

and exhibiting volume electrical resistivity of 0.11  $\Omega$  cm and thermal stability up to 205 °C was found to be an effective resistive heating element. It provided temperatures up to 134 °C at a power of up to 6.5 W, with a time up to 106 s to reach half of the maximum temperature rise. The electrical energy input to heat by 1 °C during the initial period of rapid temperature rise (5 s) was up to 3.8 J. The time to drop to half of the maximum temperature rise during cooling was much longer than the time to reach half of the maximum temperature during heating, especially when the input power was low. The efficiency of conversion from electrical energy to heat was nearly 1.00, even in the first 5 s of heating. A mat comprising Ni–Cu–Ni coated carbon fibers gave lower temperatures, due to the lower resistance, but it gave faster response.

Flexible graphite was superior to carbon fiber mats as a heating element, as it provided much higher temperatures and a much faster response.

## References

- [1] Quick JR, Mate Z. *Modern Plastics* 1982;59(5):68–73.
- [2] Council MA, Park GB, 34th Int. SAMPE Symp. and Exhibition—Tomorrow's Materials: Today, SAMPE, Covina, CA. 1989;2:1644–1655.
- [3] Armstrong-Carroll E, Cochran R. *Proc. 5th Symp. Composite Materials: Fatigue and Fracture*, ASTM, Philadelphia, PA, 1995;5(1230):124–131.
- [4] Walker NJ. *Plastverarbeiter* 1988;39(6):4.
- [5] Portnoi OA, Shub ES, Il'ina GA, Stark IM, Zosin VP, Slavinskii ST, Bushtyrkov VA, Klyukvin VA, Levit RM. *Fibre Chemistry (English Translation of Khimicheskie Volkna)* 1990;21(5):420–2.
- [6] dos Santos FSG, Swart JW. *J Electrochem Soc* 1990;137(4):1252–5.
- [7] Cattelino MJ, Miran GV, Smith B. *IEEE Trans Electron Dev* 1991;38(10):2239–43.
- [8] Hung C-C, Dillehay ME, Stahl M. *J Aircraft* 1987;24(10):725–30.
- [9] Xie J, Wang J, Wang X, Wang H. *Hecheng Shuzhi Ji Suliao (Synthetic Resin and Plastics)* 1996;13(1):50–4.
- [10] Prokushin VN, Shubin AA, Klejmenov VV. *Marmar EhN Khimicheskie Volkna* 1992;6:50–1.
- [11] Song B, Viskanta R. *J Thermophys Heat Transfer* 1990;4(3):311–7.
- [12] Higaki M, Narita M, Nakayama M. *NEC Res Develop* 1988;89:81–8.
- [13] Chung DDL. In: *Applied materials science*, Boca Raton, FL: CRC Press; 2001, pp. 184–5.
- [14] Callister Jr. WD. In: *Materials science and engineering*, 5th ed., New York: Wiley; 2000, p. 811.
- [15] Chugh R, Chung DDL. *Carbon* 2002;40(13):2285–9.

# SWNT/PAN composite film-based supercapacitors

Tao Liu<sup>a</sup>, T.V. Sreekumar<sup>a</sup>, Satish Kumar<sup>a,\*</sup>, Robert H. Hauge<sup>b</sup>, Richard E. Smalley<sup>b</sup>

<sup>a</sup>*School of Textile and Fiber Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA*

<sup>b</sup>*Center for Nanoscale Science and Technology, Rice University, Houston, TX 77005, USA*

Received 1 May 2003; accepted 31 May 2003

*Keywords:* A. Carbon nanotubes, Carbon composites; D. Electrochemical properties

Supercapacitors or electrochemical capacitors have higher power density than batteries and higher energy density than ordinary capacitors, as well as a long cycle life [1,2]. Electrically conducting metal oxide [3], conducting polymers [4], activated carbon [5], and carbon nanotubes [6–8] have been used as the active electrode materials for supercapacitors. In this letter, we report the performance of supercapacitor electrodes based on single wall carbon

nanotube/polyacrylonitrile (SWNT/PAN) composite films.

A SWNT/PAN dispersion was prepared at room temperature by mixing as-produced HiPco SWNT powder [9] with a 1.5 g/l dimethylformamide (DMF) solution of poly(acrylonitrile–methyl acrylate) (90:10) copolymer (Aldrich,  $M_w \sim 100,000$  g/mol). The weight ratio of SWNT powder to PAN copolymer is 40:60. Subsequent partial solvent evaporation from the SWNT/PAN dispersion at about 100 °C and then film casting at 85 °C in vacuum resulted in a  $\sim 10$   $\mu$ m thick SWNT/PAN composite film. Based on scanning electron microscopy results, the diameter of the as-produced HiPco SWNT ropes used in this

\*Corresponding author. Tel.: +1-404-894-7550; fax: +1-404-894-8780.

*E-mail address:* satish.kumar@tfe.gatech.edu (S. Kumar).

