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Electrical properties of polyaniline films formed in acid with and without Cs^+ ions in the electrolyte

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The effect of Cs^+ ions added to the electrolyte for polyaniline films electrosynthesized in 0.1 M aniline/0.5 M H_2SO_4 was investigated. Some properties of PANI films, such as the capacitance, the ohmic resistance and the charge-transfer resistance were obtained using electrochemical impedance spectroscopy. It was found that Cs^+ ions used during PANI synthesis change its morphology, with a consequent increase in capacitance and conductivity, and a decrease in charge-transfer resistance.

1. Introduction

Conducting polymers have been the subject of several studies due to their potential applications in batteries, electrochromic displays, electrocatalysis, antistatic and anticorrosive materials, and biomedicine [1].

Polyaniline (PANI) films have received considerable attention in the last decade regarding their usage as modified electrodes [2,3], as active electrodes in secondary batteries [4], and as pH sensors [5]. PANI films are generally electrosynthesized by continuously cycling the potential of a noble-metal working electrode (Pt, Au) in acid solutions containing aniline [6]. Both their growth kinetics and physical properties depend upon parameters such as temperature [7], nature of the electrolyte used in the synthesis [8,9], potential sweep rate [10,11], and the shape of the E/t profile used as the perturbation for polymer growth [12,13]. The effect of anions on the properties of PANI films has been extensively investigated [8,9,14–18]. On the other hand, little attention has been given to the role of cations (other than protons) on the rate of PANI growth and on its properties. Previous work [19] has demonstrated that alkaline cations, similarly to anions but to a smaller degree, affect the rate of PANI electropolymerization when it is performed by continuous potential cycling. Higher rates were observed for the less solvated cations: $Cs^+ \gg K^+ > Li^+ > Na^+$.

Electrochemical impedance spectroscopy (EIS) has been extensively employed in the characterization of different conducting polymer films. In spite of the lack of a complete model to describe their frequency response due to the complexity of these polymers, a great deal of information about their electrical properties can be found using different approaches [20–25]. EIS is an attractive technique since it allows *in situ* measurements, added to the fact that small-amplitude perturbations in a wide frequency domain do not remove the system from its steady state and allow the exploration of several processes relaxing at different time constants. In a recent review, Musiani [26] reports on the most usual systems analysed by EIS, including both redox and intrinsic conducting polymers. Specifically on PANI films there is good agreement in the results reported by two different groups [27,28]. In the oxidized conducting state, the film is claimed to behave like a combination of a resistor and a capacitor in series. In the reduced state, where two time constants can be observed, Rubinstein *et al.* [27] propose, as possible interpretations for the lower frequencies relaxing processes, the presence of a two-phase structure polymer, the presence of a diffusional controlled process, or a pseudo capacitance due to a large-thickness film and a double-layer capacitance of a porous material. Albery and Mount [29] have suggested a transmission line model to describe the charge conduction in the polymer. In this case, the electron movement is thought to be controlled by a hopping motion from one to another polymeric chain.

More recently Lang and Inzelt [30] have analysed the variation of the impedance spectra as a function of the polymer characteristic parameters through a computational simulation stressing the effects of both thickness and thickness distribution of the polymer films. The same authors have also reported the effect of temperature on the conductivity and capacitance of PANI films [31]. They suggested that the ohmic resistance determined from EIS data is connected with ionic conductivity and not with electronic conductivity. Grzeszczuk and Zabinska–Olszak [32] have used EIS to study diffusional processes of anions in PANI films with different electrolytes.

