

IV.C.1b Carbon Aerogels for Hydrogen Storage

Theodore F. Baumann (Primary Contact),
Marcus A. Worsley, Joe H. Satcher, Jr
Lawrence Livermore National Laboratory (LLNL)
7000 East Avenue, L-092
Livermore, CA 94551
Phone: (925) 423-5543; Fax: (925) 423-4897
E-mail: baumann2@llnl.gov

DOE Technology Development Manager:
Carole Read

Phone: (202) 586-3152; Fax: (202) 586-9811
E-mail: Carole.Read@ee.doe.gov

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Partner Approach

This effort is focused on the design of new nanostructured carbon-based materials that meet the DOE 2010 targets for on-board vehicle hydrogen storage. 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 into the carbon matrix in order to alter hydrogen sorption enthalpies in these materials. Since the properties of the doped CAs can be systematically modified (i.e. amount/type of dopant, surface area, porosity), novel materials can be fabricated that exhibit enhanced hydrogen storage properties. We are using this approach to design new H₂ sorbent materials that can store appreciable amounts of hydrogen at room temperature through a process known as hydrogen spillover. The spillover process 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.

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. 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 2008 Results

- Hydrogen dissociation catalysts (Ni and Pt) have been incorporated into activated CAs with different surface areas through a metal impregnation process. The Pt-doped CA material with Brunauer-Emmet-Teller surface area of ~2,400 m²/g exhibited 1.2 wt% H₂ uptake at room temperature and 100 bar. Hydrogen adsorption measurements were performed by Sorption Center of Excellence (SCoE) members at Caltech.
- Atomic layer deposition (ALD) was used to prepare Pt-loaded CAs materials (see Figure 1) that exhibited 1.2 wt% H₂ uptake at room temperature and 100 bar (see Figure 2). Hydrogen adsorption measurements were performed by SCoE members at Caltech.

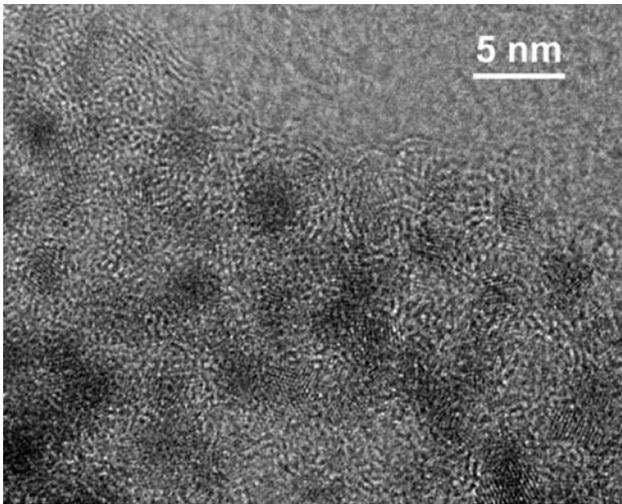


FIGURE 1. Transmission electron micrograph of an activated carbon aerogel (Brunauer-Emmett-Teller surface area $\sim 2,200$ m²/g) containing a dispersion of crystalline platinum nanoparticles prepared by atomic layer deposition.

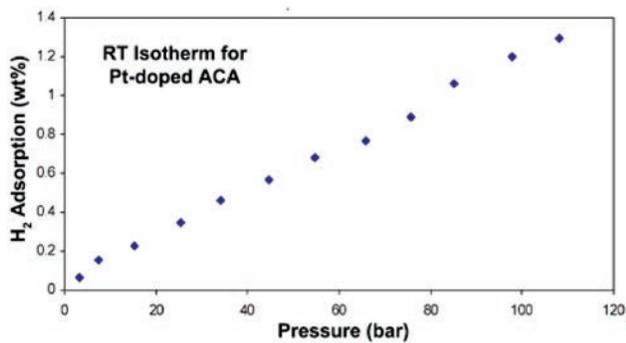


FIGURE 2. High-pressure hydrogen isotherm at 298 K for a platinum-doped activated carbon aerogel (Brunauer-Emmett-Teller surface area $\sim 2,200$ m²/g) prepared by atomic layer deposition.

- Improved methods have been developed for the fabrication of CA scaffolds that possess both large pore volumes (>2.6 cm³/g) and small average pore sizes (<15 nm).
- Novel CA scaffolds containing dispersions of carbon nanotubes (see Figure 3) were used in the preparation of a CA/LiBH₄ nanocomposite that showed a decrease in hydrogen desorption temperature relative to bulk LiBH₄. Metal hydride incorporation and desorption measurements were performed by MHCoe members at HRL Laboratories.

