

Electrochemical Doping/dedoping Behaviors of Polythiophene Derivatives in the Ionic Liquids

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Recently, various types of electrically conductive polymers are actively developed for using them to fabrication of devices such as lithium ion batteries, capacitors, organic light emitting diodes, actuators so called 'artificial muscle' and so on. Since the physical and chemical properties of electrochemical conducting polymers are easily designable by varying the molecular structures of the main and side chain, the fundamental and applied researches of syntheses and characterizations of the novel conductive polymers are still continuing. When the electrochemical conducting polymers are used as the material of devices, organic solvents are commonly used in consideration of its wide potential window. However, there are significant problems such as danger of inflammation and degradation of performance caused by evaporation of solvent, since most organic solvents are highly volatile and flammable.

Ionic liquid, which is also called as room temperature molten salt, is expected to be used as the novel solvent from a view point of safety and preservation of environment because of its non-flammability and non-volatility. In particular, the ionic liquids composed of quaternary imidazolium cation and tetrafluoroborate anion have been attracting the great attentions of researchers in many fields because it is chemically more stable in the humid air than the conventional ionic liquids such as chloroaluminate¹. Since ionic liquid is composed of only cation and anion themselves, it shows the quite unique characteristics such as extremely high ion concentration. In addition, the ionic liquid, which has various characteristics, can be obtained because the cations (and some anions) composing the ionic liquids are organic molecules, whose structures are easily designable. Some examples of the ionic liquid commonly used are shown in Figure 1. In this study, the doping/dedoping reactions of polythiophene derivatives in the ionic liquids are characterized by the electrochemical measurements like the cyclic voltammeteries.

Figure 2 shows the cyclic voltammogram showing the electrochemical oxidation and reduction of polythiophene obtained in trimethyl-n-propylammonium bis(trifluoromethanesulfonyl) imide (TMPA-TFSI). The increase in the anodic current and corresponding cathodic wave are observed at >0 V (vs. Ferrocene/Ferrocenium). These currents would be corresponding to the doping and dedoping reaction of TFSI. On the other hand, the increase in cathodic current and corresponding anodic wave are also observed at <-2.0 V. It is reported that both cation and anion doping reactions take place at some type of polythiophene derivatives in acetonitrile solution². The result obtained in Figure 2, it is suggested that the doping / dedoping reactions of cation and anion also proceed in TMPA-TFSI.

Since the doping / dedoping reactions should be influenced by the interaction between the matrices of electrochemical conducting polymers and penetrating ions, the reactivity would change by selecting the type of polymers and properties of the ions such as the size,

hydrophilicity / hydrophobicity and charge density. The result obtained by systematic experiments will be shown in this paper.

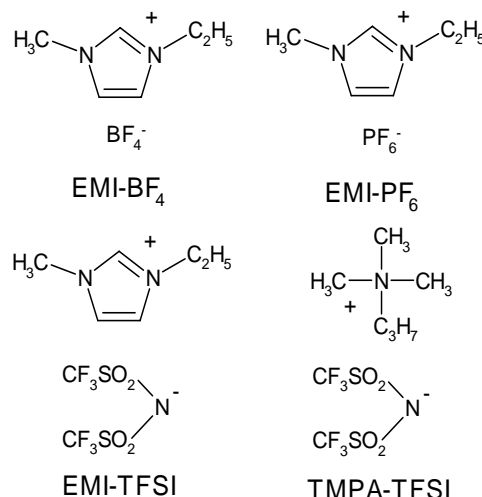


Figure 1. Molecular structure of some ionic liquids.

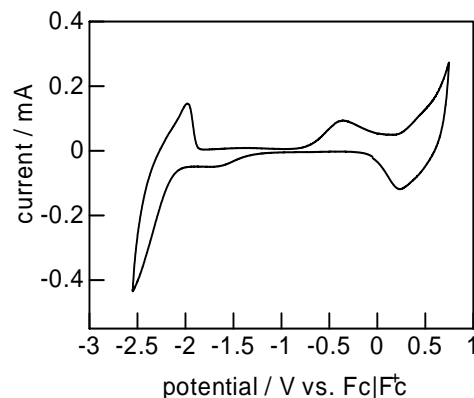


Figure 2. Cyclic voltammogram showing the electrochemical oxidation and reduction of polythiophene obtained in TMPA-TFSI. Scan rate = 20 mV s⁻¹.

References

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