Novel Metal Perhydrides for Hydrogen Storage

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Project ID: STP 26

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## Overview

### Timeline
- **Start:** April 1, 2004
- **Finish:** Phase 1, May 31, 2009; total project, May 31, 2011
- **% Complete:** Phase 1, 50%

### Budget
- **Total Project funding**
  - DOE – Phase 1: $694,816; total project: $1,719,806
  - Contractor – Phase 1: $195,677; total: $451,428
- **Funding received in FY07:** $250,000
- **Funding received in FY08:** $364,816

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

### Partners
- **Interactions/ collaborations**
  - Clemson University
  - University of Minnesota
  - NanoMas, Inc.
- **Project lead**
  - Michigan Technological University
Objectives

• **The overall focus of this project**
  – Develop a new kind of materials that are able to bind hydrogen molecules into clusters
  – Enhance hydrogen adsorption/desorption by means of hydrogen cluster formation/decomposition so that the capacity of materials for hydrogen storage and the kinetics for hydrogen release have potential to meet the DOE 2010 and 2015 target

• **The objective over the past year**
  – Study the potentials and roles of charged/polarized species on hydrogen cluster formation
  – Examine the interaction behavior of charged species with hydrogen

• **Relevance to Overall DOE Objectives**
  – By the concept of charge-induced hydrogen cluster formation, the hydrogen storage capacity of the materials has potential to exceeding 0.06kg H₂/kg system, the DOE 2010 target
Milestones

12-01-2007:  
- Material species with potential to form hydrogen clusters have been screened by computational approach  
- Mechanisms for charged species to cluster hydrogen was revealed as a charge-transfer process  
- Charge transfer between hydrogen and charged electrode was experimentally observed  
- A bench scale reactor for experimentally investigation of hydrogen storage capacity of the new material system was built

12-01-2008:  
- The enhancement effects of applied potential on hydrogen adsorption will be identified  
- Various electrode materials will be screened for optimized enhancement effect  
- Effective electrode structures will be determined for maximum adsorption  
- Suitable anode-cathode separation materials will be sought
Approach

- The study is focused on use of charged species to form H₂ clusters and thus to enhance the H₂ storage capacity

  - Proton-Hydrogen clusters:
    \[ H^+ + nH_2 \rightarrow [H(H_2)_n]^+ \]

  - Cation-hydrogen clusters:
    \[ M^{Z+} + nH_2 \rightarrow [M(H_2)_n]^{Z+} \]

  - Anion-hydrogen clusters:
    \[ X^{Z-} + nH_2 \rightarrow [X(H_2)_n]^{Z-} \]

  - Clustering H₂ around polar chemical bonds:
    \[ mH_2^+ \delta^+M-X^\delta^- + nH_2 \rightarrow \delta^+[(H_2)_mM-X(H_2)_n]^\delta^- \]

  - Clustering H₂ by charges on electrodes
    \[ \text{anode}^{q+} + mH_2 + nH_2 + \text{q-cathode} \rightarrow \text{anode-}(H_2)_n^{q+} - q^-(H_2)_n\text{-cathode} \]
Approach

• The study employed the following approaches
  – Computer modeling
    • Examine the potentials of cations, anions and polar chemical bonds for hydrogen cluster formation
    • Identify the cluster formation mechanism
    • Compare the cluster binding capabilities of different charged species
  – Experimental investigation
    • Create charges on electrodes
      \[
      \text{electrodes} + \text{applied voltage} \rightarrow \text{anode}^{q_+} - q^- \text{cathode}
      \]
    • Study interactions of hydrogen with charges on the electrodes by analyzing the changes of the anode potentials
    • If the charges on electrodes form bonds with \( H_2 \) molecules:
      \[
      \text{anode}^{q_+} + mH_2 + nH_2 + q^- \text{cathode} \rightarrow \text{anode}-(H_2)_n^{q_+} - q^- (H_2)_n^- \text{cathode}
      \]
      An anode potential change should be observed
Technical Progress/ Accomplishments Summary (I)

- Computer modeling
- The capability of cations for forming hydrogen clusters have been examined, including the ions of
  - alkaline metals
  - alkaline-earth metals
  - transition metals
- The capability of anions for forming hydrogen clusters have been examined, including O²⁻, Cl⁻, and C⁻
- The capability of polar bonds in material compounds for forming hydrogen clusters have been examined, including
  - metal-oxygen bonds in alkaline-earth metal oxides and in transition metal oxides,
  - carbon-oxygen bonds in CO and CO₂
  - H-Cl bond
- The capabilities of various charged species for forming hydrogen clusters were analyzed and compared based on
  - cluster formation energy
  - changes of bond length of H-H after and before cluster formation
  - bond length between hydrogen and the charged species
  - Charge transfer between hydrogen and the charged species
- The most promising charged species for forming hydrogen clusters have been selected, as summarized in the table below:

<table>
<thead>
<tr>
<th>Charged Species</th>
<th>Hydrogen-Storage Capacity (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cations</td>
<td></td>
</tr>
<tr>
<td>Be²⁺</td>
<td>63.7</td>
</tr>
<tr>
<td>Mg⁡⁺⁺</td>
<td>39.7</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>28.5</td>
</tr>
<tr>
<td>Anions</td>
<td></td>
</tr>
<tr>
<td>O²⁻</td>
<td>50</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>57.1</td>
</tr>
<tr>
<td>C’</td>
<td>31.1</td>
</tr>
<tr>
<td>Polar Bonds in Metal Oxides</td>
<td></td>
</tr>
<tr>
<td>Be-O</td>
<td>24.2</td>
</tr>
<tr>
<td>Cr-O</td>
<td>19</td>
</tr>
<tr>
<td>Fe-O</td>
<td>18.2</td>
</tr>
<tr>
<td>Co-O</td>
<td>17.6</td>
</tr>
<tr>
<td>Ni-O</td>
<td>17.6</td>
</tr>
</tbody>
</table>
Technical Progress/ Accomplishments Summary (II)

- An dedicated instrument, namely electrode reactor, for examining the charge transfer between hydrogen and charged species has been developed
- Using electrode reactor, experimental investigations on charging/discharging behavior, with reflects the charge transfer between hydrogen and charged species, have been carried out
- Charge transfers between hydrogen and charges on anode were observed
- Data analysis indicates the charge transfer came from charge-induced hydrogen adsorption and desorption
- Some experiments on hydrogen sorption in materials containing charged species have been done with a volumetric sorption instrument, PCTpro-2000 (HyEnergy, Inc)
- Combination of the electrode reactor with the PCTpro-2000, is close to completion, which will be dedicated to study the hydrogen storage capacity of materials, in which charges can be concurrently generated by an external electric field
**Technical Progress/ accomplishments:**

**Computer modeling: cation-hydrogen clusters**

<table>
<thead>
<tr>
<th>M(^{2+}) -8H(_2) cluster core</th>
<th>Be(^{2+})</th>
<th>Mg(^{2+})</th>
<th>Ca(^{2+})</th>
<th>Sr(^{2+})</th>
<th>Ba(^{2+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy gain from 8H(_2) + M(^{2+}) = M(^{2+})-8H(_2) (kcal/mole)</td>
<td>-154.99</td>
<td>-100.77</td>
<td>-63.35</td>
<td>-27.82</td>
<td>-20.82</td>
</tr>
<tr>
<td>Bond Length (Å)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M(^{2+})-H1</td>
<td>2.109</td>
<td>2.324</td>
<td>2.596</td>
<td>3.225</td>
<td>3.488</td>
</tr>
<tr>
<td>M(^{2+})-H2</td>
<td>2.109</td>
<td>2.324</td>
<td>2.596</td>
<td>3.225</td>
<td>3.488</td>
</tr>
<tr>
<td>H1-H2</td>
<td>0.755</td>
<td>0.755</td>
<td>0.753</td>
<td>0.747</td>
<td>0.743</td>
</tr>
<tr>
<td>Mulliken Charge</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M(^{2+})</td>
<td>-0.303</td>
<td>0.158</td>
<td>0.600</td>
<td>1.434</td>
<td>1.556</td>
</tr>
<tr>
<td>H1</td>
<td>0.144</td>
<td>0.115</td>
<td>0.088</td>
<td>0.035</td>
<td>0.028</td>
</tr>
<tr>
<td>H2</td>
<td>0.144</td>
<td>0.115</td>
<td>0.088</td>
<td>0.035</td>
<td>0.028</td>
</tr>
</tbody>
</table>

* Mulliken charge s: naked M\(^{2+}\), +2; H in H\(_2\), 0

- All cations show the capability to cluster hydrogen, but Be\(^{2+}\), Mg\(^{2+}\), and Ca\(^{2+}\) are most promising.
- Hydrogen-binding capacity: Be\(^{2+}\), 63.7%; Mg\(^{2+}\), 39.7%; Ca\(^{2+}\), 28.5%.
- The stability of the M\(^{2+}\)-H\(_2\) clusters corresponds to changes of mulliken charges on M\(^{2+}\) and H\(_2\) with and without the clusters.
- Electron transfer from H\(_2\) to M\(^{2+}\) is essential for formation of the clusters.
Anions also show capabilities to bind H\textsubscript{2} molecules into clusters

Hydrogen-binding capacity: O\textsuperscript{2-}, 50.0%; C\textsuperscript{-}, 57.1%; Cl\textsuperscript{-}, 31.1%

Electron transfer from O\textsuperscript{2-} to H\textsubscript{2} is essential for formation of the clusters

It is important for the oxygen anion to have the capability to bind H\textsubscript{2}, because metal oxides are the most common polar bond materials

It is also worthwhile to note the capability of C\textsuperscript{-} to form hydrogen clusters, since it can be made into a highly porous, lightweight electrodes

### Computer modeling: anion-hydrogen clusters

<table>
<thead>
<tr>
<th>X\textsuperscript{2-} -8H\textsubscript{2} cluster core</th>
<th>O\textsuperscript{2-}</th>
<th>Cl\textsuperscript{-}</th>
<th>C\textsuperscript{-}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy gain from 8H\textsubscript{2} + X\textsuperscript{2-} = X\textsuperscript{2-}-8H\textsubscript{2} (kcal/mole)</td>
<td>-118.9</td>
<td>-14.6</td>
<td>-</td>
</tr>
<tr>
<td>Bond Length (Å)</td>
<td>X\textsuperscript{2-} -H1</td>
<td>1.916</td>
<td>2.819</td>
</tr>
<tr>
<td></td>
<td>X\textsuperscript{2-} -H2</td>
<td>2.709</td>
<td>3.571</td>
</tr>
<tr>
<td></td>
<td>H1-H2</td>
<td>0.793</td>
<td>0.751</td>
</tr>
<tr>
<td>Mulliken Charge</td>
<td>X\textsuperscript{2-}</td>
<td>-0.776</td>
<td>-0.599</td>
</tr>
<tr>
<td></td>
<td>H1</td>
<td>0.259</td>
<td>0.040</td>
</tr>
<tr>
<td></td>
<td>H2</td>
<td>-0.412</td>
<td>-0.090</td>
</tr>
</tbody>
</table>

* Mulliken charge s: naked O\textsuperscript{2-}, -2; naked Cl\textsuperscript{-} and C\textsuperscript{-}, -1; H in H\textsubscript{2}, 0
Technical Progress/ accomplishments:

Computer modeling: hydrogen clusters around M-O bond in alkaline-earth metal oxides

<table>
<thead>
<tr>
<th>Energy gain from $4H_2 + BeO = BeO-4H_2$ (kcal/mole): -22.54</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond length between atoms in the cluster (Å)</td>
</tr>
<tr>
<td>Be-O</td>
</tr>
<tr>
<td>------</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mulliken Charge at atoms in the cluster</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
</tr>
<tr>
<td>------</td>
</tr>
<tr>
<td>0.171</td>
</tr>
</tbody>
</table>

* Be-O without $H_2$: Bond length 1.332Å; Mulliken charge Be, 0.386; O, -0.386

- Alkaline-earth metal oxides have polar M-O bonds as their structure units
- Among these metal oxides, BeO comes out as the most promising candidate
- Hydrogen binding capacity of Be-O: 24.2 $H_2$-wt.%
- Compare Be-O to Be$^{2+}$, it can be seen that the higher $H_2$-binding capacity of Be$^{2+}$ is related to its larger amount of charge transfer
Technical Progress/ accomplishments:

**Computer modeling:** hydrogen clusters around M-O bond in transition metal oxides

| Energy gain from $8\text{H}_2 + \text{CrO} = \text{CrO-8H}_2$ (kcal/mole): | -57.0 |
|---------------------------------------------------------------|
| Bond length between atoms in the cluster (Å)                  |
| Cr-O                                                         |
| O-H1 O-H2 H1-H2                                              |
| O-H3 O-H4 H3-H4 Cr-H9 Cr-H10 H9-H10 Cr-H11 Cr-H12            |
| O-H5 O-H6 H5-H6 Cr-H13 Cr-H14 H13-H14 Cr-H15 Cr-H16          |
| O-H7 O-H8 H7-H8                                              |
| 1.598 2.738 3.474 0.745 1.773 1.669 0.889 1.776 0.804       |
| Mulliken Charge at atoms in the cluster                       |
| Cr O H1, H3, H5, H7 H2, H4, H6, H8 H9, H13, H10, H14, H15, H16 |
| -0.118 -0.359 0.019 -0.027 0.451 0.069 0.070               |

* Cr-O without $\text{H}_2$: Bond length 1.553Å; Mulliken charge Cr, 0.338; O, -0.338

- Calculations on transition metal oxides indicates the Cr-O, Fe-O, Ni-O, and Co-O bonds can also bind $8\text{H}_2$ molecules
- **Hydrogen-binding capacity:** Cr-O, 19.0%; Fe-O, 18.2%; Ni-O, 17.6%; Co-O, 17.6%
- Cluster formation free binding energies (kcal/mole): Cr-O, -57.0; NiO-8H$_2$, -34.6; CoO-8H$_2$, -20.8; FeO-8H$_2$, -20.7
- Compare Cr-O to Be-O, it can be seen that Cr-O involves with larger amount of charge transfer and has more negative cluster formation energy
Technical Progress/accomplishments:

**Experimental:** hydrogen-material interaction in dc field

- With applied voltage, cations and anions can be created on the electrode surface, protons could also be generated.
- Using dc-filed reactor is a convenient approach to investigate reaction behavior of hydrogen with charged species.
- The instrument shown on the left has the function to examine charge transfer between hydrogen and electrodes. The charge transfer is anticipated to occur when hydrogen clusters form onto electrode surface.
- The anode potential detect circuit measures the real-time potentials on the anode.
- The leak-induced anode potential drop detect circuit measures the potential drop on the anode when charges flow from the anode onto the cathode.
- The voltage safe circuit makes the cathode potential safe to personnel and equipment.
- Electrodes are made from electric conductive materials.
- The HV switch is controlled by a computer program in order for data accuracy.
Technical Progress/ accomplishments:

**Experimental:** hydrogen-material interaction in dc field during charge circle

- Experiments revealed significant anode potential fluctuations when a constant voltage is applied to the hydrogen filled electrode reactor (upper left figure).
- The drops of the anode potential caused by current leak between electrodes (lower left figure) are much smaller than the amplitude of the anode potential fluctuations (upper left figure).
- The anode potential fluctuation is attributed to charge transfer between hydrogen and the anode.
- Charge-induced hydrogen adsorption/desorption on the anodes is possible:
  1) \( \text{H}_2 \text{ adsorbed to the charged anode} \)
     \[ \text{iAnode}^{q+} + n\text{H}_2 \rightarrow \text{Anode}^{q+} - n\text{H}_2 \]
  2) Electrons flow from the adsorbed \( \text{H}_2 \) to anode, anode potential drops
     \[ \text{Anode}^{q+} - n\text{H}_2 \rightarrow \text{Anode}^{(q-n)+} - n\text{H}_2^+ \]
  3) Electrons from the anode flow back to the adsorbed \( \text{H}_2 \), anode potential rises
     \[ \text{Anode}^{(q-n)+} - n\text{H}_2^+ \rightarrow \text{Anode}^{q+} - n\text{H}_2 \]
  4) Some of the \( \text{H}_2 \) on the anode may be ionized, anode potential drops
     \[ \text{Anode}^{q+} - n\text{H}_2 \rightarrow \text{Anode}^{(q-m)+} - \left( n - \frac{1}{2} m \right) \text{H}_2^+ + m\text{H}^+ \]
  5) If the protons reach the cathode and are neutralized, the corresponding signals should be observed as leak-induced anode potential drops (but the detected signals are insignificant, compare the lower figure to the upper figure).

Electrode area: 1.27 cm²; anode-cathode distance: 0.008 cm

Experiments:

5/7/2008 Michigan Technological University
Technical Progress/ accomplishments:

**Experimental:** hydrogen-material interaction in dc field during charge circle

- With larger electrode area, the anode potential fluctuates at a lower voltage level (compare the upper figure Slide 13 and the left figure in this slide)
- Again the anode potential drop is not due to the current leak from the anode to the cathode (compare the two figures below)
- This phenomenon suggests that larger electrode area is more favorable to hydrogen-anode interaction

![Graph showing anode potential during charging circle under various applied voltages and anode potential drop caused by current leak between electrodes.](image-url)
Experimental: hydrogen-material interaction in dc field during discharge circle

- Experimental data as shown in the figures revealed that the hydrogen filled electrode reactor behaves like a capacitor
- Without the hydrogen filled electrode reactor, the circuit lost this capacitor-like characteristics
- The phenomenon suggests possible release of hydrogen from the anode when the applied voltage is take off
  \[ \text{Anode}^q + n\text{H}_2 \rightarrow \text{Anode} + n\text{H}_2 + qe^- \]
- The results from the two figures suggest that, under high voltages applied, higher hydrogen pressures may hold more hydrogen
Future work
FY08-FY09

• Investigate the effects of applied electric potential on hydrogen adsorption
  – Verify the charge-induced hydrogen adsorption/desorption process
    • Using a dedicated instrument that is able to measure hydrogen sorption in the hydrogen filled electrode reactor
  – Develop electrodes with large surface area and study the adsorption/desorption enhancement effect
    • Use mesoporous/nanoporous electrode materials
    • Use multilayer electrode structure
  – Further study the adsorption/desorption enhancement effects of applied voltage and hydrogen pressure, and explore the optimization approaches
  – Examine the adsorption/desorption enhancement effects of different electrode materials (starting from the metals explored by computer calculation), and screen the best candidates
Future work

FY08-FY09

• Investigate the hydrogen adsorption capability of materials with naturally polar bonds
  ➢ Directed by our computer simulation, we will explore the following material compounds:
    BeO, Cr₂O₃, Fe₂O₃, NiO, and CoO
  ➢ The experiment will be carried out with
    o Highly porous materials
    o Using these materials to modify the electronic structure of other materials

• Investigate the hydrogen adsorption capability of materials being electrically polarized, materials being explored will include
  • Inorganic ferromaterials
  • Organic ferromaterials
  • Other materials having charge carriers that can be electrically separated
Project Summary

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

- **Approach:** Investigate charge-induced hydrogen cluster formation and develop materials systems that have charge-enhanced hydrogen adsorption/desorption

- **Technical accomplishments and progress:**
  - By computational screening a large number of various charged species, a number of most promising candidates were selected
  - Their high capacity for hydrogen storage (see Table) indicates that materials containing/consisting of these species have potentials to meet the DOE 2010 projective target
  - Experimental work observed of charge transfer between hydrogen and charged species, which indicates charge-induced hydrogen adsorption/desorption

- **Proposed future research:**
  - Verify the charge-induced H₂ sorption process using concurrent electric polarization and H₂ sorption reactor
  - Using Be, Mg, Ca as anode materials, examine the hydrogen storage capability
  - Develop new electrode structures in order to further enlarge the hydrogen storage capacity
  - Experimentally investigate the hydrogen storage capability of highly porous materials having Be-O, Cr-O, Fe-O, Co, Ni-O bonds
  - Experimentally investigate the hydrogen storage capability of materials having charge carriers that can be electrically polarized

<table>
<thead>
<tr>
<th>charged species</th>
<th>Cations</th>
<th>Hydrogen-storage capacity (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Be²⁺</td>
<td>Mg²⁺</td>
</tr>
<tr>
<td></td>
<td>Ca²⁺</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>63.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>39.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>28.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>anions</th>
<th>O²⁻</th>
<th>C⁻</th>
<th>Cl⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>57.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>31.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>polar bonds in metal Oxides</th>
<th>Be-O</th>
<th>Cr-O</th>
<th>Fe-O</th>
<th>Co-O</th>
<th>Ni-O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>24.2</td>
<td>19</td>
<td>18.2</td>
<td>17.6</td>
<td>17.6</td>
</tr>
</tbody>
</table>