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OXIDATION OF ASCORBIC ACID ON A POLYANILINE MODIFIED ELECTRODE

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ABSTRACT. The results presented in this paper reveal marked improvement in the oxidation characteristics of the physiologically active carbohydrate (ascorbic acid), when the latter is oxidized on a polyaniline derivatized carbon graphite working electrode. The pH of the system is also observed to influence significantly the role of polyaniline in influencing the oxidation characteristics of the ascorbic acid. Polyaniline conductivity is also shown to be dependent on temperature.

INTRODUCTION

It is now well over a decade since intensive research on organic conductive polymers or 'synthetic metals' began. Most of this research has focused on trying to establish/develop practical application for these conductive plastics. Considerable success has been achieved in utilizing these polymers in rechargeable batteries, 'smart windows' and in electrolytic capacitors [1-7].

A lot of work is also currently under way in attempts to try and improve their mechanical and electrical properties. This has entailed the formation of composites, whereby the conducting polymer is electrodeposited on an insulating host - matrix, or on another conducting polymer matrix [8-10]. Such composites have shown marked differences in their electrochemical characteristics from that of either component.

One area of research where possible application of these conducting polymers can be of significance is in electrocatalysis. This normally involve the mediation of electron transfer between the substrate and the electrode by an immobilized redox couple. Reactions requiring electrocatalysis are normally very slow in bare/naked electrodes [11].

In this paper we report on the electrochemical characteristics of a physiologically active carbohydrate (ascorbic acid) on a polyaniline (conducting polymer) derivatized electrode. The results obtained show improved oxidation characteristics of ascorbic acid on the conducting polymer modified electrode. The effect of pH on the electron transfer mediation role played by polyaniline is also highlighted in the paper.

EXPERIMENTAL

Apparatus. The electrochemical instrumentation used in generating the cyclical potential scans comprised of a PAR model 173 potentiostat/galvanostat used in conjunction with a PAR model 175 universal programmer. The output signal was fed into a PAR RE 0089 X-Y recorder. The three - electrode assembly used in electrochemical analysis consisted of a carbon graphite (surface area 0.38 cm^2) as the working electrode, platinum wire as the counter/auxiliary electrode and saturated calomel electrode (SCE) as the reference electrode.

Chemical Reagents. All the reagents (sulphuric acid, Aldrich), ascorbic acid (Howse McGeorge), were used as received without further purification. Aniline (Aldrich) was triply distilled prior to use until a colourless liquid was obtained and then stored under nitrogen. All the solutions were prepared using triply distilled water. The working electrode was polished with alumina on a felt polishing cloth prior to use on all occasions. A thermostated bath was used in all temperature controlled experiments.

RESULTS AND DISCUSSION

Polyaniline was electrodeposited on the working electrode by cycling the potential from -0.2 V to 0.75 V in a solution containing 0.1 M aniline and 1.3 M sulphuric acid. The oxidation and reduction peaks for polyaniline occur at 0.19 V and 0.06 V, respectively as can be seen in Fig. 1.

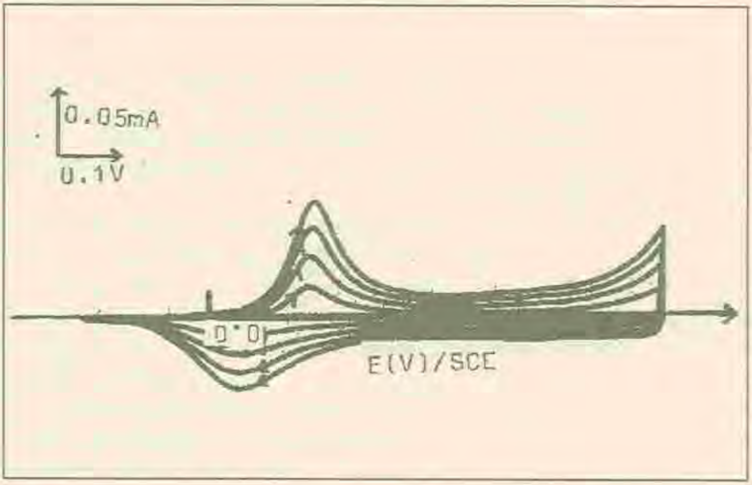

Fig. 1. The growth of polyaniline in a solution containing 0.1 M aniline and 1.0 M sulphuric acid. Scan rate 20 mV/sec.

We began our analysis by studying how the polyaniline on the electrode surface influences the cyclic voltammetric responses of ascorbic acid. This was achieved by transferring the polymer modified electrode described in Fig. 1 into a solution containing 34 mM ascorbic acid and 1 M sulphuric acid (no aniline monomer). The cyclic voltammetric response obtained is shown in Fig. 2. We observe the polyaniline oxidation peak at 0.1 V and a broad reduction peak at 0.06 V.

