Catalyzed Nano-Framework Stabilized High Density Reversible Hydrogen Storage Systems

X. Tang, D. Mosher, S. Opalka, T. Vanderspurt, B. Laube, R. Brown
United Technologies Research Center

E. Rönnebro*, T. Boyle, L. Ottley, M. Ong
Sandia National Laboratories
*(Currently at PNNL)

F.-J. Wu
J. Strickler
Albemarle Corporation

DOE Hydrogen Program
Annual Merit Review
Arlington, VA
May 19, 2009

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Project ID: ST_10_Tang
Overview

Timeline
- Start: 7/1/07
- Finish: 7/1/10
- 65% Complete

Budget
- $1.26M Total Program
  - DOE: $1.01M
    - SNL: $360k
    - Albemarle: $90k
    - Cost share: 20% (31% UTRC $)
  - FY07: $80k
  - FY08: $470k
  - FY09: $460k (planned)

Barriers Addressed
- A. System Weight and Volume
- E. Charging/Discharging Rates
- P. Lack of Understanding of Hydrogen Physisorption and Chemisorption
  www.eere.energy.gov/hydrogenandfuelcells/mypp

Partner Participation
- United Technologies Research Center (Project Lead)
- Sandia National Laboratories
- Albemarle Corporation
- Aspen Aerogels
Challenges:
- A wide range of high-capacity on-board rechargeable material candidates have exhibited non-ideal behavior related to:
  - Reversibility
  - High desorption temperatures
  - Instability at ambient temperature
- While different material compositions are continuing to be developed in the world-wide research community, the scope of novel, high-potential storage materials has its limits.

Objectives:
The use of nano-frameworks offers a distinct material design approach to improve sorption reaction behavior in a number of ways. The objectives of the current effort are to:
- Examine a variety of framework chemistries and hydride / framework combinations to make a relatively broad assessment of the method’s potential.
- These chemistries include doped, functionalized, and catalyzed frameworks.
Objectives (cont.):

- Tune hydride / framework interactions to:
  - Decrease desorption temperature for highly stable compounds.
  - Stabilize high capacity compounds, resulting in ligand elimination.
  - Influence desorption product formation to improve reversibility.

- Develop and apply atomic modeling techniques in evaluating and designing the local surface interactions.

- Activate $H_2$ dissociation on highly dispersed catalytic sites.

- Maintain nano-scale phase domains during cycling.

- As part of the MHCoE, focus on improving the performance of material candidates within the center, which have been borohydrides to date.
Plan / Approach

Combine *computational* and *experimental* methods to design & synthesize hydride / nano-framework composites.

<table>
<thead>
<tr>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hydride Candidates</strong></td>
</tr>
<tr>
<td>▪ Examine composites with Ca(BH$_4$)$_2$, a reversible borohydride with 9.6 wt% theoretical capacity, which is overly stable.</td>
</tr>
<tr>
<td>▪ Examine NaTi(BH$_4$)$_4$ as a high-capacity candidate which is unstable and requires ligands to stabilize.</td>
</tr>
<tr>
<td><strong>Atomic / Therm. Modeling</strong></td>
</tr>
<tr>
<td>▪ Evaluate hydride-framework interactions: associative stabilization, decomposition/side-products, dehydrogenation, to guide experiments.</td>
</tr>
<tr>
<td>▪ Explore heterogeneous catalysis of hydride reversibility by modeling H$_2$ dissociation, H migration, and rehydrogenation.</td>
</tr>
<tr>
<td><strong>Nano-Framework Development</strong></td>
</tr>
<tr>
<td>▪ Evaluate a range of framework chemistries, with a focus on oxides and (functionalized) carbons, for their influence on the hydride candidates.</td>
</tr>
<tr>
<td>▪ Catalyze the nano-frameworks to promote H$_2$ dissociation.</td>
</tr>
<tr>
<td><strong>Hydride Incorporation</strong></td>
</tr>
<tr>
<td>▪ Employ both melt and solution based incorporation methods.</td>
</tr>
<tr>
<td>▪ Focus on solution-based incorporation methods for unstable hydrides.</td>
</tr>
<tr>
<td><strong>Characterization</strong></td>
</tr>
<tr>
<td>▪ Screen hydride / framework combination candidates for chemical compatibility, to ensure framework integrity and cyclability.</td>
</tr>
<tr>
<td>▪ Examine hydride-incorporated frameworks.</td>
</tr>
</tbody>
</table>
### Milestones

