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Electrochemical Characterization of Single-Walled Carbon Nanotube Electrodes

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The cyclic voltammetric responses and capacitive behavior of single-walled carbon nanotube sheets or papers are described. Broad redox responses have been observed in aqueous solutions that are probably due to the presence of oxygen-containing groups bound to the surface of the nanotubes or to the impurities produced during nanotube purification. The voltammetry and capacitance of the nanotube paper do not vary significantly when the chemical nature of the electrolyte ions is changed. In nonaqueous media, no redox responses are produced except in solutions of Li^+, where an intense reduction response, possibly due to lithium insertion into the nanotube bundles, is observed. Electrochemical impedance spectroscopy in aqueous solutions reveals the typical features associated with a porous material. Electrochemical quartz crystal microbalance studies in both aqueous and nonaqueous electrolytes show that the mass of the nanotube film increases as the potential is made more negative. These mass changes are affected by, but are not directly proportional to, the cation mass. In acetonitrile solutions of Li^+, a significant increase in mass associated with the suggested insertion of the cation is observed.
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Carbon nanotubes are of significant interest due to their unique properties and potential applications.[1-4] We are interested in using single-walled carbon nanotubes (SWNTs) as an electrode material suitable for electromechanical actuators.[5] Such application requires a good understanding of the electrochemical properties of SWNTs.

In this initial report, we describe some of the basic electrochemical characteristics of sheets of SWNTs. These sheets, called nanotube paper (NTP) due to their appearance, consist of SWNT bundles joined by mechanical entanglement and van der Waals interactions. The NTP shows high porosity and large surface area.[5,6] It is generally considered[1-6] that in the material used the nanotubes ends are closed and that the interstitial spaces between individual nanotubes inside a bundle are not accessible to the electrolyte. Consequently, the pores responsible for most of the surface area correspond to the void spaces between bundles. The techniques utilized for the characterization of the NTP were cyclic voltammetry, electrochemical impedance spectroscopy, and electrochemical quartz crystal microgravimetry. Several aqueous and nonaqueous electrolytes were evaluated.

Experimental

Chemicals and materials.—All solutions were prepared using Milli-Q deionized water. The SWNTs dispersed in water were obtained from Tubes@Rice (Rice University) with a purity better than 90%. The material consists of hexagonally packed bundles of nanotubes 1.2-1.4 nm diam. Each bundle consists of about 30 nanotubes and is 10 nm average diam and several micrometers long.[6]

Instrumentation.—A conventional three-electrode cell was used for all experiments. The working electrode was a piece (0.1 cm^2) of NTP attached to a short length of thin platinum or gold wire. The reference electrode was Ag/AgCl (3 M NaCl) for aqueous media and Ag/Ag^+ (0.01 M $AgClO_4$/0.1 M tetrabutylammonium perchlorate/acetonitrile) for nonaqueous solutions. The auxiliary electrode consisted of two pieces of NTP several times larger than the working electrode and placed one on each side of the working electrode. The potentiostat comprised PAR 174 and PAR 175 modules. The output from the potentiostat was recorded using a MacLab 4e (ADInstruments) operated by Chart software (ADInstruments) and a Macintosh computer. Electrochemical impedance data were obtained with an EG&G BES potentiostat operated by PowerSuite software (EG&G) and an Optima computer.

The electrochemical quartz crystal microbalance (EQCM) instrumentation consisted of a PAR 174/175 potentiostat and an EQCN-700 system (Elchema). The quartz crystals were 10 MHz AT-cut (ICM), 14 mm diam. The gold electrodes deposited on the crystal were 100 nm thick and 5 mm diam. The outputs from the potentiostat and the EQCM were recorded simultaneously using the system described above.

Procedures.—The preparation of the NTP has been previously described.[5,6] It involved vacuum filtration of the SWNT suspension on a membrane filter, washing with water and methanol, air drying, and removal from the filter.

