



Ionic liquids at charged surfaces: Insight from molecular simulations



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ABSTRACT

Understanding of molecular level structure and mechanisms of the formation of electric double layers in realistic ionic liquid-based electrolytes on charged electrode surfaces is one of scientifically and technologically key areas that have attracted a lot of attention over the last decade. Extensive experimental, theoretical, and modeling studies have been dedicated to this challenging topic in order to establish fundamental correlations between the details of molecular structure of electrolyte and the properties of the electric double layers (EDL) forming on various electrodes. While great progress has been made in advancing our understanding of EDL properties and their influence on the performance of supercapacitors, batteries, and other energy storage devices, there are still a number of challenges and controversies that have not been resolved. In this manuscript, we demonstrate how atomistic molecular dynamics simulations provide a powerful tool for dealing with these challenges and can facilitate the design of novel materials for advancing energy storage technologies.

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1. Introduction

The behavior and properties of room temperature ionic liquids (RTILs) on charged electrode surfaces have attracted significant attention in the last decade due to potential promise for utilization of the RTIL-based electrolytes for application in the new generation of energy storage devices. A particularly significant progress in the application of RTIL-based electrolytes has been achieved in electric double layer (EDL) capacitors (EDLCs), also known as super- or ultracapacitors. In these devices, the charge/energy is stored through the rearrangement and accumulation of ions in a couple nanometers thick layer of electrolyte at high specific surface area electrodes [1]. EDLCs have great potential to complement (or replace) batteries in electrical energy storage, particularly when the high power density and fast power delivery/uptake and long cycling life are required. In purely capacitive mode, the absence of Faradic reactions during charge and discharge cycles eliminates the phase changes in the active electrode material that typically occur in batteries [2]. EDLCs can therefore, in principle, sustain millions of cycles. Substantial efforts have been dedicated to improve the energy density of EDLCs through the design of nanostructured electrodes with a high specific surface area and gaining fundamental understanding of the interplay between various phenomena defining the performance of these devices. Realization that RTILs are promising candidates as electrolytes for high energy density capacitors has opened new routes for optimizing the performance of EDLCs. RTILs are in general electrochemically and thermally more stable than conventional electrolytes, allowing for higher charging voltages.

In order to further improve the performance of EDLCs, a more advanced understanding of charge storage mechanisms and their correlations with the chemical structure and composition of electrolytes are needed. This understanding is crucial for further development of novel advanced nanostructured electrodes and electrochemically stable electrolytes. However, our understanding of correlations between properties of different EDLC components and their influence on the EDLC performance is still immature. The progress in this fundamental understanding is hindered by the complex interplay of several molecular scale phenomena that make experimental studies of EDLCs quite challenging and often resulting in inconsistent data. For example, Fig. 1 shows a comparison of several reported in the literature experimental data for differential capacitance (DC) obtained on gold, platinum, and glassy carbon electrodes for the same (or very similar) RTILs [3–7]. The DC is one of the key properties used to characterize structural changes in the EDL as a function of electrode potential as well as a direct measure of the energy stored by a given electrode/electrolyte combination. As we can see from Fig. 1, the shape and the magnitude of DC reported by different studies can significantly deviate from each other. The magnitude of DC from two different measurements can be different up to a factor of 5, particularly at low potentials. Note that the inconsistencies shown in Fig. 1 were obtained for the simplest electrode/electrolyte set up geometry, i.e., flat electrode surfaces in contact with bulk electrolyte. Needless to say that interpretation of experimental results become even more complicated for the technologically more practical nanoporous electrodes, where electrolyte EDL layers are forming in nanopores with very heterogeneous pore size, shape, and surface structure distributions [8,9]. In these electrode materials, electrolyte is subjected to nanoconfinement, local curvature, and atomic scale roughness of exposed

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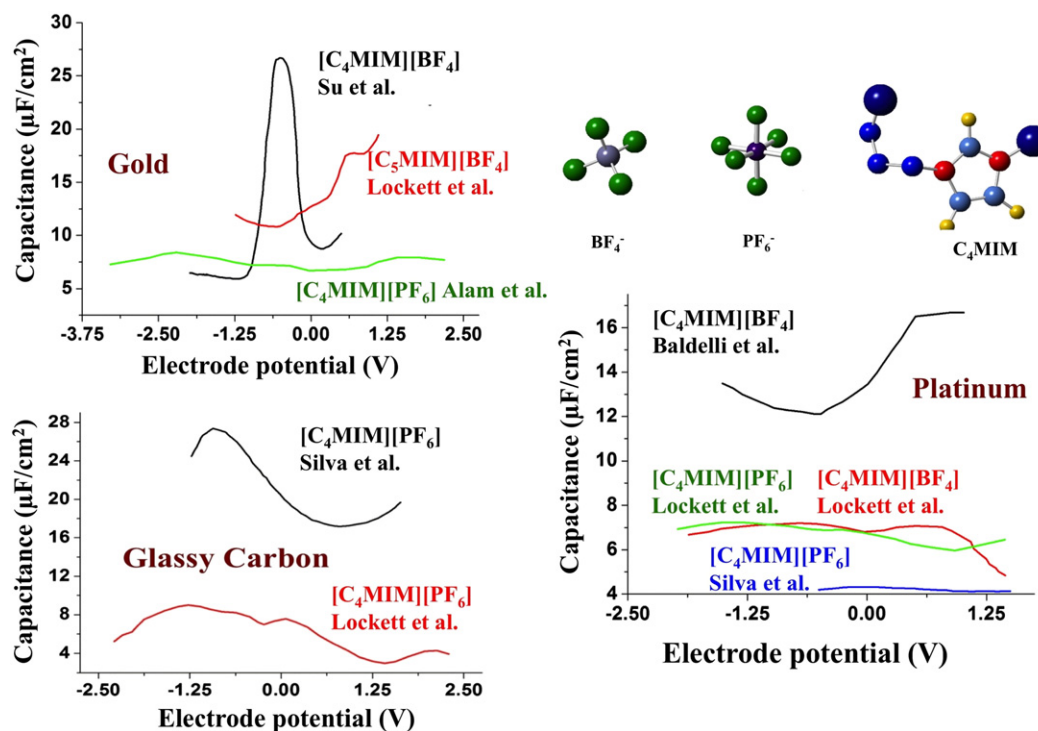


