

# On the electrical anisotropy of conducting polypyrrole

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The electrical properties of polypyrrole films prepared by electrochemical polymerization have been studied. The films were electrochemically and optically characterized. A very high anisotropy of the resistivities and mobilities, both parallel and perpendicular to the substrate, has been found. The results obtained are consistent with a hopping model for the conduction mechanism, with the interchain hopping much lower than the intrachain hopping, if it is assumed that the chains are oriented preferentially parallel to the substrate.

## 1. Introduction

Polypyrrole is one of the most stable and attractive conducting polymers suitable for several applications in batteries, electronic devices etc. [1, 2]. Its electrical properties and charge-carrier transport mechanism have been studied and described in terms of modifications that occur in the molecular orbitals of the polymer during charge transfer, which lead to the formation of defects more or less localized in the electronic structure [3]. Street and co-workers [4, 5] have suggested that conductance is due to the movement of polarons and bipolarons which are produced by doping. Though extensively studied [6], a deeper understanding of its electrical characteristics is necessary. Points related to the questions of the way in which the conducting pathways are formed, and how the current flows along these pathways are of particular interest and must be investigated further.

In this paper we present the results of an experimental study on the electrical properties in directions both perpendicular and parallel to the substrate of polypyrrole thin films prepared by electrodeposition.

## 2. Experimental procedure

Black films of polypyrrole (about 1  $\mu\text{m}$  thick) were prepared by galvanostatic electrodeposition from a solution containing 0.1 M  $\text{LiClO}_4$  and 0.1 M of polypyrrole monomer, in purified deoxygenated propylene carbonate. The electrolysis was effected by passing a constant current of 1  $\text{mA cm}^{-2}$ , and the film thickness was controlled by monitoring the charge passed during polymerization [7]. The films adhere to the electrode surface strongly. They were washed with distilled water and dried at room temperature in vacuum. Commercially available pyrrole and propylene carbonate were purified by distillation before using, and  $\text{LiClO}_4$  was previously annealed.

After the electrochemical synthesis the electrolyte was changed to 0.1 M  $\text{LiClO}_4$  propylene carbonate

solution to carry out the electrochemical experiments, which were made with a frequency response analyser (Solartron 1250) coupled with an electrochemical interface unit (Solartron 1186). All potentials are measured against a Ag-AgCl electrode.

Platinum plates (about 2  $\text{cm}^2$ ) were used as substrates and a platinum grid served as counter electrode. Optically transparent doped tin oxide electrodes were used for optical measurements.

The optical properties were studied by transmittance and reflectance measurements using a Hitachi 150-20 spectrophotometer. The method followed was similar to that reported by Bennett *et al.* [8] and takes into account the multiple incoherent reflections both in the film and in the substrate to determine the refractive index,  $n$ , and the absorption coefficient  $\alpha$  [9].

The measure of the perpendicular resistivity was made following a method initially explored by Cox and Strack [10] for contact resistivity measurements. In this method the electrical contact is made to one side of a thin film with several small discs of various diameters  $d$  and a full coverage contact on the reverse side. Gold discs deposited by thermal evaporation on the polypyrrole free surface and the back platinum electrode provided in our case good ohmic contacts. The contact resistance,  $R_c$ , is determined by measuring the voltage drop between two gold frontal discs when applying a current constant between those and the back platinum electrode.

By measuring the voltage drop between the front and back electrodes when applying a constant current between them, the total resistance  $R$  is determined. In the limit of small disc contact size to film surface size that resistance is given by

$$R = \frac{V}{I} = \frac{\rho_{\perp}}{\pi d} \tan^{-1}(4t/d) + R_c$$

where  $\rho_{\perp}$ , the perpendicular resistivity of the sample,

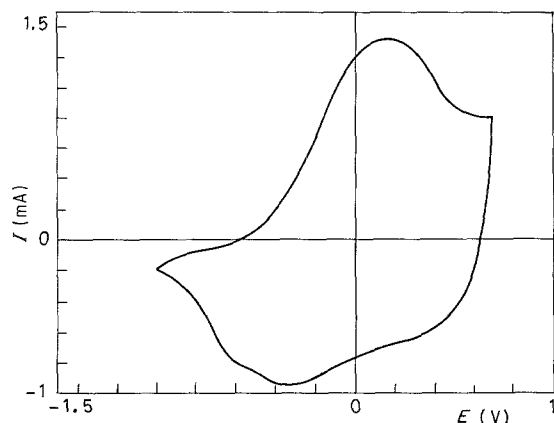


Figure 1 Cyclic voltammety of polypyrrole in 0.1 M LiClO<sub>4</sub> in propylene carbonate. Scan rate 20 mV sec<sup>-1</sup>.

is associated with electrical conduction along a direction perpendicular to the substrate.

