Thermodynamically Tuned Nanophase Materials for Reversible Hydrogen Storage

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

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Project ID #
ST18

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Overview

**Timeline**
- Project start date: March 2005
- Project end date*: Feb 2010
- Percent complete*: 45%
  * Assumes support for Phases 1 and 2

**Budget**
- **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 FY07:**
  - $117K as of 4/10/07 (DOE),
  - $150K (cost share)

**Technical System Targets**

<table>
<thead>
<tr>
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<th>2007</th>
<th>2010</th>
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<tbody>
<tr>
<td>Gravimetric capacity:</td>
<td>4.5%</td>
<td>6%</td>
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<td>Volumetric capacity:</td>
<td>0.036 kg/L</td>
<td>0.045 kg/L</td>
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<td>Min/Max delivery temp:</td>
<td>-30/85°C</td>
<td>-40/85°C</td>
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**Technical Barriers**
- System weight and cost
- Large binding energies and slow H₂ sorption kinetics in light metal hydrides

**Partners**
- Participant in DOE MHCoE
  - U. Pitt, CMU: modeling of new systems and kinetic barriers
  - Stanford: thin film systems
  - Caltech, JPL, U. Utah, Hawaii: scaffolds
  - Intematix: catalysis
Objectives

Overall

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

2006/2007

• To identify and test new high capacity Li- and Mg-based destabilized hydrides
  ➢ Screen candidate LiBH₄ + MgX destabilized systems and evaluate energetics and kinetics
  ➢ Down-select systems for additional work

• To apply nano-engineering methods to address kinetics limitations
  ➢ Determine hydrogen exchange rates in nanoscale MgH₂/Si
  ➢ Evaluate sorption kinetics and thermodynamics of LiBH₄ and Mg in carbon aerogel scaffolds
  ➢ Assess capacity penalty for hydrides in scaffolds (can they be practical?)
Hydride Destabilization
(addresses thermodynamics)

Reduce reaction enthalpy by forming dehydrogenated alloy
- If alloy is stable w.r.t metal then hydride is destabilized
- System cycles between H-containing state and metal alloy
  ⇒ lower $\Delta H$

Destabilization results in lower $\Delta H$ and $T_{1\text{ bar}}$

Nano-engineering
(addresses kinetics)

Decrease diffusion distances, nanoporous scaffolding
- Shorter diffusion distances: faster hydrogen exchange
- More efficient catalysis pathways
- Nano-scaffolds as hosts for nanostructured hydrides:
  ⇒ structure-directing agents, mitigate particle agglomeration

Enhanced reaction rate and improved cycling

From Petricevic, et al., Carbon 39, 857 (2001)
New Destabilized Systems
– LiBH₄ + MgX –

- Potential systems include: X = F, Cl, OH, O, S, Se, CO₃, Si, SO₄, Cu, Ge, & Ni
  - 12 destabilization reactions identified and characterized using HSC modeling
  - H-capacities ranging from 5.4-9.6 wt.% T₁ bar from -10°C to 430 °C
  - X = F, S, Se, CO₃ tested previously
- In FY06/07, two new systems tested, X = Cl and Cu:
  - 2LiBH₄ + MgCl₂ ↔ 2LiCl + MgB₂ + 4H₂ (5.8 wt.% T₁ bar = -10 °C)
    - No H₂ uptake from 2LiCl + MgB₂ at 150 bar, up to 250°C (T₁ bar too low)
  - 4LiBH₄ + Mg₂Cu ↔ 4LiH + 2MgB₂ + Cu + 6H₂ (6.0 wt.%)
    - From 4LiBH₄ + Mg₂Cu, only trace MgB₂ formed (4LiBH₄ + Mg₂Cu did not react with each other)
- Neither system is a good candidate for further work
- Results show kinetic limitations in destabilized systems
MgH₂/Si
– Go/No-Go Decision  Qtr 4, FY06 –

- Motivation: prototype system for nanoengineering, nearly ideal thermodynamics (T₁bar ~ 50 °C)

- Summary of effort to demonstrate reversibility
  - Catalysis (tested bulk metals, nanoparticle metals, and oxides for effect on dehydrogenation and hydrogenation). All improved dehydrogenation (nano-Ni best). No hydrogenation observed.
  - Mechanical dispersion (MgH₂ milled with excess Si to create dispersed nano-MgH₂). Onset of dehydrogenation decreased by up to 100°C. No hydrogenation observed.
  - Mg₂Si nanoparticles (tested samples of nano-Mg₂Si formed using nano-Si precursors, self-propagating reactions, and chemical vapor synthesis (CVS). No hydrogenation observed.
  - Mechano-chemistry (milled Mg₂Si formed by powder metallurgy and mechanical synthesis in 50 bar of hydrogen, varied milling conditions and included catalysts). No hydrogenation observed.