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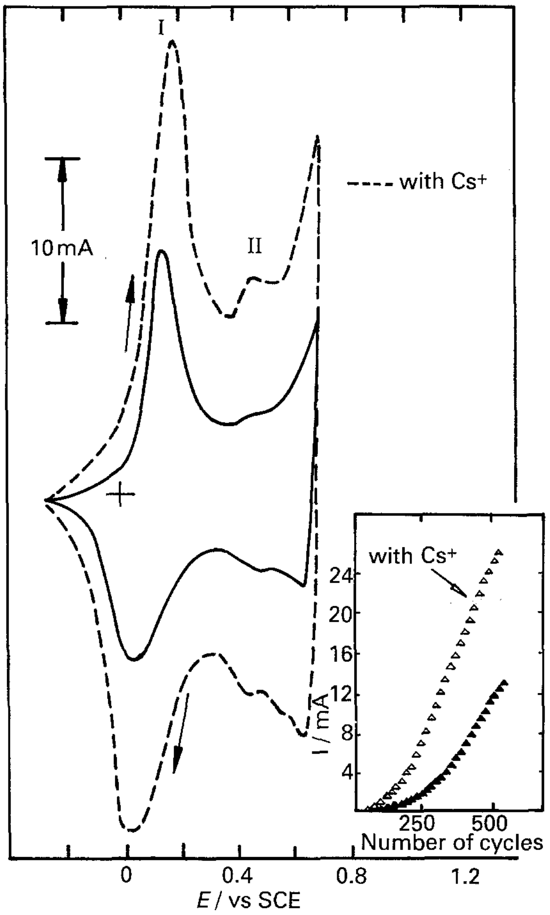

Fig. 1. Cyclic voltammograms of PANI (600 cycles) recorded at $0.1\,V\,s^{-1}$, electrosynthesized in 0.1 M aniline/0.5 M H_2SO_4 with (solid line) and without 0.2 M Cs_2SO_4 electrolyte solution. The insert displays the current for the first oxidation peak (peak I) as a function of the number of voltammetric cycles.

In continuation of previous work [19], the electrical properties of PANI films (with and without Cs^+) are now studied by the EIS technique.

2. Experimental details

Aniline (analytical grade from Merck) was distilled under low pressure and a nitrogen atmosphere and stored in the dark before use. Other chemicals (H_2SO_4 and Cs_2SO_4) were analytical grade from Merck and used without further purification. Deionized and doubly distilled water was employed to prepare all solutions. Polyaniline films were electrosynthesized on a $1\,cm^2$ geometrical area platinum sheet (99.99% purity from Johnson Matthey). The counter electrode, a 99.99% purity platinum coil, was separated from the main compartment of a three-compartment Pyrex glass cell by fritted glass during the polymer film growth. Another counter electrode configuration, a platinum grid placed symmetrically around the 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 the potentials are quoted in this work. Both the electrosynthesis and the impedance measurements were performed under nitrogen atmosphere and the temperature at 20 °C.

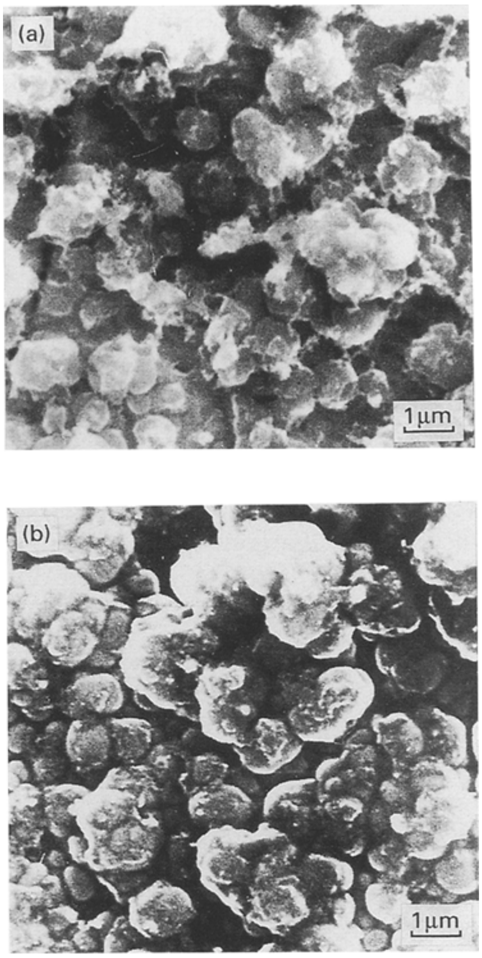

Fig. 2. Scanning electron micrographs of different PANI films obtained in 0.5 M H_2SO_4 solution with Cs^+ (a) and without Cs^+ (b).

