



NIST
National Institute of
Standards and Technology
Technology Administration
U.S. Department of Commerce



imagination at work



BROOKHAVEN
NATIONAL LABORATORY

HRL
LABORATORIES
ornl
OAK RIDGE NATIONAL LABORATORY

Intematix
 Sandia
National
Laboratories



STANFORD
MATERIALS SCIENCE
AND ENGINEERING

U
THE
UNIVERSITY
OF UTAH

Carnegie Mellon

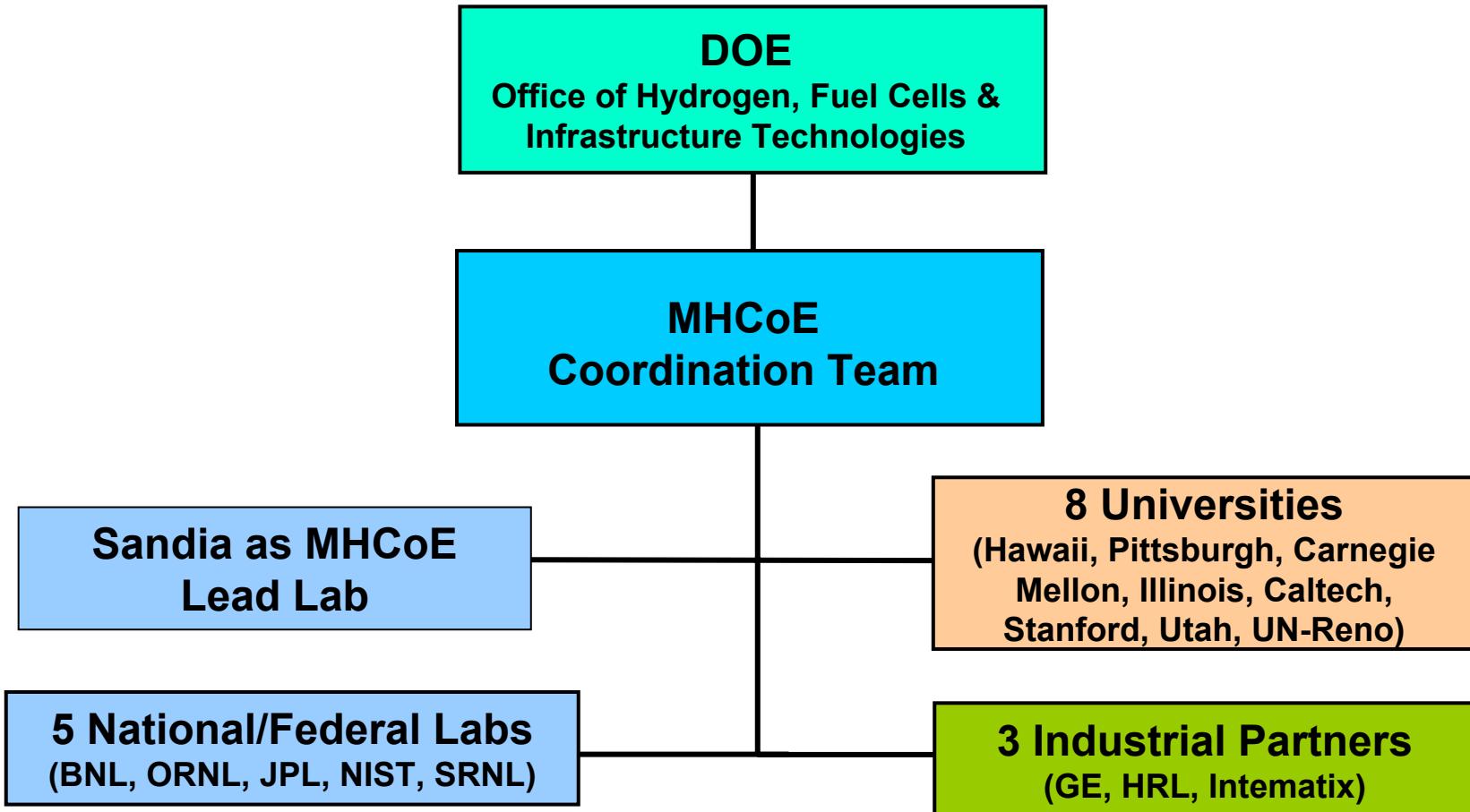
SRNL
SAVANNAH RIVER NATIONAL LABORATORY
We Put Science To Work

Overview of DOE Metal Hydride Center of Excellence (MHCoE)

James Wang, Jay Keller & Karl Gross
Sandia National Laboratories
Livermore, California

This presentation does not contain any proprietary information

DOE Metal Hydride Center of Excellence (MHCoE)



Overview

Timeline: Project start date - FY2005
Project end date - FY2009
Percent complete - New start

Budget: Total funding proposed - \$25M
DOE share asked - \$25M
Contractor share - 20%

Funding received in FY05: \$5M
Funding expected for FY06: \$5M

Partners: 8 universities, 3 industrial partners,
and 6 national/federal labs

Barriers to Success

- **Limited selection of materials to meet gravimetric targets**
- **Volumetric densities trend opposite to gravimetric gains**
- **Safety in use of light-weight reactive materials**
- **Cost of hydrogen storage systems**
- **Energy transfer requirements for H₂ storage systems**
- **Kinetics of solid-state reactions**
- **Cycle life, reliability and durability**

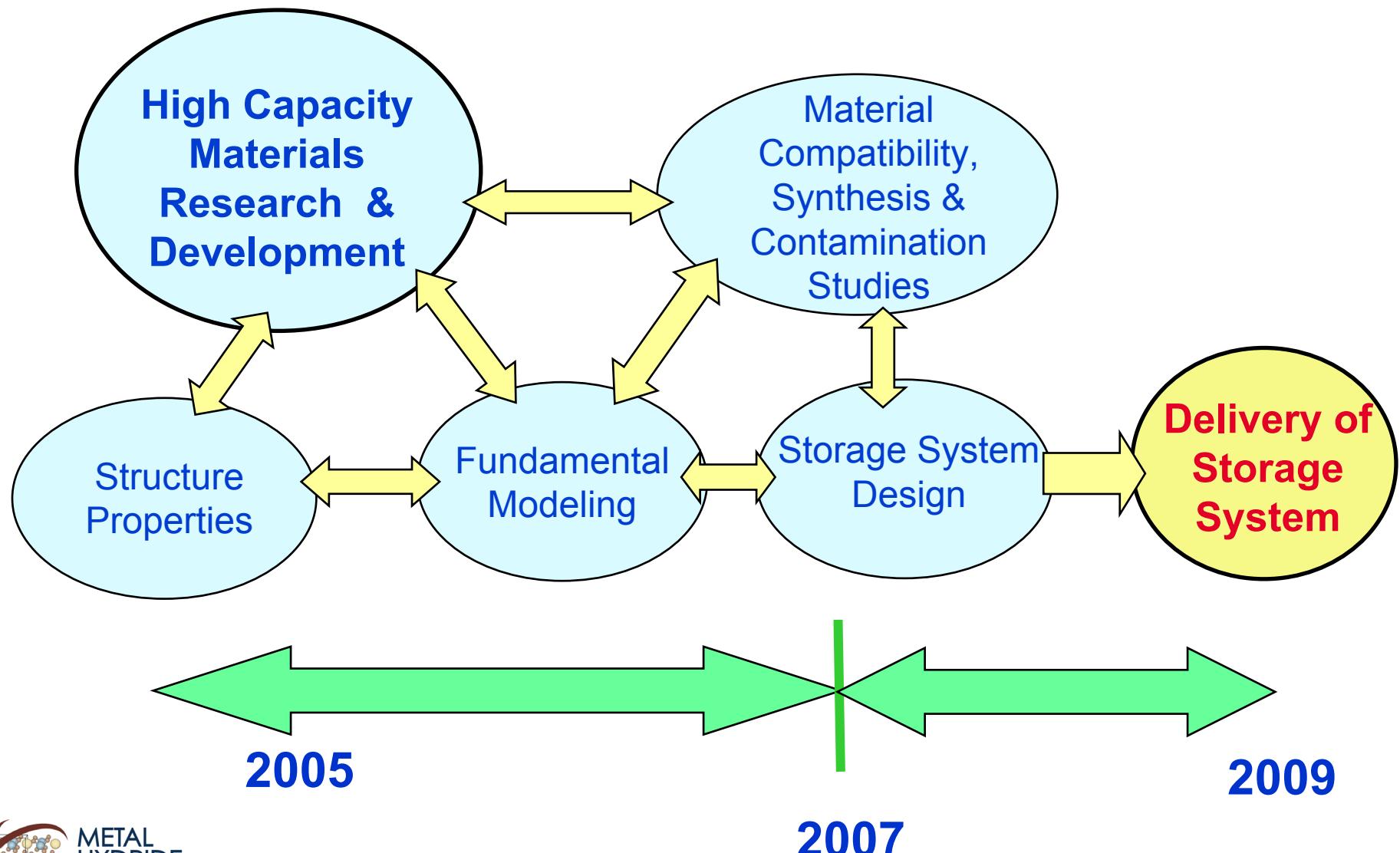
Objectives

- **Develop new reversible hydrogen storage materials that meet or exceed DOE FreedomCAR 2010 and 2015 goals**
- **Deliver a 1 kg hydrogen storage system to DOE by 2010**

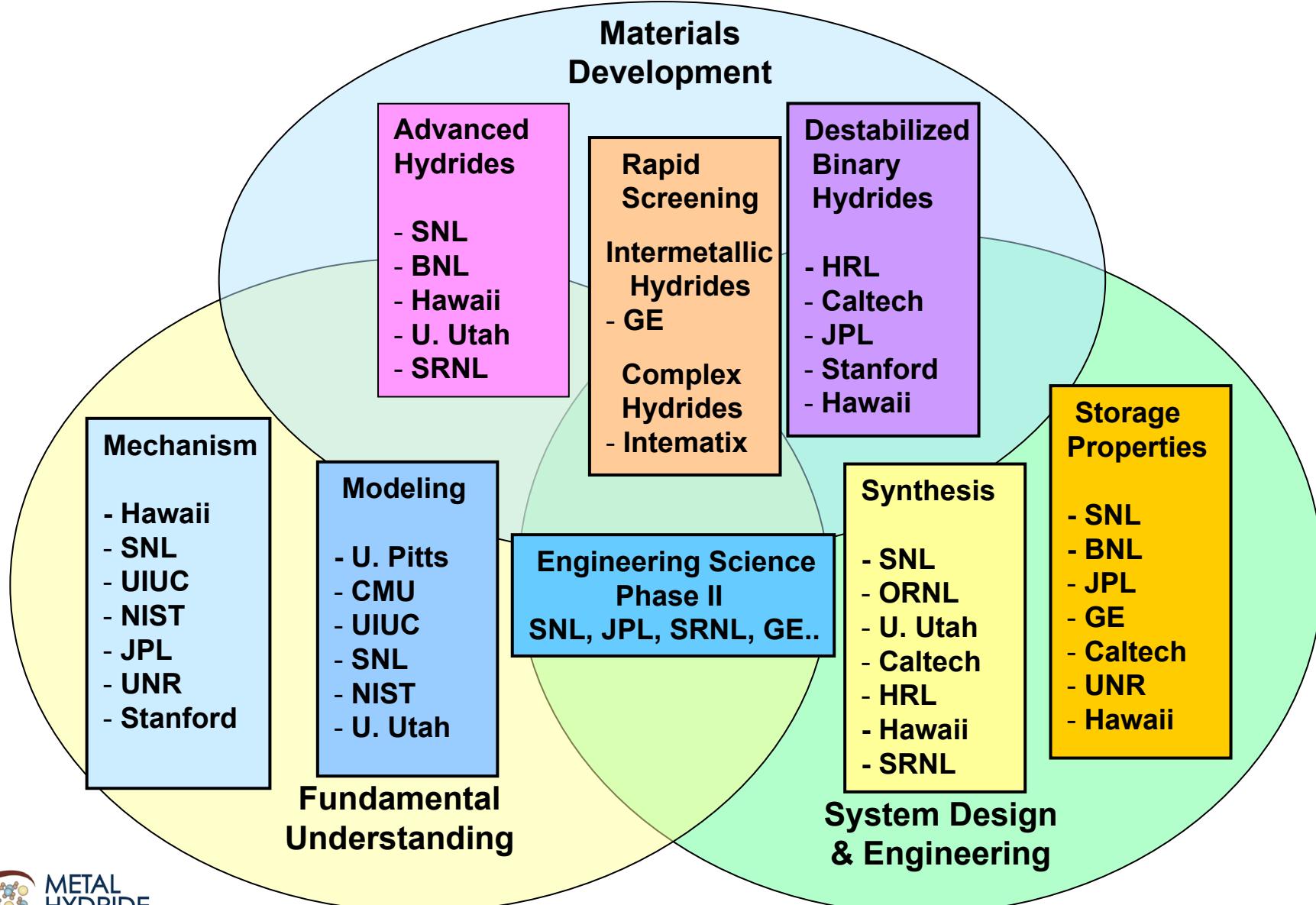
Approach

- **System engineering focus to maximize the overall performance**
- **Science based R&D to guide discovery**
 - Teaming of 1st principal modeling and experimental efforts
 - Identification and use of fundamental mechanisms to extrapolate beyond base materials
- **Combinatorial methods to screen potential materials**
 - Intermetallic hydrides
 - Complex hydrides