- Phase separation or passivation by hydrogen* prevents hydrogenation
  * suggestion by Prof. Gabor Somorjai, (MHCoE/Berkeley Hydrogen Storage meeting 3/13/07)

“No-Go” for continued work on MgH₂/Si system
Nano-scale Hydrides in Porous Scaffolds

- Scaffolds are effective structure directing agents for nano-scale hydrides
- Kinetics improved by limiting particle size and diffusion distances
- Thermodynamic changes possible through surface/interface energy effects

- Initial work on LiBH$_4$ incorporated into carbon aerogels
  - Prototype complex hydride
  - Slow kinetics
  - Poor reversibility
  - Synthesis (resorcinol/formaldehyde condensation)
  - Pore sizes (5-25 nm) and volumes (1-4 cm$^3$/g)
  - Relatively chemically inert

- Aerogels filled with LiBH$_4$ (LiBH$_4$@aerogel) by infiltration from melt:
  - 80-90% of pore space filled with LiBH$_4$
Dehydrogenation of LiBH₄@C-Aerogel

TGA (10°C/min) for H₂ desorption: LiBH₄ → LiH + B + 1.5H₂ (13.6 wt %)

- Aerogel lowers dehydrogenation temperatures up to 70°C
- Capacity penalty reduced to 40% with high pore volume aerogel

Capacity penalties for LiBH₄ in aerogel
- 13 nm (0.8 cm³/g) : 66%
- 25 nm (1.3 cm³/g) : 56%
- 40 nm (2.7 cm³/g)* : 40%
- Goal (>4 cm³/g) : < 25%

*provided by Ted Baumann, LLNL

New data
LLNL aerogel
8 wt %
0.072 kg/L H₂
**METHOD**

Determine activation energy for dehydrogenation using Ozawa analysis:

Heat samples at multiple ramp rates \( b \); measure transition temp \( T \). Fit data to:

\[
\ln(b) = -\frac{E_a}{RT} + \text{constant}
\]


- Activation energy for dehydrogenation is reduced in aerogel
- Reaction rate (Boltzmann factor) increases by ~1000x at 350 °C
Quasi-equilibrium Pressure for LiBH₄@C Aerogel

LiBH₄ → LiH + B + 1.5H₂ at 300 °C

- Desorption rate accelerates if H₂ overpressure is removed
- Result suggests that the final pressures do represent equilibrium
  * Could not obtain good data for neat LiBH₄

Aerogel increases the equilibrium pressure of LiBH₄ by 10 times (at ~ 4 wt % desorbed)
Incorporation of LiBH$_4$ into the aerogel significantly increases the dehydrogenation rate

- After ~ 0.1 hr the desorption rate for the aerogel slows significantly due to the H$_2$ pressure
- Ratio of the initial desorption rates is 150
- Rate for control sample increases with dilution by graphite
- Initial desorption rate for aerogel sample may still be influenced by hydrogen pressure
Cycling Behavior: LiBH₄@C-Aerogel

Capacity from dehydrogenation (400 °C, 2 hr) after hydrogenation (100 bar H₂, 400°C, 2 hr)

- Decreased pore size improves cycling
- Pore size of 40 nm shows bulk behavior

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<th>Sample (pore size)</th>
<th>Activated carbon (~2 nm)</th>
<th>Aerogel (13 nm)</th>
<th>Aerogel (26 nm)</th>
<th>LLNL aerogel (40 nm)</th>
<th>Control (nonporous)</th>
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Incorporation of Mg into Carbon Aerogel

- Nickel “wetting layer” enables incorporation of Mg from melt
- Hydrogenation/dehydrogenation measurements in progress
- Significant step toward incorporating LiBH₄/MgH₂ in scaffold

Oxidation in TGA indicates Ni + Mg sample contains 1.5 wt% Ni and 16 wt% Mg

26 nm average pore size (1.3 cm³/g) carbon aerogel

Intensity (arbitrary units)

Two Theta (degrees)

graphite

Mg

small MgO

Ni

Ni

Ni + Mg (900 °C, 60 hr)

Ni(NO₃)₂ (4%H₂, 500 °C, 6 hr)

No Ni, Mg (900 °C, 60 hr)
New Destabilized Systems

- Screened new LiBH₄/MgX systems, X = Cl and Cu – Destabilization reactions not observed in these systems

