Discovery of H_2 Storage Materials: LiMgN and Mg-Ti-H

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Project ID ST062

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Overview

Timeline

- Start – March 2005
- Finish – March 2011
- Percent complete – 90%

Barriers

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

Budget

- Total project funding

  DOE share: ~$950K

  Contractor share: $240K
- Funding received for FY09: $280K
- Planned Funding for FY10: $0K

MHCoE 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

FY09-10

- Study thermodynamic properties of hydrogen storage using LiMgN
- Study kinetic properties of hydrogen storage using LiMgN
- Search for catalytic additives that improve kinetics of hydrogen storage using LiMgN
- Study the kinetics of hydrogen storage of high-energy-high-pressure milled MgH_2-0.1TiH_2 system

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+3$LiNH_2$ 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.	80% complete
March - 2011	Milestone: Full report, conclusions, and recommendations on selected materials.	On track

Technical Accomplishments and Progress

Two promising materials discovered in the past three 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…down-selected due to poor kinetics.

The $Li_3AlH_6/LiNH_2$ material was "downselected", removed from further study

II. Reactions Leading to LiMgN

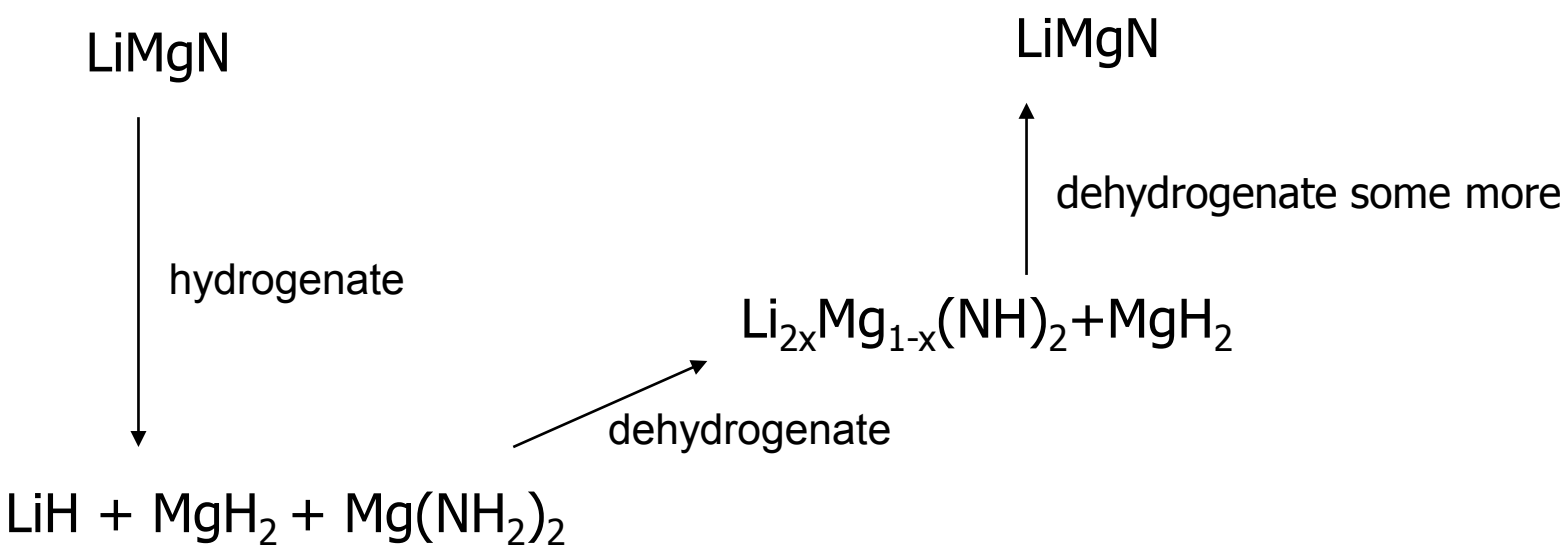
$$MgH_2 + LiNH_2 \rightarrow LiMgN + 2H_2$$

-- Theoretically predicted by MHCoE partners (Johnson, Sholl, Alapati) 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

LiMgN Status at 3/2009 (last annual review)

- Reactions leading to LiMgN – theoretically predicted by *MHCoE partners (Johnson, Sholl, Alapati) with 8.2% theoretical hydrogen capacity*
- LiMgN can be hydrogenated at T ~180 ^{o}C, confirmed by SRNL
- In-situ XRD studies (GE) of hydrogenation/dehydrogenation indicate overall reaction scheme:



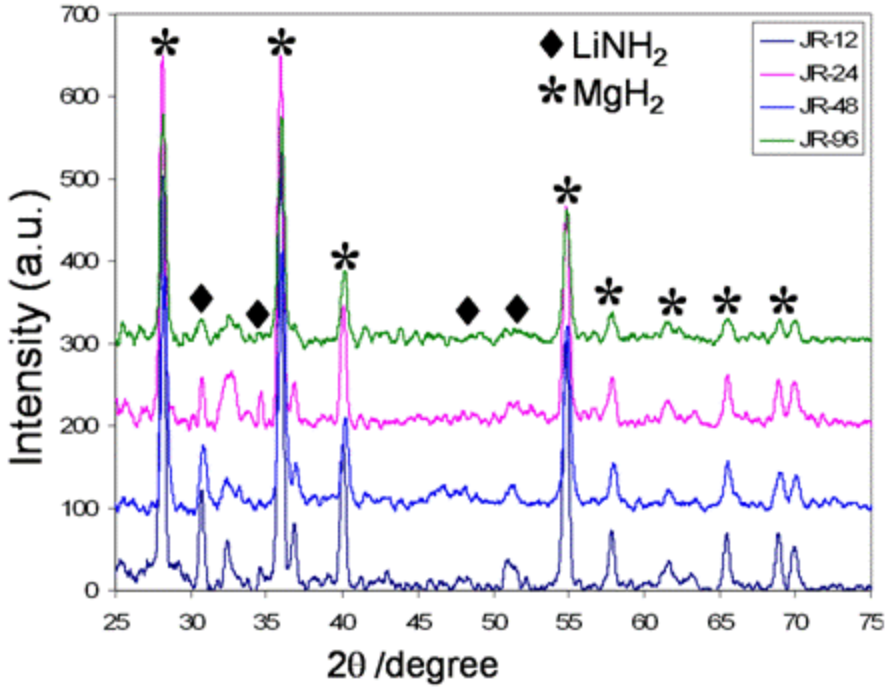
Recent results on LiMgN

I. **Preparation of LiMgN from the $LiNH_2$+MgH_2 reaction**

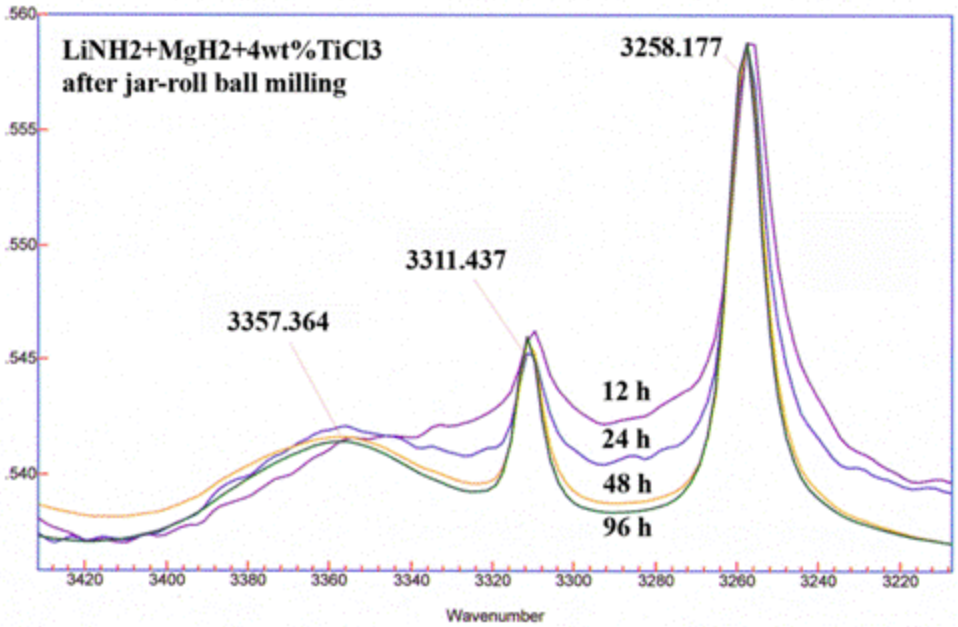
II. **PCT study of hydrogenation and dehydrogenation using LiMgN as starting material**

