Synthesis and Discovery of Nanocrystalline Reversible Hydrides

DOE

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Project ID #: STP 10

Overview

Timeline

- Start – March 2005
- Finish – March 2010
- Percent complete – 20%

Budget

- Total project funding (Expected)
  - DOE share: $645,438
  - Contractor share: $165K
- Funding for FY05: $75K
- Funding for FY06: $100K

Barriers

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

Partners

- Sandia National Lab,
- HRL
- UNR
- Hy-Energy

Objectives

Overall

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

FY05-06

- Set up CVS reactors and demonstrate the feasibility of synthesis of nanosized metal and metal hydride powders
- Discover new materials based on the combination approach of alanates and amides
- Improve / develop mechanical milling processes for materials preparation and synthesis

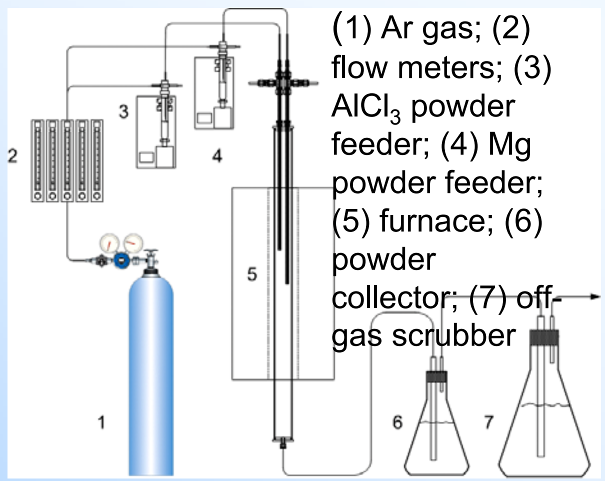
Technical Approach

Materials Discovery

- Lithium and other light metal based materials
- Lewis acid and base chemistry
- Combination of alanates with amides

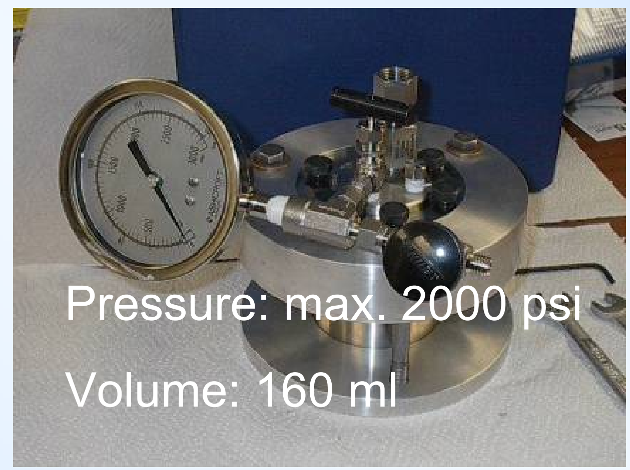
Chemical Vapor Synthesis

- Nanosized particles
- Atomic level homogeneity
- Doping at the molecular level
- Flexibility of custom engineered formula



Materials Processing

- Processing techniques affect performance
- Reactive milling
- High energy high pressure milling



Accomplishments and Progress

Highlights

I. Discovered a new Li-Al-N-H material system that shows promising properties

II. Demonstrated the feasibility of making nanosized metal and metal hydride powders using the chemical vapor synthesis (CVS) process

III. Improved the milling process for better material preparation and testing

IV. Developed a high energy high pressure (HEHP) reactive milling capability

Accomplishments and Progress - I

A Li-Al-N-H System for Reversible Hydrogen Storage

Problem based on prior arts

- $2LiAlH_4 = 2LiH + 2Al + 3H_2$ not reversible
- $LiAlH_4 + LiNH_2 = Li_2NH + Al + 5/2H_2$ not fully reversible