Partner FY 2009 Plans

Based on the promising results from FY 2008, we will continue to investigate ALD for the design of new spillover systems with improved H₂ uptake and kinetic

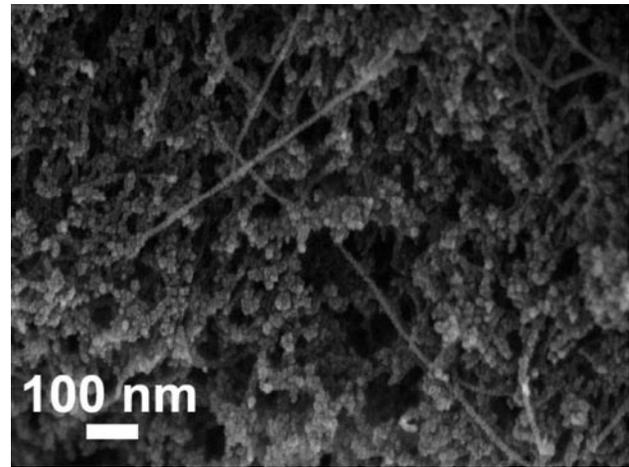


FIGURE 3. Scanning electron micrograph of a carbon aerogel scaffolding composite containing an 8 wt% dispersion of double-walled carbon nanotubes.

performance. In FY 2008, we demonstrated that ALD can be used to incorporate catalytic metal nanoparticles into our high surface area CAs and that these Pt-doped materials exhibit spillover behavior at room temperature. One of our goals for FY 2009 will be to use the ALD process to determine the optimal size, morphology and distribution of the dissociation catalyst for enhanced hydrogen sorption by the spillover process. In addition, we will investigate the incorporation of alternative dissociation catalysts, such as Ni or Ru, using the atomic layer deposition. Another critical aspect of spillover materials is the structure of the support material. Therefore, we will also continue optimization of our high surface area CA supports, both in terms of porosity and surface chemistry, to improve the capacity and kinetic performance of these sorbants. The room temperature hydrogen uptake behavior of these metal-doped CAs will be evaluated to determine the influence that the catalyst dispersion and support morphology have on the thermodynamics and kinetics of hydrogen spillover in these materials. These studies will be performed with SCoE members at Caltech. We will also initiate mechanistic studies of hydrogen spillover in these materials using advanced nuclear magnetic resonance techniques in collaboration with SCoE members at the University of North Carolina. With this approach, we can optimize the performance of these spillover materials to meet the DOE targets for hydrogen storage.

For the scaffolding effort, we will focus on the preparation of new CA structures that possess both large pore volumes (up to 4 cm³/g) and small pores sizes (10 nm or less). The flexibility associated with the aerogel synthesis will allow us to design new CA materials with the desired pore volumes and pore diameters. In FY 2008, we were able to prepare new CAs that retained the large pore volumes (~ 2.6 cm³/g)

of our original scaffolding materials, but possessed much smaller average pore sizes (~15 nm) than those original materials. Building on this progress, our efforts in FY 2009 will be focused on further improvements to the scaffold structure, both in terms of porosity and thermal conductivity. Our approach to improve the thermal transport properties of these materials is to prepare CA composites with a second material that exhibits superior thermal conductivity, such as carbon nanotubes (CNT). CNTs possess high thermal conductivities ($>1,500$ W/m K) and, due to their extremely high aspect ratios (100 to 1,000), only small volume fractions (~0.01) are needed to create a percolation network within the CA scaffold. In FY 2008, we were able to fabricate novel CA-CNT nanocomposites that exhibited enhanced thermal conductivities relative to the pristine CA materials. Performance evaluation of these CA materials as scaffolds for metal hydrides will be performed by MHCoe members at HRL Laboratories. As the CA scaffold structure evolves, our efforts will focus on the homogeneous incorporation of destabilizing agents and catalysts, such as Ni or Ti, into the scaffold structure 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 metals, such as Mg, in these materials.

FY 2008 Publications/Presentations

1. T.F. Baumann, M.A. Worsley, T.Y. Han, and J.H. Satcher, Jr., "High Surface Area Carbon Aerogel Monoliths with Hierarchical Porosity" *Journal of Non-Crystalline Solids*, **2008**, 354, 3513.
2. 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, "Ultra-low loading Pt nanocatalysts prepared by atomic layer deposition on carbon aerogels" *NanoLetters*, **2008**, *in press*.
3. M.A. Worsley, J.H. Satcher, Jr. and T.F. Baumann, "Synthesis and Characterization of Monolithic Carbon Aerogel Nanocomposites Containing Double-walled Carbon Nanotubes" *Langmuir*, **2008**, *in press*.
4. T. F. Baumann, M.A. Worsley and J.H. Satcher, Jr., "Carbon Aerogels for Hydrogen Storage" Materials Research Society Meeting, San Francisco, March 2008. (*Invited*)