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

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University of Arkansas at Little Rock
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STP 32
Overview

Timeline
- July 2006
- August 2009
- Percent complete 45%

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 FY06 $ 544,160

Partners
- University of Arkansas Nanotechnology Center, Little Rock
- National Institute for Isotopic & Molecular Technologies, Romania
- Los Alamos Neutron Diffraction Center
<table>
<thead>
<tr>
<th>PARAMETER</th>
<th>YEAR</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2007</td>
<td>2010</td>
<td>2015</td>
<td></td>
</tr>
<tr>
<td>Weight (%)</td>
<td>4.5</td>
<td>6</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Kinetics (Min.)</td>
<td>10</td>
<td>3</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>Temp. (°C)</td>
<td>-20/50</td>
<td>-30/50</td>
<td>-40/60</td>
<td></td>
</tr>
</tbody>
</table>

**PROJECT TARGETS:** 6 wt.% , 100 bar, 3 min , -30/50 deg C
• **Hydrogen Storage Characterization**
  – Design and fabrication of a Sievert Type high pressure high temperature gas titration / chemical reactor setup.

• **Develop materials for hydrogen storage based on DOE’s system storage target for 2010**
  ➢ Increase of reversible hydrogen storage capacity in complex metal hydrides by developing new systems including hydride phases
  ➢ Development of catalytic compounds to enhance the formation and decomposition of complex metal hydrides.
  ➢ Investigation of hydrogen storage capacity in metal (Ti and Li) decorated polymers.
  ➢ Investigation of enhancement of hydrogen storage capacity in metal hydrides dispersed in polymer matrix.
<table>
<thead>
<tr>
<th>Month/Year</th>
<th>Milestone or Go/No-Go Decision</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jan 08</td>
<td><strong>Milestone</strong>: Design, fabrication and testing of the Sievert Type high pressure and high temperature gas titration setup is completed and tested successfully.</td>
</tr>
<tr>
<td>Mar 08</td>
<td><strong>Milestone</strong>: An inert atmosphere synthesis and compound treatment (moisture less than 5 ppm and oxygen less than 10 ppm) facility has been installed.</td>
</tr>
<tr>
<td>Apr 08</td>
<td><strong>Milestone</strong>: Characterization of Hydrides initiated</td>
</tr>
<tr>
<td>Apr-08</td>
<td><strong>Milestone</strong>: Synthesis and characterization of Ti-decorated polymers started; 1.3 wt % of hydrogen stored in Ti-decorated polyaniline at 80 bar and 25 deg C.</td>
</tr>
</tbody>
</table>
• **H₂ absorption/desorption measurement setup**
  1. Scalable sensitivity
  2. Wide range of operating temperature and pressure conditions
  3. Increase the degree of automation

• **Metal hydrides**
  4. Decrease reaction temperature
  5. Increase reaction rates
  6. Decrease reaction pressure

• **Polymer based materials**
  7. Synthesis of metal (Ti, Li, Sc)-decorated stable polyaniline/polyacetylene
  8. Use of metal nanoparticles in synthesis
  9. Reducing cluster formation of nanoparticles
  10. Increase surface area
  11. Dispersing polymers in metal hydrides
BULK MATERIALS

TECHNICAL ACCOMPLISHMENTS

SIEVERT APPARATUS DEVELOPED IN-HOUSE

COST OF COMMERCIAL DEVICE: ~ $130,000
OUR DEVELOPMENTAL COST: ~ $20,000

Specifications

1. Pressure: Vacuum to 200 bar
2. Temperature: Ambient to 500 deg C
3. Sample volume: 10 mL
4. Computer controlled & automated

DOE funded
The measured hydrogen yield from a sample of batch certified NaAlH4 during thermal decomposition

0.02855 moles H$_2$ theoretical yield

0.02830 moles H$_2$ measured
Theory (1) predicts replacement of N-H bond by Ti in polyaniline. The IR spectra confirms that N-H bond in Ti-decorated polyaniline has disappeared. Experiments are needed to confirm that N-H has been replaced by Ti.