Solution: a new combination

System: $Li_3AlH_6 + 3LiNH_2$*

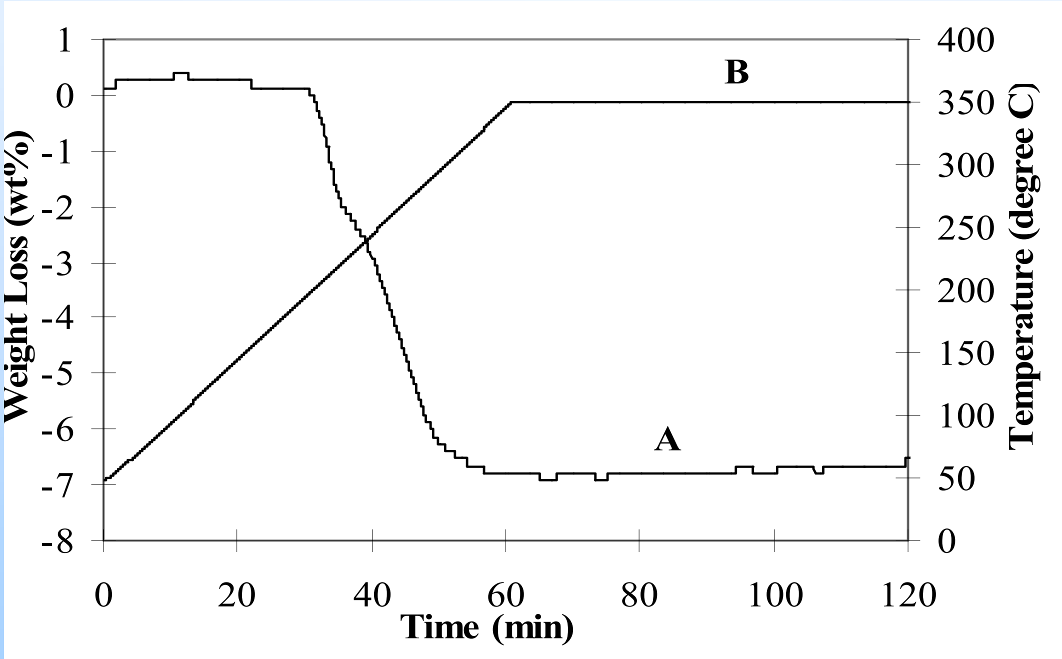
Theoretical hydrogen capacity: 7.3 wt%

* US patent pending.

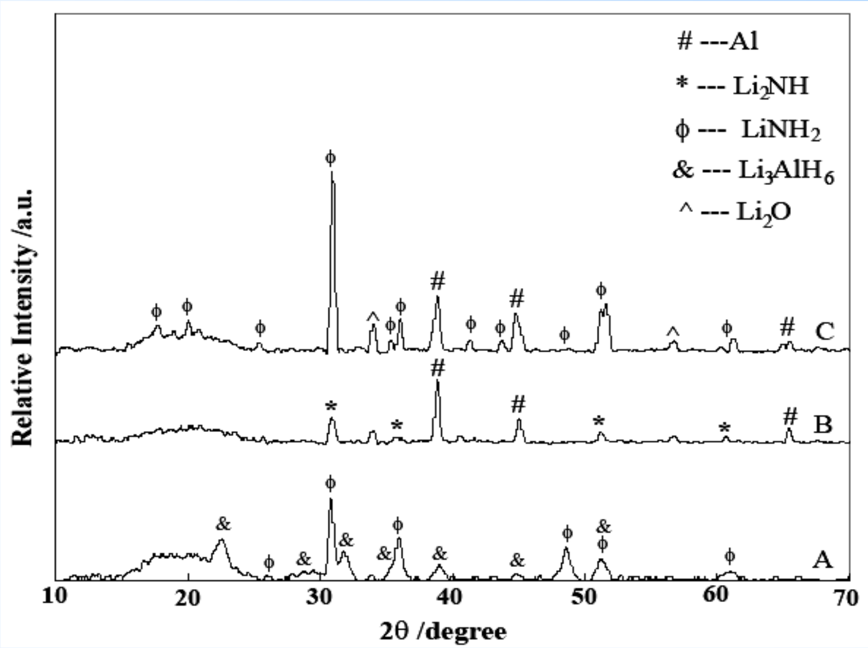
Accomplishments and Progress - I

A Li-Al-N-H System for Reversible Hydrogen Storage

Dehydrogenation by TGA measurement: 7.1%



TGA curves for sample 1 (Li_3AlH_6/3$LiNH_2$/4 wt% $TiCl_3$-⅓$AlCl_3$) system

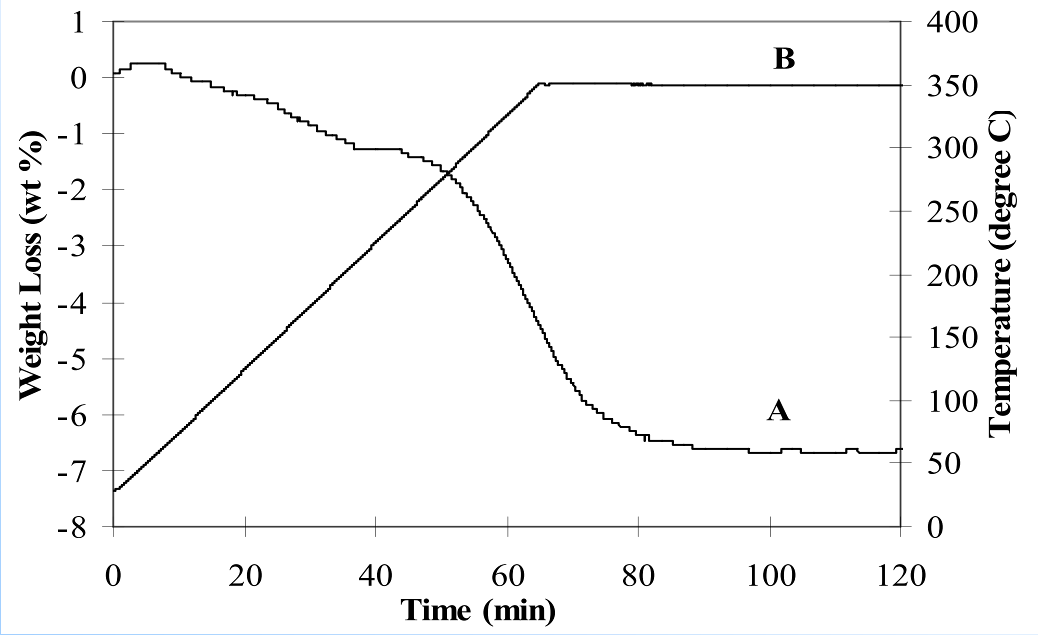


XRD patterns of A) Sample 1 after ball milling, B) Sample 1 after being heated up to 300 °C. C) Sample 1 after being heated up to 200 °C.