The ascorbic acid oxidation occurs at approximately 0.4 V. There is no corresponding reduction peak, an observation which is consistent with the well established fact that ascorbic acid electro-oxidation is an irreversible process.

To be able to ascertain the effect of the polyaniline on the ascorbic acid electrochemical response, the working electrode was polished as already described elsewhere in the paper, and then transferred to a solution containing 5.7 mM ascorbic acid and 1 M sulphuric acid only (no aniline monomer).

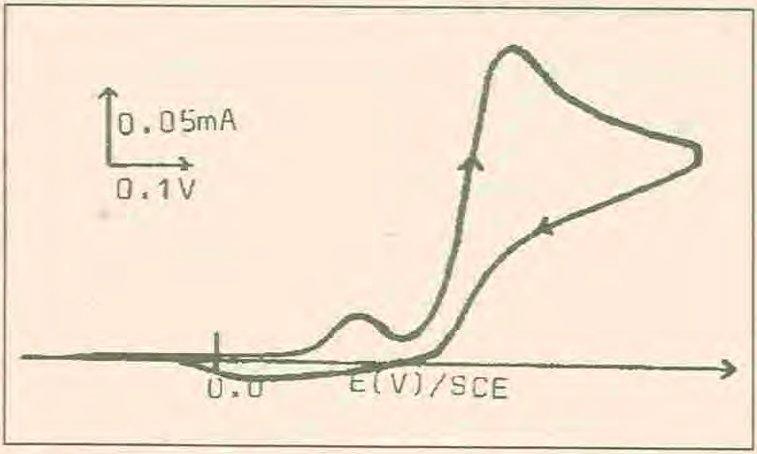

Fig. 2. Polyaniline modified electorde in a solution containing 34 mM ascorbic acid and 1 M sulphuric acid (no aniline monomer). Scan rate 5 mV/sec.

The resultant cyclic voltammetric response is shown in Fig. 3. Comparing the results obtained in Figures 2 and 3, we observed that the oxidation peak in the case of polyaniline modified electrode is much sharper and well defined than that observed in the bare electrode case.

This observation cannot be attributed to improved electron transfer dynamics (i.e., faster electron transfer), since for a fast electron transfer reaction the current becomes diffusion controlled [12]. In this case, a plot of oxidation peak current *versus* square root of scan rate does not yield a linear plot as shown in Fig. 4. This suggests that adsorption could be a factor in the electrochemical behaviour of ascorbic acid at a polyaniline derivatized electrode.

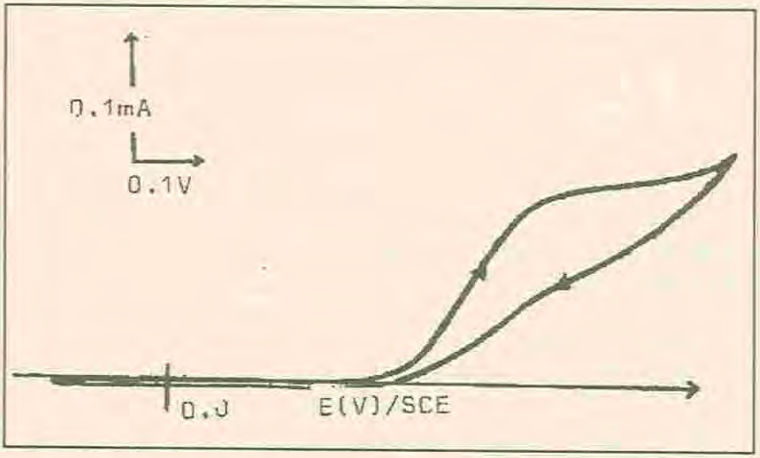

Fig. 3. Bare/naked electrode response in a solution containing 34 mM ascorbic acid and 1M sulphuric acid.

Investigations were further carried out to establish the influence of the quantity of ascorbic acid in the electrochemical system on the latter's cyclic voltammetric response. This was achieved by transferring the polyaniline modified electrode into various solutions containing 1 M sulphuric acid (constant) and 11, 17, 23 and 29 mM, ascorbic acid.

The results have been tabulated in Table 1, where the peak current of the ascorbic acid oxidation is shown *versus* the amount of ascorbic acid in the solution. The best cyclic voltammetric response was observed for the case of 34 mM ascorbic acid at a scan rate of 5 mV/sec. (It is important to mention at this point, that this observation served as a basis for our choice of using solution containing 34 mM ascorbic acid at scan rate of 5 mV/sec in subsequent analysis). The cyclic voltammetric response in solution containing large amounts of ascorbic acid, i.e, greater than 34 mM, did not show any significant improvement over the voltammogram obtained in solution containing 34 mM ascorbic acid. The voltammograms obtained in solutions containing less than 34 mM ascorbic acid exhibited less defined ascorbic acid oxidative peak. This apparent influence of the mass of the electroactive species in the solution (ascorbic acid) on the cyclic voltammetric response of the latter is a veiled pointer to a diffusion limited process, i.e., mass transport is a key factor.

