Molecular dynamics simulations of the electric double layer capacitance of graphene electrodes in monovalent aqueous electrolytes

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Abstract

Electrical double layer (EDL) capacitors based on recently emergent graphene materials have shown several folds performance improvement compared to conventional porous carbon materials, driving a wave of technology breakthrough in portable and renewable energy storage. Accordingly, much interest has been generated to pursue a comprehensive understanding of the fundamental yet elusive double layer structure at the electrode/electrolyte interface. In this paper, we carried out comprehensive molecular dynamics simulations to obtain a comprehensive picture of how ion type, solvent properties, and charging conditions affect the EDL structure at the graphene electrode surface, and thereby its contribution to capacitance. We show that different symmetrical monovalent aqueous electrolytes M^+X^- ($M^+ = Na^+, K^+, Ru^+$, and Cs^+ ; $X^- = F^-, Cl^-$, and I^-) indeed have distinctive EDL structures. Larger ions, such as, Ru^+ , Cs^+ , Cl^- , and I^- , undergo partial dehydration and penetrate through the first water layer next to the graphene electrode surfaces under charging. As such, the electrical potential distribution through the EDL strongly depends on the ion type. Interestingly, we further reveal that the water can play a critical role in determining the capacitance value. The change of dielectric constant of water in different electrolytes largely cancels out the variance in electric potential drop across the EDL of different ion type. Our simulation sheds new lights on how the interplay between solvent molecules and EDL structure cooperatively contributes to capacitance, which agrees with our experimental results well.

Keywords: graphene supercapacitor, molecular dynamics simulations, electric double layer structures, aqueous electrolyte, monovalent ions.

1. Introduction

Electrochemical capacitors, also called supercapacitors, store energy by forming an electric double layer (EDL) of electrolyte ions on conductive porous electrodes, usually made from porous carbon. Recent advance in making graphene-based nanoporous carbon materials have led to much improved capacitive energy storage performance, which directs much research efforts into investigating the fundamental charging mechanism, the formation of EDL at the electrode/electrolyte interface. Indeed, it is not until very recently do we start to understand many of the anomalous phenomena associated with the formation of EDL particularly in small nano-sized pores, for example the drastically increased capacitance and the distortion of ion solvation shell in pores below 2 nm, to name a few [1, 2]. Although the structure and property of EDLs on metal and carbon-based electrode have been widely studied via the various numeric simulation (*i.e.*, continuum modeling [3], classic MD simulation [4-6], grand canonical Monte Carlo [7, 8], and classic density functional theory [9]), many questions remain to be explored such as the effect of ion size, degree of ion hydration, dielectric constant of solvents [10-15], the potential-dependent EDL structure, and the “bell” or “U” shaped differential capacitance [16, 17]. A comprehensive understanding of the EDL structure and its dependence on various ion type and different charging conditions remains vacant.

Accordingly, in this work, we investigate the molecular structures of EDL in graphene-based electrochemical capacitor systems via molecular dynamic (MD) simulations. Specifically, we are looking at the influence of various ion type and the strength of charging electric field on the structure of EDL. The combination of MD simulations and the aid of Guoy-Chapman-Stern (GCS) model framework [18-21] has allowed a comprehensive understanding on the EDL molecular structure and an in-depth analysis of its effects on the capacitance of graphene-based electrochemical capacitors. Our results show that the ion type indeed plays a crucial role in determining the ion concentration distribution in an EDL. More importantly, our simulations have successfully revealed the significant effect of the dielectric properties of water molecules on the achievable capacitance of a certain aqueous electrolyte.

2. Methodology

Figure 1 shows a typical system in our MD simulations: graphene sheets (10.2 nm $\times$ 10.0 nm) aligned in parallel with an interlayer distance of 5 nm. The dashed box depicts the simulation supercell with periodic boundary conditions employed at all three dimensions. Symmetrical

monovalent aqueous electrolytes M^+X^- ($M^+ = Na^+, K^+, Ru^+$, and Cs^+ ; $X^- = F^-, Cl^-,$ and I^-) were used to fill the gaps between graphene sheets. The concentration was set as 1 mol/L.

Figure 1. A typical model system employed in the MD simulation to investigate the electric double layer formed at charged graphene sheets immersed in symmetric monovalent electrolyte (1 mol/L).