Science-based Materials Development



MHCoE Partners Cover a Full Range of Expertise



MHCoE System Engineering & Integration

Materials
Development

System Engineering
& Integration



Component
engineering,
design, & testing



Sandia
National
Laboratories

Team Lead

Storage system design,
integration, & testing

Fundamental
Understanding



System design,
fabrication and
testing



System design, fabrication &
commercialization



Storage engineering, design,
fabrication, & testing

MHCoE Materials Synthesis Resources

Materials Development



System Design & Engineering



Solution-based synthetic methods development



Develop chemical routes for nano-sized metal hydrides and bulk productions

Fundamental Understanding



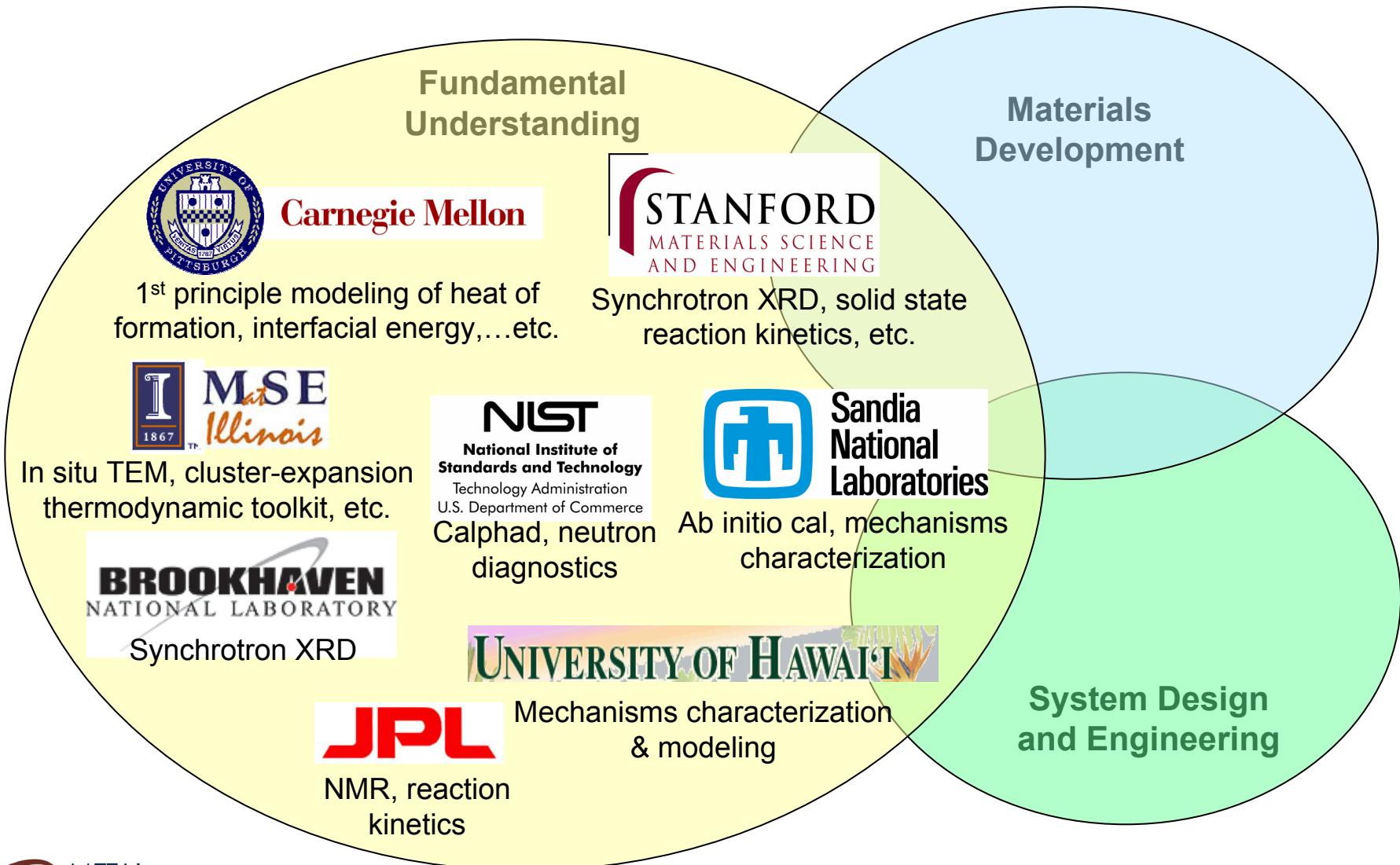
Nanostructured catalyst development & new synthesis routes

Nanoparticle synthesis (gas condensation) & materials Characterization (TEM, XRD)



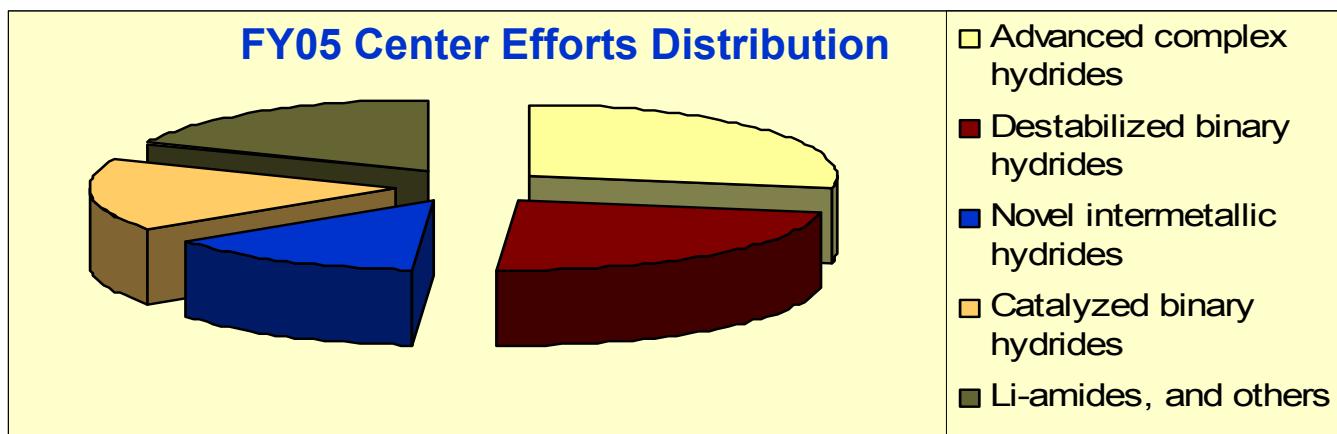
Synthesis & characterization of aluminum hydrides

MHCoE Modeling and Mechanism Resources

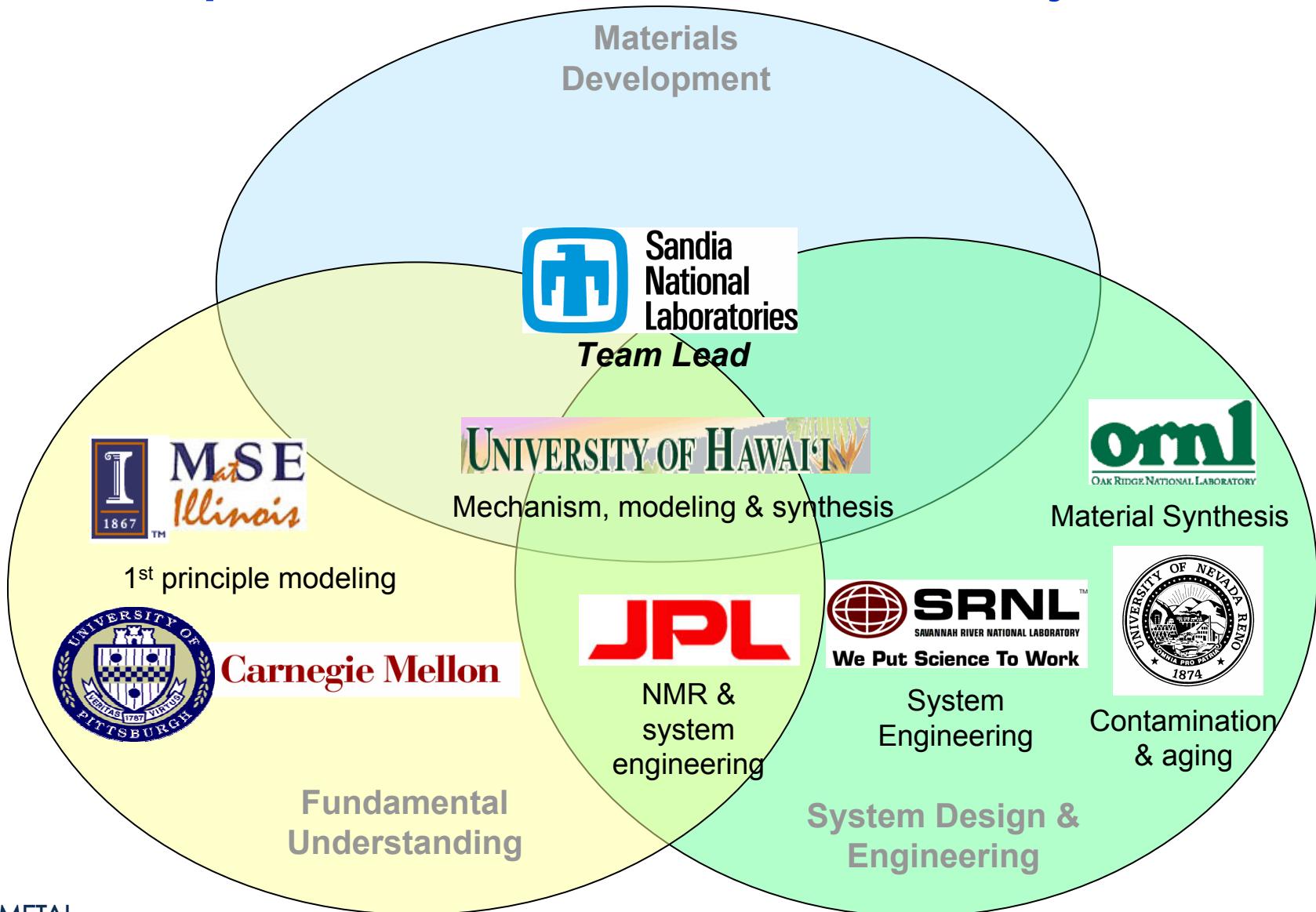


MHCoE – Materials Development Categories

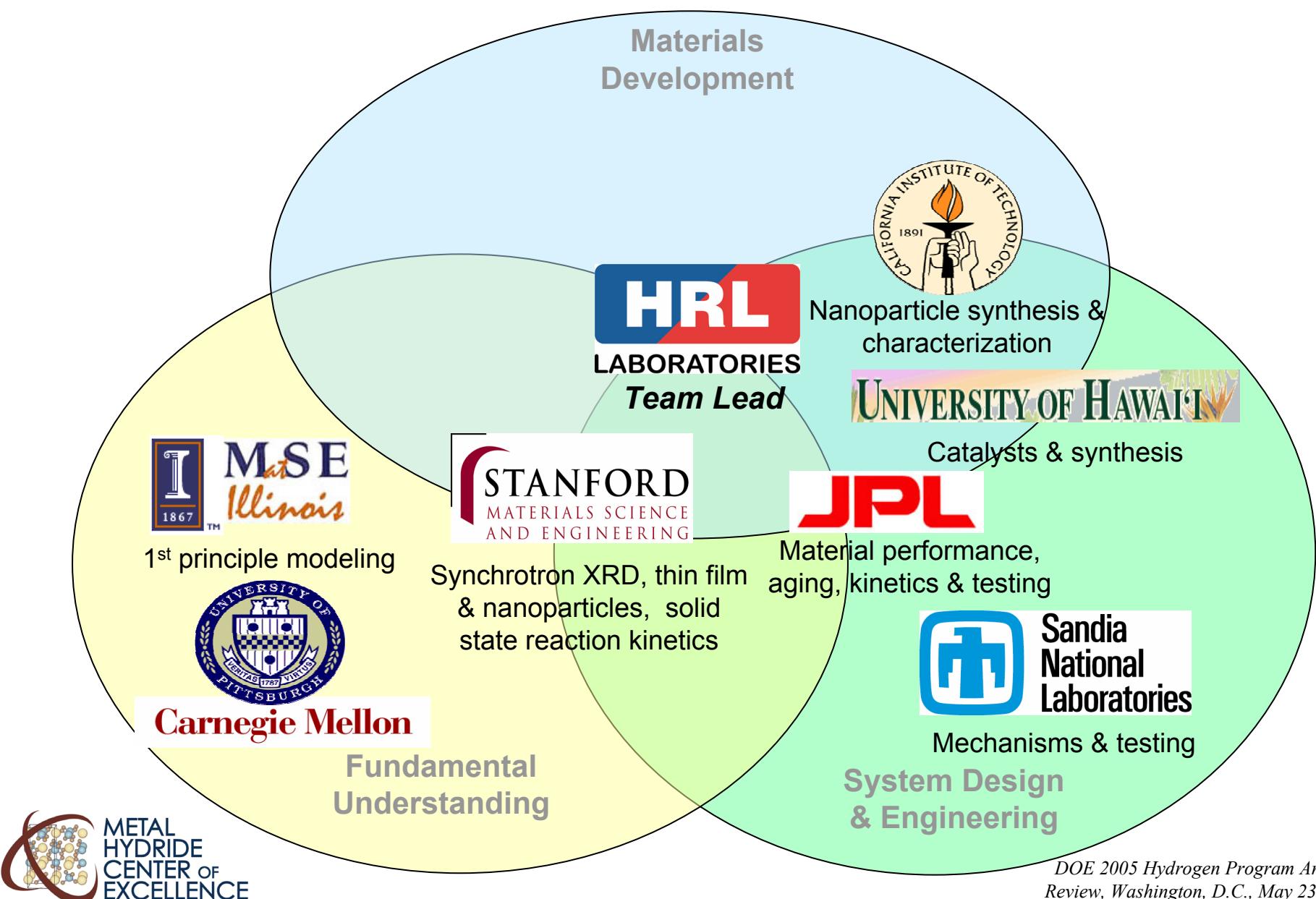
- Advanced complex hydrides ($\text{AH}_x + \text{B} + \text{H}_2 \rightleftharpoons \text{ABH}_y$)
- Destabilized binary hydrides ($\text{AB} + \text{H}_2 \rightleftharpoons \text{AH}_x + \text{B}$)
- Novel intermetallic hydrides ($\text{AB} + \text{H}_2 \rightleftharpoons \text{ABH}_x$)
- Catalyzed binary hydrides ($\text{A} + \text{H}_2 \rightleftharpoons \text{AH}_x$)
- Other reversible hydrogen storage materials
(e.g. lithium amides, non-lithium based imides)