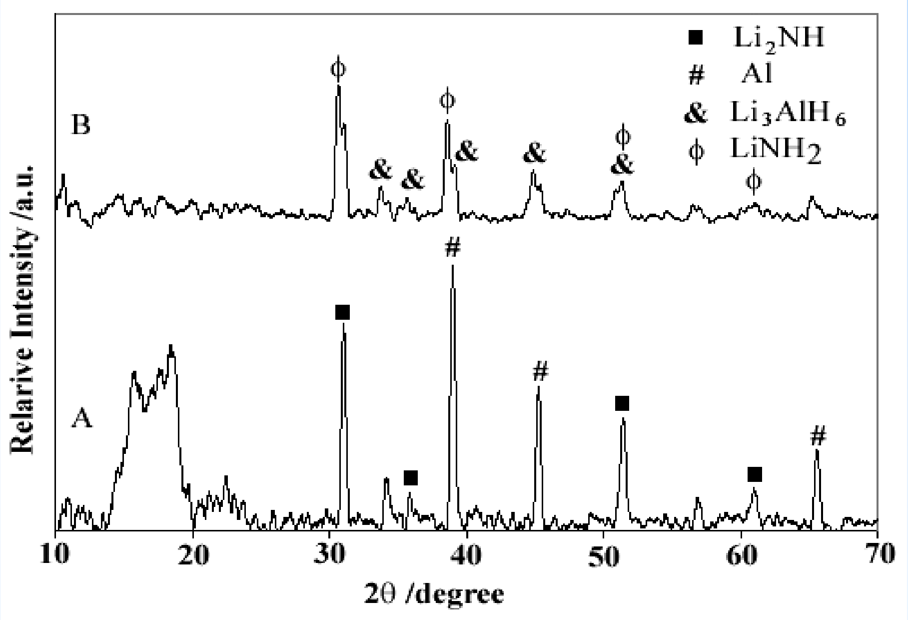
Accomplishments and Progress - I

A Li-Al-N-H System for Reversible Hydrogen Storage

TGA measurement after Re-hydrogenation: 7.0%



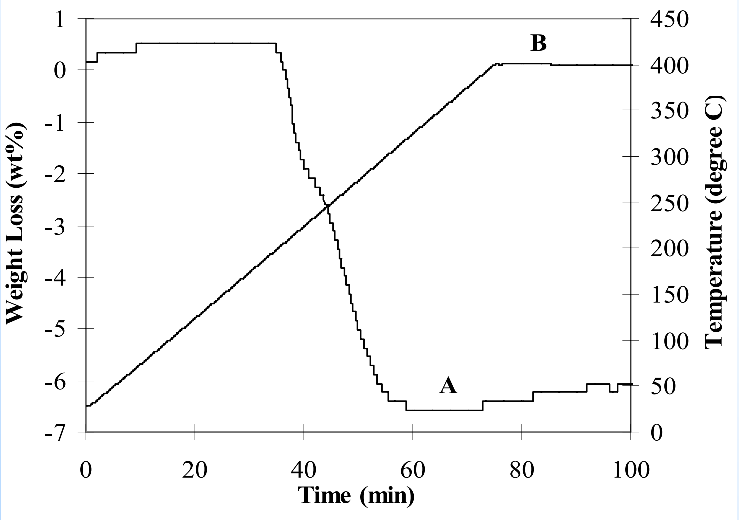
TGA curves for Sample 2 ($Al/3Li_2NH/4$ wt% $TiCl_3$-⅓$AlCl_3$) after hydrogenation.



XRD patterns of A) Sample 2 after ball milling, B) Sample 2 after re-hydrogenation.

Accomplishments and Progress - I

A Li-Al-N-H System for Reversible Hydrogen Storage



TGA measurement after six cycles of hydrogenation and dehydrogenation: 6.9%

Reversible H2 capacity:	**~7wt%**
Dehydrogenation T:	**<350°C**
Dehydrogenation kinetics:	**OK/TBD**
Hydrogenation kinetics:	**OK/TBD**
Plateau pressure:	**TBD**

The TGA wt-loss results demonstrated that this system is a very promising system for hydrogen storage. Further work are needed to characterize H_2 desorption/adsorption pressures and means to lower dehydrogenation temperature and improve the kinetics of the process.

