



Amide and Combined Amide/Borohydride Investigations

**Charles James, Christine Erdy, Jose Cortes-Concepcion,
and Don Anton (PI)**

Savannah River National Laboratory

May 11, 2011

Project ID #: ST070

Overview

Timeline

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

Budget

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

Barriers Addressed

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

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 $\text{LiMg}(\text{NH}_2)_x(\text{BH}_4)_y$, 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**.

LiMgN as a Hydrogen Storage Material



- ❖ Identified using DFT calculations as potentially reversible with a theoretical H₂ 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 hours²
- ❖ The reversible hydrogen absorption reaction involved:
 - ❖ **8 wt%** observed experimentally at 160°C and 140 bar



- ❖ Dehydrogenation is proposed to proceed through an intermediate step



- ❖ Accelerated reversibility has been observed using 4 wt% TiCl₃ dopant²

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 $\text{Mg}(\text{NH}_2)_2$ 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: $200^\circ\text{C}/1$ 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: $180^\circ\text{C}/100$ bar/ 6 hrs

TGA-RGA Procedure

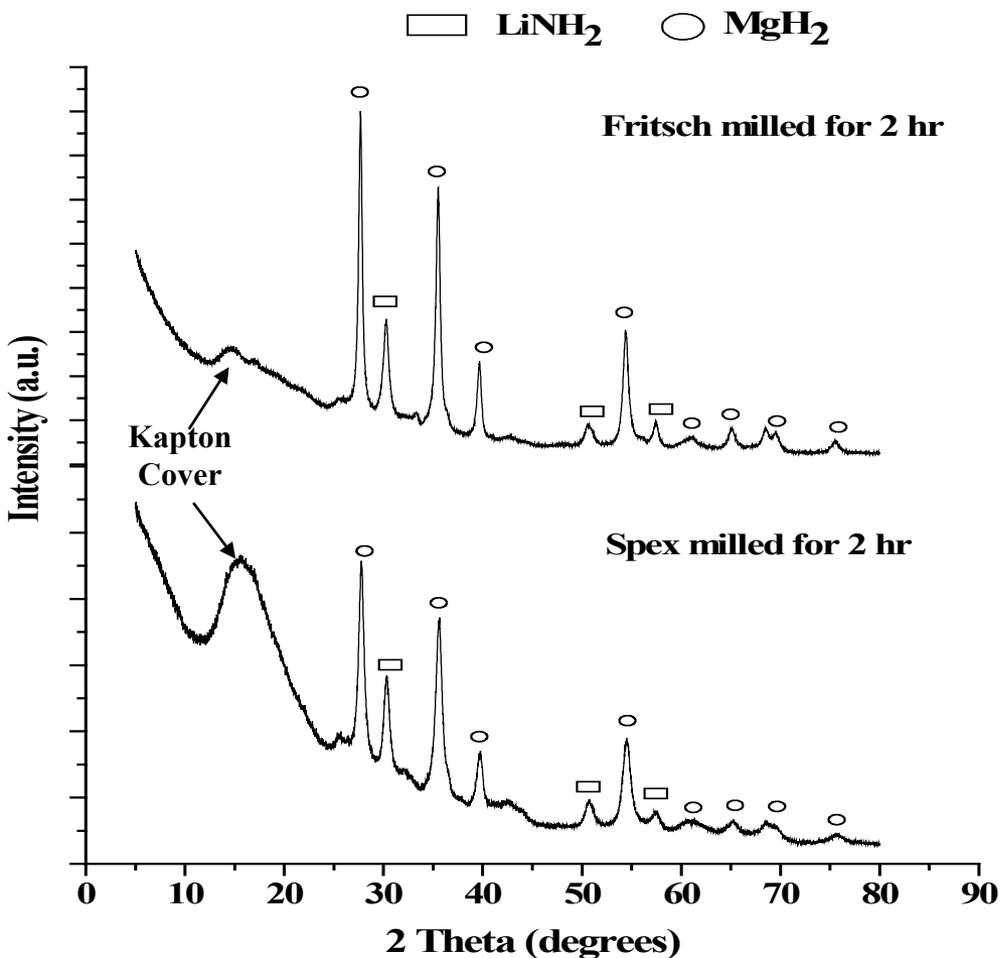
- ❖ Heating rate at $5^\circ\text{C}/\text{min}$ from RT to 400°C
- ❖ Looked at mass 2 (H_2), 16 (NH_2^-), 17 (NH_3/OH) and 18 (H_2O) in RGA

DSC Procedure

- ❖ Heating rate at $2^\circ\text{C}/\text{min}$ from RT to 400°C

Technical Accomplishment and Progress –

XRD Analysis as function of milling technique w/o modifiers

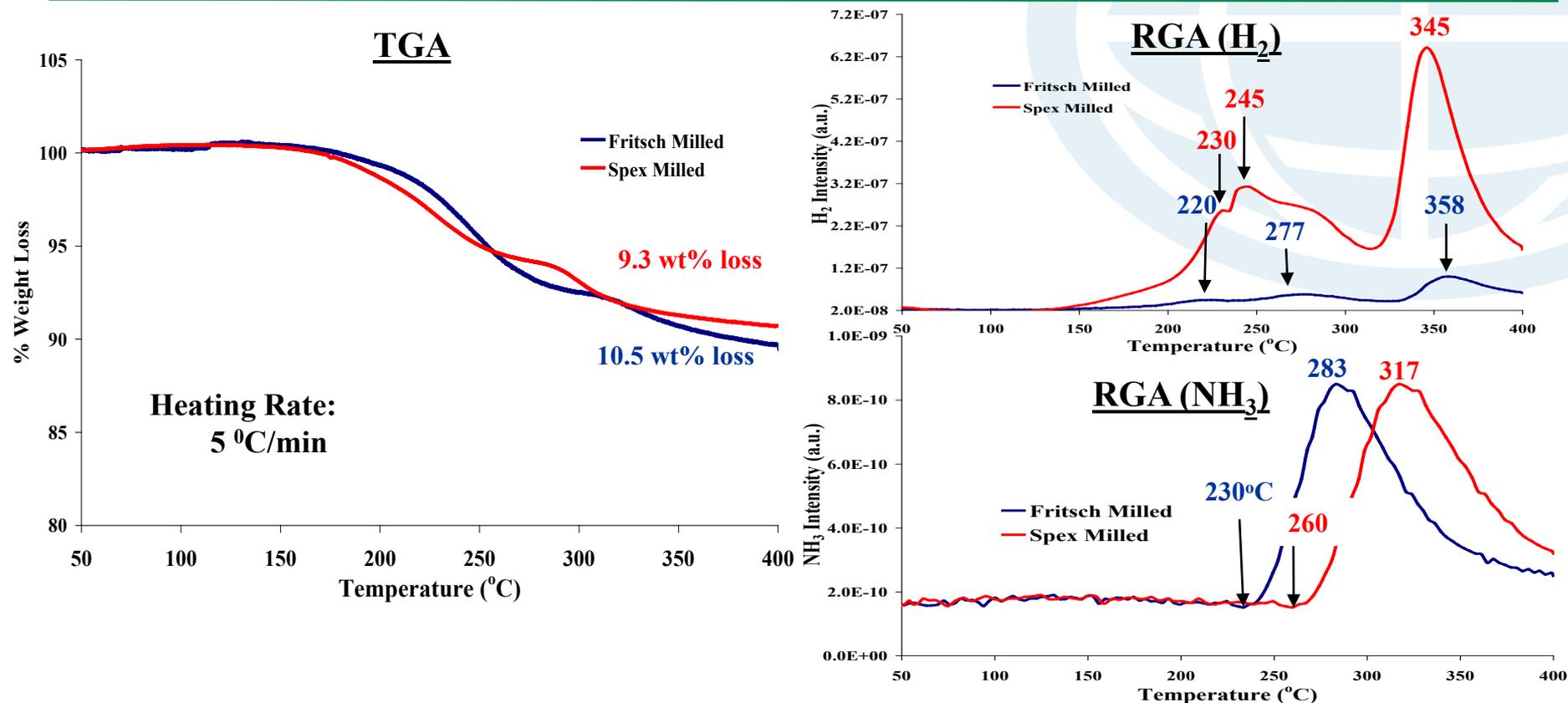


MgH_2 and LiNH_2 patterns identified

- ❖ 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

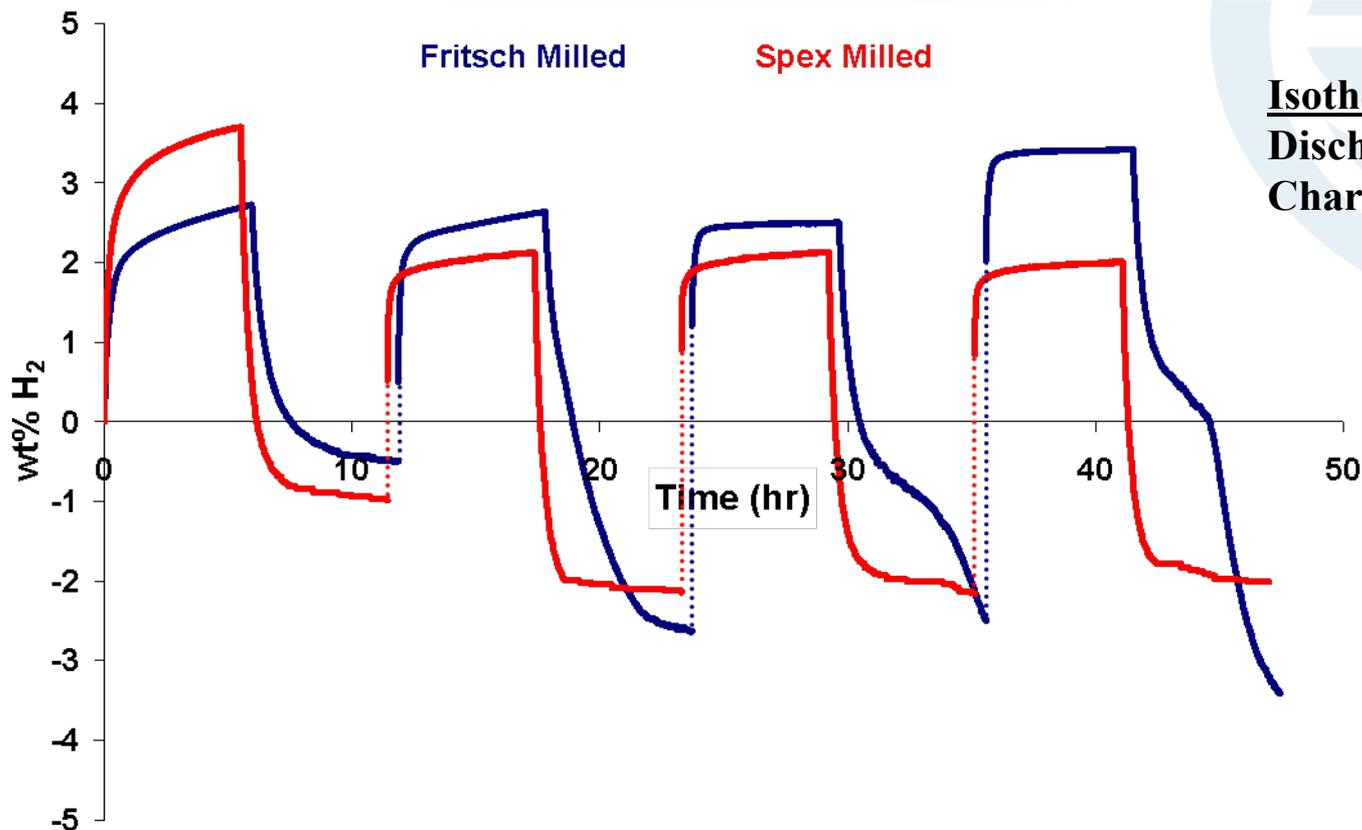


- ❖ Hydrogen desorption for the Fritsch-milled sample started at approximately 135°C; Spex-milled material started at 120°C. Reduction in temperature is attributed to the smaller particle size which resulted in increased surface area and lower surface activation energy
- ❖ Difference in max ammonia release attributed to the slow reaction kinetics between MgH₂ and NH₃ from decomposing LiNH₂, the decomposition of unreacted LiNH₂ and/or the self-decomposition of Mg(NH₂)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.

