An Integrated Approach of Hydrogen Storage in Complex Hydrides of Transitional Elements

Abhijit Bhattacharyya, Tansel Karabacak, Fatih Cansizoglu, Mike Wolverton, Ganesh Kannarpady, Anindya Ghosh, Dustin Emanis

University of Arkansas at Little Rock
May 18-22, 2009

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Overview

Timeline

• July 2006
• August 2009
• Percent complete 75%

Barriers

• Barriers addressed
  – Durability/Operability (3.3.4 D)
  – Charging/Discharging Rates (3.3.4 E)
  – Lack of understanding of Hydrogen Physisorption & chemisorption (3.3.4 P)

Budget

• Total project funding $
  – DOE share $ 544,160
  – Contractor share $ 234,991
• Funding received in FY08 $ 183,891

Partners

• University of Arkansas Nanotechnology Center, Little Rock
• National Institute for Isotopic & Molecular Technologies, Romania
• Los Alamos Neutron Science Center
### OBJECTIVES

<table>
<thead>
<tr>
<th>PARAMETER</th>
<th>2007</th>
<th>2010</th>
<th>2015</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight (%)</td>
<td>4.5</td>
<td>6</td>
<td>9</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Kinetics (Min.)</td>
<td>10</td>
<td>3</td>
<td>2.5</td>
</tr>
<tr>
<td>Temp. (°C)</td>
<td>-20/50</td>
<td>-30/50</td>
<td>-40/60</td>
</tr>
</tbody>
</table>

**PROJECT TARGETS:** 6 wt.% , 100 bar, 3 min , -30/50 deg C
OBJECTIVES

POLYMERS  METAL HYDRIDES  NANOSTRUCTURES

HYDRIDES & POLYMERS

BULK MATERIALS

BULK & NANOSTRUCTURED HYDRIDES

NANOSTRUCTURES
OBJECTIVES

BULK MATERIALS

- Investigate methods for synthesizing DFT predicted metal decorated polymers$^1$
  - Continue testing on titanium decorated polyaniline
  - Investigate feasibility of metal decoration in polyphenylacetylene.

- Work with a high capacity hydride complex based storage system to improve viability
  - Establish reliable, scalable synthesis method for Ca(BH$_4$)$_2$
  - Improve reversible decomposition facilitated by additives

- Investigate use of absorbing transition metal alloys as additives to hydride complex based storage reactions
  - Characterize sorption properties of neat LaNi$_5$ alloy
  - Investigate addition of activated LaNi$_5$ to other compound by mechanical mixing, chemical dispersion

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<table>
<thead>
<tr>
<th>Month/Year</th>
<th>Milestone or Go/No-Go Decision</th>
</tr>
</thead>
<tbody>
<tr>
<td>June 2008</td>
<td><strong>No-Go</strong>: False positive confirmed in our previous preliminary absorption results with Ti-polyaniline material. A faulty valve was the cause. The problem was corrected. Subsequent testing showed conclusively no H₂ absorption for this material.</td>
</tr>
<tr>
<td>July 08</td>
<td><strong>Go</strong>: Ca(BH₄)² selected for hydride complex work due to reports of direct formation and reversible decomposition of catalyzed material.¹,²</td>
</tr>
<tr>
<td>September 08</td>
<td><strong>Milestone</strong>: Work on synthesis of Ca(BH₄)² initiated due to repeated delays and difficulties with suppliers regarding this material.</td>
</tr>
<tr>
<td>Apr-08</td>
<td><strong>Milestone</strong>: Work with Ti-Polyphenylacetlene started as a concept proofing material for the DFT predicted hydrogen absorber Ti-polyacetlene.</td>
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</table>


**Metal Decorated Polymers**
1. Validate polymerization (IR or NMR)
2. Attempt binding with titanium through solid state reaction (grinding, milling, pressing, heating)
3. Test for hydrogen absorption (Sieverts)

**Ca(BH\(_4\))\(_2\)**
1. Analyze neat compound for comparison (XRD, DSC, IR, Sieverts)
2. Combine with additives (grinding, pressing, milling, or solvent dispersion)
3. Thermally decompose then attempt to reform Ca(BH\(_4\))\(_2\) (Sieverts)

**Absorbing alloys as additives**
1. Sorption characteristics of alloy must be well characterized (Sieverts)
2. Combination with commercial alanates and borohydrides (grinding, pressing, chemical dispersion)
3. Test for changes in decomposition, reformation of complex – alloy mixture
**TECHNICAL ACCOMPLISHMENTS**

**BULK MATERIALS**

**Ca(BH$_4$)$_2$ - Solid State Ion Exchange Synthesis**

\[
2NaBH_4 + CaBr_2 \rightarrow Ca(BH_4)_2 + 2NaBr
\]

- We successfully demonstrate that this reaction will proceed in solid state.
- Materials are ground together, and pressed into a pellet in a hydraulic press.
- The pellet is heated under vacuum or inert atmosphere at 220°C for 48 hours.
- Products need additional processing to isolate Ca(BH$_4$)$_2$.

