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# SUPPRESSION OF POLYANILINE ELECTROCHEMICAL DEGRADATION IN SALT SOLUTIONS

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**ABSTRACT**. The results presented in this paper reveal that, the electrochemical degradation of polyaniline at positive potentials (*ca* 0.70 V) *vs* SCE in the absence of aniline monomer is totally suppressed when the electrochemical process is carried in sodium chloride solution and acetic acid-sodium acetate mixture.

## INTRODUCTION

Research on conducting polymers i.e., poly-(aniline, pyrrole, thiophene and isothianaphthene) continues unabated. The research is focused primarily on trying to understand the mechanism of electrical conductivity in these films [1-9]. The effect of solvent content and ion population on the electrochemical properties has also been a subject of interest. Polyaniline has generated a lot of interest especially given the fact that, it is easily synthesized [1], has well behaved electrochemistry [4], and is stable under ambient conditions [1]. A major handicap in the electrochemical characterization/usage of polyaniline is that it undergoes electrochemical degradation at potentials above 0.70 V *versus* SCE. This behaviour makes it difficult to study, for example, the versatility of a polyaniline derivatized electrode as an electrocatalyst for a redox process involving an electrochemical species whose redox potential occurs in the potential range where polyaniline degrades. In this paper, the polyaniline film is shown to maintain its electrochemical integrity on continuous potential cycling in solutions containing sodium chloride or acetic acid - sodium acetate mixture (no aniline monomer).

## EXPERIMENTAL

All the acids and reagent grade chemicals (sodium chloride and sodium acetate (BDH)), were used as received without further purification. Aniline was triply distilled until a colourless liquid was obtained. The latter was then stored under nitrogen. A three electrode assembly comprising of saturated calomel as the reference electrode, platinum wire as the auxiliary/counter electrode and carbon graphite (surface area, 0.38 cm$^2$) as the working electrode were used in the electrochemical cell. The electrochemical instrumentation consisted of a PAR Model 173 Potentiostat/ Galvanostat used in conjunction with PAR Model 175 Universal Programmer to generate the potential sweep. The output signal was fed into a PAR RE 0089 X-Y recorder. The working electrode was polished on a felt polishing cloth, prior to electrosynthesis of a fresh film.

## RESULTS AND DISCUSSION

The polyaniline film was electrodeposited by cycling the potential from -0.2 V in a to 0.75 V in a solution containing 1 M sulphuric acid and 0.1 M aniline (Fig. 1). During the electrochemical deposition of the film there was increase in both anodic and cathodic peak currents with each subsequent cycle. The polyaniline film was rinsed with triply distilled water and then transferred to a solution containing only 1.0 M sodium chloride (no aniline monomer) and the potential cycled from -0.2 V to 0.75 V. A decrease in the oxidative peak current was observed with each subsequent cycle. The same behaviour was observed when a freshly prepared polyaniline film was transferred to a solution containing 1.0 M hydrochloric acid. The percent change in the peak currents are shown in Table 1 (a) and (b) for both cases. When polyaniline had been completely degraded i.e., peak current approximately equal to zero, one could still observe that, in the case of sodium chloride the film was still on the electrode surface (greenish/blue coloration) and this was confirmed when the electrode was transferred to a solution containing only 1 M sulphuric acid as shown in Fig. 2. The cyclic voltammetric response indicated that, no degradation had taken place, since the oxidative charge was nearly of the same magnitude as was for the initial film ($1.94\times10^{-1}$ $Ccm^{-2}$). This behaviour can best be explained based on the MaC Diarmid Model (Scheme A). When polyaniline is oxidized above 0.70 V in sulphuric acid solution (no aniline monomer), the polyaniline is deprotonated, an effect which lifts the requirement for charge compensating anions. The film at this stage will be containing excess anions and protons resulting from the deprotonation. The species to be expelled from the film will depend on the nature of excess charge in the film. But, in the case of sodium chloride solution we propose that we have sorbed electrolyte in the film and this remains even when the film is switched to its conductive state. The presence of the electrolyte in the film probably leads to the formation of ionpairs. This scenario led to stabilization of the imines to hydrolysis. Similar results were obtained when a fresh film of polyaniline was transferred to a solution containing acetic acid-sodium acetate mixture (Fig. 3).

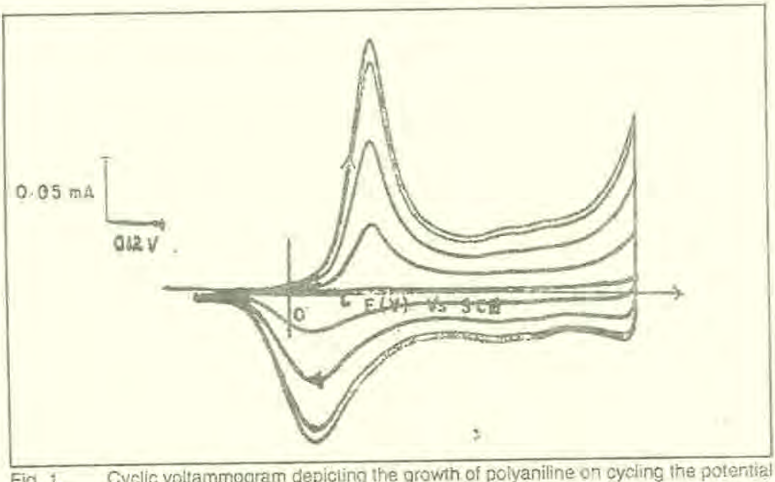

Fig. 1. Cyclic voltammogram depicting the growth of polyaniline on cycling the potential from - 0.2 V to 0.75 V. Scan rate, 20 mV/sec.

