

Chemical Vapor Synthesis and Discovery of H₂ Storage Materials: Li-Al-Mg-N-H System



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Partners

JPL, GE, SNL, U Nevada Reno, ORNL, U Hawaii, U Pitt

Overview

Timeline

- Start – March 2005
- Finish – March 2010
- Percent complete – 40%

Budget

- Total project funding (Expected)
 - DOE share: \$645,438
 - Contractor share: \$165K
- Funding received: \$100K
- Funding for FY07: \$150K

Barriers

- Inadequate kinetic properties
- Reversible hydrogen content not sufficient
- Lack of robust synthesis methods

Partners

- JPL, GE, UNR, U Hawaii
- SNL, ORNL
- U Pitt, Intematix

Objectives

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

FY06-07

- Discover and study new materials based on lithium alanates destabilized by light metal amides
- Synthesize new materials using high-energy high-pressure reactive milling process
- Synthesis of nano precursor and hydride powders using Chemical Vapor Synthesis (CVS) process

Technical Approach

- Initiate new material concepts and conduct experimental investigations based on fundamental principles of inorganic chemistry and any new knowledge or prediction made by the theory group within the Center,
- Use TGA, XRD, and FTIR as basic screening tools for rapid materials discovery and use NMR, in-situ XRD, and PCT for in-depth characterizations and understanding,
- Use high-energy high-pressure (HEHP) reactive milling to synthesize nanosized and non-equilibrium materials,
- Use Chemical vapor synthesis (CVS) process to produce nanosized precursor powders (e.g. Al, Li, Mg, LiMgN, MgB₂),
- Use CVS approach to incorporate metals in carbon aerogels.

Accomplishments and Progress

Highlights

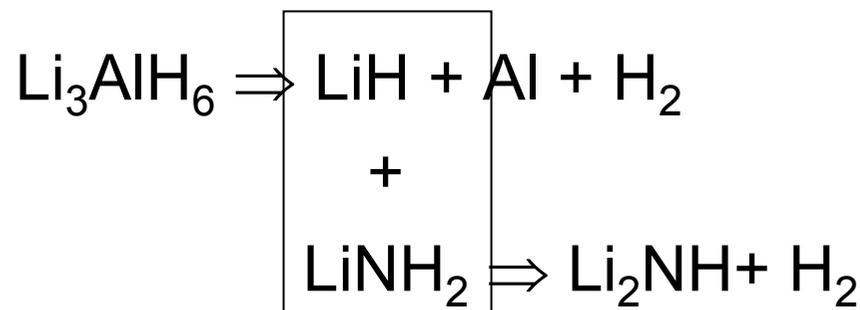
- I. Demonstrated the potential of a new Li-Al-Mg-N-H material system – 6% reversible capacity at <math><300^{\circ}\text{C}</math>
- II. Demonstrated the potential of LiMgN – a new candidate - for reversible H_2 storage
- III. Significant progress on the characterization of $\text{Li}_3\text{AlH}_6 + 3\text{LiNH}_2$ reaction
- IV. Made nanosized Al, Li, Mg, and other precursor powders using CVS process
- V. Made a number of potential candidate materials (e.g. Mg-Ti-H) using the high-energy high-pressure (HEHP) reactive milling process

Accomplishments and Progress

The concept: alanate destabilized by reacting with amides

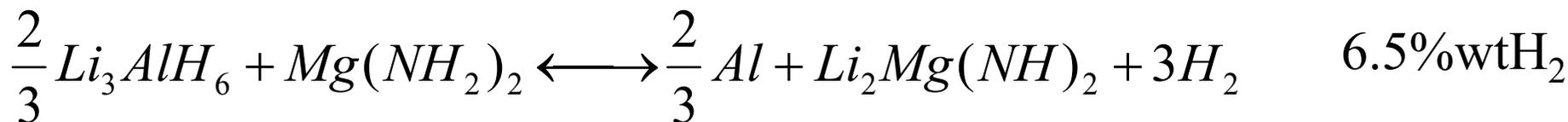
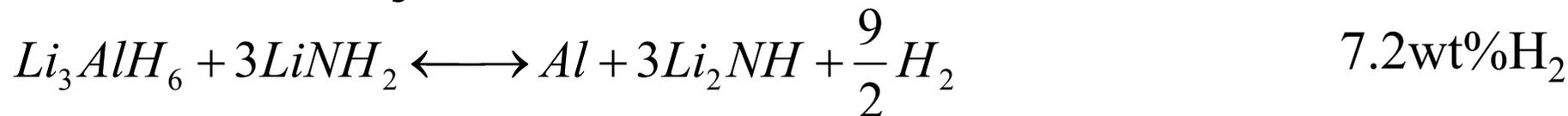
Knowledge from prior art:

- Li_3AlH_6 decompose to LiH and H_2
- LiH releases H_2 when reacting with amide



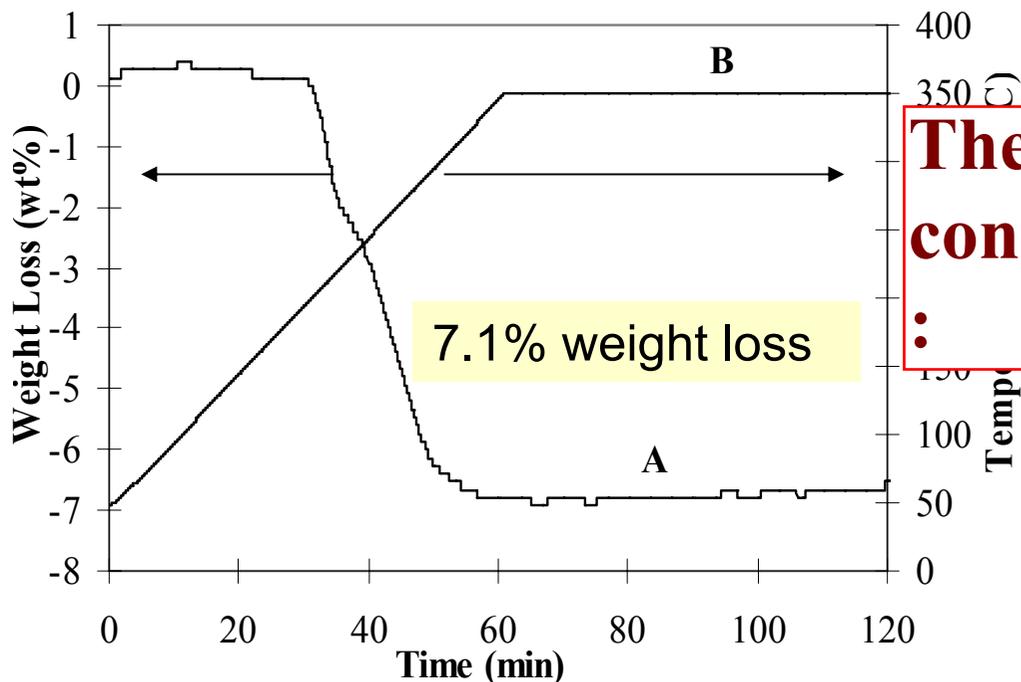
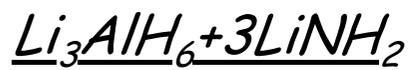
1. Chen, J.; et al. *J. Phys. Chem.* **2001**, 17, 1665
2. Chen, P.; et al. *Nature*, **2002**, 420,320
3. Luo, W.; *J. Alloys Compd.*, **2004**, 381, 284