PANI films were grown by potentiodynamically cycling the platinum working electrode in a 0.1 M aniline/0.5 M H_2SO_4 (with or without Cs^+) electrolyte, between −0.25 and 0.69 V at a sweep rate of $0.1\,V\,s^{-1}$. A series of thin (300 cycles) and thicker (600 cycles) PANI films were thus produced in acidic solutions with and without 0.2 M Cs_2SO_4.

After growth the films were rinsed with bidistilled water, dried under a nitrogen stream 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 any aniline or cesium sulphate. The frequency range extended from 5 mHz to 10 kHz and a peak-to-peak a.c. potential perturbation of 10 mV was used. For each film, the frequency response was measured under steady-state potentiostatic conditions at −0.25, −0.10, 0.03, 0.20 and 0.40 V. For potentials equal to or higher than 0.6 V dispersion of the impedance data, and drifting of the impedance profile to higher values clearly indicated the degradation of PANI films in H_2SO_4 medium. Therefore the positive potential limit was kept at 0.4 V.

The electrosynthesis was carried out by means of an EG&G Parc 273 electrochemical system, and the

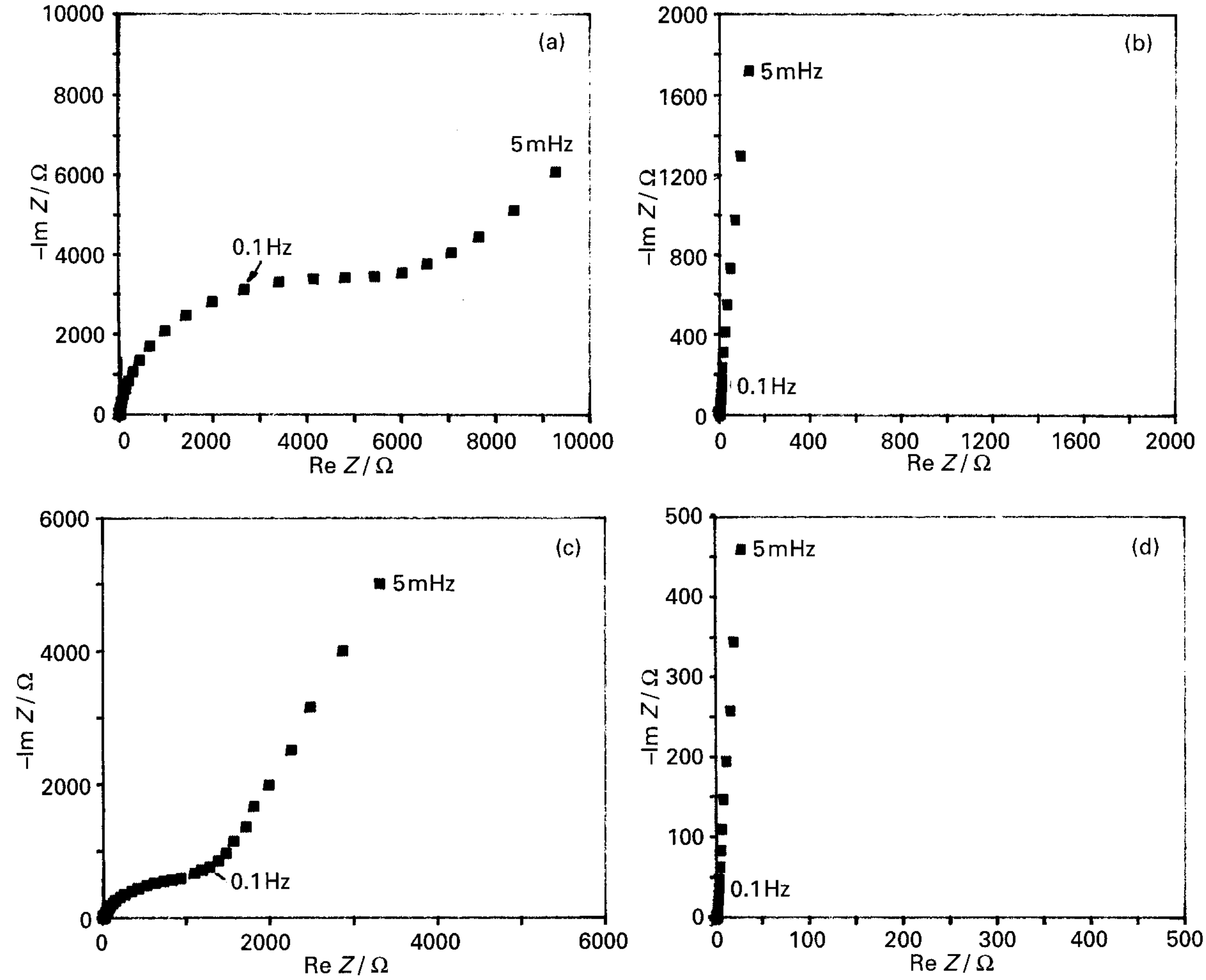

Fig. 3. Complex-plane impedance plots for reduced (a,c), $E = -0.25$ V, and oxidized (b,d), $E = 0.40$ V PANI films (600 cycles) obtained in 0.5 M H_2SO_4 solution. Films were grown without (a and b) and with (c and d) Cs^+ ions in the electrolyte.

potentiodynamic profiles were recorded on an EG&G Parc RE0089 X–Y recorder. The 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 via a Zeiss 960 scanning electron microscope.

3. Results and discussion

