SHORT COMMUNICATION

# Platinum-containing polypyrrole coatings on stainless steel electrodes for oxygen reduction in aprotic media

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## 1. Introduction

The superoxide ion may be electrochemically generated in an aprotic medium [1]. Sawyer *et al.* investigated the mechanism of decomposition of various chlorinated organic compounds [2], as well as $CCl_4$ and DDT using superoxide [3]. This work suggests that the superoxide ion preferentially degrades organic compounds which have a higher chlorine content.

The removal of chlorine from organic wastes is a costly process involving incineration [4]. Since there is less of an energy requirement with the electrochemical method, savings in costs of decomposition would be significant. Studies are currently being directed in this area [5].

This work proposes a system of generating superoxide on a large scale in an aprotic medium for the removal of chlorine from chlorinated solvent waste. This was attempted in two configurations; a fluidized bed system similar to that of Fleischmann [6] and Rolison [7] and a dispersion of platinum particles in a polypyrrole matrix. Platinum has previously been deposited in Nafion® [8], poly(4-vinylpyridine) [9], and polypyrrole [10]. Oxygen reduction in an aqueous medium has been achieved using this latter system as well as with layers containing catalytic centres such as cobalt porphyrins [11], or metallo-phthalocyanines [12]. This work consists of preliminary experiments involving depositing polypyrrole on stainless steel, incorporating platinum and using this modified electrode to decompose $CCl_4$.

## 2. Experimental details

Pyrrole (Aldrich) was distilled under nitrogen and stored in the dark until required. Potassium chloroplatinate (BDH), lithium perchlorate (Aldrich) and $CCl_4$ were used as received. DMSO (Riedel-deHaen) was dried over activated molecular sieves.

Cyclic voltammetry was carried out using a Thompson 16 bit sweep generator (model DRG16) and a Thompson ministat coupled with a J. J. Lloyd chart recorder. The cell was a conventional three electrode cell consisting of a calomel reference electrode (SCE) and a carbon auxiliary electrode.

Stainless steel (18/8 Cr/Ni) was cut and electrically bonded to copper wire with silver epoxy and encapsulated in a glass tube with Araldite exposing an electrode area of approximately 0.1 $cm^2$. The steel was polished finally down to a stage with 0.3 micron alumina.

The electrode potential was stepped from 0.4 V to 0.8 V/SCE in a solution of 0.1 M pyrrole and 0.1 M KCl. The potential was maintained at 0.8 V for periods ranging from 2 to 10 min in unstirred solution. It was found that some corrosion of the stainless steel occurred but that a black adherent layer formed. More recently work has been carried out on the deposition of polypyrrole from aqueous nitrate media onto stainless steel [13].

The electrode was rinsed and placed in 0.1 M KCl and the electrode potential stepped to − 0.5 for 20 min in order to reduce the film and expel the anions. The electrode was then transferred to a solution of potassium chloroplatinate (10 mM) in 0.1 M KCl and held at a potential of 0.5 V in order to oxidize the layer and absorb the Pt(IV).

Finally the electrode was transferred to a solution of 0.1 M KCl and the electrode potential held at − 0.5 V in order to reduce the platinum. Both the time for the deposition of polypyrrole and the time for the deposition of the platinum were varied.

In order to characterize these electrodes cyclic voltammetry for the reduction of oxygen was carried out in a solution of dimethylsulfoxide containing 0.1 M $LiClO_4$.

## 3. Results and discussion

Figure 1 shows a cyclic voltammogram for the reduction of oxygen at a Pt-containing polypyrrole coating on stainless steel. It can be seen that the reduction appears to reach a steady state value indicative of the behaviour of an array of microelectrodes [14, 15] rather than a peaked current profile obtained at macroelectrodes. It can be seen from Fig. 1(b) that there is some residual background current, though, for this range of potentials, the polypyrrole is in a reduced form. This may be due to incomplete oxygen removal.

Figure 2 shows the limiting current as a function of polypyrrole layer thickness for a given amount of platinum deposited. It can be seen that the most efficient oxygen reduction occurs at much thinner

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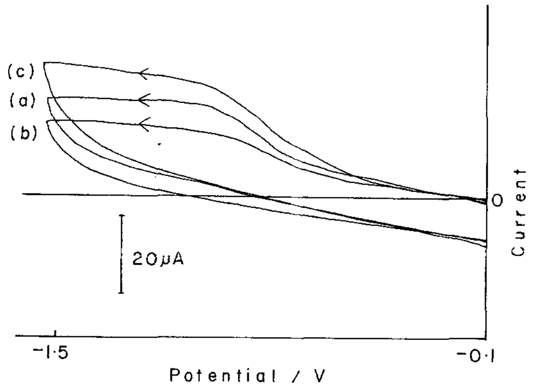

Fig. 1. Cyclic voltammogram of the Pt-containing polypyrrole coated stainless steel electrode in DMSO, 0.1 M $LiClO_4$. Scan rate = 50 mV $s^{-1}$, Pt deposition time = 20 min, polypyrrole deposition time = 4 min. Curve (a) solution equilibrated with air, (b) solution degassed with nitrogen, (c) as solution (a) but with $CCl_4$ added to a concentration of 42 mmol $dm^{-3}$.

layers. This corresponds to a very high density of platinum sites, unlike in thicker layers where there is a more dilute concentration of platinum which may cause problems with contact toward the electrode, since polypyrrole is reduced then the electrical contact is through the distribution of platinum particles suspended in the layer [10]. It has been suggested by Wang [16] that as the electropolymerized layers become thicker the permeability decreases. This implies that a 2 dimensional coating is more realistic than a three dimensional porous coating.