Technical Accomplishments and Progress –

Milling technique dependence on H₂ 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 H₂ 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 H₂ capacity starting with the 4th cycle.

Technical Accomplishment and Progress –

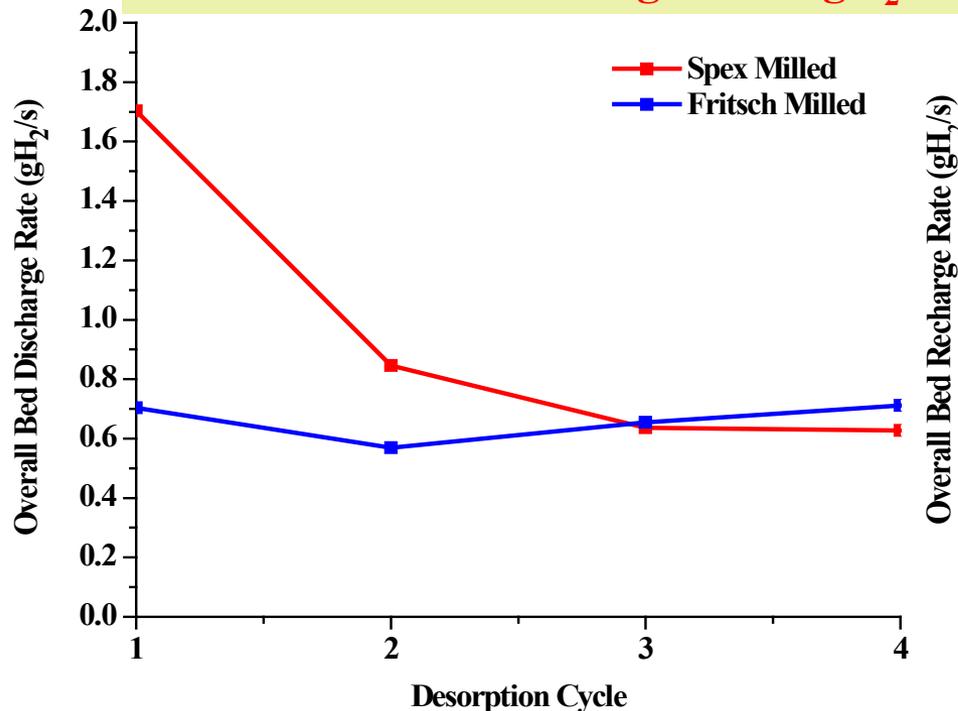
Discharge/Recharge Rate Dependence on Milling Technique

- Assumed 5 kg H₂ Capacity and average rate over 30 mins

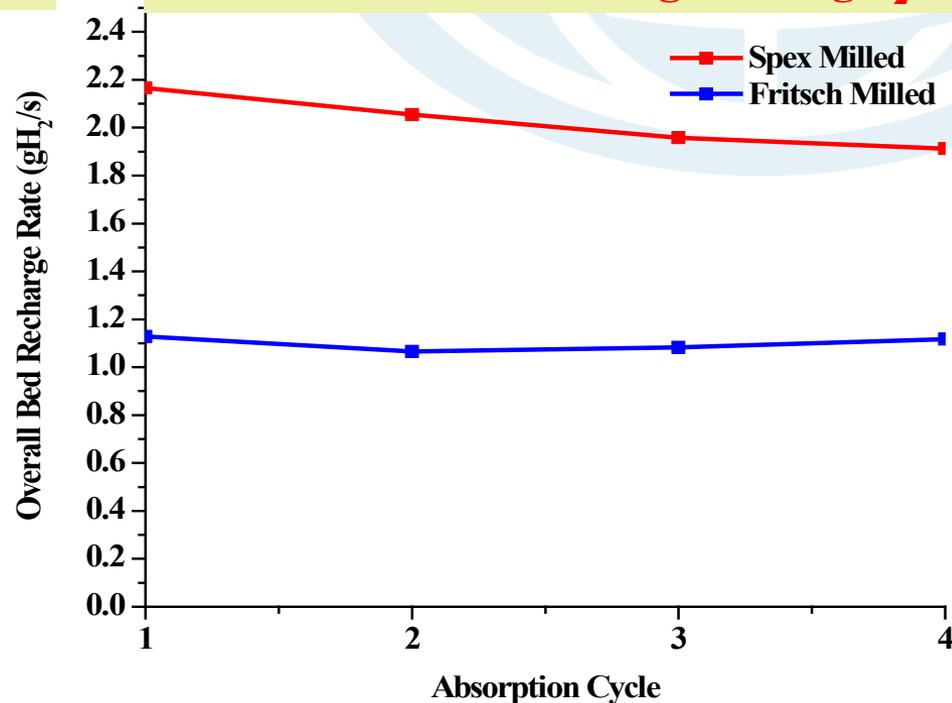
- Desorption: 200°C/1 bar/ 6hr

- Absorption: 180°C/100 bar/ 6hr

DOE 2015 Technical target = 1.6 gH₂/s



DOE 2015 Technical target = 25 gH₂/s

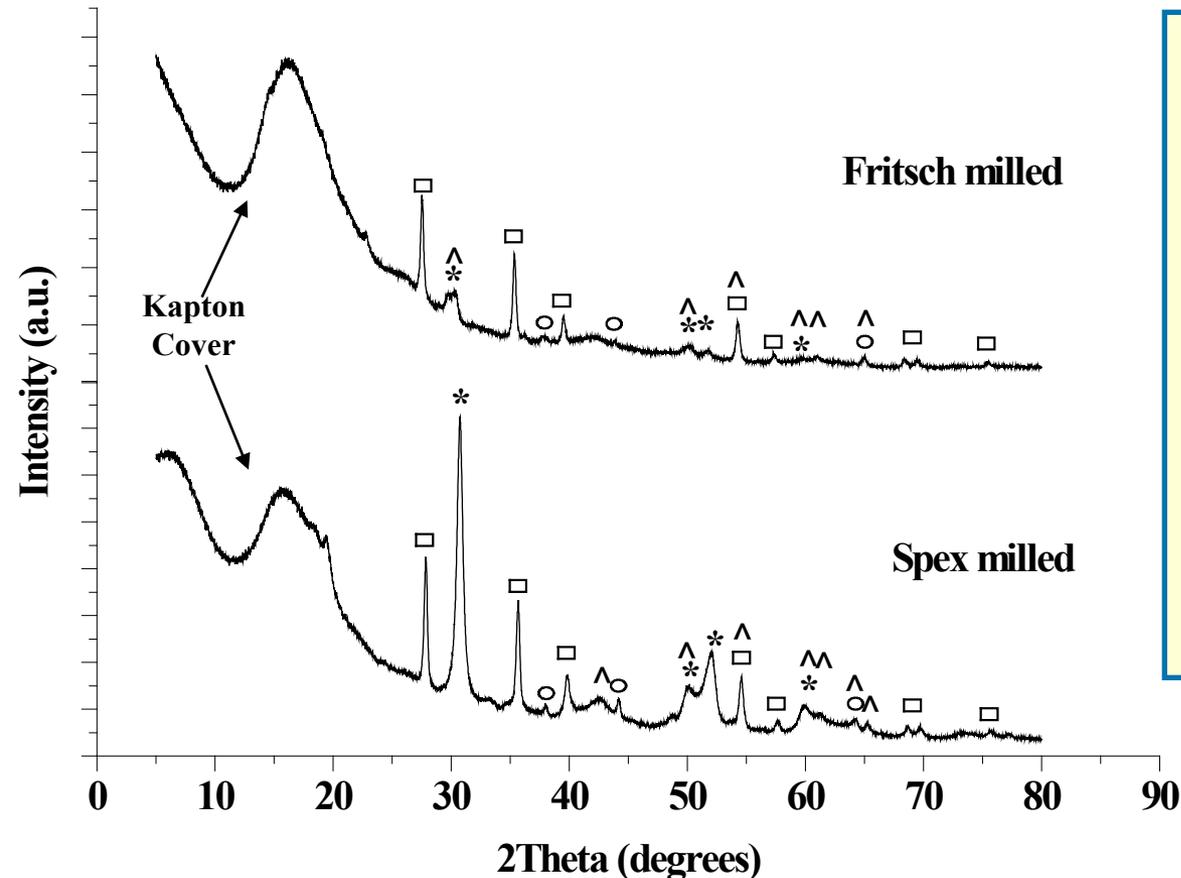


- ❖ Discharge rate is initially 2x faster for Spex milled material due to smaller particle size, but reduces to the discharge rate of Fritsch milled material by the 3rd cycle.
- ❖ Average bed recharge rates over 4 isothermal cycles showed strong dependence on milling technique w/the bed recharge rate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

