

IV.F.4 Novel Metal Perhydrides for Hydrogen Storage

Jiann-Yang Hwang (Primary Contact),
Shangzhao Shi, Stephen Hackney,
Douglas Swenson, Yunhang Hu
Michigan Technological University (MTU)
1400 Townsend Drive
Houghton, MI 49931
Phone: (906) 487-2600; Fax: (906) 487-2921
E-mail: jhwang@mtu.edu

DOE Technology Development Manager:
Grace Ordaz
Phone: (202) 586-8350; Fax: (202) 586-9811
E-mail: Grace.Ordaz@ee.doe.gov

DOE Project Officer: Katie Randolph
Phone: (303) 275-4901; Fax: (303) 275-4753
E-mail: Katie.Randolph@go.doe.gov

Contract Number: DE-FC36-05GO15003

Project Start Date: April 1, 2005
Project End Date: November 11, 2009

Objectives

- The overall focus of this project:
 - Develop new kinds 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 for Fiscal Year 2009:
 - Study the H₂ adsorption behavior of material systems having charged species in the material structure.
 - Design and 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 and develop devices for directly measuring H₂ sorption in electric field.
- Study the H₂ adsorption behavior of materials systems charged by applied electric potentials.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.0) 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 H₂ clusters and thus to enhance the H₂ storage capacity. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials and systems that meet the following DOE 2010 hydrogen storage targets, as shown in Table 1:

TABLE 1. DOE 2010 Hydrogen Storage Targets

Storage Parameter	Units	2010
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)

Accomplishments

- 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 (CGMs)
 - NiO + CGM
 - Activated carbon + 2,000 V potential
 - Pt/carbon + activated carbon + 2,000 V potential
- All of the five systems demonstrated enhanced H₂ sorption in the presence of charges.
- Electrically-charged system yields 200 to 550% hydrogen sorption enhancement with spill-over approach at room temperature under 1-5 bar pressure.
- More than 6 wt% hydrogen storage capacity has been reached at 77 K on a material basis.



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. In addition, the host materials cannot contribute to the energy content of the fuel. 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 obtained by means of conventional chemical and physical sorption. On the other hand, the charged species may affect the electronic structure of the host materials and therefore enhance the attraction of hydrogen to their surfaces. The novel materials are anticipated to uptake sufficient amounts of hydrogen and are promising for meeting the DOE 2010 and 2015 targets.

Approach

The proposed charge-induced hydrogen clusters 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, $\delta^+[(H_2)_m M-X(H_2)_n] \delta^-$; and clusters that may form on electrodes, anode- $(H_2)_n^{q+}$ - cathode- $(H_2)_n^{q-}$. Based on the charge cluster concept, we anticipated that the hydrogen sorption on sorbent materials would be enhanced if an electric field is applied.

In this year's research, we employed two approaches to introduce the electric field: directly applying an electric potential to the sorbent materials, and burying a piezoelectric element inside the sorbent materials, which could autogenously generate electric charges under hydrogen pressure. Direct measurement of hydrogen sorption under electric field was carried out with PCTPro-2000. A special sorption reactor has been developed to interface with PCTPro-2000 for carrying out the sorption experiment

Results

Our experimental results revealed that applying an electric potential to pure carbon did result in enhanced hydrogen sorption on the material. It supports our initial assumption. It was further found that the sorption enhancement could be appreciably

promoted when platinum was present. As illustrated in Figure 1, enhancement of fivefold on Pt-supported carbon could be reached under lower hydrogen pressures. It is well known that the presence of platinum could induce spillover sorption of hydrogen. By the spillover mechanism, hydrogen molecules dissociate into hydrogen atoms that diffuse toward sorption sites via low energy paths. From our own observations, we conclude that applying an electric field could make the spillover sorption more effective.

Figures 2 and 3 show the sorption curves obtained from our experiment of hydrogen sorption on carbon and NiO samples in the presence of a piezoelectric

