# Characterization of polypyrrole electropolymerized on different electrodes*

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Polypyrrole containing the toluenesulphonate counter-ion has been electrochemically polymerized on a wide range of metallic electrodes, including platinum, titanium, aluminium, mild steel and brass. The oxidation behaviour of pyrrrole monomer in the presence of these electrodes has been investigated and the influence of metal oxide layers is discussed. The redox behaviour of the polymers prepared on different electrodes suggests that the reaction appears quasi-reversible for all the oxidizable metal electrodes and only in the case of platinum is the reaction simply diffusion-controlled. Chemical and physical characterization of the materials is also presented and the presence of a distinct fibrillar second phase is reported for the first time.

**(Keywords: polypyrrole–toluenesulphonate; pyrrole oxidation; redox reaction; characterization; morphology; phase separation)**

## INTRODUCTION

Since many of the polymeric heteroaromatic compounds are conductive and have potential applications in electronic displays[1], as electrode materials in batteries[2] and as molecular electronic circuit elements[3], the electrochemical polymerization of the appropriate monomers has been intensively studied[4]. Polypyrrole is one of these electrical conducting poymers and its history dates back to 1916[5], when it was prepared as a powder by the oxidation of pyrrole and known as 'pyrrole black'. In 1968, Bocchi *et al.*[6] reported the first electrochemical preparation of polypyrrole, which was carried out in dilute sulphuric acid. In 1979, Diaz *et al.*[7] prepared the first free-standing polypyrrole films by an electrochemical method. These had sufficiently good mechanical properties to make the practical investigation of the conducting polymer possible and triggered an expansion of research[7–11] in this field.

It has been reported that polypyrrole has been prepared in aprotic[12] (e.g. $CH_3CN$, propylene carbonate) and protic solvents[13,14] (e.g. $H_2O$) with tetraethylammonium salts as the supporting electrolyte and platinum (Pt) as the working electrode. Although many physical measurements and chemical analyses have been performed on polypyrrole, e.g. mechanical properties[15,16], solid $^{13}C$ nuclear magnetic resonance (n.m.r.)[17,18], elemental analysis[12–14], ESCA[19], oxidative degradation, i.r.[20], e.s.r.[21] and Raman spectroscopy[22–24], the exact structure of polypyrrole is still unknown. It was suggested that the polypyrrole chain structure is a planar array of monomer units joined by $\alpha$–$\alpha$ bonds and with some $\alpha$–$\beta$ and $\beta$–$\beta$ cross-linkages.

Besides the above-mentioned investigations, other kinetic[25,26] and electrochemical[27,28] experiments have been carried out to elucidate the mechanism of formation of the polymer. The effect of different electropolymerization parameters, such as the temperature at which the film was grown, the water content in the aprotic solvent[4] and the nature of the working electrodes[29], have been investigated. In addition, the properties of polypyrrole have been studied as a function of temperature and other physical factors such as the degree of stretching[21].

The range of electrode materials used in previous work was limited. In this paper we report on the chemical and physical characterization of polypyrrole films containing the toluenesulphonate counter-ion (*Figure 1*) electropolymerized on different metal electrodes. This system was chosen because eariler work[15,16] has shown that this system combines reasonable electrical conductivity (up to 50 S cm$^{-1}$) with good thermal and chemical stability and excellent mechanical properties (maximum tensile strength was about 50 MPa, Young's modulus was about 4 GPa). The films were grown on a range of metal electrodes, namely platinum (Pt), titanium (Ti), aluminium (Al), mild steel (Fe) and brass, using cyclic voltammetry. Characterization included elemental analysis, Raman spectroscopy, scanning electron microscopy and conductivity measurements. These experiments were conducted in the presence and absence

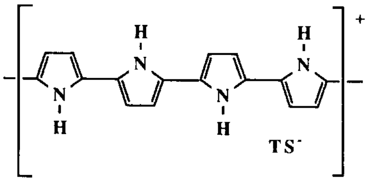

**Figure 1** Structure of polypyrrole–toluenesulphonate. TS$^-$ = $p$-$CH_3C_6H_5SO_3^-$

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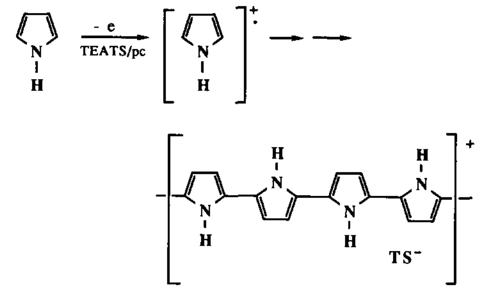


**Scheme 1** Oxidation of pyrrole monomer

of oxygen with either dry electrolyte or an electrolyte with a known addition of water.

## EXPERIMENTAL

Pyrrole monomer (Aldrich) was distilled twice under reduced pressure and stored at 0°C. The electrolyte was tetraethylammonium toluenesuphonate (TEATS) (Fluka Chemical Co.) in propylene carbonate (pc). TEATS was dried at 120°C *in vacuo* for 24 h and the propylene carbonate was purified by passing it through a column of activated 0.5 nm molecular sieve followed by vacuum distillation and nitrogen flushing. All reagents were stored in the dark. The metal electrodes for preparing the polymer films were supplied from standard stock. The microelectrodes for cyclic voltammetry were made of pure metals, e.g. Pt, Al, Ti and Fe. Brass was not investigated as a microelectrode. All electrodes were abraded and cleaned in tetrachloromethane. During the first cyclic voltammetric (c.v.) scan polymer deposited on the metal electrodes. These were then dipped in concentrated sulphuric acid, in order to soften the polymer before scraping it off, and then abraded and cleaned again before the next c.v. scans.

Electropolymerization was carried out under galvanostatic control using a Thompson Electrochem 401 potentiostat in a single compartment cell under nitrogen with an electrode size of 35 × 35 mm and a separation of 40 mm. Cyclic voltammetry of the pyrrole monomer was carried out in a glass cell[30] with a luggin pointing at the microelectrode (*ca.* 0.03 $cm^2$), a saturated calomel reference electrode (SCE) and a platinum coil counter electrode; a computer controlled Thompson Electrochem Autostat was used for these measurements. Cyclic voltammetry of the polypyrrole film was carried out in the same glass cell, but the voltammograms were generated by a sweep generator connected to a potentiostat.

