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Quantum Effects on the Capacitance of Graphene-Based Electrodes

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Abstract: Quantum capacitance has been recently measured for electric double layers (EDL) at electrolyte/graphene interfaces. However, the importance of quantum capacitance in realistic carbon electrodes is not clear. Toward understanding that from a theoretical perspective, here we studied the quantum capacitance and total capacitance of graphene electrodes as a function of the number of graphene layers. The quantum capacitance was obtained from electronic density functional theory based on fixed band approximation with an implicit solvation model, while the EDL capacitances were from classical density functional theory. We found that quantum capacitance plays a dominant role in total capacitance of the single-layer graphene both in aqueous and ionic-liquid electrolytes but the contribution decreases as the number of graphene layers increases. The total integral capacitance roughly levels off and is dominated by the EDL capacitance beyond about four graphene layers. Because many porous carbons have nanopores with stacked graphene layers at the surface, this research provides a good estimate of the effect of quantum capacitance on their electrochemical performance.

Key Words: Carbon Electrode, Quantum Capacitance, Few-layer Graphene, Classical DFT

1. Introduction

Electric double-layer capacitors (EDLCs) are a type of supercapacitors that have high power density and long cycle life. Unlike rechargeable batteries, EDLCs store electric energy at solid-electrolyte interfaces by applying a bias voltage.[1] The specific capacitance of an EDLC is on the order of hundreds of Farads per gram, much greater than that of a conventional dielectric capacitor.[2] In recent years, graphene has been found to be a potential electrode for EDLCs.[3] Unlike traditional electrodes such as metals, graphene electrodes are unique two-dimensional materials with a quantum capacitance (QC).[4] This quantum effect arises from the limited electronic density of states at the Fermi level: when the graphene electrode is charged, electrons begin to occupy higher-energy states, leading to quantum capacitance.

In an EDLC of graphene and electrolyte, the total capacitance reflects the overall effect of quantum and electric double-layer (EDL) capacitances (Equation 1). Quantum capacitance (C_Q) depends on the material's electronic structure, while EDL capacitance (C_{EDL}) depends on the electrode-electrolyte interfacial structure.[5-6]

$$\frac{1}{C_{total}} = \frac{1}{C_Q} + \frac{1}{C_{EDL}} \quad (1)$$

For a metal electrode, quantum capacitance is extremely high due to the large electronic density of states at the Fermi level. As a result, its contribution to the total capacitance is negligible given the inverse-sum relationship in Equation 1, and the experimentally measured capacitance of a metal electrode hence corresponds to the EDL capacitance. For a 2D-material such as graphene, quantum capacitance and EDL capacitance are on the same order of magnitude, thereby greatly influencing the total capacitance.

According to recent experiments[7-8] the quantum capacitance dominates the total capacitance for single-layer graphene in both ionic liquid and aqueous electrolytes. The new discovery raises an important question about the contribution of the quantum capacitance in the diverse carbon materials used in EDLCs. For example, commercial EDLCs use activated carbons as electrodes. How important the quantum capacitance is for those carbon materials remains unclear. As a first step to address this question, we consider variation of quantum capacitance with the grapheme-electrode thickness. High-resolution transmission electron miscopy (TEM) images of porous carbons show that their walls consist of a few layers of stacked graphene.[9] In this paper, we investigate the quantum capacitance and their contribution in the total capacitance at the graphene/electrolyte interface as a function of the graphene layers for both the ionic-liquid and aqueous electrolytes.

2. Computational Methods

Quantum capacitance was computed with the electronic density functional theory within an implicit solvation model as implemented in the JDFTx software.[10-11] Periodic boundary conditions (that is, the supercell model) were used to describe the interface: single layer graphene was modeled as a lateral 2.460×2.460 Å^2 rhombus sheet with a unit-cell length of 2.460 Å, close to the experimental value of 2.461 Å; the vacuum or electrolyte layer above the graphene electrode was modeled as a 20-Å slab along the z-direction. Generalized gradient approximation in the form of Perdew-Burke-Ernzerhof (GGA-PBE) functional was chosen to describe the exchange-correlation energy.[12] Ultra-soft pseudopotential was used to describe the interaction between the nuclei and the electrons,[13] with a kinetic energy cutoff of 20 hartree for the plane-wave basis. 24×24×1 k-point mesh was used to sample the Brillouin Zone. The linear

polarizable continuum model (PCM)[10] was coupled with an implicit solvent model to fill the vacuum layer to study the influence of the electrolyte on the quantum capacitance.