Table 1. Oxidative peak current (mA/cm^2) *versus* concentration (mM) of ascorbic acid in 1 M sulphuric acid solution.

Peak current (mA/cm^2)	Concentration of ascorbic acid (mM)
0.25	11
0.43	17
0.61	23
0.76	29

Table 2. Oxidative peak current (mA/cm^2) *versus* sulphuric acid concentration.

Acid concentration (M)	Peak current (mA/cm^{-2})
0.2	0.49
0.5	0.38
1.0	0.50
2.0	0.26
3.0	0.27
4.0	0.25
5.0	0.08

It is important to mention that similar response (increase in oxidative peak current) was observed also in the case of bare electrode, even though in this particular case the oxidative peak was merely a broad current envelop as opposed to the well defined peak in the polyaniline modified electrode.

When the concentration of the ascorbic acid was held constant at 34 mM, and that of sulphuric acid varied, (see Table 2), we observed that the ascorbic acid oxidative peak current varied haphazardly even though in acid concentrations larger than 3 M, there was a linear decrease in the peak current.

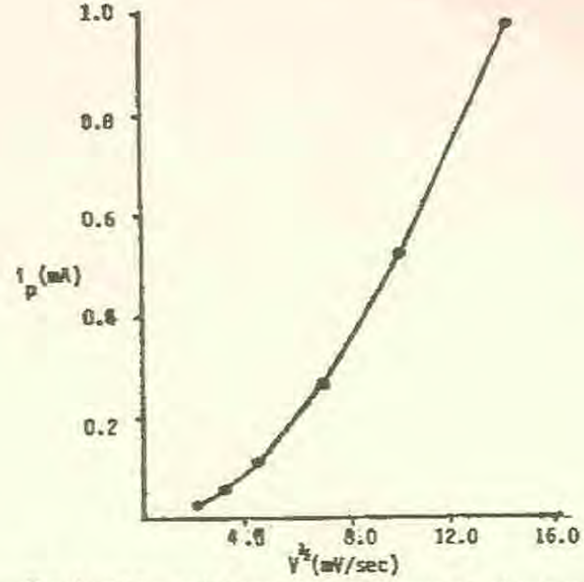

Fig. 4. Plot of oxidative peak current (i_p) *versus* square root of scan rate ($V^{1/2}$) for ascorbic acid.

The possible explanation for these observations lies on the influence of pH on the polyaniline oxidation/reduction potential. It has been observed by various researchers [13], that lowering the pH of the media shifts the polyaniline oxidation/reduction peaks towards positive potentials; hence given the fact that the formal potential of the polyaniline and that of ascorbic acid are not far apart (as already mentioned elsewhere in the paper) it is possible that, during the shift, at one point the two formal potentials nearly coincide. This probably contributes to maximizing electron transfer mediation by the polyaniline.

It is also worth mentioning that, at very low acid concentrations (high pH), there are a number of things happening to the film. The film conductivity decreases at high pH [13] and there is enhanced degradation of the film [14]. These happenings complicate the interpretation in these high pH solutions. For example as the film degrades, the surface coverage decreases. This fact affects the electrocatalytic ability of the film given the notion that film surface coverage plays a significant role in electrocatalysis, even though this is not necessarily true in our case as observed below. The influence of polyaniline film thicknesses on the oxidative peak of ascorbic acid was also investigated. Various film thickness were prepared (Polyaniline film thickness is proportional to its peak current). The various films were then immersed in a solution containing 34 mM ascorbic acid and 1 M sulphuric acid. The analysis were carried out at a scan rate of 5 mV/sec.

The results obtained indicated that, as the film thickness increases, the oxidative peak of ascorbic acid decreases (see Fig. 5) and is reduced to a mere 'shoulder' as the film becomes very thick. This observation is most probably attributable to the fact that the porosity of the polyaniline film towards the ascorbic acid molecules decreases with increasing film thickness. The observation is useful in the sense that one can use the extent of ascorbic acid oxidative peak as a pointer to the thickness of the polyaniline film, a result which has already been highlighted by the author in a short communication [15].

