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ELECTROCHEMISTRY OF POLYANILINE OBTAINED FROM POTENTIOSTATIC OXIDATION OF ANILINE ON POLYTHIOPHENE COATED ELECTRODE

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ABSTRACT. Polyaniline was electrodeposited by potentiostatic oxidation of aniline monomer in aqueous sulfuric acid solution, onto a polythiophene coated glassy carbon working electrode. The resultant cyclic voltammogram showed both polythiophene (PS) and polyaniline (PAN) redox waves. PAN electrochemistry was also observed in the case of very thick PS films, and at potentials where polythiophene is an insulator, suggesting that we are dealing with a 'composite'. Potentiostatic oxidation of equimolar amounts of aniline and thiophene monomers in sulfuric acid yielded voltammograms depicting mainly polyaniline redox wave. Results obtained from incorporation of metal ions in the 'composite' revealed that the oxidation potential of the metal cation is decreased when it is incorporated in the polymer matrix.

INTRODUCTION

A lot of work has been done in the study of electronically conducting polymers. These studies have focussed mainly on systems such as polyaniline, polypyrrole, and polythiophene (1,2). Conducting polymers have been used as electrochromic display devices , and are also serving as energy storage units. As a result of their increasing importance in electrochemical industries, attempts are being made to improve and broaden their role in the above mentioned areas, as well as in newly discovered domains.

Most of the work involve the formation of composites. This has traditionally involved the electrodeposition of a conducting polymer on an insulating host-matrix coated on the working electrode by 'dip-coating' (3,4). PVC and Nafion have served as useful host-matrices.

In this paper we report on the formation of a composite by electropolymerization of aniline on a PS coated glassy carbon working electrode. The PS had been electrodeposited by cycling the potential within the specified limits. It was possible to observe both the PAN and PS redox waves simultaneously. The results further reveal the importance of depostion pattern i.e. one is not able to electropolymerize thiophene on a PAN coated electrode from a solution containing thiophene monomer in an acid solution. Similarly electropolymerization of aniline takes precedence over that of thiophene when the potental is cycled within the specified limits in a solution containing equimolar amounts of aniline and thiophene monomers in acid solution. We also present results on the incorporation of metal ion into the polymer matrix and how the electrochemical response of the latter is affected by the matrix.

EXPERIMENTAL

Reagent grade acids and chemicals were used as received. The thiophene and aniline were doubly distilled under reduced pressure until a colorless solution was obtained. The solutions were kept under nitrogen. All the solutions were prepared using triply distilled water. During and in between the experiments the solution in the electrochemical cell was de - gassed by bubbling nitrogen.

Glassy carbon was used as the working electrode. Before each fresh experiment, the glassy carbon was polished using alumina on felt polishing cloth. Platinum wire and saturated calomel electrodes were used as auxiliary and reference electrodes respectively.

RESULTS AND DISCUSSION

Fig. 1 shows the steady state cyclic voltammogram (CV) obtained when PS was electrodeposited by continuously cycling the potential between - 0.2 and 0.9 volts in a solution containing 0.1 M thiophene in 1.0 M sulfuric acid solution, at a scan rate of 50 mV/sec. The PS oxidation and reduction waves occur at 0.33 and 0.24 volts respectively. The oxidation peak is sharper compared to the reduction peak. These peaks are a consequence of redox precesses that lead to the change in the conductivity of PS just as has been observed in the case of other conducting polymers (1,2). Reduction produces an insulating film whilst oxidation produces a conducting film. The CV shown in Fig. 1 represents a thin film of PS with a surface coverage of approximately 22 monolayers (2.2 x 10^{-9} mol/cm).

The film in Fig. 1 was then rinsed with triply distilled water prior to transfer to a solution containing 0.1 M aniline in 1.0 M sulfuric acid solution. The PAN was electrodeposited by continuously cycling the potential between - 0.2 to 0.75 volts. Cycling to very positive potentials was avoided to deter the formation of quinone derivatives (7).

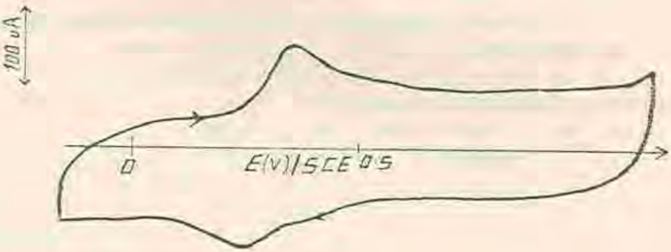


Fig. 1 CV recorded in a solution containing 0.1 M thiophene and 1.0 M sulfuric acid. Scan rate, 50 mV/sec.

