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Studies of pyrrole black electrodes as possible battery positive electrodes

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It is shown that a polypyrrole, pyrrole black, may be formed anodically in several aqueous acids. The polypyrrole film shows a redox couple at less positive potentials than that required to form the film and the charge associated with these reduction and oxidation processes together with their stability to cycling varies with the anion in solution and the potential where the polypyrrole is formed; over-oxidation of the film caused by taking its potential too positive has a particularly disadvantageous affect. In the acids HBr and HI, the polypyrrole films can act as a storage medium for Br_2 or I_2 so that they may be used as a substrate for a X_2/X^- electrode. Such electrodes may be charge/discharge cycled and the pyrrole/Br_2 electrode shows promise as a battery positive electrode.

1. Introduction

The electrosynthesis of conducting organic polymers and the study of their electrochemical properties has become a very common activity. One application of such materials would be in energy storage since the polymer could combine the rôles of electroactive species and current collector. For example, a battery based on polyacetylene has been described [1]. Indeed a rechargeable device based on aniline black dates back fifteen years [2]; both electrodes were made of polyaniline, one in its oxidized form and the other in its reduced form, and although the cell voltage and energy density were inevitably low, the polymer electrodes operated successfully.

Recently, polypyrrole has been studied intensively [3–7]. The anodic oxidation of pyrrole under a variety of conditions has been shown to lead to a polymer film which may be driven between the oxidized and reduced state but, because the reduced state is only poorly conducting, such polypyrroles are not appropriate material for secondary batteries. On the other hand it has been reported that chemical oxidation of pyrrole in aqueous acid [8, 9] leads to a pyrrole black with properties close to aniline black. Moreover there is a single report [10] that a similar material may be prepared by galvanostatic oxidation of pyrrole in H_2SO_4. Hence the purpose of this study was to examine in greater detail the oxidation of pyrrole in aqueous acids and to use cyclic voltammetry as a preliminary probe as to the performance of pyrrole blacks as battery positive electrodes. It will be shown that the behaviour of the polypyrrole electrodes depends strongly on the potential used for their preparation and the anion present in solution.

2. Experimental details

The electrochemical experiments were carried out with standard three electrode cells. Voltammetry used a vitreous carbon disc electrode, area 0.075 cm^2, while the synthetic experiments used platinum or gold sheets area 20 cm^2; much higher adhesion was obtained for the films to the carbon surface. The reference electrode was always a SCE.

Product analyses were carried out by standard methods. The pyrrole blacks sent for elemental analyses were scraped from the platinum or gold anode into a filter funnel, washed with 500 cm^3

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distilled water and then dried in a vacuum at a room temperature for 8 h.

The chemicals were all used as supplied. Pyrrole is not totally stable in acid solution due to polymerization to deeply coloured products [11–13]. The timescale of such reactions is, however, long compared to any experiment reported in this paper.

3. Results and discussion

3.1. *Aqueous sulphuric acid*

Fig. 1 shows a series of cyclic voltammograms for a solution of pyrrole (7.2×10^{-2} mol dm^{-3}) in H_2SO_4 (1 mol dm^{-3}) at a vitreous carbon electrode; the potential scan rate is 50 mV s^{-1}. On the first scan towards positive potentials, a well-formed oxidation peak is observed at + 0.8 V vs SCE (total anodic charge 120 mC cm^{-2}) but on repetitive cycling this peak rapidly diminishes and on the 4th cycle is almost totally absent indicating that the surface has become passivated. The cyclic voltammograms also show a cathodic peak ($E_p \triangleq 0.05$ V and charge 10 mC cm^{-2}) and a coupled anodic peak at $E_p \triangleq 0.3$ V and these redox processes of the film formed in the initial anodic peak diminish more slowly. Similar series of cyclic voltammograms showed that polymer was formed in all acid concentrations but the extent of passivation in subsequent cycles was a strong function of both the H_2SO_4 concentration and the anodic limit of the cycle.

