Novel Metal Perhydrides for Hydrogen Storage

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Project ID: stp_21_hwang

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Overview

Timeline
• Start: April 1, 2004
• Finish: Phase 1, May 31, 2009; total project, May 31, 2011
• % Complete: Phase 1, 98%

Budget
• Total Project funding
  – DOE – Phase 1: $694,816; total project: $1,719,806
  – Cost Share – Phase 1: $195,677; total: $451,428
• Funding received in FY08: $364,816
• Funding received in FY09: none

Barrier
- A. Cost
- B. Weight and Volume
- C. Efficiency

Partners
- Interactions/ collaborations
  – Clemson University
  – University of Minnesota
  – NanoMas, Inc.
  – Boda Corporation
  – Oak Ridge National Lab
- Project lead
  – Michigan Technological University
Objectives

- The overall focus of this project
  - Develop a new kind of materials capable of binding H₂ molecules into clusters
  - Enhance H₂ adsorption/desorption by means of the “hydrogen cluster” formation/decomposition so that the capacity of materials for H₂ storage and the kinetics for H₂ release have potential to meet the DOE 2010 and 2015 target

- The objective over the past year
  - Study the H₂ adsorption behavior of material systems having charged species in the material structure
  - Design & develop material systems capable of auto-charging under H₂ pressure
  - Study the H₂ adsorption behavior of materials systems capable of auto-charging under H₂ pressure
  - Design & develop devices for directly measuring H₂ sorption in electric field
  - Study the H₂ adsorption behavior of materials systems charged by applied electric potentials

- Relevance to Overall DOE Objectives
  - By the concept of charge-induced H₂ cluster formation, the H₂ storage capacity of the materials has potential to exceed 0.06kg H₂/kg system, the DOE 2010 target
Result Highlights

• Hypothesis of charge-induced hydrogen sorption enhancement has been experimentally demonstrated.

• Electrically charged system yields 200 to 550% hydrogen sorption enhancement for the spill over approach at room temperature under 1-5 bar pressure.
Milestones

04-30-2008:
• Materials and devices developed for direct H₂ sorption measurement in electric field
• The effect of charge-induced hydrogen sorption enhancement has been identified and verified using direct sorption measurement approach with five material systems:
  – Dehydrated vermiculite having interlayer cations
  – Activated carbon with charge generating materials
  – NiO with charge generating materials
  – Activated carbon charged by applied electric potentials
  – Pt/carbon-activated carbon (Spill Over approach) charged by applied electric potentials

04-30-2009
• Design and develop materials with high intrinsic H₂ sorption capacity
• Design and develop storage systems hosting high charge population
• Combine and optimize the high intrinsic sorption system & high charge population system to meet the DOE target

Go/No Go Milestone
Whether the new system has the potential to achieve the technical target of exceeding 6wt% hydrogen storage capacity will be the criteria for the decision
Approach

• The study is based on the concept that protons, metal and non-metal ions are capable of forming H₂ clusters and thus to enhance the H₂ storage capacity

  – Proton-Hydrogen clusters: \( H^+ + nH_2 \rightarrow [H(H_2)_n]^+ \) (e.g. \( H_3^+, H_5^+, \) etc.)
  – Cation-hydrogen clusters: \( M^{Z+} + nH_2 \rightarrow [M(H_2)_n]^{Z+} \) [e.g. \( \text{Mg}^{2+}(H_2)_4, \text{Ni}^{2+}(H_2)_8, \) etc.]
  – Anion-hydrogen clusters: \( X^{Z-} + nH_2 \rightarrow [X(H_2)_n]^{Z-} \) [e.g. \( \text{F}^-(H_2)_4, \text{O}^{2-}(H_2)_8, \) etc.]

• However, where to look for these charged species?
  – Gaseous phase? –Too dilute to be practical
  – Simple ionic compounds? –cations and anions are too close to accommodate H₂ clusters

• In the 08’ research, the following approaches were employed for studying the charge effect
  – Utilize minerals that could expose metal ions to H₂ by proper treatment
  – Utilize materials that could generate charge under H₂ pressure
  – Apply electric potential to H₂ adsorbents
Approach

- Utilize minerals that could expose metal ions to $\text{H}_2$ by proper treatment
  - Vermiculite is treated to expose interlayer $\text{Mg}^{2+}$
- Utilize pressure-induced charge generating materials (CGM)
  - Carbon and transition metal oxides are the model materials
- Apply electric potential to $\text{H}_2$ adsorbents
  - Carbon and pt/carbon are the model materials
Technical Progress/Accomplishments Summary

• Advance the research focus from computer modeling to direct H₂ sorption

• H₂ sorption on five material systems has been investigated:
  – Dehydrated vermiculite
  – Activated carbon + charge-generating materials (CGM)
  – NiO +CGM
  – Activated carbon + 2000V potential
  – Pt/carbon + activated carbon + 2000 V potential

• All of the five systems demonstrated enhanced H₂ sorption in the presence of charges