Given the theoretical intrinsic capacitance value of graphene ($21\mu F/cm$ [22]) and electric potential window for aqueous electrolytes (1 V), we estimated the maximum charge per carbon atom to be $0.0685 e/C\text{-atom}$, equivalent to a total charge of 270 electrons in one graphene sheet (3936 carbon atoms) in our system (Fig. 1). Thus a total charge of 0, ± 60 , or $\pm 160 e^-$ was imposed on one graphene layer (corresponding to 0, ± 0.015 , or $\pm 0.041 e/C\text{-atom}$), respectively, so as to consider the influence of different charging conditions on the EDL structure and the resultant capacitance values [6, 23-27]. The injected charges were homogeneous distributed in every carbon atoms across the graphene layer. Some MD simulation techniques have recently been developed to apply a constant electric potential [28, 29] on electrodes, which is more consistent with electrochemistry experiment conditions. However, they are computational demanding in comparison with the widely used constant surface charge method. In addition, recent studies showed a negligible difference of simulating the EDL structures between these methods particularly at a low electric potential (< 2 V) [30, 31]. Therefore, in this study, we adopted the conventional constant surface charge method. Water molecules were accordingly filled in the supercell to generate a pressure close to 1 bar at 300 K. The numbers of the electrolyte ions were determined with two conditions: the ion concentration being 1 M and charge neutrality of the whole system. Table 1 summarizes the numbers of water molecules and ions in our MD simulation systems.

Table 1. Number of water molecules and electrolyte ions in one MD simulation supercell under different charging conditions.

Total charge on one graphene layer (3936 carbon atoms)	M ⁺	X ⁻	Water
0e	310	310	48884
+60e	280	340	48884
+160e	230	390	48884
-60e	340	280	48884
-160e	390	230	48884

The TIP/3P model was used for water because it can best reproduce the dielectric constant of water among other popular water models and the SHAKE algorithm was employed [A1][32, 33]. In addition to the electrostatic forces, the van der Waals interactions among the ions, carbon atoms, and the water molecules were described by using the modified Lenard-Jones potential [34]. Parameters of LJ potentials of most ions and carbon atoms were taken from CHARMM27 force field [35], except those of I⁻ and F⁻ anions that were taken from these references [36, 37]. Table 2 summarizes the parameters and the charges of each type of ions. The Lorentz-Berthelot mixing rule was adopted to determine the LJ potential parameters between different types of ions, waters and carbon atoms.

Table 2. Parameters of the Lennard-Jones force fields that were used in this paper.

Atoms	ϵ (eV)	σ (Å)	Molar Mass	Valence (e)
Na ⁺	0.00203	2.430	22.990	-1
K ⁺	0.00377	3.143	39.102	+1
Cs ⁺	0.00824	3.742	132.90	+1
F ⁻ [37]	0.00781	3.118	18.998	-1
Cl ⁻	0.00650	4.045	35.450	-1
I ⁻ [36]	0.00434	5.167	126.90	-1
O (TIP3P)	0.00660	3.151	15.999	-0.834
H (TIP3P)	0.00000	0.000	1.0080	0.417
C (graphene)	0.00304	3.550	12.011	0 ~ ±0.041

Our MD simulations were carried out using the LAMMPS code. Time step was set as 1.5 fs. The van der Waals forces were truncated at 1.0 nm with long-range Columbic interactions computed using the particle-particle particle-mesh (PPPM) algorithm. Although isolated graphene layers take on a micro-corrugated texture, the corrugation amplitude of the graphene layer [38] is generally much smaller than 5 nm as selected for this simulation [39, 40]. Furthermore, previous MD studies

have showed a negligible effect of graphene surface corrugation on the structure of the first water layer, suggesting a minor effect on the EDL [41-43]. As such, we didn't consider the movement of carbon atoms and their positions were frozen. The Berendsen thermostat was adopted to control the system temperature, which was firstly increased from 298K to 373K over a period of 10ps, maintained at 373K for an additional 10ps before gradually cooled down from 373K back to 298K. Then, the NVT ensemble simulations at 298K were carried out for 1.2 ns. Results generated during the last 150ps were used to analyze the EDL structures and to calculate the capacitance. In some cases, longer MD simulations up to 2 ns were carried out to ensure that the systems indeed reached thermal equilibrium state.