Accomplishments and Progress - II

Li-Mg-N-H system: Milling processing techniques affect performance

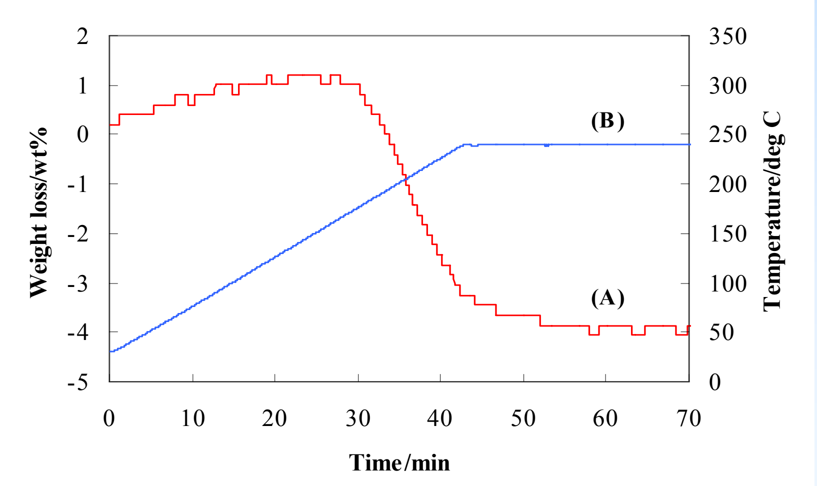
Problem based on previous experiences

- H_2 capacity less than expected when MgH_2+2$LiNH_2$ are milled and tested.
- Release of H_2 or NH_3 during milling suspected (~1 wt% lost during milling)

Solution: a new sequence for milling and testing

1. Dehydrogenate the starting material first. The following reaction occurs:
   $MgH_2 + 2LiNH_2 \rightarrow Li_2Mg(NH)_2 + 2H_2$
2. Mill the dehydrogenated product – $Li_2Mg(NH)_2$ – *There were no reactions during milling of the dehydrogenated product.*
3. Rehydrogenate the milled powder
4. Cycle

TGA curves of the milled $Li_2Mg(NH)_2$ after re-hydrogenation



~5.1 wt% hydrogen released. This is higher than if MgH_2/2$LiNH_2$ were milled directly.

