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Conductivity measurements of electrodeposited polypyrrole

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Thick, freestanding, flexible films of polypyrrole have been prepared from propylene carbonate solutions of pyrrole monomer containing tetra-ethyl ammonium *p*-toluene sulphonate electrolyte. The conductivity of the films was found to vary with orientation of the sample, deposition temperature and time. Conductivities of up to 338.4 S cm^{-1} were attained with samples prepared at 0°C. XRD analyses have revealed a difference in structure with sample orientation which affects the conductivity of the material significantly.

1. Introduction

There has been much interest in the area of conducting polymers over the last decade, with many new conducting polymers being synthesized. There are numerous applications for these materials, such as in electrocatalysis [1, 2], in antistatic coatings [3], in batteries [4–6] and in semiconductor stabilization (7–9].

One of the most widely studied conductive polymers is polypyrrole (PPyr). This material exists in two general forms, the first being the neutral, unstable and insulating form (reduced state). The second is the oxidized form which is stable, very conductive and easily prepared by electrodeposition of the monomer solution [7, 10].

The properties of PPyr films vary greatly with the conditions under which they are prepared. The main conditions affecting the polymer properties are thought to be: electrolyte type and concentration, potential [11], current density [12], pH [13], temperature [14] and the overall solution composition, this being illustrated by the many different 'recipes' used to produce PPyr films. Thus, PPyr films have been grown in aqueous solutions [9], molten salts [5] and in a variety of organic solvent systems [9, 10].

The most commonly used organic system consists of acetonitrile with 1% water as solvent, with 0.1 M tetra-ethyl ammonium tetrafluoroborate $(C_2H_5)_4N^+BF_4^-$ electrolyte and the pyrrole monomer in the concentration range 0.06–1.0 M. Other electrolytes which have been employed are tetra-ethyl ammonium perchlorate, tetra-butyl ammonium perchlorate and tetra-ethyl ammonium paratoluene sulphonate. Salmon *et al.* [10] used a large range of electrolytes containing the anions BF_4^-, PF_6^-, AsF_6^-, ClO_4^-, HSO_4^-, FSO_3^-, $CF_3SO_3^-$, $BrC_6H_4SO_3^-$, $CH_3C_6H_4SO_3^-$ and CF_3COO^-.

In place of the common tetra-alkyl ammonium salts, silver salts have also been used as the electrolyte [11]. Other organic solvents which have been employed are methylene chloride [9] and propylene carbonate [15].

The anion employed in the preparation of PPyr films has been shown to be incorporated in the deposited film. Thus, when pyrrole polymerization is conducted at 0.8 V versus saturated calomel electrode (SCE), the resulting film has been found to consist of an anion to pyrrole ratio of 1 : 3 to 1 : 4 units, with the anion making up 30–40% of the final weight of the polymer.

The conductivity of the polymer materials is one of the most important properties for most electrochemical applications. PPyr shows a large variation in conductivity between the neutral

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and oxidized state. Thus in the neutral insulating state, the conductivity is less than $10^{-5}\,S\,cm^{-1}$ [11] while in the oxidized, very conducting form, conductivities in the range 10–300 $S\,cm^{-1}$ have been reported [16–20]. Deposition temperature has been shown to affect the conductivity of PPyr films strongly. Thus, films grown at 20°C exhibited conductivities of 97 $S\,cm^{-1}$, while at −20°C the conductivity increased dramatically to 287 $S\,cm^{-1}$ [15]. Other factors which have been found to affect conductivity are the nature and amount of the anion incorporated in the structure [10, 21], pH of the polymerization solution [13], current density [13] and deposition potential [11].

From the above, it can be seen that the properties of conducting PPyr films are influenced by a large number of variables. In the present study, several variables have been investigated with a view to preparing thick, free-standing films of PPyr with both good flexibility and conductivity.

2. Experimental details

PPyr films were prepared by electropolymerization in various solutions. A simple one-compartment cell was employed, with a carbon cathode and a platinum or titanium strip as anode. The substrates were polished with 1200 grit SiC emery paper and then suspended vertically in the solution at a distance of 2 cm from the cathode. Polymerization solutions consisted of pyrrole monomer (Merck, Schurchardt) dissolved in either 1 M H_2SO_4 or propylene carbonate (Merck, Schurchardt) and containing one of the following electrolytes at a concentration of 0.05 M: $K_3Fe(CN)_6$, sodium n-lauryl sulphate, DECOL W482 (mixture of dodecyl benzene sulphonate and other undisclosed compounds; Harcros Chemicals) or tetra-ethyl ammonium *p*-toluene sulphonate (Alfa Products).

