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EFFECT OF BENZIDINE ON THE ELECTROPOLYMERIZATION OF ANILINE ON A CARBON GRAPHITE ELECTRODE

Duke Orata and Segor Fred
Department of Chemistry, University of Nairobi, P.O. Box 30197, Nairobi, Kenya

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ABSTRACT. The work presented in this paper shows that the presence of benzidine 'catalyzes' the electropolymerization of aniline. It is also shown that the oxidation potential of ascorbic acid on a benzidine modified polyaniline is reduced by approximately 140 mV relative to that on a polyaniline (no benzidine) electrode.

INTRODUCTION

Organic electronic conductors (also referred to as synthetic metals) such as poly-(aniline, pyrrole, and thiophene) are the subject of intense research [1-6]. These new class of organic materials have generated considerable interest due to their successful use in battery cells, electrolytic capacitors and in smart windows where their electrochromic dismay characteristics is of significance [7]. Metal-polymer composites have also been formed by embedding metal particles into the polymer matrix. This dispersion of metal into the polymer not only improves its conductivity but enhances its role in the areas of catalysis, photocatalysis and sensor development [8-10].

For example polyaniline - Nafion composites have been characterized electrochemically for their electrocatalytic activity [11]. In this paper, we report on the effect of benzidine on the electropolymerization of aniline and on how this benzidine modified polyaniline influences the oxidation of ascorbic acid.

EXPERIMENTAL

Benzidine (Aldrich) and sodium chloride (BDH) were used as received without further purification. Aniline was triply distilled until a colourless liquid was obtained. The aniline was then stored under nitrogen. All the solution were prepared using triply distilled water.

A three electrode assembly was used in the electrochemical analysis. These consisted of saturated calomel electrode (SCE) as the reference electrode, platinum wire as auxiliary electrode and carbon graphite (surface area 0.38 cm^2) as the working electrode. The working electrode was polished using alumina on a felt polishing cloth prior to electrodeposition of polyaniline. The cyclical potential scan was generated using PAR model 173 potentiostat/galvanostat, in conjunction with PAR model 175 universal programmer. The output signal was fed into a PAR RE0089 X-Y recorder.

RESULTS AND DISCUSSIONS

The cyclic voltammetric response of benzidine was obtained by cycling the potential from -0.2 V to 0.99 V in a solution containing 1.6 mM Benzidine in saturated sodium chloride solution (see Fig. 1). We observe an oxidation peak at approximately 0.7 V and a reduction peak at about 0.35 V.

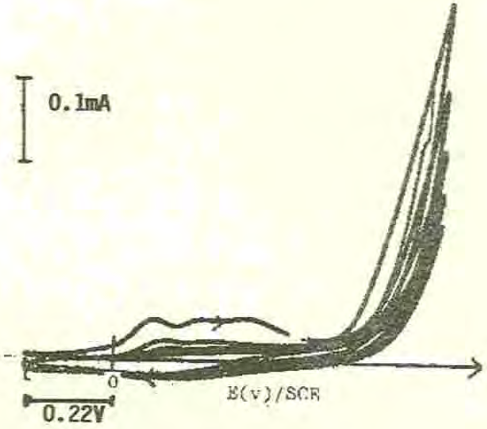

Fig. 1. Cyclic voltammetric response obtained on cycling the potential from -0.2 V to 0.99 V in a solution containing 1.6 mM benzidine in a saturated sodium chloride solution. Scan rate, 20 mV/sec.

The peak current for both processes (redox) decreases on continued cycling as shown in Fig. 2. These peaks represent the oxidation - reduction of benzidine. The decrease in the redox peaks on continued cycling of the potential indicates that the

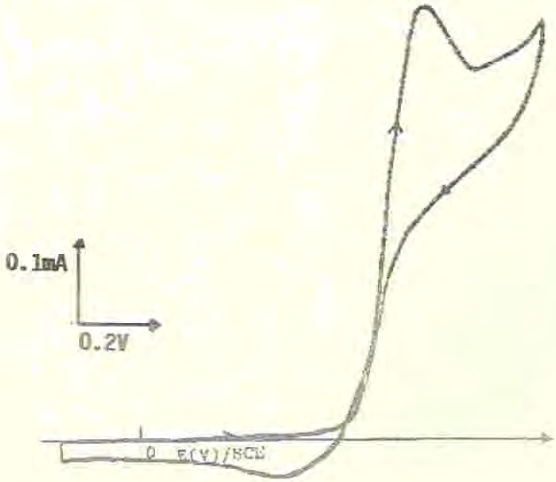

Fig. 2. Cyclic voltammetric response on continued cycling. The potential limit is from -0.2 V to 0.99 V in a solution containing 1.6 mM benzidine in a saturated sodium chloride solution. Scan rate, 20 mV/sec.

