METAL HYDRIDE CENTER OF EXCELLENCE

DOE Hydrogen Program

THE UNIVERSITY OF UTAH

Chemical Vapor Synthesis and Discovery of H_2 Storage Materials: Li-Mg-N-H System

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THE UNIVERSITY OF UTAH

Project ID ST_04_Fang

Overview

Timeline

- Start – March 2005
- Finish – March 2010
- Percent complete – 80%

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)

Budget

- Total project funding

  DOE share: ~$1.0MM

  Contractor share: $250K
- Funding received for FY08: $150K
- Planned Funding for FY09: $200K

Partners

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

Objectives and Impact

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

FY08-09

- Determine thermodynamic properties of hydrogen storage using the ternary nitride material – LiMgN
- Understand mechanisms of hydrogenation and dehydrogenation of LiMgN,
- Quantify NH_3 content during dehydrogenation of hydrogenated LiMgN
- Demonstrate effects of nanoscale particle size on properties of metal hydrides.

Approach

- Exploit potentials of ternary nitrides.
- Use an ultra-high-energy high pressure milling method and a chemical vapor reaction technique for synthesis of nano particles and study of the effect of nanosize scale (≤10nm).
- Discover and identify new candidate materials through collaborations with MHCoE Theory Group.
- Using a two-step strategy for identifying research path among multiple candidate materials:
  - ***rapid-screening using in-house tools (e.g. TGA, XRD)***
  - ***in-depth study by collaborating with MHCOE partners (NMR, in-situ XRD etc)***,
- Implement a criteria based on ΔH for select/down-select candidate materials.

Approach

Milestones and Go/No-go Decisions

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	A No-Go decision was made on $Li_3AlH_6+3LiNH_2$ system because the ΔH of the dehydrogenation reaction is to high (~60 KJ/mol.H_2)	Completed
March – 2010	Go/No-Go Decision will be made on LiMgN based on comprehensive characterizations of the thermodynamic and kinetic properties of LiMgN with additives.	50% complete
March - 2010	Milestone: Full report, conclusions, and recommendations on selected materials.	

Two promising materials discovered in the past two years:

I. Reactions of $LiNH_2$ with lithium alanate materials

$$Li_3AlH_6 + 3LiNH_2 \longleftrightarrow Al + 3Li_2NH + \frac{9}{2}H_2$$

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

II. Reactions Leading to LiMgN

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

-- Theoretically predicted by MHCoE partners (Johnson, Sholl, Alpati) to have ΔH = 32kJ/molH_2, with 8.2% theoretical hydrogen capacity.

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

Georgia Institute of Technology

Amide Go/No-go Decisions

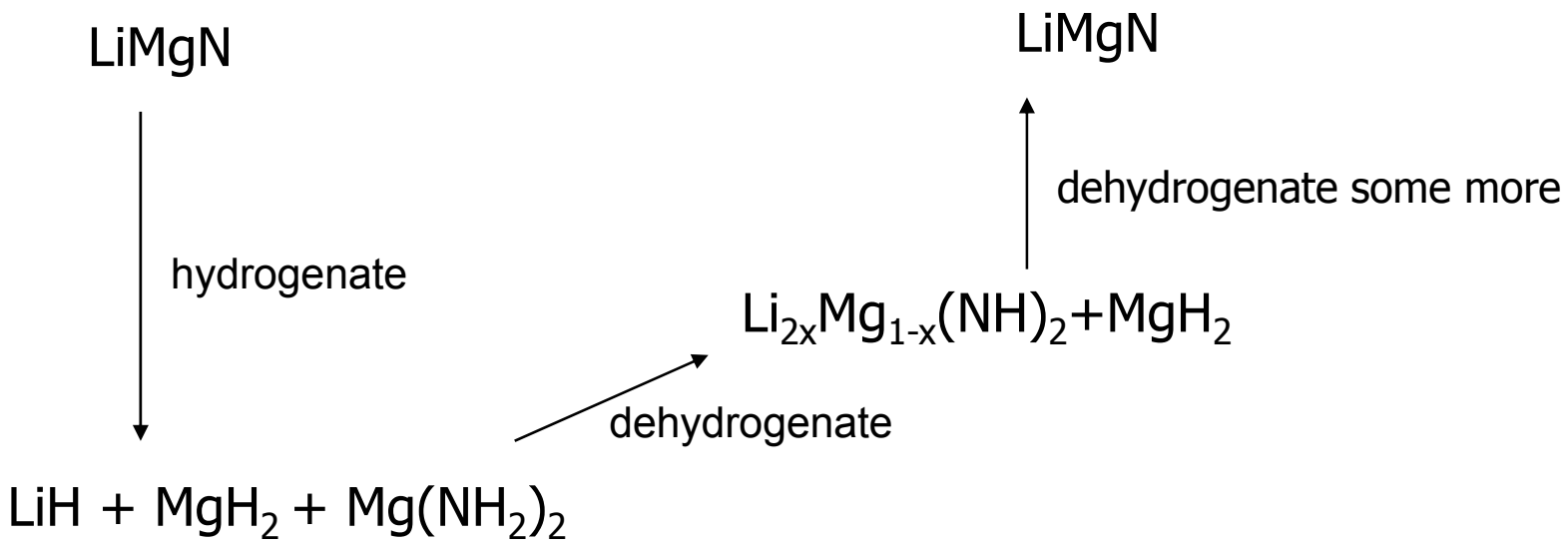
Decided <u>not</u> to pursue further $Li_3AlH_6/3LiNH_2$ material (it was down-selected)

Decided to focus on LiMgN:

- Potential H_2 storage capacity (theoretical 8.2*wt*%) is higher than that of $Li_3AlH_6/3LiNH_2$
- Predicted ΔH of LiMgN reaction is more desirable
- Dehydrogenated product (LiMgN) is one single compound, rather than a mixture, perhaps simpler?
- Better kinetics than $Li_3AlH_6/3LiNH_2$

LiMgN Status at 3/2008 (last annual review)