Nanoparticles / MgH₂-Si

- Reversibility (hydrogenation of Mg₂Si) not achieved – tried catalysts, nanoparticles by direct synthesis and mechanical dispersion, and mechanically-induced hydrogenation
- Made “No-Go” decision, Sept. 2006

Nanoporous Scaffolds

- Evaluated large pore volume carbon aerogel – reduced capacity penalty for LiBH₄ to 40% (goal is 25%)
- Measured equilibrium pressure of LiBH₄ in aerogel – ~10x increase at 300°C
- Compared rates of desorption – aerogel potentially ~150x faster at 300°C
- Incorporated Mg into carbon aerogel – Ni used as wetting layer
Future Work
– FY2007/08 –

New Destabilized Systems

• Explore additional LiBH₄ + MgX reactions; determine influence of X on kinetics

Nanoporous Scaffolds

• Incorporate LiBH₄/MgH₂ destabilized system into carbon aerogel
  - Measure intrinsic dehydrogenation rates of LiBH₄@C aerogel, i.e., at PH₂ → 0
  - Test hydrogenation/dehydrogenation behavior of Mg@C aerogel; Check U. Utrecht claims
  - Add LiBH₄ to Mg@C
  - Incorporate catalysts
  - Optimize aerogel materials (with T. Baumann, LLNL), processing, and catalysts (with Utah, Hawaii, and Intematix)
# Program Direction

## – By System –

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<tr>
<th>Destabilized System</th>
<th>Benchmark</th>
<th>2006 Status</th>
<th>2006/07 Progress</th>
<th>Future</th>
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<tr>
<td><strong>MgH$_2$/Si</strong>&lt;br&gt;5.0 wt.%,&lt;br&gt;0.083 kg/L&lt;br&gt;est. $T_{1\text{bar}}=30^\circ\text{C}$</td>
<td>Prototype system&lt;br&gt;&lt;2007 goal (including system penalty)</td>
<td>•Kinetics too slow&lt;br&gt;•$T$ (dehyd) &gt;200°C&lt;br&gt;•Hydrogenation not achieved</td>
<td>•Reversibility still not observed&lt;br&gt;•No-go decision Sept ’06</td>
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<td><strong>LiBH$_4$/MgH$_2$</strong>&lt;br&gt;11.4 wt.%, 0.095 kg/L&lt;br&gt;w/o aerogel,&lt;br&gt;est. $T_{1\text{bar}}=170^\circ\text{C}$</td>
<td>Could meet 2010 system cap. goal (assuming 25% aerogel and 25% system penalties)</td>
<td>Lowered LiBH$_4$ dehydrogenation temp by 70°C in C-scaffold</td>
<td>•Reduced capacity penalty to 40%&lt;br&gt;•Measured 10x equilibrium pressure&lt;br&gt;•Incorporated Mg into aerogel&lt;br&gt;•Measured &gt; 150x reaction rate</td>
<td>•Incorporate full destab. system in scaffold&lt;br&gt;•Optimize scaffold</td>
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<td><strong>LiBH$_4$/MgF$_2$</strong>&lt;br&gt;7.6 wt.%&lt;br&gt;est. $T_{1\text{bar}}=150^\circ\text{C}$</td>
<td>Could meet 2010 system cap. goal</td>
<td>Hydrogen uptake ~6.5% at 300-350°C&lt;br&gt;Dehydrogenation 5.3%&lt;br&gt;Not fully reversible</td>
<td>Candidate for incorporation into scaffold</td>
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<tr>
<td><strong>LiBH$_4$/MgS</strong>&lt;br&gt;8.0 wt.%&lt;br&gt;est. $T_{1\text{bar}}=170^\circ\text{C}$</td>
<td>Could meet 2010 system cap. goal</td>
<td>Hydrogen uptake ~6% at 300°C&lt;br&gt;Dehydrogenation 4.3%&lt;br&gt;Not fully reversible</td>
<td>Candidate for incorporation into scaffold</td>
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<tr>
<td><strong>Other LiBH$_4$/MgX</strong>&lt;br&gt;4-10 wt.%,&lt;br&gt;est. $T_{1\text{bar}}: -10$ to 430°C</td>
<td>Could meet 2007 goal (including moderate system penalty)</td>
<td>Sorption meas.: X=CO$_3$&lt;br&gt;No destabilization</td>
<td>Sorption meas.: X=Cl, Cu&lt;br&gt;No destabilization</td>
<td>•Test new destab. agents, X=O, OH, Ni&lt;br&gt;•Use nano-engineering to improve kinetics</td>
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