

# MICROSTRUCTURAL CHARACTERIZATION OF ACTIVATED CARBON FIBERS USING ABERRATION CORRECTED SCANNING TRANSMISSION ELECTRON MICROSCOPY

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## Introduction

The use of nanostructured carbon materials for hydrogen storage attracted a renewed interest because of the significant advantage of using a light weight and reasonably inexpensive material. Physisorption of H<sub>2</sub> on nanoporous carbon, although significant at cryogenic temperatures, is however too weak at room temperatures (David, 2005) and does not satisfy the DOE goals. Nevertheless, hydrogen uptake is enhanced on carbon materials modified either by chemical activation (Basova, 2005) or by doping with catalysts, in comparison to unmodified carbons (Anson, 2006). Previous results have shown that a significant enhancement of H<sub>2</sub> adsorption (at room temperature and 20 bar) was obtained for activated carbon fibers modified with supported Pd catalyst particles (Gallego, 2006). To control such processes in greater detail an understanding of atomistic mechanisms of metal-assisted hydrogen storage on nanostructured carbons is necessary. The objectives are to better understand the intrinsic relationship between hydrogen adsorption properties and local nanostructures in carbon, and leveraging it to produce carbon and Pd nanostructures that enhance catalytic effects in metal-assisted hydrogen storage on carbons.

The materials studied were activated carbon fibers, with and without Pd, prepared at Clemson University from an isotropic pitch precursor (Jorda-Beneyto, 2007). Their surface properties, microporosity, and equilibrium and kinetic parameters of H<sub>2</sub> uptake were characterized. The excess H<sub>2</sub> adsorbed in presence of Pd exceeds the amounts expected based solely on formation of Pd hydride, thus supporting the spillover mechanism (Lueking, 2004). Based on analysis of equilibrium and kinetic data on H<sub>2</sub> adsorption, two different processes have been identified: physical adsorption (favored by high pressure and low temperatures) and an activated process (at low pressures only and favored by an increase in temperature).

The high-pressure process in the range of ~0.4 to 20 bar is most probably physical adsorption, similar to the room-temperature process observed on Pd-free carbon. For the low-pressure process, the mechanism based on catalytic dissociation of H<sub>2</sub> on the catalyst nanoparticles, followed by surface diffusion, so called “spillover”, of atomic H and storage at sites that would otherwise be inaccessible to molecular H<sub>2</sub>, is considered highly probable.

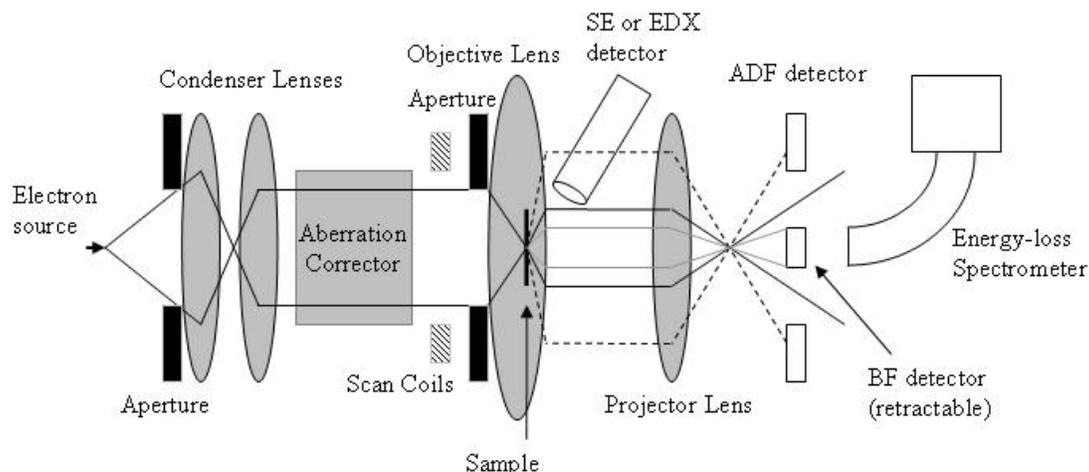
However, a detailed understanding of the microstructural evolution of activated carbon fibers in the presence of Pd catalyst particles is essential to determine active storage sites for a future design of more effective storage materials. The distribution of Pd particle sizes and its dependence on the materials processing conditions might be a critical factor for the final storage capabilities. Secondly, preexisting Pd particles in the carbonaceous precursor can have an effect on the atomic and electronic structure of carbon during the carbonization and activation process. Finally, and maybe most importantly, the local carbon microstructure in the immediate vicinity of dispersed Pd nanoparticles is expected to have significant influence on the spillover mechanism and, therefore, on the final storage capabilities. Aberration-corrected scanning transmission electron microscopy (STEM) is an ideal tool to investigate the microstructural evolution of carbon materials in the presence of heavy catalyst elements such as Pd. A combination of high resolution imaging and spectroscopy capabilities provides access to both atomic and electronic structures of the carbon fibers, the Pd nanoparticles and the atomically structured interfaces in between. In this paper, we report first preliminary results demonstrating how atomic resolution STEM provides detailed information about the activated carbon microstructure in the presence of both nano-sized Pd catalyst particles and single Pd atoms dispersed throughout the microstructure.