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

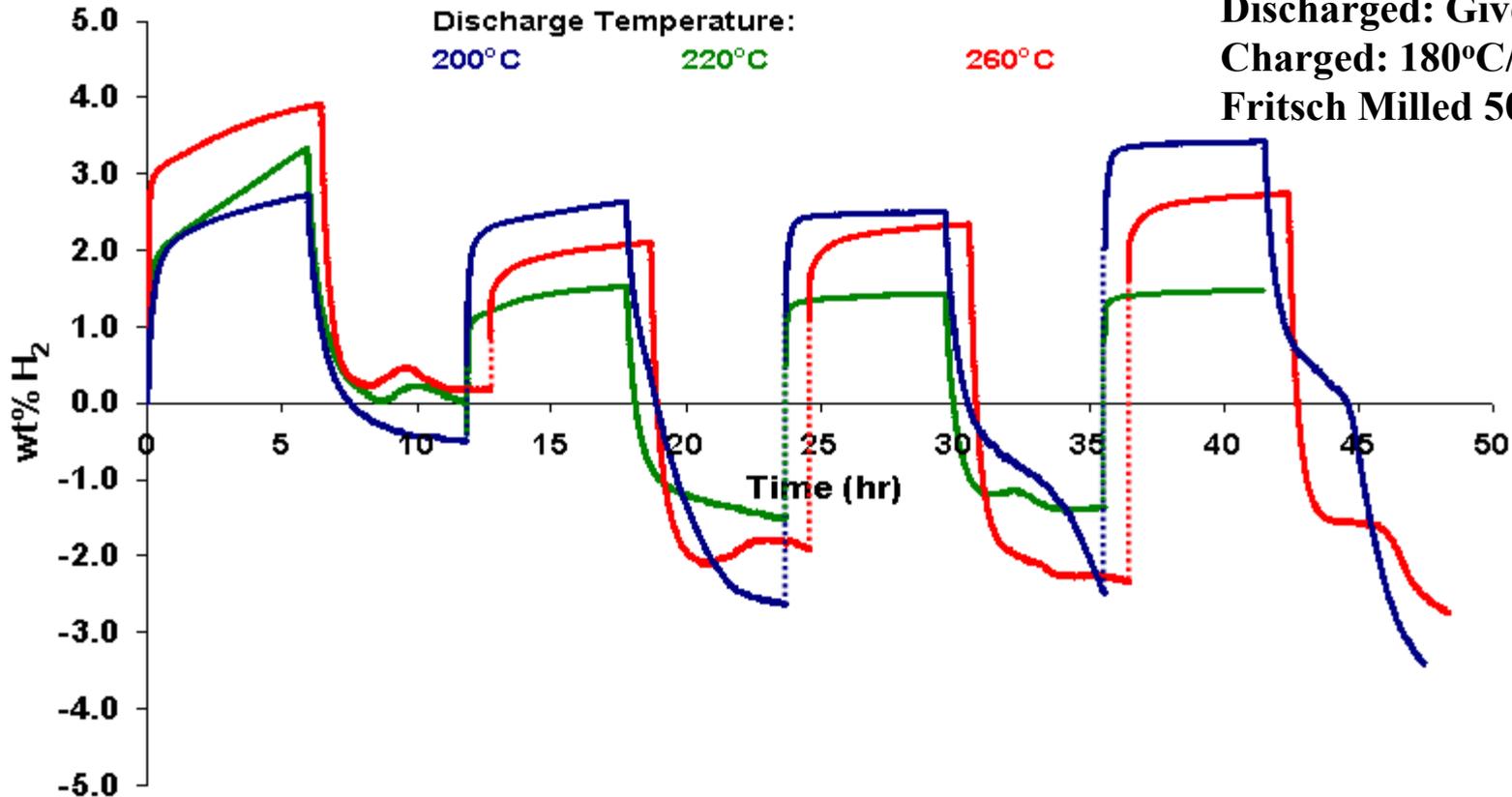
Charged State XRD:

□ MgH₂ ○ LiH * Mg₃N₂ ^ Mg(NH₂)₂



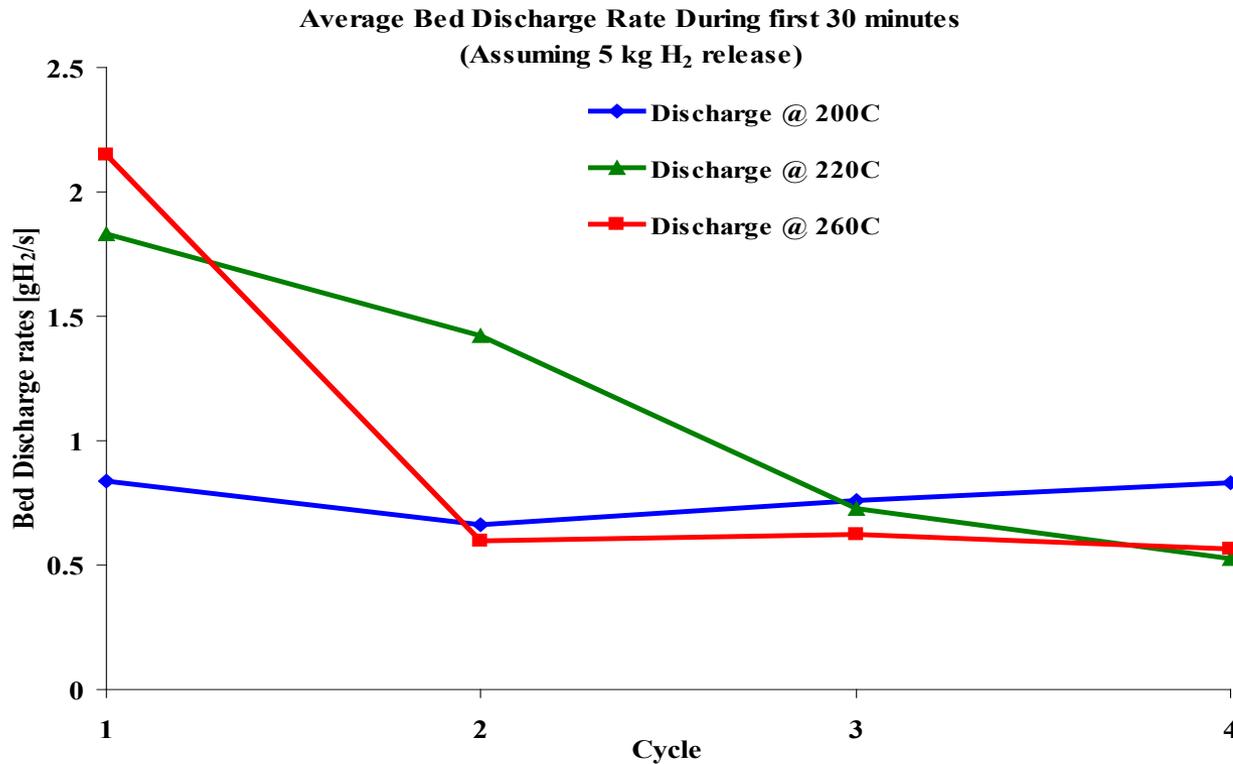
- ❖ Shows that Mg₃N₂ and MgH₂ were the predominate products accompanied by LiH formation.
 - ❖ Presence of Mg₃N₂ could indicate incomplete rehydrogenation under 100 bar at 180°C.
- ❖ Mg(NH₂)₂ not differentiated from Mg₃N₂
 - ❖ Raman: N-H stretching bands at 3273 cm⁻¹ and 3326 cm⁻¹ were observed, which are consistent with Mg(NH₂)₂ formation

Technical Accomplishments and Progress – Temperature dependence on H₂ Capacity (4 cycles)



❖ 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 $\text{Mg}_3\text{N}_2 + \text{Li}_3\text{N}$.

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

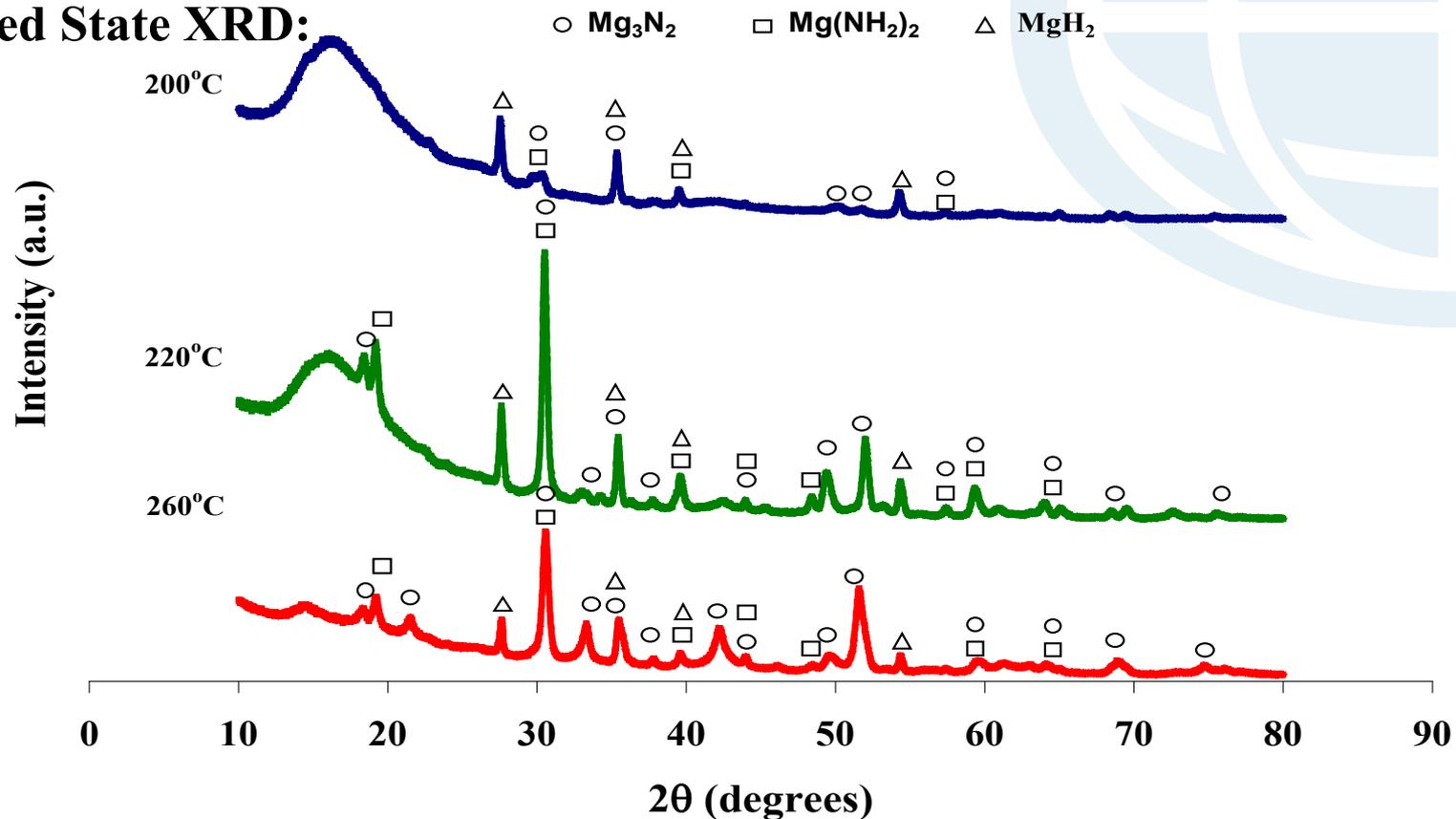
❖ **Average bed discharge rate over 4 isothermal cycles showed strong dependence on discharge temperature**

- ❖ 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 Mg₃N₂ due to loss of ammonia at high temperatures