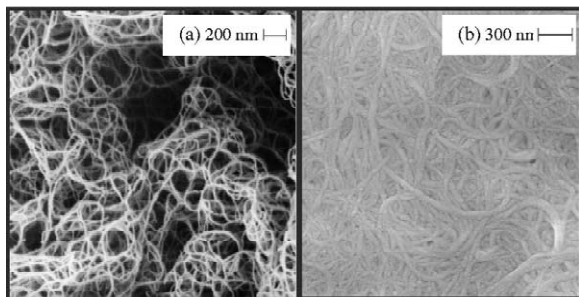


Fig. 1. Scanning electron micrographs of (a) as-produced HiPco SWNT powder, and (b) as-produced SWNT/PAN composite film.

study was  $35 \pm 7$  nm and that for the as-prepared SWNT/PAN composite film was estimated to be  $57 \pm 8$  nm (Fig. 1). The increased rope diameter indicates PAN copolymer adsorption by the SWNT ropes.

Physical or chemical activation [10,11] of polyacrylonitrile or its copolymers is generally used for producing activated carbon with high specific surface area and high porosity, and it is expected that similar activation treatments of a SWNT/PAN composite film can also be used for developing SWNT/activated carbon composite films. As-produced SWNT/PAN composite films were heat treated at  $700$  °C in argon for 30 min and subsequently activated in  $\text{CO}_2$  at the same temperature for 20 min in a Thermolyne 21100 tube furnace. During heat treatment and activation, the composite film did not exhibit significant shrinkage.

Two circular pieces of SWNT/activated carbon films (11.8 mm diameter), without further treatment, were sandwiched into a supercapacitor testing cell composed of two stainless steel current collectors and a hydrophilic

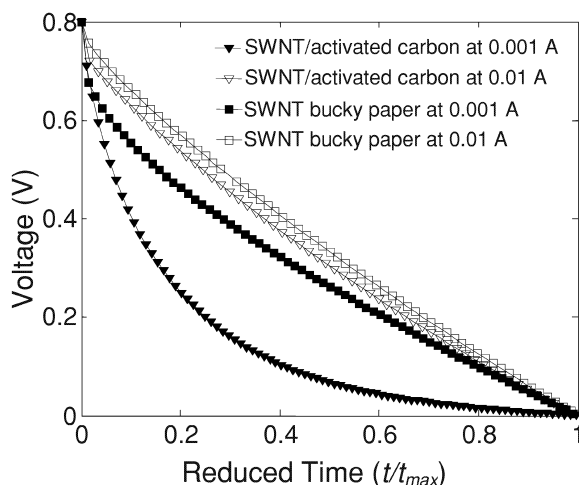


Fig. 2. Constant current discharging behavior of SWNT/activated carbon composite film and SWNT bucky paper.

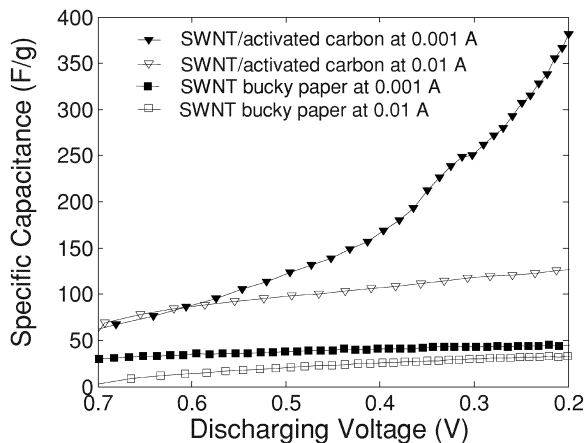


Fig. 3. Specific capacitance as a function of discharging voltage for SWNT/activated carbon and SWNT/bucky paper at different constant discharging currents.

polyethylene sheet separator (Small Parts Inc., PEH-060, average pore size  $15\text{--}45$   $\mu\text{m}$ , 1/16 inch thick). The constant current charging and discharging behavior of the composite film electrodes and that of a SWNT bucky paper (a 100% SWNT mat, provided by Carbon Nanotechnologies Inc.) was recorded with a CH Instruments 660A electrochemical workstation using a 6 N KOH aqueous solution as the electrolyte. The measured discharging curves as a function of reduced time (reduced time is the ratio of the actual discharging time,  $t$ , to the total time of the discharging process,  $t_{\text{max}}$ ), given in Fig. 2, show that the SWNT/activated carbon film exhibits significant non-linear discharging behavior, particularly at low discharging current (0.001 A). The non-linear constant current charging and discharging behavior of the SWNT/activated carbon

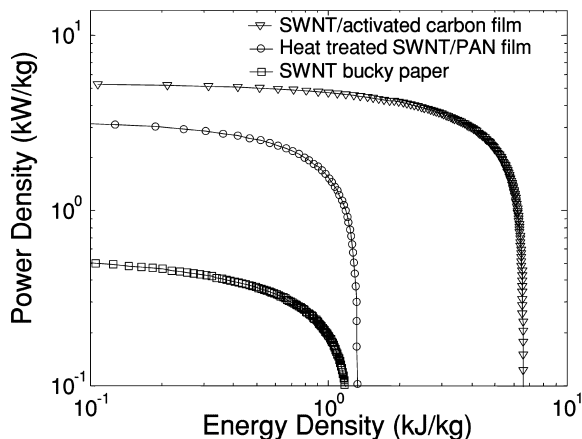


Fig. 4. Ragone plots for various electrodes evaluated at a discharging current of 0.01 A.

film is attributed to either the broad pore size distribution [12] or the pseudocapacitance [2] introduced by the surface chemistry caused by the activation treatment.

