

STABILIZATION OF POLYANILINE FILMS IN THE PRESENCE OF *p*-AMINOPHENOL

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ABSTRACT. Cyclic voltammetry was used to study the electrochemical properties of *p*-aminophenol on a polyaniline modified carbon electrode surface. The results reveal reversible redox waves. The quinone derivatives formed from *p*-aminophenol (PAP) oxidation seem to depress the rate of degradation of polyaniline (PAN) at positive potentials.

INTRODUCTION

Electronically conducting polymers continue to generate a lot of interest in scientific research. They are being used in fabrication of devices for various applications. Polyaniline is probably the most researched of all the conducting polymers. This is as a result of its excellent electrochemical characteristics and the fact that it is extremely stable under ambient conditions [1-3].

The one unfortunate aspect of polyaniline (PAN) is the degradation of its electrochemical properties when it is subjected to very positive potentials ca. 0.8 v. This severely limits the potential domain in which PAN can be used. Several researchers have assigned the products formed during the degradation to be quinone derivatives [4-6].

The results presented in this paper suggest that attachment of quinone derivatives on the 'surface' of a polyaniline film prior to subjecting it to very positive potentials substantially halts its electrochemical degradation.

The choice of quinone in stabilizing the PAN film was as a result of attempts to find a species which can relieve the oxidative stress by acting as a charge sink.

EXPERIMENTAL

p-Aminophenol (BDA), and sulphuric acid (Aldrich) were used without further purification. All the solutions were prepared using triply distilled water. The

electrochemical instrumentation comprised PAR 173 potentiostat/galvanostat, used in conjunction with PAR 175 Universal programmer. The output signal was fed into a PAR RE 0089 X-Y recorder. The three electrode assembly used included carbon graphite (surface area, 0.38 cm^2), saturated calomel electrode (SCE) and platinum wire as working, reference and auxiliary electrode, respectively. The working electrode surface was polished using alumina on a felt polishing cloth.

RESULTS AND DISCUSSION

PAN films were prepared by cycling the potential from -0.20 v to 0.70 v in a solution containing 0.1 M aniline and 1.0 M sulphuric acid. The resultant cyclic voltammogram is shown in curve A, Fig. 1. The PAN oxidation and reduction peaks occur at 0.2 v and 0.04 v , respectively [4].

The PAN film (in curve A) was then transferred to a solution containing 0.01 M *p*-aminophenol and 1.0 M sulphuric acid. The resulting redox waves are shown in Fig. 1, curve B. The *p*-aminophenol oxidation and reduction waves both occur at 0.53 volt . Since the peak potentials for the cathodic and anodic waves are the same ($E_p = 0$) and scan rate dependence studies also reveal that the latter varies linearly with the peak current (see Fig. 2). This suggests that we are dealing with surface waves, even though the peaks are on a sloping background which could be responsible for the apparent coincidence of potentials.

The oxidation peak for *p*-aminophenol has been attributed previously to a 2-electron process leading to the formation of a quinoneimine (QI) derivative as shown in Scheme 1 [7]. Studies were conducted to ascertain the influence of QI on polyaniline electrochemical degradation at potentials upto 1.0 v . Polyaniline films were transferred to solutions containing 1.0 M sulphuric acid and varying concentrations of PAP i.e., 0.01 M , 0.02 M and 0.04 M . On each occasion a freshly prepared PAN film was used. The potential was cycled from -0.2 v to 1.0 v and the resultant cyclic voltammograms recorded. In all the cases, there was a decrease in the peak current with each subsequent cycle. Another fresh PAN film was prepared in a similar manner and then transferred to a solution containing only 1.0 M sulphuric acid (no PAP). The potentials was then cycled between -0.2 v and 1.0 v and the resultant cyclic voltammogram recorded. A comparison of the peak currents are shown in Table 1. The successive lines correspond to peak heights measured in successive cycles.

