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

METAL HYDRIDE CENTER OF EXCELLENCE

THE UNIVERSITY OF UTAH

Z. Zak Fang and H.Y. Sohn
University of Utah

May 15-18, 2007

Partners

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

Project ID #: ST21

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, MgB_2),
- 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 <300°C

II. Demonstrated the potential of LiMgN – a new candidate - for reversible H_2 storage

III. Significant progress on the characterization of Li_3AlH_6+3$LiNH_2$ reaction

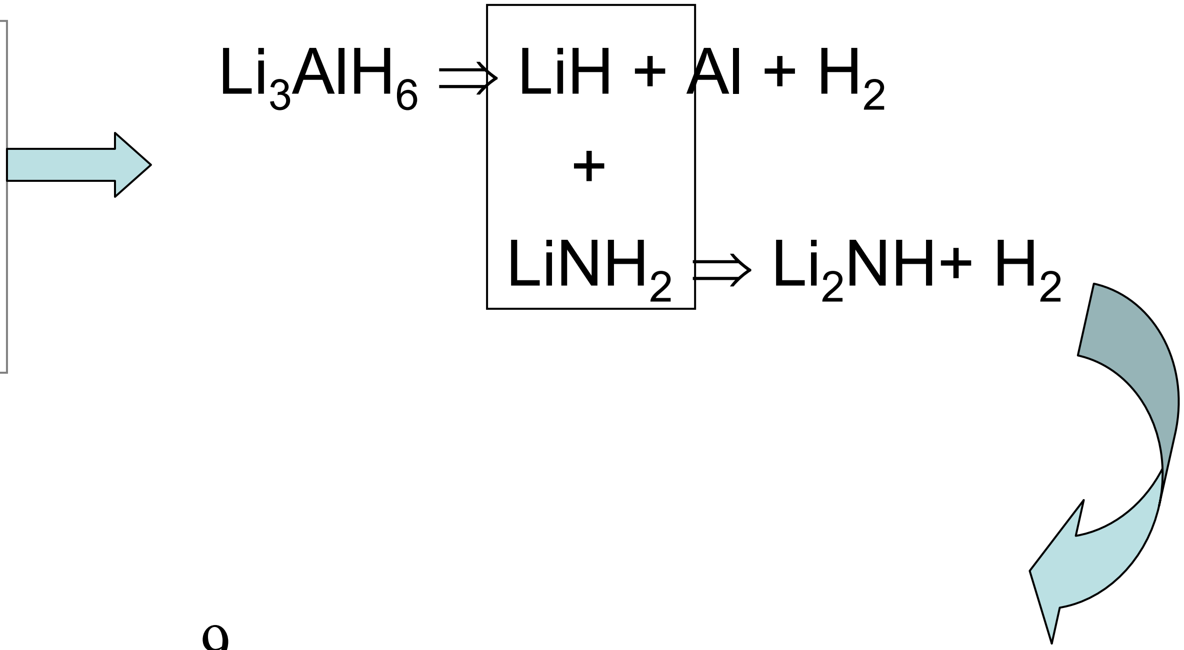
IV. Made nanosized Al, Li, Mg, and other precursor powders using CVS process

V. Made a number of potential candidate materials (e.g. Mg-Ti-H) using the high-energy high-pressure (HEHP) reactive milling process

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



$Li_3AlH_6 \Rightarrow LiH + Al + H_2$

$+$

$LiNH_2 \Rightarrow Li_2NH + H_2$

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:*

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

7.2wt%H_2

$$\frac{2}{3}Li_3AlH_6 + Mg(NH_2)_2 \longleftrightarrow \frac{2}{3}Al + Li_2Mg(NH)_2 + 3H_2$$

