

IV.C.1h Carbon Aerogels for Hydrogen Storage

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Accomplishments

- New monolithic carbon aerogels derived from sugars (i.e. sucrose, glucose) have been synthesized for use as spillover substrates. These materials possess surface areas up to 600 m²/g and can readily be doped with hydrogen dissociation catalysts, such as platinum or nickel.
- Novel CA-carbon nanotube (CNT) scaffolds have been prepared through catalyzed chemical vapor deposition (CVD) growth of CNTs on the inner pore surfaces of high surface area CA substrates. These substrates promote intimate contact between the surfaces of the CNTs and the incorporated complex hydride, thus influencing the kinetics of hydrogen exchange in the hydride.
- LiBH₄ nanocomposites prepared with the CA-CNT scaffolds showed significant decreases in the temperature of hydrogen desorption relative to that of bulk LiBH₄. These scaffolds also appear to outperform CA scaffolds prepared without CNT. Work performed in collaboration with Metal Hydride Center of Excellence (MHCoE) members at HRL Laboratories.



Objectives

- Demonstrate high-capacity hydrogen storage in high surface area carbon aerogels (CAs).
- Develop carbon-based sorbent materials that can store hydrogen at ambient temperature and reasonable operating pressures.
- Fabricate porous carbons as scaffolds for complex hydride systems to improve the kinetic performance of the hydride.

Technical Barriers

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

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
- (Q) Reproducibility of Performance

Technical Targets

This effort is focused on the design of new nanostructured carbon-based materials that meet the former DOE 2010 targets for on-board vehicle hydrogen storage of 6 percent hydrogen by weight and 45 grams of hydrogen per liter.

Introduction

Porous carbon materials are promising candidates for hydrogen sorption due their lightweight frameworks and high accessible surface areas. The low hydrogen binding energies, however, that are typical of carbonaceous sorbents (~6 kJ/mol H₂), require that cryogenic temperatures (77 K) be utilized for storage of hydrogen in these materials. In general, the amount of surface excess hydrogen adsorbed on porous carbons at 77 K and ~3.5 MPa varies linearly with Brunauer-Emmett-Teller surface area; gravimetric uptake is ~1 wt% H₂ per 500 m²/g of surface area. Our overall goal in this effort is the design of novel carbon nanostructures that exhibit enhanced binding energies for hydrogen and thus allows for reversible hydrogen storage at ambient temperature and reasonable operating pressures.

Approach

CAs are a unique class of porous materials that possess a number of desirable structural features for the storage of hydrogen, including high surface areas (over 3,000 m²/g), continuous and tunable porosities, and variable densities. In addition, the flexibility associated with CA synthesis allows for the incorporation of

modifiers or catalysts onto the surfaces of the carbon matrix in order to alter hydrogen sorption enthalpies in these materials. Since the properties of CAs can be systematically modified (i.e. surface chemistry, pore structure, amount/type of dopant), novel materials can be fabricated that exhibit enhanced hydrogen storage properties. For example, we have used this approach to prepare high surface area CAs that exhibit excess gravimetric H_2 densities over 5 wt% and volumetric H_2 capacities of 29 g/L at 77 K and 30 bar. We are now exploring the design of new H_2 sorbent materials that can store appreciable amounts of hydrogen at reasonable operating temperatures. One such approach, known as hydrogen spillover, involves the dissociative chemisorption of molecular hydrogen on a supported metal catalyst surface (e.g. platinum or nickel), followed by the diffusion of atomic hydrogen onto the surface of the support material. Due to the enhanced interaction between atomic hydrogen and the carbon support, hydrogen can be stored in the support material at more reasonable operating temperatures. While the spillover process has been shown to increase the reversible hydrogen storage capacities at room temperature in metal-loaded carbon nanostructures, a number of issues still exist with this approach, including slow kinetics of H_2 uptake and capacities (~1.2 wt% on carbon) below the DOE targets. The ability to tailor different structural aspects of the spillover system (i.e. the size/shape of the catalyst particle, the catalyst-support interface and the support morphology) should provide valuable mechanistic information regarding the critical aspects of the spillover process (i.e. kinetics of hydrogen dissociation, diffusion and recombination) and allow for optimization of these materials to meet the DOE targets for hydrogen storage.