It was previously found [19] that the presence of alkaline cations, specially Cs^+, accelerate the rate of polymerization of aniline in H_2SO_4 when the film is prepared by continuously cycling the potential. Figure 1 shows cyclic voltammograms of PANI (600 cycle films) recorded at 0.1 V s^{-1} electrosynthesized in 0.1 M aniline/0.5 M H_2SO_4 (with and without 0.2 M Cs_2SO_4) electrolyte solution. Though the potentiodynamic features of both films are almost the same after several cycles, the rate of polymer growth is affected by the presence of Cs^+ as shown by the insert in Fig. 1. Apart from the substantial differences in peak currents for peak I, an intermediate peak (peak II) becomes more pronounced when Cs^+ is present. This peak II has been attributed to cross-link formation between polymer chains [31–33]. Furthermore, Cs^+ affects the morphology of the films obtained, as illustrated in Fig. 2.

SEM micrographs of PANI films prepared by 600 cycles with and without Cs^+ in the electrolyte, presented in Fig. 2, indicate that more spherical-type structures are not only more abundant but also smaller than those obtained without Cs^+. Therefore, the alkaline cation seems to promote the formation of more nucleation sites for polymerization. Both films are porous, but with Cs^+ they become more homogeneous and compact and the pores are more evenly distributed.

The effect of cesium ions on PANI growth and properties results from a collaborative process between co-ions and counterions in the forming electrolyte. The Cs^+ ions in the electrolyte are increasingly trapped inside the polymer film during the repetitive potential cycling. Therefore an equivalent number of negative charges, acting as counter-ions of the trapped Cs^+, are also retained in the polymer. These retained anions may also be the species responsible for the enhancement of PANI electropolymerization, since they favour the formation of cross-link species between preferential chains [33–35]. The idea of cation incorporation is supported by previous work by Inzelt [36] on poly(tetra-cyanoquinodimethane), demonstrating that labelled Ca^+ co-ions

