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Electrochemically synthesized polypyrrole films: effects of polymerization potential and electrolyte type

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Polypyrrole films containing either the perchlorate or *p*-toluenesulfonate ion were prepared from an aqueous solution by applying an anodic potential in the range 0.6–2.0 V (relative to a saturated calomel electrode). The effects of applied potential on electropolymerization, morphology, chemical structure, electrochemical properties and tensile modulus have been investigated. The chronoamperometric response of pyrrole electropolymerization depends on the applied potential and not on the counterion. The electrochemical properties and structure of polypyrrole depend on the polymerization potential as well as the counterion. An empirical expression relating peak current to the scan rate and charge passed during polymerization is proposed. This relationship provides some insight into the nature of the polypyrrole switching reaction. For polypyrrole containing perchlorate, the concentration of dicationic species or dipolarons decreases as the polymerization potential increases from 0.6 to 1.0 V. The large concentration of dicationic species in polypyrrole prepared at 0.6 and 0.75 V is responsible for the second reduction peak observed in the cyclic voltammograms.

(Keywords: electropolymerization; polymerization potential; polypyrrole film)

INTRODUCTION

Conducting polypyrrole films are currently being investigated for use as battery electrodes, corrosion protection and biological sensors[1–5]. Films can be prepared by anodic electropolymerization of pyrrole in either non-aqueous[6,7] or aqueous[8–11] media using a variety of electrochemical techniques, which include potentiostatic polymerization on a substrate such as glassy carbon or indium tin oxide (ITO). The properties of the deposited film are dependent on the electropolymerization conditions. The solvent and supporting electrolyte also affect the film morphology, conductivity and mechanical behaviour. In general, polpyrrole films have poor mechanical properties. Various techniques have been used to prepare a porous matrix to improve the mechanical properties and/or to eliminate the diffusion of trapped catalytic species out of the polypyrrole film[12–15]. Polypyrrole is generally deposited into the pores of the matrix by an electrochemical technique.

Recently, a microemulsion polymerization technique was used to form a porous non-conducting matrix[11,16]. The microemulsion is prepared using a surfactant and two monomers, one hydrophilic and the other hydrophobic. The surfactant affects the pyrrole electropolymerization and the electrochemical properties of the conductive composites. Before these composites can be considered for applications such as biosensors or corrosion protection, the effect of the surfactant on the properties of the conductive composite must be determined. An investigation of conductive composites using microemulsions[11] was recently conducted in order to: (1) determine the effect of polymerization conditions on pure polypyrrole films as discussed in this paper; (2) develop a theoretical model[17] and compare the predictions with the experimental electrochemical response of polypyrrole films[18]; and (3) evaluate the effect of polymerization conditions on conductive composites[16].

Otero and co-workers[8,19] and Satoh *et al.*[20] have demonstrated that the electropolymerization potential affects the formation and properties of polypyrrole films. In the cyclic voltammetric experiments, the anodic limit was varied from 0.8 to 1.8 V relative to a saturated calomel electrode (SCE) by Otero *et al.*[8]. When the anodic limit was 1.0 V or less, the current increased with each successive sweep. However, when the anodic limit exceeded 1.0 V, the current decreased with each successive sweep. When the potential was raised from 0.55 to 0.75 V (SCE) during potentiostatic polymerization of pyrrole, the current increased from 0.07 to 0.6 mA cm^{-2} (ref. 8). More recently, Otero and Santamaria[19] reported the dependence of polypyrrole production on potential using *ex situ* microgravimetry. Satoh *et al.*[20] investigated the effect of polymerization potential on a number of physical properties including electrical conductivity. For polypyrrole films prepared in a 0.25 M pyrrole solution containing 0.8 M sodium *p*-toluenesulfonate, a steep

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increase in the conductivity from 100 to 500 S cm^{-1} was observed as the polymerization potential was raised from 0.45 to 0.6 V (SCE). The conductivity decreased sharply as the polymerization potential was increased further from 0.6 to 1.4 V.

The role of electropolymerization potential on various properties of polypyrrole is poorly understood at present. The overall objective of this investigation was to determine the effects of the applied potential and electrolyte type on pyrrole electropolymerization, and also their effects on the morphology, structure and redox couple of polypyrrole. Films were prepared using two different electrolytes, sodium perchlorate and sodium *p*-toluenesulfonate, at five different potentials: 0.6, 0.75, 1.0, 1.5 and 2.0 V. The chronoamperometric response of electropolymerization and cyclic voltammetry of the polypyrrole switching reaction were studied under different experimental conditions. A power law relationship is proposed to correlate the peak currents to the scan rate and charge passed during electropolymerization. The exponent in the power law depends on the rate-controlling step of the switching reaction. A similar approach was used by Naoi and Osaka[13] to determine the rate-controlling step in conductive composites.

EXPERIMENTAL

Polypyrrole films were prepared from an aqueous solution containing 0.1 M pyrrole (Aldrich) and either 0.1 M sodium perchlorate (Fisher) or 0.1 M sodium *p*-toluenesulfonate (Fluka). Pyrrole was vacuum distilled prior to use. All other chemicals were used as received. The water used had a resistivity exceeding 17 MΩ cm^{-1}. Prior to experimental work, all solutions were deaerated by bubbling argon for 30 min.

A BAS100 Electrochemical Analyzer was used for the electrochemical experiments. A three-compartment cell was employed. The counterelectrode was platinum foil (1 cm^2) while the reference electrode was a SCE. All potentials reported are referenced to the SCE. The working electrode in the electrochemical and morphological studies was a glassy carbon electrode (BAS, 0.067 cm^2). Prior to each experiment, the glassy carbon electrode was polished with microalumina (Buehler) down to 0.05 μm. ITO-coated glass (Applied Films Lab, 6 cm^2) was used as the working electrode to prepare polypyrrole films for investigating chemical structure, mechanical properties and electrical resistivity. *In situ* electrochemical–e.s.r. (electron spin resonance) experiments were carried out in a thin-layer cell with platinum wires as the working electrode (0.152 cm^2) and the counterelectrode (0.032 cm^2). All electrochemical experiments were performed at 25°C in an inert environment.

A JEOL 64 scanning electron microscope was used to observe the morphology of the films. A BioRad FTS-60 infra-red spectrometer was used in the investigation of the chemical structure. All i.r. spectra were measured in the transmission mode using the DRIFT technique. A Varian E-Line Centuries Series EPR Spectrometer was used to determine the spin concentration of polypyrrole films containing perchlorate. The mechanical properties and the electrical resistivity of polypyrrole films containing *p*-toluenesulfonate were measured using a Perkin–Elmer Dynamic Mechanical Analyzer (DMA) and a four-point probe conductivity meter, respectively.

RESULTS AND DISCUSSION

Electrochemical polymerization of pyrrole

Electropolymerization of pyrrole was performed using either cyclic voltammetry or the potentiostatic technique. The polymerization of pyrrole in either perchlorate or toluenesulfonate solution requires an anodic potential exceeding 0.55 V *versus* SCE, similar to the value reported by Otero *et al.*[8]. The minimum potential required to electropolymerize pyrrole is not sensitive to the electrolyte type, as shown in *Figures 1a* and *b*.

The chronoamperometric response of pyrrole polymerization to the applied potential gives an indication of hydroxyl or carbonyl groups being incorporated into the polypyrrole chain. The incorporation of termination groups, also known as overoxidation, slows the electropolymerization. Overoxidation is negligible at both 0.6 and 0.75 V, as the current never reaches a maximum (*Figure 2*). The chronoamperometric responses at 0.6 and 0.75 V are similar to the behaviour reported by Otero *et al.*[8]. At 1.0 V, overoxidation is indicated by the slow decay of the current after reaching a maximum. For both 1.5 and 2.0 V, the current decays sharply from the steep maximum observed initially, indicating significant overoxidation. The effect of potential on pyrrole electropolymerization is independent of the electrolyte type as observed by chronoamperometry. Overoxidation of polypyrrole is significant when the polymerization potential exceeds 1.0 V. Similar behaviour was observed by Otero and Santamaria[19] with 0.1 M pyrrole and 0.1 M lithium perchlorate but at higher polymerization potentials.