## Experimental Details

In the framework of this study scanning transmission electron microscopes have been used for electron microscopy investigations of the carbon fibers microstructures. Figure 1 shows a sketch view of a dedicated STEM. The electron beam, generated by a cold field-emission source is de-magnified by a set of condenser lenses and finally focused by an objective lens onto the sample. The so-formed electron probe scans across the sample and transmitted electrons can be detected by a variety of different detectors such as but not limited to annular dark-field (ADF), bright field (BF), secondary electron (SE) detectors and electron energy-loss and energy dispersive X-ray (EDX) spectrometers. The enormous advantage for an experimental setup such as the one described here is that in principle all these different signals can be acquired simultaneously, hence providing a maximal output of experimental data and direct spatial correlation of atomic and electronic structures and local chemistry.

The invention and application of aberration correctors to STEM (Krivanek, 2003) has enabled the characterization of materials with unprecedented detail. Direct effects of aberration correction include the availability of larger convergence

angles and hence the formation of electron probe sizes of less than 0.08 nm (Nellist, 2006) and a reduced depth of field to 3-4 nm enabling 3D “confocal STEM” (van Benthem, 2005 and 2006, Borisevich, 2006). Aberration correction also leads to “slower” oscillations of the phase contrast transfer function so that larger axial detectors can be used, allowing, according to the theorem of reciprocity, an aberration-corrected bright-field phase-contrast image to be formed with enhanced signal. Therefore, reliable and very high resolution BF and ADF images can be acquired simultaneously with pixel-to-pixel correlation. Due to the fact that the electron beam current is conserved upon decreasing the probe size, effectively brighter probes are formed after correcting lens aberrations. As a consequence the available signal-to-noise ratio in ADF images is significantly increased, generating enhanced sensitivity and enabling single atom detection.



**Figure 1.** Sketch of an aberration-corrected dedicated scanning transmission electron microscope. Electron trajectories at the edge of the apertures are indicated by solid lines. High angle scattering used for the formation of ADF images is represented by dashed lines while low angle scattering forming aberration-corrected bright field images is indicated by grey lines.

