Overview of DOE Metal Hydride Center of Excellence (MHCoE)

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Sandia National Laboratories
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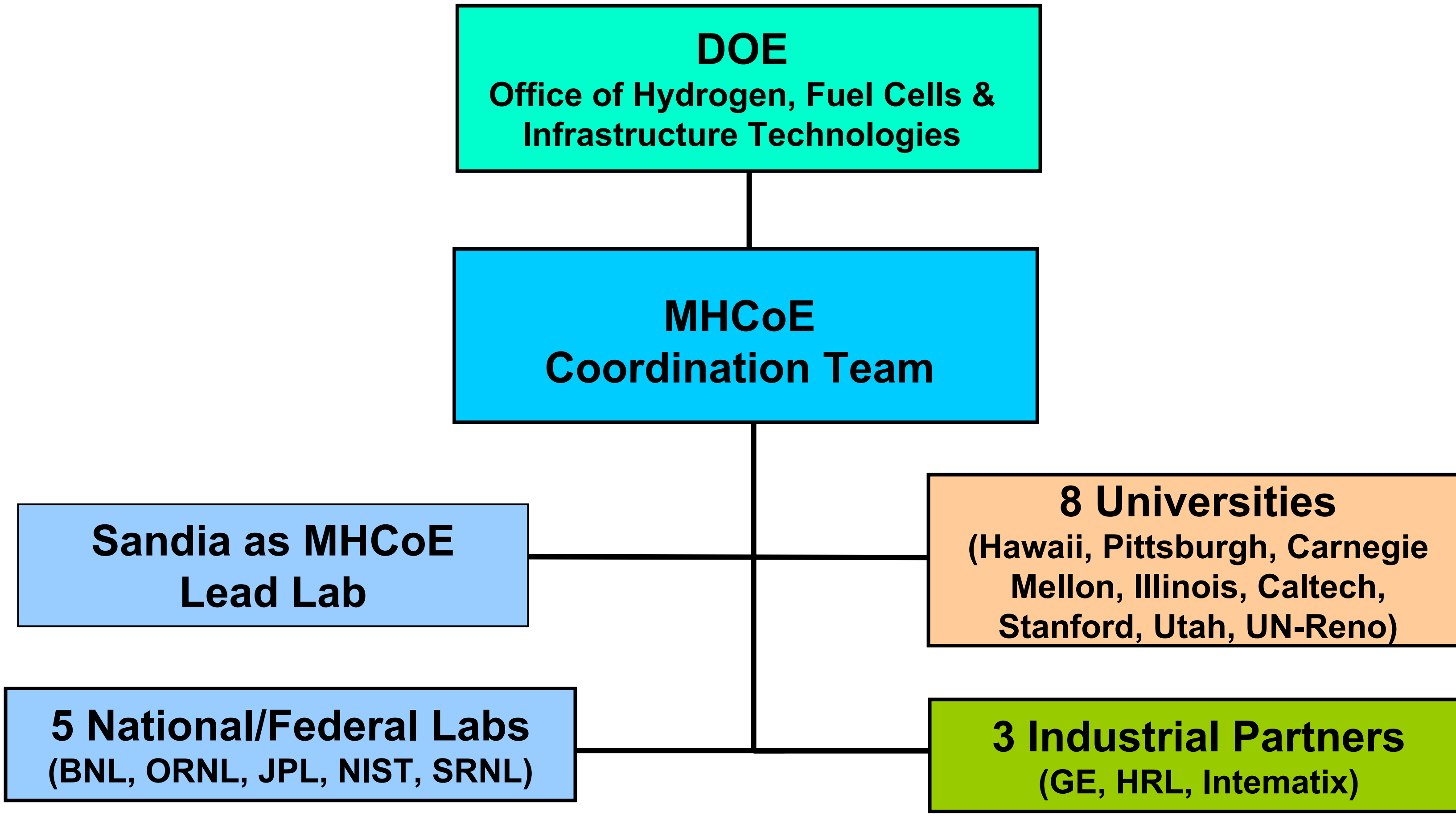
Project ID # STP15

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

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

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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 H_2 storage systems
- Kinetics of solid-state reactions
- Cycle life, reliability and durability

Objectives

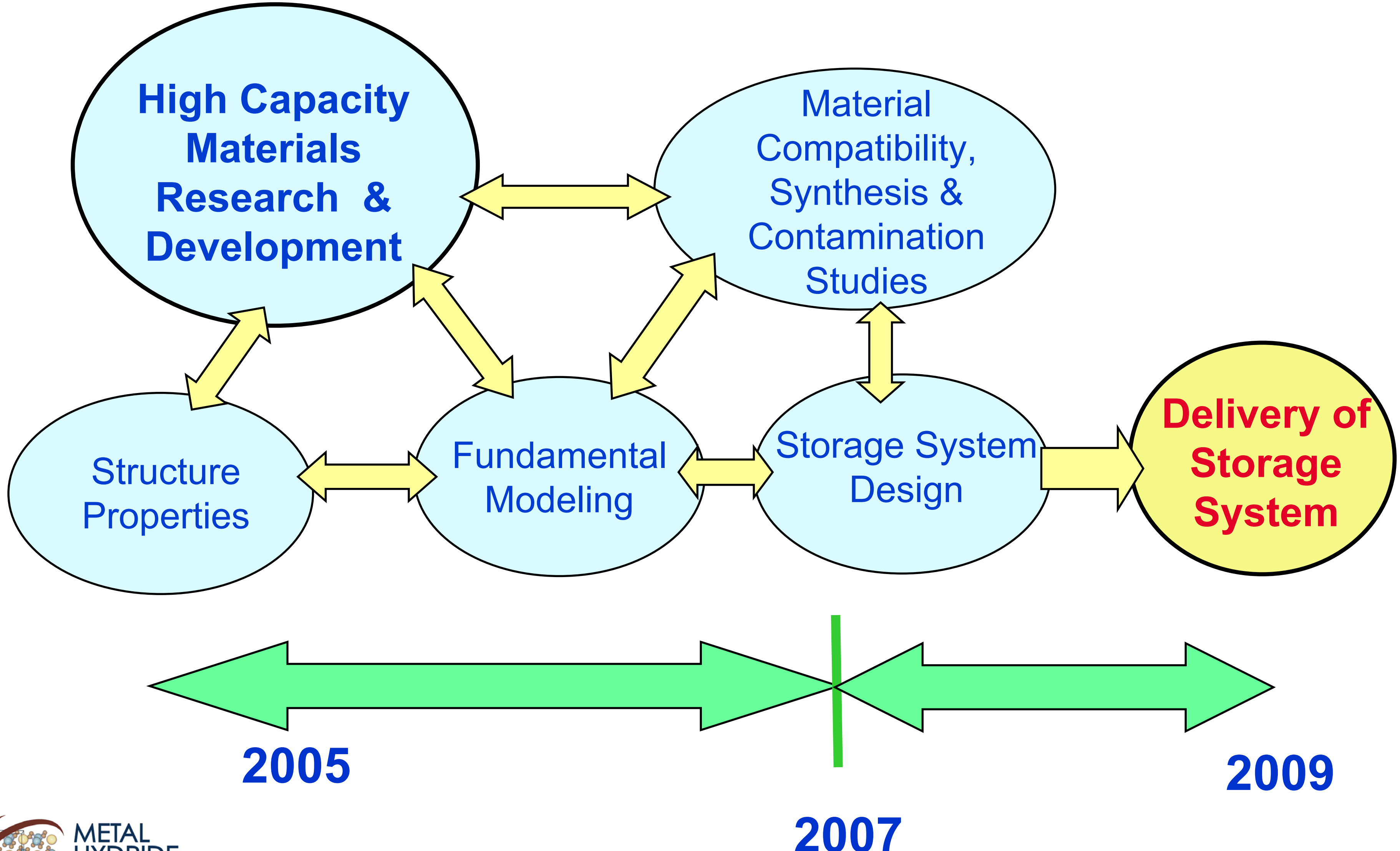
- **Develop new reversible hydrogen storage materials that meet or exceed DOE FreedomCAR 2010 and 2015 goals**

- **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



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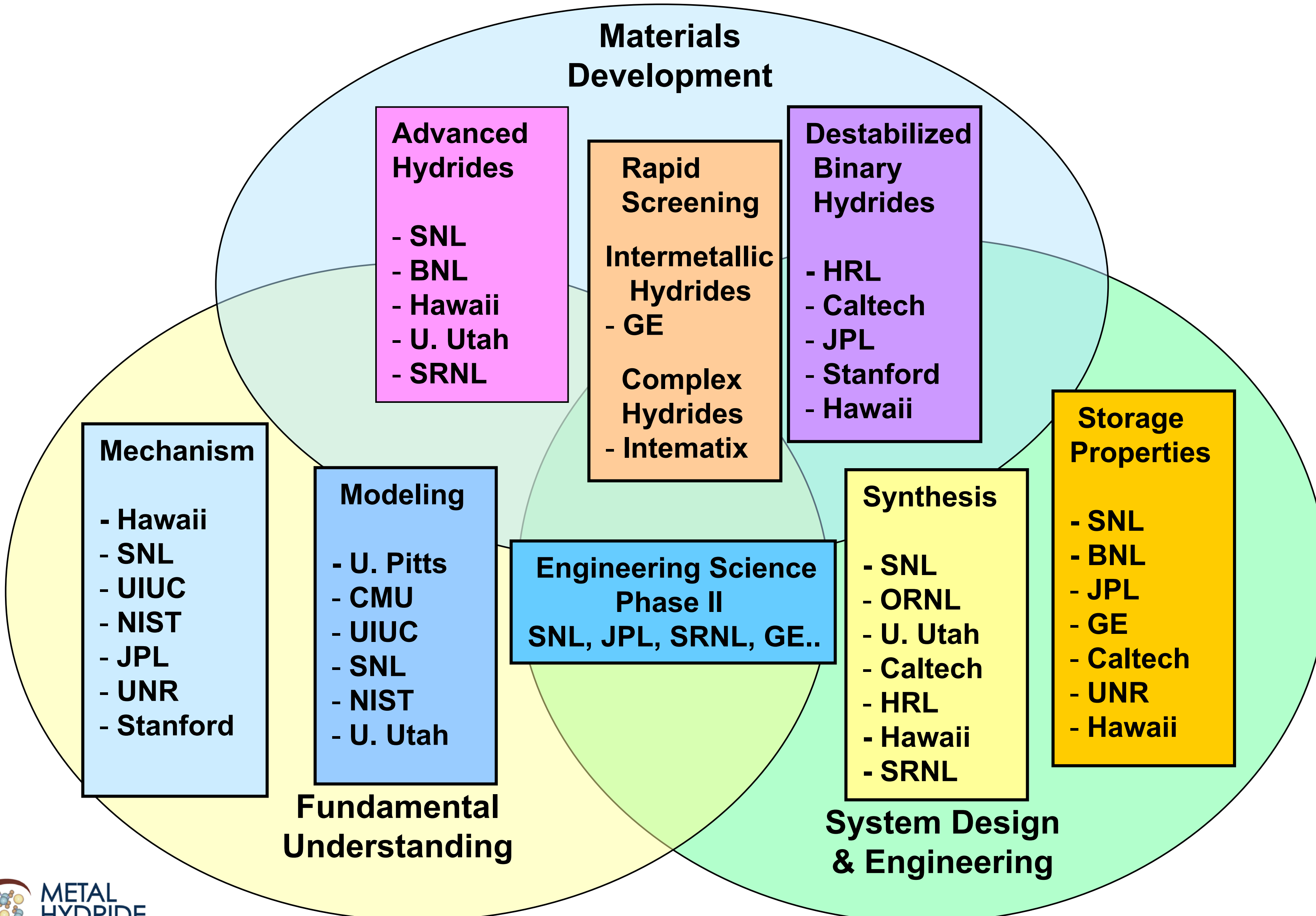
MHCoE Partners Cover a Full Range of Expertise