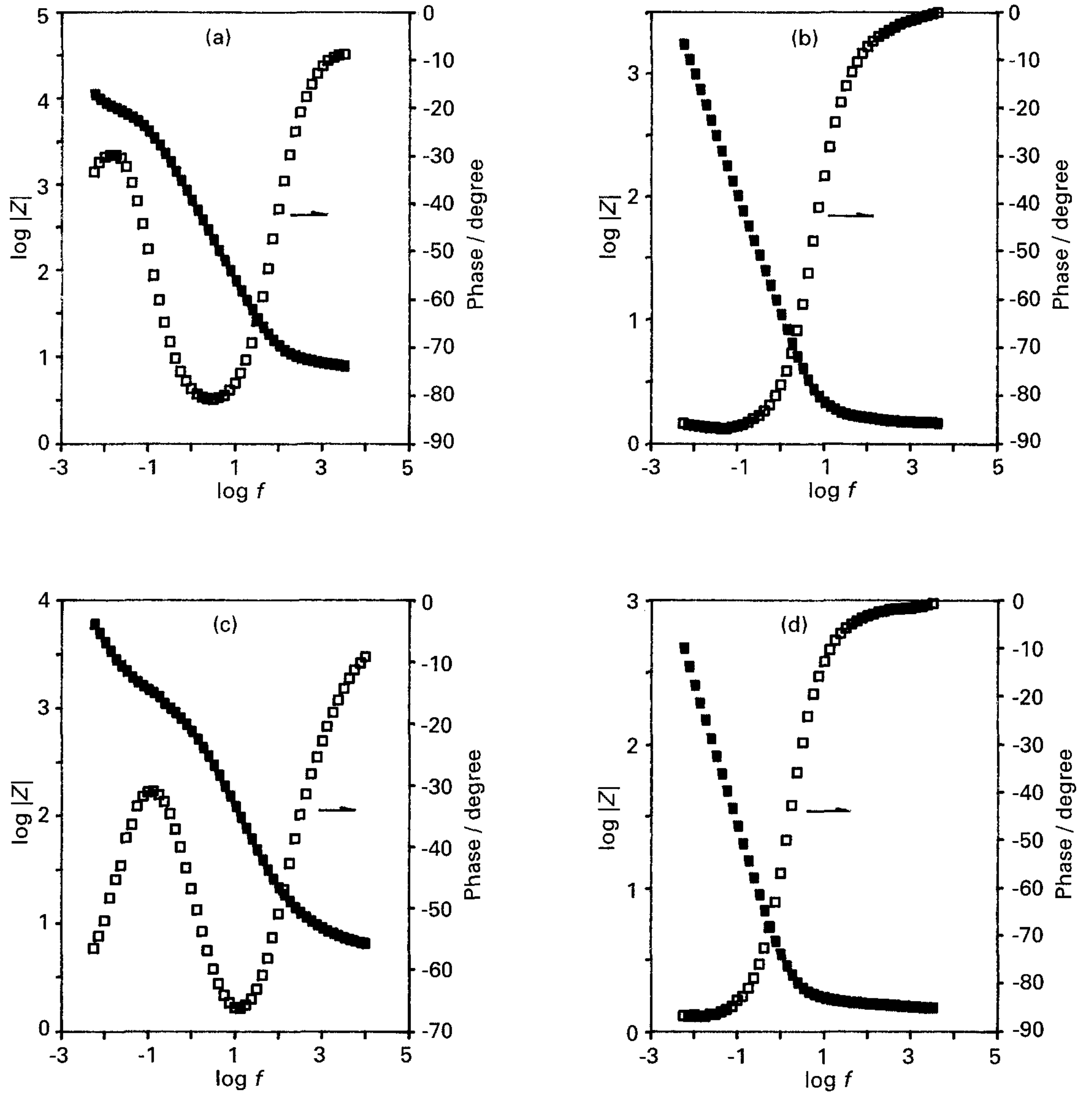

Fig. 4. Bode plots for reduced (a,c at $E = -0.25$ V) and oxidized (b,d at $E = 0.40$ V) PANI films (600 cycles) obtained in 0.5 M H_2SO_4 solution. Films were grown without (a,b) and with (c,d) Cs^+ ions in the electrolyte.

enter a polymer film during the absorption of the counterions. Moreover, Chong Lee [37] has shown for poly(3-methylthiophene) electrosynthesis, using labelled Na^+, that during the first potential cycles the amount of Na^+ in the polymer film increases irrespective of the direction of the half cycles and that, as the electrochemical polymer growth proceeds, the Na^+ content in the film decreases during the negative potential sweep. As a global effect, however, an increase of sodium ion concentration in the polymer was detected as the film was growing [37].

