



# Chemical Vapor Synthesis and Discovery of H<sub>2</sub> Storage Materials: Li-Al-Mg-N-H System

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University of Utah



Project ID ST31

# Overview

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## Timeline

- Start – March 2005
- Finish – March 2010
- Percent complete – 60%

## Budget

- Total project funding  
DOE share: ~\$800K  
Contractor share: \$200K
- Funding received for FY07: \$150K
- Funding for FY08: \$150K (+\$150K for PCT)

## Barriers

- Reversible hydrogen content not sufficient (MYPP Barrier A),
- Inadequate kinetic properties (MYPP Barrier B)
- Desorption T's too high (MYPP Barrier (MYPP Barrier B))

## Partners

- JPL, CalTech, GE, UNR, U Hawaii, SNL, SRNL, ORNL, U Pitt, CMU, Georgia Tech, Intematix,
- Project Lead: U of Utah 2

# Objectives

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## Overall

- Discover new solid hydrides that meet reversibility and kinetics requirements
- Develop chemical vapor synthesis process (CVS) for production of nanosized solid metal hydrides
- Demonstrate the effectiveness and unique properties of nanosized solid hydride materials

## FY07-08

- Understand reaction mechanisms of materials based on lithium alanates (destabilized by light metal amides), and  $\text{LiMgN}$ ,
- Establish capability and quantify  $\text{NH}_3$  co-production during dehydrogenation,
- Synthesize new materials using high-energy high-pressure reactive milling process,
- Synthesis of nano precursor and hydride powders using Chemical Vapor Synthesis (CVS) process.

# Milestones

Month/Year	Milestone or Go/No-Go Decision	Milestone Status
April - 06	Milestone: Complete design and set-up of the chemical vapor synthesis reactor systems and demonstrate their feasibility.	Achieved.
September - 08	Milestone: Demonstrate feasibility of selected materials (LiMgN and $\text{Li}_3\text{AlH}_6 + 3\text{LiNH}_2$ ) for hydrogen storage based on their capacity, reversibility, kinetics, and thermodynamic properties.	
September - 09	Go/No-Go Decision: Based on comprehensive characterizations of the thermodynamic and kinetic properties of LiMgN and $\text{Li}_3\text{AlH}_6 + 3\text{LiNH}_2$ , Go/No-Go decisions on these two material systems will be made.	
September - 10	Milestone: Full report, conclusions, and recommendations on selected materials.	

# Technical Approach

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- Collaborate with MHCoe Theory Group to identify promising candidate materials (LiMgN)
- Exploit interactions between amides, alanates, and simple hydrides to discover new reactions / material systems,
- Use TGA, XRD, and FTIR as basic rapid screening tools, and NMR, in-situ XRD, and PCT for in-depth characterizations and understanding,
- Use high-pressure high-energy (HPHE) mechanochemical milling method to synthesize nanosized and non-equilibrium materials,
- Use Chemical Vapor Synthesis (CVS) process to produce nanosized precursor powders (e.g. Al, Li, Mg, LiMgN, MgB<sub>2</sub>).

# Accomplishments Highlights

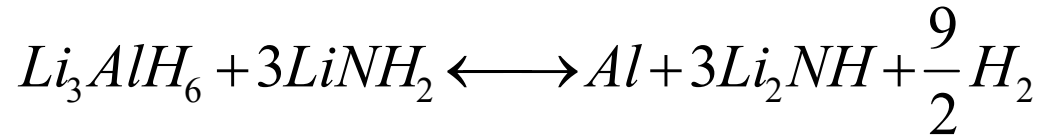
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1. Using PCT, confirmed that LiMgN is a **reversible** material with 6.6 wt. % or greater capacity, characterized reaction mechanisms with XRD, FTIR, NMR.
2. Elucidated the cycling mechanism for  $\text{Li}_3\text{AlH}_6 + 3\text{LiNH}_2$
3. Identified the critical dependence of the regeneration of  $\text{Li}_3\text{AlH}_6$  on the heating rate of hydrogenation process.
4. Developed and used pH-ion meter capability to quantify the concentrations of  $\text{NH}_3$  during dehydrogenation.
5. Identified the role of heating rate in  $\text{NH}_3$  release from hydrogenated LiMgN.
6. Conducted preliminary measurement of the reaction enthalpy of LiMgN.
7. Achieved improved desorption properties of  $7\text{MgH}_2/\text{TiH}$  system prepared by high pressure high energy milling.
8. Made nanosized Al powder using CVS method.

# Focus on 2 Promising Materials

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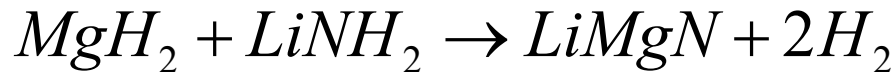
## I. Reactions of $\text{LiNH}_2$ with lithium alanate materials



*-- Expected to have theoretical hydrogen capacity in the 6-7 wt. % range, coupling known reactions...*

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## II. Reactions Leading to $\text{LiMgN}$



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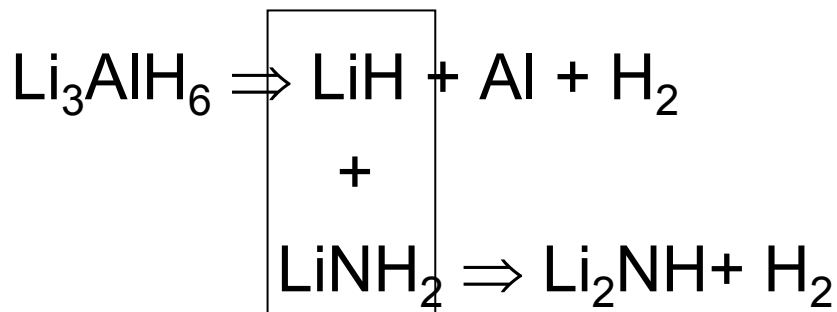


*-- Theoretically predicted by MHCoe partners (Johnson, Sholl, Alpati) to have  $\Delta H = 32\text{kJ/molH}_2$ , with 8.2% theoretical hydrogen capacity.*

## Given that:

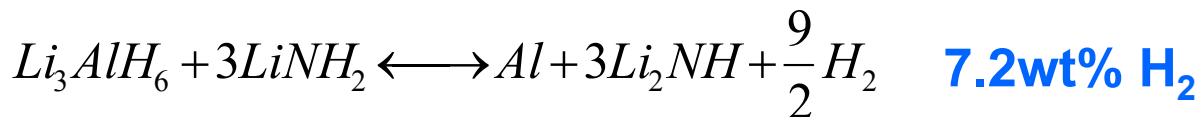
- $\text{Li}_3\text{AlH}_6$  decomposes to  $\text{LiH}$  and  $\text{H}_2$
- $\text{LiH}$  releases  $\text{H}_2$  when reacting with  $\text{LiNH}_2$

Perhaps we can place a source of  $\text{LiH}$  (from  $\text{Li}_3\text{AlH}_6$ ) in close proximity to  $\text{LiNH}_2$  to get enhanced  $\text{H}_2$  evolution:

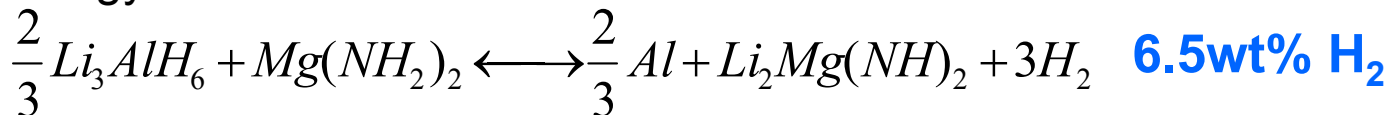


1. Chen, J.; et al. *J. Phys. Chem.* **2001**, 17, 1665
2. Chen, P.; et al. *Nature*, **2002**, 420,320
3. Luo, W.; *J. Alloys Compd.*, **2004**, 381, 284

## Anticipated Rxns (with amide in 2 forms):



or by analogy....

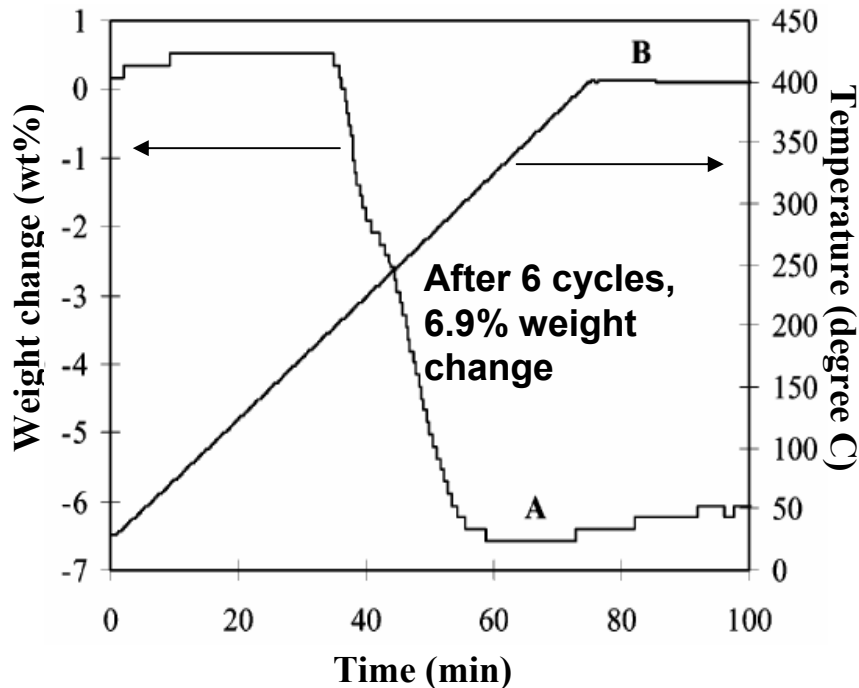




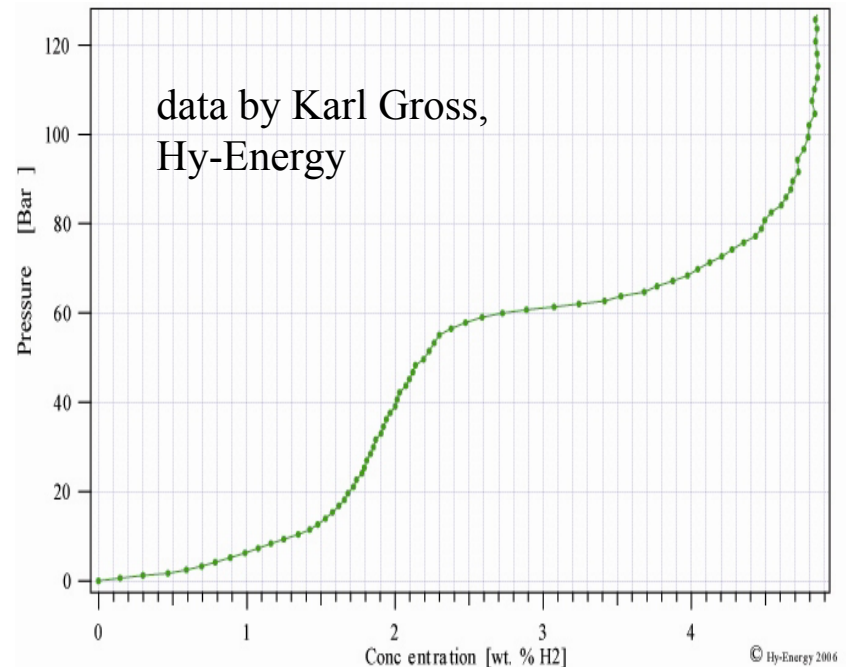
# $\text{Li}_3\text{AlH}_6 / 3\text{LiNH}_2$ Releases 4.9 wt.% $\text{H}_2$

Basic reactions, capacity, and reversibility confirmed by TGA, XRD, PCT, and NMR analysis.

TGA of hydrogenated (138 bar, 300°C) sample.