This behaviour is also reflected by the data in Table 1 which reports the charge passed during the first 180 s of oxidation of pyrrole at a series of potentials and in several aqueous H_2SO_4 solutions. It can be seen that this anodic charge varies between 200 and 2000 mC cm^{-2} and is lowest under the most oxidizing conditions, i.e. high H^+ concentration and high potential. Conversely, the largest charge is observed at 0.125 mol dm^{-3} H_2SO_4 and at potentials of 0.75 to 0.80 V, values prior to the peak on the cyclic voltammogram of Fig. 1. We believe that under strongly oxidizing conditions the film of polypyrrole undergoes a change in structure, e.g. more extensive cross linking or more likely ring opening which breaks the conjugation and thereby degrades its ability to conduct. Hence material suitable for battery applications is more likely to be formed at a lower potential and in dilute H_2SO_4. When, in fact, a polypyrrole layer was formed at + 0.80 V in a solution of 70 mmol dm^{-3} pyrrole and 0.25 mol dm^{-3} H_2SO_4 and then potential cycled between − 0.4 V and + 0.8 V in a solution containing only acid, well formed peaks for the redox properties of the film could be observed. The charge which could be cycled was approximately 8% of that consumed in the initial preparation of the film and this charge only diminished very slowly on repetitive cycling.

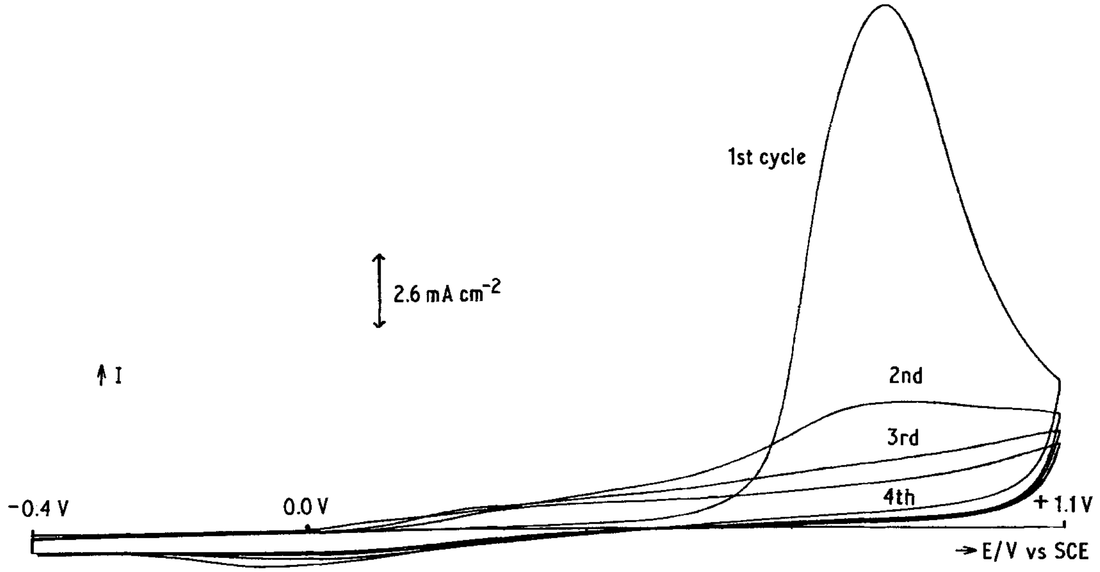

Fig. 1. Repetitive cyclic voltammograms for a solution of pyrrole (70 mmol dm^{-3}) in H_2SO_4 (1 mol dm^{-3}). Potential sweep rate 50 mV s^{-1}.

Table 1. Charge passed during the first 180 s of oxidation of pyrrole (70 mmol dm^{-3}) in various concentrations of H_2SO_4. Vitreous carbon anode. Potential stepped from − 0.4 V

E (V vs SCE)	*Charge* (C cm^{-2})				
	0.05 mol dm^{-3} H_2SO_4	0.125 mol dm^{-3} H_2SO_4	0.25 mol dm^{-3} H_2SO_4	0.50 mol dm^{-3} H_2SO_4	1.00 mol dm^{-3} H_2SO_4
0.70	0.69	0.92	1.04	1.04	1.11
0.75	1.25	1.39	1.49	1.60	0.91
0.80	1.69	1.71	1.48	1.31	0.86
0.90	0.59	0.57	0.68	0.62	0.49
1.00	0.46	0.71	0.85	0.59	0.40
1.10	0.44	0.56	0.94	0.50	0.21
1.20	0.57	0.80	0.98	0.68	0.18

Conversely if the anodic limit was increased to + 1.0 V, a new well defined oxidation peak, $E_p \simeq 0.9$ V, was seen only on the first positive going sweep and there was a rapid decrease in the charge associated with the redox cycling of the polymer at less positive potentials. Again it appears that taking the potential to + 1.0 V leads to overoxidation of the film and a degradation of its electrical properties.

