Amide and Combined Amide/Borohydride Investigations

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***University of South Carolina**

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METAL HYDRIDE CENTER OF EXCELLENCE

Project ID #: STP_40_Anton

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Overview

Timeline

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

Barriers Addressed

A. System Weight and Volume

E. Charging/Discharging Rates

P. Understanding of Hydrogen Chemisorption

Budget

- FY'08 Funding
  - $100K
- Planned FY'09 Funding
  - $400K

Partners

- Z. Fang – University of Utah
- H. zurLoye – University of South Carolina
- E. Ronnebro – SNL (now PNNL)

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Relevance: LiMgN as a Hydrogen Storage Material

$$LiNH_2 + MgH_2 \rightarrow LiMgN + 2H_2$$

- Identified with DFT calculations performed by Alapati and colleagues as potentially reversible with reasonable H_2 storage content

  (Alapati *et al*, *Phys. Chem. Chem. Physics*. 9 1438 (2007)

- Theoretical H_2 gravimetric storage capacity of system is 8.2 wt%
  - Experimentally, 8.1 wt% was observed by Lu et al. under moderate temperature (160^{O}C – 220^{O}C) using TGA (Lu et al., J. Phys. Chem. C, 111,pp. 12129. (2007))

- Recharge theorized by Lu et. al. to take different pathway
  - Theoretical H_2 storage capacity is 8.2 wt%

    (8.0 wt% observed experimentally at 160 ^{o}C and 140 bar in pressure vessel)

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

- Dehydrogenation is proposed to proceed through an intermediate step

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

- Accelerated reversibility has been observed using 4 wt.% $TiCl_3$ dopant by Lu et al.

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Li-Mg-N-H Systems Published in Literature

- Li_xMg_y-amide materials have been studied by numerous groups which have cited both NH_3 production and high discharge temperatures as limiting their utility
- Various compositional ratios of these compounds have been investigated to determine experimental hydrogen storage capacities, reaction pathways, reversibility, and rate of hydrogen release:
  - $LiNH_2 + MgH_2 \leftrightarrow LiMgN + 2H_2$
    (Lu *et al*. *J. Phys. Chem. C*, **111** ,pp. 12129. (2007);
    Alapati *et al*, *Phys. Chem. Physics*. 9 1438 (2007))
  - $Mg(NH_2)_2 + 2LiH \leftrightarrow Li_2Mg(NH)_2 + 2H_2$
    (Xiong *et al*, *Adv. Mater*. **16** 1522 (2004))
  - $3Mg(NH_2)_2 + 8LiH \leftrightarrow 4Li_2NH + Mg_3N_2 + 8H_2$
    (Leng *et al*, *J. Phys. Chem. B*. **108** 8763 (2004))
  - $3Mg(NH_2)_2 + 12LiH \leftrightarrow 4Li_2N_3 + Mg_3N_2 + 12H_2$
    (Nakamori *et al*, *J. Power. Source*. **138** 309 (2004))
  - $2LiNH_2 + MgH_2 \leftrightarrow Li_2Mg(NH)_2 + 2H_2$
    (Luo, *J. Alloys Compd*. **381** 284 (2004) / Rijssenbeek *et al*, *J. Alloys Compd*. **454** 233 (2008))

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

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Objectives

- Collaborate with University of Utah group - perform complementary experiments to analyze the LiMgN system
- Verify reversibility conditions of $TiCl_3$ doped LiMgN
- Explore the effect of catalyst loading on both charge and discharge reaction pathways and kinetics.
- Outline discharge and charge kinetics under various temperature and pressure conditions to prepare for hydrogen storage system design

Experimental Plan

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

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

M_{tr} = Ti, V, Cr, Ni…
composition = [0.5 mol% – 6 mol%]

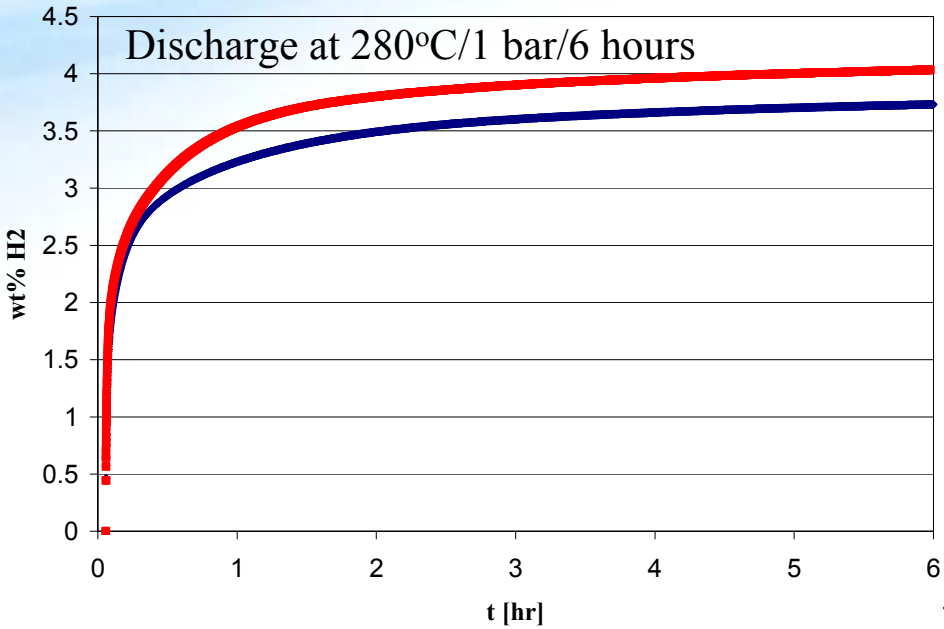
- XRD analysis at various points in hydrogenation/dehydrogenation cycle

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

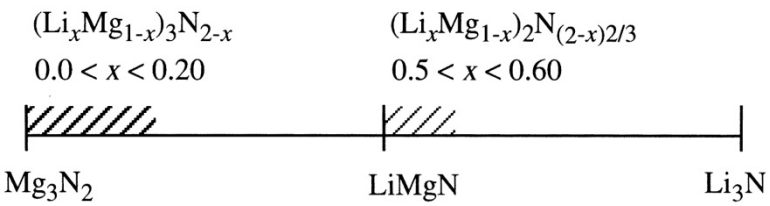
Material Synthesis and Experimental Procedure

- **Synthesis**
  - All materials prepared using Frisch mill rotational milling technique
  - FM for 3 hrs at 500 rpm, with rotational direction reversed every 3 min
  - All reactors are loaded in an inert Ar glove box
  - Standard discharge condition: 280^{o}C/1 bar/6 hr
  - Standard charge condition: 180^{o}C/150 bar/6 hr
- **Discharge Procedure**
  - Reactor is placed under high pressure (~150 bar) and heated to desired temperature
  - Manifold is controlled so that when the reactor is released to the reservoir, the nominal backpressure is equal to 1 bar
  - Temperature Programmed Desorption (TPD) performed at 2^{o}C/min into 1 bar reservoir pressure
- **Charge Procedure**
  - Reactor is placed under active vacuum and heated to desired temperature
  - Reservoir is pressurized to the desired pressure and released to the reactor

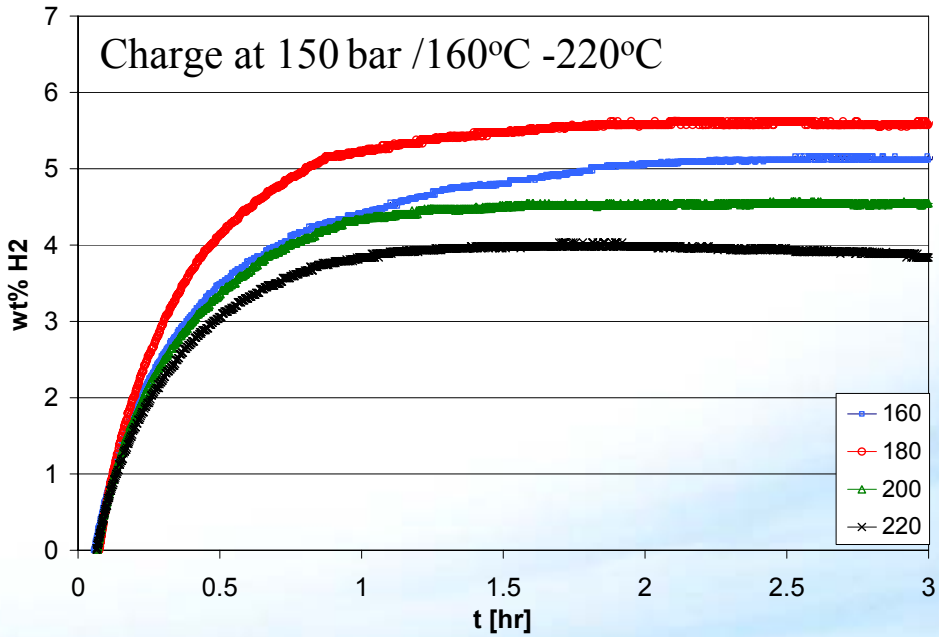
Isothermal Recharging Data – 0.667 mol% (4 wt% $TiCl_3$)



Discharge products are comprised of LiCl, Mg_3N_2, LiMgN and a minor amount of an unidentified phase (< 5%). Mg_3N_2 and LiMgN nearly iso-structural with a cation disordered anti fluorite structure type.