Quantum capacitance is defined as $C_Q = \frac{dQ}{d\varphi}$, where Q is the excessive charge on the graphene electrode, and φ is external potential. Q can be expressed by an integral term related to the electronic density of state (DOS) and the Fermi-Dirac distribution function $f(E)$. When the chemical potential of electrons is shifted by applying an electrical potential, φ/e, the graphene charge is

$$Q = e\int_{-\infty}^{+\infty} D(E)[f(E) - f(E-\varphi)]dE, \quad (2)$$

where E is the relative potential to the Fermi level. By differentiating Q with respect to φ, one obtains C_Q:

$$C_Q = \frac{dQ}{d\varphi} = \frac{e^2}{4kT}\int_{-\infty}^{+\infty} D(E)sech^2\left[\frac{E-\varphi}{2kT}\right]dE \quad (3).$$

By obtaining DOS from the electronic DFT calculations, we then calculated the quantum capacitance from Equation 3.[14] Our approach of computing quantum capacitance here is based on the fixed band approximation (that is, the band structure and density of states in the system are not affected by electron charging)[8, 15] without screening effect in inner graphene layers, for its simplicity in offering a quick estimate of the importance of quantum capacitance in total capacitance. Recent and more sophisticated simulations that took into account band-structure relaxation[16] and screening effect[17] under charging showed a more accurate estimate of quantum capacitance.

Classical density functional theory was used to obtain EDL capacitance for graphene in contact with an ionic liquid or aqueous electrolyte. The details of the CDFT calculations have

been published before.[18-23] Briefly, we obtained the EDL differential capacitances by computing the surface charge densities at various surface potentials. The ionic liquid was modeled as a mixture of charged hard spheres of single valence and equal size (0.425 nm in diameter) at a molar volume of 154 cm^3/mol at 298 K. The model system mimics that of a typical ionic liquid such as 1-ethyl-3-methylimidazolium tetrafluoroborate [emim][BF_4]. An aqueous NaF electrolyte of 1 M in 298 K was modeled as charged hard spheres of 0.116 nm and 0.119 nm in diameter for the cations and anions, respectively. The Stern layer capacitance was calculated using the bulk dielectric constant ($\varepsilon = 6$) of NaF due to the compact layer formed at the surface observed in the density profile. Compared with classical molecular dynamics,[24-28] classical DFT is much more efficient in obtaining EDL capacitance. With both quantum capacitance and EDL capacitance calculated from electronic and classical DFT, respectively, we then computed the total capacitance, following Hwang's work.[14, 29] Briefly, we first got the quantum capacitance (C_Q) as a function of the voltage $\varphi_{QC} = (E - E_{Fermi})/e$ and the EDL capacitance (C_{EDL}) as a function of the voltage $\varphi_{EDL} = \varphi - \varphi_{PZC}$, and then we used the same surface charge density to link the two capacitances in series. Namely, we summed up φ_{QC} and φ_{EDL} at the same surface charge density (σ) to get the applied voltage ($\varphi_a = \varphi_{QC} + \varphi_{EDL}$). With the σ vs. φ_a curve, we then derived the total differential and integral capacitances.