Incremental Adsorption curve of Ti decorated polyaniline following a two-step adsorption of 0.7 % at 35 bar, and an additional 0.3% at 50 bar, both at 25 deg C
### Ti-decorated polyaniline

<table>
<thead>
<tr>
<th>Pressure (bar)</th>
<th>Weight (%)</th>
<th>Kinetics (min)</th>
<th>Temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>0.7</td>
<td>40</td>
<td>25</td>
</tr>
<tr>
<td>50</td>
<td>0.7+0.3</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>80</td>
<td>0.7+0.3+0.3=1.6</td>
<td>5</td>
<td>25</td>
</tr>
</tbody>
</table>

Possible Ti clustering (1)

Hydride-dispersed polyaniline

Peak shift confirms molecular level interaction between polymer and NaAlH$_4$

Variation of optical absorption peaks as function of concentration of NaAlH$_4$ in polyaniline

<table>
<thead>
<tr>
<th></th>
<th>PANI</th>
<th>PANI/NaAlH$_4$ 2:1</th>
<th>PANI/NaAlH$_4$ 1:1</th>
<th>PANI/NaOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_1$ (nm)</td>
<td>330</td>
<td>308</td>
<td>312</td>
<td>329</td>
</tr>
<tr>
<td>$\lambda_2$ (nm)</td>
<td>618</td>
<td>571</td>
<td>597</td>
<td>636</td>
</tr>
</tbody>
</table>
BULK MATERIALS

FUTURE WORK

Synthesis, H₂ storage & Kinetics

- Ti-decorated polyaniline
  4.1 wt.%, 30 bar, 25 deg C (1)
- Ti-decorated cis-polyacetylene
  7.6 wt.%, 30 bar, 25 deg C (1)
- Ti-decorated trans-polyacetylene
  12 wt.% (2)
- Sc-decorated trans-polyacetylene
  14 wt.% (2)

(1) Lee et al., Physical Review Letters, 97 (2006) 056104

All are theoretical predictions
Promising
BULK MATERIALS

Synthesis, dissociation studies

- Magnesium Borohydride \((\text{Mg(BH}_4\text{)}_2)\) and Magnesium Alanate \((\text{Mg(AlH}_4\text{)}_2)\),

- \(\text{Mg(BH}_4\text{)}_{2-n} \text{ (AlH}_4\text{)}_n\)

- Sodium Aluminium Hydride \((\text{Na(AlH}_4\text{)})\) and Ti-Na(AlH4)) as model systems
### SUMMARY

**BULK MATERIALS**

- A state-of-the-art hydrogen storage material synthesis and characterization facility has been established at University of Arkansas at Little Rock.

- A highly automated Sievert type gas titration setup to measure the hydrogen sorption has been developed and fabricated in-house.

- Titanium nanoparticle decorated polyaniline shows promising preliminary results (1.3 wt.%, 80 bar, 25 deg C) for validating the theoretically predicted hydrogen storage capacity.
OBJECTIVES

NANOSTRUCTURES

- Investigation of maximum hydrogen storage capacity and adsorption/desorption kinetics of thin films and nanostructures of magnesium alanate and magnesium borohydride for hydrogen storage.

- Utilization of glancing angle deposition (GLAD, also known as oblique angle deposition) technique for the growth of nanorod arrays of magnesium (Mg) as a model system, magnesium alanate (Mg(AlH₄)₂), and magnesium borohydride (Mg(BH₄)₂).

- Construction and utilization of 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 Mg, magnesium alanate, and magnesium borohydride. Possible catalyst materials that we plan to incorporate are Pt, Ti, Ni, Pd, and V.
### MILESTONES

#### NANOSTRUCTURES

<table>
<thead>
<tr>
<th>Month/Year</th>
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<tbody>
<tr>
<td>Jun-07</td>
<td><strong>Milestone</strong>: Fabrication of nanostructures in the shapes of vertical nanorods using GLAD approach. Material: Mg as model system.</td>
</tr>
<tr>
<td>Dec-07</td>
<td><strong>Milestone</strong>: Started design and set-up of a QCM gas chamber for the dynamic measurement of hydrogen adsorption/desorption kinetics, thermal stability, and oxidation properties of nanostructured coatings.</td>
</tr>
<tr>
<td>May-08</td>
<td><strong>Milestone</strong>: Finished investigation of thermal stability and oxidation properties of thin films and nanostructures produced by GLAD. Material: Mg as model system.</td>
</tr>
<tr>
<td>May-08</td>
<td><strong>Milestone</strong>: Started investigation of hydrogen adsorption/desorption properties of thin films and nanostructures produced by GLAD. Material: Mg as model system</td>
</tr>
<tr>
<td>Sep-08</td>
<td><strong>Milestone</strong>: Will start the fabrication and investigation of hydrogen adsorption/desorption properties of magnesium borohydride and alanate thin films and nanostructures produced by GLAD. Materials: Mg(AlH₄)₂ and Mg(BH₄)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
## APPROACH