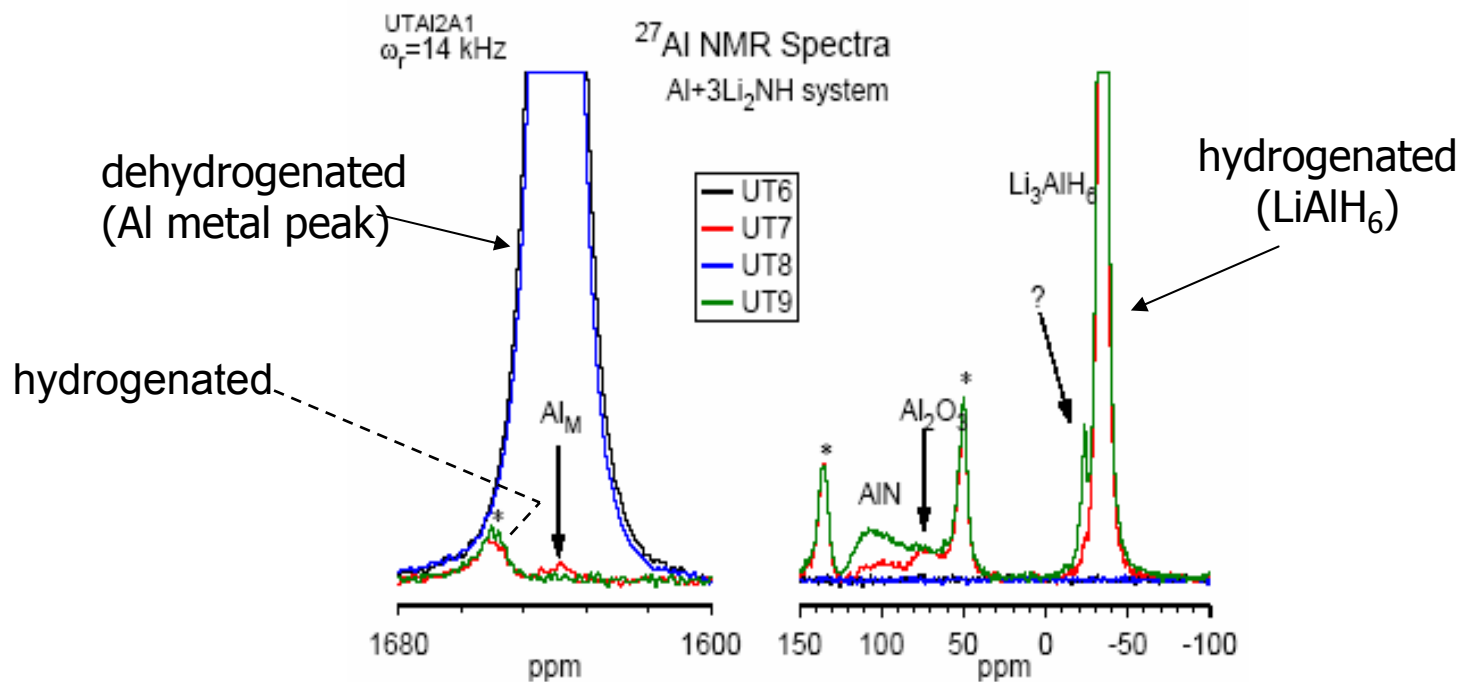
PCT of  $\text{Li}_3\text{AlH}_6 / 3\text{LiNH}_2 / 4\text{wt}\% \text{TiCl}_3$ ,  
 $T = 375^\circ\text{C}$



- Two plateau pressures at ~1 and 60 bar respectively.
- van't Hoff plot shows the material is less stable than  $\text{MgH}_2$ .

# NMR confirms $\text{AlH}_6 \leftrightarrow \text{Al}$ conversion

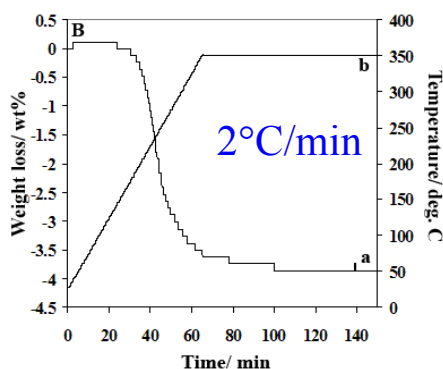
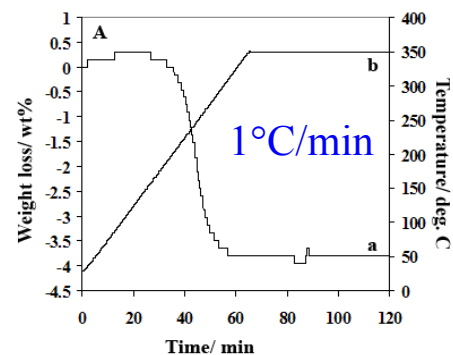
## Characterization of $\text{Li}_3\text{AlH}_6 + 3\text{LiNH}_2$ (Bowman, Hwang):



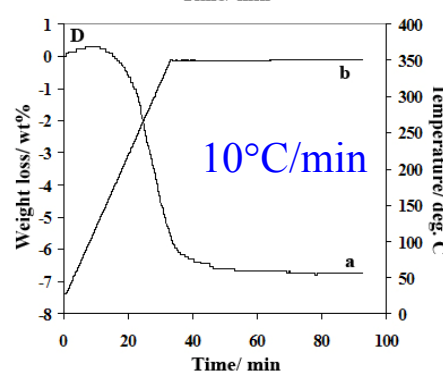
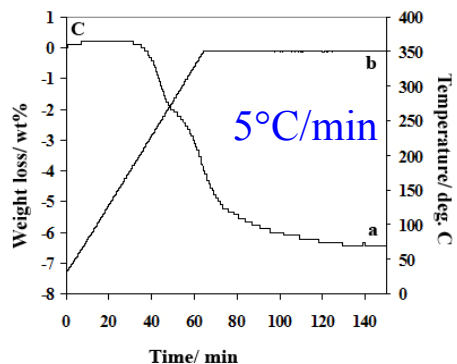
- $^{27}\text{Al}$  NMR results prove that the system shows stable cycling behavior:  
 $\text{Al} + 3\text{Li}_2\text{NH} + 9/2\text{H}_2 \leftrightarrow \text{Li}_3\text{AlH}_6 + 3\text{LiNH}_2$
- $^{27}\text{Al}$  NMR: identifies Al(M),  $\text{Li}_3\text{AlH}_6$ , AlN (small),  $\text{Al}_2\text{O}_3$  (small)
- There is unknown species found in  $^{27}\text{Al}$  NMR of hydrogenated UT9 at -23.7 ppm, while the AlN was increased noticeably as the ads/des cycle was performed

# Rehydrogenation Depends on Heating Rate

Hydrogenating Al + Li<sub>2</sub>NH (the dehydrogenated product): Hydrogenating using heating rates of 1, 2, 5 and 10 °C/min at P = 172 bar H<sub>2</sub>



Slower hydrogenation heating rate yields only ~ 4 wt. % material, no characteristic Li<sub>3</sub>AlH<sub>6</sub> peak in XRD.



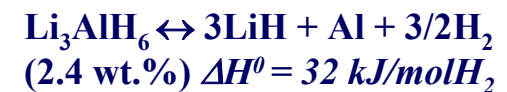
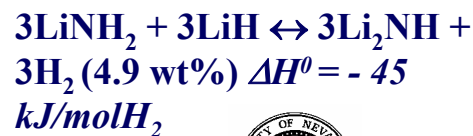
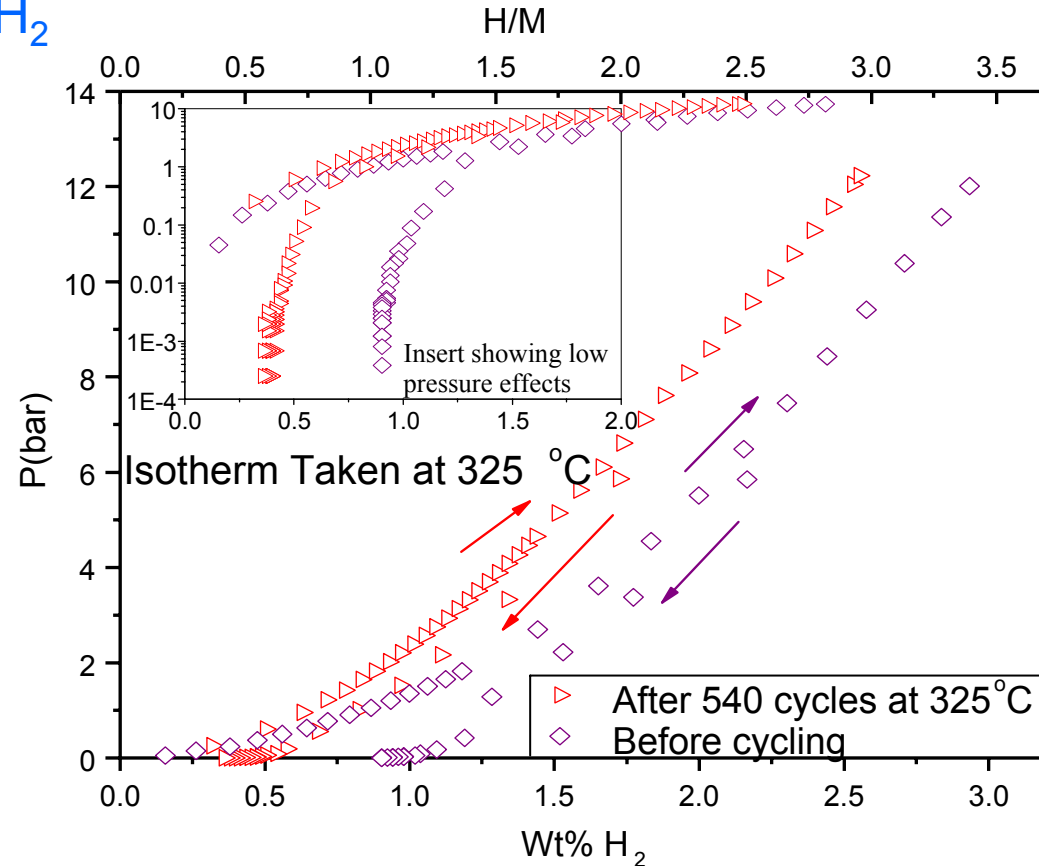
Faster hydrogenation heat rate yields ~ 6.9 wt. % material, XRD shows Li<sub>3</sub>AlH<sub>6</sub>

The heating rate needs to be higher than 5 °C/min and the reaction temperature needs to be greater than 220 °C in order to make the reversible conversion. Results confirmed by <sup>27</sup>Al and <sup>6</sup>Li NMR studies.

# (Li<sub>3</sub>AlH<sub>6</sub>+3LiNH<sub>2</sub>) Stable with Cycling and Modest O<sub>2</sub> Exposure

Start with ball-milled Li<sub>3</sub>AlH<sub>6</sub>/3LiNH<sub>2</sub>

- Isotherm taken before and after 540 cycles shows a small loss in H<sub>2</sub> capacity (~0.6%) using 100 ppm O<sub>2</sub> in UHP hydrogen.
- **Therefore, material loss by volatilization (NH<sub>3</sub>) is a negligible problem for this material under the conditions of this study.**
- Note that cycling LiNH<sub>2</sub> + LiH ↔ Li<sub>2</sub>NH + H<sub>2</sub> in Industrial hydrogen (with no Li Alanate) showed ~2.6% hydrogen loss after 500 cycles under similar cycling conditions



**A theoretically predicted reaction by MHCoe theorists  
(Alapati, Johnson, Sholl, et.al\*):**



Carnegie Mellon



## Potential Advantages:

- all the hydrogen in  $\text{MgH}_2$  and  $\text{LiNH}_2$  could be released (theoretical 8.2%)
- by-passes the undesirable imide ( $\text{Li}_2\text{Mg}(\text{NH})_2$ ) which forms when the  $\text{MgH}_2:\text{LiNH}_2$  ratio is 2:1\*\*

## Questions:

- Does the rxn proceed?
- Is it reversible?

\*. Alapati, S.V.; Johnson, K.J., Sholl, D.S.  
*J.Phys.Chem.*, 2006, 110, 8769

\*\* . Luo, W.; *J. Alloys Compd.*, 2004, 381, 284

TGA Data: first, hydrogenate Ti-doped LiMgN, then desorb....