1. LiMgN can be hydrogenated at T ~180 ^{o}C, confirmed by SRNL
2. ^{1}H, ^{6}Li NMR data (JPL/Caltech) reveal complex LiMgN hydrogenation pathways
3. In-situ XRD studies (GE) of hydrog./dehydrog. indicate overall reaction scheme:



Synthesis of Pure LiMgN

Since last AMR, we invested a significant amount of time on the synthesis of pure LiMgN from $LiNH_2$+MgH_2

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

Then, once we found the route to pure LiMgN, we focused on:

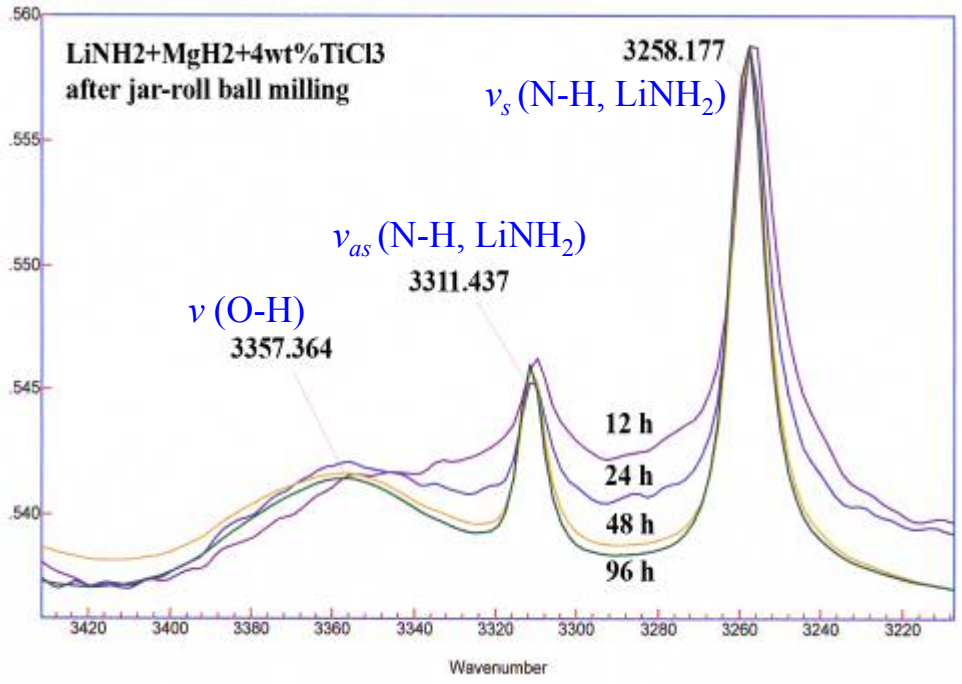
- **Reversibility and Capacity**
- **Thermodynamics**
- **Kinetics**
- **Reaction pathways**

Low-energy Milling Produces Pure LiMgN

Gentle low-energy milling using a jar-rolling set-up preserves the $LiNH_2/MgH_2$ mixture, without premature release of H_2

Reaction of the mixture during subsequent heating will produce pure (98.99%) LiMgN

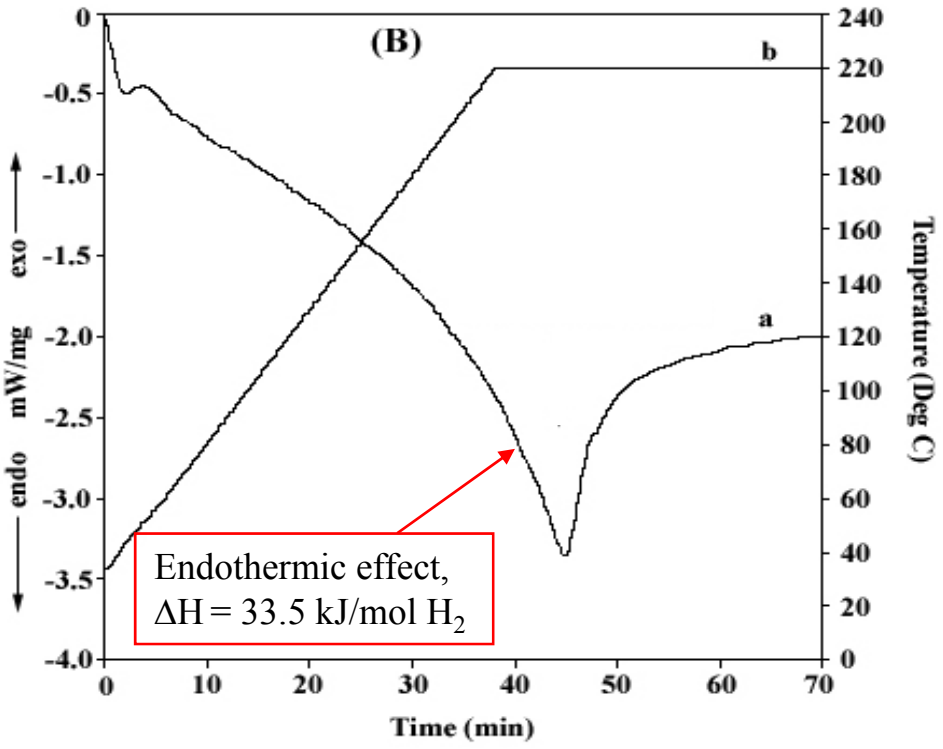
FT-IR results: N-H bond transformation during the low-energy ball-milling



Note: High-energy milling is not suitable for synthesis of LiMgN due to premature release of H_2 and production of mixed nitride products

Thermodynamics: Measured ΔH of dehydrogenation from LiMgN precursor validating Johnson/Sholl predictions.

