Effects of anion on the electric double layer of imidazolium-based ionic liquids on graphite electrode by molecular dynamics simulation

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Effects of anion on the electric double layer (EDL) structure and differential capacitance (C_d) of ionic liquid (IL), 1-butyl-3-methyl-imidazolium bis(fluorosulfonyl)imide (BMIM$^+$/FSI$^-$) and 1-butyl-3-methyl-imidazolium trifluoromethanesulfonate (BMIM$^+$/Tf$^-$) on graphite electrode were studied by molecular dynamic simulations. It is found that ILs with FSI$^-$ and Tf$^-$ anions show substantially different EDL structures and C_d features. The potential-dependent capacitance curve of the BMIM$^+$/FSI$^-$ is asymmetric camel-shaped, with the potential of zero charge at the local minimum, while the BMIM$^+$/Tf$^-$ shows much weaker C_d dependence on potential between 0 to 1.1 V. Such feature of BMIM$^+$/Tf$^-$ indicates formation of Helmholtz-like EDL structure, which consists of a parallel alignment of imidazolium-ring in BMIM$^+$ and the planar graphite electrode. A higher C_d of the both ILs at positive polarization can be attributed to the thinner effective EDL caused by the smaller size of anions compared to the cations. Apart from that, the slightly higher capacitance of BMIM$^+$/Tf$^-$ compared to BMIM$^+$/FSI$^-$ at positive polarization and the reverse trend at negative polarization is associated with the effectively shortened EDL thickness that resulted from the smaller size of Tf$^-$ in contrast to FSI$^-$.

1. Introduction

Room-temperature ionic liquids (ILs), as the "designer solvent", has received intensive interest due to their low melting point and volatility, relatively high ionic conductivity, and wide electrochemical window [1], which can enhance charge storage capacity of supercapacitors, given the square dependence of the energy density on potential windows. Properties of IL are tunable through various combinations of organic cations and organic/inorganic anions, as well as the modification of cations and anions [1,2]. Therefore, IL is one of promising electrolyte of supercapacitors that can deliver a high power density and an energy density comparable to the lead-acid battery [3,4]. Although ILs possess favorable properties for use as electrolytes in supercapacitors, the electric double layer (EDL) structure at molecular level is still not well understood [5].

EDL is generally complicated by various conformations of ILs [6], ionic correlations [5], specific adsorption [7,8], and temperature [9–11],*etc.*. Differential capacitance (C_d) provides important insight into the potential dependent EDL both from theoretical and practical points of view. The EDL structure of ILs is often experimentally probed by the potential-dependent capacitance (C_d–U) curve using electrochemical impedance spectroscopy (EIS) [12]. The available C_d data of various ILs provide invaluable information about EDL of this new kind of electrolyte. In terms of anionic effects, the trend of experimental C_d with variation of the anion size and the chemical structure is controversial. Lockett et al. [11] found the C_d decreases as the anion size increases from Cl$^-$ to I$^-$ in 1-butyl-3-methyl-imidazolium BMIM$^+$/Y$^-$ (Y$^-$ = Cl$^-$, Br$^-$, I$^-$) ILs on a glassy carbon electrode by EIS. However, Lust et al. [13] and Silva et al. [14] reported an opposite trend of ILs. Specifically, Lust et al. [13] found that the C_d of 1-ethyl-3-methyl-imidazolium EMIM$^+$/TCB$^-$ (tetracyanoborate) is higher than that of EMIM$^+$/BF$_4^-$ (tetrafluoroborate) on bismuth electrode using EIS. The C_d of BMIM$^+$/TFSI$^-$ (bis(trifluoromethylsulfonyl) imide), as studied by Silva et al. [14], is higher than that of BMIM$^+$/PF$_6^-$ (hexafluorophosphate) on both gold (Au) and platinum (Pt) electrodes. Similar contradiction also exists in the computer simulations of ILs/electrode interfacial properties. Qiao et al. [15] studied the EDL capacitance of two ILs at planar graphite electrode by using a combination of molecular dynamic (MD) simulations and density functional theory. They found that the C_d of BMIM$^+$/Cl$^-$ is higher than that of BMIM$^+$/PF$_6^-$ at the positive polarization. Feng et al. [16] studied the EDL of 1-hexyl-3-methyl-imidazolium

