Nanostructured electrochemical capacitors (ECs) are advantageous for charge and energy storage due to their intrinsically large surface area, which contributes to a large electrostatic/double layer capacitor ($C_{dl}$). However, the intrinsically small density of states in nanostructures results in a quantum capacitor ($C_Q$) in series with $C_{dl}$ which could diminish the total device capacitance value ($C_{tot}$). We investigate, through comparison with experiment, the relative magnitudes of $C_{dl}$ and $C_Q$ in electrodes constituted of carbon nanotube arrays. Consequently, we attribute the increase in $C_{tot}$ resulting from ionizing radiation to an increase in $C_Q$ and suggest limits to the capacitance in ECs.

**Abstract**

Electrochemical energy storage may be broadly classified as encompassing either batteries or electrochemical capacitors (ECs). While the former category incorporates devices with high energy density (∼100 Wh/kg) and relatively low power density (∼1 kW/kg), the latter comprises media with opposite attributes, i.e., relatively lower energy density (∼10 Wh/kg) and higher power density (∼10 kW/kg). The overarching imperative is then to devise intermediate ECs, combining the best of both energy and power densities. Moreover, characteristics such as a high cycle life, i.e., the capability of rapid charging and discharging, for millions of cycles must be incorporated.

Much EC work has focused on charge storage in a double layer comprised of the electrode charge and electrolyte charge of opposite polarity—Fig. 1. Double layer capacitance/unit area ($C_{dl}$) is directly proportional to the dielectric constant ($\varepsilon = \varepsilon_0 \varepsilon_r$, where $\varepsilon_0$ is the permittivity of free space and is equal to 8.854 × 10$^{-12}$ F/m and $\varepsilon_r$ is the relative permittivity, e.g., ∼80 for water) and inversely proportional to the charge separation distance between the positive (+) and negative (−) charges. $C_{dl}$ is further constituted of a Helmholtz capacitor, where distances are of the order of the electrolyte ionic diameters, as well as a diffusive capacitor, with mean distances of the order of the Debye length $d = \sqrt{\frac{2k_B T}{\varepsilon_0 \varepsilon_r I^2}} = 9.78 \frac{1}{\sqrt{I}}$ nm, where $k_B$ (= 1.38 × 10$^{-23}$ J/K) is the Boltzmann constant, $T$ is the absolute temperature (K), $N_A$ (≈ 6.02 × 10$^{23}$ atoms/mole) is the Avogadro number, ($\varepsilon e$) is the net charge with $e$ as the elementary electronic charge (≈1.6 × 10$^{-19}$ C), and $I$ (in moles/m$^3$) is the electrolyte concentration. For an aqueous electrolyte (at 1 M concentration), $C_{dl}$ could then potentially be of the order of 250 µF/cm$^2$. The utilization of a high surface area electrode substrate, e.g., carbon nanotubes (CNTs), where the total surface area would be much larger than the projected area would also be beneficial. However, the values reported in literature are typically an order of magnitude lower, and this has been tentatively ascribed to incomplete/inadequate utilization of the surface area. A substantial addition to total capacitance ($C_{tot}$) through the utilization of parallel redox capacitance/pseudocapacitance ($C_P$), which mimics battery like behavior, could also be obtained in ECs as discussed in a previous study. It was found that ion irradiation, facilitated through plasma processing, increased the observed $C_{tot}$ value. However, details of the underlying mechanisms were not specified. In this article, we propose a possible mechanism through detailed comparison with experiment and seek to understand the limits of capacitance that may be manifested with a given CNT configuration. The underlying principles may be adapted to other nanostructure and device types as well.

We considered quantum capacitance ($C_Q$), which is relevant when nanostructures such as CNTs, with a finite density of states (DoS) $D(E)$, as depicted in Fig. 2. The increase (decrease) of the Fermi energy ($E_F$) of the CNTs could be significant, relative to the bulk electrolyte, when charge carriers

**Figure 1**

A schematic of electrode configuration in an electrochemical capacitor, zoomed into a section of the CNT array. $C_Q$ and $C_P$ in series represented within a single CNT. As the surface area for the CNT electrode (in red) is much higher than that of the counter electrode (in green), the capacitance value of the former is much more significant.
of single type, e.g., electrons of magnitude $dQ (= e\cdot dn)$, are added (removed) due to an applied voltage change ($dV$). An effective capacitance could therefore be defined for a given electrode, considering the DoS at the $E_F$ as:

$$C_Q = \frac{dQ}{dV} = \frac{e\cdot dn}{e\cdot dE_F} = e^2 D(E_F).$$  \hspace{1cm} (1)

