging rates over 4 cycles
    - Similar discharge rates after first two cycles
  - **Oxides**
    - Lowered initial hydrogen release temperature and amount of ammonia release
    - Showed no significant increase in hydrogen sorption rates over four desorption cycles
    - Resulted from decomposition of oxides during cycling and persistent Mg_3N_2 formation
- Discharge temperature also has a significant effect on sorption rates and product composition
  - Mg_3N_2 formation predominate in high temperature cycling
- Mixtures of $Mg(NH_2)_2$ with $LiBH_4$ have shown an decrease in the dehydrogenation temperature and an increase in the amount of hydrogen released.

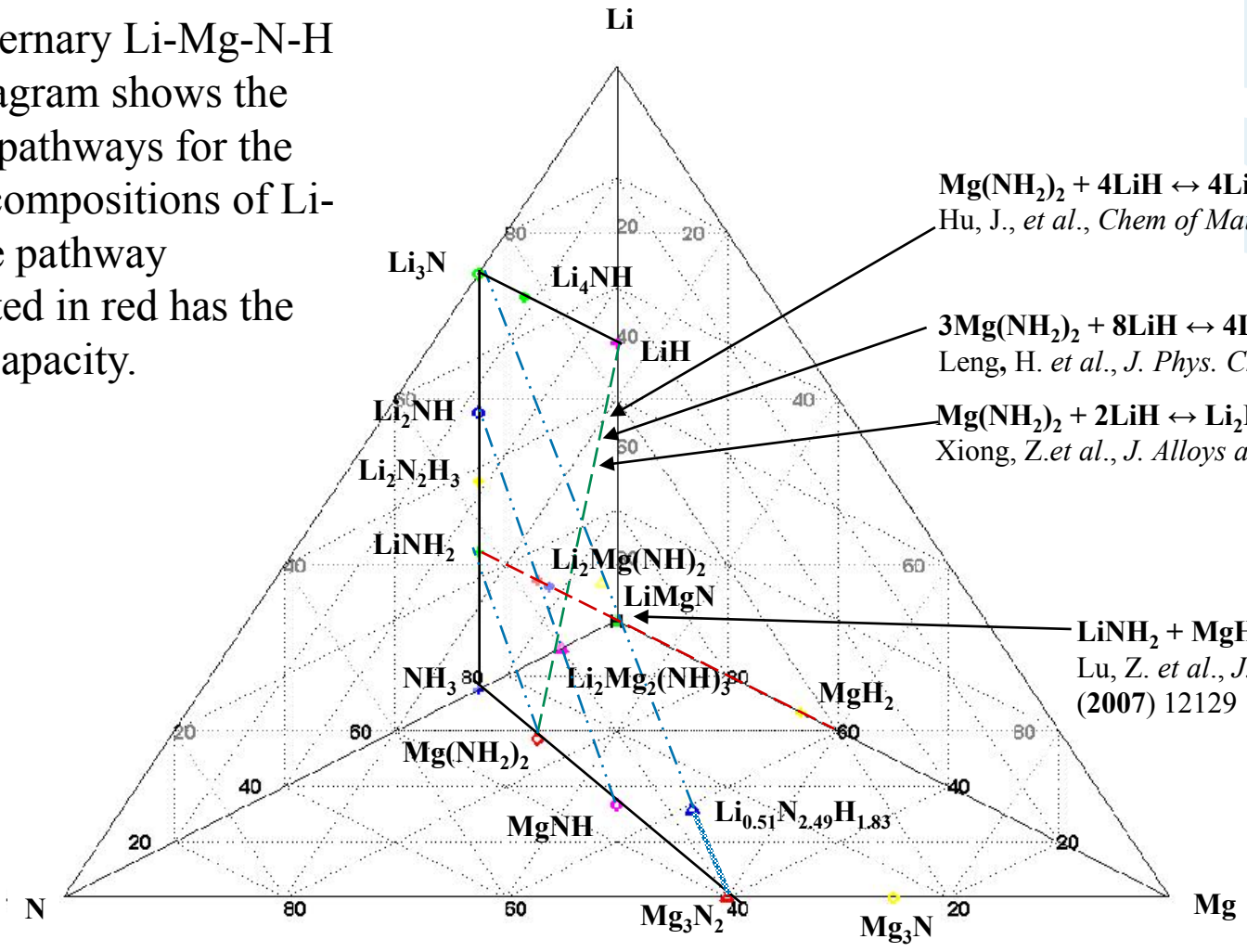
Proposed Future Work

- Couple experimental results with *ab-initio* calculations to identify kinetic enhancing mechanisms in complex metal hydride systems. *(Collaboration with Ga Tech and U. of Pittsburgh)*
