Discovery of Novel Complex Metal Hydrides for Hydrogen Storage through Molecular Modeling and Combinatorial Methods

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Project ID # ST12

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Overview

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Timeline

- Start date: 5/1/2004
- End date: 4/30/2007
- % Complete: 90

Budget

- Total project funding
  - DOE: $2,000,000
  - UOP: $2,910,618
  - Ford: $ 75,000
- FY06 DOE: $525,000
- FY07 DOE: $371,193

Barriers

- Barriers addressed (DOE-2010)
  - Useable H_2 Density
    - 2.0 kWh/kg & 1.5 kWh/L
  - H_2 Delivery Temperature Range
    - -40 to 85˚C
  - Cycle Life
    - 1000 Cycles

Partners

- Hawaii Hydrogen Carriers
- UCLA
- Ford
- Striatus

Objectives

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• **Overall**	• **Discovery of a complex metal hydride through Molecular Modeling and Combinatorial Methods which will enable a hydrogen storage system that meets DOE 2010 goals** • **Deliverables:** ◆ Optimized material ◆ Sample for independent testing at SWRI ◆ Documentation
• **2004/2005**	• **Validation and Demonstration of VHTS (Molecular Modeling)** • **Validation and Demonstration of Medium Throughput Combinatorial Tools** • **Downselect from Na, Li, Mg/AlH_4**
• **2005/2006**	• **Demonstration of High Throughput Combinatorial Tools** • **Identification of New Materials Approaching DOE Targets**
• **2006/2007**	• **Search for New Hydrogen Storage Materials using High Throughput Combinatorial Tools** • **Identification and Characterization of New Materials Meeting DOE Targets**

High Throughput vs. Traditional Approach

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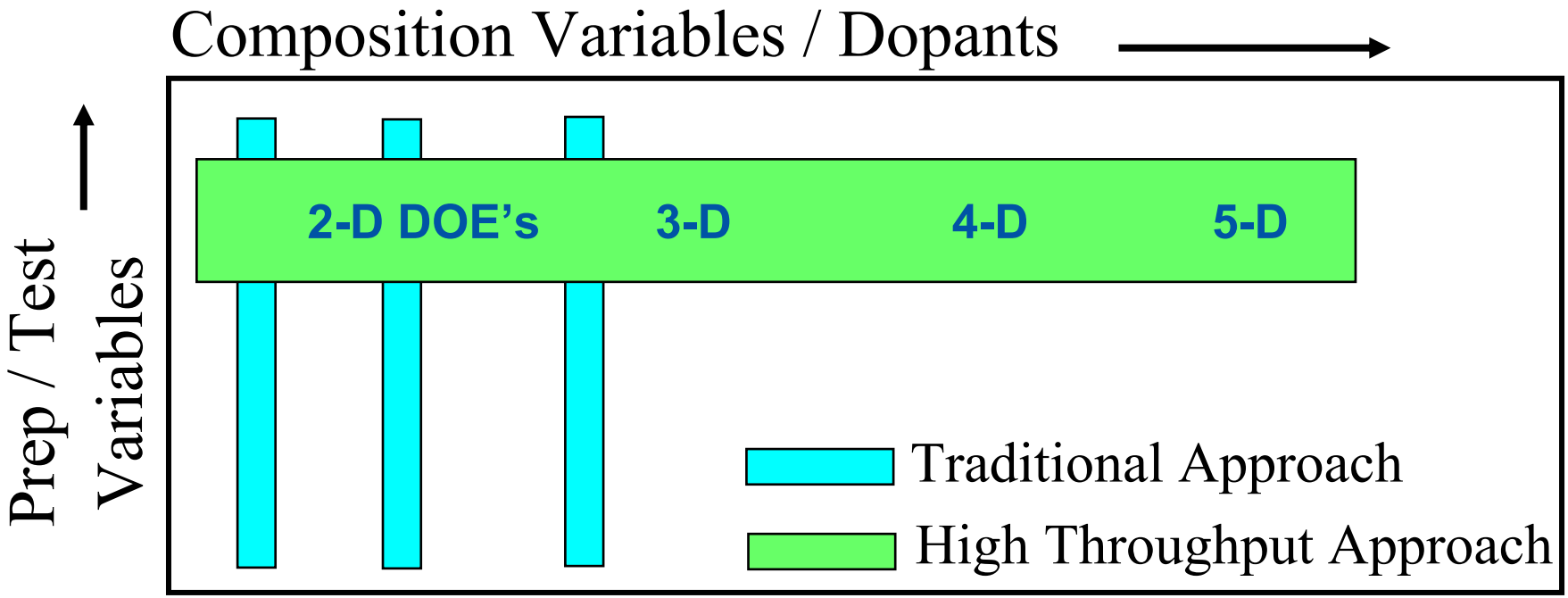
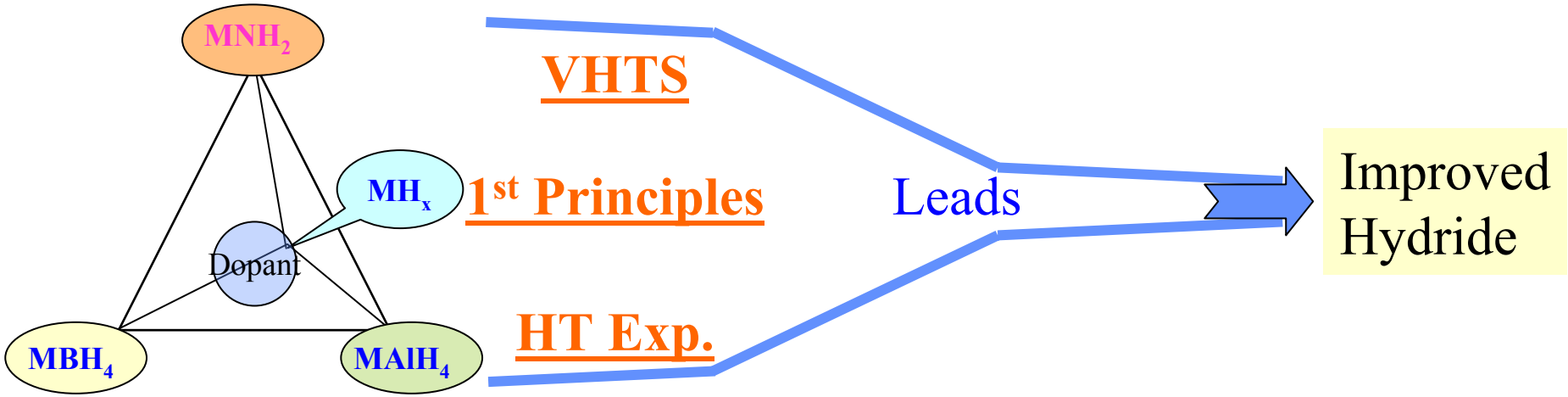