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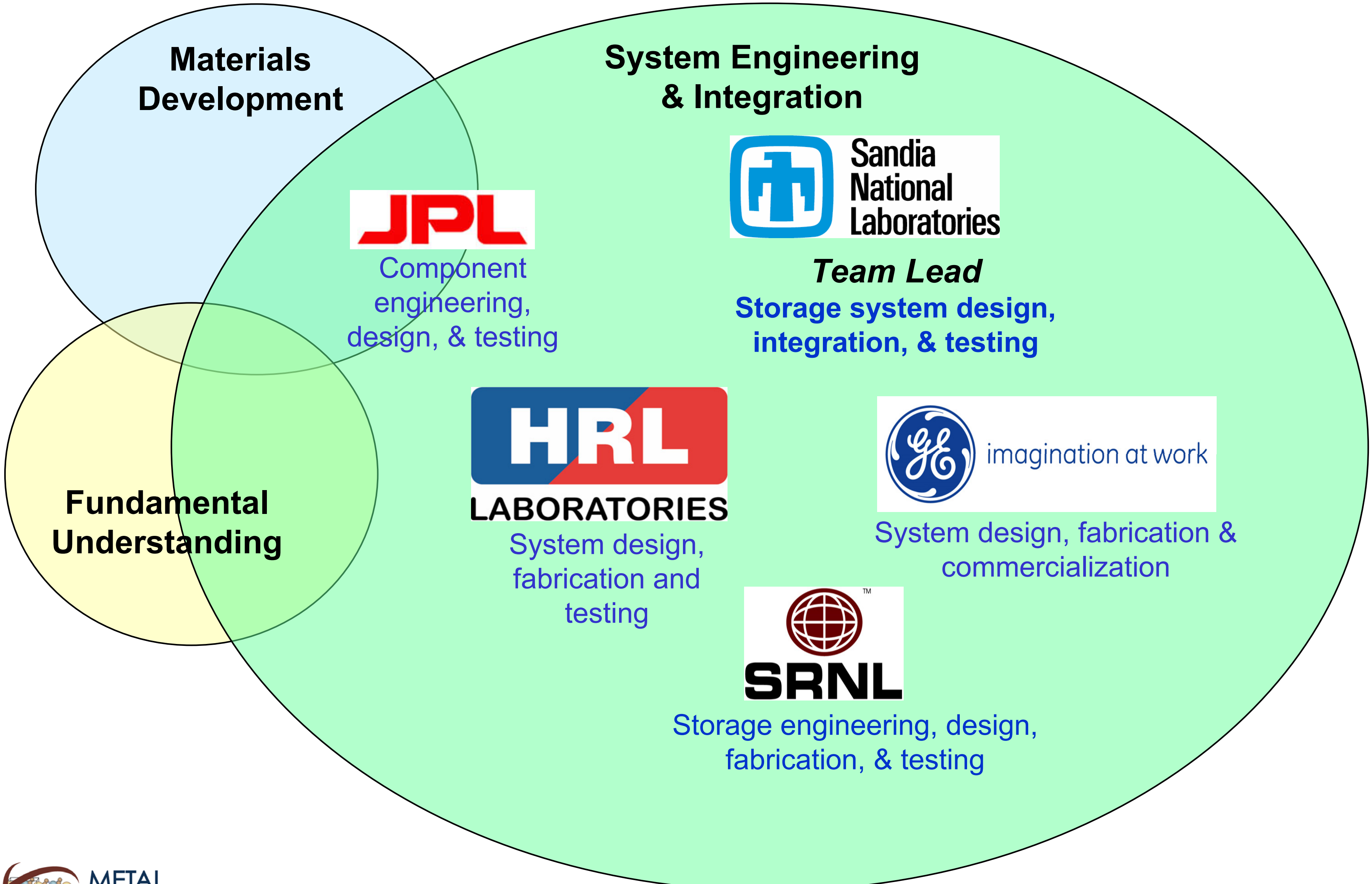
MHCoE System Engineering & Integration



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MHCoE Materials Synthesis Resources

Materials Development

System Design & Engineering

Fundamental Understanding

The University of Utah: Synthesis of nanocrystalline reversible hydrides by vapor phase reactions

ORNL (Oak Ridge National Laboratory): Solution–based synthetic methods development

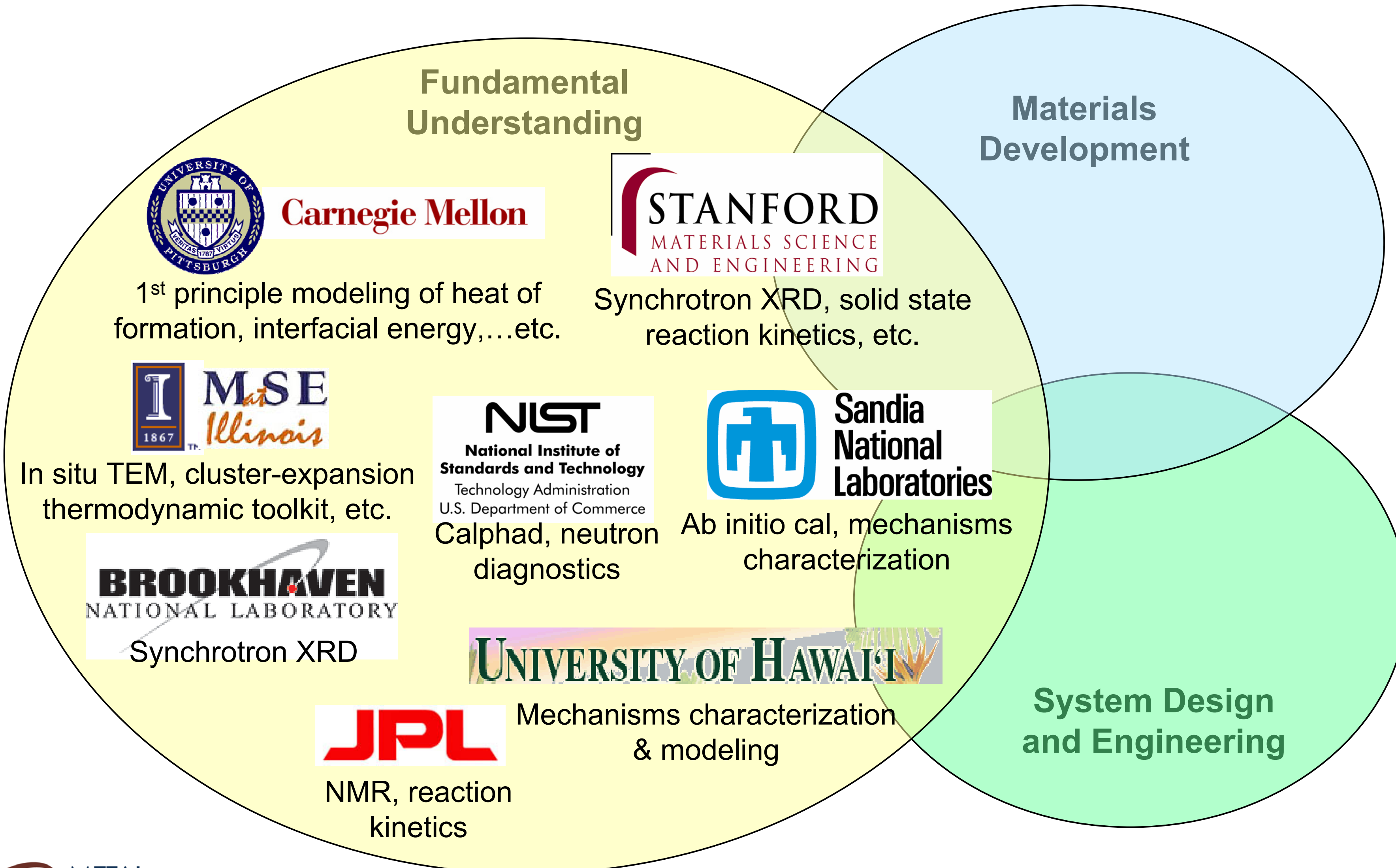
Sandia National Laboratories: Develop chemical routes for nano-sized metal hydrides and bulk productions

California Institute of Technology: Nanoparticle synthesis (gas condensation) & materials Characterization (TEM, XRD)

University of Hawai'i: Nanostructured catalyst development & new synthesis routes

SRNL: Synthesis & characterization of aluminum hydrides

MHCoE Modeling and Mechanism Resources



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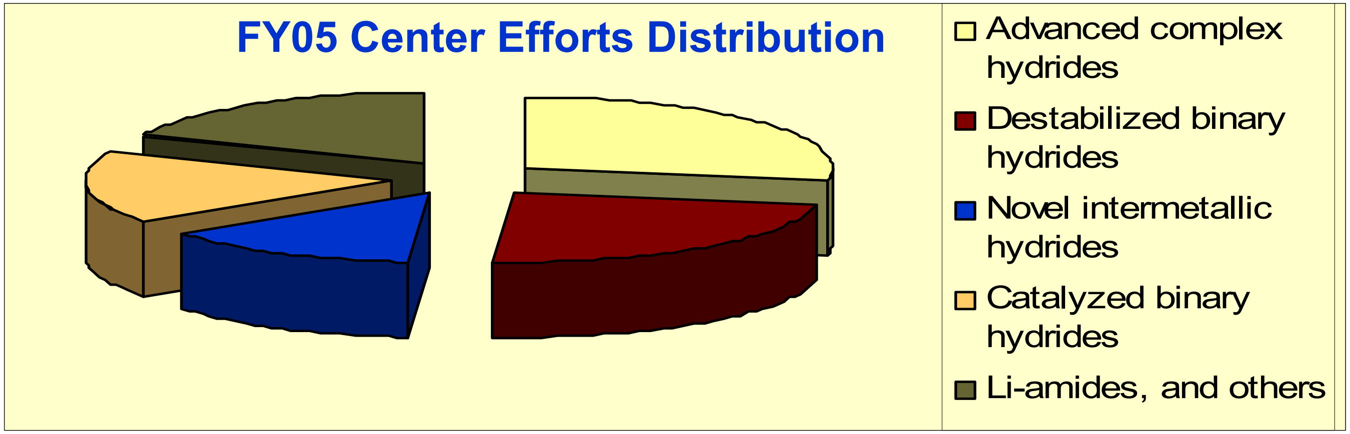
MHCoE – Materials Development Categories

- Advanced complex hydrides ($AH_x + B + H_2 \rightleftarrows ABH_y$)
- Destabilized binary hydrides ($AB + H_2 \rightleftarrows AH_x + B$)
- Novel intermetallic hydrides ($AB + H_2 \rightleftarrows ABH_x$)
- Catalyzed binary hydrides ($A + H_2 \rightleftarrows AH_x$)
- Other reversible hydrogen storage materials (e.g. lithium amides, non-lithium based imides)



