High Throughput/Combinatorial Screening of Hydrogen Storage Materials: UOP Approaches

High Throughput/Combinatorial Analysis of Hydrogen Storage Materials Meeting
Organized by DOE on June 26, 2007

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Outline

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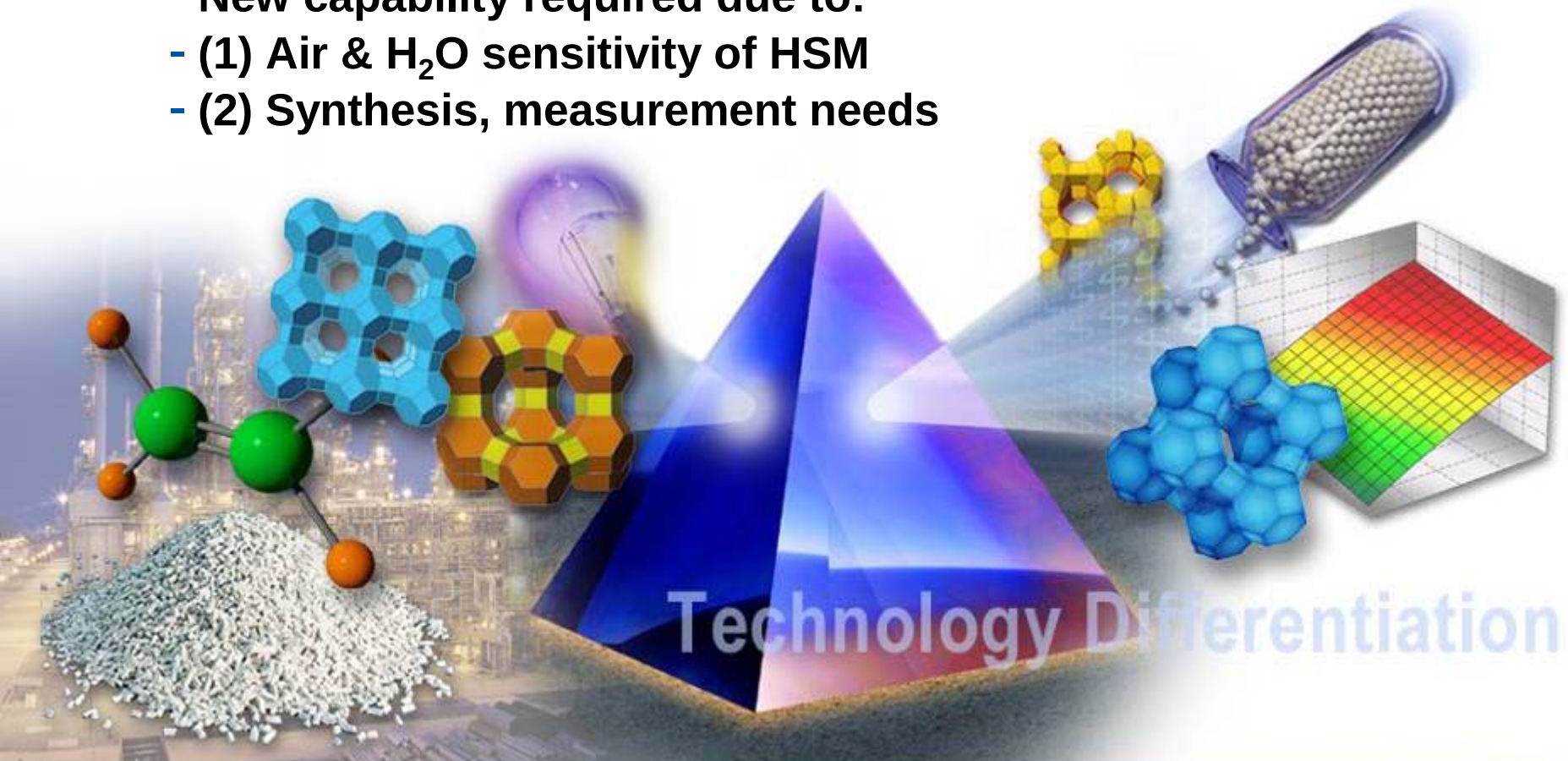
- Combi Strategy for HSM
- High Throughput Synthesis Capability
- High Throughput Testing Capability
- Example Results
- Lessons Learned

UOP Combi Capability

- **Extensive Rang e of Tools**
  - Materials & Catalysts
  - Characterization, Informatics
- **Hydrogen Storage Materials**
  - New capability required due to:
  - (1) Air & H_2O sensitivity of HSM
  - (2) Synthesis, measurement needs



Combi Strategy for HSM

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- **Test Methodology**
  - **Needs: driven by DOE targets**

DOE Target	Approach
Useable H_2 Capacity	Wt%H by desorption
Delivery Temperature	Wt%H versus T → TPD
Reversibility	Multiple TPD's w. high-P rehydriding between

- **Synthesis Methodology**
  - **Need: discrete, scalable sample preparation**
    - **Ball milling predominant in literature**
    - **Solvent approach of interest**
- **Characterization Methodology**
  - **Need: structure info**
    - **XRD**

High Throughput Challenges

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- **HT Equipment**
  - **Testing: No Comm. equipment for HSM → invent**
  - **Synthesis: Comm. equipment exists → customize**
  - **XRD: Equipment in-house → adapt for air, H_2O exclusion**
- **Informatics**
  - **Leverage Combi database, analytics**
  - **Add new unit ops. → custom programs**
- **Test Methodology**
  - **Develop rapid multi-cycle screen**
  - **Partner with Craig Jensen to accelerate**