Technical Accomplishments and Progress

Effects of ball milling intensity on the synthesis of pure LiMgN



XRD patterns of $LiNH_2/MgH_2$ mixture after Jar-roll milling



FT-IR Spectra of $LiNH_2/MgH_2$ mixture after Jar-roll milling

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

Technical Accomplishments and Progress

Effects of ball milling intensity on the synthesis of pure LiMgN

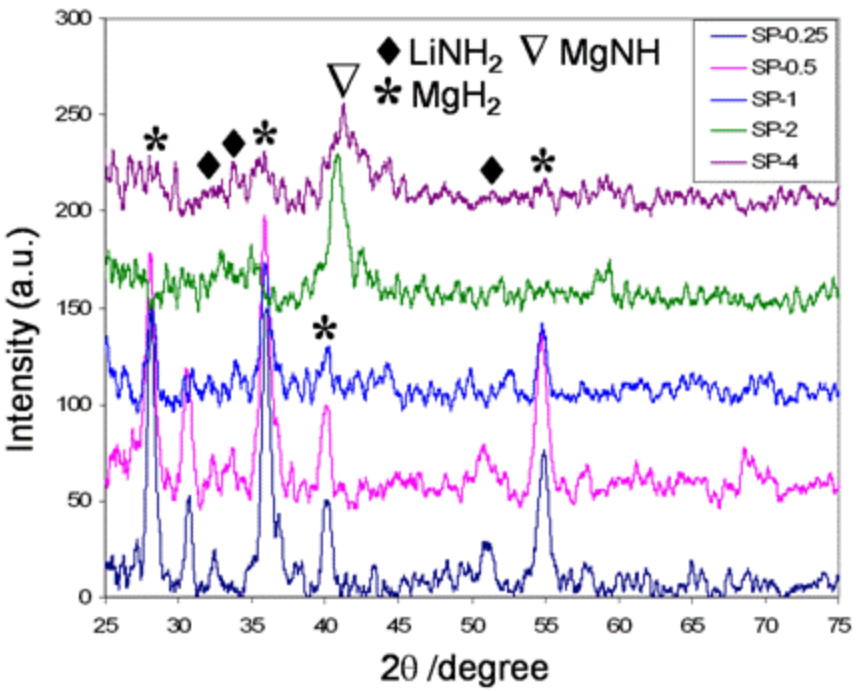
Summary of the mixture of $LiNH_2/MgH_2$ after Jar-roll milling

Low-energy mill	12 hrs	24 hrs	48 hrs	96 hrs
TGA (wt.%)	9.19	8.02	7.87	7.91
XRD after milling	MgH_2, $LiNH_2$	MgH_2, $LiNH_2$	MgH_2, $LiNH_2$	MgH_2, $LiNH_2$
FT-IR after milling	$LiNH_2$	$LiNH_2$	$LiNH_2$	$LiNH_2$
XRD after dehydrogenation	LiMgN, Li_3N	LiMgN, Li_3N	LiMgN, Mg_3N_2	LiMgN

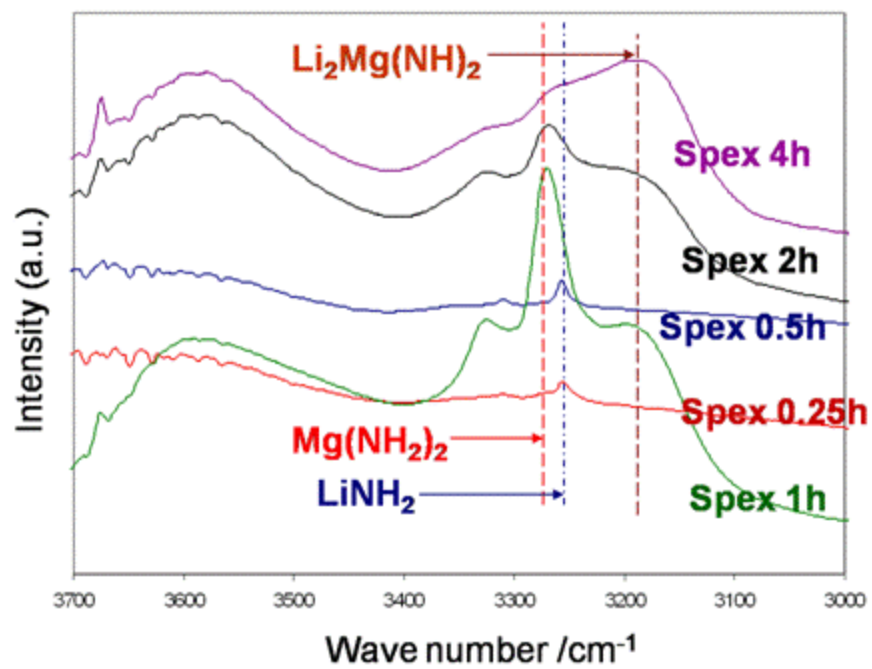
After low-energy milling, reactions during subsequent heating produce pure (98.99%) LiMgN from the sample after longer milling time (>48h)

Technical Accomplishments and Progress

Effects of ball milling intensity on the synthesis of pure LiMgN



XRD patterns of $LiNH_2/MgH_2$ mixture after Spex milling



FT-IR Spectra of $LiNH_2/MgH_2$ mixture after Spex milling

High-energy milling leading to a series of reactions during the milling process, including the reactions between $LiNH_2$ and MgH_2, and the subsequent release of hydrogen.

Technical Accomplishments and Progress

Effects of ball milling intensity on the synthesis of pure LiMgN

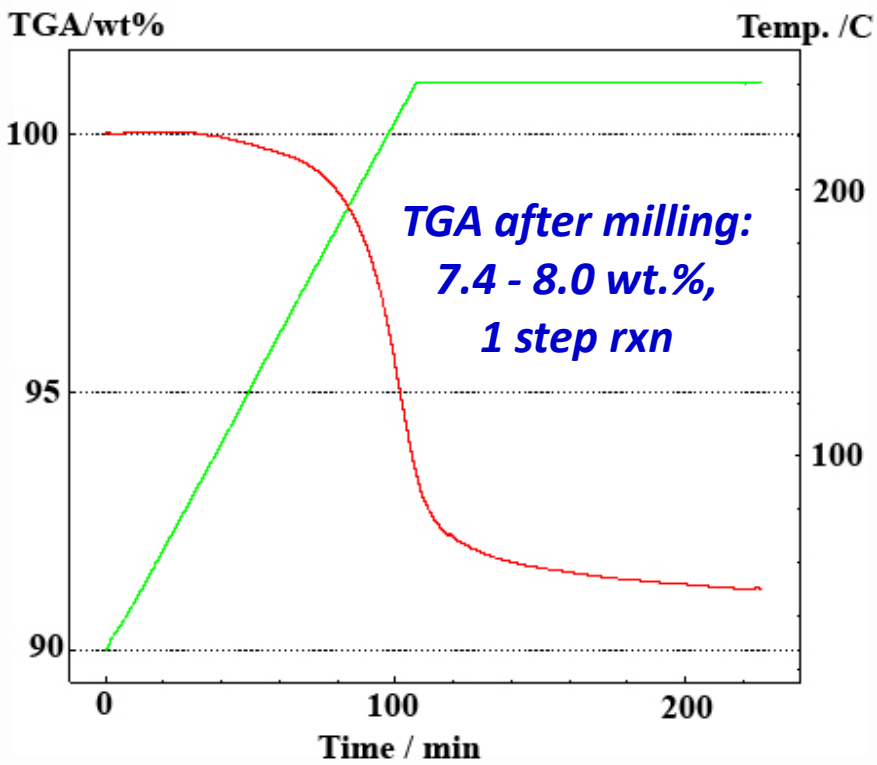
Summary of the mixture of $LiNH_2/MgH_2$ after Spex milling

