



# Effects of Alkyl Chain Length on Interfacial Structure and Differential Capacitance in Graphene Supercapacitors: A Molecular Dynamics Simulation Study



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## ABSTRACT

Supercapacitors with graphene electrodes are studied via molecular dynamics simulation. As an electrolyte, we consider three different room-temperature ionic liquids (RTILs), each of which is made up of the same anion  $\text{BF}_4^-$ , and different cations, 1- $\text{C}_n$  ( $n=2,4,6$ )-3-methylimidazolium, respectively. We investigate how the alkyl chain length of the cation affects their interfacial structure and electrical properties for electric double layer capacitors. As a whole, cations and anions make layering structures between two parallel electrodes. Cations in the nearest layer orient predominantly in parallel to the electrode. Imidazolium rings of cations form  $\pi$ -stacking with graphene, then the alkyl chains of cations align parallel to the electrode. Differential capacitances in three RTILs are found to decrease with an increase of the magnitude of electrode potentials. The ion size and orientation affect both structure and capacitance behavior. The parallel orientations of cations become stronger with an increase of the alkyl chain length for the considered RTILs. The differential capacitance tends to decrease with raising the alkyl chain length over a wide range of the electrode potential. This is ascribed to a steric effect caused by larger cation size. It is also found that anodic capacitance is higher than cathodic one due to a higher screening efficiency by small anions, and an asymmetry in the peak of capacitance biased to the cathodic side becomes weaker as the alkyl chain length increases. Comparing electrode charge with ion numbers near the electrodes, with respect to their changes in response to the electrode potential, we find that the interfacial layer of the electrolyte mainly governs capacitive behavior of the systems.

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## 1. INTRODUCTION

Room-temperature ionic liquids (RTILs) have unique physico-chemical properties such as high ion conductivity, high electrochemical and thermal stability, which allows superior performance over conventional solvents for electrochemical applications [1]. In the past decades, RTILs have been investigated as key solvents for electrodeposition, batteries, supercapacitors, and dye-sensitized solar cells [2]. Interfacial properties of the RTILs are one of the most important factors for their surface-dependent electrochemical applications. A number of experimental and computational efforts have been made to obtain insights on their interfacial behaviors. Recent theoretical and computational studies of the interfacial systems [3–20] have offered a microscopic

understanding on the electric double layer structure and associated dynamics, and capacitive properties of RTILs as electrolytes in electric double layer capacitors (EDLCs).

Electrode as well as electrolyte plays an important role in building EDLCs. A wide variation of carbon-based materials have been proposed and applied as electrodes. Graphene, a planar allotrope of carbon, has drawn considerable attention since its discovery because it is chemically stable and mechanically flexible, and has large surface area and high conductivity of heat and electron [21]. Especially, extensive computational research has been dedicated to graphene due to its well-defined chemical structure [22].

Many studies on EDLCs have devoted their attention to the shape of the differential capacitance curve with respect to the applied electrode potential for RTIL electrolytes. Experimental and theoretical studies have characterized capacitance behaviors of the RTILs as either camel-shaped [6–9,16,23–27] or bell-shaped [6,8,16,28,29] differential capacitance (DC) curves. A “lattice saturation effect” [30–32] on the capacitance was taken into

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account such that an electric double layer becomes thicker and thus the capacitance decreases with the electrode potential increasing. This accounts for the decreasing capacitance behavior from the local maxima in DC curves for RTILs. The potential difference between the local maxima in the camel-shaped capacitance curve becomes narrower with increasing ion concentration, resulting in a transition into a bell-shaped one at which the maximum occurs at potential of zero charge (PZC). On the other hand, Monte Carlo simulation studies reported a camel-shaped DC for a coarse-grained model of RTILs with neutral chain [8,33]. Neutral beads in cations first act as “latent voids” at low electrode potentials, and are replaced by charged beads at moderate electrode potentials [33]. In addition, a self-consistent mean field model was developed in which the permittivity depending on the distance from the electrode surface is responsible for the camel-shaped capacitance curve [6,7].

Experimental measurements on DCs for EDLCs have provided diverse results even though the same ionic species and electrodes are considered. For example, for the imidazolium-based tetrafluoroborate RTILs, U-shaped DC curves were observed at glassy carbon and highly oriented pyrolytic graphite (HOPG) electrodes [34,35], while camel-shaped DC curves at glassy carbon electrodes were found [23]. On the other hand, bell-shaped DC curves were observed for 1-butyl-3-methylimidazolium tetrafluoroborate at the gold electrode [29]. Molecular dynamics (MD) simulation studies on DC curve in RTILs have also been reported for the graphite electrodes. A U-shaped capacitance curve was observed over a limited potential range of  $-1.5\sim 1$  V in 1-butyl-3-methylimidazolium nitrate [4], while camel-shaped capacitance curves were found in alkylimidazolium RTILs with a hydrophobic bis(trifluoromethanesulfonyl)imide ([TFSI]<sup>-</sup>) anion [16,25].