In a parallel effort, we are also designing CA materials as nanoporous scaffolds for metal hydride systems. Recent work by others has demonstrated that nanostructured metal hydrides show enhanced kinetics for reversible hydrogen storage relative to the bulk materials. This effect is diminished, however, after several hydriding/dehydriding cycles, as the material structure coarsens. Incorporation of the metal hydride into a porous scaffolding material can potentially limit coarsening and, therefore, preserve the enhanced kinetics and improved cycling behavior of the nanostructured metal hydride. Successful implementation of this approach, however, requires the design of nanoporous solids with large accessible pore volumes ($>4 \text{ cm}^3/\text{g}$) to minimize the gravimetric and volumetric capacity penalties associated with the use of the scaffold. These scaffold materials should also be capable of managing thermal changes associated with the cycling of the incorporated metal hydride. CAs are promising candidates for the design of such porous scaffolds due to the large pore volumes and tunable porosity of aerogel framework. In addition, the synthesis

of CA allows for the dispersion of secondary materials into the carbon matrix that can serve as catalysts or destabilizing agents for the metal hydride and potentially influence the transport properties of the scaffold. Our previous efforts were focused on determining the extent to which the different structural aspects of the CA scaffold (pore diameter, interconnectivity, microporosity, surface chemistry) influence the kinetics of hydrogen exchange in LiBH_4 . This research is a joint effort with HRL Laboratories, a member of the MHCoe. Our efforts were focused on the design of new CA materials that can meet the scaffolding requirements, while metal hydride incorporation into the scaffold and evaluation of the kinetics and cycling performance of these composites was performed at HRL.

Results

Design of New Spillover Receptors Derived from Carbon Aerogels

Over the last review period, our work as part of the Hydrogen Sorption Center of Excellence (HSCoe) has been focused on the design of novel spillover receptor materials that can potentially improve both capacity and uptake kinetics in spillover materials. Specifically, we have synthesized novel CAs derived from sugars as spillover receptors. This approach builds on the concept developed by Yang et al. of using partially carbonized sugars as “bridges” to facilitate hydrogen diffusion from the catalyst to the receptor. Our material, however, is comprised entirely of “bridge” material and, therefore, these materials should provide sufficiently favorable surfaces for hydrogen spillover. The carbonized sugar aerogels are prepared through the sol-gel polymerization of simple sugars, such as glucose or sucrose, affording highly cross-linked sugar gels. These gels are then supercritically dried and subsequently pyrolyzed under an inert atmosphere to afford the sugar-derived carbon aerogels. These materials are monolithic and possess surface areas up to $600 \text{ m}^2/\text{g}$. In addition, these porous carbon structures can be readily doped with hydrogen dissociation catalysts, such as platinum, ruthenium or nickel, by either solution- or vapor-phase techniques. Room temperature hydrogen uptake in the metal-loaded sugar-derived CAs has not yet been evaluated within the HSCoe.

Carbon Aerogel as Scaffolds for Complex Hydrides

For our work with the MHCoe, we fabricated a new class of CA scaffolds that contain dispersions of CNTs within the scaffold framework. Incorporation of CNTs into the scaffold has the potential to not only improve the thermal conductivity of the scaffold, but may also affect the kinetics of dehydrogenation for

