

Characterization of Carbon Nanostructures in Pd Containing Activated Carbon Fibers Using Aberration-Corrected STEM

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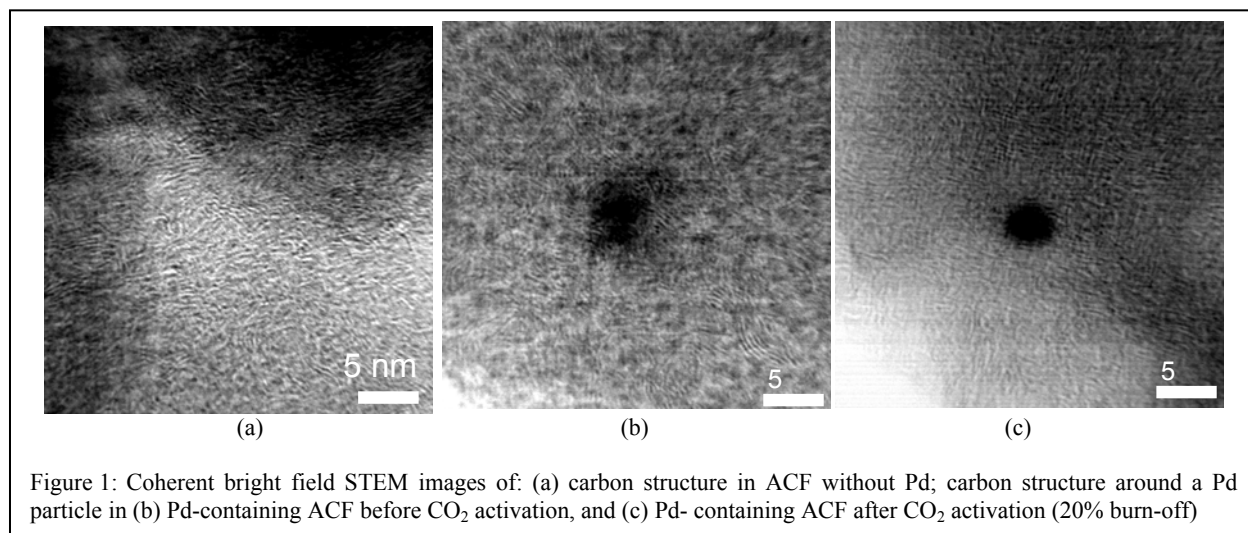
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This effort is part of the project on “Atomistic Mechanisms of Metal-Assisted Hydrogen Storage on Nanostructured Carbons”. The objective is to obtain an in-depth characterization of atomic structures in Pd-doped activated carbon fibers (ACF) using sub-angstrom resolution electron microscopy, and to correlate these structures with their hydrogen storage properties.

The aberration corrected scanning transmission electron microscope (STEM) at ORNL currently provides a lateral spatial resolution of 0.67 Å, given by the electron beam diameter. The small diameter beam also brings greatly improved sensitivity and allows for single metal atom detection on light supports, such as carbon. Particle size and shape can also be extracted directly from Z-contrast images formed by monitoring transmitted electrons scattered to high angles using an annular detector. A significant advantage of the aberration corrected STEM is that it enables a high quality conventional phase contrast image to be obtained simultaneously with the Z-contrast image; this allows direct imaging of lattice structures in carbon and carbon-supported materials. In addition, measurements of electron energy-loss spectroscopy (EELS) enable the determination of the local electronic structures at about 0.1 nm spatial resolution, and of the local bonding character on carbon atoms. In particular, the K-ionization edge of carbon atoms provides information about the unoccupied local density of states, which is used to quantify the sp^2/sp^3 hybridization ratios.

A series of carbon fiber materials both with and without Pd (in the 1-2 wt% range) were prepared from an isotropic pitch precursor. The fibers were carbonized and activated in CO_2 to various degrees of burn-off. For the Pd-containing ACF, a Pd salt was mixed with the pitch precursor prior to spinning and heat treating. This process differs from the synthesis method of most carbon-supported Pd catalysts where the metal is added to a pre-existing carbon support.

