**Cation effect on the electrolyte structure with an applied potential: a molecular level investigation using a constant potential method**

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**Introduction**

Future energy storage devices require both high power density and energy density. In general, batteries have a high energy density whereas supercapacitors have a high power density. Developing devices that achieve both is therefore of significance. A striking difference between these two systems is that no chemical reactions occur on the electrodes of a supercapacitor, while energy is stored on the electrodes of a battery through chemical reactions. Energy is stored via ion adsorption on the electrodes in supercapacitors. To advance the performance of supercapacitors, it is vital to understand the molecular-level formation of layers in the vicinity of electrodes, or the electric double layers (EDLs) as this is a key factor for their performance. In this work, we investigate the effect of the cation structure and dynamics on the layering in the electrolyte-to-electrode interface (or EDLs) using molecular dynamics (MD) simulations. We implement a constant potential method to fully capture the correct dynamics of C2mimNTf2 and N4,1,1,1NTf2 ionic liquids (IL) at varying potential differences applied across the electrochemical cell.

**Computational Method and Results**

Two ionic liquids (ILs) are examined: C2mimNTf2 and N4,1,1,1NTf2, with graphene electrodes. A constant potential method (Reed *et al*. 2007) has been applied to model electrochemical cells at the molecular level. After equilibration of the IL at 294 K in the presence of graphene electrode, a potential difference was applied. Our MD simulation results for the C2mimNTf2-based model indicate that the applied potential created ion-dense layers at both electrode interfaces (**Fig. 1-a**). This affected the charge density distribution in the EDL (**Fig. 1-b)**. Although this is symmetric when the potential difference is set to zero, asymmetric charge density distribution profiles formed in the EDL on both surfaces when we turned on the potential difference across the cell. The EDLs have substantially different compositions near both electrodes as a function of applied potential. This not only affects the charge density distribution, but also influences the orientation of the ions. We explore the potential configurations of ions on both EDLs as a function of time and potential difference to better understand the dynamics of ions for the aim of tuning and designing new ILs.

**Fig 1.** (a) A molecular level representation of a supercapacitor. (b) Charge distribution in the ionic liquid (C2mimNTf2) as function of applied potential difference at 294 K. Colour scheme: Grey, yellow and pink for graphene, cation and anion, respectively.

**References**

1. Reed, S.K. & Lanning, O.J. & Madden, P.A. (2007). Electrochemical interface between an ionic liquid and a model metallic electrode. J. Chem. Phys., 126, 084704.

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