

ELECTROPOLYMERIZATION OF ANILINE IN THE PRESENCE OF 2,2'-BIPYRIDINE

Duke Omondi Orata
Department of Chemistry, University of Nairobi
Box 30197, Nairobi, Kenya

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ABSTRACT. The experiments involved electropolymerization of aniline in the presence of 2,2'-bipyridine monomers. The results obtained show that the cyclic voltammograms (CV) obtained during electropolymerization of aniline is altered significantly by the presence of 2,2'-bipyridine. We also observed reversible oxidation/reduction peaks for Fe(II)/Fe(III) couple on the polymer modified electrode.

INTRODUCTION

Polymeric systems containing 4,4'-alkylated bipyridines have been termed viologens (1,2,3). A lot of studies is being done on these systems given that the viologens serve as electron acceptors in photoelectrochemical schemes (4), and also have been used in p-type silicon semiconductor electrodes. In this paper, attempts were made to generate a polyaniline 'analogue', by simultaneously electrodepositing polyaniline from a solution containing both aniline and 2,2'-bipyridine monomers. The redox chemistry of Fe(II)/Fe(III) was also studied on the polymer modified electrode.

EXPERIMENTAL SECTION

The aniline was triply distilled prior to use until a colorless liquid was obtained. Ferrous sulphate (BDH), 2,2'-bipyridine (Aldrich) were used as received. All the solutions were prepared using triply distilled water. The electrochemical instrumentation used was the same as that discussed in reference (5). Carbon graphite, saturated calomel electrode (SCE), and platinum wire were used as working, reference, and auxiliary electrodes respectively.

RESULTS AND DISCUSSION

The CV response shown in Fig. 1a represents polyaniline electrodeposited from a growth solution containing 0.1 M aniline and 1.0 M sulphuric acid. The potential was cycled between -0.2 V and 0.75 V. The polyaniline (PAN) oxidation and reduction peaks occur at 0.2 V and 0.04 V respectively. The electrochemical aspects of PAN have already been discussed in detail by several researchers (6). Similar procedure was followed in attempts to electropolymerize aniline from a solution containing in addition 0.1 M 2,2'-bipyridine; the results are shown in Fig. 1b. We observe that the PAN oxidation and reduction peaks now occur at 0.04 V and -0.04 V respectively. Thus, the PAN oxidation and reduction peaks have shifted by 160 and 80 mV respectively towards more negative potentials. This shift may be attributed to a higher pH in the film.

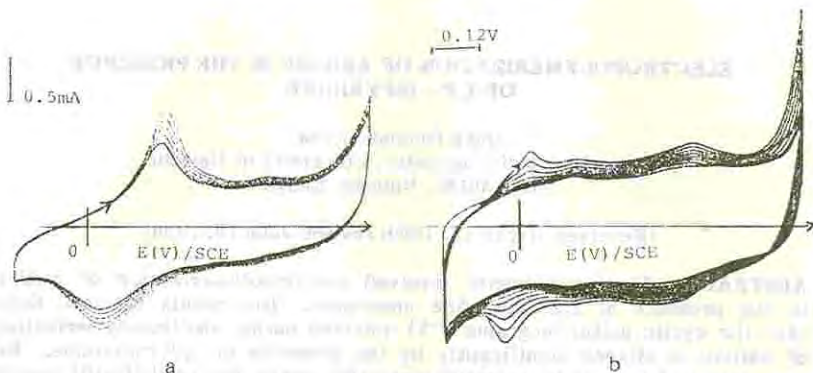


Fig. 1a. CV response during film growth in a solution of 0.1m aniline and 1.0m sulphuric acid. The potential limit is from -0.2V to 0.75V . Scan rate, 50mV/Sec .

Fig. 1b. CV response during film growth in a solution containing 0.1m aniline, 0.1m 2,2'-bipyridine under conditions similar to those in 1a.

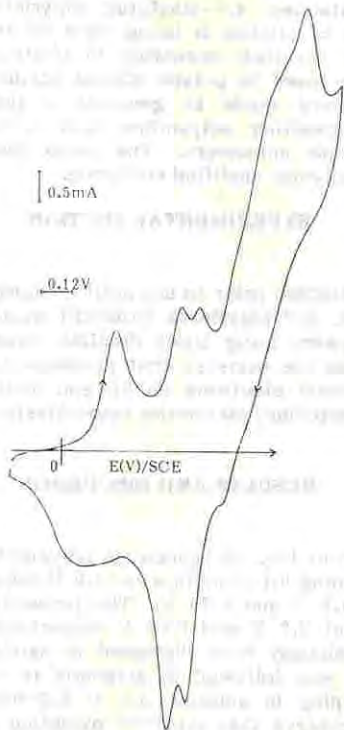


Fig. 2. Potential limit increased to 1.1V for the film discussed in Figure 1b. Scan rate, 20mV/Sec .