certain metal hydrides. Recent work by other groups have indicated that the interaction of the hydride with an electronegative surface, such as that of a carbon fullerene or nanotube, can disrupt the bonding structure of the hydride and, as a result, provide lower energy pathways for hydrogen exchange. These novel CA-CNT scaffolds (Figure 1) were prepared through the growth of CNTs by CVD on the inner porosity of high surface area carbon aerogel substrates. Because the CNTs populate the surfaces of the CA support, these scaffolds promote intimate contact between the surfaces of the CNTs and the incorporated metal hydride. To evaluate the influence of the CNTs on the kinetics of hydrogen exchange in LiBH_4 , the hydride was incorporated into the free pore volume of these scaffolds using melt infusion techniques and the temperature of dehydrogenation was determined using thermogravimetric analysis. As shown in Figure 2, LiBH_4 nanocomposites prepared with the CA-CNT scaffolds showed significant decreases in the temperature of hydrogen desorption relative to that for bulk LiBH_4 and also out-perform earlier generation CA scaffolds prepared without CNT. This approach to scaffold design appears promising and we expect further improvements in performance as the structure of these composite scaffolds are optimized.

Conclusions and Future Directions

While this project finished at the end of this review period, we believe there are a number of aspects of this work that warrant future investigation based on the promising results from Fiscal Year (FY) 2010, including:

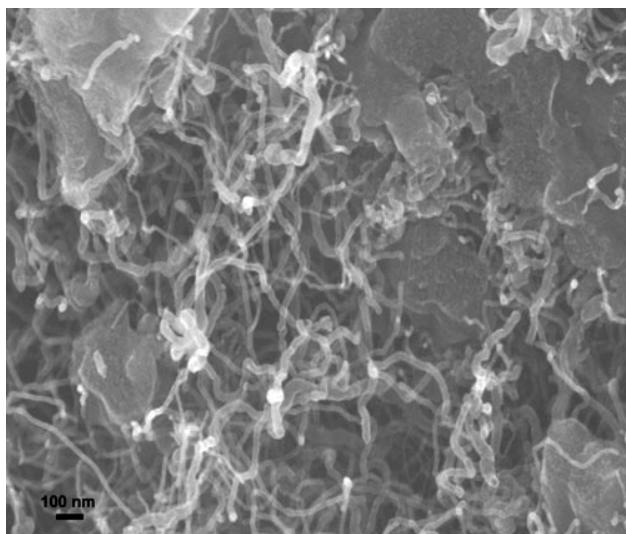


FIGURE 1. Scanning electron micrograph of a carbon scaffold in which the CNTs have been grown directly on the inner surfaces of the CA using CVD. The solid gray sections are the ligaments of the CA that are coated with multi-walled CNTs. The free pore volume within these materials is then infiltrated with metal hydride.

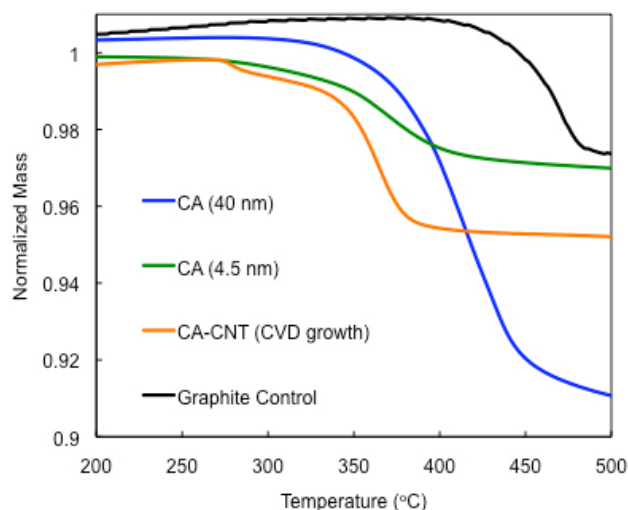


FIGURE 2. Representative thermogravimetric analysis data for LiBH_4 incorporated into various CA scaffolds showing the influence of pore size (in parentheses) and CAs on dehydrogenation reaction. The black curve is LiBH_4 mixed with nonporous graphite. The weight losses indicate dehydrogenation and scale with LiBH_4 loading.