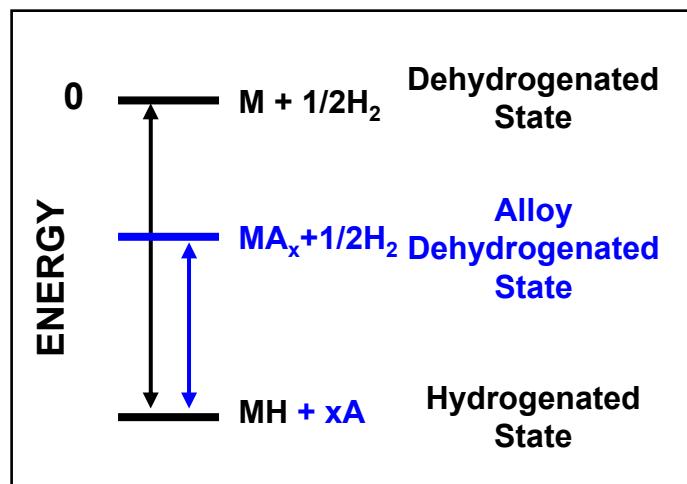
MHCoE Team on 1st Principal Modeling & Experimentation for Material Discovery



MHCoE Team on Mechanistic Approach to Destabilize Hydrides



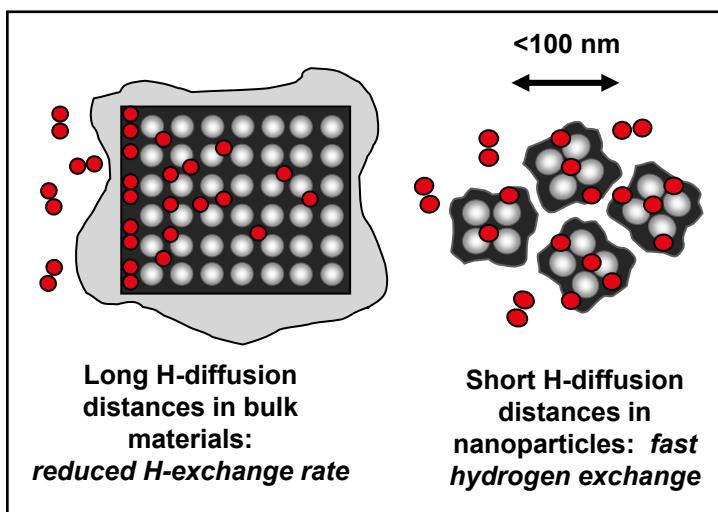
Example of Science Based Approach of Hydride Destabilization and Nano-engineering



Alter Thermodynamics by Hydride Destabilization

Reduce energy (temperature) needed to liberate H_2 by forming dehydrogenated alloy

- System cycles between the hydrogen-containing state and the metal alloy instead of the pure metal
- Reduced energy demand means lower temperature for hydrogen release

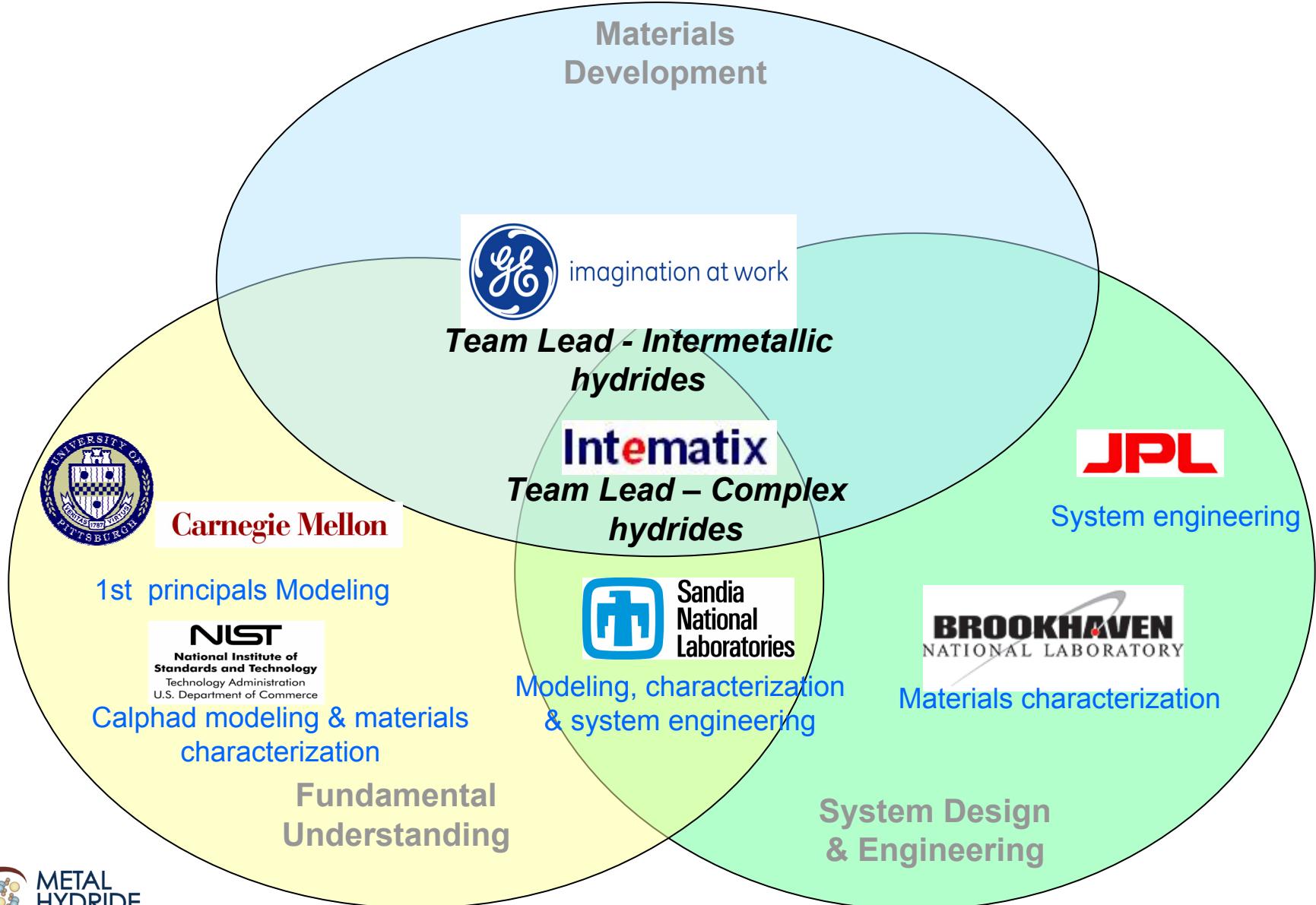


Enhance Kinetics by Nano-engineering

Increase H-exchange rate by decreasing particle size

- Overall rate controlled by hydrogen diffusion distance
- H-exchange much faster in nanoscale particles than in bulk

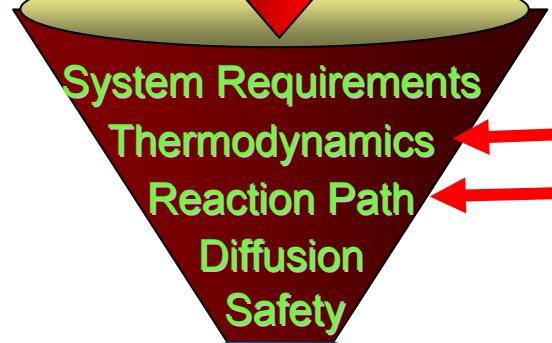
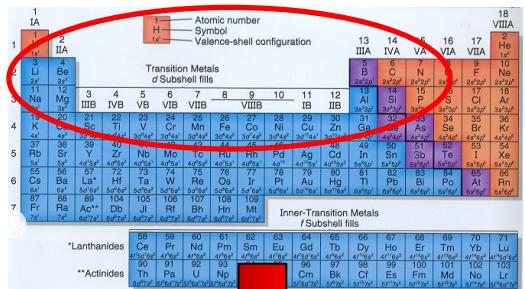
Combinatorial Approach Teams



Combinatory Approach – Intermetallic Hydride

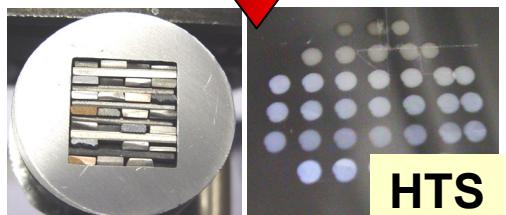


imagination at work



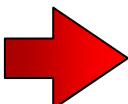
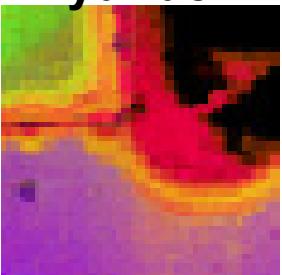
DFT
Phase
diagram
analysis