The aberration-corrected STEM was used to characterize the atomic and electronic structure of carbon atoms in the vicinity of embedded Pd particles. Preliminary results show that



the development of atomic structures in Pd-doped carbons is influenced by the presence of Pd particles. The bulk of most materials is amorphous (turbostratic carbon). Small domains of organized carbon nanostructures consisting of quasi-parallel, although undulated, graphene layers were also identified. It seems that most Pd-containing carbons showed the presence of onion-like superstructures, which have not been observed in ACF without Pd (Figure 1).

High resolution images of the Pd-carbon interface in carbonized samples prior to CO₂ activation revealed a significant degree of order in the carbon atoms around the Pd nanoparticles (Figure 1b), although no Pd atoms were seen in the Z-contrast image. These "graphitic" regions were much less visible on materials activated to a 20 % burn-off (Figure 1c) which showed a typical amorphous speckle pattern. It seems that activation in CO₂ not only contributes to

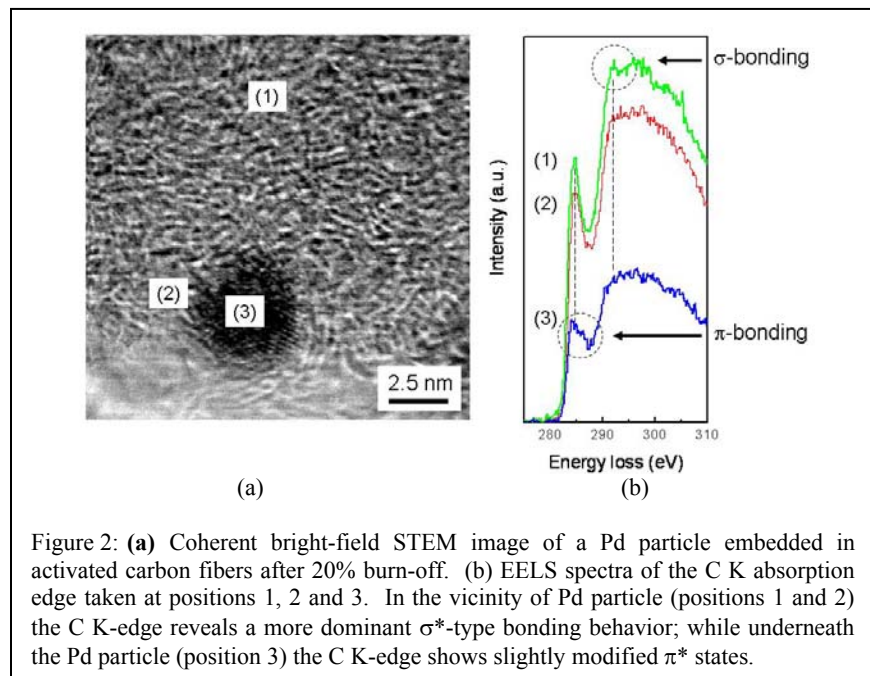


Figure 2: (a) Coherent bright-field STEM image of a Pd particle embedded in activated carbon fibers after 20% burn-off. (b) EELS spectra of the C K absorption edge taken at positions 1, 2 and 3. In the vicinity of Pd particle (positions 1 and 2) the C K-edge reveals a more dominant σ^* -type bonding behavior; while underneath the Pd particle (position 3) the C K-edge shows slightly modified π^* states.

development of microporosity in carbon, but also frees the Pd particles from surface carbon deposits; this is probably an effect of the catalytic action of Pd during carbon gasification (activation) with CO₂.

The EELS spectra collected at various positions around Pd particles revealed spatial differences between the dominant types of bonding characteristic for carbon atoms. In the vicinity of Pd particles, the bonding character was more of σ^* -type, while underneath the

Pd particles, the EELS spectra showed slightly modified π^* states (Figure 2).

Future Aspects:

Aberration corrected STEM not only enables the formation of sub-Angstrom electron probe sizes but also greatly decreases the depth of focus due to the use of larger illumination angles. By recording images through the acquisition of through-focal series, STEM imaging becomes a three-dimensional imaging technique comparable to confocal microscopy. In the future, three-dimensionally imaging of the embedded Pd particles will be used to study the three-dimensional shape and distribution of the catalyst particles and the true 3D structure of the surrounding carbon material. Furthermore, this technique will also be combined with electron energy-loss spectroscopy to record three-dimensional sp^2/sp^3 ratio volumes.