→Consequences

- **Time to develop, build, shakedown HT > [1Rx]**
  - Staged development: [8Rx] → [48Rx]
- **Capital-$: $[1Rx] < $HT < 48 *$[1Rx]**
- **Flexibility: changes 48-fold**

Multilevel Testing Approach

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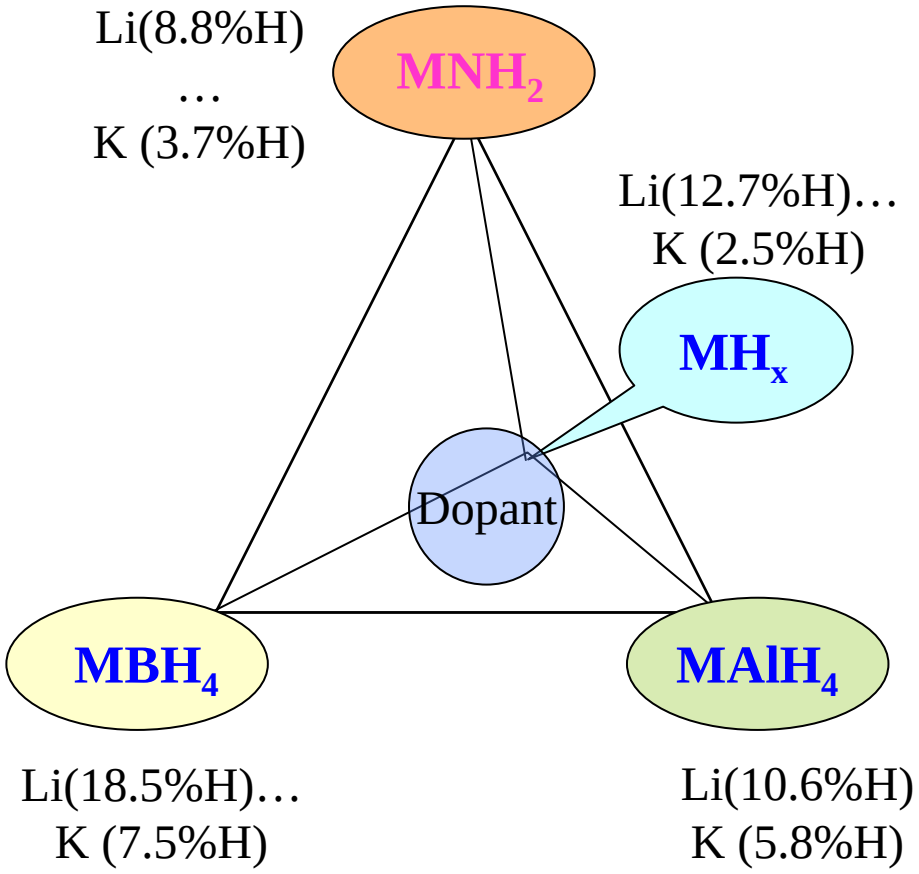
- **Issue: DOE desires many properties for HSM**
- **Answer: Multilevel Screening Approach:**
  - **(1) Steps critical for finding leads → Implement HT**
    - Sample synthesis
    - Reversible %H →TPD & Re-hydriding
    - Structure → XRD
  - **(2) Promising leads → remaining information non-HT**
    - Fewer samples → HT not needed
    - Validation using PCT
    - Characterization: HSM + desorbed gas
    - Extended multi-cycle testing
    - Additional properties per DOE specifications