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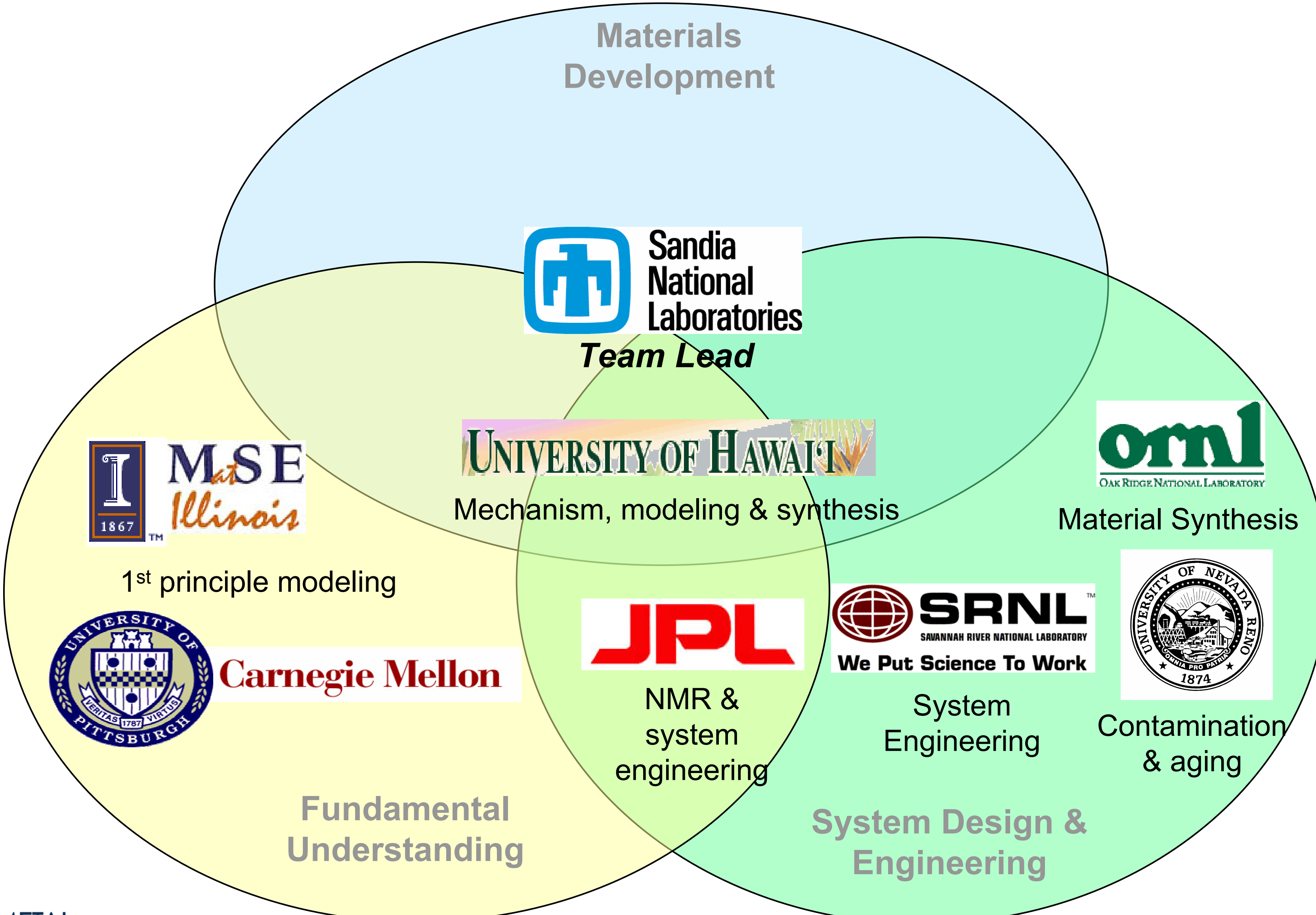
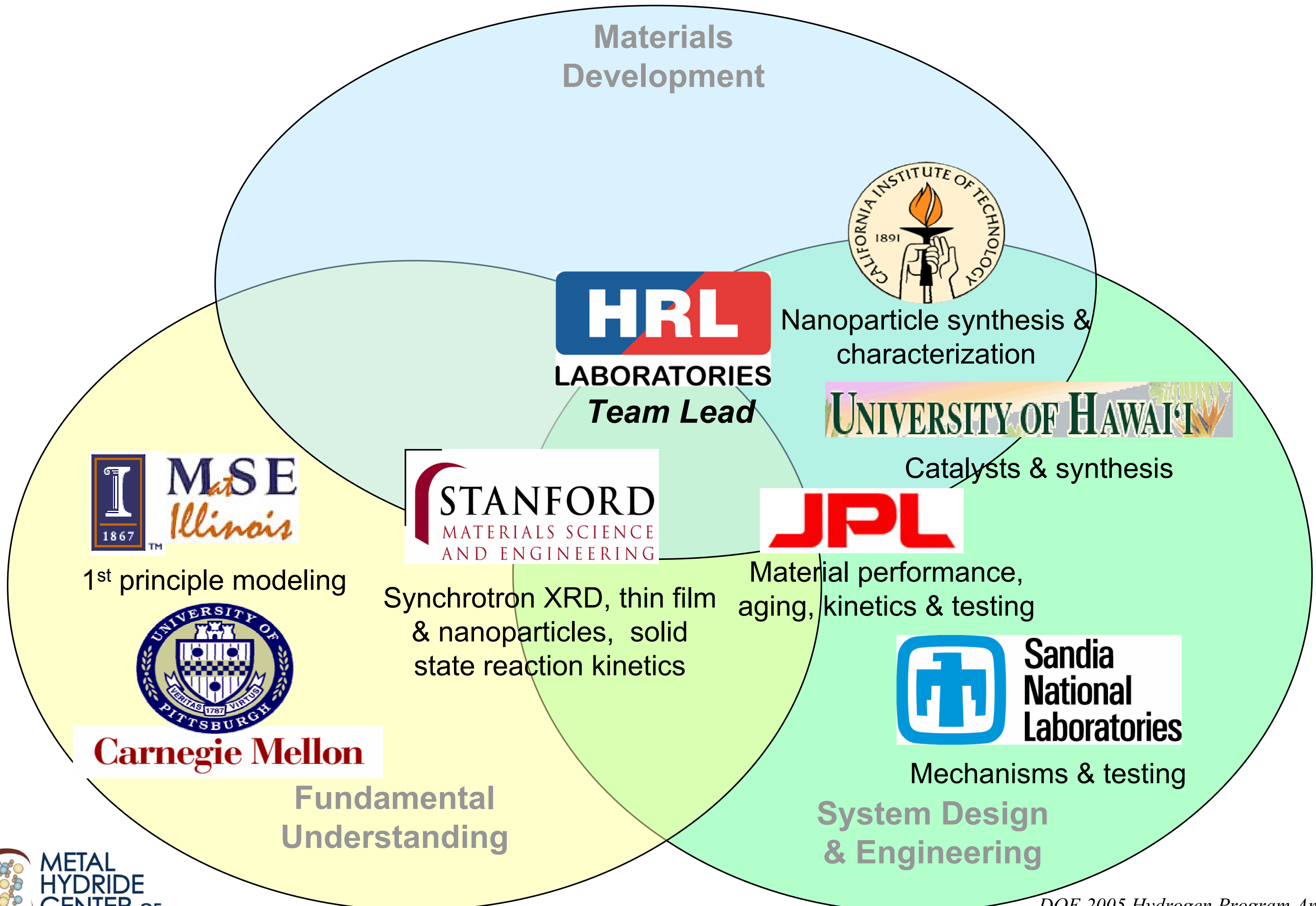
MHCoE Team on 1st Principal Modeling & Experimentation for Material Discovery

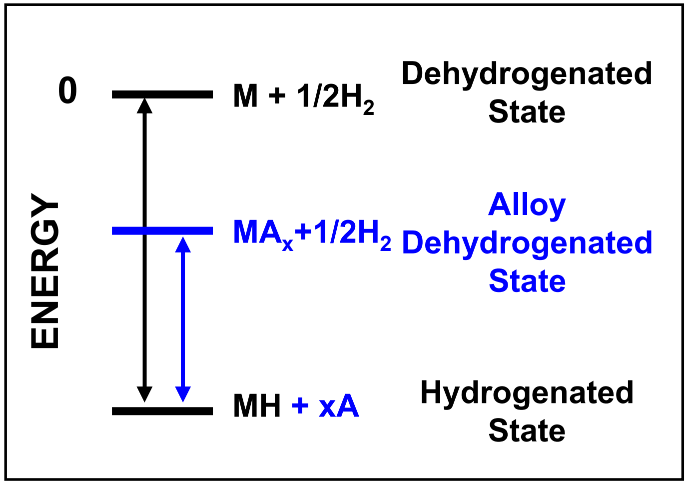


MHCoE Team on Mechanistic Approach to Destabilize Hydrides



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

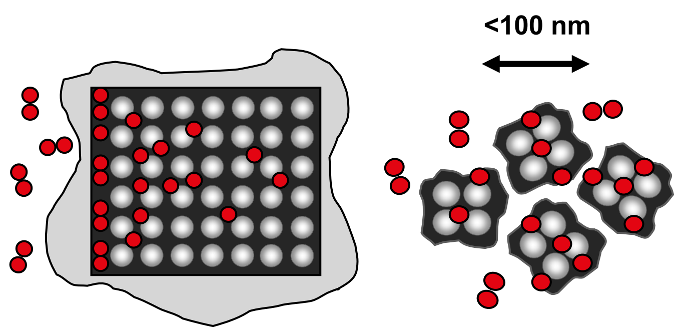
HRL LABORATORIES



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 <u>instead</u> of the pure metal
- Reduced energy demand means lower temperature for hydrogen release



Long H-diffusion distances in bulk materials: ***reduced H-exchange rate***

Short H-diffusion distances in nanoparticles: ***fast hydrogen exchange***

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

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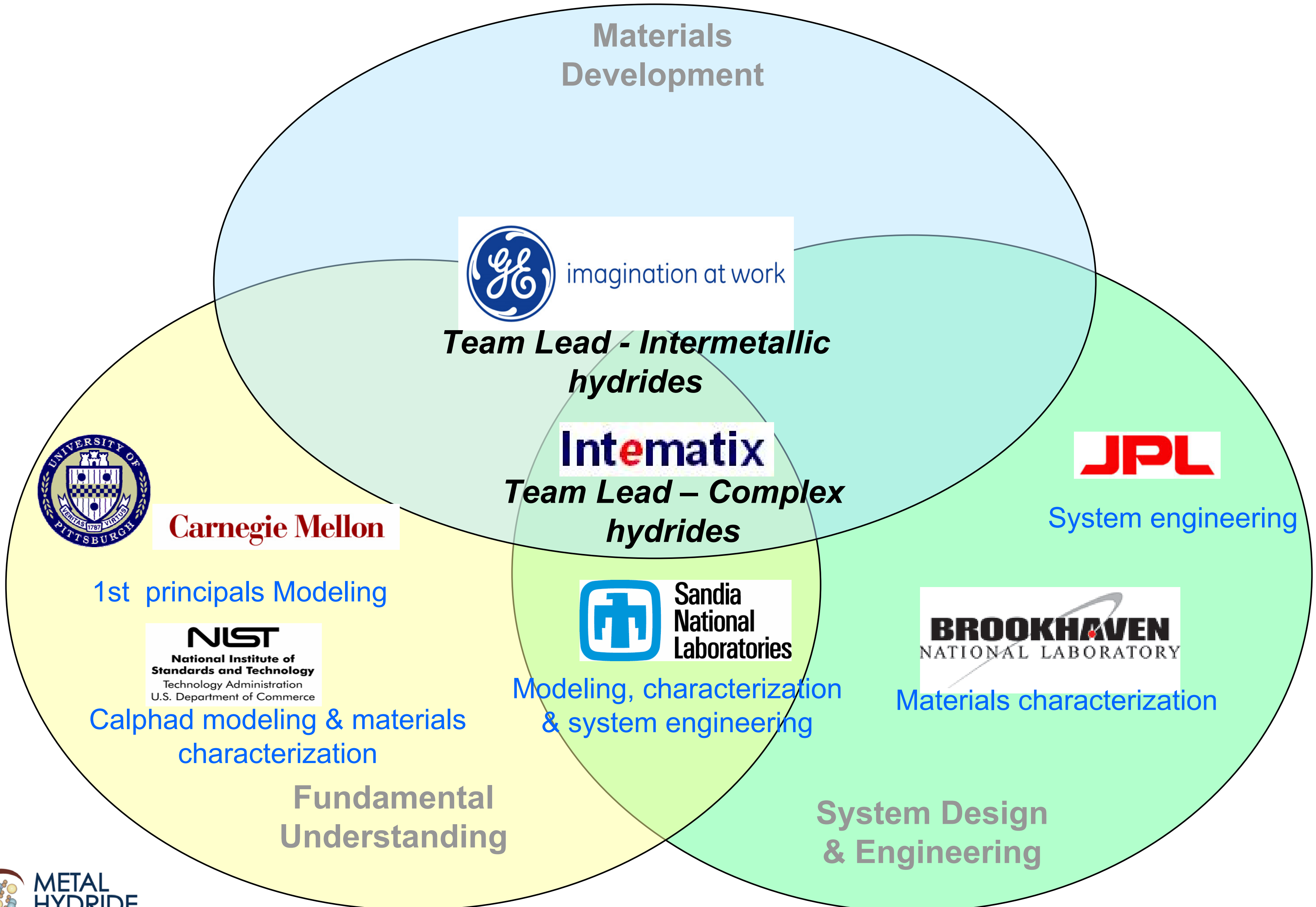
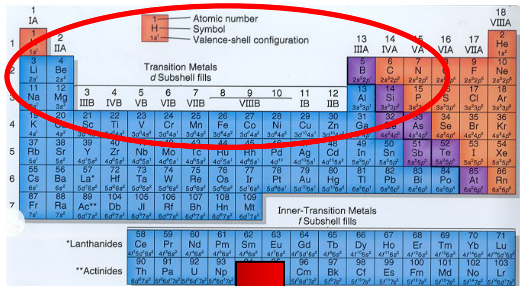
Combinatorial Approach Teams



Combinatory Approach – Intermetallic Hydride

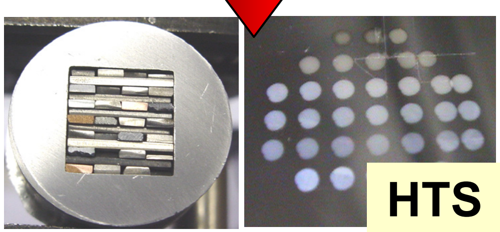
imagination at work



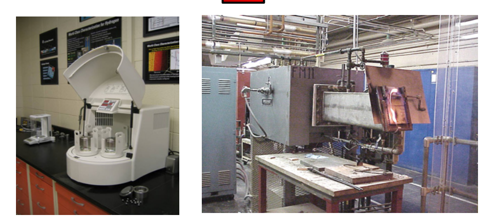
System Requirements
Thermodynamics
Reaction Path
Diffusion
Safety