Fig. 1. Compilation of experimental data of differential capacitance measured on similar RTILs on gold, platinum, and glassy carbon electrodes.

electrode surface, all of which can significantly influence the magnitude and dependence of DC [10].

Several theoretical models have focused on the prediction and explanation of correlations between the EDL structure and the dependence of DC as a function of electrode potential [11–27]. These models found that on a flat surface, in general, the DC can be either a camel-shaped with a minimum near the potential of zero charge (PZC) or a bell-shaped with a maximum at low potentials. The camel-shaped DC typically has a low-voltage minimum (the U-shaped region) flanked by two maxima at higher electrode potentials. These dependencies were explained by the analytical model of Kornyshev [28] and attributed them primarily to steric exclusion effects. Specifically, on surfaces where at PZC the EDL structure has a relatively low density of ions and, hence, can pack more ions without significant free energy penalty, the rate of electrode charge (σ) accumulation as a function of electrode potential ($U_{\text{electrode}}$) is high. Therefore the DC, defined as $DC = d\sigma/dU_{\text{electrode}}$ is increasing with the increase of electrode potential. However, at higher potentials, the electrode surface eventually becomes overcrowded with counterions and $d\sigma/dU_{\text{electrode}}$ (i.e., DC) begins to decrease with further increase of $U_{\text{electrode}}$. Therefore, on surfaces that at PZC have loosely-packed electrolyte the camel-shaped DC is expected. In contrast, if at PZC the EDL is already crowded by the counterions and/or has a high overall density due to van der Waals interactions of electrolyte with the electrode surface, i.e., the EDL is sufficiently incompressible, a further increase in applied potential will not lead to a sufficient increase of electrode charge to allow an increase in DC and, hence, a bell-shaped DC dependence can be expected.

Recent experiments [3–7,29,30] showed that both types of DC are observed in RTIL electrolytes. While many of these experimental data can be qualitatively understood/interpreted within the framework of theoretical models mentioned above, a careful examination of several recent experimental studies showed an apparent inconsistency between them (as shown in Fig. 1) as well as a qualitative disagreement with predictions of basic theoretical models. For example, Su et al. [3] studied 1-butyl-3-methylimidazolium ($C_4\text{MIM}$) cation-based RTIL, $[C_4\text{MIM}][\text{BF}_4]$, on Au(001) electrode and reported a bell-shaped DC with a surprisingly large maximum near PZC ($\sim 25 \mu\text{F}/\text{cm}^2$). In contrast,

for a very similar electrolyte $[C_4\text{MIM}][\text{PF}_6]$ Alam et al. [4] found essentially a constant DC (~ 6 to $7 \mu\text{F}/\text{cm}^2$) as a function of electrode potential. Similarly large differences in DC were observed for $[C_4\text{MIM}][\text{PF}_6]$ on glassy carbon electrode as measured by Lockett et al. [6] who reported DC fluctuating between 4 and $8 \mu\text{F}/\text{cm}^2$ and Silva et al. [5] who obtained DC in the 18–27 $\mu\text{F}/\text{cm}^2$ range.

Another controversial issue in EDL properties of RTIL-based electrolytes is the temperature dependence of EDL structure and DC. A number of experimental studies, such as Lockett et al. [6,31], Silva et al. [5,32], Alam et al. [33–35] and Siinor et al. [36] have reported a systematic increase of DC with increasing temperature for commonly studied RTIL-based electrolytes comprised of alkyimidazolium ($C_n\text{MIM}$) cations and BF_4^- , PF_6^- or bis(trifluoromethanesulfonyl) (TFSI) anions on several electrode surfaces (Au, Pt, and glassy carbon). Surprisingly, in some of those studies the capacitance magnitude showed a significant increase with increasing temperature even at large electrode potentials where the electrode surface is expected to be crowded with electrolyte ions and the EDL structure and composition to be only weakly dependent on temperature. For example, Silva et al. showed almost a factor of 2 increase in capacitance across a wide range of voltages and within a 55° temperature window [5]. In contrast, Druschler et al. [37] found that the capacitance due to the fast relaxation process, that was associated with electrolyte reordering in the EDL, had an opposite temperature dependence. Specifically, that work reported DCs ranging between 4 and $7 \mu\text{F}/\text{cm}^2$ in the investigated electrode potential window and an overall small decrease of DC with increasing temperature [37]. Alam et al. also reported only weakly changing DC with temperature for $[C_2\text{MIM}][\text{BF}_4]$ on Hg electrode [38]. A very recent experimental work of Cannes et al. on $[C_4\text{MIM}][\text{TFSI}]$ has also showed an overall decrease of DC with increasing temperature for several electrode surfaces [39].

Taking into account the outstanding issues discussed above, the vast amount of possible anion–cation combinations that can comprise an RTIL-based electrolyte, and the fact that detailed experimental characterization of a couple nanometer-wide EDLs formed in these electrolytes is very challenging, it is clear that both experimental and theoretical investigations of these systems require a complementary

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