Materials and Screening Strategy

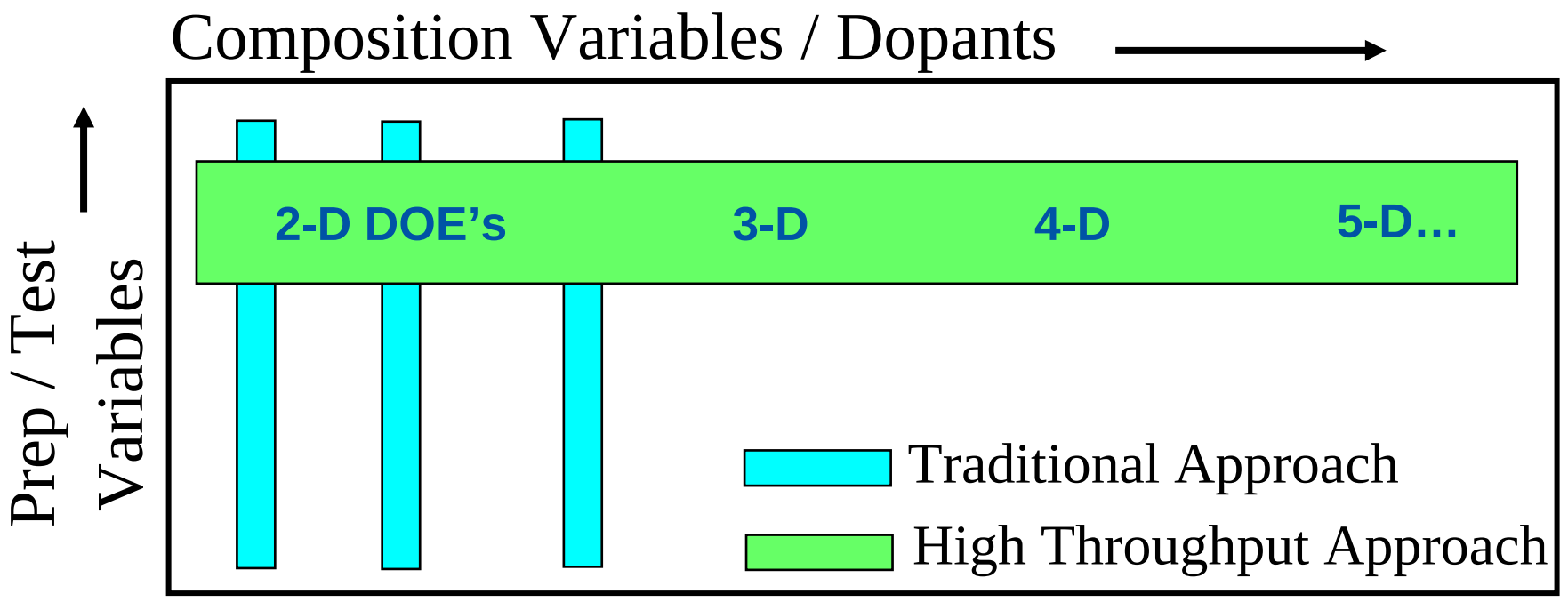


- **Multiple Dimensions:**
  - **Hydride phase space**
  - **Dopant phase space**
  - ***Preparation space***
  - ***Testing space***
- ***Preparation space:***
  - ***Target species → many starting reagents***
  - ***One reaction → multiple synthesis techniques, conditions***
- ***Testing Space:***
  - ***Desorption, re-hydriding conditions affect observed capacity, reversibility***

M = alkali, alkaline earth and transition metals

Complex compositions, huge number of combinations

High Throughput vs. Traditional Approach



- **For a given HT capability:**
  - **Rapid screening of hydride compositions, hydride precursors, dopants – up to very complex phase systems**
  - **Limited screening of preparation, testing/process variables: equipment changes difficult**

High Throughput Synthesis Capability

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- **Approaches:**
  - Ball milling
  - Solution Synthesis
- **Capability:**
  - HT milling using multi-stage traditional mills
  - HT Combi-Milling demonstrated
  - Automated solution and powder dispensing
  - Filtration, sample washing and drying
  - Sample agitation, sample heating to 250°C
- **Status:**
  - System currently being applied to project
- **Characterization:**
  - HT XRD being applied to project

High Throughput Testing Capability

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- **Capability:**
  - Comparison of Medium Throughput (MT) and High Throughput (HT) systems:

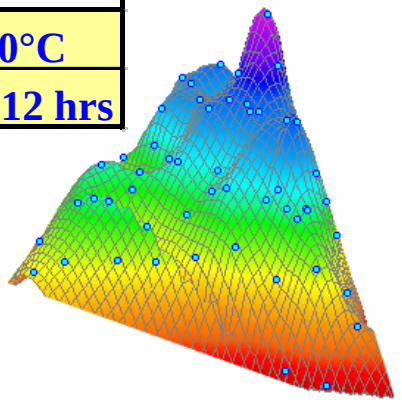
	MT Assay	HT Assay
No of Rx:	8	48
Max T:	220°C	350°C
Max P:	87 bar	120 bar
Desorption P:	Variable	~1 bar abs.

- **Test Protocol:**
  - Perform multiple cycles of temperature programmed desorption + rehydriding:

Std. Cond.	MT Assay	HT Assay
Desorption	To 220°C	Multiple T: 100-350°C
Rehydriding	125°C, 87 bar, 12 hours	100-125°C, 120 bar, 12 hrs

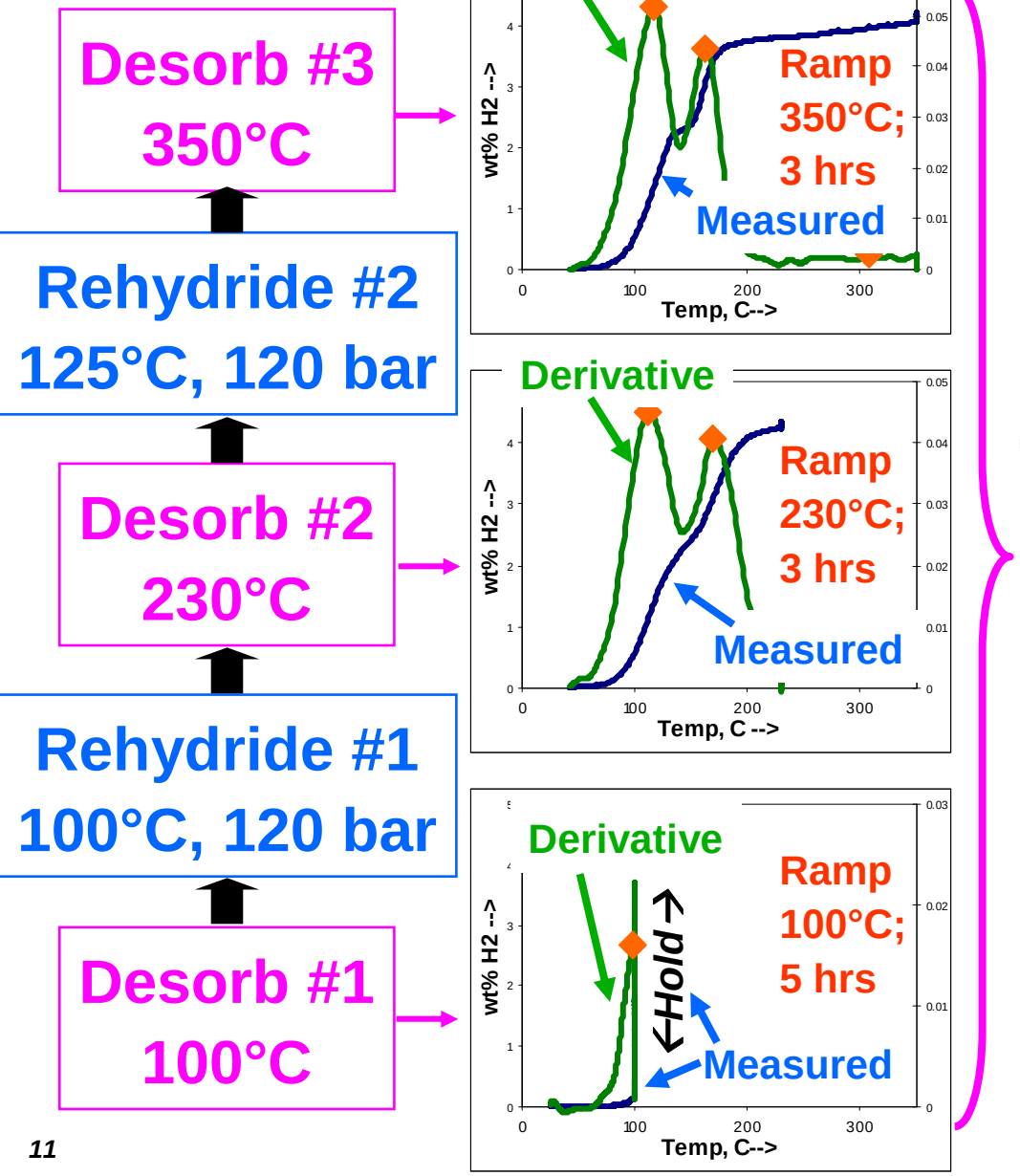
  - Second cycle represents reversible wt-%H