Technical Accomplishment and Progress –

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

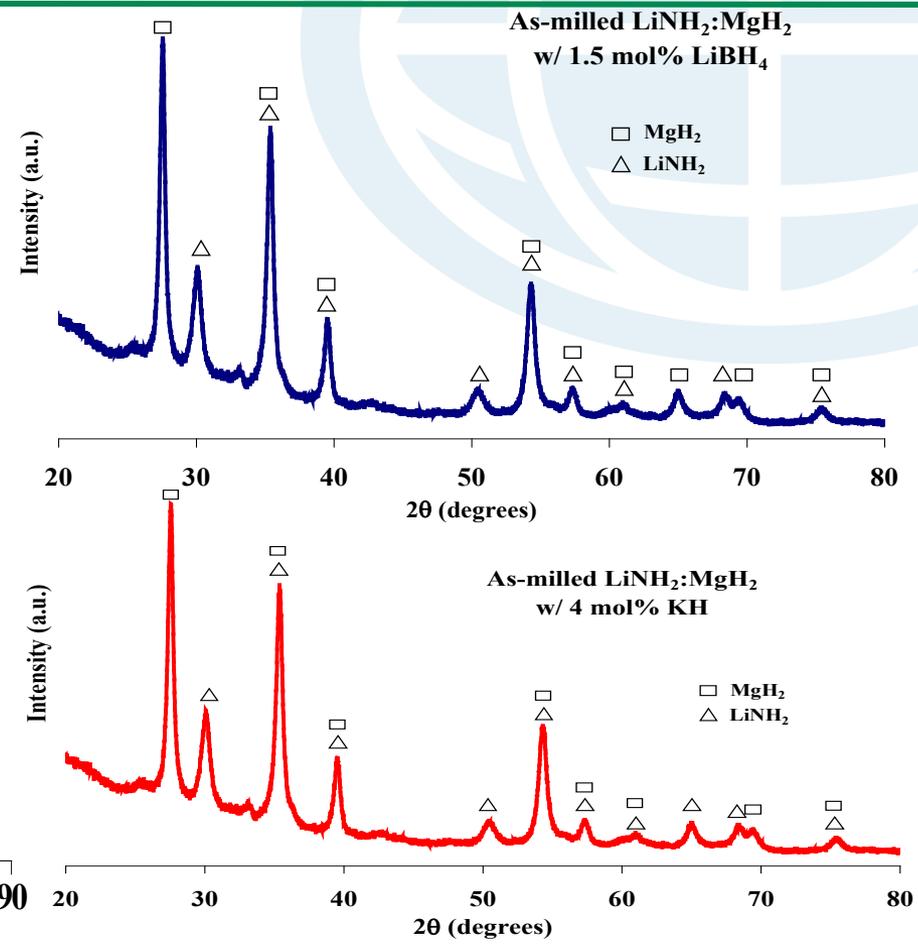
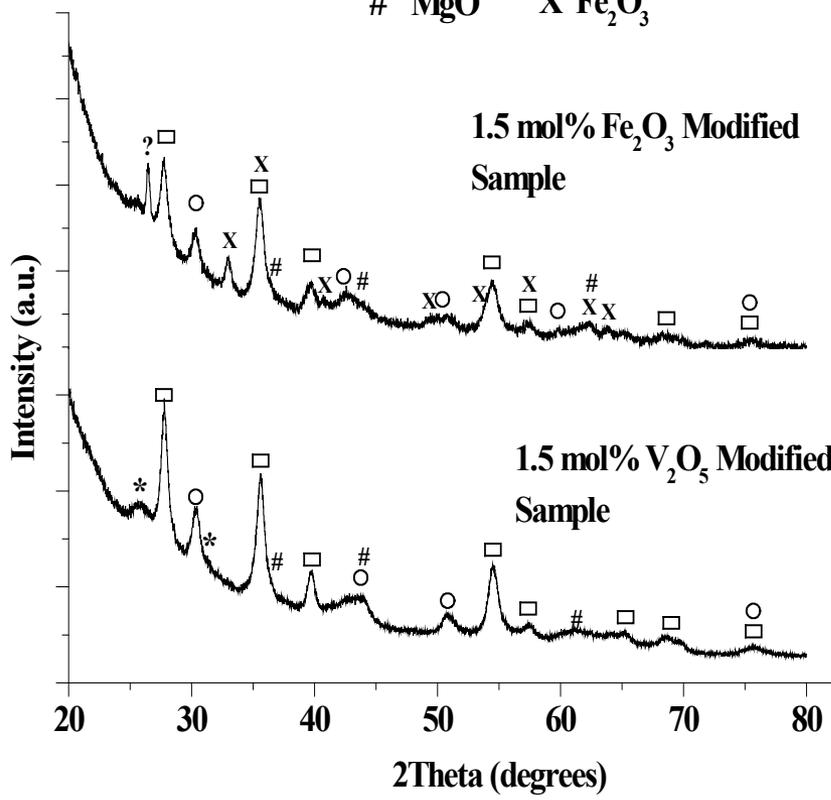
Charged State XRD:



- ❖ At 200°C, XRD results show the formation of MgH₂ and minimal Mg₃N₂ formation.
- ❖ At 220°C and 260°C, the decrease in H₂ capacity is due to enhanced Mg₃N₂ formation. The amount of Mg(NH₂)₂ is difficult to differentiate from Mg₃N₂ because of similar XRD patterns.

Technical Accomplishment and Progress – XRD Analysis of As-milled $\text{LiNH}_2:\text{MgH}_2$ w/modifiers

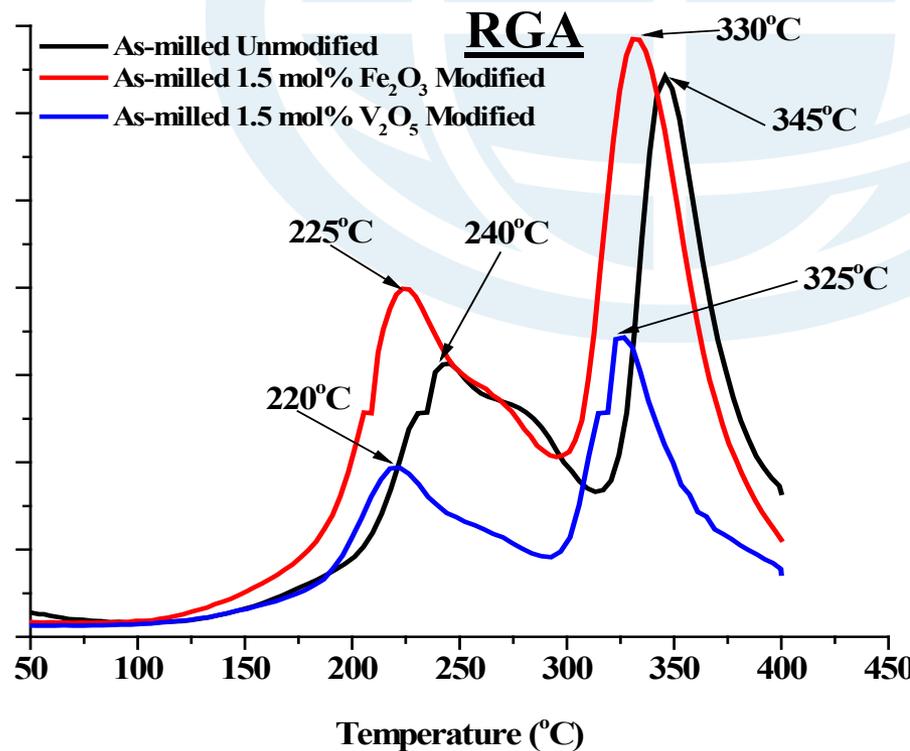
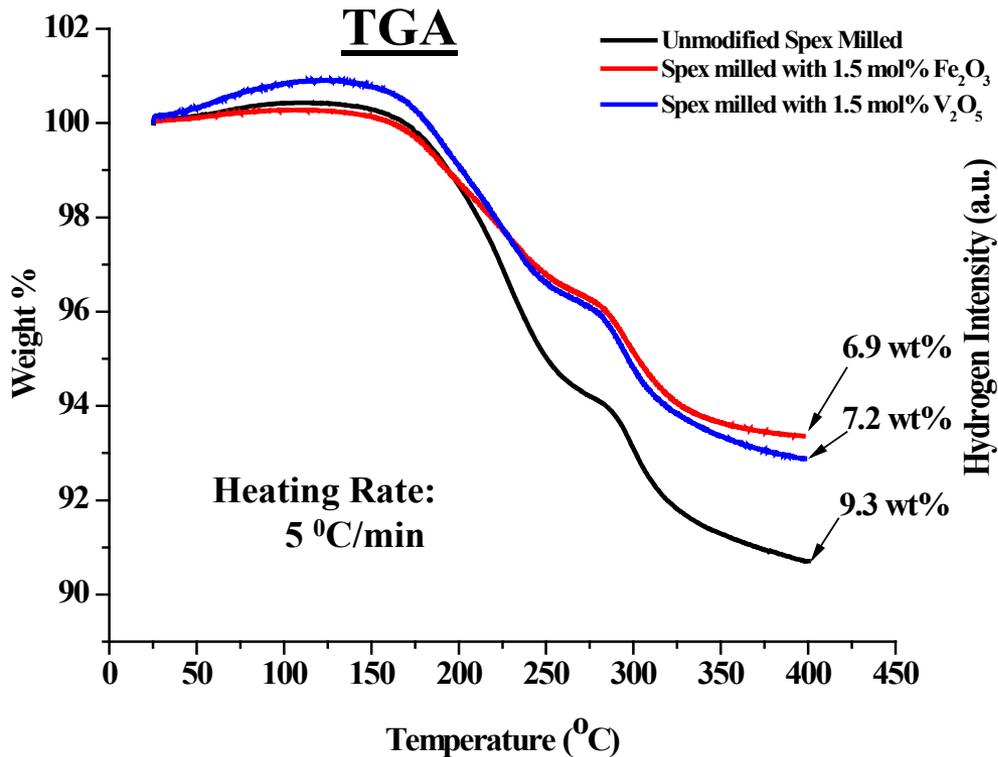
\square MgH_2 \circ LiNH_2 * V_2O_5
 $\#$ MgO \times Fe_2O_3



❖ 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.

Technical Accomplishment and Progress –

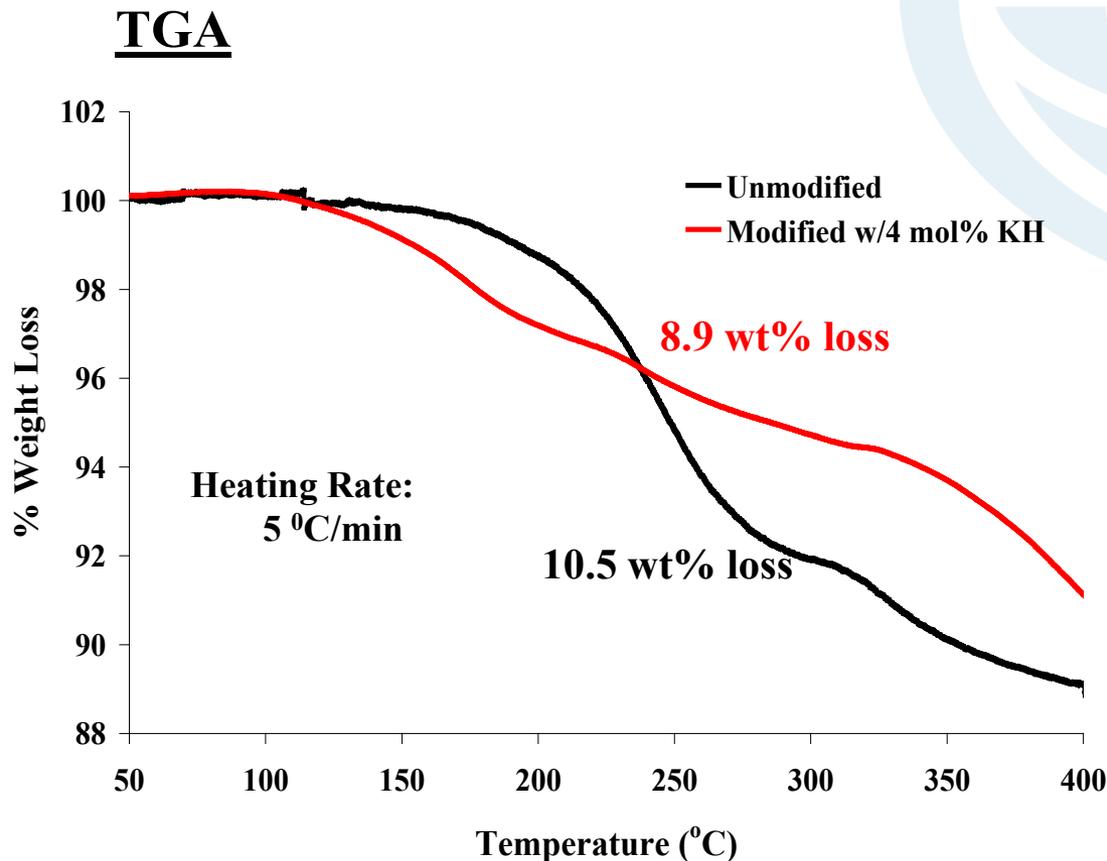
TGA/RGA results of as-milled $\text{LiNH}_2:\text{MgH}_2$ w/oxide modifiers