[XRD of reaction products]
Ca(BH$_4$)$_2$ - Other Synthesis Methods Attempted

Borane Solution / Hydride Type Reactions

\[ \text{CaH}_2 + 2\text{Et}_3\text{N} \cdot \text{BH}_3 \xrightleftharpoons{\text{reflux}} \text{Ca}(\text{BH}_4)_2 + 2\text{Et}_3\text{N} \]

- Despite numerous reaction conditions variations attempted, yields were much too low in all cases to extract Ca(BH$_4$)$_2$
- Reaction proceeds, but stalls out leaving mostly un-reacted CaH$_2$ (XRD of typical products shown)

Solvent Ion Exchange

\[ 2\text{XBH}_4 + \text{CaY}_2 \xrightleftharpoons{\text{reflux}} \text{Ca}(\text{BH}_4)_2 + 2\text{XY} \quad \text{X} = \text{Li, Na} \quad \text{Y} = \text{Cl, Br} \]

- Solvents tried include: Et$_2$O, Pyridine, (1,4)Dioxane, THF
- Ca(BH4)2 has a high affinity for ethers in which it is soluble and reacts with some solvents (notably pyridine) under certain conditions
- Some of these reactions are convenient for obtaining Ca(BH4)2 in solution, but isolating pure solid is problematic in all cases
Titanium Decorated Polyaniline

- Theoretically predicted\(^1\) to absorb 4.1% H\(_2\) by weight at 30 bar at 25°C
- Synthesis attempted by grinding powdered polyaniline with titanium nanoparticles then pressing into a pellet, and regrinding
- IR spectra revealed removal of the N-H bond suggesting possible binding of Titanium
- *Zero absorption*\(^2\) was measured for this material up to 130 bar at 25°C both before and after high temperature hydrogen soak


\(^2\) Our preliminary results had indicated some absorption for this material, but this was discovered to be a data artifact caused by a faulty valve.
Polyacetylene is predicted to absorb a large amount of H₂ by weight at 30 bar at 25°C when titanium is adjoined to the double bond.

Because of the likely difficulty with synthesizing polyacetylene, we selected polyphenylacetylene as a substitute to test the titanium bond concept.

Polymerization of phenylacetylene by a rhodium catalyst was verified by IR and NMR by verification of the double bond.

Titanium bonding was attempted by grinding with titanium nanoparticles, pressing, and heating at 200°C for 48 hours, followed by grinding again.

Zero absorption was measured for this material up to 130 bar at 25°C both before and after high temperature hydrogen soak.


2 Our preliminary results had indicated some absorption for this material, but this was discovered to be a data artifact caused by a faulty valve.
**LaNi\textsubscript{5} Alloy - Initial Characterization**

<table>
<thead>
<tr>
<th>As Alloyed (commercial)</th>
<th>After Activation and First H\textsubscript{2} Absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>(right) The raw XRD data from our area detector. Theta increases to the left. Note the high crystallinity.</td>
<td>(right) Although the crystal structure type is not changed, the lattice dilations from absorption cause fractures and the material turns into finer particulates.</td>
</tr>
<tr>
<td>(left) High crystallinity is again evident from the large grains of alloy.</td>
<td>(left) The internal stresses of lattice dilation caused by the absorption of hydrogen have pulverized the alloy into a fine powder. No mechanical processing was performed.</td>
</tr>
</tbody>
</table>
LaNi$_5$ Alloy - Initial Characterization

$LaNi_5 + 3H_2 \rightarrow LaNi_5H_6$

The initial absorption rate after activating the alloy is extremely sluggish, but increases rapidly as the alloy is cycled.

**Initial H$_2$ absorption**

Initial absorption of LaNi$_5$ after chemical activation. The sample was held at a constant 500 psia at room temperature overnight.