Materials
Concept
S

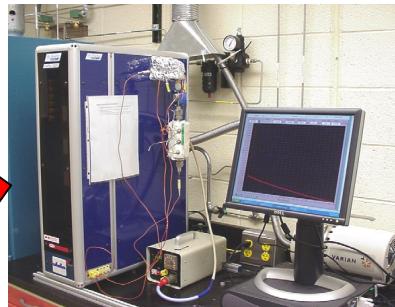


HTS

Hydride ID



Synthesis

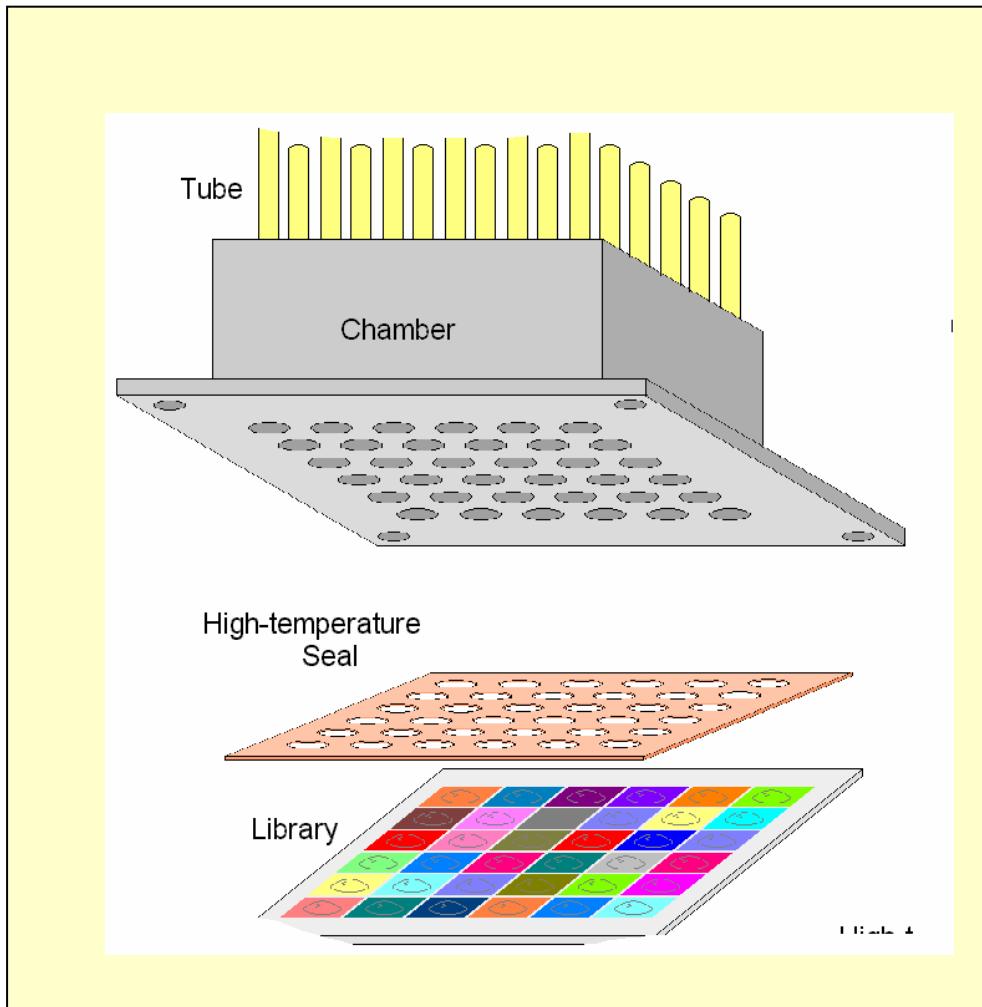
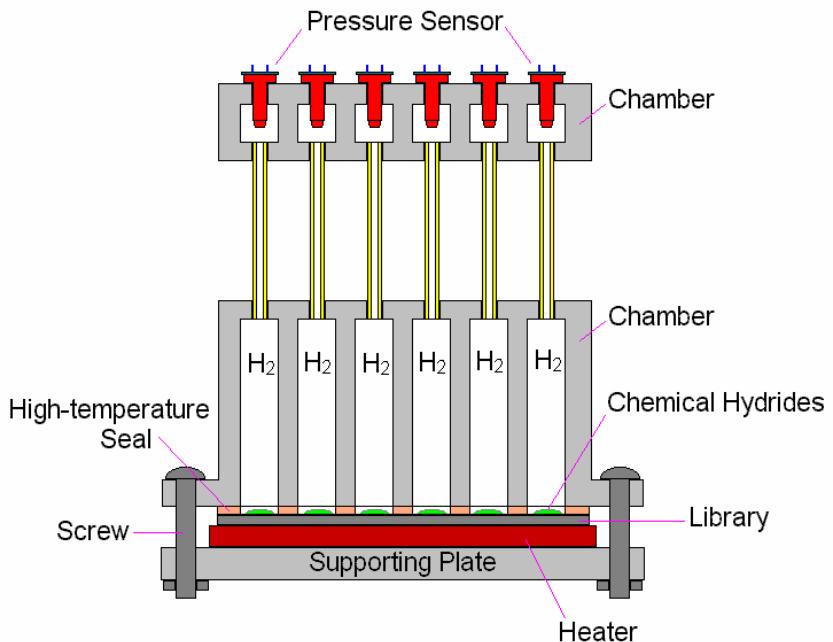


Characterization

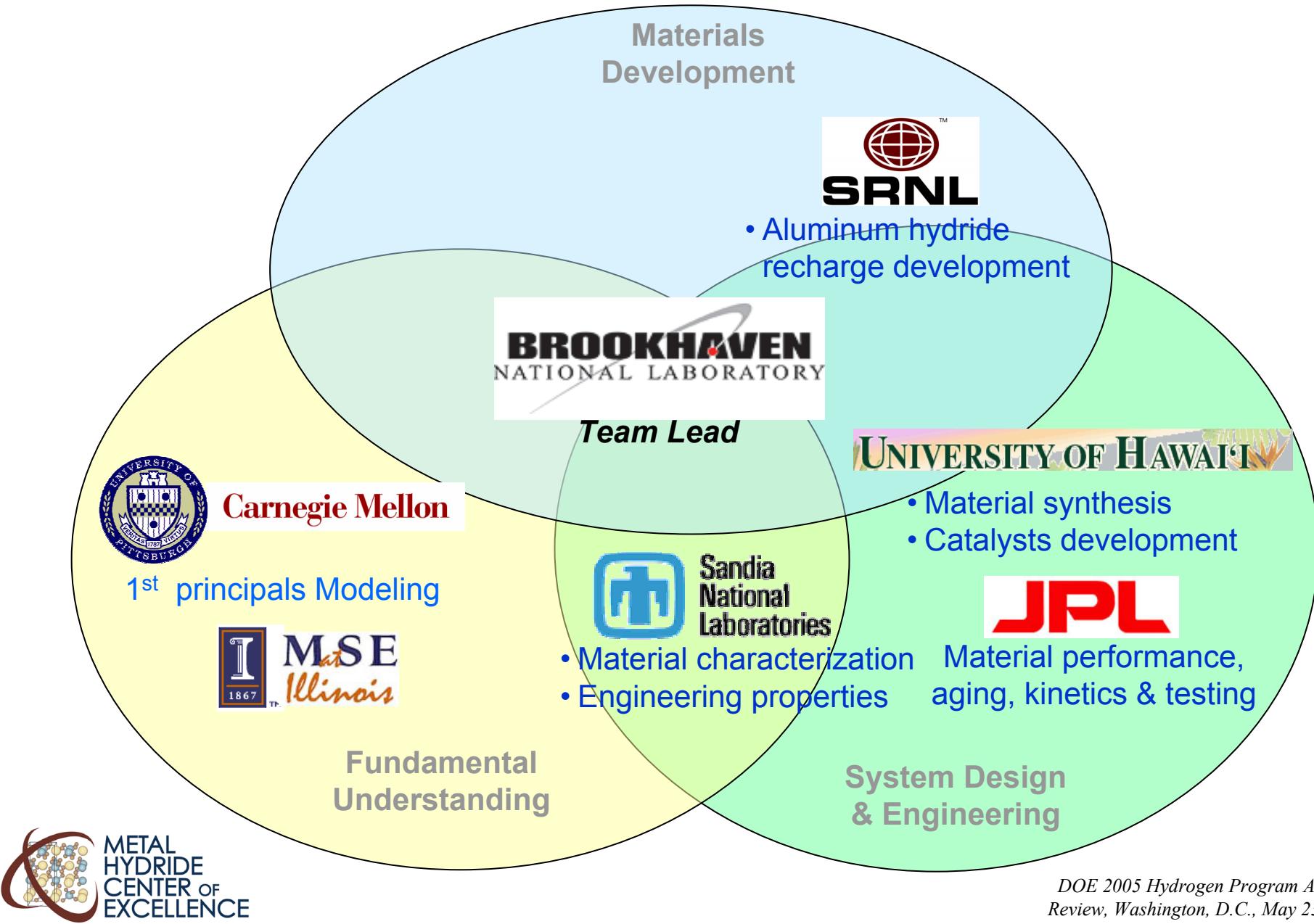
Combinatory Approach – Complex Hydride

Intematix

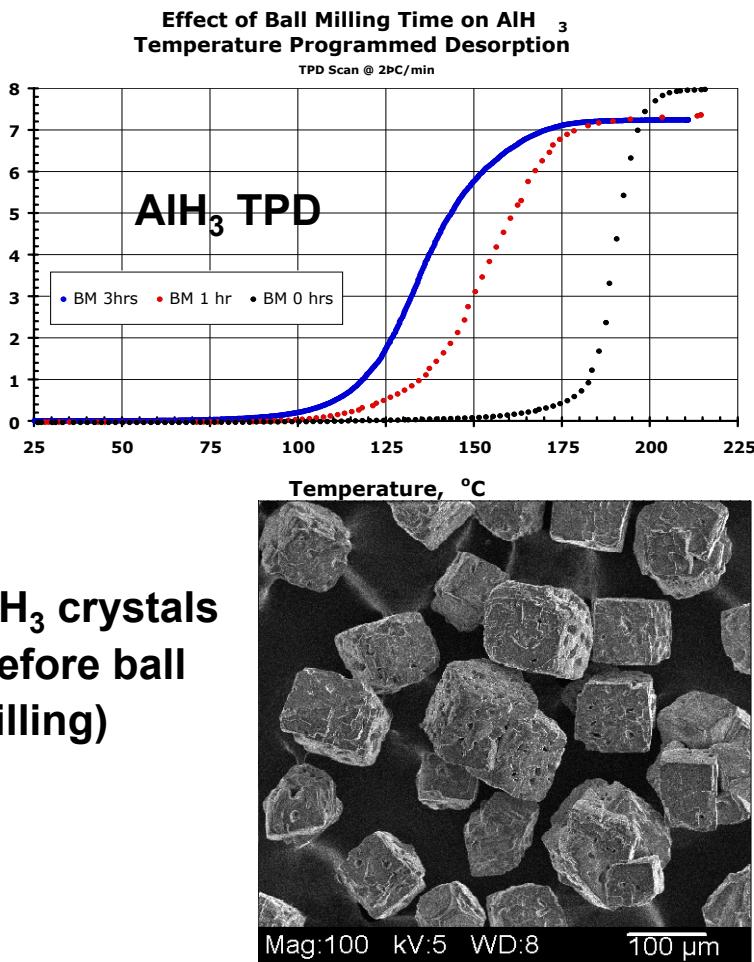
Micro-reactor



System Engineering Team – AIH₃



Crystalline and Microcrystalline AlH₃



Accomplished:

1. Demonstrated H₂ yield of 7-8 wt.% at < 175°C. Potential for 10 wt.% at lower temperatures. **But not easily reversible!**
2. Defined ball-milling (particle size) effects.
3. Found at least one “metallurgical stimulant” to increase low-temperature (100-125°C) desorption kinetics.

Target Needs:

1. Decrease desorption temperature to < 80°C (fuel cell waste heat).
2. Find a practical, low-cost way to revert spent Al powder back to AlH₃.

Summary

- **The Challenge:**
 - *Systems must be developed that deliver the best option for storing hydrogen on-board a vehicle*
- **Our Strategy:**
 - Storage System Focused / Science-based materials development incorporating
 - Phase I
 - *1st principle modeling and fundamental mechanisms as guides*
 - *Combinatorial screening for materials discovery and improvement*
 - Phase II
 - *Total systems approach to development a hydride storage system*
- **Our Team:**
 - *Covers a full range of fundamental and applied science , and systems engineering expertise*
 - *Developed powerful multi-disciplinary teams*

Acknowledgement

Point of Contact

- Channing Ahn
- Gilbert Brown
- Robert Bowman
- Dhanesh Chandra
- Bruce Clemens
- Zak Fang
- Craig Jensen
- Karl Johnson
- Ted Motyka
- Greg Olson
- Ian Robertson
- David Sholl
- Susan Townsend
- Terrence Udovic
- Jim Wegrzyn
- Xiao Dong Xiang

Institution

- California Institute of Technology
- Oak Ridge National Laboratory
- Jet Propulsion Laboratory
- University of Nevada, Reno
- Stanford University
- University of Utah
- University of Hawaii at Manoa
- University of Pittsburg
- Savannah River National Laboratory
- HRL Laboratories, LLC
- University of Illinois at Urbana-Champaign
- Carnegie Mellon University
- General Electric Company
- NIST Center for Neuron Research
- Brookhaven National Laboratory
- Intematix Corporation

Thermodynamically Tuned Nanophase Materials

Gregory L. Olson and John J. Vajo
HRL Laboratories, LLC
Malibu, CA

– A Participant in the DOE Metal Hydride Center of Excellence –

May 23, 2005

*DOE 2005 Hydrogen Program Annual Review,
Washington, D.C., May 23-26, 2005*

This presentation does not contain any proprietary or confidential information

Project ID #
STP28

Timeline

- Project start date: FY05
- Project end date: FY09
- Percent complete: *New Project*

Budget

- Expected Total Project Funding:
Phase One - 3 years: \$1.65M
 - DOE Share: \$1.20M
 - Contractor Share: \$0.45M
- Phase Two - 2 years:* \$1.1M
 - DOE Share: \$0.8M
 - Contractor Share: \$0.3M
- Funding for FY05:
\$400K (DOE), \$150K (cost share)

Barriers

Weight and volume
Efficiency
Hydrogen capacity and reversibility

Targets

Gravimetric capacity: >6%
Volumetric capacity: > 0.045 kg H₂/L
Min/Max delivery temp: -30/85°C

Partners

- Participant in DOE Metal-Hydride Center of Excellence; collaborations with MHCe partners on synthesis, modeling, and characterization
- Coordinator of sub-team on hydride-destabilized nanophase materials (Caltech, JPL, Stanford, U. Hawaii)



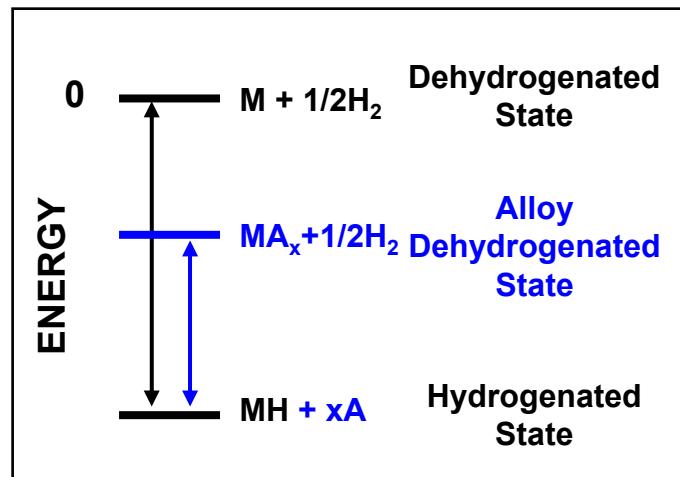
- | | | | | |
|-----------------------------------------------|---------------------------------------------|---------------------------------------|-------------------------------------------------------------------------|----------------------------------------------------------|
| • Sub-team coordination | • Nanoparticle synthesis (gas condensation) | • Nanostructured catalyst development | • <i>In situ</i> , real-time synchrotron XRD of H-induced phase changes | • Materials development (performance / aging properties) |
| • Hydride destabilization strategies | • Materials Characterization (TEM, XRD) | • New synthesis routes | • Nanoparticle synthesis | • Reaction kinetics and metal atom motion |
| • Nanoparticle synthesis | | | • Solid state reaction kinetics | • Concept testbed |
| • Hydrogen cycling: test and characterization | | | • Thin film reactions | |