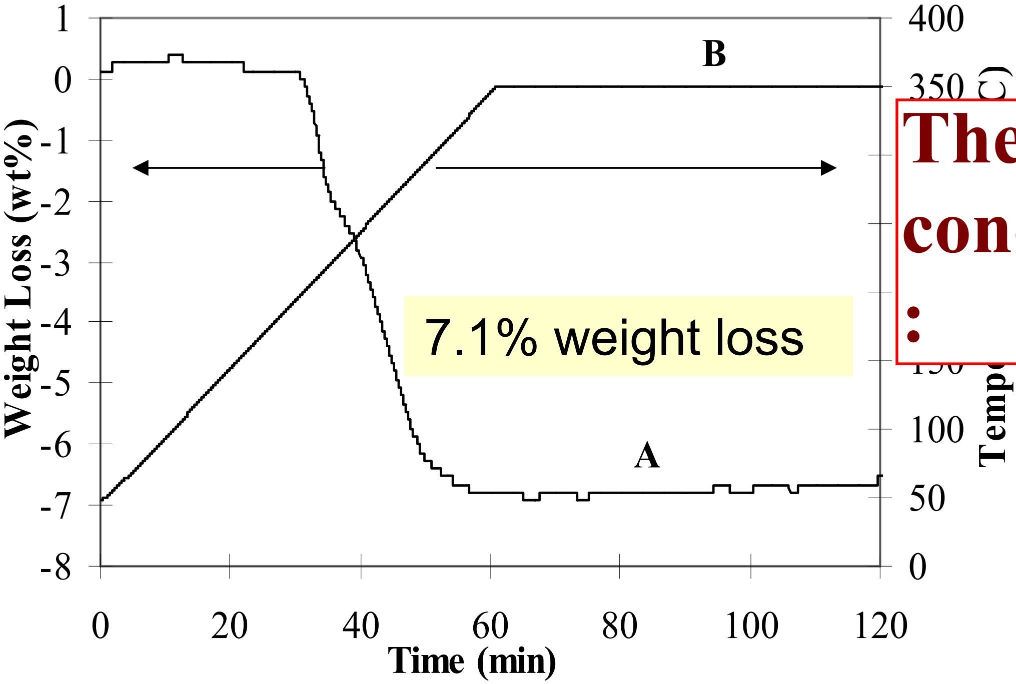
6.5%wtH_2

*US Patent pending

Accomplishments and Progress

Verification of the basic reaction hypothesis using TGA

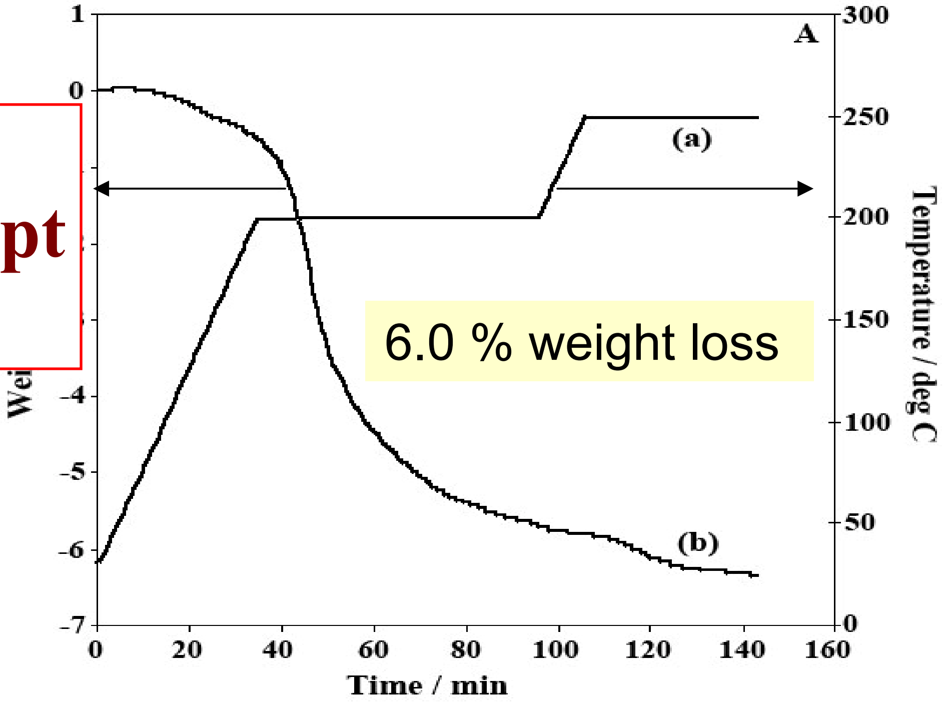
Li_3AlH_6+$3LiNH_2$



7.1% weight loss

The concept:

$2/3Li_3AlH_6$+$Mg(NH_2)_2$



6.0 % weight loss

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

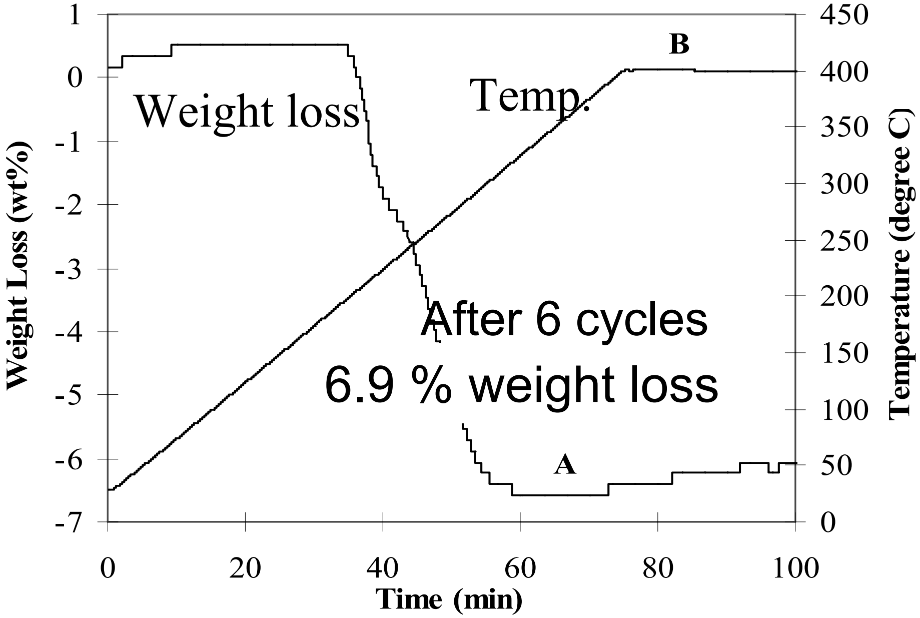
Ref. Lu, Fang, Sohn, Bowman, & Hwang, to be submitted.

Accomplishments and Progress

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

$Li_3AlH_6+3LiNH_2$ is reversible

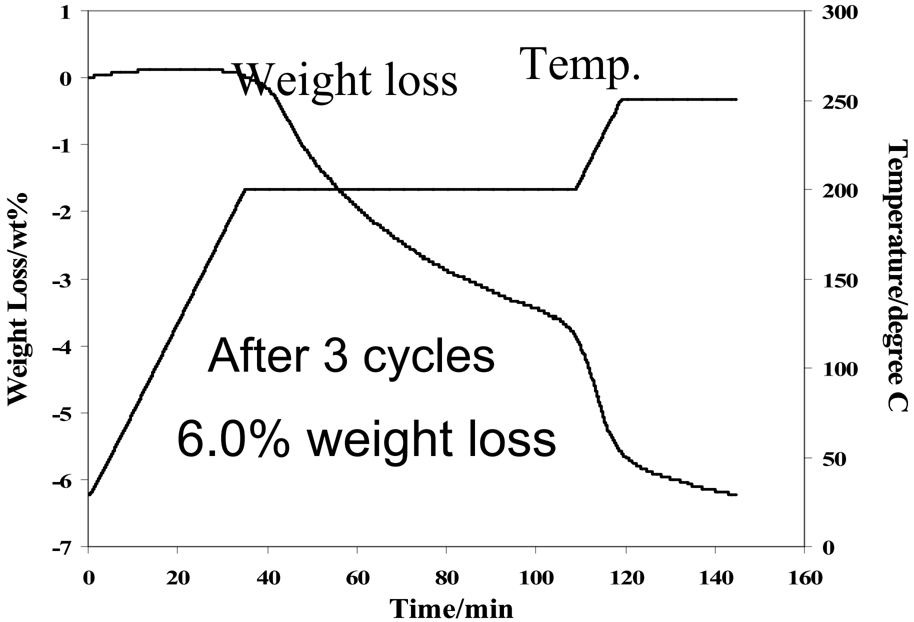
(Hydrogenation: 138 bar, 300°C)



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

$2/3Li_3AlH_6+Mg(NH_2)_2$ 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. $Mg(NH_2)_2$ does not release hydrogen by itself. Combining the two allows dehydrogenation.