DFT
Phase
diagram
analysis

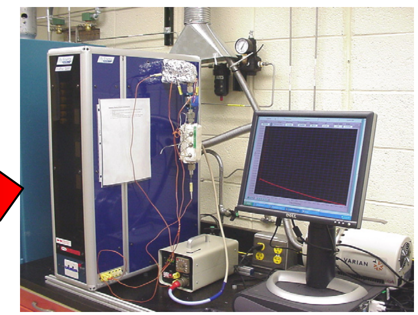
Materials
Concept
s



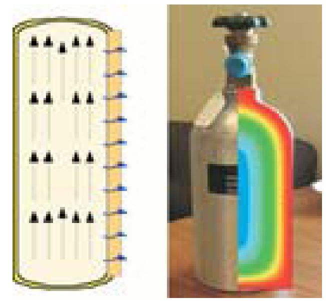
Hydride ID



Synthesis



Characterization



System-
level testing

New Hydride

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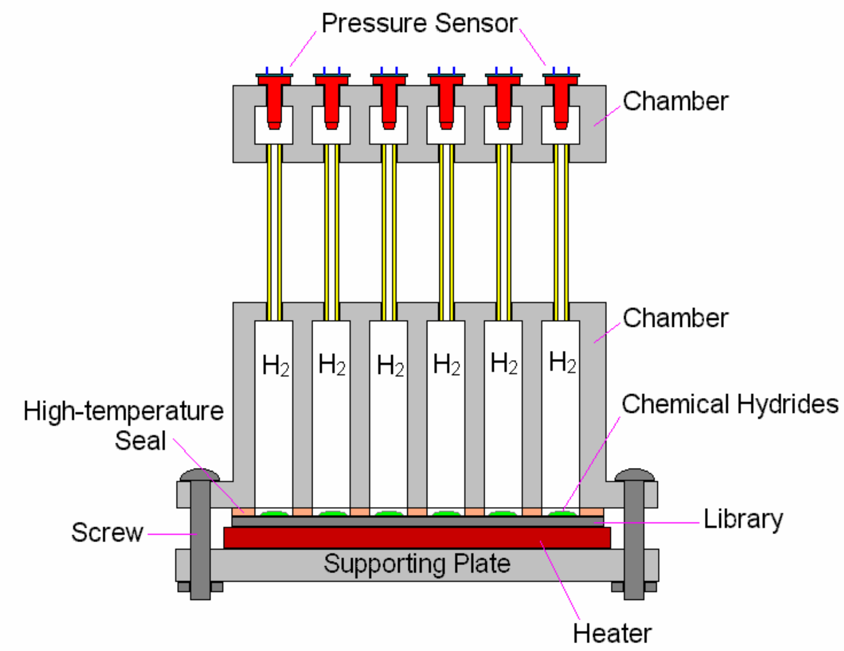
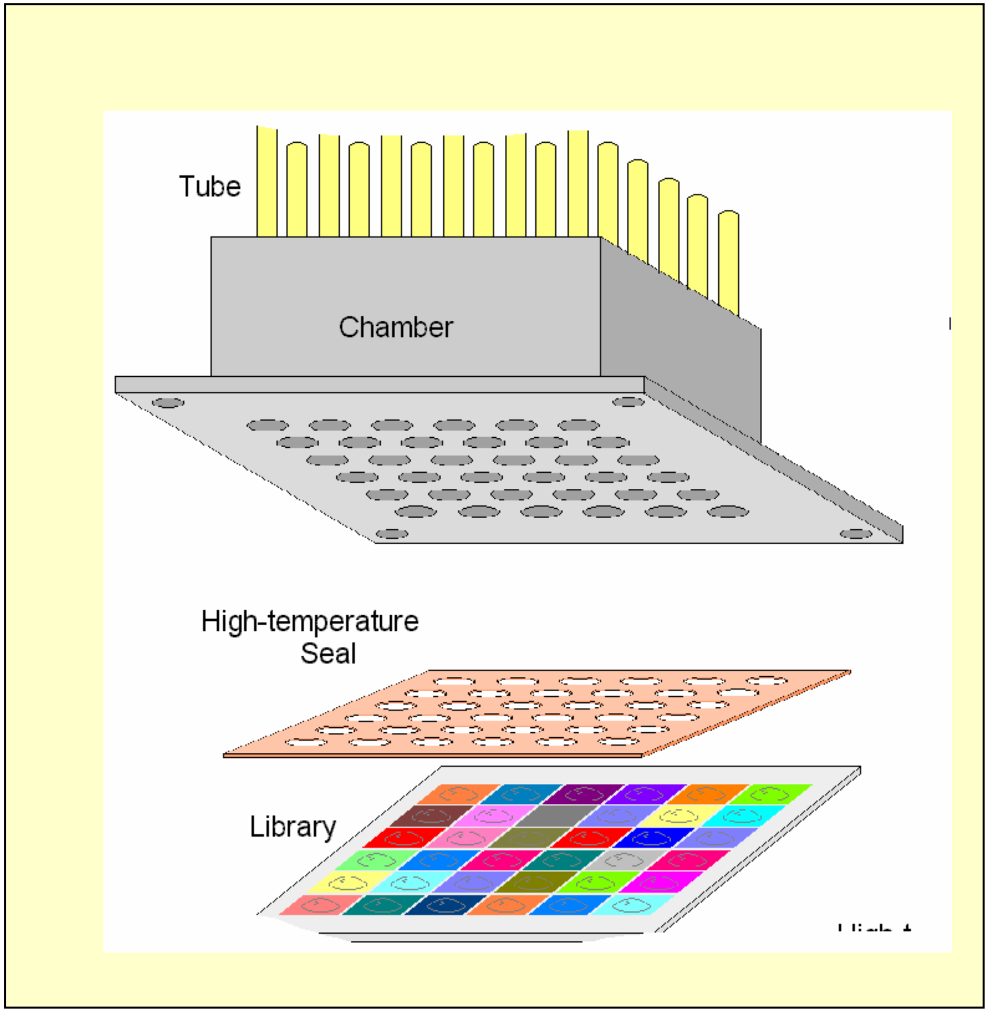
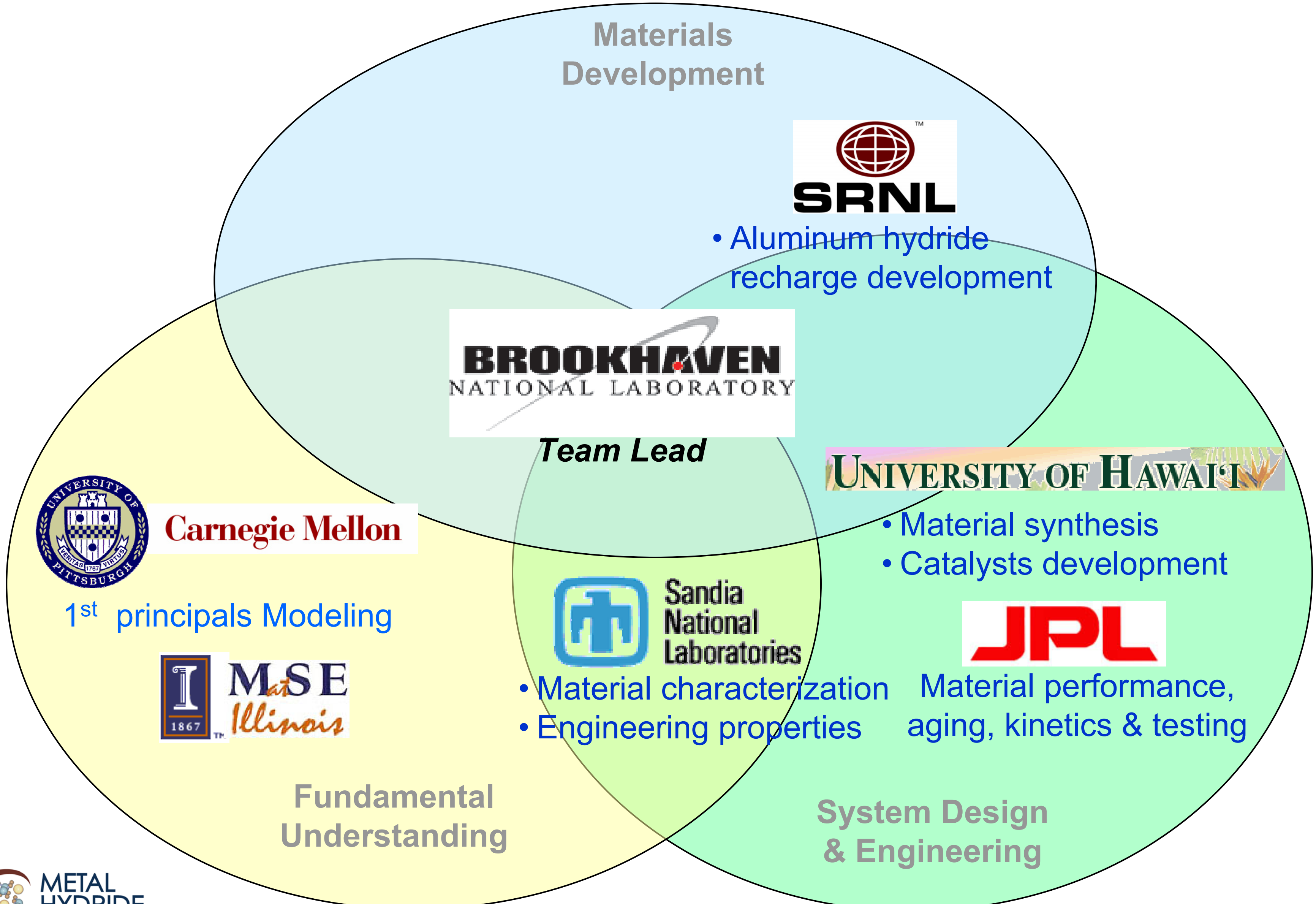
Combinatory Approach – Complex Hydride

Micro-reactor

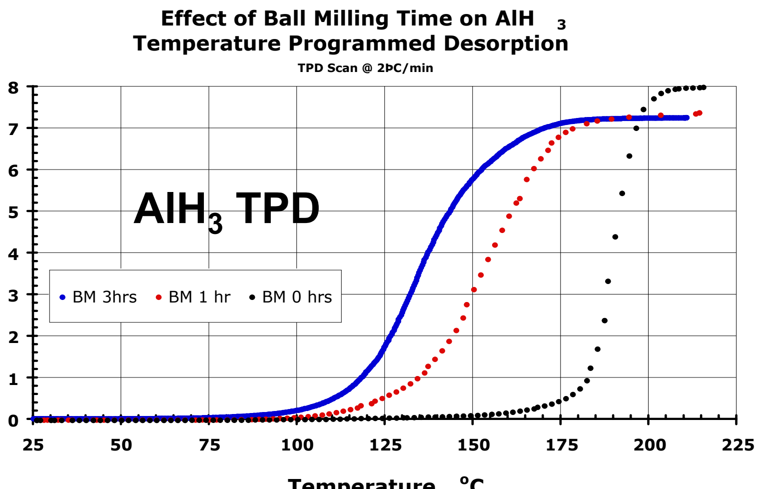




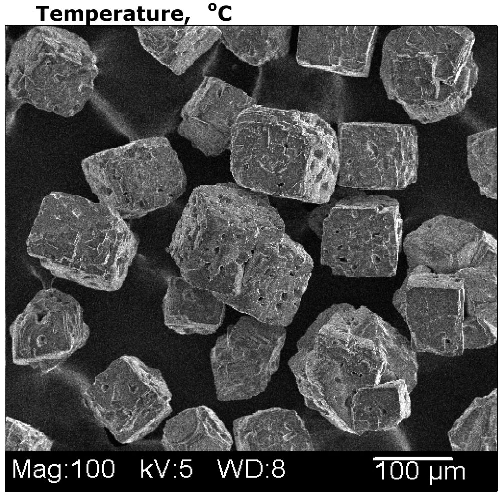
System Engineering Team – AlH_3



Crystalline and Microcrystalline AlH_3



AlH_3 crystals (before ball milling)



<u>Accomplished</u>:

1. **Demonstrated H_2 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.**

<u>Target Needs</u>:

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 AlH_3.**

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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-discinaplanary teams***

Acknowledgement

Point of Contact	Institution
• Channing Ahn	California Institute of Technology
• Gilbert Brown	Oak Ridge National Laboratory
• Robert Bowman	Jet Propulsion Laboratory
• Dhanesh Chandra	University of Nevada, Reno
• Bruce Clemens	Stanford University
• Zak Fang	University of Utah
• Craig Jensen	University of Hawaii at Manoa
• Karl Johnson	University of Pittsburg
• Ted Motyka	Savannah River National Laboratory
• Greg Olson	HRL Laboratories, LLC
• Ian Robertson	University of Illinois at Urbana-Champaign
• David Sholl	Carnegie Mellon University
• Susan Townsend	General Electric Company
• Terrence Udovic	NIST Center for Neuron Research
• Jim Wegrzyn	Brookhaven National Laboratory
• Xiao Dong Xiang	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

Overview

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 H_2/L

Min/Max delivery temp: -30/85°C

Partners

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

MHCoE Sub-Team on Thermodynamically Tuned Nanophase Materials

HRL Labs — Greg Olson/John Vajo

- Sub-team coordination
- Hydride destabilization strategies
- Nanoparticle synthesis
- Hydrogen cycling: test and characterization

Caltech — Channing Ahn

- Nanoparticle synthesis (gas condensation)
- Materials Characterization (TEM, XRD)