The specific capacitance (capacitance per unit mass of a single electrode) was calculated as a function of discharging voltage using the formula [1,2]

$$C_{sp} = \frac{I}{dV(t)/dt} \left( \frac{1}{m_A} + \frac{1}{m_B} \right)$$

where  $m_A$  and  $m_B$  are the masses of the two electrodes, and  $I$ ,  $V(t)$ , and  $t$  are the discharging current, voltage and time, respectively. The specific capacitance of the SWNT/activated carbon film is significantly higher than that of the bucky paper (Fig. 3). The specific capacitance of SWNT/activated carbon at 0.001 A discharging current is strongly dependent upon the discharging voltage, as a result of its non-linear discharging behavior. When the discharging voltage was changed from 0.7 to 0.2 V, the specific capacitance increased from 60 to 380 F/g.

Ragone plots, which are used to relate the power density (PD) to the energy density (ED) [2], have been calculated using the equations

$$ED = \int_{t=0}^t IV(t) dt / (m_A + m_B)$$

$$PD = IV(t) / (m_A + m_B)$$

The results given in Fig. 4 indicate that both the power and energy densities of the SWNT/activated carbon composite film are significantly higher than those of the SWNT bucky paper. For comparison, Fig. 4 also plots power and energy densities of heat-treated SWNT/PAN composite film without CO<sub>2</sub> activation. Although the specific capacitance of the heat-treated SWNT/PAN composite film (data not reported) without activation is comparable to the specific capacitance of the bucky paper, the power density of the heat-treated SWNT/PAN composite film is much higher than that of the SWNT bucky paper.

### Acknowledgements

We thank Professor Jiri Janata and Dr. Guofeng Li for the use of the CH Instruments 660A Electrochemical Workstation. Financial support for this work from AFOSR,

ONR, Carbon Nanotechnologies Inc., and support at Rice University in developing the HiPco™ process from NASA, the Office of Naval Research, the Texas Advanced Technology Program, and the Robert A Welch Foundation is gratefully acknowledged.

### References

- [1] Kotz R, Carlen M. Principles and applications of electrochemical capacitors. *Electrochim Acta* 2000;45(15/16):2483–98.
- [2] Conway BE. *Electrochemical supercapacitors: scientific fundamentals and technological applications*. Kluwer Academic/Plenum; 1999.
- [3] Liu TC, Pell WG, Conway BE. Self-discharge and potential recovery phenomena at thermally and electrochemically prepared RuO<sub>2</sub> supercapacitor electrodes. *Electrochim Acta* 1997;42(23/24):3541–52.
- [4] Mastragostino M, Arbizzani C, Soavi F. Conducting polymers as electrode materials in supercapacitors. *Solid State Ionics* 2002;148(3/4):493–8.
- [5] Shi H. Activated carbons and double layer capacitance. *Electrochim Acta* 1996;40(10):1633–9.
- [6] Niu CM, Sichel EK, Hoch R, Moy D, Tennent H. High power electrochemical capacitors based on carbon nanotube electrodes. *Appl Phys Lett* 1997;70(11):1480–2.
- [7] Frackowiak E, Metenier K, Bertagna V, Beguin F. Supercapacitor electrodes from multiwalled carbon nanotubes. *Appl Phys Lett* 2000;77(15):2421–3.
- [8] An KH, Kim WS, Park YS, Choi YC, Lee SM, Chung DC et al. Supercapacitors using single-walled carbon nanotube electrodes. *Adv Mater* 2001;13(7):497–500.
- [9] Nikolaev P, Bronikowski MJ, Bradley RK, Rohmund F, Colbert DT, Smith KA et al. Gas-phase catalytic growth of single-walled carbon nanotubes from carbon monoxide. *Chem Phys Lett* 1999;313(1/2):91–7.
- [10] Molina-Sabio M, Gonzalez MT, Rodriguez-Reinoso F, Sepulveda-Escribano A. Effect of steam and carbon dioxide activation in the micropore size distribution of activated carbon. *Carbon* 1996;34(4):505–9.
- [11] Addoun A, Dentzer J, Ehrburger P. Porosity of carbons obtained by chemical activation: effect of the nature of the alkaline carbonates. *Carbon* 2002;40(7):1140–3.
- [12] Conway BE, Pell WG. Power limitations of supercapacitor and capacitance distribution operation associated with resistance in porous electrode devices. *J Power Sources* 2002;105(2):169–81.