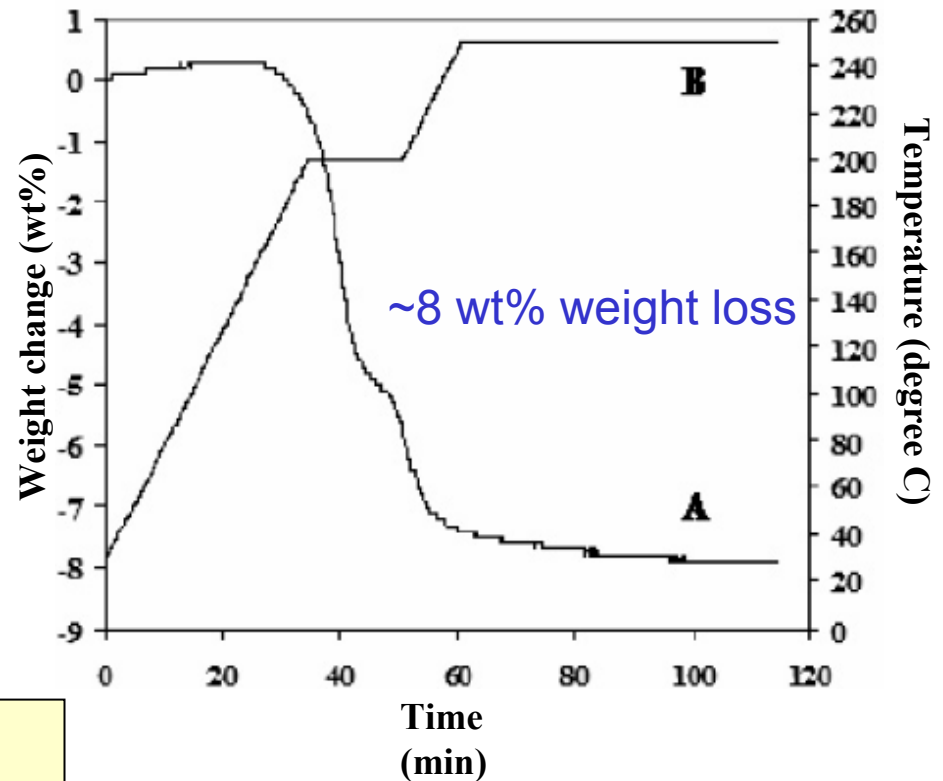
Rehydrogenation  
conditions:

Pressure: 2000 psi H<sub>2</sub>

Temperature: 160 °C

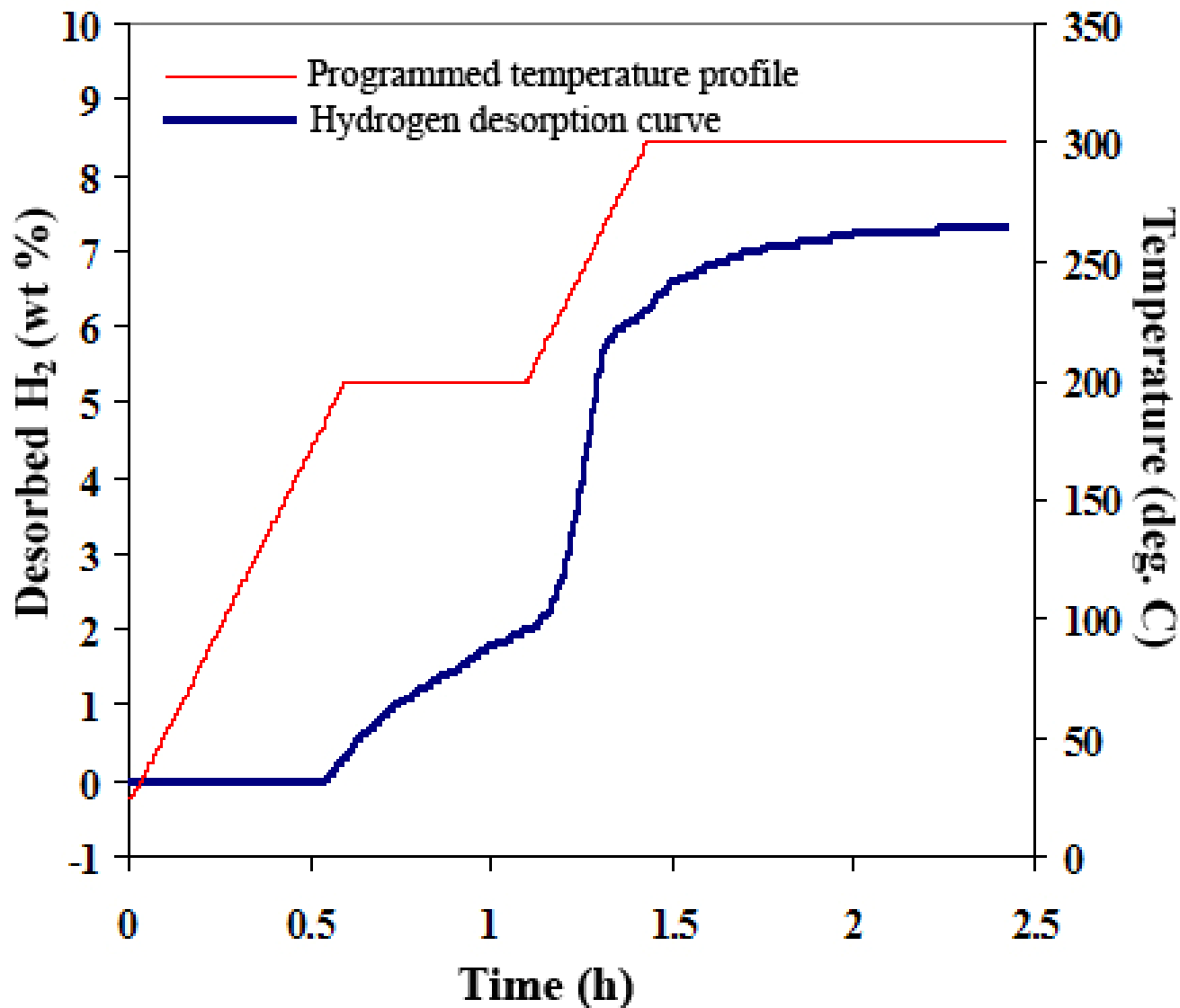
Holding time: 6 hours

TGA of rehydrogenated TiCl<sub>3</sub>-doped LiMgN



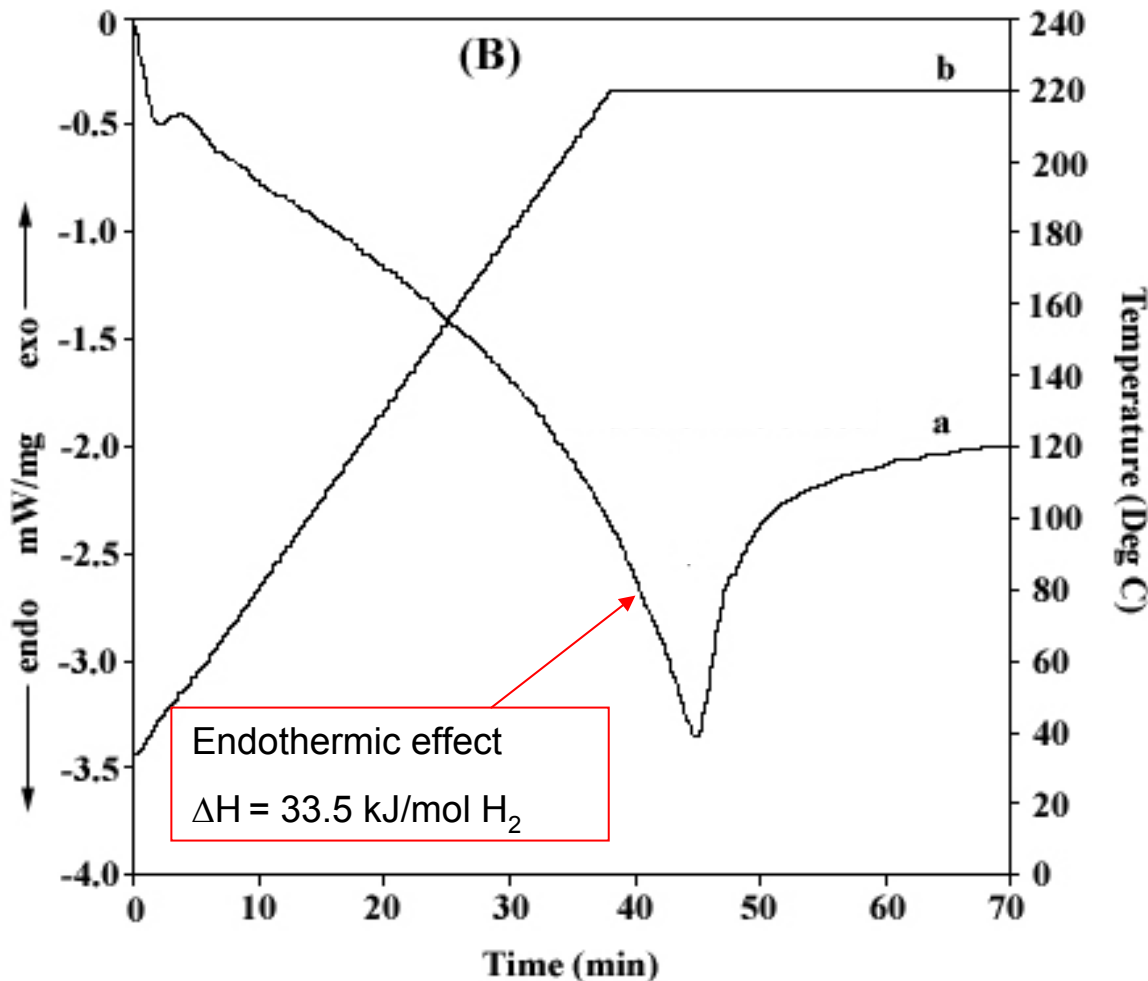
LiMgN can be hydrogenated  
at temperatures below 240 °C

# TPD for $\text{LiNH}_2 + \text{MgH}_2$ after jar-roll milling for 48 hours



# Measuring $\Delta H$ of the dehydrogenation reaction of $\text{LiNH}_2 + \text{MgH}_2$

DTA curve of the dehydrogenation reaction of  $\text{LiNH}_2 + \text{MgH}_2 = \text{LiMgN} + 2\text{H}_2$



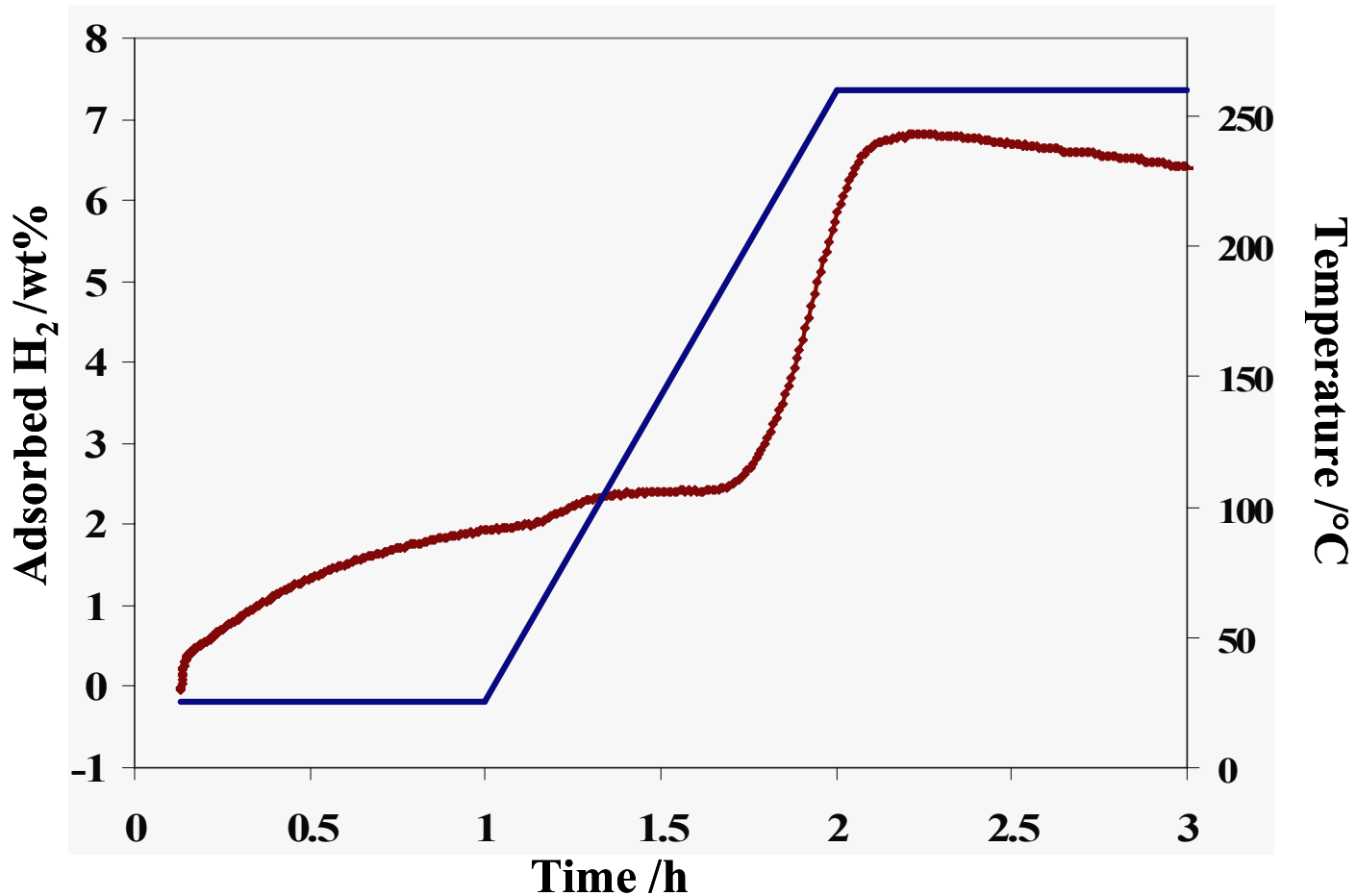
- One reaction step detected during the dehydrogenation of  $\text{LiNH}_2 + \text{MgH}_2$
- The  $\Delta H$  value for the reaction is  $33.5 \text{ kJ/mol H}_2$ , which is close to the theoretically predicted reaction enthalpy of  $29.7$  ( $31.9$ )  $\text{kJ/mol H}_2$  reported by Alapati<sup>1</sup> et al using the USPP (PAW) approach.