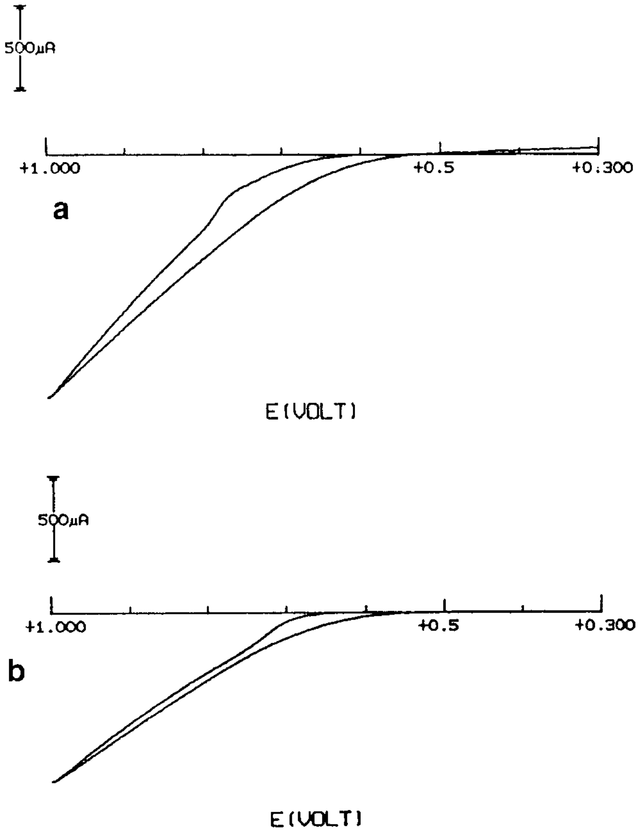


Figure 1 Cyclic voltammogram of pyrrole electropolymerization at 50 mV s^{-1} on a glassy carbon electrode in (a) 0.1 M pyrrole solution with 0.1 M sodium perchlorate, and (b) 0.1 M pyrrole solution with 0.1 M sodium *p*-toluenesulfonate

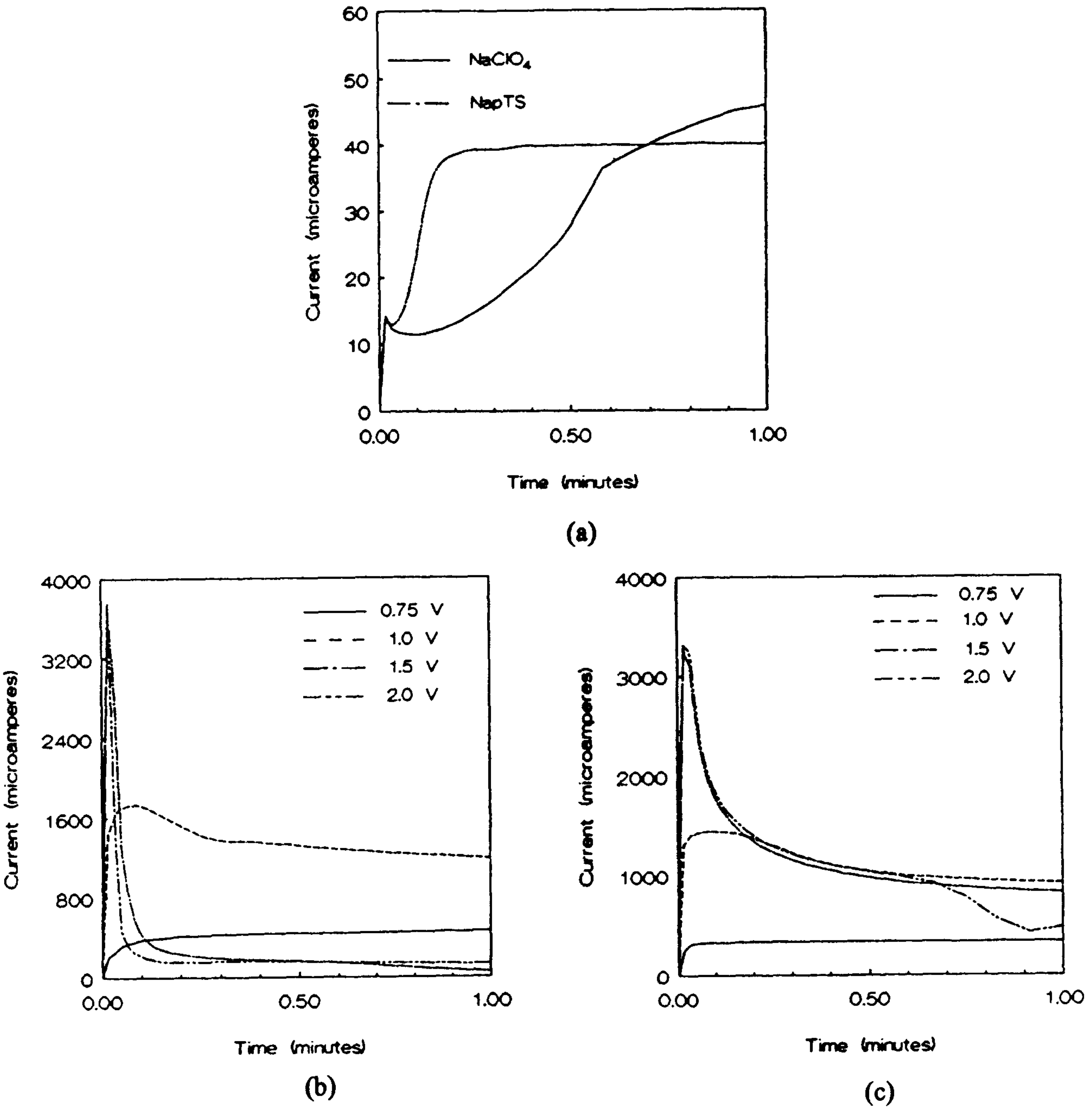


Figure 2 Chronoamperometric response of pyrrole electropolymerization on a glassy carbon electrode for films prepared in 0.1 M pyrrole solution containing (a) 0.1 M sodium perchlorate or 0.1 M sodium *p*-toluenesulfonate by applying 0.6 V; (b) 0.1 M sodium perchlorate by applying 0.75, 1.0, 1.5 and 2.0 V; (c) 0.1 M sodium *p*-toluenesulfonate by applying 0.75, 1.0, 1.5 and 2.0 V

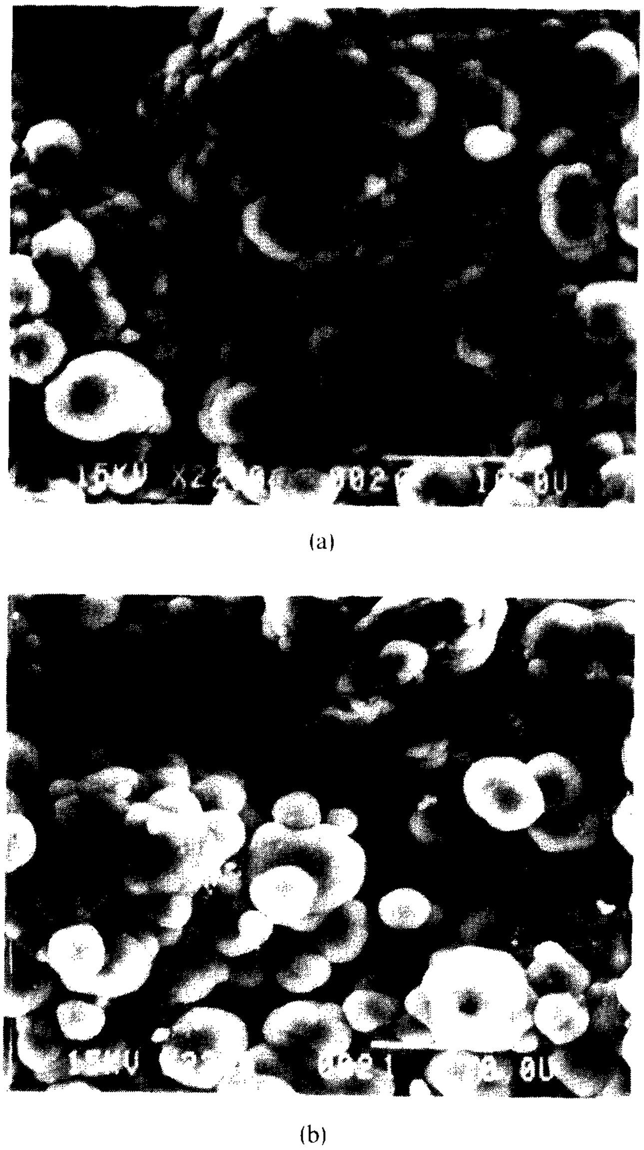
Physical properties of polypyrrole films

The physical properties were characterized in terms of the appearance of the polypyrrole film, its adhesion to the electrode, and the morphology. The physical appearance of the film is dependent on the electrolyte used during synthesis. Polypyrrole films prepared in perchlorate solution were rough and brittle while those prepared in toluenesulfonate solution were smooth and flexible. The results are consistent with the observations of Warren and Anderson[9].

The adhesion of polypyrrole to glassy carbon is dependent on both the electrolyte and the polymerization potential. Adhesion was qualitatively assessed in terms of the ease or difficulty of removing the film from the electrode. Films prepared in toluenesulfonate adhered more strongly than those prepared in perchlorate. Film adhesion decreases when the applied potential is increased. Polypyrrole films prepared at 0.6 V were difficult to remove while those prepared at 2.0 V were the easiest to remove. Polypyrrole films prepared in toluenesulfonate at 2.0 V were easily removed intact using a sharp razor. Films prepared in perchlorate were less adherent and were removed intact using a sharp razor or wiped off with a piece of cloth.

When the potential is $\leqslant 1.0$ V, the oxidation of glassy carbon electrode is slow compared with pyrrole polymerization. At higher potentials, the oxidation of glassy carbon is relatively fast and leads to the formation of carbonyl or hydroxyl groups which block the sites for pyrrole adsorption on the electrode surface[21]. Thus, overoxidation reduces the adhesion of polypyrrole.