For thin films ( $t \ll d$ )

$$R = \frac{\rho_{\perp}}{\pi(d/2)^2} + R_c$$

then

$$\rho_{\perp} = \pi(d/2)^2(R - R_c)/t$$

On the other hand, Van der Pauw's method [11] was used to determine the resistivity and the carrier mobility associated with electrical conduction along directions parallel to the surface of the sample. In this case the polypyrrole films were previously detached from the substrate. Four evaporated gold dots symmetrically distributed on the periphery of the free surface of the film provided the appropriate ohmic contacts. The carrier concentrations can also be determined by this method. As this is a scalar property of the material, the value obtained can also be used to compute the carrier mobility perpendicular to the substrate.

### 3. Results and discussion

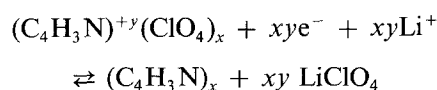
Polypyrrole films can be electrochemically switched from their reduced (insulating) state to their oxidized (conducting) state. After the electrochemical deposition, polypyrrole films were cycled in 0.1 M LiClO<sub>4</sub> propylene carbonate solution. The scan rate and the potential interval were selected to obtain a complete reduction of the polymer within the stability range of the electrolyte. Fig. 1 shows the voltammograms obtained for a polypyrrole film of about 1 μm thick-

TABLE I

<i>E</i> (V)	<i>R</i> <sub>Ω</sub> (Ω)	<i>R</i> <sub>CT</sub> (Ω)	<i>C</i> <sub>d</sub> (μF cm <sup>-2</sup> )	<i>C</i> <sub>p</sub> (μF cm <sup>-2</sup> )
+0.8	17	80	31	8.5
-0.1	30	82	13	9.1

ness. The behaviour of this curve approximates to that of a quasi-reversible couple with the distinguishing characteristics of a large capacitive current once oxidation is complete.

The polymer films are very stable between -1.0 and +0.9 V, and it is possible to obtain more than 1000 cycles in thin films (< 1 μm) without change in the coulombic capacity of the electrode. The peaks in Fig. 1 correspond to the doping and undoping of the polymer as follows



The integration of the peak gave a value of  $y = 0.33$ , in agreement with the previously reported doping level [7] and the elemental analysis of a ≈ 10 μm film (C = 46.6%, H = 2.7%, N = 17.5%, Cl = 10.1%).

Fig. 2 shows the complex impedance plot of a cycled polypyrrole film (≈ 1 μm) in the supporting electrolyte. The data represent measurements obtained in the frequency range 0.01 to 10,000 Hz and at constant potentials +0.8 V (oxidized polypyrrole) and -0.1 V (oxidation peak). At high frequencies ( $\omega > 40$  Hz) a semicircular plot is obtained. The interception with the real axis gives the ohmic resistance  $R_{\Omega}$ , which is related to both the electrolyte and films resistivities. The diameter of the semicircle drives to  $R_{CT}$ , a resistance associated with a charge transfer [12] dominated regime that reflects the average rate of injection and removal of both electrons and ions (ClO<sub>4</sub><sup>-</sup>) into the polymer. The values of these parameters are given in Table I.

At very low frequencies ( $\omega < 5$  Hz) the electrode behaves like a pure capacitor, and the impedance is almost purely capacitive reflecting the charge saturation limit set by the finite polymer thickness. The capacitance values deduced from these diagrams,  $C_p$ , are in Table I. The value of these capacitances is three orders of magnitude greater than that of the metal in this electrolyte (≈ 20 μF cm<sup>-2</sup>) and it is related to the amount of charge stored per unit volume of the polymer layer. At higher frequencies, this

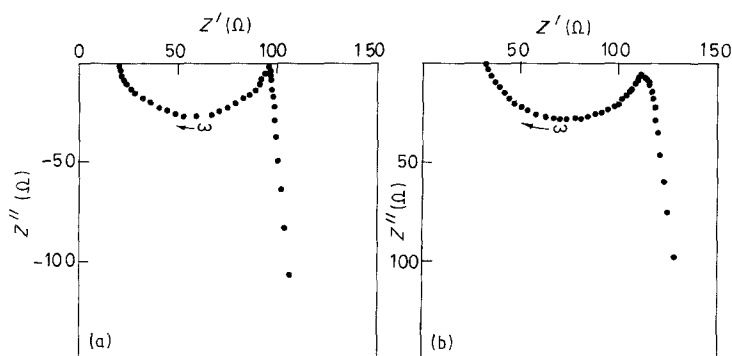


Figure 2 Complex impedance plots for Pt-PPy electrode in 0.1 M LiClO<sub>4</sub> propylene carbonate. (a)  $E = +0.8$  V, (b)  $E = -0.1$  V.