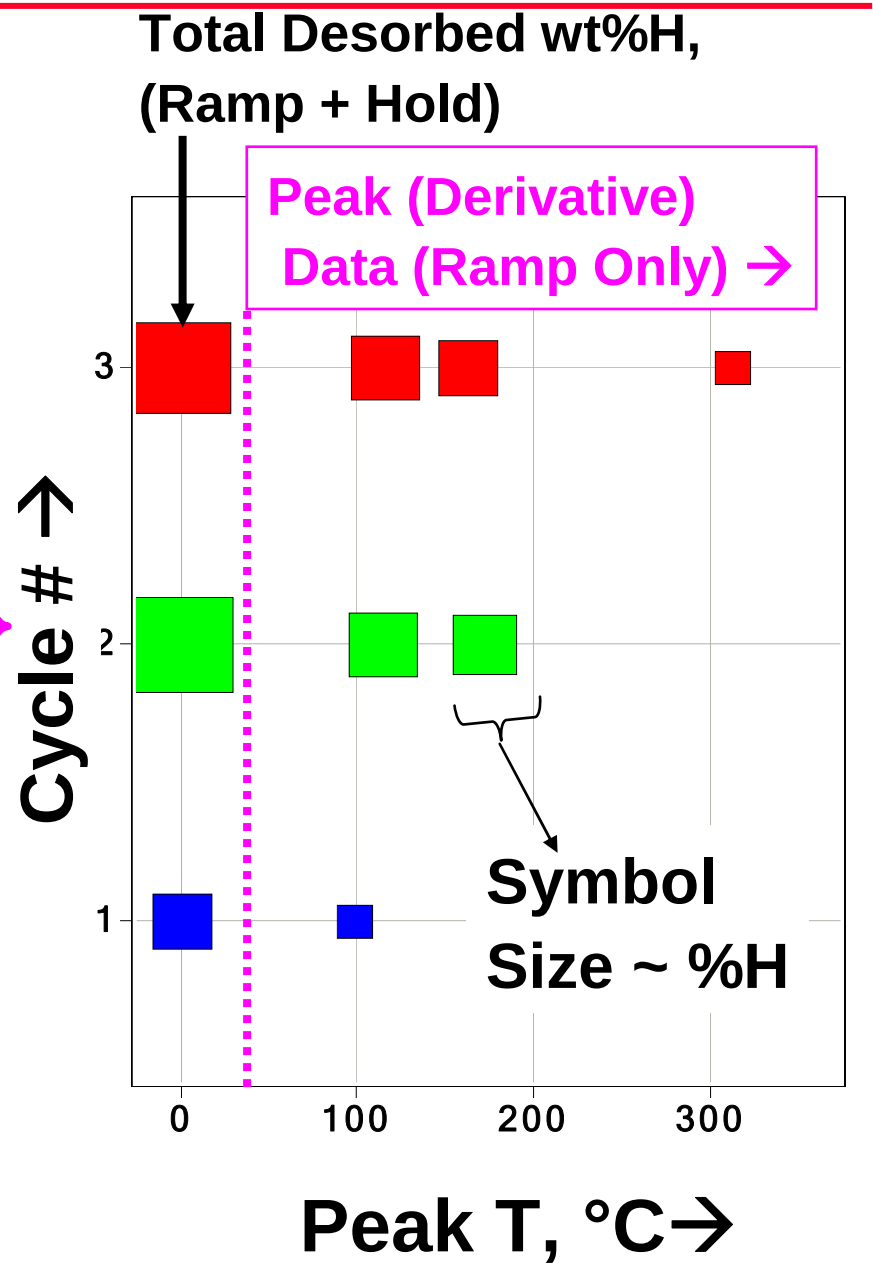
- **Status:**
  - Both MT and HT Systems are operational