The morphology of polypyrrole has been reported to



(a)

(b)

Figure 3 SEM micrographs of polypyrrole films prepared on glassy carbon by applying 2.0 V in 0.1 M pyrrole solution containing either (a) 0.1 M sodium perchlorate or (b) 0.1 M sodium *p*-toluenesulfonate. The charge passed is 0.6 C (× 1630)

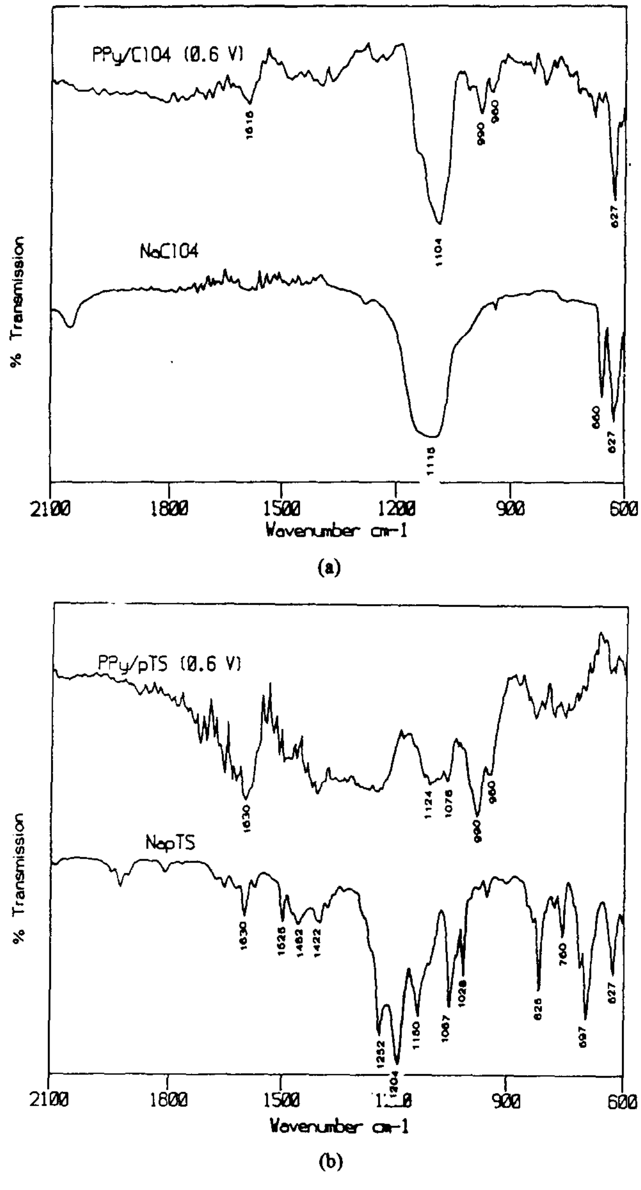
be globular in nature and dependent on the electrolyte type[6,9,10,22]. Scanning electron microscopy (SEM) micrographs of polypyrrole prepared in perchlorate and toluenesulfonate solutions are shown in *Figure 3*. Polypyrrole films containing perchlorate, *Figure 3a*, have a very rough surface which has been referred to as cauliflower-like[10,22]. Films containing toluenesulfonate, *Figure 3b*, also have globular structure but the surface is smoother than those prepared in perchlorate solution.

The morphology of films containing perchlorate ion suggests three-dimensional or isotropic growth of the polypyrrole. This agrees with previous characterization of polypyrrole using ellipsometry[23]. *Figure 3b* indicates that film growth is not uniform for polypyrrole containing toluenesulfonate since buds or branches are observed at different locations away from the surface. The alignment of the π-electrons of toluenesulfonate with the delocalized π-electrons of polypyrrole could constrain the growth of polypyrrole to certain preferred directions.

Fourier transform infra-red (FT*i.r.*) *spectroscopy*

According to the literature[24,25], polypyrrole has three weak bands at around 1610, 1490 and 1410 cm^{-1} caused by ring stretching, and has a band at around 1050 cm^{-1} caused by N–H bending. In-plane and out-of-plane bending of C–H are expected at 980 and 960 cm^{-1}, respectively. The perchlorate ion by itself has strong absorption bands between 600 and 660 cm^{-1} and around 1115 cm^{-1}, *Figure 4a*. For the toluenesulfonate ion, the absorption bands of the sulfonate ion are around 1400 and 1200 cm^{-1} while those of the disubstituted benzene are between 1430 and 1600 cm^{-1} (three peaks), between 1000 and 1280 cm^{-1} (four peaks), and a series of peaks between 600 and 850 cm^{-1} (*Figure 4b*).

Determining changes in the chemical structure by *FT*i.r. is difficult due to the overlapping of bands of oxidized polypyrrole and the counterion. Three absorption bands were observed at 960, 980 and around 1610 cm^{-1}, *Figures 4a* and *b*. These can be assigned to



(a)

(b)

Figure 4 *FT*i.r. spectra using DRIFT technique of the electrolyte and polypyrrole films prepared on ITO glass by applying 0.6 V in 0.1 M pyrrole solution containing (a) 0.1 M sodium perchlorate and (b) 0.1 M sodium *p*-toluenesulfonate

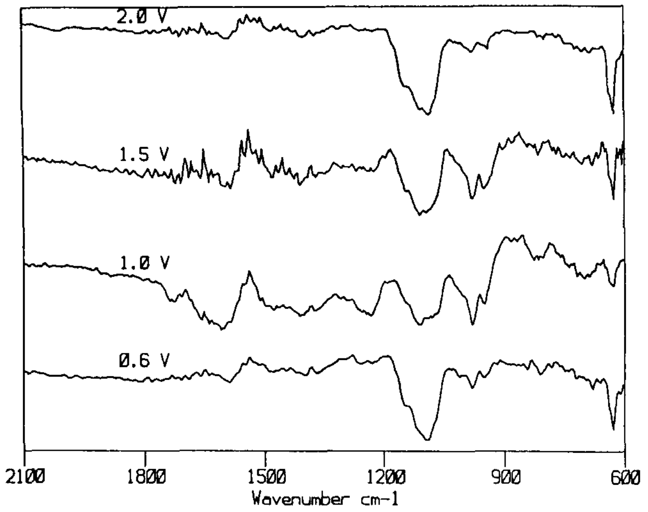


Figure 5 *FT*i.r. spectra using DRIFT technique of polypyrrole films prepared on ITO glass by applying 0.6, 1.0, 1.5 and 2.0 V in 0.1 M pyrrole solution containing 0.1 M sodium perchlorate

out-of-plane bending of C–H, in-plane bending of C–H and ring stretching, respectively. The absorption band at 1615 cm^{-1} for polypyrrole containing perchlorate, *Figure 4a*, is caused by pyrrole ring stretching. It is shifted to 1630 cm^{-1} for the film containing toluenesulfonate due to overlap with the benzene band, *Figure 4b*. For polypyrrole prepared in perchlorate solution, absorption bands of perchlorate ion are observed at 627 and 1100 cm^{-1}. The 1100 cm^{-1} band is broad because of the overlapping of the N–H bending with the perchlorate band.

The effect of polymerization potential on the chemical structure is demonstrated in *Figure 5*. The intensities of absorption at 627, 960, 990 and 1100 cm^{-1} depend on the polymerization potential. For films prepared at 0.6 or 2.0 V, the two peaks at 960 and 990 cm^{-1} are noticeably smaller than the peaks at 627 and 1100 cm^{-1}. For films prepared at 1.0 or 1.5 V, the four peaks at 627, 960, 990 and 1100 cm^{-1} are of similar height. C=O absorption bands are observed around 1700 and 800 cm^{-1}, respectively, for the film prepared at 1.0 V, *Figure 5*. Beck *et al.*[26] have ascribed the presence of these bands to overoxidation. This observation agrees with the chronoamperometric results discussed earlier. When the polymerization potential exceeds 1.0 V, C=O absorption bands are not visible, suggesting that the carbonyl groups have reacted further.

The chemical structure of polypyrrole prepared using toluenesulfonate is less sensitive to the applied potential. As in films containing perchlorate, absorption bands are observed at: 960, 990 and around 1630 cm^{-1}, *Figure 4b*. As mentioned earlier, the band around 1630 cm^{-1} overlaps with that of *p*-toluenesulfonate. The broad peak around 1100 cm^{-1} is caused by N–H bending. The magnitude of the bands at 960, 990 and around 1100 cm^{-1} are similar for all films containing toluenesulfonate except the one prepared at 2.0 V[11].

Electrochemical behaviour

The oxidation or reduction of polypyrrole requires two simultaneous processes: (i) the transfer of electrons either from or to polypyrrole, and (ii) the diffusion of the counterion, or in some cases the diffusion of the cation into or out of the polypyrrole film to maintain charge neutrality. In general, the redox mechanism of polypyrrole is described by a one-electron transfer step:

$$PPy \leftrightharpoons PPy^{+} + e^{-} \qquad (1)$$

where PPy is the neutral species (associated with three to four monomer units) and PPy^{+} is the radical cationic species or polaron (one positive charge localized over three to four monomer units). A second redox mechanism has been proposed by Genies and Pernaut[27] to explain two reduction peaks in the cyclic voltammograms:

$$PPy^{+} \leftrightharpoons PPy^{++} + e^{-} \qquad (2)$$

where PPy^{++} is the dicationic species or bipolaron (two positive charges localized over three to four monomer units). The counterion concentration will be greater for a polypyrrole film containing both cationic (polaron) and dicationic (dipolaron) species than for a film containing only cationic species.