- 180°C selected as optimal charging condition
- Time to 80% charge (τ_{80}) = 37 min
  - DOE target = 3 min



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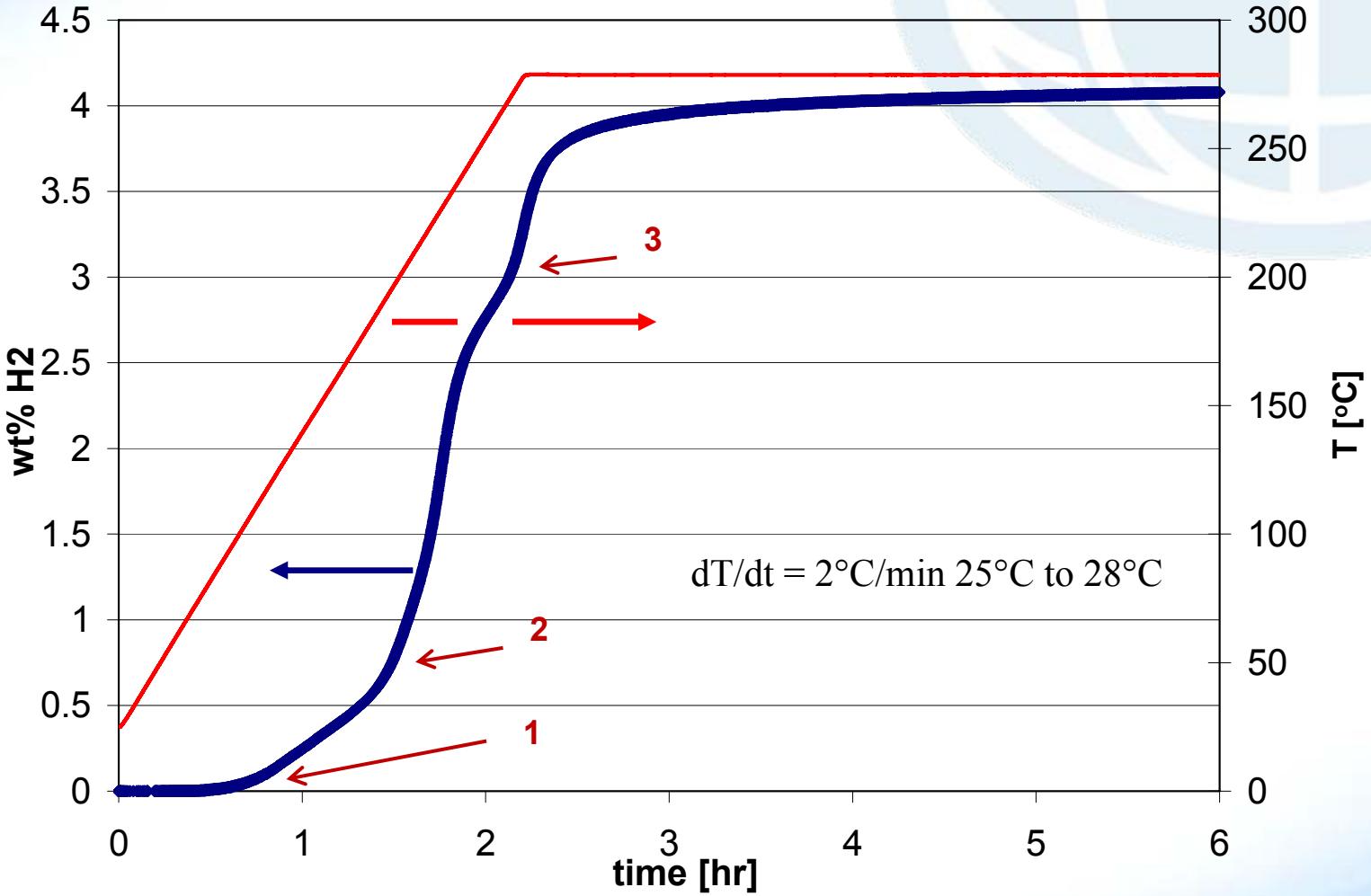
Temperature Programmed Desorption Data – 4 mol% $TiCl_3$



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

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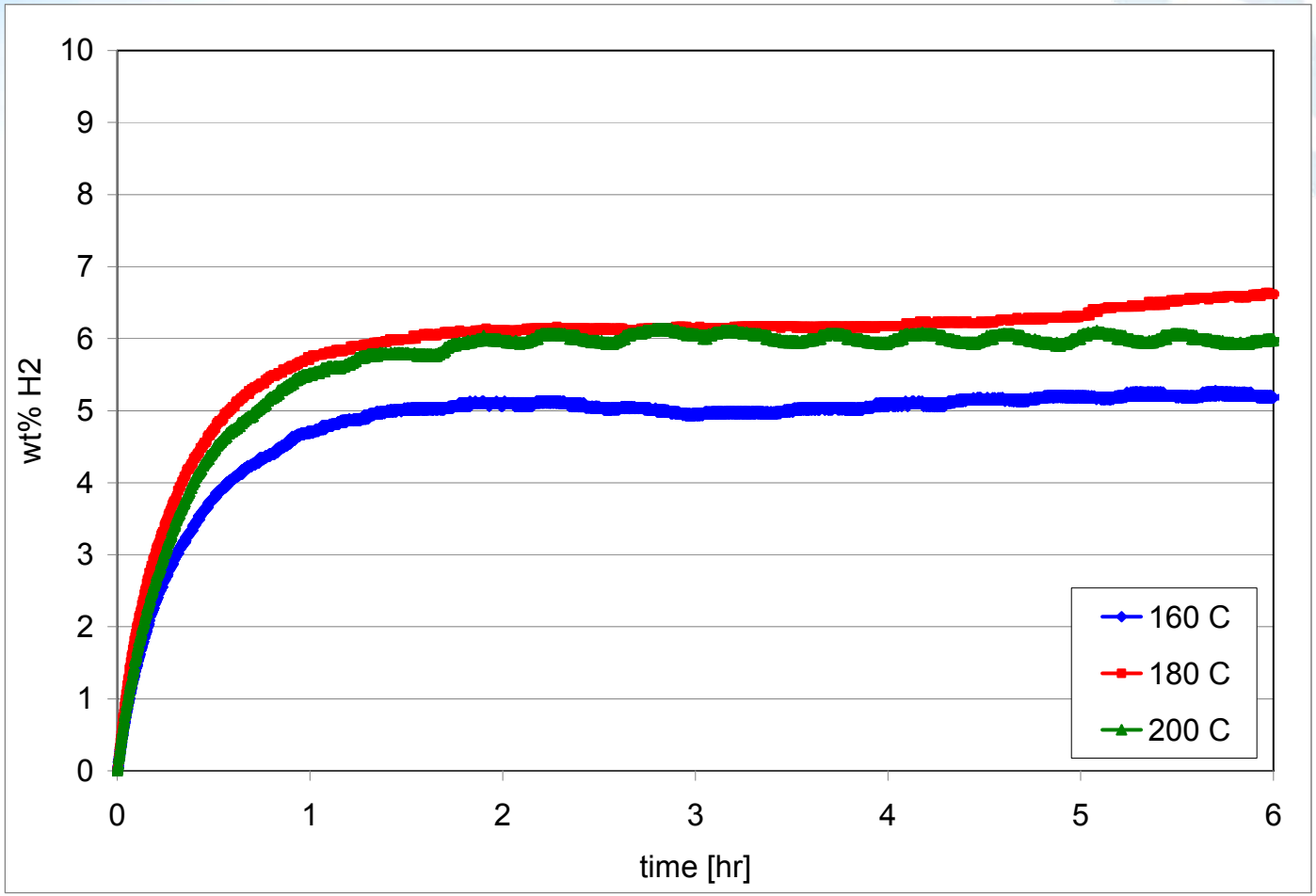
Isothermal Recharging Data – 4 mol% $TiCl_3$

Charges performed between 160°C-200°C/150 bar/10 hr



- Discharge products are similar to those obtained at 1 bar and comprised of LiCl, Mg_3N_2, LiMgN and a minor amount of an unidentified phase (< 5%).
- Time to 80% Charge (τ_{80}) = 30 min.
  - DOE target = 3 min.