DTA curve of the dehydrogenation reaction of $LiNH_2+MgH_2 \rightarrow LiMgN+2H_2$

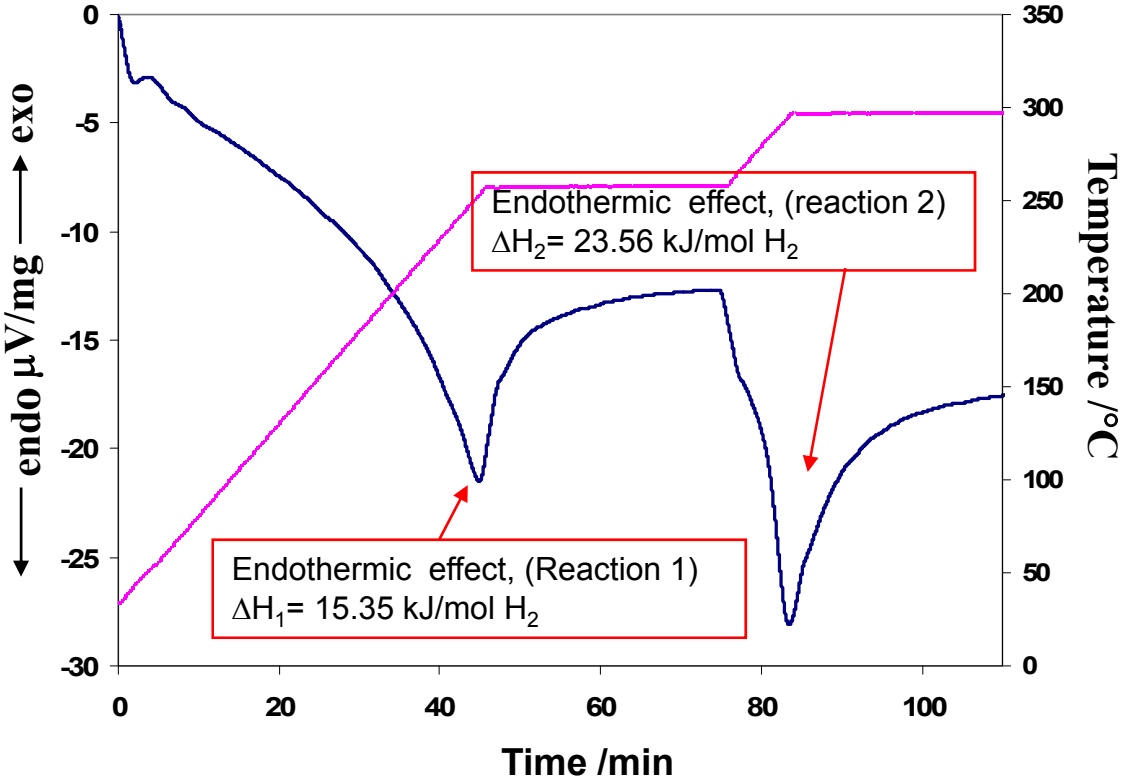


- One reaction step detected during the dehydrogenation of $LiNH_2+MgH_2$
- The ΔH value for the reaction is 33.5 kJ/mol H_2, which is close to the theoretically predicted reaction enthalpy of 29.7 (31.9) kJ/ mol H_2 reported by Alapati[1] et al.

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

Thermodynamics: Measured ΔH of dehydrogenation from hydrogenated LiMgN is close to what is deemed "ideal" range.

DTA curve of the dehydrogenation reaction of hydrogenated-LiMgN



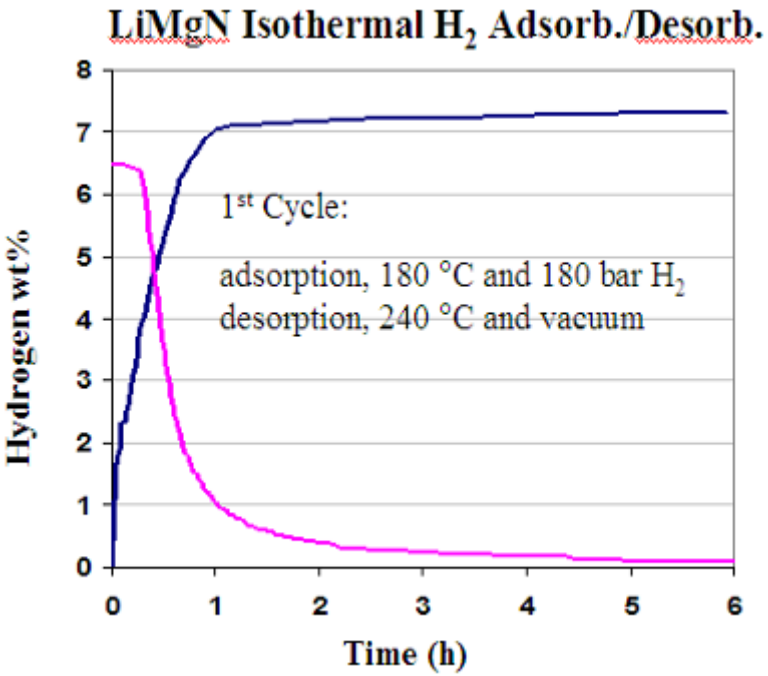
- Two reaction steps detected during the dehydrogenation of the hydrogenated LiMgN sample
- The ΔH values for the two reactions are 15.35 and 23.56 KJ/mol H2 respectively.