A typical pyrrole/electrolyte composition was *ca.* $2.0 \times 10^{-2}$ M pyrrole and 0.1 M TEATS/pc which was flushed with nitrogen. Various amounts of charge in the range 800–1000 C were passed at a current density of 0.82 mA $cm^{-2}$ to produce film thicknesses up to 0.4 mm. After polymerization the polypyrrole–toluenesulphonate (PPy–TS) films were peeled off the electrode and washed in acetone in an ultrasonic bath three times before they were dried at 40°C *in vacuo*. For c.v., 6 mg of pyrrole was used and background scans of the pure electrolyte were also recorded.

Elemental analysis of C, H, N, S and O was carried out by the University of London analysis service at University College. Checks for the other elements were made using energy dispersive spectroscopy (EDS) on the scanning electron microscope. Raman spectra were recorded using the system described elsewhere[22–24] with a laser exciting wavelength of 482.5 nm and a 180° collection geometry. Scanning electron microscopy (SEM) was performed on electrode facing and electrolyte facing surfaces and cross-sectional fracture surfaces using an Hitachi S800 field emission microscope at 10–20 kV and EDS was performed with a Kevex 8000 windowless detector. Electrical conductivity measurements were made using the four point probe method[31] at room temperature.

## RESULTS AND DISCUSSION

### *Cyclic voltammetry of the pyrrole monomer*

The oxidation potential of the pyrrole monomer was found to be greater than + 1.0 V (*versus* a SCE reference electrode) for all the metal electrodes studied (*Scheme 1*), when voltammograms were scanned over the range between 0 and + 2.0 V. *Figure 2* shows how the oxidation potentials and the current intensities of the pyrrole monomer varied with the different electrodes. Quantitative data is listed in *Table 1*.

During the cyclic voltammetric experiments, a black continuous film was seen to be deposited on each

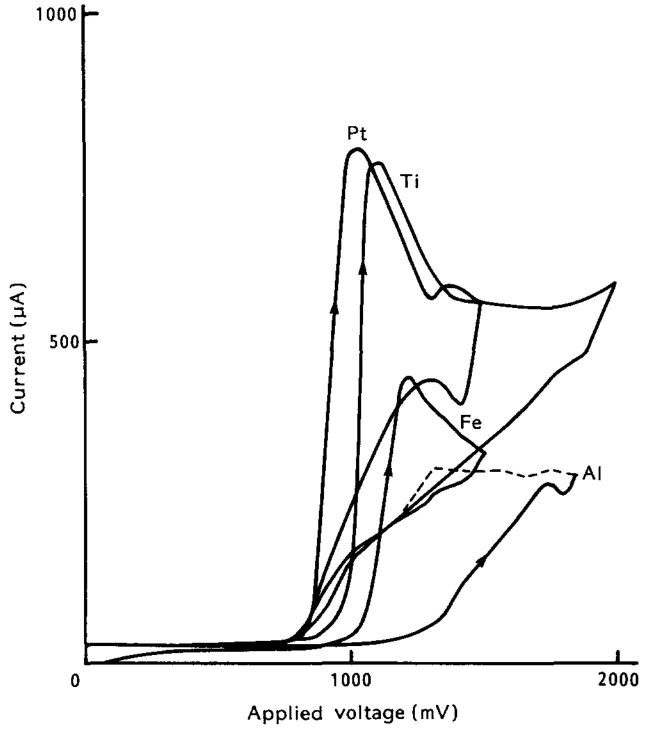


**Figure 2** Cyclic voltammograms showing the oxidation potentials of pyrrole monomer on different metal electrodes

Table 1 Oxidation potentials and current intensities of the pyrrole monomer on different electrodes

| | Pt | Ti | Fe | Al[a] |
|---|---|---|---|---|
| Oxidation potential (SCE) (V) | 1.05 | 1.10 | 1.21 | 1.74 |
| Current intensity (μA) | 800 | 780 | 460 | 280 |

[a] Concentration of pyrrole was 4 mol $l^{-1}$ in excess

**Table 2** Band-gap energies, $E_g$, and equilibrium potentials, $E^0$, of various metal oxide electrodes[41,42]

| Metal | Film | $E_g$ (eV) | $E^{\circ a}$ (V) |
|---|---|---|---|
| Al | $Al_2O_3$ | 9.5 | $Al/Al_2O_3$<br>−1.35 |
| Ti | $TiO_2$ | 3.6 | $Ti_2O_3/TiO_2$<br>−0.556 |
| Fe | $Fe_3O_4/Fe_2O_3$ | 1.6<br>2.2 | $Fe_3O_4/Fe_2O_3$<br>0.221 |
| Pt | PtO | 1.3 | Pt/PtO<br>0.98 |
| Brass | CuO | – | CuO/Cu<br>−0.439 |
|  | ZnO |  | ZnO/Zn<br>−0.262 |

[a] Equilibrium potential of the corresponding metal oxide electrode (*versus* hydrogen electrode)

electrode after the first scan, except for the Al electrode. This implies that oxidized polypyrrole is readily formed during the early stages of electropolymerization on Pt, Ti and mild steel electrodes. For Al, although a 4 M excess of pyrrole monomer was added, the current intensity was still only a third of that for, say, Pt. After one c.v. scan the polymer film obtained was discontinuous. This phenomenon suggests that an insulating layer was formed on the Al metal surface before or during the early phase of electropolymerization. Similar considerations apply to the Ti and the mild steel electrodes because their current intensities were also lower than that for Pt. This behaviour is though to be due to the formation of thin metal oxide films at the electrode surfaces.

At unoxidized metal electrodes, the rate of electron transfer is only slightly dependent on the nature of the substrate[32,33], the current intensity of a particular reaction on various metals differs by no more than one order of magnitude and the transfer coefficients are generally about 0.5. On the other hand, the presence of an oxide layer on metal electrodes has a large influence on the rate of electron transfer[34–37], which can be less than that for either Pt or Au by eight or nine orders of magnitude.

