

Thermodynamically Tuned Nanophase Materials

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

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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

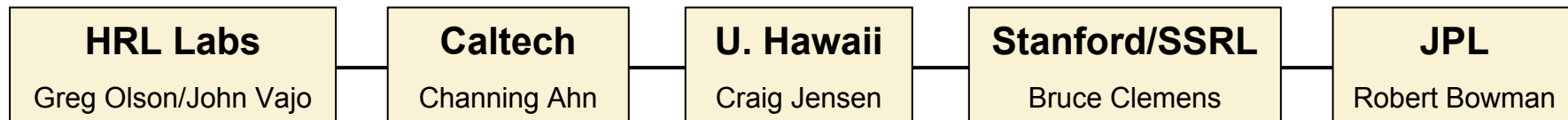
Weight and volume
Efficiency
Hydrogen capacity and reversibility

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 MHCoe partners on synthesis, modeling, and characterization
- Coordinator of sub-team on hydride-destabilized nanophase materials (Caltech, JPL, Stanford, U. Hawaii)



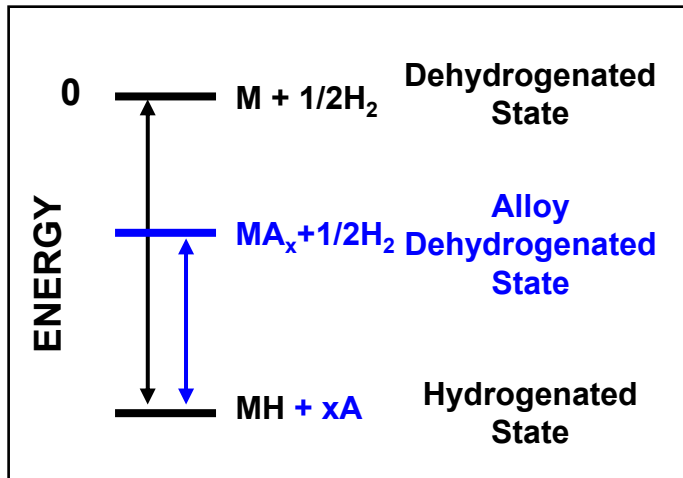
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|--|--|---|--|--|
| <ul style="list-style-type: none"> • Sub-team coordination • Hydride destabilization strategies • Nanoparticle synthesis • Hydrogen cycling: test and characterization | <ul style="list-style-type: none"> • Nanoparticle synthesis (gas condensation) • Materials Characterization (TEM, XRD) | <ul style="list-style-type: none"> • Nanostructured catalyst development • New synthesis routes | <ul style="list-style-type: none"> • <i>In situ</i>, real-time synchrotron XRD of H-induced phase changes • Nanoparticle synthesis • Solid state reaction kinetics • Thin film reactions | <ul style="list-style-type: none"> • 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

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

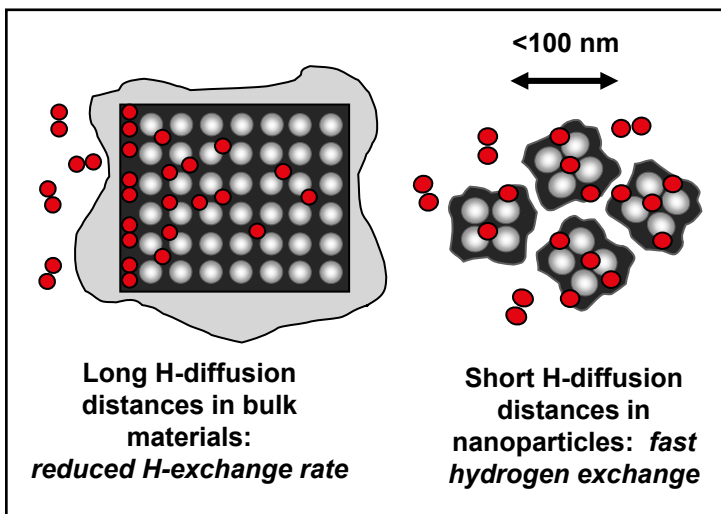
- **To develop methods for efficient and controlled synthesis of destabilized nanophase metal hydrides and to employ the materials in reversible hydrogen storage system**
 - Utilize both “top-down” (e.g., energetic ball-milling) and “bottom-up” (direct) synthesis routes (*MHCoE collaboration*)
 - Characterize 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 H₂ 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

