On the Origin of the Enhanced Supercapacitor Performance of Nitrogen-Doped Graphene

Eunsu Paek, Alexander J. Pak, Kyoung E. Kweon, and Gyeong S. Hwang*

Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas 78712, United States

ABSTRACT: Graphene-based electrodes have been widely tested and used in electrochemical double layer capacitors due to their high surface area and electrical conductivity. Nitrogen doping of graphene has recently been demonstrated to significantly enhance capacitance, but the underlying mechanisms remain ambiguous. We present the doping effect on the interfacial capacitance between graphene and \([\text{BMIM}]^{+}[\text{PF}_6]^{-}\) ionic liquid, particularly the relative changes in the double layer and electrode (quantum) capacitances. The electrode capacitance change was evaluated based on density functional theory calculations of doping-induced electronic structure modifications in graphene, while the microstructure and capacitance of the double layers forming near undoped/doped graphene electrodes were calculated using classical molecular dynamics. Our computational study clearly demonstrates that nitrogen doping can lead to significant enhancement in the electrode capacitance as a result of electronic structure modifications while there is virtually no change in the double layer capacitance. This finding sheds some insight into the impact of the chemical and/or mechanical modifications of graphene-like electrodes on supercapacitor performance.

1. INTRODUCTION

Electrochemical double layer capacitors (EDLCs), also known as supercapacitors, have garnered much attention as electrical energy storage devices owing to their high rate capabilities and long cycle lifetimes. Ionic liquids (ILs), “solvent-free” ions that are in the liquid state at room temperature, are a promising class of electrolytes due to their wide electrochemical windows, high chemical and thermal stability, extremely low volatility, and nonflammability. Carbon-based materials (such as graphene, carbon nanotubes, and porous carbon) have been regarded as a viable candidate for supercapacitor electrodes due to their high specific surface area and good electrical conductivity. However, a major drawback of EDLCs is their relatively low energy density compared to batteries; therefore, many efforts have recently been made to enhance the capacitor performance.

Recent experiments have shown that nitrogen (N) doping of graphene-like electrodes can significantly enhance EDLC capacitance in comparison to undoped electrodes. Jeong and co-workers reported a specific capacitance around 280 (225) F/g for N-doped graphene in KOH ([TEA][BF_4]), a 4-fold increase from the undoped graphene case; they claimed that the capacitance increase could be due to enhanced binding interactions between N dopants in the basal plane and electrolyte ions. Other researchers also showed that N-doped graphene can increase the capacitance to 144.6 F/g in KOH (0.2 A/g), 144.9 F/g in \([\text{Et}_4\text{N}][\text{BF}_4]/\) propylene carbonate (0.5 A/g), or 326 F/g in KOH (0.2 A/g). While the exact mechanisms remain ambiguous, the capacitance enhancements were thought to be related to an increase in the electrical conductivity of N-doped graphene or the contribution of pseudocapacitance. Among other possible factors, the important role of pseudocapacitance, together with EDL capacitance, in supercapacitors has been reported particularly when carbon-based electrodes include transition metal oxides; the involvement of faradaic reactions (e.g., redox reactions or chemisorption) at the metal sites imparts additional capacitance beyond the double-layer capacitance. For example, RuO_2 hydrates in aqueous solutions have been shown to change the valency state of Ru between Ru^{4+} and Ru^{3+} upon charge/discharge, which is balanced by electrochemical protonation. In the case of MnO_2 hydrates, it has been shown that both protonation and chemisorption of cations in alkali and alkaline solutions occur upon changes in the valency state of Mn.

While the interaction between dopants and electrolyte may influence the EDL capacitance, the total capacitance can also be affected by the doping-induced alteration of the electrode’s capacitance. Recent experimental and theoretical work have shown that the total capacitance \((C_T)\) of an IL/graphene-based electrode strongly depends on the relative contributions from both the double layer capacitance \((C_D)\) and electrode...
quantum capacitance ($C_Q$). The $C_Q$ of low dimensional materials such as graphene is proportional to the electronic density of states (DOS),

which can be altered from chemical doping. To date, however, the effects of N doping on both $C_Q$ and $C_D$ have yet to be reported.