The last column of *Table 2* shows the equilibrium potentials (*versus* hydrogen electrode) of different metals to their oxides in aqueous solution. It can be seen that Al is the easiest metal to be oxidized, and Pt the most difficult. This supports the argument that the oxide film is most readily formed on Al. The film then acts as a greater barrier for electron transfer during electropolymerization than oxide films formed on Fe and Ti and gives rise to the lower current intensity values. Similarly, the variation in oxidation potentials of the pyrrole monomers for different metal electrodes may be due to the potential drops across the metal/metal–oxide/electrolyte interfaces being different in each case.

Two reasons can be proposed for the formation of the metal oxide layers during the c.v. experiments. The first is that when the micro-electrodes were transferred to the c.v. cell after cleaning they were in contact with air and hence formed an oxide film. The second is that when a c.v. scan was first performed the metal electrodes were oxidized and hence passivated before the oxidation potential of the pyrrole monomer was reached. It is assumed that traces of water and oxygen were present as impurities in the solvent. Since the electrodes are very small, it is possible for the thin oxide layers to envelope them completely.

An interesting observation was made during the electropolymerization of pyrrole on brass. Polypyrrole was not obtained when the brass electrode had been finely abraded and cleaned with tetrachloromethane, but only when the brass electrode was cleaned in acetone. This seems to suggest that the presence of a natural oxide passivating layer was necessary for the deposition of a polymer film, at least for the brass electrode. We thought that since the equilibrium potential ($E^\circ$) of the brass (Cu and Zn) is also low (see *Table 2*), the corresponding oxide layers would easily form on clean electrodes. However, these layers are likely to be unstable because CuO dissolves in acid and ZnO dissolves both in acid and alkali, so that dissolution can occur as the acidity of the solution changes during the oxidation process. Therefore, the formation and dissolution of CuO and ZnO will occur in preference to the formation of the polypyrrole. In contrast, an unabraded electrode with a more stable oxide layer could exist which would favour the oxidation of pyrrole and the formation of a polypyrrole film. Although the $E^\circ$ of Al is even lower than that of brass, the ability to form a polypyrrole film suggests that formation of a more stable oxide layer is possible in this case.

### *Cyclic voltammetry of polypyrrole*

Polypyrrole deposited on different electrodes was scanned in the range −0.5 V to +1.0 V. The polymers were prepared separately in a small one-compartment cell in air and then transferred to a c.v. cell containing clean electrolyte devoid of any pyrrole monomer. The electropolymerization was carried out in a galvanostatic mode, and the thickness of the films was estimated from the applied current, the time of the polymerization, the area of the electrodes and the floatation density of the polymer; this thickness was about 16 $\mu$m. The voltammograms show broad peaks between 0 and +120 mV (*Figure 3* and *Table 3*) for the redox reaction of the polypyrrole films (*Scheme 2*). Large capacitive currents were observed around the anodic and cathodic potentials. This was probably due to the charging and discharging of the films during the processes of oxidation and reduction, but this could also be influenced by a change in the 'effective' electrode area due to the development of microporosity when toluenesulphonate anions are transported in and out of the films. However, electron microscopy of polymer fracture surfaces gave no evidence of microporosity. Although the anodic peaks were quite well defined, the cathodic peaks were not, except for Fe. No well defined anodic ($E_p^a$) or cathodic ($E_p^c$) peaks were observed for Ti. For Fe, $E_p^a - E_p^c = 19$ mV and $i_p^a/i_p^c = 0.73$, and it is apparent that the redox reaction is not reversible. Since the cyclic voltammograms are distorted and the baseline is difficult to assign, we did not measure the integrated anodic and cathodic currents to test reversibility. However, we consider that the rates of transport of anions into and out of the polymer are different because the diffusion gradient of the anions in the bulk polypyrrole matrix is different from the diffusion gradient of the anions in the bulk solution. Due to the difficulties in identifying a potential difference between $E_p^a$ and $E_p^c$ and also the corresponding current ratio, the exact nature of the redox process is difficult to ascertain. But on