Electrodeposition was carried out at a constant potential within the range 0.8 to 1.0 V versus SCE. The current ranged from 0.3 to 1.0 $mA\,cm^{-2}$ and deposition times of around 36 h were required to produce films 0.2 mm thick.

The deposited material was removed from the substrate with a scalpel and subjected to various tests. The four-probe technique using the Van der Paw method was employed to measure the conductivity of the deposited material [22]. Conductivities were measured both along the sample (i.e. parallel to the strip length) and across the sample (i.e. perpendicular to strip length).

A Rigaku diffractometer was employed for X-ray diffraction measurements and scanning electron micrographs were obtained with a Jeol JSM/U3 scanning electron microscope equipped with a back-scatter detector.

3. Results and discussion

Several electropolymerization solutions, both aqueous and non-aqueous, were employed in an attempt to produce thick, even and flexible films of polypyrrole.

3.1. *Aqueous systems*

Two types of aqueous systems were employed. The first solution consisted of $K_3Fe(CN)_6$ and pyrrole dissolved in 1 M H_2SO_4. Deposition was carried out at 0.8 V versus SCE for periods up to 24 h using both platinum and titanium sheets as anode. The films produced had a powdery appearance and could be easily wiped off. On standing, the solution changed from an initial yellow colour, through to green and then became black, containing a suspension of black particles. Pyrrole is thus seen to be unstable in acidic solutions, tending to polymerize in solution without the application of a voltage. This has been attributed by other workers [23] to the acid-catalysed polymerization reaction of pyrrole to saturated oligomers.

The second aqueous system employed was a solution of sodium n-lauryl sulphate and pyrrole in H_2SO_4. The films produced in this system were very brittle and crumbled easily on removal from the substrate.

3.2. *Organic systems*

The organic system employed consisted of propylene carbonate containing 0.14 M pyrrole, 1% water and one of several electrolytes which were introduced at a concentration of 0.05 M.

Fig. 1. Scanning electron micrograph of polypyrrole film grown at 25°C in propylene carbonate/tetra-ethyl ammonium *p*-toluene sulphonate system. × 43.

The films were prepared by electrodeposition at a constant potential of 1.0 V vs SCE. The following electrolytes were employed in the deposition solutions: $K_3Fe(CN)_6$, sodium n-lauryl sulphate, DECOL W482, and tetra-ethyl ammonium *p*-toluene sulphonate.

Films produced with tetra-ethyl ammonium *p*-toluene sulphonate as electrolyte exhibited the best properties, all other electrolytes yielding films which were either brittle or powdery and which did not adhere well to the substrate. All further studies were therefore carried out with tetra-ethyl ammonium *p*-toluene sulphonate as electrolyte. Uniform films of up to 1 mm in thickness could be produced from this polymerization solution. Fig. 1 is a scanning electron micrograph of a typical polypyrrole toluene sulphonate layer and illustrates the 'cauliflower' texture of the deposited material. Samples were grown at both room temperature and at 0° C and all had a similar cauliflower appearance when observed under the microscope.

The conductivity of the polypyrrole films was initally measured within 30 min of removal from the deposition solution. Measurements were made in both directions and were also taken every few days to determine any variations with time. Fig. 2 shows the conductivity of a polypyrrole film, 0.2 mm thick, grown at room temperature as a function of time. A slight difference in the conductivity can be observed with orientation of the sample. The conductivity is seen to increase within the first few days and then level off. In this particular instance, a slight decrease in the 'across sample' readings is evident for storage times over 25 days. The increase in conductivity with time during the first few days is believed to be due to the decrease in moisture–solvent content of the films on standing. The slight decrease in conductivity after long storage times is thought to be due to oxygen attack of the conjugated double-bond system.

For samples grown at 0° C, not only are the conductivity values much higher, but the variation in conductivity with orientation was also found to be more pronounced, as illustrated in Fig. 3. This variation with direction was initially thought to be due to preferential orientation of the polymer chains along scratches on the

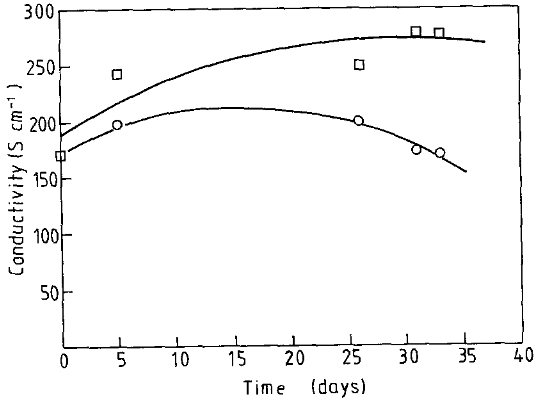

Fig. 2. Conductivity of polypyrrole films versus time. Deposition temperature 25°C. □, 'Along' sample; ○, 'across' sample.