Other partners in MHCoE will also contribute in areas of nanostructure synthesis, diagnostics and modeling/simulation

Objectives

To develop and demonstrate a safe and cost-effective light-metal hydride material system that meets or exceeds the DOE goals for on-board hydrogen storage

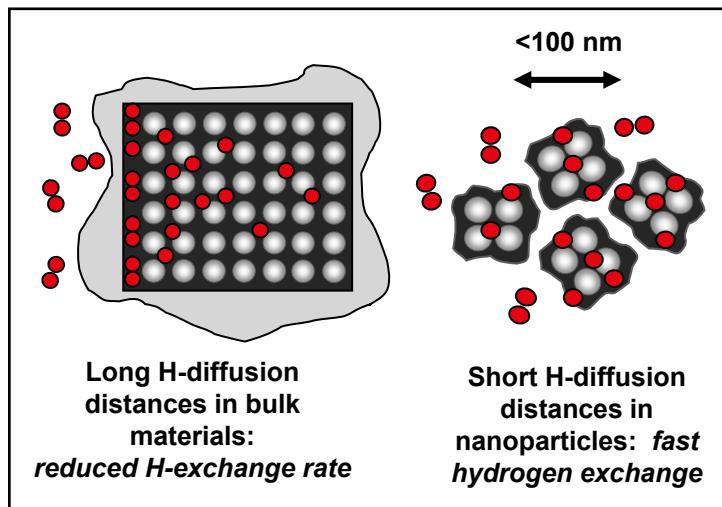
- **To implement hydride destabilization strategies for light-metal hydrides containing Li and Mg**
 - Benchmark results from destabilized Mg-Si system against conventional Mg hydrides
 - Extend to higher capacity systems, including: $\text{LiBH}_4 + \text{MgH}_2$ and $\text{LiBH}_4 + \text{Mg(X)}$
 - Down-select specific systems for continued study and system demonstration
- **To develop methods for efficient and controlled synthesis of destabilized nanophase metal hydrides and to employ the materials in reversible hydrogen storage system**
 - Utilize both “top-down” (e.g., energetic ball-milling) and “bottom-up” (direct) synthesis routes (*MHCoE collaboration*)
 - Characterize sorption behavior in nanostructured systems (*MHCoE collaboration*)
 - Evaluate role of contaminants and particle sintering – develop mitigation strategies



Alter Thermodynamics by Hydride Destabilization

Reduce energy (temperature) needed to liberate H_2 by forming dehydrogenated alloy

- System cycles between the hydrogen-containing state and the metal alloy instead of the pure metal
- Reduced energy demand means lower temperature for hydrogen release

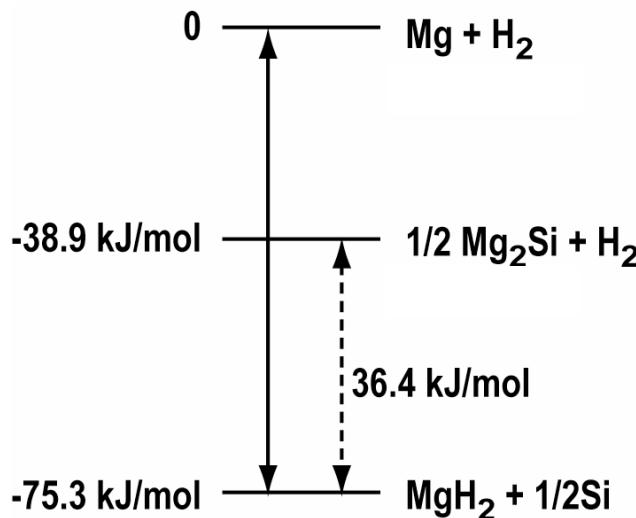


Enhance Kinetics by Nano-engineering

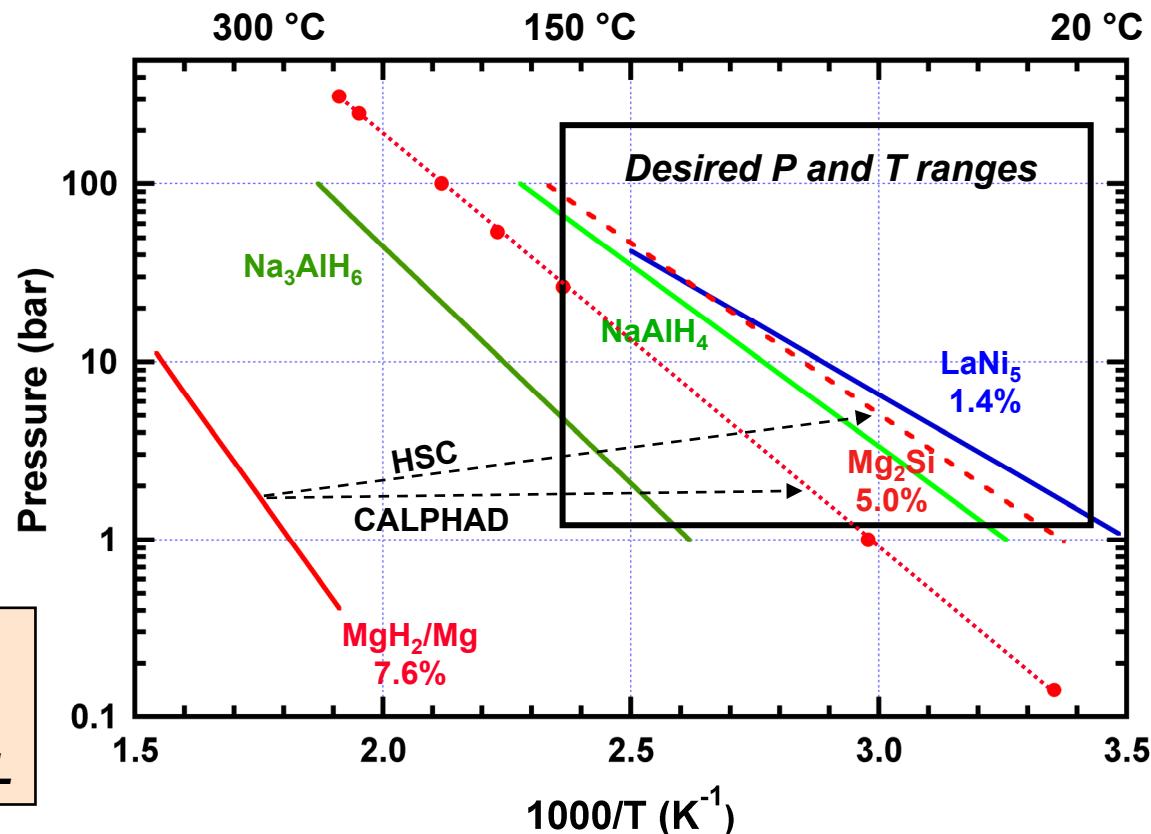
Increase H-exchange rate by decreasing particle size

- Overall rate controlled by hydrogen diffusion distance
- H-exchange much faster in nanoscale particles than in bulk

- Destabilized systems that satisfy all thermodynamic requirements for practical on-board storage not yet developed; heat removal during re-fueling remains an issue
- Dependence of nanoparticle size on diffusion rate unknown
- Efficient synthesis methods for light-metal alloy nanoparticles not yet established
- Effects of nanoparticle sintering/agglomeration during cycling reactions not characterized
- Efficient method for catalyzing nanoparticle reactions not developed



Mg₂Si:
Gravimetric Capacity: 5%
Volumetric Capacity: 0.083 kg/L



Equilibrium conditions predicted by thermodynamic modeling software (HSC and CALPHAD) for MgH_2/Si system in desired temperature and pressure range

- **Demonstrate reversibility**
 - Initiated work with Sandia (*K. Gross/E. Ronnebro*) using high pressure Sieverts system
 - Collaboration with Stanford U. (*B. Clemens, et al.*) on Mg₂Si thin films formed by sputtering (*use as model system to assess reversibility*)
- **Nano-engineer to reduce diffusion distances**
 - Collaboration with Caltech (*C. Ahn, et al.*) on generation of nanostructured Mg₂Si by gas phase condensation
 - Initiated work (*HRL*) on alternative routes for synthesis of nanoscale Mg₂Si
 - Developed approaches for forming MgH₂ in nanostructured templates
- **Characterize thermodynamics and H-diffusion**
 - CALPHAD calculations (P_{eq} vs temp.) (*NIST-U. Kattner*)
 - Collaboration with Carnegie-Mellon U. (*D. Sholl et al.*), U. Pittsburgh (*K. Johnson et al.*), and U. Ill (*D. Johnson*) on thermodynamic barriers/intermediates and phase formation mechanism(s)

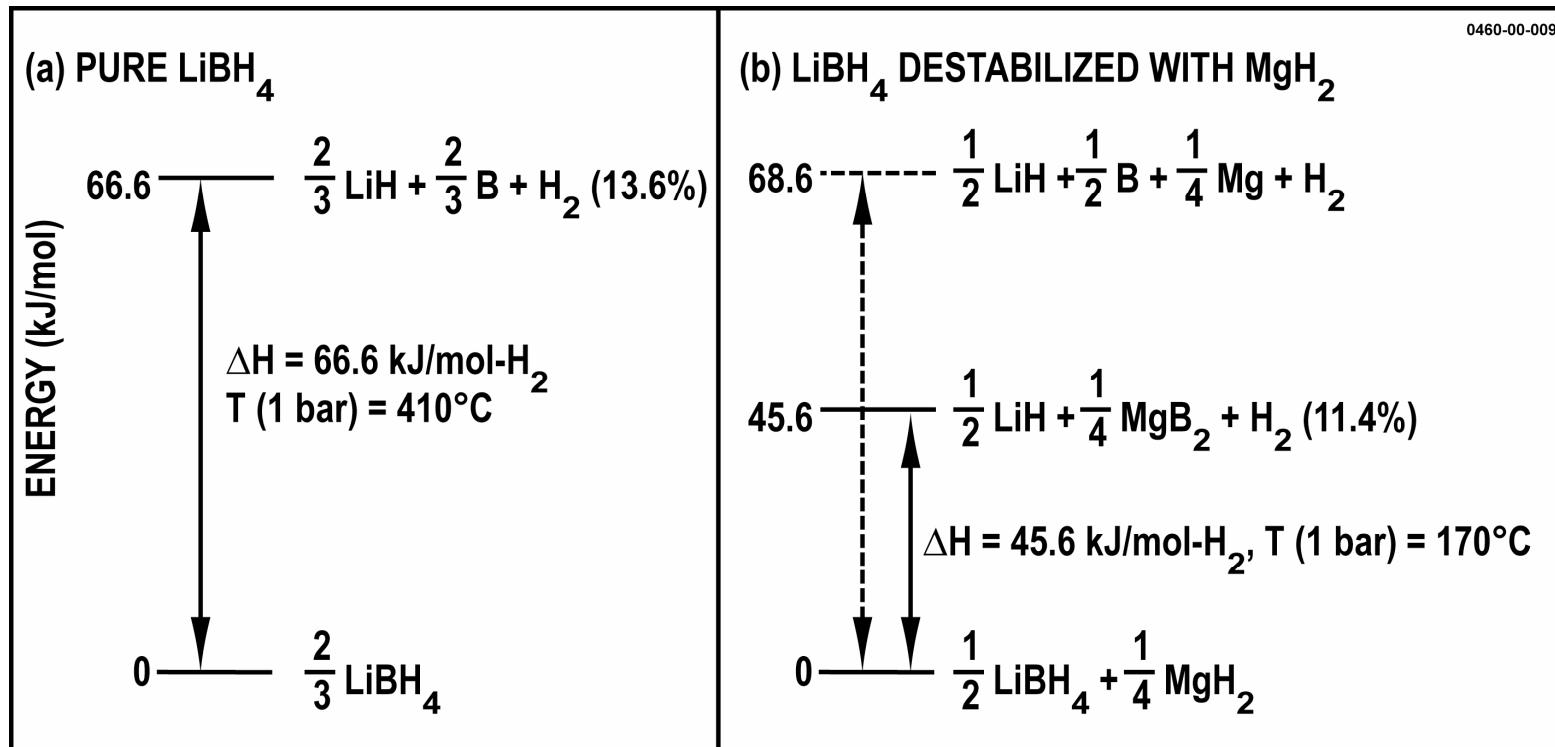
HRL

- **Metathesis reactions in pressure vessel to synthesize Mg₂Si:**
 - 4Mg + SiCl₄ ⇒ Mg₂Si + 2MgCl₂ (high vapor pressure)
 - 2MgCl₂ + SiCl₄ + 8Na ⇒ Mg₂Si + 8NaCl (stronger reducing agent)
- **Formation of MgH₂ in mesoporous hosts:**
 - Infiltrate porous alumina or carbon aerogels with dibutylMg and thermally decompose:
 - Mg(C₄H₉)₂ ⇒ 80% MgH₂ + 10% [Mg(C₄H₈)]_n + 10% Mg
 - Alternatively, decompose Grignard compounds to form MgH₂, Mg, and MgX₂
- **Synthesize Si nanoparticles and react with Mg(g) ⇒ Mg₂Si (in pressure vessel)**
- **Exploring plasma-based approaches for nanoparticle generation**

MHCoE Partners

- **Form Mg and Mg₂Si nanostructured films by sputtering (B. Clemens–Stanford)**
 - 1-D nanostructured model system
 - Cap with Pd and/or Ti ⇒ Catalyst; O₂ barrier
- **Create Mg, Mg₂Si nanoparticles by gas-phase condensation (C. Ahn-Caltech)**
 - Mg nanoparticles <100 nm demonstrated
 - Exploring direct synthesis of Si nanoparticles
- **Initiate collaboration with Z. Fang (U. Utah) on use of Chem. Vapor Synthesis process to form Mg₂Si powders**

Formation of MgB_2 estimated to reduce $T(1 \text{ bar})$ by $\sim 240^\circ\text{C}$



- Reversibility recently demonstrated*
- However, operating temperature is high and kinetics slow
- Strong candidate for nano-engineering and catalyst development

*J. Vajo, S. Skeith, and F. Mertens, Reversible Storage of Hydrogen in Destabilized $LiBH_4$, J. Phys. Chem. B, 109, 3719-3722 (2005).

