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ELECTROCHEMICAL CHARACTERISTICS OF POLYANILINE ELECTROPOLYMERIZED ON A 'PHENOL' MODIFIED CARBON ELECTRODE

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ABSTRACT. Polyaniline (PAN) film electrosynthesized on a phenolic polymer coated carbon graphite working electrode is observed to exhibit electrochemical properties 'alien' to bare polyaniline. It is observed that, the reduction process is less efficient as compared to the case of bare PAN. This suggests a kind of 'rectification' in the PAN redox process. Also of significant interest, was the ability of the PAN film to maintain its electrochemical integrity i.e., no substantial degradation at positive potentials i.e., above 0.8 V, in the absence of aniline monomer.

INTRODUCTION

A lot of research continues in the field of organic electronic conductors, and is centerd mainly on poly-(aniline, thiophene and pyrrole), [1,2].

Most of these research is geared towards improving their mechanical properties, synthesis, and possible methods on how to broaden their role as electrochromic devices, electrocatalysts in modified electrodes and as electrodes in energy storage units. Unlike PAN, the polyheterocycles - polypyrrole and polythiophene-display poor mechanical properties and conductivity in the aqueous media which has served as a barrier to expansion of their use in the fields cited above. As a result formation of composite or bilayer structures has been proposed. The host-matrix is normaly deposited on the electrode surface by dip-coating or droplet evaporation. In dip-coating, the electrode is exposed to a dilute solution of the polymer with the subsequent attachment of the polymer film on the electrode surface by adsorptive process. Droplet evaporation involves evaporation of the dilute solution of the polymer after spreading it on the electrode surface.

In most of these studies, the host-matrix is insulating. Examples include polymerization of PAN on a Nafion matrix and polymerization of pyrrole in a matrix of poly- (vinyl chloride), [3-5]. Tetrathiafulvanilinium bromide structures have also been electrochemically prepared within Nafion films [6,7].

The effect of poly-(acrylic acid) and poly-(methyl methacrylate) on electrochemical properties of PAN [8] has also been studied. In this paper, studies were conducted to ascertain the influence of the 'phenolic' polymer host-matrix on the electropolymerization of PAN.

It was also of interest to try and establish from the electrochemical data, whether the resulting material represents a composite or a bilayer structure.

Separate studies were conducted to try and observe whether the resulting 'structure' has some influence on the PAN degradation characteristics.

EXPERIMENTAL

All the chemical reagents: phenol (BDH), sodium chloride (Aldrich), and sulphuric acid (Aldrich), were used as received without further purification. The aniline

(Aldrich) was triply distilled yielding a colorless liquid. The latter was stored under nitrogen. All the solutions were prepared using triply distilled water. The electrochemical equipment and the three electrode assembly used is similar to that discussed in reference [1].

RESULTS AND DISCUSSION

The phenolic 'polymeric' films were electrodeposited on the working electrode by cycling the potential from -0.3 V to 0.75 V in a solution containing 0.1 M phenol, 0.1 M potassium hydroxide and 1.0 M sodium chloride. The resultant cyclic voltammogram (CV) is shown in Fig. 1. We observe an irreversible oxidation peak at approximately 0.43 V. This peak can be attributed to phenol oxidation, even though it is still unclear how many electrons are involved in the transfer. Subsequent cycles yield broad/misshaped voltammograms, which is indeed not surprising given the fact that we have been filming at the electrode surface [9], a characteristic which has made mechanistic studies on phenol difficult. Since our main interest was to study the possibility of electropolymerizing aniline on this 'phenolic' matrix and to study, if any, the influence of the phenolic host-matrix on PAN electrochemical properties, the cyclic voltammetric response of the phenol was thus not a handicap. To test for the stability of the 'phenolic' coating on the electrode, the latter was transfered to a solution containing 1.0 M sulphuric acid (no aniline monomer). There was no evidence of degradation in the electrochemical response of the 'phenol'. The 'phenol' coated polymer was now transfered to a solution containing 0.1 M aniline and 1.0 M sulphuric acid. The potential was then cycled from - 0.3 V to 0.8 V. The PAN film growth is illustrated in the CV response shown in Fig. 2. The PAN oxidation peak is observed at approximately 0.22 V, and the reduction peaks are observed at -0.06 V, 0.0 V, 0.18 V, and 0.40 V. The peak at 0.0 V is probably representative of the PAN reduction peak.

