

# Complex Hydride Compounds with Enhanced Hydrogen Storage Capacity

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This presentation does not contain any proprietary or confidential information

Project ID # ST10

# Program Overview

- **Timeline**

- 11/30/02 Start
- 11/30/06 End
- 80% Complete

- **Budget**

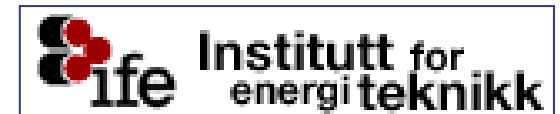
- \$2.9 M Total Program
  - \$2.1M DoE
  - \$0.8M (27%)  
UTC/ALB
- \$0.68M DoE FY'05
- \$0.59M DoE FY'06

- **Barriers**

- Gravimetric density: 2 kWh/kg
- Volumetric density: 1.5 kWh/l
- Discharging rate: 0.02 g/s/kW
- Safety: Exceeds standards

- **Partners**

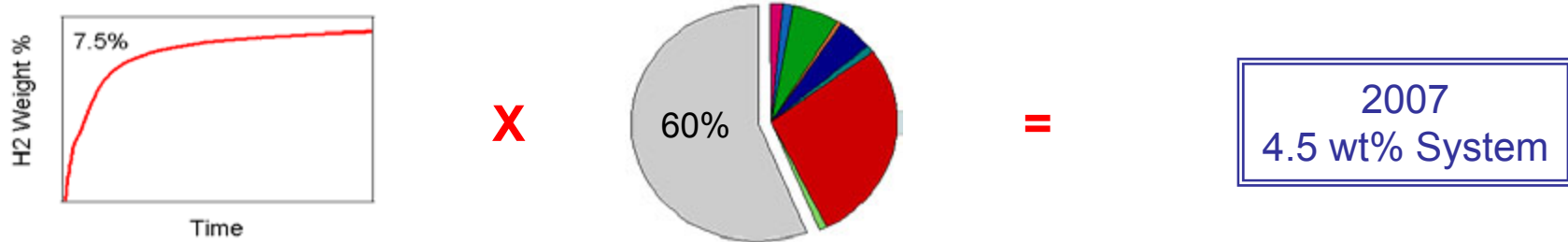
- Albemarle
- SRNL
- IFE
- QuesTek



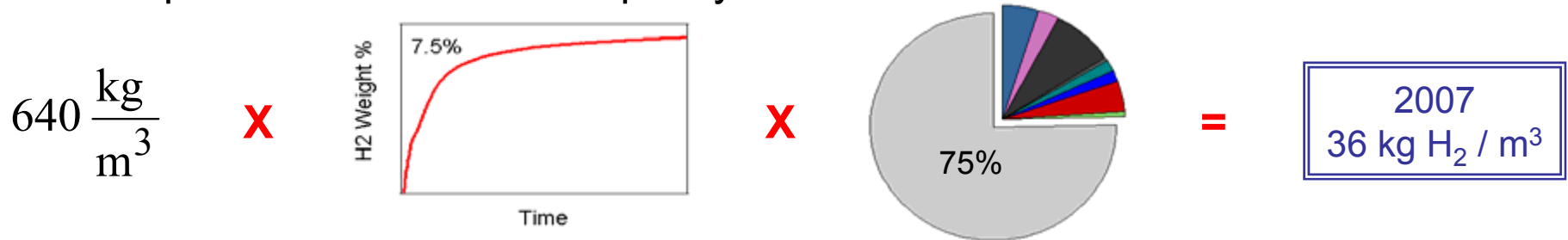
# Objectives

## Overall

- Develop new complex hydride compounds capable of reversibly storing hydrogen with capacities  $\geq 7.5$  wt % to meet DOE system **gravimetric** goals.



- Assess potential **volumetric** capacity of new materials.



## 2005

- Deploy integrated methods to search out and discover high capacity systems.
- Synthesize, characterize, and evaluate new high H capacity systems.

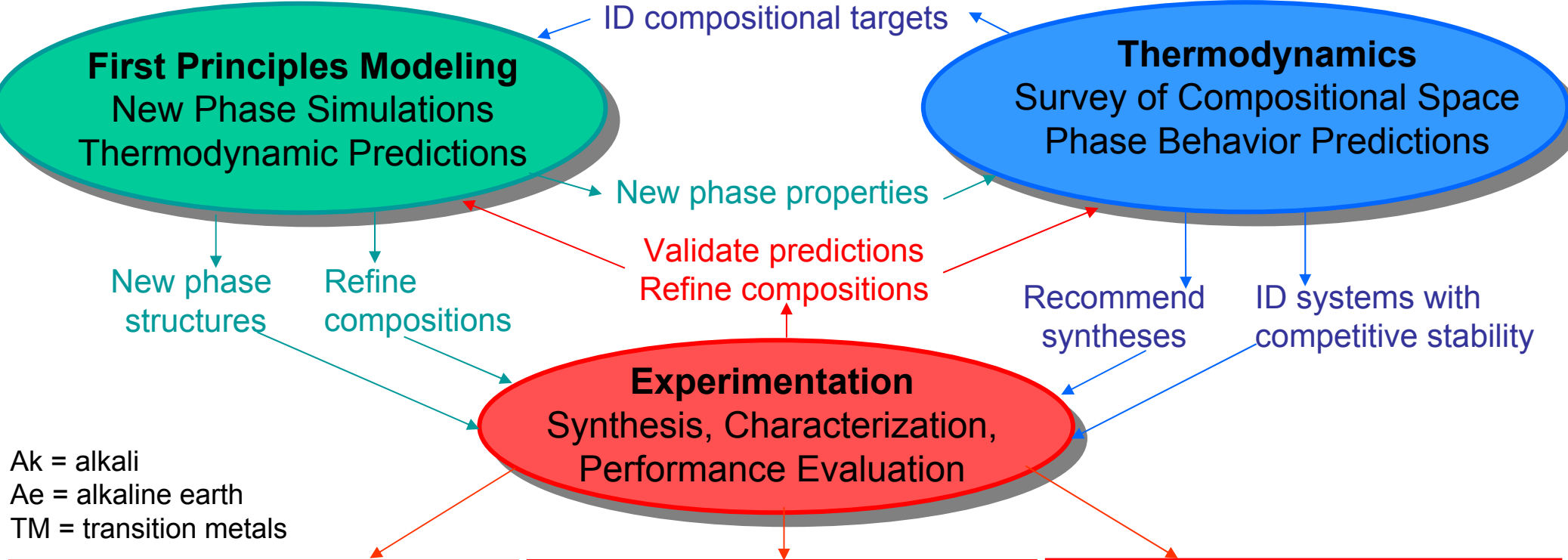
## 2006

- Design reactions with new systems to refine reversibility and capacity.
- Catalyze improved kinetic performance.

# Approach: Coupled Complex Reaction Strategy

*Design and synthesis of reversible high capacity quaternary systems*

High H Capacity Hydrides ←————→ High H Coupled Reactions



**Solid State Processing**  
Mechanochemical Mixing



**Solution Based Processing**  
Chemical Design & Synthesis



**Molten State Processing**  
High T & P Fusion



# Accomplishments Outline

Approach: Produce high H capacity compounds with diversified synthetic methods. Use atomic-thermodynamic modeling to optimize capacity & reversibility.