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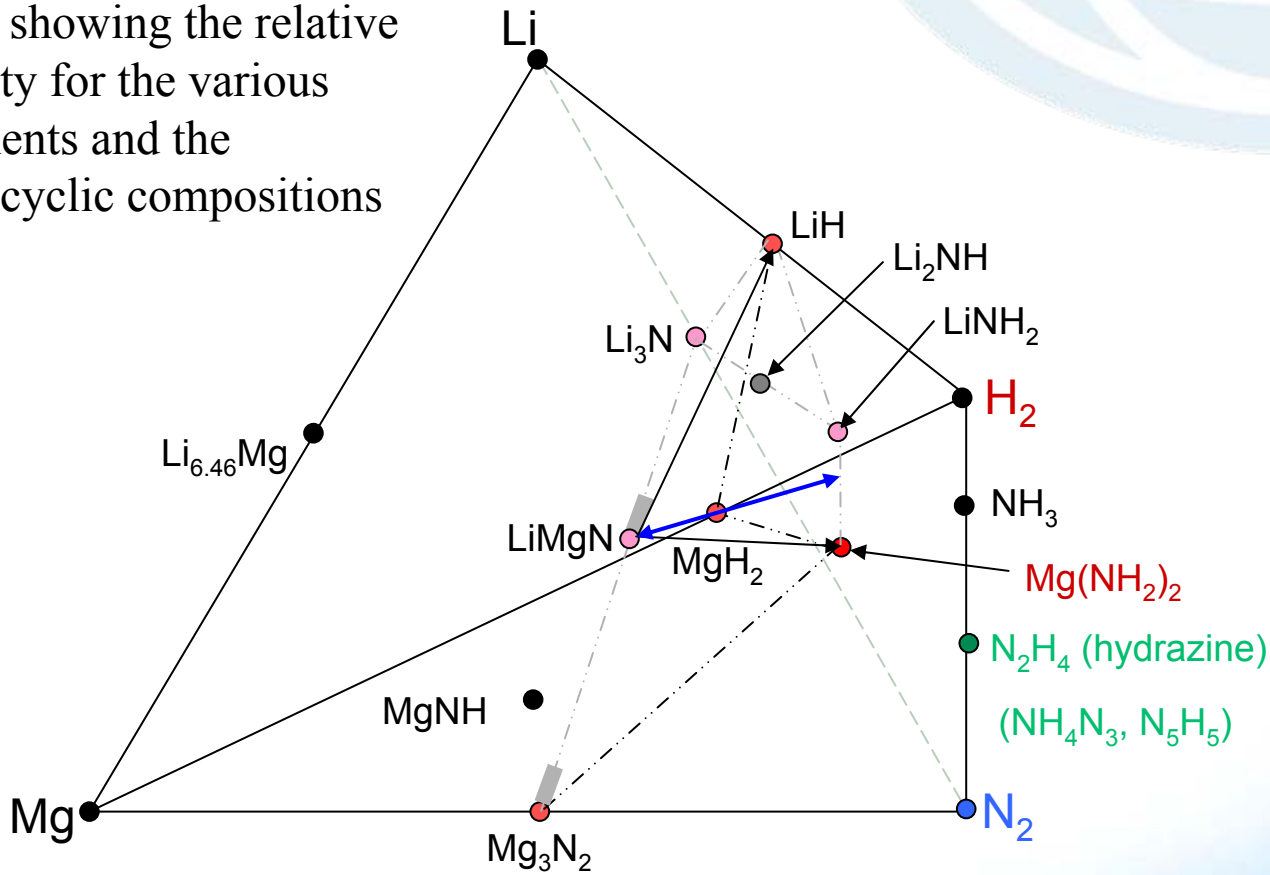
Li-Mg-H-N
Pseudo-Quaternary Phase Diagram

The quaternary Li-Mg-N-H phase diagram is given showing the relative regions of stability for the various possible components and the proposed closed cyclic compositions (in blue).



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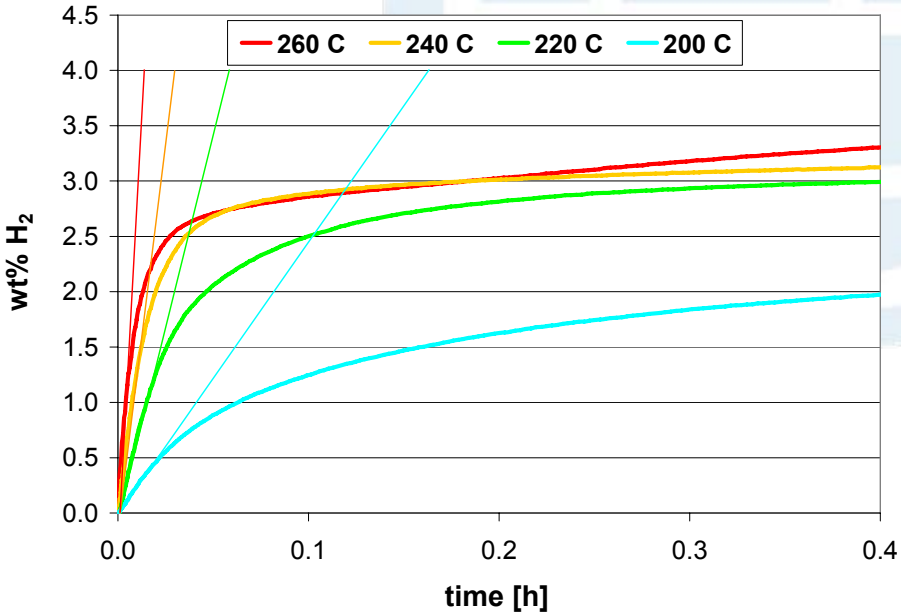
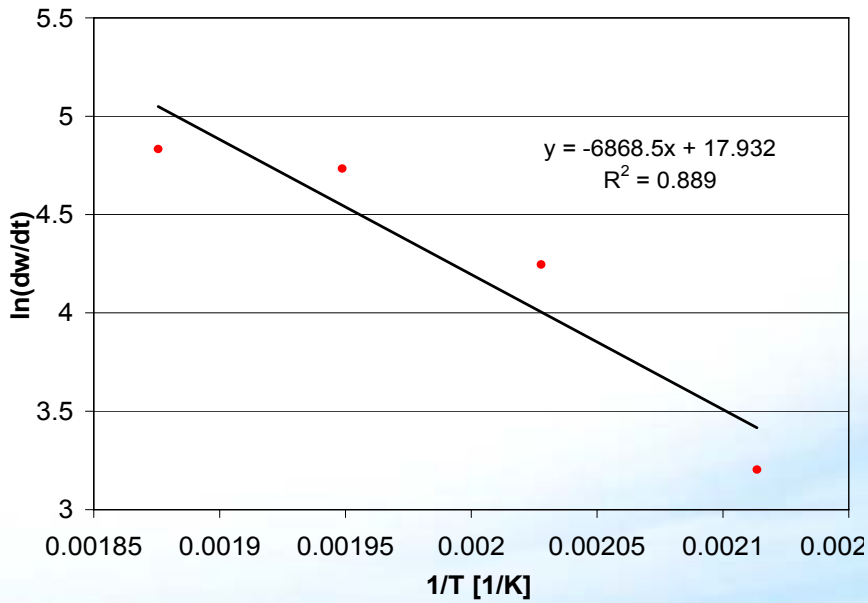
Discharge Kinetic Analysis of Li-Mg-N System

- Traditional kinetic analysis follows from Arrhenius equation



- Linear kinetics gives activation energy of 60 kJ/mol H_2 for discharge reaction