Understanding the reaction mechanisms:

Hypothesis on the reaction pathways:
e.g. $\underline{2/3Li_3AlH_6+Mg(NH_2)_2}$

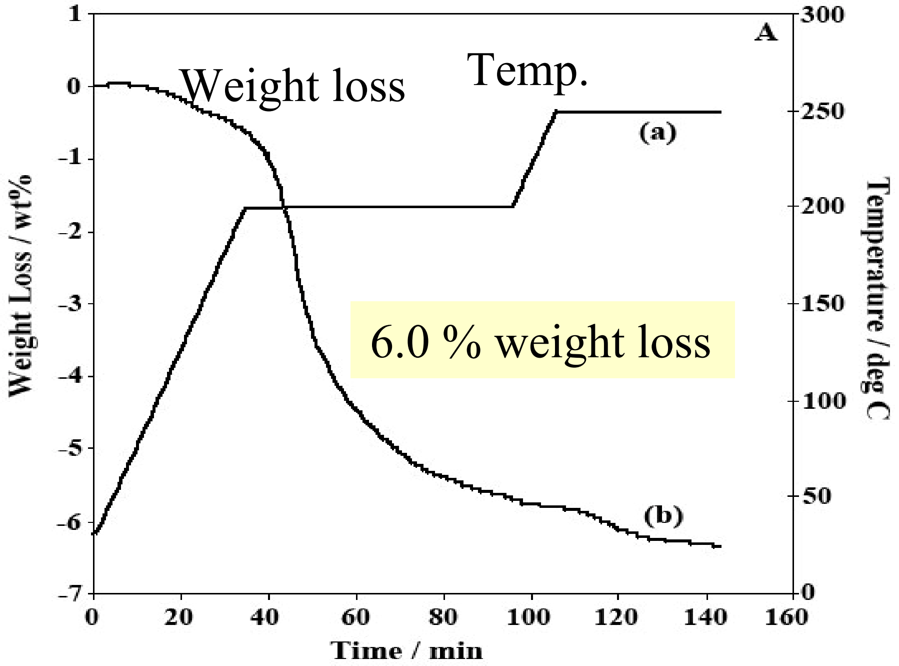
Two-step dehydrogenation:

$$\frac{2}{3}Li_3AlH_6 \longleftrightarrow \frac{2}{3}Al + 2LiH + H_2$$

$$2LiH + Mg(NH_2)_2 \longleftrightarrow Li_2Mg(NH)_2 + 2H_2$$

Overall reaction

$$\frac{2}{3}Li_3AlH_6 + Mg(NH_2)_2 \longleftrightarrow \frac{2}{3}Al + Li_2Mg(NH)_2 + 3H_2$$

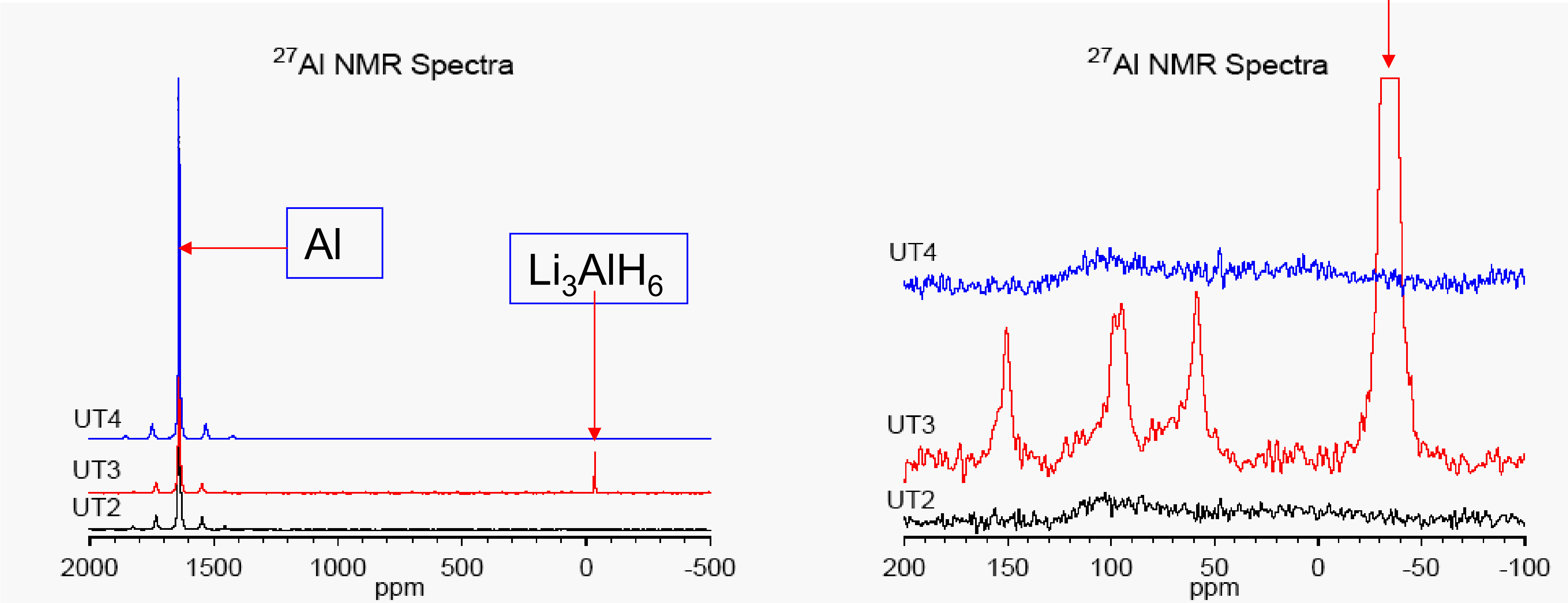


<u>Characterizations using: XRD, in-situ XRD (GE), NMR (JPL), FTIR, PCT (SNL, Hy-Energy), Cycling (UNR)</u>