❖ Modifiers reduced the temperature of the two hydrogen release by 15 to 20 $^\circ\text{C}$

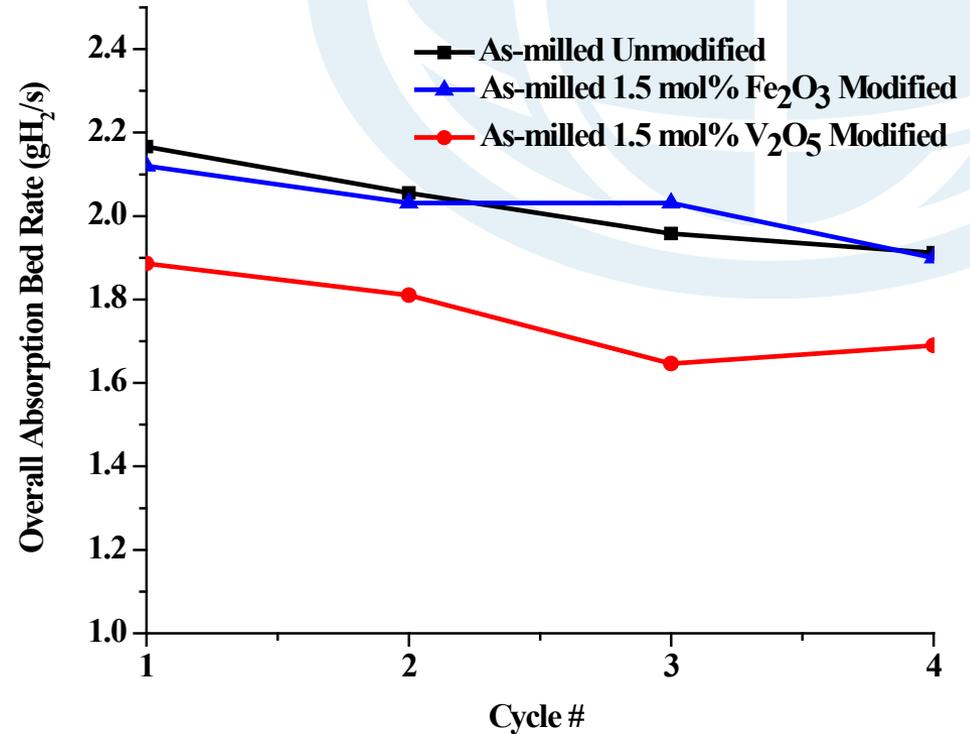
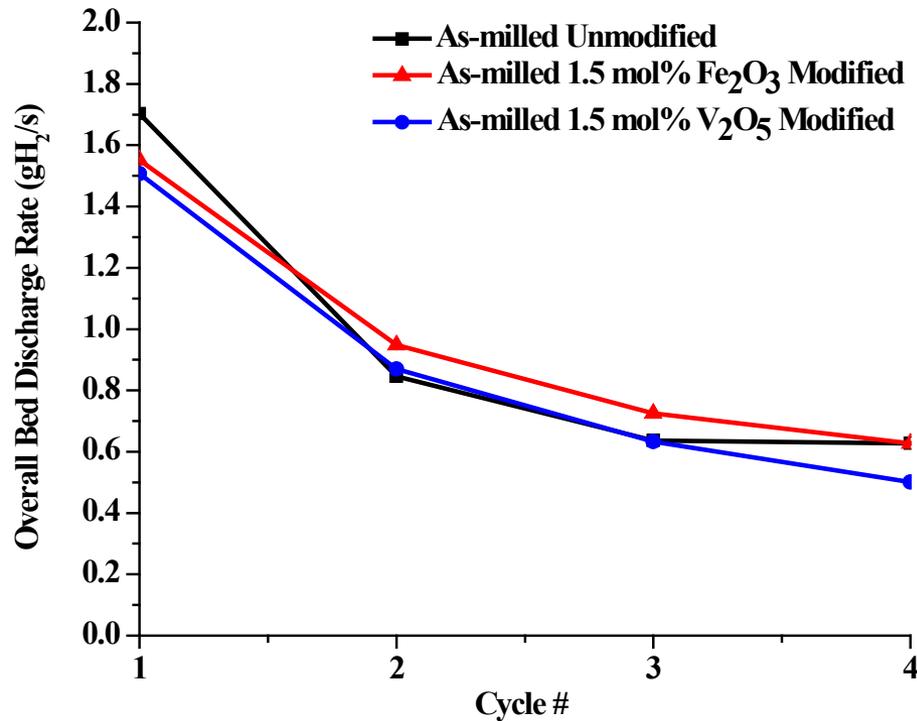
Technical Accomplishment and Progress –

TGA/RGA results of as-milled $\text{LiNH}_2:\text{MgH}_2$ 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 [gH₂/s]

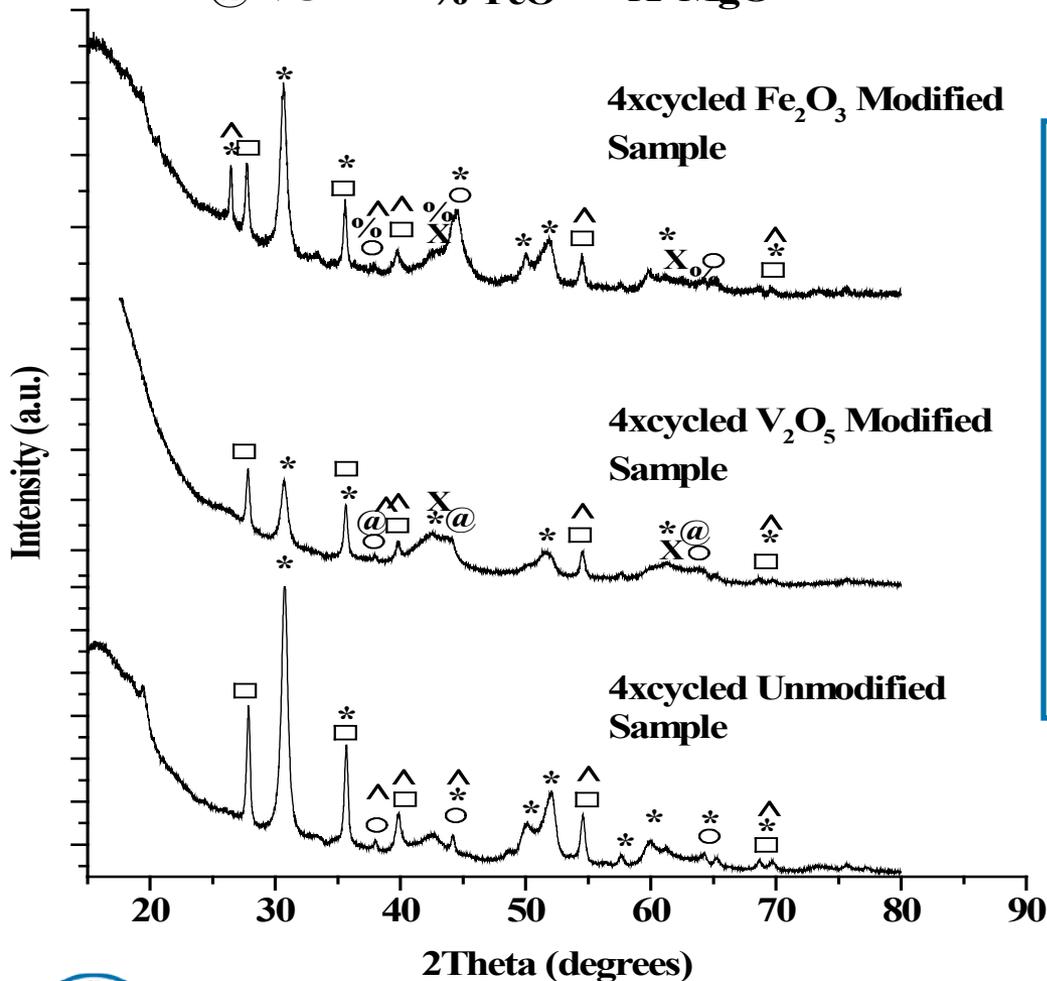


- ❖ Modifiers have no effect on the discharge rate compared to the as-milled unmodified material.
- ❖ Fe₂O₃ has no effect on the recharge rate, but the addition of V₂O₅ decreased the recharge rate by 11.6%.

Technical Accomplishment and Progress –

XRD Analysis of Cycled $\text{LiNH}_2:\text{MgH}_2$ 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.

Modified LiMgN systems of the form $\text{LiMg}(\text{NH}_2)_x(\text{BH}_4)_y$

Overall

Modified LiMgN systems through additions of alkali earth metals in the form of $\text{LiMg}(\text{NH}_2)_x(\text{BH}_4)_y$ have the potential for the formation of high hydrogen content storage materials.

