

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



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Project ID #
ST12

UOP LLC

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UOP
A Honeywell Company

This presentation does not contain any proprietary or confidential information

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

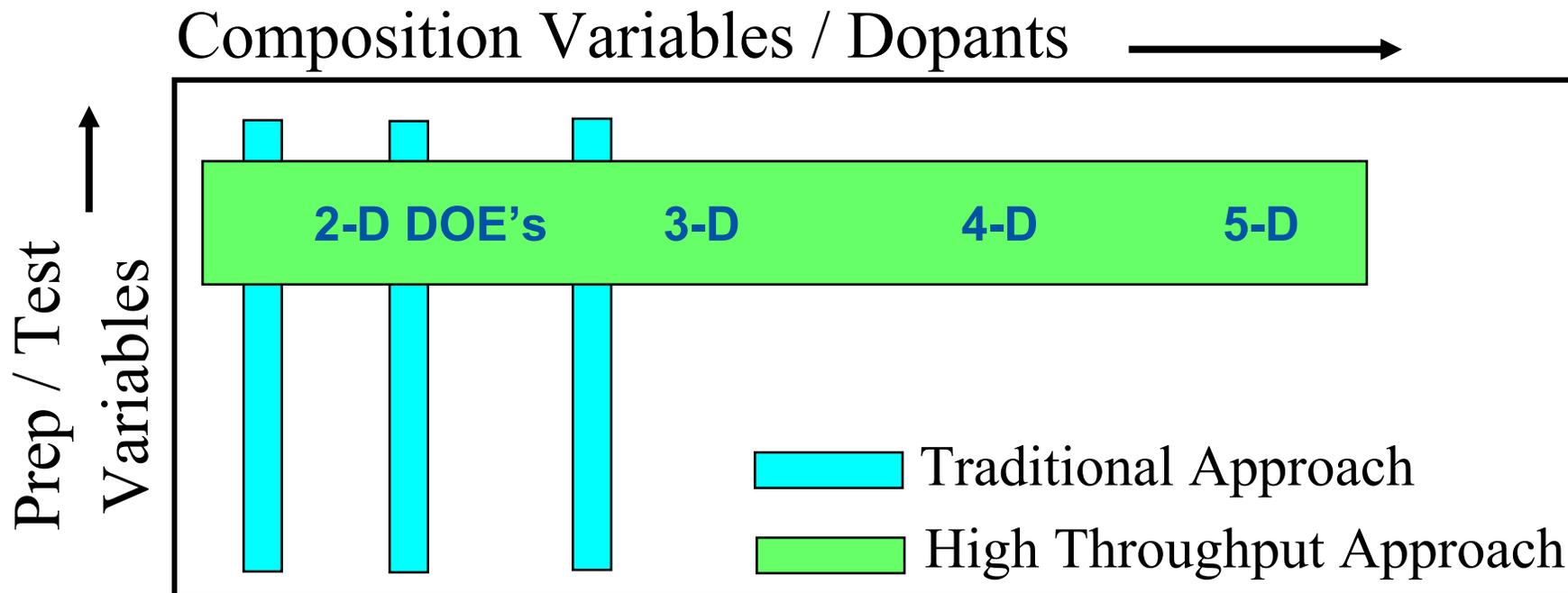
- **Barriers addressed (DOE-2010)**
 - **Useable H₂ Density**
 - 2.0 kWh/kg & 1.5 kWh/L
 - **H₂ Delivery Temperature Range**
 - -40 to 85°C
 - **Cycle Life**
 - 1000 Cycles

Partners

- **Hawaii Hydrogen Carriers**
- **UCLA**
- **Ford**
- **Striatus**

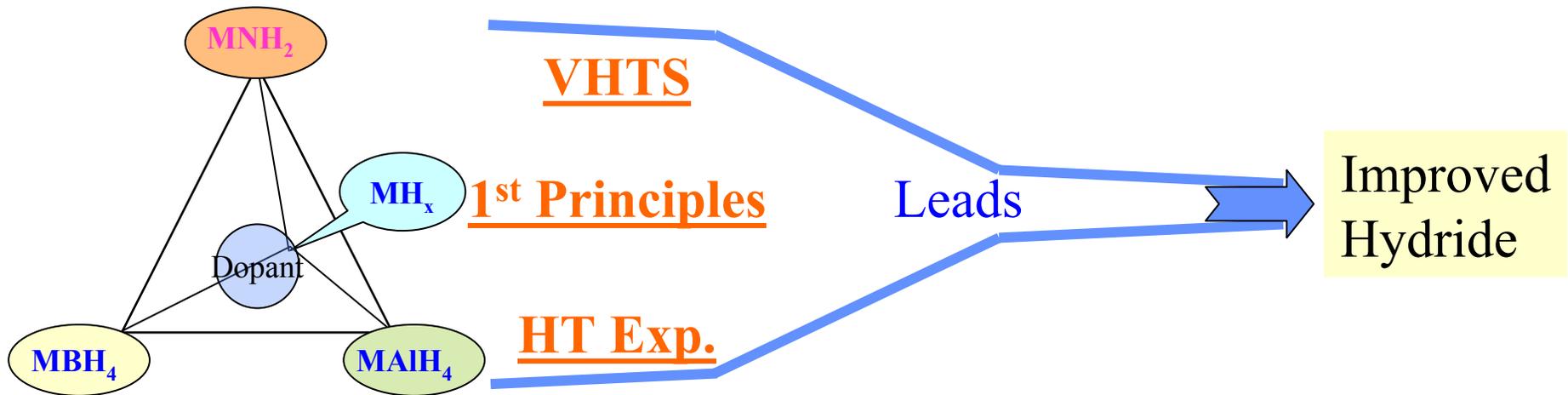
<ul style="list-style-type: none">• Overall	<ul style="list-style-type: none">• Discovery of a complex metal hydride through Molecular Modeling and Combinatorial Methods which will enable a hydrogen storage system that meets DOE 2010 goals• Deliverables:<ul style="list-style-type: none">◆ Optimized material◆ Sample for independent testing at SWRI◆ Documentation
<ul style="list-style-type: none">• 2004/2005	<ul style="list-style-type: none">• Validation and Demonstration of VHTS (Molecular Modeling)• Validation and Demonstration of Medium Throughput Combinatorial Tools• Downselect from Na, Li, Mg/AlH₄
<ul style="list-style-type: none">• 2005/2006	<ul style="list-style-type: none">• Demonstration of High Throughput Combinatorial Tools• Identification of New Materials Approaching DOE Targets
<ul style="list-style-type: none">• 2006/2007	<ul style="list-style-type: none">• 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