1. Alapati, S. V.; Johnson, K. J.; Sholl, D. S. *J. Phys. Chem. B* **2006**, *110*, 8769.

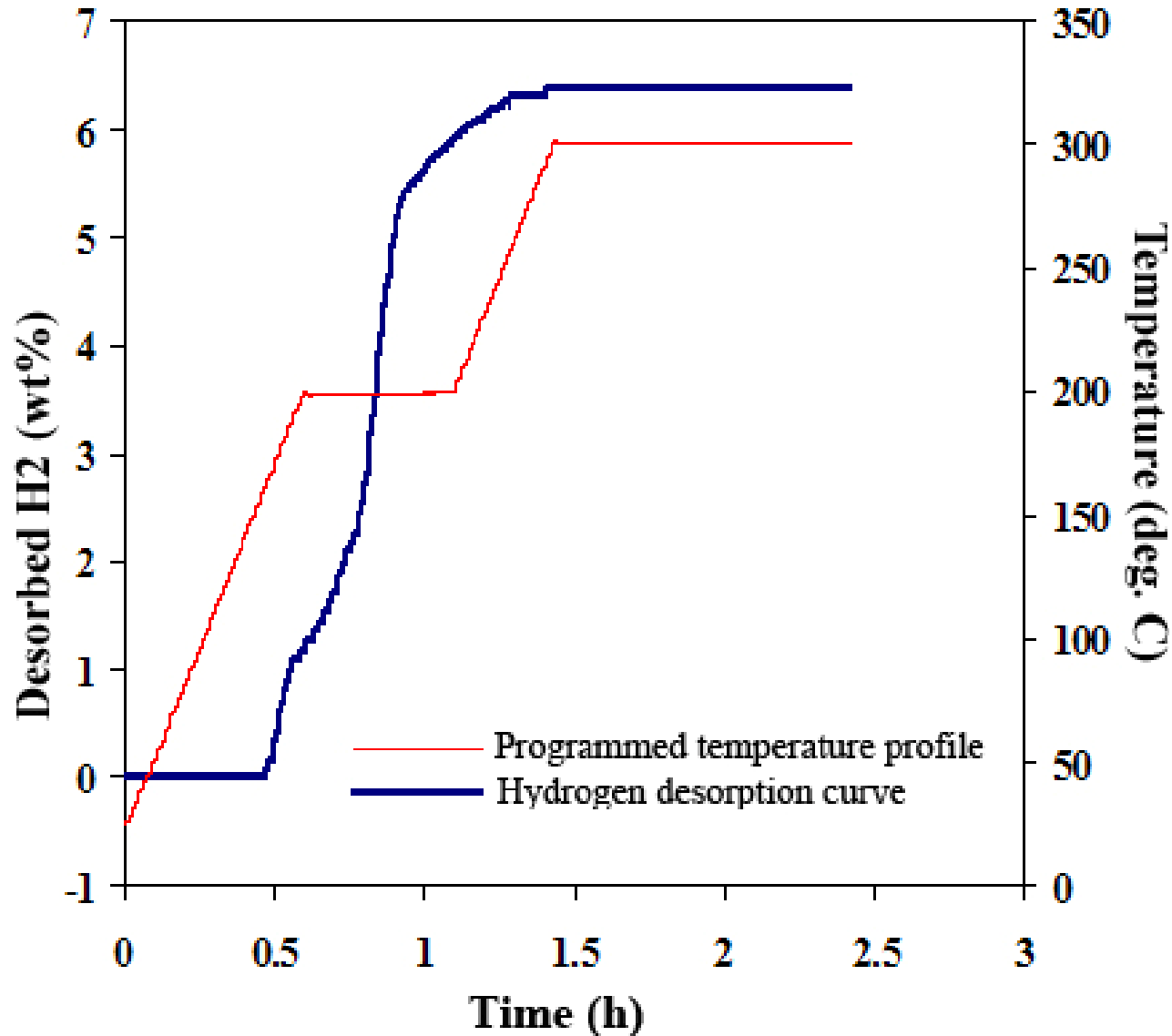


# Temperature Programmed Adsorption (TPA) of the LiMgN

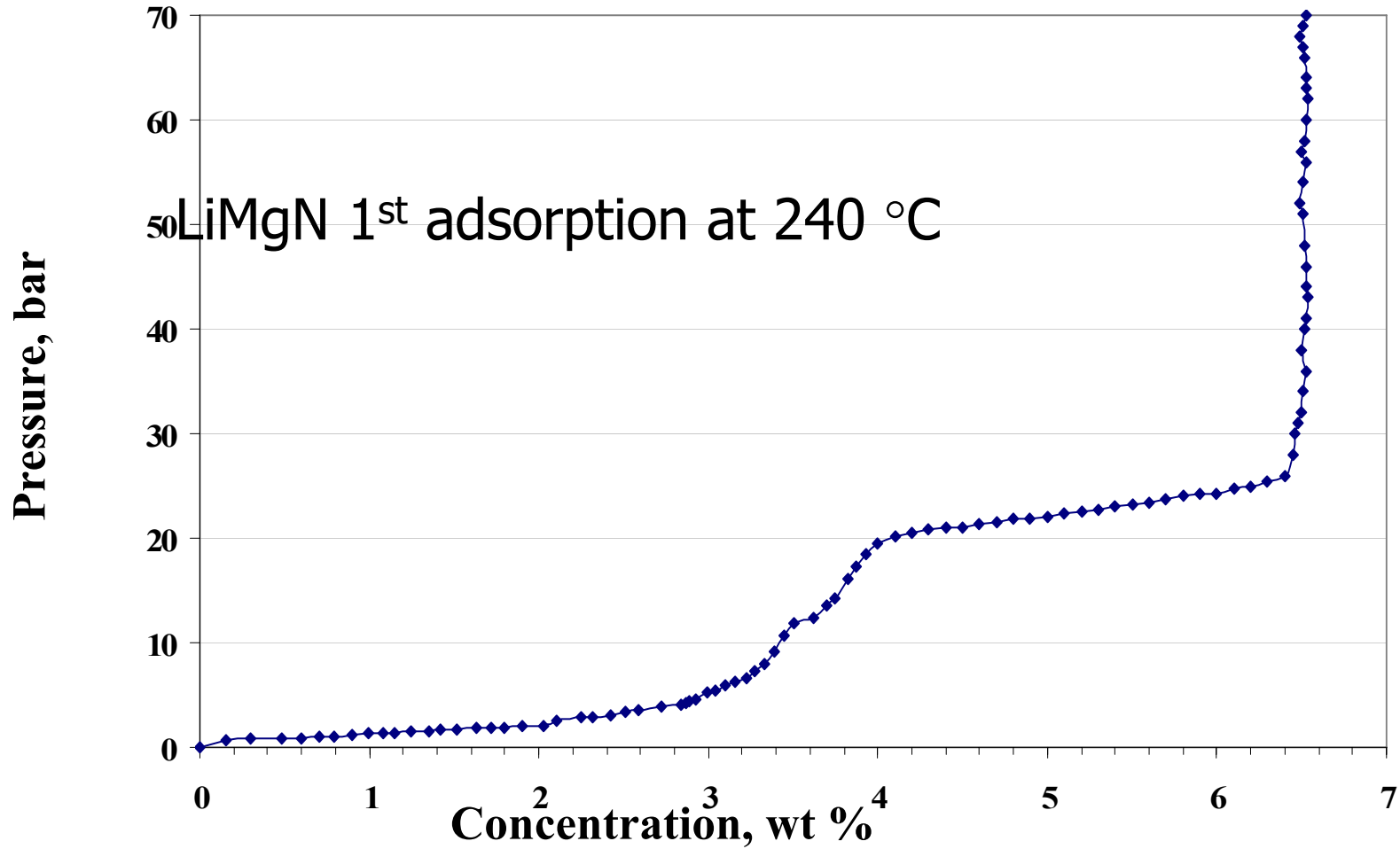
TPA of LiMgN: H<sub>2</sub> pressure 140 bar. 6.8 wt% of H<sub>2</sub> pick-up. Note that ~2 wt% of H<sub>2</sub> is adsorbed at the room temperature (further study needed).



# TPD for LiMgN after 1<sup>st</sup> hydrogenation at 172 bar and 240 °C for 10 hours



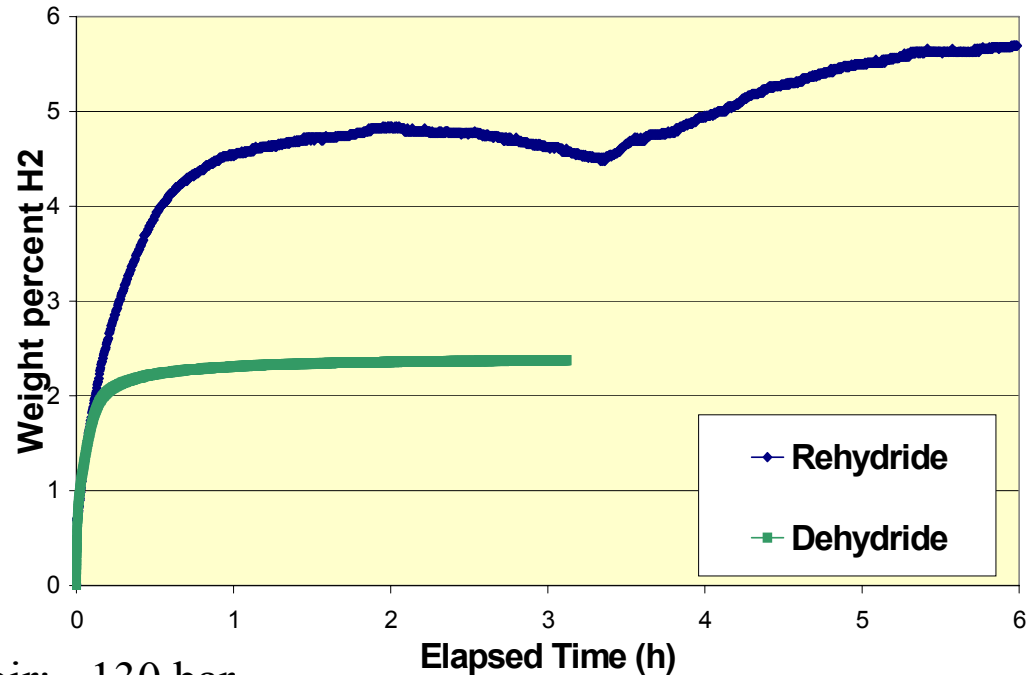
# PCT Reports LiMgN is a 6.6% reversible material