- **Total Hydride/Dopant/Process-Variable space is too large even for our Combi methods to fully explore, given time & resources.**
- **HT Tools are more difficult, costlier to develop/modify than Single-Sample tools, this limits Combi "Prep/Test" Space.**
  - **Synthesis methods, measurement conditions**
  - ***Selected milling approach based on state-of-the-art at project start***
- **Even with these limitations a vast phase space is available for searching by Combi methods.**
- **Goal of Combi is to find leads, additional measurements & characterization can be done using traditional methods.**

Overall Project Approach



- **Modeling**
  - Virtual High Throughput Screening, ~1000 compositions/month
  - DFT to predict new materials with favorable thermodynamics, refine leads
- **Combi Synthesis & Screening**
  - High Throughput (up to 48x)
  - Discrete, scalable sample preparation using ball-milling or solution-phase
- **Follow up on Leads:**
  - Characterization & modeling for increased understanding
  - Optimization, scale-up & multi-cycle testing

High Throughput Testing Protocol

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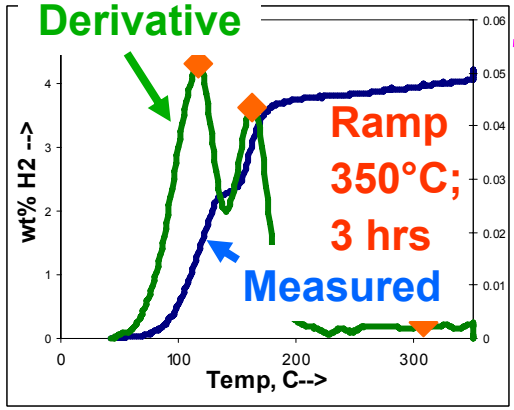
Desorb #3
350°C