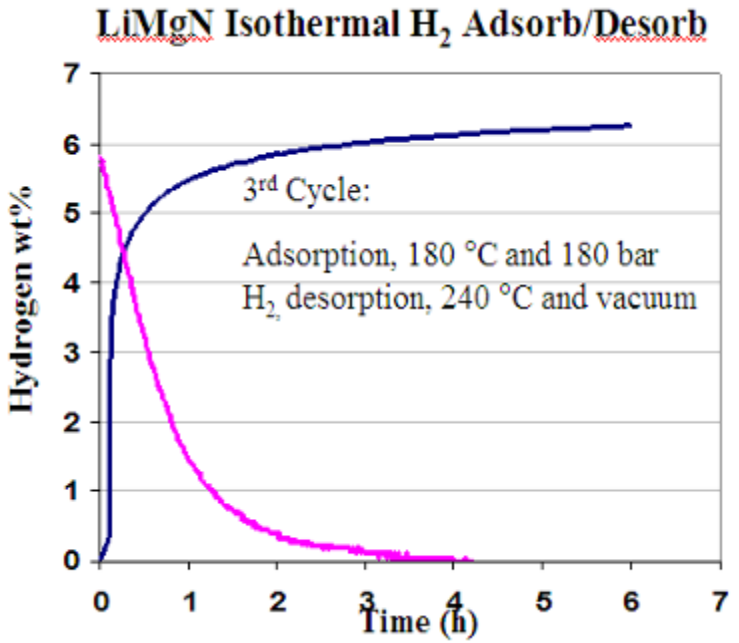
$$LiH + MgH_2 + Mg(NH_2)_2 \rightarrow Li_{2x}Mg_{1-x}(NH)_2 + MgH_2 + H_2 \quad (1)$$

$$Li_{2x}Mg_{1-x}(NH)_2 + MgH_2 \rightarrow LiMgN + H_2 \quad (2)$$

Technical Accomplishments and Progress

LiMgN Is reversible. But cycle capacity is affected by kinetics and pressure of adsorption.



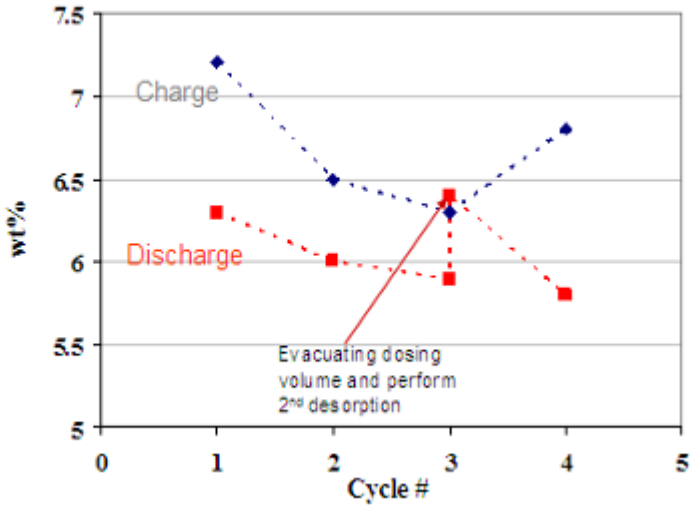


Charge:

180°C/180 bar/6h

Discharge:

240°C/vacuum/4h



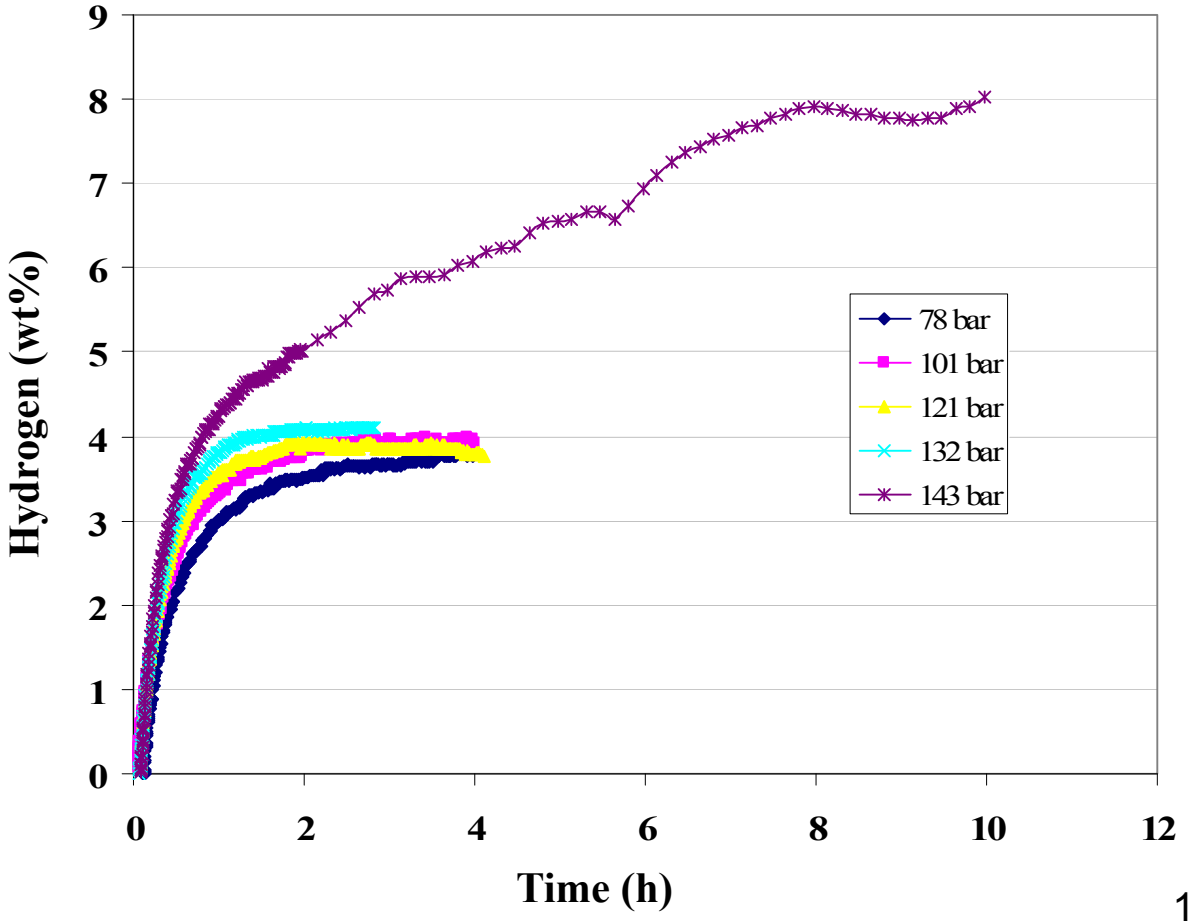
Notes:

Complete desorption was achieved by desorbing into vacuum first, then evacuate, and desorb into vacuum again – effects of back pressure and kinetics to be sorted out.