Progress:

- 1) Compositional surveys
- 2) Theoretical methodologies
  - design of reversible systems
  - thermodynamic optimization of capacity
- 3) Synthesis and characterization
  - demonstration of three new systems
  - reaction design and modification
- 5) Volumetric capacities
- 6) Material progress towards targets

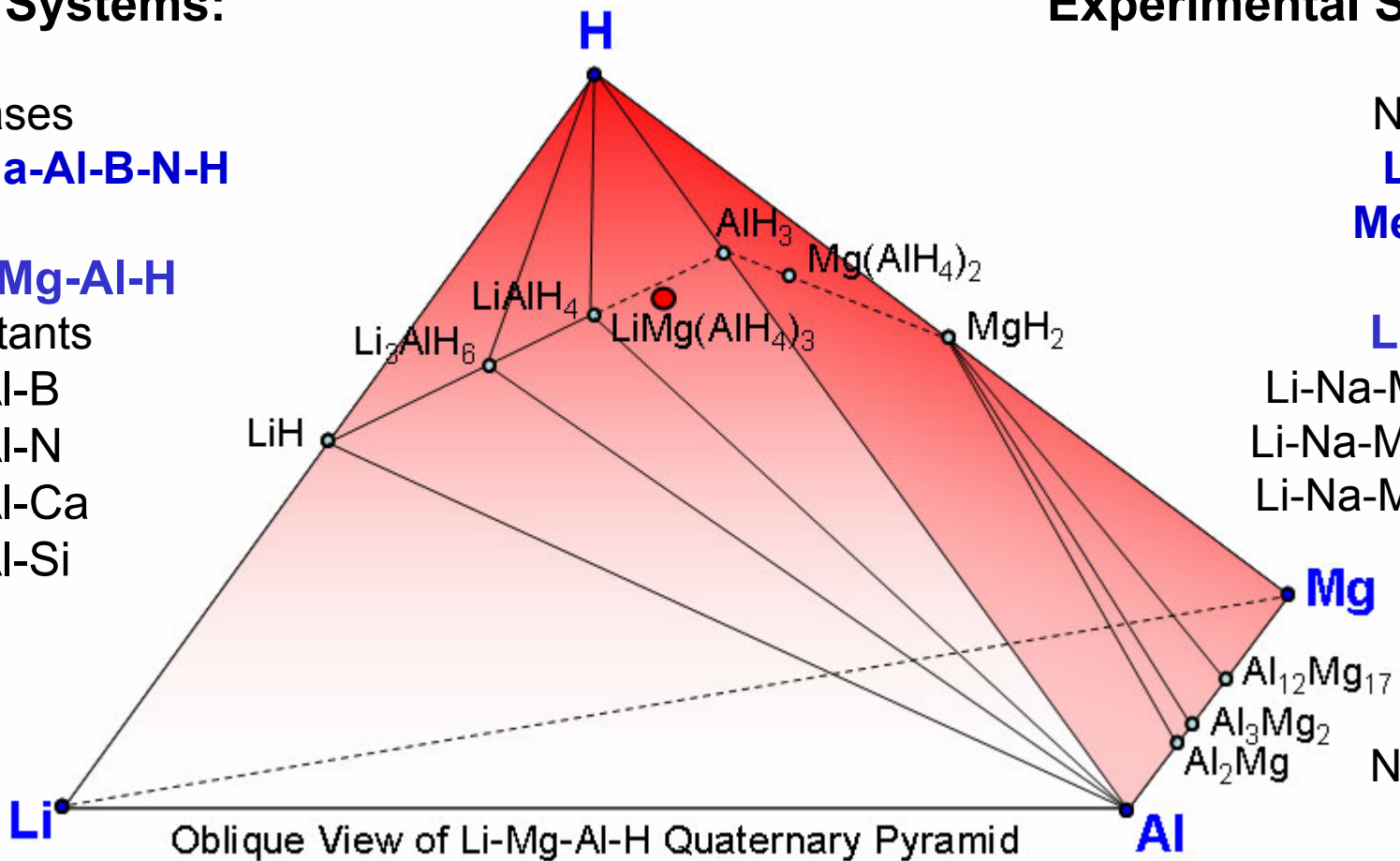
# Numerous Quaternary Surveyed Since May '05

## Virtual Systems:

- >60 Phases
- Li-Mg-Na-Al-B-N-H**
- > 30 **Li-Mg-Al-H**
- Co-reactants
- Li-Mg-Al-B
- Li-Mg-Al-N
- Li-Mg-Al-Ca
- Li-Mg-Al-Si

## Experimental Systems:

- SBP**
- Na-Mg-Al-H
- Li-Mg-Al-H**
- Metal-B-N-H**
- SSP**
- Li-Mg-Al-H**
- Li-Na-Mg-Ni-Al-H
- Li-Na-Mg-Co-Al-H
- Li-Na-Mg-Fe-Al-H
- MSP**
- Na-Mg-Ni-H

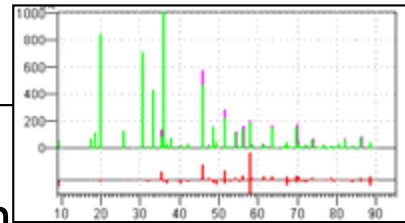


Three promising candidates synthesized from Li-Mg-Al-H & metal-B-N-H.

# Integrated Modeling with Experimentation

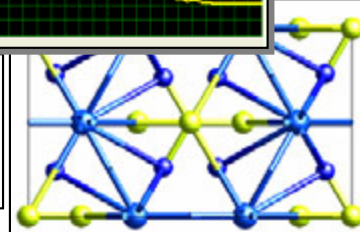
**JADE**

Crystal Indexing  
Global Optimization



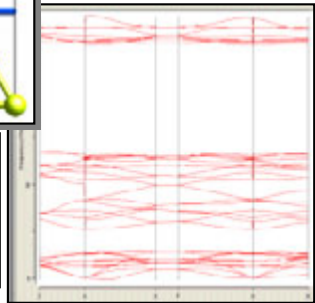
Crystallographic  
Refinement

**VASP**  
Density Functional Theory  
Ground State Minimization

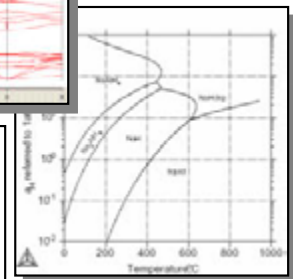


Thermodynamic  
Database Building

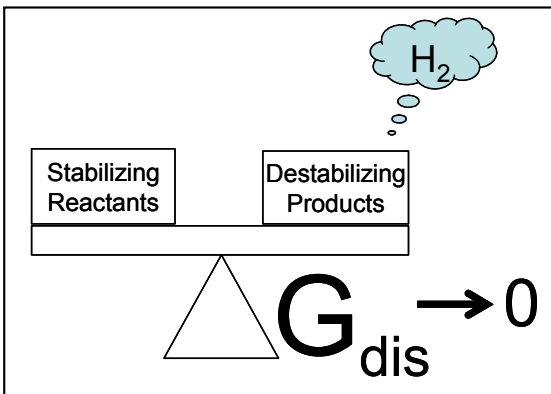
**MATERIALS DESIGN**  
Direct Method Lattice Dynamics  
Thermodynamic Property Prediction



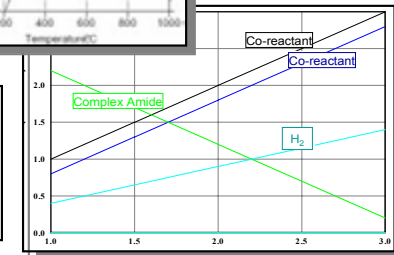
**Thermo-Calc**  
Computational Thermodynamics  
Assessment & Phase Diagrams



