High Energy Density Supercapacitor Based on a Hybrid Carbon Nanotube - Reduced Graphite Oxide Architecture

E. Bekyarova,[1,2] P. Ramesh,[1] N. Jha,[2] M. E. Itkis[1,2] and R. C. Haddon[2]

[1]Carbon Solutions Inc, [2]Center for Nanoscale Science and Engineering, Chemistry Department, University of California – Riverside, Riverside, CA

bekyarova@carbonsolution.com

ABSTRACT

We report a high energy supercapacitor device that utilizes hybrid carbon electrodes and the ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF4) as an electrolyte. The hybrid electrodes were prepared from reduced graphite oxide (rGO) and purified single walled carbon nanotubes (SWNTs). A simple casting technique gives a hybrid structure with optimum porosity and functionality that provides high energy and power density. The combination of SWNT and rGO in a weight ratio of 1:1 was found to afford specific capacitance of 222 F/g and energy density of 94 Wh/kg at room temperature.

Keywords: single wall carbon nanotubes; reduced graphite oxide; supercapacitor; synergistic effect energy density

1 INTRODUCTION

Capacitors are often used for low energy applications, which require rapid power delivery and long cycle life [1-3]. The demand for high energy density capacitors has increased tremendously as the electronics industry continues to shrink the device dimensions. Electrochemical supercapacitors are expected to meet the demand for advanced energy storage devices and to bridge the gap between batteries and capacitors. This work reports an innovative approach to the development of new supercapacitor materials and devices, which are based on carbon nanomaterials: single-walled carbon nanotubes (SWNTs) and graphene.

Carbon is traditionally used as an electrode material in supercapacitors due to its chemical stability, high surface area and well developed porosity. Among the novel carbon materials explored for supercapacitor applications, carbon nanotubes emerge as a promising candidate because they have high electrical conductivity and ability to form porous thin films [4,5]. Recently large-scale two dimensional graphene sheets have been reported to have a high specific capacitance.

Here we show that the combination of 1-D SWNTs with 2-D graphene provides a hybrid structure that has a specific capacitance of 222 F/g and that is capable of delivering an energy density of 94.5 Wh/kg at room temperature [6]. The hybrid electrode architecture provides the requisite surface morphology and porosity for high charge storage in conjunction with the use of an environmental friendly ionic liquid electrolyte. The long term stability together with high energy and power densities show that the hybrid material is a promising candidate for future advanced energy storage devices.

The hybrid structure utilizes the advantages of the two carbon nanomaterials, while eliminating the drawbacks of the individual components.

Advantages:

- high surface area, conductivity and good stability in various electrolytes
- thin film architecture with porosity that favors faster charging and discharging
- ability to introduce functional groups and tailor the electrolyte adsorption and wettability.

Drawbacks:

- graphene - strong interaction between graphene sheets leads to re-stacking and decreased surface area
- SWNTs – bundle formation and aggregation leading to reduced surface area.

2 MATERIALS AND METHODS

Material synthesis Graphite oxide (GO) was synthesized using Hummer's method [7] from natural graphite flakes (2-15 μm), obtained from Alfa Aesar. The synthesized graphite oxide (GO) was reduced to rGO using $NaBH_4$ [8] and characterized with XRD, Raman spectroscopy and TEM. The purified electric arc produced SWNTs (P3-SWNT, Carbon Solutions Inc, www.carbonsolution.com) contain

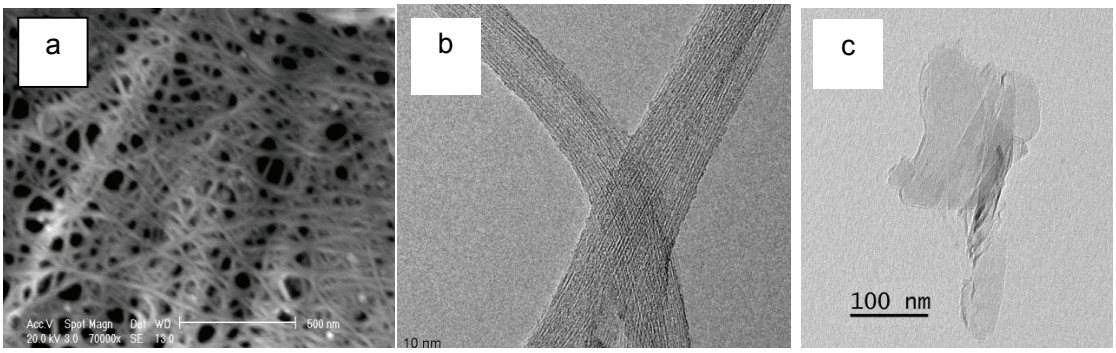


Figure 1: Images of SWNTs: (a) scanning electron microscopy (SEM) showing a network of carbon nanotubes. (b) Transmission electron microscopy (TEM) showing several nanotubes assembled in bundles. (c) TEM image of graphene sheets prepared by reduction of graphene oxide.

about ~1 mol% carboxylic acid groups [9], which affords dispersibility in water. The SWNT were dispersed in distilled water by sonication , and washed 9 times with NaOH solution in order to remove carboxylated carbon fragments [9]. The SWNTs were analyzed by near-IR spectroscopy, TGA and TEM. The conductivity of SWNT films prepared by drop casting from aqueous diepersions was 1150 S/cm.