## Isothermal Re-hydring of LiMgN (Anton)

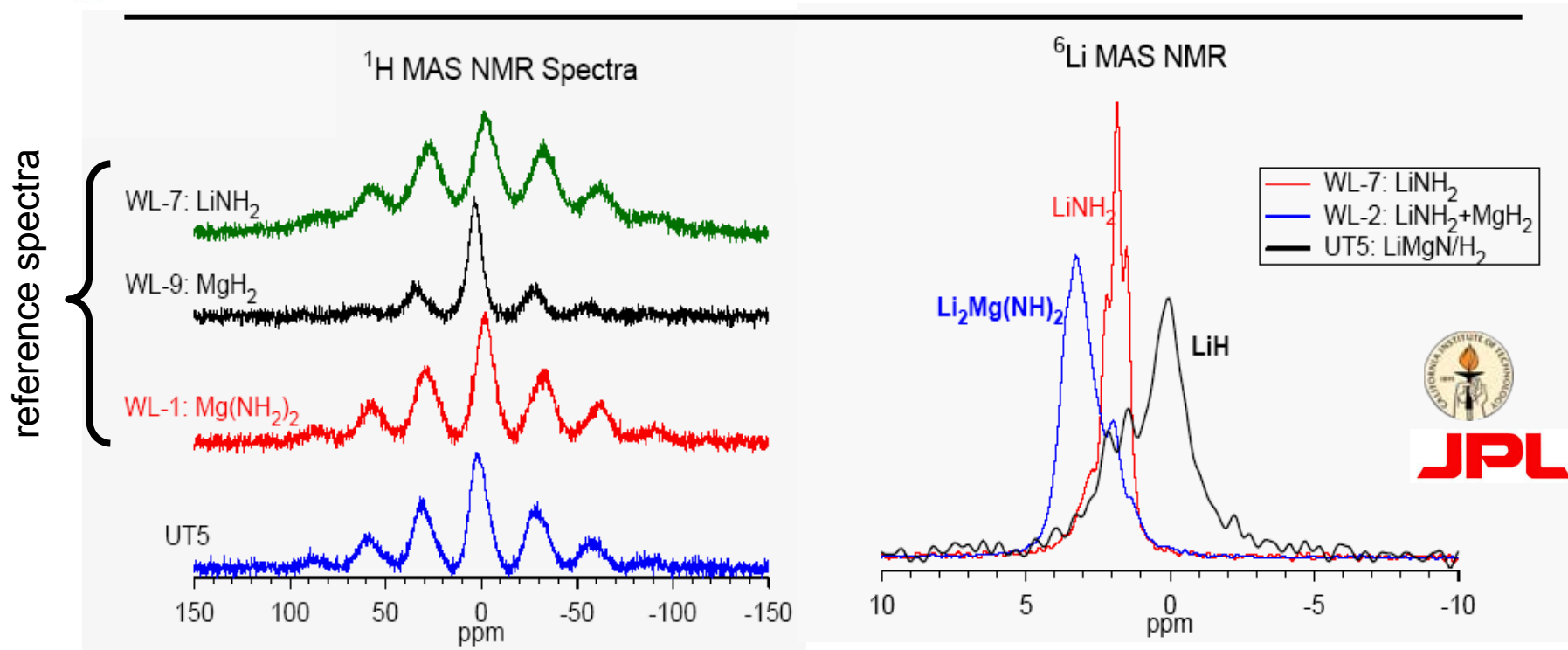


Cycle MgH<sub>2</sub>:LiNH<sub>2</sub> (4%TiCl<sub>3</sub>)



- Nominal pressure of reservoir: ~130 bar
- wt% rehydrided: ~ 5.7
- Starting material: dehydrided sample at 280 °C
- Possible 2-step rehydriding reaction in the process of being characterized. To be verified in additional experiments.

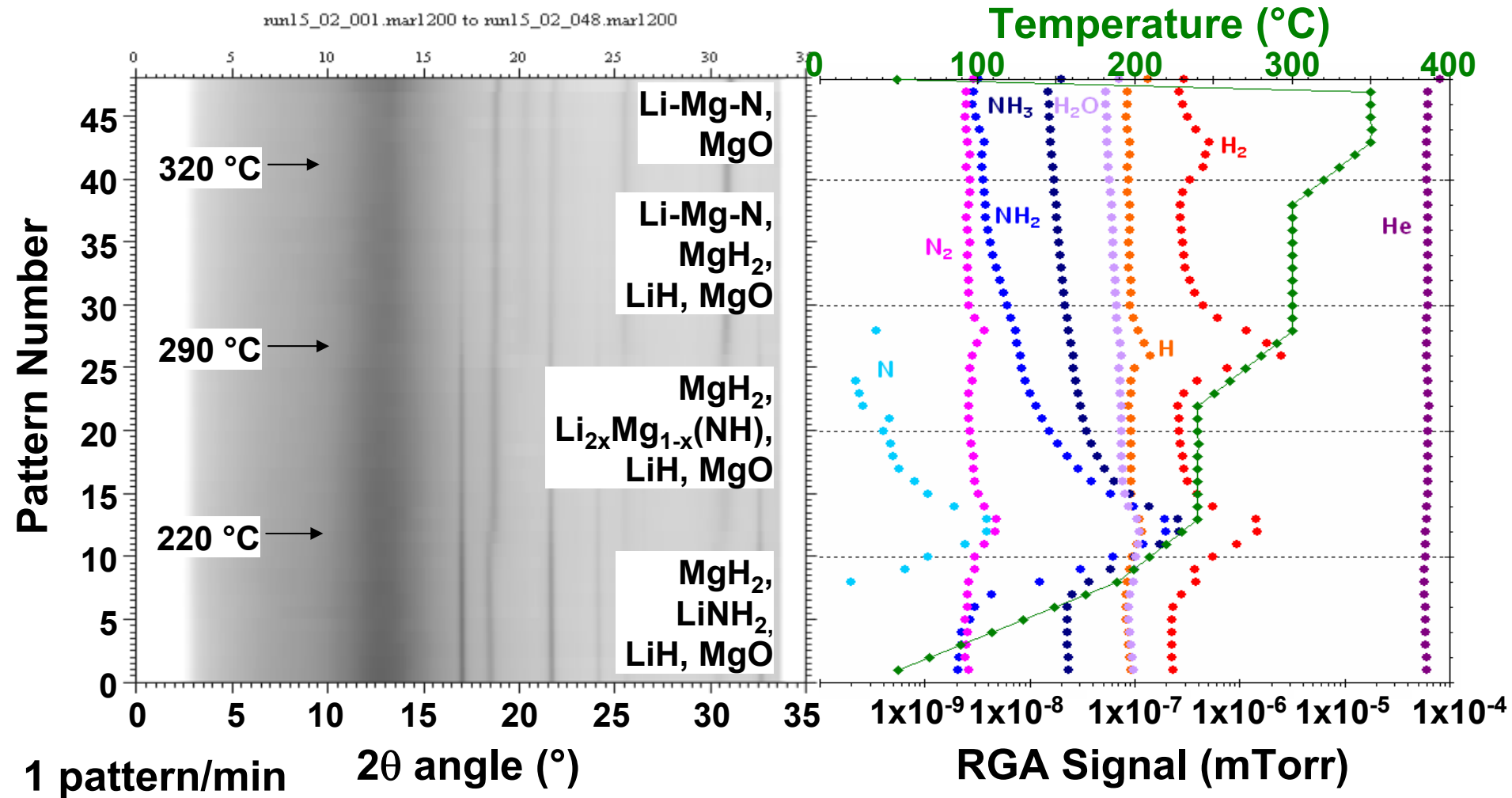
# Hydrogenated LiMgN Products Probed by NMR



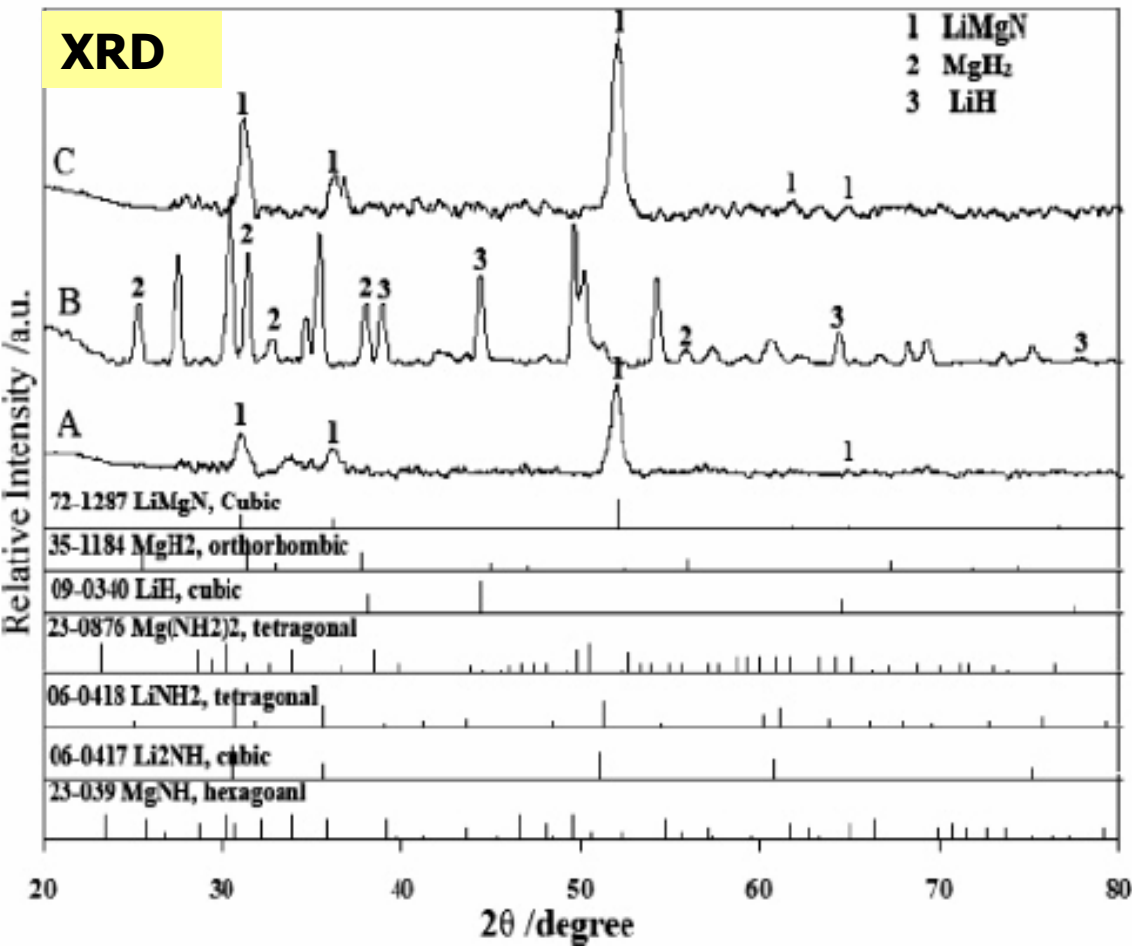
UT5: LiMgN after hydrogenation at 138 bar and 240 °C NMR by Bowman, Hwang

Hydrogenated LiMgN:  $^1\text{H}$  is inconclusive (maybe  $\text{MgH}_2 + \text{LiNH}_2$ ) while  $^6\text{Li}$  shows  $\text{LiH} + \text{LiNH}_2$ .

LiMgN hydrogenation rxn pathways are complex



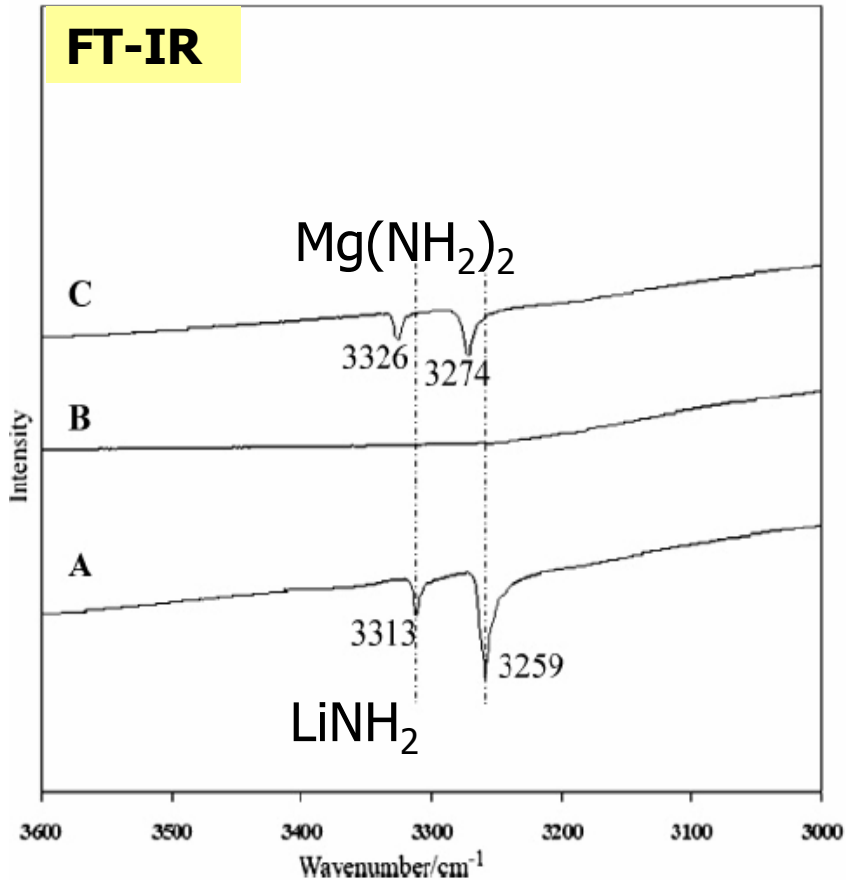
# Hydrogenated/Dehydrogenated LiMgN Probed by XRD



- A) TiCl<sub>3</sub>-doped LiMgN  
B) TiCl<sub>3</sub>-doped LiMgN  
after hydrogenation.  
C) Dehydrogenation  
products of  
hydrogenated TiCl<sub>3</sub>-  
doped LiMgN

- MgH<sub>2</sub> and LiH are formed in the hydrogenation process.
- LiMgN reformed after a hydrogenation and dehydrogenation cycle