In this work, we investigate the influence of N doping of graphene in 1-butyl-3-methyl-imidazolium hexafluorophosphate ([BMIM][PF$_6$]) IL on the interfacial capacitance ($C_I$) using combined density functional theory (DFT) and classical molecular dynamics (MD) calculations. Our particular interest lies in understanding the relative contributions of EDL capacitance and quantum capacitance to the total interfacial capacitance in the N-doped case as compared to the undoped case. Here, charge transfer at the electrode/electrolyte interface, the so-called pseudocapacitance effect, is not considered since [BMIM][PF$_6$] is chemically inert. We have chosen to separately investigate two commonly observed N configurations from experimental

characterization: (1) substitutional N ($N_1$) in which a C atom is replaced with a N atom and (2) trimerized pyridine-type N ($N_{3V}$) in which three two-coordinated N atoms surround a C vacancy. We first employ DFT to predict the impact of each type on $C_Q$, which is proportional to the DOS.

We then consider the impact of N doping on the microstructure, potential variation, and $C_D$ of the EDL using DFT/MD simulations. Finally, we compare the capacitance of the two N-doped cases to the undoped case.

II. COMPUTATIONAL METHODS

A. Density Functional Theory. The atomic and electronic structures of N-doped and pristine graphene sheets were calculated using DFT within the Perdew–Wang 91 generalized gradient approximation (GGA-PW91),

as implemented in the Vienna Ab initio Simulation Package (VASP). We employed the projector augmented wave (PAW) method to describe the interaction between ion core and valence electrons, and a planewave basis set with a kinetic energy cutoff of 400 eV. In this work, we considered two different N-doping configurations including single N atom substitution (referred to as N$_1$ hereafter) and trimerized pyridine-type ($N_{3V}$), as illustrated in Figure 1. The pristine/N$_1$ and N$_{3V}$ graphene sheets were modeled using rectangular 32-atom (corresponding to 2.7 at.% doping concentration) and 4

atom/112-atom systems and sufficiently increased the k-point mesh size to ensure convergence of electronic structure calculations. The optimized structures for the N$_1$ and N$_{3V}$ systems from our DFT-GGA calculations are presented in Figure 1; the predicted lattice distortions induced by N doping are in good agreement with previous calculation results.

N doping-induced changes in the atomic charge distribution of graphene were determined using grid-based Bader analysis. We then employ DFT to predict the impact of each type on $C_Q$, which is proportional to the DOS.

We then consider the impact of N doping on the microstructure, potential variation, and $C_D$ of the EDL using DFT/MD simulations. Finally, we compare the capacitance of the two N-doped cases to the undoped case.

B. Classical Molecular Dynamics. We employed MD simulations with the OPLS-AA force field to determine the microstructure of [BMIM][PF$_6$] near the graphene electrode; details on the force field parameters can be found in ref 27. As illustrated in Figure 2, the simulation system considered consisted of 346 [BMIM][PF$_6$] pairs between two electrodes separated by 10 Å; the lateral size of each graphene electrode was 34.18 × 34.53 Å$^2$, corresponding to 448 C atoms. The distance between the electrodes was chosen large enough such that the electrolyte maintained bulk properties in the middle region of the system.

For the N-doped graphene structures, 12 substitutional N atoms (corresponding to 2.7 at.% doping concentration) and 4 trimerized pyridine-type defects were distributed in the N$_1$ and N$_{3V}$ graphene systems, respectively. We investigated uncharged and charged electrodes with a surface charge density of $\sigma = \pm 5.43 \mu C/cm^2$. In the pristine graphene case, the atomic charges were assigned evenly throughout the lattice ($\pm 0.0089 e/atom$ when $\sigma = \pm 5.43 \mu C/cm^2$). However in the N-doped cases, excess electrons/holes appeared rather concentrated around N atoms; in MD simulations, we used the atomic charge distributions from the Bader charge analysis for the N$_1$ and N$_{3V}$ graphene systems (see Supporting Information, Table S1).

Figure 2. Schematic of BMIM, PF$_6$, and the simulation box. Planar graphene sheets are placed at the two ends of the simulation domain. White, blue, and gray balls indicate H, N, and C atoms in BMIM, and red and pink balls indicate P and F atoms in PF$_6$. Periodic boundary conditions are applied in the x and y directions.
We ran each MD simulation initially at 1000 K for 1.2 ns followed by 3 ns at 300 K to equilibrate the system using a time step of 1 fs. Production runs were carried out for 4 ns with atomic positions recorded every 4 ps. All runs were in the NVT ensemble with the temperature controlled by a Nose–Hoover thermostat\(^{37}\) with a 100 fs damping parameter. All MD simulations were performed with the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) program.\(^{38}\) MD results reported herein were obtained from the average of four independent simulations with different initial atomic configurations. Further details about the MD simulations are described in ref 27.