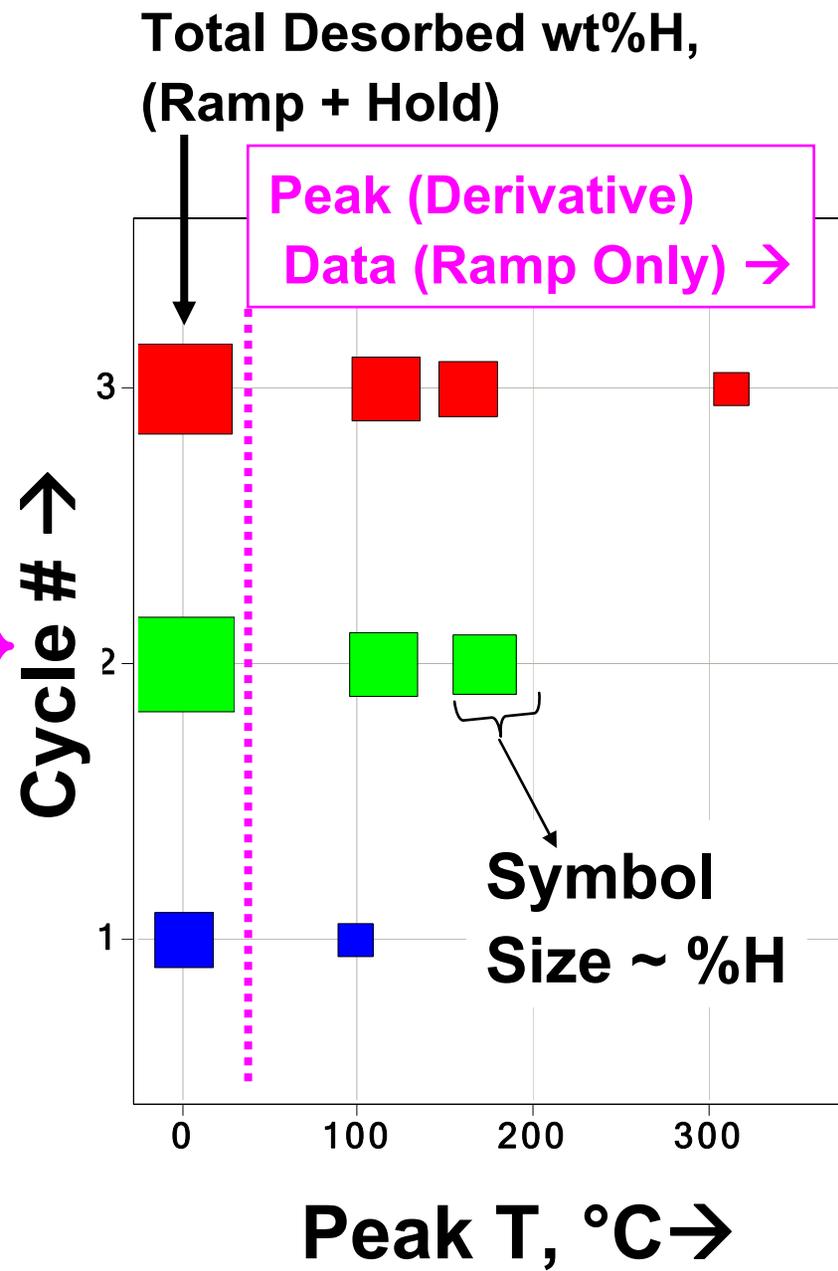
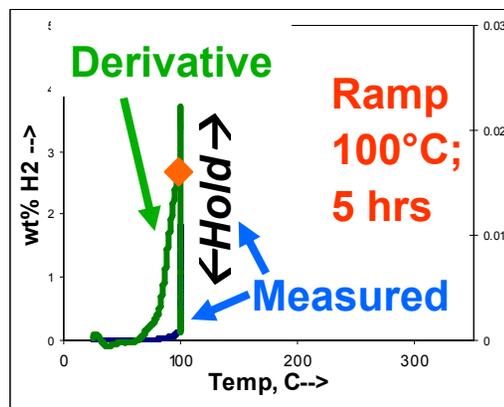
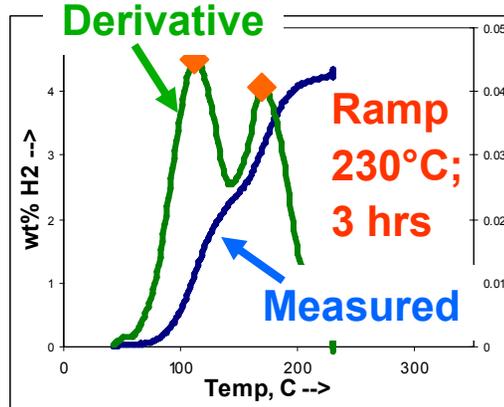
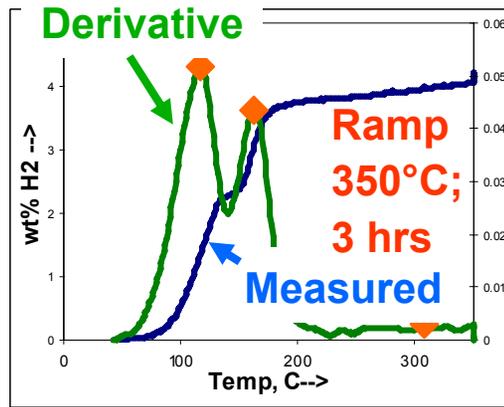
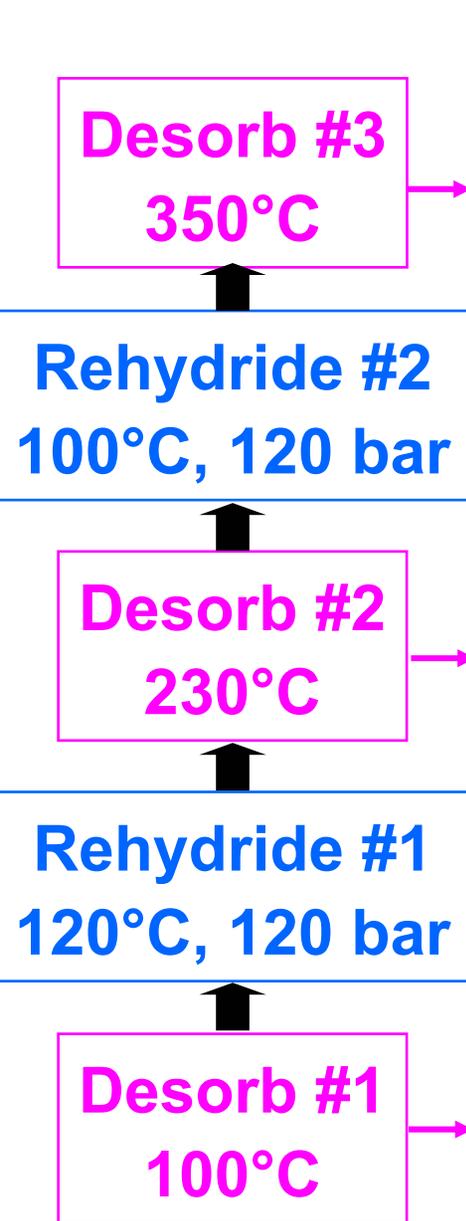
- Total Hydride/Dopant/Process-Variable space is too large even for our Combi methods to fully explore, given time & resources.
- HT Tools are more difficult, costlier to develop/modify than Single-Sample tools, this limits Combi “Prep/Test” Space.
 - Synthesis methods, measurement conditions
 - *Selected 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