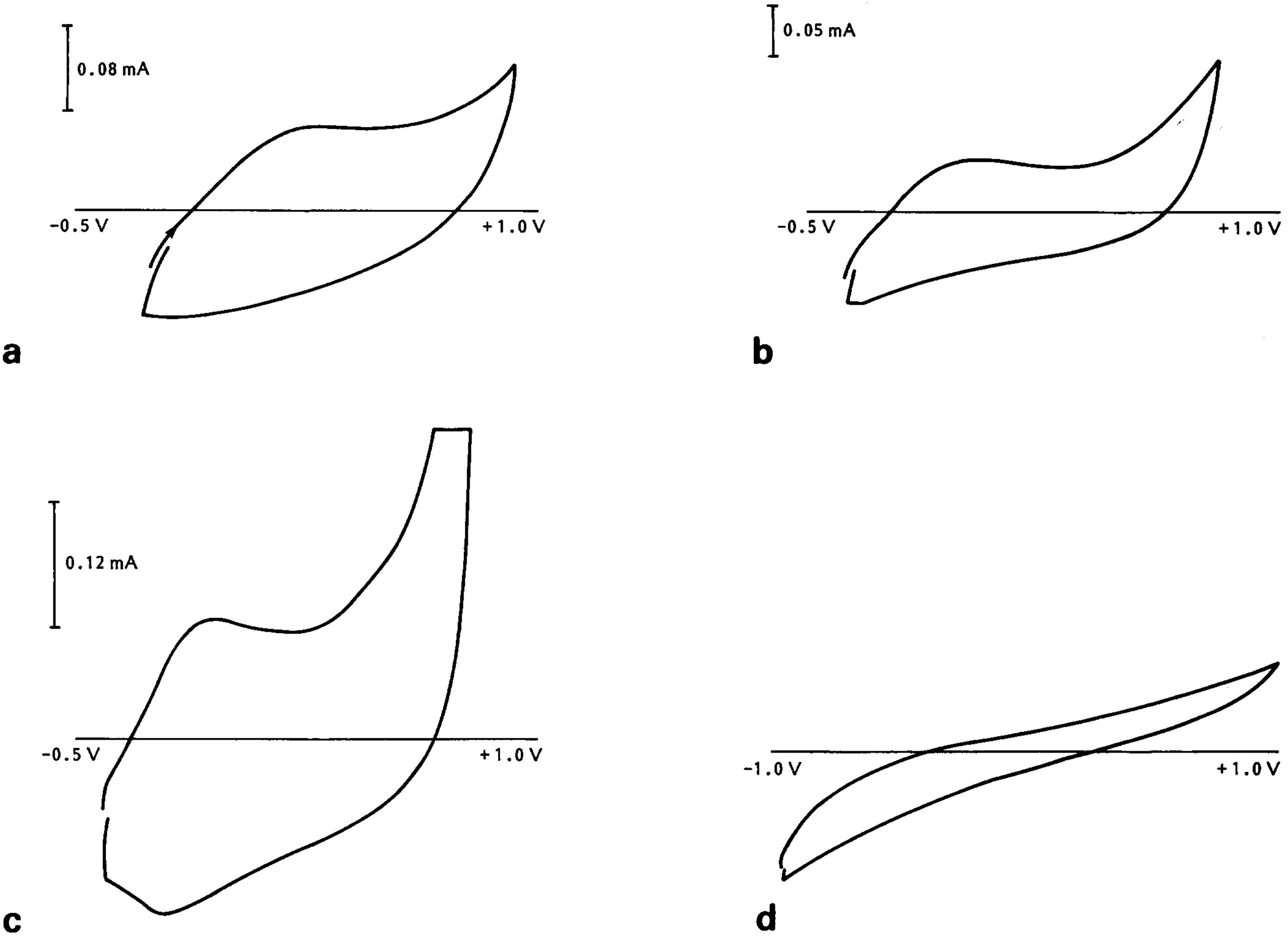


**Figure 3** Cyclic voltammograms of polypyrrole grown on: (a) Pt; (b) Al; (c) Fe; (d) Ti

**Table 3** Redox potentials of polypyrrole on different electrodes

| | Pt | Ti | Fe | Al |
|---|---|---|---|---|
| Redox potential, $E_p^a/E_p^c$ (SCE) (V) | 0.12/–$^a$ | –$^a$/–$^a$ | −0.07/−0.26 | −0.02/– |

$^a$ Not well defined

the same general grounds, the redox reactions for all the electrode materials are likely to be quasi-reversible. Graphs of $i_p^a$ *versus* scan speed ($v$) and $i_p^a$ *versus* $v^{1/2}$ for polypyrrole on different electrodes were plotted and are depicted in *Figure 4*.

For a diffusion-limited reversible reaction[38],

$$i_p \propto D_0^{1/2} v^{1/2} \qquad (1)$$

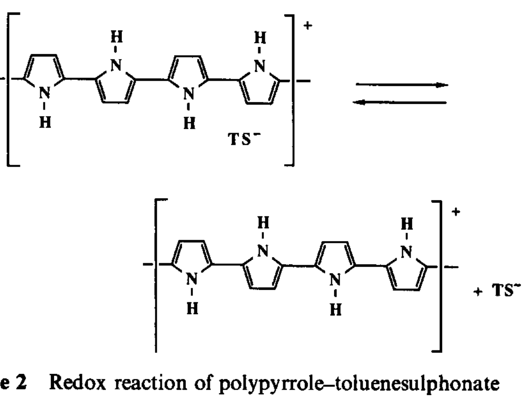
where $D_0$ is the diffusion constant and $v$ the scan speed.

For a quasi-reversible reaction,

$$i \propto D_0^{1/2} \psi(E) v^{1/2} \qquad (2)$$

where $\psi(E)$ is the current function for this case. Since $E_p$ depends upon $v$, $\psi(E)$ at the peak varies with $v$ and $i_p$ is not proportional to $v^{1/2}$.

For Pt, a straight line through the origin was obtained when $i_p^a$ was plotted *versus* $v^{1/2}$. This is the only case which follows equation (1), and we must conclude that the redox reaction of the polypyrrole film grown on Pt was diffusion-controlled. On the other hand, straight lines through the origin were obtained when $i_a^p$ was plotted *versus* $v$ for Al and Fe. This behaviour suggests that, besides diffusion control, adsorption control was also involved to some extent in the redox reaction of the polypyrrole films grown on Al and Fe.



**Scheme 2** Redox reaction of polypyrrole–toluenesulphonate

### *Elemental analysis*

Results of the elemental analysis of films grown on different electrodes are shown in *Table 4*. They do not match the required formula of $C_4H_3N_1(X)_n$ (where X is the incorporated anion and $n$ is a value between 0.2 and