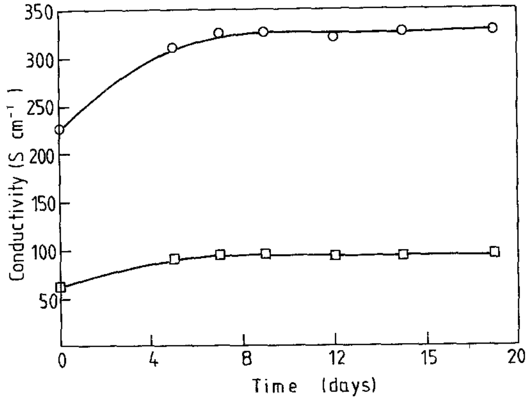

Fig. 3. Conductivity of polypyrrole films versus time. Deposition temperature 0°C. ○, 'Along' sample; □, 'across' sample.

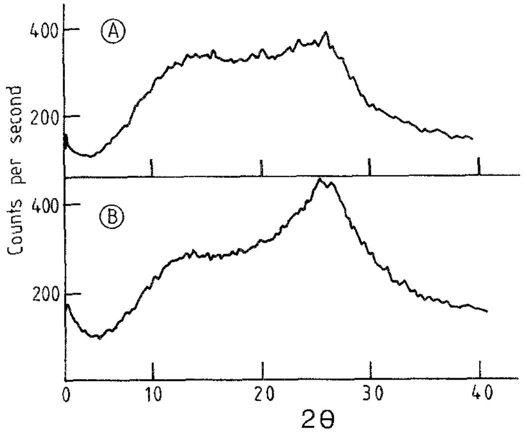

Fig. 4. X-ray diffraction spectra of polypyrrole (a) Film grown at 0°C. (b) Film rotated through 90°C.

substrate surface resulting from the mechanical polishing.

Titanium strips were therefore mechanically polished with emery paper, both in a direction parallel to and perpendicular to the strip length. An electrical contact was made at one end and the strips were positioned vertically in the electrochemical cell. Thick polypyrrole films were grown on each strip and, after removal from the substrate, were each measured for conductivity. In each case the conductivity was much higher 'along' the sample than 'across' the sample, indicating that this behaviour is not related to the surface treatment of the substrates.

As a check for anisotropy of the electrodeposited polypyrrole material, X-ray diffraction spectra were obtained for different orientations of the samples. Fig. 4A shows the X-ray diffraction spectrum for a polypyrrole film grown at 0° C, and shows the essentially broad pattern characteristic of an amorphous material. Fig. 4B shows the spectrum obtained when the same sample was rotated through 90° in the sample holder. A much sharper peak can now be observed around 20 = 25.4°, (corresponding to a D-value of 3.51) indicating a higher degree of structural order in this direction. The D-value of 3.510 Å has been attributed to the scattering from pyrrole chains at interplanar spacings close to the van der Waals distance for aromatic groups [24].

The different structural order with direction which is indicated by XRD is also consistent with the conductivity measurements which give much higher conductivity values 'along' the sample than 'across' the sample. Thus the more ordered structure would allow more efficient transfer of electrons through the material, giving higher conductivity in that direction. Evidence for anisotropy has also recently been reported by Mitchell [25].

It is not as yet clearly understood why the structural order of the material varies with direction. The way the polypyrrole chains grow and how the pyrrole monomer orientates itself before polymerizing onto the chain ends may be influenced by the electric fields within the cell. The dramatic increase in conductivity with decreasing electrodeposition temperature is also difficult to explain at this point, but also indicates a higher degree of structural order at the lower temperature. Ogasawara *et al.* [14] also noted an increase in conductivity at the lower temperature and suggested that this is due to higher conjugation within the polymer backbone.

The other interesting effect of temperature (noted in Fig. 3) is that at the lower deposition temperature, the ratio of conductivity 'along' the sample to conductivity 'across' the sample is much larger than at the higher temperature, where it is closer to unity (Fig. 2). The more ordered structure which results at lower temperatures thus produces a material which is more conductive in one direction. This attribute, if fully developed, could allow a material to be produced which will be highly conductive in one direction and insulating in other directions. This could open up a whole new range of applications for these materials which has previously not been considered.

4. Conclusions

Thick, flexible and highly conductive free-standing polypyrrole films have been grown from propylene carbonate solutions of pyrrole containing tetra-ethyl ammonium p-toluene sulphonate as supporting electrolyte. The conductivity of the polymer was found to increase for lower deposition temperatures and was also seen to be a function of sample orientation. The lower temperatures also gave rise to much greater differences in conductivity with sample orientation, this suggesting a certain degree of anisotropy which is supported by X-ray diffraction results.

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