Polypyrrole films were prepared at five different potentials: 0.6, 0.75, 1.0, 1.5 and 2.0 V. For both perchlorate and toluenesulfonate systems, different polypyrrole films were prepared by passing 15, 30, 50, 75 and 100 mC of charge. The medium used in all cyclic voltammetric experiments had the same electrolyte concentration as that used in the polymerization of pyrrole. All cyclic voltammograms and electrochemical values are reported for the first sweep.

The cyclic voltammetric response of polypyrrole films containing perchlorate is dependent on the potential applied during polymerization, *Figures 6* and *7*. The polypyrrole film prepared at 0.6 V has two reduction peaks, one strong and the other weak, and a strong oxidation peak, *Figure 6a*. The more cathodic peak becomes sharper with increasing scan rate, *Figure 7a*. For the film prepared at 0.75 V, the reduction peak has a shoulder at 75 $mV s^{-1}$. This shoulder becomes a second reduction peak at 150 $mV s^{-1}$, *Figure 7b*. The polypyrrole film prepared at 1.0 V also has a strong reduction peak and a strong oxidation peak but no additional peaks were observed as the scan rate was increased, *Figures 6b* and *7c*. For films prepared at either 1.5 or 2.0 V, the reduction and oxidation peaks are no longer symmetrical, *Figures 6c* and *d*. The cyclic voltammetric results at 10 $mV s^{-1}$ for films prepared in a perchlorate solution by passing 30 mC are summarized in *Table 1*. The oxidation peak and the switching potential, E_0, shift in the anodic direction with increasing polymerization potential. The applied potential also affects the magnitude of the peak currents but no trends could be determined.

Polypyrrole containing perchlorate, prepared by applying either 0.6 or 0.75 V, has two reduction peaks, *Figures 7a* and *b*, while polypyrrole prepared at higher potentials has only one reduction peak, *Figure 7c*. A shoulder on the reduction peak or a second reduction peak, similar to the ones described here, has also been observed in polypyrrole films containing chloride, hydrogen sulfate and methylsulfonate ions[9]. Such a shoulder or second reduction peak is caused by the presence of bipolarons. The polypyrrole film prepared at 0.6 V has few termination groups and the perchlorate concentration is greater than in films prepared at 1.0 and 1.5 V, as evident from *Figure 5*. Both cationic species (polarons) and dicationic species (bipolarons) are present

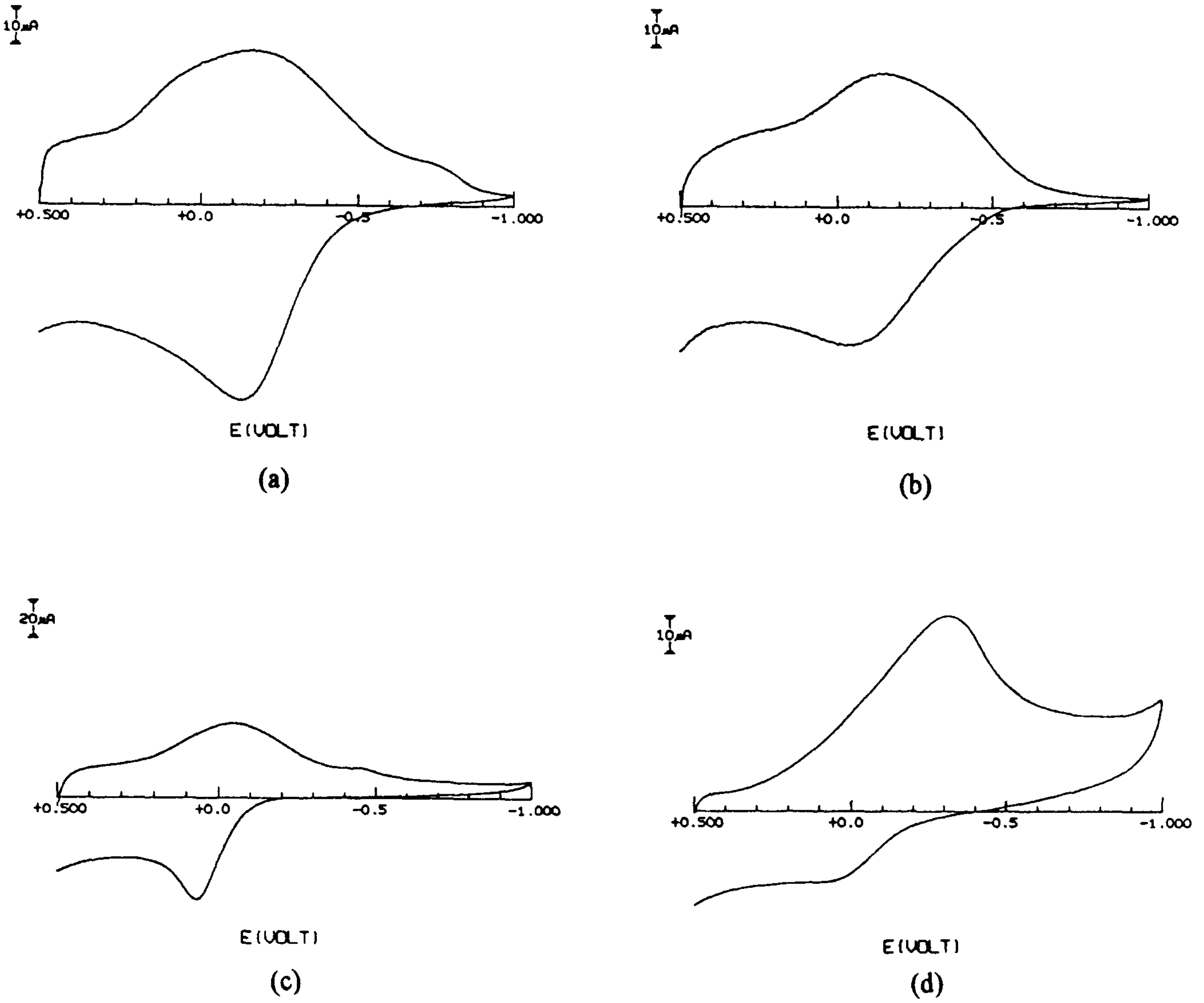


Figure 6 Cyclic voltammograms of polypyrrole on glassy carbon at 10 mV s^{-1} in a 0.1 M sodium perchlorate solution. The films were prepared in 0.1 M pyrrole solution containing 0.1 sodium perchlorate by passing 30 mC at (a) 0.6, (b) 1.0, (c) 1.5 and (d) 2.0 V

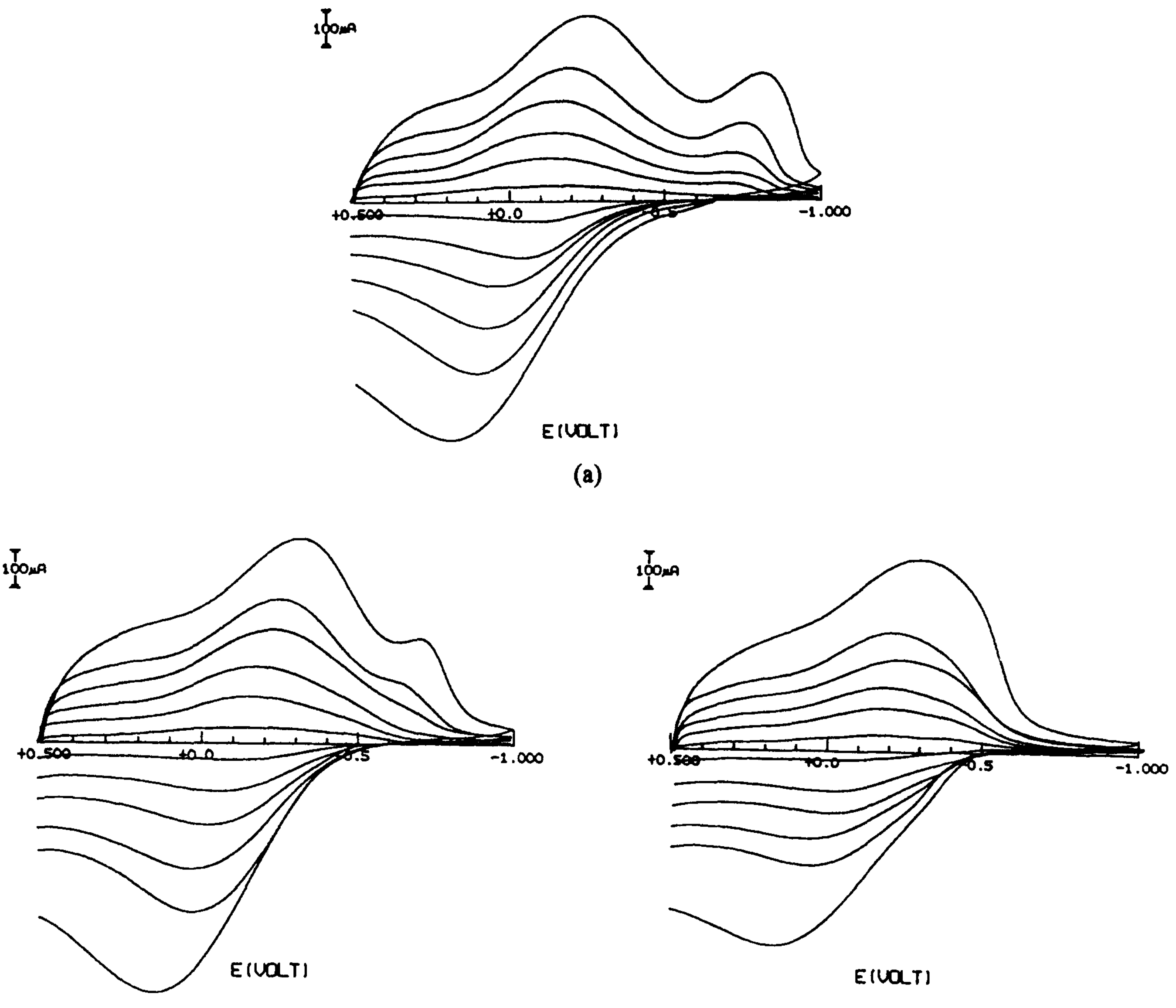
Table 1 Electrochemical data for polypyrrole containing perchlorate