$(C_6mim)_2^{2+}$-based ILs: $(C_6mim)_2^{2+}/(BF_4)_2^{2-}$ and $(C_6mim)_2^{2+}/(TFSI)_2^{2-}$ on onion-like carbon electrode via MD simulations. They found that $(C_6mim)_2^{2+}/(BF_4)_2^{2-}$ yielded a higher C_d in contrast to $(C_6mim)_2^{2+}/(TFSI)_2^{2-}$. On the other hand, Vatamanu et al. [17] investigated the EDL of N-methyl-N-propylpyrrolidinium pyr_{13}^+/FSI^- (bis(fluorosulfonyl) imide) and $pyr_{13}^+/TFSI^-$ ILs by performing MD simulations and found the smaller size of the FSI^- compared to $TFSI^-$ did not result in an increase of the C_d at the positive polarization. Subsequently, they studied the EDL of $BMIM^+/BF_4^-$ and $BMIM^+/PF_6^-$ on planar graphites [18] and observed very similar EDL structures for both ILs with an average C_d of ~5 $\mu F\,cm^{-2}$. The authors concluded that the difference in the anion structure is not important for defining C_d on the planar graphite surface. Thus, there is still a discrepancy on the trend of anion-dependent capacitance in both experiments and computer simulations, due to the complexity of the ILs/electrode interfaces.

The target of this work is to study the effects of anion on EDL structure of $BMIM^+$-based ILs by MD simulations. It is found that the C_d–U curve of $BMIM^+/FSI^-$ is asymmetric camel-shaped with a higher C_d at positive polarization, which is in good agreement with a previous MD study [19]. However, a weak dependence of C_d on potential window of 0 to 1.1 V, i.e., a nearly flat C_d–U curve is observed for $BMIM^+/Tf^-$. The potential of zero charge (PZC) of $BMIM^+/FSI^-$ is –0.077 V, while that of $BMIM^+/Tf^-$ is 0.071 V. The value of C_d at PZC decreases as the anion changes from Tf^- to FSI^-. On the other hand, the C_d of $BMIM^+/Tf^-$ is slightly higher than that of $BMIM^+/FSI^-$ at the positive polarization and such trend is reverse at the negative polarization, due to the more efficent screening of Tf^- with the smaller size in contrast to FSI^-. Apart from that, the decrease in C_d for both ILs at high polarizations was associated with the gradually increase in the effective thickness of EDL from the overcrowded counterions. Detailed analysis of EDL structure based on anatomy of the number density profiles and orientational ordering are described below.

2. Computational methods

We performed MD simulations of $BMIM^+/FSI^-$ and $BMIM^+/Tf^-$ ILs between two oppositely charged electrodes, composed of frozen graphene layers on both sides of the simulation cell. The separation between the two inner graphene layers was set to be 100 Å, allowing the EDL and the differential capacitance on the two oppositely charged walls to be studied independently [20]. The structure of $BMIM^+$, FSI^- and Tf^- are showed in Fig. 1a, b and c. The simulation process is similar to our previous studies [7,10,21]. Briefly, the $BMIM^+/FSI^-$ and $BMIM^+/Tf^-$ bulk phases contain 448 and 469 cation-anion pairs, respectively, for all systems and

