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Poly(pyrrolium tosylate) formation on a mercury anode in the presence of halide ions

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A study of poly(pyrrolium tosylate) by cyclic voltammetry in the presence of bromide and chloride ions has facilitated the determination of the oxidation potential of pyrrole on mercury. Elemental analysis and scanning electron microscope examination of a large film produced in the presence of potassium bromide indicate that any mercury formed by the anodic oxidation is removed as crystalline mercurous bromide, while about one-eighth of the tosylate dopant is replaced by bromide ions.

(Keywords: poly(pyrrolium tosylate); cyclic voltammetry; halide ions; oxidation potential; mercury)

INTRODUCTION

In a previous publication we have demonstrated that doped polypyrrole can be formed on a mercury anode in an aqueous system, resulting in flexible, free-standing films of acceptable appearance and conductivity[1]. However, it was then pointed out that a major disadvantage of mercury anodes is their ease of oxidation at potentials concurrent with those of pyrrole. We now plan to study the electrochemical polymerization of pyrrole by cyclic voltammetry in the presence of halide ions. The presence of halide ions was demonstrated by us, qualitatively, to reduce the interference due to the anodic oxidation of mercury, by removing mercurous ions as insoluble halides, thus facilitating the direct observation of the pyrrole oxidation peak by cyclic voltammetry.

A previous study by Mengoli *et al.*[2] reports on the formation of polypyrrole in aqueous halogen acids on noble metal electrode and on vitreous carbon.

EXPERIMENTAL

Pyrrole (Aldrich) was doubly distilled and stored under nitrogen at 0°C. Prior to use it was further purified by passing down a neutral alumina column under nitrogen. Mercury was purified by acid washing, rinsing first with water, then with alcohol prior to drying at 110°C and subsequently double distillation under reduced pressure.

Cyclic voltammetry experiments were conducted in a glass beaker. A glass syringe attached to a narrow nylon tube created an inverted hanging mercury drop electrode, as shown in *Figure 1*. Platinum film served as the cathode and a saturated calomel cell as a reference potential source. The cyclic voltammeter unit was in-house built and was tested with a platinum working electrode. It was shown to produce results similar to those reported in the literature[3,4]. Voltammograms were plotted on an X–Y recorder, Yew type 3025. Scanning rates of $50\,\mathrm{mV\,s^{-1}}$ were used in all of the experiments.

Larger films were produced in the manner described previously[1]. However, these were subjected to a more rigorous purification procedure than previously. This procedure, reported by Wynne and Street[5], consisted of washing with distilled water, extraction with acetonitrile, followed by pumping at 5×10^{-4} Torr and 110°C for 30 h. This treatment completely expels residual moisture and results in reproducible elemental analyses. Conductivity measurements were performed with a four-probe device[6], the current being supplied by a Wenking 121 potentiostat and the voltage measured with a multimeter.

Elemental analysis of C, H, N, S, Br and Hg was carried out at CSIRO Laboratories, North Ryde, NSW.

Scanning electron microscopy (SEM) was performed with a Jeol JSM-840 instrument.

RESULTS AND DISCUSSION

Cyclic voltammetry of pyrrole monomer

Results of a typical experiment involving the mercury drop in supporting electrolyte without pyrrole are shown in *Figure 2*. Oxidation of mercury, coincident with surface dulling, begins at about 0.4 V, a value that can be predicted from the Nernst equation for low concentrations of $\mathrm{Hg_2^{2+}}$. This process is reversible.

The following experiment, in which pyrrole is added to the electrolyte, described in *Figure 3*, reveals the mercury oxidation still beginning about 0.4 V, but is followed by a parabolic featureless current growth. As noted already, at 0.4 V the drop begins to lose its lustre but now at ~0.9 V, a fine grey deposit begins to form and slides continuously off the surface, leaving only a thin black film of polymer behind. The specific behaviour of pyrrole on a mercury drop depends on the physical arrangement of the drop, i.e. whether it is supported on top of a column (as in *Figure 1*) or whether it is suspended as in a hanging mercury drop electrode. The latter was unsuitable for the present experiments because the drop falls off the supporting tube at negative potentials, presumably due to a decreased surface tension. With the present arrangement, which also has the advantage of simulating the actual conditions used in preparing larger films, it was noted that the oxidizing current is lower than the reducing current, this being attributed to the non-conducting nature of the deposit.