The oxidation and reduction peaks observed at 0.46 V and 0.38 V respectively can be attributed to quinone derivatives (6). When the potential limit was increased to 1.1 V (see Fig. 2), in the case of the film discussed in Fig. 1b, we observed several new oxidation/reduction peaks, at 0.50 V/0.39 V, 0.59 V/0.47 V, and an irreversible oxidation peak at 1.02 V. These peaks can be attributed to the redox properties of 2,2'-bipyridine monomers in the growth solution, since similar, but slightly displaced (to more positive potentials) peaks are observed when the oxidation-reduction process is carried out in a solution containing 0.1 M 2,2'-bipyridine and 1.0 M sulphuric acid using a bare carbon electrode. Hence, the slight shift can be attributed to the polymer coating on the electrode. It is worth noting that the PAN oxidation peak has shifted to 0.23 V, and the reduction peak is now not well defined i.e., broadened. These shifts can once again be attributed to pH changes in the film. A fresh PAN film was electrodeposited from a solution free of 2,2'-bipyridine monomers. The film was then transferred to a solution containing 0.1 M ferrous sulphate, 0.1 M 2,2'-bipyridine and 1.0 M sulphuric acid. The CV response is shown in Fig. 3. We observe oxidation and reduction peaks at 0.50 V and 0.38 V respectively. This redox wave is most likely due to the Fe(II)/Fe(III) redox couple; even though a mixture of Fe(II) and bipyridine in a 1:1 ratio will contain a mixture of complexes of the form (FeL_n^{2+}) , $n = 0, \dots, 3$. (The relative concentrations of these complexes can be calculated from the known stepwise equilibrium constants (7). Hence, it is unlikely that the mixture will contain just Fe^{2+} and (FeL_n^{2+}) in the ratio 2:1). To further clarify the nature of redox waves which appear at 0.50 V and 0.38 V, CV response was taken in a solution containing 0.1 M ferrous sulphate alone, using the PAN electrode in Fig. 3. Similar redox waves were obtained (see Fig. 4). On increasing the potential limit to 1.0 V in the case of the film in Fig. 3 we observe a redox wave at 0.82 V/0.77 V. See Fig. 5. This peak is probably due to FeL based on its redox potential.

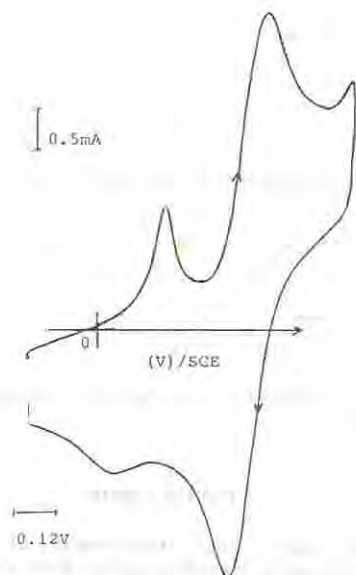


Fig. 3. CV response for PAN film in a solution containing 0.1 M 2,2'-bipyridine and 1.0 m sulphuric acid. Scan rate 50mV/Sec.

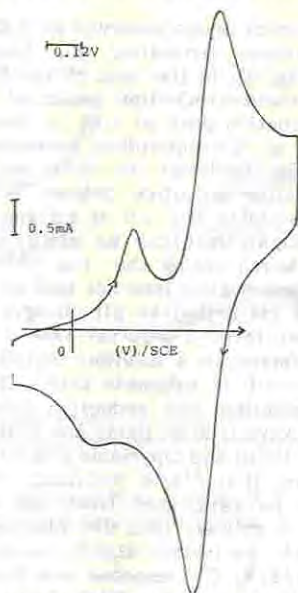


Fig. 4. CV response for PAN film in a solution containing 0.1 M 2,2'-bipyridine and 1.0 M sulphuric acid. Scan rate 50mV/sec.

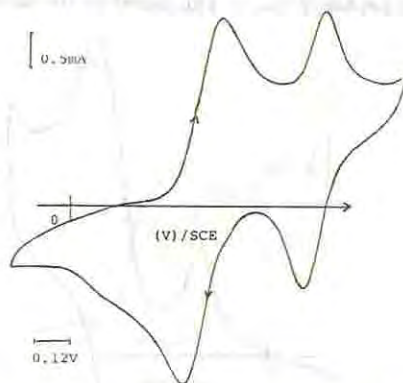


Fig. 5. Potential limit increased to 1.0V for film discussed in Figure 3. Scan rate, 50mV/Sec.

CONCLUSION

The results presented suggest that the presence of 2,2'-bipyridine monomers in the growth solution has some influence on the PAN electrochemical properties, even though the absence of a red colour suggest that the bipyridine is not incorporated into the film matrix. Currently some spectroelectrochemical studies are being conducted to allow a more conclusive discussion on this subject.

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