Potential (V)	E_{pa} (mV)	I_{pa} (μA)	E_{pc} (mV)	I_{pc} (μA)	E_o (mV)
0.6	-130 ± 14	51.9 ± 3.6	-144 ± 13	-41.1 ± 1.2	-119 ± 18
0.75	-84 ± 10	44.8 ± 0.4	-156 ± 16	-43.7 ± 0.4	-111 ± 15
1.0	-33 ± 19	37.3 ± 1.5	-139 ± 11	-36.5 ± 1.6	-83 ± 6
1.5	106 ± 27	57.5 ± 2.3	-70 ± 30	-37.5 ± 1.9	35 ± 46
2.0			-268 ± 36	-59.4 ± 8.9	

Scan rate, 10 mV s^{-1}

in the film containing perchlorate prepared at 0.6 V as observed in the voltammogram and *FT*i.r. spectrum. Films prepared by applying a potential of 1.0 V or greater have predominantly cationic species since only one reduction peak is observed. As discussed later, e.s.r. spectroscopy was used to determine the dependence of polaron and bipolaron concentrations on polymerization potential.

The redox couple of polypyrrole films containing toluenesulfonate has a strong reduction peak and a weak oxidation peak, *Figure 8*. No additional oxidation or reduction peaks were observed when the scan rate was varied. Similar behaviour was reported by Warren and Anderson[9]. The shape of the cyclic voltammogram is not dependent on the polymerization potential. However, the peak currents and their positions vary with polymerization potential as summarized in *Table 2* for films prepared by passing 30 mC of charge. The peak currents decrease while the peak positions and E_0 shift anodically as the polymerization potential is increased. When the polym-



(a)

(b)

(c)

Figure 7 The effect of scan rate on polypyrrole redox couple for films prepared in 0.1 M pyrrole solution containing 0.1 M sodium perchlorate by passing 30 mC. The cyclic voltammograms were run in a 0.1 M sodium perchlorate solution at scan rates of 10, 30, 50, 75, 100 and 150 mV s^{-1}. The films were prepared by applying (a) 0.6, (b) 0.75 and (c) 1.0 V

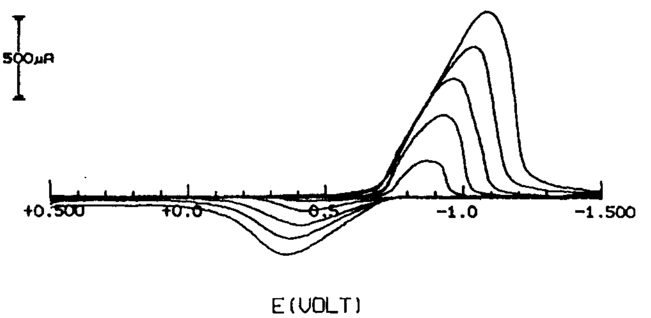


Figure 8 Cyclic voltammograms of polypyrrole on glassy carbon in 0.1 M sodium *p*-toluenesulfonate solution. The films were prepared in 0.1 M pyrrole solution containing 0.1 M sodium *p*-toluenesulfonate by passing 30 mC of charge at 0.6 V. The scan rates are 10, 30, 50, 75 and 100 mV s^{-1}

erization potential exceeds 0.75 V, the magnitude of the reduction peak current is reduced significantly due to overoxidation of polypyrrole.

Overoxidation during pyrrole electropolymerization in perchlorate is important when the applied potential exceeds 1.0 V, as mentioned earlier. Several investigators have studied overoxidation in conductive polymers in different electrolytes and solvents (e.g. refs 19, 26, 28 and 29). The changes in the shape of the voltammograms, *Figure 6*, as the polymerization potential was varied may correspond to the three polymerization regions suggested by Otero and Santamaria[19,28]: region I, growth of polypyrrole with little or no overoxidation; region II, a new reaction promotes overoxidation in the film; and region III, oxygen is released from the overoxidized film. It is interesting to note that the oxidation reactions have negligible effect on the shape of the voltammograms for polypyrrole containing toluenesulfonate.

The effects of scan rate on the peak currents of polypyrrole containing perchlorate at different potentials are illustrated in *Figure 9*. Both oxidation and reduction peak currents are linearly proportional to the scan rate. The second reduction peak of the polypyrrole film prepared by applying 0.6 V is also proportional to the

Table 2 Electrochemical data for polypyrrole containing toluenesulfonate

Potential (V)	E_{pa} (mV)	I_{pa} (μA)	E_{pc} (mV)	I_{pc} (μA)	E_o (mV)
0.6	-451 ± 3	27.3 ± 3.1	-877 ± 25	-241 ± 3	-688 ± 31
0.75	-443 ± 6	27.6 ± 1.6	-823 ± 2	-232 ± 2	-642 ± 17
1.0	-400 ± 15	26.6 ± 2.2	-849 ± 18	-159 ± 28	-567 ± 34
1.5	-301 ± 28	24.5 ± 1.9	-782 ± 46	-147 ± 6	-518 ± 21
2.0	-328 ± 30	23.7 ± 2.7	-790 ± 46	-131 ± 5	-513 ± 30

Scan rate, 10 mV s^{-1}

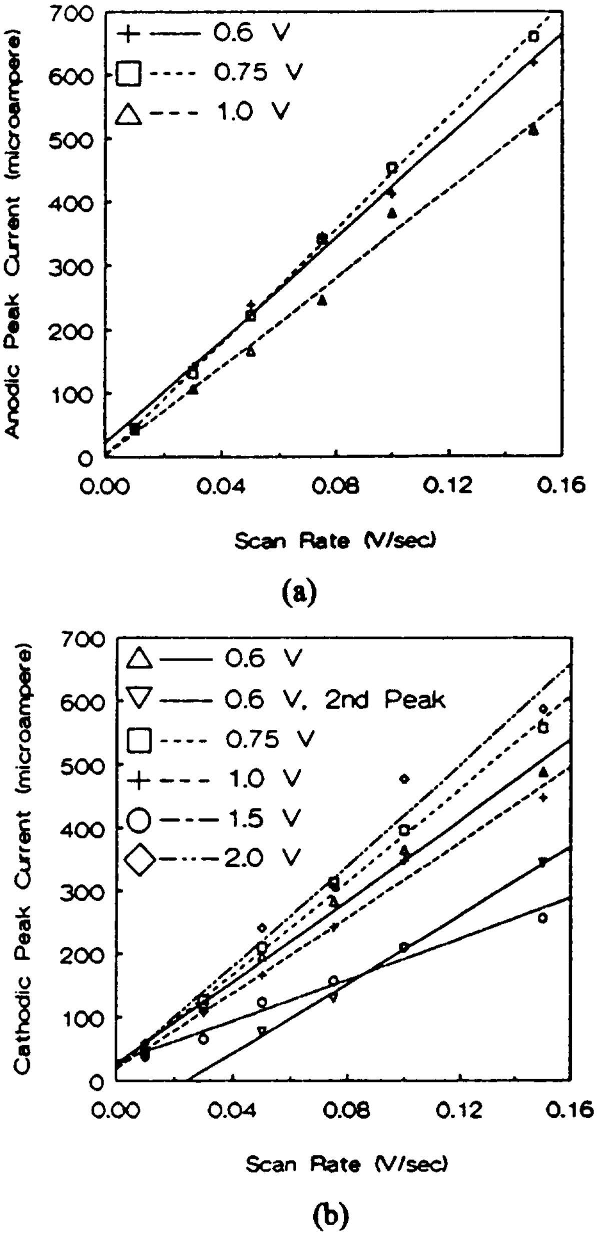


Figure 9 The effect of scan rate on the polypyrrole redox couple for films prepared by passing 30 mC in 0.1 M pyrrole solution containing 0.1 M sodium perchlorate. The cyclic voltammograms were run in 0.1 M sodium perchlorate. (a) Oxidation peak; (b) reduction peak

scan rate, *Figure 9b*. The oxidation peak of films prepared by applying either 1.5 or 2.0 V could not be measured when the scan rate exceeded 30 mV s^{-1}. For perchlorate-doped films, one of three rate-controlling steps can satisfy the linear relationship between I_p and v: (1) case II diffusion of perchlorate[10], (2) diffusion and adsorption of perchlorate[24], or (3) the electron transfer reaction of polypyrrole[30]. The diffusion coefficient of perchlorate in polypyrrole is approximately 3×10^{-9} cm^2 s^{-1} (ref. 10). Since the perchlorate ion diffuses relatively fast in polypyrrole, the diffusion-dependent steps (1) and (2) are unlikely. Thus, electron transfer is likely to control the switching reaction.