- Evaluation of room temperature hydrogen uptake (both capacity and kinetics) in the metal-loaded sugar-derived CAs. These results should provide guidance for further optimization of the surface chemistry and texture of the spillover receptors.
- Further investigation of the influence of CNTs and other graphitic nanostructures on the kinetics of hydrogen exchange in complex hydride systems. Initial results for our CA-CNT composites indicate improved kinetic performance of LiBH_4 in these scaffolds.
- Incorporation of other destabilizing agents and catalysts, such as Mg, Ni or Ti, into these CA-CNT scaffolds to facilitate the hydriding and dehydriding processes.

FY 2010 Publications/Presentations

1. “High Surface Area Carbon Aerogels as Porous Substrates for Direct Growth of Carbon Nanotubes” M.A. Worsley, M. Stadermann, Y.M. Wang, J. H. Satcher, T.F. Baumann, *Chemical Communications*, **2010**, DOI:10.1039/C0CC03457F.
2. “Synthesis of Graphene Aerogels with High Electrical Conductivity” Marcus A. Worsley, Peter J. Pauzauskie, Tammy Y. Olson, Joe H. Satcher, Jr. and Theodore F. Baumann, *Journal of the American Chemical Society*, **2010**, 132, 14067.
3. “Synthesis and Characterization of Monolithic, High Surface Area SiO_2/C and SiC/C Composites” M.A. Worsley, J.D. Kuntz, J.H. Satcher, T.F. Baumann, *Journal of Materials Chemistry*, **2010**, 20, 4840.

4. "Influence of Sodium Dodecylbenzene Sulfonate on the Structure and Properties of Carbon Aerogels" M.A. Worsley, J.H. Satcher, T.F. Baumann, *Journal of Non-Crystalline Solids*, **2010**, 356, 172.
5. "Surface Chemistry in Nanoporous Materials" J. Biener, A. Wittstock, T.F. Baumann, J. Weissmüller, M. Bäumer, A.V. Hamza, *Materials*, **2009**, 2, 2404.
6. "High Surface Area Carbon Nanotube-Supported Titanium Carbonitride Aerogels" M.A. Worsley, J.D. Kuntz, P.J. Pauzauskie, O. Cervantes, J.M. Zaug, A.E. Gash, J.H. Satcher and T.F. Baumann, *Journal of Materials Chemistry*, **2009**, 19, 5503.
7. "Properties of Single-Walled Carbon Nanotube-based Aerogels as a Function of Carbon Nanotube Loading" M.A. Worsley, S.O. Kucheyev, P.J. Pauzauskie, J.M. Zaug, A.V. Hamza, J.H. Satcher and T.F. Baumann *Acta Materialia*, **2009**, 57, 5131.
8. "High Surface Area Carbon Nanotube-Supported Titanium Carbonitride Aerogels" M.A. Worsley, J.D. Kuntz, P.J. Pauzauskie, O. Cervantes, J.M. Zaug, A.E. Gash, J.H. Satcher and T.F. Baumann, *Journal of Materials Chemistry*, **2009**, 19, 5503.
9. "Electrically conductive composites via infiltration of single-walled carbon nanotube-based aerogels," M.A. Worsley, J.D. Kuntz, S.O. Kucheyev, A.V. Hamza, J.H. Satcher, Jr., T.F. Baumann, MRS Spring Meeting Symposium R Proceedings, 2010.
10. "Mechanically robust, conductive carbon nanotube-based aerogels and their composites," M.A. Worsley, S.O. Kucheyev, J.D. Kuntz, O. Cervantes, J.H. Satcher, Jr., A.V. Hamza, T.F. Baumann, MRS, San Francisco, California, April 2010.
11. "High surface area nanocarbon-supported metal oxide aerogels," M.A. Worsley, J.D. Kuntz, O. Cervantes, P.J. Pauzauskie, J.H. Satcher, Jr., T.F. Baumann, ACS, San Francisco, California, April 2010.