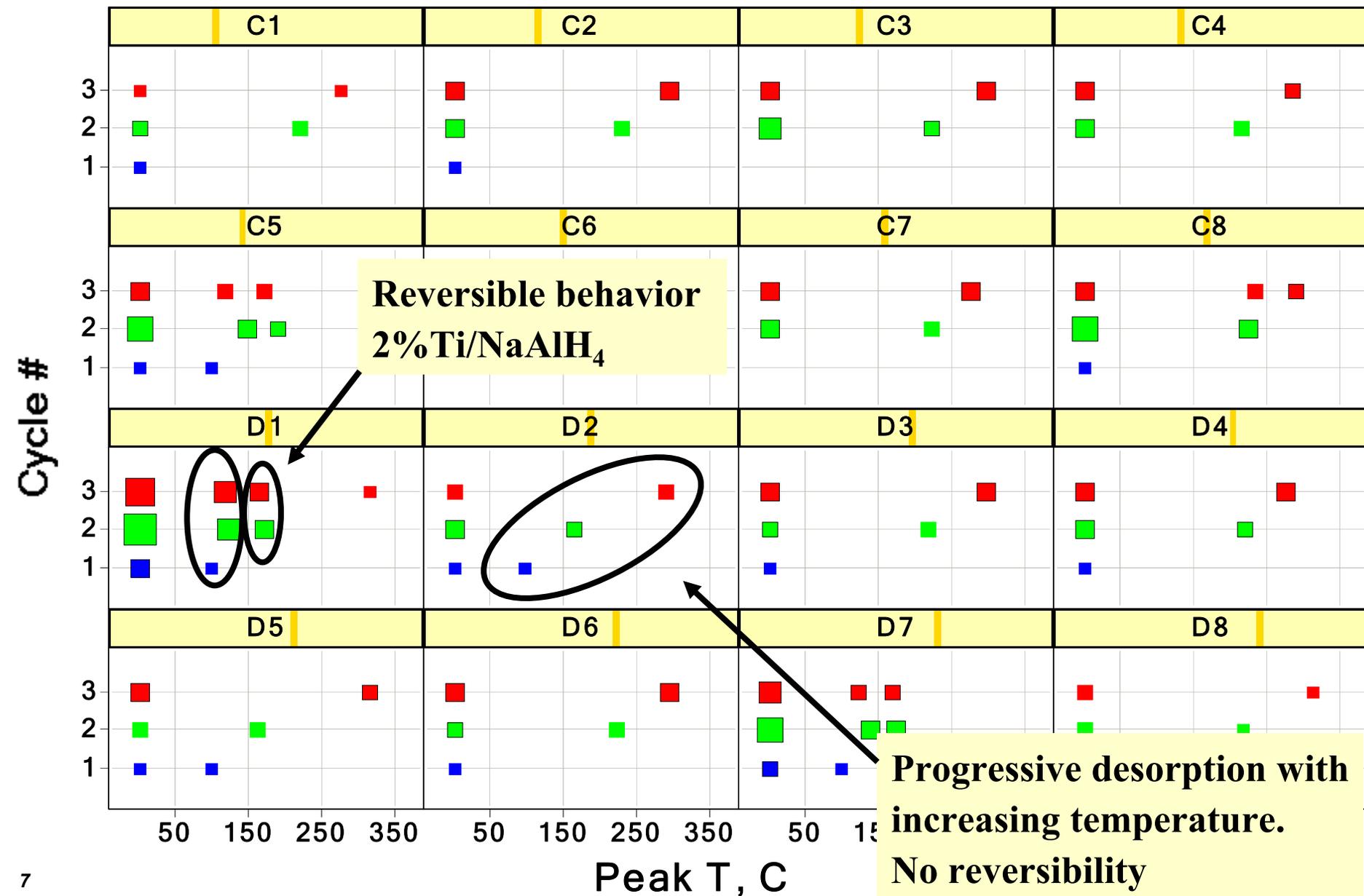


- **Modeling**
 - Virtual High Throughput Screening, ~1000 compositions/month
 - DFT to predict new materials with favorable thermodynamics, refine leads
- **Combi Synthesis & Screening**
 - High Throughput (up to 48x)
 - Discrete, scalable sample preparation using ball-milling or solution-phase
- **Follow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