To ensure proper conditioning of the sample, all NTP electrodes were cycled in the electrolyte between ±0.8 V for 5-10 cycles at 50 mV/s before any measurements were made, unless otherwise indicated. Solutions were not deoxygenated. Capacitance was measured using cyclic voltammetry.

The nanotube films used for the EQCM studies were prepared by evaporating the water from an aqueous SWNT suspension (3-5 μL) deposited on the gold electrode of the quartz crystal. The typical film mass was 20 μg.

Results and Discussion

By varying the amount or concentration of filtered nanotube suspension, samples with mass per unit area (geometric) between 1 and 2 mg/cm^2 were produced. The apparent density of most NTPs ranged between 0.30 and 0.40 g/cm^3 with an average value of 0.37 g/cm^3.

Cyclic voltammetry.—Effect of electrolyte pH and scan rate.—The potential range investigated was chosen so that formation of hydrogen or oxygen gas did not occur in the selected acidic, basic, and neutral electrolytic solutions. The cyclic voltammograms obtained after the first or second cycles were highly reproducible. However, the initial cycle was always different independent of the electrolytic solution. This cycle showed greater cathodic currents, a reduction peak at −0.25 V, and an oxidation peak at 0.65 V in 1.0 M NaCl (Fig. 1). However, the cause for the oxidation peak is not clear at this stage. The higher cathodic current and the reduction peak at negative potentials can be ascribed to the reduction of oxygen occluded inside the NTP. Removal of dissolved oxygen did not affect these features of the cyclic voltammogram; furthermore, they reappeared when the sample was left in contact with air. In addition to reducing the oxygen gas present inside the NTP, the cyclic voltammetric treatment appears to enhance the wetting of the material by the electrolytic solution. The voltammograms shown below are those obtained after conditioning.

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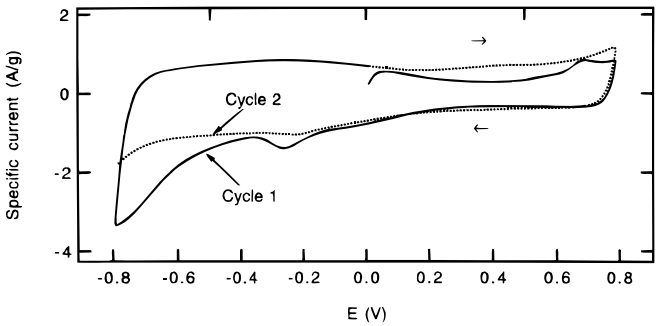

Figure 1. Cyclic voltammogram for an NTP in 1.0 M NaCl showing the first and second cycles, scan rate 50 mV/s.

Typical cyclic voltammograms in 1.0 M NaCl after the conditioning showed broad responses at around −0.15 V (Fig. 2). In sulfuric acid solutions, the potential of the redox couple shifted positively (Fig. 2), while the peaks became better defined. With some samples, particularly at high acid concentration (7.0 M), the redox response had an associated second set of small peaks. In potassium hydroxide solutions, a negative shift in the redox responses occurred (Fig. 2). These observations suggest that the redox responses are pH dependent and involve the exchange of hydrogen ions. In addition, the peak height of the oxidation response (0.1 M H_2SO_4) measured as a function of scan rate (5-100 mV/s) produced a linear plot. Based on these results, one can conclude that the voltammetric responses are due to surface redox reactions undergone by oxygen-containing functional groups (carboxylic acid, quinone) similar to those observed for other forms of carbon[7] and for nanotubes.[8] During the nanotubes' purification step in nitric acid,[9] these functional groups possibly are generated either on the surface of the nanotubes or on the amorphous carbon present as impurity in the material.[6]