<table>
<thead>
<tr>
<th>Dehydration temperature (°C)</th>
<th>150</th>
<th>500</th>
<th>700</th>
<th>900</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sorption enhancement (%)*</td>
<td>71</td>
<td>9</td>
<td>19</td>
<td>38</td>
</tr>
</tbody>
</table>

* Relative to sorption on samples dehydrated at 150 °C, 80 bar

<table>
<thead>
<tr>
<th>Hydrogen pressure (bar)</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sorption enhancement (%)*</td>
<td>12</td>
<td>19</td>
<td>24</td>
<td>27</td>
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* Comparison between sorption on samples with & w/o CGM

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* Comparison between sorption on samples with & w/o CGM

<table>
<thead>
<tr>
<th>Hydrogen pressure (bar)</th>
<th>1</th>
<th>5</th>
<th>20</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sorption enhancement (%)*</td>
<td>120</td>
<td>55</td>
<td>20</td>
<td>10</td>
</tr>
</tbody>
</table>

* Comparison between sorption on samples with & w/o e-potential

<table>
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<th>5</th>
<th>20</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sorption enhancement (%)*</td>
<td>550</td>
<td>200</td>
<td>72</td>
<td>34</td>
</tr>
</tbody>
</table>

* Comparison between sorption on samples with & w/o CGM
Technical Progress/ Accomplishment: Treated Vermiculite

- **Concept**
  - Removal of H₂O around Mg²⁺ exposes the cations to H₂ atmosphere
  - Clustering of H₂ around Mg²⁺ could lead to enhanced H₂ sorption

- **Sorption behavior**
  - Increase of sorption was observed at 77K from samples with increased treatment temperature
  - No noticeable differences of the surface properties between samples treated at different temperatures
  - **The enhanced sorption is due to the increased Mg²⁺ exposure**

<table>
<thead>
<tr>
<th>Treatment Temperature (°C)</th>
<th>BET surface (m²/g)</th>
<th>µ-pore area (m²/g)</th>
<th>Average pore diameter (Å)</th>
<th>Weight Loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>13.23</td>
<td>3.68</td>
<td>120.5</td>
<td>–</td>
</tr>
<tr>
<td>500</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>4.47</td>
</tr>
<tr>
<td>700</td>
<td>11.33</td>
<td>3.76</td>
<td>98.90</td>
<td>7.05</td>
</tr>
<tr>
<td>900</td>
<td>13.26</td>
<td>1.90</td>
<td>113.9</td>
<td>–</td>
</tr>
</tbody>
</table>
Technical Progress/ accomplishments:

Material system containing charge generating materials (CGM)

• Concept
  - CGM + pressure → CGM⁻
  - CGM⁻ + Carbon → CGM + Carbon⁻
  - Carbon⁻ + nH₂ → [CGM⁻·n(H₂)]⁻

• Material
  - Commercial activated carbon
    - Surface properties
      BET surface, 1836 m²/g;
      Micropore, 577 m²/g
  - Sorption behavior
    - Sorption difference observed from samples with and w/o CGM at H₂ pressure over 55 bar
    - No sorption difference observed from blank sample holder with and w/o CGM
    - The excess hydrogen is directly adsorbed on carbon

• The result supports the charge-induced sorption enhancement concept
Technical Progress/ accomplishments:

H$_2$ sorption on NiO enhanced by CGM

- **Concept**
  - Transition metal compounds as the charge-holding media
  - H$_2$ could cluster around the charges

- **Material**
  - Lab synthesized NiO

<table>
<thead>
<tr>
<th>BET surface area</th>
<th>Micropore area</th>
<th>Average pore size</th>
</tr>
</thead>
<tbody>
<tr>
<td>382 m$^2$/g</td>
<td>1.71 m$^2$/g</td>
<td>70.8 Å</td>
</tr>
</tbody>
</table>

- **Sorption behavior**
  - Compared to the CGM-Carbon system
    - Enhanced sorption occurred at much lower pressure
    - The enhancement amplitude is much larger

- e + Ni=O $\rightarrow$ Ni($d^f$)=O $\rightarrow$ Ni-O$^-$
- Ni-O$^-$ + n(H-H) $\rightarrow$ [Ni-O…(H-H)$_n$]"
Technical Progress/accomplishments:

Material system charged by applied electric potentials

- **Concept**
  - Anode\(^+\) + Carbon → Anode + Carbon\(^+\)
  - Carbon\(^+\) + nH\(_2\) → [Carbon·· n(H\(_2\))]\(^+\)

- **Material**
  - Commercial activated carbon
  - Surface properties
    - BET surface, 1836 m\(^2\)/g; Micropore, 577 m\(^2\)/g

- **Sorption behavior**
  - Applying an electric potential of 2000V induced an enhancement of hydrogen adsorption on activated carbon
  - The enhancement appears more noticeable when the hydrogen pressure is below 60 bar
  - Hydrogen pressure >60 bar, Adsorption enhancement <10%
  - Hydrogen pressure <60 bar; Up to over 100% adsorption enhancement observed

- **Conclusion**
  - E-potential induced sorption enhancement is supported
  - Polarization or ionization of H\(_2\) could be a responsible mechanism
CGM enhanced H₂ Sorption at 77°K

Carbon: BET 3211 m²/g, micropore 3051 m²/g
Technical Progress/accomplishments:
Enhanced sorption by charging Pt/carbon

- Concept
  - Spill-over of H⁺

- Material
  - Commercial activated carbon mixed with Pt/carbon
  - BET surface: 1613 m²/g
  - Micropore: 481 m²/g

- Sorption behavior
  - Sorption difference between samples with & w/o electric potential observed
  - Sorption enhancement is much more higher than samples without Pt

- Conclusion
  - The concept of proton spill-over on polarized surface is supported
Collaborations

• Partners
  – Clemson University (Academic): collaboration on development of charge-holding materials for the system
  – Boda Corporation (industry): collaboration on development of instrument components for study of H₂ in electric field
  – NanoMas, Inc. (industry): collaboration on development of carbon-based materials for charge-induced H₂ sorption
  – Oak Ridge National Lab (Federal): collaboration to study the charge-induced H₂ clustering using neutron diffraction

• Technology transfer
  – Collaboration with ORNL to utilize neutron facility to get insight into the mechanisms of charge-enhanced H₂ sorption
  – Collaboration with Boda corporation to utilize its expertise on instrument prototype fabrication
  – Collaboration with Clemson University and NanoMas, Inc. to utilize their expertises on electric materials and nanomaterials synthesis and processing
Future work: FY-09-10

1. Materials Improvement

2. System improvement

3. Combination of the improved system and materials and optimization
Future Work: FY09-FY10

1. Materials improvement

Develop the charge-induced H₂ storage system with materials having high intrinsic sorption capacity (sorption without charge effects) for H₂ storage

- 08’ research has just used conventional, commercially available materials
- In the 09’-10’ research, the composition, the surface and the pore properties of the sorbent materials will be tuned so that materials with high intrinsic sorption capacity for H₂ storage will be produced
- **High intrinsic sorption materials in-consideration**

<table>
<thead>
<tr>
<th>Materials</th>
<th>Intrinsic H₂ sorption capacity (wt.%)</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>High-surface area activated carbon</td>
<td>8.0 (77k, 40bar); 3.0 (298K, 160 bar)</td>
<td><em>Carbon</em> 45 (2007) 293–303</td>
</tr>
<tr>
<td>Pt/Carbon bridged with IR-MOF8</td>
<td>4.0 (298k, 100bar)</td>
<td><em>J. Am. Chem. Soc.</em> 2006, 128, 8136-8137</td>
</tr>
</tbody>
</table>
Future Work: FY09-FY10

2. System improvement
   Develop a system that will amplify the effect of charge-induced H$_2$ adsorption enhancement

2A. Introduce counter charges
   - Limited charge population in current system
     Due to mono-signed charge that can be held
   - New system will be developed capable of including counter charges
   - The plus and minus signed charges will be mutually balanced
   - Charge population in the system will increase
   - Charge-induced H$_2$ sorption enhancement will be amplified
Future Work: FY09-FY10

2B. Introduce charge-holding domains into the system

- The 09’-10’ research will further introduce charge-holding domains into the system
- Each domain will hold a certain number of charges and the corresponding counter charges
- The domain sizes will be tuned and optimized
- The system is of long-range neutral
- Sufficient charges could be populated in the system
- Charge-induced H₂ sorption enhancement could be substantially increased
Future Work: **FY09-FY10**

2C. Spill over H's concurrently with H⁺'s

- The 08’ research introduced H⁺ spill-over mechanism (Slide 13)
- The charge dipoles in the dielectric material was not fully utilized
- The work in 09’-10’ research will introduce H⁻ spill-over mechanism into the system
- These two mechanisms may double the spill-over effect

3. **Finally, combine the improved materials and systems, and develop an optimized H₂ storage system**
Project Summary

• Relevance:
  By the concept of charge-induced hydrogen cluster formation, the hydrogen storage capacity of the materials has potential to exceed 0.06kg H₂/kg system, the DOE 2010 target

• Approach
  Create H₂ sorption system with charged species by depriving H₂Os around Mg²⁺ in vermiculite structure, by introducing charge generating materials in the sorption system, and by applying electric potentials to sorbents in the system

• Technical accomplishments and progress:
  - H₂ sorption on five material systems has been investigated
  - Substantial sorption enhancements induced by charges were observed

<table>
<thead>
<tr>
<th>Sorption systems</th>
<th>Charge-induced sorption enhancement (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interlayer cations in vermiculite</td>
<td>38</td>
</tr>
<tr>
<td>Activated carbon + CGM</td>
<td>27</td>
</tr>
<tr>
<td>NiO + CGM</td>
<td>87</td>
</tr>
<tr>
<td>Activated carbon + 2000V</td>
<td>27</td>
</tr>
<tr>
<td>Pt/Carbon-carbon + 2000V</td>
<td>550</td>
</tr>
</tbody>
</table>

• Proposed future research:
  1. Materials improvement: develop high intrinsic H₂ sorption materials
  2. System improvement: develop charge-carrying systems capable of hosting large population of charges
  3. Combine the improved materials and systems and develop an optimized H₂ storage system