Since the film thicknesses are not the same and also as the potential prior to oxidation can influence first oxidation cycle (memory effect), the data for PAN and PAP (0.02 M) has been presented in the form of charge fraction, $Q_{\text{remaining}}/Q_{\text{original}}$ where, Q_{original} represents the initial switching charge as shown in Table 2.

Figure 1. CV response of PAN obtained in solution (A) containing 0.1 M aniline and 1.0 M sulphuric acid and (B) 0.01 M *p*-aminophenol and 1.0 M sulphuric acid. Scan rate = 50 mV/sec.

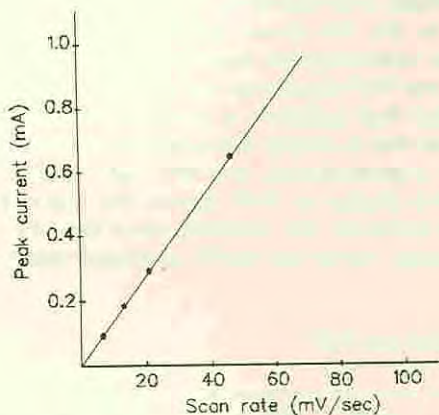
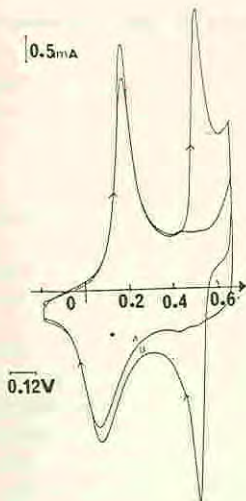
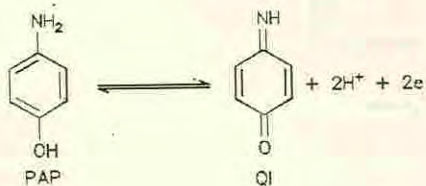


Figure 2: The variation of scan rate (mV/sec) with peak current (mA).



Scheme 1:

Table 1. Oxidative peak currents (mA) observed in varying concentrations of PAP.

Number of cycles	PAN (no PAP)	PAP (0.01)	PAP (0.02)	PAP (0.04)
1	1.0	1.7	1.7	2.0
2	1.45	1.4	1.4	1.7
3	1.05	1.1	1.15	1.5
4	0.75	0.91	0.95	1.3
5	0.55	0.75	0.8	1.1
6	0.4	0.65	--	0.95
7	--	--	--	0.8

From the results shown in Table 1, it is apparent that the decrease in the PAN oxidative peak current (height of peak above its apparent base) is least in case of 0.04 M PAP and greatest in the case where we have no PAP.

The results shown in Table 2 also show that the fractional charge left on PAN degradation is greater in the case where *p*-aminophenol is present.

It is important to mention that as the film decay approaches completion computation of the charge under the voltammogram becomes less reliable.

A possible explanation as to how the PAP depresses the degradation of PAN can be explained in terms of the fact that oxidation at very positive potential creates a chemical form in the polymer that is subject to irreversible degradation, even though, in the presence of *p*-aminophenol, the film can relieve the "oxidative stress" by transferring the charge to PAP before the irreversible degradation occurs. For this to be achieved, the *p*-aminophenol need not be bound to the film for this effect to operate, hence any readily oxidizable substrate should show the same effect.

Table 2. The charge fractions for PAN and PAP

Number of cycles	PAN	PAP (0.02M)
1	0.70	0.86
2	0.57	0.63
3	0.41	--
4	0.33	0.29

CONCLUSION

The results presented in this paper suggest that there is a possibility of controlling the electrochemical degradation of PAN in the presence of *p*-aminophenol. This would in essence allow the use of PAN at positive potentials.

Research is still being conducted using other readily oxidizable substrates. Optimum experimental conditions, e.g pH, which will broaden the potential 'window' of PAN stability are also being investigated.

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