The capacitance (at 0.4 V) of the tested NTPs in 1.0 M NaCl varied between 18 and 40 F/g, suggesting the importance of controlling the preparation conditions. Impurities, principally the carbonaceous material already mentioned, that aggregate on the bundle surface and different average nanotube bundle diameters resulting from different preparative conditions can influence the surface area and capacitance and probably explain the observed variations. The capacitance did not vary markedly even for large changes in sodium chloride concentration (0.01 to 5.0 M). The capacitance (at 0.6 V) for the samples investigated ranged between 25 and 90 F/g in 7.0 M H_2SO_4, representing an average increase of around 60% with respect to the values obtained in sodium chloride solutions. In potassium hydroxide solution (5.0 M), a smaller increase (10 to 30%) in capacitance (at 0.0 V) was observed in relation to that noted for sulfuric acid. As is the case with other forms of carbon,[7] concentrated sulfuric acid provides high capacitance, making it an excellent electrolyte for energy storage applications.

The effect of the scan rate on the capacitance of the NTP was studied in 1.0 M NaCl, 7.0 M H_2SO_4, and 5.0 M KOH over the 5-500 mV/s range. Results showed that an increase in capacitance was produced by decreasing scan rates. The average change was around 15%, which is substantially smaller than the variation (30%) observed for other porous carbon materials[10] over a narrower scan-rate range. It would appear that "slow" and "fast" charging processes associated with active sites offering different accessibility to the electrolye do not occur in these NTPs within the time scale investigated.

Effect of electrolyte type.—To test the effect of the electrolyte anion, aqueous solutions (0.1 M) of sodium salts containing anions with a range of chemical properties, sizes, and electrical charges were utilized. They included Cl^-, NO_3^-, SO_4^{2-}, HPO_4^{2-}, p-toluene sulfonate, (0.1 mM) polystyrene sulfonate, (5% w/v) dextran sulfate, and (13% w/v) polyvinyl sulfate. The cyclic voltammograms showed shape and current levels similar to those for 1.0 M NaCl (Fig. 2). Consistent with these results were the capacitance values (at 0.4 V) for the NTP investigated, which ranged between 14 and 16 F/g, with the greater value being typical for the "small" (Mw < 100) anions.

Nitrate salts of Li^+, Na^+, and tetramethylammonium (TMA) were used to study the influence of the electrolyte cation. The differences observed in either the cyclic voltammograms or the capacitance values (around 17 F/g) of the investigated sample were not significant. Other cations, from nitrate as well as other anion salts, were also tested, as shown in the EQCM section, with similar results.

The absence of strong scan-rate effects on the capacitance in conjunction with the lack of influence of the electrolyte nature on the voltammetry and capacitance of the NTPs indicate that all the ions, regardless of size and charge, penetrate the pores of the material with similar facility. At this stage, the actual average pore size is not known, but it is estimated to be significantly larger than the nanotube diameter (1.2 nm) and the intertube separation within a bundle (1.7 nm).[5,6] Therefore, the inner areas of the tubes and the bundles are probably excluded from contact with the electrolytic solution. On this basis, one can suggest that the structure of the NTP is characterized by the existence of readily accessible pores consisting of relatively large interbundle channels and spaces.

For nonaqueous studies, solutions of $LiClO_4$ and tetrabutylammonium tetrafluoroborate (TBATFB) in acetonitrile were selected. The cyclic voltammogram in 0.1 M TBATFB displayed no redox activity within a wide potential range (±1.5 V). However, in the presence of 0.1 M $LiClO_4$, well-defined reduction and oxidation responses were observed (Fig. 3). These redox responses possibly are associated with the insertion and ejection of Li^+ into and from the interstitial areas existing inside the nanotube bundles,[2,11,12] respectively. The value of the capacitance (at 0.4 V) was similar in both electrolytes.