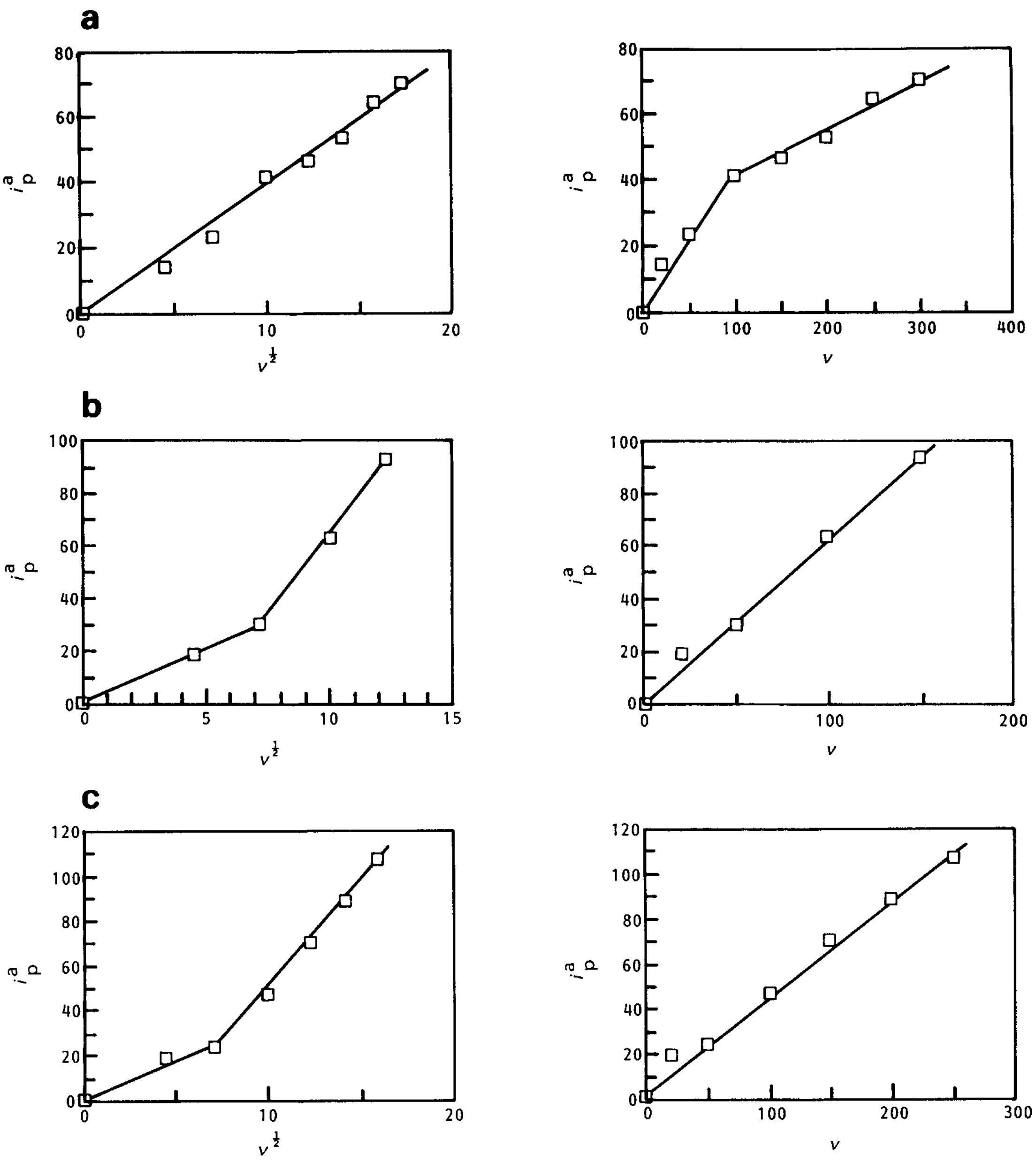


**Figure 4** Graphs of $i_p^a$ *versus* $v^{1/2}$ and $i_p^a$ *versus* $v$ plotted from the cyclic voltammograms of polypyrrole grown on: (a) Pt; (b) Fe; (c) Al at different scan speeds

**Table 4** Elemental analyses of polypyrroles grown on different metal electrodes

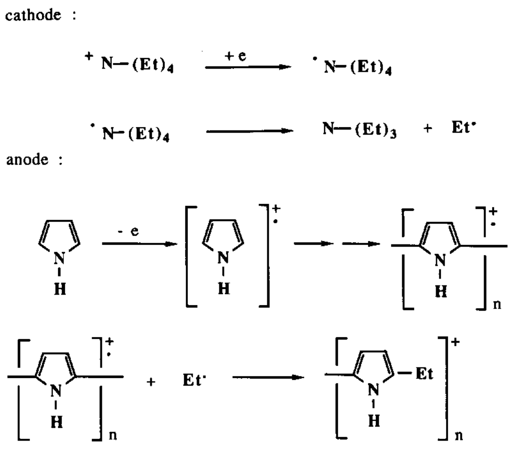
| Polypyrrole grown on | C | H | N | S | O[a] | Formula[b] | Total composition |
|---|---|---|---|---|---|---|---|
| Pt | 58.84 | 4.63 | 10.35 | 8.06 | 15.17 | $C_{4.29}H_{3.92}N_{1.00}(TS)_{0.34}$ | 97.05 |
| Pt (−11°C) | 56.86 | 4.83 | 8.82 | 7.96 | 17.05 | $C_{4.78}H_{4.93}N_{1.00}(TS)_{0.40}$ | 95.52 |
| Ti | 57.71 | 4.86 | 8.64 | 6.87 | 18.03 | $C_{5.31}H_{5.35}N_{1.00}(TS)_{0.34}$ | 96.11 |
| Mild steel | 57.23 | 4.96 | 8.58 | 7.62 | 18.23 | $C_{5.03}H_{5.36}N_{1.00}(TS)_{0.39}$ | 96.62 |
| Al | 56.82 | 4.96 | 8.49 | 7.95 | 18.96 | $C_{4.94}H_{5.31}N_{1.00}(TS)_{0.41}$ | 97.18 |
| Brass | 57.93 | 4.86 | 8.78 | 7.33 | 17.63 | $C_{5.10}H_{5.14}N_{1.00}(TS)_{0.37}$ | 96.53 |
| Pt (reduced) | 64.20 | 6.20 | 12.35 | 5.10 | 12.16 | $C_{4.79}H_{5.76}N_{1.00}(TS)_{0.18}$ | 100.21 |

[a] Direct measurements
[b] TS, toluenesulphonate

0.4). This implies that a more complex mechanism than that proposed in *Scheme 1* is involved. The carbon and hydrogen contents reported here are slightly higher than those reported elsewhere[12].

For Pt, the elemental analysis is the closest to the theoretical value. For the other electrodes, the proportion of C, H and O is relatively high. This suggests that the chain length, the chain structure and the amount of solvent trapped are different in each case.

