Thermodynamically Tuned Nanophase Materials

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

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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	Caltech	U. Hawaii	Stanford/SSRL	JPL
Greg Olson/John Vajo	Channing Ahn	Craig Jensen	Bruce Clemens	Robert Bowman

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

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

U. Hawaii
- Nanostructured catalyst development
- New synthesis routes

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

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

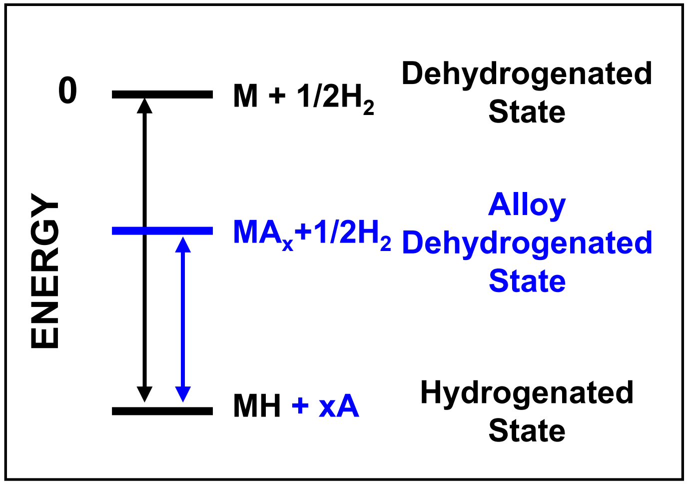
Other partners in MHCoE will also contribute in areas of nanostructure synthesis, diagnostics and modeling/simulation

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: $LiBH_4 + MgH_2$ 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

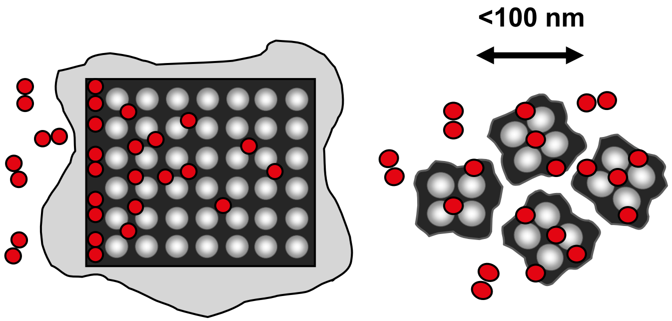
Approach:
– Hydride Destabilization and Nano-engineering –



