Determination and enhancement of the capacitance contributions in carbon nanotube based electrode systems

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(Received 7 August 2009; accepted 12 October 2009; published online 5 November 2009)

We characterize the methodology of, and a possible way to enhance, the capacitance of carbon nanotube (CNT) electrode based electrochemical capacitors. Argon irradiation was used to controllably incorporate extrinsic defects into CNTs and increase the magnitude of both the pseudocapacitance and double-layer capacitance by as much as 50% and 200%, respectively, compared to untreated electrodes. Our work has implications in analyzing the prospects of CNT based electrochemical capacitors, through investigating ways and means of improving their charge storage capacity and energy density. © 2009 American Institute of Physics. [doi:10.1063/1.3258353]

Carbon nanotubes (CNTs) have been proposed for electrodes in electrochemical capacitors (ECCs)/supercapacitors primarily due to their large surface area and abundance of reaction sites^{1–5} with the possibility of large charge storage capacity and capacitance (C). Consequently, in an electrolyte where electrochemical reactions can occur over a wide voltage range (V), large energy densities^{1,2} (W) per unit mass (m) can be achieved through $W = (CV^2)/(2m)$. While possessing superior power densities due to the capability of fast charge/ discharge, presently CNT based ECCs have lower energy densities (1-10 W h/kg) compared to batteries^{3,6} (with 10-100 W h/kg), making them less competitive with the latter technology. In this paper, we aim to probe the total CNT capacitance (C_T) and suggest ways through which it can be improved. Consequently, we focus on the accurate characterization and analysis of the electrostatic/double layer⁷ (C_{dl}) and faradaic/pseudocapacitive⁸ (C_p) components of C_T . It should be noted that C_{dl} arises primarily due to charge separation across the electrode/electrolyte interface while C_p requires adsorption of electroactive species coupled with charge transfer.⁸ We then suggest a method aimed at increasing C_{dl} and C_p , based on the controlled introduction of defects into the CNTs through argon irradiation. Characterization of the CNT electrodes through Raman spectroscopy and cyclic voltammetry (CV) was used to understand the contributions to C_T .

Vertically aligned CNT mats were grown via thermal chemical vapor deposition at 615 °C on Si substrates, using a 5 nm thick Fe catalyst. A feed gas mixture composed of 50 SCCM acetylene for 1 min (SCCM denotes standard cubic centimeter per minute) and 500 SCCM argon was employed. Through scanning electron microscopy and transmission electron microscopy (TEM), the synthesized CNTs were determined to be $100\pm 5 \ \mu m$ long with a diameter of 17 ± 3 nm, with 200 ± 10 nm separation [Fig. 1(a)]. With the aim of investigating how defects create additional reactive sites and affect charge capacity, the as-grown CNT samples were then subject to argon irradiation under various conditions in a reactive ion etching chamber. We report re-

sults on CNT samples subject to an argon flow rate of 10 SCCM, under a background pressure of 30 mTorr, and applied power of 100 W for 30-90 s of irradiation. Raman spectroscopy analysis, using a 514.5 nm, 1.49 mW Ar ion laser (Renishaw), was used to monitor the influence of the argon exposure on CNT structural order and charging characteristics. The performance of the CNTs as electrodes was then characterized through CV experiments using a PCI4-300 potentiostat (Gamry Instruments) where the CNTs were used as the working electrode, with Pt as the counterelectrode and a standard calomel electrode (SCE) as the reference electrode—Fig. 1(a). The electrochemistry of the CNTs was probed over a voltage range of -0.4 to 0.8 V using $K_3Fe(CN)_6$ (0.5–10.0 mM) in a KCl (1*M*) supporting electrolyte over a scan rate range of 5-100 mV/s. This range was carefully chosen to eliminate the possibility of hexacyanoferrate complex adsorbate formation on the electrodes which could possibly affect electron transfer kinetics.