these systems were run at 450 K under 1 bar. Table 1 summarizes the total number of ions and carbon atoms present in each simulated system containing IL/carbon interfaces. The force field parameters are taken from Pádua's work [22–24], and the carbon atoms of the graphite (0001) surface interact with $BMIM^+/FSI^-$ and $BMIM^+/Tf^-$ via the Lennard-Jones potential corresponding to the sp^2 hybrid carbon atoms in the AMBER force field [25]. The van der Waals and the real space electrostatic interaction cutoff distance was set to be 12 Å, and the smoothed particle-mesh Ewald (SPME) algorithm [26] elongated up to 700 Å in z direction (i.e. the direction perpendicular to the graphite electrode surface) was used to handle the long-range electrostatic interactions in reciprocal space, whilst a slab correction [27] is induced along the z direction for such an essential two-dimensional periodic system along the xy-directions. For each system, 14 MD runs were performed with a fixed charge density σ on the two inner graphene layers in the internal from –15.6 to +15.6 $\mu C\,cm^{-2}$, with an increment of 1.2 $\mu C\,cm^{-2}$. Charges with opposite signs were put on the carbon sites of the two inner graphene layers in contact with the $BMIM^+/FSI^-$ and $BMIM^+/Tf^-$, so that the whole system was charge neutral. For each simulation, after initial annealing from 1000 to 450 K within 20 ns, a trajectory of 50 ns was gradually generated at 450 K, coupled to a Nosé-Hoover-chain thermostat [28,29] to generate a converged EDL because dynamics of IL was slow [30,31]. The integration time step was 2 fs with a SHAKE/RATTLE algorithm [32,33] applied on constraining all the C-H bonds. The simulation was performed with a home-made MD package and the image charges were not considered in the current work.

3. Results and discussion

3.1. Influences of anion on C_d

The simulated results of the electrode surface charge density (σ) and the applied electrode potential (U) of $BMIM^+/FSI^-$/graphite and $BMIM^+/Tf^-$/graphite is shown in Fig. 2a. The σ–U curves were interpolated with B-spline interpolation [36]. Subsequently, C_d–U curves were obtained by differentiating the interpolated σ–U curves in Fig. 2a, $C_d = d\sigma/dU$, which are depicted in Fig. 2b. Several features can be observed from the C_d–U curves, i.e., (1) The overall trend of C_d–U curves of $BMIM^+/FSI^-$ and $BMIM^+/Tf^-$ are asymmetric camel-shaped, with a higher C_d at positive polarization. Such trend of C_d–U curves can be ascribed to the thinner effective EDL caused by the smaller size of anions compared to the cations. The C_d–U curve of $BMIM^+/FSI^-$ on planar graphite electrode is in excellent agreement with a previous MD study of the same system [19]. Also, the camel-shaped C_d–U curve of $BMIM^+/Tf^-$ on planar
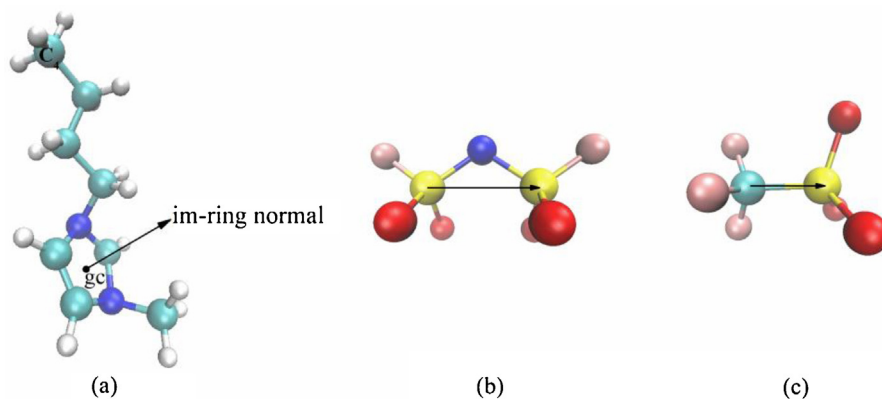

Fig. 1. Structures of $BMIM^+$ (a), FSI^- (b) and Tf^- (c), the geometrical center of the im-ring of $BMIM^+$, the butyl head carbon of $BMIM^+$, denoted as gc and C_4. Carbon (C), nitrogen (N), hydrogen (H), sulfur (S), oxygen (O), and fluorine (F) atoms are displayed in cyan, blue, white, yellow, red, and chartreuse spheres, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).