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Tomography and Spectroscopy of Structure and Degradation in Carbon Electrode Materials for Energy Conversion and Storage

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Carbon materials such as activated carbon and carbon black are popular for use in electrodes for energy conversion and storage due to their conductivity and relative inertness. However, these materials are not thermodynamically stable and show various forms of degradation after long-term use [1]. Because electrode systems are inhomogeneous at a variety of length scales, improving performance and diagnosing degradation mechanisms requires characterization techniques on the microscale and nanoscale. We use (scanning) transmission electron microscopy ((S)TEM), electron tomography, and electron energy-loss spectroscopy (EELS) alongside optical microscopy and spectroscopy to characterize the structure and degradation of carbon supercapacitor and fuel cell electrode materials.

Characterizing the 3D microstructure of electrode materials is crucial to understanding their behavior. In supercapacitors, the storage capacity is directly dependent on the electrode pore structure and surface area. Tomography is thus an invaluable characterization tool, allowing study of structural details and morphology that cannot be resolved in conventional 2D imaging [1]. In Figure 1, we image a Vulcan carbon black aggregate in the FEI Tecnai T12. Figure 1a shows the microstructure while Figure 1b shows the aggregate surface extracted from a tomographic reconstruction.
Many chemical changes that occur in energy storage electrodes exhibit energy transitions that are accessible to optical spectroscopy [2]. Here we study an activated carbon supercapacitor cathode, which upon electrochemical aging shows a dramatic shift toward the blue-violet over large areas of the cathode in optical imaging and spectroscopy (Figure 2). The same chemical changes observed in optical spectroscopy on the micron scale can be probed at the nanoscale using valence EELS. Valence EELS also enables determination of electronic structure information such as the optical gap of the material. In energy-filtered TEM (EFTEM) these features can be mapped spatially across a sample on the nanoscale. Investigating microtomed sections of this material using STEM-EELS and EFTEM in a monochromated FEI Tecnai F20, we find that a 100 nm passivating layer has formed on the carbon surface (Figure 3). Valence EELS measurements (Figure 3a) on the layer show the absence of a free carrier tail, indicating that the layer has an optical gap and poor conductivity. The primarily elastic 0 eV EFTEM images show the layer covering the surface of the activated carbon (Figure 3b). The EFTEM images selecting the π-π* peak at 6 eV highlight the activated carbon, while the surface layer show more saturated bonds.

The combination of electron tomography, EELS, and optical spectroscopy allow thorough characterization of the structural, chemical, and electronic properties of electrode materials at the micron and nanoscale. Together they are powerful tools for understanding the performance and degradation of devices for energy storage and conversion.[3]

References:
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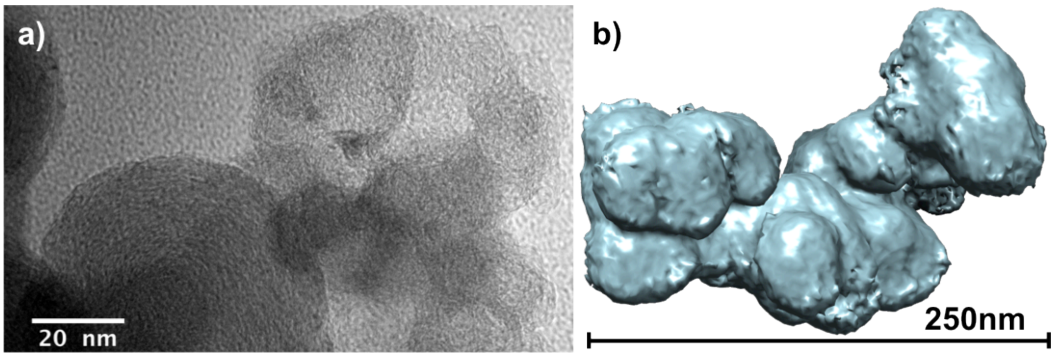

Fig. 1. (a) BF TEM of Vulcan carbon black primary particles. (b) Tomogram of a Vulcan aggregate.

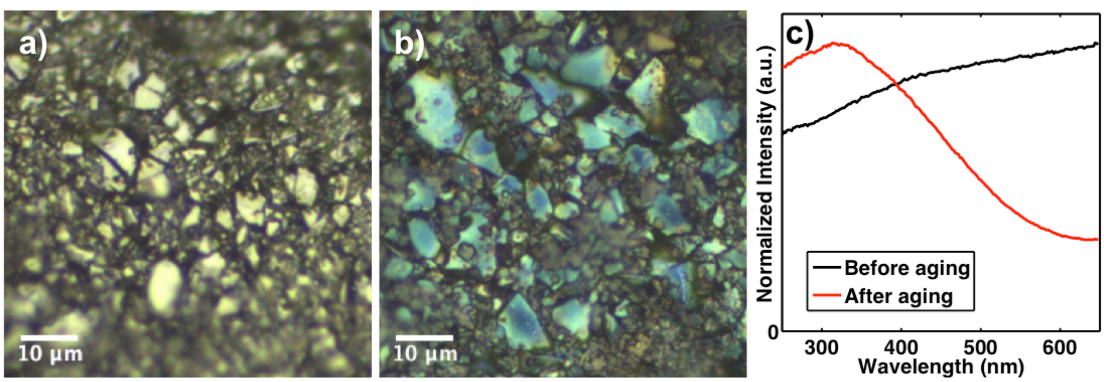

Figure 2. Optical images of a supercapacitor cathode taken (a) before and (b) after electrochemical aging, which resulted in a color change of many of the carbon grains. (c) UV-visible reflection spectroscopy shows a shift towards reflection in the blue/violet.

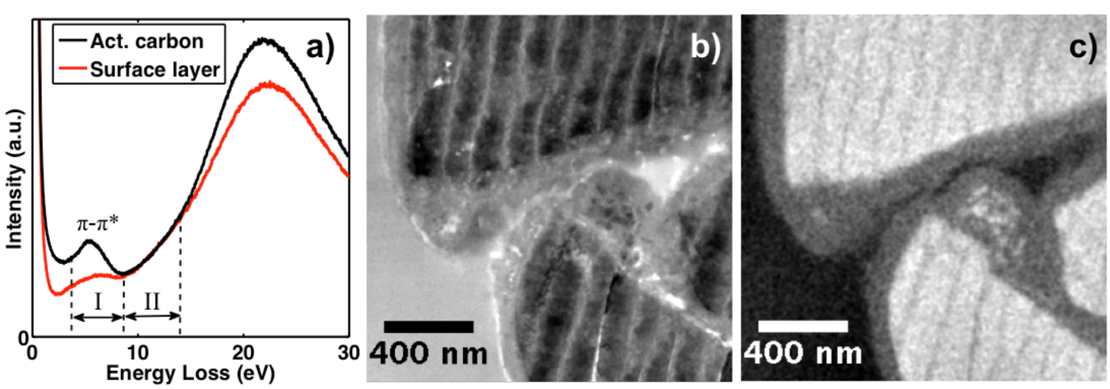

Figure 3. Valence EELS and EFTEM of an activated carbon supercapacitor electrode, which developed a passivating layer on the surface after electrochemical aging. (a) Valence EELS of activated carbon shows a π-π* transition peak and a free-carrier tail, indicating conductivity. These features are absent in the surface layer spectrum. EFTEM with 2.5eV slit of carbon and passivating layer: (b) elastic zero-loss image and (c) averaged EFTEM images in energy window I selecting the π-π* peak normalized by images in window II. The activated carbon is highlighted due to its π