

IV.C.1j Carbon Aerogels for Hydrogen Storage

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Partner Approach

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, including capacity targets of 6 percent hydrogen by weight and 45 grams of hydrogen per liter. Carbon aerogels (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 H₂ densities over 5 wt% and volumetric H₂ capacities of 29 g/L at 77 K and 30 bar. We are now exploring the design of new H₂ 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 H₂ 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. As an alternative approach to enhanced hydrogen uptake, we are also investigating the functionalization of the skeletal aerogel network with molecular units that can stabilize isolated metal atoms or organometallic species capable of reversibly binding H₂ molecules. The synthesis of aerogel materials allows for the incorporation of different types of metal-binding sites, including phosphorous-, nitrogen-, or sulfur-containing functional groups. This flexibility should allow for the design of new sorbent materials that can bind multiple H₂ molecules at the appropriate binding energies for room temperature 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 cm³/g) to minimize the gravimetric and volumetric capacity penalties associated with the use of the scaffold. In addition, these scaffold materials should 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. For example, we have demonstrated that the incorporation of carbon nanotubes into the CA framework not only improves the thermal conductivity of the scaffold, but may also affect the kinetics of dehydrogenation for certain metal hydrides. This research is a joint effort with HRL Laboratories, a member of the DOE Metal Hydride Center of Excellence (MHCoE). LLNL's efforts

have 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 is performed at HRL.

Partner FY 2009 Results

- Improved synthetic methods have been developed for the fabrication of CA scaffolds that possess both large pore volumes ($\sim 5 \text{ cm}^3/\text{g}$) and small average pore sizes ($<20 \text{ nm}$).
- Novel CA-carbon nanotube (CNT) scaffolds (see Figure 1) with improved thermal transport properties were used in the preparation of a CA/ LiBH_4 nanocomposite that showed a decrease in hydrogen desorption temperature relative to bulk LiBH_4 . Metal hydride incorporation and desorption measurements were performed by MHCoe members at HRL Laboratories.
- New aerogel substrates containing functional groups capable of binding and stabilizing organometallic species have been synthesized. For example, high surface area silica aerogels ($750 \text{ m}^2/\text{g}$) containing diphenylphosphine groups have been prepared. Metal incorporation and hydrogen uptake experiments are being performed by Hydrogen Sorption Center of Excellence (HSCoe) members at the National Renewable Energy Laboratory (NREL).
- Methods developed to readily modify surface chemistry of CA substrates for both spillover

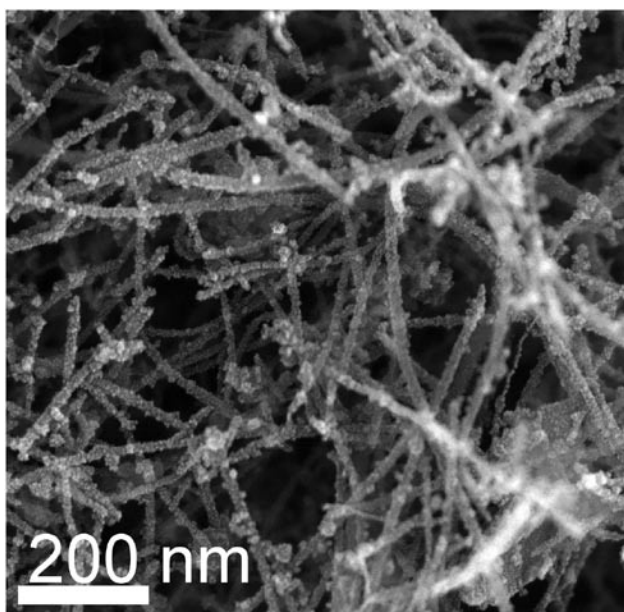


FIGURE 1. Scanning electron micrograph of a carbon scaffold composite containing 55 wt% single-walled carbon nanotubes.

materials and metal hydride scaffolds. For example, high surface area CAs with increased oxygen content ($>20 \text{ wt}\%$) have been prepared for testing as spillover substrates. In addition, we have also demonstrated the ability to incorporate destabilizing agents into scaffold materials. For example, scaffolds coated with a thin layer of nanocrystalline titania (TiO_2) have been prepared (Figure 2).