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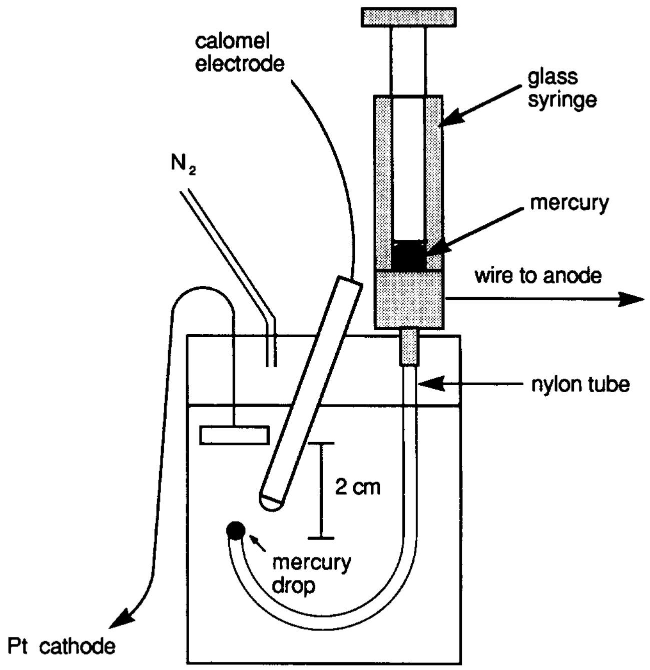

Figure 1 Experimental arrangement of the electrochemical cell used

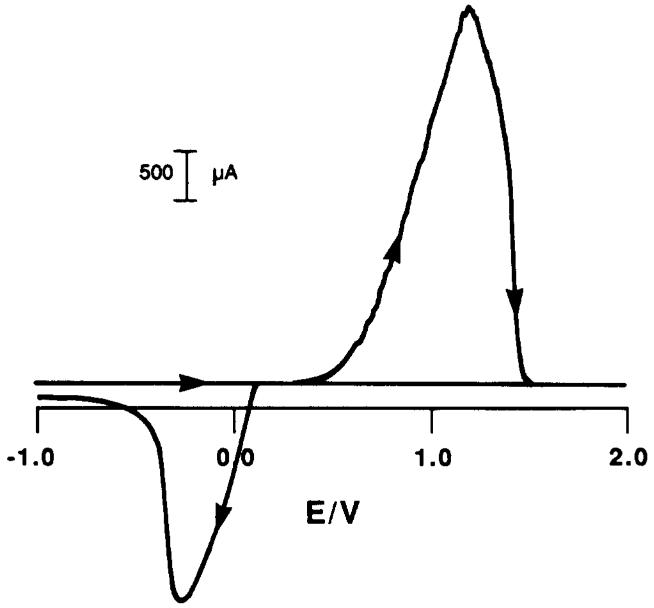

Figure 2 Cyclic voltammogram of mercury in 0.3 M sodium tosylate solution

With potassium bromide as an additional electrolyte, the composite oxidation behaviour of pyrrole and mercury is resolved, resulting in the familiar shape occurring at the expected potentials, as indicated in *Figure 4*. Visually, the grey deposit is absent; instead a thick jet black deposit of polypyrrole appears at around 1.0 V. A sharp oxidation peak appearing at 0.08 V and a corresponding reduction potential at about −0.08 V must be associated with the mercurous bromide/bromide couple. When the experiment is conducted at several different concentrations of KBr, the peaks around ±0.1 V show a direct dependence on the concentration. It was noted that the pyrrole oxidation peak was dependent on the mercury drop size but independent of the potassium bromide concentration.

When the experiment is performed in the presence of potassium chloride (*Figure 5*), similar results to those obtained with the bromide are obtained. The only difference between the two voltammograms is that the oxidation peak associated with the mercurous chloride/chloride couple appears at a slightly more positive potential, estimated to be 0.12 V. Absence of the reduction peak associated with the mercurous chloride/chloride couple is unexpected.

Considering the experiment conducted in the presence of iodide ions, the voltammogram shows a more complex situation. Although the major features are still present, i.e. a pyrrole oxidation peak separated from a mercurous iodide/iodide couple, the process is more complicated, as is indicated by means of points (a), (b) and (c) in *Figure 6*. At point (a), −0.12 V, a green deposit covers the mercury drop; at point (b) at a slightly more positive potential than shown in *Figures 5* and *6*, +1.15 V, polypyrrole deposit appears; at point (c) the dark deposit lifts off the anode and drifts towards the cathode.