species formed after the oxidation reduction process is either soluble in the solution or it does not adhere to electrode surface i.e., via adsorptive forces. Our next objective was to try and establish how the presence of benzidine in the electrochemical system affects the electropolymerization of aniline, given the fact that benzidine can be thought of as consisting of two aniline units fused together. Aniline monomer is the building block in polyaniline. The working electrode described in Fig. 1 was polished as described in the experimental section. The electrode was transferred to a solution containing 1.6 mM benzidine and 0.1 M aniline in a saturated sodium chloride solution.

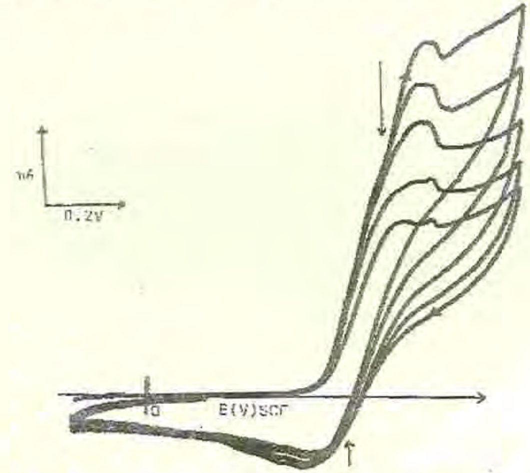

Fig. 3. Cyclic voltammetric response obtained on cycling the potential from 0.35 V to 0.50 V in a solution containing 1.6 mM benzidine and 0.1 M aniline in saturated sodium chloride solution. Scan rate, 4 mV/sec.

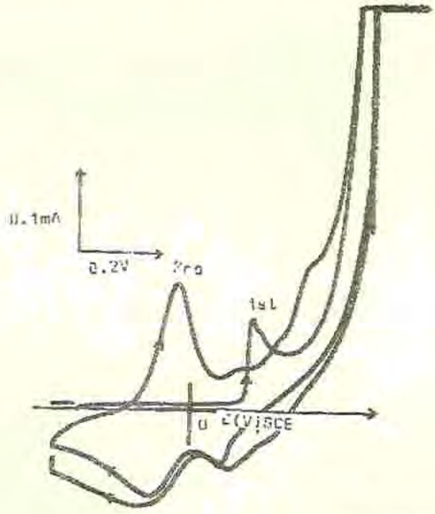

Fig. 4. Cyclic voltammetric response obtained on cycling the potential from -0.2 V to 0.75 V in a solution containing 0.1 M aniline and 0.5 M sodium chloride. Scan rate, 20 mV/sec.

During the first scan we observe a 'fast switching' double humped peak at approximately 0.15 V. There is corresponding reduction peak at 0.07 V, and another broad reduction peak at approximately 0.1 V. This 'fast switching' peak at approximately 0.15 V, resembles that of polyaniline peak in solution of high acid concentration. This has been previously attributed to the solvent population in the film [1].

It is important to mention that while we have drawn an analogy between the behaviour of the 'fast switching' peak and that of polyaniline, the former is not a polyaniline peak. It probably results from benzidine derivatives.

On the second scan, the oxidation peak at 0.15 V disappears with new oxidation/reduction peaks emerging at -0.03 V/-0.1 V (see Fig. 3). These peaks are attributed to polyaniline even though, when compared to the case where the film is electropolymerized in an acid media [8], the shift in the oxidation and reduction potentials is 230 mV and 200 mV towards negative potentials, respectively. This is not surprising given the fact that in this particular instance we are in a high pH solution. The polyaniline redox peaks are thus expected to shift towards negative potentials. Even though there are conflicting reports on electrosynthesis of polyaniline in a non-acidic media [12-14], we have been able to show that one can electrosynthesize polyaniline in a non-acidic media (see Fig. 4).

The polyaniline oxidation peak occurs at approximately 0.1 V. The poor film conductivity is attributed to protonation/deprotonation equilibria in the film.