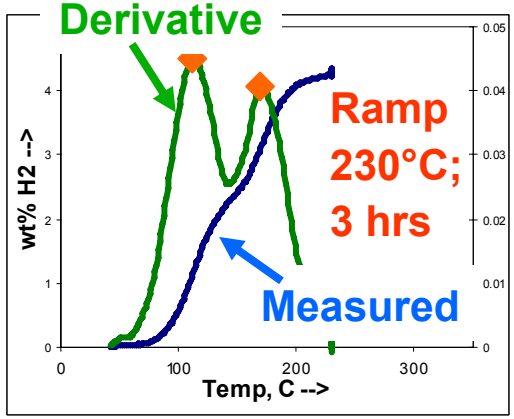
Rehydride #2
100°C, 120 bar

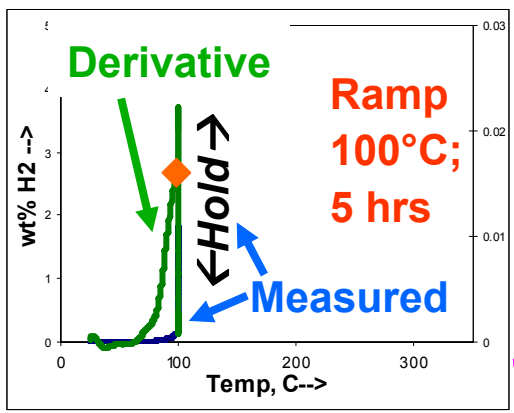
Desorb #2
230°C

Rehydride #1
120°C, 120 bar

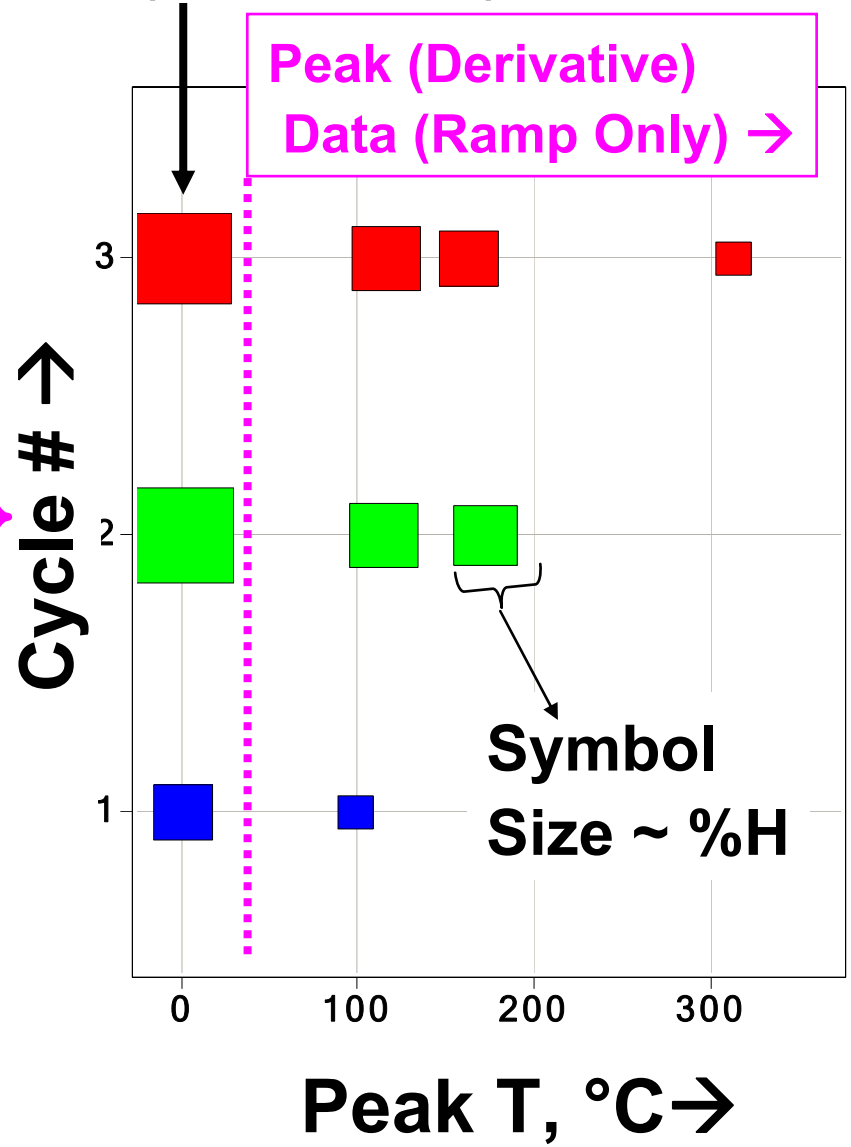
Desorb #1
100°C



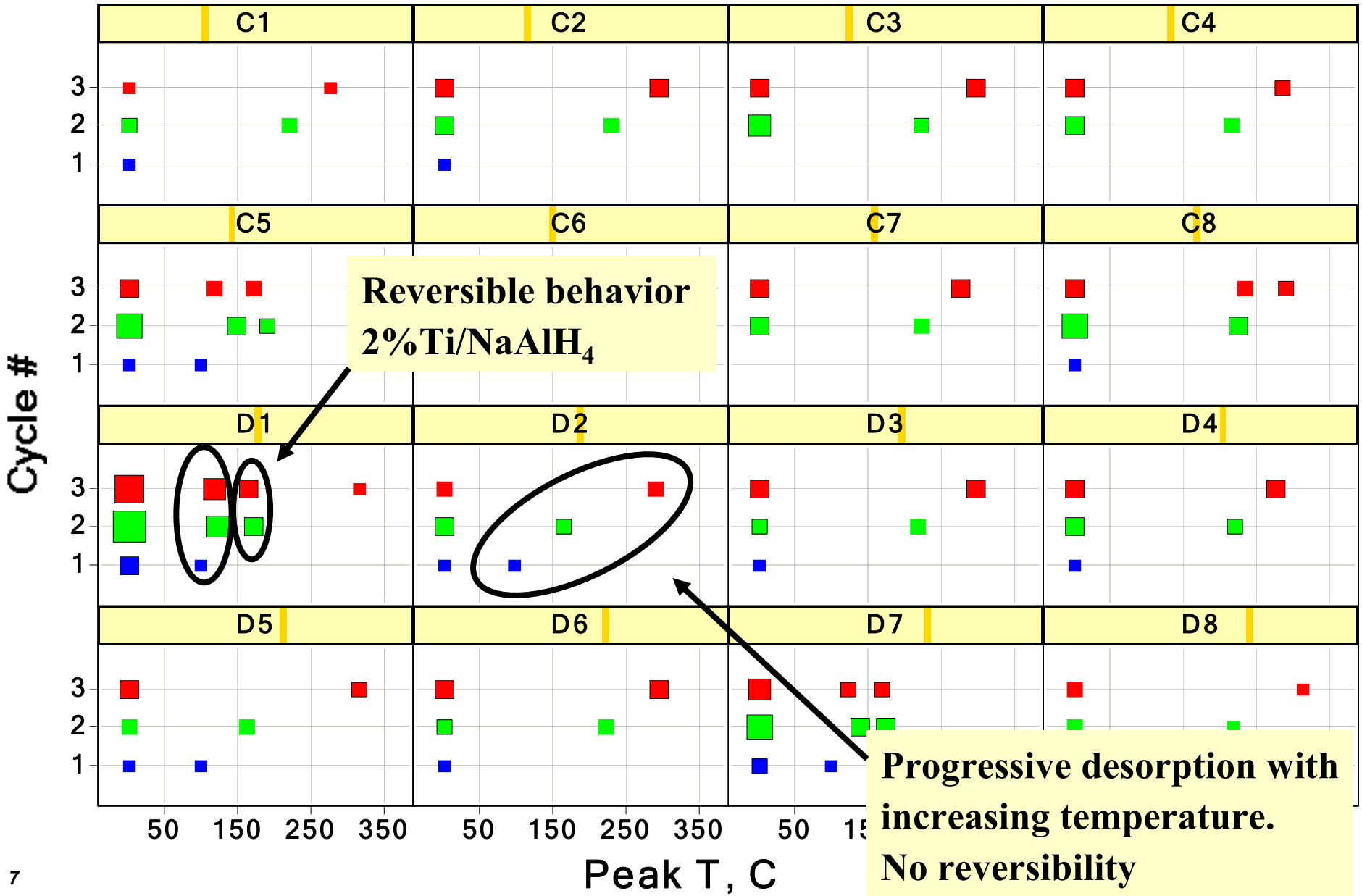




Total Desorbed wt%H,
(Ramp + Hold)



Multi-Cycle Visualization for one Run (16 of 48 Samples)



Technical Accomplishments 2006-2007

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Since last Peer Review:

- **Nearly 900 samples prepared, characterized by XRD, and tested**
  - **16 Ternary / quaternary / pentenary phase diagrams investigated**
  - **Hydrogen-containing components include $LiNH_2$ and $LiBH_4$**
  - **Metal components include Li, Na, Mg, Al, Ti, Zr, Mn, V, Cr, Mo, Co, Ni, Cu, Zn, and some mixtures**
- **High Throughput Synthesis System on line**
  - **Doping Studies carried out**
    - 2 different base materials (non - alanates)
    - 15 different dopants