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



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

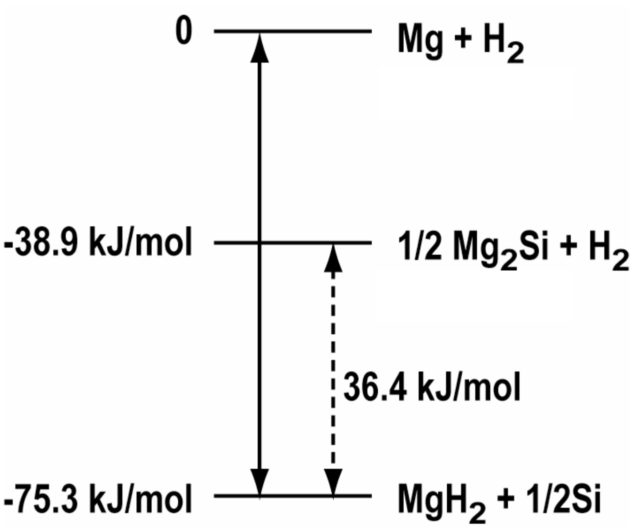
Destabilization and Nano-engineering

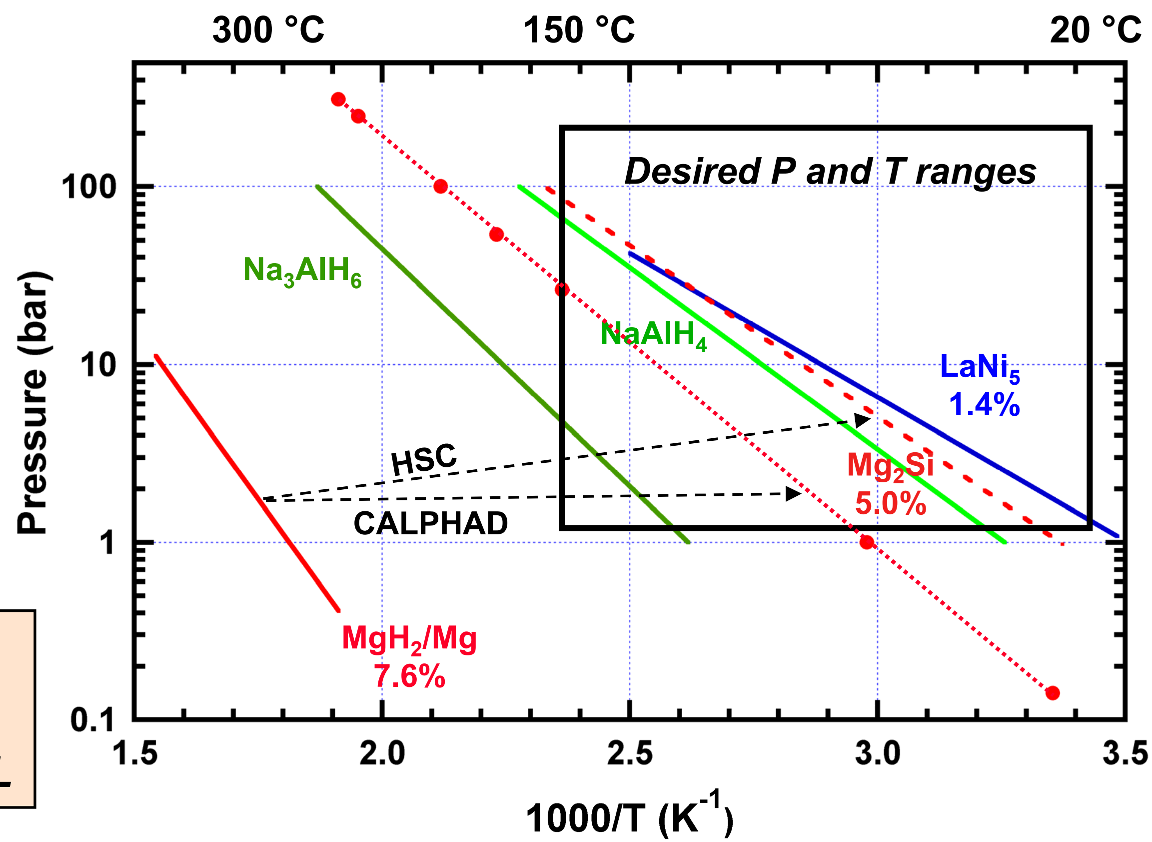
– Issues and Challenges –

- 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***

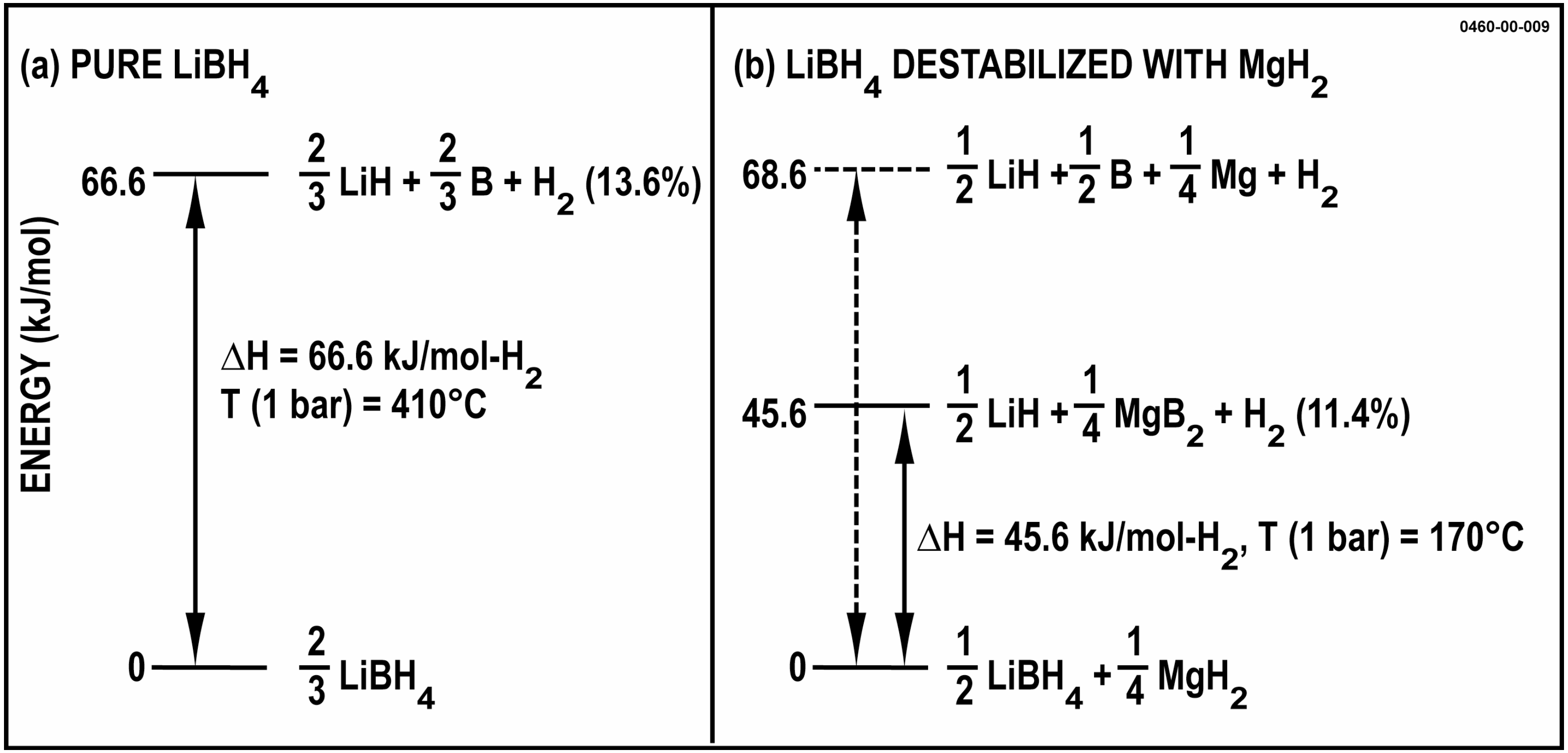
MHCoE Partners

- ***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