Another particularly interesting observation is the enhancement in the rate of growth of polyaniline in the presence of benzidine. In the absence of benzidine the first polyaniline redox peak appears after more than ten cycles (see Table 1).

Table 1. Oxidation peak current and potential of polyaniline electropolymerized in a solution containing benzidine.

Number of Cycles	Oxidation potential (mV)	Oxidative peak Current (mA cm^{-2})
1	--	--
2	-30	0.41
3	0.0	0.49
4	20	0.49
5	30	0.43
6	50	0.41
7	60	0.43
8	60	0.39
9	70	0.39

From the results depicted in Table 1, it is apparent that there is a substantial increase in the oxidative peak current, after which there is a slight drop during subsequent cycles (5th - 9th cycle). We also observe a shift in the oxidation potential towards positive potentials as we continue cycling, and the shift is approximately 100 mV by the end of the eight cycle.

It is important to note that the largest shift in oxidative potential (30 mV) corresponded to the biggest change in oxidative peak current (2nd and 3rd cyclic scans), even though the shift in oxidative potential continued consistently throughout, as opposed to the rather unpredictable change in oxidation peak currents. It is important to mention that the reduction peak potential was unaffected during the cycling.

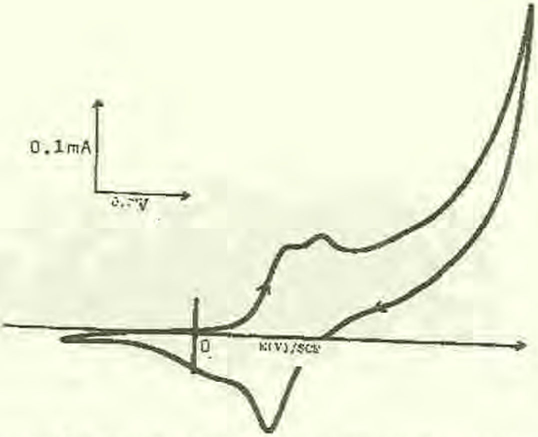

Fig. 5. Cyclic voltammetric response for a benzidine 'modified' polyaniline electrode in a solution containing 34 mM ascorbic acid and 1 M sulphuric acid. Scan rate, 5 Mv/sec.

This latter observation makes it difficult to attribute the shift in the oxidative potential to possible changes in the film internal pH, since one would have expected both the oxidation and reduction peaks to shift as is observed in the case of bare polyaniline (no benzidine).

It is thus possible that modification of polyaniline 'character' by the benzidine, i.e., by possible juxtapositioning of benzidine molecules in the polyaniline matrix, makes the polyaniline more difficult to oxidize, as more benzidine is incorporated in the film matrix on continued cycling. The mode of benzidine action is possibly through its influence on electron transfer in the film. Since one of our objectives had been to study the possibility of polyaniline electrocatalyzing the oxidation of ascorbic acid [15], we transferred the benzidine 'modified' polyaniline discussed in the foregoing paragraphs, to a solution containing 34 mM ascorbic acid and 1 M sulphuric acid. The potential was cycled at a rate of 5 mV/sec. The cyclic voltammetric response obtained is shown in Fig. 5. We observe a double humped (oxidation) peak at approximately 0.2 V and 0.27 V, and a reduction peak at 0.17 V. The oxidation/reduction peak at 0.2 V/0.17 V represents the polyaniline redox process, and that at 0.27 V represents the ascorbic acid oxidation peak.

When one compares the ascorbic acid oxidation peak, on a bare polyaniline (no benzidine), it is apparent that the ascorbic acid oxidation is suppressed even though the ascorbic acid is now much easier to oxidize i.e., 0.27 V as compared to 0.41 V in the bare polyaniline case.

Even though the ascorbic acid is easier to oxidize in the case of benzidine 'modified' polyaniline, it will be merely speculative to assert the possibility of electrocatalysis of ascorbic acid oxidation by benzidine, since the very poor solubility of benzidine makes investigations of all the experimental parameters extremely difficult.

CONCLUSION

The results presented in this paper describe the effect of benzidine on aniline electropolymerization. The observed effects can probably be attributed to copolymerization of the two species. It is also important to note that, since we are dealing with unbuffered solution, the local pH at the electrode surface may change during electropolymerization hence complicating the interpretation of the observations. More work is currently in progress to try and address these issues.

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