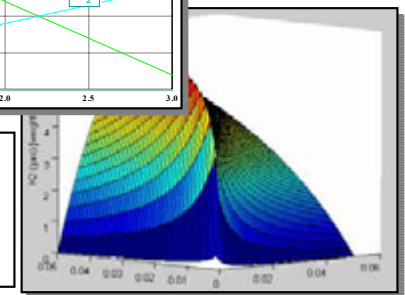
Experimental  
Guidance



**Outokumpu**  
Thermochemistry  
Design of Reversible Reactions



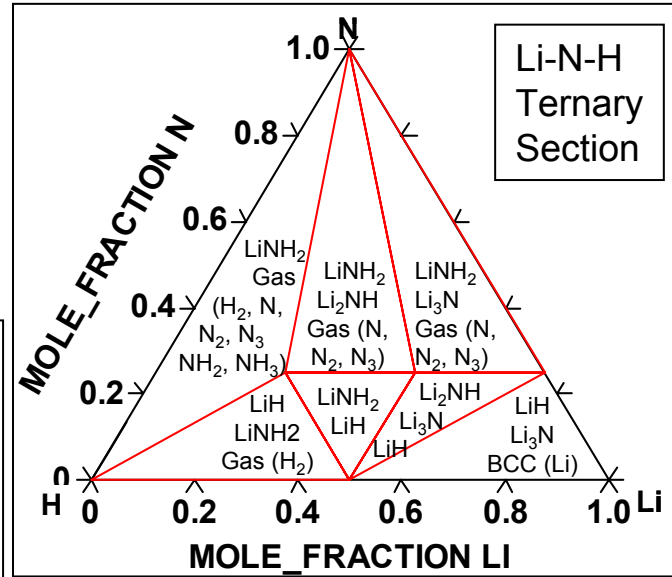
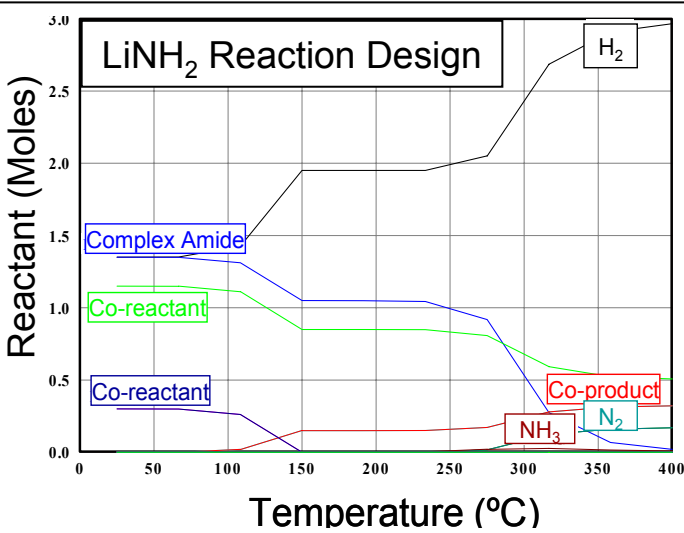
**MATLAB**  
Thermodynamic Optimization  
of Theoretical H Capacity



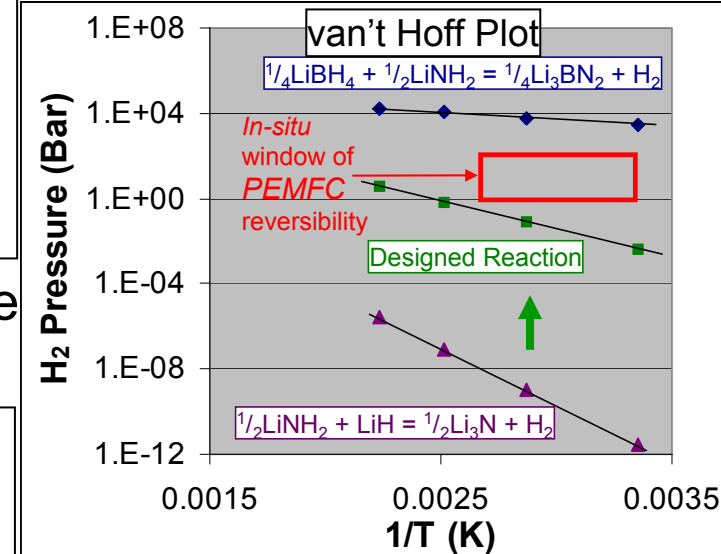
# Designed High Capacity, Reversible Reactions

Integrate theory and experiment.

Iterate and refine.

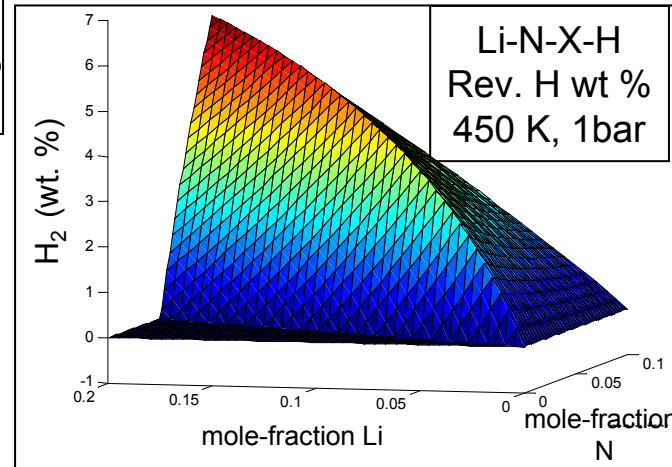


1) Select candidates, make & validate predictions.



4) Experimentally evaluate new designed reactions.

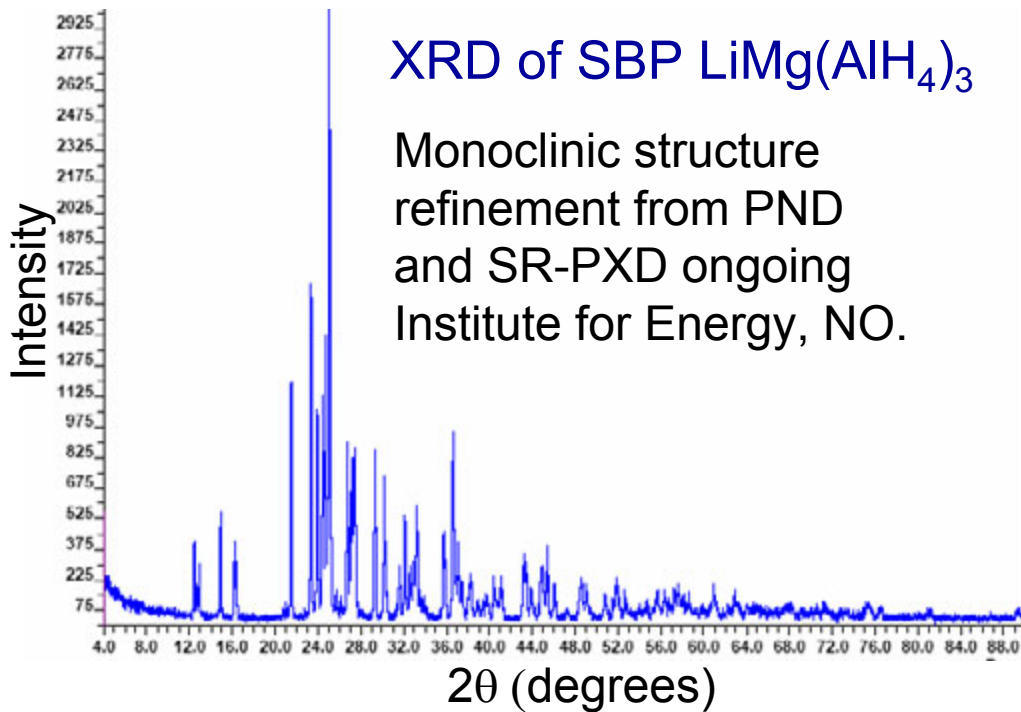
2) Screen for reversible H-exchange reactions.



3) Thermodynamically optimize H capacity.



# Synthesized and Confirmed $\text{LiMg}(\text{AlH}_4)_3$ Phase



## Elemental Analysis by Inductively Coupled Plasma

	Li wt.%	Mg wt.%	Al wt.%	Li/ Mg	Al/ Mg	(Li+Mg+Al) wt.%
$\text{LiMg}(\text{AlH}_4)_3$						
Measured	5.5	19.1	63.9	1.0	3.0	89.6
Theoretical	5.6	19.6	65.1	1.0	3.0	90.3

Trace organics confirmed by TGA/MS.

