

## IV.C.1d Metal-Doped Carbon Aerogels for Hydrogen Storage

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Projected End Date: Project continuation and  
direction determined annually by DOE

### Partner Approach

This effort is focused on designing 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 mesoporous materials that possess a number of desirable structural features for storing hydrogen, including high surface areas (up to 2,600 m<sup>2</sup>/g), continuous and tunable porosities, and variable densities (0.02 to 1.0 g/cm<sup>3</sup>). 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. For example, we have recently developed the capability to incorporate uniform dispersions of metal nanoparticles into the aerogel framework. We believe these doped CAs are ideally suited for hydrogen storage since the materials combine the high mass storage capacity of the aerogel with high surface-to-volume metal nanoparticles that can potentially influence the energetics associated with hydrogen uptake and release (i.e. hydrogen spillover). Since the properties of the doped CAs can be systematically modified (e.g. amount/type of dopant, surface area, pore size/volume), novel materials can be fabricated that exhibit enhanced hydrogen storage properties. Optimizing these CA materials for hydrogen storage, however, requires a fundamental understanding of the interaction between molecular hydrogen and the carbon-based sorbent. Therefore, we are also developing advanced nuclear magnetic resonance (NMR) techniques to investigate the mechanisms associated with hydrogen physisorption and chemisorption in these carbon-based materials.

### Partner FY 2006 Results

- High surface area CAs (up to 2,600 m<sup>2</sup>/g) were prepared through a CO<sub>2</sub> activation process. The increase in surface area (SA) was correlated to activation time and temperature as well as the density and morphology of the CA.
- The H<sub>2</sub> gravimetric density in undoped CAs was shown to track with the surface area of the material, following the “Chahine rule” of 1 wt% H<sub>2</sub> per 500 m<sup>2</sup>/g of surface area. For example, an undoped CA with SA ~2,000 m<sup>2</sup>/g exhibited a hydrogen gravimetric density of ~4.2 wt% at 77 K and 30 bar (see Figure 1). The hydrogen adsorption experiments were performed by Carbon-based Hydrogen Storage center members at Caltech.
- Incorporation of metal dopants into the CA framework appears to alter sorption enthalpy in these materials. Preliminary studies on CAs doped with Ni nanoparticles showed an increase in the isosteric heat of adsorption (~7.15 kJ/mol) relative

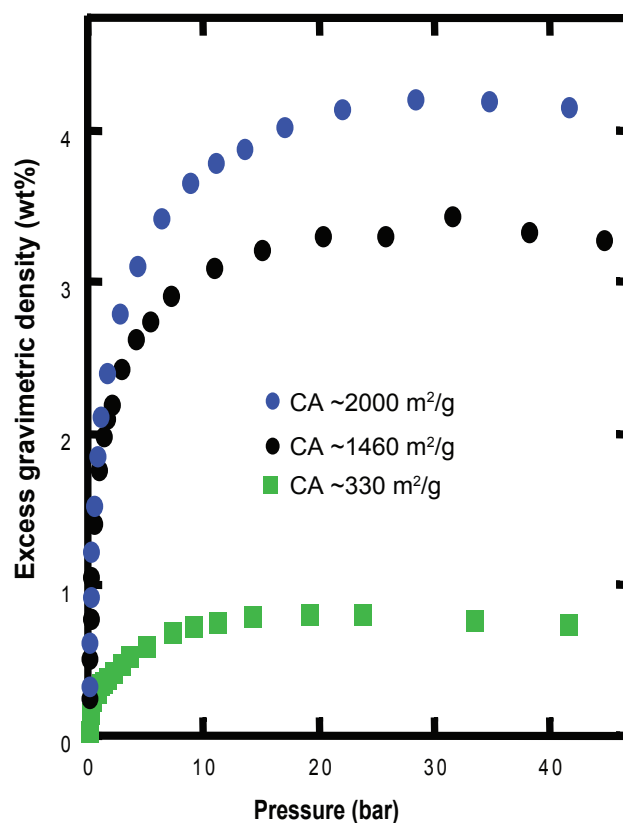


FIGURE 1. Excess Adsorption at 77 K for Undoped Carbon Aerogels with Different Surface Areas

to an equivalent undoped CA material (~4.93 kJ/mol).

### Partner FY 2007 Plans

Based on the promising results from FY2006, we will continue to optimize the undoped CA structure for hydrogen storage. Specifically, we will focus on increasing the microporosity (pore sizes < 2 nm) in these materials, while maintaining their high surface areas and large pore volumes. In addition, the densities of these CA structures will have to be modified to increase the volumetric capacity in these materials. As the CA structure evolves, we will continue to incorporate dopants, such as metal nanoparticles or boron, into these optimized materials with the goal of further improving their interaction with hydrogen. We previously demonstrated two approaches (i.e. ion exchange, atomic layer deposition) that allow for uniform incorporation of metal dopants into the CA framework. Preliminary studies from FY 2006 showed that these metal dopants appear to alter the sorption enthalpy in these

materials. Additional investigation into these metal-doped CAs is required in order to understand the real effects of incorporating the metal nanoparticles on the adsorption potential of the materials. We will also initiate mechanistic studies of hydrogen uptake in these materials using advanced NMR techniques. Para-hydrogen induced polarization (PHIP) NMR will be used to examine interactions between molecular hydrogen and the carbon aerogel network.

### LLNL FY 2006 Publications/Presentations

1. H. Kabbour, A. Saulnier, T. F. Baumann, J. H. Satcher, C. C. Ahn "Surface Area Dependence of Hydrogen Gravimetric Density in Carbon Aerogels" *209<sup>th</sup> Meeting of the Electrochemical Society*, March 2006.
2. Moudrakovski, I. L.; Ratcliffe, C. I.; Ripmeester, J. A.; Wang, L.-Q.; Exarhos, G. J.; Baumann, T. F.; Satcher, J. H. "Nuclear Magnetic Resonance Studies of Resorcinol-Formaldehyde Aerogels" *J. Phys. Chem. B* **2005**, 109, 11215.