Electroanalytical Performance of Nitrogen-Containing Tetrahedral Amorphous Carbon Thin-Film Electrodes

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The diamond-like carbons, of which ta-C belongs, is a class of materials that has been comparatively unstudied in terms of their electrochemical properties and electroanalytical performance is diamond-like carbon.[1-5] These are composite materials consisting of a mixture of sp^2 and sp^3-bonded carbon. Impurities can be incorporated during growth (e.g., N) further adding to their complex structure. Tetrahedral amorphous carbon (ta-C) is one material that has received study over the years.[6] These films typically possess 40-60% sp^3-bonded carbon. It has been widely used as a protective coating due to its hardness, high wear resistance and low coefficient of friction. The growth temperature for ta-C is usually from 25 to about 100 °C. This means that non-traditional materials, such as plastics, can be used as substrates for deposition. Ta-C films generally need to be grown thin (100's of nanometers) in order to minimize internal stress. Stressed films tend to delaminate from a substrate. We will report on the characterization and basic electrochemical properties of these new electrode materials.

Small-spot EELS measurements were made to assess the local carbon bonding in ta-C films with different levels of incorporated nitrogen. The carbon K-edge spectra for the ta-C and ta-C:N films are presented in Figure 1A. Figure 1B presents characteristic reference spectra for a pure sp^3 carbon material, diamond, and a pure sp^2 material, multiwall carbon nanotubes (MWCNTs). Unlike the reference spectrum for diamond that consists of a well-defined σ^* absorption edge at 289.5 eV and a second bandgap feature at ca. 302.0 eV, the spectra for the ta-C and ta-C:N films all consist of a π^* peak at 285.4 eV that arises from the sp^2-bonded carbon domains, as well as a broad and more intense sp^3 carbon σ^* absorption edge. The spectrum for each of the films is characteristic of a mixed-microstructure (sp^2/sp^3) material.

The curve area between 280 and 285.4 eV is reflective of the amount of sp^2-bonded carbon (π) in the probed region while the curve area from 285.4 to 292.4 eV is indicative of the sp^3-bonded carbon (σ) content. Therefore, the σ/π area ratio provides an estimate of the sp^3 relative to the sp^2-bonded carbon content in the films. The fraction of sp^2-bonded carbon increases with increasing nitrogen incorporation.
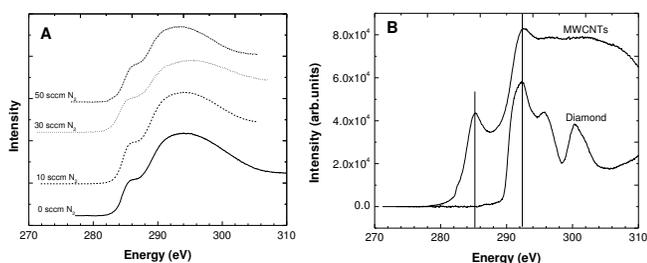
Figure 1. (A) Electron energy loss spectra (EELS) at the C K edge for (A) ta-C films deposited with 0, 10, 30 and 50 sccm N_2. (B) Reference spectra for single crystal diamond (pure sp^3) and multiwall carbon nanotubes (pure sp^2).[7]

Figure 2 shows cyclic voltammetric i-E curves for the ta-C and ta-C:N films in the presence of 1mM $Ru(NH_3)_6^{2+/3+}$ in 1 M KCl. $Ru(NH_3)_6^{2+/3+}$ is classified as outer-sphere redox couple and generally involves simple electron transfer at carbon electrodes. k^o for this redox couple is relatively insensitive to the surface microstructure, surface oxides and the adsorbed monolayers on sp^2 carbon electrodes.[7] The heterogeneous electron-transfer rate constant is mainly controlled by the electronic properties of the electrode (i.e., carrier mobility and carrier concentration). Well-defined, peak-shaped curves are seen for all the films. Essentially reversible (Nernstian) behavior is seen as the peak separation potential, ΔE_p, is 59 mV for all four films. Plots of i_p^{red} vs. $v^{1/2}$ were linear for all four films between 0.1 and 0.7 V/s ($R^2 > 0.99$),
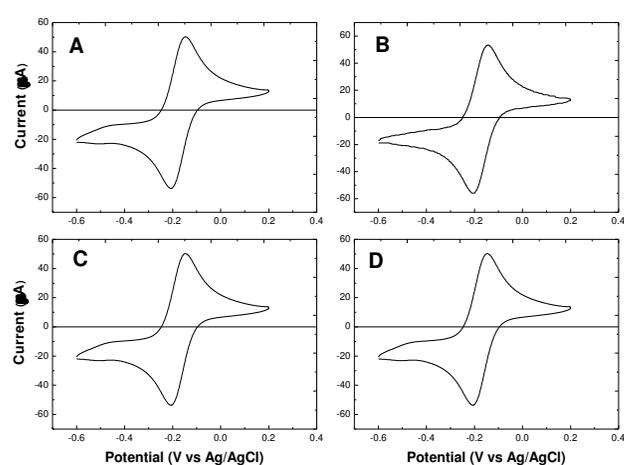
Figure 2. Cyclic voltammetric i-E curves for (A) ta-C, (B) 10 sccm N_2, (C) 30 sccm N_2, and (D) 50 sccm N_2 ta-C:N films in 1 mM $Ru(NH_3)_6^{2+/3+}$ + 1 M KCl. Scan rate = 0.1 V/s. Geometric area = 0.2 cm^2.[7]

which indicates the current is controlled by semi-infinite linear diffusion of the analyte to the electrode surface. The i_p^{ox}/i_p^{red} ratios were near unity for all four electrodes confirming the chemical reversibility of the redox reaction. Near-Nernstian behavior was observed for this redox system at all the ta-C films at the scan rates employed. Therefore, we were unable to extract k^o_{app} (est. ~0.1 cm/s) values from the data as the system was behaving reversibly.

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