High Throughput Testing Protocol



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



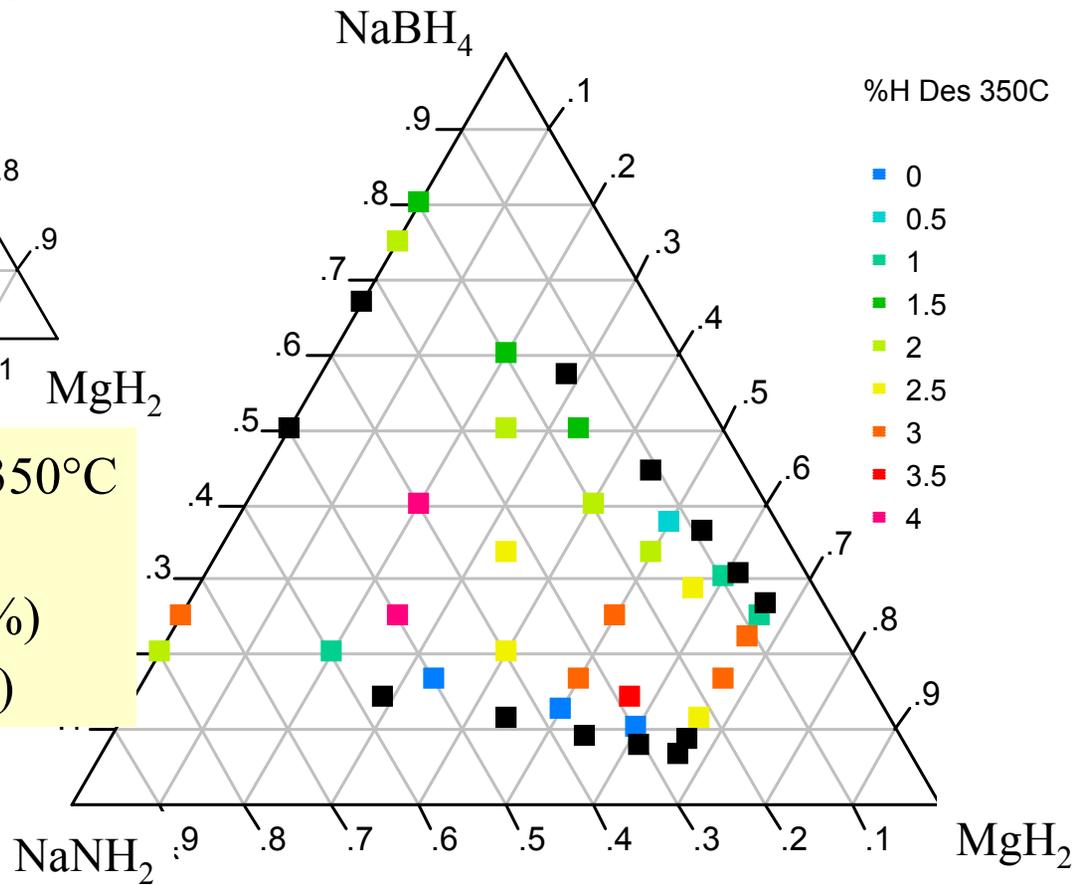
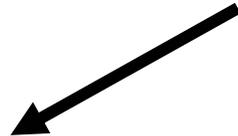
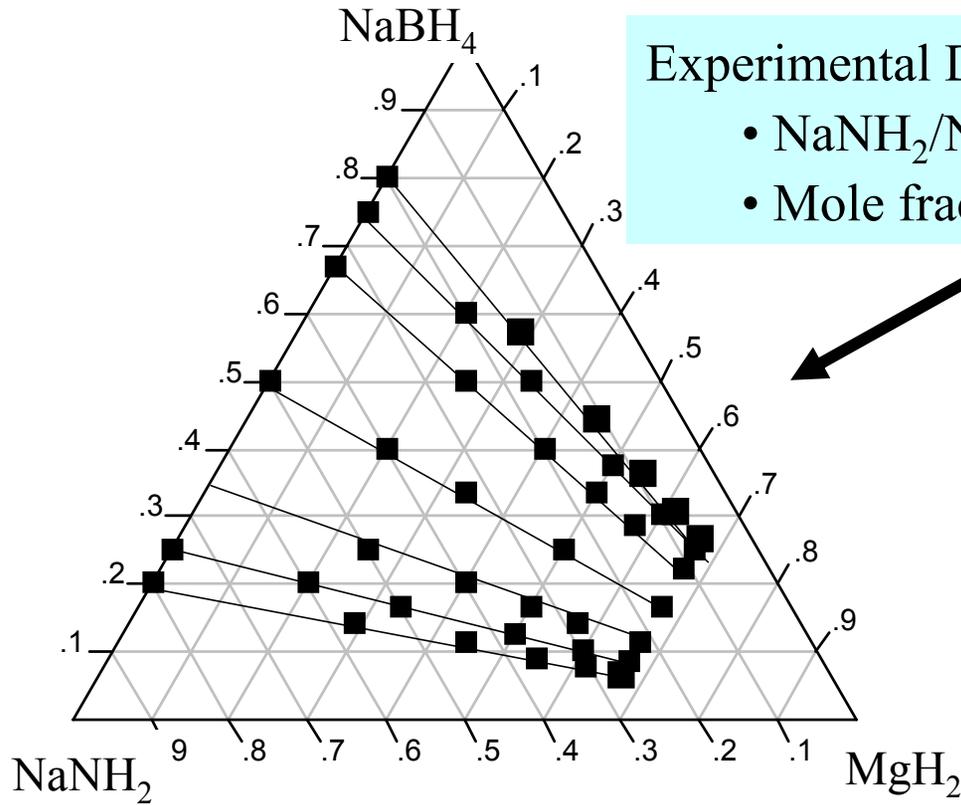
Since last Peer Review:

- **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

NaNH₂ – NaBH₄ – MgH₂ Phase Diagram

Experimental Design for NaBH₄-NaNH₂-MgH₂ System

- NaNH₂/NaBH₄ = 4, 3, 2, 1, 0.33, 0.25, 0.2
- Mole fraction MgH₂ varies from 0 – 0.66