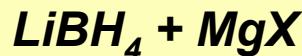
- **Explore reaction fundamentals**

- Nucleation and phase formation, rate-limiting steps, intermediate species, structure (*Stanford, JPL, U.Ill. CMU/Pitt*)
- CALPHAD calculations of equilibrium pressures/phase diagrams (*NIST*)

- **Improve kinetics using nano-engineering**

- Explore solution-based synthetic methods and mechanical attrition (energetic ball milling) for nanoparticle/nanocrystal formation (*HRL Labs*)
- Measure sorption characteristics (*HRL/JPL/Caltech/Stanford/Other MHCoE*)
- Explore kinetics phenomena unique to nanoscale (*Stanford*)

- **Identify and optimize catalyst(s) for reversible borohydride reactions**
(*U. Hawaii, HRL*)



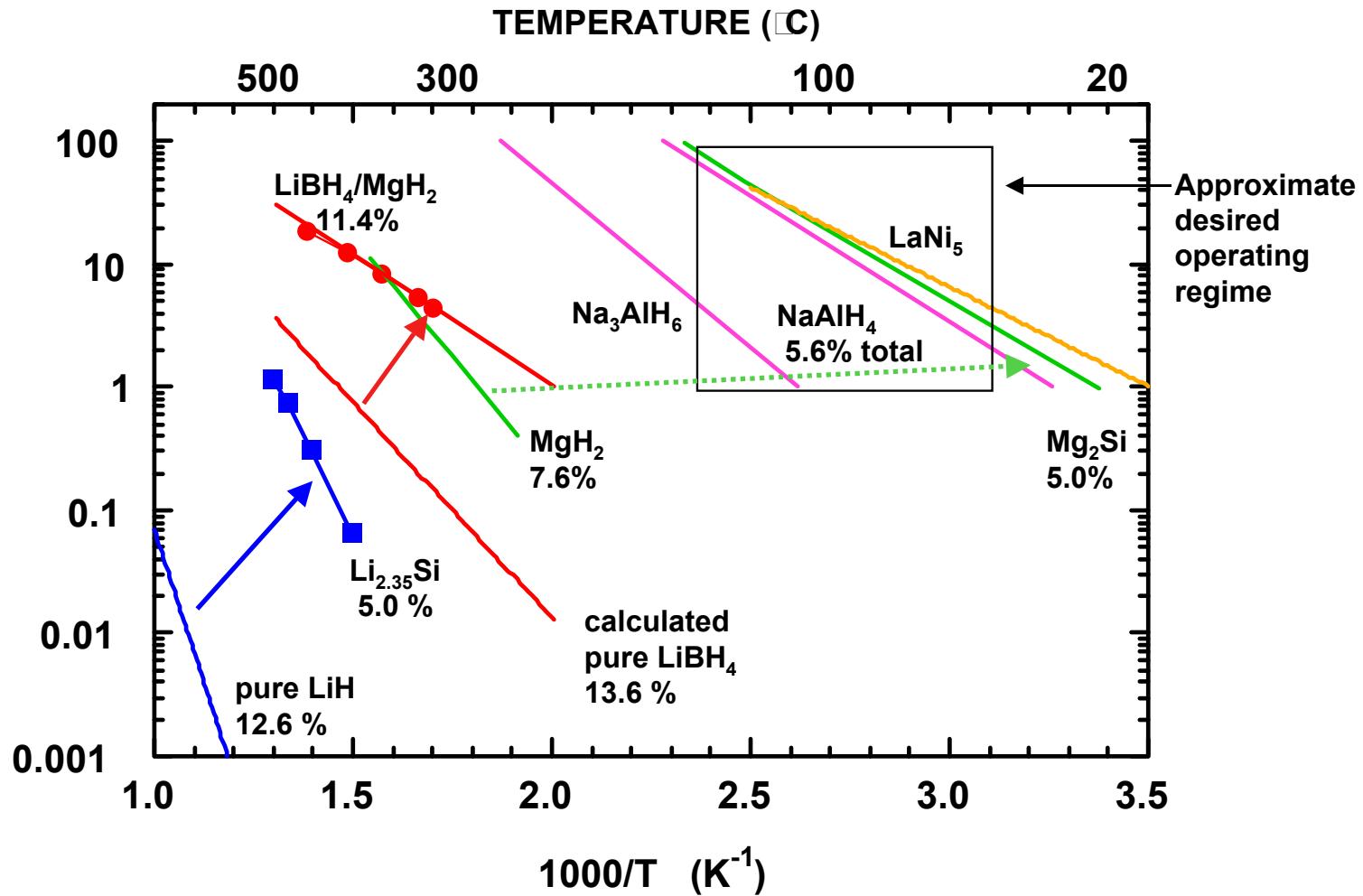
- The reversible system $2LiBH_4 + MgH_2 = 2LiH + MgB_2 + 4H_2(11.4\%)$ established.
- Analogous systems include: $LiBH_4 + MgX$ (where X = F, Cl, OH, O, S, Se, CO_3 , Si, etc.)
 - 8 destabilization reactions identified and characterized (*HSC modeling*)
 - H-capacities ranging from 5.4-9.6 wt.%, T(1 bar) from -10°C to 430°C



- Destabilize $LiNH_2$ and $LiBH_4$ using C or Si
 - 9 destabilization reactions identified; 1 characterized using HSC modeling
 - Thermodynamic properties of reaction products largely unknown (*modeling underway with MHCoE partners - Carnegie Mellon U., Univ. Pittsburgh*)

Hydride Destabilization

– Progress and Goals –



- Destabilization provides pathway to achieving desired temperature and pressure
- Ideal destabilized system not yet established

TASK	2005	2006	2007	2008	2009
Task 1: Destabilized Hydrides					
CALPHAD calcs (NIST)		■			
Thermo. modeling (CMU, Pitt, Ill)		■			
Demo. reversibility in MgH_2/Si		■	●		
Expt'l eval of new Li/Mg systems		■	●	■	
Task 2: Nanoparticle Synthesis					
Mg_2Si nano-synthesis		■			
– MgH_2/Si films (<i>Stanford</i>)		■			
– Gas condensation (<i>Caltech</i>)		■			
– Metathesis rxns (<i>HRL</i>)		■			
– CVS (<i>Utah</i>)		■			
Synth. of $\text{LiBH}_4/\text{MgH}_2$ & analogs		■		■	
Eval. sintering/agglomeration; develop mitigation approach			■	■	
Design/fab prototype system (w/ all MHCOE)			■	■	
Task 3: Characterization and Testing					

Lightweight Intermetallics for Hydrogen Storage

J.-C. Zhao,

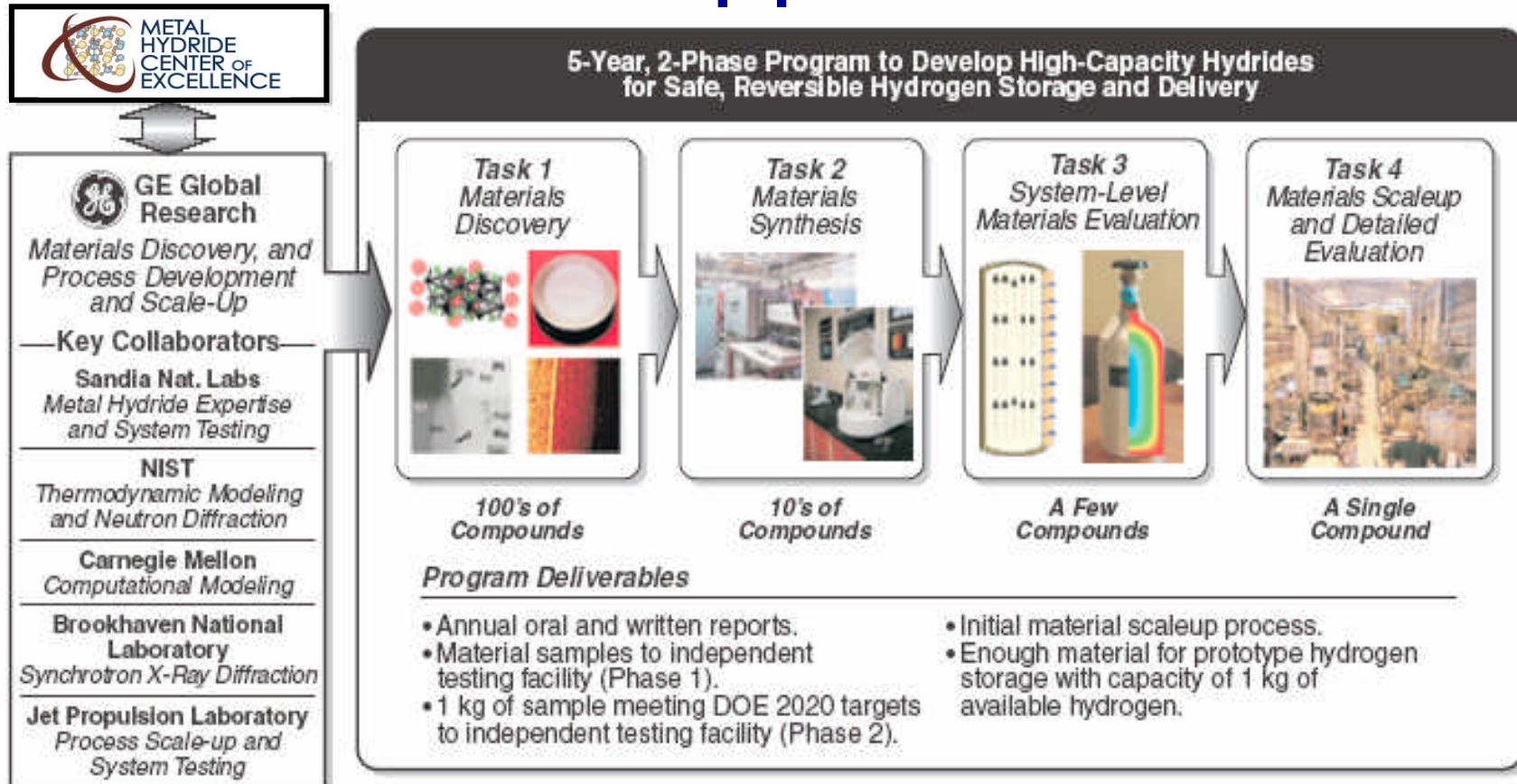
Jun Cui, Yan Gao, John Lemmon, Tom Raber,
Job Rijssenbeek, Gosia Rubinsztajn, Grigorii Soloveichik