Possible  $\text{LiMg}(\text{AlH}_4)_3$  overall decomposition scenarios:

7.2 wt. % H theoretical capacity likely:

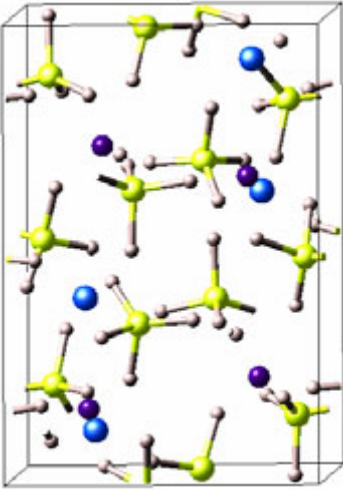


8.8 wt. % H theoretical capacity possible:

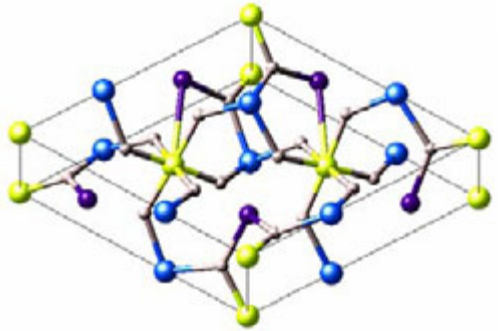


The quaternary phase,  $\text{LiMg}(\text{AlH}_4)_3$ , synthesized by SSP and SBP, has a powder density of  $\sim 0.11$  g/cc, and potential for 7.2-8.8 wt. % H and 0.019 kg  $\text{H}_2$ /L capacity.

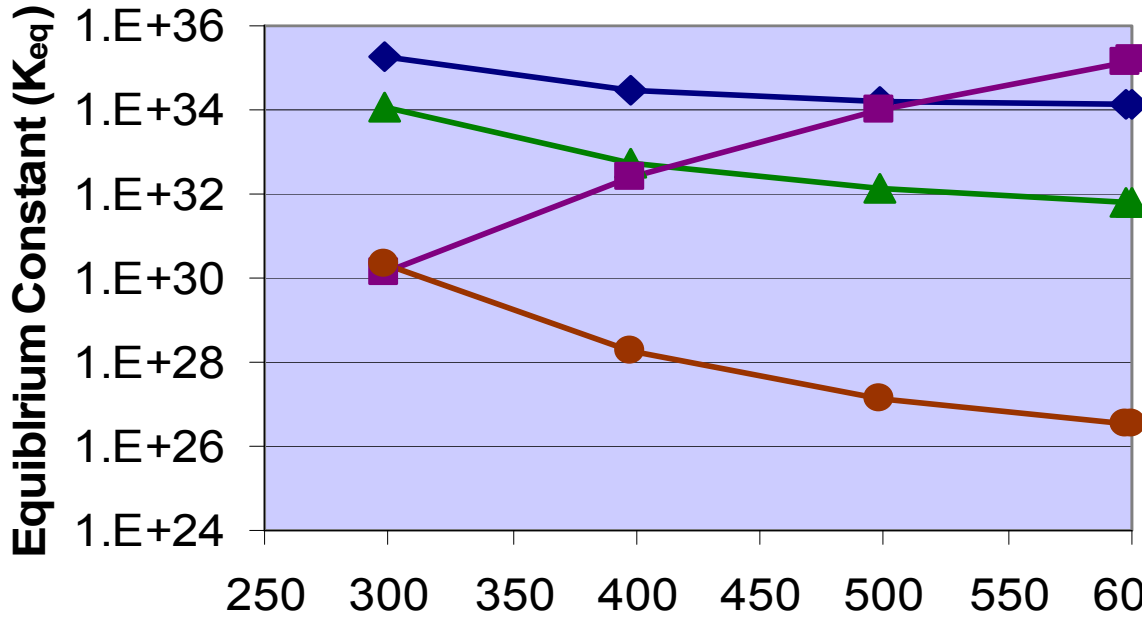
# High Reactivity Predicted for Li-Mg-Al-H Phases



**LiMg(AlH<sub>4</sub>)<sub>3</sub>**



**LiMgAlH<sub>6</sub>**

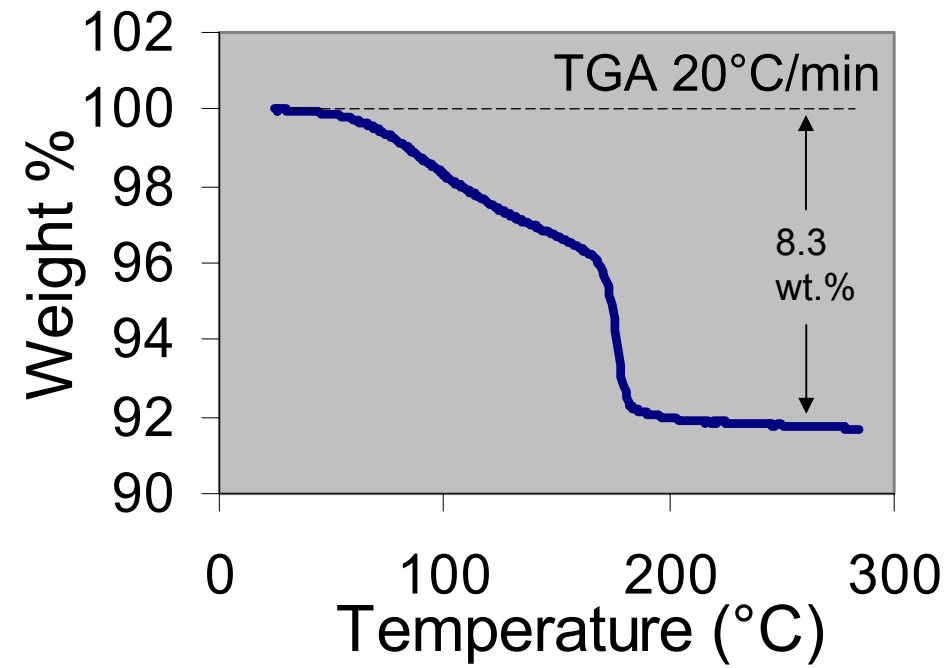
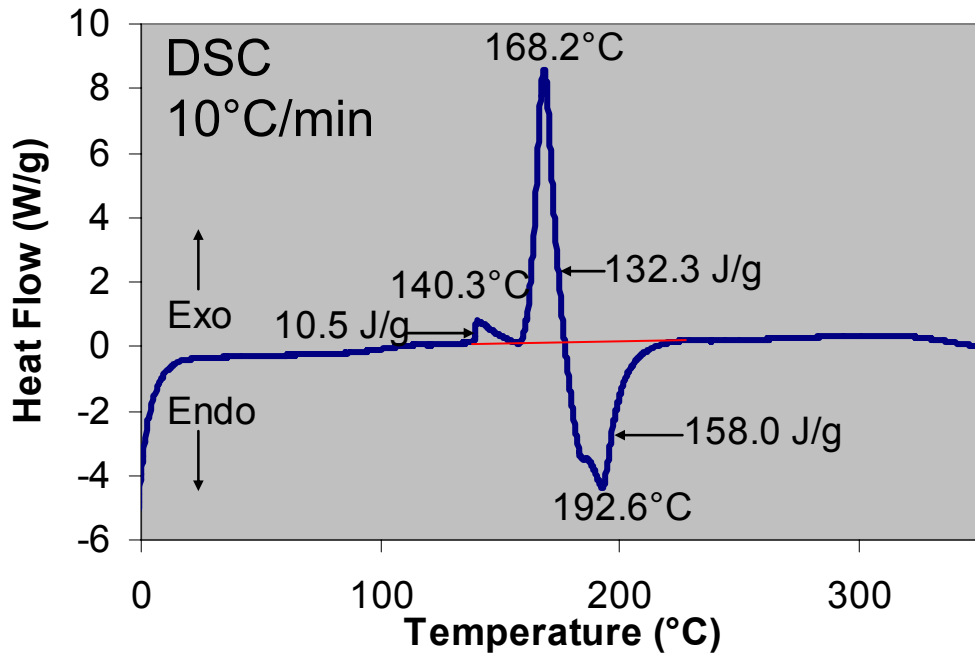


