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The Electrochemical Investigation of MEH-PPV in Ionic Liquid

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Abstract The electrochemical properties of MEH-PPV were studied in ionic liquid ($[bmim]^+[PF_6]^-$) by cyclic voltammetry, chronoamperometry and AC impedance measurements. Both *p*- and *n*-doping of MEH-PPV were observed in the cyclic voltammograms. The chronoamperometric and AC impedance results indicate that the *p*-doping of MEH-PPV was controlled by the linear diffusion of counterions.

Keywords: MEH-PPV, electrochemistry, ionic liquid

Ionic liquids are a new kind of room-temperature molten organic salts. It can be used as solvents in the organic/polymeric syntheses, and some of them are called “green” solvents because of its recyclability[1]. Ionic liquids possess the superior properties, such as thermal stability up to 200°C, involatility and re-designability(for both cation and anion). The ionic liquid employed in this work is $[bmim]^+[PF_6]^-$ (butylmethylimidazolium hexafluorophosphate) which is immiscible with water and hexane[2]. This electrochemical investigation of MEH-PPV [poly (2-methoxy-5- (2’-ethylhexyloxy)-1,4-phenylene vinylene) , a typical luminescent polymer used in light-emitting devices] in the ionic liquid is to see the possibility of the ionic liquid to be used in the fabrication of light-emitting electrochemical cell[3] (LEC).

In the electrochemical measurements with Zahner Im6e electrochemical workstation, MEH-PPV was cast on a Pt working electrode (0.8 mm^2), Pt plate and Ag wire were used as the counter electrode and reference electrode respectively. For the calibration of the Ag wire quasi-reference electrode, the half-wave potential ($E^{1/2}$) of ferrocene/ferroceniom (Fc/Fc^+) couple measured in the ionic liquid is ca. 0.21 V vs. Ag wire.

The cyclic voltammograms of MEH-PPV in $[bmim]^+[PF_6]^-$ are shown in Fig.1. The *n*-doping of MEH-PPV can be observed with a peak potential at *ca.* –1.4V. The *p*-doping starts at ca. 0.9V, but the peak of the *p*-doping didn’t appear even with the extended electrochemical scanning range up to +1.5V. The band gap of MEH-PPV determined from the onset potentials of *p*-doping (ca. 0.9 V) and *n*-doping (ca. –1.0 V) is ca. 1.9eV which is comparable with that determined in the CH_3CN solution with $(Bu)_4NPF_6$ as supporting electrolyte[4]. This shows that both *p*- and *n*-doping of MHE-PPV in ionic liquid occur though the doping/dedoping process is irreversible to some extent.

In order to understand the movement of counterions (disassociated from ionic liquid, here $[bmim]^+$ and PF_6^-), chronoamperometry was conducted in the potential range of *p*-doping because the *n*-doping is quite sensitive to experimental environment. As shown in Fig.2, linear relationship between current and $t^{-1/2}$ are obtained (see inset of Fig. 2), which indicates that the *p*-doping process of MEH-PPV is controlled by the linear diffusion of counterions. AC impedance shows the diffusion-controlled electrode reaction, which is consistent with the results of chronoamperometry, no clearly finite diffusion characteristics is found. On the contrary, the similar AC measurements in $CH_3CN(PF_6^-$ as the counterion) showed the finite diffusion responses. This means that PF_6^- from ionic liquid moves slowly in MEH-PPV, which can explain why no clear oxidation peak is observed in Fig. 1.

In conclusion, we have observed the *p*- and *n*-doping of MEH-PPV in the ionic liquid without additional other supporting electrolytes. The chronoamperometry and AC impedance investigation uncover that the diffusion of counterions(derived from ionic liquid) control the *p*-doping reaction. These results indicate that ionic liquid can be applied in the fabrication of LEC. Further works on LEC with ionic liquid is under way in our laboratory.

Figure 1, Cyclic voltammogram of MEH-PPV in $[bmim]^+[PF_6]^-$. Scan rate is 20mV/s. The arrows indicate the initial scan direction.

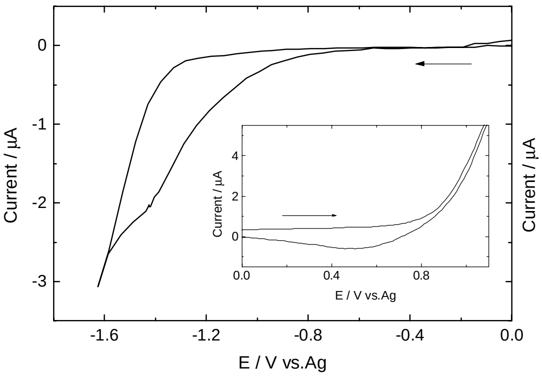
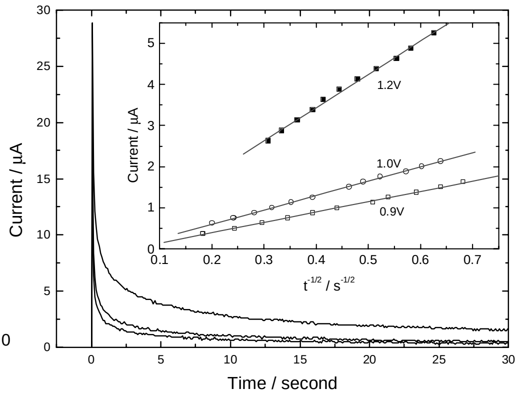


Figure 2, Chronoamperometric curves of MEH-PPV in $[bmim]^+[PF_6]^-$. Potential steps from 0.0V to 0.9V, 1.0V and 1.2V. Inset shows the current/$t^{-1/2}$ plot derived from current/t curves



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