

Stability and electrical properties of polyaniline films formed with EDTA and FeEDTA in the electrolyte

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The incorporation of EDTA and Fe(II/III)EDTA into polyaniline films has been achieved by electropolymerization of aniline in acid solutions at constant potential. The stability and electrical properties of these films have been studied by cyclic voltammetry and electrochemical impedance spectroscopy. The presence of FeEDTA species inhibits the second redox process in the polymer film corresponding to the emeraldine/permanganine transition and decreases degradation of these films upon cycling to positive potentials. EDTA increases the degree of cross-linking reactions within the film and leads to less conducting and thinner films compared to those obtained with FeEDTA in the electrolyte.

1. Introduction

Doping ions can be incorporated into conducting polymers films by either growing the film in the presence of the ions or cycling the preformed films in a solution of such ions [1]. Different anionic species have already been incorporated into these films during the electropolymerization processes. For example, MoS_4^{2-} has been incorporated into polypyrrole [2], without causing a substantial change in its conductivity. Iron and cobalt phthalocyanines tetrasulfonated anions have also been incorporated into polypyrrole and polyaniline (PANI), producing films with catalytic activity for oxygen reduction [3], but lacking long-term stability [4, 5]. PANI films have been doped with $[\text{Fe}(\text{CN})_6]^{3-/4-}$ but these species do not remain within the film and cause its degradation [6]. Oxametallates incorporated into PANI give very stable cyclic voltammetric profiles [7, 8]. However, there are few reports in the literature concerning the stability of PANI films containing incorporated electroactive species [9–11].

In this paper, the incorporation of Fe(II/III)(EDTA) species during the electrosynthesis of PANI generated potentiostatically is described. The stability and electrical properties of these films are investigated by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS).

2. Experimental details

Aniline (analytical grade from Merck) was distilled under low pressure and nitrogen atmosphere and stored in the dark before use. Other chemicals

(H_2SO_4 , $\text{Fe}(\text{NO}_3)_3$ and Na_2EDTA) were analytical grade from Merck and used without further purification. The Fe(EDTA) species was obtained by mixing stoichiometric quantities of both $\text{Fe}(\text{NO}_3)_3$ and Na_2EDTA to give a final concentration of $5 \times 10^{-2} \text{ M}$ and the pH was adjusted with a 0.5 M H_2SO_4 aqueous solution. Doubly-distilled deionized water was employed to prepare all solutions. Polyaniline films were electrosynthesized on a 2 cm^2 geometrical area Pt sheet (99.99% purity from Johnson Matthey). The counter electrode, a 99.99% purity Pt coil, was separated from the main compartment of a three-compartment Pyrex glass cell by fritted glass during polymer film growth. A platinum grid, arranged cylindrically around the Pt/PANI working electrode, was used to perform the electrochemical impedance measurements.

A saturated calomel electrode (SCE), separated from the working electrode compartment by a Luggin probe, was used as reference to which all potentials are quoted. Both synthesis and impedance measurements were performed keeping the solutions under nitrogen at 20°C .

PANI films were grown potentiostatically at 0.69 V in 0.1 M aniline/ $5 \times 10^{-2} \text{ M}$ Fe(EDTA) $^-$ at pH 2.5 and 3.7 and 0.1 M aniline/ $5 \times 10^{-2} \text{ M}$ EDTA at the same pHs. Polymer growth was performed in two steps. (a) First, the working electrode was polarized at 0.69 V for 25 min. After this, the electrode was thoroughly washed with bidistilled water and then cycled in 0.5 M H_2SO_4 between -0.2 and 0.69 V for 10 min, until a reproducible potentiodynamic profile was obtained. (b) Second, the PANI electrode was reintroduced in the initial solution containing aniline and polarized for 30 min more at 0.69 V .

After growth the film was rinsed with bidistilled

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water, dried under nitrogen and placed in the electrochemical impedance cell. All PANI films were analysed by EIS measurements in fresh 0.5 M H_2SO_4 solutions without aniline. The frequency range extended from 5 mHz to 10 kHz and a peak-to-peak a.c. potential perturbation of 10 mV was used. The frequency response was measured under steady-state potentiostatic conditions at -0.25 , -0.10 , 0.0 , 0.20 , 0.40 and 0.47 V.

