Electrochemical Preparation of a Metallic Polythiophene Film

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Electrolytic polymerization of thiophene gives a metallic film with a conductivity of *ca.* 100 S/cm, and which becomes a semiconductive polymer with an optical absorption edge of 2.0 eV when reduced by electrochemical or chemical means.

Electrochemical preparation of conjugated organic polymers has recently been shown to be a useful method for obtaining high conductivity, good quality, flexible films,[1,2] when compared to chemical polymerization.[3] Electrochemical polymerization of thiophene[2] unlike the polypyrrole film[1] has been little studied. The electrochemical oxidation of the monomer unit initiates the polymerization by an anodic reaction, giving rise to insoluble polymer film with a suitable amount of anion.[1,2] The *in situ* film with metallic properties easily becomes a semiconductive film by electrochemical and chemical undoping.[1,2]

The conditions for electrochemical polymerization and the results of conductivity measurements on polythiophene films are summarized in Table 1. An In–Sn oxide conducting glass and a Pt plate served as anode and cathode, respectively. Details of the purification of solvents and electrolyte salts have been reported in our previous papers.[2,4] In Table 1, V_{applied} and $I_{\mathrm{polymerization}}$ are the typical polymerization voltage and current, respectively, and V_{OC} is the open circuit voltage measured immediately after the removal of the applied voltage. V_{OC} should be the cell potential of the battery with the same construction. The application of a high voltage of 20 V to the electrolyte consisting of thiophene (0.4 mol dm^{-3}) and $LiBF_4$ (0.5 mol dm^{-3}) in benzonitrile at *ca.* 30 °C results in a homogeneous fine film with a conductivity of more than 100 S/cm and an activation energy of 23 meV, a result contrary to that with a low applied voltage.[2] The electrochemically prepared film in this electrolyte contained *ca.* 30 mol% of BF_4^- per thiophene molecule, a figure estimated from the weight change of the film before and after the undoping by chemical compensation with gaseous ammonia. A similar result was also obtained by elemental analysis of polythiophene perchlorate.[2] The elemental analysis of this undoped polythiophene gave an empirical composition of $C_{4.02}H_{2.09}S_{1.00}$, indicating a considerable degree of polymerization.

Table 1. The electrolytic conditions for the polymerization[a] of thiophene and the electrical properties of the film.

Electrolyte	V_{applied} /V	$I_{\mathrm{polymerization}}$ /(mA/cm^2)	V_{OC} /V	σ /(S/cm)	E_a /meV
$LiBF_4$–MeCN	10	10	4.1	20	29
$LiBF_4$–PhCN	20	10	4.2	106	23
$NaAsF_6$–PhCN	20	20	2.6	97	19
$NaPF_6$–PhCN	20	20	2.7	55	21

[a] At *ca.* 30 °C.

The electrical conductivity of the undoped film and its activation energy (E_a) were *ca.* 2 × 10^{-8} S/cm at room temperature and 0.36 eV, respectively. The undoped film appears greenish gold in reflected light and has an interband optical absorption spectrum with a band gap energy of *ca.* 2.0 eV.[4] This undoped film is quite stable in air up to 200 °C

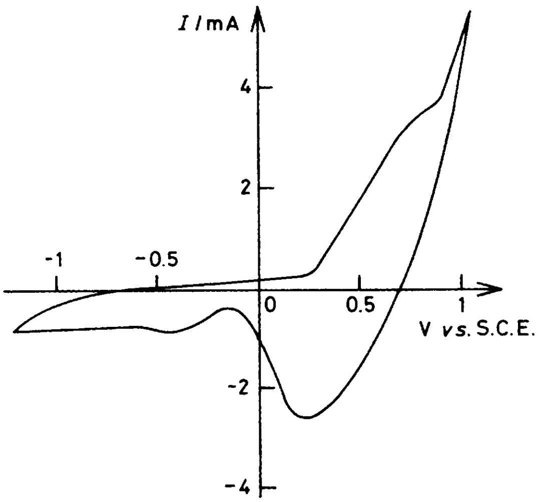

Figure 1. Cyclic voltammogram of polythiophene at a 25 mV/s scan rate.

and also in all solvents examined. However, the oxidized polythiophene film is not stable in air or protic solvents such as water and methanol. For instance, the electrical conductivity decreases by more than one order of magnitude by just washing the film with methanol for several minutes, which seems to indicate the chemical reduction of oxidized polythiophene in protic media.

Figure 1 shows the cyclic voltammogram of polythiophene in an electrolyte comprising thiophene–$LiBF_4$–acetonitrile *vs.* S.C.E. (saturated calomel electrode) at a 25 mV/scan rate. The shoulder at +0.75 V and the steep increase of current above +0.8 V were associated with the oxidation of polythiophene and the polymerization of thiophene, respectively. The signal at *ca.* +0.2 V should be due to the reduction current of oxidized polythiophene. The oxidation and reduction current are comparable as shown in Figure 1, indicating that the electrochemical oxidation and reduction are reproducible processes. These electrochemical properties of polythiophene demonstrate the electrochromatic switching and memory effects of transmitted light from red to blue and *vice versa.*[5]

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