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

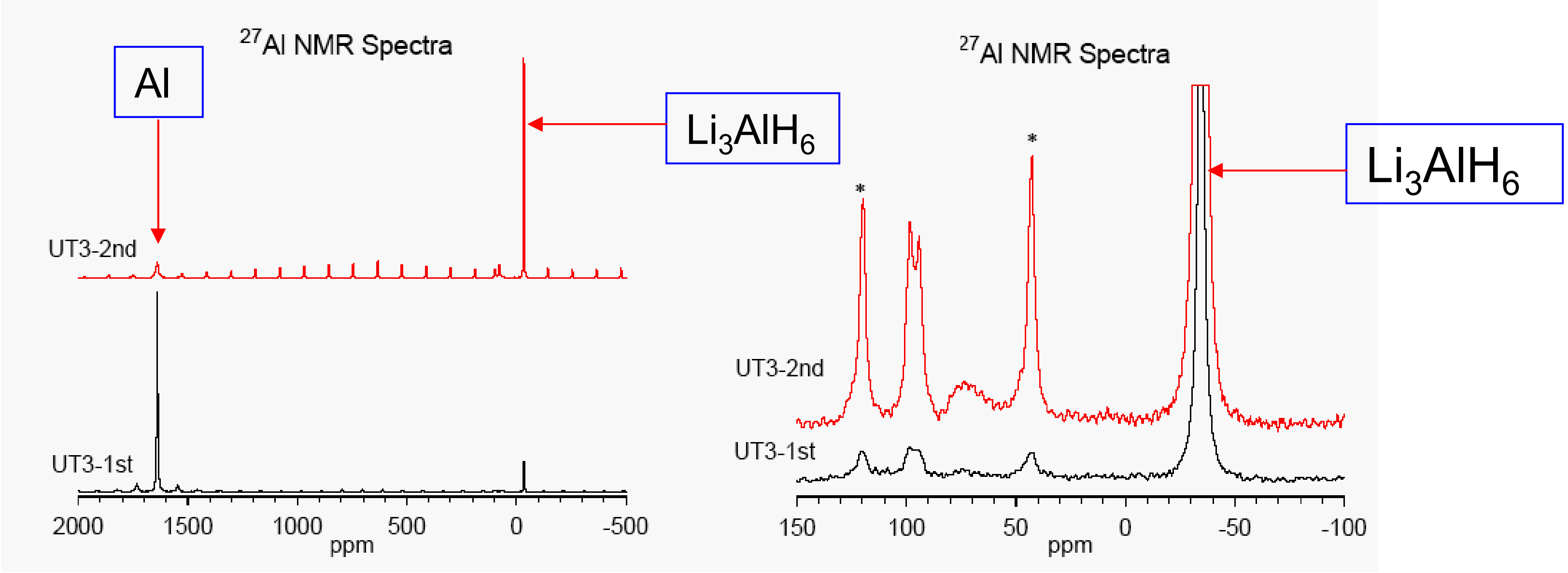
Li_3AlH_6

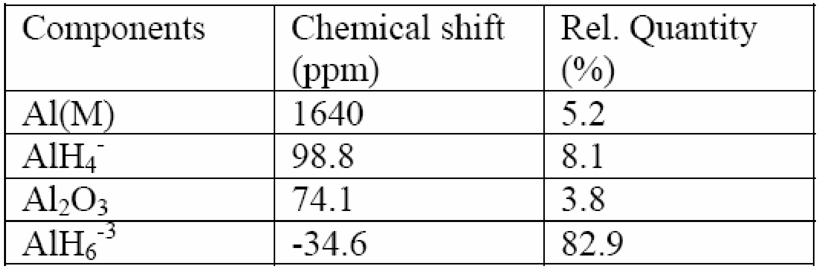


- ➢ Li_3AlH_6 has been regenerated (UT3)