U. Hawaii — Craig Jensen

- Nanostructured catalyst development
- New synthesis routes

Stanford/SSRL — Bruce Clemens

- *In situ*, real-time synchrotron XRD of H-induced phase changes
- Nanoparticle synthesis
- Solid state reaction kinetics
- Thin film reactions

JPL — Robert Bowman

- Materials development (performance / aging properties)
- Reaction kinetics and metal atom motion
- Concept testbed

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

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Objectives

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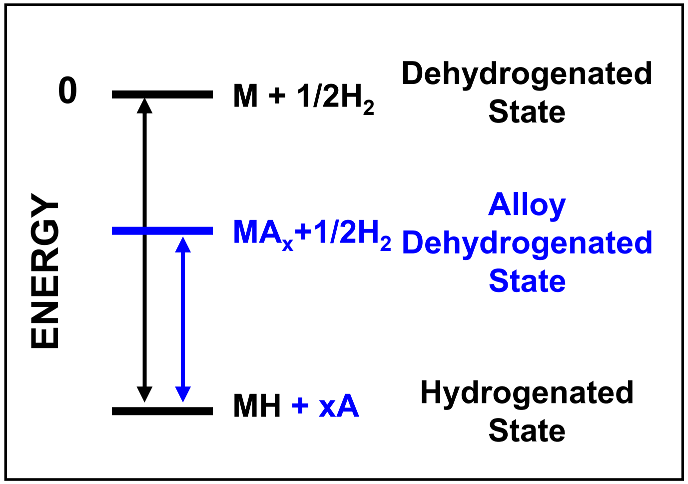
To develop and demonstrate a safe and cost-effective light-metal hydride material system that meets or exceeds the DOE goals for on-board hydrogen storage

- **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: $LiBH_4 + MgH_2$ and $LiBH_4 + Mg(X)$
  - 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

Approach:

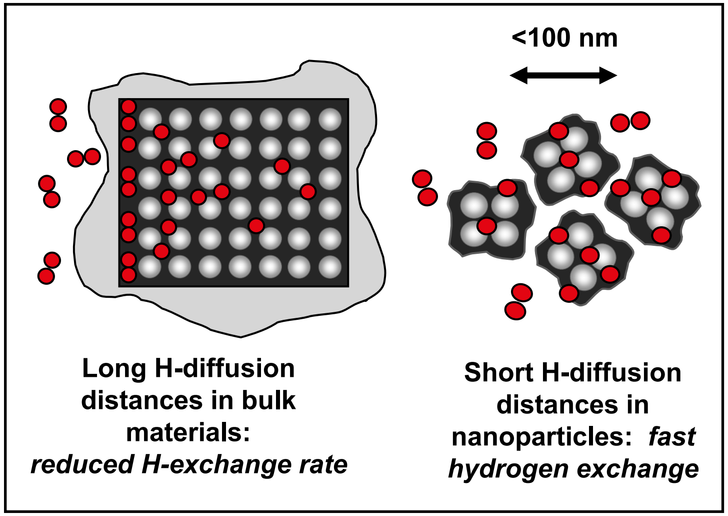
– Hydride Destabilization and Nano-engineering –



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

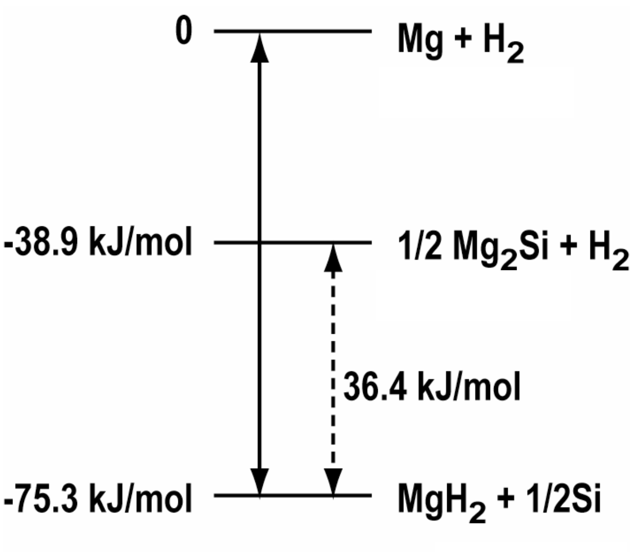
- Overall rate controlled by hydrogen diffusion distance
- H-exchange much faster in nanoscale particles than in bulk

Destabilization and Nano-engineering
– Issues and Challenges –

- 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

MgH_2 / Si

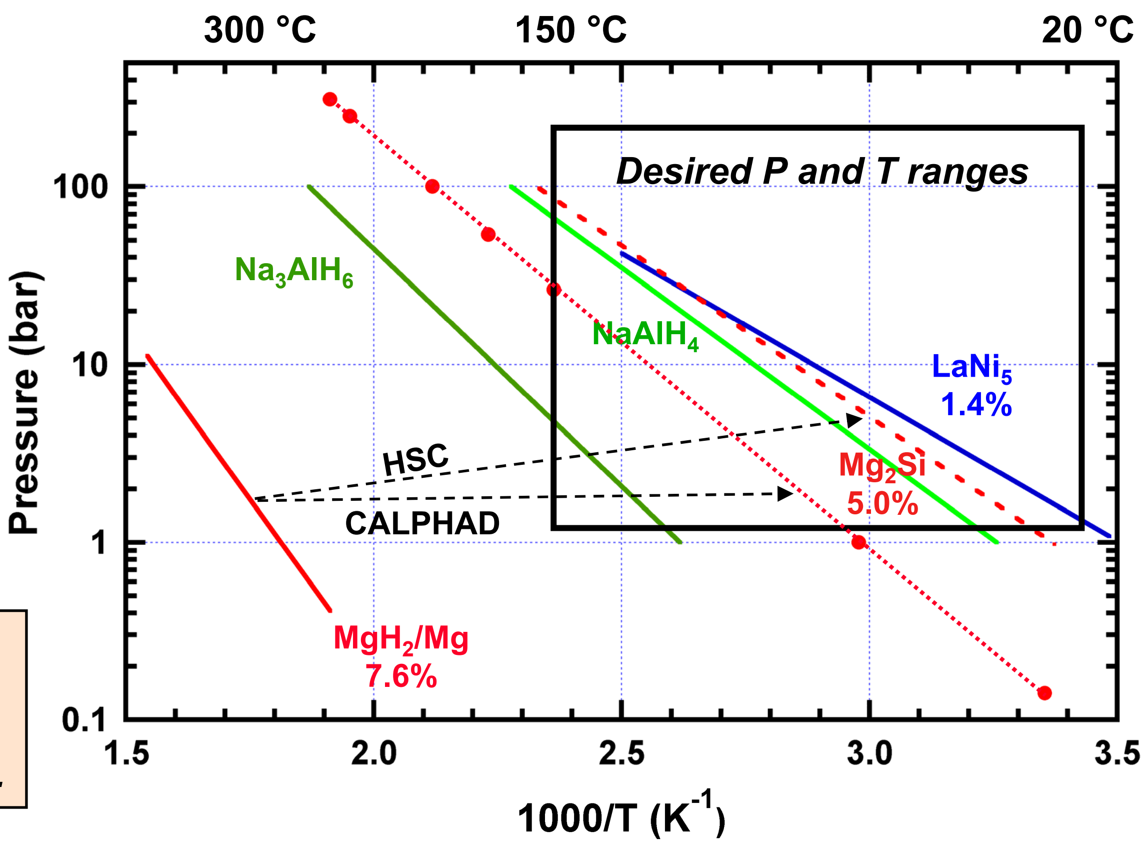
– Prototype Destabilized Hydride System –



Mg_2Si:

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

MgH_2 / Si System
– Accomplishments and Future Work –

- **Demonstrate reversibility**
  - Initiated work with Sandia *(K. Gross/E. Ronnebro)* using high pressure Sieverts system
  - Collaboration with Stanford U. *(B. Clemens, et al.)* on Mg_2Si 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 Mg_2Si by gas phase condensation
  - Initiated work *(HRL)* on alternative routes for synthesis of nanoscale Mg_2Si
  - Developed approaches for forming MgH_2 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)

MgH_2 / Si System

– Nanoscale Synthesis Work in Progress –

HRL

- ***Metathesis reactions in pressure vessel to synthesize Mg_2Si:***
  - $4Mg + SiCl_4 \Rightarrow Mg_2Si + 2MgCl_2$ (high vapor pressure)
  - $2MgCl_2 + SiCl_4 + 8Na \Rightarrow Mg_2Si + 8NaCl$ (stronger reducing agent)
- ***Formation of MgH_2 in mesoporous hosts:***
  - Infiltrate porous alumina or carbon aerogels with dibutylMg and thermally decompose:
    - $Mg(C_4H_9)_2 \Rightarrow$ 80% MgH_2 + 10% $[Mg(C_4H_8)]_n$ + 10% Mg
    - Alternatively, decompose Grignard compounds to form MgH_2, Mg, and MgX_2
- ***Synthesize Si nanoparticles and react with Mg(g) $\Rightarrow$ Mg_2Si (in pressure vessel)***
- ***Exploring plasma-based approaches for nanoparticle generation***

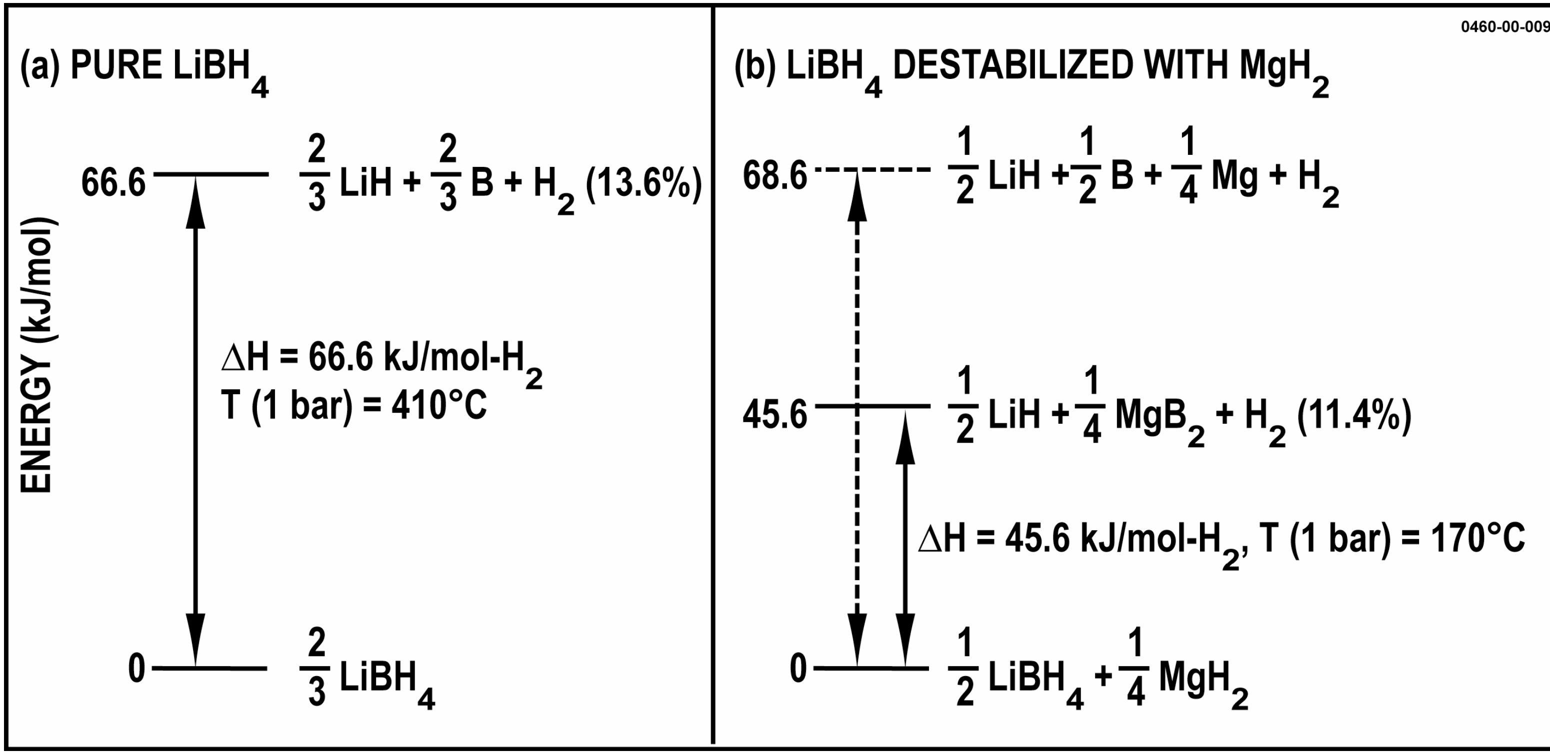
MHCoE Partners

- ***Form Mg and Mg_2Si nanostructured films by sputtering (B. Clemens–Stanford)***
  - 1-D nanostructured model system
  - Cap with Pd and/or Ti $\Rightarrow$ Catalyst; O_2 barrier
- ***Create Mg, Mg_2Si 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 Mg_2Si powders***

$LiBH_4$ / MgH_2

– New system (11.4 wt. % and 0.095 kg/L) –

Formation of MgB_2 estimated to reduce T(1 bar) by ~ 240 °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).