Two reaction systems*:



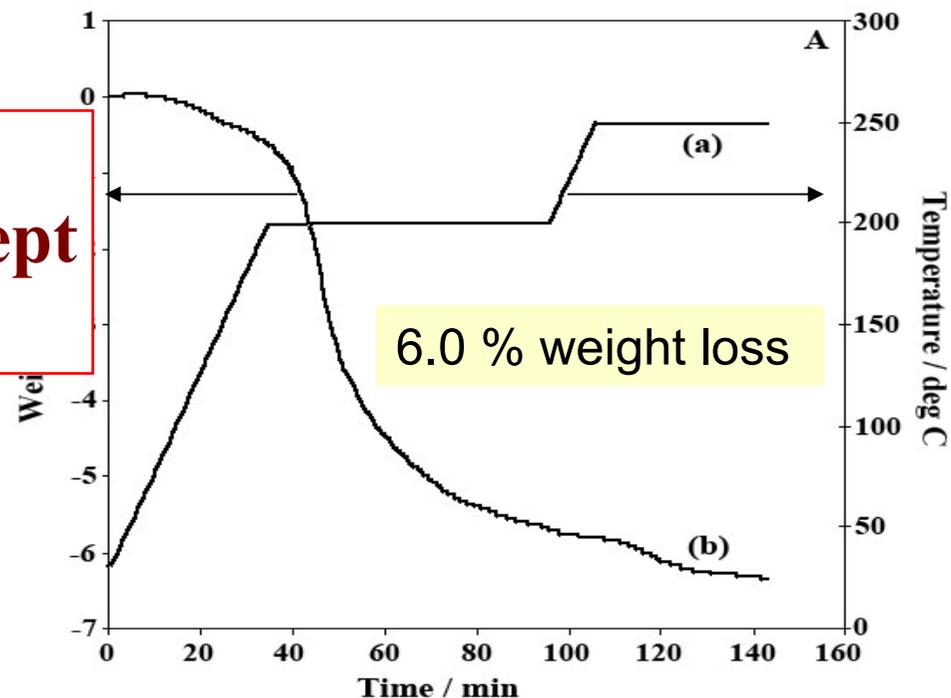
Accomplishments and Progress

Verification of the basic reaction hypothesis using TGA



The
concept

:



Ref. J. Lu, Z.Z. Fang, H.Y. Sohn *J. Phys. Chem. B*, 110(29), 14236-14239, 2006

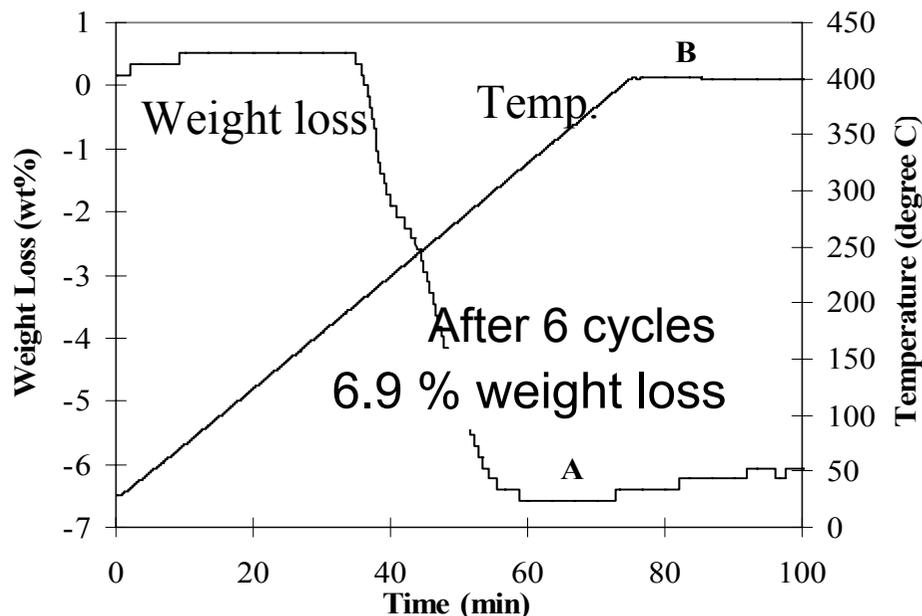
Ref. Lu, Fang, Sohn, Bowman, & Hwang, to be submitted.

Accomplishments and Progress

The reactions are **REVERSIBLE** after short cycles:

$\text{Li}_3\text{AlH}_6 + 3\text{LiNH}_2$ is reversible

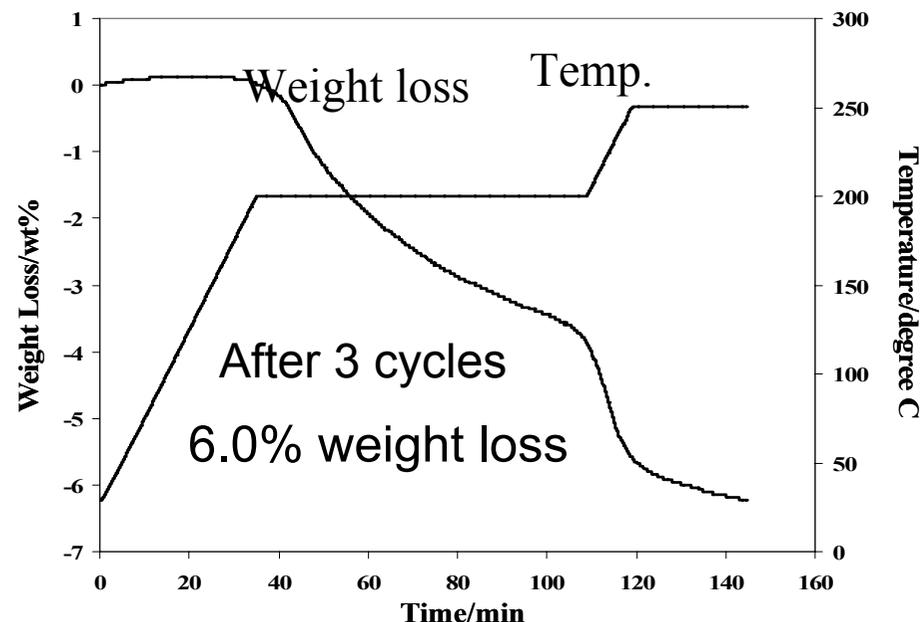
(Hydrogenation: 138 bar, 300°C)



Ref. J. Lu, Z.Z. Fang, H.Y. Sohn *J. Phys. Chem. B*, 110(29), 14236-14239, 2006

$2/3\text{Li}_3\text{AlH}_6 + \text{Mg}(\text{NH}_2)_2$ is reversible

(Hydrogenation: 172 bar, 300°C)



Ref. Lu, Fang, Sohn, Bowman, & Hwang, to be submitted.