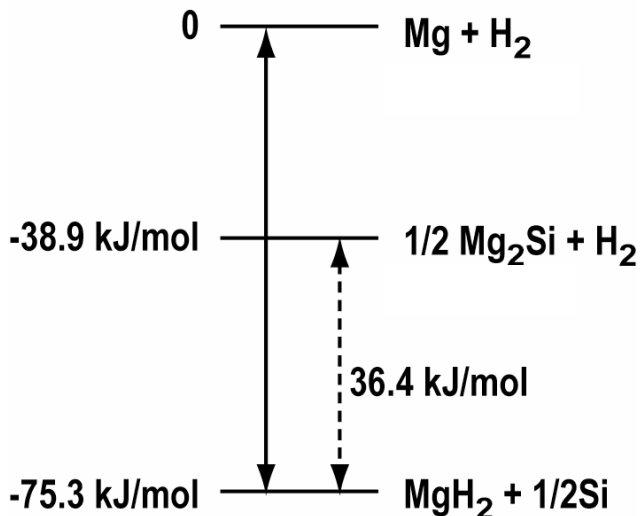


Enhance Kinetics by Nano-engineering

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

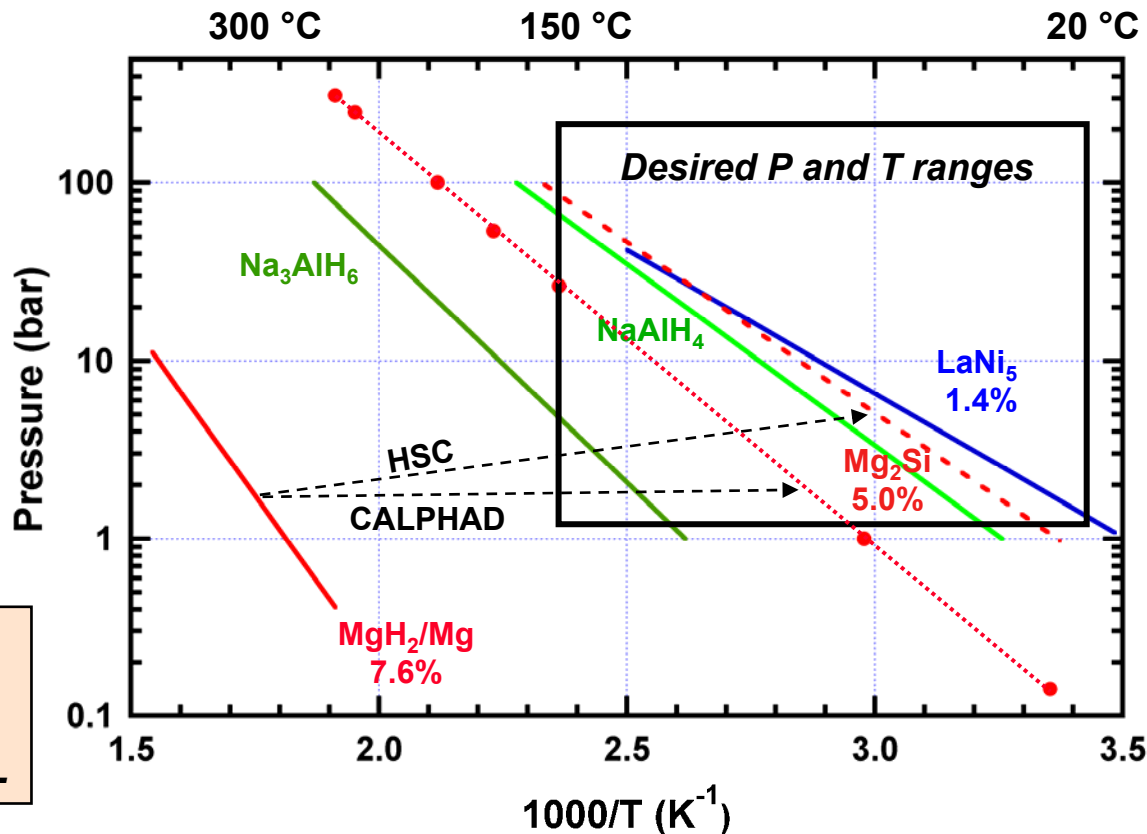
- **Destabilized systems that satisfy all thermodynamic requirements for practical on-board storage not yet developed; heat removal during re-fueling remains an issue**
- **Dependence of nanoparticle size on diffusion rate unknown**
- **Efficient synthesis methods for light-metal alloy nanoparticles 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 MgH₂/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 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)

