

Ionic Liquid Kinetics on Polarizable Electrode Surface

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The dynamical behavior of electrolyte molecules on an electrode surface is one of the most important factors to determine the performance of electrochemical devices. For example, the charging/discharging rate of the electrical double layer (EDL) capacitors is closely linked to the kinetics of the EDL reconstruction at the electrode surface, and the kinetics is expected to originate from the adsorption (desorption) dynamics of interfacial electrolyte molecules or ions onto (from) the electrode. To improve the device performance, it is quite essential to understand the fundamental interfacial dynamics. These dynamics/kinetics at the molecular level have become an active research field in both experiments and simulations. However, not much is known yet about the dynamics compared to the structural properties.

Here we present a classical molecular dynamics (MD) simulation study on the interfacial ionic liquid kinetics at a graphite electrode surface. In particular, we focus on the nonequilibrium relaxation kinetics of the EDL upon the electrode charge change [1]. The electrochemical cell in this study was constructed with 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF₄] ion pairs sandwiched between two three-layered graphite electrodes (Figure 1). For the computational efficiency, the ion pairs were described by a coarse-grained model [2] which can reproduce the experimental bulk diffusion coefficient. Each cation was modeled by a three-site rigid model, while each anion was represented by one spherical particle. The electrode was represented with a polarizable model to appropriately describe electrostatic interaction between ions and the conductive electrode surface. The electrode atomic charges were determined at each MD time step to satisfy the constant electrostatic potential (ESP) condition inside the electrode according to the constant potential MD method [1,3]. In other words, the ESPs acting on each electrode atom were used as parameters specifying the electrode charge density.

The EDL relaxation process was investigated as follows. An equilibrium state at $t < 0$ was initially prepared under the electrode ESP of -0.75 V and then the ESP was

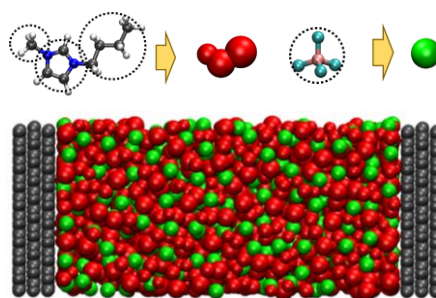


Figure 1. The computational modeling of ions and the electrochemical cell to study the interfacial ionic liquid kinetics.

suddenly dropped to 0 V at $t = 0$. The relaxation to the equilibrium at $t > 0$ was monitored with the change of the electrode charge density reflecting the EDL reconstruction. The relaxation thus simulated was found to occur in the sub-nanosecond timescale in the present case (Figure 2). In comparison with the constant potential simulation, the constant charge simulation, where the electrode charge was completely removed at $t = 0$ and the charge was fixed to zero after that, showed much faster relaxation (several picosecond timescale). The slow relaxation observed in the polarizable electrode originates from the fact that most electrode charges remain as image charges against the interfacial ions. As a result, the small bias (electric field) is imposed on the ions, leading to the quite gradual relaxation. Therefore, the difference in timescale suggests that the electrode polarization effect plays an essential role in the kinetics of nonequilibrium processes like the EDL relaxation.

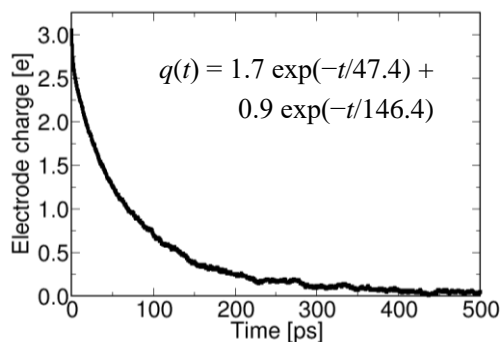


Figure 2. The time evolution of the amount of electrode charge $q(t)$ observed in the relaxation simulation.

The relaxation kinetics observed in the constant potential simulation was further analyzed and found to have approximately two time constants, 47 and 146 ps (Figure 2). This indicates that the relaxation includes two different dynamical processes at least. To obtain molecular insights into the relaxation, we analyzed dynamics of the ions on the basis of the van Hove time-space correlation functions. As a result, we found that the lighter anions contribute largely to the relaxation compared to the cations. In addition, diffusive dynamics of anions were classified into three groups according to initial positions at $t = 0$, that is, the first layer, second layer, and bulk. The analysis showed that the ions in the second layer respond first to the potential drop, which is followed by the ions in the bulk, and the ions in the first layer are most insensitive. This observation suggests that the initial relaxation occurs in the intermediate region between the electrode surface and the bulk due to the delicate balance between the potential drop and the electrode surface interactions. The difference in response rate is expected to be related to the two time constants obtained from the electrode charge reduction curve (Figure 2). Along with the ion dynamics present under the kinetics, the findings gained here are expected to be valuable information to understand interfacial molecular kinetics from computational studies.

[1] T. Inagaki, M. Nagaoka, *J. Comput. Chem.* **2019**, *40*, 2131. [2] C. Merlet, M. Salanne, B. Rotenberg, *J. Phys. Chem. C* **2012**, *116*, 7687. [3] J. I. Siepmann, M. Sprik, *J. Chem. Phys.* **1995**, *102*, 511.