Technical Accomplishments and Progress

Recharge of LiMgN Is pressure dependent. >140 bar is required to fully recharge the material.

LiMgN Isothermal Adsorption at 180 °C under different H_2 pressure



Kinetic Analysis of LiMgN

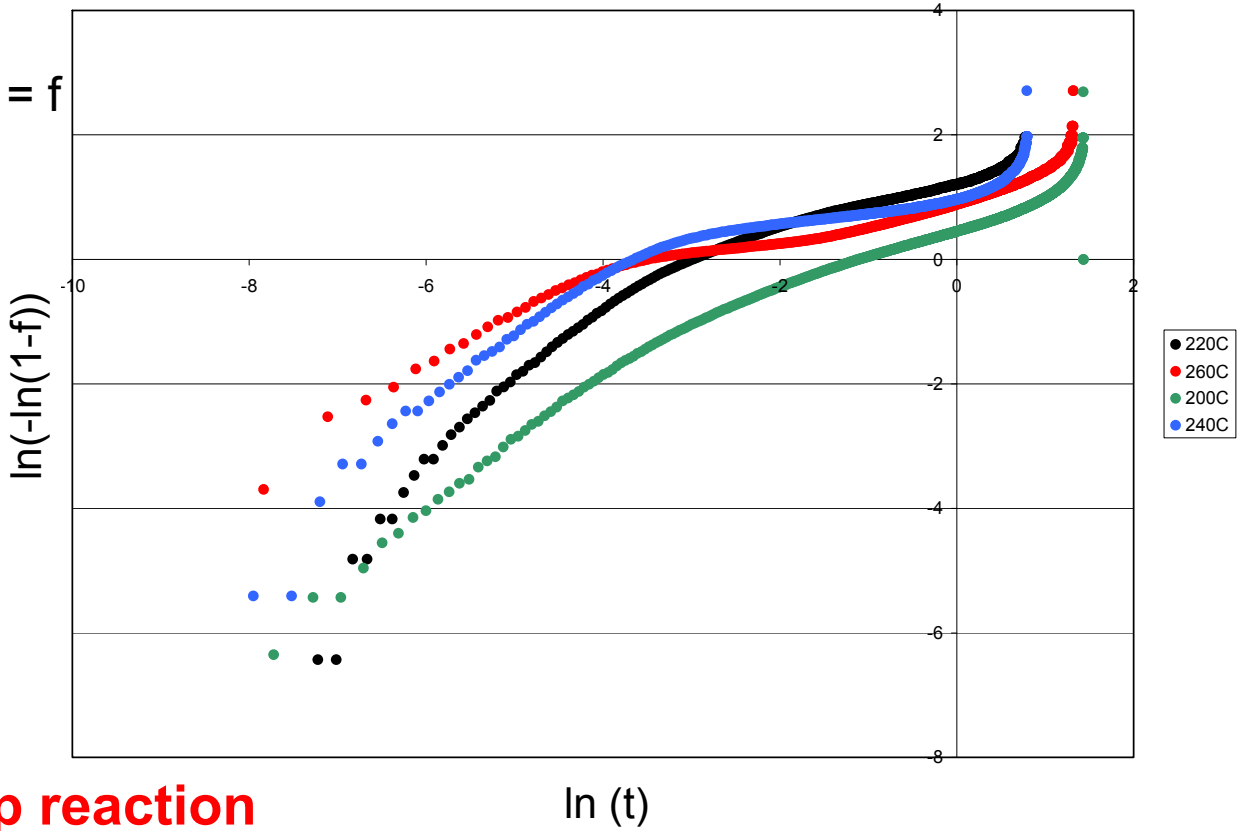
– **Common equation for crystallization and solid phase transformation processes**

Def. α(t)= fraction transformed = f

- $\alpha(t)=1-\exp(-ktn)$

  $d\alpha/dt=k*nt^{(n-1)}*\exp(-kt^n)$

- $\ln(-\ln(1-\alpha)) = n\ln(t) + \ln(k)$



– **Transformations between different linear segments indicative of changes in reaction mechanism**

– **Evidence of multi-step reaction mechanism observed**

Kinetic Analysis of LiMgN

Kinetic rate of H_2 release and uptake using LiMgN are within an order of magnitude of the targets, but the temperature is still too high

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	2.0×10^{-5}	1.43
	180°C	2.4×10^{-5}	1.73
	200°C	1.9×10^{-5}	1.38
	220°C	1.7×10^{-5}	1.26
Temp	160°C	Charge	
P	70 bar	4.6×10^{-6}	0.330
	100 bar	1.2×10^{-5}	0.811
	150 bar	2.0×10^{-5}	1.43
Discharge			
T = 280°C	P = 1 bar	1.0×10^{-5}	0.737