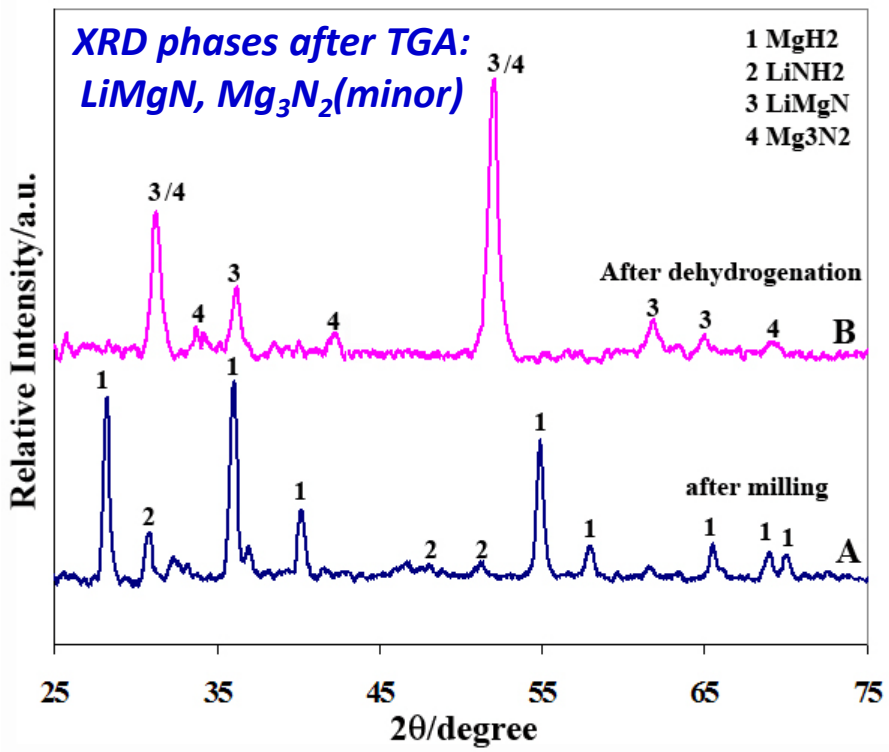
High-energy mill	0.25 hr	0.5 hr	1 hr	2 hrs	4 hrs
TGA wt.%	9.124	8.192	5.723	4.511	3.422
XRD after milling	$LiNH_2$, MgH_2	$LiNH_2$, MgH_2	MgH_2	MgNH	MgNH
FT-IR after milling	$LiNH_2$	$LiNH_2$	$Mg(NH_2)_2$, $Li_2Mg(NH)_2$, MgNH	$Mg(NH_2)_2$, $Li_2Mg(NH)_2$, MgNH	$Li_2Mg(NH)_2$, MgNH
XRD after dehydrogenation	LiMgN, Mg_3N_2	LiMgN, Mg_3N_2	LiMgN, Mg_3N_2	LiMgN, Mg_3N_2,	LiMgN, Mg_3N_2,

The product after high milling is a complex mixture of multiple phases. Pure LiMgN cannot be obtained from High-energy method

Technical Accomplishments and Progress

Effects of ball milling intensity on the synthesis of pure LiMgN





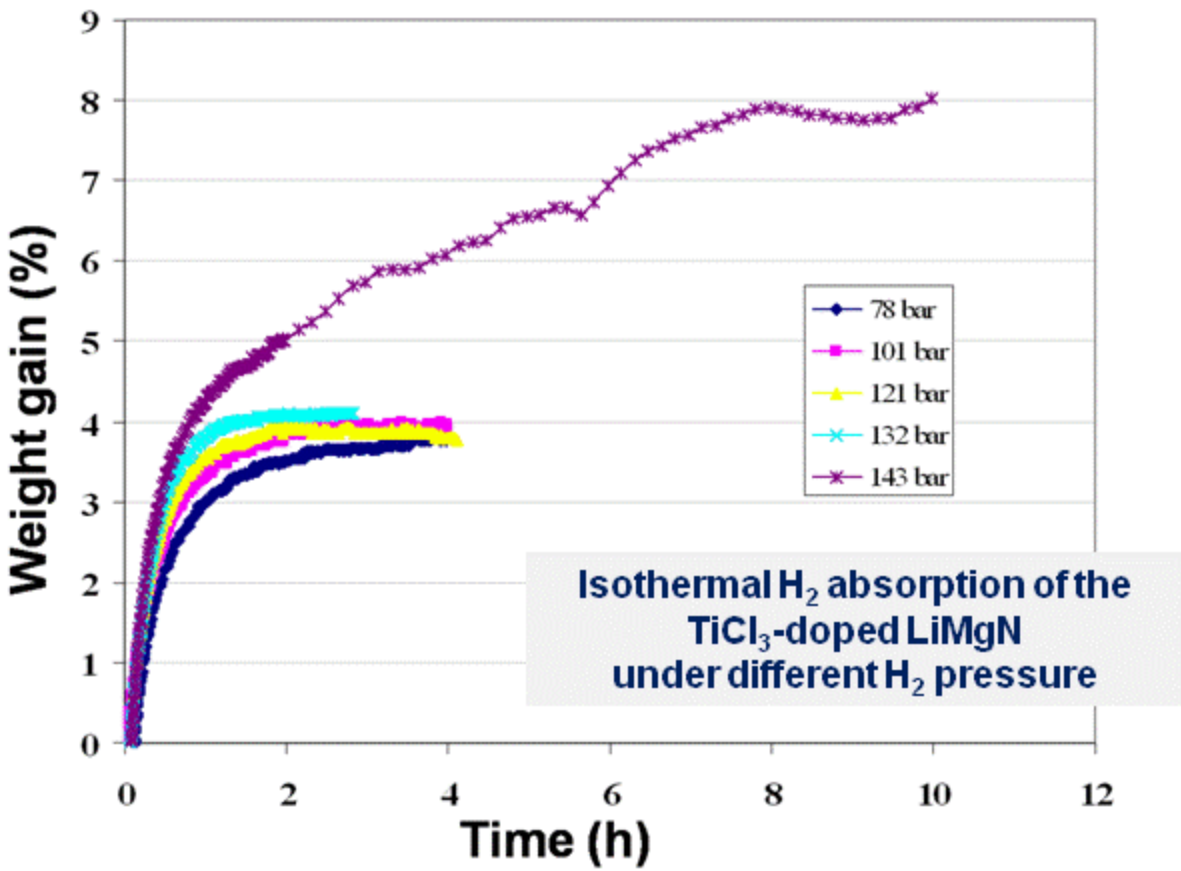
Optimum milling procedures:

1). Spex milling separately ($LiNH_2$ & $MgH_2/TiCl_3$)(4h) +

2). Jar-roll milling together ($LiNH_2+MgH_2+TiCl_3$)(96h)

