



## Electrochemical Transformation of SWNT/Nafion Composites

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The electrochemical performance of single wall carbon nanotube (SWNT)/Nafion composite electrodes were studied in sulfuric acid solutions. Electrochemical oxidation of the highly dispersed SWNTs within the Nafion matrix results in a dramatic morphological change in the SWNTs. As evidenced by transmission electron microscopy, small bundles of straight-line SWNTs change into curved bundles with relatively sharp contours. Electrochemical impedance spectroscopy indicates increased electrochemical impedance in the oxidized SWNT/Nafion composites. Reduction of the composites at low potentials reverses impedance to near original values. However, the morphological change of the SWNTs is irreversible. In addition, the electrochemical capacitance of the composite electrode increases significantly after the oxidation-reduction cycle. Our results demonstrate that electrochemical oxidation and reduction treatment of the composite is also potentially useful for modifying the SWNT sidewalls, which results in an enhancement of the electrochemical capacitance of SWNTs.

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Since their discovery in the 1990s, single wall carbon nanotubes (SWNTs) have been examined as active electrodes for energy storage applications. For example, reports already exist on the evaluation of SWNTs as electrodes for lithium batteries,<sup>1,2</sup> supercapacitors,<sup>3,4</sup> and electrochemical hydrogen storage.<sup>5-8</sup> With respect to supercapacitors, the high surface area and excellent electronic conductivity of SWNTs make this material an attractive candidate for use as an active electrode. A capacitance value of 40 F/g has been reported when an SWNT electrode was evaluated in 6 M KOH.<sup>3</sup> It was suggested that redox reactions involving surface functional groups contribute significantly to the capacitance.<sup>3</sup> Consequently, oxidation of SWNTs should lead to increased capacitance. In addition, SWNTs may form composites with other electroactive materials such as conducting polymers to generate much higher capacitance.

For applications beyond energy conversion and storage, there is an increasing need in side-wall modification of SWNTs to make them more applicable to use in polymer composites as well as to open new materials chemistry opportunities in such areas as sol-gels and ceramics. The most effective approach in sidewall modification involves free-radical reactions. For example, electrochemical reduction of diazonium salts can readily functionalize SWNTs in a non-aqueous environment.<sup>9</sup> There are few studies concerning the electrochemistry of SWNTs in aqueous media. Most of the experiments were conducted in a potential range so that the oxidation or reduction of water does not occur. In this range, SWNTs behave like a capacitive material with an often featureless cyclic voltammogram (CV) with a very large capacitive current. Redox reactions involving surface functional groups are expected, while fundamental structural or electrical properties of SWNTs do not change in this voltage range.

In this paper, we report on an examination of the electrochemistry of SWNT/Nafion composites in aqueous media over a wide potential range so as to include both hydrogen and oxygen evolution. Prior to oxygen evolution, SWNTs within the composite undergo an oxidation reaction which appears to alter their morphology within the polymer matrix which has the additional effect of variations in electrochemical impedance. A subsequent reduction process of the oxidized SWNTs can also be observed which again changes the composites electrochemical impedance properties. We have also found that the electrochemical capacitance can be significantly enhanced by the oxidation-reduction cycle.

The SWNTs used in this study were purchased from Carbon

Nanotechnologies, Inc., *i.e.*, HiPco or h-SWNTs. The h-SWNTs were purified according to the procedure established by Chiang *et al.* The purity of the final SWNT samples was determined quantitatively using thermogravimetric analyses (TGA) in conjunction with inductively coupled plasma spectroscopy,<sup>10</sup> and qualitatively by field emission scanning electron microscopy (FESEM), UV-vis-NIR spectroscopy, Raman spectroscopy, and transmission electron microscopy (TEM). The end result was a purified material that consistently contained at least 95 wt % single wall carbon nanotubes. Composites of Nafion and nanotube materials were prepared by dispersion of the SWNTs in a 5 wt % Nafion/2-propanol solution (Aldrich).<sup>11</sup> The appropriate amounts of purified h-SWNTs were added to the Nafion-2-propanol solutions to achieve 0.1 wt % nanotube loading within the final polymer membranes. The SWNT-Nafion solutions were first homogenized for five 10 min intervals to effectively disperse the SWNTs. The solutions were then exposed to high shear stirring at room temperature for 72 h. The solutions were subsequently centrifuged to remove any nondispersed materials. After centrifugation, the mass of any residue was determined and the percent by weight was adjusted accordingly. SWNT-Nafion composite electrodes containing 0.1% of SWNT by weight were fabricated by applying two drops of the solution directly onto a glassy carbon (GC) electrode. After the solvent evaporated, the electrode was heated for 15 min at 70°C. The average mass of the composites tested was 10 mg. The counter and reference electrodes were a platinum wire and a Ag/AgCl electrode, respectively. The electrolyte was a solution of 4.5 N H<sub>2</sub>SO<sub>4</sub>. Electrochemical impedance spectroscopy (EIS) measurements were carried out with a Solartron 1285 frequency response analyzer and a potentiostat Solartron 1260 controlled by a computer with the software Zplot and Corrware. The frequency range studied was 630 to 1 Hz. All measurements were made at the rest potential of the cell after each polarization steps. The  $\Delta V$  signal amplitude applied was  $\pm 5$  mV.