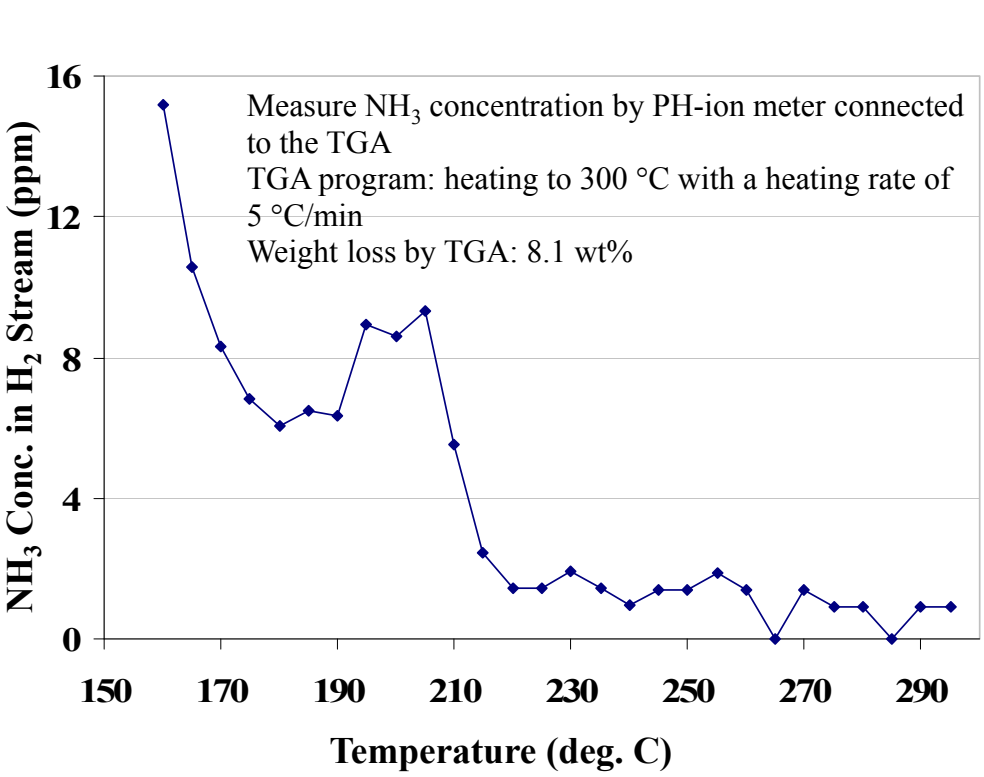
4 mol% $TiCl_3$ (13.7 wt%)		Rate [g H_2 / (s·g_s)]	Rate 72 kg bed*
P	150 bar	Charge	
Temp	160°C	1.9×10^{-5}	1.40
	180°C	2.5×10^{-5}	1.80
	200°C	2.3×10^{-5}	1.68
Temp	180°C	Charge	
P	70 bar	6.0×10^{-6}	0.430
	100 bar	1.2×10^{-5}	0.882
	150 bar	2.5×10^{-5}	1.80
Discharge			
T = 280°C	P = 1 bar	2.4×10^{-5}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

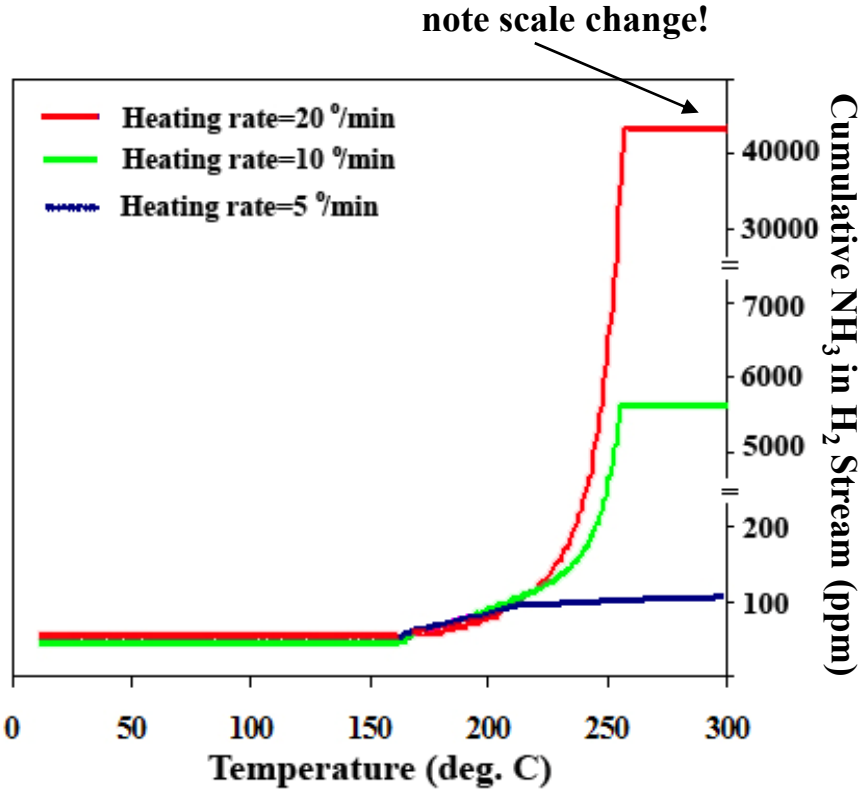
**Assumes 7 wt% with 5 kg H_2 stored*

- >6 w% cyclic hydrogen charging observed
- Catalyst loading has significant effect on discharge rate
- Catalyst loading has little effect on charging rate
- Charging rate is strongly pressure dependent
- Terminal compound tentatively identified as $Li_{0.51}Mg_{2.49}N_{1.83}$ awaiting IR confirmation

- 4 mol% material discharge rate is 57% of DOE technical target at 280 °C
- 4 wt% material is10% of target charge rate at 180 °C