# Cycled LiMgN Probed by FTIR



- A) TiCl<sub>3</sub>-doped LiNH<sub>2</sub>+MgH<sub>2</sub> (starting mat.)
- B) LiMgN
- C) LiMgN after hydrogenation

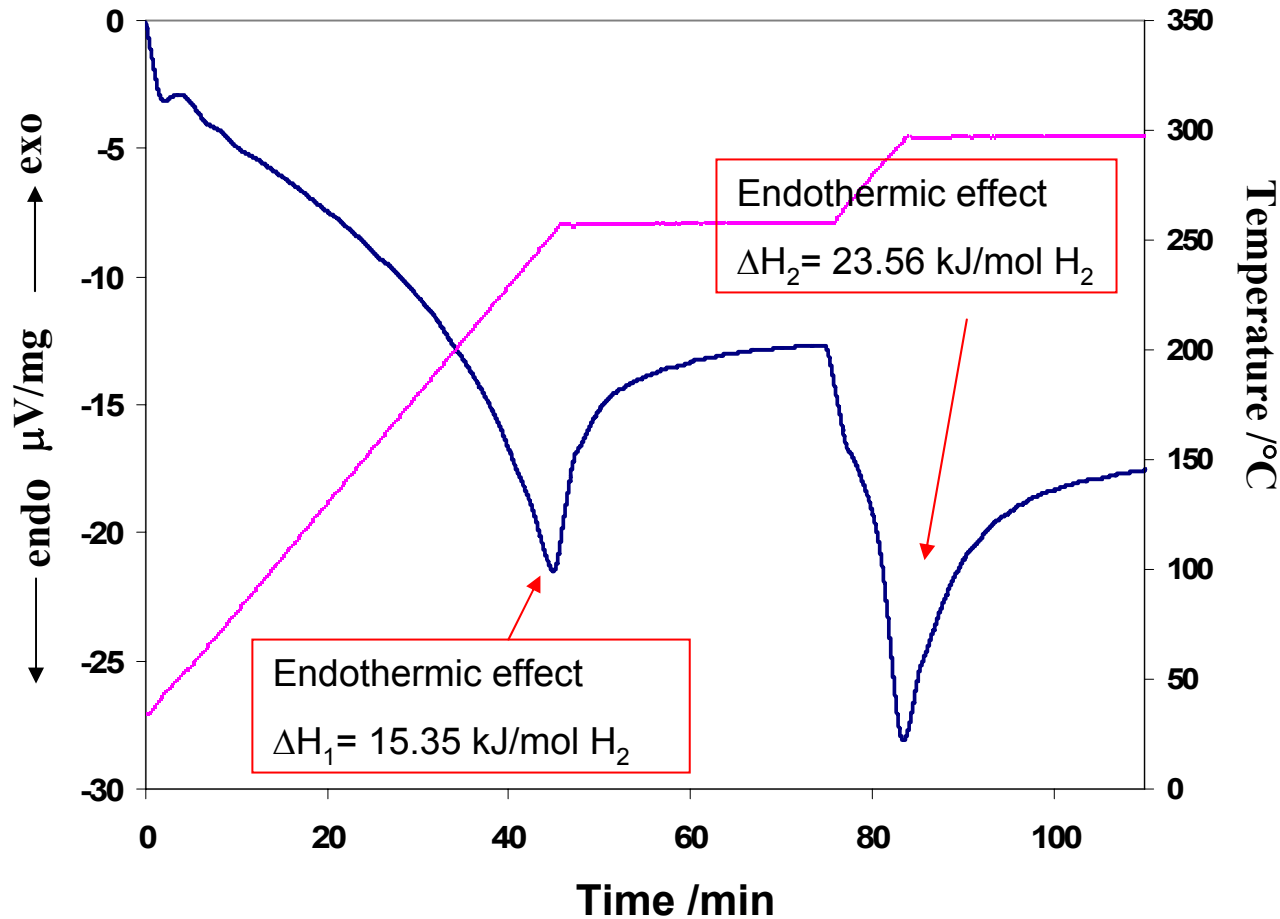
FTIR results showed:

Mg(NH<sub>2</sub>)<sub>2</sub> is formed in the hydrogenation process.



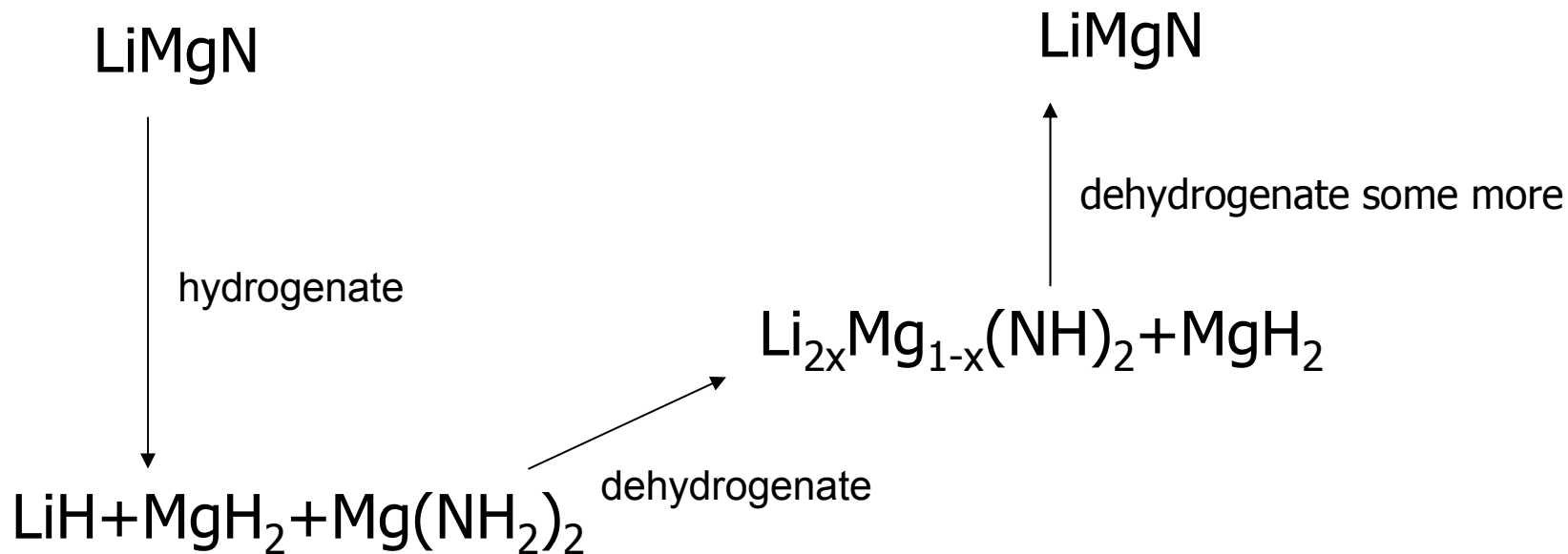
# Measuring $\Delta H$ of the dehydrogenation reactions of hydrogenated-LiMgN

DTA curve of the dehydrogenation reaction of hydrogenated-LiMgN



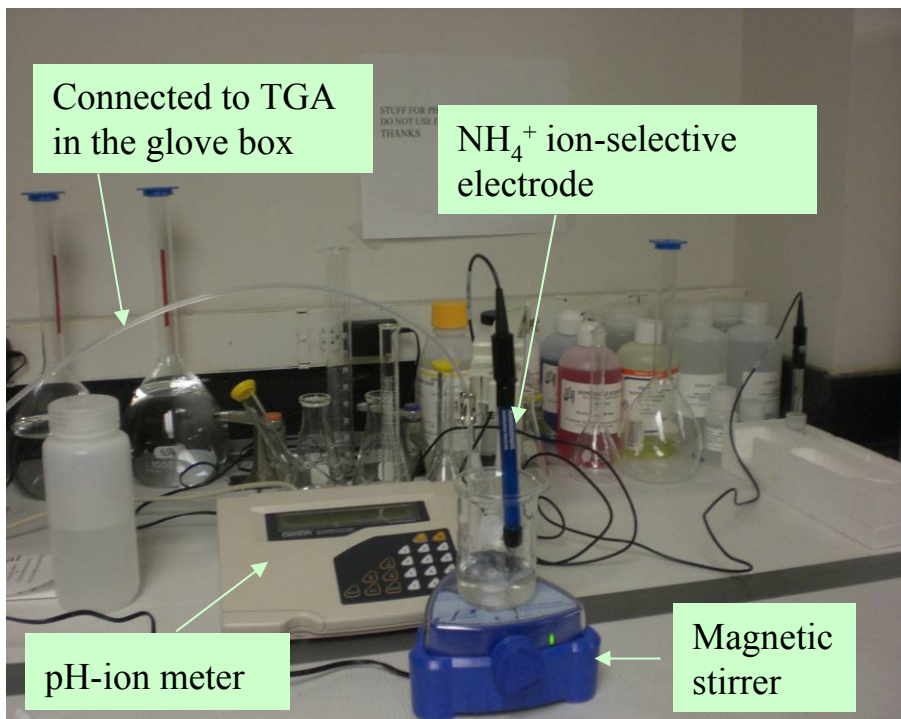
- Two reaction steps detected during the dehydrogenation of the hydrogenated LiMgN sample
- The  $\Delta H$  values for the two reactions are 15.35 and 23.56 KJ/mol H<sub>2</sub> respectively.

# Proposed Reaction Scheme for LiMgN



Proposed reaction pathway based on XRD, FTIR and in-situ XRD results to date. Results in partial agreement with theoretical expectations

# Measuring $\text{NH}_3$ Emission from Amides



## Measuring $\text{NH}_3$ using pH-ion meter connected to TGA:

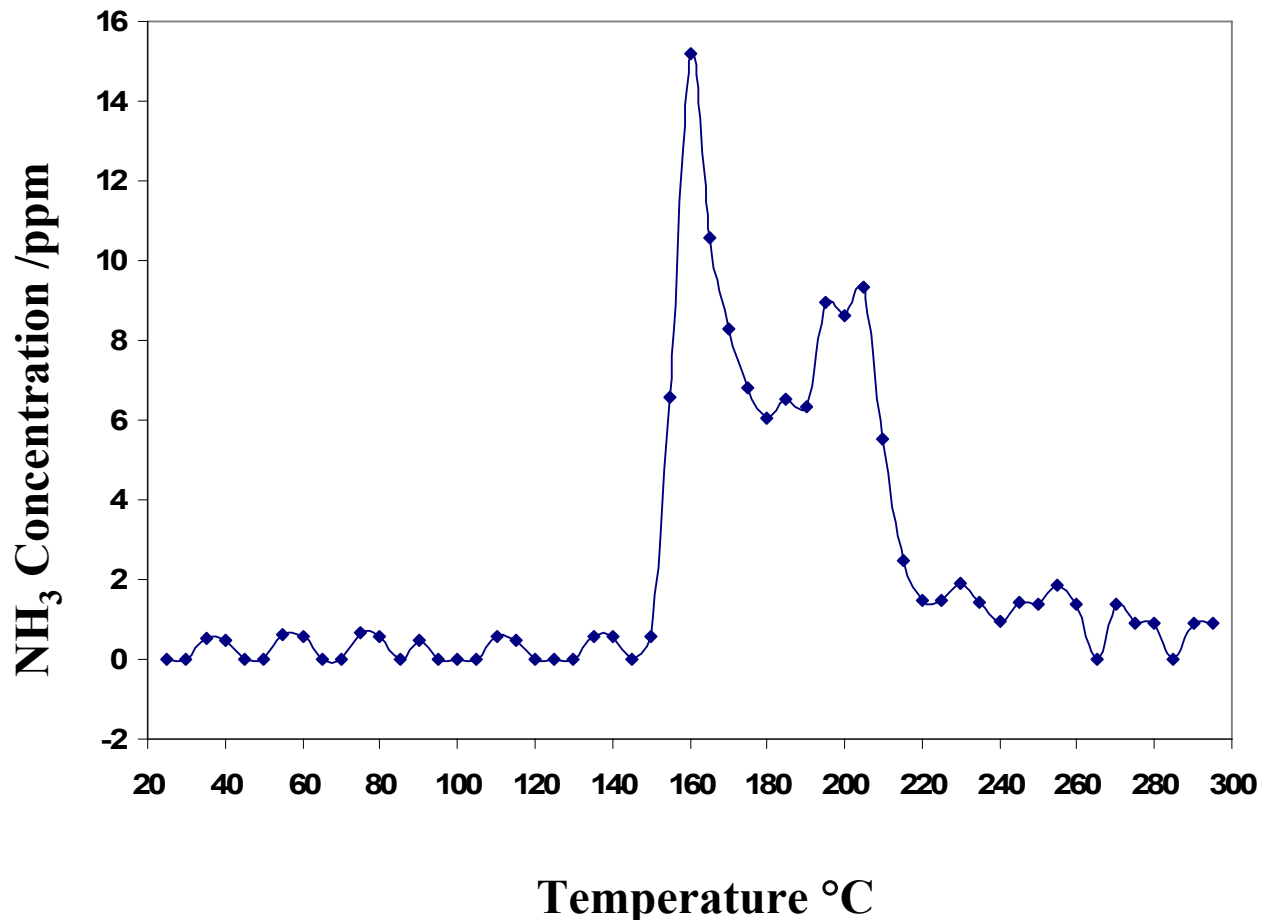
- pH-ion meter measures the changes of pH value of the solution
- The pH-ion meter is calibrated by 3-point calibration using the standard pH buffers (4, 7, 10) before any measurements.
- When the gas containing  $\text{NH}_3$  is fed into the solution,  $\text{NH}_3$  reacts with  $\text{H}^+$  to form  $\text{NH}_4^+$ , which changes the pH value.
- The concentration of  $\text{NH}_4^+$  is measured based on the changes in pH values.