We split the channels into a set of bins (of 0.05 Å in width) along the direction (x) perpendicular to the graphene surface. The averaged number density of particles (e.g., water, electrolyte ions) within a bin during the last 150ps of our MD simulations was calculated to represent the number densities ρ of the corresponding particles. Such a number density $\rho(x)$ is widely used to represent the EDL structures. The resultant electric potential $V(x)$ can be computed by integrating the following one-dimensional Poisson equation:

$$\frac{\partial^2 V(x)}{\partial x^2} = -\frac{q(x)}{2A_G \epsilon_0} \quad (1)$$

where x is the distance to the graphene surface ($x > 0$), $q(x)$ is the total charge quantity at x , A_G is the cross-section area of MD simulation, namely the size of graphene sheet, and ϵ_0 is the vacuum dielectric constant. Note that $q(x)$ includes the electrode charge, electrolyte ion charge, and charges of hydrogen and oxygen atoms of water molecules. The term $2A_G$ in Eq. (1) is due to double accounting of electrolyte charges from both sides of graphene surface. We used numerical integration of Eq. (1) to obtain $V(x)$. The $V(x)$ value in the middle of the channel ($x = \pm L/2$) was used as a reference. Since the channel is symmetrical, the dV/dx value at $x = L/2$ should be equal to zero. The integral of Eq. (1) yields the potential $V(x)$.

$$V(x) = -\int_{L/2}^x \frac{q(x)}{2A_G \epsilon_0} dx \quad (2)$$

3. Results and Discussions

3.1 Structures of the EDL

We normalized the number densities ρ of ions and water molecules with respect to their number densities in the bulk aqueous solution to obtain the relative number densities ρ^* . Figure 2 summarizes the results of the electrolyte ions Na^+ , K^+ , Rb^+ , Cs^+ cation and co-ion Cl^- in different aqueous electrolyte close to the negatively charged graphene surfaces. Figure 3 shows the results for F^- , Cl^- , I^- anions and counter-ion Na^+ close to the positively charged graphene surfaces. Figure 4 shows the results for water molecule close to graphene surfaces with either positive or negative charges.

Figure 2. Relative number density ρ^* of different electrolyte ions as a function of distance from the graphene cathode surface with a charge of 0, -0.015 and -0.041 e/C-atom, respectively. The shaded regions represent the inner Helmholtz layer (IHL) and outer Helmholtz layer (OHL).

Figure 3. Relative number density ρ^* of different electrolyte ions as a function of distance from a graphene anode surface with a charge of 0, +0.015 and +0.041 e/C-atom, respectively. The shaded regions represent the IHL and OHL.

Figure 4. Relative number density ρ^* of water molecules as a function of distance from a graphene anode surface with a charge of +0.041, +0.015, 0, -0.015 and -0.041 e/C-atom, respectively. A negligible change of water distribution is seen in different electrolyte. The presented results are for the NaCl electrolyte.

The sharp relative number density peaks in Figs. 2 and 3 represent the accumulation of electrolyte ions as a result of the electrical interactions from the charged electrode surfaces. The regions between the peaks and the electrode surface are regarded as the impact Helmholtz layers (HLs) in the Grahame model. The ionic density gradually decays as the distance increases from the electrode surface, and ultimately to the nominal density in the bulk solution, the region of which is known as the diffusion layer. As the electrolyte in our MD simulations has a relatively high concentration of 1 M, the EDL is fairly compact and has a thickness of ~ 1.0 nm (Figs. 2 and 3). This is generally consistent with the classic GCS model [44, 45]. Nevertheless, Figs. 2 and 3 clearly show an oscillating ρ^* , in contrast to the continuous exponential decay ionic density stated in the continuum GCS model. We found that the first electrolyte ion layer next to the graphene surface contains more opposite charges than the total charge of graphene electrode. As such, a following ion layer with an opposite charge is needed to counterbalance the surplus charges. The finite size of water molecules and ions in MD simulations has resulted in this over-screening effect [6, 26, 27, 46-48], which has been identified to negatively contribute to capacitance since it effectively increases the distance between electrode and counter-ions [49-52].

