Thermodynamically Tuned Nanophase Materials for Reversible Hydrogen Storage

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Overview

Timeline
• Project start date: March 2005
• Project end date: Feb 2010
• Percent complete: 60%

Budget
• Total Project Funding:
  *Phase I - 3 years: $1.65M*
    - DOE Share: $1.20M
    - Contractor Share: $0.45M
  *Phase II - 2 years: $1.1M*
    - DOE Share: $0.8M
    - Contractor Share: $0.3M

• Funding for FY08:
  $350K as of 4/1/07 (DOE),
  $150K (cost share)

Technical Barriers
• A. System weight and volume
• C. Efficiency
• E. Charging and discharge rates

Partners
• MHCoE collaborations:
  - U. Pitt, Georgia Tech: modeling of new systems and kinetic barriers
  - Stanford: thin film systems
  - Caltech, JPL, Hawaii, NIST: scaffolds
  - Intematix: catalysis

• DOE collaborations:
  - Drexel, LLNL, PNNL: carbon scaffolds

• International collaboration
  - Norway IFE: synchrotron XRD
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

2007/2008
• To identify and test new high capacity Li- and Mg-based destabilized hydrides
  ➢ Screen candidate LiBH$_4$ + MgX destabilized systems and evaluate energetics and kinetics
  ➢ Down-select systems for additional work
• Evaluate sorption kinetics and thermodynamics of LiBH$_4$ and Mg in carbon aerogel scaffolds
  ➢ Investigate effects of pore size and pore size distribution on reaction rates of LiBH$_4$
  ➢ Incorporate Mg into the aerogel and measure its kinetics
# Milestones

<table>
<thead>
<tr>
<th>Month/Year</th>
<th>Milestone or Go/No-Go Decision</th>
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<tbody>
<tr>
<td>June-07</td>
<td><strong>Milestone: Incorporate Mg into carbon aerogel.</strong> Facilitated Mg incorporation with Ni or Cu as a wetting layer. Continue to improve process to reduce aerogel destruction and increase Mg loading.</td>
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<td>Sept-07</td>
<td><strong>Milestone: Complete screening of LiBH₄+MgX system and down select for further studies.</strong> Tested X=Si and Ni and found Ni system to be reversible with promising kinetics; work to continue on this system.</td>
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<tr>
<td>Sept-08</td>
<td><strong>Milestone: Incorporate the LiBH₄/MgH₂ destabilized system into nanoscale scaffold.</strong> Successfully incorporated LiBH₄ and MgH₂ separately. Working to encapsulate the combined system. Measure hydrogen sorption thermodynamics and kinetics; incorporate catalysts into the system and investigate their effect on reaction rate.</td>
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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**

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 software
  ➢ H-capacities ranging from 5.4-9.6 wt.%, T₁ bar from -10°C to 430 °C
  ➢ X = F, S, Se, CO₃, Cl, and Cu tested previously

• In FY07/08, two new systems tested, X = Si and Ni:
  4LiBH₄ + Mg₂Si ↔ 4LiH + 2MgB₂ + Si + 6H₂ (7.3 wt.%, T₁ bar = 230 °C)
  4LiH + 2MgB₂ + Si absorbs 5.5 wt % H₂ at 150 bar, 350°C
  Hydrogenation forms LiBH₄ and Mg₂Si
  However upon dehydrogenation Mg₂Si does not react

  4LiBH₄ + Mg₂NiH₄ ↔ 4LiH + 2MgB₂ + Ni + 6H₂ (8.3 wt.%)
  System cycles forming ternary boride(s) -- see following slides

Results for LiBH₄/Mg₂Ni may indicate new class of systems
LiBH$_4$/Mg$_2$NiH$_4$ Dehydrogenation

- Sample prepared by ball milling
- Dehydrogenation done in 4 bar H$_2$
- Hydrogenations between desorption cycles done at 100 bar, 350 °C, 2 hr

See 2 steps at low T
- both from Mg$_2$NiH$_4$
  or
- Mg$_2$NiH$_4$ + MgH$_2$??