The gas products from the system can be carried to an acid solution by inert gas (Ar). If  $\text{NH}_3$  is formed during the dehydrogenation process, the acid solution can catch all the  $\text{NH}_3$  gas to convert to  $\text{NH}_4^+$ . Then the pH-ion meter can measure the  $\text{NH}_4^+$  concentration via a  $\text{NH}_4^+$  ion-selective electrode.

-- the instrument was calibrated by measuring  $\text{NH}_3$  release from  $\text{LiNH}_2$ , combined with TGA measurements

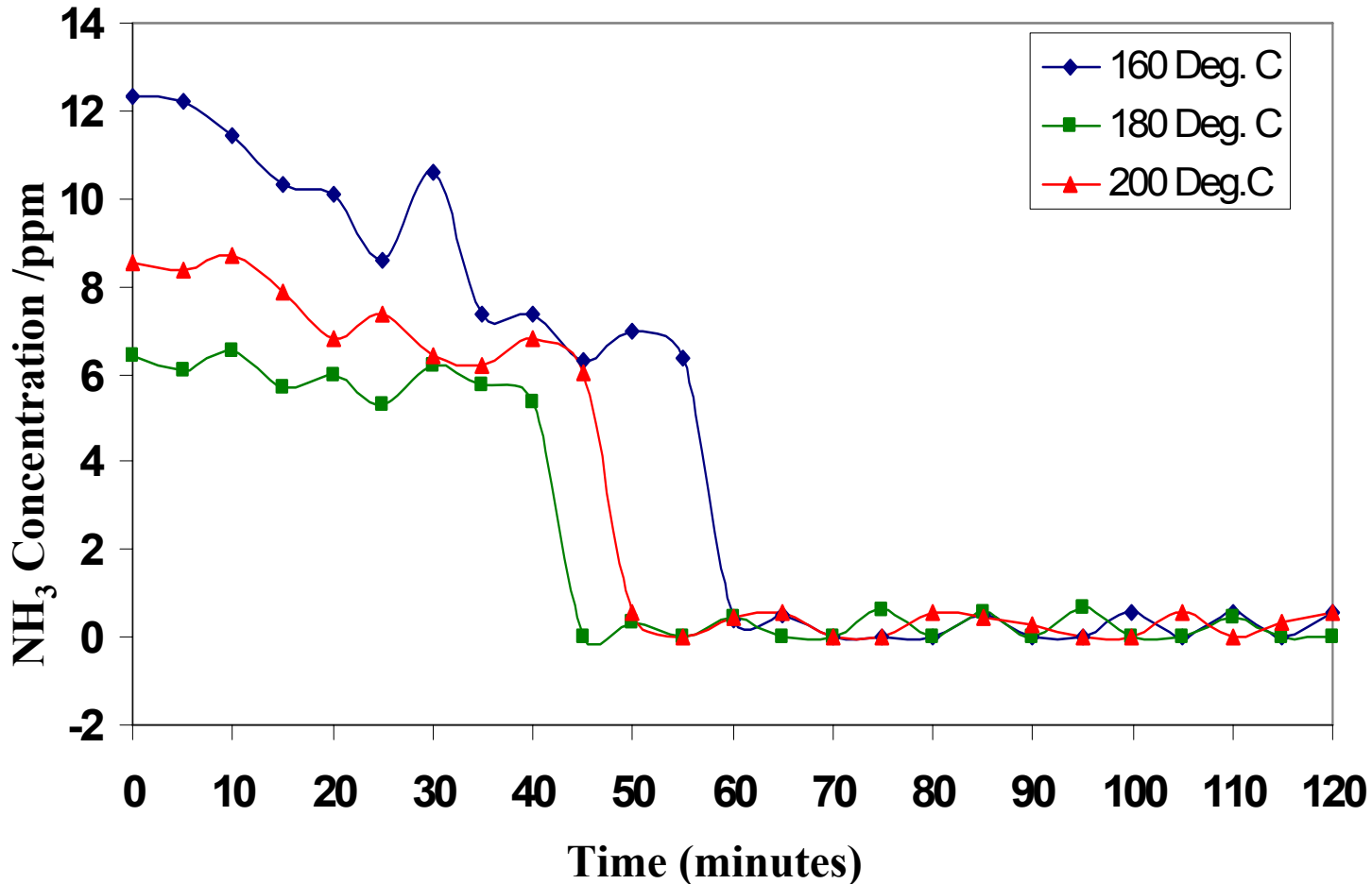
# Measuring $\text{NH}_3$ concentration

$\text{NH}_3$  concentration during dehydrogenation of the hydrogenated-LiMgN as a function of the temperature. The heating rate is 5 °C/min.



# Measuring $\text{NH}_3$ concentration

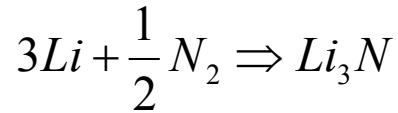
$\text{NH}_3$  concentration as a function of time during isothermal dehydrogenation of the hydrogenated-LiMgN. The heating rate prior to isothermal holding is  $5\text{ }^\circ\text{C}/\text{min}$ .



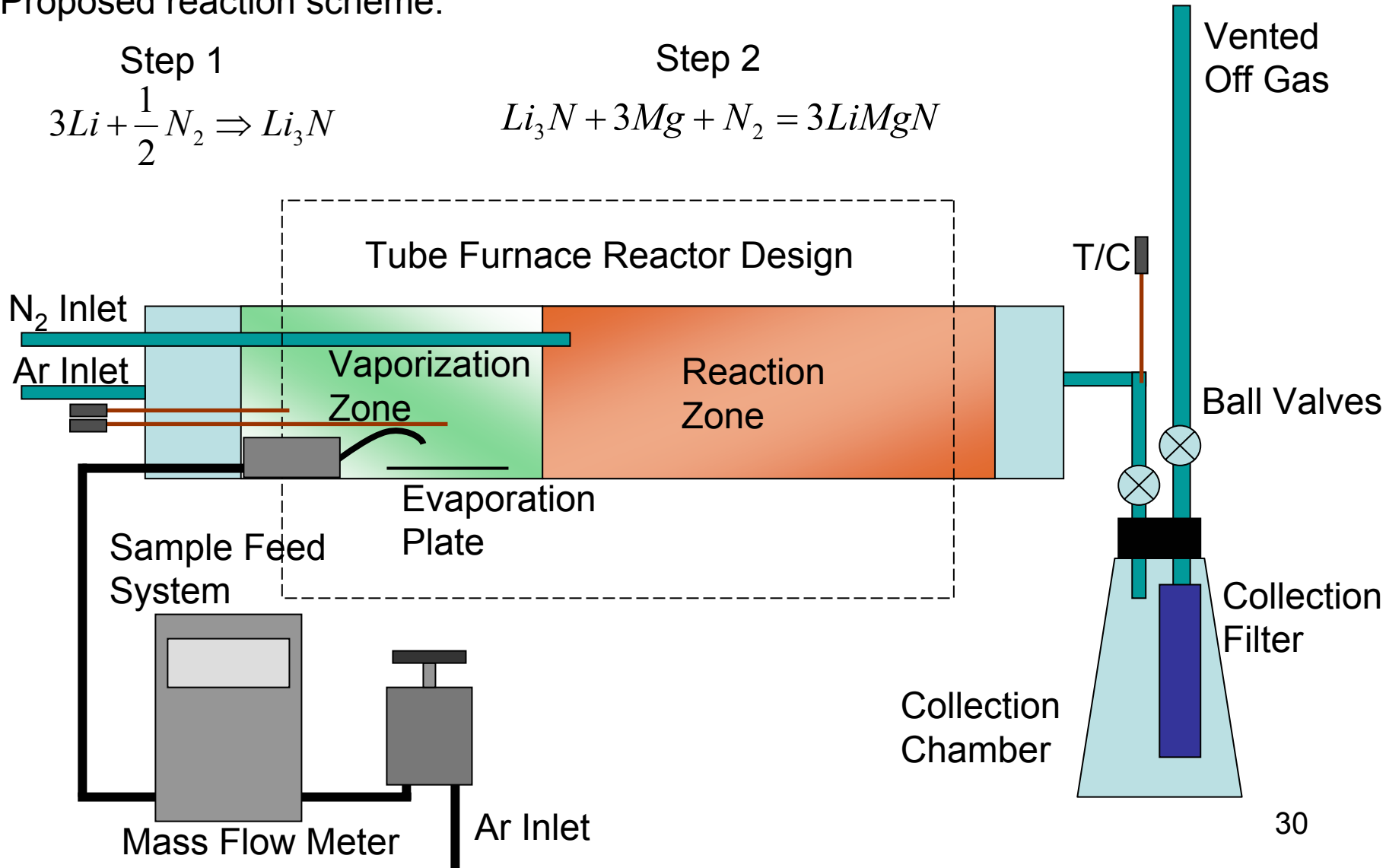
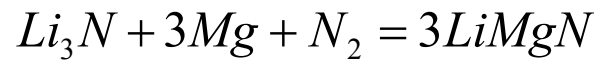
# Chemical vapor synthesis of LiMgN

Proposed reaction scheme:

Step 1

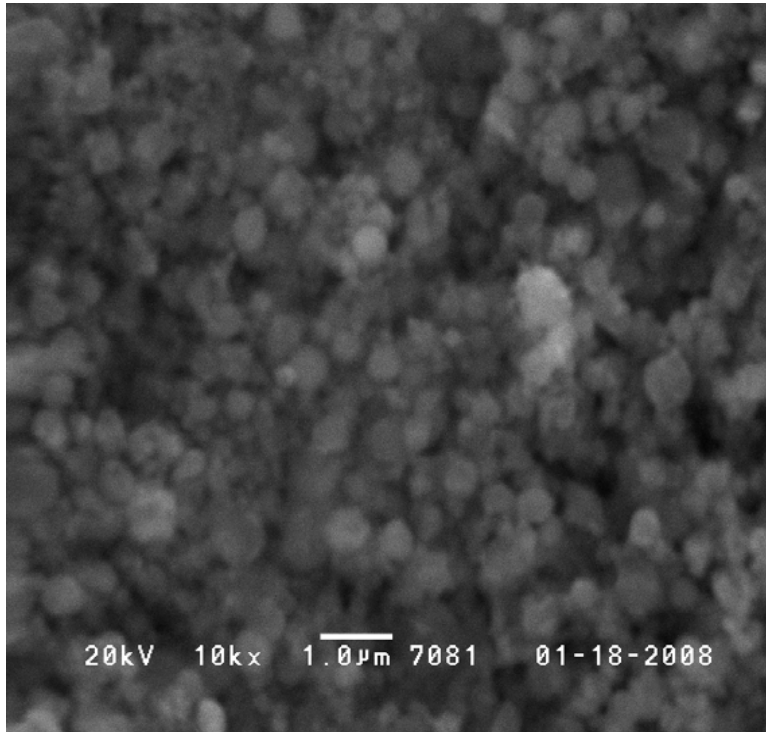


Step 2

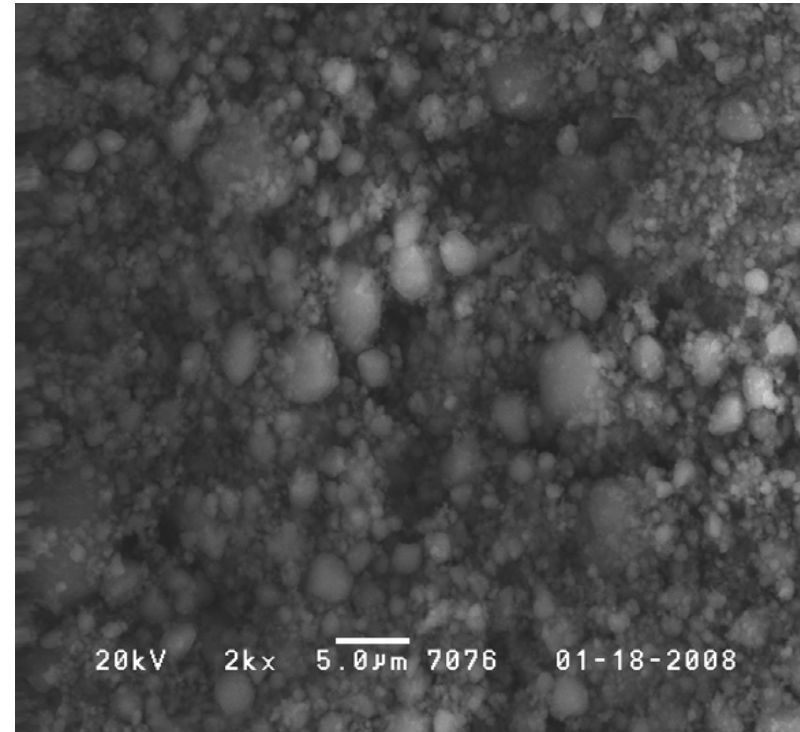


# Chemical vapor synthesis of LiMgN

Ultrafine LiMgN powders made by CVS process was successfully hydrogenated/dehydrogenated.