The dependence of peak currents on scan rate for polypyrrole containing toluenesulfonate is different. For films prepared by applying either 0.6 or 0.75 V, the oxidation peak current is proportional to v, *Figure 10a*. Therefore, electron transfer is the rate-controlling step. However, the oxidation peak current is proportional to $\sqrt{v}$ for films prepared by applying 1.0 V or greater, *Figure 10b*. Hence, the rate-controlling step is the diffusion of the counterion, toluenesulfonate. The reduction peak current is proportional to $\sqrt{v}$, *Figure 10c*.

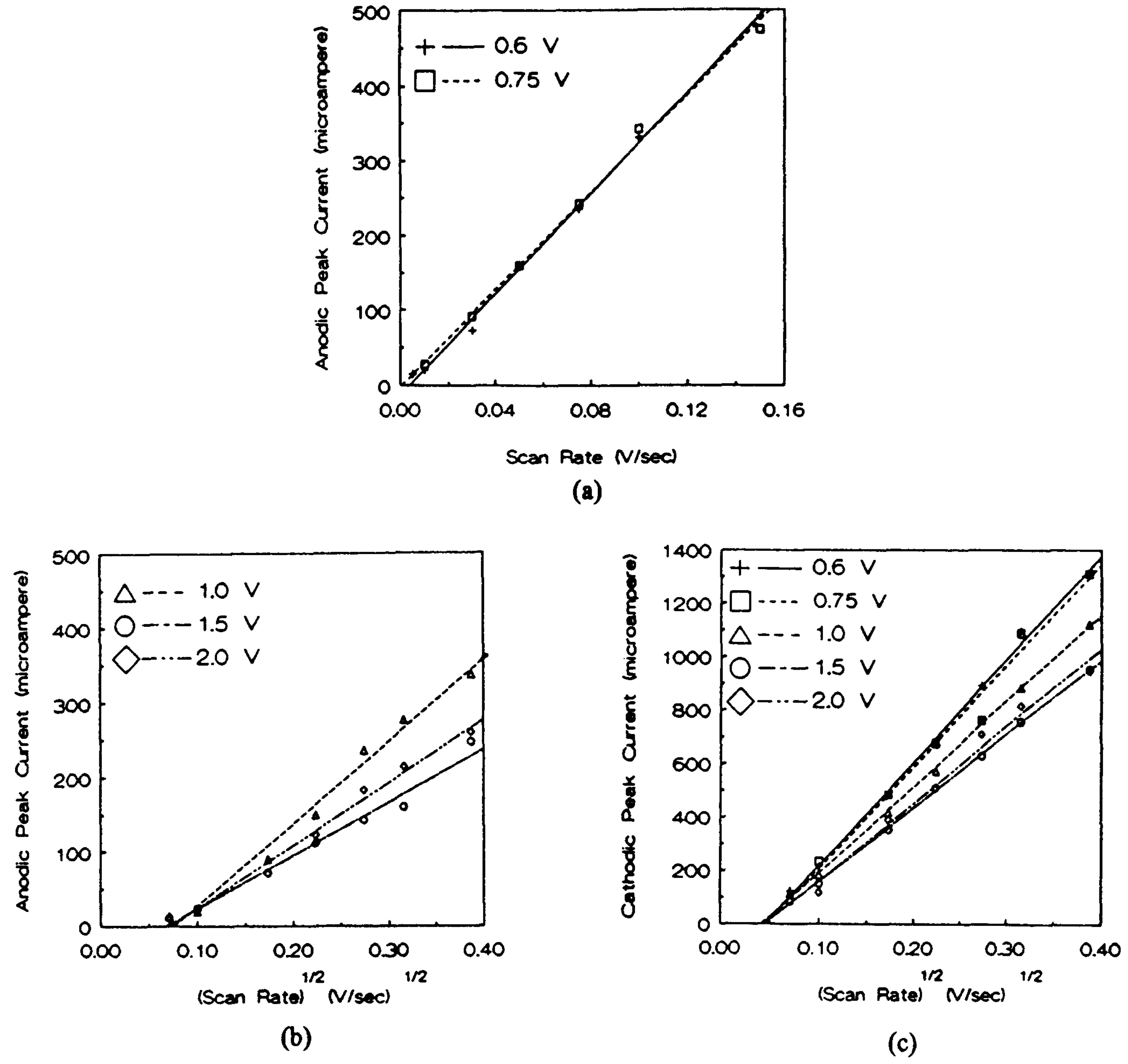
When I_p is proportional to $\sqrt{v}$, the diffusion coefficient of toluenesulfonate can be estimated at 25°C by using the relationship[31]:

$$I_p = 2.69 \times 10^5 n^{3/2} A D_o^{1/2} v^{1/2} C \tag{3}$$

where n is the number of electrons transferred per molecule ($n = 1$), A is the electrode area ($A = 0.067$ cm^2), D_o is the diffusion coefficient of toluenesulfonate, v is the scan rate and C is the concentration of diffusing species (toluenesulfonate). For simplicity, the concentration of toluenesulfonate in the film is assumed to be independent of the polymerization potential. The film density of polypyrrole containing toluenesulfonate is 1.364 g cm^{-3} (ref. 24) and the number of anions per pyrrole unit is 0.35 (ref. 10). The diffusion coefficient of toluenesulfonate for reduction is of the order of 10^{-10} cm^2 s^{-1}, while for oxidation it is of the order of 10^{-11} cm^2 s^{-1}, as summarized in *Table 3*. Volk *et al.*[10] estimated a diffusion coefficient of 4.3×10^{-11}, which falls in the range of calculated values.

The observed relationship between peak current and scan rate is complex (*Figures 9* and *10*). The behaviour is dependent on both electrolyte type and polymerization potential. Relationships like the Integrated Cottrell equation[31] used by Volk *et al.*[10] and the linear potential sweep equation (equation (3)) are not accurate since the film thickness is not considered. The film thickness and the total amount of counterion are dependent on the charge passed during electropolymerization.

The peak currents of polypyrrole containing either perchlorate or toluenesulfonate ion are strongly dependent on the charge passed during electropolymerization,



(a)

(b)

(c)

Figure 10 The effect of scan rate on polypyrrole redox couple for films prepared in 0.1 M pyrrole solution containing 0.1 M sodium *p*-toluenesulfonate by passing 30 mC of charge. The cyclic voltammograms were run in 0.1 M sodium *p*-toluenesulfonate. (a) Oxidation peak current *versus* scan rate; (b) oxidation peak current *versus* square root of scan rate; (c) reduction peak current *versus* square root of scan rate

Table 3 Calculated diffusion coefficients for toluenesulfonate in polypyrrole

Potential (V)	Diffusion coefficient ($cm^2 s^{-1}$)	
	Oxidation	Reduction
0.6	–	2.11×10^{-10}
0.75	–	2.04×10^{-10}
1.0	1.71×10^{-11}	1.47×10^{-10}
1.5	0.72×10^{-11}	1.08×10^{-10}
2.0	1.00×10^{-11}	1.19×10^{-10}

Figure 11. The polymerization reaction involves two electrons per monomer unit and the oxidation of polypyrrole accounts for a partial electron, approximately 0.25, per monomer unit[6]. The excess charge in polypyrrole film is dependent on the counterion and proportional to the charge passed during electropolymerization. When the film is reduced, the excess charge will be neutralized. If charge transfer is rate-controlling, the peak current will be linearly proportional to the charge passed and the scan rate. For a diffusion-controlled process, the relationship between peak current and charge passed will not be linear. The following empirical relationship is proposed:

$$I_p = K(Q_p v)^m \quad (4)$$

where I_p is the peak current in amperes, Q_p is the charge passed during electropolymerization in coulombs, v is the scan rate in $V s^{-1}$, and K and m are power law parameters. The parameter K is a function of the electron transfer coefficient and the degree of anion incorporation per monomer unit in the film. If ion diffusion is rate-controlling, K would also depend on the diffusion coefficient of the counterion in the film. The correlation constants based on films prepared by passing 15, 30, 50,