We model the net device capacitance in Fig. 1 as a series combination of $C_{dl}$ and $C_Q$. If, as hypothesized, the role of ion irradiation (e.g., through plasma processing) was to introduce fixed charges, then $C_Q$ increases significantly with increasing processing time. The series combination of $C_Q$ and $C_{dl}$ would allow an increase in $C_{tot}$ consistent with the experiment as can be understood through

$$\frac{1}{C_{tot}} = \frac{1}{C_{dl}} + \frac{1}{C_Q}. \hspace{1cm} (2)$$

It should be pointed out that our work focuses on correlating capacitance contributions from multi walled CNTs (MWCNTs) (with concentric nanotubes of gradually decreasing perimeters) while previous works, e.g., by Fang et al.\cite{12} and Xia et al.,\cite{13} are on graphene sheets or nanoribbons, the latter of which have sub-bands due to the finite width and become graphene sheets in the infinite width limit. The $C_Q$ values of nanoribbons and graphene were discussed in Ref. 12 for MOSFET (metal oxide semiconductor field effect transistor)-like devices. While they discussed the series addition of the gate oxide capacitance and $C_Q$, we discuss the series addition of $C_{dl}$ with $C_Q$, as appropriate for an electrochemical capacitor. The maximum carrier concentration ($n$) studied in Ref. 12 was less than $2 \times 10^{12}$ cm$^{-2}$ with concomitant $C_Q$ values of the order of $10 \mu$F/cm$^2$, which seem to be comparable with the values calculated in this article. In Ref. 13, they fabricated experimental MOSFET-like devices using a graphene sheet and analyzed their data. Accordingly, there was no need to consider sub-band contributions, but for our purposes, counting contributions of several tens of all relevant sub-bands are critical and that is what will be performed below.

We modeled MWCNT characteristics, in accordance with the previous experiments which used such ensembles (with average individual MWCNT diameter of 20 nm and spacing 200 nm on a 5 mm $\times$ 5 mm Si substrates) as electrodes.\cite{8,11} We calculated the DoS of a constituent wall in a MWCNT, following previous methodology,\cite{10,14} modeled as a rolled graphene sheet (infinite in the y-direction and both periodic and finite in the orthogonal x-direction). It was assumed that the walls are independent of each other,\cite{15} with the implication that the total DoS can be obtained as the sum of the DoS for each constituent wall. We considered zigzag CNTs (involving rolling of the graphene sheet in the x-direction), as this category encompasses both semiconducting and metallic CNTs.\cite{16} As we consider relatively large diameter CNTs,\cite{11} the details as to how graphene is rolled to yield CNTs, i.e., whether zigzag or armchair or chiral,\cite{17} will not influence $C_Q$. The exact dispersion relation for a graphene sheet, through the tight-binding approximation\cite{10,18} is

$$E(k_x,k_y) = \pm \gamma_1 \sqrt{1 + 4\cos\left(\frac{3\pi k_x}{2}\right) \cos\left(\frac{ak_x}{2}\right) + 4\cos^2\left(\frac{ak_x}{2}\right)}.$$  \hspace{1cm} (3)

In the above equation, $a = \sqrt{3}a_0$ where $a_0$ ($= 0.142$ nm) is the C-C bond length and the overlap integral $\gamma_1 = 2.9$ eV.\cite{15} The 20 nm MWCNT with 15 walls was approximately indexed through $[N, 0]$ (with $N = 250$ for the outermost wall, and decreasing by 10 for each successive inner wall), and was effectively one dimensional since $k_{x,n}$ is a function of $\gamma_1$ and $k_y$ is continuous. The DoS for a single sub-band is then $\frac{d\Delta V}{d\Delta E_F}$ with $\gamma_1$, $\gamma_2$, and the 4 in the numerator accounted for the electron spin degeneracy and the positive/negative $k_y$.