We observed that argon irradiation could be used to tune the number of defects in CNTs through monitoring the changes in the Raman peak intensities and peak widths [Fig. 1(b) inset]. The ratio of the integrated D-peak intensity (at ~1350 cm⁻¹, originating from noncollinear stretches of



FIG. 1. (Color online) (a) Use of CNTs as the WE, with Pt as the counter electrode in a CV setup. A SCE was used as the reference. The inset illustrates a TEM image sample of the individual CNTs. (b) The correlation length (L_a) of the CNTs decreases with increasing argon exposure. The inset depicts the Raman spectra for the as-prepared and argon irradiated (for times $\sim 30-90$ s) CNT electrodes.

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TABLE I. Characterization of untreated (time=0) and argon irradiated CNTs through Raman spectroscopy.

Ar irradiation times (s)	G peak (cm ⁻¹)	D peak (cm ⁻¹)	$(I_D/I_G)_L$	$\Delta \omega_{ m G} \ (m cm^{-1})$	$\Delta \omega_{ m D} \ (m cm^{-1})$	L _a (nm)
0	1586.4 ± 2.1	1347.0 ± 0.7	0.64 ± 0.02	70.0 ± 1.3	116.4 ± 7.5	68.4 ± 1.7
30	1586.0 ± 1.2	1353.0 ± 1.0	0.98 ± 0.08	89.5 ± 3.6	101.9 ± 2.0	45.2 ± 4.0
60	1587.4 ± 1.4	1353.0 ± 1.0	1.10 ± 0.03	89.2 ± 7.4	95.6 ± 7.2	40.1 ± 1.0
90	1588.2 ± 0.5	1353.6 ± 1.2	1.12 ± 0.04	89.3 ± 2.1	99.5 ± 0.5	39.3±1.4

C-C bonds) to the integrated G-peak intensity (at \sim 1580 cm⁻¹, from the linear stretching of the *sp*² bonds), $(I_D/I_G)_L$ was used to determine the defect correlation length (L_a) , as defined through the Tuinstra-Koenig relation⁹ $L_a(\text{nm}) = 4.4/(I_D/I_G)_L$ and characterize the defect density [Fig. 1(b) and Table I]. It was seen that with increasing argon exposure, L_a decreases [Fig. 1(b)], indicating an increase in the number of defects on the CNTs. The G-peak width also broadens due to argon exposure, as indicated by the enhanced full width at half maximum $(\Delta \omega_{\rm G})$ in Table I, and is upshifted in frequency suggestive of CNT charging.^{10,11} It is thought that the upshift is due to electron density being abstracted away from the carbon-carbon bonds effectively decreasing the bond length¹² and increasing the vibration frequency. Additionally, a decreased $\Delta \omega_{\rm D}$ could indicate a more uniform distribution of the defect energies.

We hypothesize that tuning the CNT charge and defect densities through argon irradiation can influence both C_{dl} and C_p . We probed the electrochemical characteristics of asprepared and defect tuned CNTs in CV by deconvoluting the total capacitive current $I_T(=C_T v)$, into contributions from the double-layer and pseudo-capacitive currents $(I_T=I_{dl}+I_p)$ using standard procedures, where v is the scan rate.^{13,14} To quickly summarize, the values of I_{dl} and I_p were carefully determined by first linearly fitting the current baseline (I_C) and then calculating $I_p[=I(E_p)-I_C]$ and $I_{dl}(=I_{C,cathodic})$

 $-I_{C,\text{anodic}}$ [Fig. 2(a)], where E_p is the voltage at which the current due to the faradaic reaction is maximum.