3. Results and discussion

3.1. Quantum capacitance of single-layer and multi-layer graphenes. Figure 1a shows the quantum capacitance of a graphene electrode of different thickness next to the vacuum. One can see that the quantum capacitance exhibits a "V" shape near the Fermi level with the slope increasing proportionally to the number of layers. The thickness effect can be expected from the definition of quantum capacitance in Equation 3.[14] As the number of layers increases, the total

electronic DOS per unit area of the electrode surface increases proportionally. The non-zero quantum capacitance at the Fermi level can be interpreted by the thermal broadening function in Equation 3, consistent with the experimental observation.[15]

To examine the effect of an electrolyte on the quantum capacitance, we computed the quantum capacitance for a 1.0 M NaF aqueous electrolyte. The results (Figure 1b) indicate that the presence of an electrolyte only slightly affects the quantum capacitance of a graphene electrode of few layers. The electrolyte effect is negligible for the single-layer graphene. In our calculation of the quantum capacitance using JDFT, the total Hamiltonian and free energy functional have included the implicit solvation part via an exact dielectric function and the Debye screening effect.[10] In the free-energy functional, all terms including the fluid part are electron-density dependent. An electrolyte affects the quantum capacitance by shifting the Dirac point; however, the shift is small for a single-layer graphene as found previously.[30] In addition, both experimental observation[15, 31] and *ab initio* molecular dynamics simulation[32] have shown that the quantum capacitance of a single-layer graphene is insensitive to the presence of an electrolyte.

Direct measurements of quantum capacitance of a graphene electrode have been reported recently. Tao et al. measured quantum capacitance of single layer graphene in an ionic liquid electrolyte,[15] and obtained a value of about 6.7μF/cm^2 at the Fermi level. Wang et al. obtained quantum capacitance by capacitance bridge technique in a vacuum[31] and found a value of about 0.8 μF/cm^2 at the Fermi level in vacuum. Our calculated quantum capacitance is about 1.3 μF/cm^2, close to Wang's result. Tao et al. explained their abnormally high quantum capacitance at the Fermi level in terms of the charge impurity effect induced by electrolyte during measurement.[15] At higher voltages (such as +/- 0.6 V), our predicted quantum capacitance

is consistent with a previous computational study[29] but about twice that of the experimental measurements.[15,31] This could be due to the fixed band approximation that we used to obtain the quantum capacitance, which has shown to overestimate the quantum capacitance.[17]

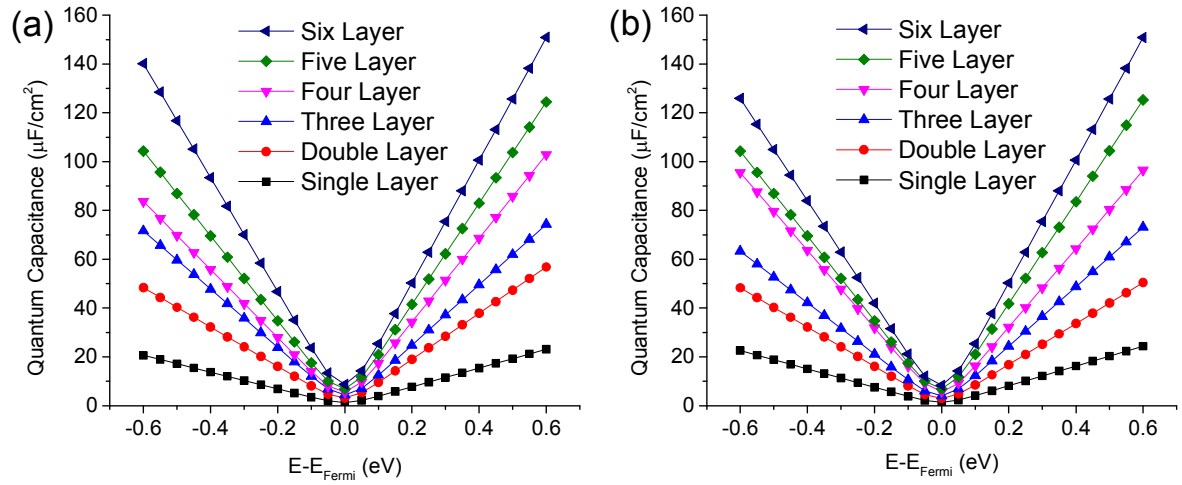

Figure 1. Quantum capacitance of a graphene electrode with different numbers of graphene layers in (a) vacuum; (b) a 1.0 M NaF aqueous electrolyte.