Predictions based on best candidate LiMg(AlH<sub>4</sub>)<sub>3</sub> and LiMgAlH<sub>6</sub> structures

Possible Disproportionation Reactions		$\Delta H_{dis}$ kJ/mole H <sub>2</sub>	wt. % H
—	$LiMg(AlH_4)_3 = LiH + MgH_2 + 3Al + 4.5H_2$	-2.8	7.2
—	$LiMg(AlH_4)_3 = \frac{1}{3}Li_3AlH_6 + MgH_2 + \frac{8}{3}Al + 4H_2$	-6.3	5.5
—	$LiMg(AlH_4)_3 = LiH + 0.06Al_{12}Mg_{17} + 2.29Al + 5.5H_2$	10.4	8.8
—	$LiMg(AlH_4)_3 = LiMgAlH_6 + 2Al + 3H_2$	-14.4	4.8

LiMg(AlH<sub>4</sub>)<sub>3</sub> decomposition predicted to be irreversible. Stable intermediate LiMgAlH<sub>6</sub> formation probable. Intermetallic formation predicted T > 240°C.

# Thermal Analyses Substantiate High $\text{LiMg}(\text{AlH}_4)_3$ H Capacity

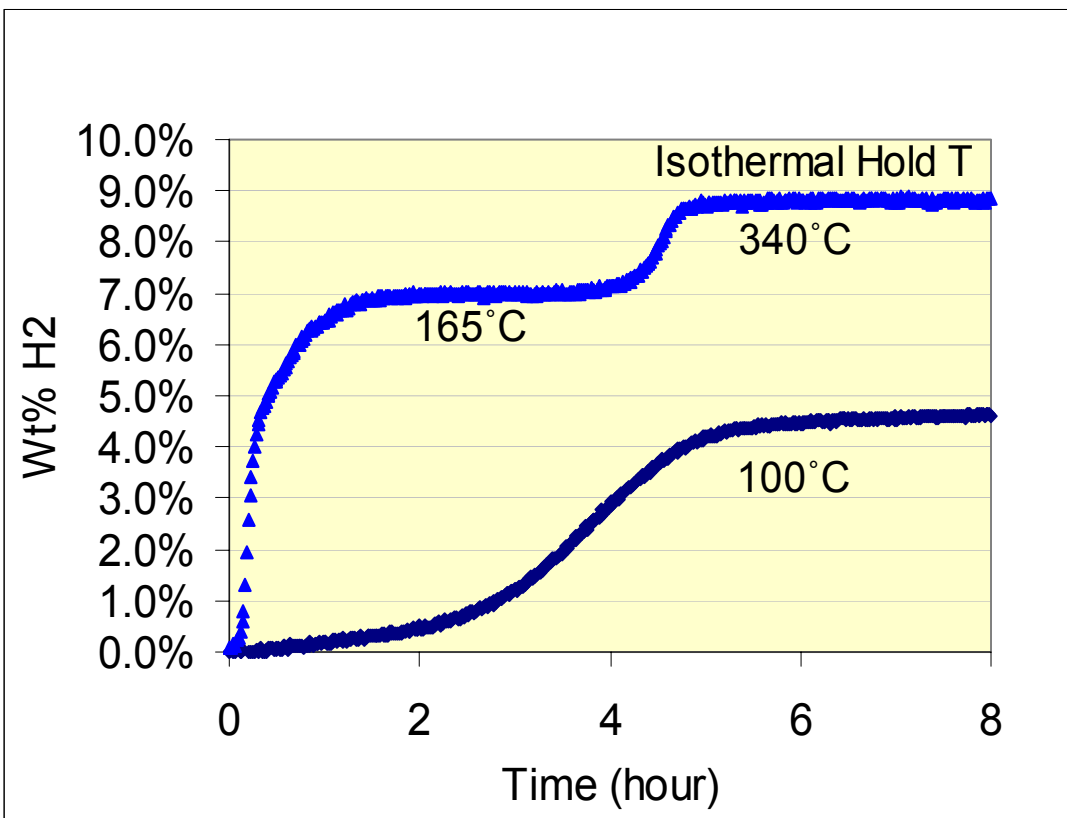


Possible overall decomposition reaction to release 8.8 wt. %  $\text{H}_2$ :  
 $\text{LiMg}(\text{AlH}_4)_3 = \text{LiH} + 0.06\text{Al}_{12}\text{Mg}_{17} + 2.29\text{Al} + 5.5\text{H}_2$

Uncatalyzed, unmilled  $\text{LiMg}(\text{AlH}_4)_3$  spontaneously decomposes to release 8 wt. %  $\text{H}_2$ .

# LiMg(AlH<sub>4</sub>)<sub>3</sub> Capacity Increase with Temperature

## LiMg(AlH<sub>4</sub>)<sub>3</sub> H<sub>2</sub> Desorption



## First Hour Average H Discharge Rate

Compound	100°C	150°C
LiMg(AlH <sub>4</sub> ) <sub>3</sub>	0.16%	6.79%
4%TiCl <sub>3</sub> catalyzed NaAlH <sub>4</sub>	2.10%	3.34%

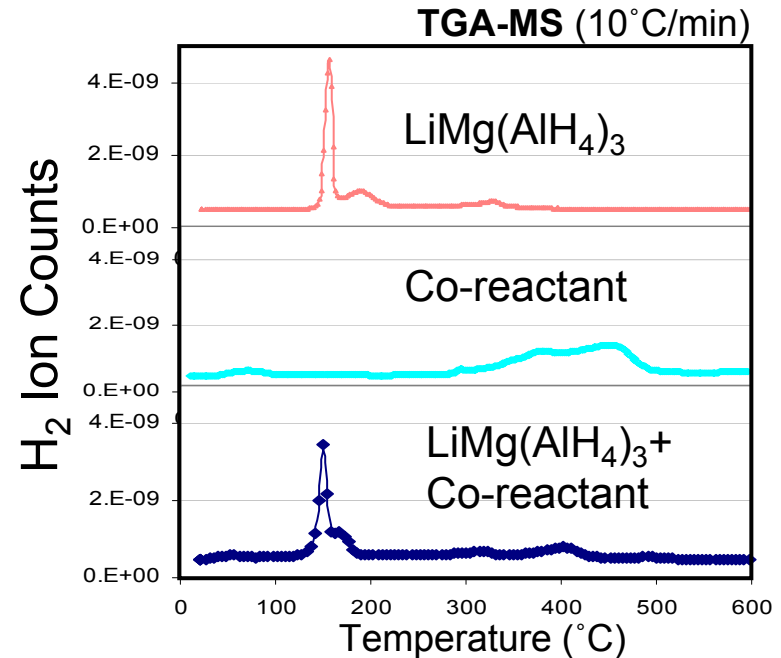
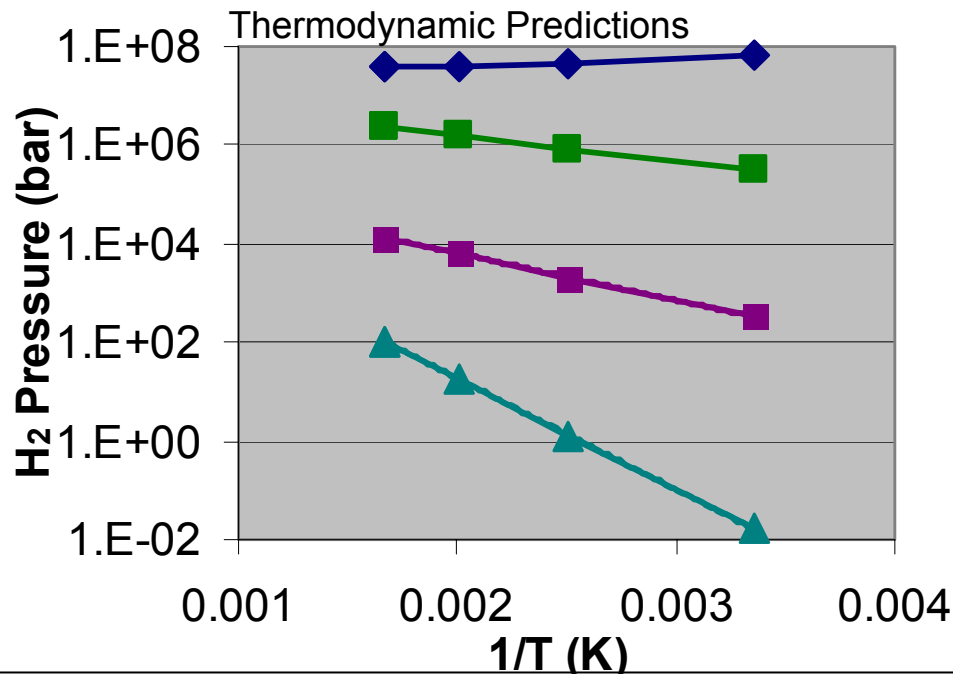
## Phases Identified by XRD