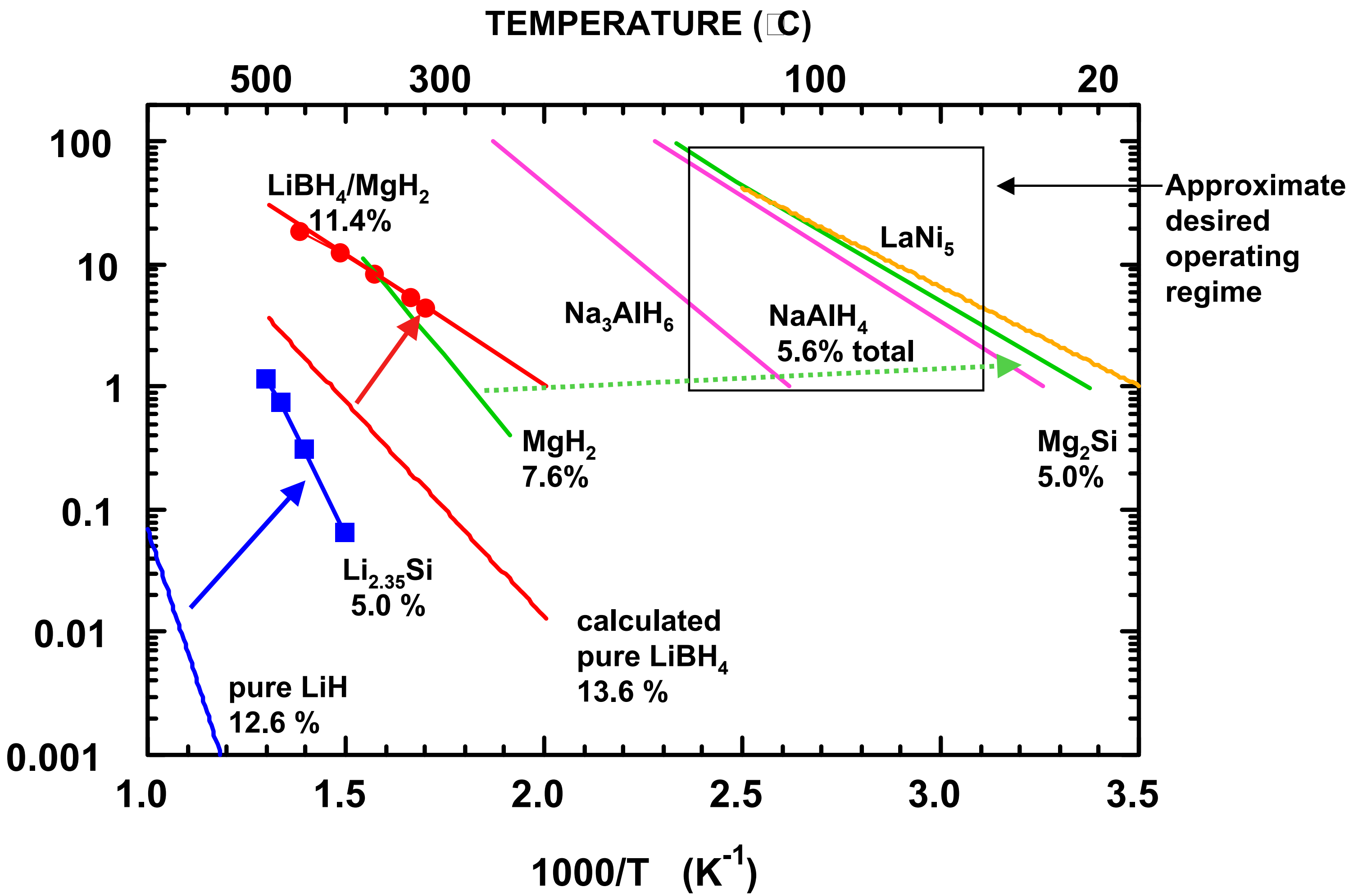
- **The reversible system $2LiBH_4 + MgH_2 = 2LiH + MgB_2 + 4H_2$(11.4 %) established.**
- **Analogous systems include: $LiBH_4$ + MgX (where X = F, Cl, OH, O, S, Se, CO_3, Si, etc.)**
  - 8 destabilization reactions identified and characterized *(HSC modeling)*
  - H-capacities ranging from 5.4-9.6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

Summary of Program Plans