**H$_2$ Absorption Time Vs cycle**

Absorption rates increase with initial cycling of LaNi$_5$. Conditions for absorption cycles were 145 psia of H$_2$ constant and 33°C. Dehydriding occurred at 80°C.
Calcium Borohydride Decomposition and Reformation Study

\[ \text{Ca}(BH_4)_2 \xleftarrow{\text{catalyst}} \xrightarrow{} \text{CaB}_6 + 2\text{CaH}_2 + 10\text{H}_2 \]

Maximum Reversible \( \text{H}_2 \) by weight: 9.6%

Minimum Theoretical Release Temperature\(^1\): 94ºC

Interest: Among the few borohydride reactions that has been proven to be reversible,\(^2,3\) this reaction has some of the most favorable thermodynamic characteristics.

Method: We wish to test additives which have yet to be applied to this material that have documented catalytic effects\(^4\). We also wish to elucidate the mechanism which allows the borohydride to reform from gaseous hydrogen. (Sieverts, XRD, DSC, IR)

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DFT Predicted Destabilized Borohydride Reaction

\[ 5\text{Ca}(BH_4)_2 + 2\text{LiBH}_4 \rightarrow \text{Li}_2\text{B}_{12}\text{H}_{12} + 5\text{CaH}_2 + 13\text{H}_2 \]

Maximum Reversible H\(_2\) by weight: 6.7%

Minimum Theoretical Release Temperature\(^1\): 83ºC

Interest: This reaction, predicted to occur recently by Ozolins et al. is (to our knowledge) yet untested. The reaction temperature is slightly below that of pure Ca(BH\(_4\))\(_2\)

Method: Initially the reaction will be treated as simply as possible: commercial reagents simply ground or milled together. Focus will be on validation of the reaction conditions and byproducts. (Sieverts, XRD, DSC, IR)

\(^1\) Ozolins, V.; Majzoub, E. H.; Wolverton, C. “First-Principles Prediction of Thermodynamically Reversible Hydrogen Storage Reactions in the Li-Mg-Ca-B-H System” JACS 131 2009. 230-237
FUTURE WORK

BULK MATERIALS

Absorbing Alloy Interactions with Reversible Hydride Complexes

Alloy:  $\text{LaNi}_5$

Reactions: I.  \[ \text{NaAlH}_4 \leftrightarrow \frac{1}{3} \text{Na}_3\text{AlH}_6 + \frac{2}{3} \text{Al} + \text{H}_2 \leftrightarrow \text{NaH} + \text{Al} + \frac{3}{2} \text{H}_2 \]

II. $\text{Ca(BH}_4\text{)}_2 \xleftarrow{\text{catalyst}} \text{CaB}_6 + 2\text{CaH}_2 + 10\text{H}_2$

Interest:  $\text{LaNi}_5$ is selected because of the wealth of information available, its quick kinetics, and room temperature absorption of hydrogen. We have characterized it well, and can differentiate between effects caused by the alloy and competing effects.

Method:  We will initiate study on I. which is a reversible, well known system. This will make it easier to see what effects the alloy has using different incorporation techniques. We will then move to higher capacity reversible systems with more unknowns such as II. (Sieverts, XRD, DSC, IR)
• More rigorous examination of the polymers we have prepared has shown that they do not absorb hydrogen. The reason for this is unclear, as direct evidence of titanium bonding was never demonstrated.

• We intended to begin decomposition / reformation studies with Ca(BH4)2 over the last 6 months. Delays with chemical suppliers made this infeasible. We initiated some work on chemical synthesis of this compound instead until the delays subside.

• Curious about potential interactions between alloy systems and complexes, we initiated study of the well known hydrogen absorption alloy LaNi₅. We have characterized the neat alloy sufficiently to proceed to combination.
• Investigation of **maximum hydrogen storage capacity, thermal stability, and adsorption/desorption kinetics** of thin films and nanostructures of magnesium (model system), magnesium alanate, and magnesium borohydride for hydrogen storage.

• Utilization of **glancing angle deposition (GLAD)** technique for the growth of **nanorod arrays of magnesium (Mg) as a model system, magnesium alanate (Mg(AlH$_4$)$_2$), and magnesium borohydride (Mg(BH$_4$)$_2$).**

• Utilization of a new **quartz crystal microbalance (QCM)** gas chamber system for the dynamic investigation of **maximum hydrogen storage capacity and adsorption/desorption kinetics** of the nanostructures produced with nanograms measurement sensitivity.