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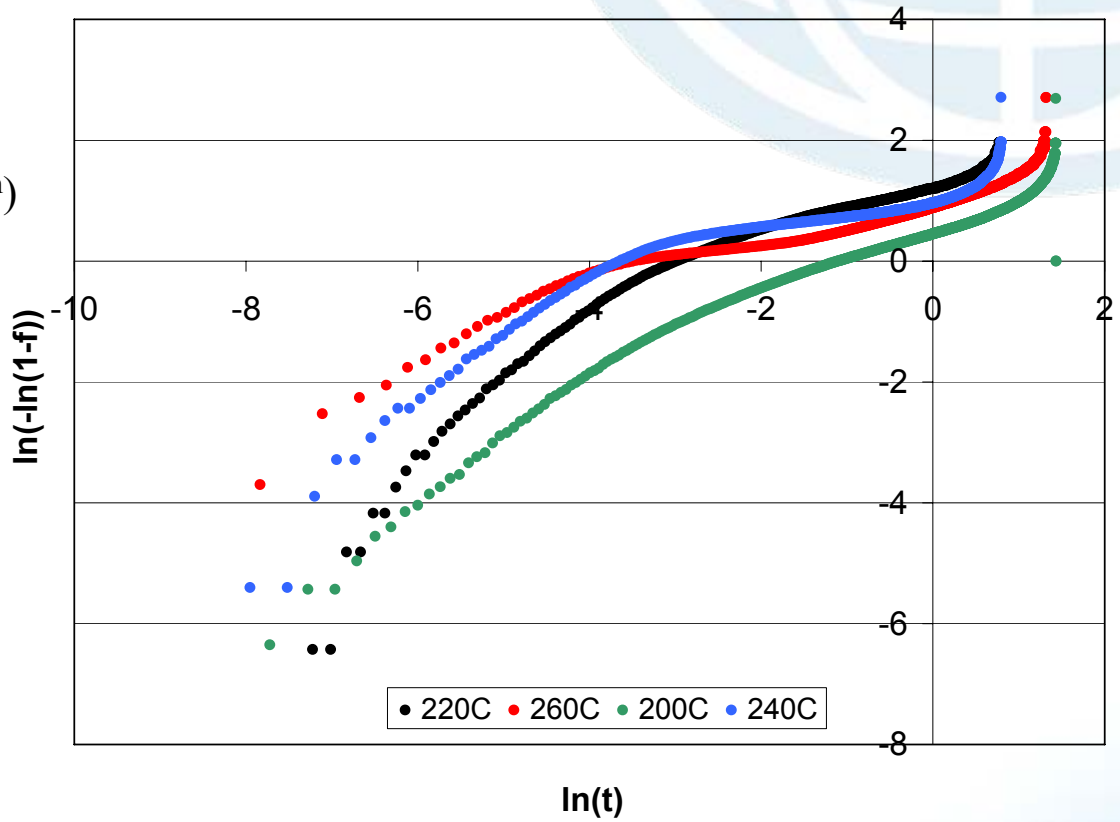
Discharge Kinetic Analysis

Johnson-Mehl-Avrami Approximation

- $\alpha(t)=1-\exp(-kt^n)$
  - $d\alpha/dt=k*nt^{(n-1)}*\exp(-kt^n)$
- $\ln(-\ln(1-\alpha)) = n\ln(t) + \ln(k)$
- Transformations between different linear segments indicative of changes in reaction mechanism



Evidence of multi-step reaction mechanism observed

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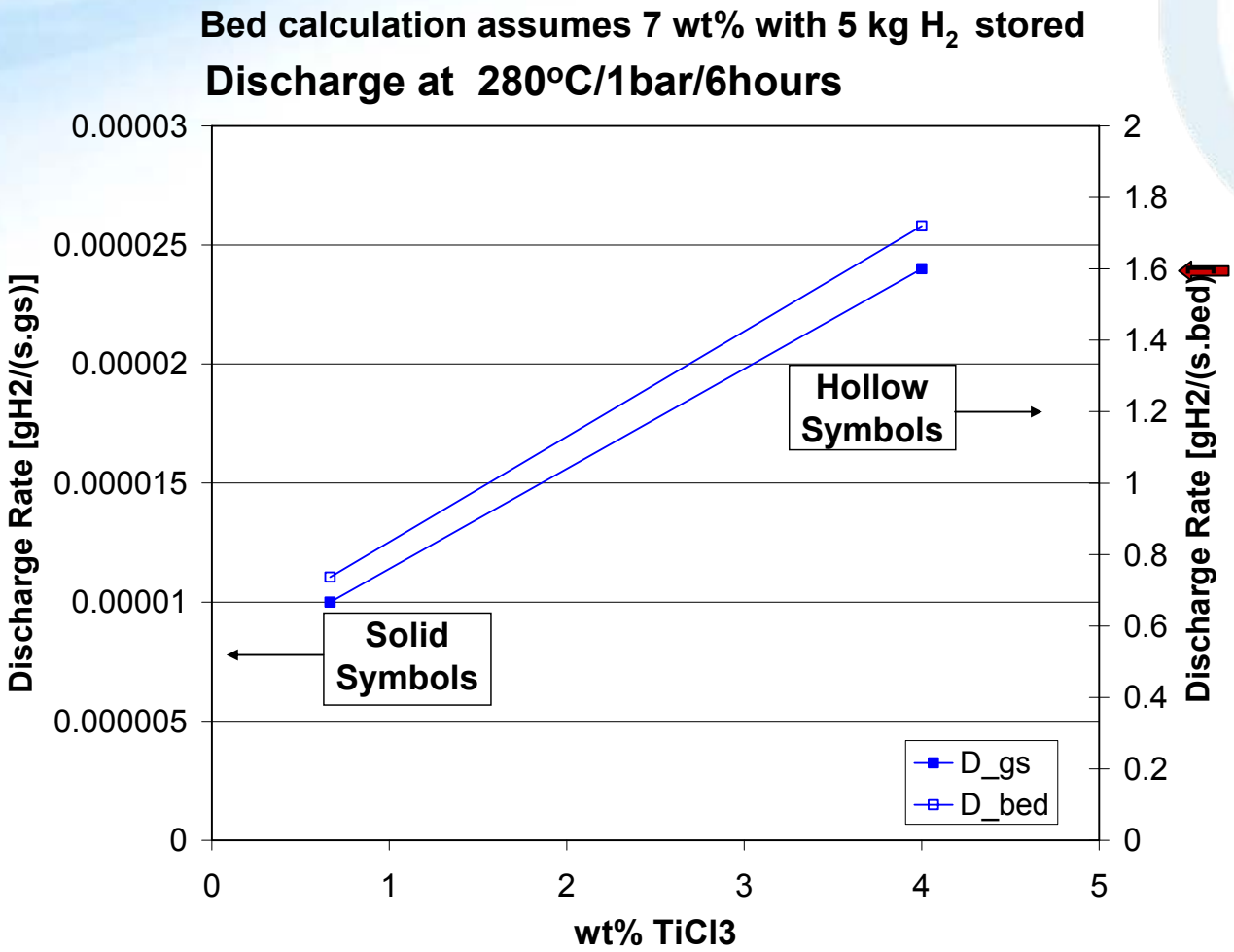
Li-Mg-N Discharge Kinetics