Electrochemical impedance spectroscopy.—Measurements were performed at open circuit in aqueous solutions (1.0 M) of sodium chloride, sulfuric acid, and potassium hydroxide using a 10 mV amplitude sinusoidal wave with a frequency range between 5 kHz

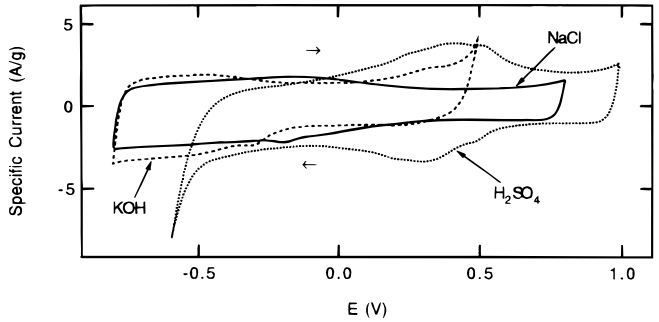

Figure 2. Cyclic voltammograms for an NTP in 1.0 M NaCl, 1.0 M H_2SO_4, and 1.0 M KOH, scan rate 50 mV/s.

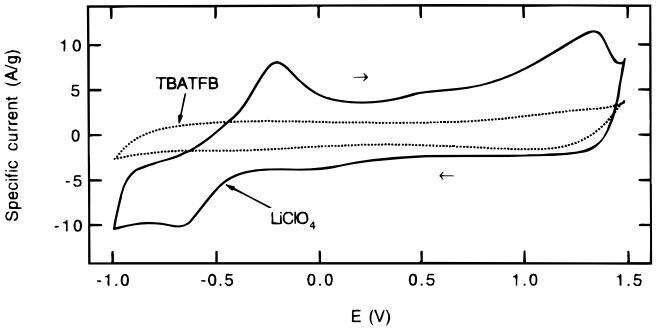

Figure 3. Cyclic voltammogram for an NTP in acetonitrile solutions of 0.1 M $LiClO_4$ and 0.1 M TBATFB, scan rate 50 mV/s (reference electrode Ag/Ag^+).

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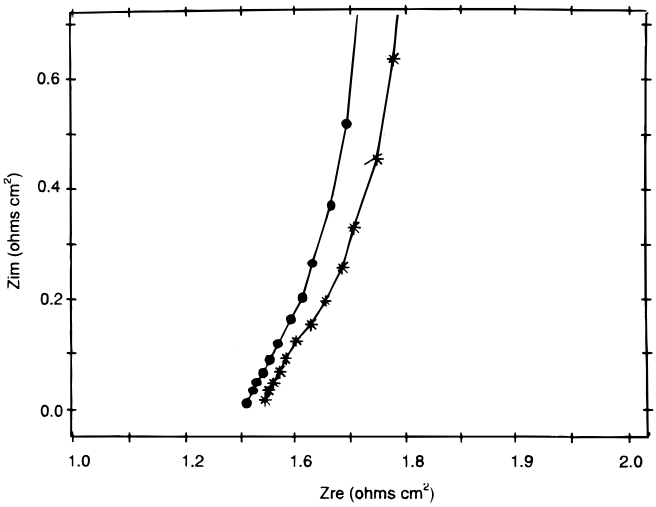

Figure 4. Complex-plane impedance plot for an NTP, (*) before and (•) after cyclic voltammetric conditioning in 1.0 M NaCl.

and 50 mHz. A comparison of the impedance spectrum of an NTP before and after cyclic voltammetry in 1.0 M NaCl (Fig. 4) reveals that the electrochemical treatment produces a decrease (2%) in the electrical resistance and an increase (25%) in the ac capacitance. This suggests, as noted earlier, that the electrochemical conditioning induces a higher degree of wetting of the NTP surface and a better penetration of the solution into the pores. The effect of conditioning is similar in the other electrolytes evaluated. The overall shape of the curves, similar also for the three electrolytes, indicates a behavior typical of a porous electrode characterized by a distributed resistor-capacitor time constant. The slight initial curvature of the plot suggests the existence of a faradaic pseudocapacitance, in agreement with the cyclic voltammetric data. The nearly vertical line reflects a predominant double-layer capacitive component at low frequencies, where the influence of the pores becomes relatively more important.

