

## Direct Observation of Pseudocapacitor Electrode Behavior During Electrochemical Biasing using *in-situ* Liquid Stage Electron Microscopy

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With the rapid rise of global energy demand and the negative environmental consequences incurred from decades of reliance on fossil fuels, there is a tremendous need to develop and implement cleaner, more sustainable, and renewable energy production methods. The performance of these alternative energy generation technologies is intimately linked, and thus limited by the ability to efficiently store and retrieve the electrical energy produced. Wind, solar and geothermal energy generation, as well as electric-powered automobiles and mobile devices, all require storage systems that combine high energy density and high power density electrical energy storage capabilities to enhance performance and become viable alternatives to current fossil fuel based equivalents. Recently, highly porous carbide-derived carbon (CDC) structures have attracted attention for electrical energy storage as supercapacitor electrodes. These high surface area carbon structures store charge through the formation of an electric double layer at the electrode-electrolyte interface, enabling rapid charging and discharging (high power density) but possess relatively low energy density. For many energy storage applications, the low energy density of supercapacitors is prohibitive to large-scale implementation and the used of batteries is usually preferred, which charge/discharge much more slowly than supercapacitors, but can provide high energy density to a composite storage system. For this reason, increasing the energy density (the amount of charge that can be stored) is a major goal for next generation supercapacitor-based storage materials, broadening their range of suitable applications [1].

By synthesizing CDCs with imbedded transition metal-oxide nanoparticles within the carbon's pore structure, significant increases in specific capacitance and energy density have been obtained. This new class of energy storage materials, called pseudocapacitors, store charge through a combination of the electric double-layer at the CDC surface and reversible redox reactions (faradaic) at the metal-oxide nanoparticle surface. In the case of Nb<sub>2</sub>O<sub>5</sub>/CDC pseudocapacitors, it has been observed through *ex-situ* TEM, XRD and voltammetry that the phase of the Nb<sub>2</sub>O<sub>5</sub> nanoparticles largely determines the storage properties of the material, with crystalline Nb<sub>2</sub>O<sub>5</sub> phases showing much larger specific capacitance than amorphous Nb<sub>2</sub>O<sub>5</sub>. In this system, ~5-20 nm Nb<sub>2</sub>O<sub>5</sub> nanoparticles, both crystalline and amorphous, are distributed throughout the pore structure of the CDC support, both on the surface and deep within pores (Figure 1). After electrochemical operation (lithiation) of the Nb<sub>2</sub>O<sub>5</sub>/CDC in a 3-electrode cell with Li counter/reference electrodes, a 3% increase in crystalline lattice spacing occurs in the Nb<sub>2</sub>O<sub>5</sub> nanoparticles and a solid electrolyte interface (SEI) builds up at the nanoparticle/electrolyte interface.

Upon delithiation, no evidence of structural changes to the enlarged  $\text{Nb}_2\text{O}_5$  lattice or SEI layer have been seen by *ex-situ* analysis, but the study of this step has been limited thus far [2]. The changes to the  $\text{Nb}_2\text{O}_5$  electrode structure and electrolyte that develop during electrochemical operation are critical to both the capacitive properties of the energy storage system during a single charge/discharge cycle and the long term functionality and stability of the system over many cycles. To provide a deeper understanding into these dynamic processes at the atomic scale, an *in-situ* characterization technique is needed that enables direct observation of structural changes during electrochemical operation.

*In-situ* liquid stage electron microscopy is a rapidly growing field of materials characterization and has been used to study the growth and dynamics of inorganic and organic structures within many different liquid environments on the atomic scale [3,4]. New developments in this field allow electric potentials to be applied to two/three electrode systems while imaging under the electron beam. In this study we use a Hummingbird *in-situ* liquid stage and electrochemical biasing chips with Pt electrode contacts over the electron transparent windows (Li counter/reference electrodes) to observe the  $\text{Nb}_2\text{O}_5$ /CDC working electrode during electrochemical cycling in the presence of EC/DMC electrolyte. No longer being limited to *ex-situ* characterization and inferences about the dynamic processes that have transpired, we are able to directly observe the changes in lattice structure and volume occurring in the  $\text{Nb}_2\text{O}_5$  nanoparticles during lithiation/delithiation as well as the process of SEI formation at the electrode/electrolyte interface [5].

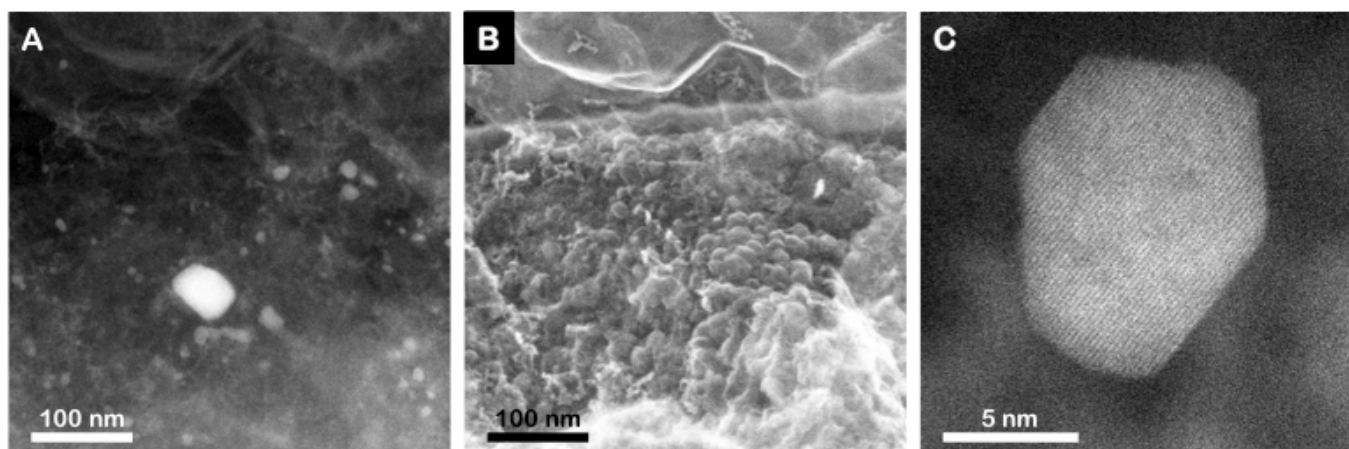
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**Figure 1.** Z-contrast STEM (A) and secondary electron (B) images of identical region of pristine  $\text{Nb}_2\text{O}_5$ /CDC pseudocapacitor electrode. The CDC support is highly porous (B), and  $\text{Nb}_2\text{O}_5$  nanoparticles ( $\sim 5$ -20 nm, with one large NP) are predominantly located within the CDC pore structure with some on the outer CDC surface. (C), high magnification Z-contrast STEM image of pristine crystalline/faceted  $\text{Nb}_2\text{O}_5$  nanoparticle within the CDC structure. All images are prior to electrochemical biasing.