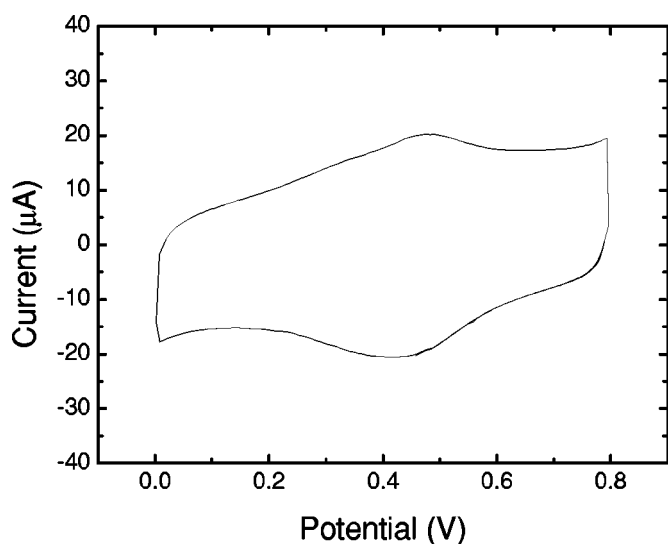
The electrochemistry of the SWNT-Nafion composite was studied with CV. Figure 1 shows a representative CV curve of an SWNT/Nafion composite electrode cycled between 0 and 0.8 V. The square shape of the CV curve indicates capacitive behavior of the electrode. In addition, a pair of broad, reversible redox peaks is superimposed over the square shaped curve. These two peaks are most likely associated with redox reactions of the surface functional groups of the SWNTs. It is well known that the openings at the ends of SWNTs are decorated with organic groups generated during the chemical oxidation process used for purification and tube opening.<sup>12</sup>

Figure 2a displays CV curves of a SWNT/Nafion composite coated on a GC electrode when the potential range was expanded to  $-0.7$  to  $+2.25$  V. On the first anodic scan, a broad oxidation peak was observed with a peak potential of 1.7 V. Significant oxygen evolution was not observed until after 2 V. On the subsequent cathodic scan, a reduction peak was centered at  $-0.1$  V. Even at  $-0.7$