3.2. Total capacitance for an aqueous electrolyte next to a single-layer graphene. It is computationally challenging to directly model the total capacitance of an electrode/electrolyte interface, as one has to simultaneously model both the electronic response in the electrode and the mobile-ion response in the electrolyte. Although JDFT[10-11] can in principle solve this problem, the classical DFT part in the JDFT approach is still under development. We instead employed a more practical and commonly used approach,[8, 14, 29] by simulating quantum capacitance and electric double layer capacitance separately and then combining them together to obtain total capacitance.

Figure 2a shows the surface charge density vs. the potential for the quantum, EDL, and total charging of single-layer graphene in a 1M NaF aqueous electrolyte, while Figure 2b presents the corresponding total differential capacitance. Qualitatively, our calculated total capacitance of single-layer graphene is in good agreement with recent experimental results,[8, 33] which also show a V-shaped capacitance-potential curve. As shown by the charging curves in Figure 2a, the total capacitance is mostly dominated by quantum capacitance around the potential of zero charge (PZC; which is zero in our classical DFT simulation) from -0.2 to 0.2 V. Thus, in single-layer graphene, the quantum capacitance always plays an important role.

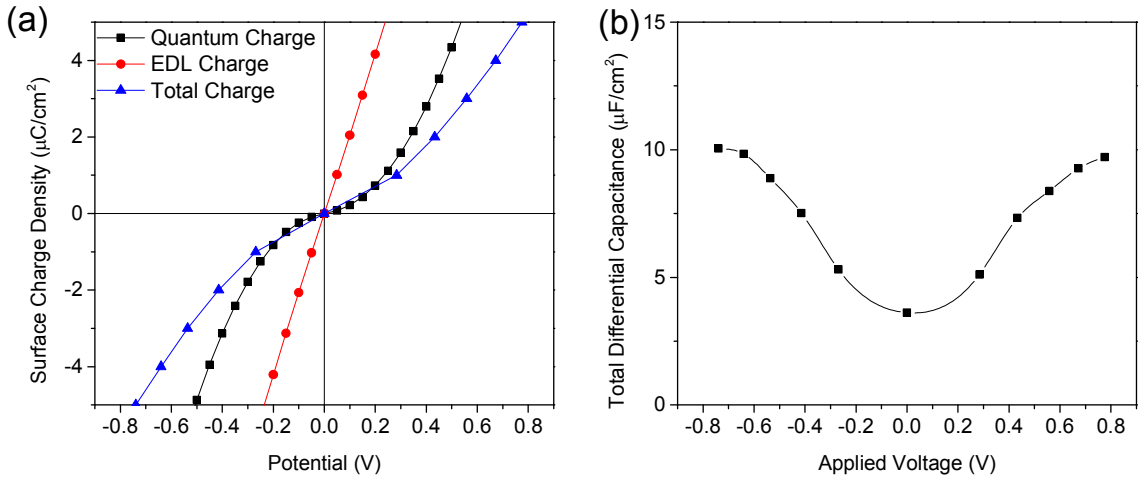

Figure 2. Single-layer graphene in1 M NaF aqueous electrolyte: (a) charging curve corresponds to C_Q, C_{EDL} and C_{tot}; (b) total differential capacitance.

3.3. Total capacitance for an ionic-liquid electrolyte next to a single-layer graphene. As shown by our earlier studies, classical DFT is a powerful tool for studying the EDL capacitance in ionic liquids.[34-36] Figure 3a shows the surface charge density vs. the potential for the quantum, EDL, and total charging of single-layer graphene in an ionic-liquid electrolyte, while Figure 3b presents the corresponding total differential capacitance. The calculated total capacitance shows a V-shaped capacitance-potential curve, which matches the experimental measurement in ionic

liquid very well.[7] Around the PZC (within +/- 0.4 eV), quantum capacitance also dominates the total capacitance in the ionic liquid, as in the case of an aqueous electrolyte.