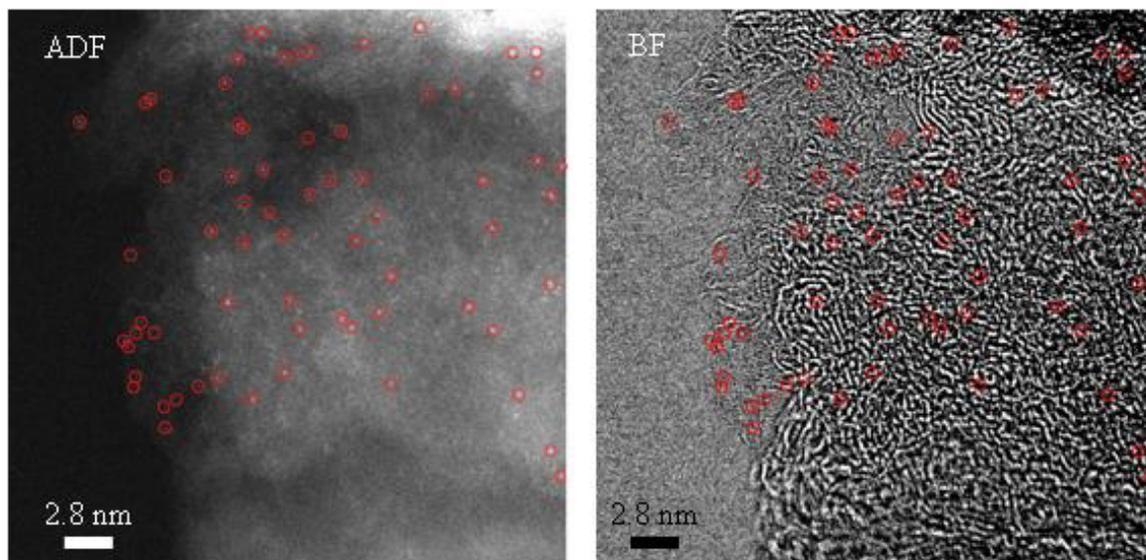
In this report we demonstrate the electron microscopic capabilities for microstructural investigations of activated carbon fibers with embedded Pd catalyst particles. The results shown were obtained from a sample processed at Clemson University. An isotropic pitch precursor was mixed with about 1% Pd salt before melt-spinning. The traditional subsequent carbonization and activation processes were combined into a single stage process of “direct carbonization and activation” in pure CO<sub>2</sub>, and samples with various levels of burn-off were generated. The particular material used for the results presented below is characterized by the direct activation process and a burn-off level of 40%. Further details of the materials processing can be found in (Tekinalp, 2007). The hydrogen storage characteristics are not subject of this report and are reported elsewhere (Contescu, 2007)

## Results and Discussion

ADF images, often referred to as Z-contrast images, are very sensitive to heavy elements since the scattering cross-section is roughly proportional to the squared atomic number  $Z^2$  of the illuminated species (ref11). At the same time, BF images are very sensitive to light elements in the sample, so that simultaneous acquisition of these images with pixel-to-pixel correlation at very high resolution becomes a very powerful tool for the investigation of carbon microstructures in the presence of catalytic Pd particles. Figure 2 shows a pair of ADF and BF images, which were acquired with a VG Microscopes HB603 U STEM operated at 300 keV. The microscope is equipped with a Nion third-order aberration corrector, as it is sketched in Figure 1. Bright contrasts in the ADF image shown in Figure 2 represent small Pd clusters and, in many times, even single isolated Pd atoms distributed throughout the carbon microstructure. Through-focal series acquisition of ADF images was used to determine whether the observed bright contrasts are due to single or multiple Pd atoms. The vertical resolution for this type of “confocal” STEM is 7-8 nm (van Benthem, 2006; Borisevich, 2006), which is comparable to an observed visibility range of 7-10 nm. Therefore, we conclude that the observed bright contrasts labeled in the ADF image in Figure 2 are due to single isolated Pd atoms. However, in many cases the Pd atoms became very mobile due to illumination with the electron beam and could not be imaged at the exact same region in a subsequently acquired frame but at a nearby location.

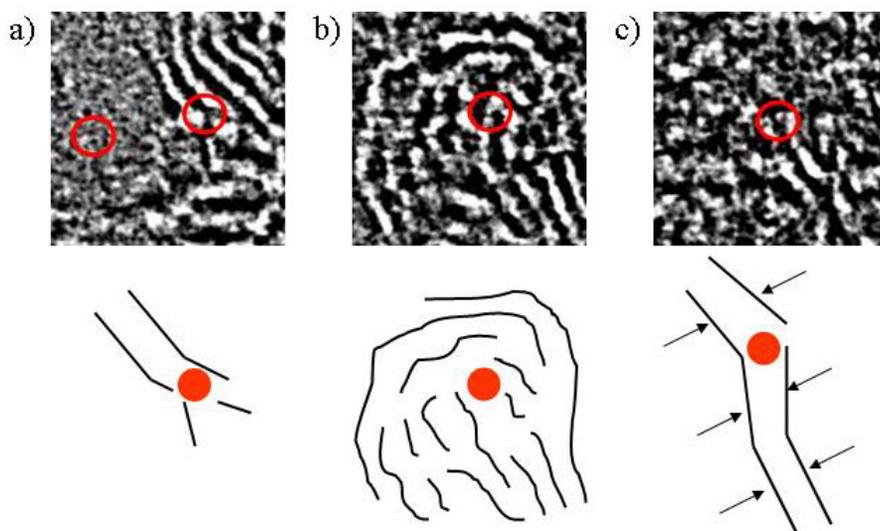
The simultaneously acquired BF image clearly shows the carbon microstructure exhibiting graphene sheets in various different orientations. However, it is evident that the carbon fiber material is somewhat disordered on a larger length scale, but reveals some structural ordering with parallel but bent graphene layers. The overall contrast in the ADF image varies in

steps from dark on the left to lighter gray on the right side, indicating different specimen thicknesses in the direction parallel to the electron beam. In the upper right corner the ADF image shows a bright contrast region which appears significantly dark in the BF image. This contrast is due a larger Pd particle extending into the field of view when this set of images was acquired.