Fig. 2 shows the CV obtained during the first scan on transfer to the aniline containing media. We observe both the PAN and PS redox waves. The PAN oxidation and reduction waves occur at 0.12 and - 0.02 volts respectively. We also observe a 'shoulder' immediately after the PS oxdation peak. As was already suggested, the fact that we observe the electrochemical reactions of aniline at potentials negative of the polythiophene wave indicates that, both the polymers are electrode accessible, thus, we are not dealing with a two - polymer bilayer where the electroactivity of the outer polymer is via mediation by the polymer nearest the electrode (see Scheme 1). We also do not observe any charge trapping or rectification as would have been expected for a bilayer case, where the interface between the two polymer films act as a charge rectifying junction provided the redox levels in the two polymers are appropriately situated (8,9).

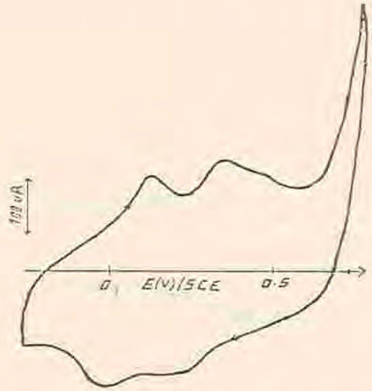
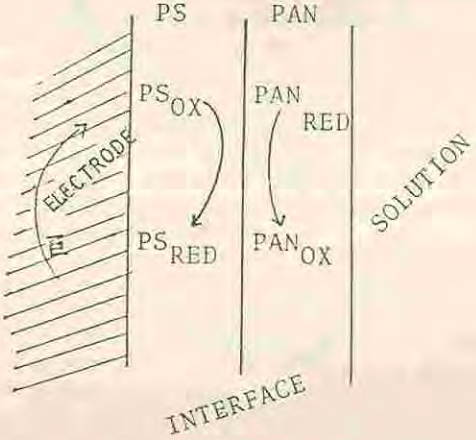


Fig. 2 CV response recorded on first scan after transferring the polythiophene coated electrode (described in Fig. 1) to a solution containing 0.1 M aniline and 1.0 M sulfuric acid. Scan rate 50 mV/sec.

Scheme 1



It is also oberved that the PS oxidation and reduction peaks have shifted by 10 and 40 millivolts respectively. The electrical resistance of the film could be a possible cause for this shift. On continued cycling, there was a reduction in the currents, and the PS wave degenerated, as the PAN wave continued to grow, as shown in Fig. 3. The CV were recorded at intervals of 240 seconds. Table 1 shows how the anodic peak current varied with time. The rate of change of anodic peak current is approximately 0.1 μA per second. This indicates that the growth of PAN is relatively constant.

Table 2 shows the variation of anodic peak current with scan rate for the PAN redox wave. We observe that the scan rate varies approximately linearly as the peak current, as is typical of surface attached species.

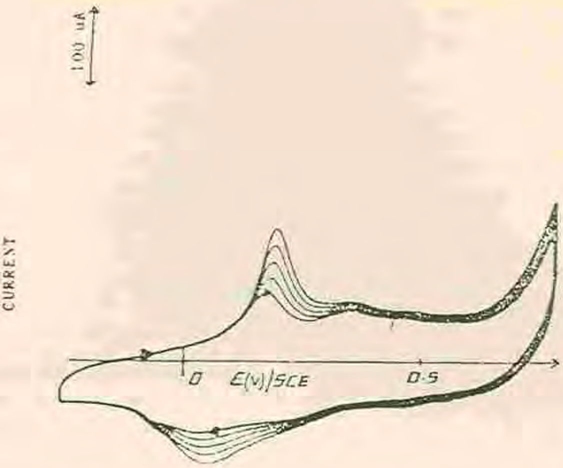


Fig. 3. CV showing the growth of PAN in a solution containing 0.1 aniline and 1.0 M sulfuric acid. Scan rate, 50 mV/sec.

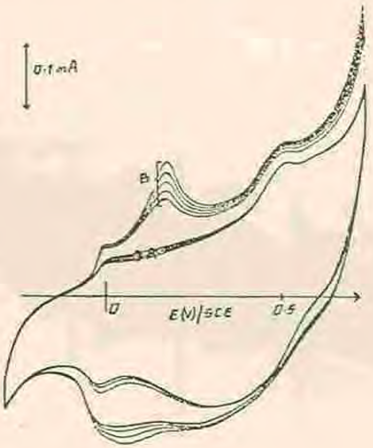


Fig. 4. CV response showing the PAN redox wave, obtained from the electrodeposition of aniline on a carbon graphite electrode coated with a 'thick' PS film. The sets of voltammograms A and B show film growth. Between sets A and B the recorder pen was 'lifted'.

