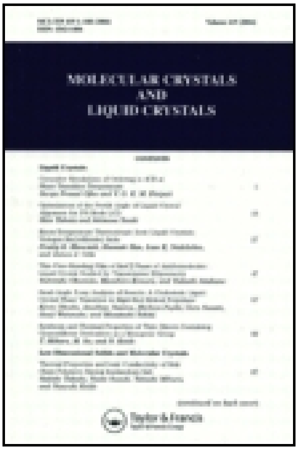

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A Chemical Process Initiated by an Electrochemical Process of Electrochromic Conducting Polymer PEDOT

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A Chemical Process Initiated by an Electrochemical Process of Electrochromic Conducting Polymer PEDOT

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Spectroscopic analysis of conducting polymer PEDOT showed that polaron and bipolaron were the species involved in full range redox. The unusual potential hysteresis for the P^0/P^+ redox pair was attributed to the chemical process initiated by an electrochemical process.

Keywords: PEDOT; UV/VIS; hysteresis; chemical process

INTRODUCTION

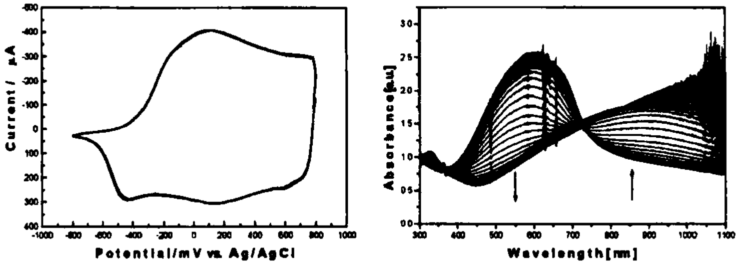
Poly(3,4-ethylenedioxythiophene)(PEDOT) is a conducting polymer of low band gap having electrochromic properties[1]. While the UV/VIS spectroscopy clearly shows the evolution of charge carriers, cyclic voltammogram(CV) shows unresolved current peaks with a large potential hysteresis for the neutral state(P^0)/polaron(P^+) pair. A lot of authors reported spectroelectrochemical data having two isosbestic points[2, 3]. But no one concerned about the unusual hysteresis appearing in the CV. In this study, we tried to elucidate the hysteresis was caused by a chemical P^+ forming process initiated by the electrochemical reduction of bipolaron (P^{2+})state using spectroelectrochemical analysis.

EXPERIMENTAL

Chemicals were purchased from Aldrich (USA) and used as received otherwise noticed. Preparation of PEDOT are described in detail elsewhere[1]. Electrochemical system was composed of a potentiostat (BAS 100B, USA) and an electrolytic cell having a Pt counter and a Ag/AgCl reference electrodes. The electrolyte was 0.1M $LiClO_4$ solution of CH_3CN. Electrochemical polymerization of EDOT produced PEDOT thin films on ITO electrodes(Samsung Corning, Korea). *In situ* UV/VIS absorption measurements were done using HP8453 (HP, USA).

RESULTS AND DISCUSSION

Spectroelectrochemistry of PEDOT films on ITO electrodes produced CV (a) and UV/VIS absorption spectra (b) in Fig.1. The CV shows a broad oxidation peak at 0V (all the potential values were quoted from Ag/AgCl) and reduction peaks at –0.5V and 0.15V[1]. The first peak pair shows very large potential difference. The spectra show two isosbestic points at 730 and 850nm due to the absorption changes at λ_{max}, *i.e.* 600,



(a) (b)

FIGURE 1. CV(a) and UV/VIS spectra(b) of PEDOT

900nm, and the one beyond 1100nm. This implies that three species are involved in this redox process, namely P°, P^{+}, and P^{2+} of PEDOT[2, 3]. But the poor resolution of the CV hardly shows the existence of the two one-electron reactions involved in redox process.

The potential dependent absorption at each λ_{max} was differentiated with respect to the potential in order to obtain the abs-CV without capacitive current effect. Fig. 2 shows well resolved oxidation peaks at 0V (from 600nm curve) and 0.4V (from 800nm and 1000nm curves) indicate that three independent species (P°, P^{+}, P^{2+}) are involved in the oxidation process. Implying the existence of a chemical complexity, the reduction process gives three different potentials at -0.5, -0.1, and 0.3V.

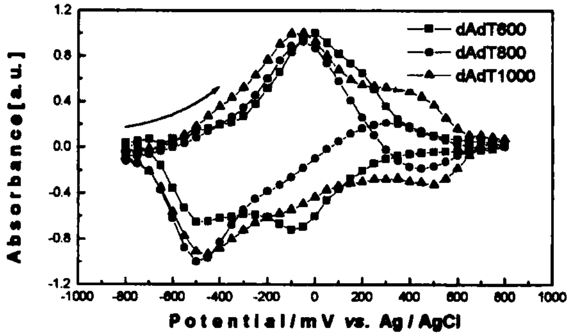


FIGURE 2. Normalized Abs-CV(dA/AE) at 600, 800, 1000 nm

In order to clarify the complexity, CV's at different scan rates were obtained. Fig. 3 shows the relative current ratio, $I_{-0.5V}/I_{0V}$, is decreasing as the scan rate increases. This indicates the species responsible for the peak at -0.5V is P^{+} produced by the chemical process between $P^{0}$and P^{2+}. This reaction is initiated by the electrochemical reduction of P^{+} to P^{0}.

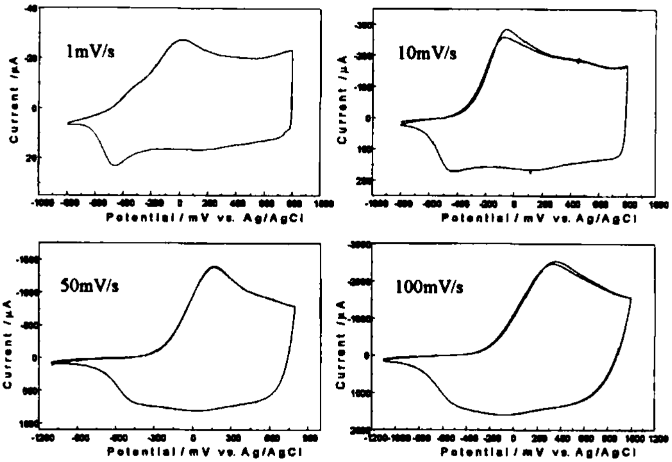


FIGURE 3. Cyclic voltammograms of different scan rates.

Potential sweep is reducing a part of P^{2+} to P^{+} at 0.3V and continuously to P^{0} at -0.1V. In this moment, the remainder part of P^{2+} chemically reacts with the P^{0} and produces P^{+}. The swept potential far away from –0.1V easily reduces the P^{+} produced *via* this chemical process to P^{0} and makes an additional peak at –0.5V. This electrochemical reduction of chemically produced P^{+} makes the large hysteresis in redox potential for P^{0}/P^{+} pair.

Acknowledgments

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