System cycles at ~ 6.5 wt % with some degradation
• LiBH₄/Mg₂NiH₄ appears to have formed upon hydrogenation
• Ternary borides formed upon dehydrogenation; appear to cycle
• Further characterization (FTIR, NMR) required
Possible Reactions

\[ 4\text{LiBH}_4 + \text{Mg}_2\text{NiH}_4 \leftrightarrow \frac{1}{5}\text{Li}_{2.4}\text{Ni}_5\text{B}_4 + 3.52\text{LiH} + 1.6\text{MgB}_2 + 0.4\text{Mg} + 8.3 \text{ wt\% } \text{H}_2 \]
\[ 4\text{LiBH}_4 + \text{Mg}_2\text{NiH}_4 \leftrightarrow \frac{1}{3}\text{MgNi}_3\text{B}_2 + 4\text{LiH} + 1.6\text{MgB}_2 + 8.0 \text{ wt\% } \text{H}_2 \]
\[ 4\text{LiBH}_4 + \text{Mg}_2\text{NiH}_4 \leftrightarrow \frac{1}{7.5}\text{Mg}_3\text{Ni}_{7.5}\text{B}_6 + 4\text{LiH} + 1.6\text{MgB}_2 + 8.0 \text{ wt\% } \text{H}_2 \]

- Three ternary borides have XRD patterns consistent with our observations
- Further work to characterize reaction with NMR is planned
- Suggests computational and experimental efforts to search for other Li(Mg)-transition metal borides
Motivation:

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

Initial work demonstrated feasibility using LiBH₄ incorporated into carbon aerogels (in collaboration with T. Baumann, LLNL)

Current Effort:

- optimize pore size and pore size distribution
- incorporate Mg into aerogels
- incorporate full LiBH₄/MgH₂ destabilized system into aerogel
Dehydrogenation of LiBH₄@Aerogel

LiBH₄ → LiH + B + 1.5H₂

1. Heat to 300 °C in 100 bar H₂
2. Quickly (~1 min) vent/pump H₂
3. Dehydrogenate with P < 0.05 bar

In 13 nm aerogel
12.5 wt% LiBH₄/hr

With graphite
0.2 wt%LiBH₄/hr

Desorbed H₂ (wt % LiBH₄)

Time (hr)

Rate for LiBH₄@aerogel ~60X rate for LiBH₄/graphite control sample
Smaller Pore Size Improves Kinetics

- Rate for 13 nm > 25 nm, indicates influence of pore size
- Relatively slow rate for 4 nm indicates requirement for access

TGA: $\text{LiBH}_4 \rightarrow \text{LiH} + \text{B} + 1.5\text{H}_2 (13.6 \text{ wt }\%)$

Desorbed $\text{H}_2$ (wt % $\text{LiBH}_4$) vs. Time (hr)

Pore size distributions

- 13 nm
- 25 nm
- 4 nm (LLNL)

Pore Volume (cm$^3$/g-nm) vs. Pore Size (nm)
2007 Status: Mg@Carbon Aerogel

- Nickel “wetting layer” enables incorporation of Mg from melt
- However, 900 °C is too high to preserve aerogel structure
- Lower temperatures needed
Lower Temperature Process Improves Mg Encapsulation

- Lower temperature (700 °C vs. 900 °C) reduces aerogel break down
- Cube samples contain bulk Mg impurity

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

Aerogel with bulk Mg impurity

Ni + Mg (700 °C, 24 hr)

Ni(NO₃)₂ (4%H₂, 500 °C, 6 hr)

TEM (C. C. Ahn, Caltech)

No change in aerogel
Dehydrogenation of MgH$_2$@Aerogel

~10 wt% Mg (700 °C, 24 hr) with Ni@13 nm aerogel

- MgH$_2$ in aerogel can be fully dehydrogenated ✓
- $P_{eq}(250$ °C) equal to bulk value, no change in thermodynamics
Encapsulation Improves MgH₂ Desorption Kinetics

Isothermal desorption at 250 °C (~10 wt% Mg@13 nm aerogel)

- Mg with Ni (700°C)
- Mg with Cu (700°C)
- No wetting layer (~3.3 wt% Mg)

- Ni & Cu wetting layers catalyze dehydrogenation
- Rate without wetting layer still higher than (uncatalyzed) milled MgH₂
1. Gravimetric and Volumetric Penalties
   • Current aerogels:
     • ~ 1 cm$^3$/g for 5 to 10 nm pore sizes
     • up to > 4 cm$^3$/g for pore sizes > 20 nm
   • If kinetic improvements are sufficient, then will need:
     • ~ 5 to 10 nm pore sizes with > 3 cm$^3$/g pore volume