NH_3 release from Hydrogenated LiMgN





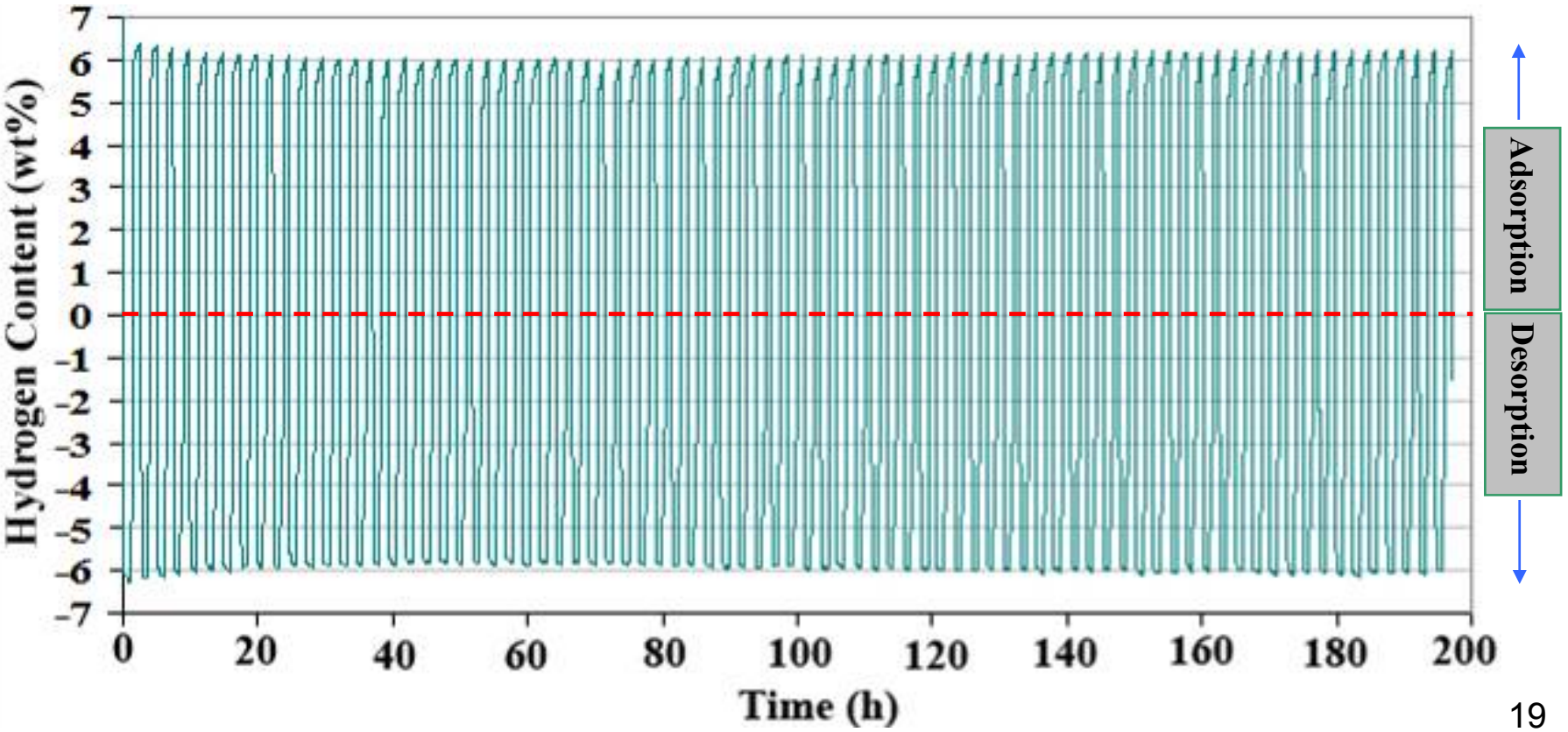
- NH_3 113ppm in the H_2 stream when heating rate is slow, as measured by TGA and pH- ion meter.
- NH_3 concentration is dramatically increased when the heating rate is increased.
- Will conduct isotherm measurements as the next step.

Summary of Ternary Nitride LiMgN:

- Reversible,
- Reversible capacity 6-8wt%
- Thermodynamics: ΔH = 33-38 KJ/mol.H_2,
- Kinetics – Reasonable at 280 °C.
- NH_3 issue: ~14 ppm in H_2 stream, Cumulative ~100 ppm.
- ***Must reduce the reaction temperature. Efforts underway to use additives and nano engineering.***

Effects of nano size scale: MgH_2-8mol%TiH_2, particle size – 5-10 nm

Excellent stability after 100 cycles at 290 °C. ~6.0 wt% reversible capacity.

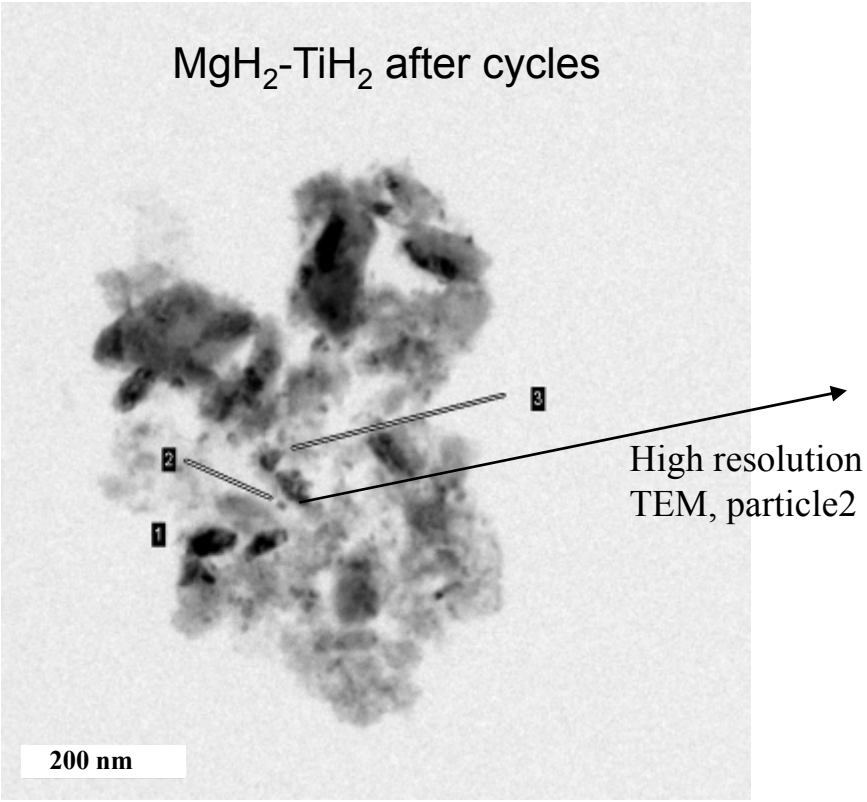


Technical Accomplishments and Progress

Effects of nano size scale: MgH_2-8mol%TiH_2, particle size – 5-10 nm

Particle size very stable during cycling in the presence of TiH_2.