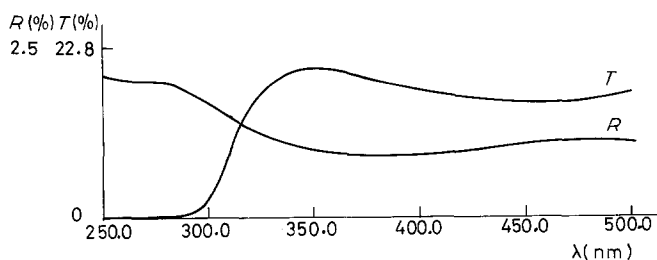


Figure 3 Transmittance ( $T$ ) and Reflectance ( $R$ ) plotted against photon energy for a polypyrrole sample in oxidized state.

charge can not follow the fluctuations of the electric field, and so the value of the double layer capacity,  $C_d$ , is obtained from the medium frequencies range. The magnitude of these values is quite typical of the double layer capacitance at an electrolyte polymer interface, they are given in Table II. The high values of the low frequency capacity,  $C_p$ , can be considered as a characteristic of the oxidized state of polypyrrole, as was suggested by Feldberg [13] and deduced from impedance measurements by Bull *et al.* [14], and it suggests that oxidized polypyrrole is effectively like a "porous metal" electrode with a high surface-to-volume ratio.

Fig. 3 shows the measured transmittance and reflectance as a function of the incident photon energy ( $E$ ) for a sample grown in oxidized state. Fig. 4 shows  $\alpha^2$  plotted against  $E$  (eV). A least square fitting method was used to evaluate the direct gap. The value obtained is 4.1 eV and the refractive index (at 500 nm) is 2.56. The heat treatments do not substantially change the transmittance of the samples.

In Table II the electrical properties at polypyrrole films are given.

It has been estimated from the value at the density ( $\rho = 1.48 \text{ g cm}^{-3}$ ) that the total  $\pi$  electrons in polypyrrole are  $7 \times 10^{22} \text{ cm}^{-3}$  [15]. As the hole concentration of the films (Table II) is much lower ( $N = 5 \times 10^{17}$ ) it is clear that only a few holes in the filled  $\pi$ -band contribute to the transport phenomenon. Nevertheless, the high value of the mobility in planes parallel to the substrate ( $\mu = 480 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ ) allows a rather high conductivity in those planes ( $\sigma = 38 \Omega^{-1} \text{ cm}^{-1}$ ).

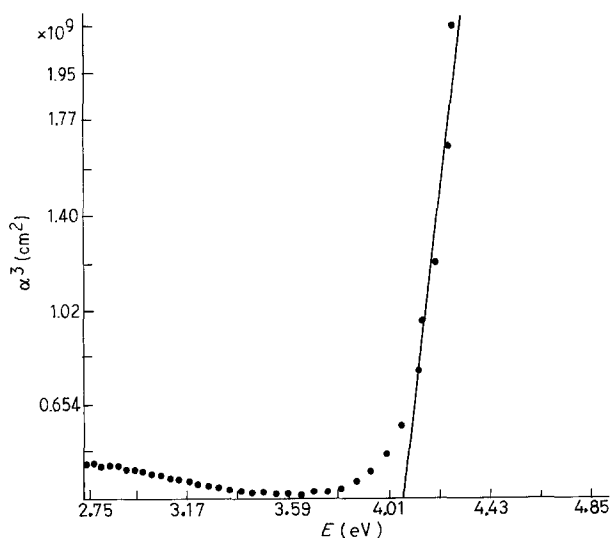


Figure 4 Determination of the band gap for a polypyrrole sample in oxidized state.

TABLE II Resistivities, carrier concentration and mobilities of polypyrrole thin films grown on platinum substrates

	AS-grown	After cycling	Reduced
$t$ ( $\mu\text{m}$ )	1	1	1
$R_c$ ( $\Omega$ )	0.05	0.05	0.05
$P_{\perp}$ ( $\Omega \text{ cm}$ )	20	23.7	28.8
$\rho$ ( $\Omega \text{ cm}$ )	$2.6 \times 10^{-2}$	$2.3 \times 10^{-2}$	-
$N$ ( $\text{cm}^{-3}$ )	$5 \times 10^{17}$	-	-
$\mu_{\perp}$ ( $\text{cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ )	0.625	-	-
$\mu_{\parallel}$ ( $\text{cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ )	480	-	-

The most striking feature is, however, the high electrical anisotropy of the samples, being the parallel resistivity three orders of magnitude lower than the perpendicular resistivity, ratio which is maintained after successive cycling. When the polymer was in reduced state (non-conducting) the parallel resistivity become extremely high while the perpendicular resistivity resulted very close to the value obtained in the conductive state.

These results are consistent with a hopping conduction mechanism with the intrachain resistivity much lower than the interchain resistivity, being the polypyrrole chains arranged in planes parallel to the substrate.

## Acknowledgement

Thanks are due to Comisión Asesora de Investigación Científica y Técnica for providing financial help to carry out this work (Project PA85-0175).

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*Received 16 June  
and accepted 22 November 1989*