<table>
<thead>
<tr>
<th>Date</th>
<th>Milestone or Go / No Go Decision</th>
</tr>
</thead>
<tbody>
<tr>
<td>2008 Q1</td>
<td>Select advanced nano-framework structure</td>
</tr>
<tr>
<td>2008 Q1</td>
<td>Demonstrate synthesis of desired nano-framework structure</td>
</tr>
<tr>
<td>2008 Q1</td>
<td>Synthesize top Sandia candidate hydride material</td>
</tr>
<tr>
<td>2008 Q2</td>
<td>Synthesize top UTRC / Albemarle candidate hydride material</td>
</tr>
<tr>
<td>2008 Q4</td>
<td>Evaluate relative performance of framework / catalysts</td>
</tr>
<tr>
<td>2008 Q4</td>
<td>Synthesize optimal catalyzed nano-framework structure</td>
</tr>
<tr>
<td>2009 Q1</td>
<td>Demonstrate loading of UTRC / Albemarle hydride into framework</td>
</tr>
<tr>
<td>2009 Q2</td>
<td>Demonstrate loading of Sandia hydride into framework</td>
</tr>
<tr>
<td>2009 Q3</td>
<td>Go / No Go on whether to proceed with original plan or redirect based on:</td>
</tr>
<tr>
<td></td>
<td>&gt; 50% hydride deposition into the catalyzed framework materials</td>
</tr>
<tr>
<td></td>
<td>Reasonable absorption/desorption behavior for at least one cycle</td>
</tr>
<tr>
<td></td>
<td>Performance relative to the state-of-the-art material shows promise</td>
</tr>
</tbody>
</table>

To date greater emphasis has been placed on evaluating uncatalyzed systems.
Concept
Hydride-filled nano-framework

Materials
Ca\textsubscript{5}(BH\textsubscript{4})\textsubscript{10} cluster
Ca\textsubscript{5}(BH\textsubscript{4})\textsubscript{10} cluster

Role
Conduct atomic modeling to investigate and prescreen:

- Hydride thermodynamics
- Interfacial physi-/chemisorption reactions influence on hydride stability and dehydrogenation
- Nano-framework stability and modification:
  a) doping to tune reactivity
  b) loading with H\textsubscript{2} activation catalysts for reversibility
  c) surface functionalization

Approach

Density Functional Theory Ground State Minimization

Direct Method Lattice Dynamics Thermodynamic Property Prediction

Exploratory mechanistic simulations to guide material selection & design.
Experimental

Solid State Processing
- Rapid, low cost screening for undesired reaction products between hydrides and framework and impact on reversibility

Nano-Framework
- Synthesize and characterize uncatalyzed and catalyzed nano-frameworks

Solution Based Incorporation
- Solvated hydride
- Solvents selected for ease of removal

High-Pressure station
- Solid state reactions
- Wide range of P and T (20,000 psi, 600°C)
- Autoclave with six samples capability

NaTi(BH₄)₄*DME Synthesis
- Synthesize NaTi(BH₄)₄*DME by solution based processing
- Incorporation in aerogel

[Diagram showing synthesis and characterization processes]
Technical Achievement

Summary

Last Year:
- Down selected ZrO$_2$ as most stable oxide nano-framework material using LiBH$_4$ as baseline hydride.

This Year:
- **Atomic Modeling:**
  - Evaluated interaction of Ca(BH$_4$)$_2$ with ZrO$_2$ framework and its impact on Ca(BH$_4$)$_2$ dehydrogenation.
  - Investigated the effect of Pt catalyzed ZrO$_2$ on hydrogen dissociation and Ca(BH$_4$)$_2$ rehydrogenation.
- **Framework and Hydride (Experimental):**
  - Conducted evaluation of the reactivity of Ca(BH$_4$)$_2$ with Y$_2$O$_3$ stabilized ZrO$_2$ (YSZ) and functionalized carbon aerogels.
  - Identified the impact of uncatalyzed framework materials on Ca(BH$_4$)$_2$ rehydrogenation.
  - Incorporated Ca(BH$_4$)$_2$ and NaTi(BH$_4$)$_4$*DME (dimethoxy ether) in aerogels.
When interfaced with ZrO₂, Ca(BH₄)₂ was predicted to have:
* Increased dehydrogenation enthalpy, with an increase of < +14 kJ/m H₂.
* The same order of favorability for competing dehydrogenation reactions.
Spontaneous H$_2$ dissociation and H adsorption on ZrO$_2$ supported Pt$_{10}$ nano-raft