From the determination of $I_{dl}(=C_d v)$ and a known v, we estimate C_{dl} . To understand C_{dl} , we assume that $C_{dl}[=(\varepsilon_o \varepsilon_r A)/(L_D)]$ can be modeled as a parallel plate capacitor¹⁵ in which L_D was used as a measure of the diffuse ion layer thickness around the electrode of area A, in an electrolyte with a dielectric constant ε_r . We estimate⁷ ε_r as ~80, ε_o =8.854×10⁻¹² C²/Nm², and the A of the CNT electrode to be ~100 m²/g by considering the surface area of each nanotube,¹⁶ which is equivalent to treating each CNT as an individual electrode. Assuming a coupling between the individual CNTs and taking the projected area of the electrode (~mm²) leads to unrealistically high values^{1,17} for the capacitances of the order of mF/cm² and L_D of the order of 0.005 nm.

The pseudo-capacitance, $C_p(=I_p/v)$, which arises from the faradaic reactions at the CNT surface, e.g., due to redox reactions from adsorbed species such as $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$, was then derived from the cathodic/anodic peak current values [Fig. 2(a)]. At 298 K, I_p is defined through the Randles–Sevcik equation,¹⁴ i.e., $I_p=2.65 \times 10^5 n^{1.5} c_i \sqrt{D_o v}$ $=Bc_i \sqrt{v}$, where $D_o(\sim 6.9 \times 10^{-6} \text{ cm}^2/\text{s})$ is the diffusion coefficient of the cyanide species,¹⁸ n is the number of electrons transferred for a given redox reaction, and B (/B', see



FIG. 2. (Color online) (a) The deconvolution of observed CV spectrum, or argon exposed CNT electrodes, e.g., with a $K_3Fe(CN)_6$ concentration of 6 mM and a v (scan rate) of 20 mV/s, into the peak (I_p) and double-layer (I_{dl}) currents, using a baseline current (I_c) . (b) The variation of the total CNT capacitance (C_T) with $1/\sqrt{\nu}$ at various concentrations. (c) The variation of C_T with concentration at various v. (d) The C_p correlates inversely to the L_a (e.g., at a v of 5 mV/s and 6 mM).

TABLE II. The variation of C_p with argon irradiation time as a function of scan rate (ν). The K₃Fe(CN)₆ concentration was fixed at 6 mM.

Ar irradiation times (s)	0	30	60	90
Scan rate (mV/s)	$C_p (\mu \mathrm{F/cm^2})$	$C_p (\mu \mathrm{F/cm^2})$	$C_p (\mu \mathrm{F/cm^2})$	$C_p (\mu \mathrm{F/cm}^2)$
5	255 ± 13	285 ± 4	338 ± 5	395 ± 14
20	155 ± 8	170 ± 9	166 ± 1	247 ± 9
50	110 ± 6	124 ± 4	111 ± 3	188 ± 8
100	82 ± 4	101 ± 4	94 ± 8	116 ± 4

below) is a constant. From $I_T=I_{dl}+I_p$, we deduce that C_T varies with the v as $C_T=(B'/\sqrt{\nu})+C_{dl}$, where C_p varies as $1/\sqrt{\nu}$ and C_{dl} is constant. Plots of C_T versus $1/\sqrt{\nu}$ [Fig. 2(b)] were then used to extract the individual values of C_p and C_{dl} for both untreated and argon exposed CNTs, which have then been tabulated as a function of scan rate (Table II for C_p) and concentration (Tables III and IV for C_p and C_{dl} , respectively). The error bars for all the determined values have been estimated through the standard deviation of the sample data over multiple measurements. As expected, larger values of C_p are manifested at smaller scan rates (Table II). It was interesting then to note a monotonic increase in C_p with increased argon exposure, with an ~50% rise at a given ν , e.g., ~255 μ F/cm² enhanced to ~116 μ F/cm² at 100 mV/s.

