Overview of DOE Metal Hydride Center of Excellence (MHCoE)

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This presentation does not contain any proprietary information

Project ID # STP15

DOE Metal Hydride Center of Excellence (MHCoE)

DOE
Office of Hydrogen, Fuel Cells & Infrastructure Technologies

MHCoE
Coordination Team

Sandia as MHCoE Lead Lab

5 National/Federal Labs
(BNL, ORNL, JPL, NIST, SRNL)

8 Universities
(Hawaii, Pittsburgh, Carnegie Mellon, Illinois, Caltech, Stanford, Utah, UN-Reno)

3 Industrial Partners
(GE, HRL, Intematix)
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 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

High Capacity Materials Research & Development

Structure Properties

Fundamental Modeling

Material Compatibility, Synthesis & Contamination Studies

Storage System Design

Delivery of Storage System

2005

2007

2009
MHCoE Partners Cover a Full Range of Expertise

Materials Development

- Advanced Hydrides
  - SNL
  - BNL
  - Hawaii
  - U. Utah
  - SRNL
- Rapid Screening
- Intermetallic Hydrides
  - GE
- Complex Hydrides
  - Intematix
- Destabilized Binary Hydrides
  - HRL
  - Caltech
  - JPL
  - Stanford
  - Hawaii

Fundamental Understanding

- Mechanism
  - Hawaii
  - SNL
  - UIUC
  - NIST
  - JPL
  - UNR
  - Stanford
- Modeling
  - U. Pitts
  - CMU
  - UIUC
  - SNL
  - NIST
  - U. Utah
- Engineering Science Phase II
  - SNL, JPL, SRNL, GE...

System Design & Engineering

- Synthesis
  - SNL
  - ORNL
  - U. Utah
  - Caltech
  - HRL
  - Hawaii
  - SRNL

Storage Properties

- SNL
- BNL
- JPL
- GE
- Caltech
- UNR
- Hawaii

MHCoE Materials Synthesis Resources

Materials Development

Fundamental Understanding

System Design & Engineering

- Synthesis of nanocrystalline reversible hydrides by vapor phase reactions
- Nanostructured catalyst development & new synthesis routes
- Nanoparticle synthesis (gas condensation) & materials Characterization (TEM, XRD)

- Develop chemical routes for nano-sized metal hydrides and bulk productions
- Synthesis & characterization of aluminum hydrides

**MHCoE Modeling and Mechanism Resources**

**Fundamental Understanding**
- Carnegie Mellon: 1st principle modeling of heat of formation, interfacial energy, etc.
- MSE, Illinois: In situ TEM, cluster-expansion thermodynamic toolkit, etc.
- Brookhaven National Laboratory: Synchrotron XRD
- University of Hawaii: Synchrotron XRD
- JPL: NMR, reaction kinetics

**Materials Development**
- Stanford Materials Science and Engineering: Synchrotron XRD, solid state reaction kinetics, etc.
- Calphad, neutron diagnostics
- Ab initio cal, mechanisms characterization

**System Design and Engineering**
- Sandia National Laboratories: Mechanisms characterization & modeling

MHCoE – Materials Development Categories

- Advanced complex hydrides \((AH_x + B + H_2 \rightleftharpoons ABH_y)\)
- Destabilized binary hydrides \((AB + H_2 \rightleftharpoons AH_x + B)\)
- Novel intermetallic hydrides \((AB + H_2 \rightleftharpoons ABH_x)\)
- Catalyzed binary hydrides \((A + H_2 \rightleftharpoons AH_x)\)
- Other reversible hydrogen storage materials (e.g. lithium amides, non-lithium based imides)
MHCoE Team on 1st Principal Modeling & Experimentation for Material Discovery

- Materials Development
  - Team Lead
  - Sandia National Laboratories

- Mechanism, modeling & synthesis
  - University of Hawaii
  - MSE at Illinois

- 1st principle modeling
  - Carnegie Mellon

- Fundamental Understanding
  - NMR & system engineering

- System Design & Engineering
  - System Engineering
  - Contamination & aging

MHCoE Team on Mechanistic Approach
to Destabilize Hydrides

Materials Development

1. Mechanisms & testing
2. Nanoparticle synthesis & characterization
3. Catalysts & synthesis
4. Material performance, aging, kinetics & testing
5. Mechanisms & testing

1. Principle modeling
2. Synchrotron XRD, thin film & nanoparticles, solid state reaction kinetics
3. Fundamental Understanding
4. System Design & Engineering

Carnegie Mellon
Illinois
MSE
Stanford
JPL
HRL
University of Hawai'i
Sandia National Laboratories

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

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
Combinatory Approach – Intermetallic Hydride