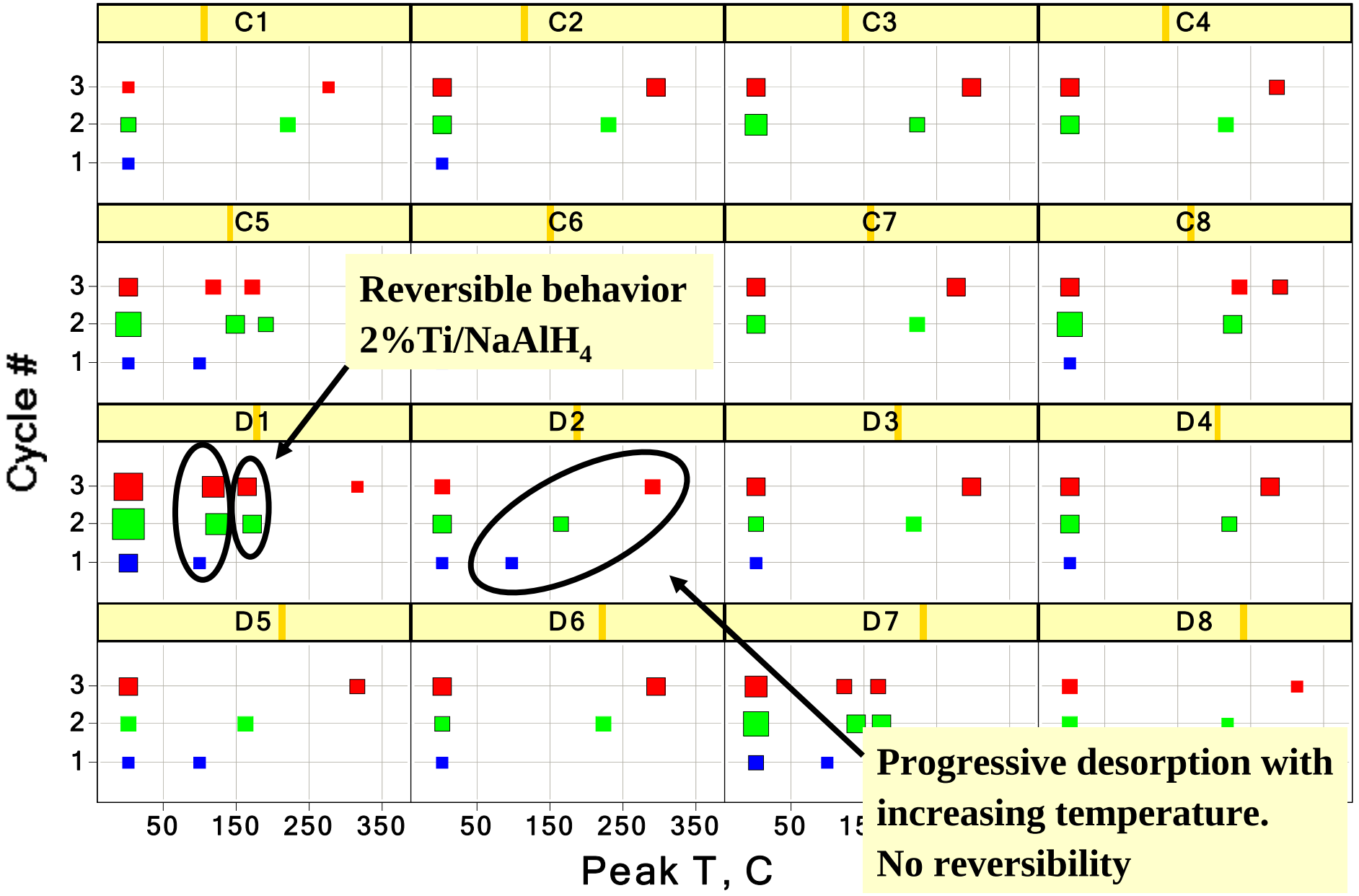
Phase Diagram measured by HT Assay

High Throughput Testing Methodology





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