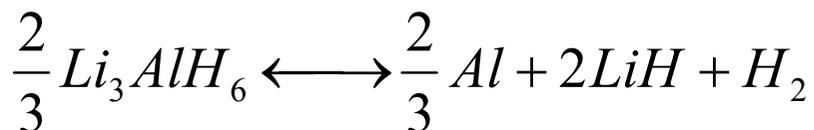
Note: Reversibility of Li_3AlH_6 is limited by itself. $\text{Mg}(\text{NH}_2)_2$ does not release hydrogen by itself. Combining the two allows dehydrogenation.

Understanding the reaction mechanisms:

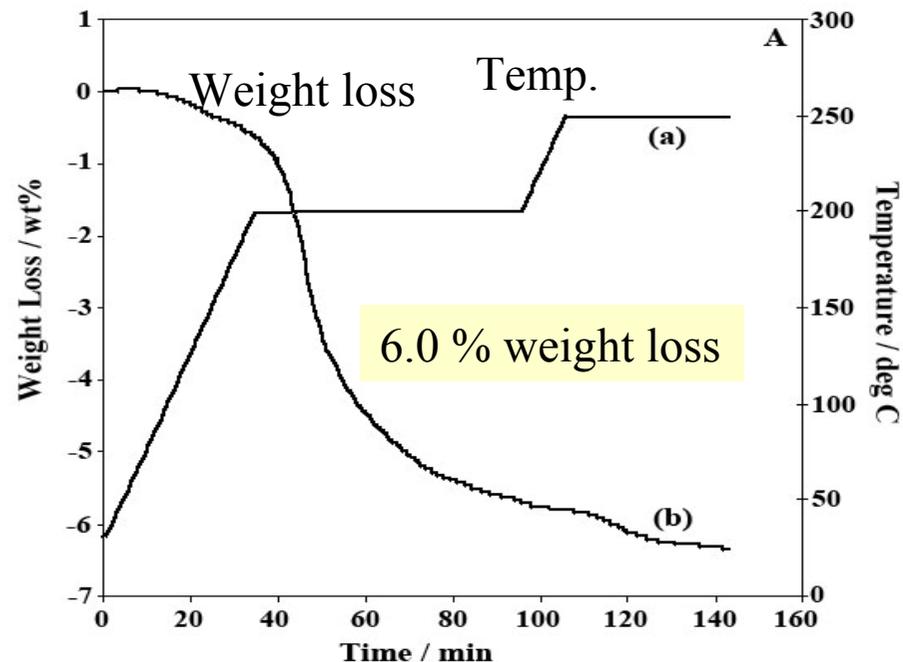
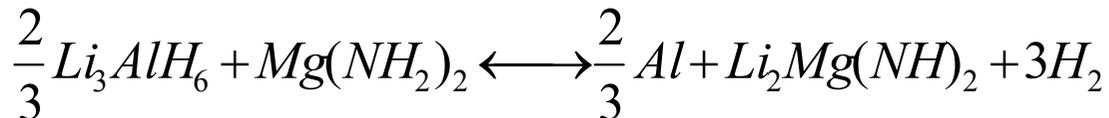
Hypothesis on the reaction pathways:

e.g. $\underline{\underline{2/3Li_3AlH_6 + Mg(NH_2)_2}}$

Two-step dehydrogenation:



Overall reaction



Characterizations using: XRD, in-situ XRD (GE), NMR (JPL), FTIR, PCT (SNL, Hy-Energy), Cycling (UNR)

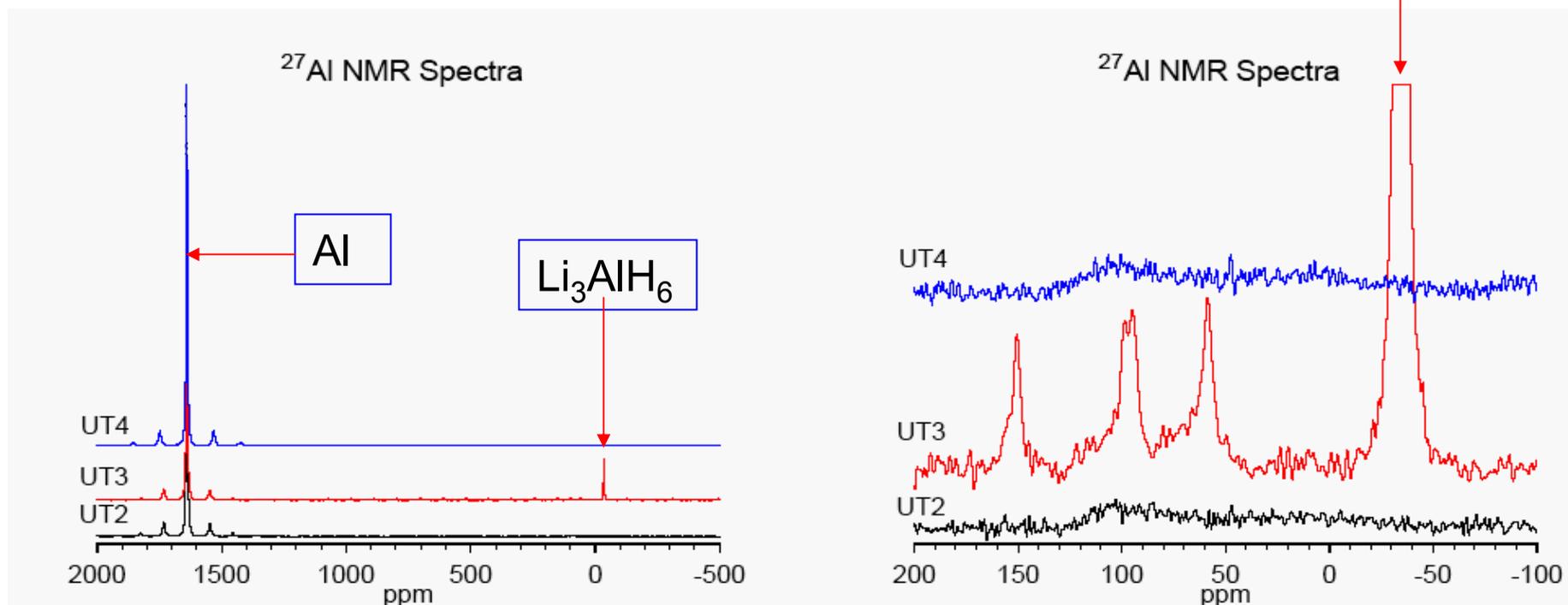
Study of the reaction pathways using NMR

UT1: Raw material: Al, LiNH₂, MgH₂, catalyst, (Not shown here)