Further evidence for the redox cycling of the polymer and the influence of the state of oxidation of the polymer film was obtained by measurement of the open circuit potential of the films after three pretreatments, one reductive and two oxidative at different potentials. The potentials were not completely stable and the data is reported for three times in Table 2.

Electrolytic oxidations of pyrrole were carried out at large platinum and gold anodes. After the passage of 50 to 100 C cm^{-2} the polymer film was weighed and in some cases it was also subjected to micro-analysis. The results, in terms of the weight of pyrrole black formed/coulomb and the mean molecular formulae are reported in Table 3. It was also shown that the yield of a polymer increased linearly with the charge passed. In fact, a much wider range of electrolysis conditions were investigated, but although the length of time required for the passage of 50 C cm^{-2} reflected the data of Table 1, it was not possible to discern any trend in polymer yield. It was, however, found from the elemental analyses that the N/C ratio decreases with increasing potential. The values were 1.0/4, 0.97/4 and 0.94/4 at 0.75, 0.95 and 1.10 V, respectively. These changes may appear small but will occur by ring opening (and hydrolysis leading to loss of nitrogen atoms) and will lead to a loss of conjugation which will affect strongly the conductivity of the polymer.

The yields of polypyrrole black and assuming that the polymer has the mean structures reported in the table, would lead to the conclusion that 3 to 4 electrons/molecule pyrrole is involved in the anode reaction. A simple coupling of the rings

Table 2. Open circuit potentials for polypyrrole electrodes after three pretreatments. The polypyrroles were prepared on vitreous carbon by passing 4 C cm^{-2} in a solution of pyrrole (70 mmol dm^{-3}) in the acid shown and then polarized at the three potentials (400–700 mC cm^{-2}) in the solution of the acid alone. Potentials in V vs SCE. The weight of polypyrrole formed averaged 0.1 g

Medium (mol dm^{-3})	*Open circuit potentials after t(s)*								
	After oxidation at 0.8 V			*After oxidation at* + 1.0 V			*After reduction at* − 0.40 V		
	30	300	600	30	300	600	30	300	600
H_2SO_4 (0.25)	0.61	0.51	0.44	0.63	0.54	0.50	−0.09	−0.04	−0.01
HCl (0.50)	0.69	0.61	0.57	0.65	0.55	0.50	−0.15	−0.10	−0.07
HBr (0.50)	0.73	0.66	0.63	0.75	0.70	0.68	−0.19	−0.10	−0.07
HI (0.10)	0.32	0.30	0.29				−0.29	−0.14	−0.09

Table 3. Yields from the anodic oxidation of pyrrole (70 mmol dm^{-3}) in aqueous acids and molecular formulae of product based on C, H, N, S, Br, Cl microanalysis

Acid (mol dm^{-3})	*Anode*	*Potential* (V vs SCE)	*Yield polypyrrole* (mg C^{-1})	*Molecular structure based on elemental analysis*†
H_2SO_4 (0.25)	Pt	0.75	0.28	$C_4H_{2.9}N(SO_4)_{0.15}O_{1.1}$
	Au	0.75	0.27	
HCl (0.5)	Pt	0.75	0.29	$C_4H_{2.3}NCl_{0.4}O_{0.99}$
	Au	0.95	0.31	
HBr (0.5)	Pt	0.75	0.37	$C_4H_{3.15}NBr_{0.8}O_{1.1}$
		0.95	0.37	$C_4H_{3.35}NBr_{0.8}O_{1.0}$
HI (0.5)	Pt	0.75	–	$C_4H_{1.7}N_{0.95}I_{1.07}O_{0.5}$
H_2SO_4 (0.25)/HBr (0.5)*	Pt	0.75	0.28	$C_4H_{2.3}N_{0.97}Br_{0.71}(SO_4)_{0.10}O_{1.32}$