- Investigate the role of additional additives, which have been identified in other studies, on the kinetics using isothermal Sievert's measurements
- Study the role of ammonia release during cycling of (un) modified $LiNH_2$: MgH_2
- Determination of the transformation mechanism in $LiNH_2$:MgH_2 using Raman and IR spectroscopy and a spallation neutron source. *(Collaboration with U. of South Carolina and Rutherford Appleton Laboratory)*
- Long-term cyclability studies to determine hydrogen capacity.
- Regeneration of $LiH/Mg(NH_2)_2$ using mix H_2/N_2 and H_2/NH_3 gas feeds for prolong cyclability.
- Further investigate the sorption characteristics of the $LiBH_4$ modified LiMgN system.

Technical Back-Up Slides

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

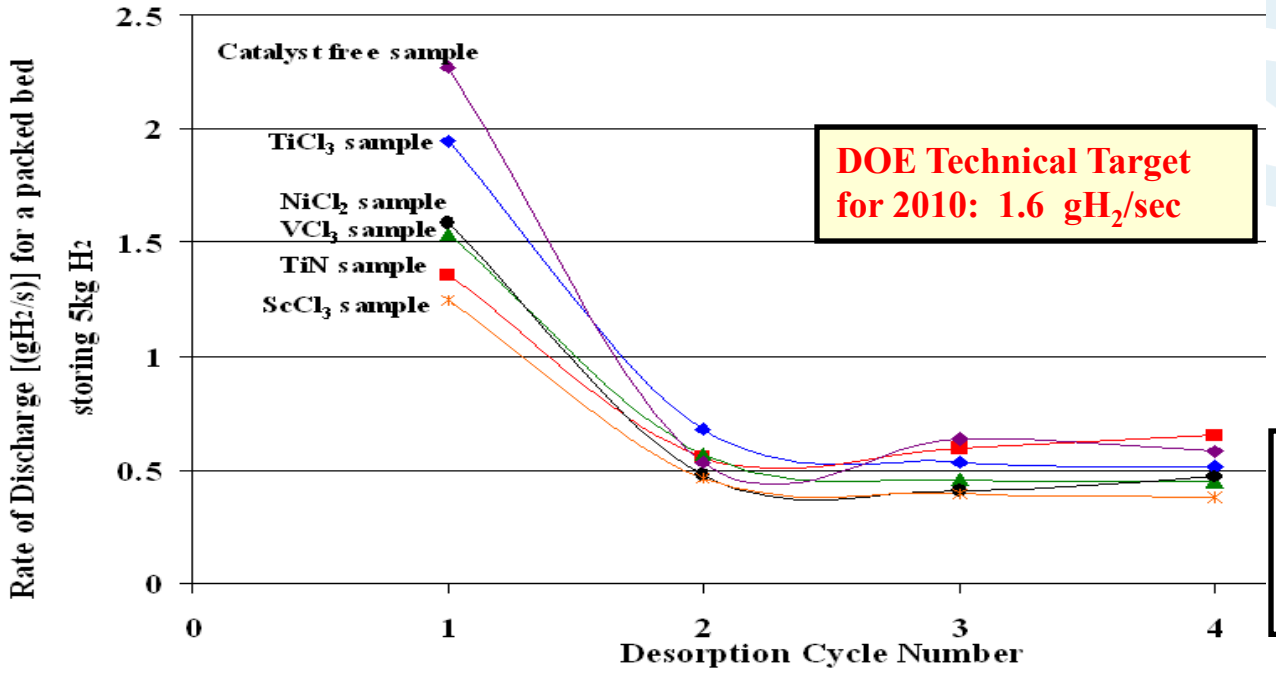
$3Mg(NH_2)_2 + 8LiH \leftrightarrow 4Li_2NH + Mg_3N_2 + 8H_2$
Leng, H. *et al*., *J. Phys. Chem. B* 108 (**2004**) 8763