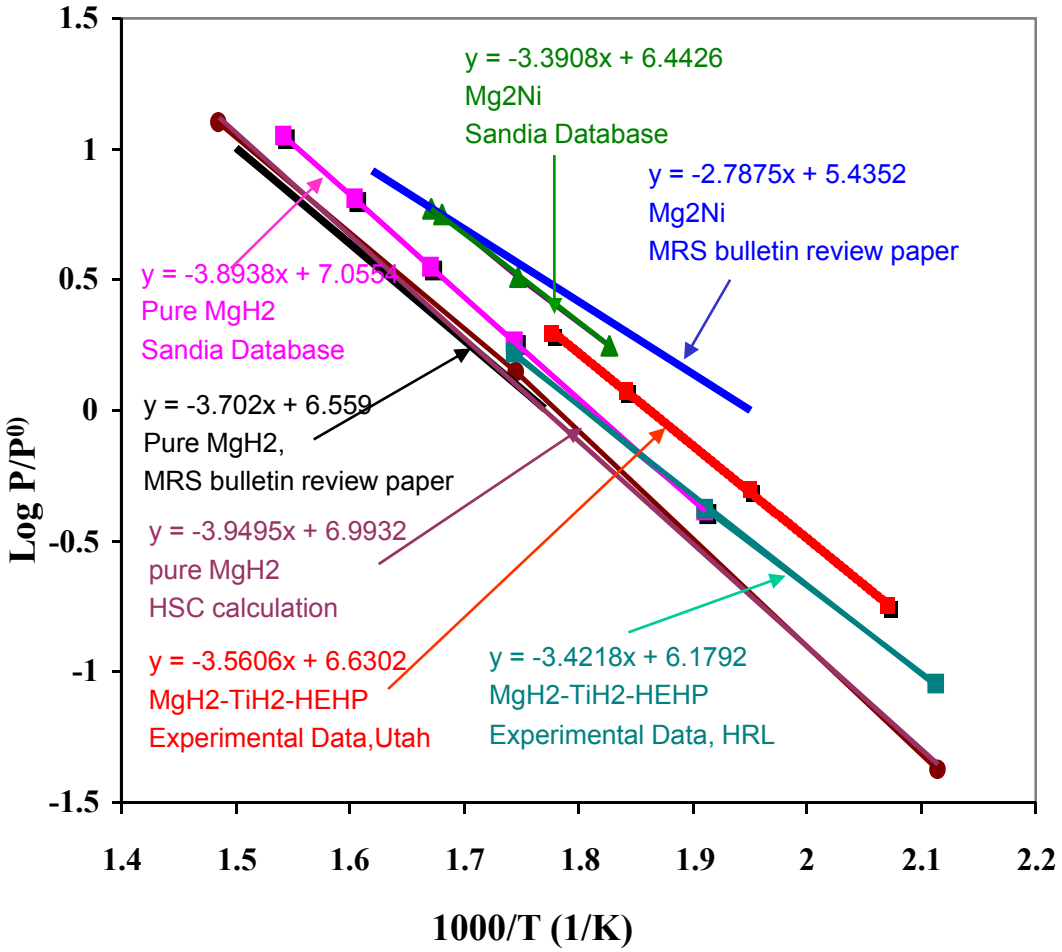
TEM Images show the size of crystallites <10 nm after cycling.



Technical Accomplishments and Progress

Effects of nano size scale: MgH_2-8mol%TiH_2, particle size – 5-10 nm

Using nano size (5-10 nm) and TiH_2 additives, the ΔH value was changed, but so was ΔS. The net effect on ΔG very small. Thus, P_{eq}, did not change significantly.



System	ΔH (kJ/K mol H_2)	ΔS (J/mol H_2)
Pure MgH_2, (Sandia Database)	-74.6	-135.1
Pure MgH_2, (MRS Bull. Sept. 2002)	-70.8	-125.6
Pure MgH_2, (HSC calculation)	-75.6	-133.9
MgH_2-TiH_2-HEHP (Exp. Data, U Utah)	-68.2	-126.9
MgH_2-TiH_2-HEHP (Exp. Data, HRL)	-65.5	-118.3
Mg_2Ni, (Sandia Database)	-64.9	-123.4
Mg_2Ni, (MRS Bull. Sept. 2002)	-53.4	-104.1

Collaborations

- Collaborations with the MHCOE Theory Group (U Pitt and Georgia Tech) on reactions mechanisms of hydrogen reactions based on LiMgN,
- Collaboration with SRNL on kinetics of LiMgN
- Collaborations within MHCOE (JPL, Cal Tech) on using NMR for in-depth characterizations,
- Collaborate with Univ of Nevada-Reno on detailed study of phase transformations in Li-Mg-N-H systems.
- Collaborations with SNL on non-equilibrium Mg-Ti-H.
- Collaboration with MHCoE Additive Screening Group on finding additives to improve kinetics.

Proposed Future Work

FY 2009 -2010:

- Search for LiMgN additives to lower H_2 release temperature
- Thermo and kinetic studies of LiMgN with additives cycling using PCT instrument
- Explore techniques (thermal, chemical) to minimize NH_3 release during H_2 desorption
- Continue to search new materials based on new concepts.

Summary

Relevance Discovering and synthesis of solid hydrides that can reversibly store hydrogen.

Approach Exploit potentials of ternary nitrides.

Technical Accomplishments and Progress

Characterized and studied thermodynamic and kinetic properties of reversible H_2 storage using LiMgN.

Demonstrated effects of nanosize scale (10 nm) on cyclic H_2 storage of MgH_2 with TiH_2 additive with greater than 6*wt*% capacity.

Technology collaborations Active partnership with theory and analytical characterization group.

Future plan Investigate effects of additives on kinetics of H_2 storage using LiMgN.

Investigate the potential of a new class of materials for H_2 storage (to be disclosed).