

Density functional theory for differential capacitance of planar electric double layers in ionic liquids

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Achievement: The emerging of ionic liquids as a new type of energy carrier and medium brought new life to theoretical investigations of electrolyte-electrode interface in non-aqueous environments. In 2007, two pioneering analytical theories¹⁻² predicted the bell and camel shapes of differential capacitance versus the surface potential for the electrolyte-electrode interface, instead of the conventional U-shape predicted by the Gouy-Chapman theory. In this paper, we introduce the classical density functional theory (DFT) to the problem of the differential capacitance of electric double layers in ionic liquids and its correlation with the surface charge density, ion size and concentration. As prescribed by the two previous analytical theories, DFT is able to reproduce the transition in the differential capacitance curve from the “camel” shape to the “bell” shape when the ionic density increases (see figure a). Moreover, DFT predicts alternating layers of cations and anions at the charged surface (see figure b). This work demonstrates that DFT is a useful and efficient computational tool for further exploring the electrolyte/electrode interface for incorporating more sophisticated electrolyte models and substrate geometries.

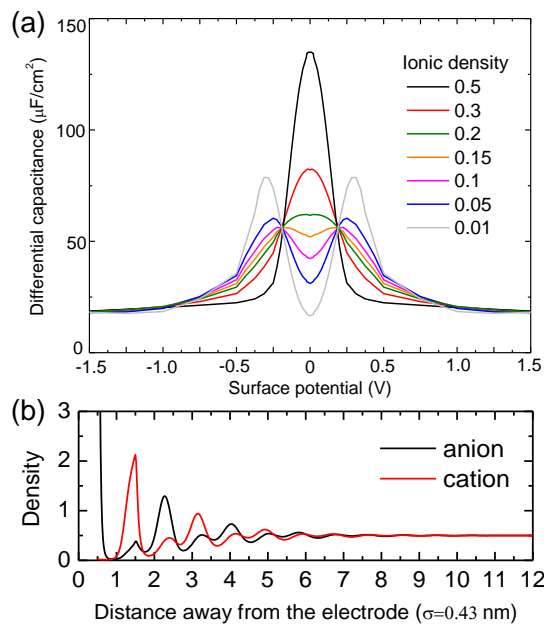


Figure: (a) Differential capacitance versus surface potential at various ionic densities (for an ionic liquid, the density is close to 0.5); (b) density profile of anions and cations near a moderate positively charged wall.

Significance: For the first time, classical DFT was used to explain differential capacitance at the ionic liquid/electrode interface. The results show that the differential capacitance of an ionic liquid reaches its maximum at zero surface potential and decreases with increasing potential, in stark contrast with what the conventional Gouy–Chapman theory predicts. Moreover, classical DFT predicts alternating layers of cations and anions at the charged surface that cannot be described by the conventional Gouy–Chapman–Stern model and its modifications. These findings clearly show the unique features at the ionic liquid/electrode interface for electrical energy storage that require further atomistic modeling for deeper understanding.

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