The influence of argon irradiation in increasing both C_p and C_{dl} was also seen as a function of the K₃Fe(CN)₆ concentration. For a particular CNT treatment (i.e., as synthesized or argon exposed) C_p increases with concentration [Fig. 2(c) and Table III], in accordance with the Randles-Sevcik equation. A further enhancement of C_p by 30%–60%, at any given concentration, was seen due to the argon, presumably due to the creation of additional electroactive defects and reactive sites. The C_p increase was correlated with the decreased L_a [Fig. 2(d)], which again indicates the importance of defects for increased charge storage. However, the influence of argon seems to be even more strongly felt through a 120%–200% increase in $C_{\rm dl}$ (Table IV), e.g., ~3 μ F/cm² enhanced to ~10 μ F/cm² at 0.5 mM, and $\sim 23 \ \mu F/cm^2$ enhanced to $\sim 58 \ \mu F/cm^2$ at 10 mM. The change of the ambient conditions around the electrode as a function of CNT exposure to argon can also be indicated through a reduced L_D , which was estimated from C_{dl} (Table IV). For example, it was noted that the changes in C_{dl} with concentration was due to the changes in the Debye length

TABLE III. The variation of C_p with argon irradiation time, as a function of K₃Fe(CN)₆ concentration. The scan rate (ν) was fixed at 20 mV/s.

Ar irradiation times (s)	0	30	60	90
Concentration (mM)	$C_p (\mu \mathrm{F/cm^2})$	$C_p (\mu \mathrm{F/cm^2})$	$C_p (\mu \mathrm{F/cm^2})$	$C_p (\mu \mathrm{F/cm}^2)$
0.5	11 ± 0	10 ± 1	13 ± 1	15 ± 1
3	83 ± 6	83 ± 1	84 ± 4	108 ± 4
6	155 ± 8	170 ± 9	166 ± 1	247 ± 9
10	316 ± 21	261 ± 3	309 ± 2	413 ± 34

TABLE IV. The variation of $C_{\rm dl}$ with argon irradiation time, as a function of K_3 Fe(CN)₆ concentration. The scan rate (ν) was fixed at 20 mV/s.

Ar irradiation times (s)	0	30	60	90
Concentration (mM)	$\begin{array}{c} C_{\rm dl} \ (\mu {\rm F/cm^2}) \\ [L_D({\rm nm})] \end{array}$	$\begin{array}{c} C_{\rm dl} \; (\mu {\rm F/cm^2}) \\ [L_D({\rm nm})] \end{array}$	$\begin{array}{c} C_{\rm dl} \ (\mu {\rm F/cm^2}) \\ [L_D({\rm nm})] \end{array}$	$\begin{array}{c} C_{\rm dl} ~(\mu {\rm F/cm^2}) \\ [L_D({\rm nm})] \end{array}$
0.5	3±0[~21]	9±0[~8]	8±1[~9]	10±1[~7]
3	$7 \pm 0 [\sim 9]$	$10 \pm 0 [\sim 7]$	$13 \pm 2[\sim 6]$	$16 \pm 0[\sim 4]$
6	$16 \pm 1[\sim 4]$	$16 \pm 3[\sim 4]$	$20 \pm 2[\sim 4]$	$44 \pm 1[\sim 2]$
10	$23 \pm 2[\sim 3]$	$23 \pm 1[\sim 3]$	$41 \pm 1[\sim 2]$	58±3[~1]

 (κ) ,⁷ where we found that the $\kappa(\sim 1/\sqrt{c_i})$ was approximately equal to L_D . Essentially, an increased number of reaction sites allows for a greater ion concentration around the electrode and concomitantly higher residual charge. The values of $C_{\rm dl}$ were then slightly larger than previously observed¹ due to a decreased L_D .

In summary, we have shown that argon irradiation of CNTs could be used to further increase the total capacitance of CNT based electrodes, possibly due to the introduction of electroactive reaction sites, through an individual enhancement of both the double-layer and pseudo-capacitive components. Such a strategy of artificial introduction of defects¹⁹ may be able to harness the electrical conductivity of the CNTs along with an enhanced effective specific surface area.

We gratefully acknowledge support from the National Science Foundation (Grant No. ECS-05-08514 and the Office of Naval Research (Grant No. N00014-06-1-0234). We are thankful to Professor Frank Talke's group at UC, San Diego for use of the Raman spectrometer.

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