$LiBH_4$ / MgH_2

– Future Work (FY05 - FY07) –

- **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)*

Other Destabilized Systems
– Future Work (FY05/06) –

$LiBH_4$ + MgX

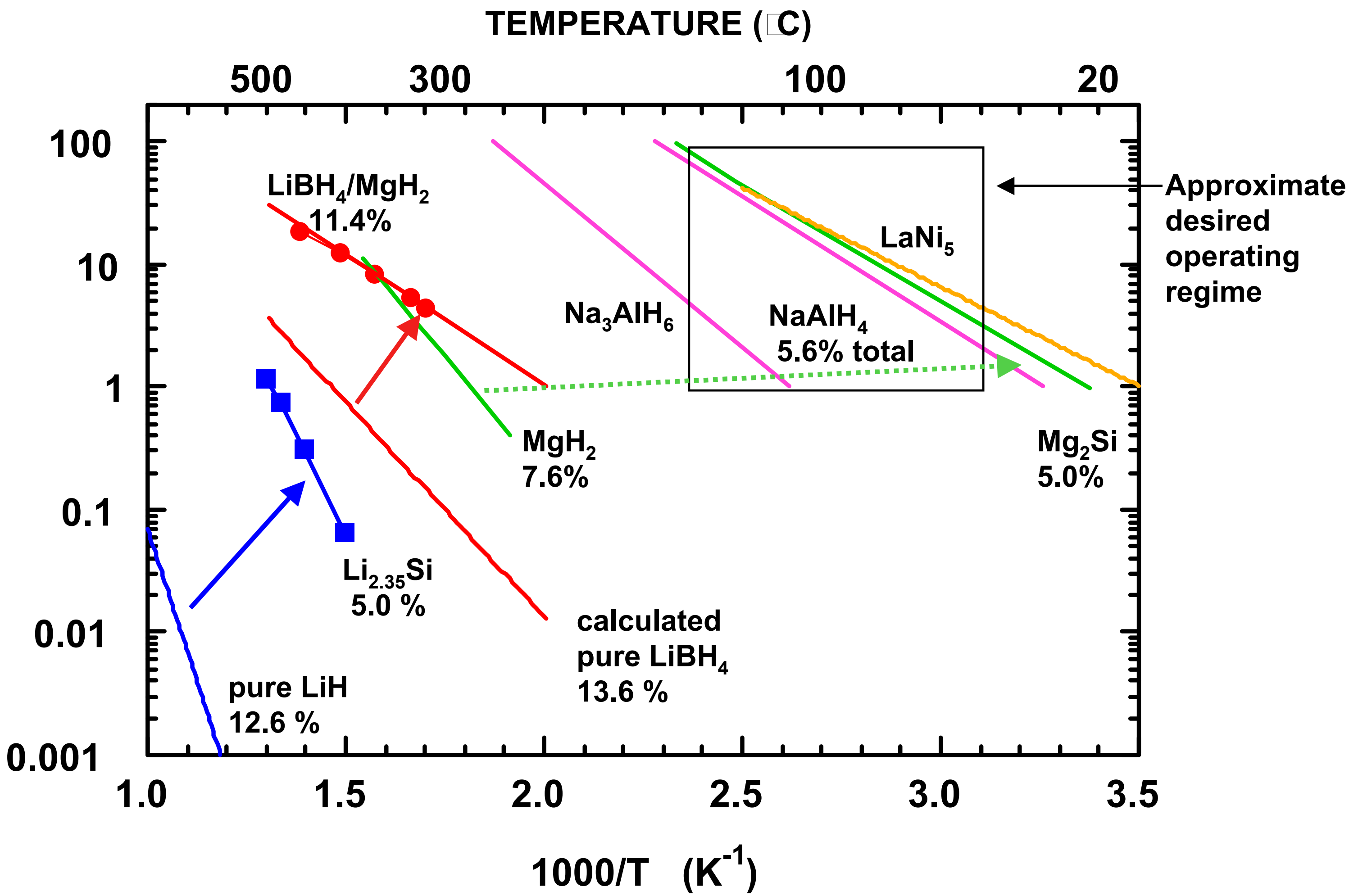
- **The reversible system $2LiBH_4 + MgH_2 = 2LiH + MgB_2 + 4H_2$(11.4 %) established.**
- **Analogous systems include: $LiBH_4$ + MgX (where X = F, Cl, OH, O, S, Se, CO_3, Si, etc.)**
  - 8 destabilization reactions identified and characterized *(HSC modeling)*
  - H-capacities ranging from 5.4-9.6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

$LiNH_2$ ($LiBH_4$) + C (Si)

- **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

HRL LABORATORIES

Summary of Program Plans

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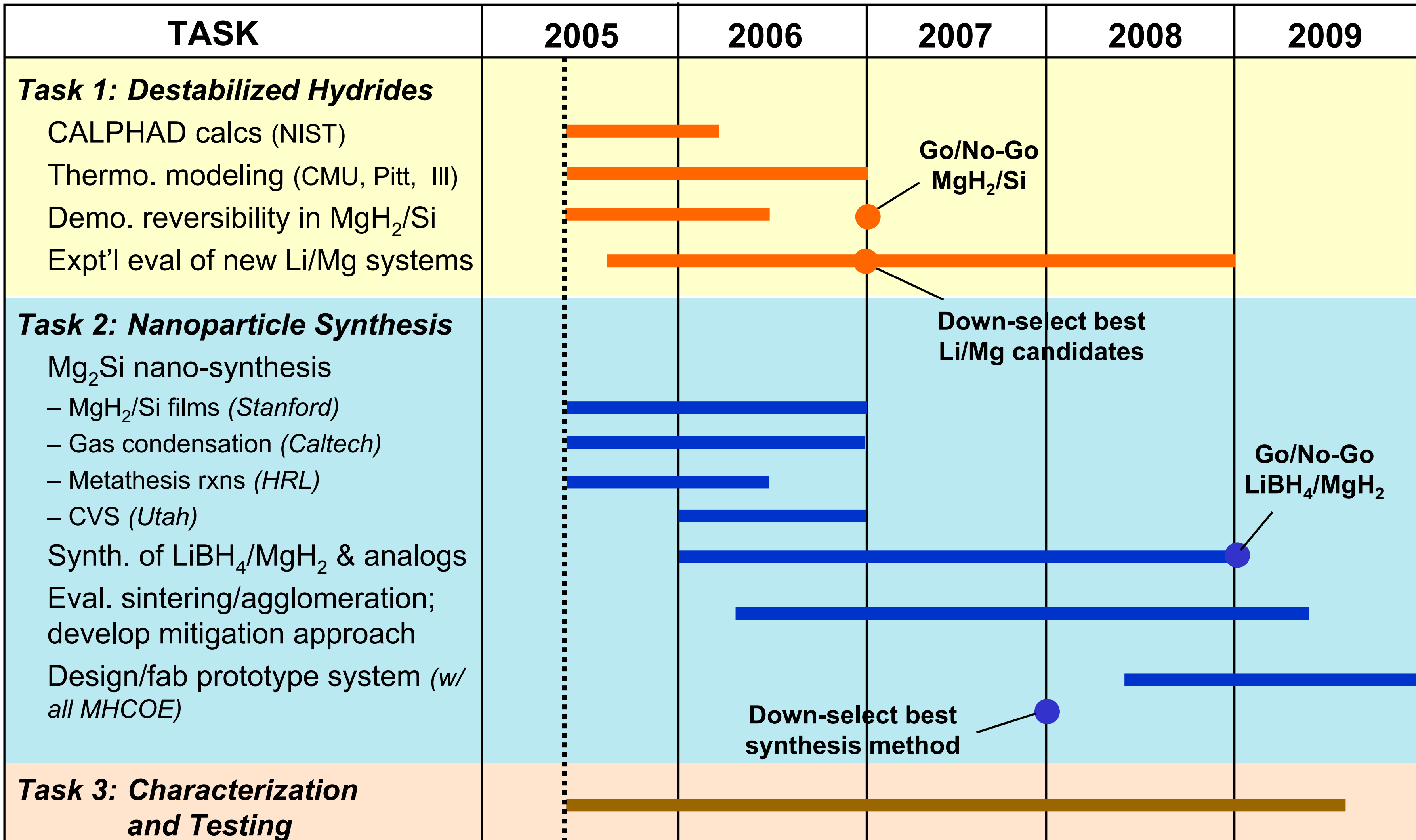


