

### Electrochemical Behavior of EMIBF<sub>4</sub> Studied by Density Functional Theory (DFT) Method and In situ Infrared Spectroscopic Measurement

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#### Introduction

Room temperature ionic liquids (ILs) are a class of organic salts that exhibit liquid phase in their pure state around room temperature. These organic salts have attracted considerable attention as novel electrolytes in electrochemistry and green solvents for synthesis because of their interesting properties such as negligible vapor pressures, low melting points, high electroconductivities, and wide potential windows. When the ILs are used as the electrolyte, they would provide unique reaction fields at the electrode | IL interface. It is therefore of much interest to investigate structures of the electrode | IL interface at molecular level by theoretical calculation and spectroscopic methods. In this research, we report the electrochemical reaction process of 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF<sub>4</sub>), one of the most popular ILs, around its reduction potential window.

#### Experimental

The calculations were carried out with the density parameter hybrid function combined with the Lee-Yang-Parr correlation function (B3LYP) with 6-31G(d) basis sets by using the GAUSSIAN98 program package on a Dell Precision Workstations 450.

In situ Fourier transform infrared reflection absorption spectra (FT-IRAS) were obtained on an FTS-6000 Fourier transform infrared spectrometer (BioRad Laboratories) equipped with a wide-band MCT detector cooled with liquid N<sub>2</sub>. Polarization of incident light was controlled with a wire grid polarizer.

A polycrystalline platinum disk, 10 mm in diameter, which was embedded in one end of a poly(tetrafluoroethylen) rod, was used as the working electrode. A platinum wire (1.0 mm diameter) and Ag | AgCl (KCl sat.) were used as the auxiliary and the reference electrodes, respectively.

#### Results and Discussion

Figure 1 shows the equilibrium molecular structure of EMI<sup>+</sup> (1), the first reduced form of EMI<sup>+</sup> (EMI<sup>0</sup>) (2) and the second reduced form of EMI<sup>+</sup> (EMI<sup>-</sup>) (3) calculated with DFT method. The hydrogen atom connected to C2 atom of imidazolium ring of the EMI<sup>+</sup> is in plane of the imidazolium ring, whereas those of EMI<sup>0</sup> and EMI<sup>-</sup> are not positioned in the same plane of the imidazolium rings. This is attributed to different hybridization of C2 orbitals in EMI<sup>+</sup> (sp<sup>2</sup>) and EMI<sup>0</sup> or EMI<sup>-</sup> (sp<sup>3</sup>). Since the LUMO of EMI<sup>+</sup> is anti-bonding in the imidazolium ring, reduction of EMI<sup>+</sup> makes the ring distort.

Figure 2 shows a series of potential-step IRAS of EMIBF<sub>4</sub> (a) and the theoretical IR spectra for EMI<sup>+</sup> (b), EMI<sup>0</sup> (c) and EMI<sup>-</sup> (d). In Fig.2 (a), upward and downward peaks indicate the increase and the decrease in number density of ions at the electrode | IL interface, respectively. One can recognize that the absorption bands assignable to both EMI<sup>+</sup> and BF<sub>4</sub><sup>-</sup> decreased in accordance with the potential step to the negative direction. It is considered that the phenomenon is due to electric repulsion between BF<sub>4</sub><sup>-</sup>

anion and the electrode that has negative charges in one hand, and the consumption of EMI<sup>+</sup> during electrochemical reduction. With the passage of time, an upward peak gradually appeared at 1670 cm<sup>-1</sup>, followed by three weak upward peaks around 2800 cm<sup>-1</sup>. These upward peaks are thought to be assigned to reduction forms of EMI<sup>+</sup>, since these peaks are not present in the IRAS of EMIBF<sub>4</sub> at the rest potential. On comparison between these peaks and theoretical harmonic frequencies of EMI<sup>0</sup> (Fig.2(c)) and EMI<sup>-</sup> (Fig.2(d)), these peaks are in good agreement with those of EMI<sup>-</sup>, therefore it is suggested that two electron reduction reaction of EMI<sup>+</sup> occurred at -2.5 V vs. Ag | AgCl.

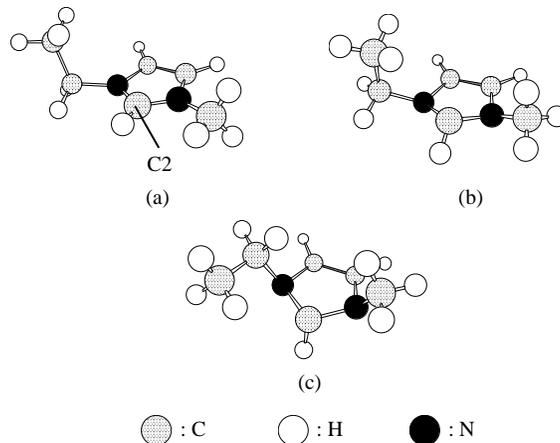


Fig. 1. Equilibrium structures (B3LYP / 6-31G(d)) of (a) EMI<sup>+</sup>, (b) EMI<sup>0</sup> (the first reduced form of EMI<sup>+</sup>), and (c) EMI<sup>-</sup> (the second reduced form of EMI<sup>+</sup>).

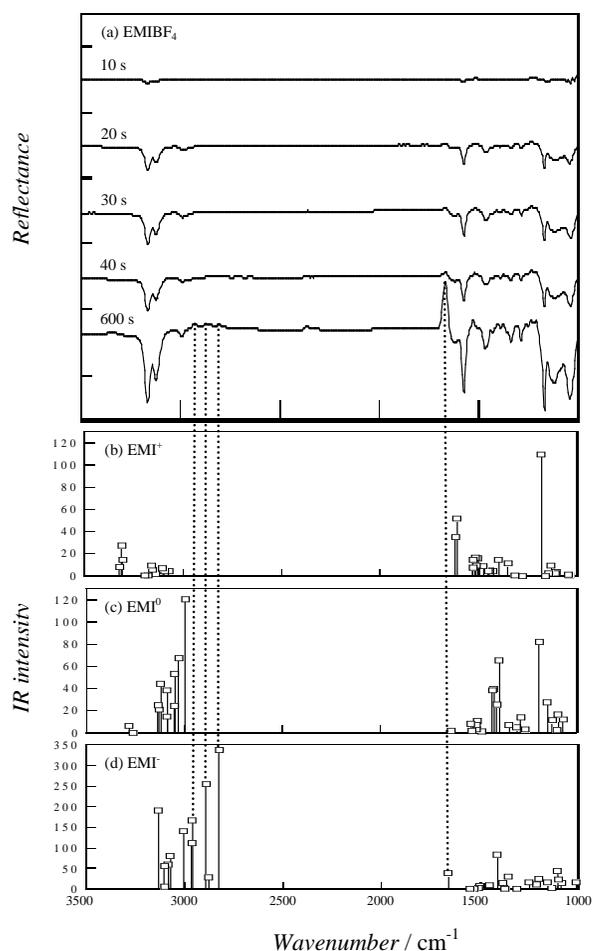


Fig. 2. Comparison between (a) a series of potential step IRAS (stepped to -2500 mV vs. Ag | AgCl) and the theoretical IR spectra (B3LYP / 6-31G(d)) calculated for (b) EMI<sup>+</sup>, (c) EMI<sup>0</sup>, and (d) EMI<sup>-</sup>.