Figure 4 shows a clear water layer adsorbed on the graphene surface. The relative number density ρ^* of O atom is estimated between 3 and 4 depending on the electrode surface charges (or the resultant electric field). It is often called as “the first water layer” in literatures [42, 53, 54]. The formation of this layer can be attributed to the interruption of continuous hydrogen-bonding network by the hydrophobic graphene surface. Without electrode surface charge, the ρ^* of oxygen is about 3 and the distance to the electrode surface is about 3.2 Å (Figs. 2 and 3), in good agreement with previous MD results [6, 26, 27, 55]. In the first water layer, the density profiles of hydrogen atoms are slightly closer to the graphene surface than those of oxygen atoms, indicating the water molecules having one of its OH bond pointing toward the graphene surface. It is worth noting that we did not see noticeable influences of the different electrolyte ions on the number density of the first water layer. Thus we only show results of electrolyte with Na⁺ and Cl⁻ solute ions in Fig. 4.

Figure 2 shows clear structural differences of EDL for different electrolyte cations. The first water layer hinders the hydrated cations from moving towards the charged graphene surface [3, 56], resulting in the first density peaks of Na⁺ and K⁺ located behind the first water layer. Such a concentrated hydrated cation layer is known as the outer Helmholtz layer (OHL) [18, 57, 58]. The EDL structures of Rb⁺ and Cs⁺ cations are very different. For a surface charge of graphene cathode of -0.015e/C-atom and above, a new ionic density peak starts to appear next to the electrode surface, overlapping with the first water layer. This new ionic density peak corresponds to the inner-Helmholtz layer (IHL) [57, 58], which arises from the distortion of the weak hydration shell of large-sized ions when approaching to an electrode surface under a strong external electrical field [25, 59-63].

Figure 3 summarizes the different EDL structures for the electrolyte anions close to the graphene anodes. The F⁻ anion only forms OHL, which is similar to Na⁺ and K⁺ but with a much larger distance from electrode surface. For the Cl⁻ anion, only an OHL forms under a low surface charge of +0.015e/C-atom. The result is in contrast to the previous report of specific absorption of Cl⁻ on metal surface [64]. But an IHL emerges under a relatively high surface charge of +0.041e/C-atom. The I⁻ anion, even under a zero electrode surface charge, has a clear IHL ionic density peak shown in Fig. 3. This should be attributed to a strong affinity of I⁻ to graphene, arising from its pronounced lone-pair electron densities [64]. Similar ions/electrode affinity has been discovered in the ionic-liquid/graphene system, leading to peculiar ionic distribution and orientation in the EDL [14, 16, 65, 66].

Some quantitative information of EDL structures for different electronic ions, such as the thickness of the IHL and OHL and the relative number density ρ^* , are summarized in Figs. 5 and 6. Overall,

the thickness of the IHL/OHL increases with the cation/anion size, which is easy to understand. But in terms of the ρ^* magnitude of OHLs, there is no clear trend on the ionic size in the case of $0.015 \pm e/C$ -atom electrode surface charge. The K^+ ion has the largest ρ^* value of OHL among the cations and the Cl^- has the largest ρ^* value of OHL among the anions. Under a higher graphene surface charge, *i.e.*, $0.041 \pm e/C$ -atom, the ρ^* of OHL exhibits a clear trend: decreasing with the ionic size. Note that the ρ^* of IHL shows an opposite trend: increasing with the increase of the ion size. This is because it is relative easier for larger ions to dehydrate, leading to a more pronounced accumulation near the charged electrode surface (*i.e.*, IHL). This effect partly contributes to the reduction of ρ^* of OHL.

Figure 5. Thickness of the IHL and OHL at the graphene cathode surface and the relative ionic number density in the cases of electrode surface charge of $-0.015e/C$ -atom or $-0.041e/C$ -atom.

Figure 6. Thickness of the IHL and OHL at the graphene anode surface and relative ionic number density in the cases of electrode surface charge of +0.015e/C-atom or +0.041e/C-atom.

The different graphene surface charges significantly change the EDL structures as well as the first water layers. Generally, a larger surface charge leads to a reduction of the IHL/OHL thickness (*i.e.*, ions moving toward the charged graphene surface) and an enhancement of the relative number density of the IHL/OHL layers (Figs. 5 and 6). There are two exceptions. There is nearly no change of OHL thickness for Na⁺ cation. This may be due to the strong hydration shell of Na⁺. For the I⁻ anion, the OHL thickness increases with an increase of electrode surface charge. The formation of stronger IHL could push the OHL further away. Note that the enhancement of the ρ^* of OHL and IHL is not proportional to the electrode surface charge change, *e.g.*, 5 times increase of ρ^* of the Na⁺ OHL *vs.* a 2.67 times increase of electrode surface charges.

