

Hysteresis of Potential-Dependent Changes in Ion Density and Orientation of Ionic Liquids on an Au Electrode: An Surface-Enhanced Infrared Study

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1. Introduction

Room temperature ionic liquids (RTILs) are promising electrolyte materials owing to their fascinating properties, such as non-volatility, non-flammability, wide electrochemical window, and high ionic conductivity. However, the structure and dynamics of RTILs at the vicinity of electrodes are still under debate. Electrochemical techniques have probed a potential-induced slow, hysteretic relaxation of RTILs,^{1, 2} but it requires to be supplemented by spectroscopic technique for uncovering the details of the restructuring. Surface enhanced infrared absorption spectroscopy (SEIRAS) that can selectively probe solid/liquid interfaces is suited for this purpose. In the present work, we investigated the potential-dependent changes in ion density and orientation of 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide [BMIM][TFSA] on an Au electrode by SEIRAS.

2. Experimental

SEIRAS experiments have been performed on a chemically deposited Au thin film electrode on a Si prism in an evacuated glass cell (5×10^{-6} Torr). The electrode potential was controlled by a potentiostat against a Pt quasi-reference electrode. The potential was corrected by the redox potential of Fc/Fc⁺ couple.

3. Results and discussion

SEIRA spectra of [BMIM][TFSA] were found to change depending on the applied potential due to the reorientation of [BMIM] and changes in density of both ions at the vicinity of the electrode. The spectral change observed during positive- and subsequent negative-going potential scans exhibited significant hysteresis as shown in Figure, where the intensity of a C-F stretching mode of the anion is plotted as a function of electrode potential. The hysteresis was larger at slower potential scan rates, showing that an irreversible process requiring overpotential is involved in the potential-dependent restructuring at the interface. The gradual change of the band intensity corresponds to the change in anion density at overlayers, while the steeper change of the band intensity corresponds to the exchange of the cation and anion in the first layer to compensate the change in the surface charge. We revealed that the change in ion density in overlayers precedes adsorption/desorption of the ions at the first layer during potential scan.

Such hysteretic behavior was observed also for various RTILs. The threshold potentials for the replacement of the first layer ions for these RTILs were different even if that have common cations or anions. This result suggests that the energy barrier for the ion exchange in the first layer involves the contribution of ion-ion interaction. Layered structure of ions formed at the vicinity of the electrode, which is characteristic for RTIL/electrode interfaces, possibly suppresses the ion exchange in the first layer and the suppression is the origin of the observed hysteresis.

4. References

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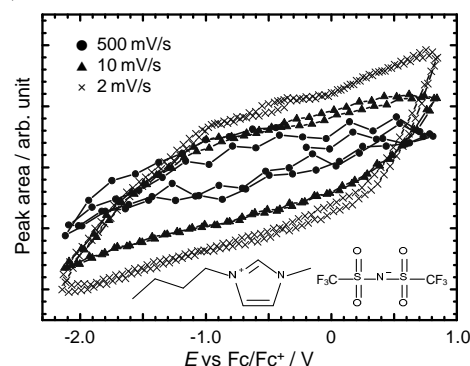


Figure. SEIRAS band intensity of C-F stretching mode of the anion of [BMIM][TFSA]/Au as a function of electrode potential at different potential scan rates. An inset shows the structures of [BMIM] and [TFSA].