Since $C_Q$ is a function of $E_F$ from Eq. (1), we needed to estimate an appropriate value for $E_F$. In a graphene sheet with no impurities, each carbon atom provides one electron to the $p_z$ orbital, yielding semi-metallic behavior and implying $E_F = 0$ eV, and zero carrier density ($n$) at $T = 0$ K. However, $n$ could range around $4.6 \times 10^{12}$ cm$^{-2}$, corresponding to the two-dimensional carrier density interpolated from the experimental value for bulk graphite\cite{15} of $10^{10}$ cm$^{-2}$, i.e., through $(10^{19})^{1/3}$. With variability in $n$, e.g., due to defects,\cite{13} etc., attempting an exact $E_F$ would yield imprecise values, and it could then be appropriate to estimate $n$ by approximating the CNTs as sheets of graphene and calculating the DoS, as was
done here. The \( n = 4.6 \times 10^{12} \text{ cm}^{-2} \) is then only posited as a representative number for the purpose of illustrating the concepts. The actual \( n \) in any sample could either be below or above\(^{20} \) this number with a corresponding decrease/increase in \( C_{dl} \).

From the total carrier concentration at the Fermi energy, \( n(E_F) \), the \( \frac{d}{dE} \int_0^{E_F} D(E)f(E)dE \). The \( f(E) \) is the Fermi-Dirac function and was approximated as a step function in our calculations, as the difference between the value of \( f(E) \) with a finite temperature \( (T=300 \text{ K}) \) and with \( T=0 \text{ K} \) was at most 5\%. The \( E_F \) values were found to range around 105 meV (with \( n = 4.6 \times 10^{12} \text{ cm}^{-2} \)). Computing \( E_F \) \((k_x,n,k_y)\) from Eq. (3), and then \( C_{dl}(k_x,n,k_y) \) from Eq. (1), pairs of \( E_F \) and \( C_{dl} \) for all sub-bands \( k_x,n \) over the Brillouin zone for \( k_y \) are plotted in Fig. 2(b). \( C_{dl}(E_F) \) is constant initially due to the metallic CNTs, up to \( \sim E_F = 50 \text{ meV} \), due to the constituent metallic CNTs with finite and constant DoS, where \( C_{dl} \) does not increase as there is no sub-band contribution from the CNTs. The staircase like structure in the variation results from the contribution of successive sub-bands to the DoS. The variation of capacitance per unit length is the product of the obtained \( C_{tot} \) value, the average CNT length, \( \sim 100 \mu \text{m} \), and the estimated CNT density on the substrate, \( \sim 2.5 \times 10^9 \text{ cm}^{-2} \), yielding an expected capacitance value per projected area of \( \sim 1200 \mu \text{F/cm}^2 \). Dividing this value by the weight of the CNTs \( \sim 40 \mu \text{g} \), the capacitance values, in \( \mu \text{F/g} \), were computed and are shown in comparison to the experimental values (details have been previously reported\(^{8,11} \)) in Fig. 3. The figure then indicates the relative magnitudes of \( C_Q \) relevant to the measured capacitance values and indicates variable \( C_Q \), being more significant (for a series combination of \( C_{dl} \) and \( C_Q \)) at lower electrolyte concentrations when the CNT is sufficiently isolated so that its DoS is small. We generally observe from the figure that while higher electrolyte concentrations may be adequately modeled through the use of \( C_{dl} \) alone, lower concentrations need \( C_Q \) as well. \( C_Q \) is significant when the CNT is sufficiently isolated so that its DoS is small. As \( I \) increases, charge transfer between CNT and electrolyte may be more likely, reducing isolation and increasing the CNT DoS effectively so that \( C_Q \) increases and becomes insignificant, as per Eq. (2).

Several insights are obtained through our analyses. For example, the magnitudes of both \( C_Q \) and \( C_{dl} \) are comparable and suggest an explanation for the considerable \( (\sim 300\%) \) increase in \( C_{tot} \) when the CNT constituted electrodes are subject to argon plasma processing.\(^{8,11} \) Such exposure was hypothesized to introduce charged acceptor like defects into the CNT’s carbon lattice, through argon abstracting electronic charge from the carbon bonds. Much like surface states in semiconductors,\(^{22} \) the fixed charges in the CNT lattice are immobile, and do not respond to applied voltage and would not contribute directly to \( C_{dl} \). However, the added charge density (which would be proportional to the exposure time) affects the Fermi energy and enhances \( C_Q \). A higher \( C_Q \) closer to \( C_{dl} \) enhances the maximum \( C_{tot} \) value that could be obtained from a given system. We can also conclude that the limits to the magnitude of the capacitance value that can be obtained from CNT or nanostructure based electrochemical capacitors are a function of the series combination of both the electrostatic/double layer capacitor as well as the quantum capacitor. In a situation where both are comparable, one would need to increase the quantum capacitance value, say through varying the charge density, in order to maximize total capacitance.

![Figure 3](image-url)
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