The electrosyntheses were done using an EG&G Parc 273 electrochemical system, and the potentiodynamic profiles recorded on an EG&G Parc RE0089 X-Y recorder. EIS measurements were carried out by interfacing the Parc 273 potentiostat to a Solartron-Schlumberger 1255 frequency response analyser (FRA). Data acquisition was computer assisted via Parc M388 software. The micrographs were obtained with a Siemens Autoscan electron microscope.

3. Results and discussion

3.1. Potentiodynamic analysis

The voltammetric profiles of a PANI film formed in $\text{Fe}(\text{EDTA})^-$ electrolyte at pH 2.5 and 3.7, after 25 and 55 min of polymerization at 0.69 V are depicted in Fig. 1. The film obtained after 25 min of polarization shows potentiodynamic features typical of films obtained in electrolytes such as H_2SO_4 or HCl under potentiodynamic conditions [12]. However, films obtained after 55 min at both pH exhibit a new peak

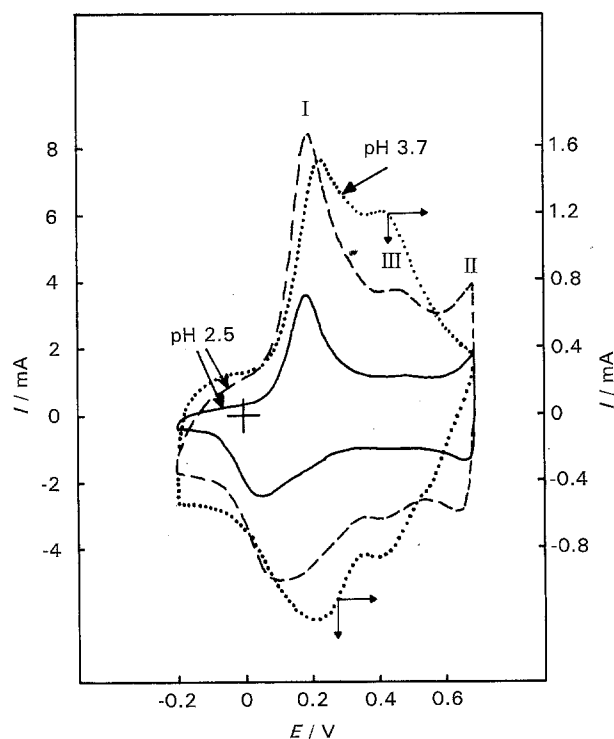


Fig. 1. Voltammetric profiles of PANI films formed in $\text{Fe}(\text{EDTA})^-$ electrolyte at pH 2.5 after 25 min (—) and 55 min (---), and at pH 3.7 after 55 min (···) of growth at 0.69 V. Voltammograms recorded in 0.5 M H_2SO_4 at 0.1 V s^{-1} .

at about 0.45 V (peak III). Several authors [13–15] have attributed this peak to the response of both soluble and insoluble degradation products of PANI. The soluble degradation products would correspond to quinone and hydroquinones, while the insoluble degradation products to cross-link reactions between chains in the polymer. The $\text{Fe}(\text{II})/\text{Fe}(\text{III})$ couple also gives a signal in this potential region but it is unlikely that peak III is due to this couple, since this peak is also observed with PANI films obtained with EDTA and no iron present. Peak III may be attributed mainly to cross-link reactions, since it remains the same when a new CV profile is obtained after washing the film and then introducing it into fresh electrolyte. The effect of soluble degradation products on peak III in this case is eliminated.

Figure 2 shows the effect of cycling a film for one hour in 0.5 M H_2SO_4 between -0.2 and 0.69 V, prepared after 55 min of polymerization in $\text{Fe}(\text{EDTA})^-$ at constant potential. The response corresponds to the voltammogram shown in solid lines. The voltammogram in dashed lines illustrates the response of a PANI film prepared under potentiodynamic conditions in 0.5 M H_2SO_4 and is included for comparison. Cycling the PANI- $\text{Fe}(\text{EDTA})^-$ film in acid has two effects, namely: (i) peak I shifts to more positive potentials and (ii) peak II, corresponding to the emeraldine-*pernigraniline* couple practically disappears as compared to the responses of films previous to cycling (Fig. 1). Similar results have been reported when cycling films grown at pH higher than 3 [16]. This result is interesting since this does not happen to PANI films grown potentiodynamically in acid without $\text{Fe}(\text{EDTA})^-$ and gives the response shown in dashed lines in Fig. 2. The latter films degrade upon cycling and both peak I and II decrease to the same extent. Thus, some net effects of preparing films with $\text{Fe}(\text{EDTA})^-$ are to make them more stable to degradation and to inhibit the second redox process when the films are cycled up to positive potentials, as this second redox process is associated with degradation due to the formation of soluble oxidation products at those potentials.