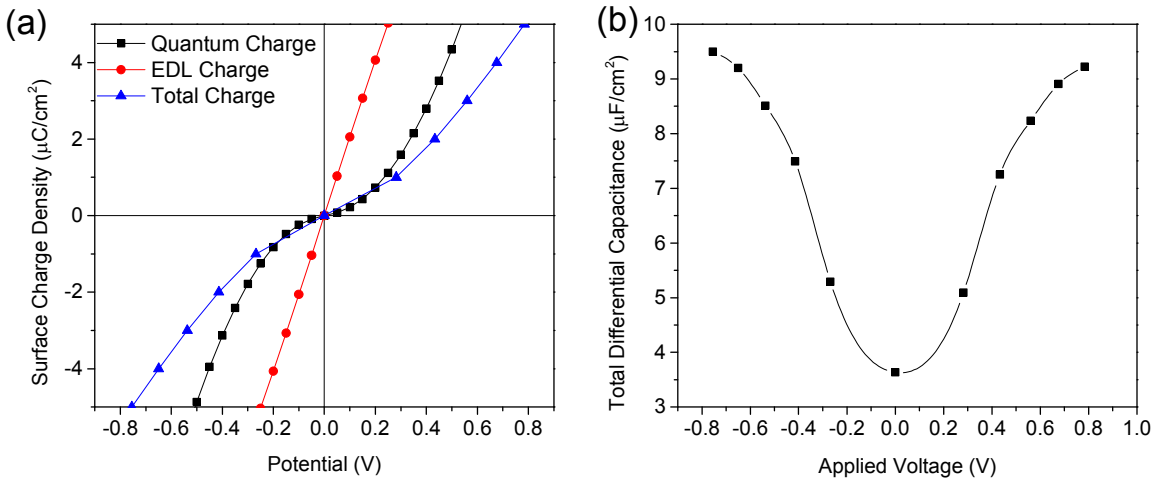

Figure 3. Single-layer graphene in an ionic liquid electrolyte: (a) charging curves corresponds to C_Q, C_{EDL} and C_{tot}; (b) total differential capacitance.

3.4. Total capacitance as a function of the number of graphene layers. The results above show that quantum capacitance is very important for the single-layer graphene electrode both in aqueous and ionic-liquid electrolytes. However, as the number of graphene layers increases, the quantum capacitance rises significantly (Figure 1) and thus it would be interesting to see how the corresponding total capacitance changes. Figure 4a presents the surface charge density vs. the potential for the total-capacitance charging of few-layer graphenes in an aqueous electrolyte, while Figure 4b shows the corresponding total differential capacitance. The capacitance increases significantly from single layer to double-layer graphene. As the number of layers further increases, however, the capacitance increase becomes smaller and the V shape of the total capacitance profile tends to converge beyond around four layers. In addition, the V shape near

the PZC (zero voltage in this case) becomes narrower due to the decreasing contribution of the quantum capacitance.

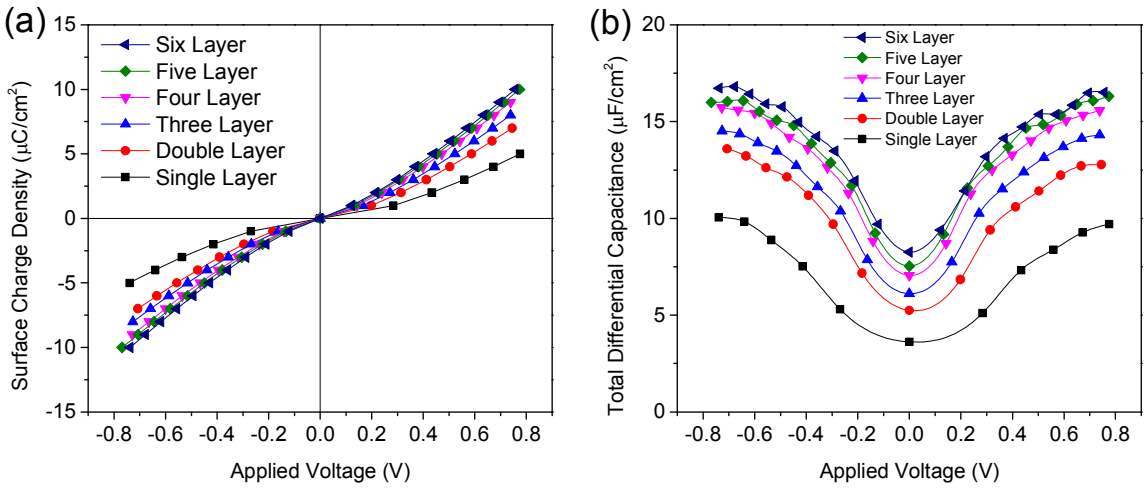

Figure 4. Few-layer graphene in1 M NaF aqueous electrolyte for different numbers of layers: (a) surface charge density vs. potential drop; (b) total differential capacitance vs. potential drop.