DOE 2015 goal for 80 KW PEMFC

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

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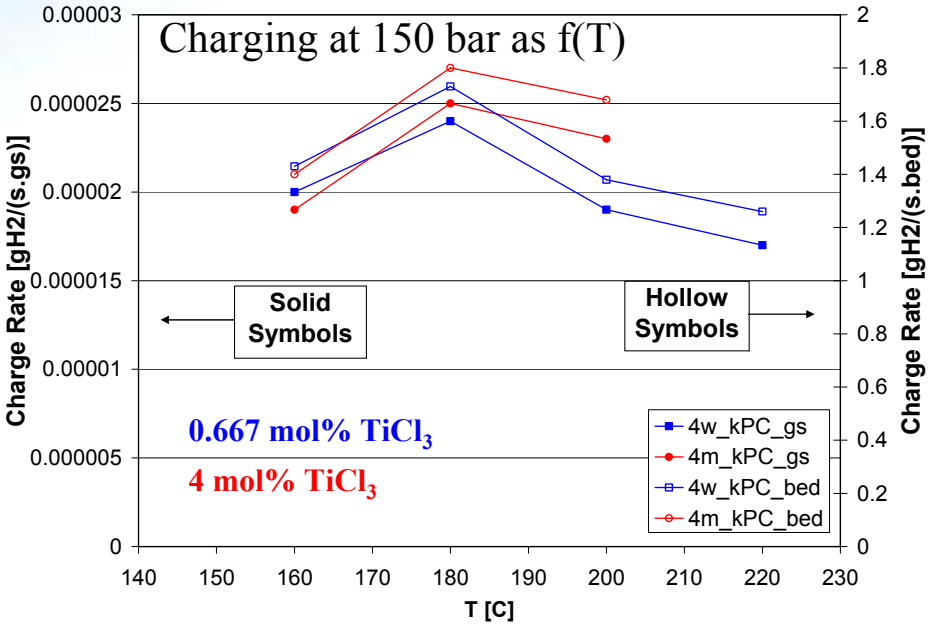
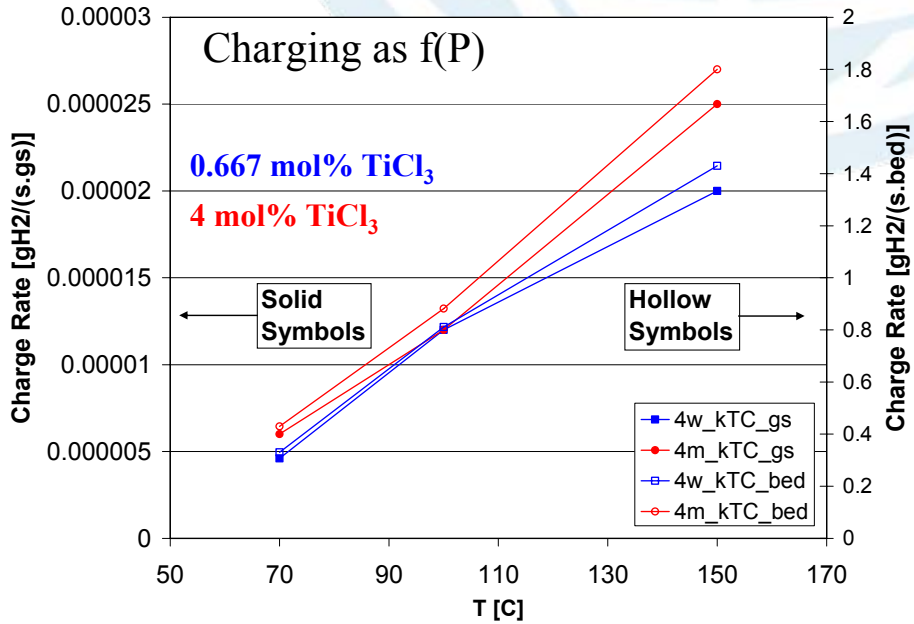
Li-Mg-N Charge Kinetics

Bed calculation assumes 7 wt% with 5 kg H_2 stored





Catalyst loading has little effect on charging rates

Charging rate strongly affected by pressure

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Technical Target Comparison

4 mol% material discharge rate is 57% of DOE technical target at 280°C
0.667 mol% material discharge rate is 24% of target at 280°C

0.667 mol% $TiCl_3$ (4 wt%)		Rate [g H_2 / (s·g_s)]	Rate 72 kg bed*
P	150 bar	Charge	
Temp	160°C	2.0 x 10^{-5}	1.43
	180°C	2.4 x 10^{-5}	1.73
	200°C	1.9 x 10^{-5}	1.38
	220°C	1.7 x 10^{-5}	1.26
Temp	160°C	Charge	
P	70 bar	4.6 x 10^{-6}	0.330
	100 bar	1.2 x 10^{-5}	0.811
	150 bar	2.0 x 10^{-5}	1.43
Discharge			
T = 280°C	P = 1 bar	1.0 x 10^{-5}	0.737

4 mol% $TiCl_3$ (13.7 wt%)		Rate [g H_2 / (s·g_s)]	Rate 72 kg bed*
P	150 bar	Charge	
Temp	160°C	1.9 x 10^{-5}	1.40
	180°C	2.5 x 10^{-5}	1.80
	200°C	2.3 x 10^{-5}	1.68
Temp	180°C	Charge	
P	70 bar	6.0 x 10^{-6}	0.430
	100 bar	1.2 x 10^{-5}	0.882
	150 bar	2.5 X 10^{-5}	1.80
Discharge			
T = 280°C	P = 1 bar	2.4 x 10^{-5}	1.72

**Assumes 7 wt% with 5 kg H_2 stored*

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

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Conclusions

- Desorption products at both ambient and higher pressures (1, 150 & 180 bar) appear to be the same (mixture of LiCl, Mg_3N_2 and LiMgN a minor amount of an unidentified phase (< 5%)).
- Increased catalyst loading has significant effect on H_2 discharge rate
- Different kinetic modeling approaches are being applied to characterize and understand reaction kinetics to enable prediction of charge/discharge rates under varying engineering conditions

Future Directions

- Resolve $Li_{0.51}Mg_{2.49}N_{1.83}$ vs. LiMgN characterization issue (IR, NMR…)
  - Further characterization of the unidentified discharge product
- Test other catalysts to render faster kinetics, lower temperatures of operation (e.g. VCl_3, $NiCl_3$, $FeCl_3$…)
- Analyze the purity of the discharged H_2 as a function of temperature using RGA and FTIR
- Conduct a study to determine the effect of milling time on isothermal kinetics

Amide-Borohydride Systems

$M(BH_4)_i(NH_2)_j$

- Tailoring the electronegativity of the metal ion M^+ in the borohydride BH_4^- complex, *Nakamori et al., 2006*
- Adding secondary reactant to form a stable boron containing product, $2LiBH_4 + MgH_2 \rightarrow MgB_2 + 2LiH + 4H_2$ *Vajo & Olsen, 2007*
- Synthesis of new $Li_4(BH_4)(NH_2)_3$ [$Li_4BN_3H_{10}$], by mechanico-chemical milling of $LiNH_2$ and $LiBH_4$, *Chater et al., 2006*
- Confirmation that $Li_4(BH_4)(NH_2)_3$ desorbs >10wt% H_2 at 250 ^oC, *Pinkerton 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*

$M(BH_4)_i \bullet xNH_3$

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

$M(NH_2)_j \bullet x(BH_3)$

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

Literature Conclusions

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

Objective

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

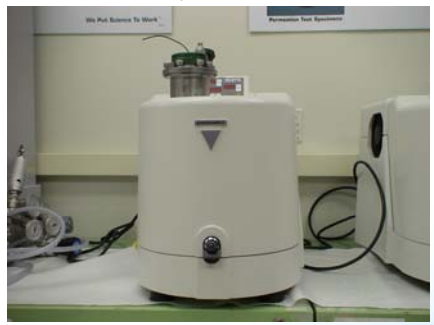
where:
M^1= Li, Na, K and
M^2=Mg, Ca, Ti and/or other transition metals.

Existing Borohydride and Amide Compounds Opportunities for Materials Discovery

Precursor 1	Precursor 2	Mixed Borohydride/Amides	ΔH_{mix} (kJ/mol H_2) Dehydriding
		NH_3BH_3	-20
LiH	NH_3BH_3	$LiNH_2BH_3$ [Xiong et.al. 2008]	-5
$LiBH_4$	$LiNH_2$	$Li_4BN_3H_{10}$ [Chater et.al. 2006]	13
$NaBH_4$	$NaNH_2$	Na_2BNH_6 [Chater et.al. 2006]	
KBH_4	KNH_2		
$Mg(BH_4)_2$	$Mg(NH_2)_2$		
$Ca(BH_4)_2$	$Ca(NH_2)_2$		
M_1 BH_4 M_1=Li, Na, K, Mg, Ca	M_2NH_2 M_2=Li, Na K, Mg, Ca		