The previous analysis was also done for PANI films

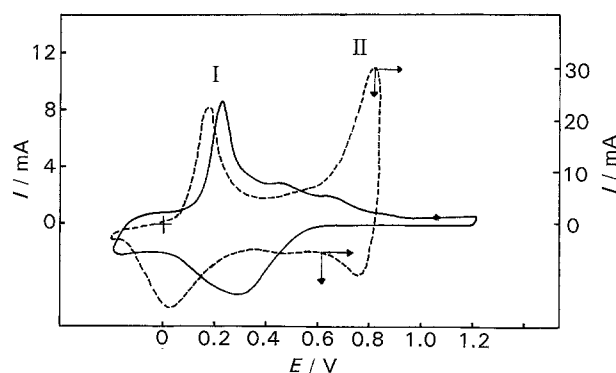


Fig. 2. Potentiodynamic profiles of a PANI film grown for 55 min in $\text{Fe}(\text{EDTA})^-$ at pH 2.5 after cycling for 1 h in 0.5 M H_2SO_4 at 0.1 V s^{-1} (—), and grown potentiodynamically in 0.5 M H_2SO_4 at 0.1 V s^{-1} (---).

grown in the presence of EDTA alone in order to see its effect on the appearance of the intermediate peak, since an enhancement of cross-link reactions with EDTA is possible. Due to the low solubility of Na_2EDTA at pH values lower than 3.7, the electro-synthesis at pH 2.5 was performed at an EDTA concentration lower than 0.05 M and in the presence of the precipitated salt. The ionic strength of the solution was maintained by adding NaNO_3 . Figure 3 displays the potentiodynamic profiles of two PANI films grown in the EDTA electrolyte at pHs 2.5 and 3.7. Both films exhibit the intermediate peak (peak III). However, for films grown at pH 2.5 the first redox process (peak I) is the most important, while for films grown at pH 3.7 it is smaller comparatively to peak III. The response of the film prepared at pH 3.7 indicates the low rate of electropolymerization of PANI at this pH (low current density for peak I) and a higher rate of cross-link reactions when the EDTA concentration is higher (the ratio peak III/peak I is increased). The extent of the hydrolysis products incorporation (or of cross-linkings in this case) has been measured in terms of the peak III/peak I ratio [17]. When cycling the film obtained at pH 3.7, in H_2SO_4 up to 1.2 V, the anodic currents progressively increase for potentials higher than the intermediate peak's potential (Fig. 4). This can be attributed to the oxidation of EDTA trapped in the film, partially precipitated due to the pH of the working electrolyte solution. Contributions due to Pt oxide formation at the Pt/pore solution interface should be also considered.