* Polymer formed in H_2SO_4 at 0.75 V then anodized in HBr at 0.75 V.
† Elemental analyses normalized to C_4.

requires 2 electrons/pyrrole and the excess charge corresponds to either cross coupling of the chains or further oxidation to quinoid structures (note excess oxygen is present in the structure). It should also be noted that the oxidation leads to the formation of proton and the sulphate in the film may be present as sulphuric acid bonded to the nitrogen atoms. A detailed interpretation of the reactions involved in the polymerization of pyrrole and in the redox reactions of the polymer film is, however, totally hampered by a lack of knowledge of the structure of the film. This, however, is also the case with pyrrole blacks formed chemically. For the purposes of comparison the elemental composition of polypyrrole blacks formed by persulphate oxidation of pyrrole were also determined. The structures were apparently identical to the ones formed electrochemically. The similarity is not restricted to elemental composition since it has been reported that the conductivity of pressed pellets (10 tons in^{-2}) of polymer decreased dramatically as the ratio $S_2O_8^{2-}$/pyrrole used in their preparation was increased [8, 9]. Also the elemental analysis showed the *N/C* ratio to decrease with increasing persulphate to pyrrole ratio; when the persulphate/pyrrole ratio was 0.25, the *N/C* ratio was 0.99/4 while when the ratio was 1.0, the *N/C* ratio was 0.96/4. For a low $S_2O_8^{2-}$/ pyrrole ratio, the conductivity found was 1 Ω^{-1} cm^{-1}.

3.2. *Aqueous HCl, HBr and HI solutions*

The cyclic voltammograms in the hydrochloric acid medium were similar to those discussed above. The changes with cycling of the potentials, however, occurred more slowly and the data in Tables 2 and 3 for this system show small but interesting changes. Firstly, after oxidation the open circuit potential takes up a higher value while it is clear from the elemental analyses that more chloride than sulphate is to be found in the film. Quite clearly, however, there is no major breakdown of the film as might be expected if chlorine were, for example, to add across double bonds.

When the study was extended to HBr solutions it was immediately clear that a pyrrole black could still be formed and that the Br^-/Br_2 oxidation does not inhibit the reaction. Indeed the potential for pyrrole oxidation is the same as in H_2SO_4 and HCl solutions. The other major feature of these curves is the reduction peak at + 0.6 V which is particularly prominent if the potential is taken, or better held constant, well positive to the peaks. This peak is due to the reduction of bromine or tribromide to bromide. The redox processes for the polypyrrole film are still observed in this medium; for example when a film formed at + 0.8 V was cycled in 0.5 mol dm^{-3} HBr between − 0.4 V and + 0.8 V, the redox couple could clearly be seen and the charge under the peaks was of the order of 20% of that used in the polymer synthesis. Moreover the change could be cycled many times before significant loss of charge was observed. In this medium the polymer was also more resistant to irreversible overoxidation although the Br^-/Br_2 peak appears as soon as the potential is taken more positive than + 0.8 V. The film could, however, be damaged by taking its potential too positive. For example, after prolonged oxidation at + 1.15 V the peaks for the redox couple were much reduced and more surprisingly the Br_2/Br^- reduction peak was almost totally missing.

These data would suggest that the polypyrrole films may be suitable substrates for bromine positive electrodes in, for example, a Zn/Br_2 battery. With this application in mind a number of further features should be noted.

(i) When a polypyrrole film was held at 0.8 or 1.0 V in HBr and then its open circuit potential determined, it is clear that the electrode takes up a value more positive than that achieved in H_2SO_4 media. The potential is determined by the Br^-/Br_2 couple (see Table 2).

(ii) When a film is formed in HCl solution and then cycled in HBr the peak at + 0.6 V for the Br_2/Br^- process appears slowly. Conversely if the film is formed in HBr and then cycled in HCl the peak disappears only slowly. On the other hand the size of the Br_2/Br^- peak is less affected by prolonged immersion (in either HBr or HCl) without cycling.

(iii) When films of increasing thickness were prepared, the charge for the Br_2/Br^- reduction peak increased almost linearly. With thick films, however, there is a kinetic problem and to obtain well shaped peaks, it is necessary to use a slow potential scan rate.