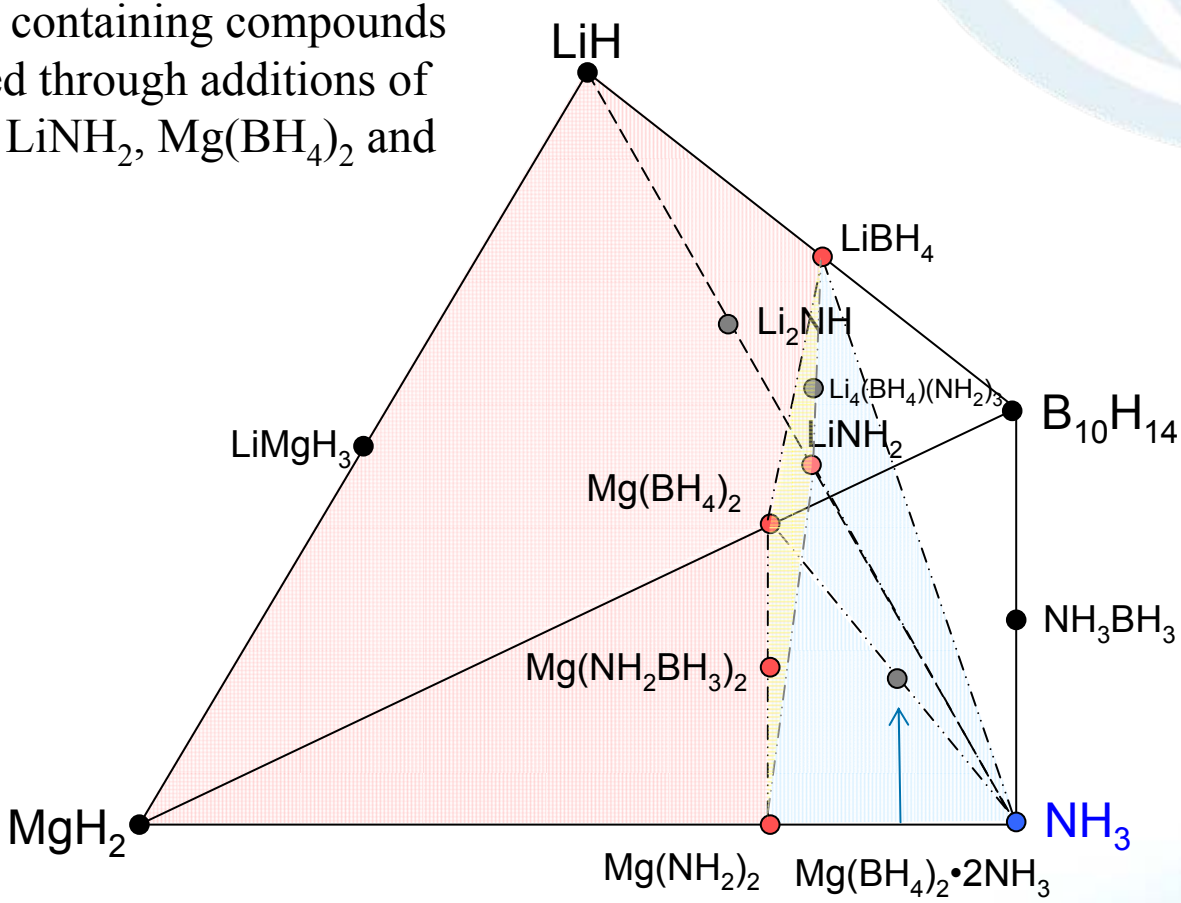
opportunities for novel materials discovery

Borohydride and Amide Precursors Used

BORO HYDRIDE	COMMERCIALLY AVAILABLE	AMIDE	COMMERCIALLY AVAILABLE
$LiBH_4$	Yes	$LiNH_2$	Yes
$NaBH_4$	Yes	$NaNH_2$	Yes
KBH_4	Yes	KNH_2	Yes
NH_3BH_3	Yes		
$Ca(BH_4)_2$	Yes	$Ca(NH_2)_2$	Synthesis via [Hino et al., 2005]
$Mg(BH_4)_2$	Synthesized via [Zanella et al., 2007] 	$Mg(NH_2)_2$	Synthesis via [Nakamori et al., 2004] or Ball milling MgH_2 under P_{NH_3} = 7 bar 

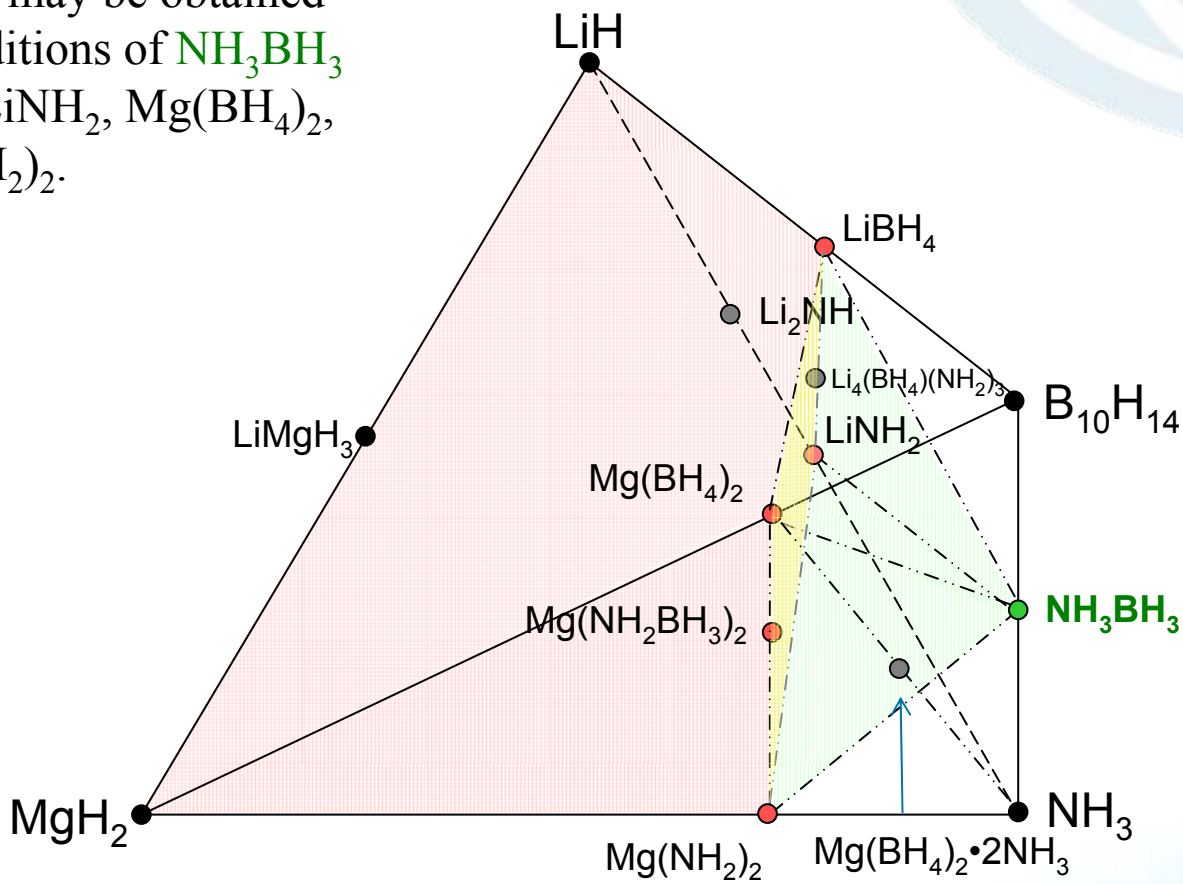
LiH-MgH_2-BH_x-NH_y Phase Diagram: Map of Identified Stable Compounds

High hydrogen containing compounds may be obtained through additions of NH_3 to $LiBH_4$, $LiNH_2$, $Mg(BH_4)_2$ and $Mg(NH_2)_2$.