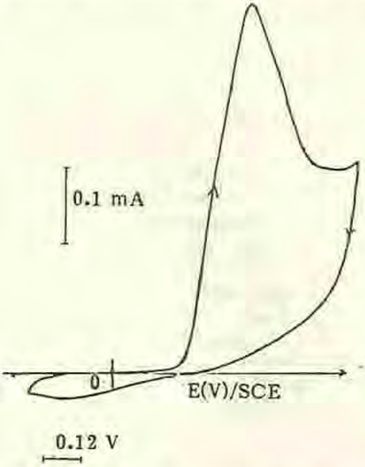

Fig. 1. Cyclic voltammetric response on cycling the potential from -0.3 V to 0.75 V in a solution containing 0.1 M phenol, 0.1 M sodium chloride and 0.1 M potassium hydroxide. Scan rate, 50 mV/sec.

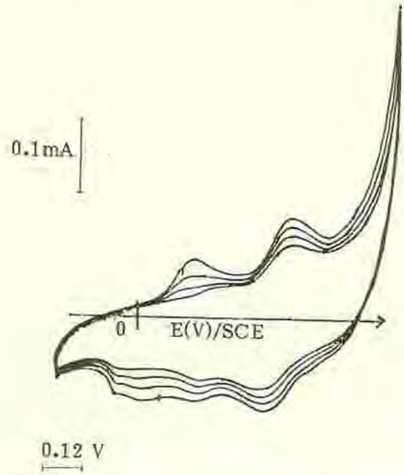

Fig. 2. Cyclic voltammogram obtained on electropolymerizing PAN on a 'phenolic' polymer coated carbon electrode. Scan rate, 50 mV/sec.

This assertion is based on a comparison of the cyclic voltammograms shown in Figs. 2 and 3. The extra reduction peaks can be attributed to the influence of the phenolic host-matrix on the redox properties of PAN. These effects probably result from the new environment in which the PAN film finds itself, assuming that the latter grows inside the matrix pores forming PAN microdomains inside the matrix. Under such circumstances, the transport of dopant ions can be affected substantially, by the now increasingly 'viscous/non-porous', medium. This would manifest itself by the shifts in the oxidation and reduction potentials. We actually observe a shift of 20 mV towards the negative potentials for the oxidation peak (see Figs. 2 and 3). The reduction peak apears to be invariant. Specification of the extent of shift, if any, is complicated even more by the fact that the peak at 0.0 V is quite broad, hence making it difficult to determine the actual shift in potential.

At this juncture, it is worth emphasizing that, our choice of the PAN reduction peak in the PAN-phenol structure was arbitrary i.e., assuming the behaviour of bare PAN. But, even if any of the peaks could have represented the PAN reduction peak, it is clear that, in all the cases, the phenolic matrix influences the PAN reduction potential. Another important factor to bear in mind is that, pH variation in the film interior can also account for the shifts in redox potentials i.e., high pH will result in a shift of the PAN oxidation potential towards negative potentials.

Another interesting observation is that, the reduction process is less 'efficient' in the PAN - phenol structure as compared to the bare PAN case (see Figs. 2 and 3), when one considers the total charge passed (charge under the CV). This 'inefficiency' is not as a result of oxidized species diffusing away from the electrode surface or reacting to form a non-electroactive species (ECtype mechanism) as evidenced from scan rate studies. Such a 'rectification' in the redox process is a veiled pointer to a bilayer structure, even though, as the film thickness increases, the reduction peak becomes more apparent with the other peaks vanishing. The reduction peak potential is now the same as that for the bare PAN. This observation can be attributed to the fact that the system

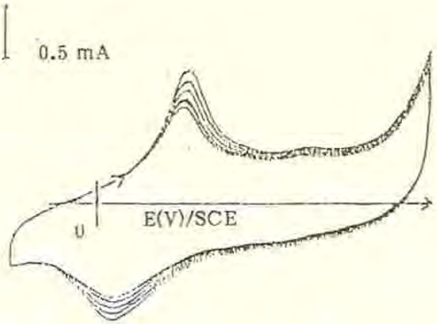

Fig.3. Cyclic voltammetric response obtained during PAN film growth in a solution containing 0.1 M aniline and 1.0 M sulphuric acid. Scan rate, 50 mV/sec.