$NaNH_2$ – $NaBH_4$ – MgH_2 Phase Diagram

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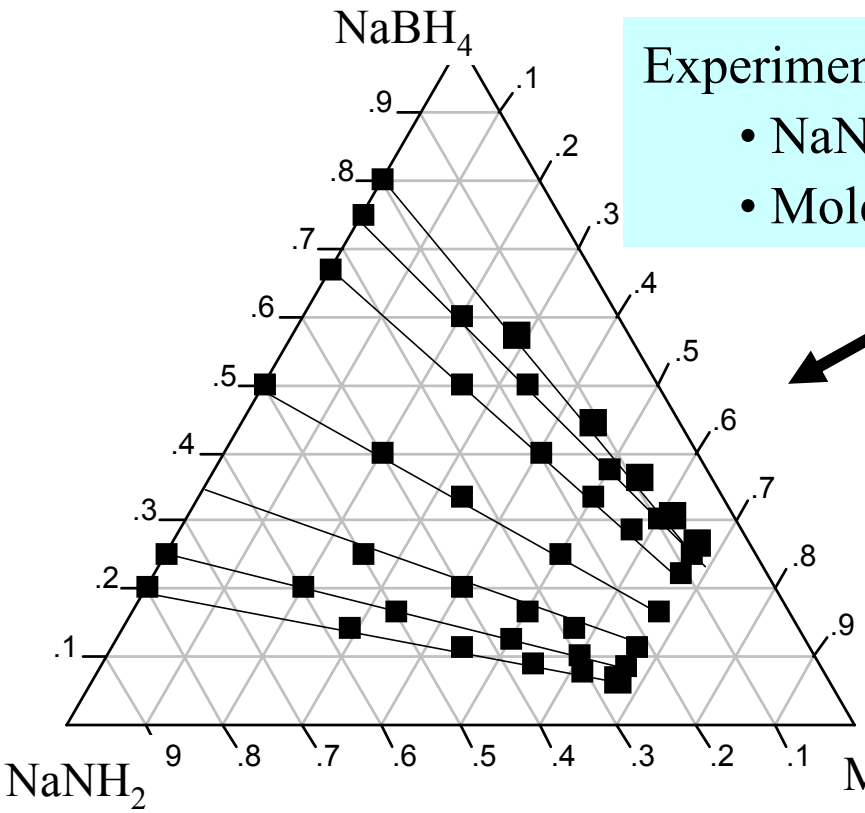
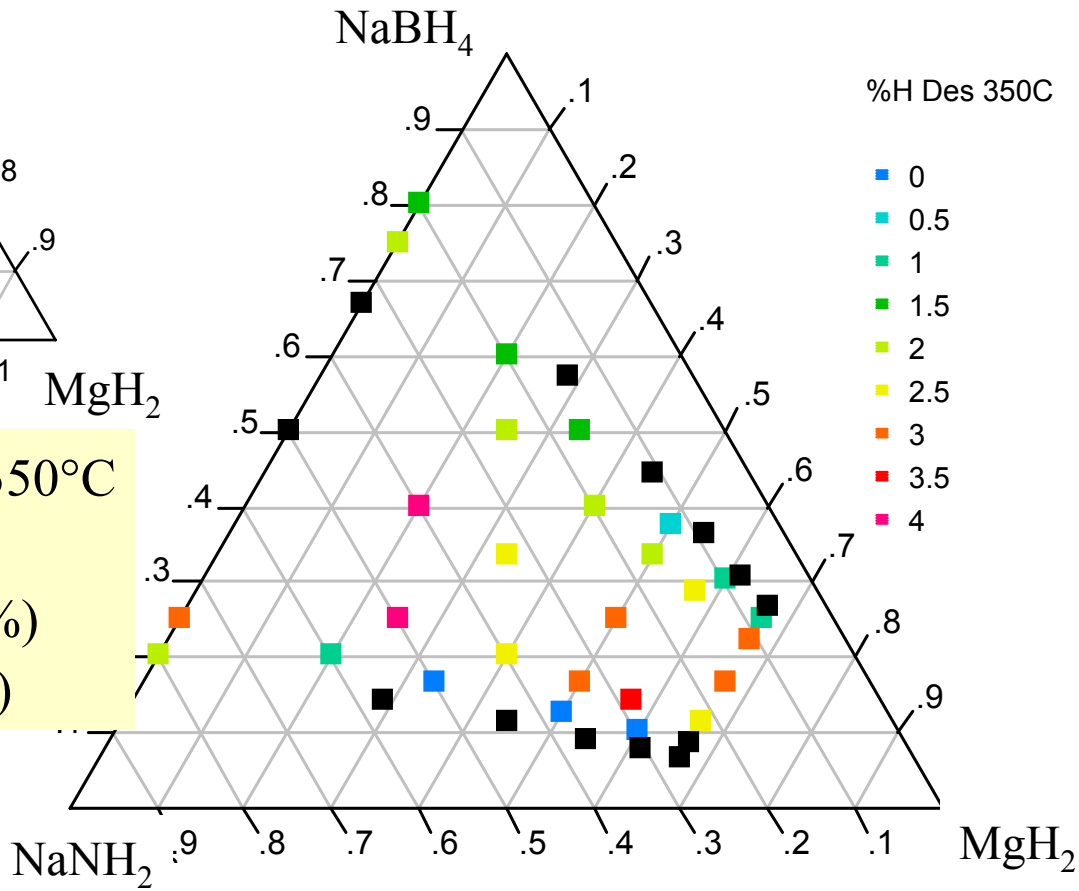


Experimental Design for $NaBH_4$-$NaNH_2$-MgH_2 System

- $NaNH_2/NaBH_4$ = 4, 3, 2, 1, 0.33, 0.25, 0.2
- Mole fraction MgH_2 varies from 0 – 0.66

Cumulative results for desorption to 350°C

- Up to 4.5 wt. % H_2 desorption
- 2 $NaBH_4$–1 $NaNH_2$–1 MgH_2 (4.49 %)
- 1 $NaBH_4$-1 $NaNH_2$-1MgH_2 (4.25 %)