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

- ❖ Synthesis of $\text{Li}_4(\text{BH}_4)(\text{NH}_2)_3$ and desorption $>10\text{wt}\%$ 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 LiNH_2 and 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 $\Delta\text{H} \sim 13$ 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 $\text{LiNH}_2 + \text{LiBH}_4 + \text{MgH}_2$ 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: $\text{M}(\text{BH}_4)^-\cdot\text{NH}_3$

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

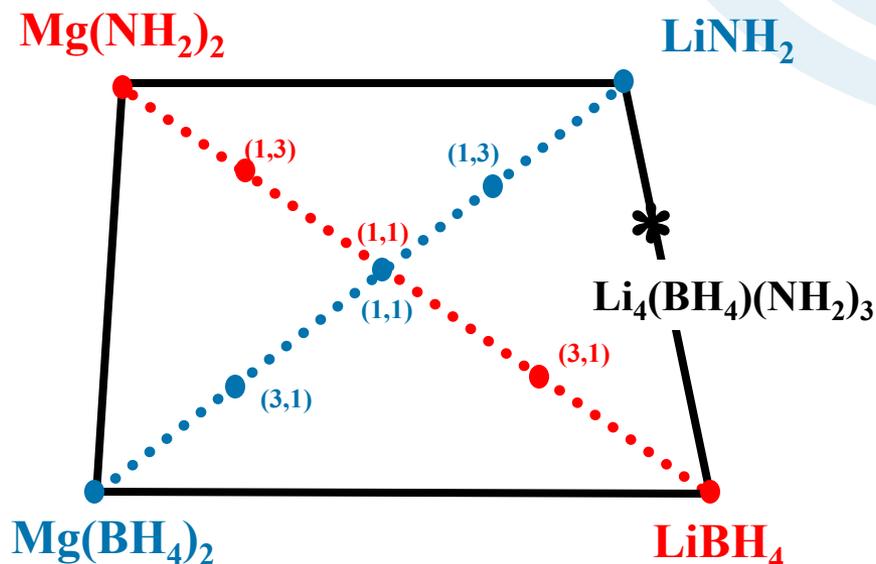
Amidoborane Complexes: $\text{M}(\text{NH}_2)^-\cdot\text{BH}_3$

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

Approach –

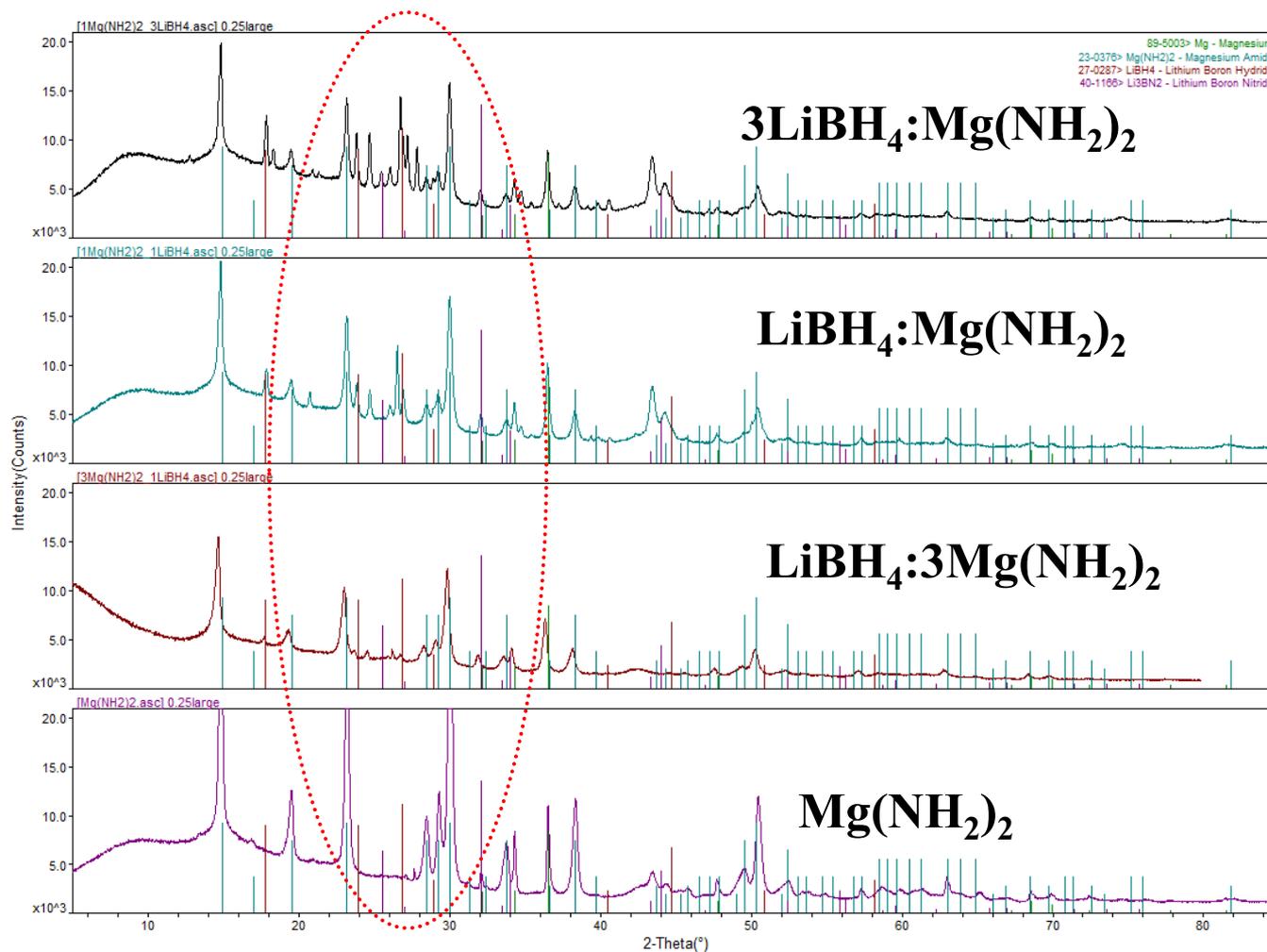
Target system $\text{Mg}(\text{NH}_2)_2$ w/large additions of LiBH_4

Amide/Borohydride Plane of Quaternary Phase Diagram



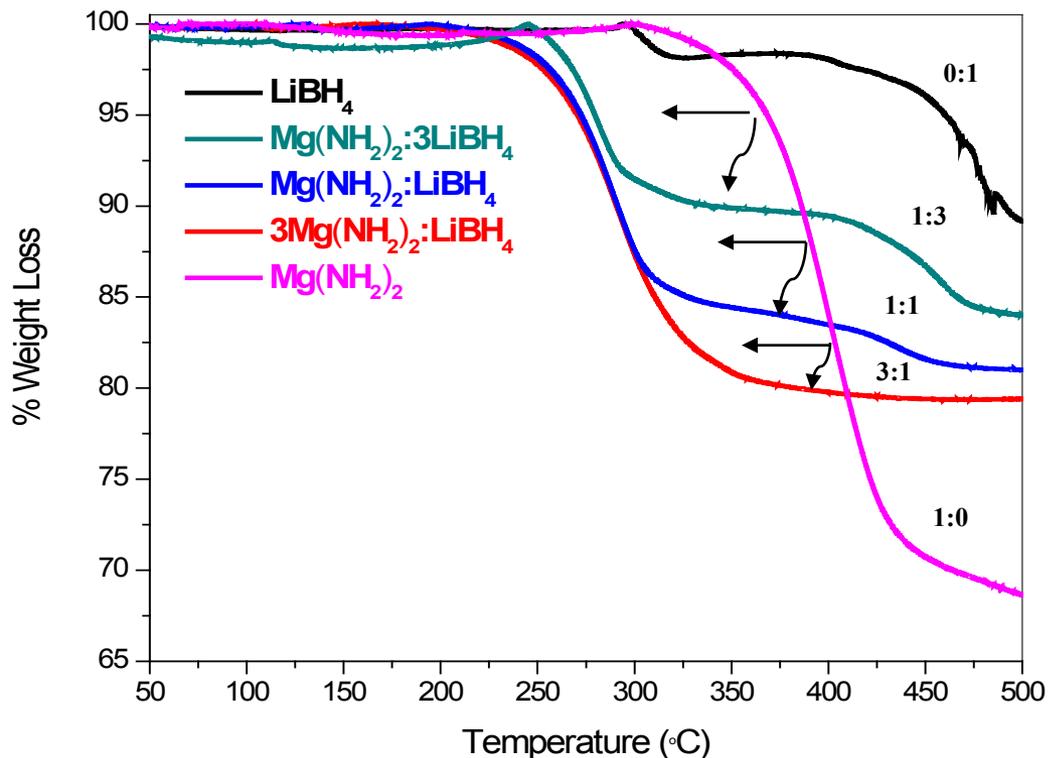
- ❖ Mixtures are formed using planetary ball-milling techniques.
- ❖ Identify isothermal/isobaric sorption properties of mixed phases using Sievert's apparatus.
- ❖ XRD analysis after ball milling process and after cycling.
- ❖ TGA-RGA to determine composition of hydrogen during dehydrogenation.

Technical Accomplishments and Progress – XRD analysis of mixed $\text{Mg}(\text{NH}_2)_2/\text{LiBH}_4$



❖ No chemical reaction observed upon Fritsch milling of $\text{Mg}(\text{NH}_2)_2$ and LiBH_4 .

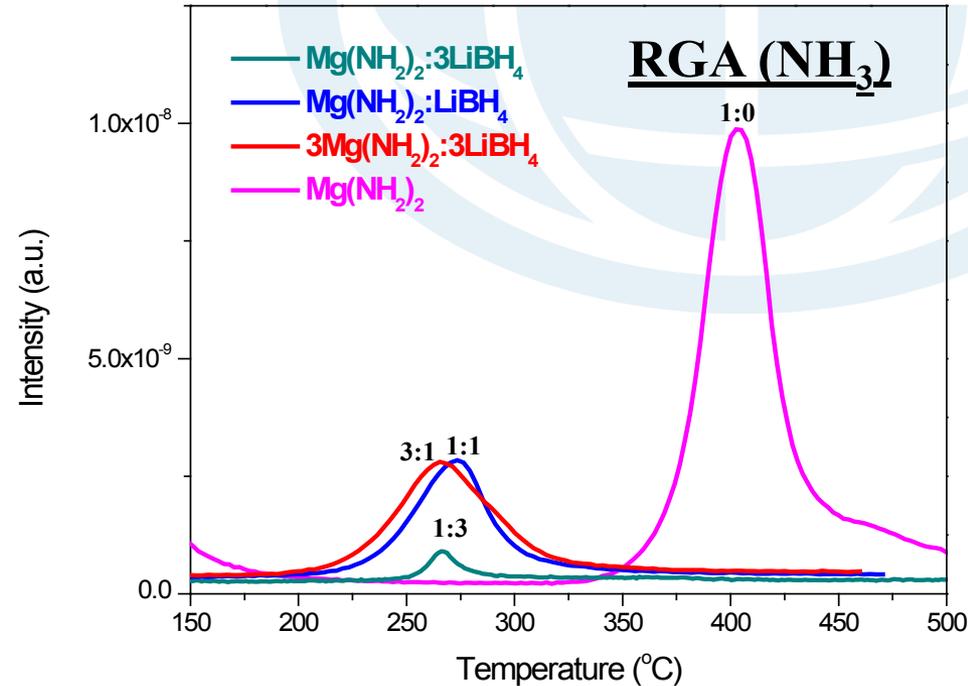
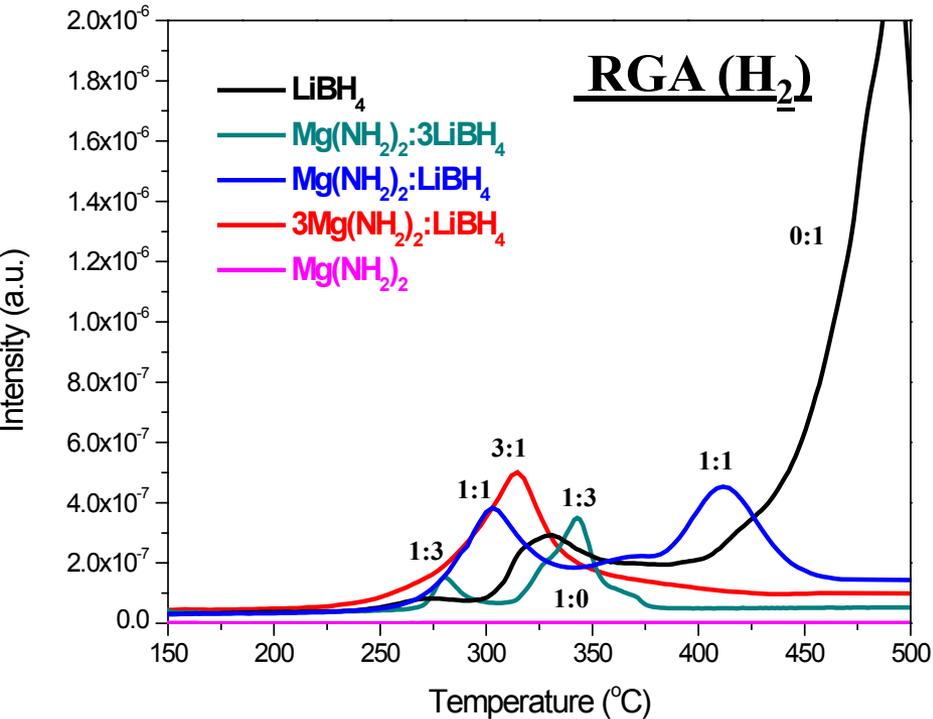
Technical Accomplishments and Progress – TGA analysis of mixed $\text{Mg}(\text{NH}_2)_2/\text{LiBH}_4$