### III. RESULTS AND DISCUSSION

The total interfacial capacitance \(C_Q\) between graphene and [BMIM][PF\(_6\)] IL was computed from a series of the EDL capacitance \(C_D\) and the quantum capacitance of graphene \(C_Q\), i.e., \(1/C_Q = 1/C_D + 1/C_Q\). In the following sections, we present the calculations of \(C_Q\) and \(C_D\) and based on the results, discuss their relative contributions to the \(C_Q\) of the graphene/IL system.

#### A. Quantum Capacitance

The quantum capacitance of graphene is defined as \(C_Q = \epsilon^2 / \int_{-\infty}^{+\infty} D(E) F(T) (E - \mu) dE\)

\[ (1) \]

where \(D(E)\) is the electron density of states (DOS), \(F(T)\) is the thermal broadening function \([=(4kT)^{-1}\text{sech}^2(E/2kT)]\), \(E\) is the relative energy with respect to the Fermi level \(E_{\text{F}}\), and \(\epsilon\) is the elementary charge.

For pristine graphene, the valence and conduction bands touch and both bands exhibit conical band dispersion near the Dirac point, where the Fermi level is located (Figure 3a). As also shown in Figure 3a, the calculated DOS of graphene using DFT-GGA is clearly demonstrated to be symmetric and linear near the Dirac point.

The electronic structure of graphene can be substantially altered by the presence of N impurities and/or C vacancies. Figure 3 also shows the band structure and DOS of N-doped graphene sheets considered. In the case of N\(_1\) (single N atom substitution) graphene (Figure 3b), the Fermi level shifts up into the conduction band of pristine graphene due to electron injection into the \(\pi\)-electron system; note that N has one more electron than C, and thus each N \(\rightarrow\) C substitution provides an extra electron to the graphene. The extra electron tends to spread rather broadly over the N atom and its neighboring C atoms, as demonstrated by the isosurface plot of the corresponding band-decomposed charge densities (Figure 3b). While the Fermi level position is a function of N concentration, at the 3.1 at.% doping level, there exists one partially filled defect state near the Fermi level; therefore, we can expect that the largely delocalized state will be first emptied (or filled) when extra holes (or electrons) are added (see the corresponding charge density isosurface plots in Figure 3b).

In the case of N\(_3V\) (trimerized pyridine-type) graphene (Figure 3c), the Fermi level moves down inside the valence band of pristine graphene due to electron deficiency; note that N\(_3V\) has one less electron than C\(_4\) (defect-free graphene). At 2.7 at. % of N-doping, our band structure calculation shows the existence of three states near the Fermi level, that is, two degenerate quasi-localized states and one partially filled delocalized state. The distinct DOS peak at 0.05 eV below \(E_{\text{F}}\) is due primarily to the quasi-localized states associated with N lone pairs, as shown by the corresponding (band-decomposed) charge density isosurface plot. We can expect, therefore, that when excess holes are injected, the states associated with the N lone pairs will be emptied first.

Using eq 1 with the calculated DOS, we obtained the \(C_Q\) of the pristine, N\(_1\), and N\(_3V\) graphene systems at 300 K, as presented in Figure 4. The \(C_Q\) of pristine graphene is U-shaped with a minimum around 0.45 \(\mu\)F/cm\(^2\) at \(\phi_{\text{G}} = 0\) V. The \(C_Q\) for N\(_1\) and N\(_3V\) at \(\phi_{\text{G}} = 0\) V are around 22 and 44 \(\mu\)F/cm\(^2\), respectively; this dramatic improvement is apparently due to the additional impurity states near \(E_{\text{F}}\). In the N\(_1\) graphene case, \(C_Q\) gradually increases as \(\phi_{\text{G}}\) increases and peaks at 45 \(\mu\)F/cm\(^2\) at \(\phi_{\text{G}} = 0.3\) V. As \(\phi_{\text{G}}\) decreases below 0 V, \(C_Q\) tapers toward 0 \(\mu\)F/cm\(^2\) at \(-0.85\) V. In the N\(_3V\) graphene case, \(C_Q\) sharply decreases to around 5\(–10\) \(\mu\)F/cm\(^2\) when \(\phi_{\text{G}} < -0.2\) V and 0 \(\mu\)F/cm\(^2\) when \(\phi_{\text{G}} = 0.4\) V.