Cumulative results for desorption to 350°C

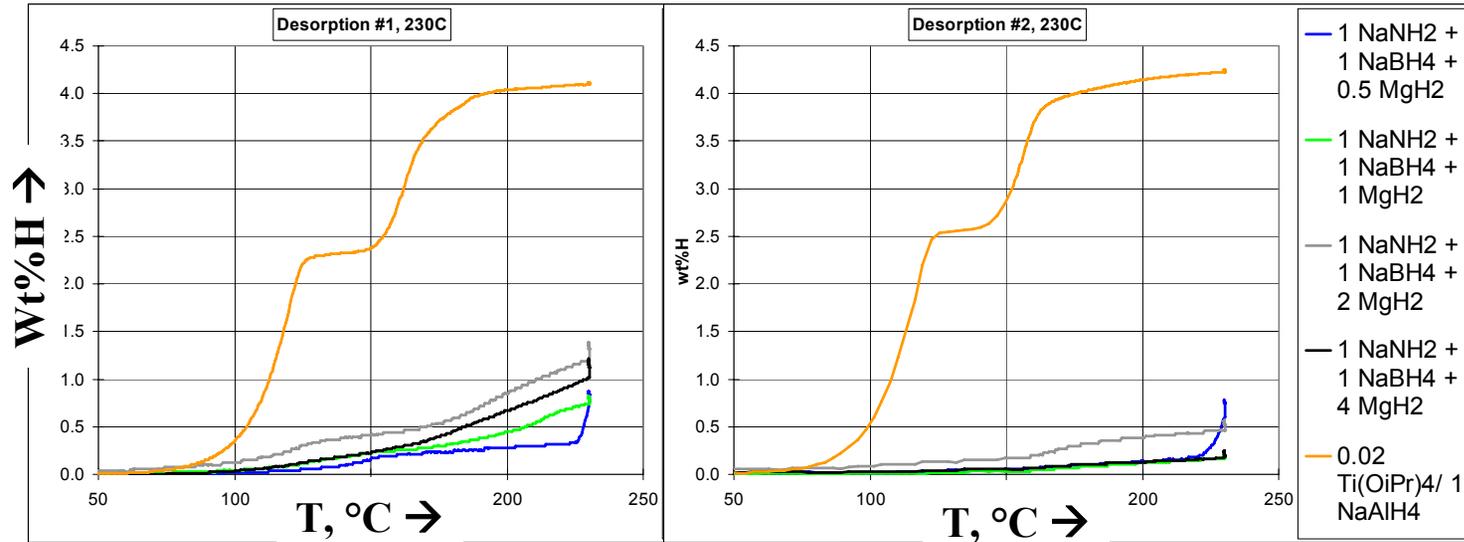
- Up to 4.5 wt. % H₂ desorption
- 2 NaBH₄-1 NaNH₂-1 MgH₂ (4.49 %)
- 1 NaBH₄-1 NaNH₂-1MgH₂ (4.25 %)



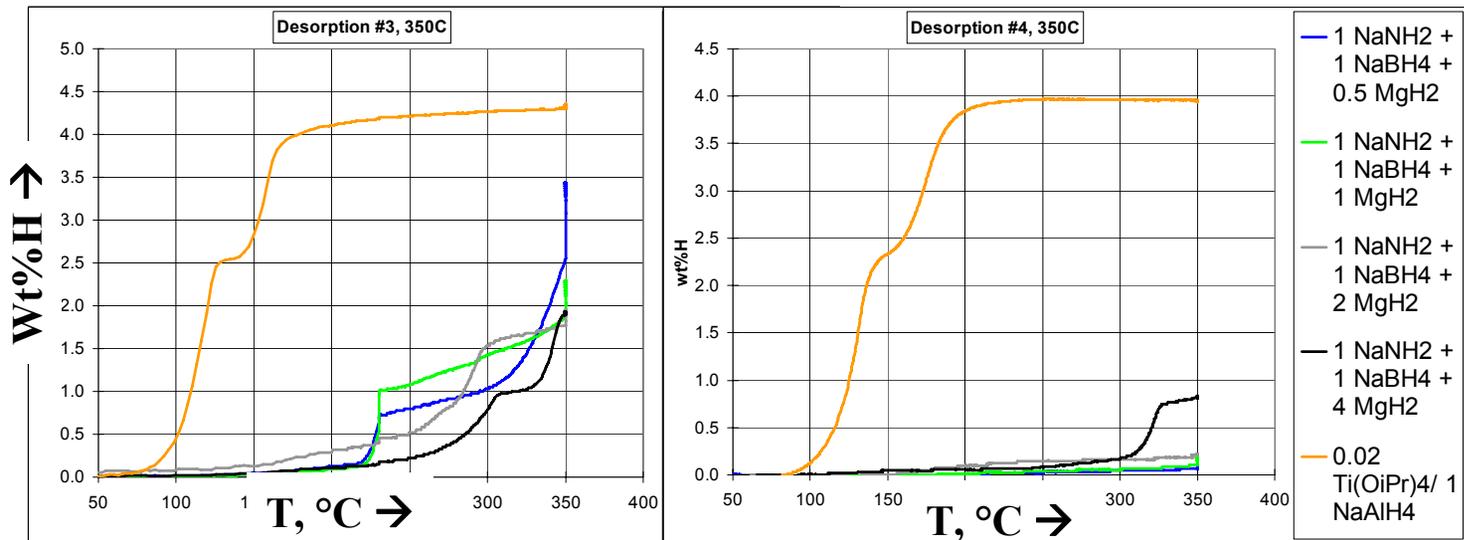
NaNH₂ – NaBH₄ – MgH₂ Phase Diagram

- First desorption often <2 wt%H by 250°C, 3 – 4 wt.% H₂ by 350°C
- Low reversibility for samples upon multiple desorption runs

2 Cycles 230°C



2 Cycles 350°C



Staged approach – increasing complexity:

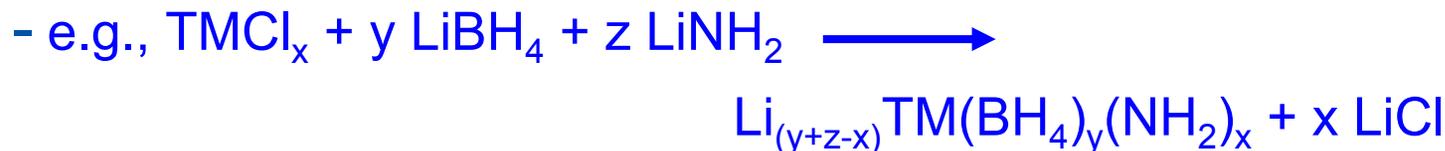
- Synthesize simple Transition Metal (TM) borohydrides or amides



- Stabilize TM borohydrides/amides with alkali:



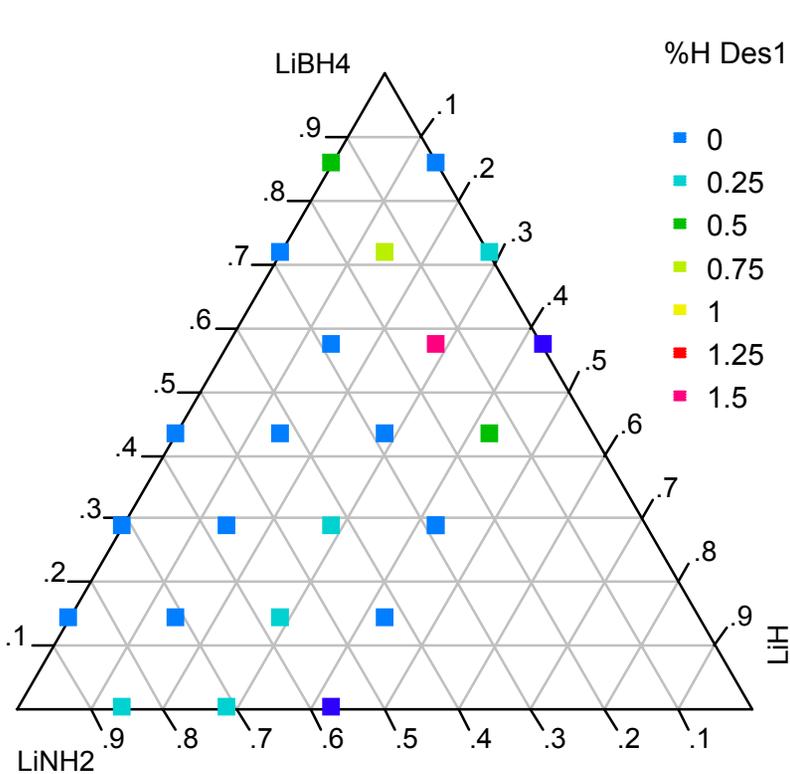
- Expand to complex mixtures of borohydrides + amides:



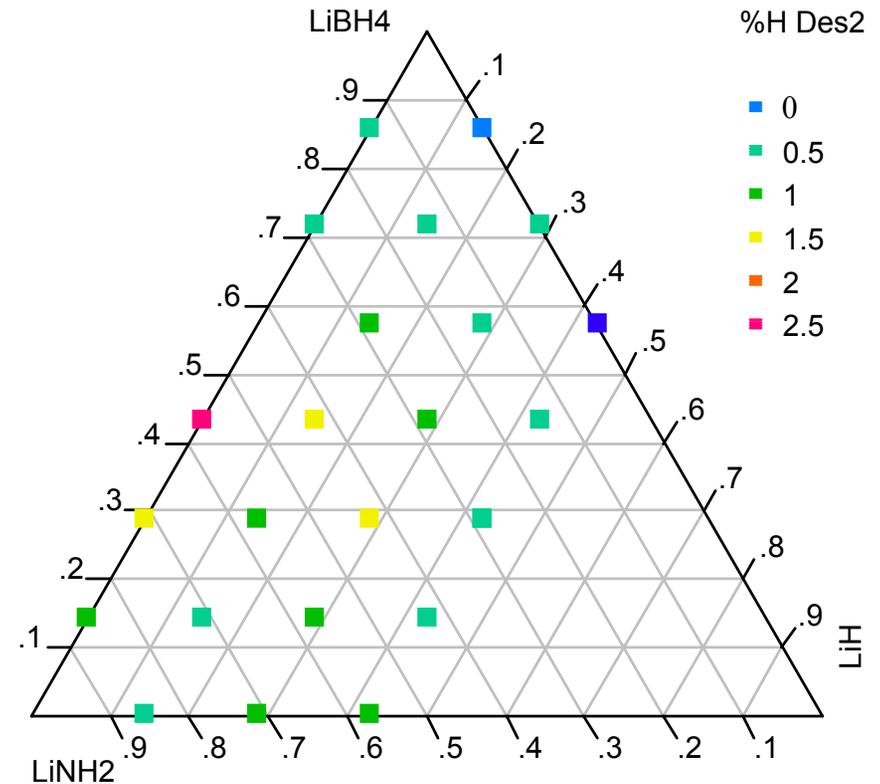
- Facilitate transport by including $\text{Li}(\text{NH}_2)_3\text{BH}_4$ which is known to melt
- These materials may dehydride to form complex as yet unknown imides, nitrides, borides, or mixtures of such