The electrode surface charge also alters the molecular structure of the first water layer, mainly manifested as the partial re-orientation of the water dipoles. The negative charge on the graphene cathode leads to the water dipole pointing toward the graphene surface, leading to the enhancement of hydrogen atom density (in front of the oxygen atom density peak) in Fig. 4. The positive charge of graphene anode yields an opposite effect. The changes in the water molecular network are expected to alter the dielectric of aqueous solution, and hence the capacitance values. This effect will be discussed in next section.

In a short summary, different electrolyte ions have profound effects on the EDL structures. The large size ions and those with specific affinity to the graphene could form IHL next to the charged electrode surface. The thickness of IHL and OHL increases with the ionic size. But the ionic density

of IHL and OHL has no clear trend under a relative low surface charge (*i.e.*, $0.015e/C\text{-atom}$). An increase in surface charge generally causes a reduction of the thickness (except Na^+ and I^-) and enhancement of the ionic density of the IHL and OHL (except I^-). Note that different types of electrolyte ions have negligible effect on the water density profile. But different surface charge status has clear influences on water molecule re-orientation in the first water layer. The EDL structure and water solvent will determine the electric potential distribution and thus the capacitance results, which will be discussed in next section.

3.2 Electric potential in the EDLs

Based on the EDL structures obtained from MD simulations, this section analyzes the electric potential results and calculates the capacitance values of the graphene-based supercapacitors using different aqueous electrolytes and under different electrode surface charging states. The theoretical results are compared with our experimental results. The influences of ionic EDL structures and dielectrics of H_2O solvent on the capacitance are carefully examined.

Figure 7. The electric potential V as a function of distance x from the graphene cathode surface for the NaCl and CsCl electrolyte under two charging cases: -0.015e/C-atom and -0.041e/C-atom . The total electrical potential U_{tot} is decomposed into two components: U_{ion} calculated from the ion EDL $\rho(x)$ and the cathode surface charge, and U_{water} calculated from the water molecular dipoles.

Figure 8. The electric potential V as a function of distance x from the graphene cathode surface for the NaF and NaI electrolyte under two charging cases: $+0.015\text{e/C-atom}$ and $+0.041\text{e/C-atom}$. The total electrical potential U_{tot} is decomposed into two components: U_{ion} calculated from the ion EDL $\rho(x)$ and the anode surface charge, and U_{water} calculated from the water molecular dipoles.

Figure 7 shows the calculated electric potentials $V(x)$ for the NaCl and CsCl electrolyte under two charging cases: a surface charge of -0.015e/C-atom or -0.041e/C-atom , at a graphene cathode. Figure 8 summarizes the results for NaF and NaI electrolytes next to a graphene anode. To clearly examine the roles of electrolyte ions and water solvent on capacitance results, the electric potentials U_{tot} were decomposed into contributions from the ionic EDL (U_{ion}) and the water solvent (U_{water}) separately. The U_{ion} is computed based on ionic EDL $\rho(x)$ and the electrode surface charge. The U_{water} is computed by only considering the polarized water molecules.

With the obtained U_{tot} , we calculated the capacitance value and summarized the results in Table 3 and 4. First, the calculated capacitance values in our simulations (100~280 F/g) are quite close to the experiment results (130 ~ 300F/g) [39, 67, 68]. Our experimental results have indicated that the capacitance of cathode would be ~100F/g higher than that of anode, which reasonably agrees with our simulation results (see supporting information). Second, increasing the cathode surface charge density leads to significantly reduced specific capacitance values (Table 3). But such a reduction is not observed for graphene anodes. Our experiments appear to show a more significant change of capacitance values for cathodes when varying from -0.25V and -0.4V than that of the anodes, *i.e.*, 5.75F/g *vs.* 0.83F/g (see supporting information), which is consistent with our MD results. But magnitude of the changes in MD simulations (Table 3) is much higher. This could be partly attributed to the much higher voltage in our MD simulations (Table 3). Third, it is a surprise to notice that the specific capacitance values of the cathodes and anodes weakly depend on the electrolytes ions types, despite the significantly different EDL structures as observed in Figs. 2 and 3. This is supported by our experimental results that capacitance values of graphene cathode using the LiCl, NaCl, KCl, and CsCl electrolytes are all around 240F/g [69]. In the following, we will provide an in-depth analysis to understand these observations.