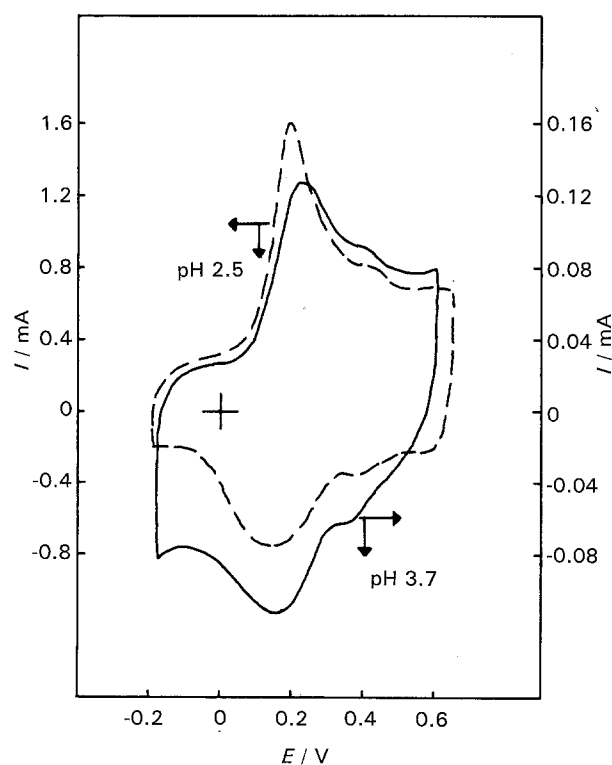


Fig. 3. Potentiodynamic profiles of two PANI films grown in EDTA electrolyte at pH 2.5 (---) and 3.7 (—), recorded in 0.5 M H_2SO_4 at 0.1 V s^{-1} for 10 min.

3.2. Morphological features

As shown in the literature, PANI films grown potentiostatically incorporate more impurities than when grown by continuous potential cycling [18]. Furthermore, PANI films grown at constant potential are less adherent to the substrate and micrographs show poorly defined pulverulent-like structures [18]. These poorly defined films are also obtained when the electro-synthesis is carried out potentiodynamically at 500 mV s^{-1} [17]. By contrast, PANI films obtained by continuous potential cycling show morphological changes (due to degradation) after polarization at 1.0 V for 30 min [19].

Morphological features of PANI films grown in three different conditions can be seen in Fig. 5. Films grown potentiostatically in $\text{Fe}(\text{EDTA})^-$ and EDTA electrolytes are compared to one grown in H_2SO_4 by cycling the potential between -0.2 and 0.69 V . The latter presents spherical-type structures, while the one formed in $\text{Fe}(\text{EDTA})^-$ presents cauliflower-like structures, which emerge from fractures developed in the noncontinuous film initially grown. On the other hand, those films grown in EDTA appear to be very thin with many fractured regions. This is consistent with the voltammetric responses of the last type of films, which show resistive profiles and lower charges associated with peak I. As in this work, it has been reported that polypyrrole/EDTA films, grown galvanostatically, show a non-conductive behaviour [19, 20]; the potential-time profile shifts

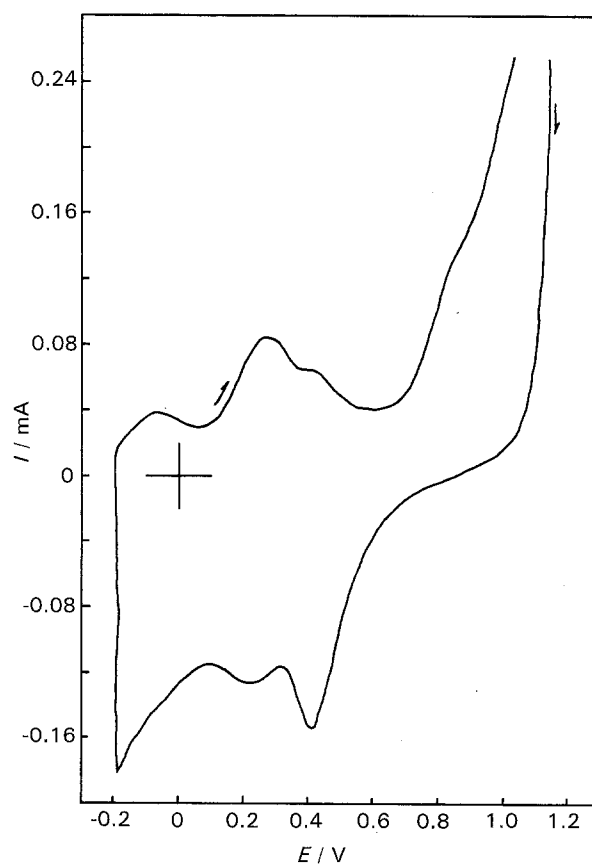


Fig. 4. Potentiodynamic profile of a PANI film grown in EDTA electrolyte at pH 3.7, recorded in 0.5 M H_2SO_4 at 0.1 V s^{-1} .

to more positive potentials during polymer synthesis, indicating a progressive deactivation of the electrode.