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

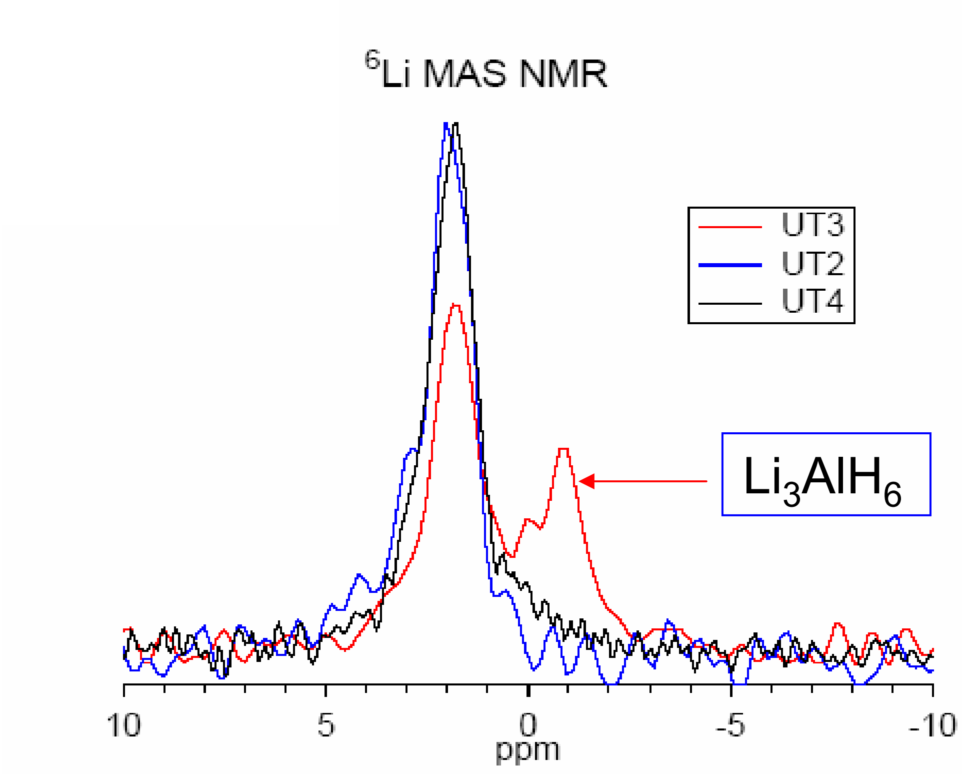


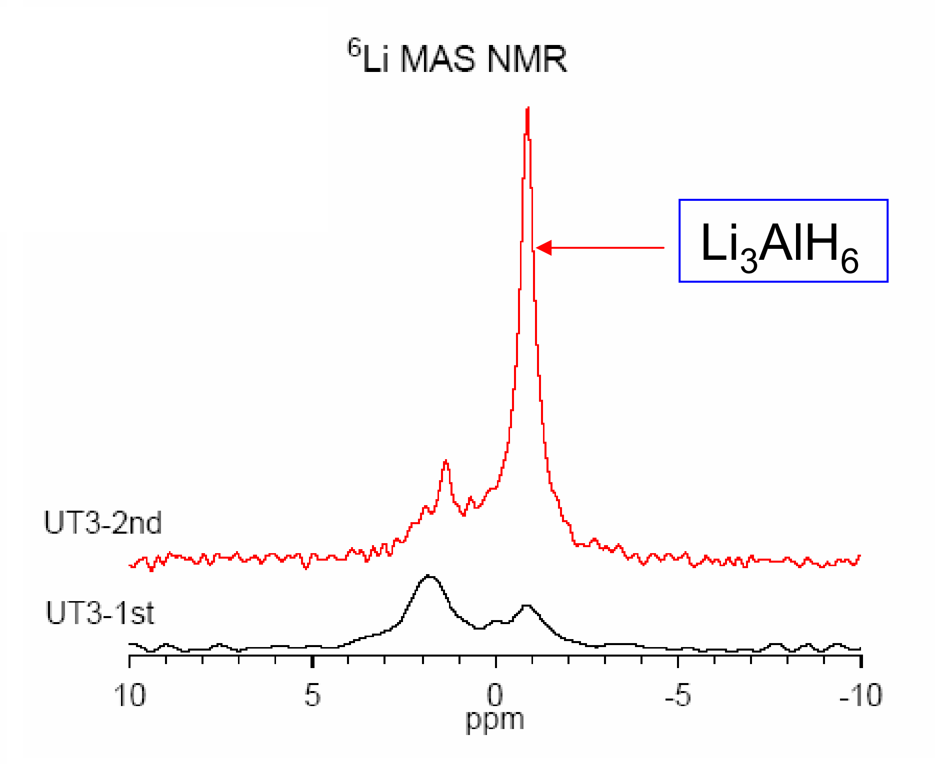


Components	Chemical shift (ppm)	Rel. Quantity (%)
Al(M)	1640	5.2
AlH_4^-	98.8	8.1
Al_2O_3	74.1	3.8
AlH_6^{-3}	-34.6	82.9

- Conversion to Li_3AlH_6 is more than 80% based on NMR results.

Study of the reaction pathways using NMR



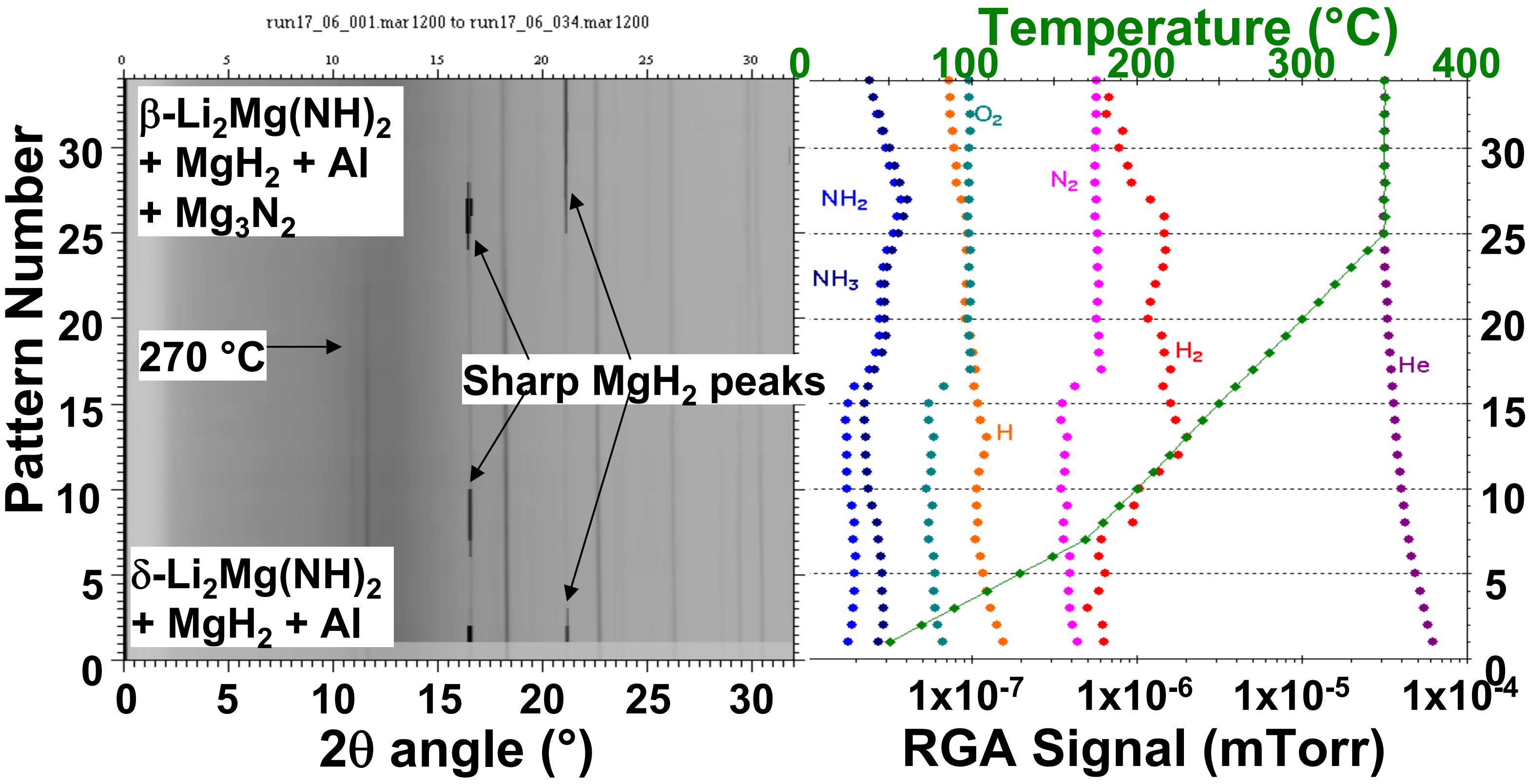


- Li is mostly in Li_3AlH_6 form in the UT-3 sample (hydrogenated status) with small portion in $LiNH_2$, which confirms the regeneration of Li_3AlH_6.

Investigating the issue of ammonia generation

In-situ XRD characterization

$$\frac{2}{3}Li_3AlH_6 + Mg(NH_2)_2 \longleftrightarrow \frac{2}{3}Al + Li_2Mg(NH)_2 + 3H_2$$