The layer effect in an ionic liquid is plotted in Figure 5. Unlike the V shape capacitance-potential curve obtained from the aqueous electrolyte, the total capacitance in the ionic liquid changes from a “V shape” to a “camel shape” as the number of graphene layers increased. For the single-layer graphene, the capacitance is dominated by the quantum capacitance, so its total capacitance is V-shaped. As the number of graphene layers increases, the total capacitance is still dominated by the quantum capacitance near the PZC, but away from the PZC (for example, more than 0.4 eV away), the total capacitance is dominated by the bell-shaped EDL capacitance. Consequently, the overall potential dependence shows a camel shape. Similar to the case of the aqueous electrolyte (Figure 4), the total-capacitance profile tends to converge beyond four layers of graphene.

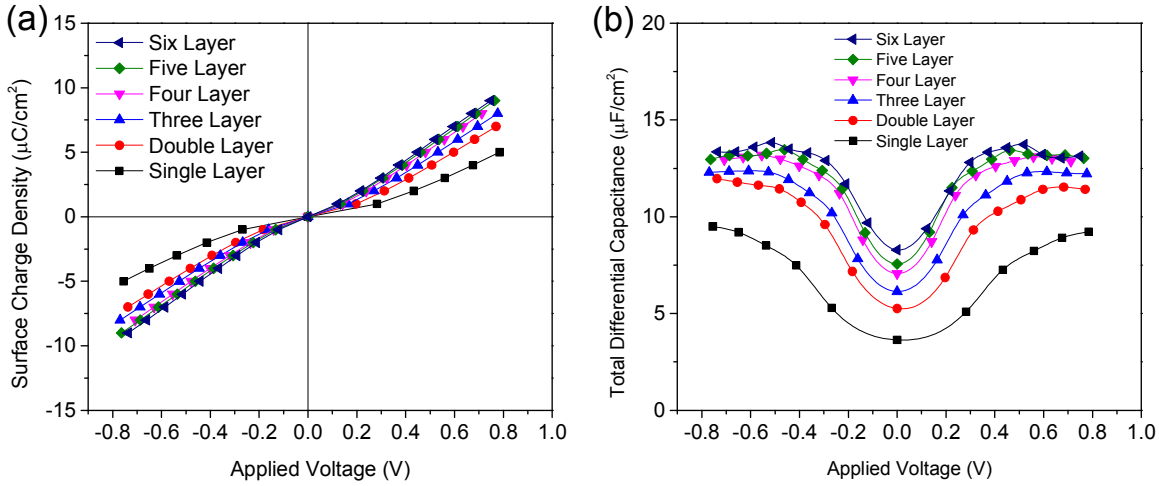

Figure 5. Few-layer graphene in ionic liquid for different numbers of layers: (a) surface charge density vs. potential drop; (b) total differential capacitance vs. potential drop.

3.5. Comparison of integral capacitance from -0.6 V to 0.6 V. In practical operations, a supercapacitor typically consists of two symmetric carbon electrodes that are charged up to the electrochemical window of the electrolyte: 1.2 V for aqueous electrolytes and 2.5 to 3.0 V for ionic liquids. It would be more informative to compare the integral capacitance at an experimentally reasonable voltage range sufficiently away from the PZC and evaluate the influence of the quantum capacitance. Toward that end, we chose -0.6 to 0.6 V for the sweep range of electrode voltage, and the results for both aqueous and ionic liquid electrolytes are plotted in Figure 6a. In both cases, the capacitance almost levels off beyond four layers of graphene. In the case of the aqueous electrolyte, Figure 6b shows that integral C_Q becomes greater than integral C_{EDL} after three layers of graphene; the trend is similar in the case of the ionic liquid. Our results agree well with a recent experiment for the ionic-liquid/graphene interface, which shows that total capacitance is limited by quantum capacitance when the number of graphene layers (N) is less than four and by EDL capacitance for $N > 4$.[7]