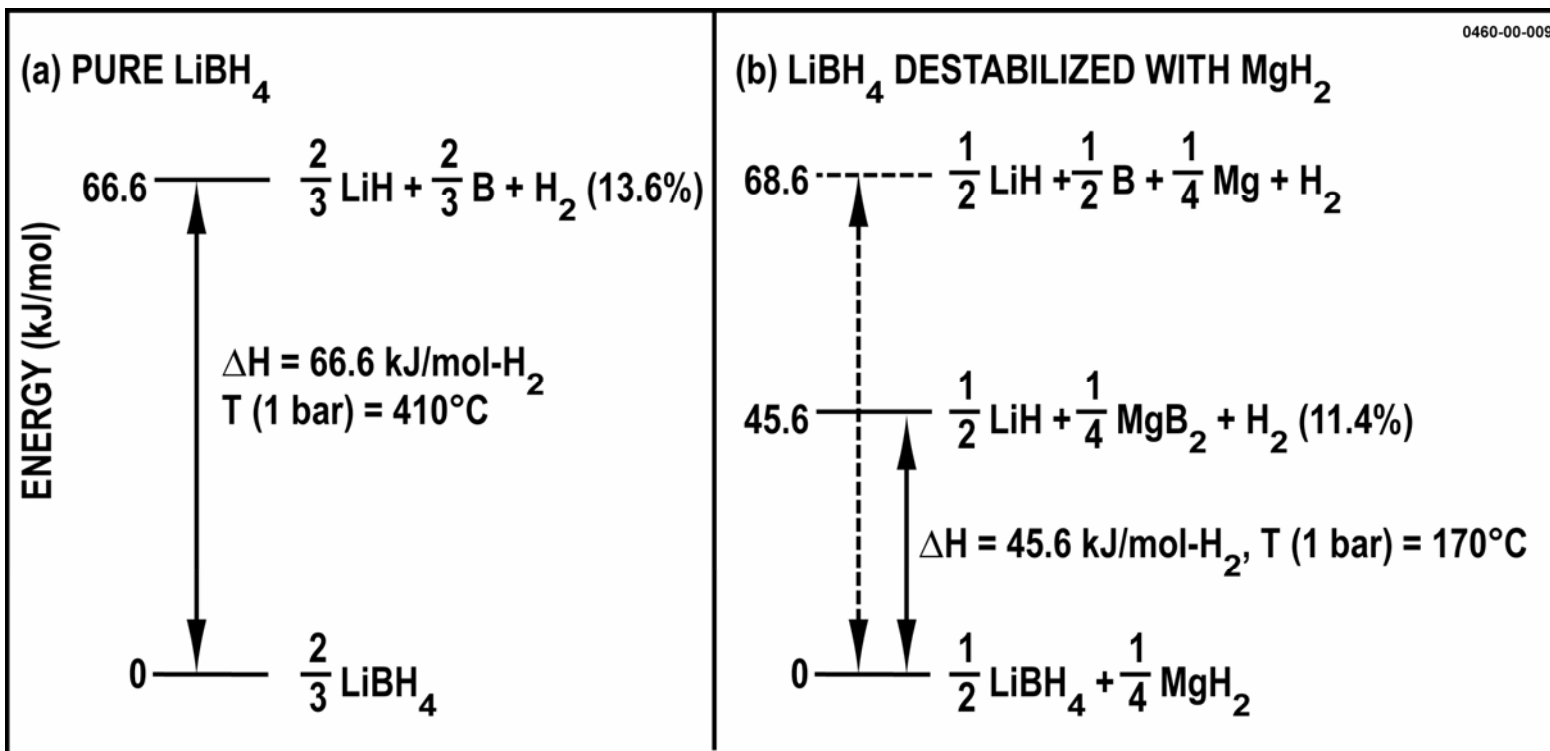
HRL

- **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).