UT2: Sample UT1 after dehydrogenation

UT3: Sample UT2 after rehydrogenation

UT4: Sample UT3 after dehydrogenation

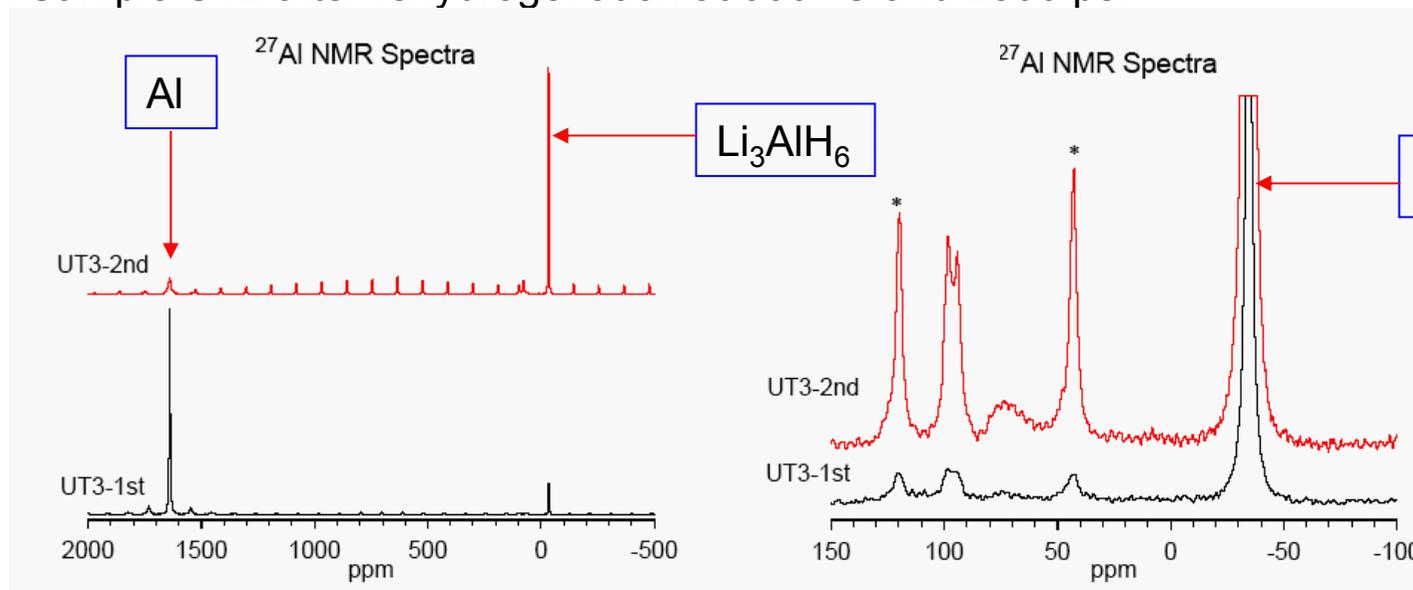


➤ Li₃AlH₆ has been regenerated (UT3)

Study of the reaction pathways using NMR

UT3-1st: Sample UT2 after rehydrogenation at 300 °C and 2000 psi

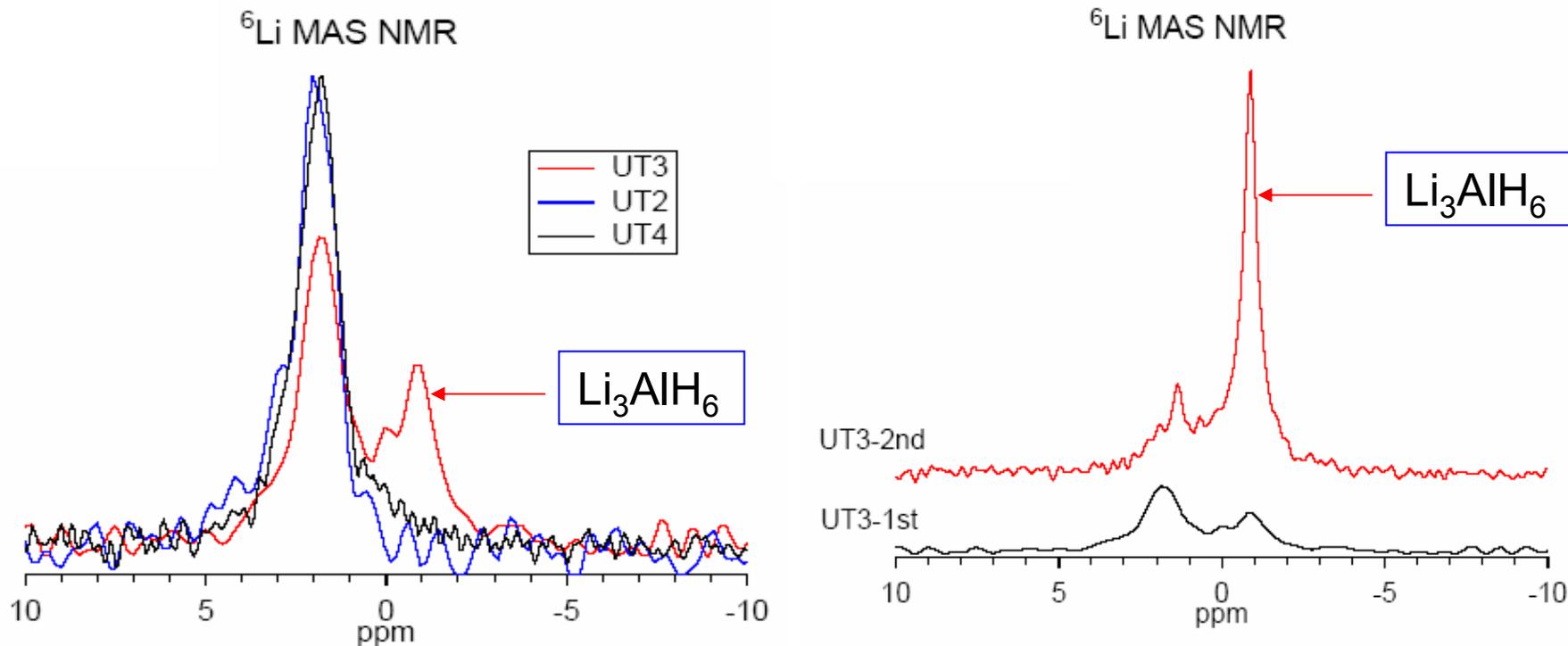
UT3-2nd: Sample UT2 after rehydrogenation at 300 °C and 2500 psi



Components	Chemical shift (ppm)	Rel. Quantity (%)
Al(M)	1640	5.2
AlH ₄ ⁻	98.8	8.1
Al ₂ O ₃	74.1	3.8
AlH ₆ ⁻³	-34.6	82.9

➤ Conversion to Li₃AlH₆ is more than 80% based on NMR results.