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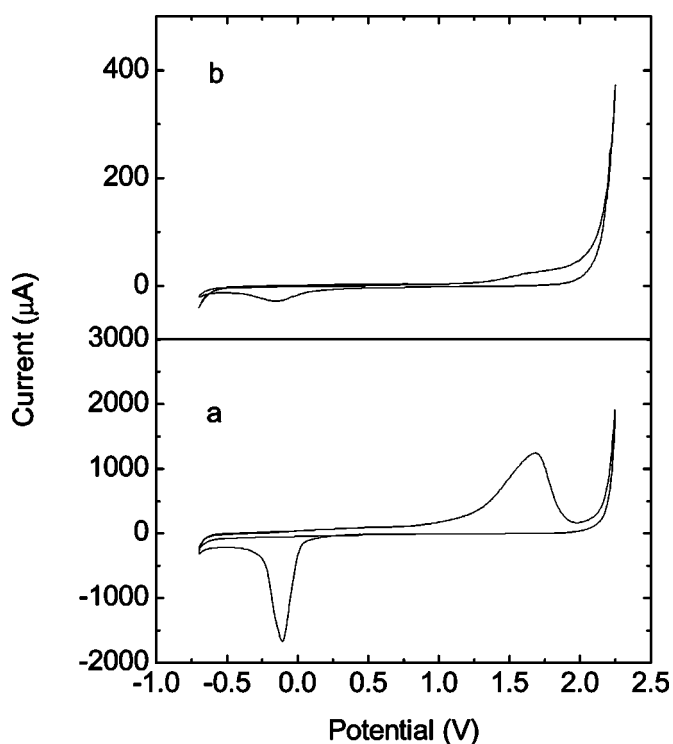
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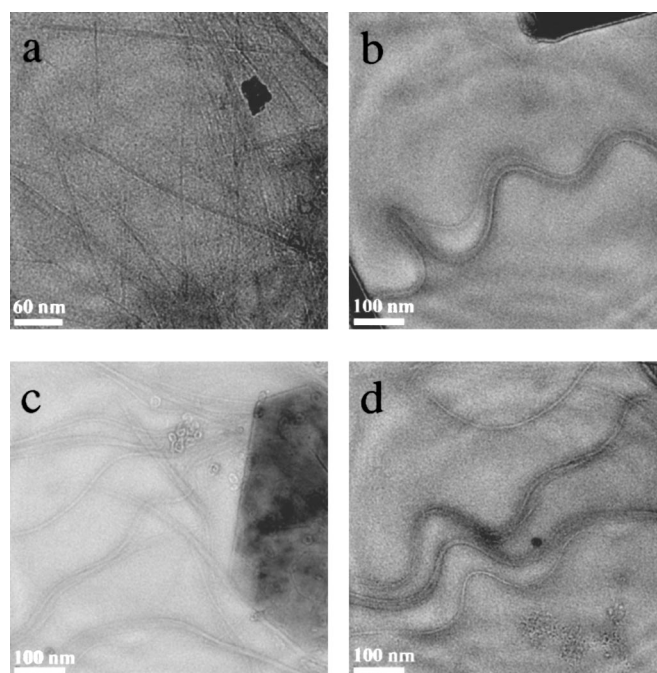


**Figure 1.** CVs of an as-prepared SWNT/Nafion composite electrode in 4.5 M  $\text{H}_2\text{SO}_4$ . Scan rate 50 mV/s.

V, no major hydrogen evolution took place. We found that the oxidation and reduction peaks, being 1.8 V apart, were in fact correlated to each other. It is suggested that the oxidation peak corresponds to oxidation reactions on the sidewalls of SWNTs. There have been extensive reports on the electrochemical activation of glassy carbon materials by themselves: an electrochemical oxidation process at extremely high potentials.<sup>13,14</sup> Figure 2b shows the CV curves of a GC electrode cycled in the same potential range as the SWNT/Nafion composite coated electrode. Indeed, a small broad peak can be seen from 1.5 to 2 V followed by a reduction process from 0.2 to -0.6 V. As evidenced by the CV plots, the similarities in the redox behavior between the composite coated electrode and the



**Figure 2.** CVs of carbon electrodes in 4.5 M  $\text{H}_2\text{SO}_4$ . (a) SWNT/Nafion composite and (b) glassy carbon electrode. Scan rate 20 mV/s.



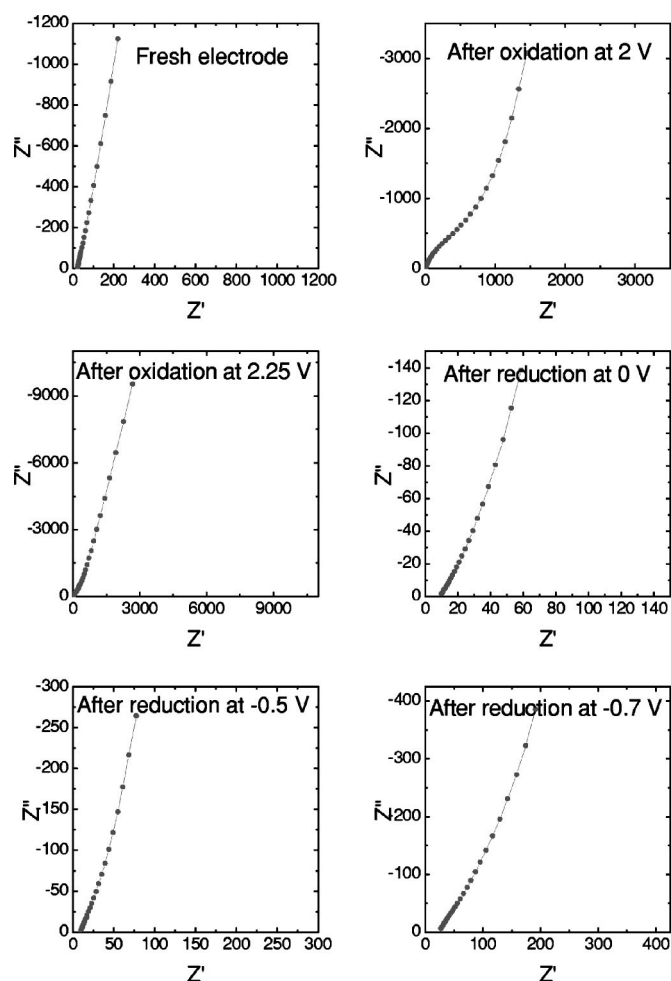
**Figure 3.** TEMs of SWNT/Nafion electrodes. (a) As-prepared, (b and c) oxidized at 2.0 V for 10 min followed by at 2.25 V for 10 min, and (d) subsequently reduced at 0.0 V for 10 min.