$NaNH_2 – NaBH_4 – MgH_2$ Phase Diagram

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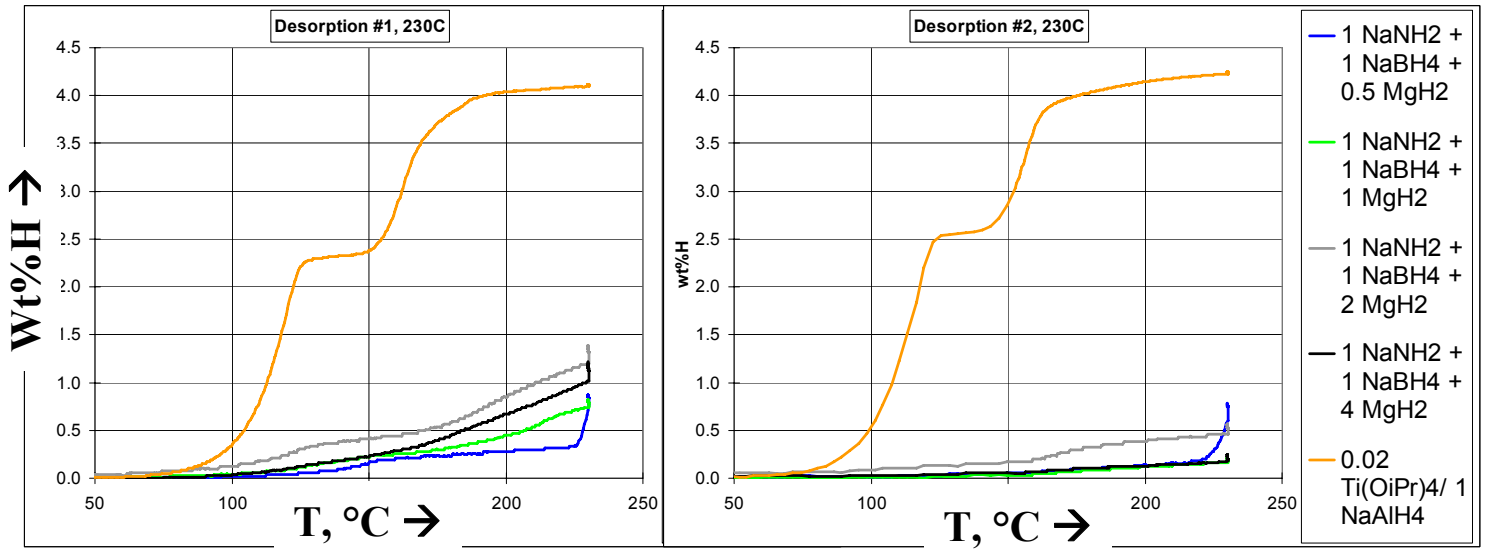
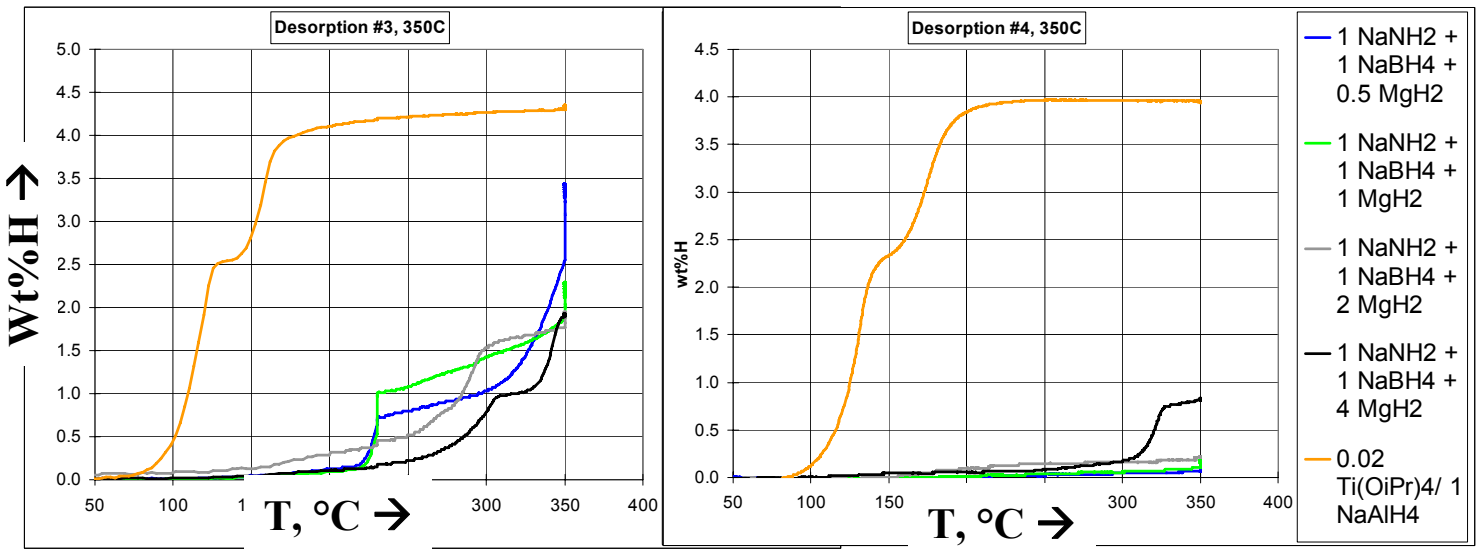
- First desorption often <2 wt%H by 250°C, 3 – 4 wt.% H_2 by 350°C
- Low reversibility for samples upon multiple desorption runs

2 Cycles 230°C



2 Cycles 350°C



Transition Metal – Borohydride – Amide Phase Diagrams

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Staged approach – increasing complexity:

- Synthesize simple Transition Metal (TM) borohydrides or amides
  - e.g., $TMCl_x + x\ LiBH_4 \longrightarrow TM(BH_4)_x + x\ LiCl$
- Stabilize TM borohydrides/amides with alkali:
  - e.g.,$TMCl_x + x+2\ LiBH_4 \longrightarrow Li_2TM(BH_4)_{x+2}$
- Expand to complex mixtures of borohydrides + amides:
  - e.g., $TMCl_x + y\ LiBH_4 + z\ LiNH_2 \longrightarrow$

    $Li_{(y+z-x)}TM(BH_4)_y(NH_2)_x + x\ LiCl$
- Facilitate transport by including $Li(NH_2)_3BH_4$ which is known to melt
- These materials may dehydride to form complex as yet unknown imides, nitrides, borides, or mixtures of such

$LiNH_2$ – $LiBH_4$ – LiH – VCl_3 Phase Diagram

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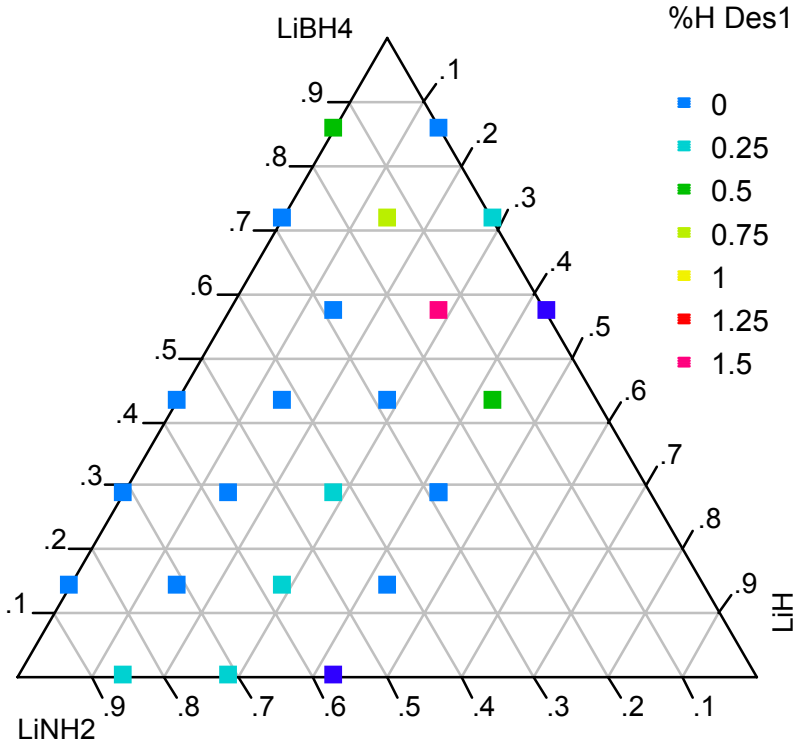
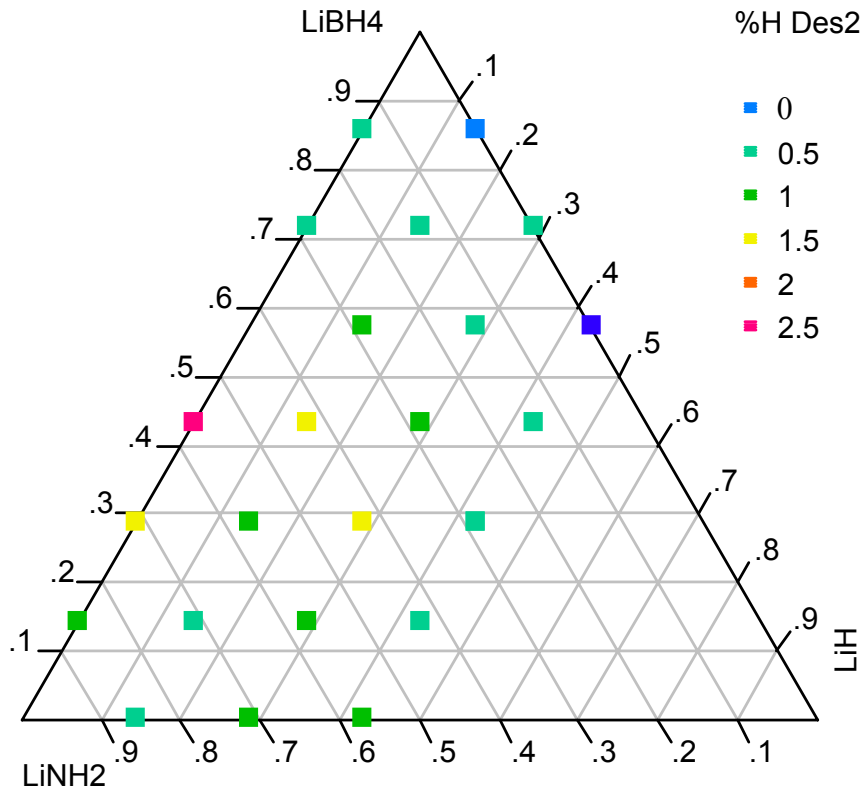
- Three desorption cycles: 100°C, 230°C, 350°C
- $VCl_3/(LiNH_2 + LiBH_4 + LiH) = 0.125$
- Hydrogen release sometimes observed during milling