Lightweight Intermetallics for Hydrogen Storage

J.-C. Zhao,

Jun Cui, Yan Gao, John Lemmon, Tom Raber,

Job Rijssenbeek, Gosia Rubinsztajn, Grigorii Soloveichik

GE Global Research

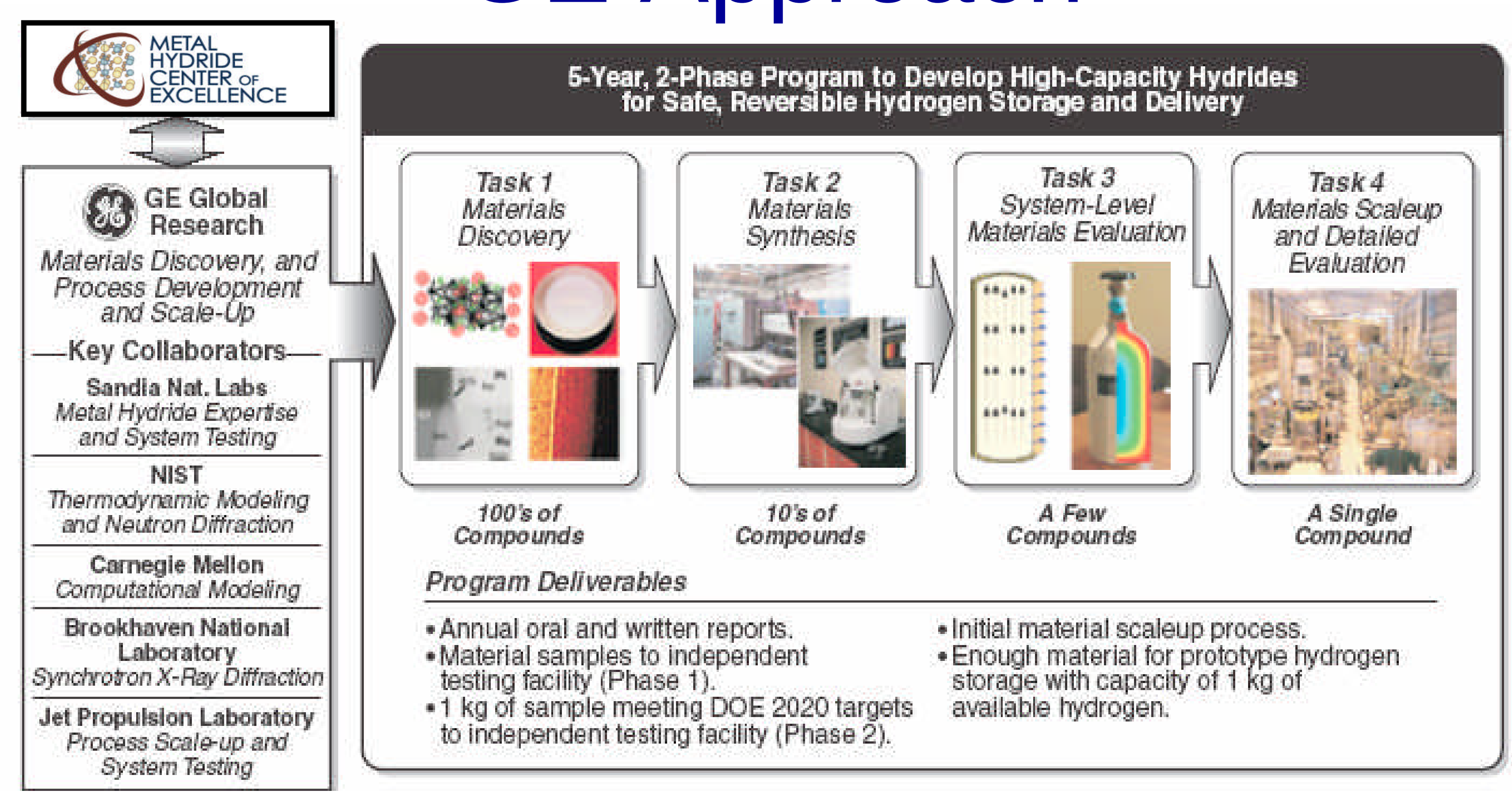
Niskayuna, NY

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

May 23-24, 2005

Project ID # STP27

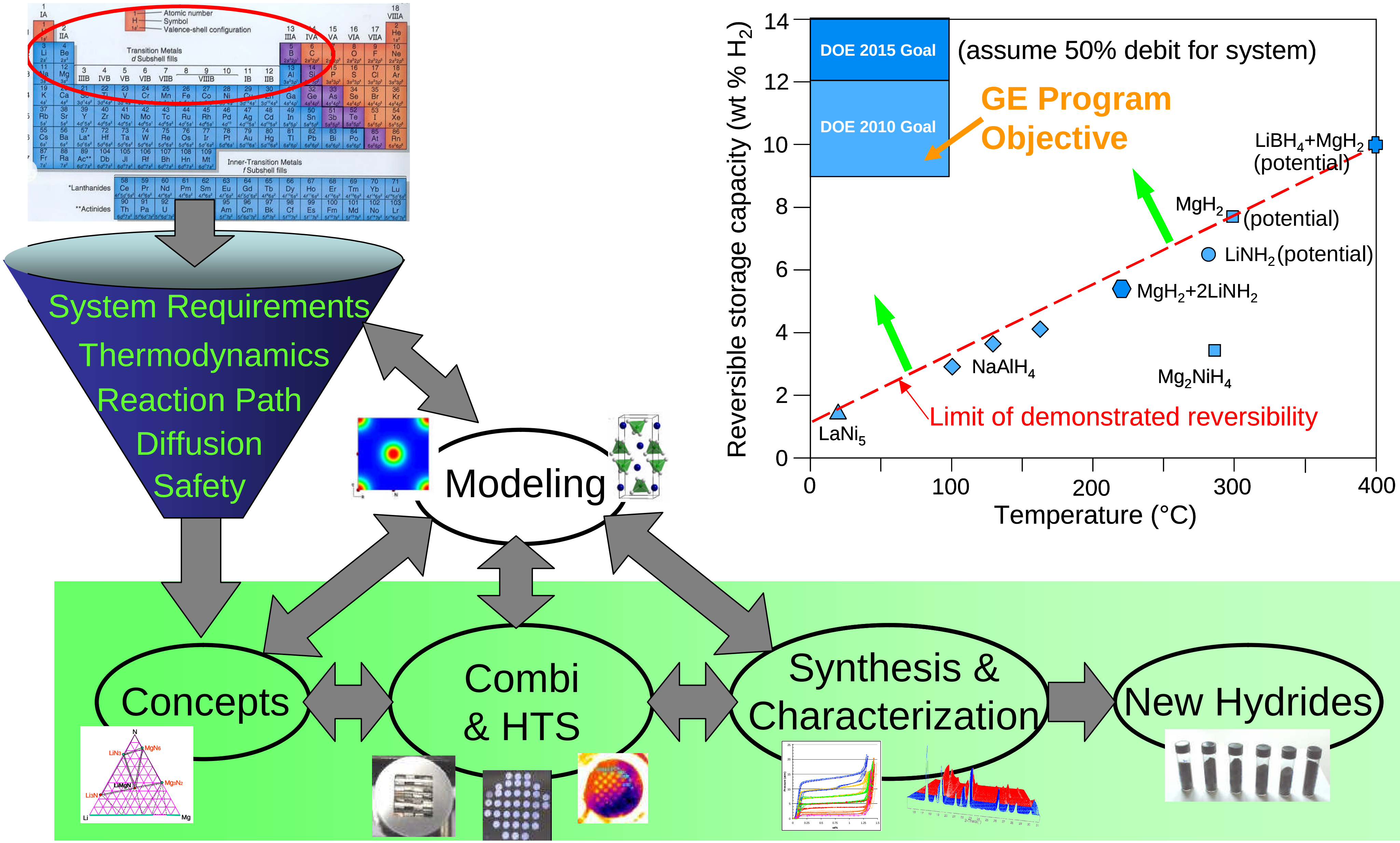
GE Approach



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

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GE Lightweight Intermetallics Approach

- **Focus:**

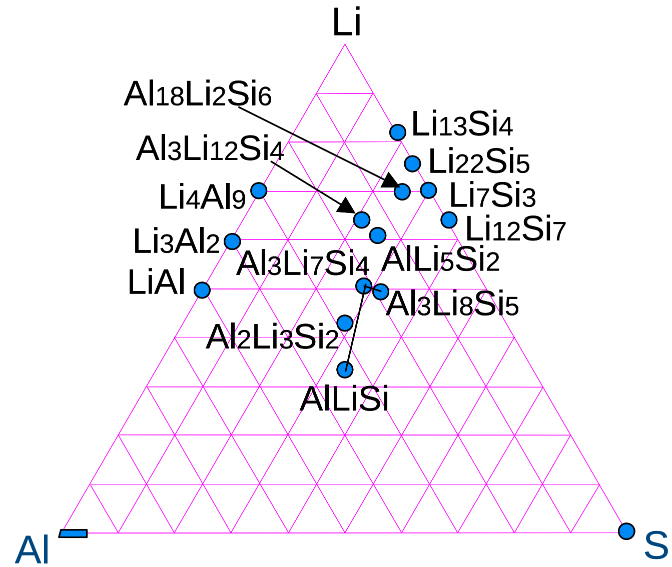
  Lightweight aluminides & silicides of Li, Mg, and Na (potential to 6 wt.%)

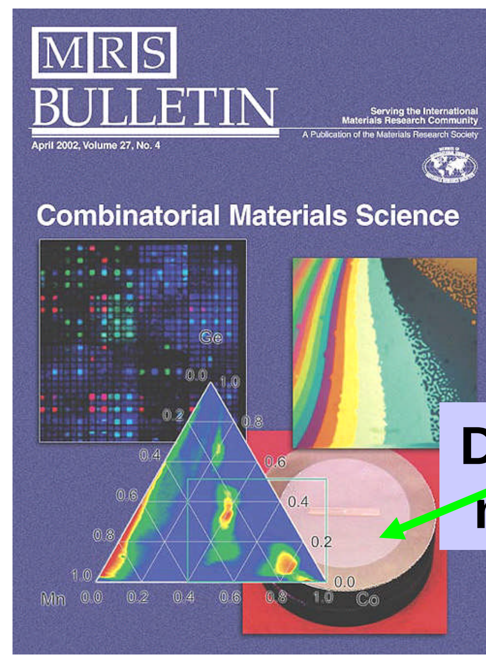
- **Opportunity:**

  Many intermetallic compounds exist in aluminide and silicide systems

- **Develop & Validate:**

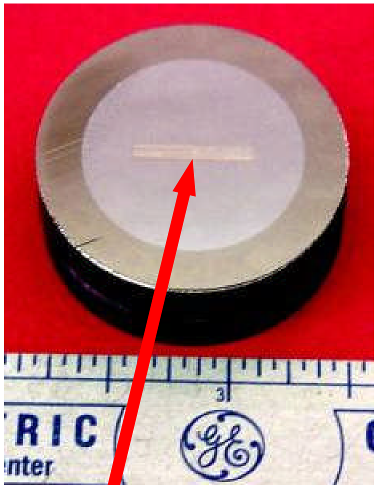
  Combinatorial synthesis and high-throughput screening methodologies for hydride discovery in the target temperature – pressure – kinetics design space