Reference Run: 2%Ti/NaAlH4, Des #2, 33 Rx

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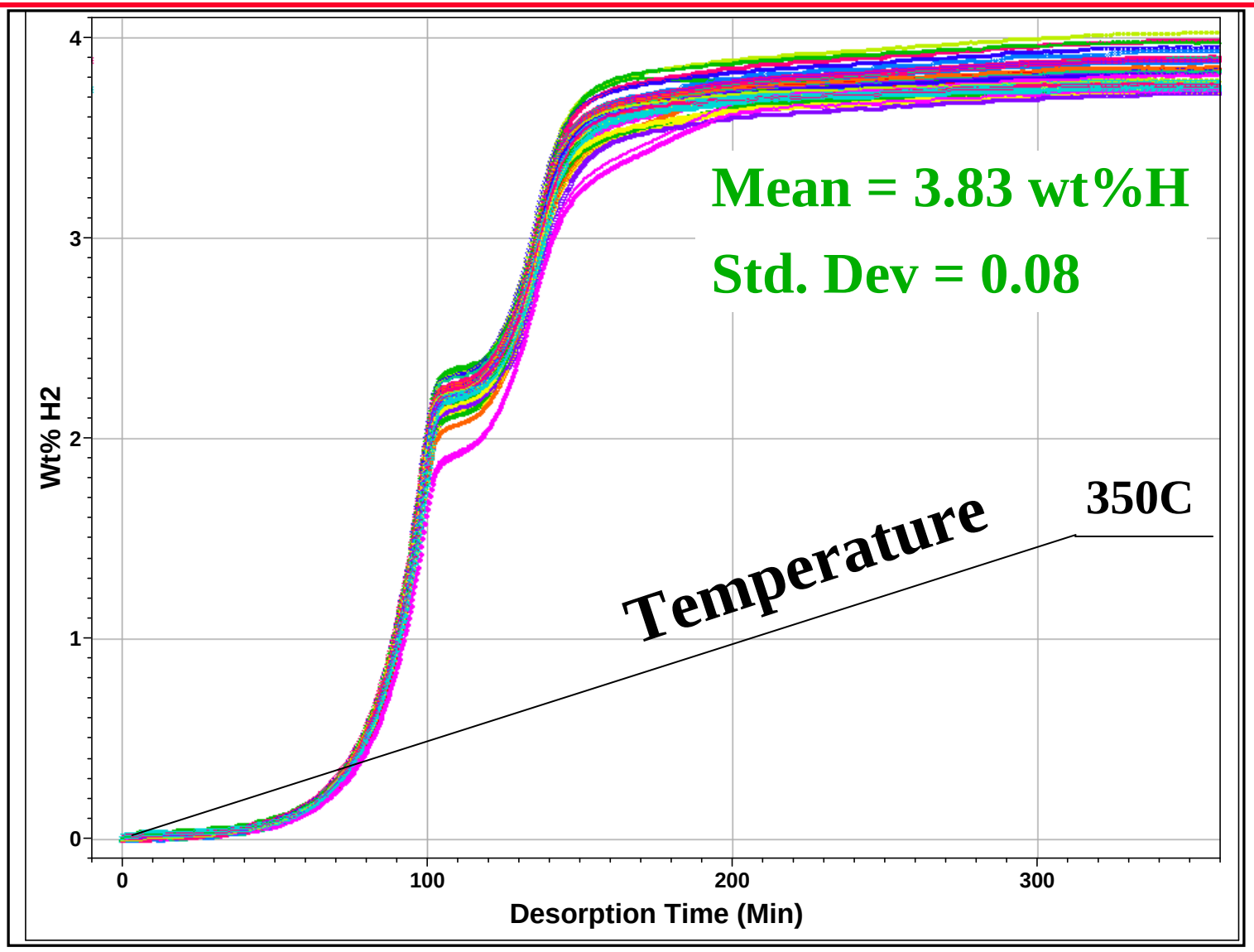
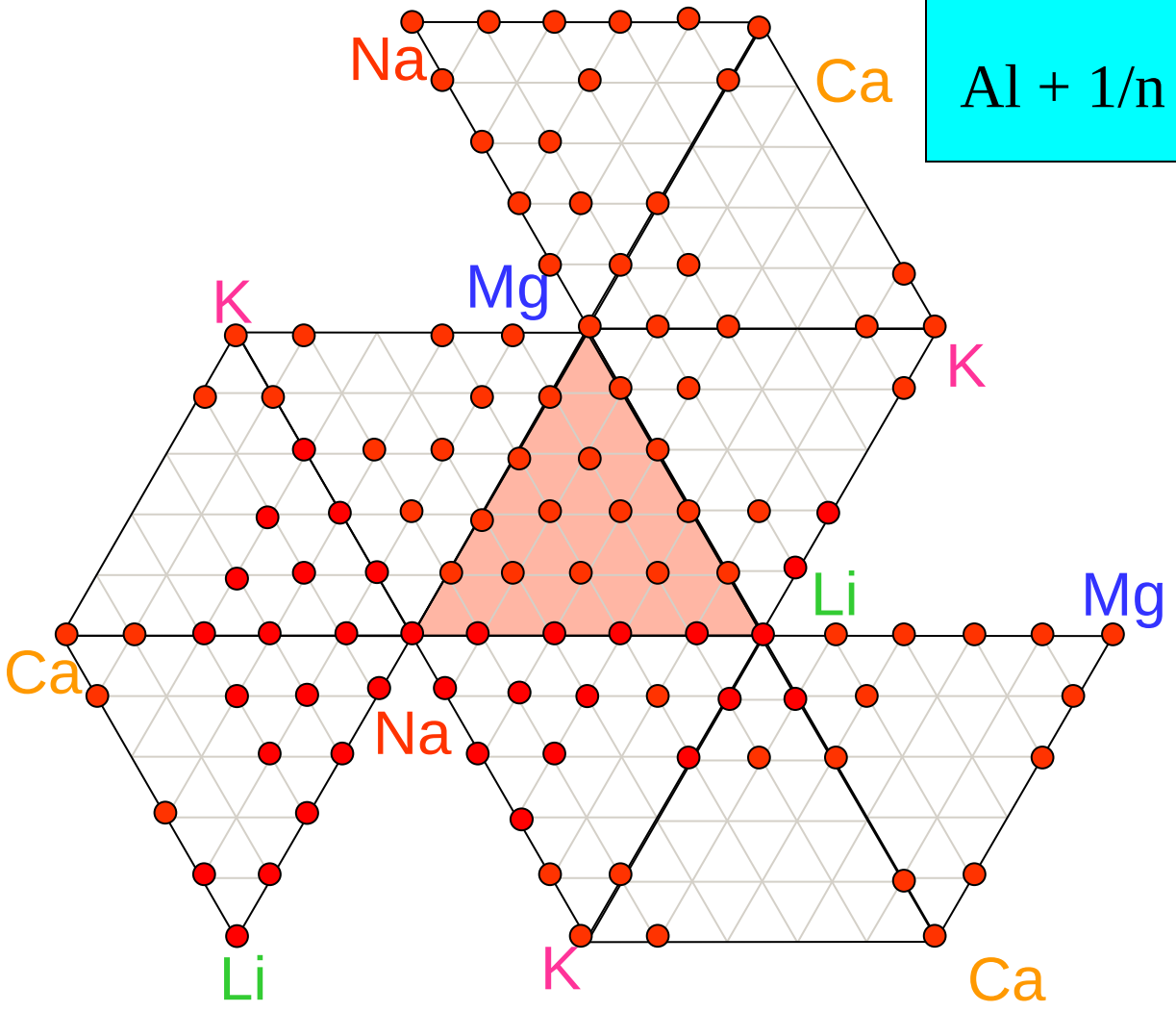


