

Modeling carbon nanotube ultracapacitor

Antonios Orphanou, Toshishige Yamada*, and Cary Y. Yang

Center for Nanostructures, Santa Clara University, Santa Clara, California, 95053, USA

Abstract— We report a study on modeling carbon nanotube (CNT) ultracapacitor performance, utilizing molecular dynamics to obtain solutions of Poisson's equation within the capacitor cell. For a given voltage, the total current is computed based on the electric field generated from the nanotube electrodes and the friction caused by the motion of the electrolyte ions, yielding the frequency-dependent impedance. From the current and impedance behavior at a given frequency, we extract the Nyquist and Cyclic-Voltammetry plots for the simulated ultracapacitor. These plots compare well with existing experimental data. The behavior of the capacitor is further analyzed based on simulated spatial distributions of electrolyte ions.

Index Terms – Ultracapacitor, carbon nanotube, Nyquist plot, Cyclic Voltammetry plot

The analysis of ultracapacitor (UC) is quite primitive and phenomenological, using an equivalent circuit model to fit the measured Nyquist plot [1]. Further, there are no detailed science-based models describing how electrolyte ions move. We propose a particle-based approach to model the behavior of carbon nanotube ultracapacitor (CNU), using molecular dynamics [2] to obtain solutions of Poisson's equation within the capacitor cell. Vertically grown CNT arrays increase the effective capacitor plate area and the capacitor energy storage capacity drastically [3,4]. Because we use only 200 particles in our simulation, we need to establish a systematic scaling relation. Current in our simulation is due to electronic conduction (not requiring actual movement of charges such as displacement current) and ionic convection (actual movement of ions between electrodes), which obey different scaling rules. Our current, voltage, and time are all scaled, and because of the presence of various transport mechanisms, scaling rules are complicated.

Figure 1(a) shows a measured Nyquist plot for a CNU [5] compared with our simulation results at an applied voltage of 0.6 V. A Nyquist plot displays the capacitor's frequency-dependent reactance $\text{Im}(Z)$ as a function of resistance $\text{Re}(Z)$ with the applied voltage frequency as a parameter. The measured plot was obtained from Electrical Impedance Spectroscopy (EIS) measurements for a CNU consisting of a 6 mole/liter KOH electrolyte solution subject to an applied voltage. Figure 1b shows the results of our simulation at a voltage of 1.4 V versus measurements at 0.2 V and 0.6 V, confirming the correct trend as voltage increases.

*Email: tyamada@scu.edu

Figure 2(a) shows the simulated Cyclic Voltammetry (CV) characteristics for a sweep rate of 1.42 V/ms. In CV measurements, the capacitor is linearly charged and subsequently allowed to discharge, yielding the total current as a function of the electrode voltage during the charging and discharging cycles. Thus it provides qualitative information about the CNU total capacitance and parasitics, based on how the measured CV plot deviates from the one for an ideal capacitor. Figure 2(b) shows the measured CV plot for the same capacitor setup at 1 mV/s. In our simulations, we employ a much smaller CNU cell compared to those in the reported experiments. Thus, when comparing our modeling results to experiment, we must scale current, voltage, and time accordingly. Appropriately scaled quantities are used in our simulation results shown here. Details of this scaling procedure will be presented elsewhere. The presence of voltage-dependent drift current in the real capacitor gives rise to a distorted parallelogram for the measured CV plot, unlike that of the simulated capacitor in Fig. 2(a).

Figure 3 illustrates the electrolyte ion distributions in the simulated CNU unit cell for three different frequency ranges, (a) low-frequency, (b) mid-frequency, and (c) high-frequency. From the ionic motion and distribution, the total current in the capacitor is calculated as a function of frequency. For the ionic distribution at low frequency in Fig. 3(a), we observe that the CNU exhibits virtually pure capacitive behavior. The immobile electrolyte ions are attached to the electrodes yielding strong displacement currents, weak drift-convection currents, and a high electrode resistance. For the mid-frequency range in Fig. 3b, the ions start to drift toward the center and mix, but are still separated, creating non-uniformity in the electrolyte charge distribution. Thus, the current consists of a strong drift-convection and a weak displacement component. At high frequencies in Fig. 3(c), the ions cannot follow the applied voltage, and the current is primarily due to drift motion of the electrons. The simulated ionic distributions for the three frequency ranges are consistent with the observed decrease in capacitance with decreasing frequency in the Nyquist plot shown in Fig. 1.

We have developed a particle-based model to study the ionic motion in a carbon nanotube ultracapacitor. Using the ionic properties and distribution of the liquid electrolyte, we have successfully calculated the total current within the CNU. Further, we have extracted Cyclic Voltammetry and Nyquist plots from our simulated results, which compare well with published experimental data.

REFERENCES

[1] Koetz R.; Carlen M.; *Electrochem. Acta* **2000**, 45, 2483.
 [2] Yamada T.; Ferry D. K.; *Phys. Rev. B*, **1993**, 47, 6416.
 [3] Chen P. C.; Shen G.; Sukcharoenchoke S.; Zhou C. W.; *Appl. Phys. Lett.* **2009**, 94, 043113.