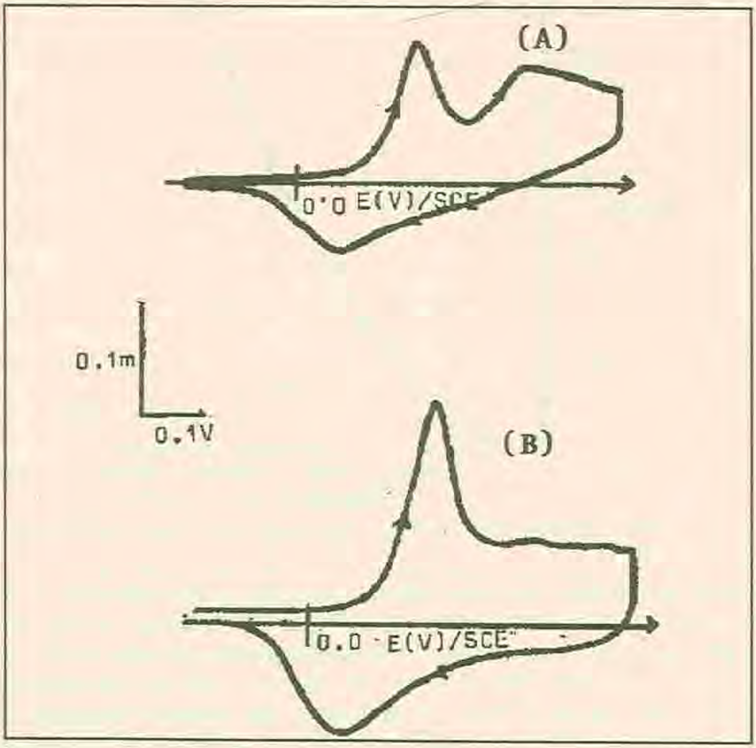

Fig. 5. Cyclic voltammogram of a solution containing 34 mM ascorbic acid and 1 M sulphuric acid. Scan rate 5 mV/sec. A) Thin polyaniline film; B) Thicker polyaniline film.

Experiments were also conducted to ascertain the effect of temperature on the conductivity of polyaniline. The polyaniline was electrodeposited as described in Fig. 1. The film and solution of analysis (1 M sulphuric acid, no aniline monomer) were left in a thermostated bath for 2 hr. The temperature of the solution was then measured to establish whether it was the same as that of the bath.

Assuming the oxidative peak current is an indicator of polyaniline film conductivity, we observed that, as the temperature is increased, the conductivity of the polyaniline film increases (see Fig. 6). A similar experiment was conducted where the polyaniline coated electrode was once again left in the bath for 2 hr, but this time the solution contained 34 mM ascorbic acid and 1 M sulphuric acid.

Our preliminary observations revealed very high oxidative peak currents for ascorbic acid. This probably can be attributed to the lowering of the activation energy for electrochemical oxidation and/or improved polyaniline film conductivity at the elevated temperatures.

We are still pursuing further work in attempts to unravel possible link between polyaniline film conductivity and ascorbic acid oxidation.

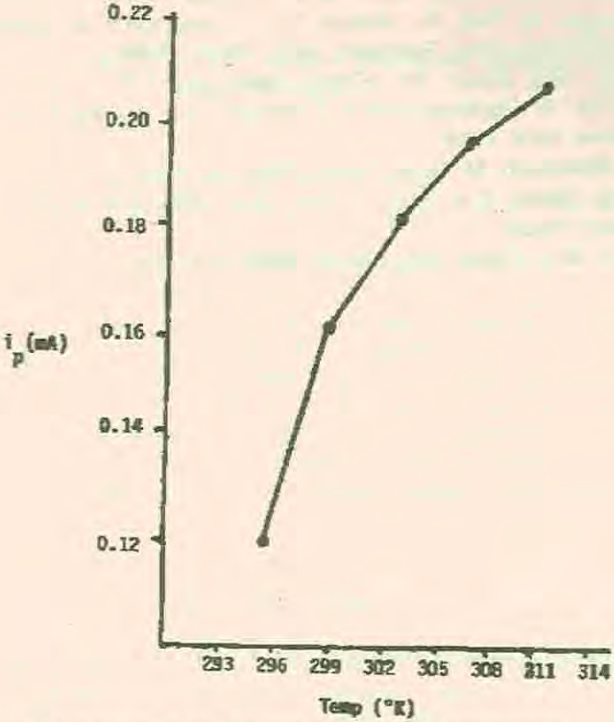

Fig. 6. Plot of polyaniline oxidative peak current (i_p) *versus* temperature.

CONCLUSION

It is apparent from the results presented in the foregoing work that derivatization of the working electrode surface with the conducting polymer, polyaniline, markedly improves the oxidation characteristics of the ascorbic acid. But it is important to mention that one should not assign polyaniline an electrocatalytic role despite this observations, since there is still deficiency in explanations pertaining to electronic properties of these polymers i.e., how electrical current passes through them.

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