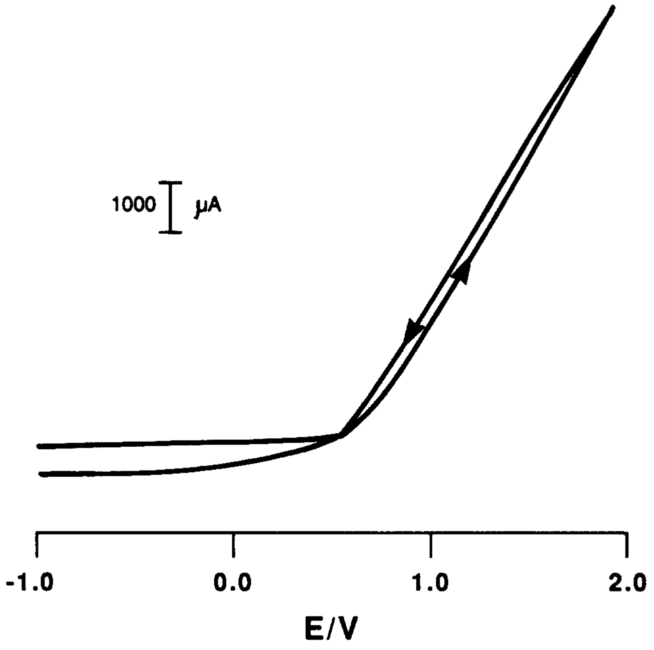

Figure 3 Cyclic voltammogram of pyrrole on a mercury anode in 0.3 M sodium tosylate solution

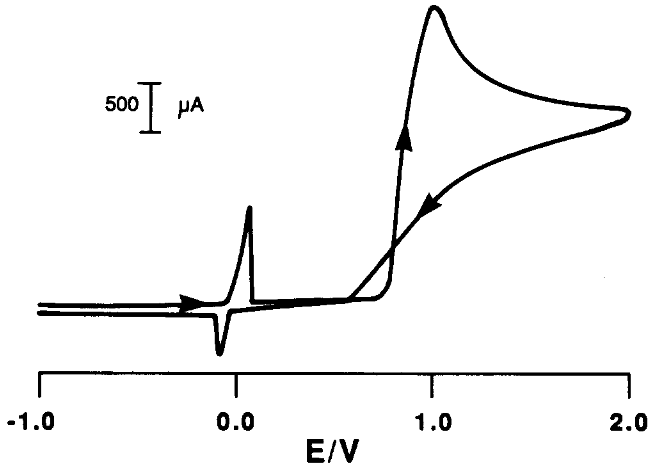

Figure 4 Cyclic voltammogram of pyrrole on a mercury anode in a solution of 0.3 M sodium tosylate and 0.2 M KBr

Table 1 Elemental analysis of poly(pyrrolium tosylate) grown on a mercury anode

Sample	C	H	N	S	Br	Hg	Formula
Film A	59.06	4.49	11.52	7.2	–	0.08	$C_{4.07}H_{3.35}N_{1.00}(TS)_{0.273}$
Film B	54.54	4.35	11.30	5.5	4.0	2.12[a]	$C_{4.14}H_{3.86}N_{1.00}(TS)_{0.213}Br_{0.49}$

[a] Analysis was not as reproducible as for C, H, N S since Hg_2Br_2 distribution on the surface was not uniform. Four determinations (1.5, 1.9, 1.9, 3.2%) led to the averaged value in the table. Similarly for film A the value given represents an average of two determinations (0.06, 0.1%)

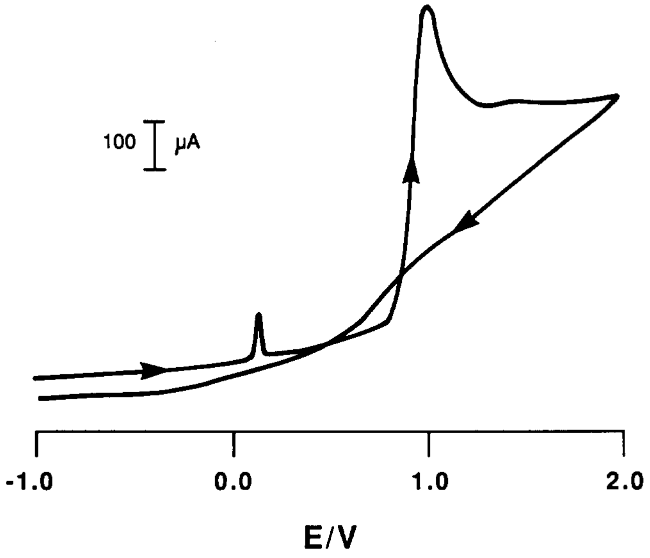

Figure 5 Cyclic voltammogram of pyrrole on a mercury anode in a solution of 0.3 M sodium tosylate and 0.2 M KCl