Cell fabrication and electrochemical tests The charge storage measurements were performed using a stainless steel current collector based supercapacitor cell. The supercapacitor was fabricated in a glove box under an argon atmosphere. The supercapacitor unit cell consisted of two electrically isolated electrodes, joined together by a porous filter paper soaked in the ionic liquid $BMIMBF_4$.

Cyclic voltammetry (CV) and galvanostatic charge-discharge measurements were performed using the CHI Model 1140 at room temperature. CV curves were measured at several scan rates ranging from 10-100 mV/s to analyze the electrochemical behavior including the pseudo-capacitance of the materials.

The specific capacitance (C) of the electrode materials was calculated from the galvanostatic (constant current) charge-discharge and the slope of the discharge curve (dv/dt): $C = i\ (m\ dv/dt)$, where m is the mass of the electrode material.

The energy density, E, was calculated from the total capacitance (C) of the supercapacitor device and the potential window (V) using the equation: $E = \frac{CV^2}{2}$

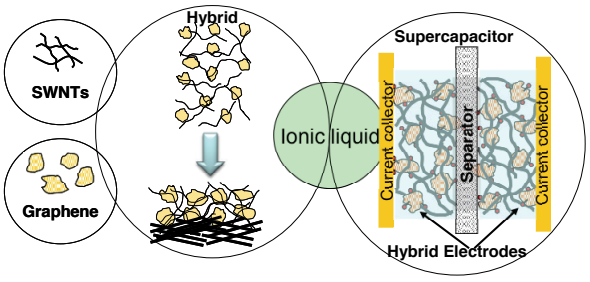
The power density (P) is defined as the rate at which energy is delivered $P = \frac{E}{\Delta t}$, where E is the energy density and Δt is the discharge time [10,11].

3 RESULTS AND DISCUSSION

The single-walled carbon nanotubes (SWNTs) used in this study are produced by the electric arc method and purified with nitric acid, which leaves the material functionalized with carboxylic acid groups (~1 at%). The carbonaceous purity of the purified material was monitored with solution phase near-IR spectroscopy [12,13] to assure SWNT content above 90%. The SWNTs were further washed with a NaOH solution in order to remove carboxylated carbon fragments that remained after the nitric acid treatment [9]. The presence of carboxylic acid groups facilitated the dispersibility of the SWNTs in water; the dispersions were used to prepare thin films, which showed conductivity in the range of 1150 S/cm.

The graphene, which was derived from graphene oxide by chemical reduction (rGO) was characterized with XRD and Raman spectroscopy. The successful reduction of the graphene oxide was confirmed with EDX analysis, which showed the C/O ration doubled after the reduction and this also resulted in an increase of the electrical conductivity, which for films of rGO was estimated to be 0.5 S/cm; GO, which is highly resistive in nature, showed conductivity of 7×10^{-3} S/cm. Typical SEM and TEM images of the carbon nanomaterials are shown in Figure 1.

For the fabrication of hybrid supercapacitor cells, the carbon materials - rGO and SWNTs, were separately dispersed in distilled water by ultrasonication and cast on the surface of the stainless steel current collector in the form of thin films. The hybrid structures were obtained by combining aliquots of the suspensions to obtain mixtures of a specific composition. The use of highly conducting SWNTs removes the need for a binder and conducting agent in the preparation of the supercapacitor cells. A schematic of the fabricated hybrid architecture comprised of SWNT and rGO is presented in Scheme 1.



Scheme 1: Schematics of hybrid SWNT-graphene supercapacitor electrodes.

The electrochemical performance of the electrodes, which were assembled in a symmetric two electrode supercapacitor cell, was tested using cyclic voltammetry (CV) and galvanostatic charge-discharge measurements. Stable operating voltage range for all materials was determined using CV and stability up to 3.5 V was observed for the electrolyte. The CV curves for each material and the hybrid structure rGO:SWNT (1:1) measured at scan rates from 10 – 100 mV/s are compared in Figure 2.