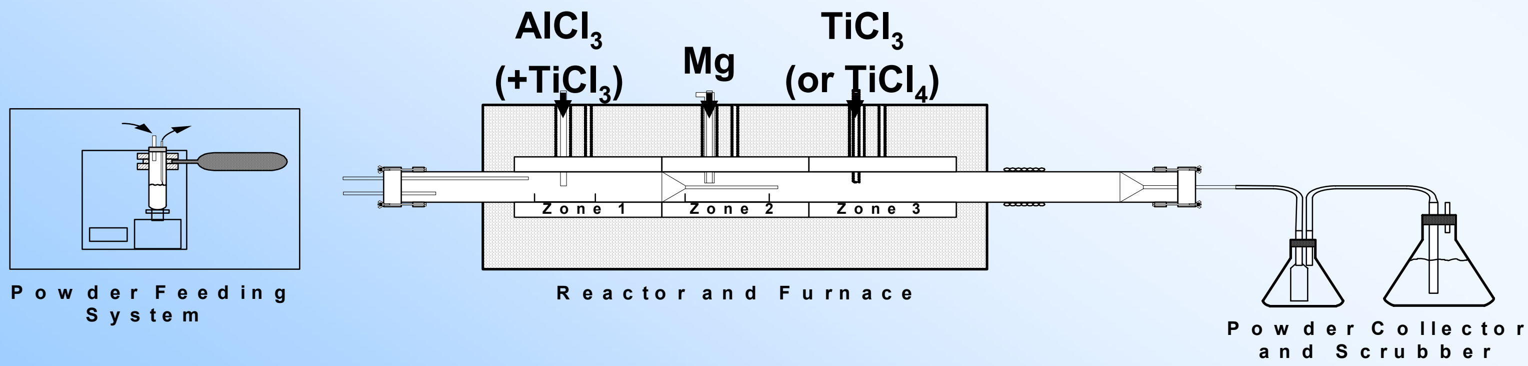
Accomplishments and Progress - III

Demonstrated feasibility of CVS Process - Application to Metal Hydride Synthesis

Chemistry principles

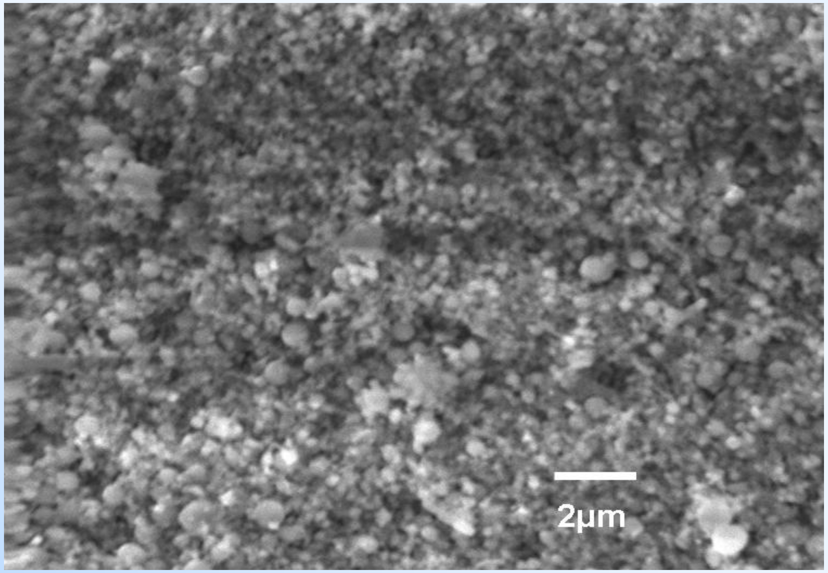
- Aluminum nanopowder:
  $AlCl_3(g) + wMg(g) + xMCl_y(g) = (AlMg_y+xM)(s) + zMgCl_2(g)$
  (M = Doping or Alloying Element: Ti, etc.)
- Mg_2Si Powder and Thin film:
  $SiCl_4(g) + wMg(g) + xMCl_y(g) = (Mg_2Si+xM)(s) + yMgCl_2(g)$

Experimental Set-up

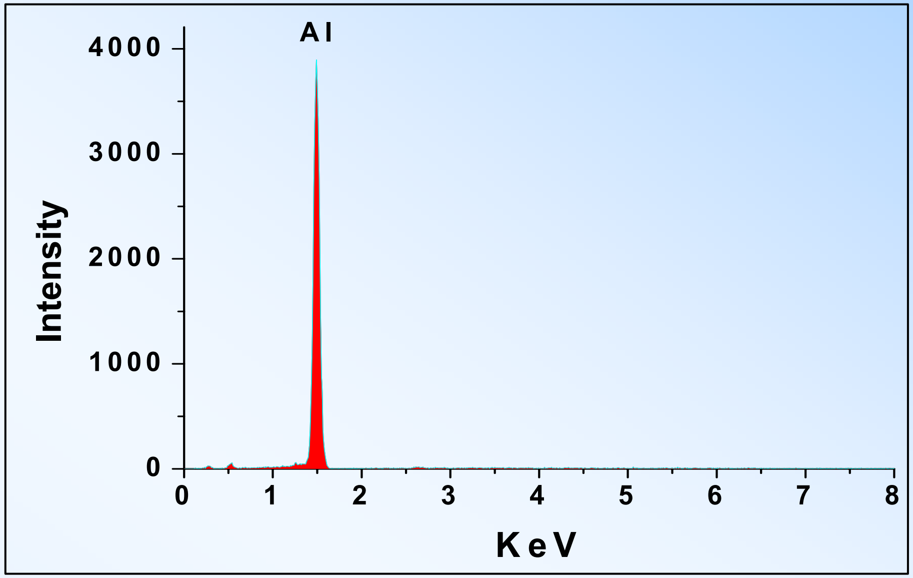


Accomplishments and Progress - III

Nano aluminum powder synthesis – precursor for metal hydrides containing Al



SEM micrograph



EDX

- Pure aluminum powder was produced (~500nm).
- Impurities were successfully removed by the modified system.
- In Ti doping process, the intermetallic compound (Al_5Ti_2) was produced.