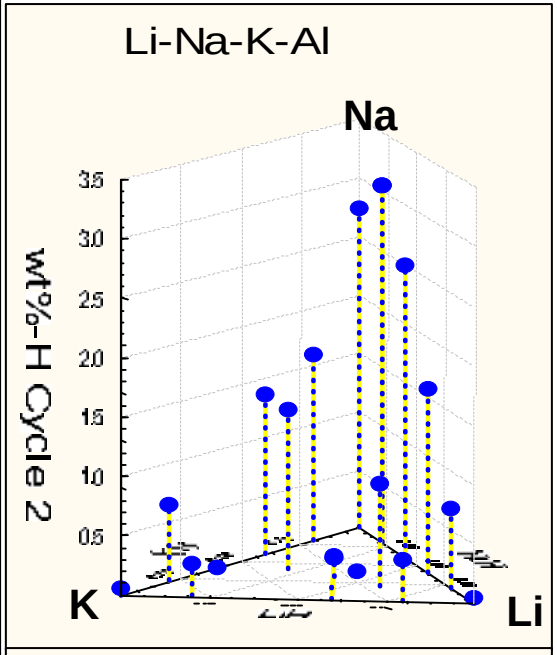
Example Result: Mixed Alanates DOE

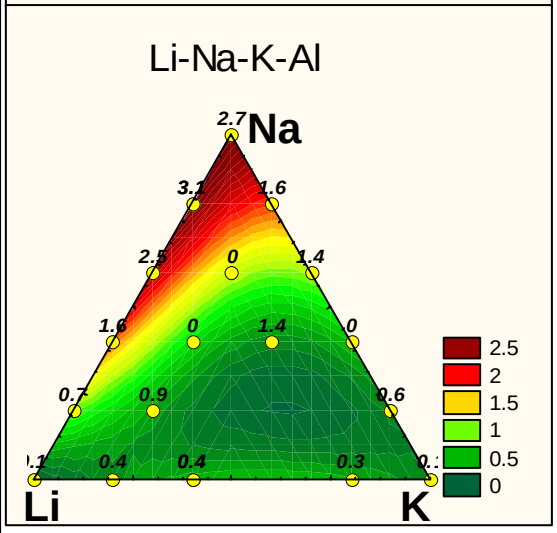


$$Al + 1/n\ MH_n \underset{}{\overset{H_2}{\rightleftharpoons}} M_{1/n}AlH_4$$

- **Experimental DOE = collection of ternary diagrams**
- ***Molecular modeling scanned 891 hexanary mixtures of Li + Na + K + Be + Mg + Ca Alanates***