GC electrode indicate that the electrochemical reactions may also be similar. Electrochemical oxidation of GC is known to generate carboxylic acid and quinone functional groups<sup>15,16</sup> and it is reasonable to suggest that the same products are formed during the oxidation of SWNTs.

The structural changes in SWNT/Nafion composites during the electrochemical oxidation have been examined by TEM. Figure 3 shows TEMs of a SWNT-Nafion composite electrode before and after electrochemical treatment. SWNTs dispersed in the as-prepared composite exist as small bundles (of 6-7 SWNTs, ~8 nm diam). The bundling effect is due to the strong Van der Waals interactions between the SWNTs dispersed in the Nafion matrix. Figure 3b and c show selected images of the composite subjected to a two-step oxidation process (at 2 V for 10 min followed by oxidation at 2.25 V for an additional 10 min). Some remarkable changes in tube morphology are observed. The tube bundles are curved and bent due to the 2-step oxidation processes. Figure 3c appears to show that the act of bending the bundles may actually lead to separation of the SWNTs. Such dramatic changes in tube morphology are consistent with our suggestion that side wall oxidation can take place at high oxidative potentials which in turn introduce defects to the tube walls and cause the tubes to bend into curved shapes.

We also studied the impedance changes during redox reactions of the composite electrode via electrochemical impedance spectroscopy. The composite coated electrode was polarized sequentially at 2, 2.25, 0, -0.5, -0.7 V for 10 min each step. Data from 630 Hz to 1 Hz are shown at 10 data points per decade of frequency. As shown in Fig. 4, the Nyquist plot of the as-prepared electrode is a straight line indicative of capacitive behavior, which is consistent with the CV results. The impedance behavior starts to deviate from the ideal capacitive behavior after the electrode is oxidized at 2 V when a high frequency feature of a semicircle developed, which usually indicates a slower interfacial charge transfer process.<sup>17</sup> As shown in the accompanying Bode plot (Fig. 5), the real impedance (over the investigated frequency range) increased significantly upon oxidation. This trend continues when the electrode is further oxidized at 2.25 V.

The electrode was subsequently reduced by polarizing at increas-

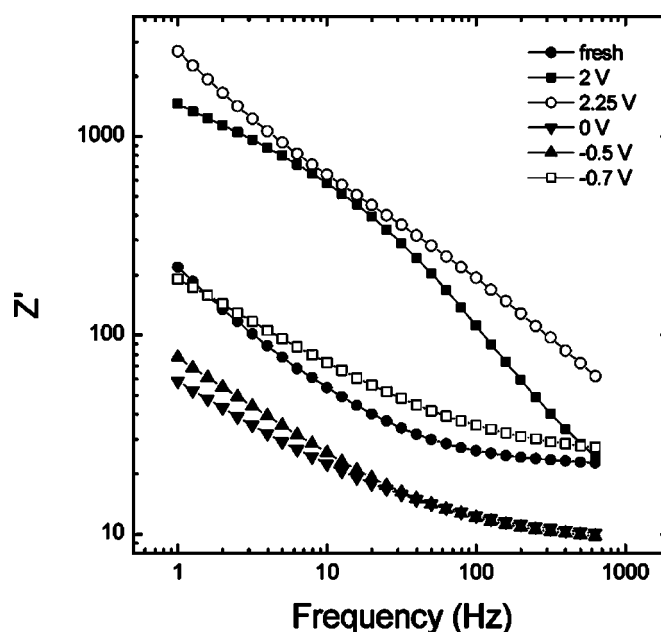


**Figure 4.** Nyquist plots of an SWNT/Nafion composite electrode. The composite coated electrode was polarized sequentially at 2, 2.25, 0,  $-0.5$ , and  $-0.7$  V for 10 min each step. Data from 630 to 1 Hz are shown at 10 data points per decade of frequency.