2nd Discharge

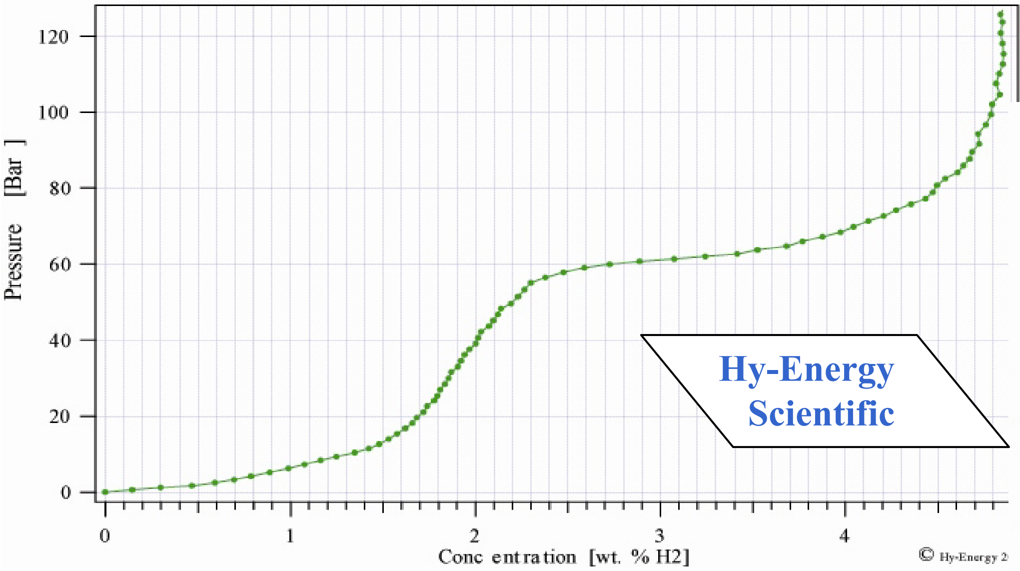
The generation of ammonia during this reaction is minimum. Exact content of NH_3 in ppm is yet TBD, pending funding for equipment.

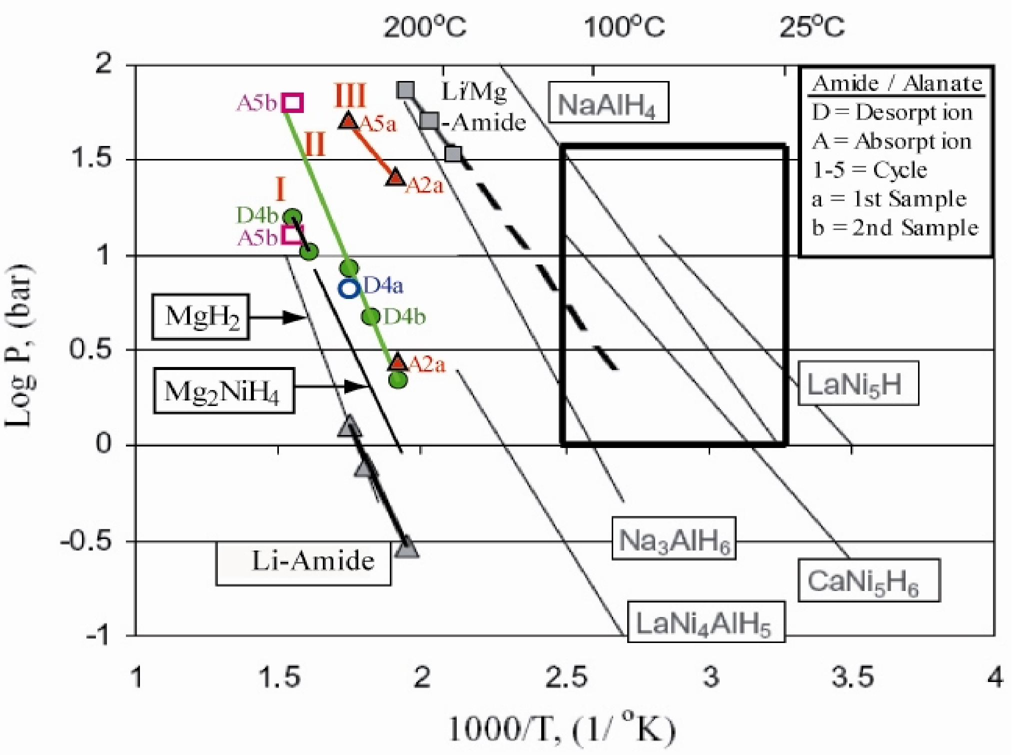
Accomplishments and Progress

Thermodynamic and kinetic properties – PCT characterization:

$Li_3AlH_6/3LiNH_2/4wt\%TiCl_3$

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





Two plateau pressures at ~1 and 60 bar respectively.

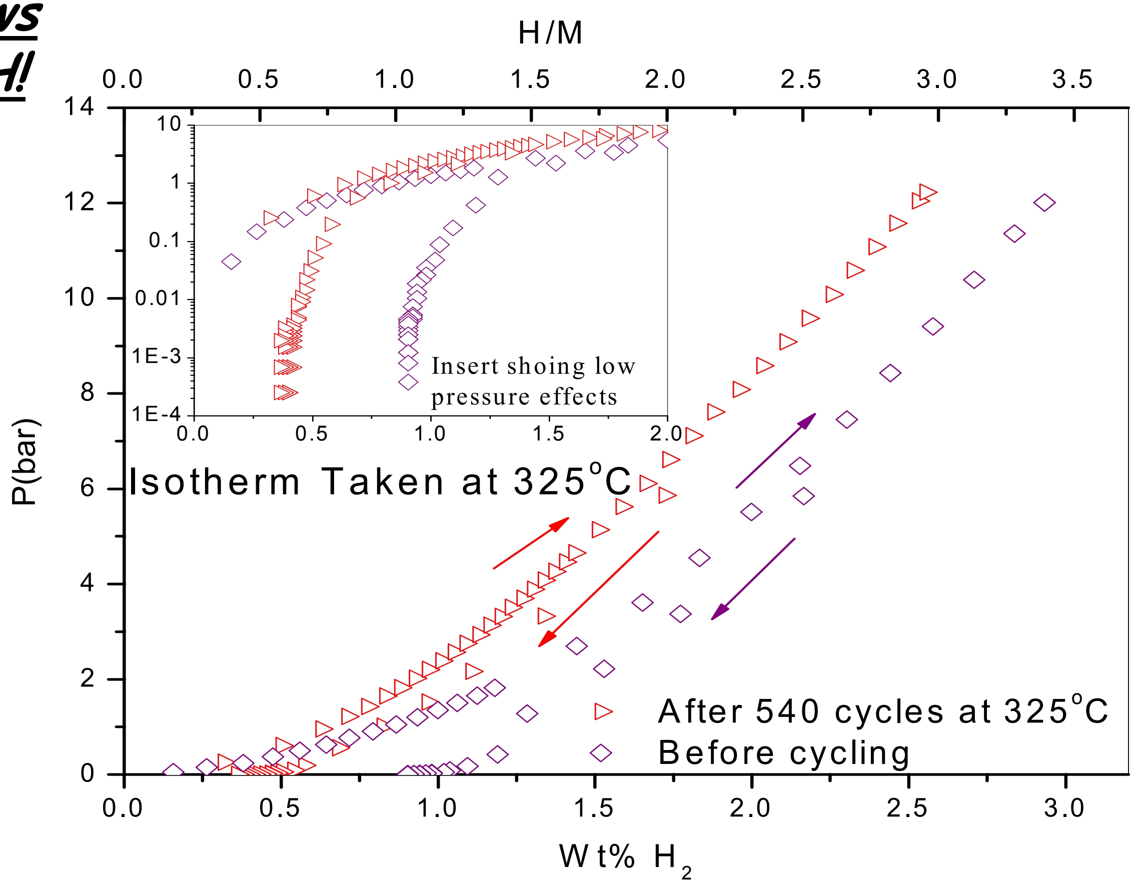
Accomplishments and Progress

Cycling of Li_3AlH_6+3$LiNH_2$ 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 ~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 $Li_2NH \leftrightarrow LiNH_2$ in Industrial hydrogen (with no Li Alanate) showed ~2.6% hydrogen loss after 500 cycles under similar cycling conditions*

*See UNR poster for details.