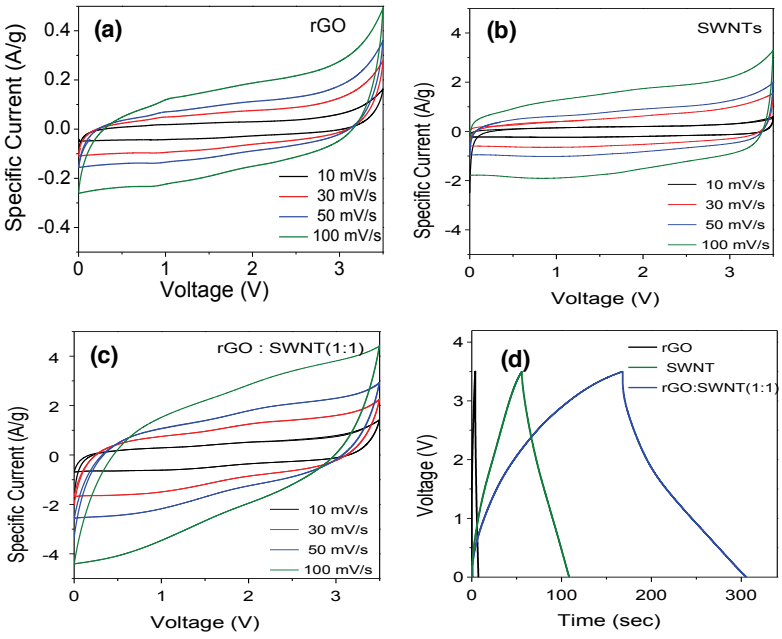


Figure 2: Cyclic voltammetry (CV) curves of (a) reduced graphite oxide, rGO, (b) SWNTs and (c) hybrid material, rGO+SWNT (1:1) at different scan rates from 10 to100 mV/s. (d) CV curves of the materials at 10 mV/s. Charge discharge cycles of rGO, SWNTs and a hybrid rGO+SWNT (1:1) at constant current of 1A/g.
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Almost rectangular curves were obtained for each sample, indicating that the stored charge is due mainly to an electrochemical double layer with a minor contribution from the pseudocapacitance, which is due to Faradaic processes occurring at the oxygen groups in the carbon materials. The rectangular shape indicates good capacitive behavior and rapid diffusion and transport of the electrolyte ions from the solution to the pores of the electrode materials. The charge-discharge curve illustrates the amount of charge stored and it can be seen that the hybrid material shows a tremendous improvement in charge storage.

The specific capacitance and energy density calculated from the charge-discharge curves show the synergy of the component nanomaterials which is realized in the hybrid material and this is illustrated in Figure 3.

The reduced graphite oxide, rGO, possesses a very low specific capacitance (*Csp*) of 6 F/g, which can be attributed to the stacking of the sheets and the reduced surface area available for electrolyte adsorption at the electrode. The SWNT material showed a specific capacitance of 66 F/g; addition of rGO to the SWNTs in equivalent weight ratio (1:1) enhanced the capacitance to 222 F/g, which represents an 37-fold increase in comparison to rGO and three-fold improvement over SWNTs alone. The strong enhancement of the capacity of the hybrid material indicates a synergistic effect, which cannot be explained by the rule of mixtures or by the addition of the individual capacitances for SWNTs and rGO.

The measurements also confirmed that a hybrid material with a composition rGO:SWNT = 1:1 gives superior performance as compared to other hybrid compositions (Figure 3c). The excellent lifetime stability of the hybrid electrode material rGO:SWNT (1:1) was confirmed by running a constant current charge-discharge for 1000 cycles at a current density of 1 A/g. The specific capacitance and the energy density were largely preserved giving values of 219 F/g and 93.2 Wh/kg, respectively. Thus the hybrid rGO+ SWNT (1:1) supercapacitor retains ~ 99% of its performance after 1000 cycles.

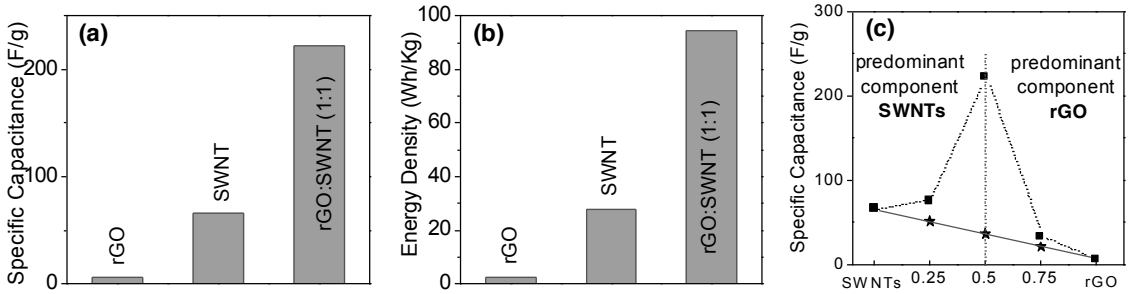

Figure 3: (a) specific capacitance and (b) energy density of the fabricated supercapacitor devices. (c) Specific capacitance Csp, of hybrid materials comprised of reduced GO (rGO) and SWNTs as a function of the composition (square symbols), and calculated Csp from the rule of mixtures (star symbols). Reprinted with permission from ref. [6] Copyright 2012, Wiley-VCH.