A thick film (approximately 100 monolayers) of polythiophene was electrodeposited on the working electrode by continuously cycling the potential between - 0.2 and 0.9 volts, in a solution containing 0.1 M thiophene and 1.0 M sulfuric acid. The PS coated electrode was then transferred to a solution containing 0.1 M aniline and 1.0 M sulfuric and the aniline electrodeposited as described in Fig. 1. We observed both the PS and PAN redox waves on the first scan, as was the case for electrode coated with a thin PS film (see Fig. 4). On continuous cycling we observe the PAN redox properties distinctly.

Table 1.

TIME (secs)	ANODIC CURRENT (μA)
240	73
480	90
720	110
960	128
1200	145

Table 2.

ANODIC CURRENT (mA)	SCAN RATE (mV/sec)
0.4	10
0.6	20
2.2	50
4.0	100

The PAN oxidation potential occurs at 0.17 volts and the reduction potential at 0.04 volts, indicating that the PAN oxidation and reduction peaks have shifted by 50 and 60 mV respectively towards positive potentials in the thick film case. This shift can also be attributed to the electrical resistance of the film. The fact that we can still observe PAN electrochemical properties on a thick PS film enhances the suggestion that we are dealing with a composite, whereby both films are electrode accessible as already mentioned. The dominance of PAN electrochemical response over that of PS is expected since the solution does not contain any thiophene monomer. Studies involving thick PS films can be complicated as a result of the films undergoing morphological transition, with increasing film thickness (5a, 5b).

To observe whether the sequence followed in the deposition process was of significance, experiments were conducted in which PAN served as the host-matrix in place of PS. On transferring the PAN coated electrode to a solution containing 0.1 M thiophene in 1.0 M sulfuric acid, and cycling the potential from - 0.25 to 0.80 volts, electropolymerization of thiophene was not observed. It is thus possible that the PAN matrix was impervious to thiophene monomer. Attempts to electropolymerize PAN and PS simultaneously from a solution containing equimolar amount of thiophene and aniline in a solution containing 1.0 M sulfuric acid yielded CV depicting only the PAN redox wave.

A fresh 'PAN-PS' film was prepared as already discussed. The film was then transferred to a solution containing 1.0 mM ammonium ferrous sulfate, 0.1 M pyridine and 1.0 M sulfuric acid. The cyclic voltammetric response is shown in Fig. 5 (The pyridine was included based on previous observation (6) that it modifies the porosity of the film to metal ions). We observe an oxidation peak at 0.49 V and a reduction peak at 0.34 V. We anticipate that these peaks represent the ferrous/ferric redox process. The CV obtained on a bare glassy carbon electrode in a solution containing 1.0 mM ferrous ammonium sulfate and 0.1 M pyridine showed oxidation and reduction peaks at 0.52 and 0.32 volts respectively. The cyclic voltammogram also displayed peak tailing typical of diffusion-limited systems. This strongly contrasted with the surface attached species shown in Fig. 5. We note that the oxidation wave was shifted by 30

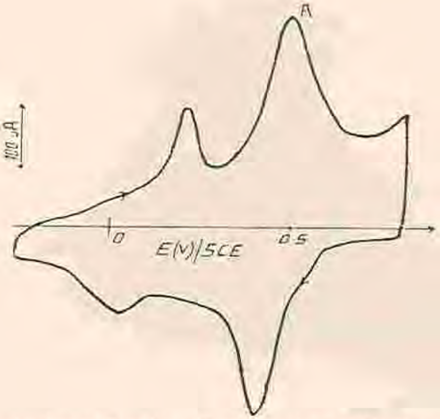


Fig. 5. CV obtained on transferring the film to a solution containing 1.0 mM ammonium ferrous sulfate, 0.1 M pyridine and 1.0 M sulfuric acid.

mV and the reduction wave by 20 mV. One can thus infer that, once the metal ion is incorporated into the polymer matrix, it becomes easier to oxidize, but much more difficult to reduce. This is probably as a result of electrostatic interactions between the metal ion and the polymer matrix, interactions which lower the oxidation potential of the metal ion, coupled with the change in coordination of the metal ion upon incorporation into the polymer.

CONCLUSION

The results obtained in this work indicate that we are dealing with a 'PAN-PS' composite rather than a bilayer. This assertion is supported by the fact that we do not observe characteristics typical of bilayers (8,9). Thus, both polymers are accessible to the electrode.

Studies on incorporation of metal ions into the polymer matrix and the results obtained therein, will enable detailed comparative studies to be conducted to establish how such a robust polymer system modifies/influences the electrochemistry of the metal ion, as compared to macrocyclics typical of biochemical systems.

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