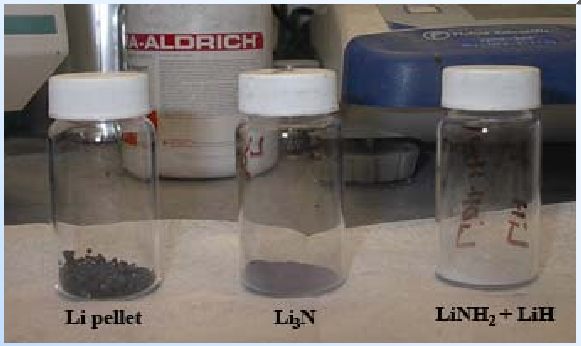
Accomplishments and Progress - III

Vapor Phase Synthesis - nano Li and Li/Mg powders

Li (pellets) → **Vaporization & condensation** → **Li (nano powder)**

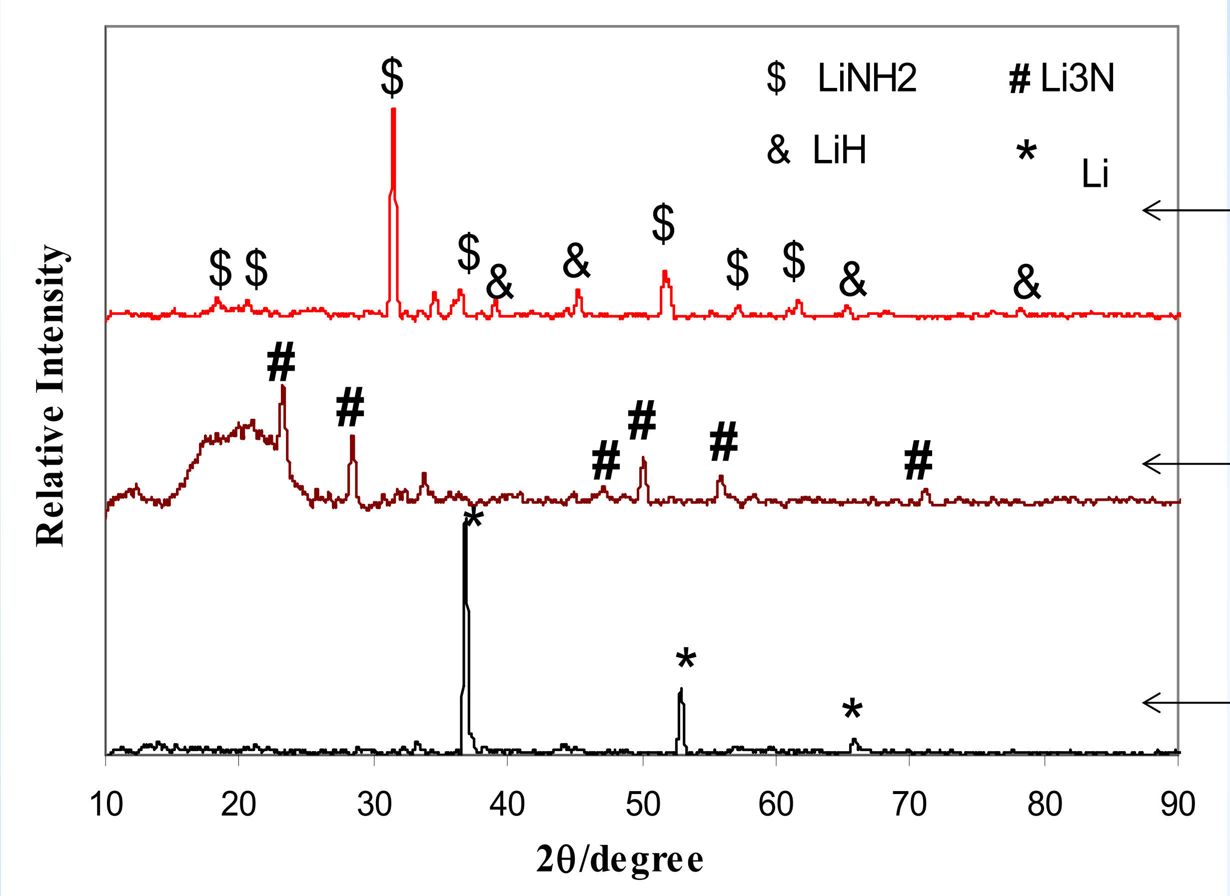
- **NH_3** → **$LiNH_2$**
- **N_2** → **Li_3N** → **H_2** (250°C,1000 psi) → **$LiNH_2$+LiH**
- **H_2** → **LiH**

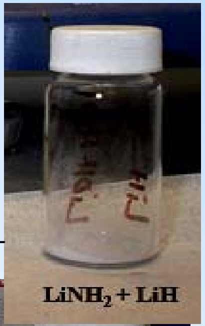
Vapor phase synthesis of Li as precursor for Li-based hydrogen storage materials



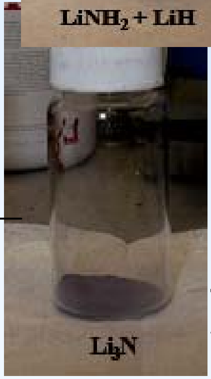
Accomplishments and Progress - III

Vapor phase synthesis - nano Li and Li/Mg powders





~20 nm
Scherrer Eqn.



~17nm
Scherrer Eqn.