Impedance measurements were carried out on a series of PANI films grown with and without Cs^+ in order to examine the effect of thickness (expressed as the number of cycles), applied potential and morphology on their electrical parameters. Figure 3 summarizes the most representative complex-plane impedance data for PANI films grown with and without Cs^+ in the electrolyte, as a function of the applied potential. The chosen potentials were those for polyaniline films in their reduced (nonconducting) and oxidized (conducting) states, since the impedance profile gradually changed from a resistive to a capacitive one as the potential increased. However, EIS measurements were also performed at intermediate states under steady-state potentiostatic polarization.

Figure 3 also shows a well-defined semicircle in the high frequency ranges for the reduced state of PANI films. This behaviour is similar to that reported by Fiordiponti and Pistoia [38] for PANI films grown in H_2SO_4 alone. Cs^+ does not seem to affect the features of the complex-plane representations, but otherwise displaces the whole spectrum to lower impedance values. The low frequency range is characterized by a dispersion which may be related to both the diffusion of ions inside the polymer and the capacitance of a highly porous material [27]. The nearly capacitive nature of the oxidized PANI films is depicted on Fig. 3(b) and (d). Though a slight CPE behaviour can be found in this frequency region (as pointed out by Inzelt *et al.* [31]), the capacitive behaviour was expected since the polymer becomes conductive at those positive potentials. At these potentials, the high frequency dispersion can be only

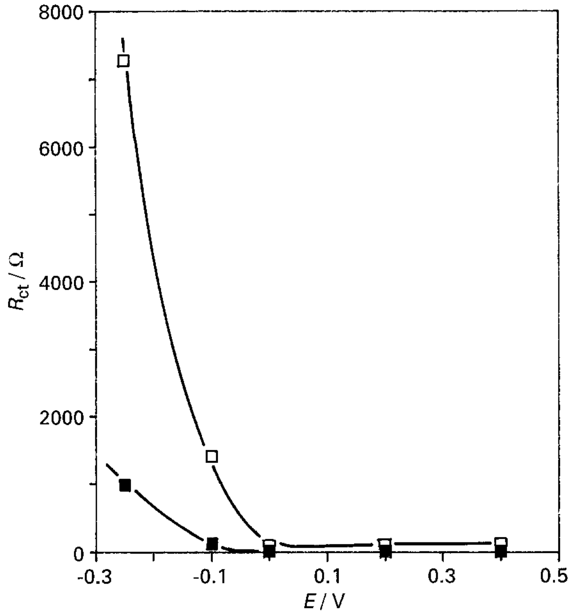

Fig. 5. Charge transfer resistance as a function of applied potential for thick (600 cycles) PANI films grown with (closed squares) and without (open squares) Cs^+ ions in the electrolyte.

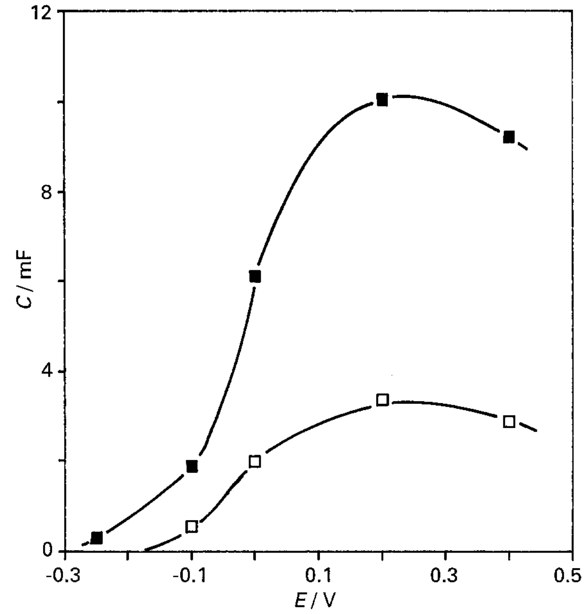

Fig. 6. Capacitance as a function of applied potential for thin (300 cycles) PANI films grown with (closed squares) and without (open squares) Cs^+ ions in the electrolyte.