The slight excess of C and H may be due to the reaction between the polymer in the oxidized form and the alkyl radicals produced at the cathode, resulting in the



Scheme 3 Probable mechanism for formation of alkyl terminating groups

Table 5 Excess C, H and O values for different metal electrodes used in the estimation of the amounts of propylene carbonate (pc) and $C_2H_5$ terminating groups

| | Excess formula | Estimate of no. of pyrrole eq. to 1 mol pc | Estimate of no. of pyrrole eq. to 1 mol $C_2H_5$ |
|---|---|---|---|
| Pt | $C_{0.29}H_{0.92}O_{0.25}$ | 14.3 | 200.0 |
| Pt (−11°C) | $C_{0.78}H_{1.93}O_{0.49}$ | 6.2 | 15.4 |
| Ti | $C_{1.31}H_{2.35}O_{0.69}$ | 4.4 | 5.0 |
| Fe | $C_{1.05}H_{2.36}O_{0.69}$ | 4.4 | 15.4 |
| Al | $C_{0.94}H_{2.31}O_{0.73}$ | 4.3 | 200.0 |
| Brass | $C_{1.10}H_{2.14}O_{0.64}$ | 4.7 | 8.0 |
| Pt (reduced) | $C_{0.79}H_{2.76}O_{0.31}$ | 9.8 | 5.7 |

formation of alkyl terminating groups (*Scheme 3*). Also, the solvent, propylene carbonate is assumed to be trapped[39] in the matrix of the polypyrrole film during electropolymerization (*Table 5*). In *Table 5*, the calculation of the amount of propylene carbonate was based on the excess O content obtained from the difference between the experimental and the theoretical $[C_4H_3N_1(TS)_x]$ elemental analysis values. Then the remaining C and H composition was used to estimate the alkyl terminating group concentration. The water content was ignored because the solvent was dried and the polypyrrole films which were peeled off the electrodes were washed with acetone and dried at 40°C *in vacuo*. In *Table 5*, we can see that from the estimation of the $C_2H_5$ terminating group concentrations, there are 10–400 pyrrole monomer units in the polymer chain. This estimate is lower than the one determined using tritium labelling[43]. The estimates of propylene carbonate and $C_2H_5$ terminating group concentrations have such a large range because of other variables which can affect the composition of the polypyrrole, such as the physical adsorption of oxygen and the oxidation of polypyrrole to form carbonyl groups, e.g. pyrrolidinone end groups (*Scheme 4*). In addition, hydrogenation and over-oxidation of the pyrrole moiety coincident with loss of nitrogen are possible but highly unlikely under the conditions employed here. The total elemental composition is not equal to 100% (see *Table 4*); the remaining 3–4% may result from traces of different metals attached to the polymer film in the form of pure metal or metal oxide.

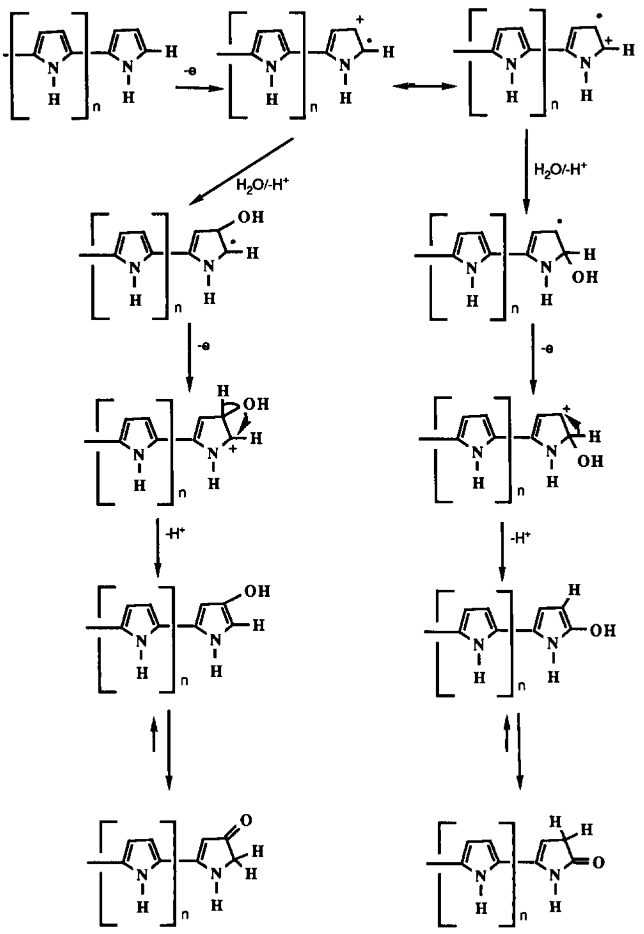
Finally, it can also be seen that the amount of toluenesulphonate anions present in the reduced polypyrrole films was less than that in the oxidized ones but was not zero. Thus, although the same amount of charge used to oxidize the films was also passed during the galvanostatic reduction, toluenesulphonate anions were still left in the film. It is possible that, during reduction, the polymer film swelled up and part of it was not in contact with the metal electrode, or that some of the counter-ions are strongly bound to the polymer; hence 100% reduction was difficult to achieve.

## Electrical conductivity

The conductivities of the polymers were measured by a four-prove technique, the current being supplied by a Farnell L30DT stabilized power supply and the voltage measured with a multimeter. The polymers were held tightly underneath four gold-coated copper strips and measurements were made in air, at room temperature. The conductivities obtained are all very similar and in the range 20–50 S cm$^{-1}$ (*Table 6*).

## Resonance Raman spectroscopy

Resonance Raman spectroscopy has proved to be a powerful method for the study of other conjugated polymers[38]. In principle, it provides a method for the characterization of polypyrrole films. In our previous paper[22], a detailed investigation was reported of Raman spectroscopy on polypyrrole grown on different



Scheme 4 Probable mechanism of formation of pyrrolidinone at the end groups of polypyrrole during electropolymerization

**Table 6** Physical form and conductivities of polypyrrole films prepared on different electrodes

| Electrode | Nature of product | Conductivity (S cm$^{-1}$) |
|---|---|---|
| Pt | Strong, dense, flexible | 48.5 |
| Pt (−11°C) | More elastic at first, then inflexible | 35.7 |
| Ti | Brittle, uniform, smooth | 22.0 |
| Al | Brittle, inflexible, rough | 27.5 |
| Brass | Ductile, flexible, tough | 25.0 |
| Mild steel | Brittle, inflexible, smooth | 44.6 |