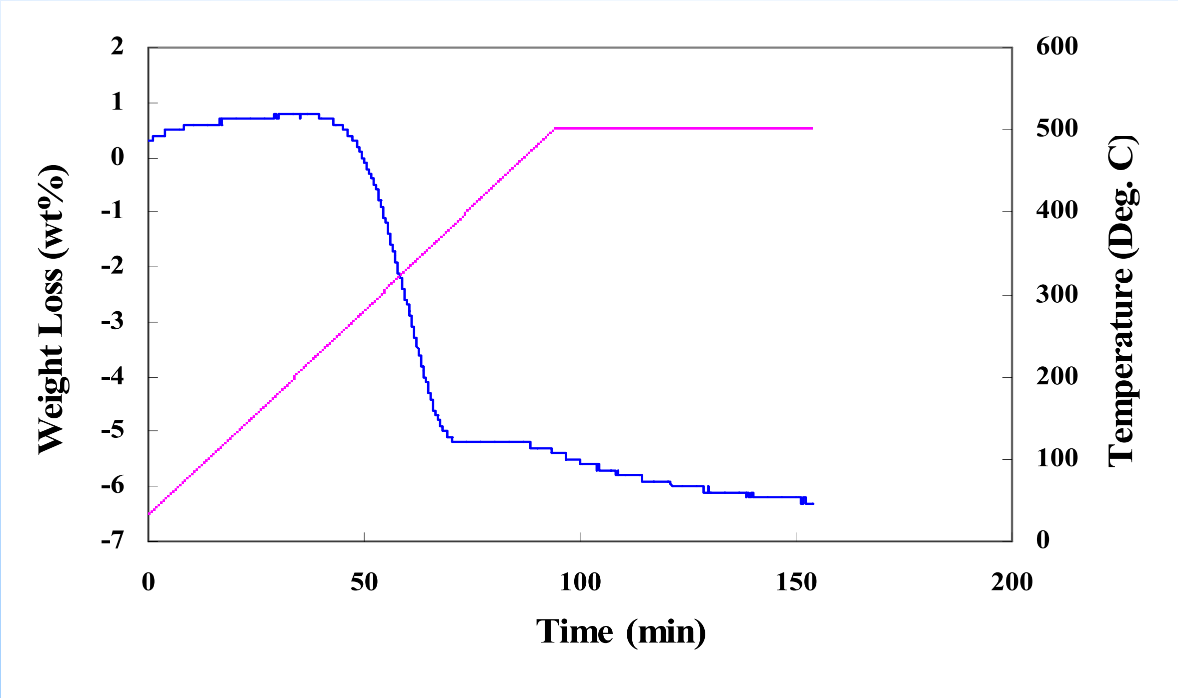
-- No Li_2NH in the hydrogenation product.

-- Complete hydrogenation of Li_3N to $LiNH_2$+LiH?

Accomplishments and Progress - III

Vapor phase synthesis - nano Li and Li/Mg powders

Dehydrogenation characteristics of vapor phase synthesized nano ***$LiH+LiNH_2$***