### NANOSTRUCTURES

### 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>Mg(AlH$_4$)$_2$ Magnesium Alanate [1]</td>
<td>9.3</td>
<td>200</td>
</tr>
<tr>
<td>Mg(BH$_4$)$_2$ Magnesium Borohydride [2]</td>
<td>14.9</td>
<td>320</td>
</tr>
<tr>
<td>Mg</td>
<td>7.6</td>
<td>300</td>
</tr>
</tbody>
</table>

Catalyst Incorporation

- Pt
- Ti
- Ni
- Pd
- V

TECHNICAL ACCOMPLISHMENTS

NANOSTRUCTURES

GLAD SPUTTER/EVAPORATION DEPOSITION SYSTEM

Sputter source (target) & plasma glow
Substrate holder with rotation and tilt control

DOE funded (in part)

COST OF COMMERCIAL DEVICE: ~ $160,000
OUR DEVELOPMENTAL COST: ~ $80,000
NANOSTRUCTURES

TECHNICAL ACCOMPLISHMENTS

QUARTZ CRYSTAL MICRO-BALANCE (QCM) SYSTEM DEVELOPED IN-HOUSE

DOE funded

SPECIFICATIONS

- Operating Pressure Range: $10^{-3}$ – 30 bars
- Gasses available: Hydrogen, argon, oxygen
- Stable Temperature Range: room temperature – 500 deg C
- Nanostructure/thin film coating surface area: ~ 1 cm$^2$
- Mass Sensitivity: down to 0.001 ng/cm$^2$

COMMERCIAL DEVICE:
Not Available
OUR COST: ~ $6,000
**TECHNICAL ACCOMPLISHMENTS**

**NANOSTRUCTURES**

**Thin film**
- Evaporated thin film 3000 nm (top view SEM image)
- Evaporated thin film 3000 nm (x-view SEM image)

**Nanoblades**
- Evaporated nanorod 300 nm (top view SEM image)
- Evaporated nanorod 300 nm (top view SEM image)

**Deposition conditions:**
- Tilt angle:
  - Thin films: 0°
  - Nanorods: 83.7°
- Pressure: 6.9 *10^{-6} mbar
- Rotation: 1 RPM
- Substrate: Si (100)

**Thermally Evaporated Mg Nanoblades and Thin Films**
Deposition conditions:

- Tilt angle:
  - Thin films: 0°
  - Nanorods: 83.7°
- Power: 80 watts
- Pressure: 2.7 * 10^-3 mbar
- Rotation: 1 RPM
- Substrate: Si (100)

Sputter Deposited Mg Nanorods and Thin Films
Microstructure and Crystal Orientation of Sputtered Deposited Mg Thin Films: XRD and SEM results

- Growth in (002) direction
- Surface porosity
Growth in (002), (101), (102), and (103) directions, unlike 002 Mg thin films
• Highly columnar microstructure
Reduced oxidation and enhanced evaporation in Mg nanorods; needs to be accounted for during hydrogen adsorption studies.
Enhanced evaporation in Mg nanorods at low temperatures; needs to be accounted for during hydrogen adsorption experiments.
Identified magnesium borohydride and alanate as materials of choice for nanofabrication and hydrogen storage studies.

Mg nanostructures as model material system: Hydrogen storage capacity, adsorption/desorption kinetics, thermal stability, crystal orientation, and oxidation properties.

Glancing angle deposition (GLAD) technique is utilized for the growth of nanostructured arrays in the shapes of vertical nanorods and nanoblades.

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

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,
- Nanorod arrays of Mg as a model system.
SUMMARY
(OVERALL PROJECT)

POLYMERS
- Polyaniline
- Polyacetylene

METAL HYDRIDES
- Magnesium Borohydrides & Alanates

NANOSTRUCTURES
- Magnesium Borohydrides & Alanates

FOCUS

HYDRIDES+POLYMERS

BULK & NANOSTRUCTURED HYDRIDES