[4] Schindall J.; *IEEE Spectrum*, Nov. **2007**.
 [5] Frackowiak E.; Metenier K.; Bertagna V.; Beguin F.; *Appl. Phys. Lett.* **2000**, 77, 2421.

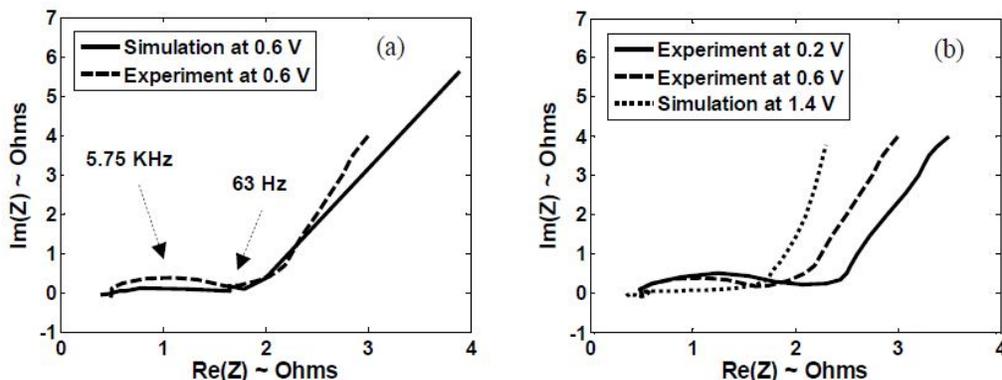


Figure 1. Experimental and simulated Nyquist plots for a CNU with a 6 mole/liter KOH electrolyte at 0.6 V (a) and at 0.2 V, 0.6 V, and 1.4 V (b). The effect of electrode double layer capacitance (DLC) is clearly visible around the 5.75 kHz mark in the simulated data in (a). DLC is created by the electrode and electrolyte ions, when the latter are not completely attached to their respective electrodes. Thus DLC increases the UC reactance, creating the "bump" in the Nyquist plot around 5.75 kHz.

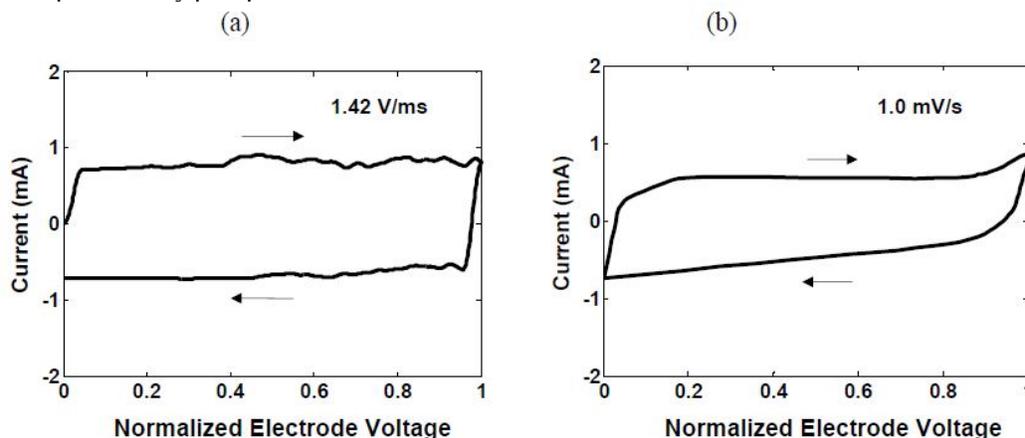


Figure 2. Experimental and simulated CV plots for the same CNU as in Fig. 1. (a) Simulated CV plot. The arrows indicate the sweep directions. (b) Experimental CV plot at 1 mV/s.

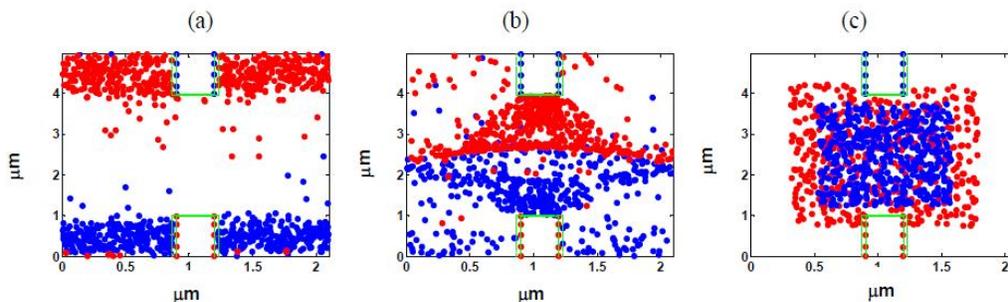


Figure 3. Ionic distribution snapshots at (a) low, (b) mid, and (c) high frequencies in the simulated CNU cell, where the CNT electrodes are situated along the green lines. Negative charges are indicated in red and positive in blue.