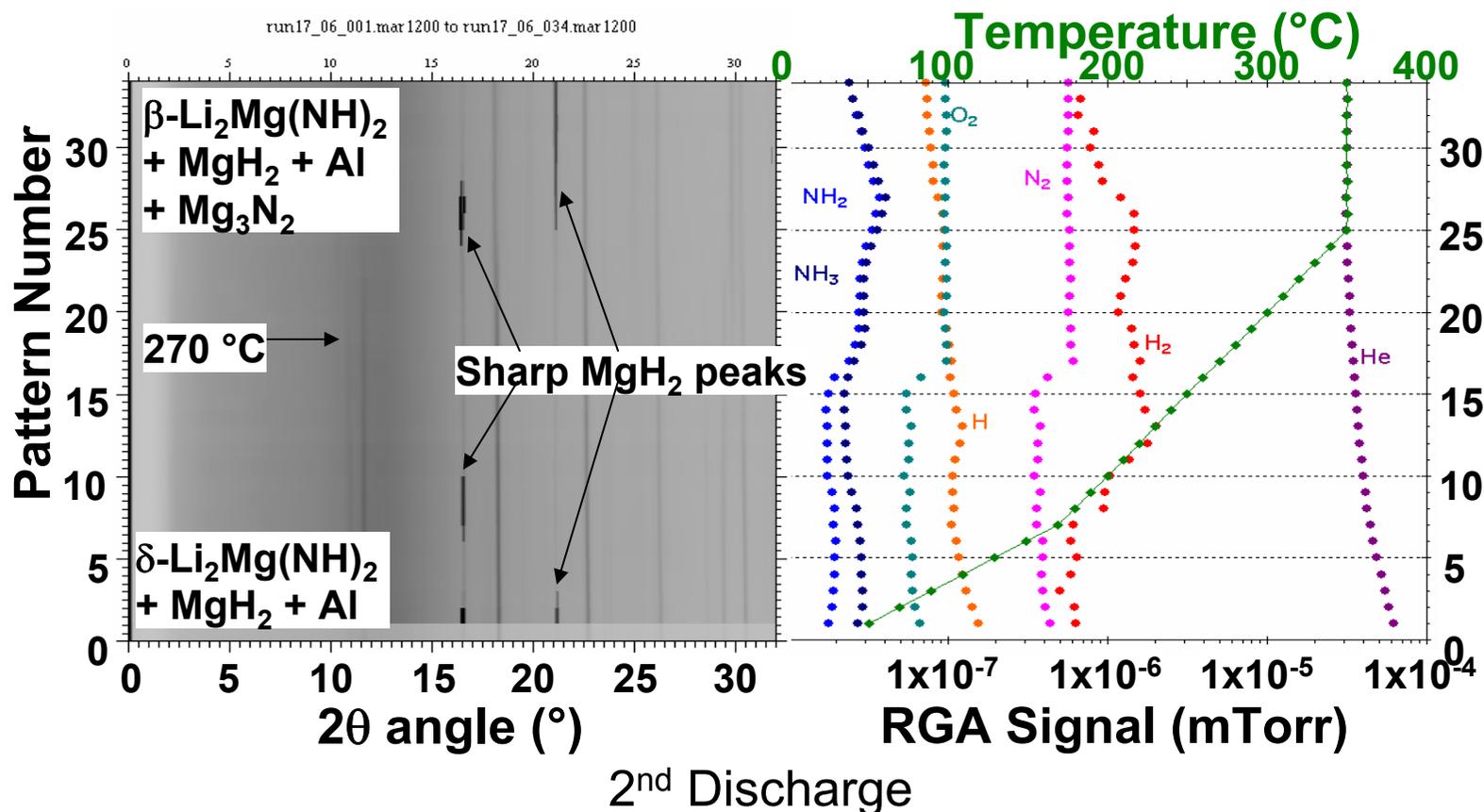
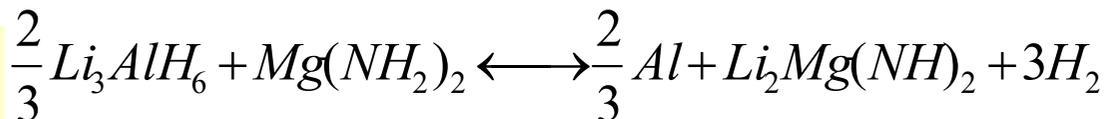
Study of the reaction pathways using NMR



- Li is mostly in Li_3AlH_6 form in the UT-3 sample (hydrogenated status) with small portion in LiNH_2 , which confirms the regeneration of Li_3AlH_6 .

Investigating the issue of ammonia generation

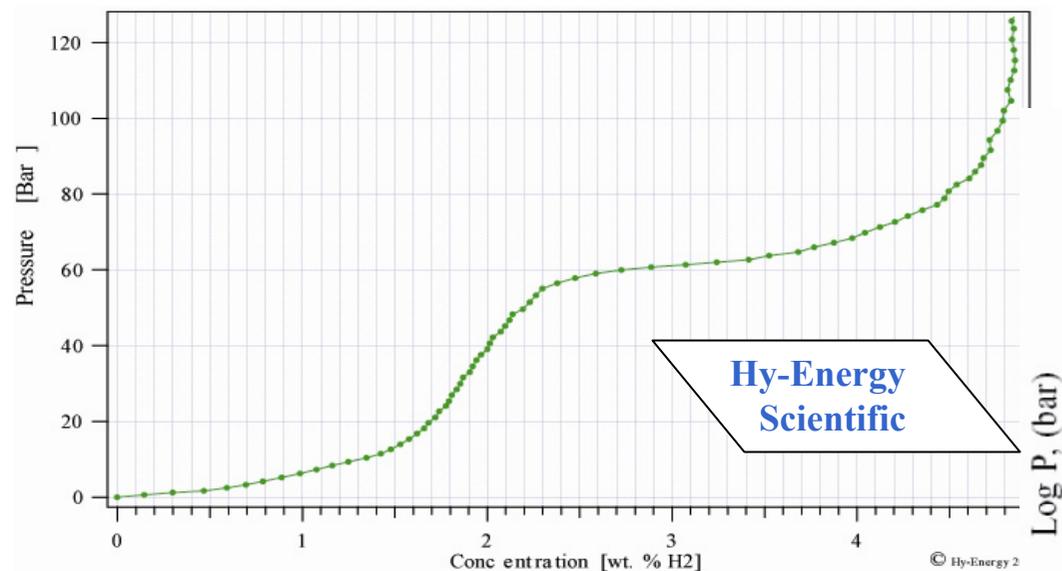
In-situ XRD characterization



The generation of ammonia during this reaction is minimum. Exact content of NH₃ in ppm is yet TBD, pending funding for equipment.