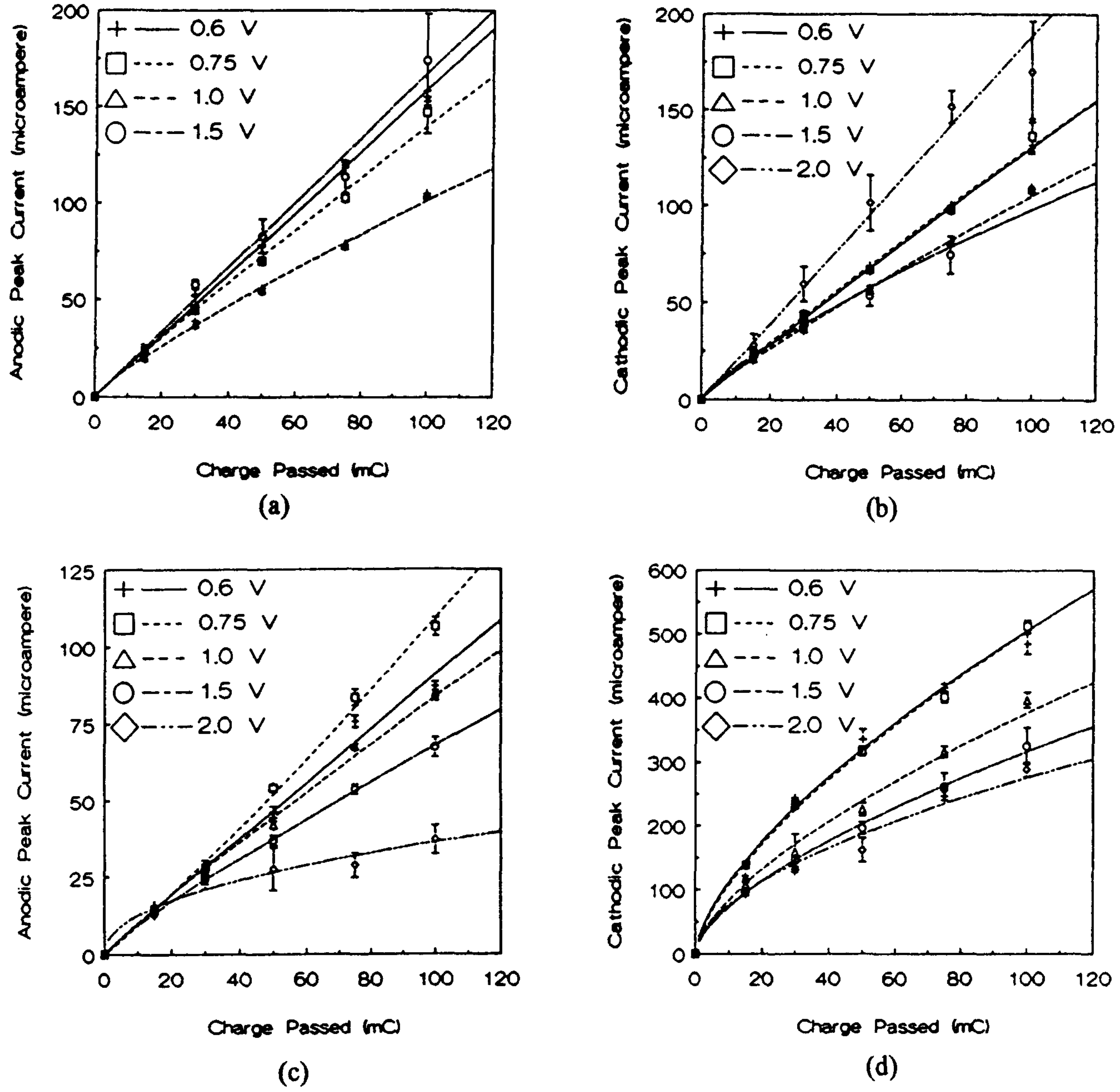


Figure 11 The peak current of polypyrrole redox couple as a function of charge passed during electropolymerization for films prepared on glassy carbon using 0.1 M pyrrole solution with ((a) and (b)) 0.1 M sodium perchlorate or ((c) and (d)) 0.1 M sodium p-toluenesulfonate. The cyclic voltammograms were run in (a), (b) 0.1 M sodium perchlorate or (c), (d) 0.1 M sodium p-toluenesulfonate. The scan rate is $10\,\mathrm{mV\,s^{-1}}$

Table 4 Dependence of correlation constants of equation (4) on pyrrole polymerization potential

		Oxidation peak		Reduction peak	
Electrolyte	Potential (V)	m	K	m	K
Perchlorate	0.6	0.96	0.12	0.93	0.077
	0.75	1.00	0.14	0.96	0.10
	1.0	0.96	0.083	0.90	0.056
	1.5	1.00	0.17	0.77	0.020
	2.0	–	–	1.07	0.031
Toluenesulfonate	0.6	1.05	0.13	0.70	0.067
	0.75	1.04	0.14	0.66	0.047
	1.0	1.00	0.090	0.70	0.050
	1.5	0.91	0.036	0.71	0.047
	2.0	0.96	0.048	0.71	0.047

75 and 100 mC of charge are summarized in *Table 4*. The exponent m is dependent on redox peak, polymerization potential and electrolyte type. For polypyrrole containing perchlorate, m is approximately unity in most cases, suggesting that charge transfer is the rate-controlling step. The exponent for the reduction of polypyrrole containing toluenesulfonate is approximately 2/3 but a diffusion-controlled process in an infinite medium should have an exponent of 1/2 (ref. 10). For these films, the exponent of approximately 2/3 could suggest that diffusion of the counterion in a finite medium is the rate-controlling step or that the switching reaction is not entirely diffusion-controlled. This is another reason why the diffusion coefficient cannot be calculated accurately using either equation (3) or the Integrated Cottrell equation.

E.s.r. spectroscopy

The polaron–bipolaron interactions of polypyrrole have been studied by *in situ* electrochemical–e.s.r. experiments[32,33]. For e.s.r. spectroscopy, pyrrole was electropolymerized in a thin-layer cell from a 0.1 M pyrrole solution containing 0.1 M sodium perchlorate by passing 60 mC charge at 0.6 or 1.0 V. The polypyrrole film was rinsed and placed in a clean thin-layer cell containing 0.1 M sodium perchlorate. The electrochemical cell was then placed in the e.s.r. cavity of the spectrometer. A voltage of 0.5 V was applied to the polypyrrole film for 10 s, then the voltage was stepped between 0.5 and −1.0 V. An e.s.r. spectrum was recorded after each voltage change. The observed spectra for polypyrrole are similar to those observed by Waller and Compton[33]. The spin concentration (*S*, proportional to the number of polarons) was measured by integrating the area under the spectrum.

The spin concentration is dependent on the state of charge or discharge of polypyrrole film[32,33]. As the potential decreases from 0.5 V, the spin concentration increases until it reaches a maximum as shown in *Figure 12*. In the region anodic to the maximum, the bipolarons become polarons as the applied potential is decreased and thus the spin concentration increases[33]. The polaron and bipolaron concentrations approach zero as the potential continues to decrease in the region cathodic to the maximum.

The spin concentration of films prepared at different polymerization potentials produced distinct responses (*Figure 12*). The spin concentration at the maximum is higher for the film prepared at 1.0 V. Since the two polypyrrole films exhibit approximately the same peak current (*Figure 6* and *Table 1*), the excess charge in the films must also be equal. Thus, the total polaron and bipolaron concentration should be approximately equal. Since the spin concentration of polypyrrole prepared at 0.6 V is less than the spin concentration of the film prepared at 1.0 V, the bipolaron or dication concentration is greater, *Figure 12*. Thus, the e.s.r. results support the interpretation of the *FT*i.r. spectra (*Figure 5*). The dependence of the bipolaron concentration on the polymerization potential also explains the two reduction peaks observed in the cyclic voltammograms, *Figure 7*.

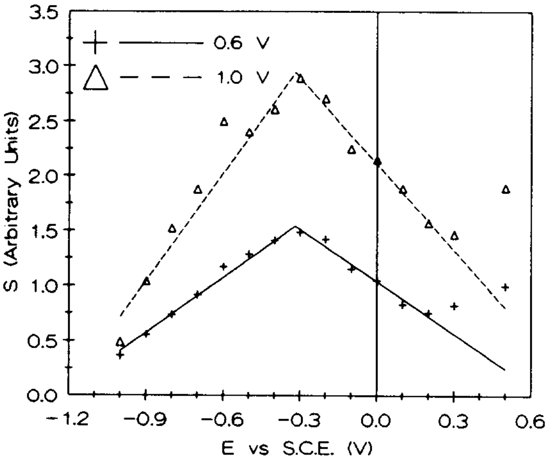


Figure 12 Dependence of spin concentration of polypyrrole containing perchlorate on potential in 0.1 M sodium perchlorate solution. The films were prepared by passing 60 mC in 0.1 M pyrrole solution containing 0.1 M sodium perchlorate

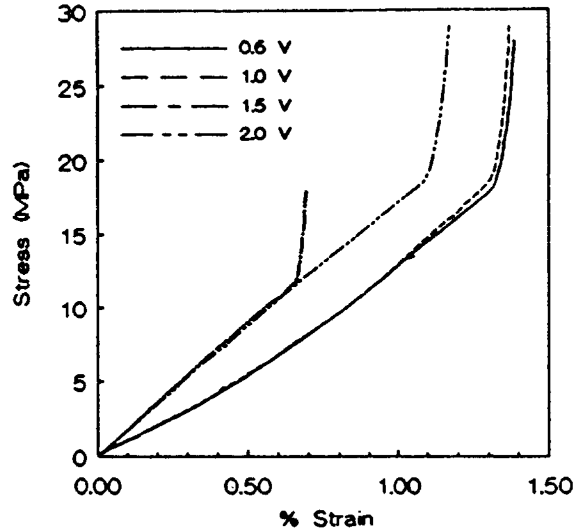


Figure 13 The stress–strain curve of polypyrrole containing *p*-toluenesulfonate for films prepared on ITO glass by applying 0.6, 1.0, 1.5 or 2.0 V. The draw rate is 130 mN min^{-1}