• Investigation of **effect of catalyst** on hydrogen adsorption/desorption properties of magnesium, magnesium alanate, and magnesium borohydride. Possible **catalyst materials that we plan to incorporate are Pt, Ti, Ni, Pd, and V.**
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<tr>
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<tbody>
<tr>
<td>July-08</td>
<td><strong>Milestone</strong>: Fabrication of nanostructures in the shapes of vertical “nanoblades” using GLAD approach. Material: Mg as model system.</td>
</tr>
<tr>
<td>Sep-08</td>
<td><strong>Milestone</strong>: Finished the set-up and up-gradation of a QCM gas chamber with an RGA attachment for the dynamic measurement of hydrogen adsorption/desorption kinetics, thermal stability, and oxidation properties of nanostructured coatings.</td>
</tr>
<tr>
<td>Sep-08</td>
<td><strong>Milestone</strong>: Finished further investigation of thermal stability and oxidation properties of thin films and nanostructures produced by GLAD. Material: Mg as model system.</td>
</tr>
<tr>
<td>Dec-08</td>
<td><strong>Milestone</strong>: Using new QCM set-up, started to obtain hydrogen storage capacity and adsorption/desorption properties of thin films and nanostructures produced by GLAD. Material: Mg as model system.</td>
</tr>
<tr>
<td>May-09</td>
<td><strong>Milestone</strong>: Will start the investigation of hydrogen adsorption/desorption properties of magnesium borohydride and alanate thin films and nanostructures produced by GLAD. Materials: Mg(AlH$_4$)$_2$ and Mg(BH$_4$)$_2$</td>
</tr>
</tbody>
</table>
NANOSTRUCTURES

Glancing Angle Deposition (GLAD)

- Large surface-to-volume ratio
- Control of crystal orientation
- Lower oxidation rate
- Porosity allows for volumetric changes

- Quartz Crystal Microbalance (QCM) method for the investigation of hydrogen storage, thermal stability, and oxidation properties of nanostructures and thin films produced
### Nanostructured Materials to be Studied

<table>
<thead>
<tr>
<th>Nanostructured Material</th>
<th>Hydrogen Storage (wt %)</th>
<th>Decomposition T (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mg(AlH₄)₂</strong></td>
<td>9.3</td>
<td>200</td>
</tr>
<tr>
<td>Magnesium Alanate [1]</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Mg(BH₄)₂</strong></td>
<td>14.9</td>
<td>320</td>
</tr>
<tr>
<td>Magnesium Borohydride [2]</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Mg</strong></td>
<td>7.6</td>
<td>300</td>
</tr>
<tr>
<td>Magnesium [3]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Catalyst Incorporation**
- Pt
- Ti
- Ni
- Pd
- V

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TECHNICAL ACCOMPLISHMENTS

NANOSTRUCTURES

UP-GRADIATION of a QUARTZ CRYSTAL MICRO-BALANCE (QCM) SYSTEM with RESIDUAL GAS ANALYZER (RGA) DEVELOPED IN-HOUSE

SPECIFICATIONS

• Operating Pressure Range: $10^{-4}$ – 50 bars
• Gasses available: Hydrogen, argon, oxygen
• Stable Temperature Range: room temperature – 500 °C
• Nanostructure/thin film coating surface area: ~ 1 cm$^2$
• Mass Sensitivity: down to 0.001 ng/cm$^2$
• Capable of measuring two sample at a time
• In-situ Residual Gas Analysis (RGA) analysis capability

COMMERCIAL DEVICE: Not Available
OUR COST: ~ $10,000

DOE funded
TECHNICAL ACCOMPLISHMENTS

NANOSTRUCTURES

Mg Nanoblades by GLAD

Deposition conditions:
GLAD Thermal Evaporation
Tilt angle: 80°
Pressure: 7.5 *10^{-6} mbar
Rotation: 1 RPM
Substrate: QCM crystal

Length of nanoblade-trees: ~ 7 μm
Thickness of nanoblade-leaves: ~30nm

Cross-Section SEM Images
Top-View SEM Images
Development of Experimental Procedures for QCM Hydrogen Storage Measurements

- **Procedure 1:** A single QCM crystal is used for reference and storage measurements. Experimental procedure is performed first on an empty QCM crystal for baseline measurements followed by thin film or nanostructure coating on the same crystal, and then by measuring the QCM data of the coated crystal.  
  Pros & Cons: 1. Temperature and pressure effects on measurements are minimized, 2. Longer sample preparation

- **Procedure 2:** Dual QCM crystals are used one for reference and the other coated one for storage measurements.  
  Pros & Cons: 1. Quick sample preparation, 2. Bare and coated crystals might have different response to the changes in temperature and pressure, that can lead to limitations in dynamic adsorption/desorption analysis