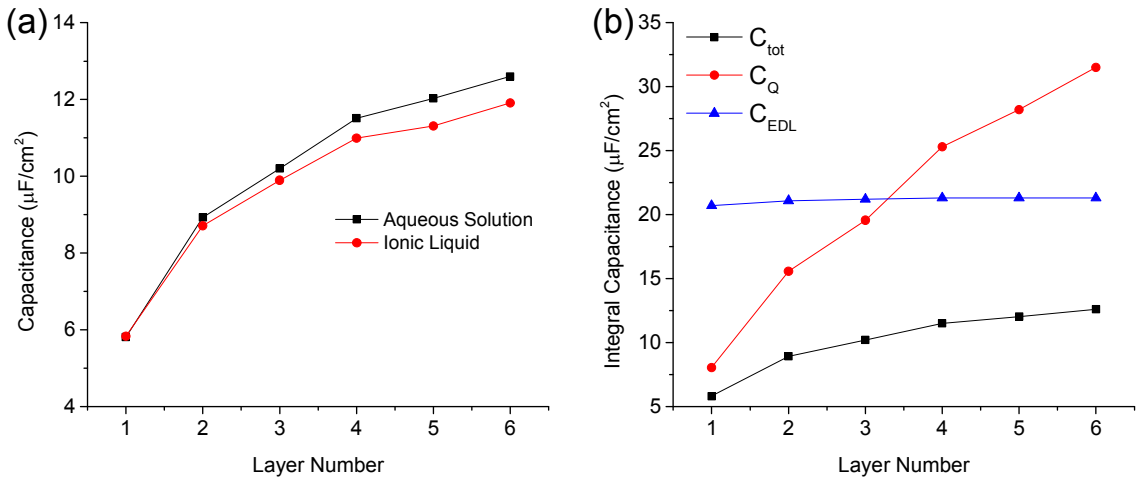

Figure 6. (a) Integral capacitance from -0.6 V to 0.6 V of applied voltage as a function of the number of graphene layers in both aqueous and ionic liquid electrolytes. (b) Quantum and EDL contributions to the total integral capacitance as a function of graphene-layer number in the aqueous electrolyte.

We have further analyzed the relative contribution of quantum capacitance and EDL capacitance in total differential capacitance for the case of the six-layer graphene at different surface potential. Figure 7 shows that, away from the PZC, the total capacitance is dominated by EDL capacitance although quantum capacitance is comparable to EDL capacitance at PZC. Due to the inverse-sum relationship in Equation 1, when the quantum capacitance is much greater than the EDL capacitance, its contribution to the total capacitance becomes negligible and the EDL capacitance dominates the total capacitance. In addition, from partial voltage analysis on C_Q and C_{EDL}, we can also see that as the applied voltage go up, the partial voltage on C_Q becomes less dominative. When the total applied voltage is 0.2 V, the partial voltage contribution of C_Q is 0.11 V, more than half of the total. When the applied voltage goes up to 0.6

V, the voltage contribution of C_Q is 0.24 V and that of C_{EDL} is 0.36 V. Thus, the total capacitance is dominated by EDL capacitance.