Example Experimental Result: Li-Na-K-Al

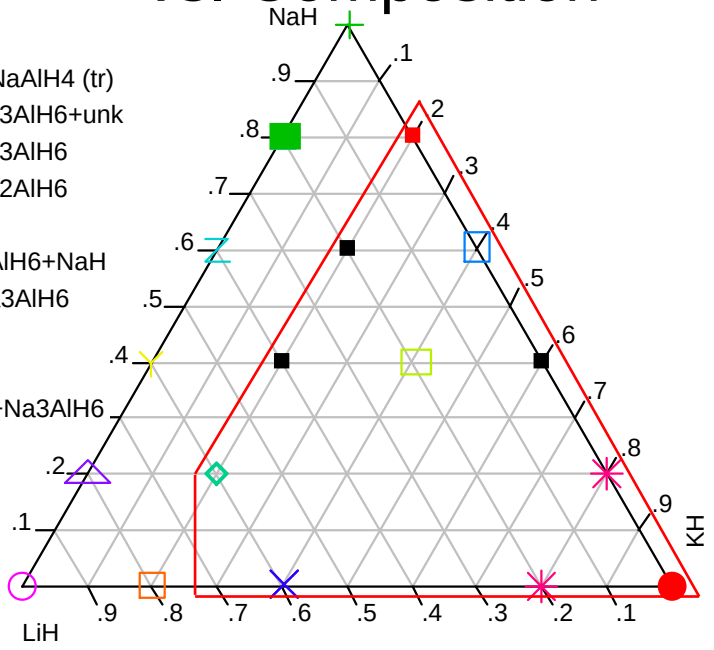




Products

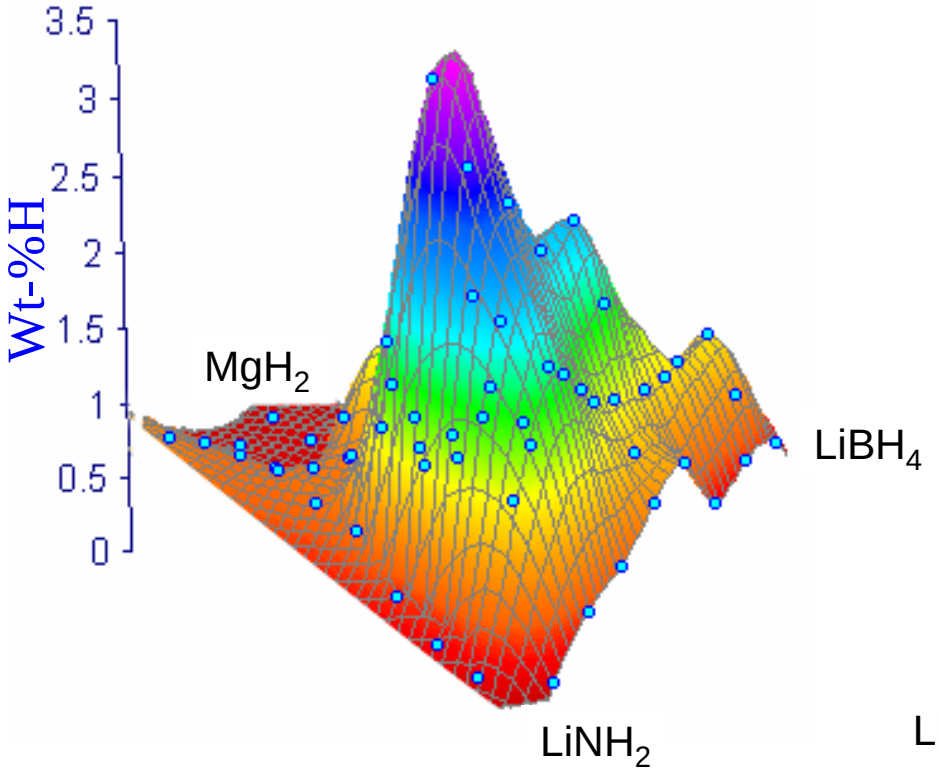
- Al+Na3AlH6+KAlH4+NaH
- Al+NaH+Na3AlH6+Na3AlH6
- Al/LiH+KAlH4
- Al/LiH+KH+unk
- Al/LiH+LiNa2AlH6+KAlH4+NaAlH4 (tr)
- Al/LiH+LiNa2AlH6+NaH+Na3AlH6+unk
- Al/LiH+NaH+LiNa2AlH6+Na3AlH6
- Al/LiH+NaH+Na3AlH6+LiNa2AlH6
- Al/LiH+unk
- K2NaAlH6+KAlH4+Al+Na3AlH6+NaH
- K2NaAlH6+KAlH4+NaH+Na3AlH6
- KAlH4
- KAlH4+KOH*H2O
- NaAlH4+LiNa2AlH6+Al/LiH+Na3AlH6

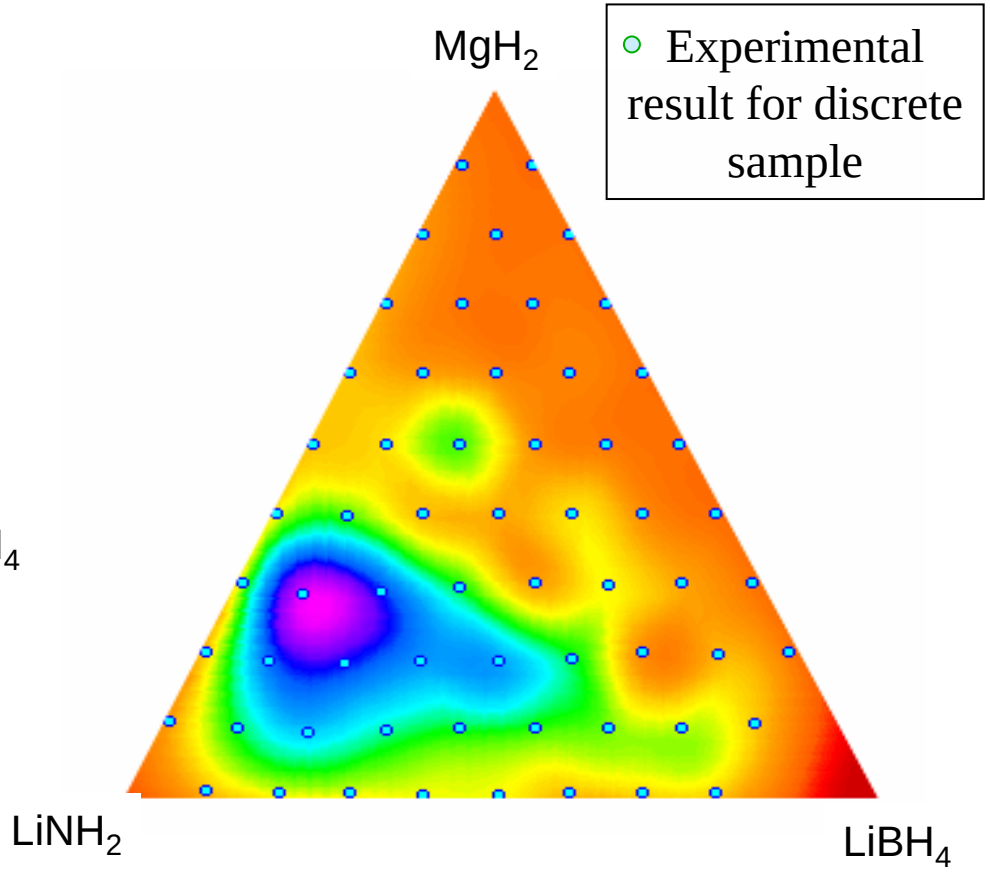
XRD of Products vs. Composition



Full phase diagram readily measured XRD before and after testing

Experimental Result: $LiNH_2 + MgH_2 + LiBH_4$ Reversible %H (Des#2 to 220°C)





Prior literature → few compositions along edges
HT screening → full phase diagram
Discovered New Optimum for Ternary System

Lessons Learned

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- **Combi great for finding optima in phase diagrams**
- **Capability development slower than 1-Rx methods**
- **Medium Throughput Assay (8 Reactor)**
  - **+ Worked well**
- **High Throughput Assay (48 Reactor)**
  - **+ Screened ~ 1000 experimental samples (+ refs.)**
  - **- Labor intensive, high maintenance**
  - **- Not enough sample for spent analysis**
    - Run interesting samples in MT system
- **High Throughput Synthesis System**
  - **+ Wide synthesis capability**
  - **- Development, shakedown**
    - Accurate handling of milled powders
    - Sample transfer equipment

The Team

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DOE Project Manager

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