Exothermic H saturation of Pt$_{10}$ surface and migration to ZrO$_2$ support

Spontaneous initiation of CaB$_6$ rehydrogenation adjacent to H-saturated Pt$_{10}$

Modeling investigations demonstrated utility of H$_2$ activation catalysts to:
* Facilitate formation, adsorption, and transfer of atomic H,
* Enhance binding and rehydrogenation of dehydrogenated phases.
Ca(BH₄)₂ – Framework Interaction

XRD Analysis

Rehydrided

Rehydrided

Rehydrided

Dehydrided

(As desolvated)

Ca(BH₄)₂ + C(PI*)(SPEX milled) → * ZrO₂

Ca(BH₄)₂ + YSZ (SPEX milled) → * ZrO₂

Ca(BH₄)₂ (SPEX milled) → *

Ca(BH₄)₂ (SPEX milled) → *

Ca(BH₄)₂ → *

* PI: Polyimide derived C aerogel, Dehydriding: 350°C/1 bar, Rehydriding: 350°C/190 bar

• Ca(BH₄)₂ (low temperature phase) formed in recharged Ca(BH₄)₂ and Ca(BH₄)₂-C systems, but not in recharged Ca(BH₄)₂-YSZ.
• Small amount of products from Ca(BH₄)₂ reaction with C framework.
Enhanced desorption was observed in Ca(BH\(_4\))\(_2\) - C systems.

C aerogel from PF has faster Ca(BH\(_4\))\(_2\) desorption after rehydriding.
Ca(BH$_4$)$_2$ Incorporation (Solution Method)

Ca(BH$_4$)$_2$ Precursors Investigated: 
Ca(BH$_4$)$_2$*2THF, Ca(BH$_4$)$_2$(py)$_4$•py and Ca(BH$_4$)$_2$*2DME

Solvent: THF and Pyridine

Aerogels: Carbon (PI) (583 m$^2$/g, 25 nm pore size, 3.67 cc/g pore volume) 
Y-stabilized ZrO$_2$ (138 m$^2$/g, 12 nm pore size, 0.72 cc/g pore volume)

Incorporation methods for C aerogel:
- Dissolve Ca(BH$_4$)$_2$*2THF in THF
- Submerge for 48 h
- Remove aerogel from solvent
- Remove solvent from aerogel at 160ºC/vacuum for 24h

- Incorporation of Ca(BH$_4$)$_2$ in C aerogel lowered H$_2$ desorption temperature.
- Desorption capacity needs to be optimized.

Technical Achievement

Ca(BH$_4$)$_2$ incorporated in C(PI) (50 wt% loading)

H$_2$ Desorption

Temperature

Ca(BH$_4$)$_2$ + C (SPEX Milled)

Ca(BH$_4$)$_2$ (SPEX Milled)

Ca(BH$_4$)$_2$ incorporated in C(PI) (50 wt% loading)
Melt incorporation of Ca(BH$_4$)$_2$ into four different nano-frameworks at elevated $T$ and $P$:
- C-aerogel (from HRL)
- Polyimide-derived C-aerogel
- Phenolic-derived C-aerogel
- Y-stabilized ZrO$_2$

From a visual inspection, it appears that Ca(BH$_4$)$_2$ wets the surface but also may have been infused into the polyimide-derived C-aerogel.

Melt incorporation increases the proportion of hydrogen released at elevated temperatures.