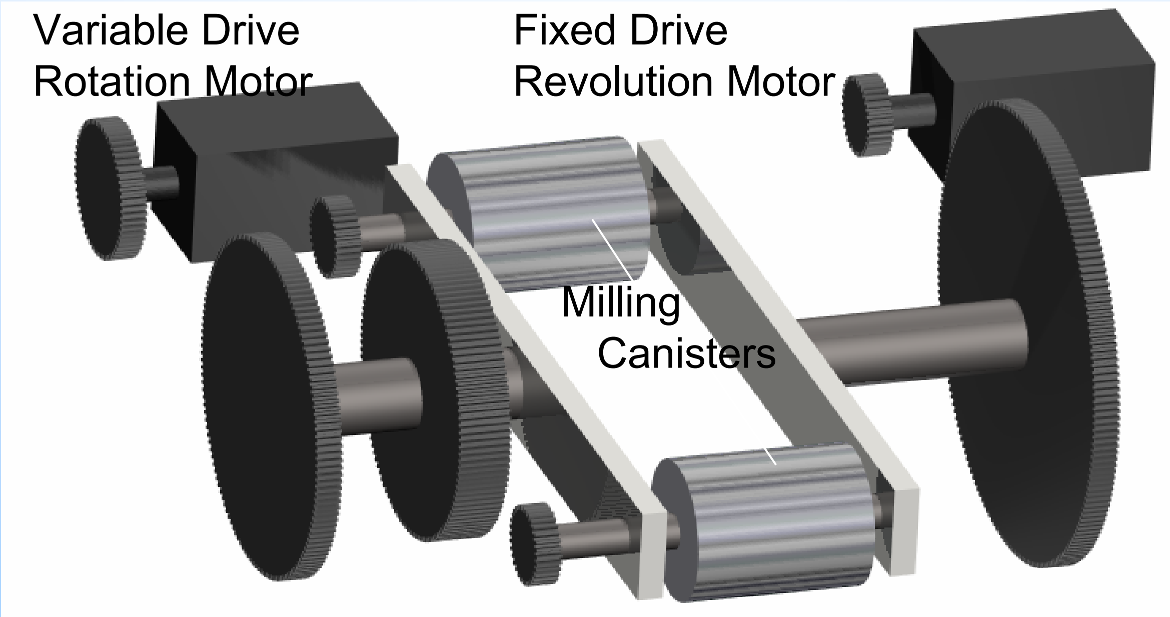


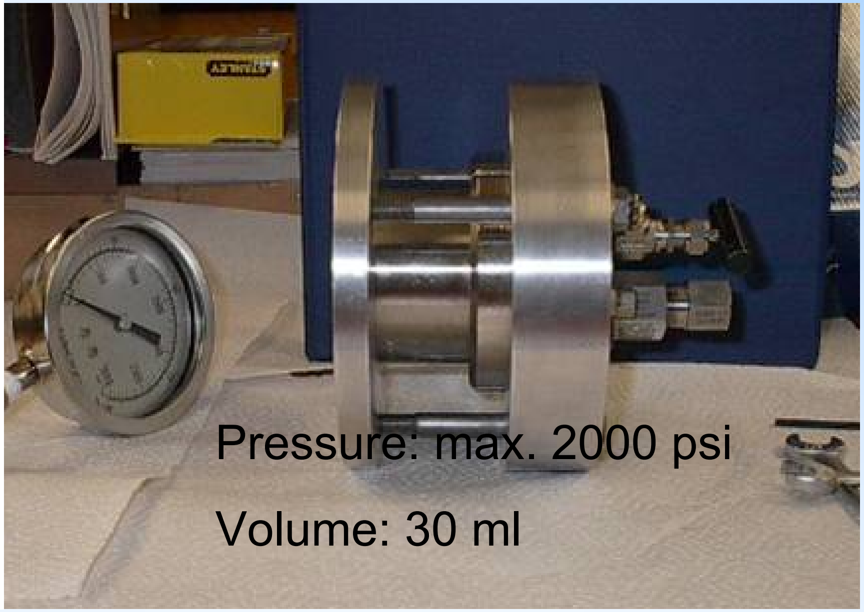
~ 5% Hydrogen release to form Li_2NH

➢ ***Next step***: **Synthesis of Li/Mg powders.**

Accomplishments and Progress - **IV**

Established an High Energy High Pressure (HEHP) Reactive Milling Capability





The HEHP reactive milling process will be immediately applied to the following two tasks: 1) Hydrogenation of Mg_2Si; and 2) Solid state synthesis of ternary systems of M-Si-H.

Future Work – FY06-07

Materials Discovery and Development

- Comprehensive investigation of Li-Al-N-H materials
- Characterize hydrogen storage properties: isothermal plateau pressures, desorption/adsorption kinetics, thermal conductivity and thermal expansion characteristics
- Continue to explore other combinations

CVS Synthesis – nano metals and metal hydrides

- Chemical vapor synthesis of Li/Mg powders to be used as precursor for metal hydride --- *collaboration with SNL and HRL*
- Synthesis of nanosized Mg_2Si --- *collaboration with HRL*
- Synthesis of nanosized aluminum powder and determine its potential for manufacturing of metal hydride.

Future Work – FY06-07

High Energy High Pressure (HEHP) Milling

Materials Processing and Synthesis

- Solid state synthesis of ternary metal hydrides such as Na-Si-H --- *collaboration with SNL*
- Hydrogenation study of Mg_2Si --- *collaboration with HRL*
- Optimize mechanical milling processes to maximize metal hydride performance --- *collaboration with SNL*

Summary

- A candidate Li-Al-N-H material system with 7% reversible hydrogen storage capacity at <300°C was demonstrated.
- Nanosized metal powders including Li, Li/Mg, and Al were produced via chemical vapor synthesis (CVS) process.
- A high energy high pressure reactive milling capability was established.
- An improved milling process for preparation of metal hydride materials was established.

Responses to Previous Year Reviewers' Comments

N/A. This was a new project in FY05-06.

Publications and Presentations

1. Jun Lu and Zhigang Zak Fang, "Dehydrogenation of a combined $LiAlH_4/LiNH_2$ system", The Journal of Physical Chemistry B, *109(44)*, 20830-20834, 2005
2. Jun Lu, Zhigang Zak Fang, and H. Y. Sohn, "A Hybrid Method for Hydrogen Storage and Generation from Water", submitted, The Journal of Physical Chemistry B, March 2005
3. Jun Lu, Zhigang Zak Fang, and H. Y. Sohn, "A New Li-Al-N-H System for Reversible Hydrogen Storage", submitted, J. Physical Chemistry B, April, 2006
4. Jun Lu, Zhigang Zak Fang, and H. Y. Sohn, "Destabilization of Metal Hydrides Based on Negatively Charged Hydrogen (H–) and Positively Charged Hydrogen (Hδ+) Interactions", Journal of Alloys and Compounds, submitted, February, 2006
5. Jun Lu, Zhigang Zak Fang, and H. Y. Sohn, "A New Li-Al-N-H System for Reversible Hydrogen Storage", presented during MRS Spring Meeting, San Francisco, April 20, 2006
6. Two provisional patent applications were filed by the University of Utah.

METAL HYDRIDE CENTER OF EXCELLENCE

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Critical Assumptions and Issues

- The dehydrogenation temperatures of the material systems that are studied are higher than required. Therefore, it is an assumption that the dehydrogenation temperatures of these materials can be lowered by finding catalysts and fine tuning of chemistries.
- All material systems that contain nitrogen faces a challenge of reducing NH_3 content in the output H_2. It is therefore another critical assumption this problem will be solved.

Summary Table

Properties of $Li_3AlH_6/3LiNH_2$ – *to date*

On-Board Hydrogen Storage System Targets (**Data is based on material only, not system value)				
Storage Parameter	**Units**	**2010 System Target**	**FY05 materials****	**FY06 Result materials****
Specific Energy	kWh/kg (wt. % H2)	2.0 (6 wt.%)		(7.1wt%)
Volumetric Energy Capacity)	kWh/L (kgH2/L)	1.5 (0.045)		(0.101kgH2/L)
Desorption Temperature	°C	~85		100-300°C
Plateau Pressure	Bar	1-10		TBD