$Mg(NH_2)_2 + 2LiH \leftrightarrow Li_2Mg(NH)_2 + 2H_2$
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

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

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



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

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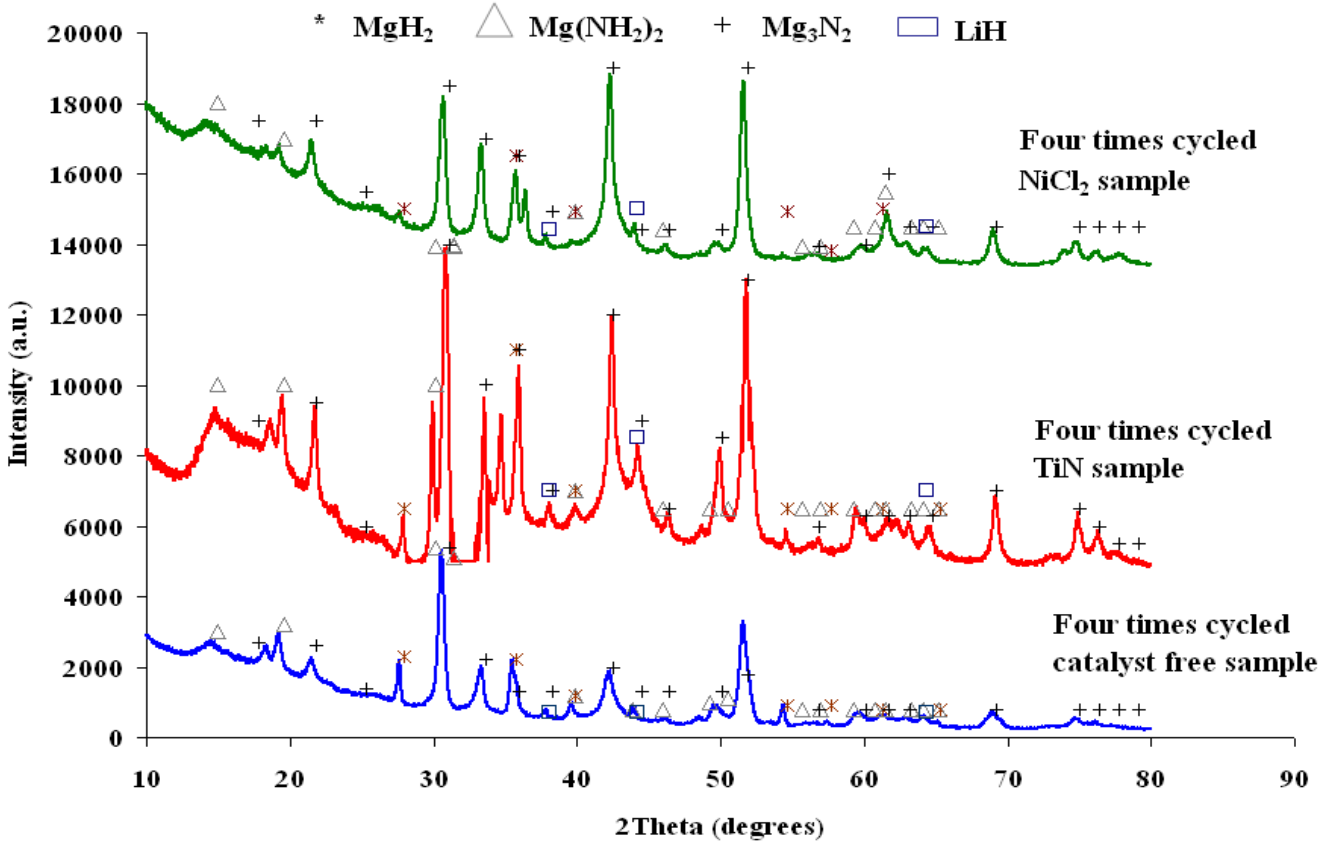
Technical Accomplishments and Progress – XRD Analysis of four cycled 1:1 $LiNH_2$:MgH_2 $^{w}/_{w/o}$ modifiers