3.3. Electrical properties

The ohmic resistance, R_{ohm} , the double-layer capacity and the pseudo capacity of the polymer film, C_{dl} and C_{p} , and the charge-transfer resistance, R_{ct} , were determined using the impedance data as reported earlier [21]. The oxidized PANI films, independently of the way they were prepared, present a nearly capacitive behaviour. R_{ohm} values were obtained for either oxidized or reduced films at the limit of high frequencies, ranging from 1.5 to 2.5 Ω for all cases. These values have the contribution of the resistance of the electrolyte within the pores of the film in addition to the intrinsic resistance of the film.

Though in the complex-plane plots for the reduced films the shape are similar to that obtained for films grown in other acid electrolytes, that is, just one semi-circle associated to one relaxation process, one can distinguish in the Bode plots (Fig. 6) two relaxation processes for films grown with $\text{Fe}(\text{EDTA})^-$ in the electrolyte. This seems to be related to the iron complex incorporated within the polymer film.

Figure 7 shows the charge-transfer resistance (R_{ct}) dependence on the potential for PANI films with and without the second redox processes, peak II (as in Figs 1 and 2). The film presenting the second redox process shows an R_{ct} variation similar to that obtained for PANI films synthesized only in acid electrolytes [21, 22], that is, it decreases sharply as the polymer becomes conducting. On the other hand, the film inhibiting the second redox process shows