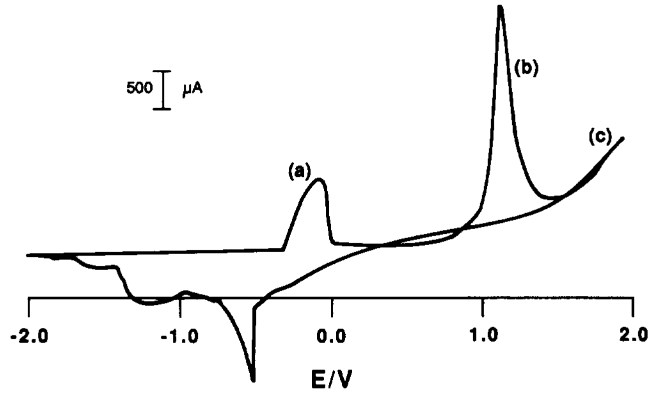

Figure 6 Cyclic voltammogram of pyrrole on a mercury anode in a solution of 0.3 M sodium tosylate and 0.2 M KI

Formation and characterization of large films

Two large doped polypyrrole films (78 cm^2) were prepared galvanostatically with a current of 60 mA over a period of 4 h on a mercury anode in the manner described previously[1]. Film A was prepared in buffered sodium tosylate (0.3 M), while film B was prepared similarly but with a mixed electrolyte of sodium tosylate (0.3 M) and potassium bromide (0.1 M). These films were purified and submitted to elemental analysis, conductivity and SEM examinations.

Compositions of the two films in terms of their elemental analysis are described in *Table 1*. The elemental analyses given are the average of duplicate results. The chemical composition of film A (omitting the mercury) is in good agreement with previously published data for poly(pyrrolium tosylate) formed in aqueous systems[5]. It should be noted that the purification treatment resulted in excellent reproducibility. Two features of the analyses are noteworthy. First, film A was found to have only 0.08% w/w Hg compared to 3.3% reported in the earlier study[1]. Such a difference is real and is attributed to removal of mercury by the heating/pumping procedure. Secondly, film A is more heavily doped with tosylate ions than film B, but it is more lightly doped than samples prepared on pyrolytic carbon in aqueous solution[5], or on platinum in organic solvents[4,7]. Film B contains some bromide in the form of mercurous bromide, and some as free bromide ion, which appears to be a partial dopant, replacing some of the tosylate ions. The persistence of mercury in film B must be due to involatile Hg_2Br_2, which is observed as small crystals on the film surface, when it is examined by SEM.