(iv) The preparative experiments, Table 3, show that the polymer yield is higher in HBr than H_2SO_4 media. The polymer yield increases linearly with charge, Fig. 2. Moreover, the elemental analysis suggests that the pyrrole ring/bromine atom ratio approaches 4:3, maybe due to the presence of one tribomide ion/pyrrole ring; the elemental analysis did not vary with the charge passed during the synthesis and a similar polymer film could be achieved by formation of the film in H_2SO_4 solution, followed by prolonged oxidizing at + 0.75 V in HBr (see also Table 3).

The polypyrrole films were also formed and studied in HI solution. Although the I^-/I_2 couple is less positive than the potential for the formation of polypyrrole, in some solutions (e.g. 0.1 mol dm^{-3} pyrrole, 0.1 mol dm^{-3} HI), a pyrrole black is still formed. Again after formation of the film, it takes up an open circuit potential expected for the halogen couple. With I_2/I^- this potential is of course less positive, see Table 2. Fig. 3 demonstrates the displacement of one halogen by another in the polypyrrole film. The film was formed in HI media and then cycled in 0.5 mol dm^{-3} HBr. It can clearly be seen that the I_2/I^- reduction peak at + 0.35 V diminishes on cycling while the Br_2/Br^- peak at + 0.6 V increases.

Finally it is interesting to note that bromine is not readily incorporated when the polypyrrole is formed by chemical oxidation with persulphate in

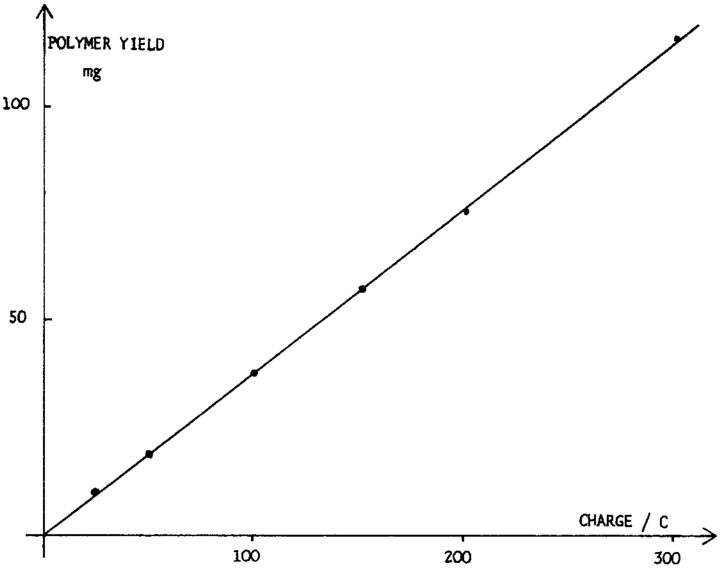

Fig. 2. Plot of polypyrrole yield at Pt as a function of charge passed. Solution pyrrole (70 mmol dm^{-3}) + HBr (0.5 mol dm^{-3}). Potential + 0.8 V vs SCE.