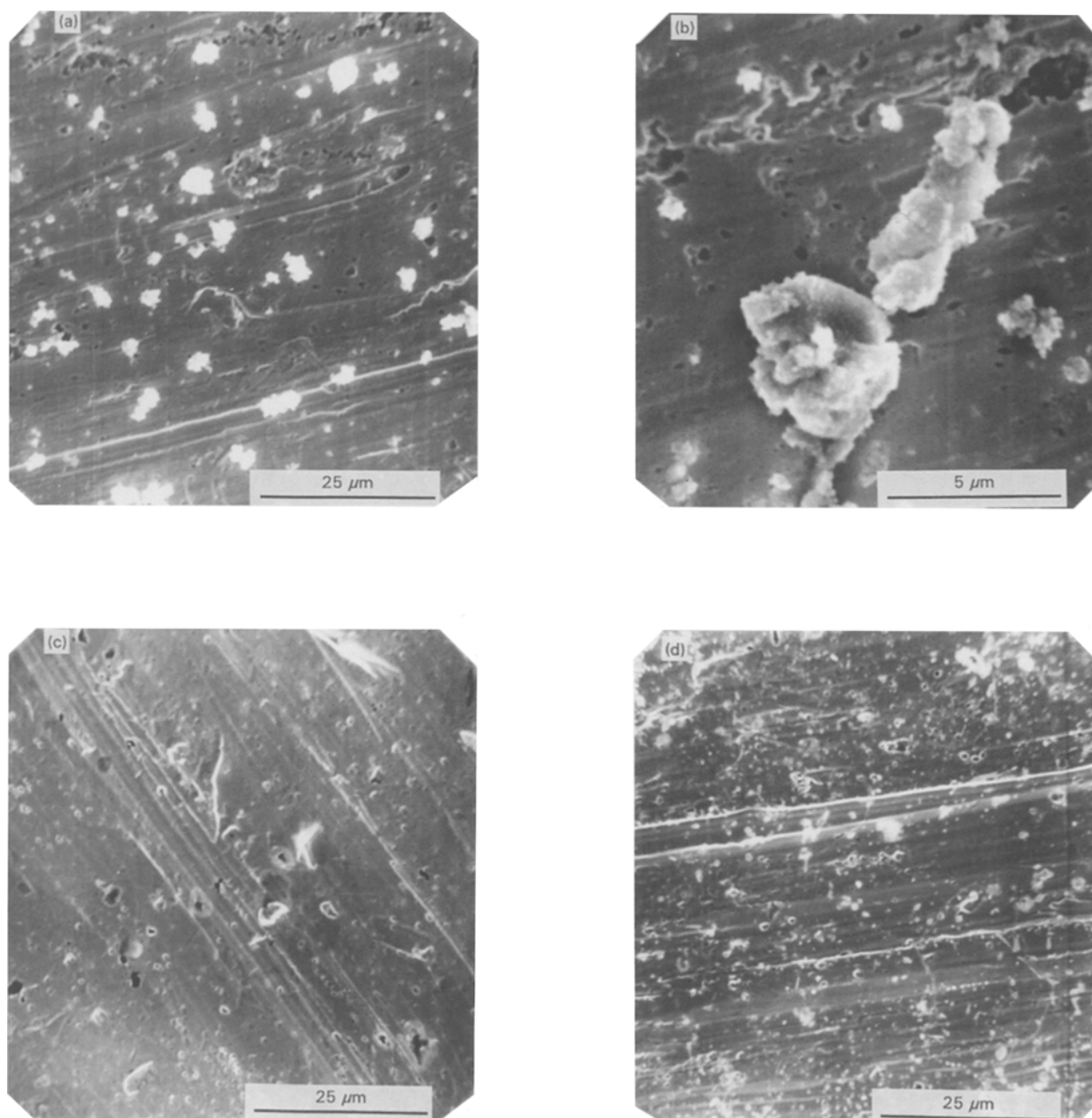


Fig. 5. Micrographs of PANI films grown potentiostatically at 0.69 V in $\text{Fe}(\text{EDTA})^-$ (a) and (b), EDTA (c), H_2SO_4 by cycling between -0.2 and 0.69 V (d).

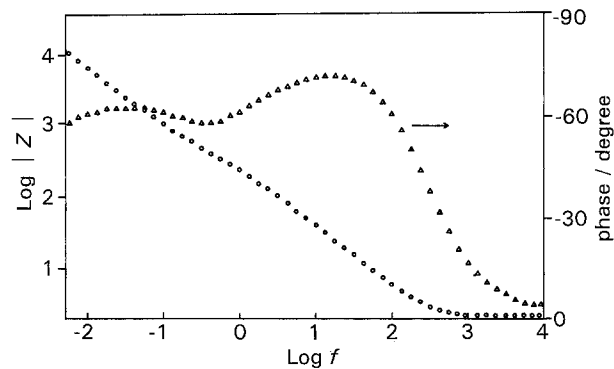


Fig. 6. Bode plots obtained at -0.2V for a PANI film formed in $\text{Fe}(\text{EDTA})^-$ electrolyte at pH 2.5.

much higher R_{ct} values at positive potentials at which the film was expected to be a conductor. This behaviour may be related to a progressive deactivation of the latter, as already shown in Fig. 2, and is consistent with the lower capacity values displayed in Fig. 8. The pseudo capacities (obtained at low frequencies and proportional to the amount of electrodeposited polymer) for the film inhibiting the second redox process is about 50% lower than the pseudo capacities for the film presenting that redox process, indicating a loss of activity of the $\text{Fe}(\text{EDTA})^-$ -containing film when it is cycled in H_2SO_4 solution for one hour or more.

The incorporation of the iron complex also affects the double layer capacitances obtained at high frequencies. As seen in Fig. 9, the polymer film presenting the second redox process shows a remarkable increase of the C_{dl} values at potentials more positive than 0.2V , where the $\text{Fe}(\text{II})/\text{Fe}(\text{III})$ redox process could occur (this process is not supposed to exist for films inhibiting peak II). The C_{dl} values increase gradually as the polymer is oxidized, due to the influx of counter ions to stabilize the positive charges

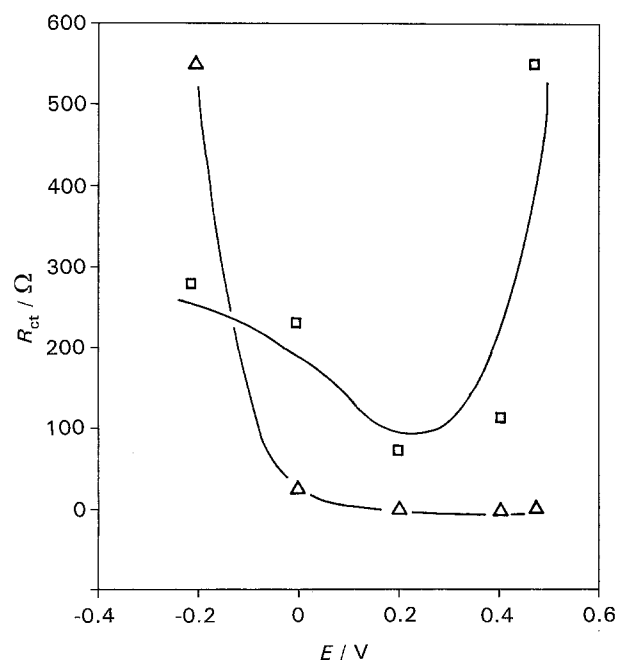


Fig. 7. Charge-transfer resistance dependence on potential for PANI films grown in $\text{Fe}(\text{EDTA})^-$ electrolyte with (Δ) and without (\square) the second redox process.