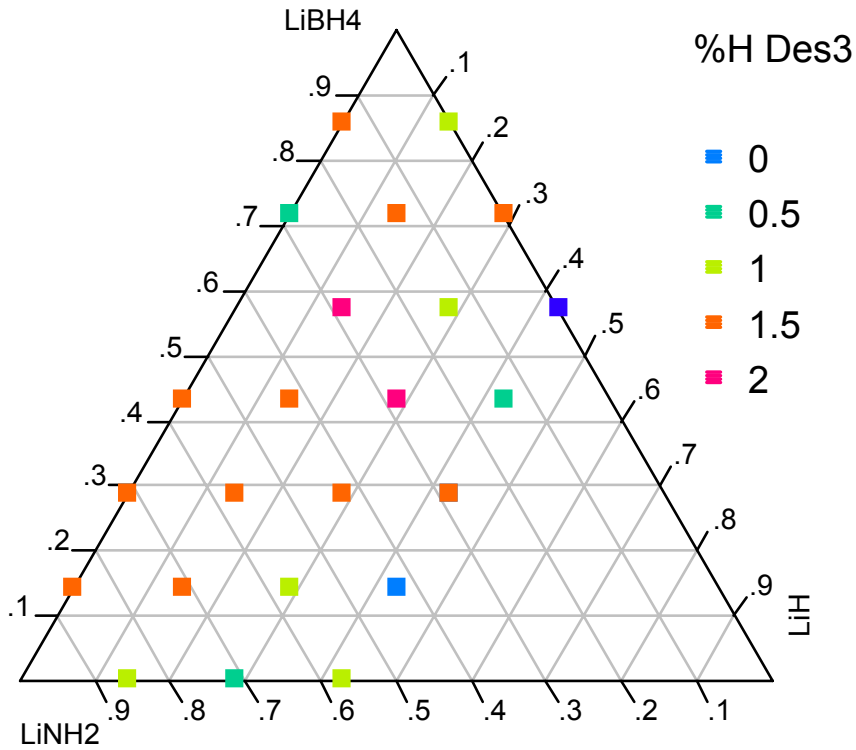


Desorption 1, 100°C

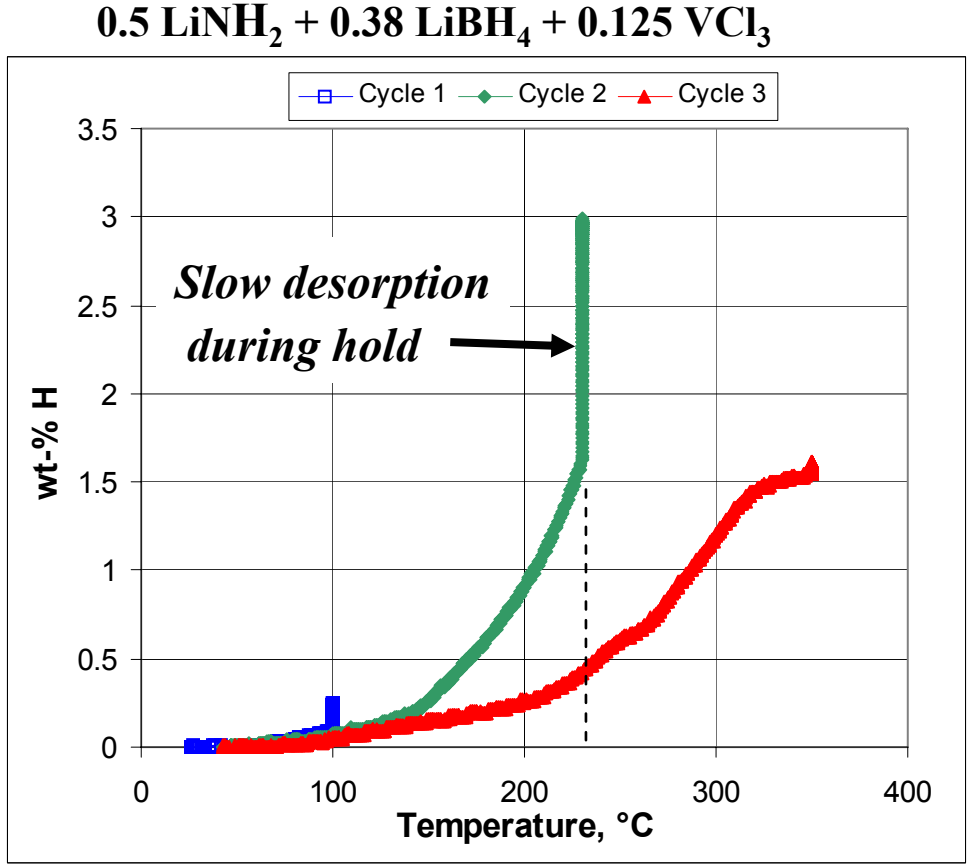


Desorption 2, 230°C

$LiNH_2$ – $LiBH_4$ – LiH – VCl_3 Phase Diagram



Desorption 3, 350°C



Following a single composition, 0.5 $LiNH_2$ – 0.375 $LiBH_4$ – 0.125 VCl_3 through the desorption cycles illustrates the general trend of poor reversibility often observed