4 CONCLUSIONS

In conclusion a hybrid electrode material comprised of rGO and SWNTs (weight ratio 1:1) provides a supercapacitor with a specific capacitance of 222 F/g that is capable of delivering an energy density of 94.5 Wh/kg at room temperature. This structure utilizes the high conductivity of SWNTs and their ability to form a two-dimensional microporous network with interconnected SWNTs, in conjunction with chemically modified two-dimensional graphene. The introduction of functional groups, particularly in graphene, is explored to improve the pseudocapacitance. The incorporation of the two-dimensional graphene within the SWNT network allows for design of a hybrid structure with tunable porosity for enhanced electrolyte accessibility.

REFERENCES

[1] Conway, B. E., *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications*. Kluwer Academic/Plenum Publisher: Newyork, 1999.

[2] Kotz, R.; Carlen, M., Principles and Applications of Electrochemical Capacitors. *Electrochim. Acta* **2000,** 45, 2483-2498.

[3] Frackowiak, E.; Beguin, F., Carbon materials for the electrochemical storage of energy in capacitors. *Carbon* **2001,** 39, 937-950.

[4] Bekyarova, E.; Itkis, M. E.; Cabrera, N.; Zhao, B.; Yu, A.; Gao, J.; Haddon, R. C., Electronic Properties of Single-Walled Carbon Nanotube Networks. *J. Am. Chem. Soc*. **2005,** 127, 5990-5995.

[5] Ramesh, P.; Itkis, M. E.; Tang, J. M.; Haddon, R. C., SWNT-MWNT hybrid architecture for proton exchange membrane fuel cell cathodes. *J. Phys. Chem. C* **2008,** 112, 9089-9094.

[6] Jha, N.; Ramesh, P.; Bekyarova, E.; Itkis, M. E.; Haddon, R. C., High Energy Density Supercapacitor Based on a Hybrid Carbon Nanotube–Reduced Graphite Oxide Architecture. *Adv. Energy Mater*. **2012**, 2, 438-444.

[7] Hummers, W. S.; Offeman, R. E., Preparation of Graphitic Oxide. *J. Am. Chem. Soc*. **1958,** 80, 1339-1339.

[8] Bourlinos, A. B.; Gournis, D.; Petridis, D.; Szabo, T.; Szeri, A.; Dekany, I., Graphite Oxide: Chemical Reduction to Graphite and Surface Modification with Primary Aliphatic Amines and Amino acids. *Langmuir* **2003,** 19, 6050-6055.

[9] Worsley, K. A.; Kalinina, I.; Bekyarova, E.; Haddon, R. C., Functionalization and Dissolution of Nitric Acid Treated Single-Walled Carbon Nanotubes. *J. Am. Chem. Soc*. **2009,** 131, 18153-18158.

[10] Yan, J.; Wei, T.; Shao, B.; Fan, Z. J.; Qian, W. Z.; Zhang, M. L.; Wei, F., Preparation of a Graphene Nanosheet/polyaniline Composite with High Specific Capacitance. *Carbon* **2010,** 48, 487-493.

[11] Liu, C. G.; Yu, Z. N.; Neff, D.; Zhamu, A.; Jang, B. Z., Graphene-Based Supercapacitor with an Ultrahigh Energy Density. *Nano Lett*. **2010,** 10, 4863-4868.

[12] Itkis, M. E.; Perea, D.; Niyogi, S.; Love, J.; Tang, J.; Yu, A.; Kang, C.; Jung, R.; Haddon, R. C., Optimization of the Ni-Y Composition in Bulk Electric Arc Synthesis of Single-Walled Carbon Nanotubes by Use of Near-Infrared Spectroscopy. *J. Phys. Chem. B* **2004,** 108, 12770-12775.

[13] Itkis, M. E.; Perea, D.; Niyogi, S.; Rickard, S.; Hamon, M.; Hu, H.; Zhao, B.; Haddon, R. C., Purity Evaluation of As-Prepared Single-Walled Carbon Nanotube Soot by Use of Solution Phase Near-IR Spectroscopy. *Nano Lett*. **2003**, 3, 309-314.