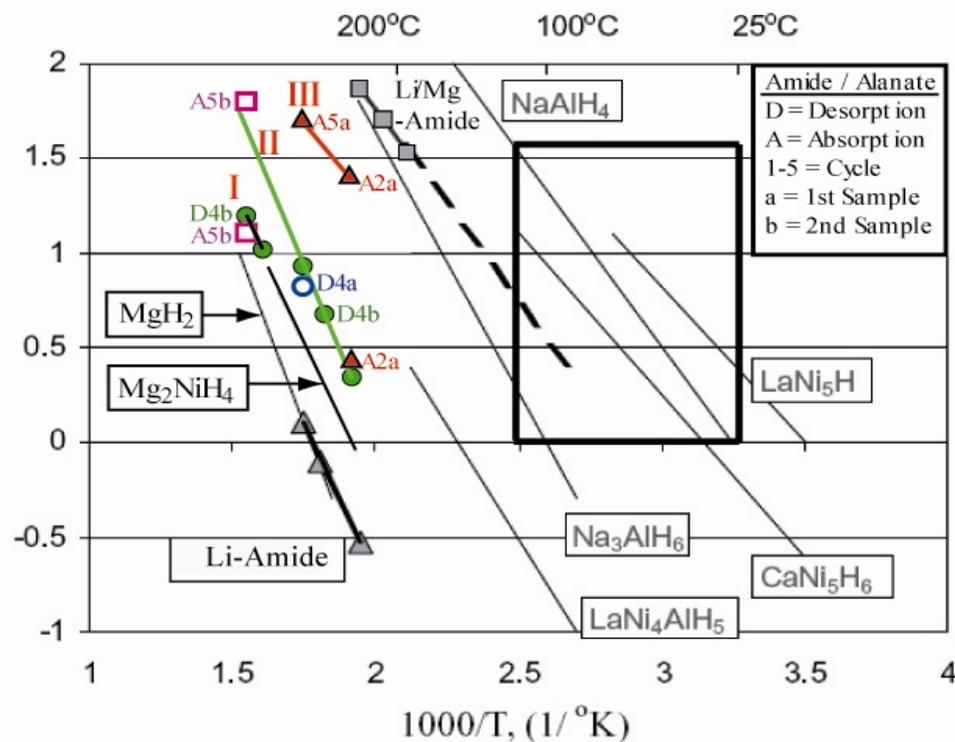
Accomplishments and Progress

Thermodynamic and kinetic properties – PCT characterization:



Two plateau pressures at ~1 and 60 bar respectively.

van't Hoff plot shows the material is less stable than MgH_2 .



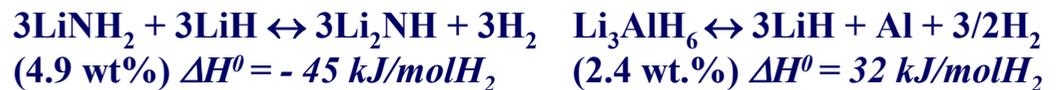
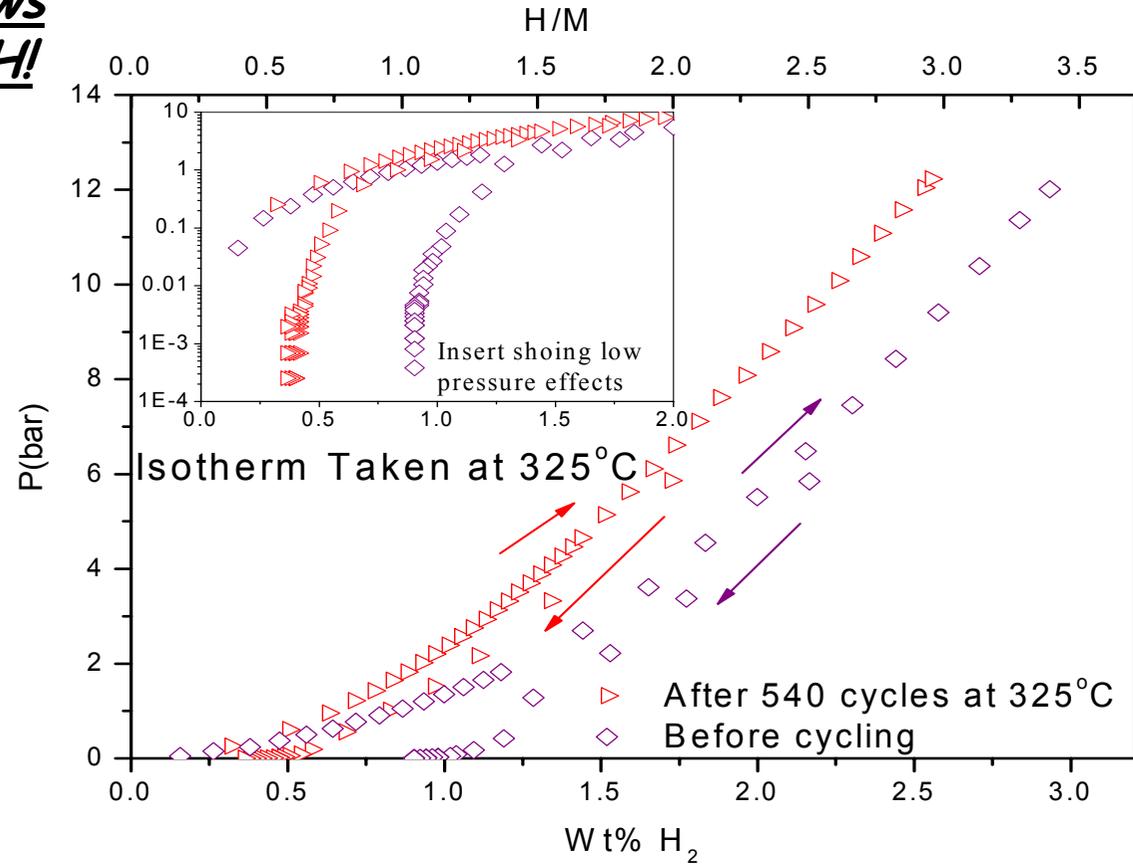


Accomplishments and Progress

Cycling of $\text{Li}_3\text{AlH}_6 + 3\text{LiNH}_2$ in O_2 partial pressure:

Mixture of alanate with amides shows better property than LiNH_2 with LiH !

- Isotherm taken before and after 540 cycles shows a small loss in capacity $\sim 0.6\%$ hydrogen using 100 ppm O_2 in UHP hydrogen.
- Therefore, ammonia release is a negligible problem for this materials under the conditions of this study.
- Note that cycling $\text{Li}_2\text{NH} \leftrightarrow \text{LiNH}_2$ in Industrial hydrogen (with no Li Alanate) showed $\sim 2.6\%$ hydrogen loss after 500 cycles under similar cycling conditions*



*See UNR poster for details.

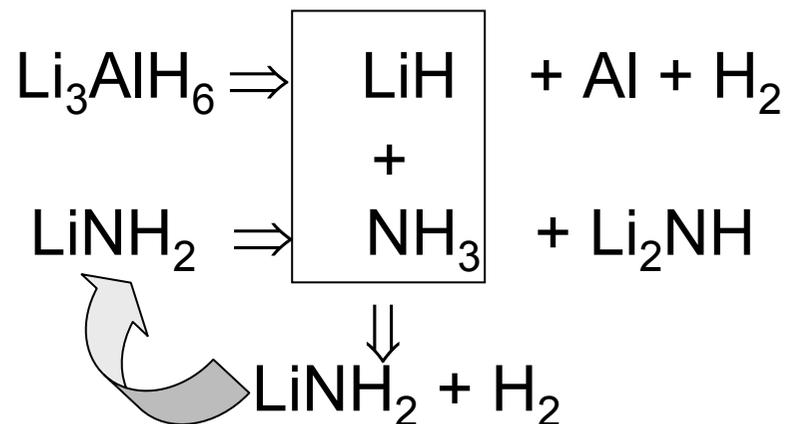
Accomplishments and Progress

Role of LiH produced during the **alanate+amide** reaction

- Reversibility of lithium alanate is limited, partially due to the poisoning of LiH by H₂O,