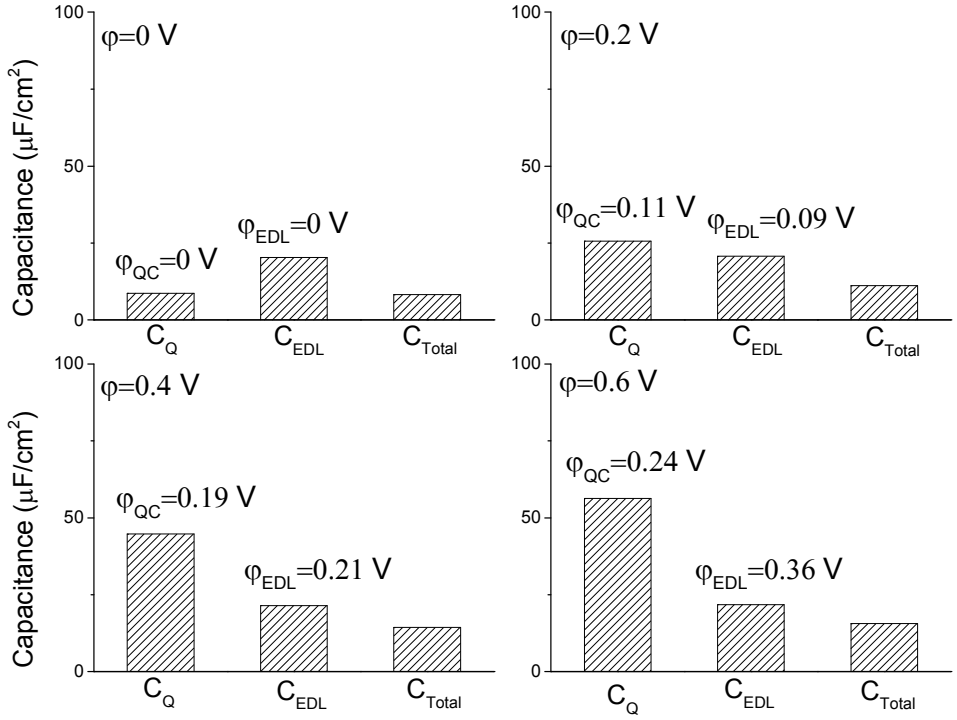

Figure 7. Relative contributions of quantum and EDL capacitances to the total differential capacitance of a six-layer graphene electrode at different voltages.

3.6. Relevance to realistic carbon electrodes. Activated carbon represents the most widely used electrode material for EDLCs; recent developments use other carbons such as carbide-derived carbons, onion-like carbons, and mesoporous carbons.[37-38] High-resolution TEM images indicate that all these carbons consist of stacked graphene layers at the pore walls.[9, 39] In other words, the electrode surfaces are typically made of a few layers of graphene. Our work suggests that, for these realistic carbons and away from the PZC, the quantum capacitance is probably insignificant for the performance of EDLC devices if the carbon pore-wall thickness is above three. In addition, our partial voltage analysis shows that even when the layer number go up to six and

total capacitance is converged due to large quantum capacitance, C_Q can still account for one third of the applied voltage. This means that there is still room for further improving total capacitance by increasing the quantum capacitance.

4. Summary and conclusions

We have studied the quantum capacitance and the total capacitance of graphene electrodes as a function of the number of graphene layers for both aqueous and ionic-liquid electrolytes. The quantum capacitances were predicted from electronic density functional theory based on fixed band pproximation with an implicit solvation model; the electric-double layer (EDL) capacitances were from classical density functional theory. For both aqueous and ionic-liquid electrolytes, quantum capacitance plays a dominant role in the total capacitance of a single-layer graphene electrode. The overall potential-dependent profile of total capacitance increases with the number of graphene layers but the extent diminishes quickly. When the number of layers reaches four, the total capacitance tends to converge and the EDL capacitance dominates at voltages sufficiently different from the potential of zero charge. Our work here shows that for supercapacitors with realistic carbon electrodes, the capacitance performance depends on the pore-wall thickness.

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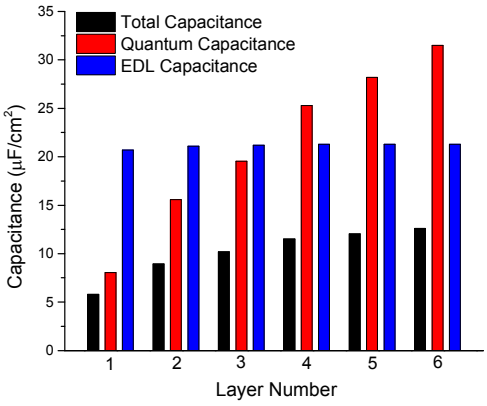
Table of Contents: