Electrochemical and Solid-State Letters, **2** (11) 577-578 (1999)
S1099-0062(99)06-057-5 CCC: $7.00

Electrochemical Characterization of Films of Single-Walled Carbon Nanotubes and Their Possible Application in Supercapacitors

Chong-yang Liu,[a] Allen J. Bard,[a,*,z] Fred Wudl,[b] Iris Weitz,[b] and James R. Heath[b]

[a]*Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712, USA*
[b]*Department of Chemistry and Biochemistry, The University of California, Los Angeles, California, 90095 , USA*

Films of single-wall carbon nanotubes (SWCNTs) were cast from suspensions in several solvents on the surface of a Pt or Au electrode. Cyclic voltammetry of the films in MeCN did not show well-resolved waves (as distinct from films of C_{60} prepared in a similar manner). However, the increase in the effective capacitance of the electrode with a SWCNT film at 0.5 V *vs.* an AgQRE was 283 F/g, which is about twice that of carbon electrodes in nonaqueous solvents.

Manuscript submitted June 9, 1999; revised manuscript received July 30, 1999. Available electronically September 7, 1999.

We describe here, for the first time, studies of thin films of single-wall carbon nanotubes (SWCNT) deposited on Pt or Au electrode surfaces and their voltammetric response. SWCNTs are interesting materials, since their electronic properties are significantly modulated by slight structural variations in diameter and the helicity of the carbon atoms in the wall.[1,2] We were interested in comparing the behavior of such SWCNT films with those of the fullerenes, C_{60} and C_{70}.[3,4] We show that, while these films give no distinct voltammetric peaks, probably because of a broad tube size distribution, they show a very high "effective capacitance" which might make them of interest as electrodes in supercapacitors.

Films of the fullerenes can be cast from solutions of C_{60} or C_{70} in benzene or other solvents. However, SWCNTs are insoluble in all solvents; therefore films had to be cast from SWCNTs in benzene, acetonitrile (MeCN), acetone, or water containing sodium dodecylsulfate (SDS, 0.5 g in 100 mL) after strong sonication. A greater amount of SWCNTs could be dispersed in SDS solution than in other solvents due to the self-aggregation of surfactant molecules into micelles. Thin films of SWCNTs[c] were prepared by evaporation on a Pt or Au electrode surface of a few microliters of a suspension similar to a procedure used for the C_{60} studies.[3,4] When the thin films were cast from SDS solutions, the electrodes were kept in an oven (104°C) for about 45 min before transfer into a dry box where electrochemical experiments were conducted in MeCN under a helium atmosphere. A CH Instruments model 660 was employed for the cyclic voltammetric (CV) measurements in MeCN solutions containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate ($TBAPF_6$). A platinum mesh served as the counter electrode, and a silver wire was used as a quasi-reference electrode.

Films prepared from C_{60} suspensions were studied first to compare their CV characteristics to those films prepared from solutions of C_{60} in benzene, which produce well-defined waves. These C_{60} suspensions in solvents like water/SDS and MeCN produced films that showed essentially identical CV behavior to those cast from solutions (Fig. 1). For example, the reduction $C_{60} \rightarrow C_{60}^{-} \rightarrow C_{60}^{2-}$ and corresponding oxidation peaks were well-defined over the given potential region. A third reduction wave (not shown) was observed at more negative potentials. As reported earlier,[3,4] the film became less stable for scans beyond the third reduction peaks in MeCN/$TBAPF_6$. Similar results were also obtained from films prepared from a MeCN suspension of C_{60}. These results demonstrate that good CV results can be obtained with C_{60} films prepared from suspensions and suggest a similar procedure would be suitable for SWCNTs.

However, CVs obtained from SWCNT films prepared from suspensions of different amounts of nanotube material in water/SDS, benzene, MeCN, and acetone showed only a featureless voltammogram, such as that shown in Fig. 2. In this experiment, the voltammogram of a bare Pt flag (6 x 7 mm) was measured first, and then a

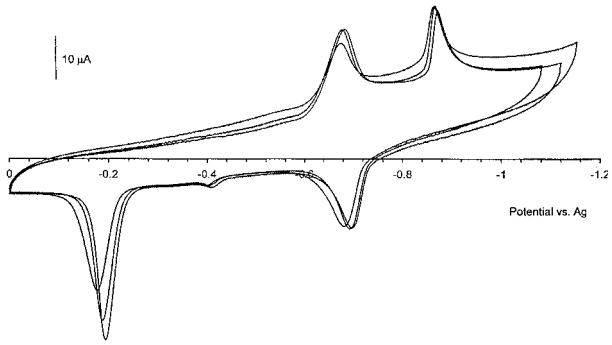

Figure 1. CVs of a C_{60} film cast as a suspension from acetone on a Pt electrode in MeCN containing 0.1 M $TBAPF_6$. Scan rate, 50 mV/s.