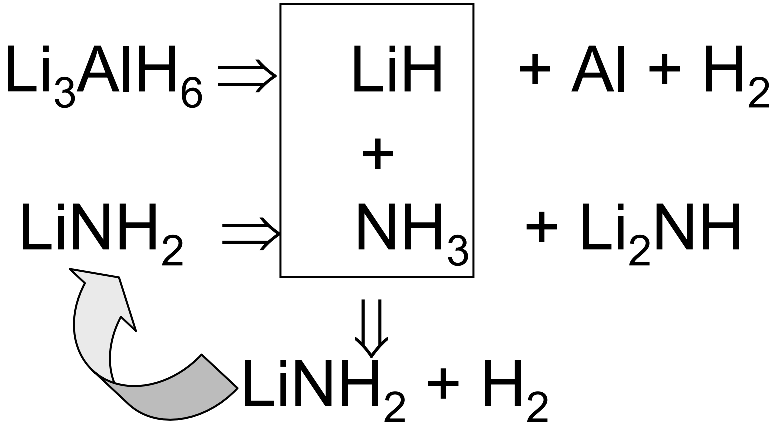
$3LiNH_2 + 3LiH \leftrightarrow 3Li_2NH + 3H_2$ (4.9 wt%) $\Delta H^0 = -45$ kJ/molH_2

$Li_3AlH_6 \leftrightarrow 3LiH + Al + 3/2H_2$ (2.4 wt.%) $\Delta H^0 = 32$ kJ/molH_2

Role of LiH produced during the alanate+amide reaction

- Reversibility of lithium alanate is limited, partially due to the poisoning of LiH by H_2O,

  Poisoning for OH monolayer: $LiH+H_2O \rightarrow LiOH+H_2+1.30eV/H_2O$*
- Amide alone, by itself, does not release hydrogen, instead, it release NH_3, unless a catalytic agent is present reacting / decomposing NH_3,
- The combination of alanates with amides allows fresh and active LiH to react with NH_3, releasing hydrogen from both LiH and amide.



$Li_3AlH_6 \Rightarrow \boxed{LiH} + Al + H_2$

$+$

$LiNH_2 \Rightarrow \boxed{NH_3} + Li_2NH$

$\Downarrow$

$LiNH_2 + H_2$

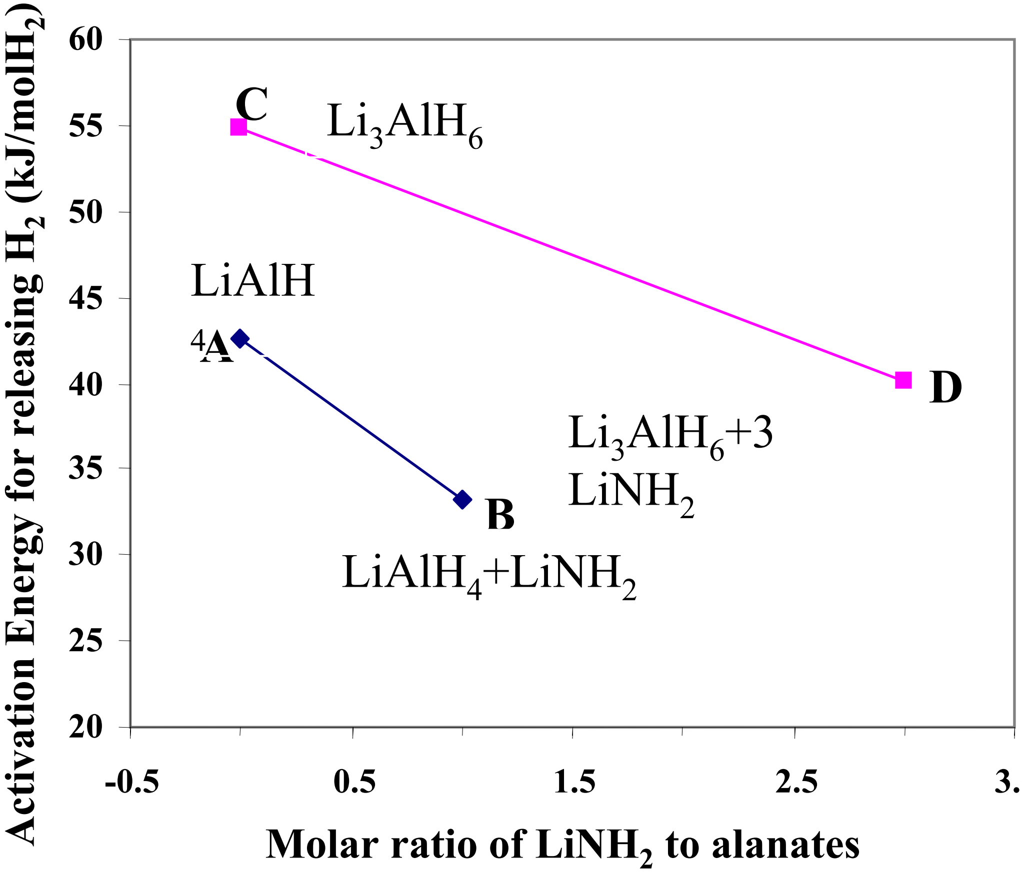
---

* Duane Johnson (UIUC, MHCoE theory group)

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

$Li_3AlH_6+3LiNH_2$

Reversible H_2 capacity:	**~ 5~7wt%**
Dehydrogenation T:	**<300°C**
Dehydrogenation kinetics:	**TBD**
Hydrogenation kinetics:	**TBD**
Plateau pressure:	**1 & 60 bar**

$2/3Li_3AlH_6+Mg(NH_2)_2$

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

Note 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_3AlH_6 /$3LiNH_2$	$2/3Li_3AlH_6$ /$Mg(NH_2)_2$
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 theorests (Alapati, Johnson, Sholl, et.al*)

$$MgH_2 + LiNH_2 \rightarrow LiMgN + 2H_2 \qquad \Delta H = 32 kJ/molH_2$$

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

Note: By this reaction all the hydrogen in MgH_2 and $LiNH_2$ can be released. It bypasses the formation of imide ($Li_2Mg(NH)_2$)** which forms when the molar ratio of MgH_2: $LiNH_2$ is 2:1. Imide is too stable to be useful.