Poisoning for OH monolayer: $\text{LiH} + \text{H}_2\text{O} \rightarrow \text{LiOH} + \text{H}_2 + 1.30\text{eV}/\text{H}_2\text{O}^$*

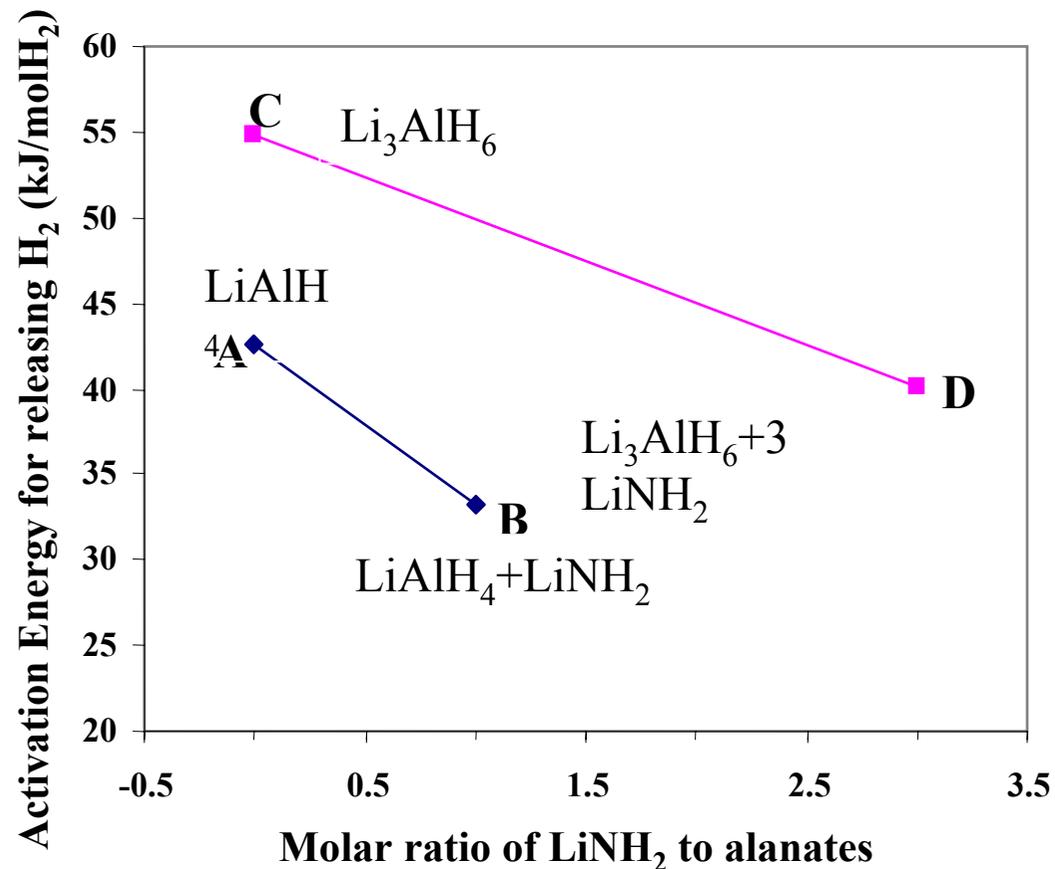
- Amide alone, by itself, does not release hydrogen, instead, it release NH₃, unless a catalytic agent is present reacting / decomposing NH₃,
- The combination of alanates with amides allows fresh and active LiH to react with NH₃, releasing hydrogen from both LiH and amide.



Accomplishments and Progress

Lithium amide destabilizes lithium alanate

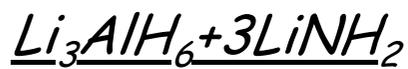
The activation energy for lithium alanates (LiAlH_4 or Li_3AlH_6) to release hydrogen are lower when they are reacted with lithium amide. That is, in effect, lithium amide destabilized lithium alanates.



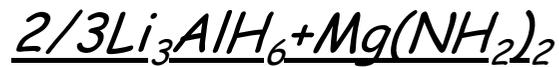
$$\log \beta = -\frac{0.457 E_a}{RT} - 2.315 - \log \left(\frac{R}{AE_a} \int_0^a \frac{d\alpha}{f(\alpha)} \right)$$

Accomplishments and Progress

Summary of Li-Al-Mg-N-H Systems



Reversible H ₂ capacity:	~ 5~7wt%
Dehydrogenation T:	<300°C
Dehydrogenation kinetics:	TBD
Hydrogenation kinetics:	TBD
Plateau pressure:	1 & 60 bar



Reversible H ₂ capacity:	~6 wt%
Dehydrogenation T:	<250°C
Dehydrogenation kinetics:	TBD
Hydrogenation kinetics:	TBD
Plateau pressure:	TBD

Using the reactions of alanates and amides is a promising approach for discovering new candidate materials for reversible hydrogen storage.

Accomplishments and Progress

Comparing Li-Al-Mg-N-H to other candidate materials



All things considered, alanate/amide combinations are still some of the more promising materials discovered to date.

	Selected reversible hydrogen storage material systems						
Properties	MgH ₂ / Ni ^{nano}	NaAlH ₄	2LiH/ LiNH ₂	MgH ₂ / 2LiNH ₂	LiBH ₄ / 1/2MgH ₂	Li ₃ AlH ₆ / 3LiNH ₂	2/3Li ₃ AlH ₆ / Mg(NH ₂) ₂
Theoretical reversible wt% H ₂	7.6	6.5	10.4	5.6	11.4	7.3	6.5
Demonstrated reversible wt% H ₂	6.5	5.5~6.0	9.3	5.2	8-10	7.1	6.1
Desorp. Temp (°C)	150-250	150~250	200~450 vacuum	100~250	315-400	160-300	100~240
Adsorp. Temp (°C)	150	180	170-255	100~200	315-400	200-300	200-300
Isothermal Plateau Pressure	<1 (250)	~10 (180) ~130 (180)	0.2 (230°C) 1.0 (255°C)	46 (200 °C)	1 (255)	1 (255°C) 60 (375°C)	TBD
Kinetics	Slow	Good	Good	Good	Very Slow	TBD	TBD

Another new candidate material - LiMgN

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



- Theoretical 8.2% hydrogen
- No experimental verification
- Reversibility?

Note: By this reaction all the hydrogen in MgH₂ and LiNH₂ can be released. It bypasses the formation of imide (Li₂Mg(NH)₂)** which forms when the molar ratio of MgH₂: LiNH₂ is 2:1. Imide is too stable to be useful.