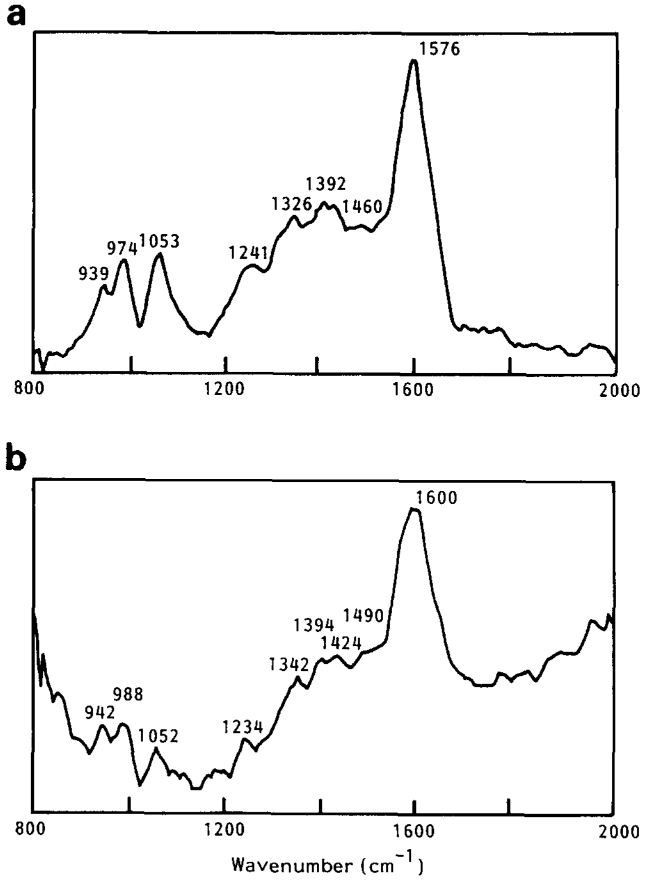


**Figure 5** Raman spectra of polypyrrole prepared on a Pt electrode recorded with laser excitation at 482.5 nm in: (a) oxidized form; (b) reduced form. These spectra have been smoothed by multipoint averaging to improve the signal-to-noise ratio

electrodes. In addition, there have been other reports of Raman spectra for polypyrrole[22–24].

Raman spectra of oxidized polypyrrole films grown on Pt, Ti, Al, mild steel and brass are very similar to those shown in *Figure 5(a)*. The general peak intensities are low. The band with the highest intensity at 1576 cm$^{-1}$ is assigned to the backbone stretching of the oxidized polymer. The Raman spectrum of the partially reduced polypyrrole film grown on Pt is shown in *Figure 5(b)*, in which the bands are less clearly resolved. This Raman experiment was carried out in ordinary atmosphere, and little attention was paid to the oxygen effect. The backbone stretching frequency was 1600 cm$^{-1}$, higher than that of the fully oxidized polypyrrole. This is to be expected because the electrons in the backbone are more delocalized in the oxidized form. Besides the backbone stretching band, other ring stretching bands (from 1340 to 1500 cm$^{-1}$), the weak NH in-plane deformation band (1053, 1052 cm$^{-1}$), the ring C–H in-plane deformation band (1241, 1234; 974, 988 cm$^{-1}$) and the ring C–H out-of-plane deformation band (939, 942 cm$^{-1}$) are also assigned (*Table 7*). These assignments were made on the basis of comparisons with the spectra of substituted pyrrole monomers[44] and deuterated polypyrrole films[45].

### *Film character and morphology*

All of the PPy–TS films grown on various metal electrodes were fully dense and showed no evidence at their surfaces or in the bulk of voiding. However, the flexibility and electrolyte surface character of the films differed significantly, as summarized in *Table 6*. In general, the material formed on Pt and brass electrodes was much more flexible than the others and appeared to be stronger. Higher current densities invariably lead to the formation of rougher films for a given electrode material, but aluminium and brass were more prone to producing rough globular surfaces.

Detailed SEM, to be reported at greater length separately, revealed that the materials exhibited fracture surfaces typical of glassy polymers but containing a fine microstructure below 0.1 $\mu$m which was also seen on growth surfaces. Such structures could arise from a colloid-like polymerization process at the polymer film growth surface. More surprisingly, a distinct separate phase was observed on the fracture surfaces and electrolyte surfaces of many films for all of the metal electrodes. However, the texture of this second phase varied dramatically for material formed on different metals, as illustrated in *Figures 6*, *7* and *8*. *Figure 6* shows the fibrillar structures found in materials polymerized on Pt and mild steel and the large and small fibril clustering which is commonly observed. *Figure 7* shows the more globular structures observed in materials polymerized on brass and *Figure 8* shows the highly connected microfibrils usually seen in materials polymerized on Al and Ti.

A further common feature is shown in *Figure 8*; this is the region immediately adjacent to the metal electrode surface which is devoid of any second phase. This region is usually about 2–5 $\mu$m thick and has a well defined boundary with the start of the second phase. The exact nature of this second phase is currently being investigated. Early results show that although it has an elemental composition similar to that of the bulk polymer, it is sulphur-rich and it is never observed in films which have been reduced. This second phase will probably influence bulk properties but we have not yet examined this aspect in detail.

**Table 7** Raman peak frequencies of oxidized and reduced polypyrrole–toluenesulphonate and their peak assignments

| Peak frequencies of polypyrrole (cm$^{-1}$) | | |
|---|---|---|
| Oxidized | Reduced | Peak assignments |
| 1576 | 1600 | C=C backbone stretching |
| 1460 | 1490 | Ring stretching |
| – | 1424 | Ring stretching |
| 1392 | 1394 | Ring stretching |
| 1326 | 1342 | Ring stretching |
| 1241 | 1234 | C–H in-plane deformation |
| 1053 | 1052 | N–H in-plane deformation |
| 974 | 988 | C–H in-plane deformation |
| 939 | 942 | C–H out-of-plane deformation |