ingly negative potentials. Reduction at 0 V immediately reduced the impedance of the electrode to a level slightly lower than that of the as-prepared electrode. Moreover, the Nyquist plot of Fig. 4 again indicates a capacitive behavior. In essence, the impedance of the composite electrode is reversible during the redox cycle. Previous work on GC electrode reported similar reversible phenomenon.<sup>11</sup> While carboxylic groups are observed in infrared spectra after oxidation, release of carbon dioxide during reduction takes place before hydrogen evolution. However, the morphological changes observed in TEM after oxidation are not reversible. The curved features of the SWNT bundles remain intact as shown in Fig. 3d.

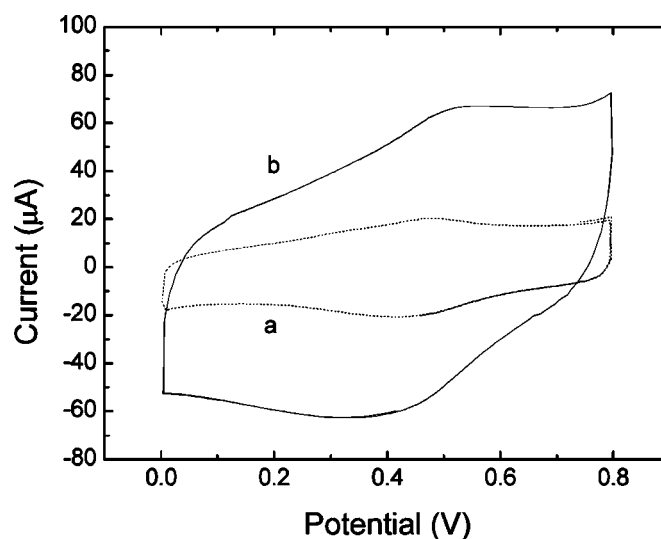
The redox cycle imposed on the SWNTs also enhances their electrochemical capacitance. Figure 6b shows the CV curves of an electrode after the redox cycle. When tested between 0 to 0.8 V, the capacitive current increased approximately three times when compared to that of the as-prepared electrode of Fig. 1. Such a significant enhancement in electrochemical capacitance is most likely due to the unraveling of SWNT bundles as observed in our TEM work of Fig. 3c. Impedance studies have shown that electrochemical reduction is required to regenerate the capacitive behavior. Oxidized SWNTs do not function as electrochemical capacitors as indicated by high charge transfer resistance data (2 V curve of Fig. 4).

In summary, we have shown that electrochemical oxidation of SWNT/Nafion composite electrodes at high potentials in a strong acidic media provides a new method of chemical modification of the SWNTs. The remarkable morphological changes derived after elec-



**Figure 5.** Bode plots of the electrode shown in Fig. 4.

trochemical oxidation are attributed to side-wall chemical modification of the SWNTs. Electrochemical impedance studies reveal that oxidized SWNTs exhibit high impedance values which can be reversed by electrochemical reduction of the SWNTs. The redox cycle also significantly enhances the electrochemical capacitance of the SWNT/Nafion composite electrode. The electrochemical oxidation method used in this study represents a new technique to modify the side-walls of SWNTs. Side-wall modification will make it more compatible for use in composites by providing reaction sites to attach other chemical functional groups. The electrochemical oxidation and reduction treatment of the SWNT/Nafion composite is potentially useful for modifying the SWNT sidewalls, which results in an enhancement of the electrochemical capacitance of SWNTs.



**Figure 6.** CVs of an SWNT/Nafion composite electrode in 4.5 M  $\text{H}_2\text{SO}_4$ . (a) For comparison, the CV curve of the as-prepared electrode of Fig. 1 is plotted as a dashed line, and (b) after oxidation at 2.25 V for 10 min followed by reduction at  $-0.5$  V for 5 min. Scan rate 50 mV/s.

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