Temp	Phases
100°C	LiMgAlH <sub>6</sub> <sup>*</sup> , Li <sub>3</sub> AlH <sub>6</sub> , LiH, MgH <sub>2</sub> , Al
150°C	LiH, MgH <sub>2</sub> , Al
340°C	LiH, MgH <sub>2</sub> , Al <sub>3.11</sub> Mg <sub>2</sub> , Al

\* New peaks attributed to possible LiMgAlH<sub>6</sub> phase.

Capacity (7.2-8.8 wt. %H) depends on competitive stability of end-products.

# Designed $\text{LiMg}(\text{AlH}_4)_3$ Coupled Reactions

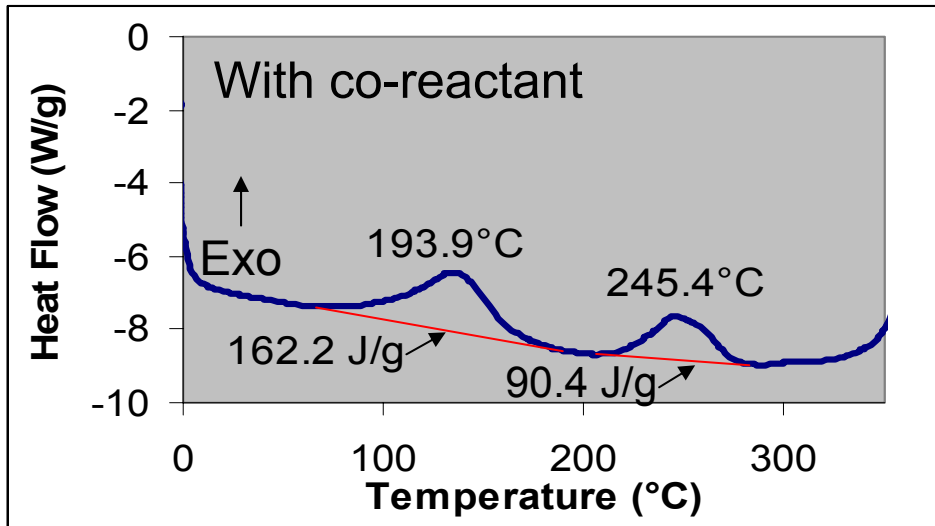
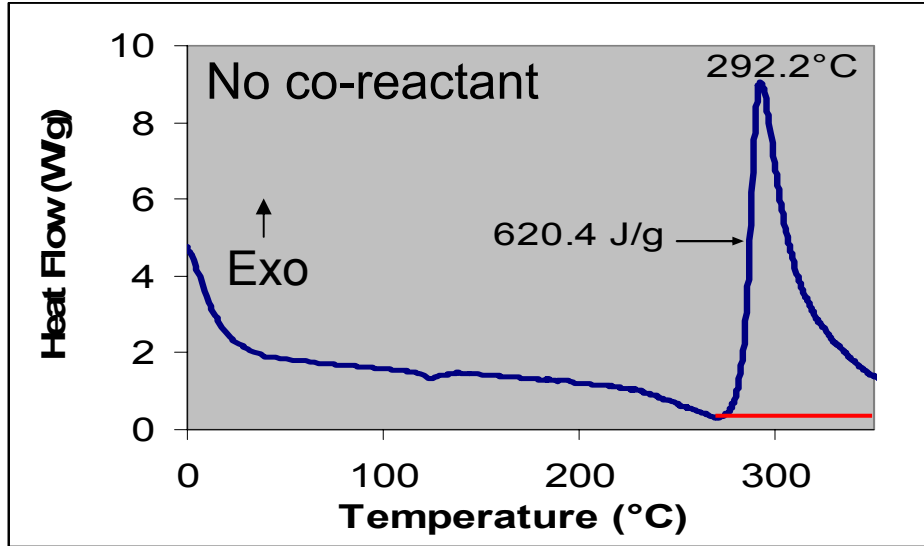


Reaction	Predicted $\Delta H_{\text{dis}}$ (kJ/mole $\text{H}_2$ )
◆ $\text{LiMg}(\text{AlH}_4)_3 = \text{LiH} + \text{MgH}_2 + 3\text{Al} + 4.5\text{H}_2$	-2.8
■ $\text{LiMg}(\text{AlH}_4)_3 = \text{LiH} + 0.06\text{Al}_{12}\text{Mg}_{17} + 2.29\text{Al} + 5.5\text{H}_2$	10.4
■ $\text{LiMg}(\text{AlH}_4)_3 + a\text{Reactant} = b\text{LiH} + c\text{Product} + d\text{Al} + >10 \text{ wt. } \% \text{H}_2$	18.3
▲ $\text{LiMg}(\text{AlH}_4)_3 + e\text{Reactant} = f \text{LiH} + g\text{Product} + h\text{Al} + >10 \text{ wt. } \% \text{H}_2$	43.2