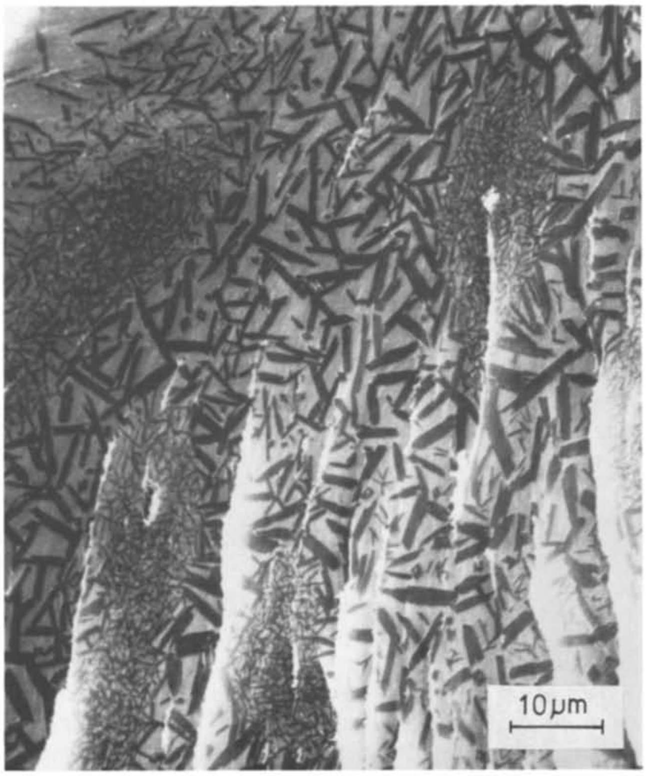


**Figure 6** Fibrillar structures of the second phase found in polypyrrole grown on mild steel

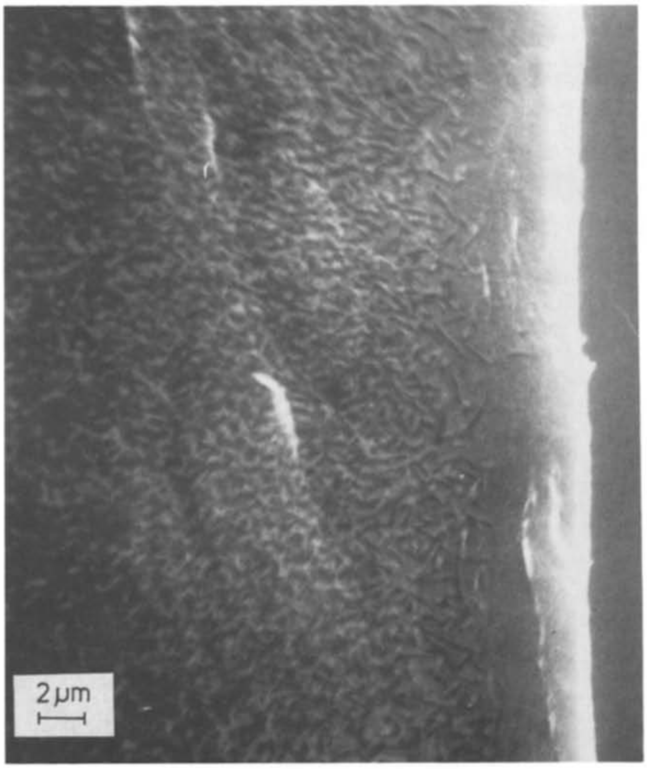


**Figure 8** Microfibrillar structures of the second phase found in polypyrrole grown on Al, and the second-phase deficient region adjacent to the electrode

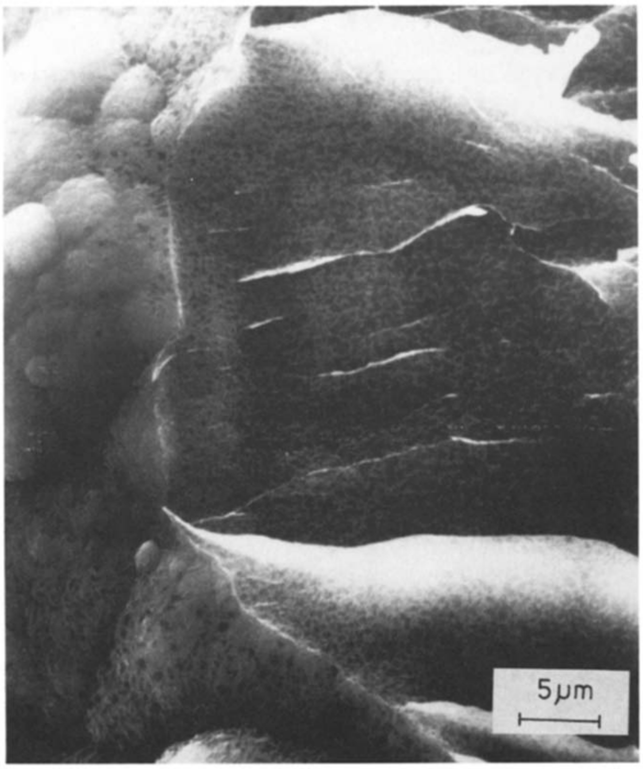


**Figure 7** Globular structures of the second phase found in polypyrrole grown on brass

## CONCLUSIONS

Polypyrrole–toluenesulphonate (PPy–TS) films can be electropolymerized on a wide range of metal electrodes. In comparison with Pt the oxidation potential of pyrrole is increased and the current intensity reduced when Ti, Fe and Al are used. This is a consequence of metal–oxide film formation which impedes electron transfer during electropolymerization. Brass is unusual in that the presence of an oxide film is necessary for electropolymerization to proceed. The redox potentials of PPy–TS films are different in each case. Materials polymerized on these metal electrodes display behaviour typical of quasi-reversible reactions. In the case of Pt, the redox reaction is diffusion-controlled, whereas in the other cases, the redox reactions appear to be controlled by both diffusion and adsorption processes. In spite of these differences, the electrical conductivities of fully oxidized free-standing films at room temperature are in the range 20–50 S cm$^{-1}$, and are independent of the nature of the electrode.

Uncertainties still exist regarding the exact chain structure of electropolymerized polypyrrole. While it is not possible to identify the exact chain or network structure using Raman spectroscopy, the spectra observed for PPy–TS produced on the different electrodes studied here are very similar. Distinct differences have been observed, however, for polymerization at low temperatures and on Si electrodes[22]. Elemental analysis suggests that there is an excess of C and H over that expected for an idealized chain structure. This can be accounted for if chain-terminating or $\beta$-coupled alkyl groups are present. Differences were observed in the general character and morphology of the materials produced on different electrodes. The morphological differences relate to the presence of a well defined second phase which is present in fully oxidized materials and ranges from well separated fibrils in material polymerized on Pt and mild steel to microfibrillar clustering on Al and Ti, and globular structures on brass.

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