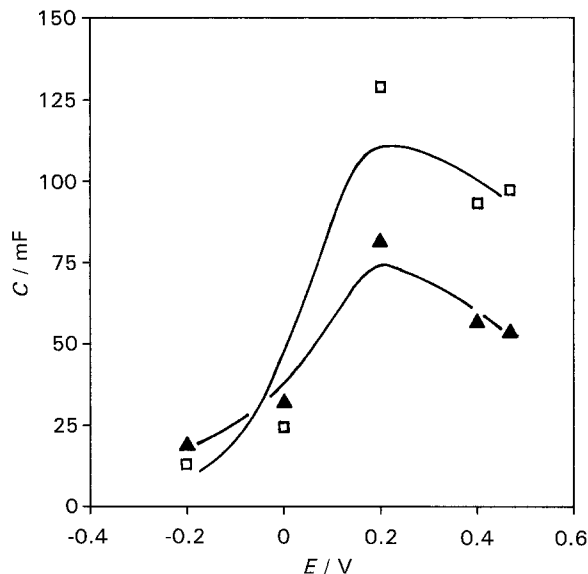


Fig. 8. Capacitance dependence on potential for PANI films grown in $\text{Fe}(\text{EDTA})^-$ electrolyte with (\square) and without (Δ) the second redox process.

generated in the polymer film. Nevertheless, this fact alone cannot explain the notable increase in C_{dl} for just one of the films. This phenomenon can be interpreted in terms of a change in the oxidation state of Fe trapped in the film with a consequent incorporation of more anions from the electrolyte. The Fe content in the PANI films was obtained by atomic absorption spectroscopy after dissolving them in hot nitric acid. While for the film presenting peak II the Fe content is $6.2 (\mu\text{g}(\text{Fe})/\text{mC})\text{cm}^{-2}$, it is $1.6 (\mu\text{g}(\text{Fe})/\text{mC})\text{cm}^{-2}$ in the film inhibiting the second redox process. These results suggest that $\text{Fe}(\text{EDTA})^-$ species incorporated within the polymer film progressively diffuse out to the bulk electrolyte when cycling the electrode in H_2SO_4 . The loss of $\text{Fe}(\text{EDTA})^-$ inside the film may also occur, together with cross-linking reactions leading to less-conducting films.

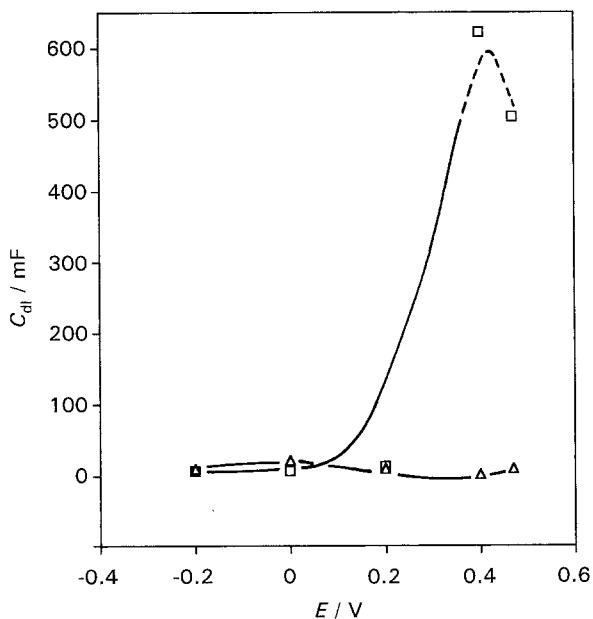


Fig. 9. Double-layer capacitance dependence on potential for PANI films grown in $\text{Fe}(\text{EDTA})^-$ electrolyte with (\square) and without (Δ) the second redox process.