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

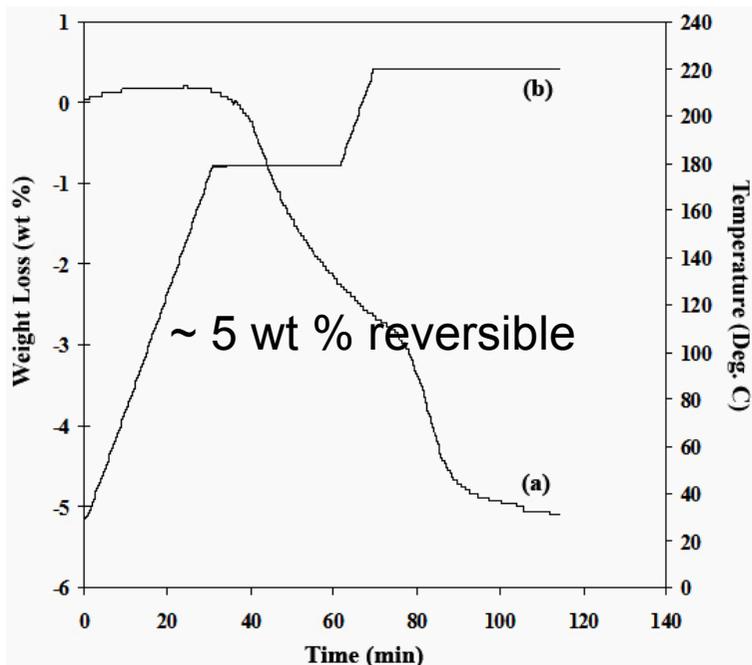
** . Luo, W.; *J. Alloys Compd.*, **2004**, 381, 284

Accomplishments and Progress

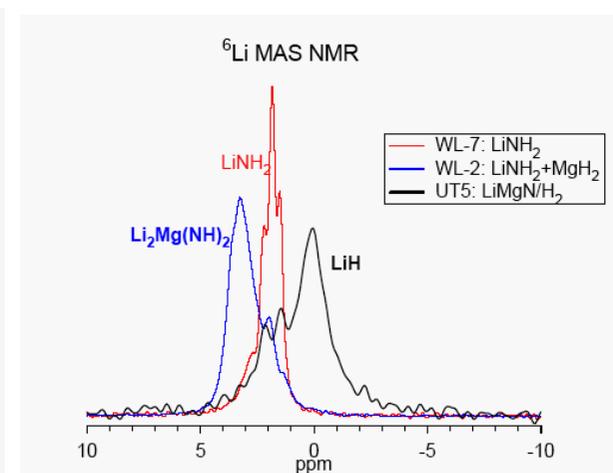
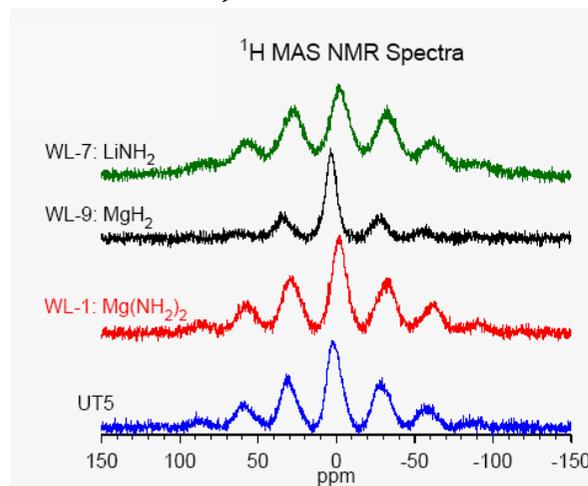
The potential of binary nitride - LiMgN

Hydrogenation of LiMgN: 138 bar, 240°C

TGA of hydrogenated LiMgN

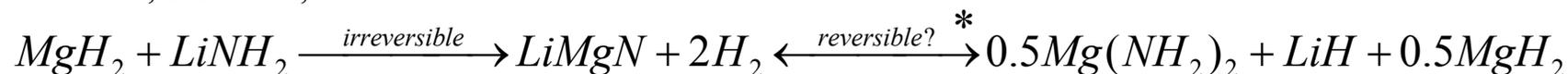


Ref. J. Lu, Z.Z. Fang, H.Y. Sohn, *Chem. Materials*, submitted, 2007



UT5: LiMgN after hydrogenation at 138 bar and 240°C

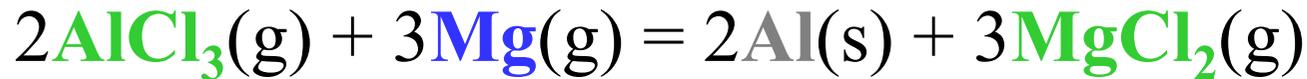
- Hydrogenated products are complex
- Hydrogenation mechanisms are unclear



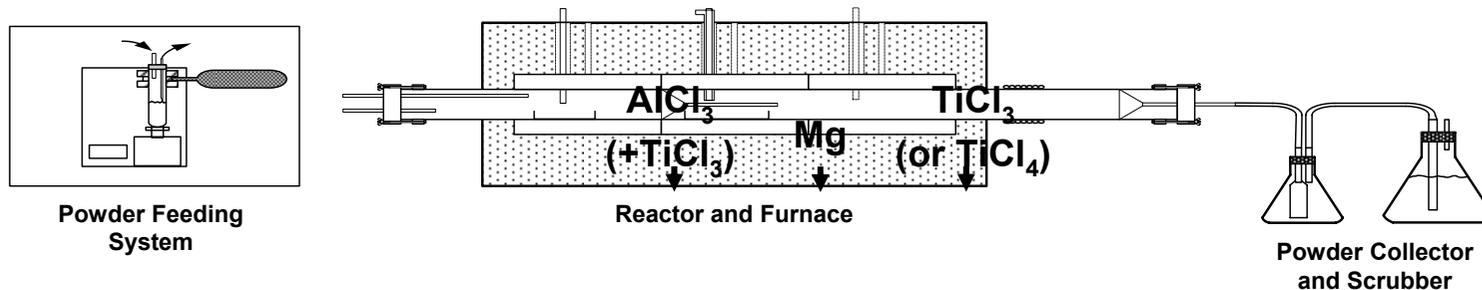
Chemical vapor synthesis (CVS)

Chemistry principles

- Aluminum nanopowder:



Experimental Set-up



Nano powders produced to date:

Al, Li, Li/Mg, Li₃N, LiMgN, ...

Precursors for metal hydrides – support the Center partners.

Future Work: FY07-08

Materials Discovery and Development

- Continue comprehensive investigation of alanate reactions with amides and Li-Al-Mg-N-H materials including LiMgN
- Characterize hydrogen storage properties including thermodynamic isothermal plateau pressures and kinetics,
- Quantify ammonia generation and develop means to mitigate NH₃ generation

CVS and High Energy High Pressure Reactive Milling

- CVS synthesis of Li/Mg powders as precursor for metal hydride
- CVS synthesis of MgB₂ to support center partners
- HEHP reactive milling synthesis of non-equilibrium metal hydrides based on Mg, Ti, Li, etc.

Summary

- ❑ Initiated and led the research effort on reactions of alanate with amides – MHCoE Group C lead
- ❑ Demonstrated the potential of the Li_3AlH_6 when reacting with LiNH_2 or $\text{Mg}(\text{NH}_2)_2$
- ❑ Demonstrated possibility of LiMgN – a new candidate material for hydrogen storage.
- ❑ Nanosized metal powders including Li, Li/Mg, and Al were produced via chemical vapor synthesis (CVS) process.
- ❑ Material discovery and synthesis by high energy high pressure reactive milling is on-going