EQCM studies.—Aqueous solutions.—Solutions (0.1 M) of the following salts were investigated: NaCl, CsCl, benzyltriethylammonium chloride, $LiNO_3$, $NaNO_3$, $Ca(NO_3)_2$, and $TMANO_3$. The potential range was chosen so that redox processes associated with the electrolytic solution or the gold electrode were avoided.

In neutral solutions, a continuous mass increase was observed for a cathodic potential scan below 0.6 V. The opposite effect occurred during the anodic scan (Fig. 5). Typically, the mass change was around 1% of the sample mass. Examination of the mass changes at negative potentials, the average slope of the mass curves, or the slope of these curves divided by the current shows no linear relation with the cation mass. This may be due to simultaneous changes in the amount of cation, anion, and solvent present in the NTP pores resulting from double-layer charging/discharging.

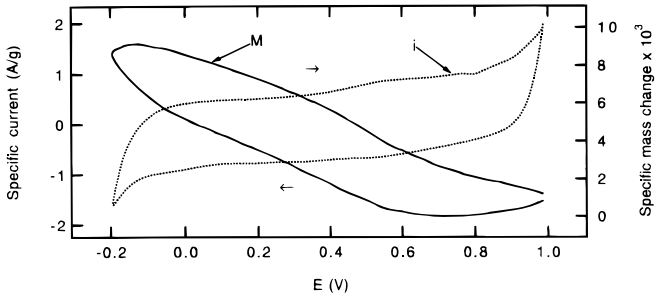

Figure 5. Specific current (current/sample mass) and specific mass (mass change/sample mass) as a function of applied potential for a nanotube film in 0.1 M $TMANO_3$, scan rate 50 mV/s.

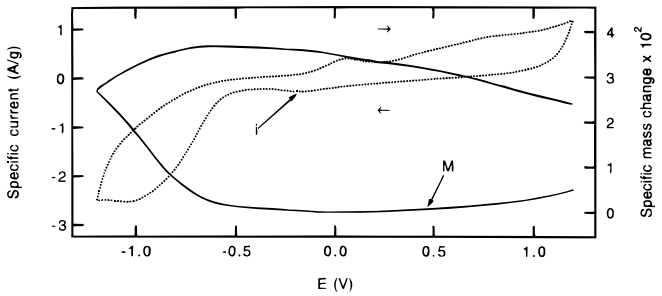

Figure 6. Specific current (current/sample mass) and specific mass (mass change/sample mass) as a function of applied potential for a nanotube film in 0.1 M $LiClO_4$ in acetonitrile, scan rate 50 mV/s (reference electrode Ag/Ag^+).

The absence of mass changes at positive potentials is possibly due to the existence of negative charges immobilized on the carbon nanotubes, which tend to become negatively charged in aqueous suspensions.[13] Immobilization of these charges inside the nanotube film possibly forces the predominant exchange of cations necessary to maintain electroneutrality of the double layer.

Nonaqueous solutions.—The acetonitrile solutions described above were utilized. In 0.1 M TBATFB, the mass variation with applied potential was similar to those seen in aqueous solutions. In contrast, in 0.1 M $LiClO_4$, a larger (3 to 4%) mass increase was observed at −0.7 V (Fig. 6). An intense reduction peak is also observed at this potential, as noted earlier. The mass gained on the negative scan was not readily lost when the potential was scanned in the positive direction. A significant but slow change occurred only when a constant positive potential above 1.0 V was applied. These observations seem to be consistent with the suggested insertion or intercalation of Li^+ in the interstitial sites within the nanotube bundles.[2,11,12]

Conclusions

These intitial studies of NTP have shown that the material exhibits broad redox responses in aqueous solutions, probably as a result of the presence of functional groups attached to the surface of the nanotubes or to the impurities produced during nanotube purification. The capacitance of the material varies with the sample, probably due to differences in surface area introduced during the NTP preparation process. The voltammetry and capacitance of the NTP do not vary substantially with the chemical nature of the electrolyte ions. This suggests that the NTPs are characterized by an interbundle open structure with relatively large pores. Insertion of Li^+ appears to occur readily by the application of moderately negative potentials in acetonitrile medium. However, the reverse process is more difficult.