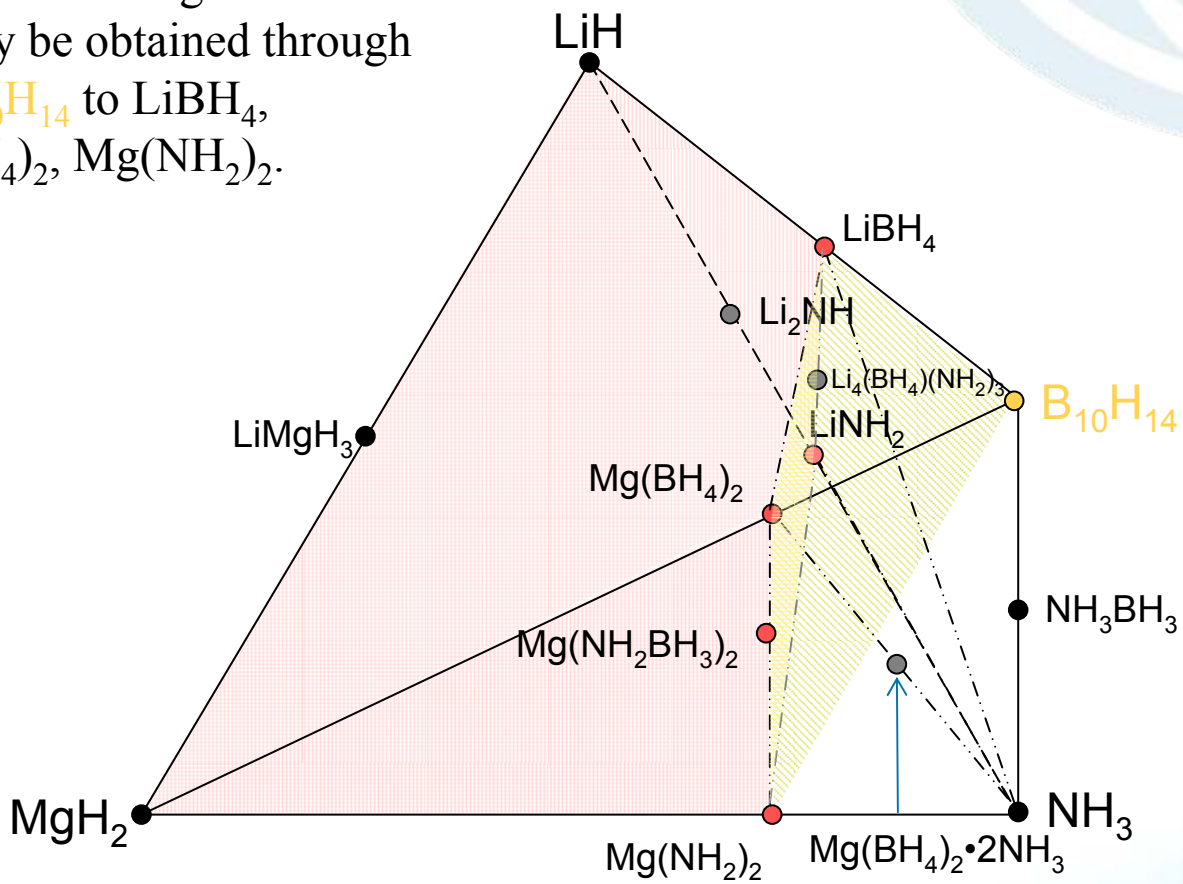
LiH-MgH_2-BH_x-NH_y Phase Diagram: Map of Identified Compounds

High hydrogen containing compounds may be obtained through additions of NH_3BH_3 to $LiBH_4$, $LiNH_2$, $Mg(BH_4)_2$, and $Mg(NH_2)_2$.



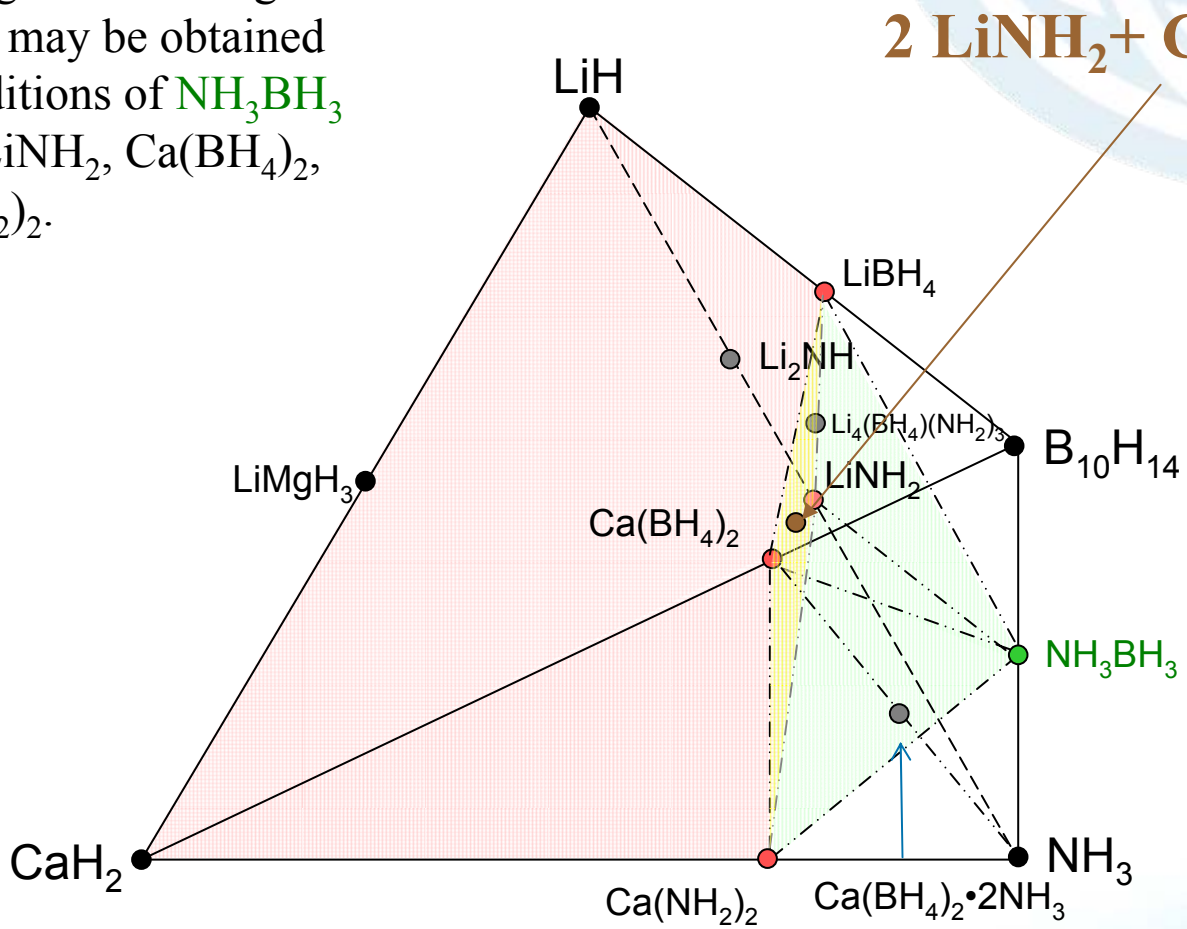
LiH-MgH_2-BH_x-NH_y Phase Diagram: Map of Identified Compounds

High hydrogen containing compounds may be obtained through additions of $B_{10}H_{14}$ to $LiBH_4$, $LiNH_2$, $Mg(BH_4)_2$, $Mg(NH_2)_2$.



LiH-CaH_2-BH_x-NH_y Phase Diagram: Map of Identified Stable Compounds

High hydrogen containing compounds may be obtained through additions of NH_3BH_3 to $LiBH_4$, $LiNH_2$, $Ca(BH_4)_2$, and $Ca(NH_2)_2$.



Synthetic Plan for Materials $M^1M^2(BH_4)_x(NH_2)_y$

$LiNH_2 + Ca(BH_4)_2$ ball milling

Calcium Borohydride $Ca(BH_4)_2$	*Lithium Amide $LiNH_2$*	*Product*
1 mole	1 mole	in progress
1 mole	2 mole	$Li_xCa(BH_4)_x(NH_2)_y$
2 mole	1 mole	in progress

$LiBH_4 + Ca(NH_2)_2$ ball milling

Calcium Amide $Ca(NH_2)_2$	*Lithium Borohydride $LiBH_4$*	*Product*
1 mole	1 mole	in progress
1 mole	2 mole	in progress
2 mole	1 mole	in progress