GE Global Research
Niskayuna, NY

– A Member of the DOE Metal Hydride Center of Excellence –

May 23-24, 2005

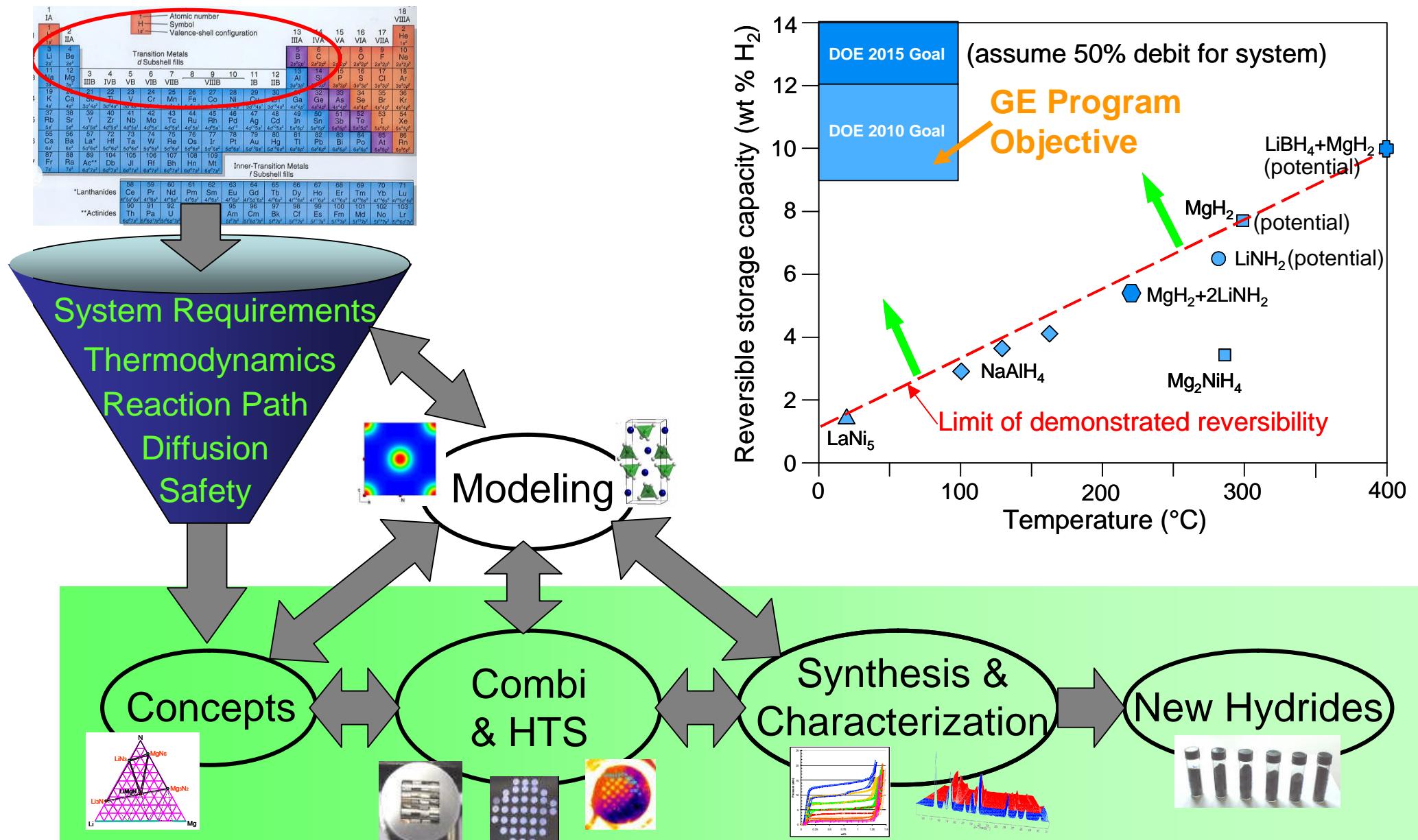
GE Approach



Materials Discovery Acceleration: *Design for Six Sigma coupled with...*

- Materials Expertise: Development & Processing
- High Throughput Screening (HTS): Composition Design Space
- Characterization: Composition, Microstructure & Performance
- System Performance: Characterization & Predictive Modeling
- Focused multi-disciplinary team

GE Metal Hydride Discovery Process



imagination at work



GE Lightweight Intermetallics Approach

- **Focus:**

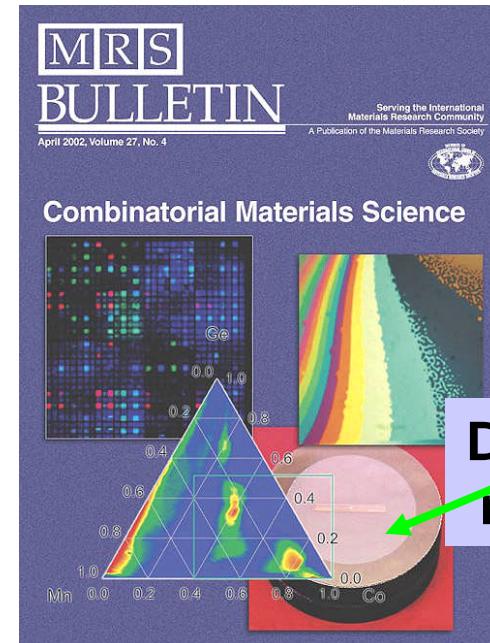
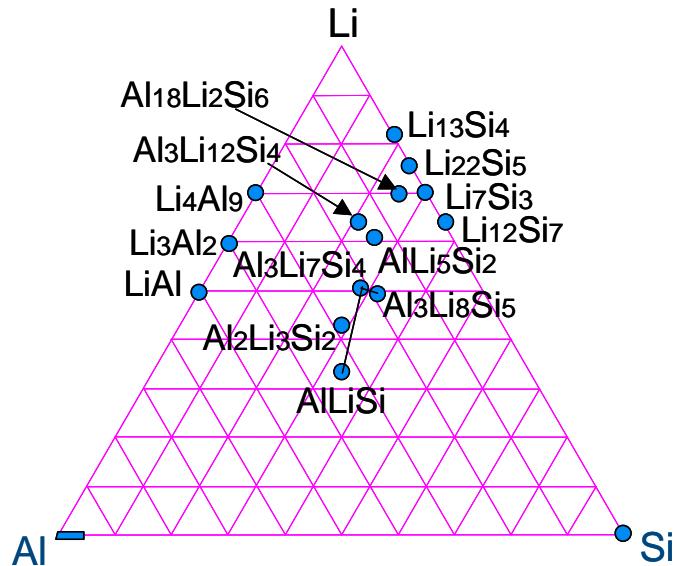
Lightweight aluminides & silicides of Li, Mg, and Na (potential to 6 wt.%)

- **Opportunity:**

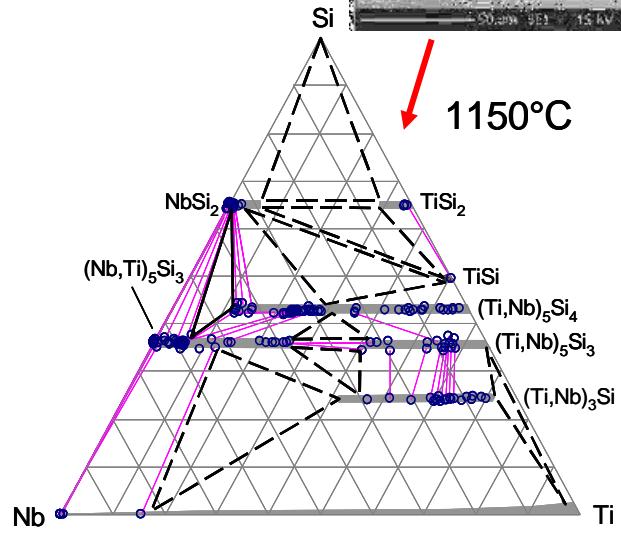
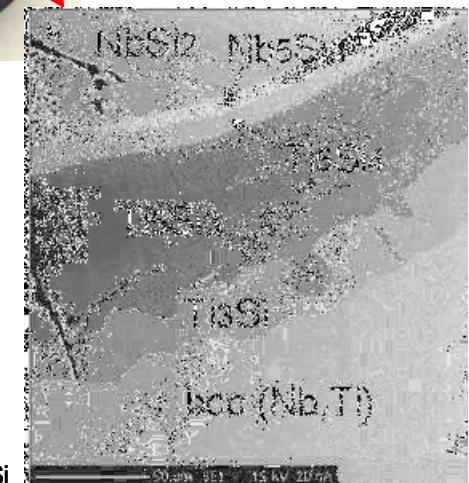
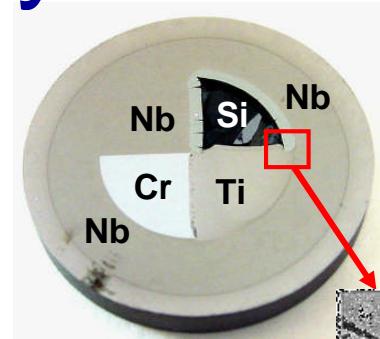
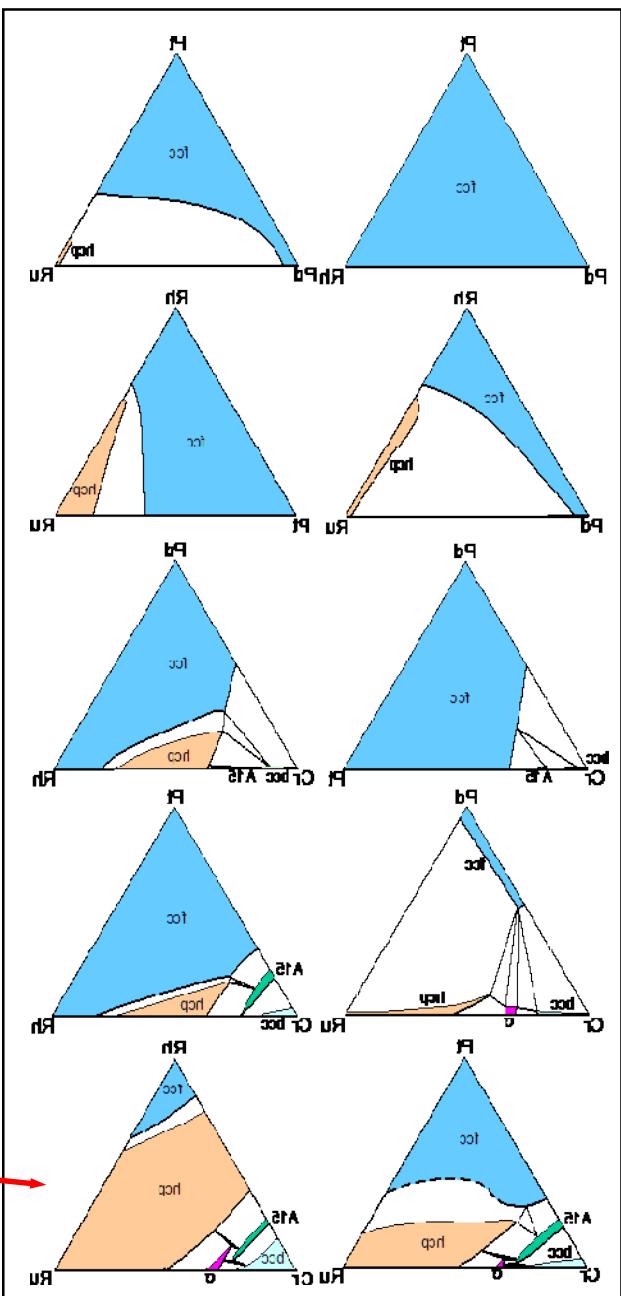
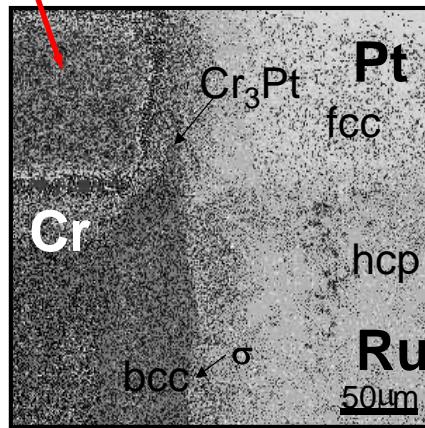
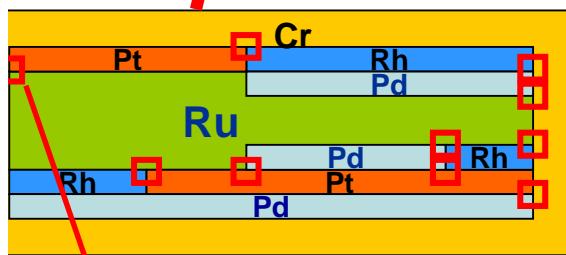
Many intermetallic compounds exist in aluminide and silicide systems