related to the ohmic resistance (R_{ohm}) of the system, i.e. the sum of the resistances of the solution (R_{sln}) and the polymer film (R_p):

$$R_{ohm} = R_{sln} + R_p \tag{1}$$

The different relaxation time phenomena are better illustrated as Bode plots (Fig. 4). While two relaxation processes are observed in a reduced polyaniline (Fig. 4(a) and (c)), its oxidized state can be represented by a capacitor with a phase angle of about 90° in series with the ohmic resistance of the system (Fig. 4(b) and (d)), regardless of whether Cs^+ was present or not during film formation.

The data for the charge transfer resistance (R_{ct}), the capacitance (C) and the ohmic resistance (R_{ohm}) were obtained by the partial NLLS fit method [39] applied to the different frequency regions. The charge-transfer resistance data were obtained by extrapolating the semicircle from the high-to-intermediate frequency region to the real component of the impedance axis. For example in Fig. 3(c), the extrapolation for -0.25 V gives a value for R_{ct} of approximately $1 \times 10^3\ \Omega$, disregarding any ohmic contribution from the system. Different values were obtained in this fashion for different potentials and plotted in Fig. 5. As seen in this figure, the R_{ct} values decrease dramatically as the potential of the PANI films becomes more positive. This figure illustrates that the nonconducting/conducting transition takes place at about 0.0 V. The R_{ct} values for the PANI films obtained with Cs^+ are much smaller at negative potentials than those observed for the film prepared without Cs^+. This agrees with the voltammetric response shown in Fig. 1, where much higher currents are observed with the film obtained with Cs^+. The presence of Cs^+ during the PANI synthesis also favours a more close-packed structure of the porous polymer film as was discussed above and illustrated in the micrograph of Fig. 2. Cross-linking is favoured, giving rise to more compact structures. It is also possible that Cs^+ favours the attraction of parallel aromatic rings in the PANI chains resulting in more close-packed structures. All these phenomena favour charge transfer processes within the PANI film when the polymer is a poor conductor at negative potentials. The film becomes conductive when oxidized and all these effects are less pronounced, as illustrated in Fig. 5. For thinner (300 cycles) films the behaviour was found to be the same, however, the R_{ct} values were higher: $1.16 \times 10^4\ \Omega$ (with Cs^+) and $6.0 \times 10^4\ \Omega$ (without Cs^+), at -0.25 V. These results are reasonable considering the preceding discussion.

Capacitances were obtained from the low frequency region from plots such as in Fig. 3. Capacitance values as a function of applied potential for thin PANI films grown with and without Cs^+ in the electrolyte are shown in Fig. 6. A similar plot for thick films is presented in Fig. 7. The capacitance increases as the potential becomes more positive and reaches a constant value at about 0.2 V, where the film becomes conductive. This indicates that the oxidized film stores more charge due to an increase of redox sites by the oxidation of active centres. This occurs together with film swelling, which facilitates the influx of counter ions. The capacity of PANI films obtained with Cs^+ ions is much larger than that prepared without Cs^+. This essentially agrees with the fact that PANI–Cs^+ is thicker and has more redox active centres as discussed above. Film thickness is probably the predominant factor for giving higher capacitances. This becomes clear when comparing the data from Figs 6 and 7.