We have thus far presented an analysis pertaining to two ideal types of N doping in graphene; in reality, however,
fabricated N-doped graphene electrode may have numerous types of N-dopants and/or C vacancies and/or structural defects. In such a mixed system, the impact of the individual dopant types does not alter the electronic structure in simply an additive manner. Additional interactions between dopant types can also create unique states and alter the electronic structure (see Figure S5), but numerous combinations of these mixed dopants exist and are outside the scope of this study. We should also note that the possible influence of graphene-IL interactions on the DOS and $C_{\text{el}}$ have been neglected in this analysis for simplicity. However, it is clear that N-doping can lead to significant changes in the electrode capacitance.

**B. Electric Double Layer Capacitance.** The capacitance of an EDL can be obtained from the relationship between excess electrode surface charge ($\sigma$) and potential drop $\phi_\sigma$ within the EDL $\phi_\sigma = \sigma / \epsilon_0 / \varepsilon_{\text{ff}}$ (integral) or $\phi'_\sigma = d\sigma / d\varphi_{\text{el}}$ (differential). We first calculated the integral capacitances at $\sigma = \pm 5.43 \, \mu\text{C/cm}^2$ for the pristine, N1, and N3V graphene cases. For each system, the EDL capacitance was evaluated based on the microstructure of [BMIM][PF6] IL near the electrified electrode determined using MD simulations, as described in the following section.

Figure 5 presents a comparison between the mass density profiles of BMIM and PF$_6$ at $\sigma = \pm 5.43 \, \mu\text{C/cm}^2$ for pristine (a), N1 (b), and N3V (c) graphene. Each of the panels (a-c) displays an alternating cation/anion layering that extends 25–30 Å from the electrodes, after which the IL structure becomes nearly bulk-like; this layering behavior is consistent with previous experimental observations. Near the positive electrode ($z = 0$ Å), PF$_6$ exhibits three distinct peaks adjacent to the electrode (in a-c); these peaks correspond to planar aligned F, P, and F atoms, which arise primarily due to the electrostatic attraction between the positive electrode and the negatively charged F atoms. Near the negative electrode ($z = 100$ Å), the sharp peak (in a-c) corresponds to BMIM ions which tend to align parallel to the electrode surface.

The presence of N dopants and/or C vacancies affects the charge distribution throughout the electrode surface as stated earlier, which in turn influences the IL arrangement near the surface. In both N1 and N3V graphene cases, the positively charged BMIM rings have a tendency to lie near the negatively charged N atoms as a result of their electrostatic attraction (Figure S4). However, the influence of N doping on the IL distribution along the normal ($z$) direction appears to be insignificant (when the N concentration is about 2.7% as considered here); note that the average density of the first IL layer deviates at most by 3.3% compared to the undoped case.

For each system, the space charge variation in the IL electrolyte was calculated based on the distribution of IL ions with fixed atomic charges. We then obtained $\phi$ along the surface normal direction for a given $\sigma$ from Poisson’s equation

$$\varphi(z) = -\frac{\sigma z}{\varepsilon_0} - \frac{1}{\varepsilon_0} \int_0^z (z - z') \rho(z') \, dz'$$

where $z$ is the distance from the electrode, $\rho$ is the charge density averaged over a lateral $z$-cross section, and $\varepsilon_0$ is the vacuum permittivity.

Figure 6 shows a calculated potential profile for the pristine graphene case near the positive (left panel) and negative (right panel) electrodes with respect to the bulk potential (which is set equal to 0 V) for $\sigma = \pm 5.43 \, \mu\text{C/cm}^2$. Here, a bin size of 0.1 Å was used in obtaining laterally averaged $\rho(z)$. The results show that the potential variation mostly occurs across the EDL, indicating that the accumulated counterions effectively screen the surface electric field. The $\phi_D$ near the positive (negative) electrode was 1.30 (−1.02) V. The potential profiles for the N1 and N3V graphene cases (not shown) are found to exhibit similarity to the pristine graphene case; the variations in $\phi_D$ among the three systems considered appears to be less than 5% (see Table 1).