- **Develop & Validate:**

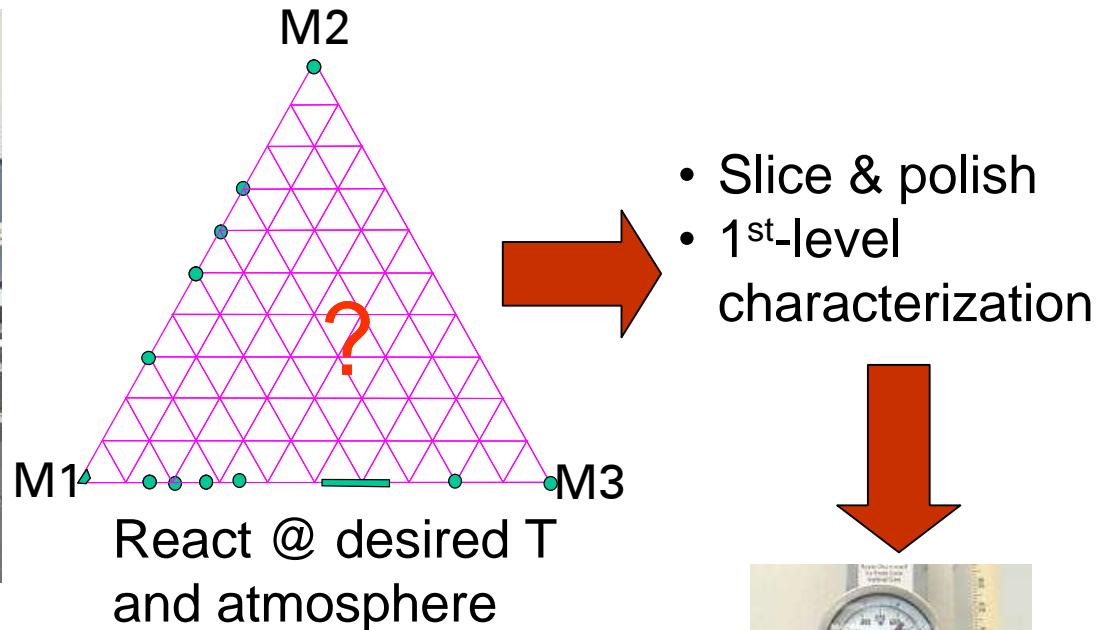
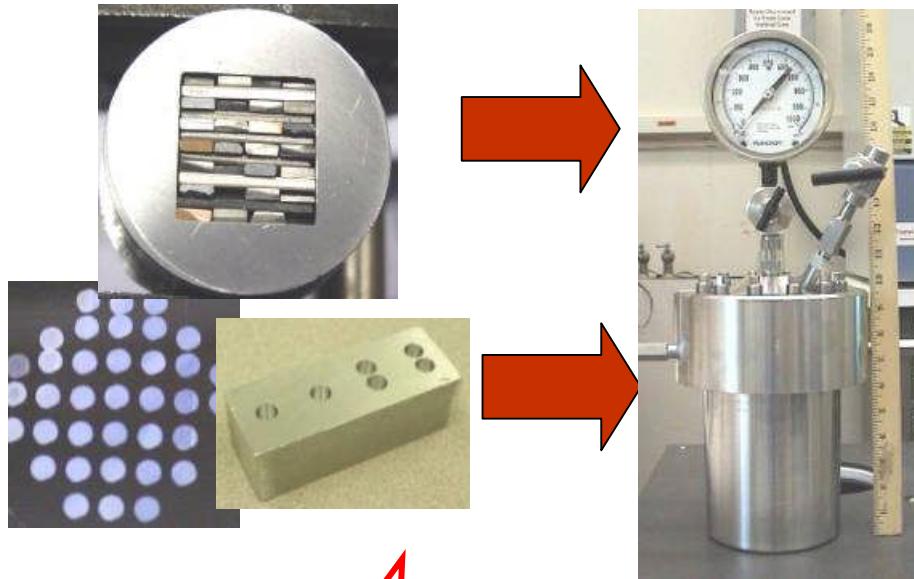
Combinatorial synthesis and high-throughput screening methodologies for hydride discovery in the target temperature – pressure – kinetics design space



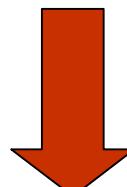
Diffusion Multiples & Alloy Development



Combinatorial Synthesis & HTS



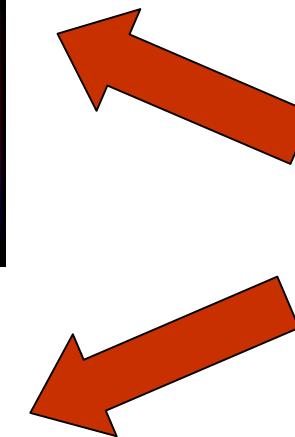
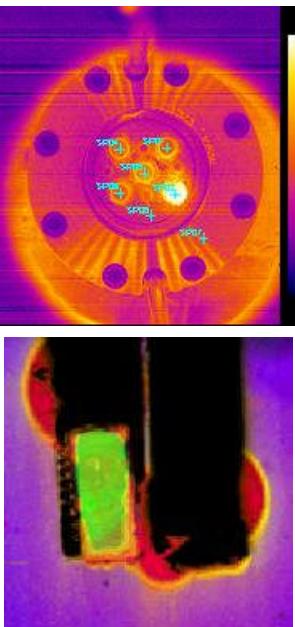
- Slice & polish
- 1st-level characterization



Identify,
synthesize
& test
leads

Screening with
thermography

Screening with
time-of-flight
secondary ion
mass spectroscopy



Charge with D₂

Combinatorial Synthesis & HTS: Results

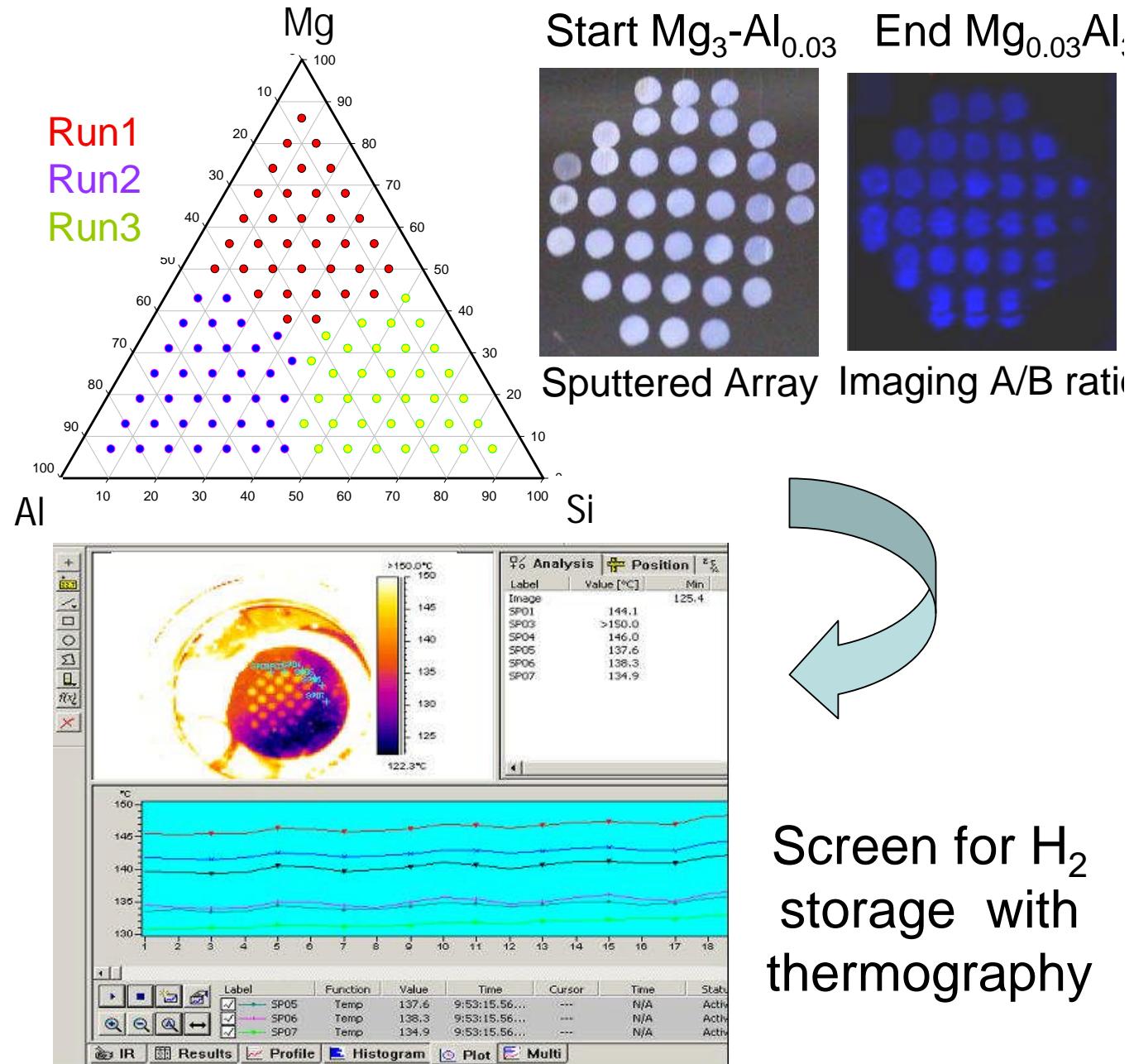
Thin-film methods

Synthesis

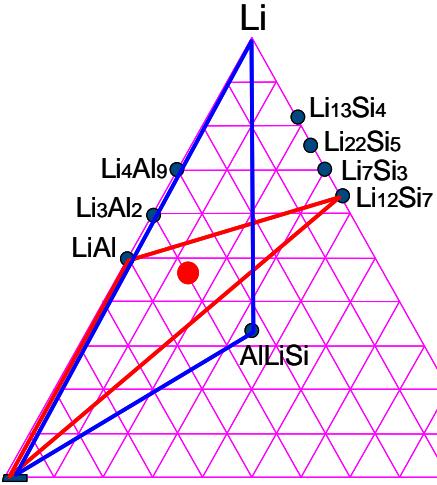
- Complementary to diffusion multiple
- Great for exploring Mg, Al, Si alloys
- Map phase diagram at 6% intervals, 3 runs, 5hrs.
- 7 target co-sputtering, DC and RF power

Screening

- Optical reactor capability, 350 °C, 55 atm.



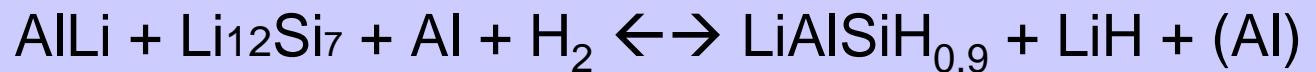
In-Situ XRD: Results



Literature:



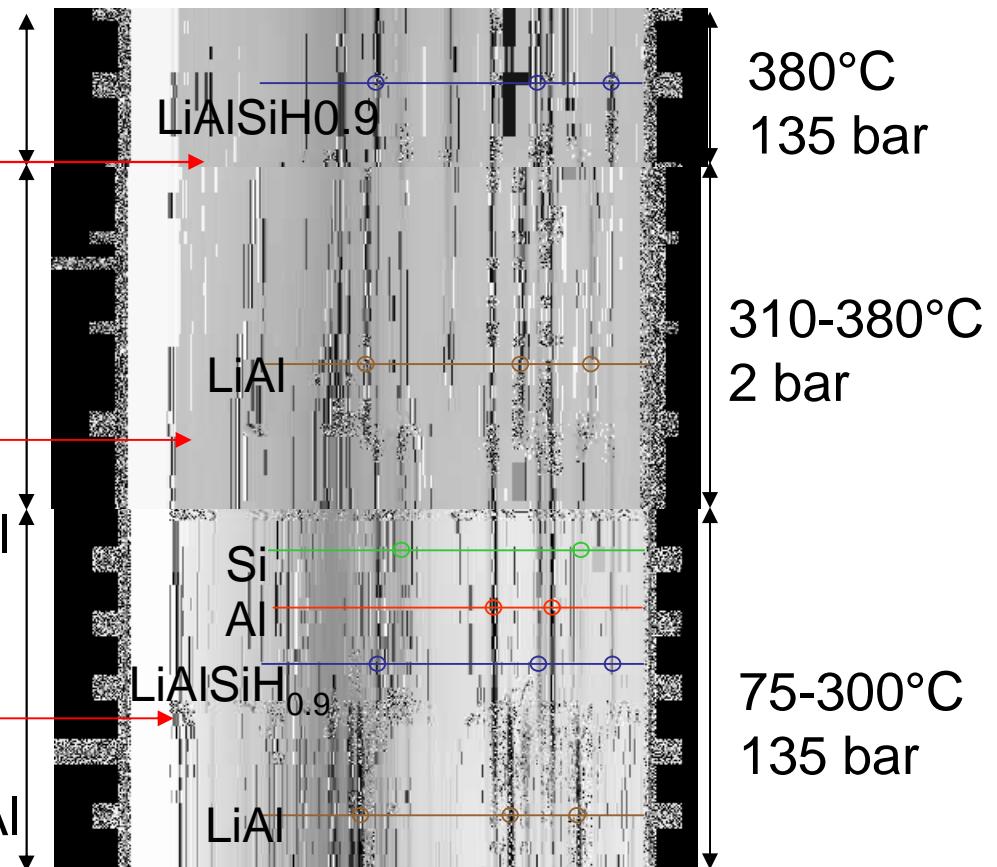
New result: $300-380^\circ\text{C}$, $< 135 \text{ bar}$



Charging kinetics
are very fast

LiAl (Al)
Decomposition without
intermediates at 380°C

Hydrogenation via
intermediates at 300°C
 $\text{LiAl} + \text{Li}_{12}\text{Si}_7 + \text{Al} \rightarrow \text{LiAlSiH}_{0.9} + \text{Si} + \text{Al}$



First intermetallic hydride in non-transition metal alloys

GE Lightweight Intermetallics Progress

1. Designed new diffusion multiple configuration and tested for alkali metals
2. Demonstrated the screening capability of thermography and ToF-SIMS
3. Studied/screened several compounds in the Li-Al-Si ternary system
 - *This system has the first reversible intermetallic hydride in non-transition metal alloys*

FY05 Deliverable:

Develop Combi / HTS methods & validate with gram-quantity bulk tests