LiNH₂ – LiBH₄ – LiH – VCl₃ Phase Diagram

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

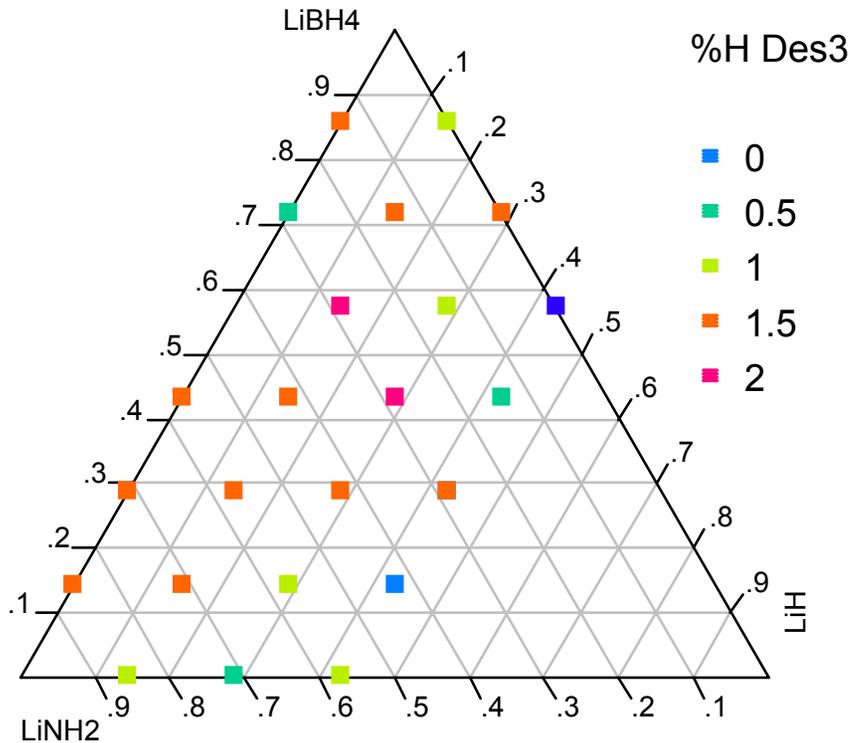


Desorption 1, 100°C



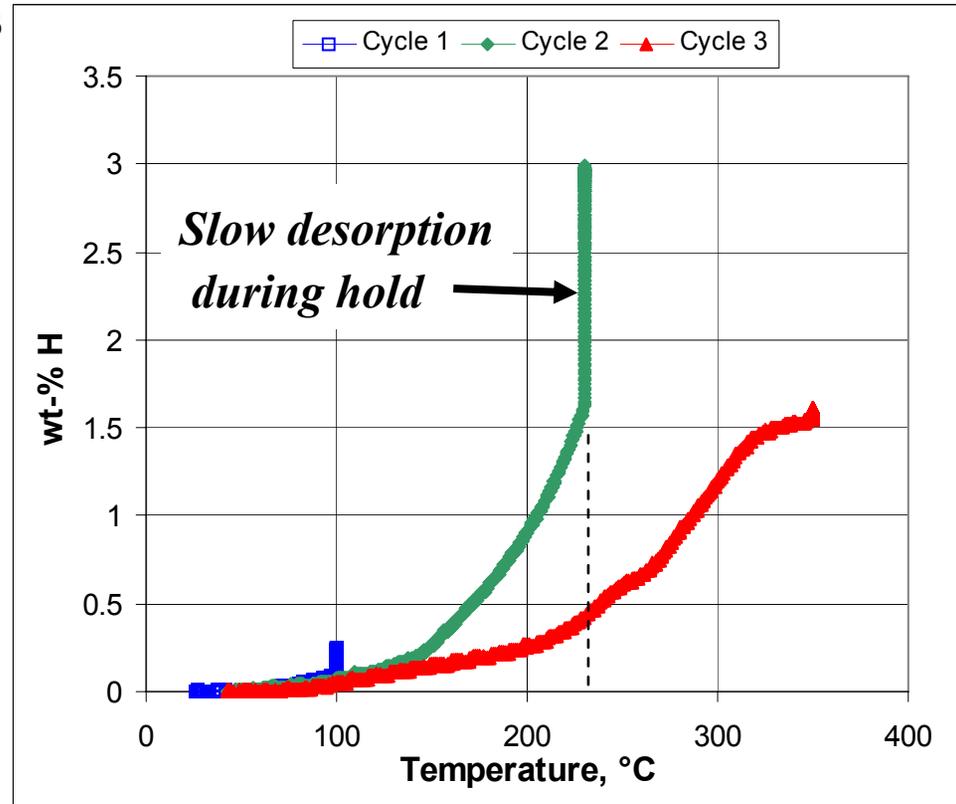
Desorption 2, 230°C

LiNH₂ – LiBH₄ – LiH – VCl₃ Phase Diagram



Desorption 3, 350°C

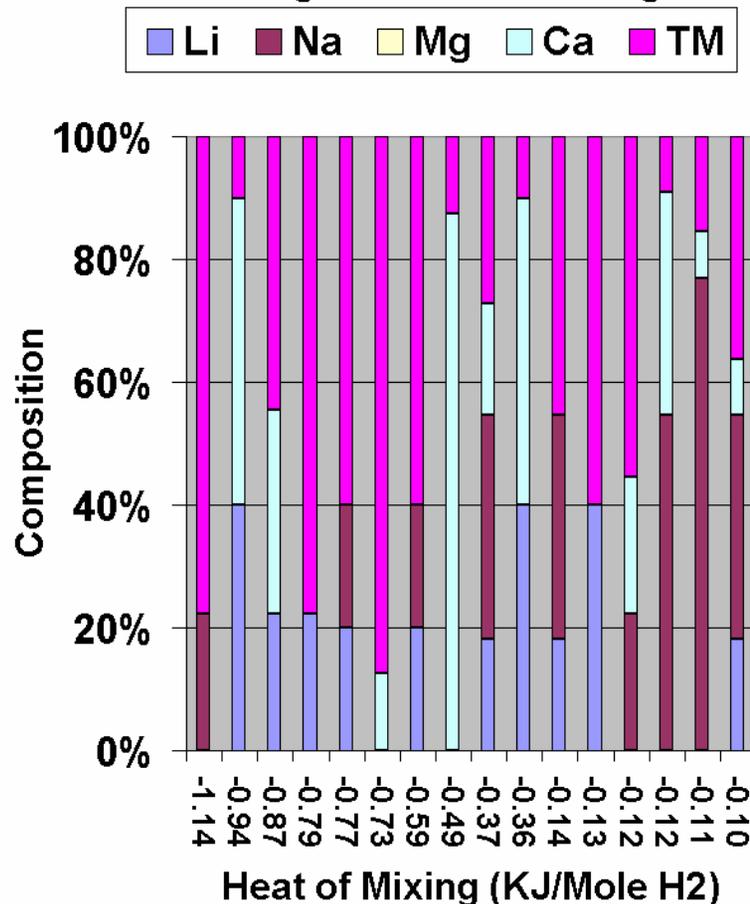
0.5 LiNH₂ + 0.38 LiBH₄ + 0.125 VCl₃



Following a single composition, 0.5 LiNH₂ – 0.375 LiBH₄ – 0.125 VCl₃ through the desorption cycles illustrates the general trend of poor reversibility often observed

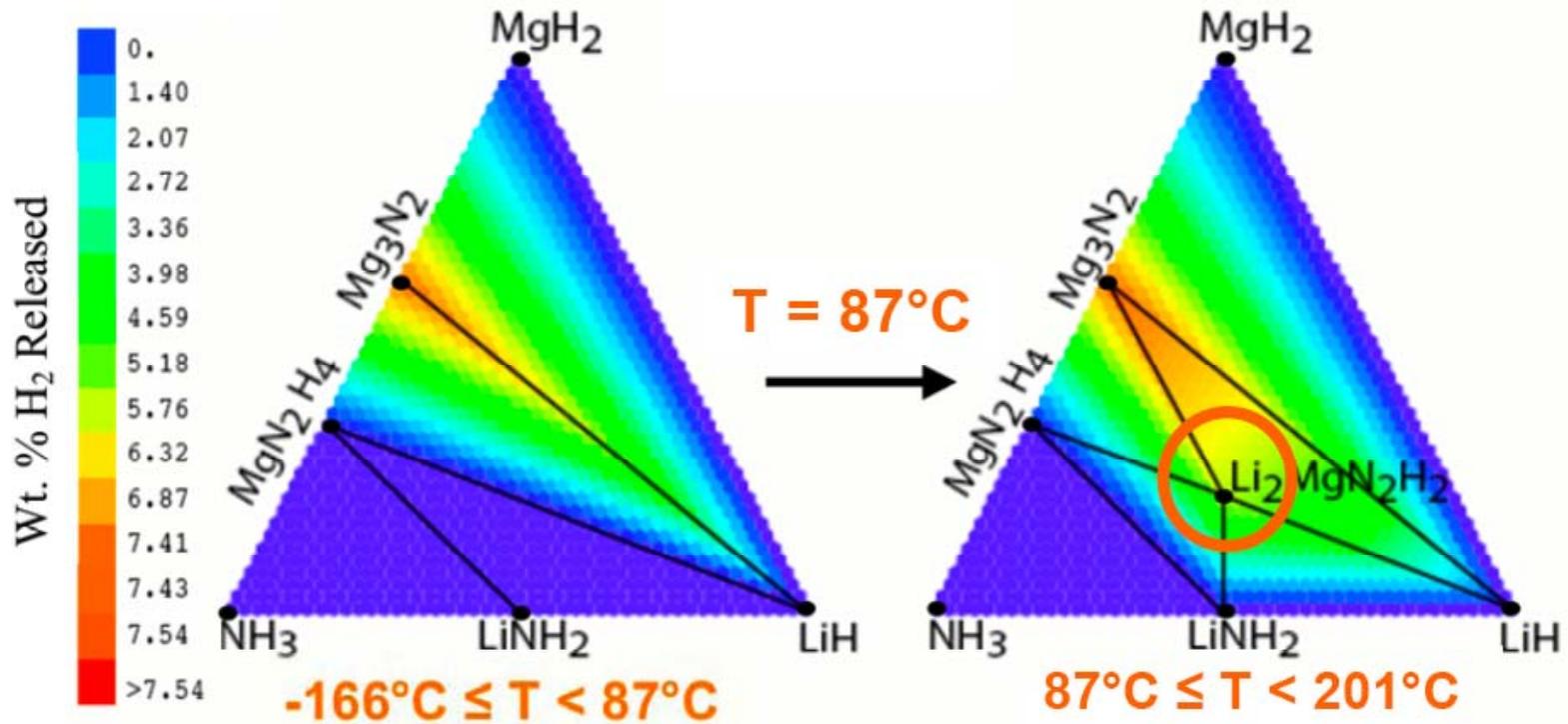
VHTS Screening of Alkali, Alkaline-Earth and Transition Metal Borohydrides

Composition of mixed borohydrides with negative heats of mixing



- Screened ~1200 pentenary Borohydride mixtures
- Heats of mixing not large enough to stabilize any mixture versus dehydrating
 - Need an additional 15 kJ/mol*H₂ to stabilize mixtures

First-principles phase diagrams of complex hydrogen storage mixtures



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,

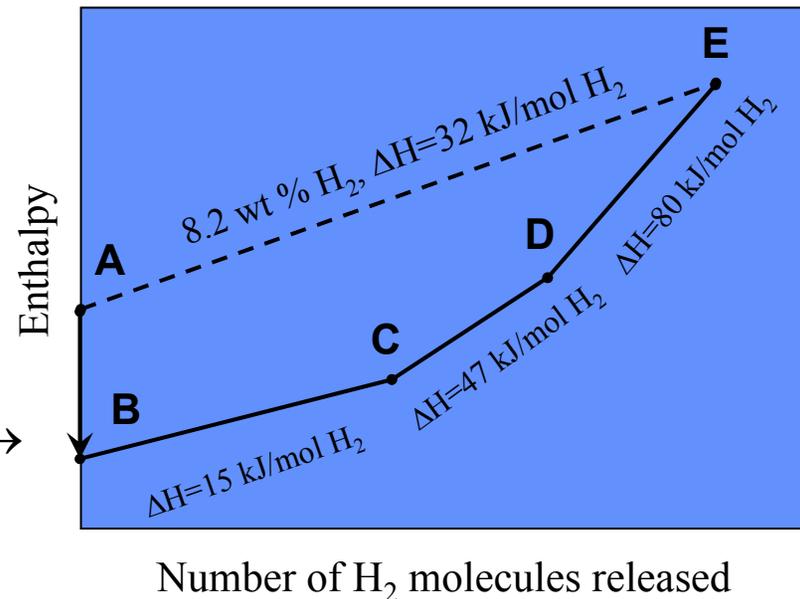
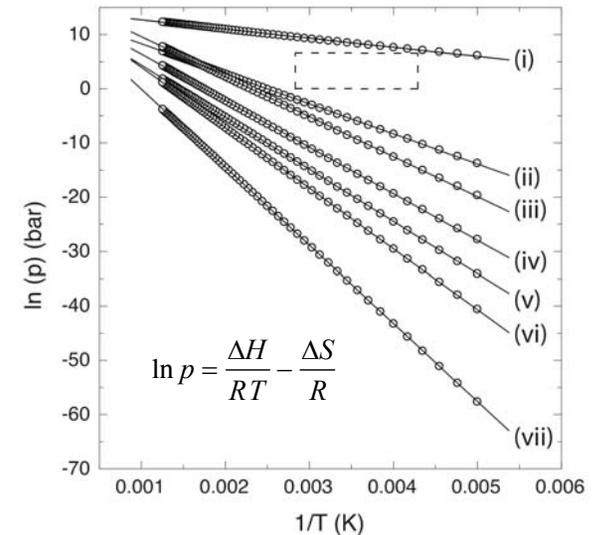


Alapati et al., J. Phys. Chem. 110, 8769 (2006)

will instead proceed via intermediate steps:



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



- **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 - $\text{Mg}(\text{AlH}_4)_2$ /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 $\text{Li}_4(\text{NH}_2)_3\text{BH}_4$, 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.**

- **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**

- **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 $\text{LiNH}_2 - \text{MgH}_2 - \text{LiBH}_4$ 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