Figure 8 illustrates the ohmic resistance (R_{ohm}) as a function of applied potential for thick PANI films

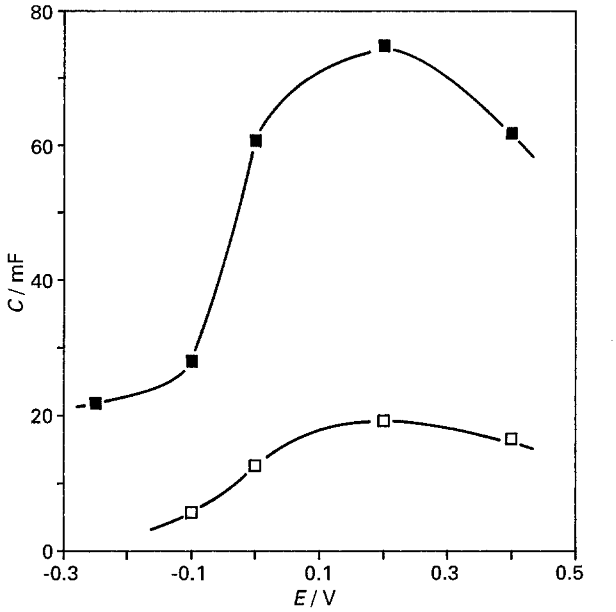

Fig. 7. Capacitance as a function of applied potential for thick (600 cycles) PANI films grown with (closed squares) and without (open squares) Cs^+ ions in the electrolyte.

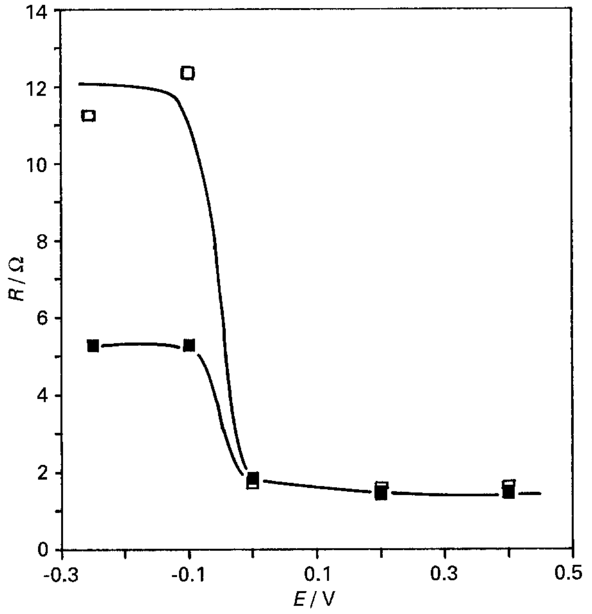

Fig. 8. Ohmic resistance as a function of applied potential for thick PANI films grown with (closed squares) and without (open squares) Cs^+ ions in the electrolyte.

grown with and without Cs^+. For potentials higher than approximately 0 V the resistance is independent of the applied potential, which suggests that, according to Equation 1, most of the measured resistance comes from the electrolyte and not from the polymer. However, at potentials more negative than 0 V, the resistance increases due to the reduction of the PANI film. Higher values are observed for the films prepared without Cs^+ as they have a more open structure (Fig. 2). A linear emeraldine structure resulting from tail to head couplings during polymerization is supported by i.r. spectra interpretation [40,41], but electronic conductivity may well depend upon defects such as interchange cross-links, which seem to occur with films prepared with Cs^+. The mechanism for the intermolecular transport process necessary for electronic conductivity remains unclear. One hypothetical route is through cross-linked N–N bridges [28]. For reduced films, the local structure could then resemble that of tetraphenylhydrazine. Unfortunately, structural changes taking place in these films upon reduction or oxidation cannot be identified by electrical measurements. However, changes in electronic conductivity strongly suggest structural variations. It would be necessary to carry out *in situ* spectroscopic measurements in order to identify the structural changes.

4. Conclusions

The improved electrical properties of PANI films obtained in the presence of Cs^+ ions may be of great importance in possible applications of these conductive polymers such as matrix supports for electrocatalysts, sensors and active electrodes for batteries. Different potential perturbation programs during the polymer synthesis, which improve the electrical properties of the films, could be used in combination with Cs^+ ions to obtain more interesting PANI films.

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