

Determination and enhancement of the capacitance contributions in carbon nanotube based electrode systems for CNT based electrochemical capacitors/supercapacitors

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Introduction

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] 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 (W) per unit mass (m) can be achieved, through $W = \frac{CV^2}{2m}$.

While possessing superior power densities due to the capability of fast charge/discharge, presently CNT based ECCs have lower energy densities (1-10 Wh/kg) compared to batteries[2] (with 10-100 Wh/kg), making them less competitive compared to the latter technology. In this paper, we aim to probe the total CNT capacitance (C_T) and suggest ways in which it can be improved. Consequently, we focus on the accurate characterization and analysis of the electrostatic/double layer[3] (C_{dl}) and faradaic/pseudo-capacitive[4] (C_p) components of the C_T . The 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.[4] 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 CNTs through Raman spectroscopy and Cyclic Voltammetry (CV) was used.

Experimental

Vertically aligned CNT mats ($\sim 100 \mu\text{m}$ long with a diameter of $\sim 20 \text{ nm}$, with 200 nm separation) were grown via thermal chemical vapor deposition (CVD) at 615°C on Si substrates. 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 Trion reactive ion etching (RIE) chamber. Raman spectroscopy analysis 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 counter electrode and a standard calomel electrode (SCE) for reference – Fig. 1a. The electrochemistry of the CNTs was probed over a voltage range of -0.4 to 0.8 V using $\text{K}_3\text{Fe}(\text{CN})_6$ (0.5 - 10.0 mM) in a KCl (1 M) supporting electrolyte over a scan rate range of 5 - 100 mV/s . 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. 1b). The ratio of the integrated D- peak intensity (at $\sim 1350 \text{ cm}^{-1}$) to the G-peak intensity (at $\sim 1580 \text{ cm}^{-1}$) was used to determine the defect correlation length (L_a), as defined through the Tuinstra-Koenig relation[5] $L_a \text{ (nm)} = 4.4/(I_D/I_G)$ and characterize the defect density. It was seen that with increasing argon exposure, L_a decreases (Fig. 1b), indicating an increase in the number of defects on the CNTs. The G-peak width also broadens due to Ar exposure, and is up-shifted in frequency suggestive of CNT charging[6].

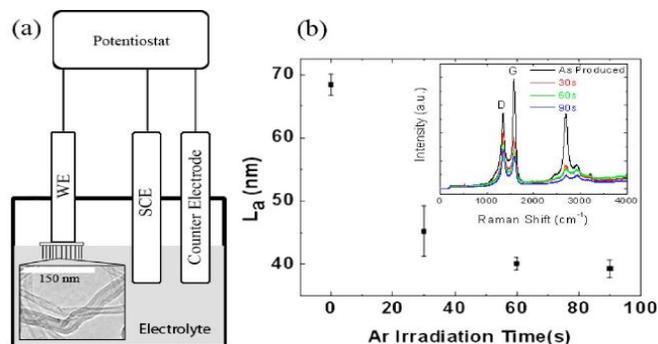


Fig. 1(a) Use of CNTs as the working electrode (WE), with Pt as the counter electrode in a Cyclic Voltammetry (CV) setup. A Standard Calomel Electrode (SCE) was used as the reference. **(b)** The correlation length (L_a) of the CNTs decreases with increasing argon exposure. The inset depicts the Raman spectra for the as-prepared and argon irradiated CNT electrodes.

Results and Discussion

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 as-prepared and defect tuned CNTs in CV by deconvoluting the total capacitive current $I_T (= C_T v)$, where v is the scan rate, into contributions from the double-layer and pseudo-capacitive currents ($I_T = I_{dl} + I_p$), using standard procedures. 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 $I_{dl} (= I_{C, cathodic} - I_{C, anodic})$ (Fig. 2a), where E_p is the potential/voltage at which the current due to the faradaic reaction is maximum.

From the determination of $I_{dl} (= C_{dl} v)$ and a known v , we estimate C_{dl} . To understand C_{dl} , we assume that $C_{dl} (= \frac{\epsilon_o \epsilon_r A}{L_D})$ can be modeled as a parallel plate capacitor in which

L_D can be 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 estimate[3] ϵ_r as ~ 80 , $\epsilon_o = 8.854 \times 10^{-12} \text{ C}^2/\text{Nm}^2$, and the A of the CNT electrode to be $\sim 100 \text{ m}^2/\text{g}$ by considering the surface area of each nanotube[7], 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 ($\sim \text{mm}^2$) leads to unrealistically high values[8, 9] for the capacitances of the order of mF/cm^2 and L_D of the order of 0.005 nm.