**Figure 2.** Pair of annular dark field (ADF) and bright field (BF) STEM images acquired simultaneously. The frames have pixel-to-pixel correlation, so that the location of single Pd atoms in the ADF images (circled) can be superimposed on the BF image, which is sensitive to the local carbon microstructure.

Figure 3 shows three magnified areas extracted from the BF image shown in Figure 2. In Figure 3a one Pd atom is located within a highly disordered, most likely amorphous region in the carbon microstructure, while a second Pd atom is located in between two graphene sheets. At the location of this Pd atom, a third graphene sheets terminates, as it is sketched below. Figure 3b contains a different case in which a Pd atom is surrounded by multiple almost concentric graphene sheets. A third configuration was observed in which Pd atoms are located in between two quasi-parallel sheets which reveal slightly increased distances at and close to the Pd atom location.



**Figure 3.** Three areas extracted from the BF image in Figure 2. The location of single Pd atoms is marked. In the lower sketches white image contrasts are represented by lines while the Pd atoms are marked by filled circles.

The combined ADF and BF imaging analysis shown in Figures 2 and 3 demonstrates that graphene sheets are bent close to embedded Pd atoms, which indicates local strain variations in the carbon microstructure. Such bending and associated straining exhibits the presence of nano-sized voids or pores in the carbon microstructure, which are therefore correlated with the presence of single Pd atoms. At this stage we can so far not determine whether these nano-pores result from the presence of isolated Pd atoms during the carbonization process, or whether the Pd atoms are primarily embedded into already existing nano-pores during this process. However, it is very likely that the identified configurations shown in Figure 3 may represent local storage sites for atomic hydrogen after the spillover process, encouraged by the presence of the metal catalyst. First but still preliminary data indicated that a through-focal series acquisition of BF images has indicated some three-dimensional information about the carbon microstructure.

## Conclusions and Outlook

Aberration-corrected STEM was used to simultaneously acquire ADF and BF images of activated carbon fibers with embedded Pd catalyst particles. Electron probes with diameters below 1 Ångström provide single atom sensitivity in ADF and increased signal-to-noise ratios in BF STEM images. Due to pixel-to-pixel correlations in both images, the local carbon microstructure was correlated with single Pd atom locations. Some structural configurations were identified which were observed many times in many different areas of the microstructure. In the future, through focal series acquisition of simultaneous ADF and BF images might be able to provide three-dimensional atomic structure data of these configurations.

The occurrence of quasi-parallel (though bent and undulated) carbon layer features (graphenes) is a clear sign of incipient short range ordering in the carbon microstructure. Such short range ordering induces local changes in the electronic structure, since for parallel graphene sheets stronger  $sp^2$  hybridization is expected (Capehart, 1989). Therefore, the near-edge structures of the C-K absorption edge in electron energy-loss spectroscopy can be used to locally determine  $sp^2/sp^3$  hybridization ratios (Muller, 1993). In the future, we plan to use such techniques to characterize local bonding behaviors in areas such as those shown in Figure 3. It was shown that the occurrence of aromatic layer stacking, lateral associations and preferred orientation of basic structural units in carbon materials can be correlated with the Li storage capacity of Li ion battery electrodes (Hayashi, 2000). It may be hypothesized in an analogous way that the carbon microstructure revealed by high resolution electron microscopy and the distribution of local  $sp^2/sp^3$  hybridization ratios could possibly be correlated with the presence of specific local structures in carbon that might be responsible for the hydrogen uptake on the macroscopic scale. We expect that after a high spatial resolution mapping of hybridization ratios with aberration-corrected STEM atomic length-scale building blocks can be identified, which are most effective for hydrogen storage. Such fundamental understanding of the materials functionality will then lead to more effective design of future storage materials with significantly increased gas uptakes.

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