   This is difficult but not impossible (requires thinner scaffold walls which will exacerbate mechanical stability issues)

2. Other issues
   • Chemical stability, i.e., CH$_4$ formation from carbon scaffolds
   • Mechanical stability over multiple cycles? (Note: volume changes during cycling are contained within aerogel particles)

Aerogels are a useful research tool for studying nanoscale effects. Practical use will require advances in the aerogels themselves
Future Work  
– FY2007/08 –

**New Destabilized Systems**

- Further characterize the LiBH$_4$ /Mg$_2$Ni reaction
- Explore oxide-based destabilized reactions  
  Ex:  $6\text{LiBH}_4 + \text{B}_2\text{O}_3 \rightleftharpoons 3\text{Li}_2\text{O} + 8\text{B} + 12\text{H}_2$ (12.0%)

**Nanoporous Scaffolds**

- Continue to work towards incorporating full LiBH$_4$/MgH$_2$ destabilized system into carbon aerogel  
  - Complete work on Mg incorporation (*evaluate U Hawaii samples*)  
  - Add LiBH$_4$ to selected Mg@aerogel samples (*test full system*)  
  - Continue to understand effects of pore size and pore size distribution  
  - Optimize aerogel materials for pore size and volume
New Destabilized Systems

• Screened new LiBH$_4$/MgX systems, X = Si and Ni
  • Observed new Ni based destabilized system with reversible capacity of ~ 6.5%
  • Observed the formation of ternary borides, pointing to potential new direction of discovery

Nanoporous Scaffolds

• Quantified rates for LiBH$_4$ dehydrogenation in aerogel:
  – at 300 °C, rate in aerogel is 60X rate for control sample
• Incorporated Mg into aerogel at reduced temperature to minimize degradation of aerogel (in progress)
• Measured dehydrogenation rates for Mg@aerogel
  – with Ni wetting layer/catalyst, the rate at 250°C comparable to best catalyzed bulk samples
• Began to understand effects of pore size and pore size distribution
  – smaller pores lower reaction temperatures; hydrogen access is important
### Program Direction
– By System –

<table>
<thead>
<tr>
<th>Destabilized System</th>
<th>Benchmark</th>
<th>2007 Status</th>
<th>2007/08 Progress</th>
<th>Future</th>
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<tbody>
<tr>
<td>LiBH₄ / MgH₂ @C aerogel</td>
<td>Could meet 2010 system weight and volume capacity goals (assuming 25% aerogel and 25% system penalties)</td>
<td>Lowered LiBH₄ dehydrogenation temp by 70°C in C-scaffold</td>
<td>•Reduced capacity penalty to 40%  •Measured 10x equilibrium pressure  •Incorporated Mg into aerogel  •Measured &gt; 150x reaction rate</td>
<td>•Incorporate full destab. system in scaffold  •Optimize scaffold</td>
</tr>
<tr>
<td>LiBH₄ / Mg₂NiH₄</td>
<td>Could meet 2010 system capacity goal (but only small system penalty)</td>
<td>Reversible capacity of ~6.5% at 350°C  Slight degradation observed</td>
<td></td>
<td>Candidate for incorporation into scaffold</td>
</tr>
<tr>
<td>LiBH₄ / MgF₂</td>
<td>Could meet 2010 system capacity goal (but only small system penalty)</td>
<td>Hydrogen uptake ~6.5% at 300-350°C  Dehydrogenation 5.3%  Not fully reversible</td>
<td></td>
<td>Candidate for incorporation into scaffold</td>
</tr>
<tr>
<td>LiBH₄ / MgS</td>
<td>Could meet 2010 system capacity goal (but only small system penalty)</td>
<td>Hydrogen uptake ~6% at 300°C  Dehydrogenation 4.3%  Not fully reversible</td>
<td></td>
<td>Candidate for incorporation into scaffold</td>
</tr>
<tr>
<td>Other LiBH₄ / MgX</td>
<td>Could meet 2007 goal (including moderate system penalty)</td>
<td>Sorption meas.: X=CO₃  No destabilization</td>
<td>Sorption meas.: X=Cl, Cu  No destabilization</td>
<td>•Test new destab. agents, X=O, OH, Ni  •Use nano-engineering to improve kinetics</td>
</tr>
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