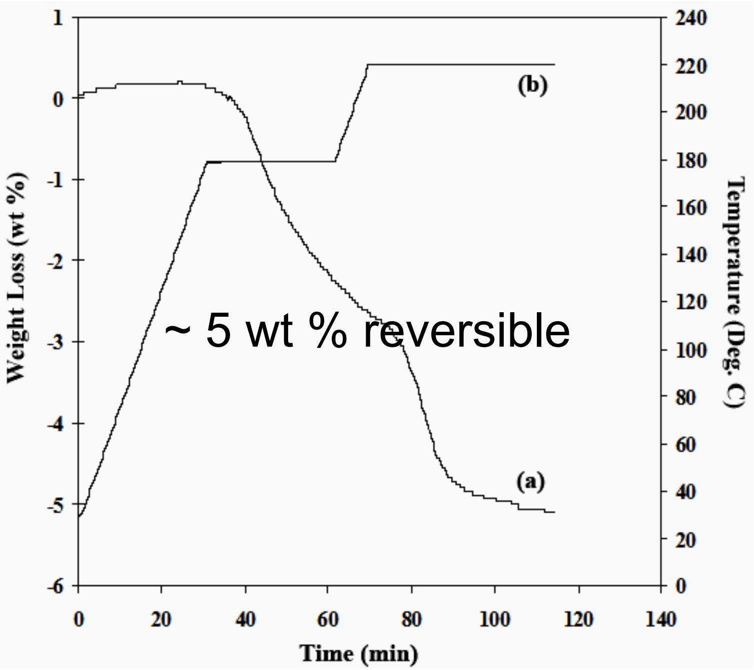
*. Alapati, S.V.; Johnson, K.J., Sholl, D.S. *J.Phys.Chem.*, ***2006***, *110,* 8769

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

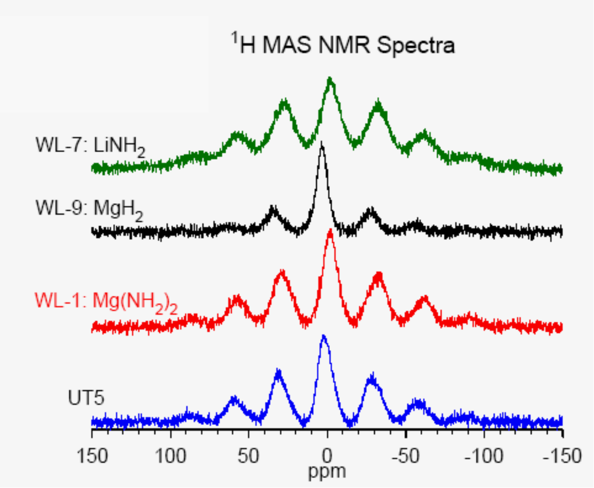
The potential of binary nitride - LiMgN

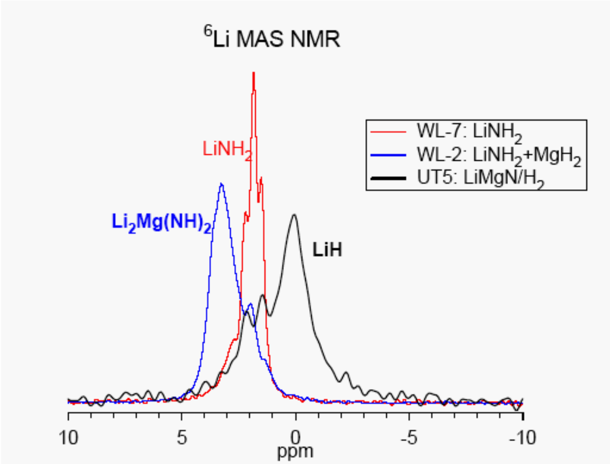
Hydrogenation of LiMgN: 138 bar, 240°C

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

$$MgH_2 + LiNH_2 \xrightarrow{irreversible} LiMgN + 2H_2 \overset{*}{\xleftrightarrow{reversible?}} 0.5Mg(NH_2)_2 + LiH + 0.5MgH_2$$

*US Patent pending

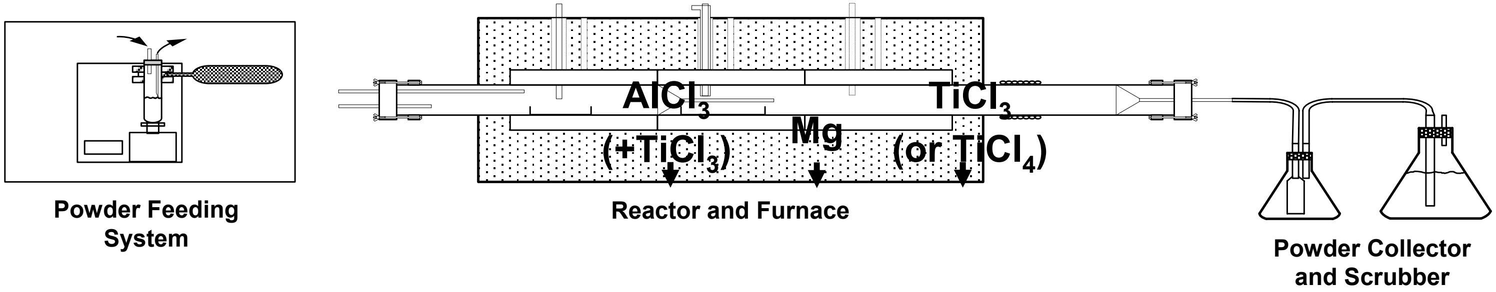
Chemical vapor synthesis (CVS)

Chemistry principles

- Aluminum nanopowder:

$$2AlCl_3(g) + 3Mg(g) = 2Al(s) + 3MgCl_2(g)$$

Experimental Set-up



Nano powders produced to date:

Al, Li, Li/Mg, Li_3N, 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 NH_3 generation

CVS and High Energy High Pressure Reactive Milling

- CVS synthesis of Li/Mg powders as precursor for metal hydride
- CVS synthesis of MgB_2 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 $Mg(NH_2)_2$
- 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