Table 3. Specific capacitance of a graphene cathode immersed in different electrolytes, with a surface charge of -0.015e/C-atom or -0.041e/C-atom .

(F/g)	-0.015e/C-atom	-0.041e/C-atom
NaCl	279.8	176.4
KCl	282.7	175.5
RbCl	254.9	178.2
CsCl	237.9	174.5

Table 4. Specific capacitance of a graphene anode immersed in different electrolyte, with a surface charge of 0.015e/C-atom and 0.041e/C-atom .

(F/g)	$+0.015\text{e/C-atom}$	$+0.041\text{e/C-atom}$
NaF	89.14	99.47
NaCl	90.53	100.9
NaI	87.70	99.66

The U_{ion} results of different electrolyte ions are significantly different (Figs. 7 and 8). For the U_{ion} , a linear relation is observed in the EDL region 4–6 Å from graphene surface. This region corresponds to the OHL/IHL in Fig. 2. It can be treated as a parallel plate capacitor composed of the Helmholtz layer and the charged electrode, manifested by the linear electric potential. In the diffusive layer, U_{ion} gradually approaches the reference state (i.e., zero in bulk electrolyte). The NaCl has larger U_{ion} values at the graphene electrode than the CsCl under both charging cases. This can be understood by the formation of IHL in the CsCl case (Fig. 2), which effectively reduces the thickness of EDL. For the same reason (Fig. 3), the NaI has a smaller U_{ion} value at electrode surface than NaF (Fig. 8).

The U_{water} exhibits a significant oscillation. An electric potential plateau is observed in the water depletion region (between the graphene and the first water layer). The dipoles caused by the reorientation of water molecules being subjected to external electric field (Fig. 4) result in the sharp potential drop in U_{water} from 2 to 3 Å (Figs. 7 and 8). The U_{water} has an opposite sign to U_{ion} . Additionally, a higher U_{ion} value is always accompanied by a higher U_{water} value for different electrolyte cases. Both facts reflect the dielectric nature of water solvent.

Despite the distinct EDL structures and the U_{ion} results of NaCl, KCl, RuCl, and CsCl aqueous electrolytes (Figs. 2 and 7), their total electric potential profiles U_{tot} are quite similar, resulting in a similar capacitance value (Table 2 and 5). Similar situation is observed for the graphene anode cases (Fig. 8 and Table 3 and 6). It is clear that the dielectric water molecules play a critical role in determining the overall potential drop in EDLs [70, 71].

The critical role of water solvent in determining the capacitance values of different electrolyte can be understood in terms of the dielectric constants in the EDL (ϵ_{water}), as summarized in Table 5, Table 6, and Table S2. We found a general trend that a larger ion tends to have a lower ϵ_{water} : 9.744 (Na^+) > 7.266 (Rb^+) > 6.788 (Cs^+) and 3.693 (F^-) > 2.151 (Cl^-) > 1.991 (I^-). It is such a reduction in dielectric constant that largely cancels out the beneficial effect on capacitance from a thinner EDL (thus a small U_{ion}) for those large ions Rb^+ , Cs^+ , Cl^- , and I^- , which results in small differences in the calculated capacitance values of different electrolyte ions. Note that recently a similar phenomenon was reported in supercapacitors using the organic ionic liquid (IL) electrolyte, in which the beneficial nanofinement effect for the ILs was cancelled by the reduction of the dielectric constant of the organic solvent [72]. Thus, variation of the dielectric constant of water or other solvent in the EDLs should be taken into account for the design of supercapacitors.

Table 5. The electric potential drop (in unit of V) next to a graphene cathode with a charge of -0.015e/C-atom or -0.041e/C-atom .

	NaCl		KCl		RuCl		CsCl	
Surface charge (e/C-atom)	+0.015	+0.041	+0.015	+0.041	+0.015	+0.041	+0.015	+0.041
U_{ion}	4.267	7.918	2.341	7.533	3.492	7.621	3.496	7.469
U_{water}	-3.829	-6.066	-1.907	-5.671	-3.011	-5.787	-2.981	-5.598
U_{tot}	0.4379	1.852	0.4334	1.862	0.4806	1.834	0.5150	1.872
ϵ_{water}	9.744	4.275	5.401	4.046	7.266	4.155	6.788	3.990

Table 6. The electric potential drop (in unit of V) next to a graphene anode with a charge of $+0.015\text{e/C-atom}$ or $+0.041\text{e/C-atom}$.