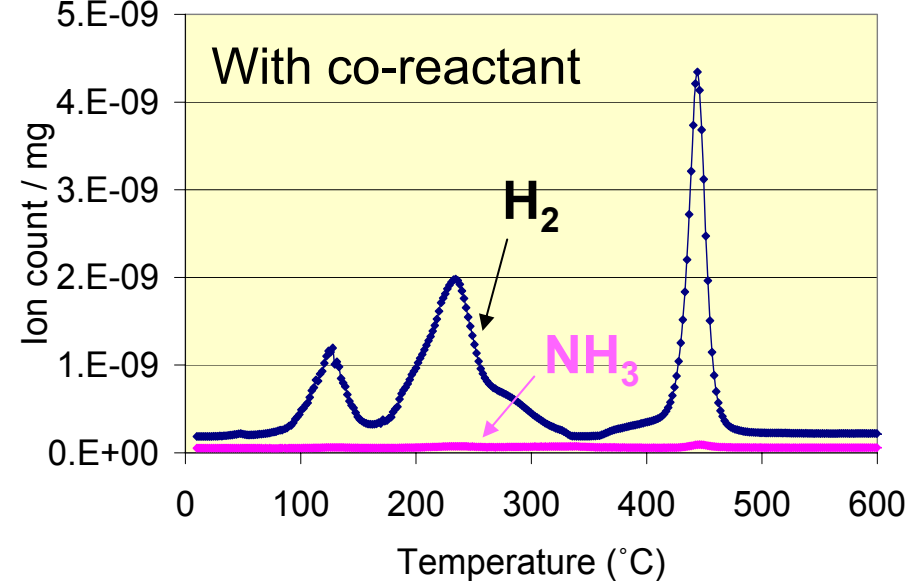
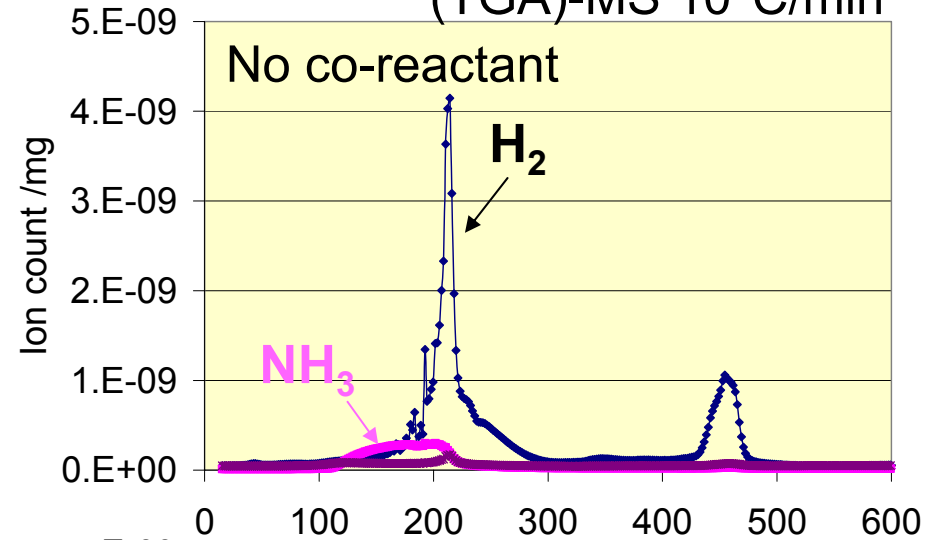
Thermodynamically surveyed & designed new reactions with Li-, B-, N-, Ca-, and Si-containing co-reactants to improve reversibility and capacity of  $\text{LiMg}(\text{AlH}_4)_3$  phase. 13

# Designed Reaction of New M-B-N-H System A

DSC 10°C/min



(TGA)-MS 10°C/min

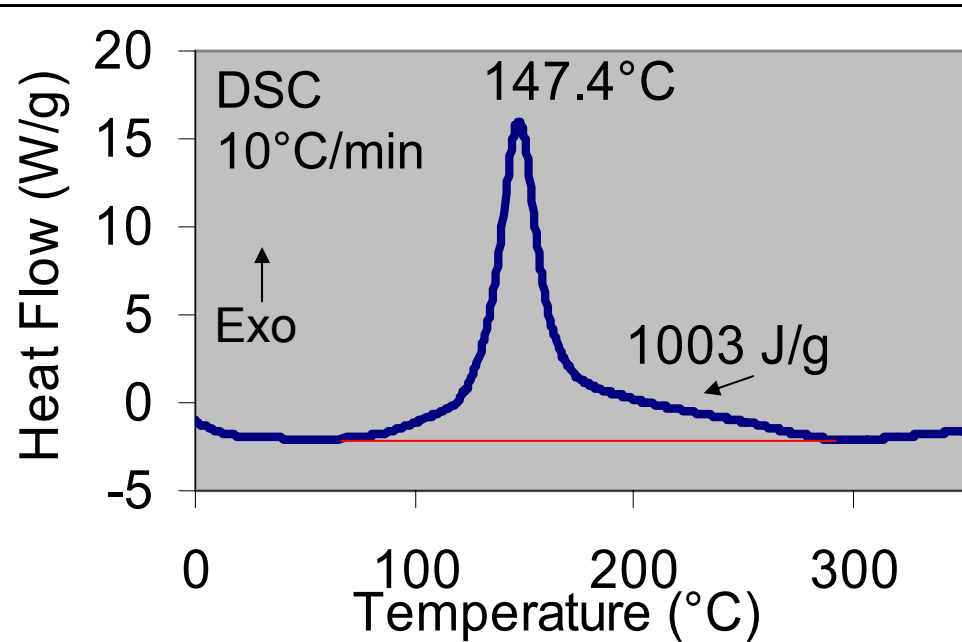


14

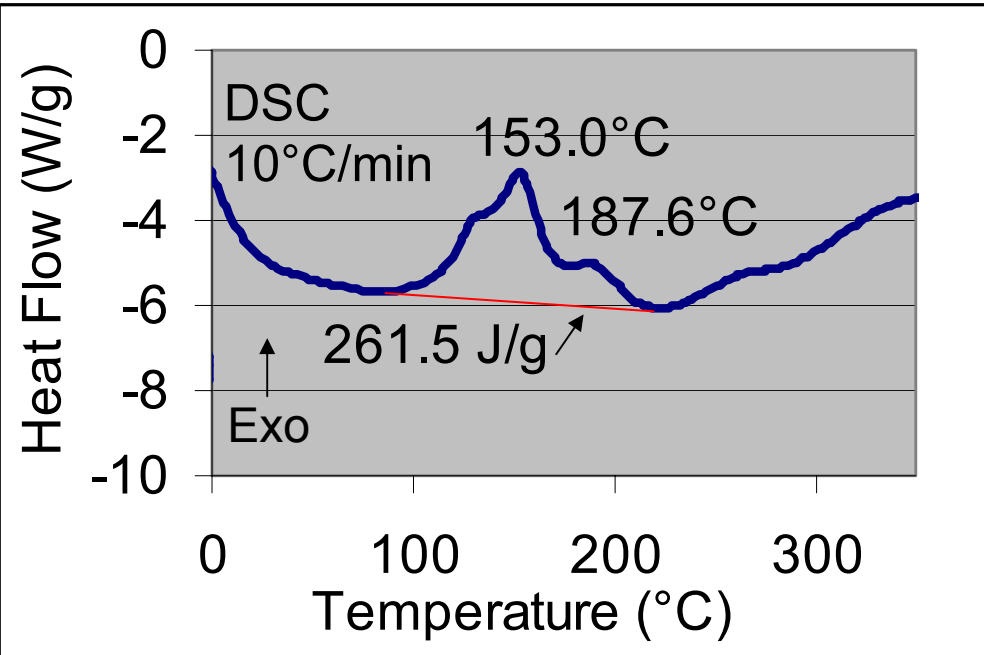
New system has powder density 0.40 g/cc, potential > 8 weight % H & 0.042 kg H<sub>2</sub>/L capacity. Co-reactant prevents NH<sub>3</sub> formation and reduces discharge onset T < 100°C.

# Modified Reactivity of New M-B-N-H System B

Original



Modified



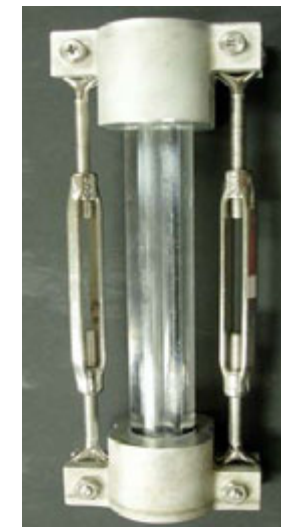
New system has powder density  $\sim 0.42$  g/cc, and potential  $> 8.0$  wt. % H &  $0.044$  kg  $H_2$ /L capacity with discharge onset  $T \sim 70^\circ\text{C}$ . Modification significantly reduced dehydrogenation exotherm and prevents undesired side-product formation.

# New Materials Have High Volumetric Capacity

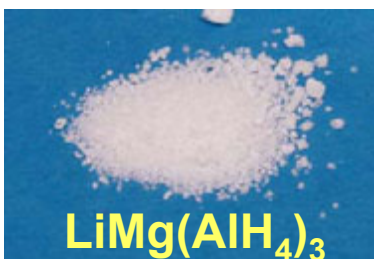
Compound	Theoretical Rev. H <sub>2</sub> wt fraction	Initial Density kg H <sub>2</sub> /liter	Vibratory Settling kg H <sub>2</sub> /liter	Enhanced Settling kg H <sub>2</sub> /liter
LiMg(AlH <sub>4</sub> ) <sub>3</sub> *	0.089	0.010	0.014	0.019
M-B-N-H System A *	0.088	0.033	0.041	0.042
M-B-N-H System B *	0.082	0.035	0.044	0.044
NaAlH <sub>4</sub> - best result **	0.056	0.026	0.041	0.042

\* Densification of as-received new materials, with no further processing.