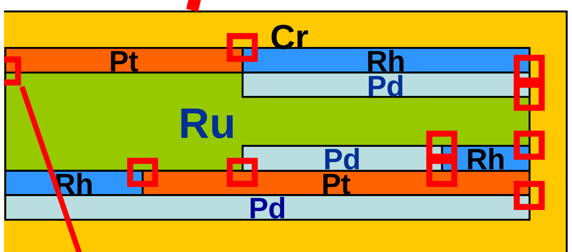


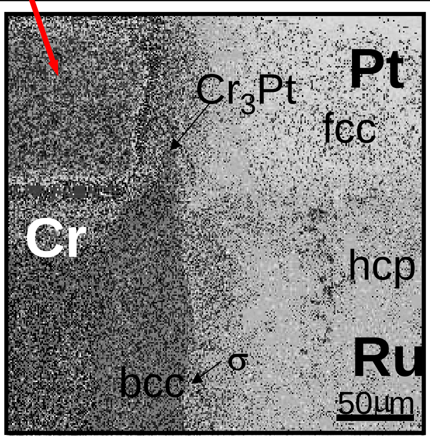


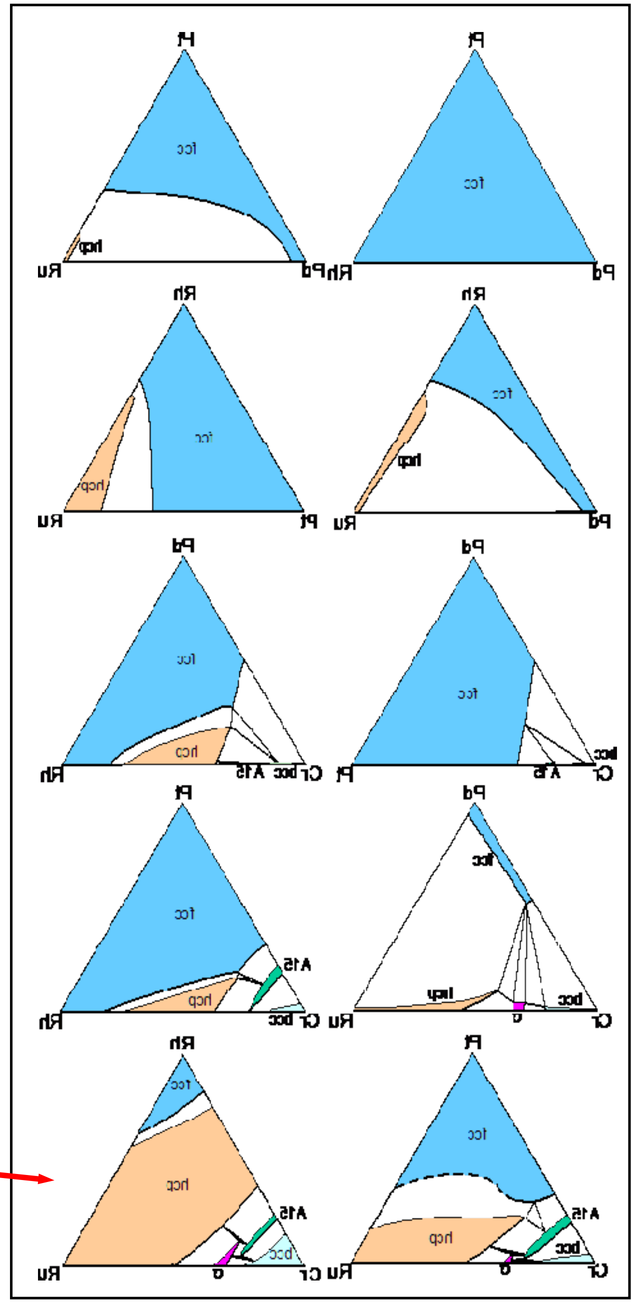
Diffusion multiple

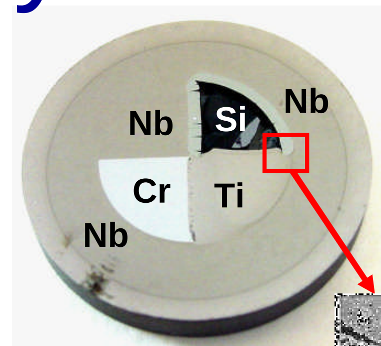
Diffusion Multiples & Alloy Development

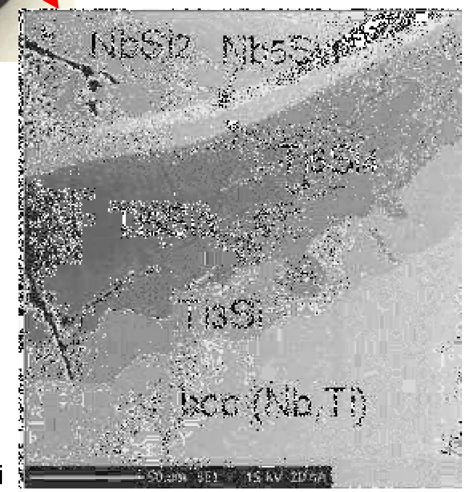


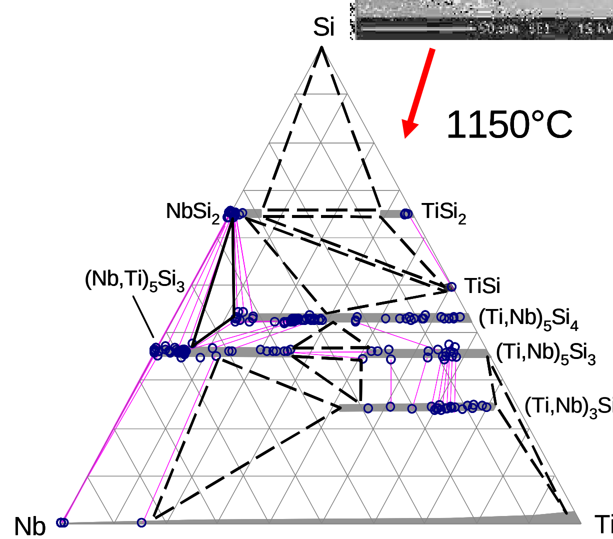












imagination at work

Synthesize many compounds simultaneously

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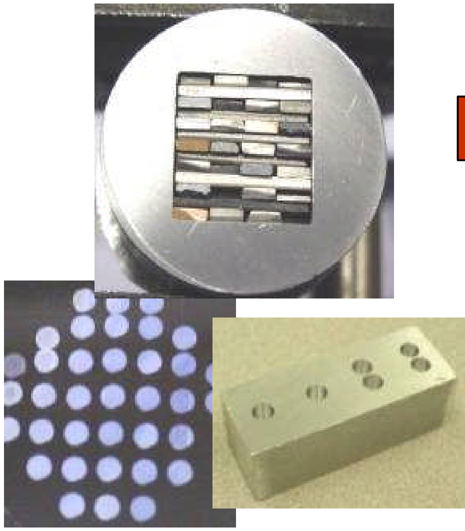
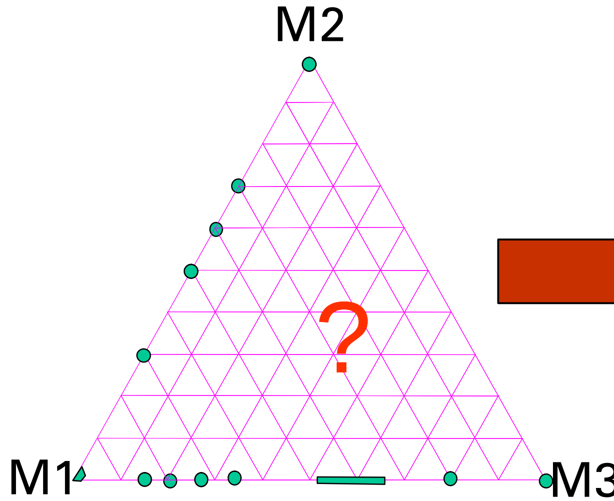
Combinatorial Synthesis & HTS

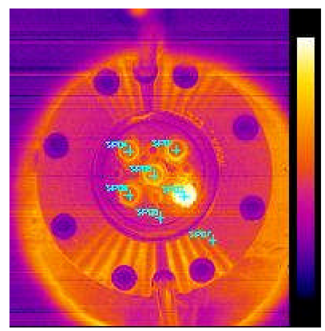




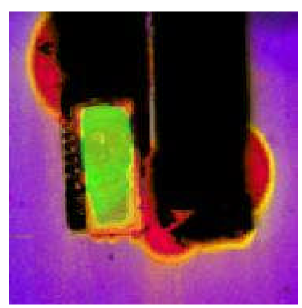
React @ desired T and atmosphere

- Slice & polish
- 1st-level characterization

Charge with D_2



Screening with thermography



Screening with time-of-flight secondary ion mass spectroscopy

Identify, synthesize & test leads

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Effective combi synthesis methods developed

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Combinatorial Synthesis & HTS: Results

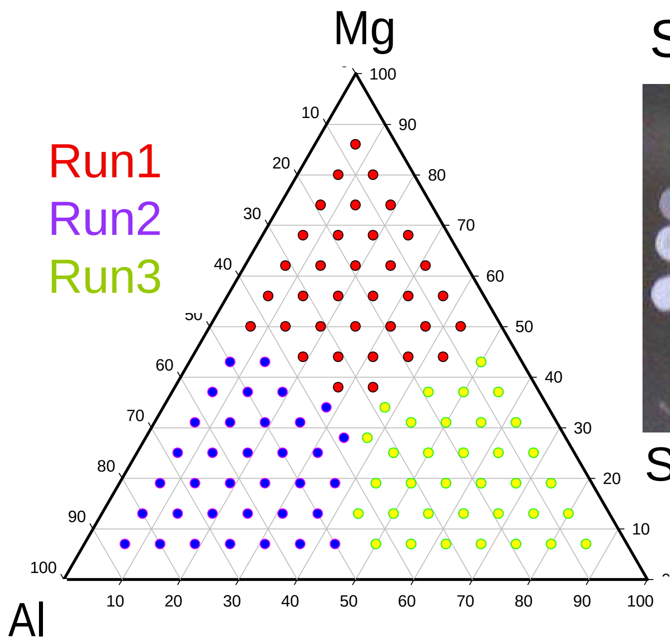
Thin-film methods

Synthesis

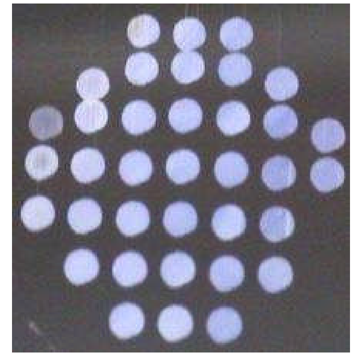
- Complementary to diffusion multiple
- Great for exploring Mg, Al, Si alloys
- Map phase diagram at 6% intervals, 3 runs, 5hrs.
- 7 target co-sputtering, DC and RF power

Screening

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

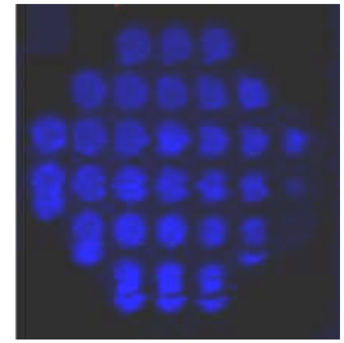


Start Mg_3-$Al_{0.03}$

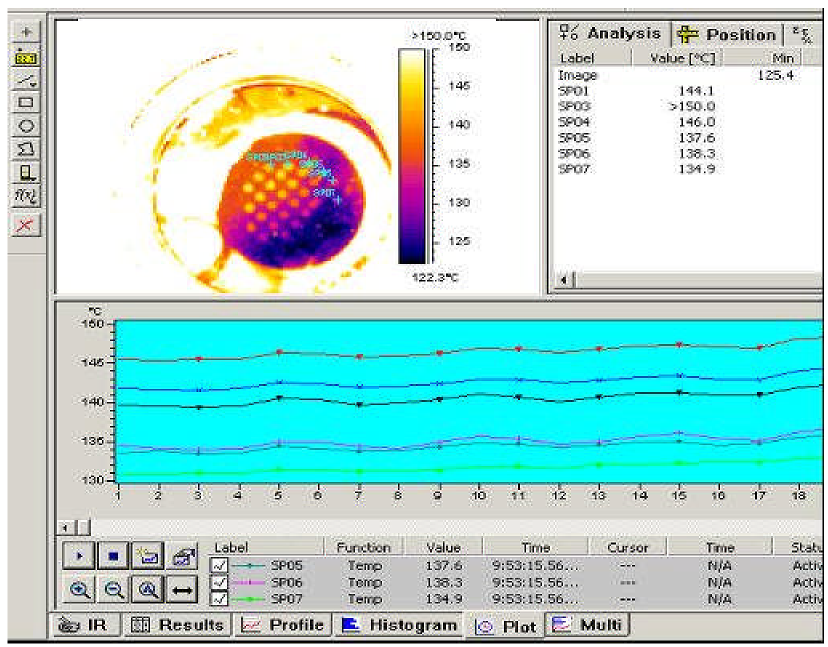


Sputtered Array

End $Mg_{0.03}$Al



Imaging A/B rati



Screen for H_2 storage with thermography

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Thermography is an effective screening tool

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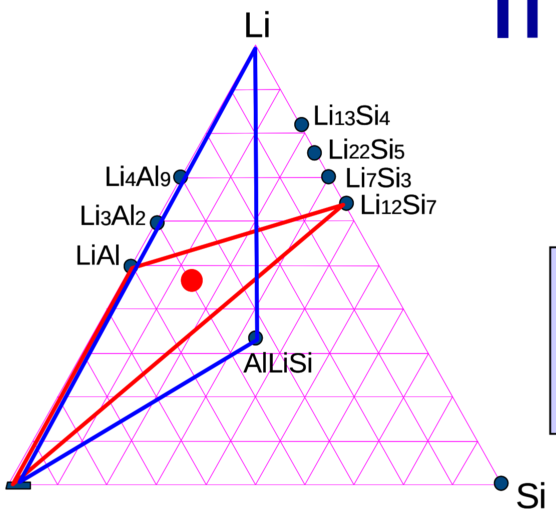
In-Situ XRD: Results

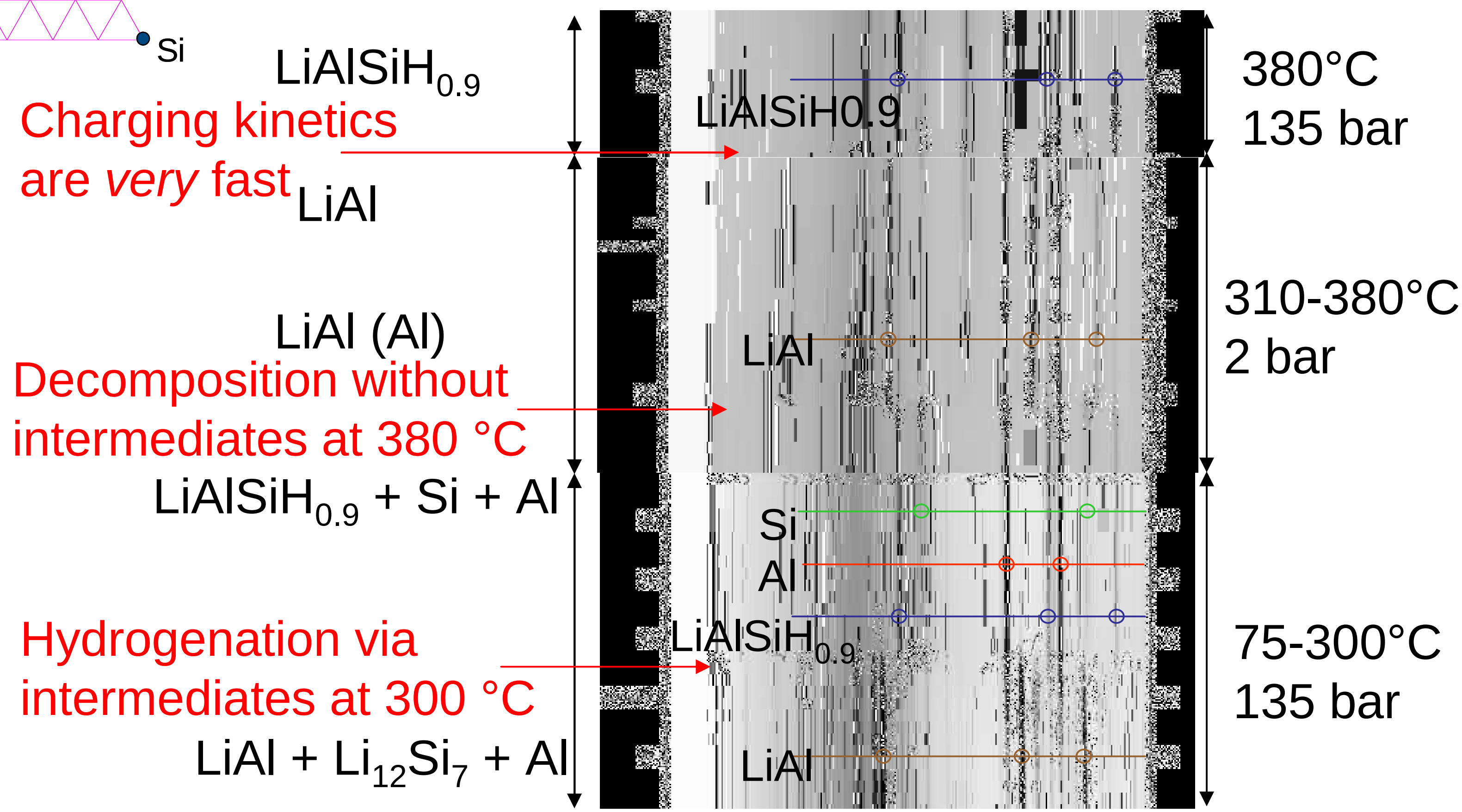


Literature:

LiAlSi + 0.45 H_2 ←→ $LiAlSiH_{0.9}$ 535°C, 80-82 bar

New result: 300-380°C, < 135 bar

AlLi + $Li_{12}Si_7$ + Al + H_2 ←→ $LiAlSiH_{0.9}$ + LiH + (Al)



First intermetallic hydride in non-transition metal alloys

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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