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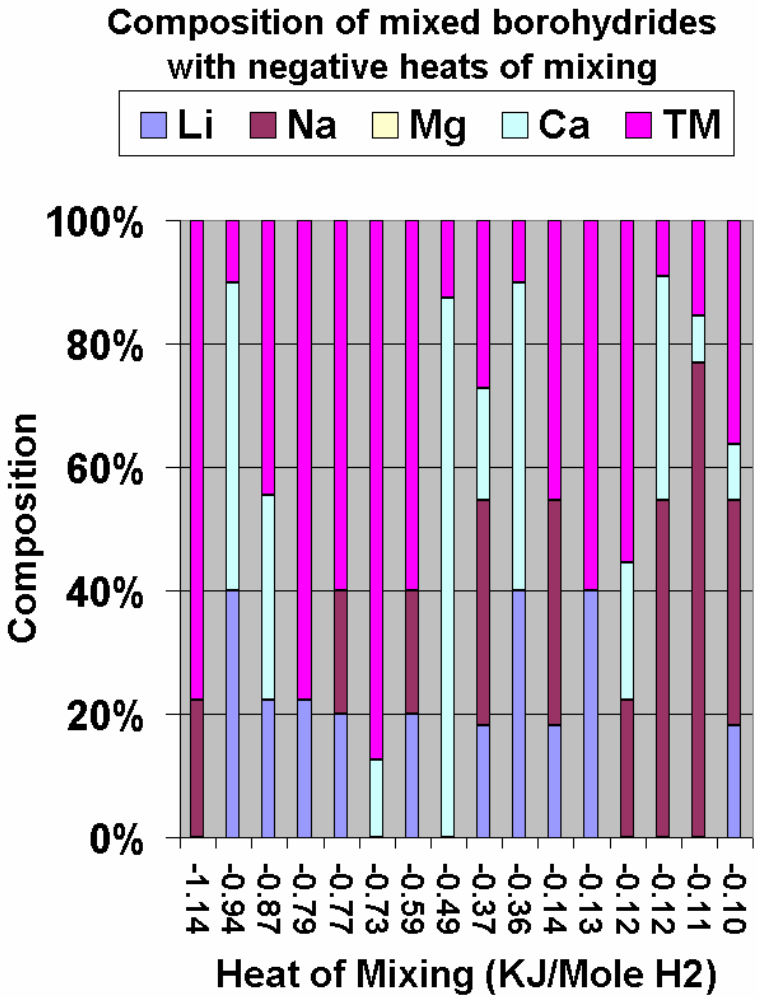
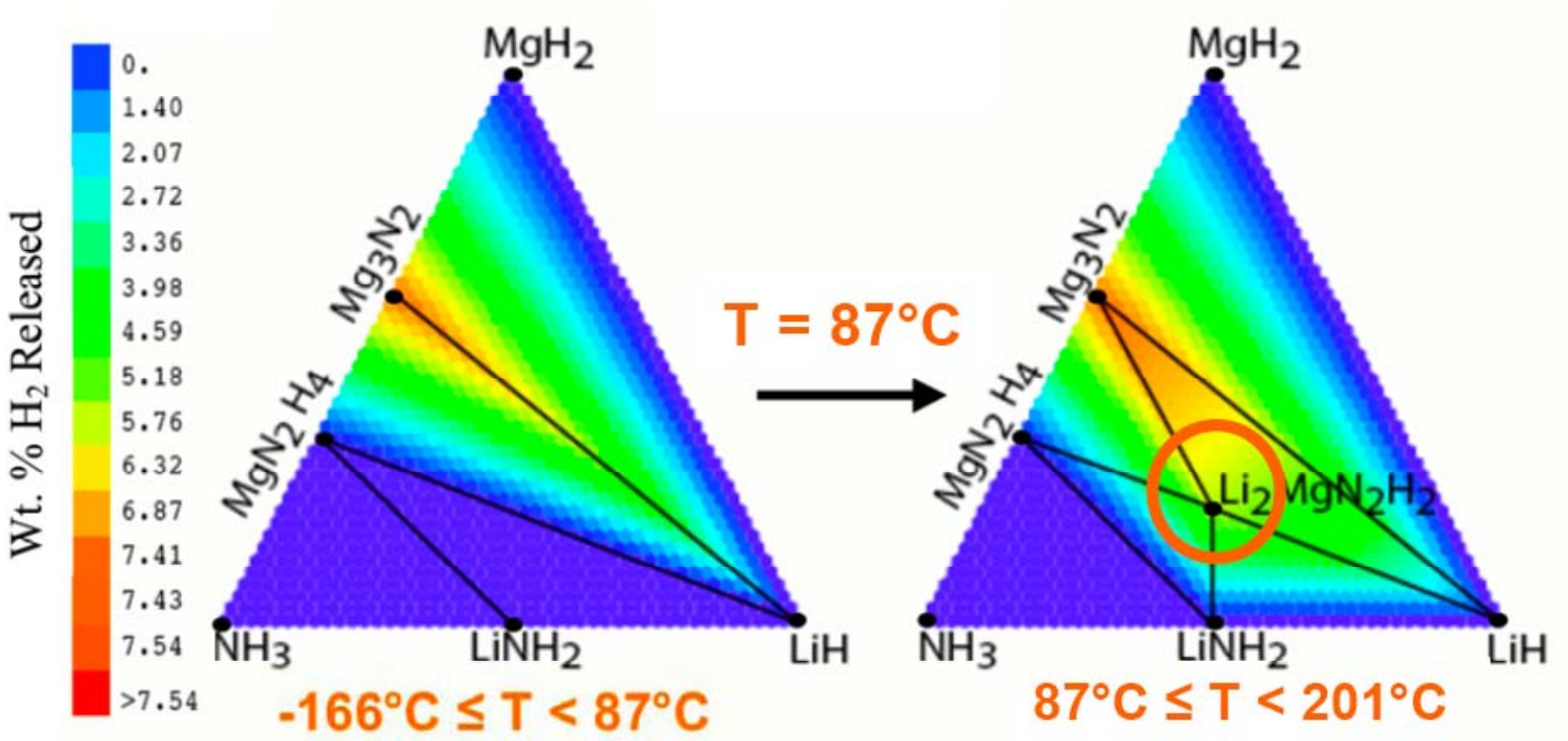
VHTS Screening of Alkali, Alkaline-Earth and Transition Metal Borohydrides



- Screened ~1200 pentenary Borohydide mixtures
- Heats of mixing not large enough to stabilize any mixture versus dehydriding
  - Need an additional 15 kJ/mol*H_2 to stabilize mixtures

First-principles phase diagrams of complex hydrogen storage mixtures



$$2\ LiH + Mg(NH_2)_2 \rightarrow Li_2Mg(NH)_2 + 2\ H_2 \qquad 5.6\ \text{wt. \%}\ H_2$$

Tests for the quaternary Li-Mg-N-H system show good agreement with experiment. Has been applied to the Li-Mg-B-N-H system.