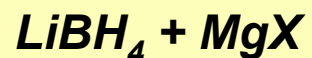
- **Explore reaction fundamentals**

- Nucleation and phase formation, rate-limiting steps, intermediate species, structure (*Stanford, JPL, U.III. 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*)

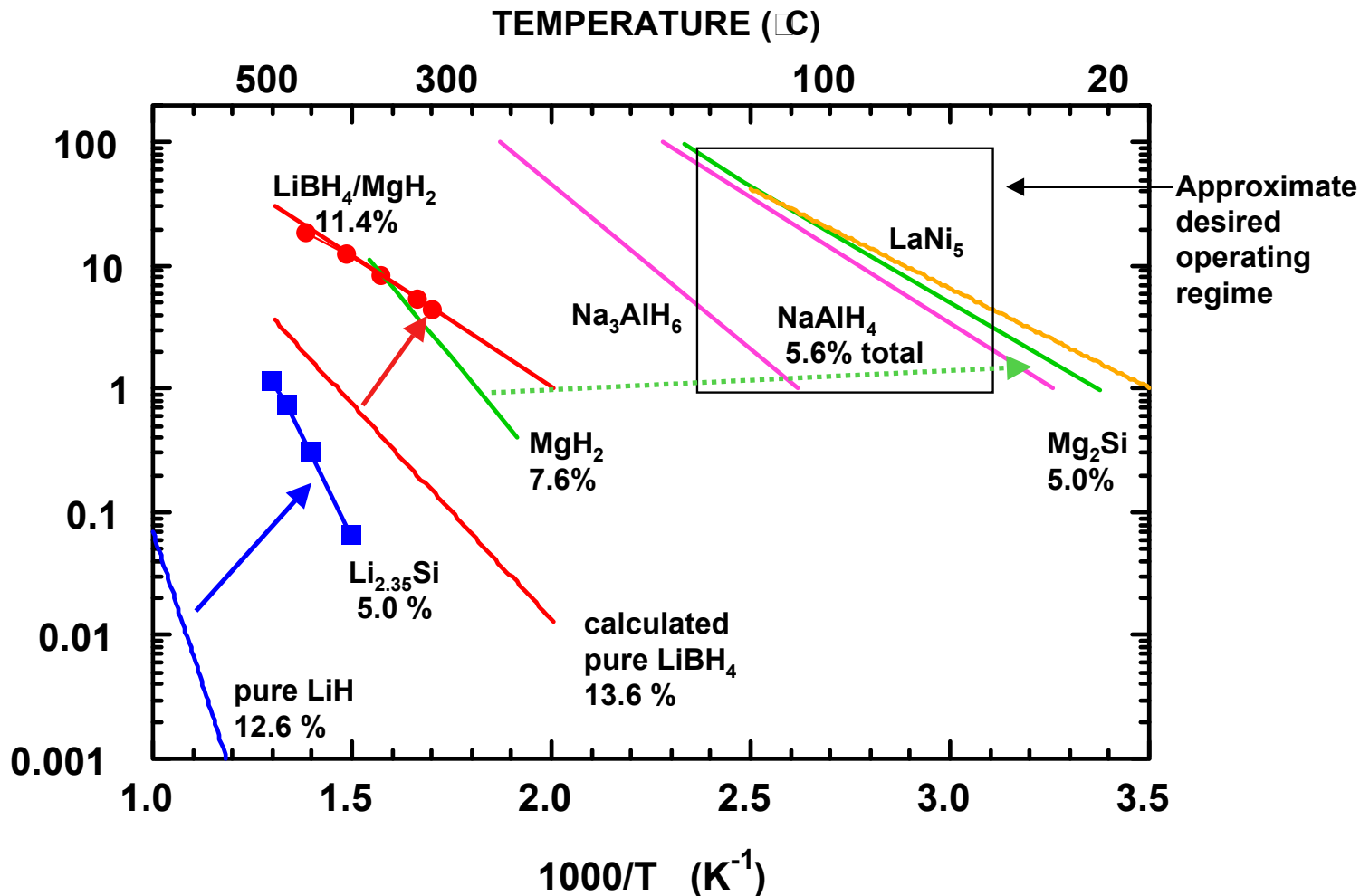
- **Identify and optimize catalyst(s) for reversible borohydride reactions**
(*U. Hawaii, HRL*)



- The reversible system $2\text{LiBH}_4 + \text{MgH}_2 = 2\text{LiH} + \text{MgB}_2 + 4\text{H}_2$ (11.4 %) established.
- Analogous systems include: $\text{LiBH}_4 + \text{MgX}$ (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*)



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