- ❖ Pronounced interaction between the LiBH_4 and $\text{Mg}(\text{NH}_2)_2$ results in a 100°C decrease in decomposition temperature.
- ❖ Weight loss seen in $\text{Mg}(\text{NH}_2)_2$ 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
$\text{Mg}(\text{NH}_2)_2:3\text{LiBH}_4$	15.6	16.0	0.4
$\text{Mg}(\text{NH}_2)_2:\text{LiBH}_4$	12.8	19.0	-6.2
$3\text{Mg}(\text{NH}_2)_2:\text{LiBH}_4$	9.9	20.6	-10.7
$\text{Mg}(\text{NH}_2)_2$	7.1	32.4	-25.3

Technical Accomplishments and Progress – RGA analysis of mixed $\text{Mg}(\text{NH}_2)_2/\text{LiBH}_4$



- ❖ Pure $\text{Mg}(\text{NH}_2)_2$ has negligible release of hydrogen and a large NH_3 release at 400°C .
- ❖ $3\text{Mg}(\text{NH}_2)_2:\text{LiBH}_4$ has a single release of hydrogen close to 225°C .
- ❖ $\text{Mg}(\text{NH}_2)_2:\text{LiBH}_4$ and $\text{Mg}(\text{NH}_2)_2:3\text{LiBH}_4$ 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.

Overview – Decomposition of TiCl₃ doped material from University of Utah

? mol% TiCl₃ used as modifier

Preparation: Spex mill LiNH₂ and MgH₂/TiCl₃ for 4 hours separately jar rolled together for 96 hours

Lu, et al. observed 8.0 wt% lost between RT and 220°C at 5°C/min TGA for hydrogenated TiCl₃ doped LiMgN

Lost 9.57 wt% during ramping from RT to 400°C at 5°C/min at SRNL

- Initial Hydrogen release started **100°C** and peaked at 256°C and 301°C
- Ammonia release started at **211°C** and peaked at 250°C

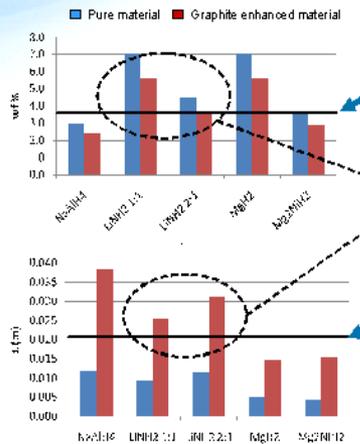
Overview – Initial Decomposition of Doped Material milled at SRNL

- Transition metal halides and nitrides used as modifiers
- Preparation: Fritch mill LiNH₂, MgH₂ & modifier for in 30 minute cycles

Composition of Mod. function	Theoretical H ₂ Weight %	Total Weight % Released	Initial Hydrogen Release Temperature	H ₂	H ₂	H ₂
Re Modification	8.14	10.5	135°C	204	240	340
1.5 mol% TiCl ₃	7.61	7.37	105°C	201	240	287
1.5 mol% VCl ₃	7.44	6.7	117°C	150	247	250
1.5 mol% TaCl ₅	7.94	7.19	120°C	210	255	325
1.5 mol% ZrCl ₄	7.45	10.32	105°C	170	337	-
1.5 mol% HfCl ₄	7.57	7.59 (by 300°C)	120°C	210	250	-

- All catalysts reduce 1st cycle hydrogen desorption temperature by 10-20°C
- Possible metathesis reaction between LiNH₂ and M₂Cl₆ promote H₂ release
- Only TiN increased the temperature of initial ammonia release by 10°C

Accomplishments: System Architect Analysis: Applying Acceptability Envelope Model to Various Materials



Accomplishments: Metal Hydride Models: Novel Concepts

Longitudinal Fins

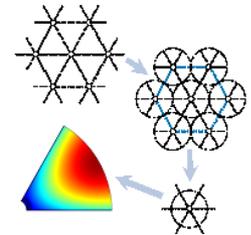
- Symmetry assumed
- Each tube independent
- End effects neglected (Assumed 2-D)
- 60° wedge
- Spatially uniform H₂ pressure assumed
- Explicit fin and tubes
- Media-metal thermal contact resistances included
- Conditions (Adjustable)
 - 50 bar H₂ feed pressure
 - 100°C cooling fluid

- Advantages**

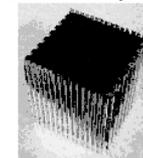
 - Media Packing

Disadvantages

 - Construction Cost (also applies to MHS (below))

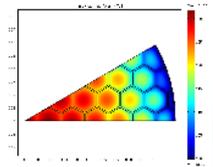


Metallic Honeycomb Structure (MHS)



Thickness t (in)	0.04
Cell size l (in)	1 1/2 3/8

- Symmetry assumed (30°)
- Axial hydrogen injection at 50 bar
- Contact resistance not considered



Summary

- ❖ Milling technique and modifier composition have a significant effect on initial H₂ and NH₃ 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 Mg₃N₂ formation
- ❖ Discharge temperature also has a significant effect on sorption rates and product composition
 - ❖ Mg₃N₂ formation predominate in high temperature cycling
- ❖ Mixtures of Mg(NH₂)₂ with LiBH₄ 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 $\text{LiNH}_2:\text{MgH}_2$
- ❖ Determination of the transformation mechanism in $\text{LiNH}_2:\text{MgH}_2$ 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 $\text{LiH}/\text{Mg}(\text{NH}_2)_2$ 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.