Table 5 Tensile moduli of polypyrrole containing toluenesulfonate

Potential (V)	Modulus (GPa)		
	Elastic I	Transition	Elastic II
0.6	1.0	1.5	17
1.0	1.1	1.6	19
1.5	1.8	–	23
2.0	1.7	–	15

Mechanical properties

The tensile modulus of polypyrrole containing toluenesulfonate has been measured to be 2.5 GPa[14]. The ultimate tensile strength is reported to vary between 54 (ref. 12) and 61 MPa (ref. 14). The mechanical behaviour of polypyrrole film containing *p*-toluenesulfonate was tested by increasing the tensile force on the film at a constant rate of 130 mN min^{-1}. A maximum force of 1300 mN was applied to the film during d.m.a. measurements. The films did not always break at the maximum load. The dimensions of the films were measured using a micrometer. The mechanical properties of polypyrrole films containing perchlorate could not be measured since the films were too brittle and broke during measurement.

The stress–strain curve for a polypyrrole film containing *p*-toluenesulfonate prepared by applying 0.6 or 1.0 V has three regions of behaviour, while films prepared at 1.5 and 2.0 V have only two distinct domains, *Figure 13*. The first range (elastic I) observed in films prepared at 0.6 and 1.0 V is linear elastic where the modulus is approximately 1.0 GPa (*Table 5*). The second (transition) range is slightly inelastic with a modulus around 1.5 GPa. Finally, the modulus increases sharply by an order of magnitude in the third range, elastic II. This increase is probably due to polymer chain ordering or orientation effects. The slightly inelastic behaviour was not observed for polypyrrole prepared at 1.5 or 2.0 V. Thus, the mechanical properties of polypyrrole are dependent on the polymerization potential. The increase in the modulus with an increase in the applied potential may be caused by an increase in the degree of crosslinking[34]. In few cases, defects or irregularities in the film caused it to break at the point of the sharp change in modulus.

Table 6 Sheet resistance of polypyrrole containing toluenesulfonate

Potential (V)	Resistance (Ω/□)
0.6	27.65
0.75	11.70
1.0	12.58
1.5	10.93
2.0	11.25

Sheet resistance

The sheet resistance of polypyrrole containing *p*-toluenesulfonate was measured using a four-point probe conductivity meter. The resistance varied between 10.9 and 27.7 Ω/□. Measurement of the electrical conductivity requires an accurate measurement of the film thickness, which was not feasible. As noted by Warren and Anderson[9], the sheet resistance is a more convenient measurement since it does not require the film thickness. The sheet resistance is dependent on the polymerization potential, as shown in *Table 6*. For films prepared by applying 0.6 to 0.75 V, the sheet resistance decreased sharply. The sheet resistance remains relatively constant for films prepared at a potential exceeding 0.75 V. These data support the conclusion based on *FT*i.r. and electrochemical measurements that films containing toluenesulfonate were less prone to overoxidation.

SUMMARY

The electropolymerization of pyrrole as shown in the chronoamperometric responses is primarily dependent on the applied potential and not on the counterion. At 1.0 V, there is an indication of overoxidation of polypyrrole during polymerization. The polypyrrole structure, the extent of oxidation and the incorporation of termination groups are dependent on the polymerization potential, and consequently affect the electrochemical and mechanical properties as well as the sheet resistance. The electrochemical properties of polypyrrole are extremely sensitive to variations in the chemical structure. Films prepared with *p*-toluenesulfonate behave differently from those prepared with perchlorate.

A second reduction peak is observed in the cyclic voltammograms of polypyrrole containing the perchlorate ion. This peak is observed for films prepared at 0.6 and 0.75 V and indicates a large concentration of dicationic species or bipolarons. As the polymerization potential increases, the concentration of dicationic species decreases, as shown by e.s.r. experiments. At 1.0 V, the concentration of dicationic species is small enough to produce only one reduction peak in the cyclic voltammetric responses.

A power law model is proposed to relate peak current to the scan rate and charge passed during electropolymerization. For films containing perchlorate, charge transfer is rate-controlling since the peak current is linearly proportional to the scan rate and the charge passed, and the perchlorate ion diffusion coefficient is high. The controlling step for oxidation of polypyrrole containing toluenesulfonate is not obvious. The exponent is approximately 2/3 for the reduction of films containing toluenesulfonate. The rate-controlling step is not diffusion of the counterion in an infinite medium. Instead, the rate-controlling step could be either ion diffusion in a finite medium or some intermediate process.

The electropolymerization of pyrrole and the side-reactions are potential-dependent, as confirmed in this investigation. The galvanostatic technique should not be used to prepare polypyrrole since it is difficult to control the composition and related properties of the film.

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REFERENCES

1 Panero, S., Prosperi, P. and Scrasati, B. *Electrochim. Acta* 1987, **32**, 1465

2 Ferreira, C. A., Aeiyach, S., Delamar, M. and Lacaze, P. C. *J. Electroanal. Chem.* 1990, **284**, 35

3 Foulds, N. C. and Lowe, C. R. *Anal. Chem.* 1988, **60**, 2473

4 Mizutani, F. and Asai, M. *Bull. Chem. Soc. Jpn* 1988, **61**, 4458

5 Couves, L. D. and Porter, S. J. *Synth. Met.* 1981, **28**, C761

6 Diaz, A. F., Casillo, J. I., Logan, J. A. and Lee, W.-Y. *J. Electroanal. Chem.* 1981, **129**, 115

7 Ko, J. M., Rhee, H. W., Park, S.-M. and Kim, C. Y. *J. Electrochem. Soc.* 1990, **137**, 905

8 Otero, T. F., Tejada, R. and Elola, A. S. *Polymer* 1987, **28**, 651

9 Warren, L. F. and Anderson, D. P. *J. Electrochem. Soc.* 1987, **134**, 101

10 Volk, F. T. A., Schuermans, B. C. A. M. and Barendrecht, E. *Electrochim. Acta* 1990, **35**, 567

11 Kaplin, D. *PhD Dissertation* Case Western Reserve University, USA, 1993

12 Niwa, O., Kakuchi, M. and Tamamura, T. *Polym. J.* 1987, **19**, 1293

13 Naoi, K. and Osaka, T. *J. Electrochem. Soc.* 1987, **134**, 2479

14 Koga, K., Iino, T., Ueta, S. and Takayanagai, M. *Polym. J.* 1989, **21**, 303

15 Janssen, W. and Beck, F. *Polymer* 1989, **30**, 353

16 Kaplin, D. A. and Qutubuddin, S. *Synth. Met.* 1994, **63**, 187

17 Kaplin, D. A. and Qutubbudin, S. *J. Electrochem. Soc.* 1993, **140**, 3185

18 Kaplin, D. A. and Qutubuddin, S. *Electrochim. Acta* Submitted for publication

19 Otero, T. F. and Santamaria, C. *Synth. Met.* 1992, **51**, 313

20 Satoh, M., Kaneto, K. and Yoshino, K. *Synth. Met.* 1986, **14**, 289

21 Rodriguez, M., Marcos, M. L. and Gonzalez-Velasco, J. *Electrochim. Acta* 1987, **32**, 1181

22 Quian, R. and Qiu, J. *Polym. J.* 1987, **19**, 157

23 Hammett, A., Higgins, S. J., Fisk, P. R. and Albery, W. J. *J. Electroanal. Chem.* 1989, **270**, 479

24 Cheung, K. M., Bloor, D. and Stevens, G. C. *Polymer* 1988, **29**, 1709

25 Socrates, G. 'Infrared Characteristic Group Frequencies', John Wiley, New York, 1980

26 Beck, F., Braun, P. and Oberst, M. *Berlin Bunsensges. Phys. Chem.* 1987, **91**, 967

27 Genies, E. M. and Pernaut, J.-M. *J. Electroanal. Chem.* 1985, **191**, 111

28 Otero, T. F. and Santamaria, C. *J. Electroanal. Chem.* 1991, **312**, 285

29 Krische, B. and Zagorska, M. *Synth. Met.* 1989, **28**, C257

30 LaCroix, J.-C. and Diaz, A. F. *J. Electrochem. Soc.* 1988, **135**, 1457

31 Bard, A. J. and Faulkner, L. R. 'Electrochemical Methods, Fundamentals and Applications', John Wiley, New York, 1980

32 Nechtschein, M., Devreux, F., Genoud, F., Vieil, E., Pernaut, J. M. and Genies, E. *Synth. Met.* 1986, **15**, 59

33 Waller, A. M. and Compton, R. G. *J. Chem. Soc., Faraday, Trans. 1* 1989, **85**, 977

34 Street, G. B. 'Handbook of Conducting Polymers' (Ed. T. A. Skotheim), Vol. 1, Marcel Dekker, New York, 1986, Ch. 8, p. 265