	NaF		NaCl		NaI	
Surface charge (e/C-atom)	+0.015	+0.041	+0.015	+0.041	+0.015	+0.041
U_{ion}	-5.074	-9.526	-2.910	-6.462	-2.781	-5.385
U_{water}	3.700	6.241	1.556	3.223	1.383	2.106
U_{tot}	-1.374	-3.285	-1.353	-3.239	-1.397	-3.278
ϵ_{EDL}	3.693	2.900	2.151	1.995	1.991	1.643

The water solvent also plays an important role in determining the capacitance values at graphene cathodes and anodes. From Table 5 and 6, NaCl has a weaker U_{ion} than that of graphene cathode, yet the U_{tot} shows an opposite trend. This is because the calculated ϵ_{water} values in graphene anode side (Table 6) are significantly lower than the results for that in cathode (Table 5). This might be understood in terms of the re-orientation of the water molecules in the first water layer under different electrical fields. As shown in Fig. 4, the water molecules in the first water layer naturally have one of its O-H bonds pointing toward the graphene surface (with zero charge). At the anode surface, the positive charge has to overcome such a tendency to re-orientate the OH bond pointing away from the anode surface. In other words, the water molecules near the anode surface are relatively more difficult to be polarized and thus the dielectric constant is smaller. In the end, the calculated capacitance values of graphene anodes are about 100F/g lower than that of cathodes, which agrees with our experimental observation quite well (see supporting information).

The surface charging conditions also affect the overall capacitance values. First, a higher density of electrode surface charges will enhance the attraction of counter-ions towards graphene electrode and thus reduce the thickness of EDLs (Fig. 4 and 5). The increase of U_{ion} is less proportional to the increase of surface charge, suggesting a tendency of capacitance enhancement. But when subjected to a high electric field, the water molecules are highly orientated (or ordered) thus have less capability to re-orientated further. The dielectric constants are smaller than those in the weak electric field (the so-called “dielectric saturation”) [44, 73, 74], which can be seen in our calculated results in Table 5 and 6. Overall, for graphene cathode, the dielectric saturation effect dominates at strong surface charging. We, therefore, obtain significantly reduced capacitances, i.e., about 30-40% reduction (Table 3). But for anodes, these two contributions almost cancel out each other. There is, therefore, a negligible change in capacitance (Table 4).

3. Conclusion

In summary, MD simulations were carried out for a comparative study on the EDL molecular structures of M^+X^- ($M^+ = \text{Na}^+, \text{K}^+, \text{Ru}^+, \text{and } \text{Cs}^+$; $X^- = \text{F}^-, \text{Cl}^-, \text{and } \text{I}^-$) electrolytes at the graphene cathodes and anodes, under different charging conditions. The role of electrolyte ion types, water solvent, and the surface charging condition on the total capacitance values are investigated. We found that the larger ions, such as $\text{Rb}^+, \text{Cs}^+, \text{Cl}^-$ and I^- , will be dehydrated subject to the external electric field (with certain strength) and penetrate the first water layer to form the impact Helmholtz layer (IHL). Generally, thickness of the IHL and OHL layer increases with the size of ions. But there is no clear trend for the ionic number density of the OHL/IHL with respect to the ionic size. The formation of IHL will effectively reduce the thickness of the whole EDL, leading to a smaller electric potential drop U_{ion} for the large ions under the same electrode charging condition. Our results reveal the critical role of water solvent in determining the capacitance values. First, despite the significant difference observed in EDL structure and the U_{ion} values for different electrolyte, the changes of water dielectric constants cancel out the influences, leading to a nearly the same capacitance value, which agrees with our experiments. Second, the electric potential drop U_{ion} from the EDL of graphene anodes is smaller than that of the graphene cathodes, potentially could lead to a higher capacitance value. Nevertheless, the water orientation at graphene anode surface results in a much smaller dielectric constant, and the graphene cathodes actually have a much higher capacitance than anodes. This is in a good agreement with our experimental results. Third, we notice that a higher surface charging condition will reduce the water dielectric constants and thus cause a significant drop of capacitance, which is also discovered within the experiments.

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