Analysis on Structuring and Dynamics of Ionic Liquid Forming Electric Double Layer at Electrode Interfaces

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Ionic liquids (ILs) are promising electrolytes for electrochemical devices such as secondary battery, capacitor, electric double layer (EDL)-FET, etc., due to their high chemical stability with negligible vaporization. Structuring and dynamics of the interfacial IL faced to charged graphite electrodes were analyzed by molecular dynamics (MD) calculations [1].

The MD simulations were performed with AMBER 11. The graphite substrate consisted of unit cells of linear dimensions 83.0×72.1 ×30.2 $Å^3$, respectively. Around 800 BMIM-TFSI ion pairs (46000 atoms) were sandwiched between the substrates and a vacuum layer (> 4 nm) (Fig. 1). The systems were equilibrated at a constant volume for 100 ps, followed by a constant volume simulation for 5 ns with fixing all of the substrate atoms. The MD simulations were performed at 300, 350, 400, and 450 K.

Fig. 2 shows the side view of the first-layer ions (z < 6.5 Å) and the total atom number density profiles as a function of the surface charge. The total atom number density profile of the BMIM cation (blue) at pzc (center) indicates a single peak (z = 3.5 Å) with shoulders, whose intensity increases with the negative potential and decrease with the positive potential without changing the overall shape. In contrast, the profile of the TFSI anion (red) at pzc (center) has three peaks at 3.0, 4.0, and 5.5 Å, and its potential dependence is more complicated at negative potential compared to the BMIM cation. These changes reflect a significant difference in the ionic arrangement on the graphite between the checkerboard type at the positive potential and the bilayer type at the negative potential and strongly affect the mobility of interfacial ions.

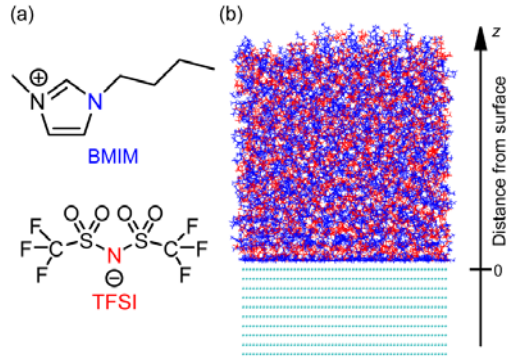

Fig. 1: (a) Ionic liquid (BMIM-TFSI) and (b) a MD snapshot for graphite the interface. BMIM cations and TFSI anions are represented by blue and red colors, respectively.

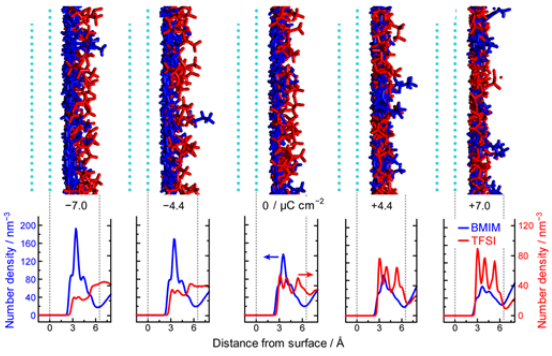

Fig. 2: (top) Side-view snapshots of the first layer ions (z < 6.5 Å) and (bottom) the total atom number density profiles for the indicated charge density of on the graphite electrode. BMIM cations and TFSI anions are represented by blue and red colors, respectively. Each cyan-colored dot represents a carbon atom in the graphite substrate.

Reference

[1] H. Miyamoto, Y. Yokota, A. Imanishi, K. Inagaki, Y. Morikawa, K. Fukui, *Phys. Chem. Chem. Phys.* **20**, 19408 (2018)