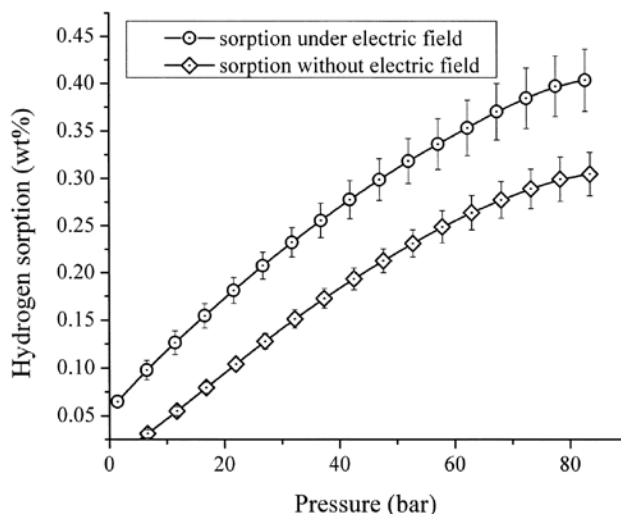


FIGURE 1. Hydrogen Sorption on Pt-Supported Carbon with and without Electric Field

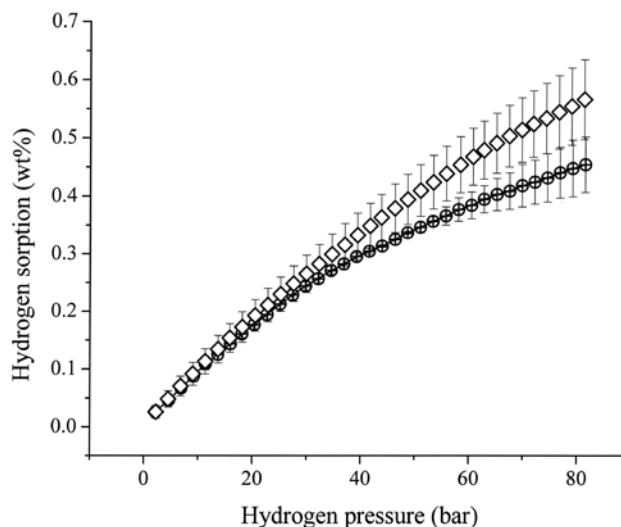


FIGURE 2. Hydrogen Sorption on Carbon in Presence and Absence of Electric Field

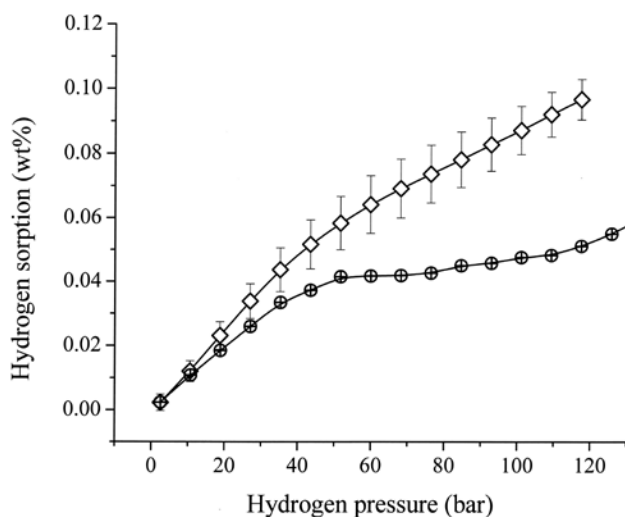


FIGURE 3. Hydrogen Sorption on NiO in Presence and Absence of Electric Field

element, respectively. It is obvious that on both samples, the presence of the piezoelectric element increased the hydrogen sorption. Once again, this verified our concept that electrical charges could have stronger forces to bind hydrogen. The sorption enhancement trends illustrated by the sorption curves are consistent with the charge-generating capability of the piezoelectric elements. Under higher hydrogen pressure, stresses in the piezoelectric element would become more intensified. More electrical charges could be generated at the surface of the piezoelectric elements.

It is interesting to note that in the case of NiO, the enhancement appeared to be more distinctive in the low pressure range and more significant in the high pressure range, compared to that of the carbon samples. The greater enhancement of sorption on NiO is attributed the catalytic characteristics of NiO. Similar to Pt-supported carbon, the nickel species could split hydrogen molecules into hydrogen atoms and make the electric field-induced enhancement more effective.

The accomplishment on electric field-induced sorption enhancement has led our efforts to address structure characteristics of the sorbent materials. Besides the catalytic species, we have investigated other measures to improve the accessibility of charges in the sorbent structure. A special material, termed a structure modifier, was found that could dramatically increase the hydrogen uptake of carbonaceous materials. Figure 4 illustrates the sorption curves of a pure carbon (C), carbon + piezoelectric element, and carbon + piezoelectric element + structure modifier. The result demonstrated that, in electric field, the 77 K hydrogen uptake capacity of structure modified carbon exceeded the target of 6.0 wt%.