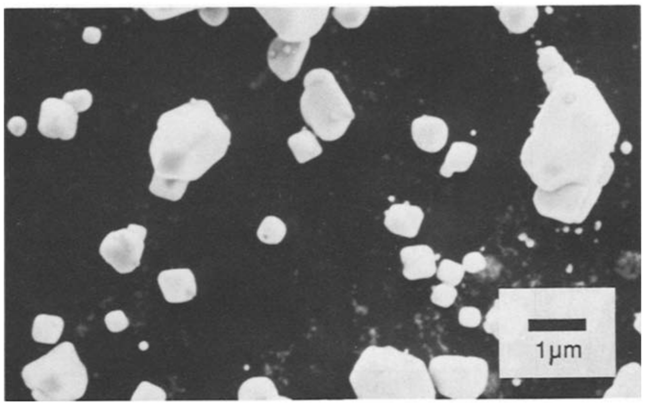

Figure 7 Mercury-facing side of film B

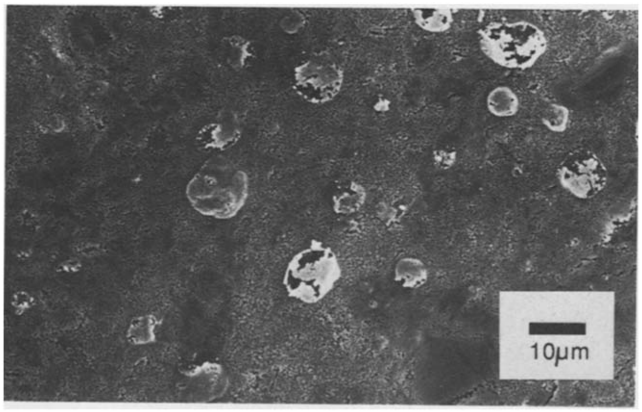

Figure 8 Mercury-facing side of film A

Examination by SEM of films A and B reveals that only the side of the film facing the mercury surface differs in the two samples. With film B (*Figure 7*), a smooth surface denuded of nodular features and covered by mercurous bromide crystals ($\leqslant 2\,\mu m$) is displayed, whereas the corresponding surface of film A (*Figure 8*) is rougher and is covered occasionally with large (~10 μm) burst spherical structures, which probably originally contained mercury or mercury compounds formed in the polymerization process. Both films displayed a typical dendritic structure, similar to previously reported surfaces[8], on the electrolyte-facing side of the film.

There was little difference in conductivity between the two films: A, 28 $\mathrm{ohm}^{-1}\,\mathrm{cm}^{-1}$; B, 18 $\mathrm{ohm}^{-1}\,\mathrm{cm}^{-1}$. These values are within the range of those reported earlier[1], although on the low side. Some loss of conductivity may have occurred during the purification procedure.

CONCLUSIONS

Examination of pyrrole oxidation in the presence of halide ions by cyclic voltammetry shows that it is feasible to resolve completely the oxidation peaks of mercury and pyrrole, by the removal of oxidized mercury as highly insoluble mercurous halides. The position of the polypyrrole peak formed in electrolyte solutions containing Cl^- and Br^- appears at identical potentials (1.0 V vs SCE) while in the presence of I^- this potential is slightly higher (1.15 V vs SCE). In each case a small oxidation peak associated with the mercurous halide/halide ion couple appears at the approximate potentials expected for the three halide solutions by applying the Nernst equation to the standard potentials. Oxidation peak values for the Cl^-, Br^- and I^- systems are observed at +0.12, 0.08, −0.11 V vs SCE, respectively. These can be compared with predicted values of +0.07, −0.06, −0.24 V vs SCE, respectively. Lack of better coincidence between the observed and expected values is not entirely surprising, since the solutions are non-ideal. Further, it is not the intention of this study to measure such potentials accurately, a task that is rendered difficult by variation in mercury drop size, but rather to confirm the nature of the proposed oxidation processes.

In this investigation the pyrrole oxidation potential on mercury observed in an aqueous electrolyte system agrees favourably with that previously reported for a platinum electrode in aqueous electrolytes[3]. When several different types of metallic electrodes were used, all with tosylate as the dopant anion in an organic solvent, the oxidation potential was found to vary[4]. Nevertheless, the value on platinum was also found to be 1.0 V vs SCE, in agreement with that reported for an aqueous electrolyte[3] and with the value reported in this study.

In the absence of halide ions the cyclic voltammogram results (*Figure 3*) suggest that the mercurous ions interact with pyrrole, forming the observed grey precipitate in the presence of tosylate ions. Control experiments have indeed demonstrated that reaction. Insufficient quantities of the grey precipitate have prevented its detailed structure determination, although it is probably similar to the product of mercurous ions with ammonia. What may be concluded is that the material is non-ionic and therefore non-conducting, and that it most likely decomposes at 110°C, allowing the volatilization of the resultant mercury.

Film B, produced in the presence of KBr, is darker than film A and other similar films produced in the earlier study. Examination of these films by SEM revealed the presence of white crystals, about 1–2 μm in size, of Hg_2Br_2 dispersed along the surface of film B. The possibility of some Br^- replacing some TS^- as dopant has been discussed. Yet, from the conductivity measurements it seems that there is no significant difference between the two types of films.

Observation of the same oxidation potential for pyrrole on Pt and Hg and in the presence of Cl^- and Br^- supports the view that no halogenation of the pyrrole ring occurs. However, in the case of I^- as electrolyte a certain amount of iodination is likely, and at potentials higher than 1.2 V there is evidence of strong adsorption on the polypyrrole surface of negative species, perhaps I_3^- because of the attraction of the film to the cathode (point (c) in *Figure 6*). Iodination of polypyrrole is evident in the study by Mengoli *et al.* from their elemental analysis of the product[2].

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