

Project Objectives

Approach

Na-Li-Mg/AlH₃ Phase Diagram: Experimental Design

Experimental Setup

Overall Program:

- Discovery of a complex metal hydride through Molecular Modeling and Combinatorial Methods which will enable a hydrogen storage system that meets DOE 2010 goals
- Project completion in three years
- Deliverables:
 - One kilogram of optimized material
 - Potential manufacturing process
 - Design for a hydrogen storage system
 - Documentation

Program Year #1:

- Downselect from Na, Li, Mg/AlH₃
- Validation and Demonstration of VHMS (Molecular Modeling)
- Validation and Demonstration of Medium Throughput Combinatorial Tools

Virtual High Throughput Screening

- Molecular Mechanics VHMS (~1000 compositions/month)
- DFT to refine leads, predict thermodynamics
- >>> Guide experiments to find optimal system faster

Combi Synthesis & Screening

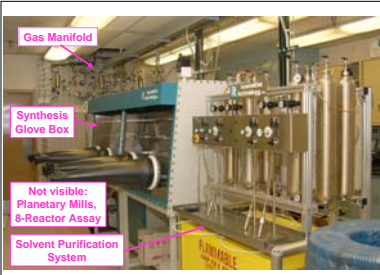
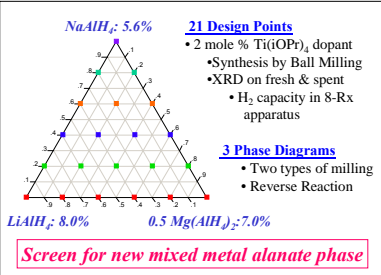
- Medium Throughput (8x), then High Throughput (48x)
- Representative sample preparations – powders by ball-milling
- >>> Feedback to theoretical efforts to refine models

Follow up on Leads:

- Additional testing, characterization & modeling for increased understanding
- Intermediate scale-up & multi-cycle testing

Material Meeting Targets:

- Optimization & scale-up to 1 kg
- Identify commercial manufacturing routes
- Design storage system & develop cost estimate



Medium-Throughput Testing Methodology

Medium Throughput Validation: Synthesis & Testing

NaAlH₄+LiAlH₄+Mg(AlH₃)₂ Phase Diagram As-Synthesized wt-% H (1st Cycle)

NaAlH₄+LiAlH₄+Mg(AlH₃)₂ Phase Diagram Reversible wt-% H (2nd Cycle)

Temperature Programmed Desorption

- Ramp to 220°C @ 2°C/min
- Hold at 220°C, 1 hour
- Closed cell, wt-%H from pressure measurement
- 8 Reactors in parallel (simultaneous)

Rehydrating

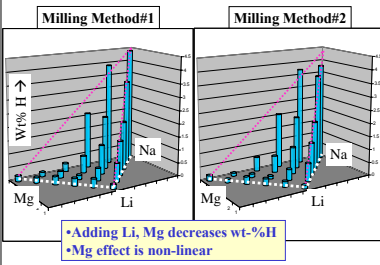
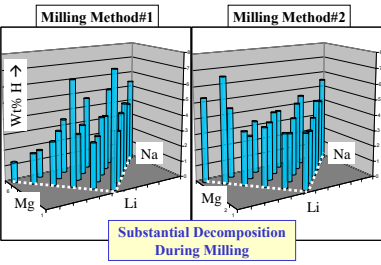
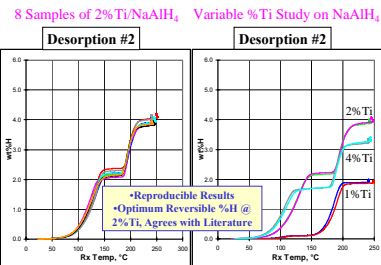
- 125°C, 1250 psig (87 bar), 12 hours

Cycles

- Two cycles is standard for screening
- Cycle #2 → Reversible wt-%H
- Original protocol ended after 2nd desorption; recently added a final rehydrating for characterization

Optional Pretreatment

- Perform hydriding step before first desorption

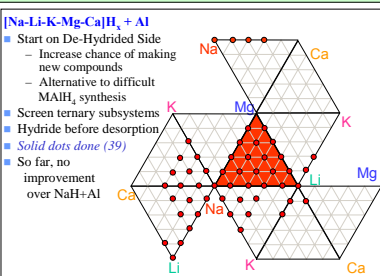
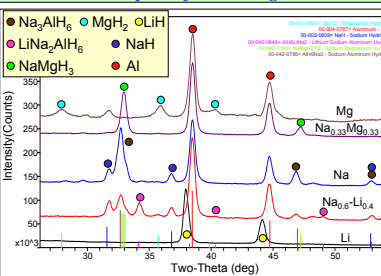
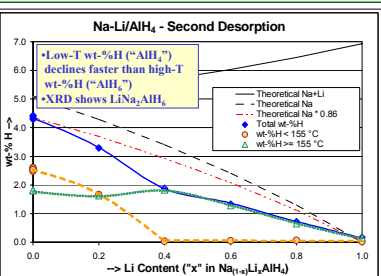
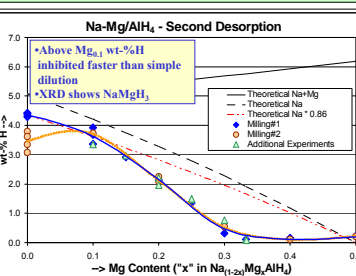


Na-Mg/AlH₃ Binary Sub-System

Na-Li/AlH₃ Binary Sub-System

Phases Observed In Li-Na-Mg/AlH₃ System: Samples After Testing

Phase Diagrams From Dehydried Side

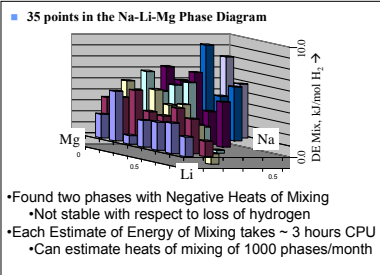
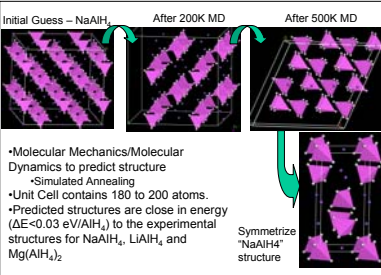
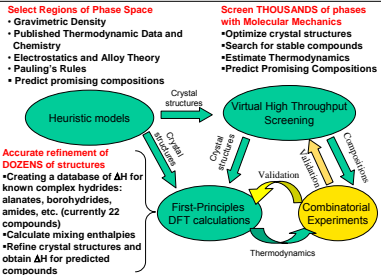
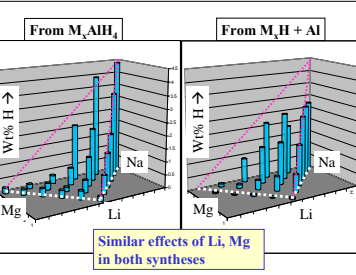


Phase Diagram From Dehydried Side

Molecular Modeling

Virtual High Throughput Screening

Virtual High Throughput Screening

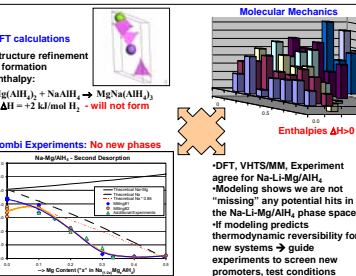


Application Of Models To Na-Mg-Li Alanates

High-Throughput Combi System

Summary

Plans - I: Alanates



Synthesis

- Capability
 - Automated solution and powder dispensing
 - Vacuum, filtration, sample washing & drying
 - Sample agitation, sample heating to 250°C
- HT Milling

Characterization

- HT XRD fully operational

Testing

- Using TPD, against atmospheric pressure
- Higher T,P capability than 8-Rx: 350°C, 120 bar

System builds on UOP's extensive Combi expertise

- Material synthesis, catalyst preparation & testing, DOE, informatics

Medium Throughput Synthesis & Testing

- Results match literature data
- Used in production mode

Na-Li-Mg/AlH₃ Phase Diagram Downselect

- Experiments + MM Modeling + DFT Modeling => no promising new compositions in this system

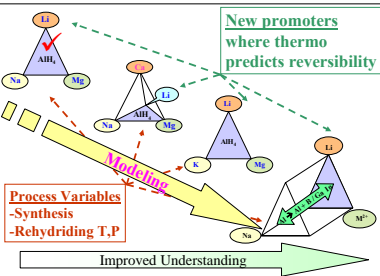
Modeling

- Three-Tier approach demonstrated for Na-Li-Mg/AlH₃
- VHMS demonstrated and checked against experiment
- Modeling indicates that we are not "missing" any promising compositions in the Na-Li-Mg/AlH₃ phase space
- Ready to start screening new UOP's

Extension to other elements

- K, Ca phase diagrams started

High-Throughput system construction on schedule



Plans - II: Other Systems

Project Timeline

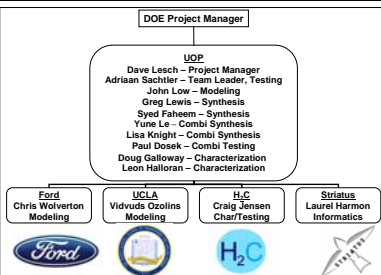
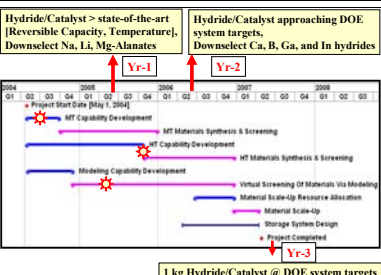
The Team

Acknowledgement

Since our proposal was written, several new interesting approaches have been published, including:

- Amides
 - 2 Li(NH₂) + MgH₂ → Li₂Mg(NH)₂ + 2H₂
 - Y. Nakamori and S. Orimo *J. Alloys Compd.* 370, 2004, 271.
 - S. Orimo, Y. Nakamori, G. Kitahara, K. Miwa, N. Ohba, T. Naito, and S. Towata *Appl. Phys. Lett.* 2004, 79, 1765.
 - W. Luo *J. Alloys Compd.* 381, 2004, 284.
- Destabilization of Hydrides
 - 4LiH + Si → SiLi₄ + 2H₂
 - 2LiBH₄ + MgH₂ → 2LiH + MgB₂ + H₂
 - J.J. Vajo, et al. *J. Phys. Chem. B* 108(2004)13977, 104(2005)3719

In addition to completing the alanate systems we plan to pursue approaches building on or extending concepts like this, and other idea's.



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