It can be seen from Fig. 3 that as the loading of platinum increases, for a given thickness of polypyrrole, the limiting oxygen reduction current also increases marginally. The effect of varying platinum deposition time is not as great as that of the polypyrrole. In order to observe the decomposition properties of the superoxide, a model compound, $CCl_4$, was added to the electrolyte solution and the limiting current was seen to increase corresponding to the catalytic decomposition of the $CCl_4$ (Fig. 1(c)). The increase in current is due to the catalytic regeneration of oxygen where the complete reaction is

$$O_2 + e^- \rightleftharpoons O_2^{-\cdot} \quad (1)$$

$$CCl_4 + 6O_2^{-\cdot} \rightleftharpoons CO_4^{2-} + 4Cl^- + 4O_2 \quad (2)$$

Partial decomposition also regenerates oxygen, which is further reduced at the electrode. The $CO_4^{2-}$ reacts with DMSO to form dimethylsulphone and $CO_3^{2-}$ which was determined by titration with HCl [3]. The oxygen concentration is approximately 4 mM [3] and the $CCl_4$ is destroyed at a rate of $10^{-9}$ mol $min^{-1}$ for an electrode area of 0.1 $cm^2$. It can be seen that conditions may be reached where, taking into account residual current, a current density of 0.1 A $cm^{-2}$ can be obtained for oxygen reduction which compares favourably with a peak current of $1.3 \times 10^{-3}$ A $cm^{-2}$ as a peak current at a platinum electrode [3]. Thus the effective area is greater due to the edge effect of an array of microelectrodes [17].

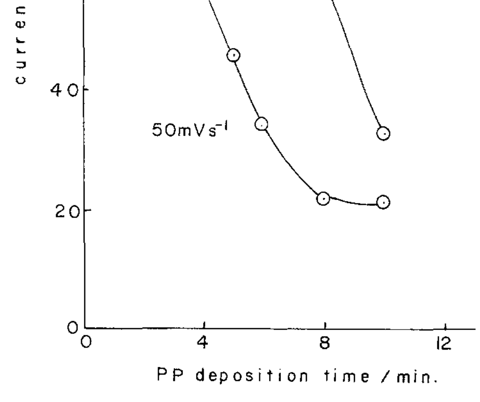

Fig. 2. Variation of limiting current for oxygen reduction with polypyrrole deposition time, with a constant amount of platinum (deposited for 20 min.), under conditions in Fig. 1.

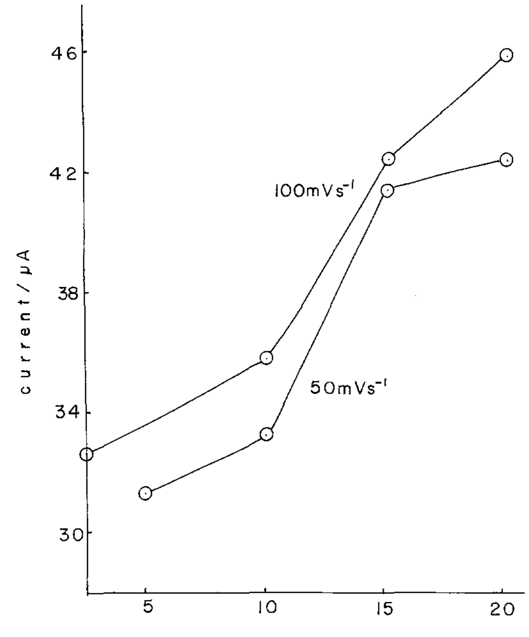

Fig. 3. Variation of limiting current for oxygen reduction with platinum loading, with a constant amount of polypyrrole (deposited for 4 min.), under conditions in Fig. 1.

## 4. Conclusion

As a result of this work the following conclusions may be drawn.

(i) The electrochemically generated superoxide ion can be used to decompose chlorinated organics. This is a useful reagent since it is environmentally less harmful than other electrochemical mediating species consisting of organometallics within micelles [18–20].

(ii) The optimum nature of the layers are thin polypyrrole layers with high platinum loading. In this work the platinum loading varied from about $8 \times 10^{-8}$ mol $cm^{-2}$ to $3.4 \times 10^{-7}$ mol $cm^{-2}$.

Finally it was found that the polypyrrole did not totally passivate the stainless steel and that some pitting occurred beneath the layer. It was also found that the presence of water is a large impediment to the scale-up of the process since the superoxide reacts preferentially with water rather than the highly chlorinated organics [1]. It would therefore be necessary to include a drying step for the chlorinated waste prior to decomposition. A concentric tubular reactor for this means of $CCl_4$ decomposition is currently under study.

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