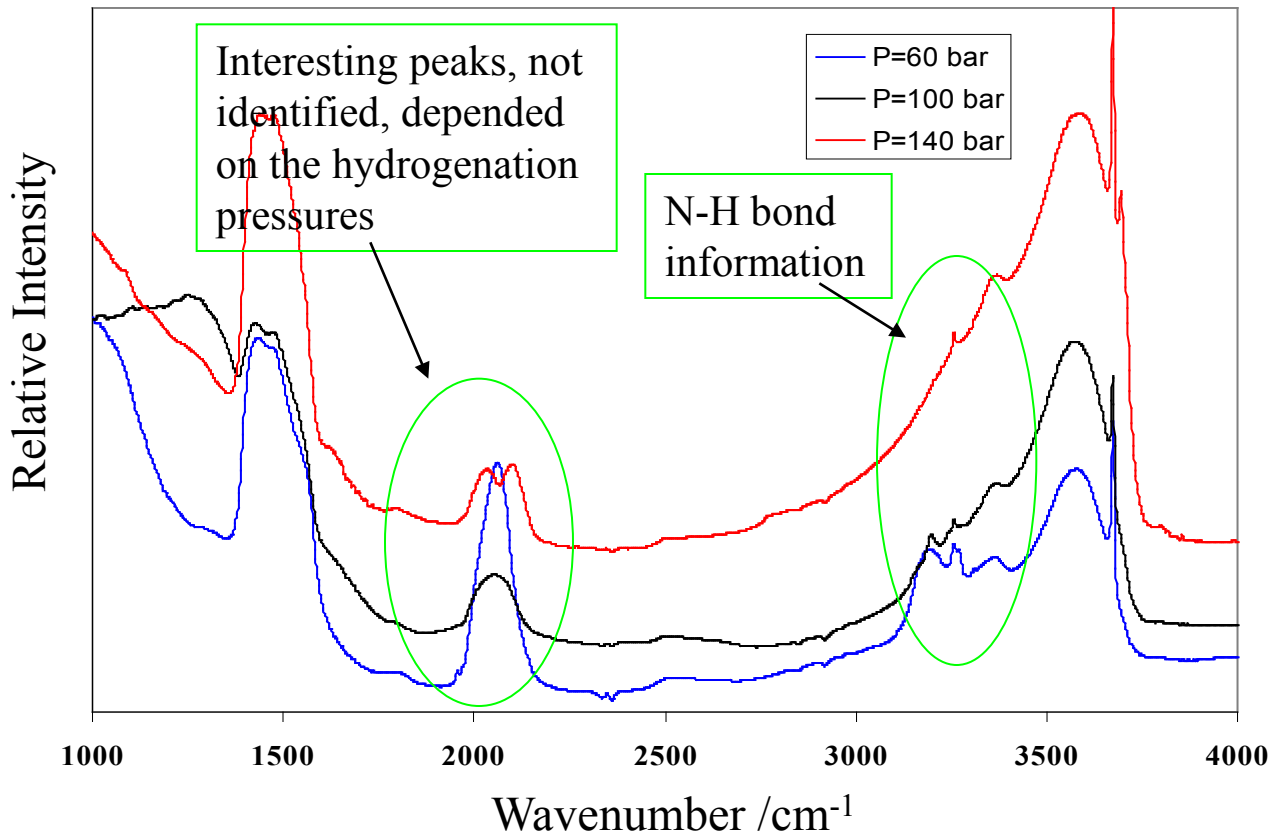
3). Dehydrogenation at 260°C with 2°C/min for 4h

Hydrogenation of LiMgN by PCT



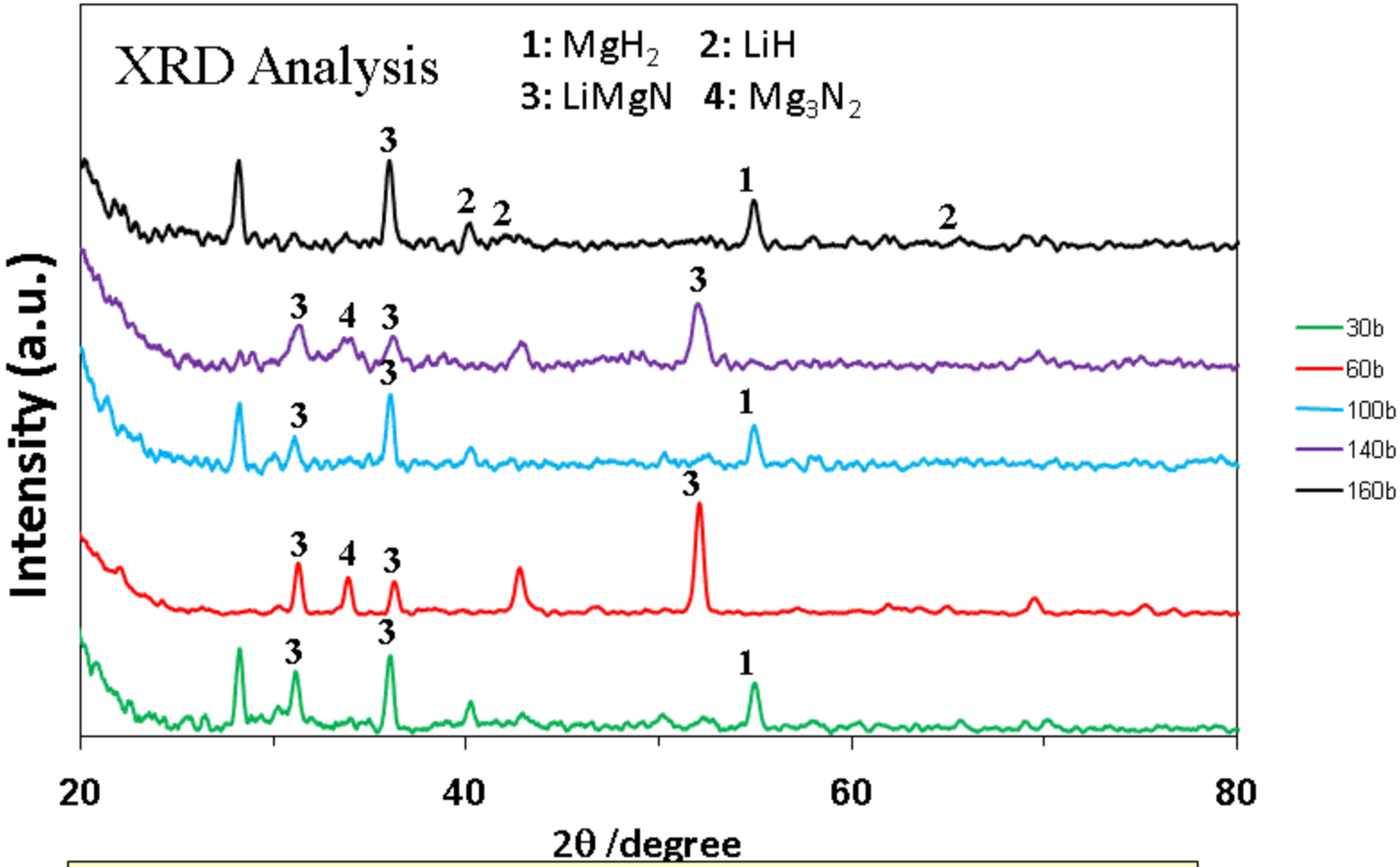
- *Hydrogenation of LiMgN is pressure sensitive*
- *>140 bar is required for full recharging*

Hydrogenation of LiMgN by PCT



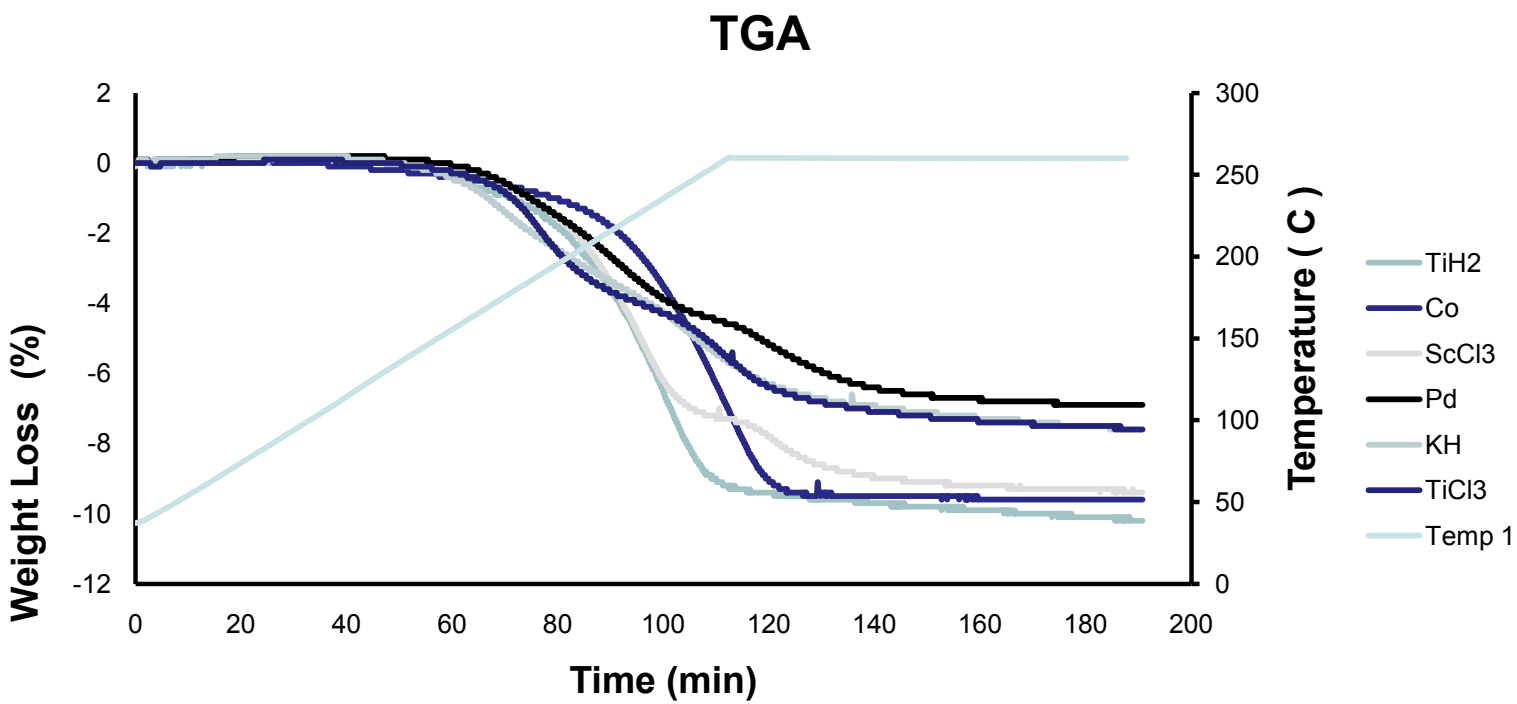
FTIR spectrum analysis consistent w/ TGA and XRD data.