H$_2$ Evolution from Ca(BH$_4$)$_2$

Simultaneous Thermo-gravimetric Modulated-Beam Mass Spectrometer (STMBMS)
- Red: Ca(BH$_4$)$_2$ melt - incorporated in C-aerogel (from HRL)
- Black dashes: Uncatalyzed Ca(BH$_4$)$_2$
- Dotted red: Catalyzed Ca(BH$_4$)$_2$ by milling
**Hydride Precursor:** NaTi(BH₄)₄•3DME and NaTi(BH₄)₄•DME

**Solvent:** DME (Dimethoxyethane)

**Aerogel:**
- SiO₂ (312m²/g, 39nm, 1.58cc/g)
- YSZ

**Incorporation by solvent route (incipient wetness):**
- 40 wt% NaTi(BH₄)₄•3DME in SiO₂
- 50 wt% NaTi(BH₄)₄•3DME in SiO₂
- 25.8 wt% NaTi(BH₄)₄•DME in SiO₂
- 33.5 wt% NaTi(BH₄)₄•DME in SiO₂

**Stability:**
- Baseline precursor material: < 2 days
- Incorporated materials > 10 days

* High loading of borohydrides in a SiO₂ aerogel was achieved.
* SiO₂ framework improved stability of unstable hydride, but still not sufficient.
Collaborations

- **HRL**: John Vajo  
  Discussions on related efforts & exchange of aerogels.

- **Aspen Aerogels**: Wendell Rhine, Sara Rosenberg  
  Synthesis and characterization of aerogels.

- **LLNL**: Ted Baumann  
  Discussions on processing of aerogels.

- **Ohio State University**: J. C. Zhao  
  Initiated synthesis of borohydrides.

- **Oak Ridge National Laboratory**: Gilbert Brown  
  Initiated synthesis of borohydrides.

- **U Hawaii**: Craig Jensen  
  Incorporation of Mg(BH₄)₂.

- **University of Missouri – St. Louis**: Eric Majzoub  
  Atomic modeling of mixed metal borohydrides.

- **Sandia National Laboratory, Livermore**: Tim Boyle, Vitalie Stavila, Joe Cordaro, Ewa Rönnebro (now with PNNL)  
  Synthesis of mixed metal borohydrides.
Future Work

Atomic Modeling

- Design doped-ZrO₂ to balance interfacial interactions of hydried and dehydried storage material candidates.
- Survey influence of candidate ligands on hydride / nano-framework interactions.

Framework and Hydride

- Evaluate the impact of catalyzed nano-frameworks.
- Examine stabilization effect of YSZ and C aerogels on the stability of NaTi(BH₄)₄•DME and removal of ligand.
- Consideration of alternate hydride candidates.
- Characterize hydride incorporated in nano-framework (uncatalyzed and catalyzed) with BET, SEM, etc.
- Optimize hydrogen storage performance.

Go / No-Go decision affecting project execution & emphasis in final year.
Summary

To advance the understanding of how nano-frameworks can enhance the performance of storage candidates, a range of material / framework combinations and effects has been investigated including:

- Down-selected functionalized C and ZrO₂ as most suitable framework materials for future catalyzation investigations.
- Simulated the atomic mechanism for heterogeneously catalyzed H₂ dissociation and H transfer to kinetically facilitate rehydrogenation of Ca(BH₄)₂ dehydrogenation products.
- Obtained a decrease in H₂ desorption temperature of the stable borohydride Ca(BH₄)₂ incorporated in C aerogels by solution based incorporation.
- Demonstrated high loading of NaTi(BH₄)₄*ligand in SiO₂ aerogel and improved hydride stability with the aerogel.
Additional Slides
Framework Characterization

In-house BET Analysis

- Determine pore size distribution and pore volume for nano-framework
- Provide guidance in optimizing calcination conditions
- Evaluate hydride incorporation

### Yttria Stabilized Zirconia

<table>
<thead>
<tr>
<th>Calcination Conditions</th>
<th>Surface Area [m²/g]</th>
<th>Average Pore Diameter [nm]</th>
<th>Pore Volume [cc/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>417</td>
<td>11.8</td>
<td>1.65</td>
</tr>
<tr>
<td>550°C / 1h</td>
<td>148</td>
<td>11.7</td>
<td>0.72</td>
</tr>
<tr>
<td>550°C / 1h **</td>
<td>199</td>
<td>13.8</td>
<td>0.69</td>
</tr>
<tr>
<td>400°C / 6h</td>
<td>221</td>
<td>15.2</td>
<td>0.92</td>
</tr>
</tbody>
</table>

** Pt loaded YSZ