System Requirements
Thermodynamics
Reaction Path
Diffusion
Safety

Materials Concepts

DFT Phase diagram analysis

HTS

New Hydride

System-level testing

Characterization

Synthesis

Combinatory Approach – Complex Hydride

Micro-reactor

- Pressure Sensor
- Chamber
- High-temperature Seal
- Chemical Hydrides
- Library
- Heater

Tube

Chamber

High-temperature Seal

Library
System Engineering Team – AlH₃

- Materials Development
  - Aluminum hydride recharge development

Team Lead

- SRNL
  - Material synthesis
  - Catalysts development

- Brookhaven National Laboratory
  - Material characterization
  - Engineering properties

- University of Hawaii
  - Material performance, aging, kinetics & testing

- Carnegie Mellon
  - 1st principals Modeling

- Sandia National Laboratories
  - System Design & Engineering

- Mase Illinois
  - Fundamental Understanding

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

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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
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 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)
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
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: LiBH₄ + MgH₂ and LiBH₄ + 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 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
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
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$_2$Si 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$_2$Si by gas phase condensation
  - Initiated work *(HRL)* on alternative routes for synthesis of nanoscale Mg$_2$Si
  - Developed approaches for forming MgH$_2$ in nanostructured templates

- **Characterize thermodynamics and H-diffusion**
  - CALPHAD calculations ($P_{eq}$ vs temp.) *(NIST-U. Kattner)*
**MgH₂ / Si System**  
– Nanoscale Synthesis Work in Progress –

**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)₃]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**
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

• 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 $2\text{LiBH}_4 + \text{MgH}_2 = 2\text{LiH} + \text{MgB}_2 + 4\text{H}_2$ (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

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<tr>
<th>TASK</th>
<th>2005</th>
<th>2006</th>
<th>2007</th>
<th>2008</th>
<th>2009</th>
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<tr>
<td><strong>Task 1: Destabilized Hydrides</strong>&lt;br&gt; CALPHAD calcs (NIST)&lt;br&gt; Thermo. modeling (CMU, Pitt, Ill)&lt;br&gt; Demo. reversibility in MgH₂/Si&lt;br&gt; Expt'l eval of new Li/Mg systems</td>
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<td><strong>Task 2: Nanoparticle Synthesis</strong>&lt;br&gt; Mg₂Si nano-synthesis&lt;br&gt; – MgH₂/Si films (Stanford)&lt;br&gt; – Gas condensation (Caltech)&lt;br&gt; – Metathesis rxns (HRL)&lt;br&gt; – CVS (Utah)&lt;br&gt; Synth. of LiBH₄/MgH₂ &amp; analogs&lt;br&gt; Eval. sintering/agglomeration; develop mitigation approach&lt;br&gt; Design/fab prototype system (w/ all MHCOE)</td>
<td><img src="timeline1.png" alt="Timeline" /></td>
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<td><strong>Task 3: Characterization and Testing</strong></td>
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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
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

System Requirements
- Thermodynamics
- Reaction Path
- Diffusion
- Safety

Modeling

Concepts

Combi & HTS

Synthesis & Characterization

New Hydrides

Graph showing reversible storage capacity vs. temperature for various hydrides and targets.

- **DOE 2015 Goal**
- **DOE 2010 Goal**
- **GE Program Objective**

Chemical reactions and formulas:
- LiBH₄ + MgH₂ (potential)
- MgH₂ (potential)
- LiNH₂ (potential)
- Mg₂NiH₄
- NaAlH₄
- Mg₂NiH₄
- LiNi₅

Limit of demonstrated reversibility

(assume 50% debit for system)
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

Synthesize many compounds simultaneously

1150°C
Combinatorial Synthesis & HTS

Identify, synthesize & test leads

Screening with thermography

Screening with time-of-flight secondary ion mass spectroscopy

React @ desired T and atmosphere

- Slice & polish
- 1st-level characterization

Charge with D₂

Effective combi synthesis methods developed
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.

Screen for H₂ storage with thermography

Thermography is an effective screening tool
In-Situ XRD: Results

Literature:
LiAlSi + 0.45 H₂ ⇌ LiAlSiH₀.₉ 535°C, 80-82 bar

New result: 300-380°C, < 135 bar
AlLi + Li₁₂Si₇ + Al + H₂ ⇌ LiAlSiH₀.₉ + LiH + (Al)

Charging kinetics are very fast

LiAlSiH₀.₉

LiAl (Al)
Decomposition without intermediates at 380 °C
LiAlSiH₀.₉ + Si + Al

Hydrogenation via intermediates at 300 °C
LiAl + Li₁₂Si₇ + 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