We observed that, the film was non-conducting after the first scan. Thus, unlike in the case of sodium chloride we do not observe a systematic decrease in peak current. This film gave a well defined cyclic voltammogram on transfer to a solution containing 1 M sulphuric acid. In this case it appears as though oxidation during first scan, produces an electroinactive layer which quickly becomes electroactive at low pH. This probably explains why polyaniline electroactivity is restored on transfer to a medium containing 1 M sulphuric acid. This assertion(s) is speculative and must remain so, subject to further research.

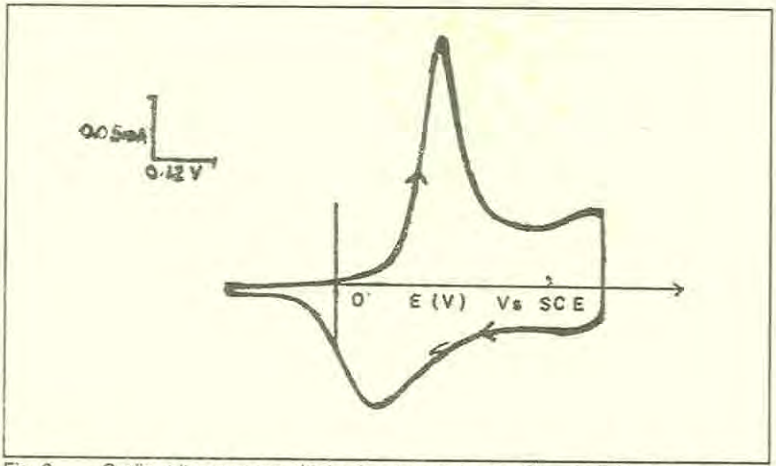

Fig. 2. Cyclic voltammogram obtained on transfering the 'degraded' film into a solution containing 1 M $H_2SO_4$. Scan rate, 20 mV/Sec.

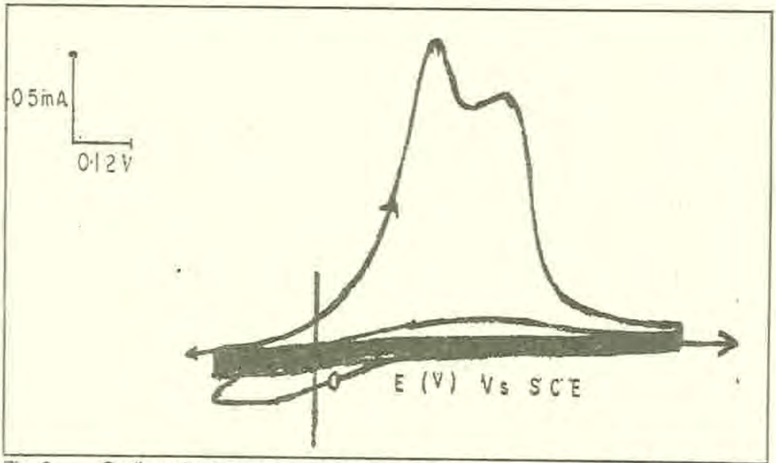

Fig. 3. Cyclic voltammogram obtained on transfering polyaniline film to a solution containing acetic acid-sodium acetate mixture. Scan rate, 20 mV/sec.

## CONCLUSION

Work is still in progress in our laboratory to try and establish whether this is a broad spectrum salt effect on the electrochemical degradation of polyaniline or if it is specific to given cations/anions. These investigations will be particularly important, given the fact that the major handicap in the use of polyaniline is its instability at far positive potentials.

Table 1. Percent change in oxidative peak currents.

a) 1 M sodium chloride solution

| Time (min.) | Scan | % Relative to $i_{p1o}^{*}$ |
|---|---|---|
| 0 | 1 | 100 |
| 1.57 | 2 | 39.6 |
| 3.13 | 3 | 24.1 |
| 4.70 | 4 | 17.2 |

b) 1 M hydrochloric acid

| Time (min.) | Scan | % Relative to $i_{p1o}^{*}$ |
|---|---|---|
| 0 | 1 | 100 |
| 18.83 | 2 | 90.4 |
| 37.67 | 3 | 81.4 |
| 56.50 | 4 | 73.4 |
| 75.33 | 5 | 65.4 |
| 94.17 | 6 | 58.5 |

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