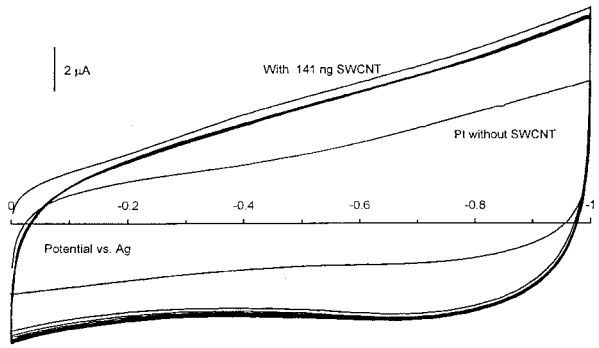

Figure 2. Cyclic voltammograms of a Pt electrode with and without a SWCNT film cast from acetone in MeCN containing 0.1 M $TBAPF_6$. Scan rate, 50 mV/s.

2 μL suspension of SWCNT in acetone was coated on the same Pt surface. After drying in He, the electrode was replaced in the cell and CVs were recorded again under identical conditions. All procedures were performed inside a He atmosphere dry box, and the electrode surface was kept horizontal to prevent possible loss of material from the electrode. Note that CVs obtained within a larger potential window than that shown (0 to -2 V *vs.* Ag quasi-reference electrode) still did not show waves. An increase in the total amount of SWCNT material on the electrode by successive deposition of the suspension on different locations at the Pt surface produced the same shaped voltammogram with an increase in the charge passed during the sweep. Variation of the electrode temperature from 24 to 150°C during deposition also did not make a difference. The featureless CV (compared to the waves seen with the fullerene films) probably

* Electrochemical Society Fellow.
z E-mail: ajbard@mail.utexas.edu

[c] WCNTs were a gift from D. T. Colbert (Rice University) and were purified by a procedure developed by one of us (I.W.) at UCLA.

S1099-0062(99)06-057-5 CCC: $7.00

result from a distribution of nanotubes. The electronic properties of the carbon nanotubes are sensitive to structural variations, such as the length, diameter, and helicity of the carbon atoms in the shell, and each nanotube is somewhat different from others in their electronic properties. Therefore, the featureless CV might be an average of many closely spaced peaks representing electron transfer into each nanotube. Indeed, different electronic properties were reported with different nanotubes based on a four-probe measurement with individual carbon nanotubes; SWCTs can show conductivities ranging from metallic to semiconducting depending upon the helicity of the particular tube structure.[5] Another possibility is that the layer of SWCNTs might simply behave like a bulk carbon material rather than individual molecules.[6]

However, the results in Fig. 2 show that the electrochemical capacitance of the Pt electrode had increased substantially by the addition of the SWCNT layer. To obtain a quantitative estimate of the amount of charge stored per unit mass of SWCNT, an electrochemical quartz crystal microbalance[7] was employed. A gold contact to the crystal was employed as an electrode. The mass of SWCNT deposited from an acetone suspension produced a frequency change equivalent to 141 ng mass increase. The capacitance was calculated from the CV curves, with $C = i/v$, where i is the current and v the sweep rate (V/s). At a potential of -0.5 V, for example, the increase of the effective capacitance per unit weight of SWCNT was about 283 F/g. This is over twice that of the largest value reported so far (120 F/g) with an active carbon electrode in a nonaqueous solution.[8] This high capacitance is consistent with the large surface area of the single-walled nanotubes and is equivalent to charging about 2% of the C atoms in the nanotubes. The high capacitance per unit weight, at least for thin films, suggests a possible application to supercapacitors.[8] The material was stable on cycling and no significant difference was seen after continuous cycles over 30 min at 50 mV/s.

Acknowledgments

We thank Dr. D. Cliffel and Dr. F. R. F. Fan for assistance. The support of this work by grants from the National Science Foundation and the Robert A. Welch Foundation is gratefully acknowledged.

The University of Texas at Austin assisted in meeting the publication costs of this article.

References

1. J. W. Mintmire, B. I. Dunlap, and C. T. White, *Phys. Rev. Lett.*, **68**, 631 (1992).
2. N. Hamada, S. Sawada, and A. Oshiyama, *Phys. Rev. Lett.*, **68**, 1579 (1992).
3. C. Jehoulet, A. J. Bard, and F. Wudl, *J. Am. Chem. Soc.*, **113**, 5456 (1991).
4. J. Chlistunoff, D. Cliffel, and A. J. Bard, *Thin Solid Films*, **257**, 166 (1995).
5. T. W. Ebbesen, H. J. Lezec, H. Hiura, J. W. Bennett, H. F. Ghaemi, and T. Thio, *Nature*, **382**, 54 (1996).
6. J. Liu, A. G. Rinzler, H. Dai, J. H. Hafner, R. K. Bradley, P. J. Boul, A. Lu, T. Iverson, K. Shelimov, C. B. Huffman, F. Rodriquez-Macias, Y.-S. Shon, T. R. Lee, D. T. Colbert, and R. E. Smalley, *Science*, **280**, 1253 (1998).
7. D. A. Buttry, in *Electroanalytical Chemistry*, A. J. Bard, Editor, Marcel Dekker, New York (1991).
8. B. E. Conway, *Electrochemical Supercapacitors-Scientific Fundamentals and Technological Applications*, Plenum, New York (1999).