The current due to the pseudo-capacitance, $I_p (=C_p \nu)$, 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 the $\text{Fe}(\text{CN})_6^{4-}$, was then derived from the cathodic/anodic peak current values (Fig. 2a).

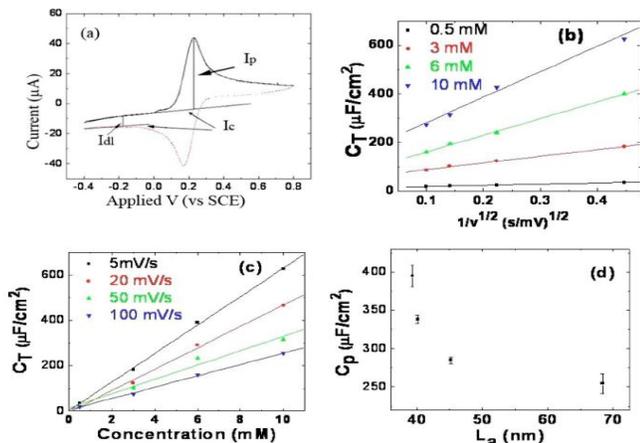


Fig. 2 (a) The deconvolution of observed CV spectrum, or argon exposed CNT electrodes, e.g., with a $\text{K}_3\text{Fe}(\text{CN})_6$ concentration of 6 mM and a ν (scan rate) of 20mV/s, into the peak (I_p) and double-layer (I_{dl}) currents, using a baseline current (I_c). (b) The variation of the total CNT capacitance (C_T) with $1/\sqrt{\nu}$ at various concentrations. (c) The variation of C_T with concentration at various ν . (d) The C_p correlates inversely to the L_a (e.g., at a ν of 5mV/s and 6 mM).

At 298 K, I_p is defined through the Randles-Sevcik equation, i.e., $I_p = 2.65 \cdot 10^5 n^{1.5} c_i \sqrt{D_o \nu} = B c_i \sqrt{\nu}$, where D_o ($\sim 6.9 \times 10^{-6} \text{ cm}^2/\text{s}$) is the diffusion coefficient of the cyanide species[10], n is the number of electrons transferred per a given redox reaction, and B (B' - see below) is a constant. From $I_T = I_{dl} + I_p$, we deduce that C_T varies with the ν as: $C_T = \frac{B'}{\sqrt{\nu}} + C_{dl}$, where C_p varies as $\frac{1}{\sqrt{\nu}}$ and C_{dl} is constant. Plots

of C_T vs. $1/\sqrt{\nu}$ (Fig. 2b) were then used to extract the individual values of C_p and C_{dl} for both untreated and argon exposed CNTs. For a particular CNT treatment (i.e., as synthesized or argon exposed) C_p increases with concentration (Fig. 2c). 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 to the decreased L_a (Fig. 2d), which indicates the importance of defects for increased charge storage. The influence of argon seems to be even more strongly felt through a 120-200% increase in C_{dl} (Table I), e.g., $\sim 3 \mu\text{F}/\text{cm}^2$ enhanced to $\sim 10 \mu\text{F}/\text{cm}^2$ at 0.5 mM

Table I A significant enhancement ($> 200\%$) of the C_{dl} due to increased argon irradiation at a given scan rate can be used for defect tuned CNTs in supercapacitor applications

The change of the ambient conditions around the electrode, as a function of CNT exposure to argon can also be

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

indicated through a reduced L_D , as estimated from C_{dl} (see Table I). The changes in C_{dl} with concentration was due to the changes in the Debye length (κ)[3], which was approximately equal to L_D . The values of C_{dl} were then slightly larger than previously observed¹ due to a decreased L_D .

Conclusions

We have shown that argon irradiation 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 may be able to harness the electrical conductivity of the CNTs along with an enhanced specific surface area, for CNT based electrochemical capacitors / supercapacitors.

Acknowledgments We appreciate support from the National Science Foundation (Grant ECS-06-43761)

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