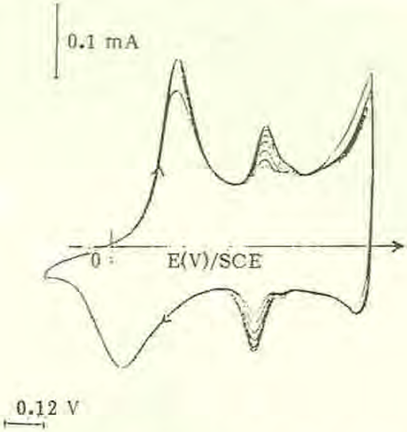

Fig. 4. Cyclic voltammogram showing the decrease in oxidative peak current on cycling the potential from -0.2 V to 0.8 V. Scan rate, 50 mV/sec.

now has more PAN 'character', eclipsing the influence/effect of the matrix. Thus, it is possible that the changes just discussed also depend to some extent on the 'level' of contact between the two 'phases'.

A fresh PAN-phenol film was electrosynthesized as already desribed. The PAN film was thicker than that shown in Fig. 2 (compare the oxidative peak currents). The film was then transfered to the phenolic polymer growth solution (see Fig. 1), in attempts to see whether we can grow more phenolic polymer on phenol-PAN matrix, and to establish whether this could render the matrix surface electro-inactive. Surprisingly, on rinsing and transfering the matrix/film to a solution containig 1.0 M sulphuric acid (no aniline monomer), a decrease in the PAN oxidation peak current was observed during the first six potential scan (cycling from - 0.2 V to 0.8 V), before it remained unchanged. During this decrease, the reduction peak current was invariant (see Fig. 4). In most cases when PAN is cycled in the absence of aniline monomer to very positive potentials i.e., above 0.7 V, its electrochemical properties degrade (characterized by a decrease in the redox peak currents).

This behaviour was not registered in the case of PAN - phenol structure when the potential was cycled above 0.7 V (see Fig. 4). This preliminary observation is as yet inconclusive, and more work is going on to establish the potential 'window' within which this observation holds.

CONCLUSION

The results presented in this paper suggest that phenolic polymer can influence the electrochemical properties of the PAN film substantially. Even though how it achieves this is purely speculative, it is apparently not acting as an electron transfer medium, based on the fact that, on its own, it displays poor electrochemistry as evidenced in the broad/misshaped voltammograms mentioned earlier in the paper.

At this stage, it is also important to mention that, the 'rectification' in the redox process does not neccesarily highlight the formation of bilayer structure. Investigations are still going on in our laboratory, to establish from optical data whether we are dealing with a composite or bilayer structure. This is even more important given the fact that, an heterojunction in this case can usher in a new generation of semi-conductor type materials.

REFERENCES

1. D. Orata, Bull. Chem. Soc. Ethiop., **3**(1), 41 (1989).
2. D. Orata and D. Buttry, J. Am. Chem. Soc., **109**, 3574 (1987).
3. D. Orata and D. Buttry, J. Electroanal. Chem., **257**, 71 (1988).
4. M. De Paoli, R. Waltman, A.F. Diaz and J. Bargon, J. Polym. Sci., Polym. Chem. Ed., **23**, 1687 (1985).
5. O. Niwa and T. Tamamura, J. Chem. Soc., Chem. Commun., 817 (1984).
6. T. Henning, H.S. White and A.J. Bard, J. Am. Chem. Soc., **103**, 3937 (1981).
7. T.P. Henning and A.J. Bard, J. Electrochem. Soc., **130**, 613 (1983).
8. J.C. LaCroix and A.F. Diaz, Makromol. Che. Macromol. Symp., **8**, 17 (1987).
9. F.J. Vermillion, and I.A. Pearl, J. Electrochem. Soc., **111**, 1392 (1964).