IV.D.4 Novel Metal Perhydrides for Hydrogen Storage

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Objectives

- Develop 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 the potential to meet DOE 2010 and 2015 targets.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume
(B) System Cost
(C) Efficiency

Technical Targets

This project is focused on the use of charged species to form H_2 clusters and thus to enhance H_2 storage capacity. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials and systems that meet the DOE 2010 hydrogen storage targets listed in Table 1.

TABLE 1. Target Parameters Addressed by this Project

Storage Parameter	Units	2010 target
Usable, specific-energy from H_2	kWh/kg	2
(net useful energy / max system mass)	(kg H_2/kg system)	(0.06)
Usable energy density from H_2	kWh/L	1.5
(net useful energy / max system volume)	(kg H_2/L system)	(0.045)
Storage system cost	Fuel cost $/kWh net ($/kg H_2)	$2-3 2 (67)

Accomplishments

- Computational study revealed charged species have a universal capability to cluster hydrogen, the charged species include cations, anions and polar molecular bonds.
- By computational screening a large number of various charged species, a number of most promising candidates were selected, the hydrogen storage capacity for the selected ions ranges from 28.5 to 63.7 wt% and that for the selected polar molecular bonds ranges from 17.6 to 24.2 wt%.
- Experimental work observed charge transfer between hydrogen and charged species, which indicates charge-induced hydrogen adsorption/desorption.
- Preliminary experimental study on materials with naturally polar bonds observed 4.5 wt% of hydrogen adsorption under 77 K.

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Introduction

Research on hydrogen storage materials has been pursued for many years, and has proven to be a difficult task. The key problem involved in reversible hydrogen storage materials is perhaps that most of the candidate materials are much heavier than carbon but their capabilities to bind hydrogen (in atomic ratios) are lower. It becomes more and more apparent that hydrogen storage could not solely rely on surface properties of host materials. Additional attracting forces have to be introduced.

This project is to develop novel materials that use charged species to cluster hydrogen in the material structures. The clustering approach is anticipated to lead to higher hydrogen uptake than that by means

of conventional chemical and physical sorption and therefore have potential to meet the DOE 2010 and 2015 targets.

Approach

The charge-induced hydrogen clusters under investigation include proton-hydrogen clusters, $[H(H_2)_n]^+$; cation-hydrogen clusters, $[M(H_2)_n]^{z+}$; anion-hydrogen clusters, $[X(H_2)_n]^{z+}$, clusters around polar chemical bonds, $^{\delta+}[(H_2)_m M\text{-}X(H_2)_n]^{\delta-}$; and clusters that may form on electrode surfaces, anode-$(H_2)_n{}^{q+}-{}^{q-}(H_2)_n$-cathode. A computational approach was employed to examine the potential for formation of these hydrogen clusters, identify the cluster formation mechanism, and compare the cluster binding capabilities between the different charged species. Volumetric adsorption measurement was employed to examine the hydrogen adsorption on materials rich in charged species. A dedicated electrode reactor was developed and used to carry out experimental studies on the interaction of hydrogen with charges created on electrode surfaces.

Results

Studies on hydrogen cluster formation capabilities of protons and transition metal ions/atoms have been reported by a number of researchers [1-6]. Since the protons are barely naked cations and the transition metal ions/atoms have *d* electrons, those studies did not clarify whether electrical charges played a universal role on the formation of hydrogen clusters. In this project, the hydrogen-clustering capabilities of various ions was investigated, including almost all of the cations of metals in the first three rows of the periodic table and the anions of oxygen, chlorine and carbon. All showed the capability for clustering hydrogen. Unlike protons and transition metal ions/atoms, these ionic species do not have special structures. This observation led to the conclusion that electrical charges play a universal role. Further, charge transfers from the hydrogen molecules to the ions were found, corresponding to cluster formation. While the transfer is negative in the case of cations, the transfer is positive when the ions are anions. The more the charge is transferred, the more the energy gain from the formation of the clusters. The charge transfer can be attributed to the mechanism of the hydrogen cluster formation. A cationic cluster and an anionic cluster were combined into a polar bond-hydrogen cluster and similar behavior was observed for polar bonds in clustering hydrogen molecules. Based on the computational results from various ionic and polar bond hydrogen clusters, several of the most promising candidates were screened out and their predicted hydrogen-storage capacities are shown in Table 2.

TABLE 2. Hydrogen Storage Capacity of Various Promising Ionic and Polar bonded Materials

Charged species	Hydrogen-storage capacity (wt%)				
Cations	Be^{2+}	Mg^{2+}	Ca^{2+}		
	63.7	39.7	28.5		
Anions	O^{2-}	C^-	Cl^-		
	50.0	57.1	31.1		
Polar bonds	Be-O	Cr-O	Fe-O	Co-O	Ni-O
	24.2	19	18.2	17.6	17.6

Based on these computational results, experimental study was conducted on the hydrogen storage capability of a material containing naturally charged species. The preliminary result is illustrated in Figure 1. Please note that, although the measured hydrogen adsorption ability appears a few percentages lower than the DOE 2010 target, the specific surface of the material is much lower than that of most of the material systems that are reported to have similar hydrogen storage capacity. A further task is to pursue materials of this kind with sufficiently high specific surface areas.

In order to create charged species on material surfaces, an electrode reactor was developed. The reactor and data acquisition system are illustrated in Figure 2. With this system, significant fluctuations of the anode potentials during application of an electric voltage to the hydrogen-filled electrodes were observed, as shown in Figure 3. These fluctuation patterns and magnitudes were compared to those induced by current leak, as shown in Figure 4. These fluctuations apparently are not caused by current leak directly from the anode to the cathode, but can be attributed to a process of charge-induced adsorption/desorption, which may assume the following mechanisms:
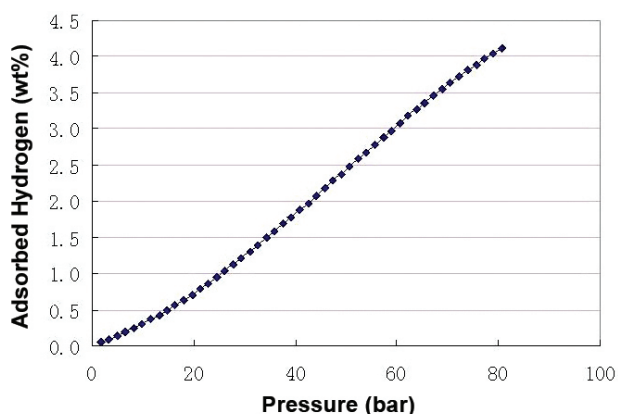

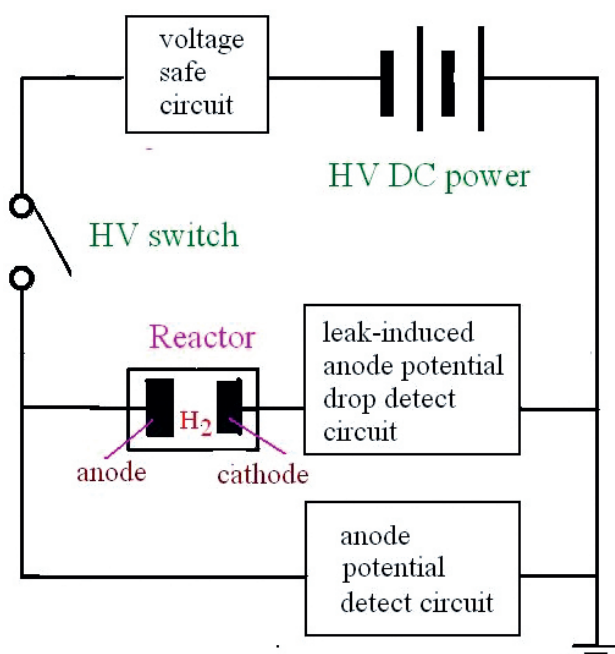**FIGURE 1.** Hydrogen Adsorption on a Material Rich in Ionic Species

FIGURE 2. Instrument System for Studying Interaction of Hydrogen with Charges Created on Electrode Surfaces
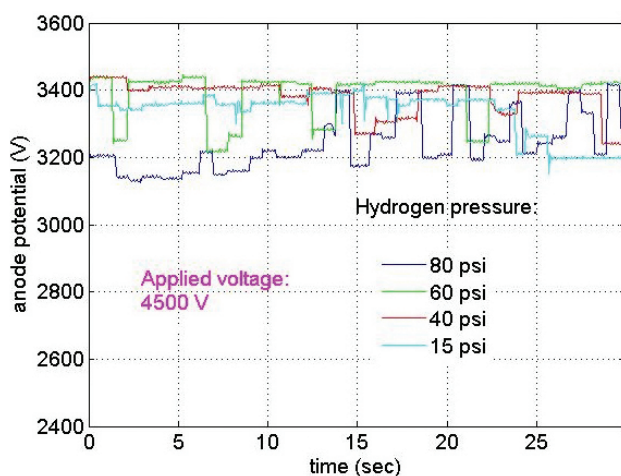

FIGURE 3. Anode Potential Changes as Electric Voltages were Applied to the Hydrogen Filled Electrode Reactor

- H_2 adsorbed to the charged anode:
  - $Anode^{q+} + nH_2 \rightarrow Anode^{q+}\text{-}nH_2$
- Electrons flow from the adsorbed H_2 to anode, anode potential drops:
  - $Anode^{q+}\text{-}nH_2 \rightarrow Anode^{(q-n)+}\text{-}nH_2^+$
- Electrons from the anode flow back to the adsorbed H_2, anode potential rises:
  - $Anode^{(q-n)+}\text{-}nH_2^+ \rightarrow Anode^{q+}\text{-}nH_2$
- Some of the H_2 on the anode may be ionized, anode potential drops:
  - $Anode^{q+}\text{-}nH_2 \rightarrow Anode^{(q-m)+}\text{-}(n\text{-}\tfrac{1}{2}m)H_2^+ + mH^+$
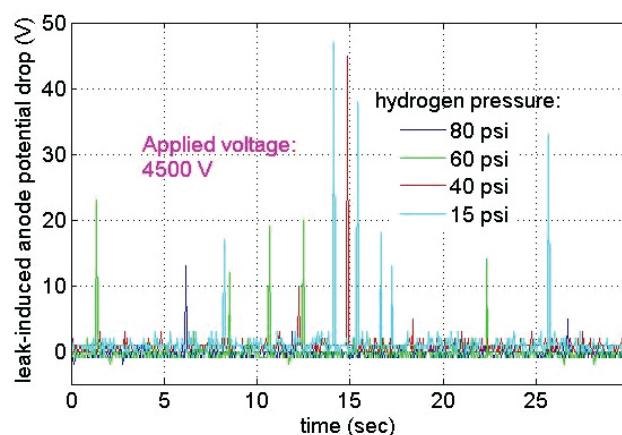

FIGURE 4. Anode Potential Drops Caused by Current Leak from the Anode to the Cathode

The significance of these findings can be viewed in the following ways:

- Polar bonds exist in many chemical compounds. Therefore it should be possible to transform the individual ionic hydrogen clusters into real-world material systems that are electrically neutral for practical applications.
- There are several natural minerals that are rich in ionic species (cations with types of negative counter ions). Appropriate treatment of these ion pairs could make these minerals useful for hydrogen storage.
- Cations and anions could be created on material surfaces by applying an electric field to material systems, thus adding a new hydrogen-binding force for hydrogen storage materials.

Conclusions and Future Directions

Conclusions

- Computational study revealed that all the charged species have a universal capability to cluster hydrogen. The binding force between charged species and hydrogen molecules comes from charge transfers between them.
- Several most promising charged species have been selected by computational screening. Material systems containing these species have potential to meet the DOE 2010 hydrogen storage target.
- Experimental study was carried out on a material rich in ionic species. Preliminary results indicate that the hydrogen storage capacity of this material achieved >4 wt%, although its specific surface area is much lower.
- An abnormal anode potential change was observed when electric voltage was applied to a hydrogen-

filled electrode reactor. The anode potential change is attributed to charge transfer between the anode and hydrogen molecules, which would lead to electric field enhancement of hydrogen adsorption.

Future Directions

- Continue the experimental investigation on materials rich in ionic species. Verify and further improve their hydrogen storage capacity.
- Experimentally investigate materials that contain polar bonds, examine and further improve their hydrogen storage capacity.
- Verify the charge-induced H_2 sorption process using concurrent electric polarization and H_2 sorption reactor.
- Using materials that containing the selected candidate ionic species to fabricate electrodes and 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 materials having charge carriers that can be electrically polarized.

FY 2008 Publications/Presentations

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2. Z. Xu, J.Y. Hwang, B. Li, X. Huang and H. Wang, "The Characterization of Various ZnO Nanostructures using Field Emission SEM", *JOM*, v.60, no. 4, pp. 29-32, 2008.

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