The resistive character of films grown with EDTA disodium salt alone as electrolyte at pH 3.7 is illustrated in Fig. 10. The higher R_{ct} values obtained at more positive potentials indicate that PANI is a non-conducting polymer when grown in that electrolyte. On the other hand, the polymer film grown in EDTA at pH 2.5 presents the same R_{ct} dependence as for PANI films grown in other acid electrolytes (Fig. 10). Furthermore, Fig. 11 shows lower pseudo capacity values for the films grown in the solution at pH 3.7, confirming the previous idea of unfavoured kinetics and thinner films formed under these conditions.

4. Conclusions

These modified electrodes do not seem to be appropriate as electrocatalysts since they lack the necessary long-term stability, due to the loss of Fe(EDTA) species from the polymer matrix. Lower pHs of the electrolyte, which enhance both polyaniline formation and conductivity, are not favourable to stabilize FeEDTA species within the film.

The presence of EDTA does not improve film conductivity because of cross-linking formations between polymer chains, hindering conductivity via hopping mechanisms. However, the presence of FeEDTA substantially modifies the redox response of PANI films assigned to the emeraldine/permanganiline transition, since this process, which is typical of PANI films prepared in acid electrolytes, does not appear, or is inhibited after cycling. If not stable enough to be used in electrocatalysis, the incorporation of FeEDTA species decreases the degradation of PANI films when cycling them in sulfuric acid solutions, as degradation occurs at potentials close to the second redox process. The disappearance or inhibition of the same redox process for some films is probably due to a hindering effect to the emeraldine/permanganiline redox process which involves eight aniline units in the polymer chain. If cross-linking occurs within distances corresponding

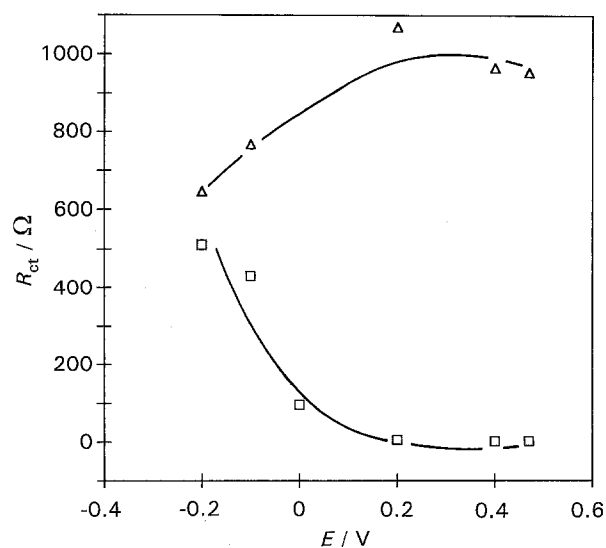


Fig. 10. Charge transfer resistance dependence on potential for two PANI films grown in EDTA electrolyte at pH 2.5 (\square) and 3.7 (Δ).

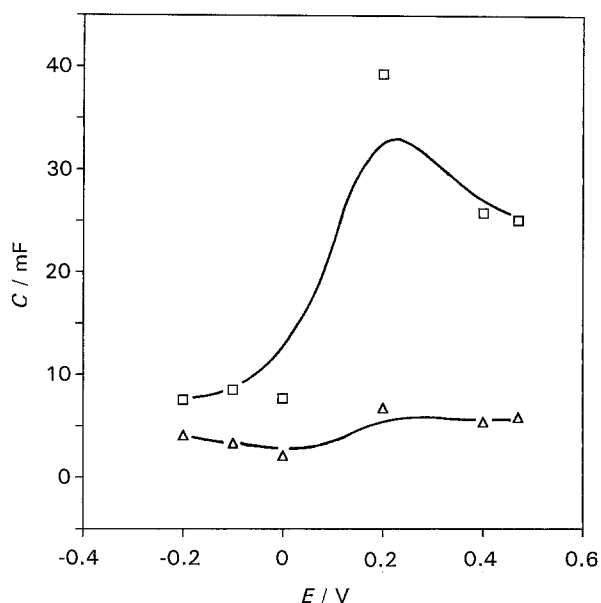


Fig. 11. Capacitance dependence on potential for two PANI films grown in EDTA electrolyte at pH 2.5 (\square) and 3.7 (Δ).

to the length of eight aniline units, then the redox process becomes unfavourable due to steric restrictions. Further studies are required to clarify this point.

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