Hydrogenation of LiMgN by PCT



XRD data consistent with TGA and XRD data.

Search for catalysts for LiMgN



A series of catalytic additives affect the kinetics of $LiNH_2$+MgH_2 reactions.

Search for catalysts for LiMgN

Catalyst Formula	Weight Loss (%)	Onset temperature	Onset Time (min)	Time needed for 90% conversion
TiH_2	6.9	104	38	~ 20
Co	9	76	24	~ 25
$ScCl_3$	9.6	93	33	~ 17
Pd	7.3	98	35	~ 22
KH (50% Paraffin)	7.9	80	30	~ 23
$TiCl_3$	6.2	110	40	~ 17

A series of catalytic additives affect the kinetics of $LiNH_2$+MgH_2 reactions.

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.
- ***First plateau pressure is very low (<<1 bar) reducing usable wt%.***
- ***Must reduce the reaction temperature. Efforts underway to use additives and nano engineering.***

Non-equilibrium Mg-Ti-H Material System

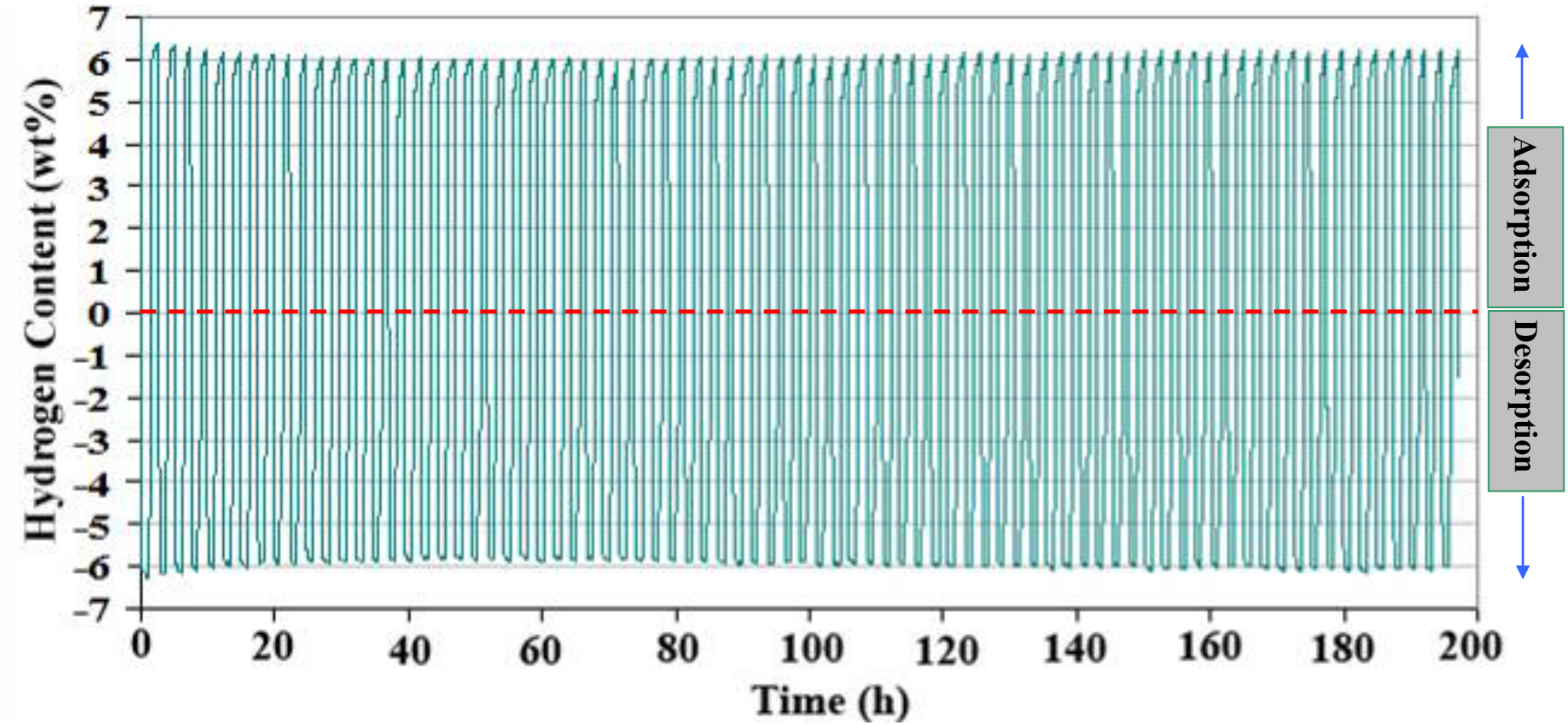
- Non-equilibrium Mg-Ti thin film systems have been demonstrated to have significant reversible hydrogen storage capacities[1,2].
- Can thin film material be replicated in powder or bulk form?
- Hydrogen storage of nano-sized MgH_2 with TiH_2 additives, synthesized by high energy high pressure ball milling process was studied.

[1] P. Vermeulen, R.A.H. Niessen, P.H.L. Notten, "Hydrogen storage in metastable MgyTi(1- y) thin films", Electrochem. Commun. 8 (2006) 27-32.

[2]. B. Clemens et al. MHCoE internal communication.