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

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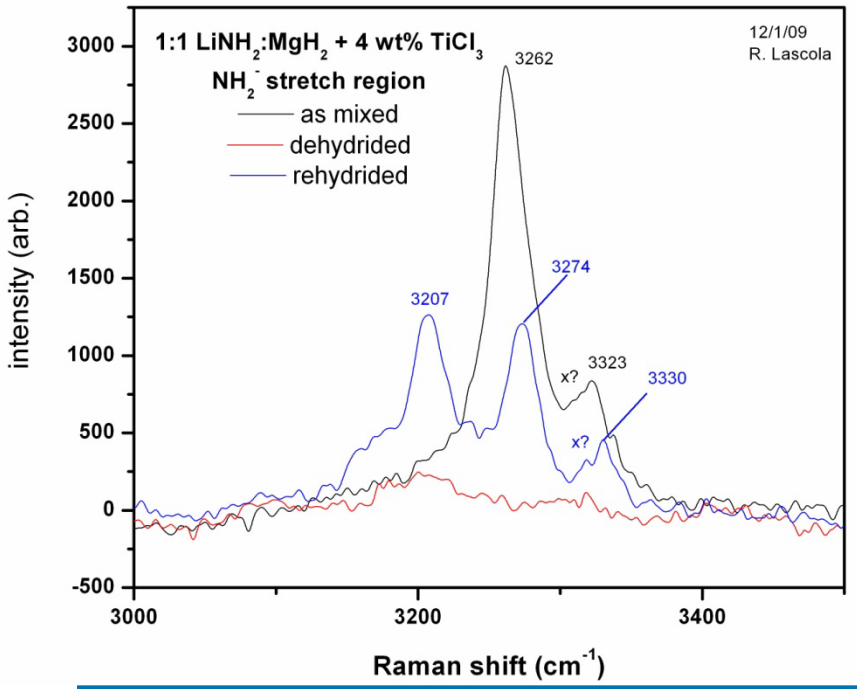
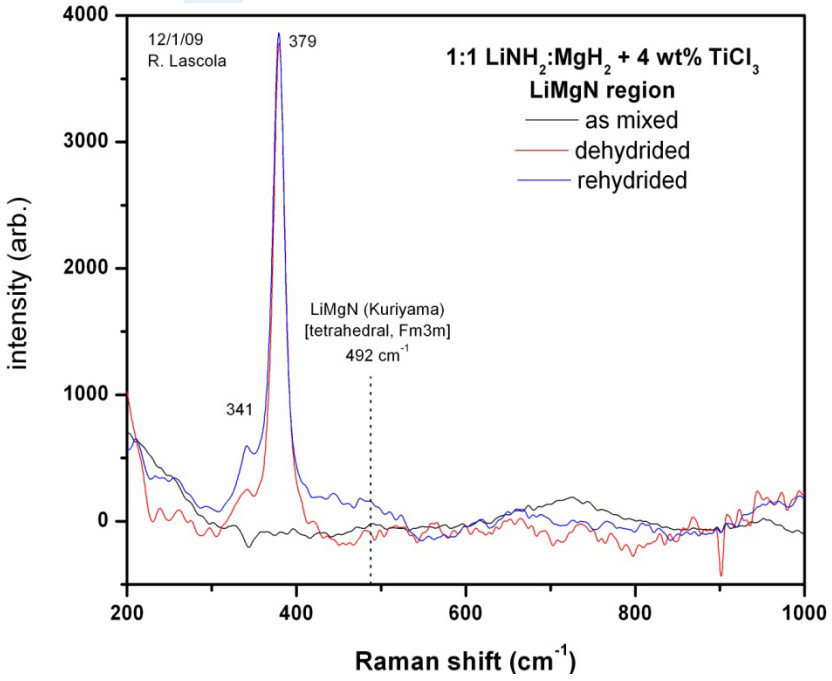
Technical Accomplishments and Progress – Raman Spectroscopy Analysis





- ❖ <u>As-milled</u>: High-shift region shows spectrum consistent with $LiNH_2$ amide stretches
- ❖ <u>Discharged:</u> 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
- ❖ <u>Recharged:</u> The bands at 3274 and 3330 cm^{-1} are consistent with the formation of $Mg(NH_2)_2$

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