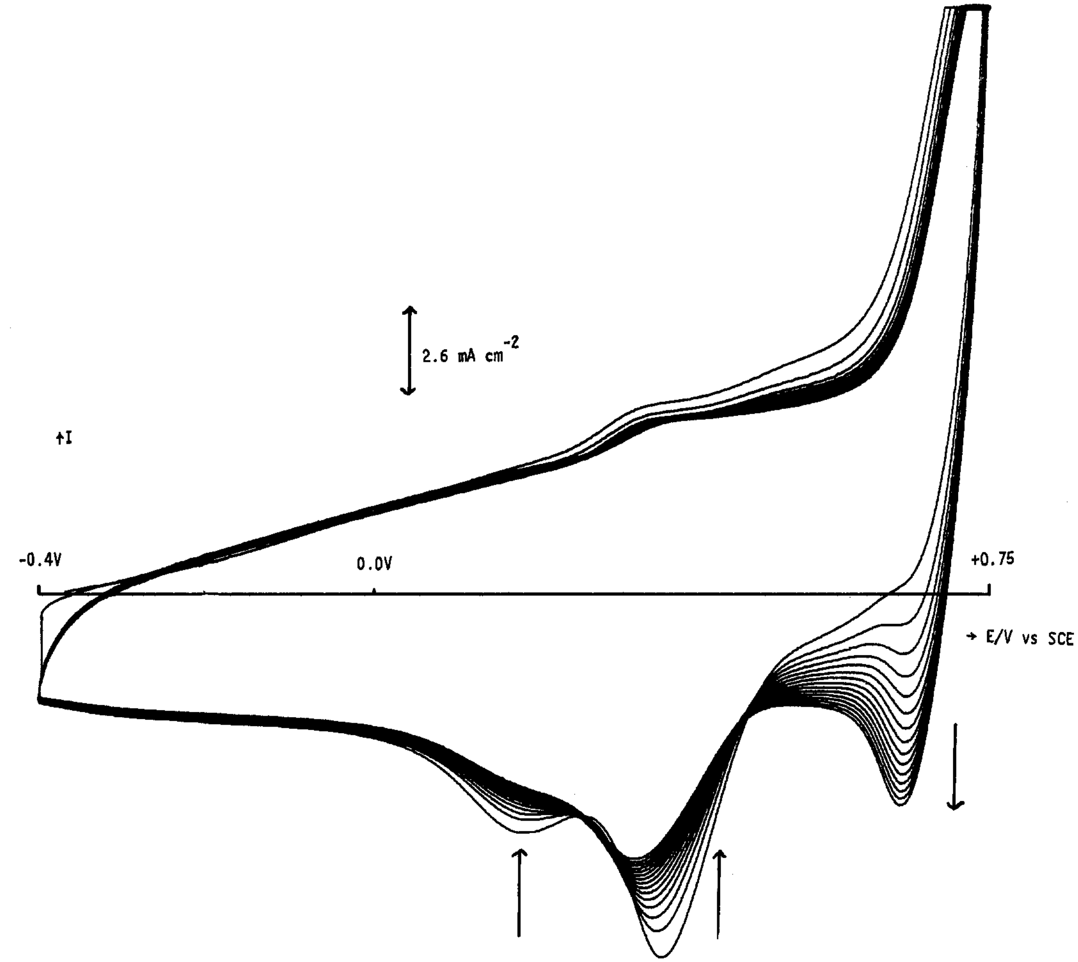

Fig. 3. Repetitive cyclic voltammograms for a polypyrrole film formed in a solution of pyrrole (70 mmol dm^{-3}) in HI (0.5 mol dm^{-3}) and then cycled in a solution of HBr (0.5 mol dm^{-3}). The arrows indicate the ways in which the voltammograms change with cycling. Potential scan rate 20 m V s^{-1}.

HBr solution. The elemental analysis of this polymer gave a structural formula $C_4H_{3.2}N Br_{0.1}(SO_4)_{0.13}O_{0.5}$,

4. Conclusions

The results presented here show that pyrrole blacks can be formed in several aqueous acids. Each shows a redox couple at lower potentials and the charge associated with this couple is significant and can be cycled several times. The polymer film is damaged if its potential is taken too positive and the resistance of this film to overoxidation depends on the anion in solution.

More interesting from a battery viewpoint, the polypyrrole seems to provide a medium for the storage of bromine and the polypyrrole/bromine electrode may be cycled several times. Before, however, these electrodes can be assessed for battery applications, longer term tests are essential. The films prepared anodically may have a similar structure to that prepared chemically and doped with Br_2 vapour [14]. In such polymers, however, the bromine was largely present as Br^- and may therefore more reasonably be equated with the reduced form of the film (with respect to the Br_2/Br^- couple).

Throughout this and other studies there is a correlation between the *N/C* ratio and either the conductivity of the polymer or its ability to store charge. This has been noted above with respect to both anode potential and persulphate/pyrrole ratio in chemical preparations (see also [9]). Diaz *et al.* [14] have described the preparation of a pyrrole black with a *N/C* ratio of 0.8/4 and described the material as an insulator. It should also be noted that the more stable films formed in HCl and HBr the elemental analysis showed the N/C ratio to be 1/4. This emphasized the importance of a highly conjugated structure for any polypyrrole to have a practical use.

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