\*\* 6% TiF<sub>3</sub>-NaAlH<sub>4</sub>, dehydrided, and paint shaken, close to “as-received.”



Subscale densification rig



These results realistically include the void space between powder particles. Best preliminary theoretical H density is >1/2 liquid H<sub>2</sub> density of 0.07 kg H<sub>2</sub>/liter. 16



# Material Progress Toward On-Board Hydrogen Storage System Targets

Storage Parameter	Units	2010 System Target	Material Result Through FY04	Material* Result FY05 to date
Specific Energy	kWh/kg (wt. % H <sub>2</sub> )	2.0 (6)	1.9 (5.6)	2.3-2.9** (7.0 -8.8)
Volumetric Energy Capacity	kWh/L (kg H <sub>2</sub> /L)	1.5 (0.05)	0.7 (0.02)	0.7-1.3** (0.02-0.04)
Desorption Temperature	°C	<100	120	150-340***

\* Relation of material results to system targets depends on system design, the material is nominally 50-60% of system mass, and capacities should be adjusted accordingly.

\*\* Enhanced settling technique on LiMg(AlH<sub>4</sub>)<sub>3</sub>, and M-B-N-H systems A & B.

\*\*\* Results for LiMg(AlH<sub>4</sub>)<sub>3</sub>. M-B-N-H Systems A and B have onset T's of <100°C. 17

Gravimetric and volumetric targets are feasible, but reversibility is a challenge.

# Summary of Accomplishments

Progress:

- 1) Compositional surveys-
  - synthetic surveys of 7 quaternary systems
  - virtual surveys of septenary & 4 co-reactant quaternary systems
  
- 2) Theoretical methodologies-
  - implemented coupled complex reaction strategy
  - integrated methods span from structure refinement, thermo. property prediction, reaction design, and thermo. optimization
  
- 3) Synthesis and characterization-
  - identified and evaluated three new high capacity systems
  - improved stability, lowered H discharge T, and prevented side-product formation by reaction design and complex modification
  
- 5) Volumetric capacities-
  - demonstrated significant progress towards volumetric targets

Other Collaborations: Participation in International Energy Agency, Task 17.  
Collaboration with Metal Hydride Center of Excellence.

# Future Plans

1) **Synthesize and screen high capacity complex hydrides**

2) **Design reversible reactions with newly synthesized candidates**

a) **Stabilize dehydrogenation**

- crystal refinement & thermodynamic predictions
- thermodynamic screening of co-reactions
- experimental evaluation of best co-reactions

b) **Tune H capacity**

- thermodynamic optimization of gravimetric capacity
- experimental performance tests

→final system selection October '06←

c) **Maximize kinetics**

- theoretically and experimentally screen activating agents for H<sub>2</sub> recharge

3) **Material Application and Synthesis Scale-up**

# Back-Up Slides

# Responses to 2005 Reviewers' Comments

“The approach does not give a clear indication about the selection of materials really suitable for the DOE goals.”

*-In response to reviewer recommendations, program scope was expanded beyond quaternary alanate systems. Program now includes Al, B, and N-based complexes and co-reactants based on the light elements, including first row transition metals.*

“PI should coordinated with UTRC System Prototype Project in order to better tailor research on metal hydride candidates.”

*-Due to common leadership and teaming for both programs, we are naturally able to apply our systems experience to realistically guide the development of new materials. Case in point: use of the densification rig to quantify new media volumetric capacity.*

“Would be good to expand collaborations, particularly with CoE’s.”

*-A collaboration has been in place over 8 months with the Metal Hydride Center of Excellence, to combine theory and experiment for the discovery of new titanium<sup>21</sup> based complex hydride compounds.*

# Publications and Presentations Since May 2005

S. M. Opalka, O. M. Løvvik, H. W. Brinks, P.W. Saxe, and B. C. Hauback, "Integrated experimental –theoretical investigation of the Na–Li–Al–H system," submitted for publication in J. Am. Chem. Soc., 4/24/06.

C. Qiu, S. M. Opalka, G. B. Olson, and D. L. Anton, "Thermodynamic modeling of the sodium alanates and the Na–Al–H system," submitted for publication in Int. J. Mat. Res., 1/30/06.

O. M. Løvvik and S. M. Opalka, "The stability of Ti in NaAlH<sub>4</sub>," accepted for publication in Physical Review Letters.

O. M. Løvvik, O. Swang, and S. M. Opalka, "Modelling alkali alanates for hydrogen storage by density-functional band-structure calculations," J. Mater. Res., 20(12) 3199-3213 (2005).

C. Qiu, S. M. Opalka, G. B. Olson, and D. L. Anton, "The Na-H System: from first principles calculations to thermodynamic Modeling," Int. J. Mat. Res. in press for June 2006.

S. M. Opalka, T. H. Vanderspurt, S. C. Emerson, D. A. Mosher, Y. She, X. Tang, and D. L. Anton, "Theoretical contributions towards the development of storage media and related materials for hydrogen processing", invited presentation, 2006 TMS Annual Meeting, San Antonio, Texas, March 13-16, 2006.

C. Qiu, G. B. Olson, S. M. Opalka, and D. L. Anton, "Thermodynamic modeling of sodium alanates and the effect of Ti," presentation, 2005 Fall MRS Meeting, Boston, MA, Nov. 29-Dec. 3, 2005.

O. M. Løvvik, O. Swang, S. M. Opalka, and P. N. Molin, "Alanates for hydrogen storage – density functional calculations of structural, electronic, and thermodynamic properties," invited presentation 2005 Fall MRS Meeting, Boston, MA, Nov. 29-Dec. 3, 2005.

S. M. Opalka, D. A. Mosher, X. Tang, D. L. Anton, R. Zidan, K. Shanahan, J. Strickler, F.-J. Wu, O. M. Løvvik, H. Brinks, and B. Hauback, "Complex hydride compounds with enhanced hydrogen storage capacity," presentation, SemiAnnual Workshop of the IEA Hydrogen Implementing Agreement Task 17 – Solid and Liquid State Hydrogen Storage at Tatehina, Japan, October 23-27, 2005.

C. Qiu, S. M. Opalka, D. L. Anton, G. B. Olson, "Thermodynamic modeling of sodium alanates," Materials for the Hydrogen Economy Symposium, presentation, Materials Science & Technology 2005, Pittsburgh, PA, September 25-28, 2005.

S. M. Opalka, O. M. Løvvik, H. W. Brinks, B. Hauback, P. W. Saxe, and D. L. Anton, "Combined experimental-theoretical investigations of the Na-Li-Al-H system," presentation, Materials Science & Technology 2005, Pittsburgh, PA, September 25-28, 2005.

# Critical Assumptions and Issues

- 1) Hydrogen storage media reactions must be reversible within the temperature range of 25-~100 °C, and pressure range of 1-100 bar.

*A wider operating window is possible, depending on H storage media:*  
*-Heat exchanger of an integrated H storage-PEMFC system may be redesigned to enable higher dehydrogenation temperatures to be used.*  
*-Composite hydrogen storage vessels capable of charging pressures of up to 300 bar, could be used without incurring a substantial weight penalty.*

- 2) Hydrogen storage media must be recharged on-board vehicle.

*-Materials discovery may lead to new media that can only be recharged off-board, due to specific reaction requirements. Irreversible new media may be considered as chemical hydride candidates.*

- 3) Hydrogen storage media comprises 60 % of total system weight, and 75 % of total system volume.

*-Actual contributions uniquely dependent on material characteristics.*