Electrochemical impedance spectroscopy indicates that increased wetting of the NTP occurs as a result of the electrochemical treatment provided by cyclic voltammetry. The complex-plane impedance curves show features that can be associated with a porous material exhibiting probably a faradaic pseudocapacitance.

A first EQCM study shows mass changes of the nanotube films associated with changes in applied potential. The mass increases for negative potential scans are not linearly proportional to the mass of the cation. A possible reason for this effect are complex movements of anions, cations, and solvent molecules in the pores of the nanotube films during potential scanning. In acetonitrile solutions of Li^+, a substantial increase in mass associated with a well-defined reduction response occurs, possibly as a result of the suggested lithium insertion in the nanotube bundles.

Acknowledgments

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References

1. *Carbon Nanotubes, Preparation and Properties*, T. W. Ebbesen, Editor, CRC Press, Boca Raton, FL (1997) and references cited.
2. C. Liu, A. J. Bard, F. Wudl, I. Weitz, and J. R. Heath, *Electrochem. Solid-State Lett.*, **2**, 577 (1999).
3. E. Frackowiak, S. Gautier, H. Gaucher, H. Bonnany, and F. Beguin, *Carbon*, **37**, 61 (1999).
4. P. J. Britto, K. S. V. Santhanam, and P. M. Ajayan, *Bioelectrochem. Bioenerg.*, **41**, 121 (1996).
5. R. H. Baughman, C. Cui, A. A. Zakhidov, Z. Iqbal, J. N. Barisci, G. M. Spinks, G. G. Wallace, A. Mazzoldi, D. De Rossi, A. G. Rinzler, O. Jaschinski, S. Roth, and M. Kertesz, *Science*, **284**, 1340 (1999).
6. A. G. Rinzler, J. Liu, H. Dai, P. Nikolaev, C. B. Huffman, F. J. Rodriguesmacias, P. J. Boul, A. H. Lu, D. Heymann, D. T. Colbert, R. S. Lee, J. E. Fisher, A. M. Rao, P. C. Eklund, and R. E. Smalley, *Appl. Phys. A*, **67**, 29 (1998).
7. R. L. McCreery, in *Electroanalytical Chemistry*, A. J. Bard, Editor, Vol. 17, p. 221, Marcel Dekker, New York (1990) and references cited.
8. G. Che, B. B. Lakshmi, E. R. Fisher, and C. R. Martin, *Nature*, **393**, 346 (1999).
9. J. Liu, A. G. Rinzler, H. Dai, J. H. Hafner, R. Kelley Bradley, P. J. Boul, A. Lu, T. Iverson, K. Shelimov, C. B. Huffman, F. Rodriguez-Macias, Y. Shon, T. Randall Lee, D. T. Colbert, and R. E. Smalley, *Science*, **280**, 1253 (1998).
10. Y. Oren and A. Soffer, *J. Electroanal. Chem.*, **186**, 63 (1985).
11. B. Gao, A. Kleinhammes, X. P. Tang, C. Bower, L. Fleming, Y. Wu, and O. Zhou, *Chem. Phys. Lett.*, **307**, 153 (1999).
12. G. T. Wu, C. S. Wang, X. B. Zhang, H. S. Yang, Z. F. Qi, P. M. He, and W. Z. Li, *J. Electrochem. Soc.*, **146**, 1696 (1999).
13. J. Liu, A. G. Rinzler, H. Dai, J. H. Hafner, R. Kelley Bradley, P. J. Boul, A. Lu, T. Iverson, K. Shelimov, C. B. Huffman, F. Rodriguez-Macias, Y. Shon, T. Randall Lee, D. T. Colbert, and R. E. Smalley, *Science*, **280**, 1253 (1998).