Technical Accomplishments and Progress

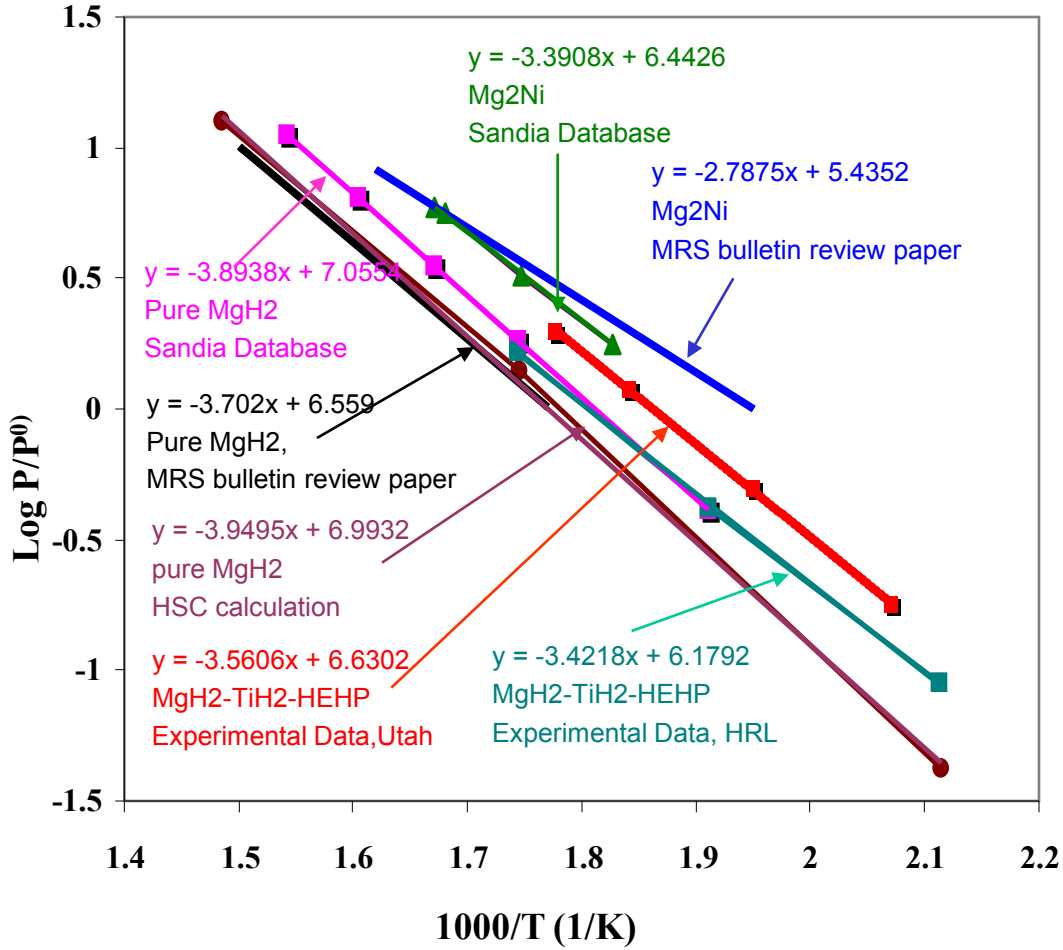
Hydrogen Storage of nano sized scale: MgH_2-8mol%TiH_2, particle size – 5-10 nm



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

Technical Accomplishments and Progress

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

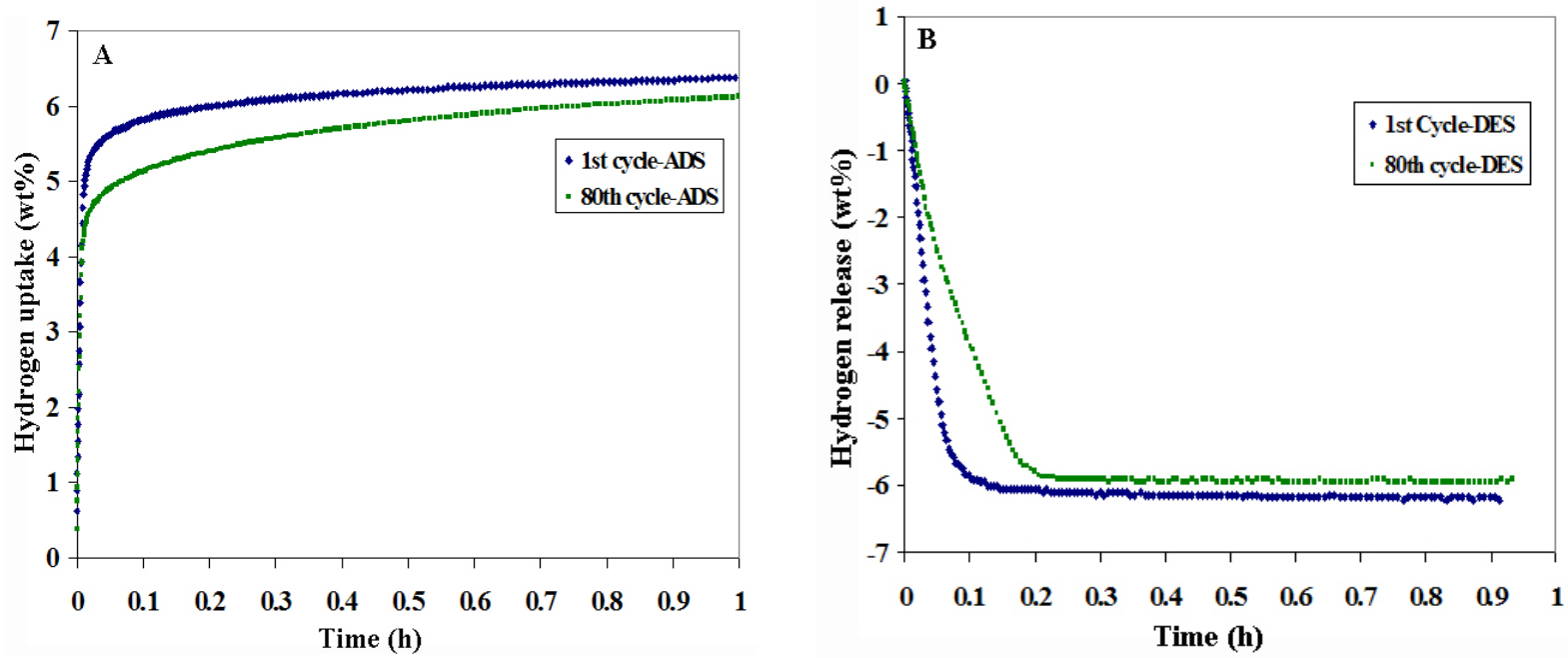


System	ΔH (kJ/K mol H_2)	ΔS (J/mol H_2)
Pure MgH_2, (Sandia Database)	-74.6	-135.1
Pure MgH_2, (MRS Bull. Sept. 2002)	-70.8	-125.6
Pure MgH_2, (HSC calculation)	-75.6	-133.9
MgH_2-TiH_2-HEHP (Exp. Data, U Utah)	-68.2	-126.9
MgH_2-TiH_2-HEHP (Exp. Data, HRL)	-65.5	-118.3
Mg_2Ni, (Sandia Database)	-64.9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

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.

Hydrogen Storage of nano sized scale: MgH_2-8mol%TiH_2

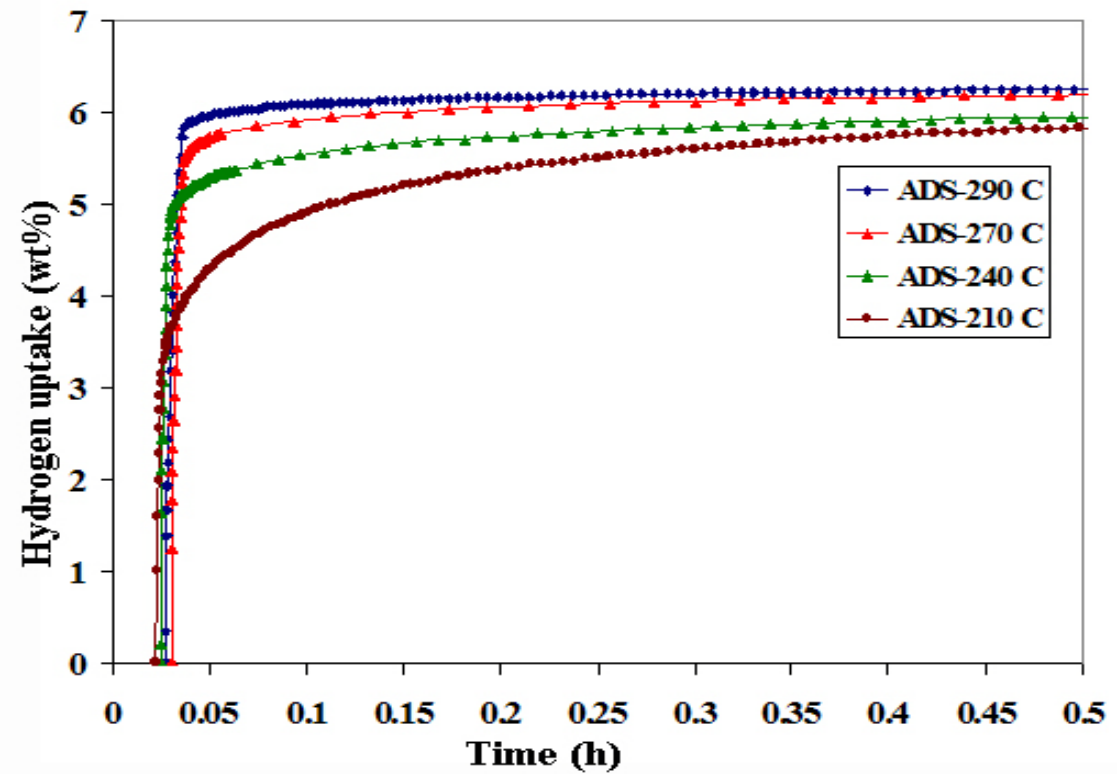
Comparison of hydrogen uptake and release at the 1st and 80th cycle



A) Isothermal dehydrogenation of the milled MgH_2/0.1TiH_2 under 1kPa hydrogen pressure at 300 °C during the 1st and 80th cyclic kinetics measurements, respectively; B) Isothermal hydrogenation of the dehydrogenated MgH_2/0.1TiH_2 under 2 MPa hydrogen pressure at 300 °C during the 1st and 80th cyclic measurements, respectively.