We can pinpoint those compositions and reactions which show the greatest promise for further experimental study.

First-Principles phase diagrams – Key Advantages

1. Can identify all thermodynamically favored reactions in a given multicomponent system with known structures (e.g. Li-Mg-N-H).

2. Can determine thermodynamically favored reaction pathways and end products for a given mixture.

3. Can determine which destabilized reactions are thermodynamically reversible. For instance,

$$LiNH_2 + MgH_2 \leftrightarrow LiMgN + 2H_2 \qquad (A \rightarrow E)$$

Alapati et al., J. Phys. Chem. 110, 8769 (2006)

will instead proceed via intermediate steps:

$$LiNH_2 + MgH_2 \rightarrow$$

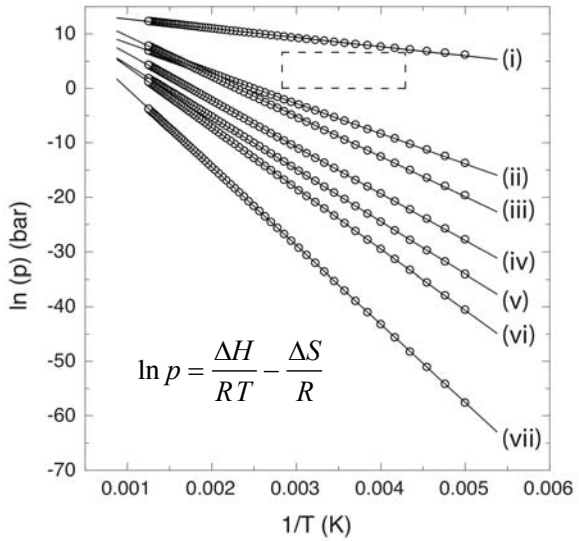
$$(A \rightarrow B) \quad LiH + \tfrac{1}{2}Mg(NH_2)_2 + \tfrac{1}{2}MgH_2 \rightarrow$$

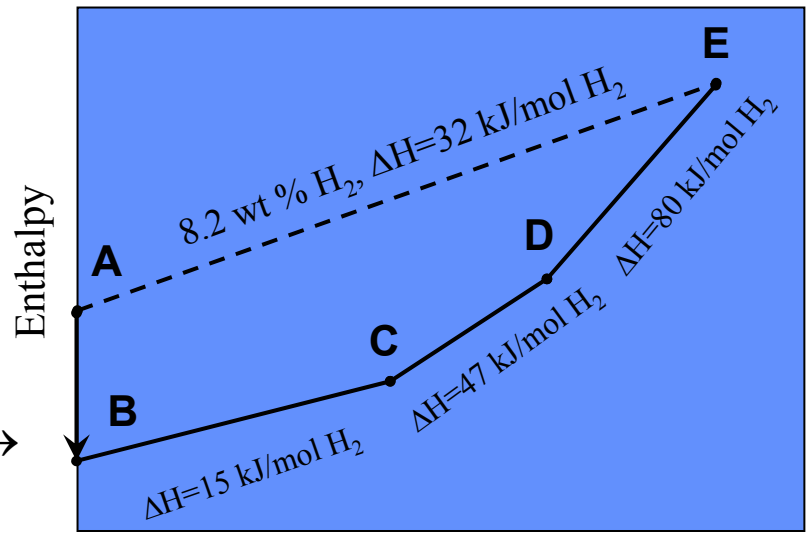
$$(B \rightarrow C) \quad LiH + \tfrac{1}{4}Mg(NH_2)_2 + \tfrac{1}{4}Mg_3N_2 + H_2 \rightarrow$$

$$(C \rightarrow D) \quad \tfrac{1}{2}LiH + \tfrac{1}{4}Li_2Mg(NH)_2 + \tfrac{1}{4}Mg_3N_2 + \tfrac{3}{2}H_2 \rightarrow$$

$$(D \rightarrow E) \quad LiMgN + 2H_2$$

All reactions in the Li-Mg-N-H system





Project Summary

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- VHTS and First Principles modeling capabilities
  - Predicted alanate mixtures do not meet DOE targets
  - Identified several potential reactions with desired energetics
- Medium Throughput Assay (8 Reactors)
  - Investigated $LiAlH_4$-$NaAlH_4$-$Mg(AlH_4)_2$/Ti phase diagram
  - Investigated rehydriding reactions with Al, alkali and alkaline earth hydrides/Ti
  - Confirmed modeling results that alanates do not meet DOE targets
  - Also applied to non-alanate studies
- High Throughput Assay (48 Reactors)
  - Measured multi-cycle capacities 1000+ samples in many phase diagrams
  - Investigation of $LiNH_2$-$LiBH_4$-MgH_2 phase diagram found kinetic enhancement due to the formation of $Li_4(NH_2)_3BH_4$, which melts during desorption/absorption
- High Throughput Synthesis System
  - Scan of 15 dopants carried out on two base materials
- Mixtures of Complex Hydrides have yielded few new compounds, and those found have not met DOE targets for hydrogen storage.

Lessons Learned

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- Combinatorial approach works very well for finding optimum compositions in multinary phase diagrams
- High throughput equipment is more complex, takes longer to develop than single-sample methods
- Medium Throughput Assay (8 Reactor)
  - [+] Worked well
- High Throughput Assay (48 Reactor)
  - [+] Screened ~ 1000 experimental samples (+ refs. in every run)
  - [-] Labor intensive - high maintenance
  - [-] Sample size too small for characterization after test
- High Throughput Synthesis System
  - [+] Wide synthesis capability
  - [-] Development, shakedown
  - [-] Accurate handling of milled powders
  - [-] Sample transfer equipment

Lessons Learned, cont.

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- **Virtual High Throughput Screening**
  - [+] When models ready, very fast & covers high-dimensional space
  - [+] Even negative results are valuable (after experimental validation): give confidence to move focus elsewhere
  - [+] Not limited to known structures
  - [+] Provided insight to alanates: heats of mixing too low to yield mixtures with desired thermodynamics
  - [-] Development of new force fields takes a long time
- **First Principles Modeling**
  - [+] Provided insights into thermodynamics of $LiNH_2$ – MgH_2 – $LiBH_4$ system
  - [+] Generated several new leads with promising thermodynamics
  - [-] Experimental follow up disappointing – kinetics?
  - [-] Computationally expensive, dev. of high-throughput algorithms
  - [-] Accuracy highest for known structures
- **Modeling Needs:**
  - Ability to predict kinetics & dopant effects