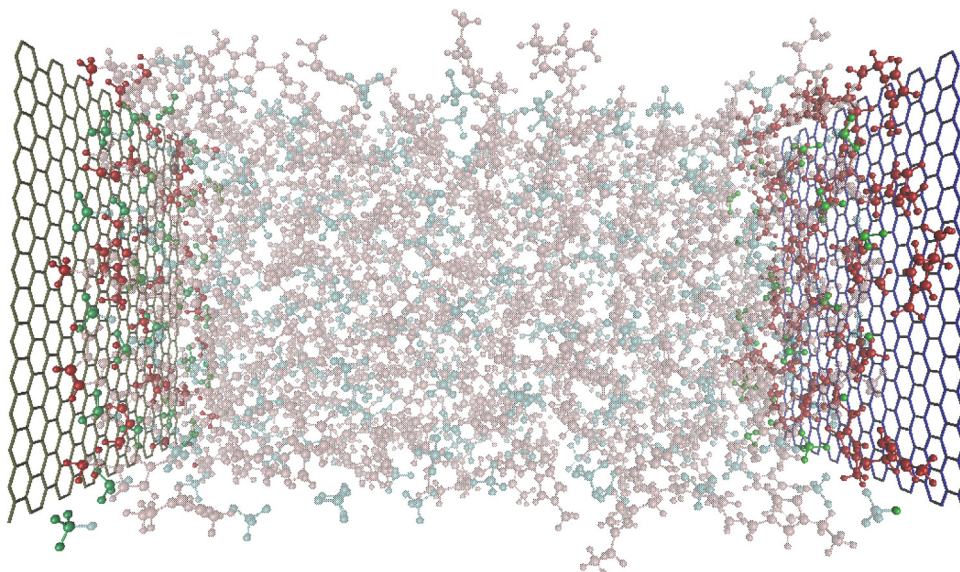
Differential capacitance is affected by various factors such as effective permittivity and dispersion force in RTILs [8,36], topology and material of electrodes [16,17,25,26,37–42]. Among other things, the alkyl chain length in imidazolium-based cations of RTILs can have a great influence on electrolyte properties for EDLCs such as viscosity, conductivity and capacitance. On the whole, as the alkyl chain becomes longer, the viscosity gets larger while the conductivity smaller in imidazolium-based RTILs due to an enhanced steric hindrance [25]. It was found that RTIL electrolytes with longer alkyl chain length provide lower differential

capacitances for various electrodes [25,28]. Although there have been numerous studies on RTIL-electrode interfacial systems, microscopic understanding of the capacitance behavior of the system is far from clear. In this article, we pay attention to the effect of the alkyl chain on structure and differential capacitance at the graphene electrode, employing various imidazolium-based RTILs with tetrafluoroborate anion.

The outline of this paper is as follows: We first give in Section 2 a brief description of the model system and simulation methods employed in this study. MD results are compiled in Section 3, where interfacial structures and differential capacitances of EDLC systems, comprising two graphene sheets and 1-C<sub>n</sub>(n=2,4,6)-3-methylimidazolium tetrafluoroborate ionic liquids, are analyzed to examine their variations with alkyl chain length. Finally, concluding remarks are given.

## 2. MODELS AND METHODS

The simulation cell comprised 256 pairs of an imidazolium-based RTIL confined between the parallel graphene plates [Fig. 1]. Three different RTILs, 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim]<sup>+</sup>BF<sub>4</sub><sup>-</sup>), 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]<sup>+</sup>BF<sub>4</sub><sup>-</sup>) and 1-hexyl-3-methylimidazolium tetrafluoroborate ([hmim]<sup>+</sup>BF<sub>4</sub><sup>-</sup>) were employed as RTILs. Each electrode was modeled as a rigid and flat layer of 448 sp<sup>2</sup>-hybridized carbon atoms, *i.e.*, a single graphene sheet, with dimensions 34.3×34.0 Å<sup>2</sup>. For convenience, we employed a Cartesian coordinate system, where the graphene electrodes at  $z = \pm z_0$  span the  $xy$ -plane ( $-x_0 < x < x_0$ ,  $-y_0 < y < y_0$ ) and its normal defines the  $z$ -direction. Electrode separation  $d$  ( $=2z_0$ ) was fixed to be 66 Å for [emim]<sup>+</sup>BF<sub>4</sub><sup>-</sup> of which density was determined previously using NPT ensemble simulation at 350 K and 1 atm [14]. Electrode separations for the other two RTILs were adjusted to reproduce the ratios in their experimental bulk densities [43–45], the values of which are 78 and 91 Å for [bmim]<sup>+</sup>BF<sub>4</sub><sup>-</sup> and [hmim]<sup>+</sup>BF<sub>4</sub><sup>-</sup>, respectively. Flexible all-atom force fields [46,47] were used for cations. Partial charge and force field description for BF<sub>4</sub><sup>-</sup> anion were taken from the ref 43 and 44, respectively. Surface charge densities at the electrodes were varied in the total charge  $Q_e$  from 0 to  $\pm 8.5 e$ , with a uniform increment of 0.5  $e$ , where  $e$  is an elementary charge. Electronic polarizability for both the graphene



**Fig. 1.** Snapshot of one of the systems. Yellow: anode with charge  $Q_e = +8e$ , Blue: cathode with the opposite charge, Red: [emim]<sup>+</sup> cation, Green: BF<sub>4</sub><sup>-</sup> anions. Ions in the interfacial layers are highlighted. We can see that a charged electrode attracts counterions and expels coions.

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