Hydrogen Storage of nano sized scale: MgH_2-8mol%TiH_2

Hydrogenation rate is high when the temperature is >210°C

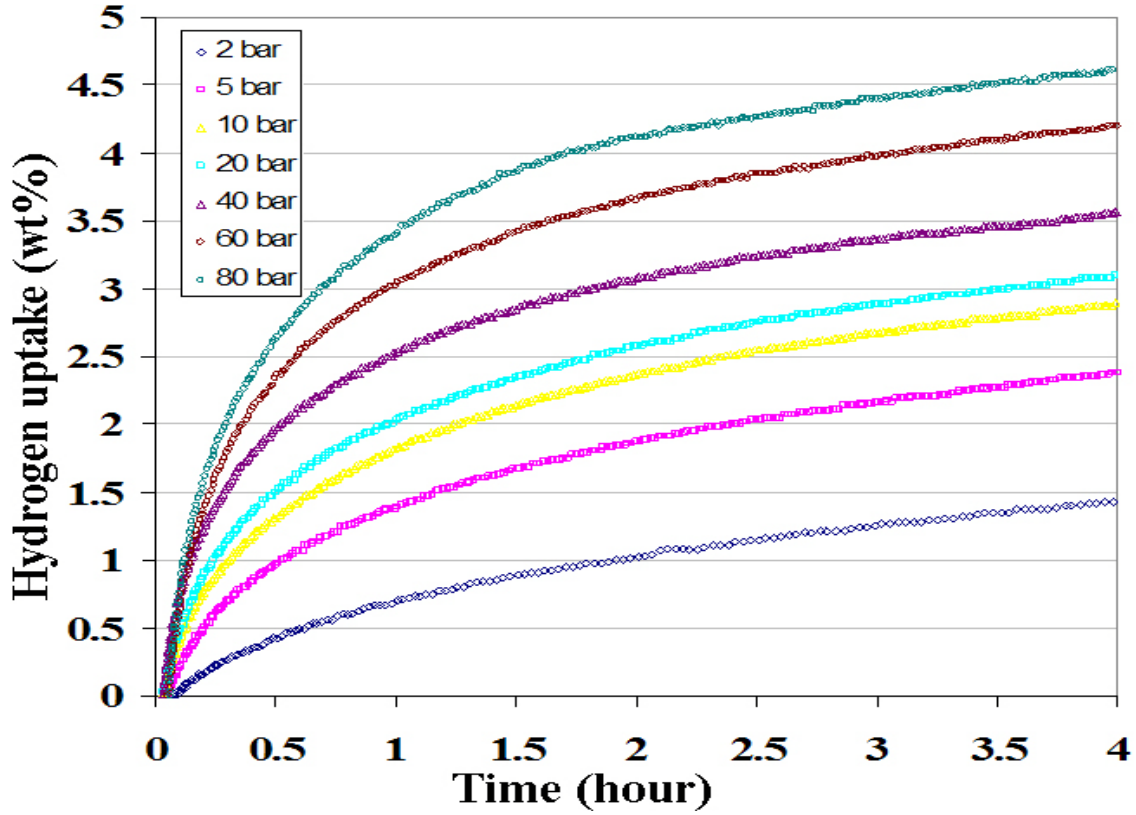


Isothermal hydrogenation of the milled Mg-Ti-H under 2MPa H_2 pressure at 210, 240, 270 and 290 °C, respectively.

Technical Accomplishments and Progress

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

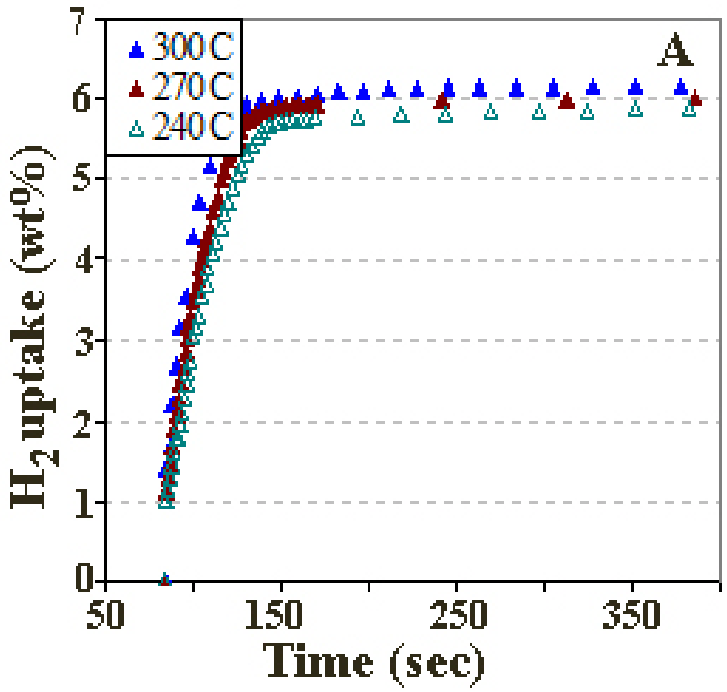
Significant H_2 uptake by Mg at room temperature

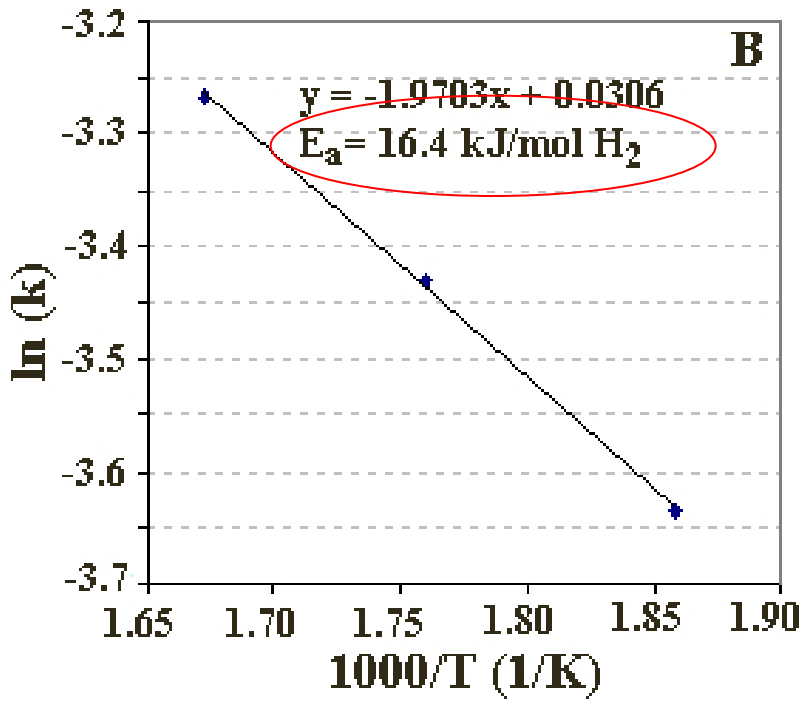


Isothermal hydrogenation profiles of the Mg-Ti-H system at room temperature.