$LiBH_4 + Mg(NH_2)_2$ ball milling

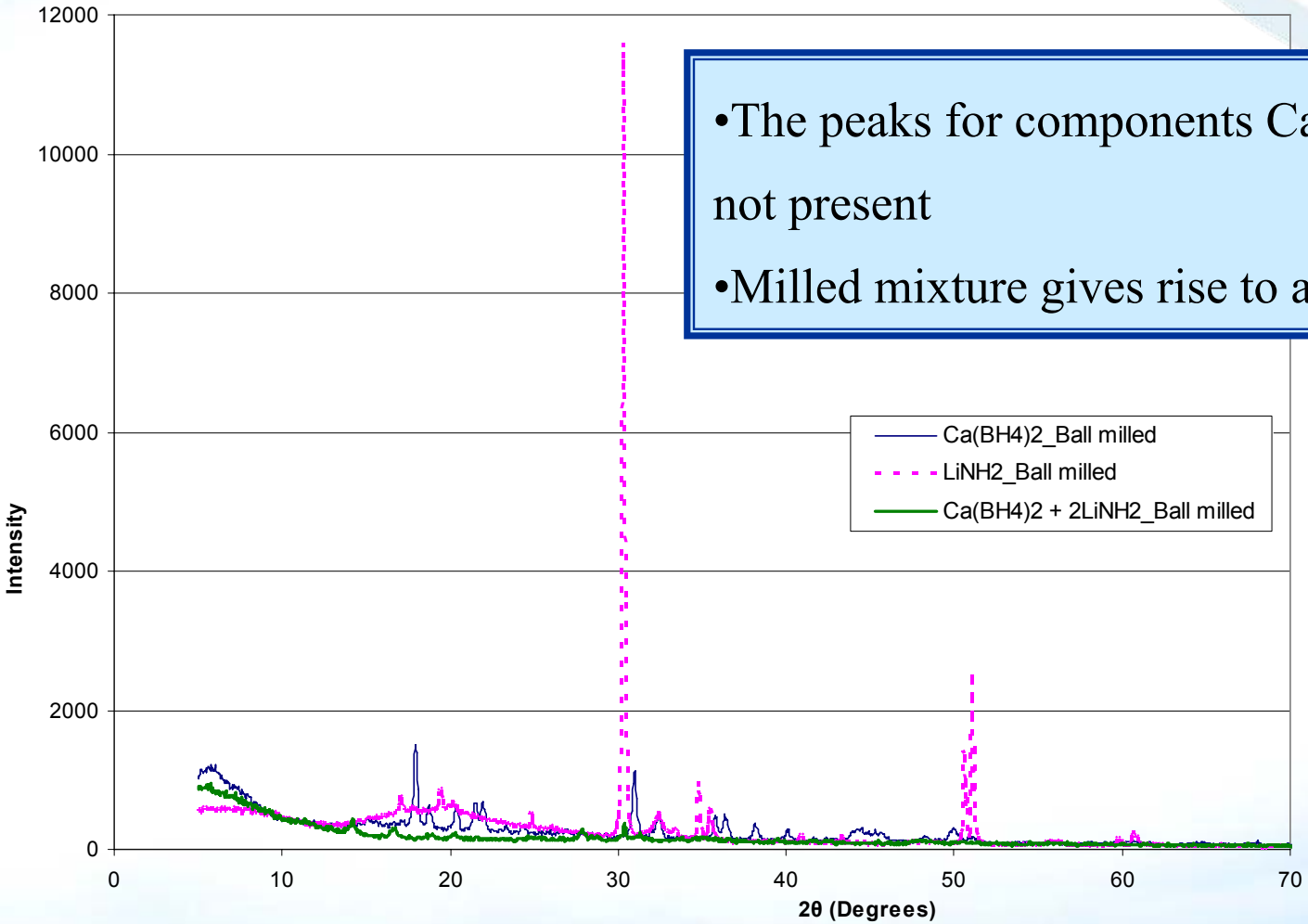
Magnesium Amide $Mg(NH_2)_2$	*Lithium Borohydride $LiBH_4$*	*Product*
1 mole	1 mole	in progress
1 mole	2 mole	in progress
2 mole	1 mole	in progress

$LiNH_2 + Mg(BH_4)_2$ ball milling

Magnesium Borohydride $Mg(BH_4)_2$	*Lithium Amide $LiNH_2$*	*Product*
1 mole	1 mole	in progress
1 mole	2 mole	in progress
2 mole	1 mole	in progress

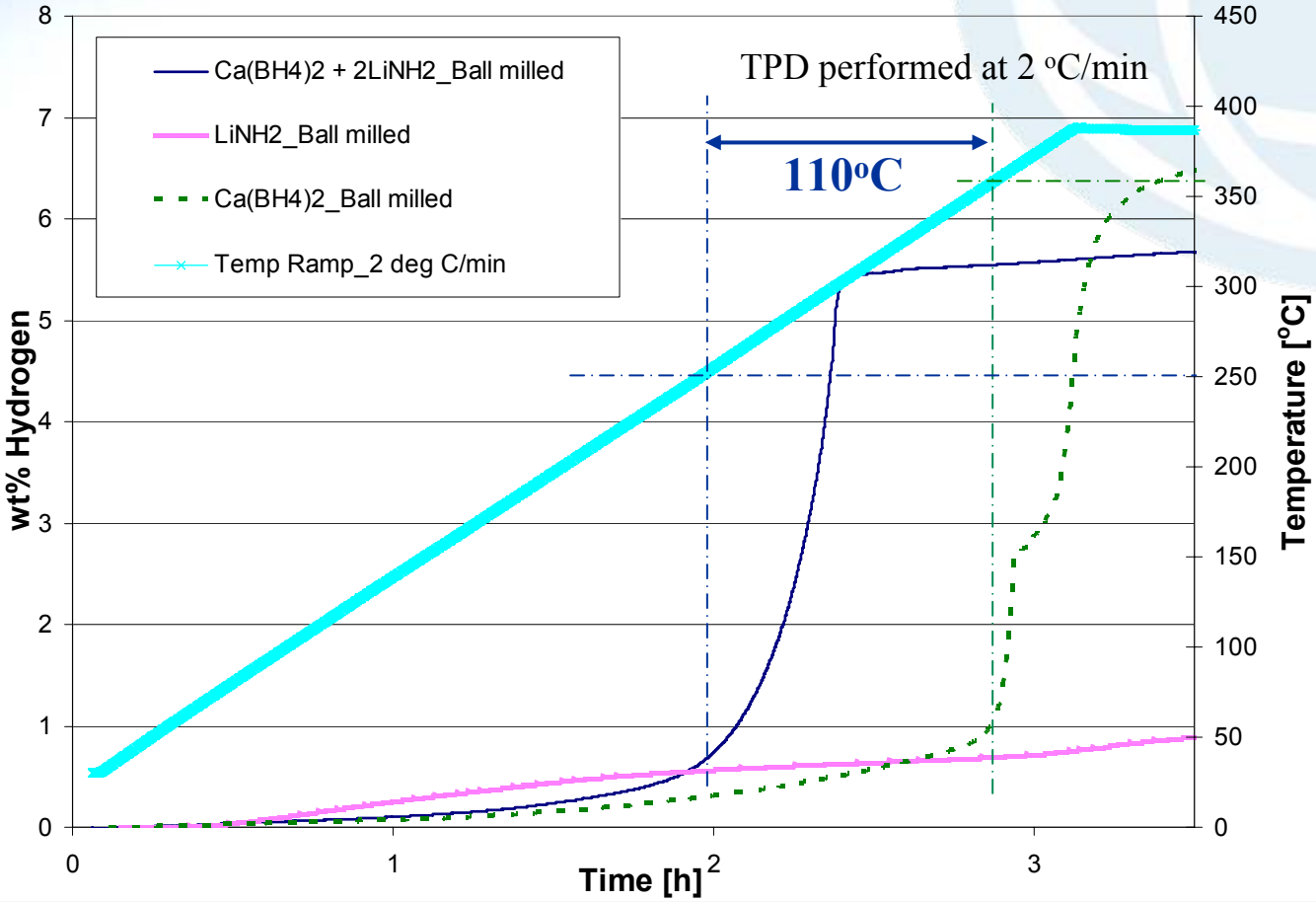
$2LiNH_2 + Ca(BH_4)_2$ ($Li_2Ca(BH_4)(NH_2)_2$) Fritsch Milled

$$2\ LiNH_2 + Ca(BH_4)_2 \xrightarrow[2\ h]{\text{(Fritsch)}} Li_xCa(BH_4)_x(NH_2)_y$$



- The peaks for components $Ca(BH_4)_2$ and $LiNH_2$ not present
- Milled mixture gives rise to an amorphous phase.

$Ca(BH_4)_2$:$2LiNH_2$ Temperature Programmed Desorption



- $Ca(BH_4)_2$ dehydrogenates rapidly at ~360°C.
- $Ca(BH_4)_2$:$2LiNH_2$ rapid dehydrogenation at ~250 ˚C completed at ~310 ˚C.
- Dehydriding temperature of the $Ca(BH_4)_2$:$2LiNH_2$ mixture is ~100 ˚C lower than that of $Ca(BH_4)_2$. Need to determine reversibility of this compositional ratio.

Summary

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

- An amorphous phase was achieved by ball milling $LiNH_2$ and $Ca(BH_4)_2$ (2:1 mole ratio).

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

Future Directions

- Identify structures and compositions of $Li_xCa(BH_4)_x(NH_2)_y$.

- Synthesize $Mg(NH_2)_2$ and $Ca(NH_2)_2$.

- Synthesize and characterize $LiMg(BH_4)_x(NH_2)_y$ and $LiCa(BH_4)_x(NH_2)_y$.

- Elucidate the origin of the reduction in dehydriding temperature.