- **Procedure 3:** Dual QCM crystals, which are both coated with thin film or nanostructures, are used for simultaneous measurement of H2 storage values of two samples. Comparison of crystals’ initial and final frequencies at the same temperature (e.g. after heating followed by cooling) are used in order to determine storage levels in nanostructures and thin films. A multi cycle storage process can also be performed in order to calculate total H2 storage that occurs between two temperature points. For the first cycle, storage is measured by heating from room temperature to a set temperature and cooling back to RT. Then in the following cycle, crystal is heated to a higher temperature then in the first cycle and cooled back to RT again in order to calculate the H2 storage gain occurred in the second cycle.  
  Pros & Cons: 1. Quick sample preparation and ability to measure two samples at a time, 2. Only storage values can be measured at this time; kinetic adsorption/measurements needs some theoretical temperature effect corrections, which are currently under investigation
TECHNICAL ACCOMPLISHMENTS

NANOSTRUCTURES

QCM Hydrogen Storage Measurements

Mg Thin Film at 30 bar H₂

Procedure 1

- Argon exhaust + H₂ introduction
- H₂ absorption
- H₂ desorption

Percentage change in the mass (% wt)

Time (sec)

Procedure 2

- Heating from 30°C to 300°C + Cooling back to 30°C

Percentage change in the mass (% wt)

Time (sec)

Low Temperature Mg Thin film Storage
@ 30°C -100 °C → 0.35 wt %

Mg Thin Film Storage
@ 30°C-300 °C → 5.01 wt %
TECHNICAL ACCOMPLISHMENTS

NANOSTRUCTURES

QCM Hydrogen Storage Measurements

Mg Nanoblades at 30 bar H₂

Procedure 2

Hydrogen introduction at 30 bar

~ 4.8 %

Vacuum

Heating

Time (sec)

Percentage change in the mass (% wt)

Temperature (°C)

Procedure 1

Argon exhaust + H₂ introduction

H₂ exhaust

H₂ desorption

Percentage Change in the Mass (wt %)

Argon

Heating + H₂ absorption

Low Temperature Mg Nanoblade Storage

@ 30°C-100 °C → 4.8 wt %

@ 30°C -150 °C → 6.71 wt %
QCM Hydrogen Storage Measurements

Mg Nanoblades at 30 bar H₂, Procedure 3

加热从60°C→100°C→60°C→300°C→60°C

1st cycle

2nd cycle

低温度Mg纳米刀片存储

@60°C -100°C → 4.60 wt %

总Mg纳米刀片存储 @60°C -300°C

→ 7.35 wt % (= 4.6 wt% 1st cycle + 2.75 wt% 2nd cycle)
Hydrogen Storage in Mg Thin Film and Nanoblades at different Temperature Intervals

Mg Nanoblades at 30 bar $H_2$

Mg Thin Film at 30 bar $H_2$
A cross-section image of Mg nanorods sputter deposited on an alumina substrate.

**TECHNICAL ACCOMPLISHMENTS**

**NANOSTRUCTURES**

**Thermal Stability and Oxidation of Mg Nanorods under Atmospheric Conditions: Isothermal TGA results**

Reduced oxidation and enhanced evaporation in Mg nanorods at temperatures $T<150 \, ^\circ\text{C}$; enhanced oxidation at $T>150 \, ^\circ\text{C}$ needs to be accounted for during low pressure hydrogen adsorption/desorption studies.
Glancing angle deposition (GLAD) technique was utilized for the growth of nanostructured arrays in the shapes of vertical nanoblades and nanorods.

**Mg nanostructures as model material system:** Hydrogen storage capacity, adsorption/desorption kinetics, thermal stability, and oxidation properties have been studied.

Significant increase in low temperature H2 storage values (e.g. ~4.8 wt% @ 100 °C) has been observed for Mg nanostructures compared to Mg thin films (e.g. ~0.8 wt% @ 100 °C).

A new quartz crystal microbalance (QCM) system was developed and upgraded for the kinetic investigation of hydrogen storage capacity and adsorption/desorption kinetics properties of nanostructured and thin film coatings.

Has started investigating magnesium borohydride and alanate for GLAD nanofabrication and hydrogen storage studies.
NANOSTRUCTURES

Study of hydrogen storage capacity & kinetics

- Thin films and nanostructures of magnesium alanate and borohydride,
- Effect of catalysis,
- Effect of nanostructure size, shape & separation,
- Nanoblades and nanorod arrays of Mg as a model system.