Hydrogen Storage of nano sized scale: MgH_2-8mol%TiH_2

Activation for Hydrogenation Reaction



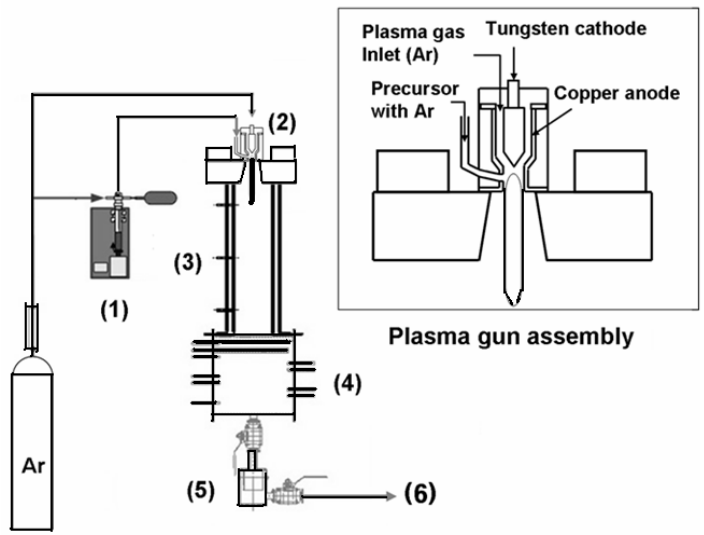


$$E_a = -RT \ln(k/k_0) \quad (1)$$

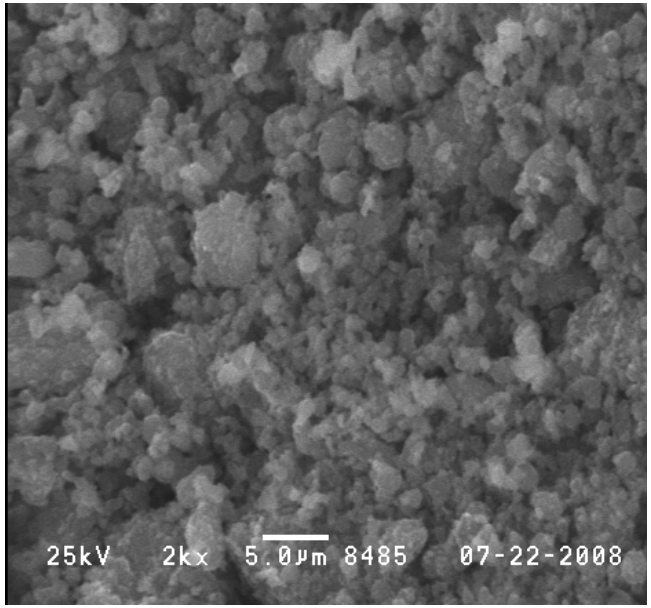
$$d\alpha/dt = k \cdot f(\alpha) \quad (2)$$

$$kt = -\ln(1-\alpha) \quad (3)$$

Synthesis of Ti-doped Mg nanopowder by a thermal plasma process

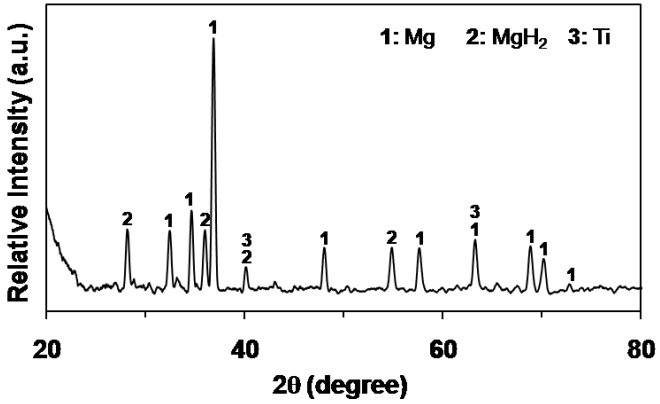


Schematic diagram of the plasma reactor system
(1) entrained-flow powder feeder for precursors (MgH_2+$TiCl_3$)
(2) plasma gun, (3) cylindrical reactor, (4) cooling chamber,
(5) powder collector, (6) offgas exhaust system.

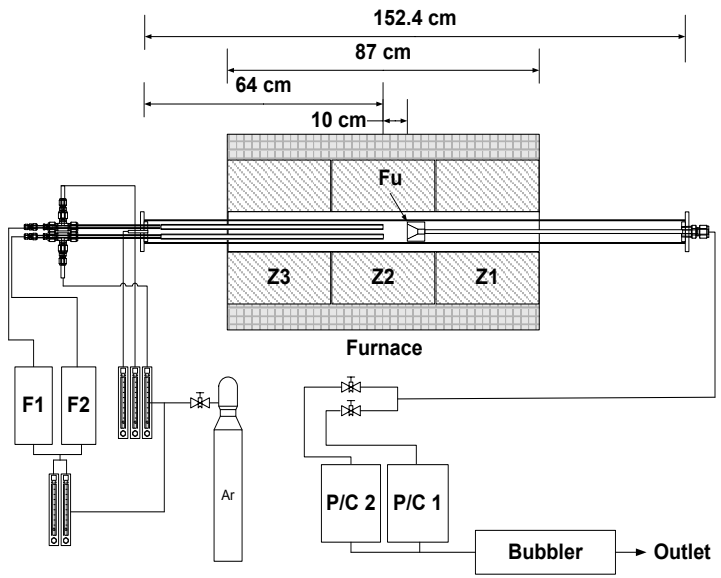


SEM micrograph of the product powder

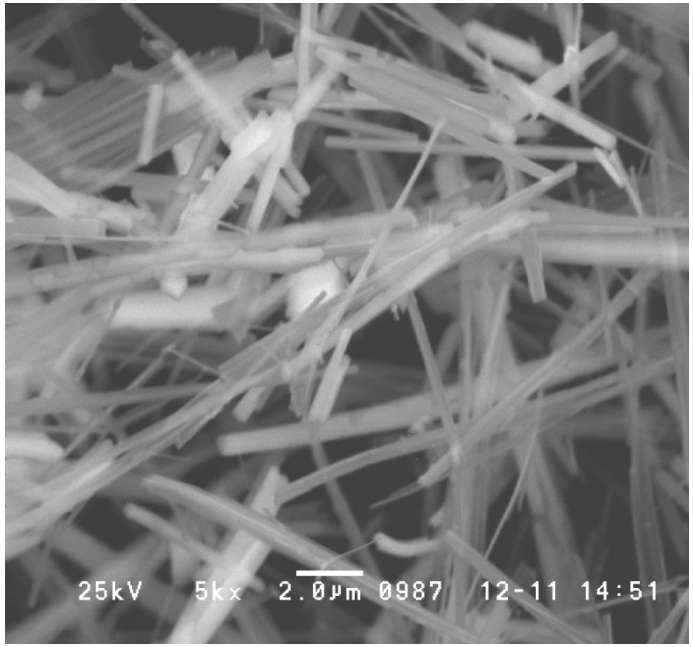
X-ray diffraction patterns of the product powder



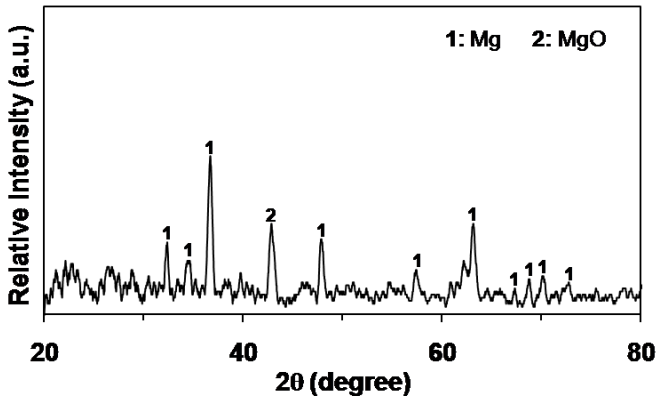
Synthesis of Mg nanowire by electric furnace



Schematic diagram of the furnace reactor system



SEM micrograph of the product Mg nanowire



X-ray diffraction patterns of the product Mg nanowire

Proposed Future Work

FY 2010 -2011:

- Search for LiMgN additives to lower H_2 release temperature
- Thermo and kinetic studies of LiMgN with additives cycling using PCT instrument
- Understand the effects of TiH_2 on MgH_2
- Continue to search new materials based on new concepts.

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.

Summary

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

Approach Exploit potentials of ternary nitrides and non-equilibrium alloys of Mg (Mg-Ti)

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.

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).