*(a). CVS Powder Hydrogenated*



*(b). LiNH<sub>2</sub> + MgH<sub>2</sub> Ball Milled 96 hours*

CVS produces LiMgN with more uniform sized particles than that of ball milling.

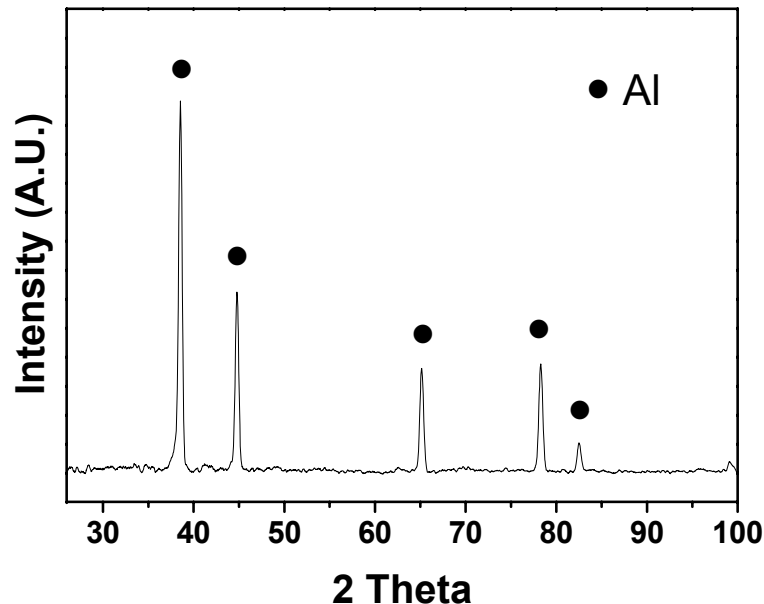


# CVS synthesis of nanosized Al powder

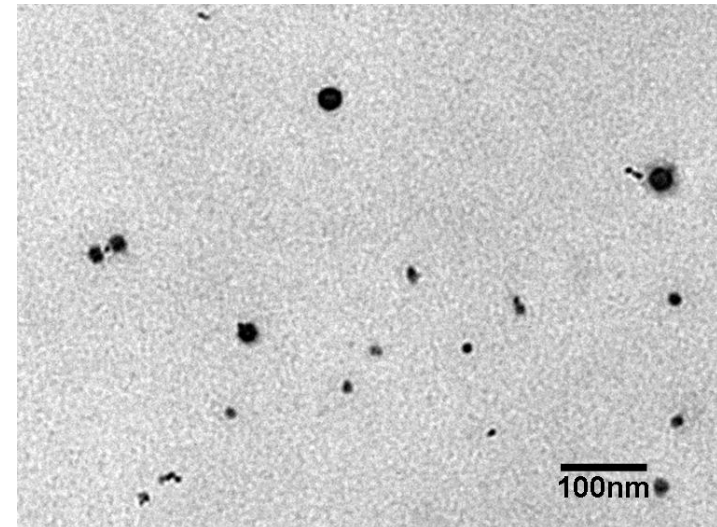
- To support MHC OE partners' efforts to regenerate  $\text{AlH}_3$ ,
- Modified the reactor from last year by controlling the residence time of the gas phase to reduce particle size,
- The average size of the produced powder is  $< 50$  nm.

Nanosized Al powder was successfully produced

XRD Result



TEM Micrograph





- $\text{Mg}_y\text{Ti}_{(1-y)}\text{H}$  thin film was found to store hydrogen reversibly with better kinetic properties compared to that of  $\text{MgH}_2$ .

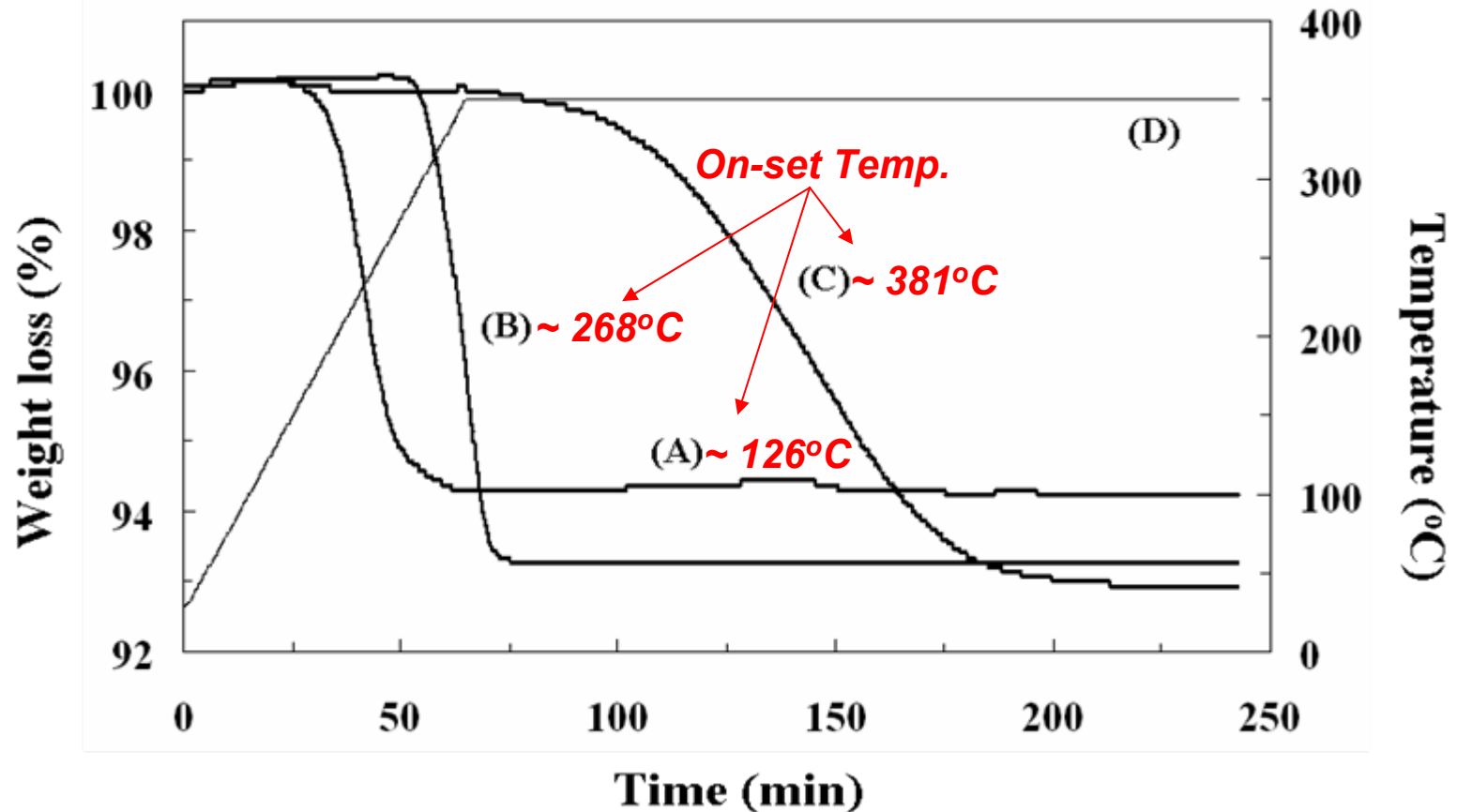
*Reference: P. Vermeulen, R.A.H. Niessen, P.H.L. Notten, "Hydrogen storage in metastable  $\text{Mg}_y\text{Ti}_{(1-y)}$  thin films", *Electrochem. Commun.* 8 (2006) 27-32.*

- Challenge: synthesize this compound in powder form and maintain reversibility
- High-energy high-pressure (HEHP) mechanochemical approach was employed: mixtures  $x\text{MgH}_2+y\text{TiH}_2$  were high-energy milled under 2000 psi  $\text{H}_2$  pressure.



HPHE Milling Reactor 33

# HEHP milled $7\text{MgH}_2\text{-TiH}_2$ - - significantly improved properties.



TGA curves of (A) milled  $7\text{MgH}_2\text{-TiH}_2$  (B) milled  $\text{MgH}_2$  (C) as-received  $\text{MgH}_2$  (D) temperature profile for (A), (B), (C).

# Summary

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- LiMgN found to be reversible at moderate temperatures, a promising material that will be investigated further.
- The reversible reaction of  $\text{Li}_3\text{AlH}_6/3\text{LiNH}_2$  was found to depend strongly on heating rate due to competing reactions and relative product stabilities.
- The co-generation of  $\text{NH}_3$  during dehydrogenation of hydrogenated LiMgN is quantified, preliminary data is now available.
- CVS is a proven approach for synthesizing nanosized or ultrafine powders for hydrogen storage applications.
- The high pressure high energy mechanochemical method is once again demonstrated as a unique approach for making non-equilibrium materials.

# Where the Amides Stand

	Selected reversible hydrogen storage material systems						
Properties	MgH <sub>2</sub> / Ni <sup>nano</sup>	NaAlH <sub>4</sub>	2LiH/ LiNH <sub>2</sub>	MgH <sub>2</sub> / 2LiNH <sub>2</sub>	Li <sub>3</sub> AlH <sub>6</sub> /3LiNH <sub>2</sub>	2/3Li <sub>3</sub> AlH <sub>6</sub> /Mg(NH <sub>2</sub> ) <sub>2</sub>	LiMgN
Theoretical reversible wt% H <sub>2</sub> (w/o catalyst)	7.6	5.6	10.4	5.6	7.3	6.5	8.2
Volumetric density (g/L) (w/o catalyst)	112	92	101	71	99		107 (estimated)
Demonstrated reversible wt% H <sub>2</sub> (with catalyst)	6.5	~5	9.3	5.2	4.9 (PCT)	6.1 (TGA)	6.6 (PCT)
Desorp. Temp (°C) (with catalyst)	150-250 (low P)	100-160	200~450 vacuum	100~250	160-300	100~240	160-240
Adsorp. Temp (°C) (with catalyst)	150	120	170-255	100~200	200-300	200-300	160-300
Isothermal Plateau Pressure, with catalyst, (Bar) (temp °C)	1 (280)	1 <sup>st</sup> step 1 (~40) 10 (~90)	0.2 (230°C) 1.0 (255°C)	46 (200 °C)	1 (255°C) 60 (375°C)	TBD	1, and 20 (240 °C)
Kinetics (with catalyst)	moderate	Good	Good	Good	TBD	TBD	TBD

## FY 2008:

- Complete quantitative characterizations of the release of  $\text{NH}_3$  during dehydrogenation from  $\text{Li}_3\text{AlH}_6/3\text{LiNH}_2$ , and  $\text{LiMgN}$ .
- Continue PCT studies of plateau pressures and the kinetics of hydrogenation and dehydrogenation for  $\text{LiMgN}$  and  $\text{Li}_3\text{AlH}_6/3\text{LiNH}_2$ ,
- Continue to study the reaction mechanisms with XRD, FTIR, NMR.
- Begin catalyst studies to improve kinetic performance of materials
- Begin studies of  $2\text{LiNH}_2 + \text{C} = \text{Li}_2\text{CN}_2 + 2\text{H}_2$  (rxn. predicted by Theory Group)
- Perform cycling studies of the  $\text{LiMgN}$  system
- Use CVS approach to make catalyzed nano Al for regeneration of  $\text{AlH}_3$ ,
- Continue explore new materials using high pressure high energy ball milling

## FY 2009:

- Continue to explore new materials, catalysts
- Explore techniques (thermal, chemical) to minimize  $\text{NH}_3$  release
- Continue to study cycle stabilities



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