Future Directions

Based on the promising results from FY 2009, we will continue to investigate surface modification of aerogel materials as a strategy for the design of sorbents with improved H_2 uptake. In FY 2009, we developed methods that allowed us to tailor the surface chemistry of the aerogel sorbent. Future work in this area will focus on the design of functionalized aerogels that can stabilize organometallic species capable of reversibly binding multiple H_2 molecules at reasonable operating temperatures. In addition, we will examine the influence of substrate surface chemistry on the capacity and kinetics in spillover materials. These studies will be performed with HSCoe members at NREL and Caltech. For the scaffolding effort, we will continue to focus on the preparation of new CA composite structures that possess the requisite pore structure, transport properties and surface chemistry. In FY 2009, we were able to fabricate CA nanocomposites containing dispersions of CNTs that exhibited enhanced thermal conductivity relative to unloaded CA materials. In addition, we developed methods that allowed for the incorporation of destabilizing agents (i.e. TiO_2) onto the surfaces

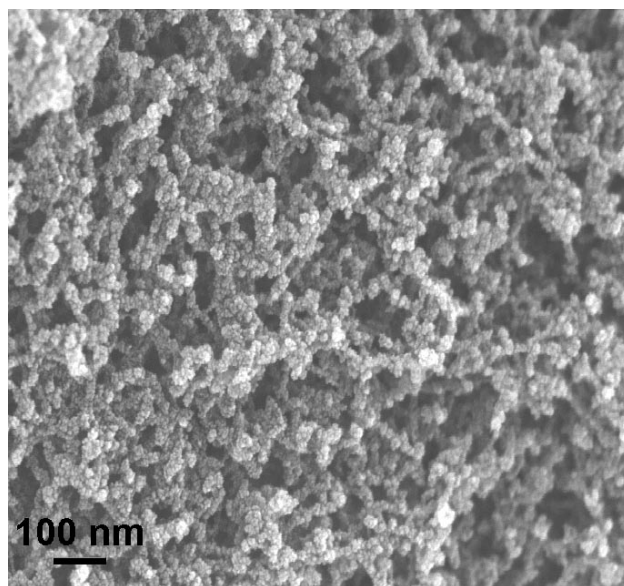


FIGURE 2. Scanning electron micrograph of a carbon aerogel scaffold coated with a conformal layer of nanocrystalline TiO_2 (37 wt%).

of the scaffold network. As the structures of these scaffolds continue to evolve, our efforts will focus on the homogeneous incorporation of other destabilizing agents and catalysts, such as Ni or Ti, into these matrices to facilitate the hydriding and dehydriding processes. We will also develop methods for controlling the surface chemistry of the CA to improve the wetting behavior of destabilizing entities, such as Mg, in these materials. Evaluation of the metal hydride scaffolds will be performed by MHCoe members at HRL Laboratories.

FY 2009 Publications/Presentations

1. “High Surface Area Carbon Nanotube-Supported Titanium Carbonitride Aerogels” M.A. Worsley, J.D. Kuntz, P.J. Pauzaskie, O. Cervantes, J.M. Zaug, A.E. Gash, J.H. Satcher and T.F. Baumann, *Journal of Materials Chemistry*, **2009**, *in press*.
2. “Enhanced Thermal Transport in Carbon Aerogel Nanocomposites containing Double-walled Carbon Nanotubes” M.A. Worsley, J.H. Satcher, and T.F. Baumann, *Journal of Applied Physics*, **2009**, 105, 084316.
3. “Mechanically Robust and Electrically Conductive Carbon Nanotube Foams” M.A. Worsley, S.O. Kucheyev, J.H. Satcher, Jr. and T.F. Baumann, *Applied Physics Letters*, **2009**, 94, 073115.
4. “Ultra-low loading Pt nanocatalysts prepared by atomic layer deposition on carbon aerogels” J.S. King, A. Wittstock, J. Biener, S.O. Kucheyev, Y.M. Wang, T.F. Baumann, S.K. Giri, A.V. Hamza, M. Baeumer, and S.F. Bent, *NanoLetters*, **2008**, 8, 2405.
5. “Synthesis and Characterization of Monolithic Carbon Aerogel Nanocomposites Containing Double-walled Carbon Nanotubes” M.A. Worsley, J.H. Satcher, Jr. and T.F. Baumann, *Langmuir*, **2008**, 24, 9763.
6. T.F. Baumann, M.A. Worsley and J.H. Satcher, Jr., “Carbon Aerogels for Hydrogen Storage” American Chemical Society Meeting, Philadelphia, August 2008. (*Invited*)