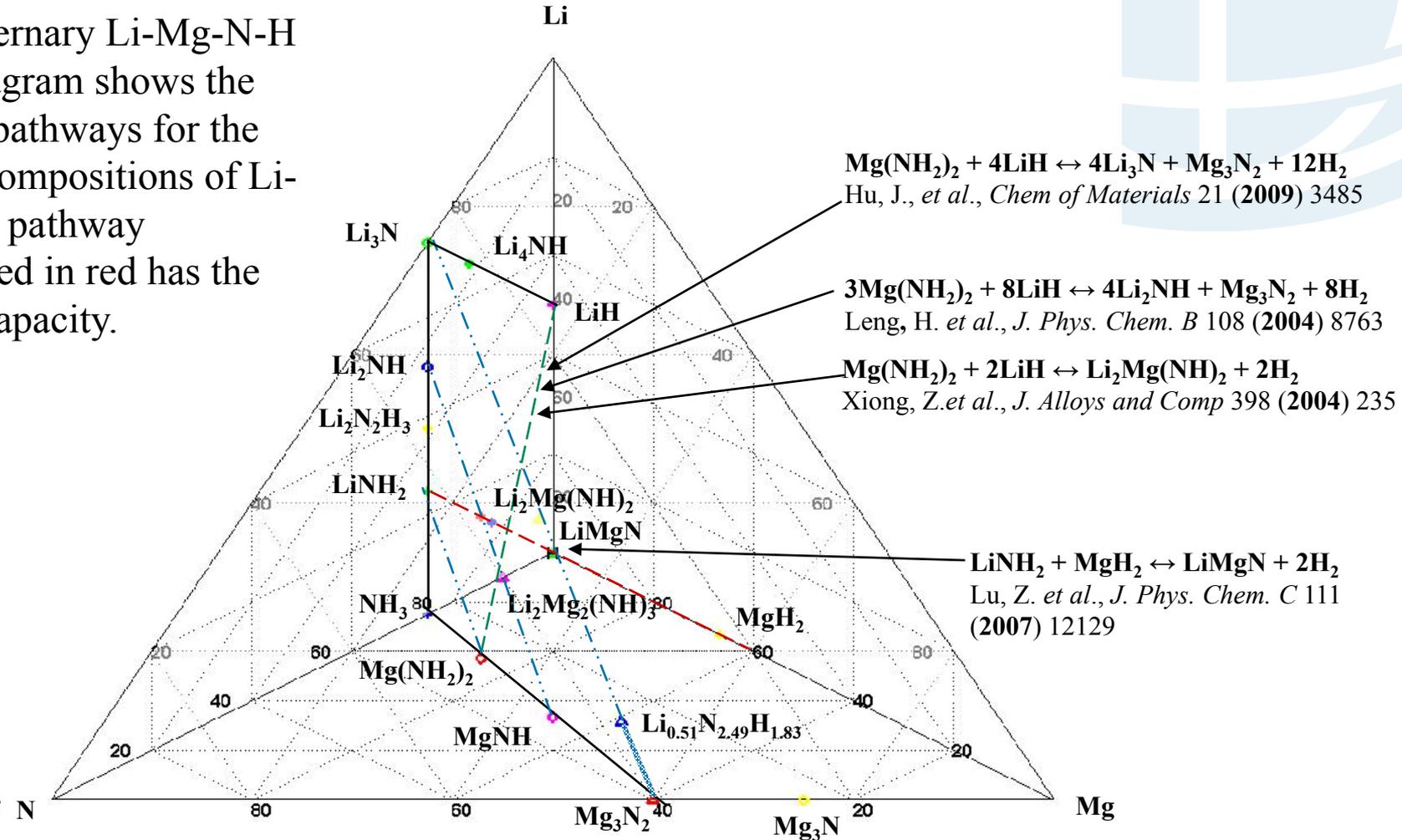


Technical Back-Up Slides

Approach –

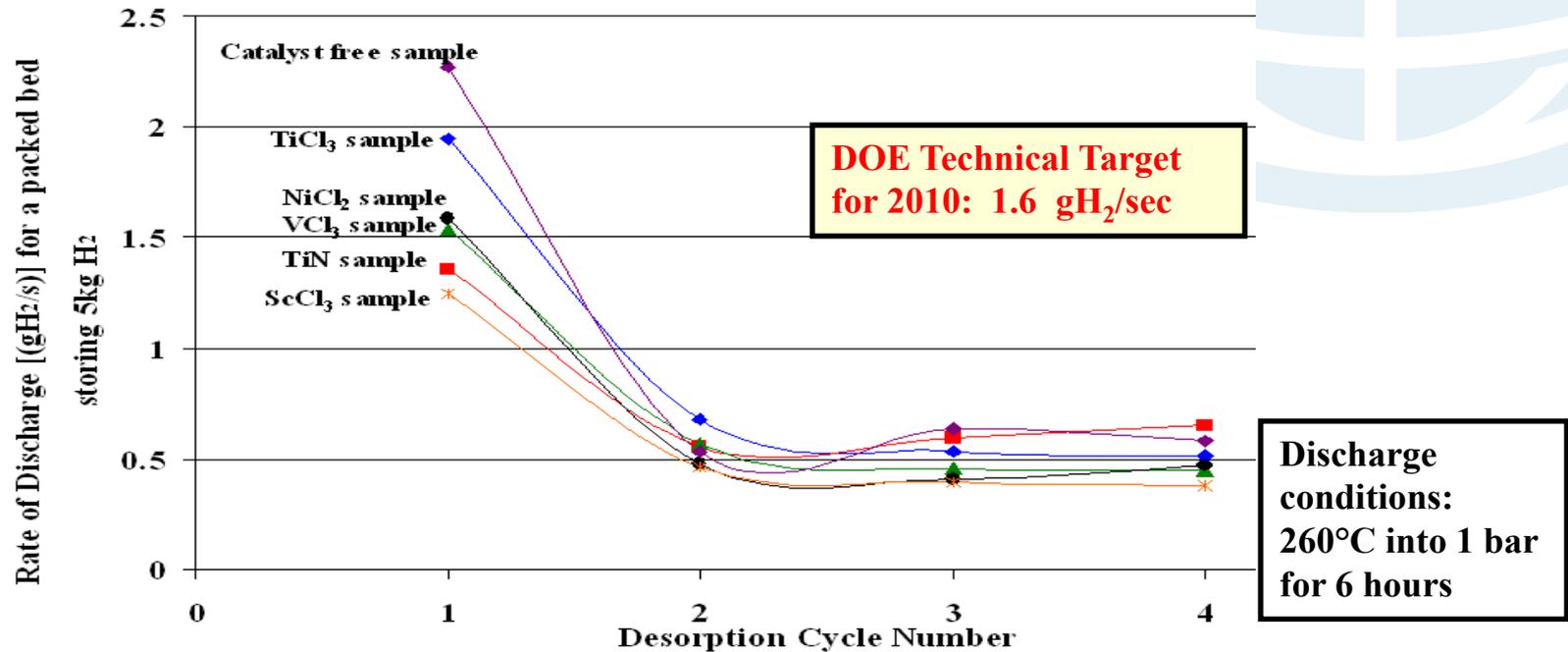
Li-Mg-N-H Quaternary Phase Diagram

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.



Technical Accomplishments and Progress – Average Discharge Rate of Hydrogen Discharge [gH₂/s]

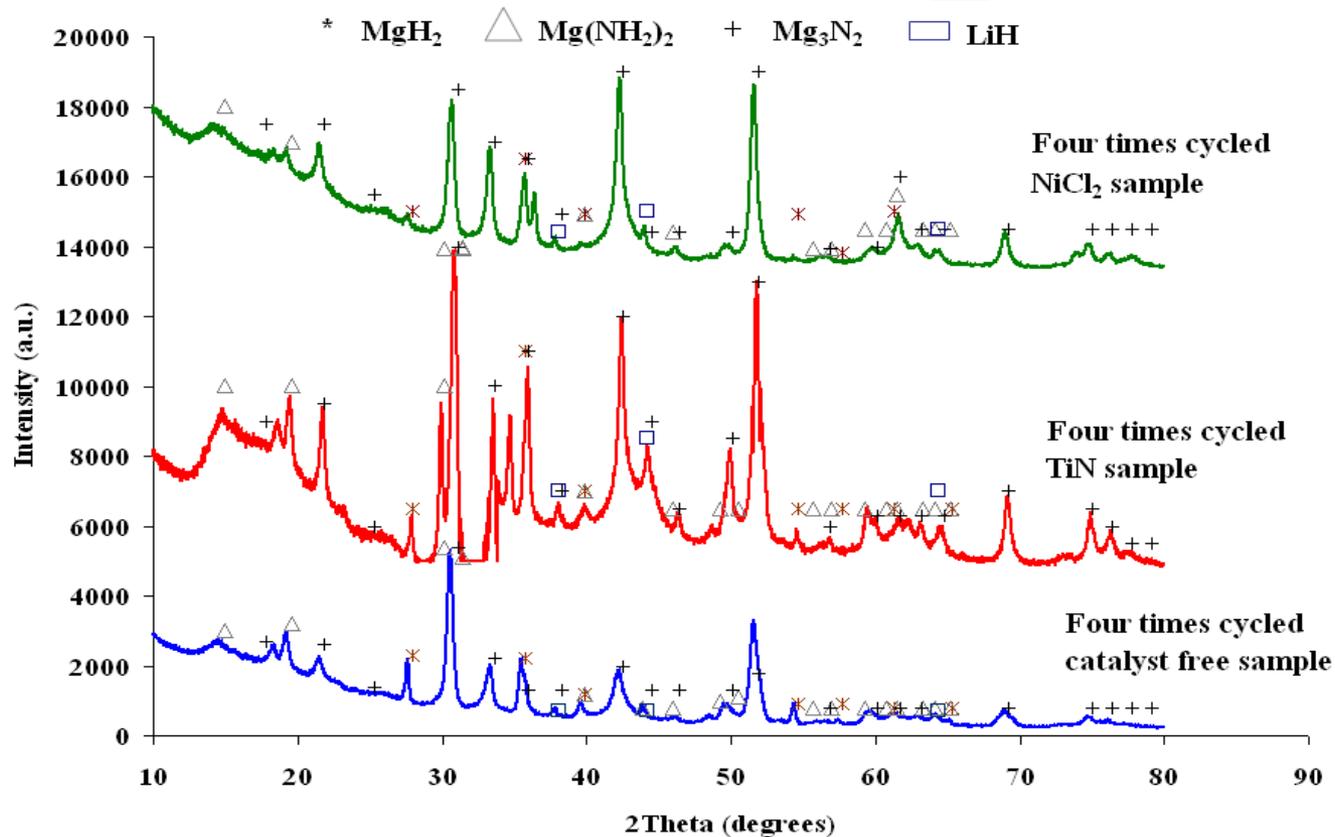
Average Rate of Hydrogen Discharge for a packed bed storing 5kg H₂



- ❖ 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 M_{tr}Cl₃: $\text{LiNH}_2 + \text{TiCl}_3 \rightarrow \text{LiCl} + \text{Ti}(\text{unknown state}) + \text{NH}_2$

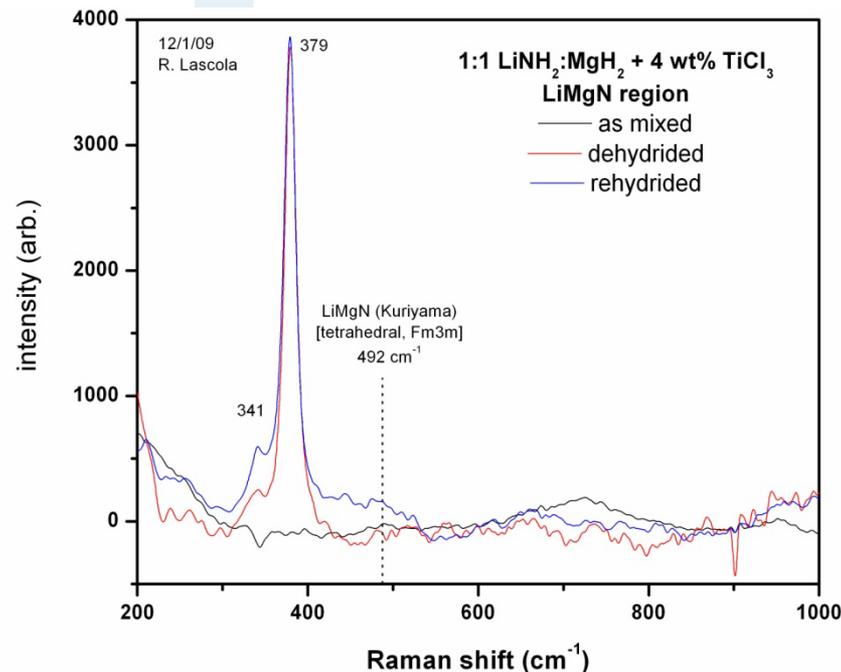
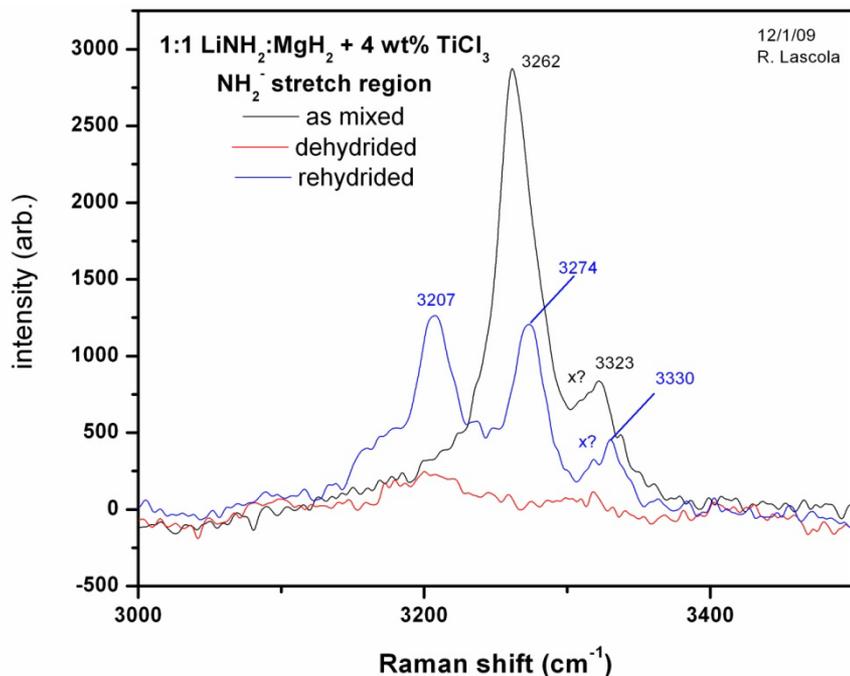
Technical Accomplishments and Progress –

XRD Analysis of four cycled 1:1 LiNH₂:MgH₂ ^{w/w/o} modifiers



- ❖ Mg(NH₂)₂, MgH₂ and LiH identified showing $\text{LiMgN} \leftrightarrow \text{LiH} + \frac{1}{2} \text{MgH}_2 + \frac{1}{2} \text{Mg(NH}_2)_2$
- ❖ Mg₃N₂ also identified, possibly forming from $\text{Mg(NH}_2)_2 + 2\text{MgH}_2 \rightarrow \text{Mg}_3\text{N}_2 + 4\text{H}_2$ [$\Delta H = 15 \text{ kJ/mol H}_2$ at 500K, Akbarzadeh, *et al.*, *Adv Mat.* **19** (2007) 3233] or $\text{LiMgN} + \text{H}_2 \rightarrow \text{LiH} + \text{Mg}_3\text{N}_2$

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_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 $\text{Mg}(\text{NH}_2)_2$