In Table 1, we present the predicted $C_1$ at $\sigma = 0$ and $\pm 5.43 \, \mu\text{C/cm}^2$ for each case. Note that in actuality, $C_1 = \sigma / (\phi_D - \phi_\sigma)$, where $\phi_\sigma$ is the potential of zero charge (which refers to the potential drop in the interface region due to a charge imbalance when $\sigma = 0 \, \mu\text{C/cm}^2$). For [BMIM][PF$_6$] near the intrinsic graphene sheet, $\phi_\sigma$ is nearly zero ($\approx 0.02$ V). Similarly, the $\phi_\sigma$ for the N1 and N3V graphene cases are also
Table 1. Potential Drop across the EDL ($\phi_D$) and Integral Capacitance ($C_I$) for Pristine, N$_1$, and N$_3$V Graphene Systems at $\sigma = \pm 5.43 \, \mu C/cm^2$

<table>
<thead>
<tr>
<th></th>
<th>pristine</th>
<th>N$_1$</th>
<th>N$_3$V</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi_D - \phi_L$ (V)</td>
<td>1.30</td>
<td>1.26</td>
<td>1.33</td>
</tr>
<tr>
<td>$C_I$ (µF/cm$^2$)</td>
<td>4.18</td>
<td>4.30</td>
<td>4.09</td>
</tr>
</tbody>
</table>

The predicted $C_D-\phi_D$ curve is nearly flat for $|\phi_D| < 0.6$ V with a maximum of 4.7 $\mu F/cm^2$ at $\phi_D = 0.7$ V. Note that the peak position appears at a positive value of $\phi_D$ which is related to the difference in packing efficiency between cation and anion. The smaller PF$_6$ anions are more effectively packed than larger BMIM cations, yielding a smaller $\Delta \phi_D$ for a given $\Delta \sigma$ and consequently a larger $C_D$. Likewise, the $C_D$ value monotonically decreases with increasing |$\phi_D$| due to the gradually reduced packing efficiency, while the PF$_6$ side consistently exhibits a higher $C_D$ at a given |$\phi_D$| than the BMIM side (not shown).

Figure 8 shows predicted $C_T-\phi$ curves for the pristine (b), N$_1$ (c), and N$_3$V (d) graphene systems, from the calculated $C_Q$,

![Figure 7](image)

Figure 7. Differential double layer capacitance ($C_D$) as a function of the potential drop across the EDL ($\phi_D$) for the pristine graphene system.

![Figure 8](image)

Figure 8. (a) Schematic of the idealized potential profile at the graphene/IL interface, and the total interfacial capacitance for (b) pristine, (b) N$_1$, and (c) N$_3$V graphene systems as a function of applied potential ($\phi_a$).
capacitance in the range $|\phi| < 0.6$ V compared to the intrinsic case, which is in qualitative agreement with experimental studies;\textsuperscript{14} it is apparent that this is due to the contribution from $C_0$ near $\phi = 0$ V. As mentioned above, however, this analysis only pertains to two ideal and probable types of N-doped graphene and does not extend toward systems with mixed N-dopant types. Nonetheless, our study clearly highlights that the enhanced capacitance observed in N-doped supercapacitors can be attributed to modification of the electrode capacitance.

IV. SUMMARY

We evaluated the interfacial capacitance of N-doped graphene in [BMIM][PF$_6$] IL using a combination of DFT and classical MD calculations, with particular attention to the relative contributions of the electrode and EDL capacitances. We considered two commonly observed N configurations from experiments, substitutional N (N$_s$) and trimerized pyridine-type N (N$_t$V). According to our DFT calculations, both types of N doping significantly tend to enhance the quantum capacitance of graphene near the Fermi level when compared to the undoped case; the N$_s$ graphene showed broad enhancement while N$_t$V graphene had sharp enhancement over a 0.4 V window. Our MD simulations for N$_s$ and N$_t$V graphene in [BMIM][PF$_6$] show that the positively charged BMIM rings have a tendency to lie near the negatively charged N atoms. However, the EDL microstructure and capacitance are found to be virtually unaffected at N doping concentrations of about 3 at. % considered in this work. In addition, the dependence of the total interfacial capacitance on voltage is strongly associated with the electrode capacitance when $|\phi| < 0.6$ V since the EDL capacitance is nearly constant in this voltage window. Our computational study clearly highlights that the enhanced capacitance observed in N-doped supercapacitors can be attributed to an increase in the electrode’s capacitance. This finding may suggest that other structural and/or chemical modifications to graphene-based electrodes could significantly contribute to enhancing the performance of supercapacitors and warrants further investigation.

■ ASSOCIATED CONTENT

Supporting Information

Figures showing the mass density profiles with uncharged electrodes, the charge distribution on graphene as a result of N-doping, the configuration of ions near the doped electrodes, and the quantum capacitance as a result of mixed systems of N-dopants. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*E-mail: gshwang@che.utexas.edu.

Notes
The authors declare no competing financial interest.

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