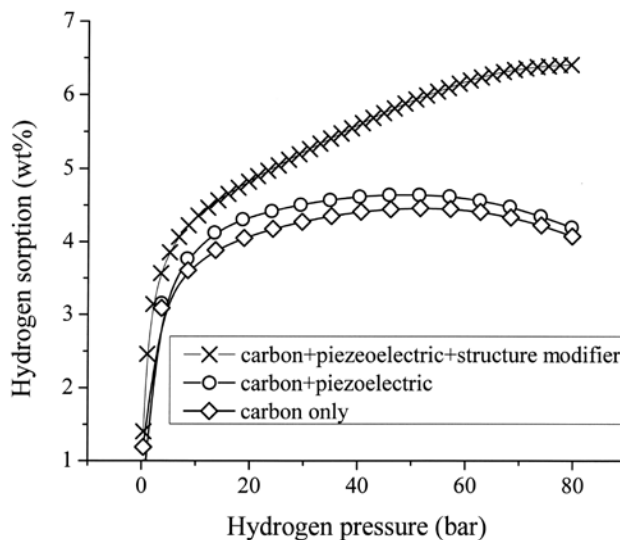


FIGURE 4. Effect of Electric Field and Structure Modifier on Hydrogen Sorption at 77 K

Conclusions and Future Directions

The criterion for the Go/No-Go decision of the MTU project is “The decision to go forward to Phase II will be based on the demonstration of at least 6 wt% hydrogen storage capacity (on a material basis) for at least one of the metal perhydride materials developed in Phase 1”. The MTU Phase I project has been able to achieve more than 6 wt% hydrogen storage capacities at 77 K on a material basis so far. It is predicted that a significant improvement over the 6 wt% hydrogen sorption capacity will be realized in the Phase II study since the fundamentals of the perhydride has been well established in the Phase I study. In Phase II, we will optimize the sorbent materials and the storage system structures. The combination of the optimized material and system structures would be able to hold a high population of electric charges and therefore perhydride species of high density could be produced. Approaches for harvesting the electrical charges during the hydrogen release cycle will also be developed, so that the hydrogen storage system could act concurrently as a battery. The overall energy storage capacity could be further increased.

FY 2009 Publications/Presentations

1. 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.
2. S. Shi, J.Y. Hwang, X. Li, X. Sun and B.I. Lee, “Enhanced hydrogen sorption on carbonaceous sorbents under electric field,” submitted to *International Journal of Hydrogen Energy*.

3. S. Shi, J.Y. Hwang, X. Li, X. Sun, “Enhanced hydrogen sorption on carbon and NiO in the presence of a piezoelectric element,” submitted to *Energy and Fuels*.

References

1. Hiraoka, K.; Kebarle, P. *J. Chem. Phys.* **1975**, *62*, 2267-2270.
2. Okumura, M.; Yeh, L.I.; Lee, Y.T. *J. Chem. Phys.* **1988**, *88*, 79-91.
3. Kemper, P.R.; Weis, P.; Bowers, M.T.; Maitre, P. *J. Am. Chem. Soc.* **1998**, *120* 13494-13502.
4. Bushnell, J.E.; Maitre, P.; Kemper, P.R.; Bowers, M.T. *J. Chem. Phys.* **1997**, *106*, 10153-10167.
5. Kemper, P.R.; Bushnell, J.; von Helden, G.; Bowers, M.T. *J. Phys. Chem.* **1993**, *97*, 52-58.
6. Matsubara, T; Hirao, K. *J. Phys. Chem. A.* **2003**, *107*, 2505-2515.
7. Wang, X.; Andrews, L. *J. Phys. Chem. A.* **2004**, *108*, 1103-1106.
8. Andrews, L.; Wang, X. *J. Am. Chem. Soc.* **2003**, *125*, 11751-11760.
9. Baur, R.; Macholdt, H.-T. *J. Electrostatics.* **1993**, *30*, 213-222.
10. Anderson, J.L.; Armstrong, D.W. *Anal. Chem.* **2005**, *77*, 6453-6462.
11. Banerjee, S.; Santhanam, A.; Dhathathreyan, A.; Rao, P.M. *Langmuir* **2003**, *19*, 5522-5525.
12. Zielinski, M.; Wojcieszak, R.; Monteverdi, S.; Mercy, M.; Bettahar, M. M. *International Journal of Hydrogen Energy.* **2007**, *32*, 1024 – 1032.
13. Lin, C.; Xu, T.; Yu, J.; Ge, Q.; Xiao, Z. *J. Phys. Chem. C.* **2009**, *113*, 8513-8517.