

# A Review About the Charge Conduction Process at Poly(*o*-aminophenol) Film Electrodes

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**Abstract:** This review, which is divided into two parts, concerns charge-transport and charge-transfer processes at poly(*o*-aminophenol) film electrodes. The first part deals with the case where the solutions contacting poly(*o*-aminophenol) films only contain ions that do not possess a redox activity (“background electrolyte”). The second part refers to the transport properties of poly(*o*-aminophenol) films contacting redox active solutions. In the first part, I have attempted to document the most significant evidence, which proves that the electrochemical behaviour of poly(*o*-aminophenol) can be explained on the basis of a chemical reaction coupled with a reversible electron-transfer process. In this connection, it was demonstrated that the response of poly(*o*-aminophenol) is highly dependent on the solution *pH*. This indicates that protons and electrons take part in the electrode reaction of the polymer. Different studies about the charge conduction across poly(*o*-aminophenol) films indicate the existence of a diffusion-limited charge-transport process. It was suggested that the transport process might be electron hopping-assisted by the corresponding counterion motion. In this regard, transport parameters, such as apparent or effective diffusion coefficients, have been employed to characterise the whole charge conduction process at poly(*o*-aminophenol) film electrodes. In some papers, electron and ion movements have been separately treated through electron and ion diffusion coefficients. It was found that these transport parameters depend not only on the type and concentration of the electrolyte solution contacting the polymer film but also on polymer film thickness. With regard to the electrochemical behaviour of poly(*o*-aminophenol) in the presence of solutions containing redox active couples, it has been reported that at negative potentials (-0.250 V *versus* SCE) the polymer can act as a mediator in electron-transfer reactions at the polymer solution interface. However, at positive potentials (higher than 0.8 V *versus* SCE) the species dissolves into the polymer with a partition equilibrium at the film solution interface.

At the end of this review (Section 4) I have tried to collect common and different viewpoints on the charge conduction process at poly(*o*-aminophenol) film electrodes reported in the literature. In Section 5 I describe some critical aspects related to charge-transport parameter values extracted from different electrochemical models applied to studying the polymer. Finally in Section 6, emphasis is laid on the effects of conduction and permeation processes at poly(*o*-aminophenol) on some of its practical applications, such as those where the polymer acts as an electrochemical sensor.

**Keywords:** Poly(*o*-aminophenol) films, charge conduction processes, redox activity.

## 1. INTRODUCTION

Electroactive polymers contain electron donor and acceptor sites that usually consist of up to hundreds of molecular layers. Oxidation and reduction of fixed sites introduce charged sites into the polymer, which, to achieve charge neutrality, require the ingress of counter-ions from the contacting electrolyte solution and, according to the Donnan relation, the egress of co-ions. Electron hopping is believed to be the mechanism for electron transport, but it is also possible that ion motions may partially or totally control the rate of charge transport. Thus, the charge-transport rate in electroactive polymer films is quantitatively characterised by a heterogeneous constant of charge transfer and an effective (or apparent) diffusion coefficient for charge transport across the film. The factors governing the magnitude of these parameters are not well understood. Furthermore, in general, these transport parameters depend on different variables such as degree of oxidation of the polymer, polymer film thickness,

type of electrolyte, ionic strength and pH of the solution in contact with the polymer film. A combination of different techniques was employed to determine the rates of the charge-transfer and charge-transport processes in electroactive polymers, such as Cyclic Voltammetry (CV), Rotating Disc Electrode Voltammetry (RDEV), Normal Pulse Voltammetry (NPV), Potential Step Chronoamperometry (PSCA), Potential Step Chronocoulometry (PSCC), EQCM measurements, Electron Spin Resonance (ESR), Probe Beam Deflection (PBD), Surface Resistance (SR) and Electrochemical Impedance Spectroscopy (EIS).

This short review concerns charge-transfer and charge-transport processes occurring in the course of redox reactions of poly(*o*-aminophenol) (POAP) film electrodes. The first part deals with the case where the solutions contacting POAP films only contain ions that do not possess a redox activity (“background electrolyte”). Thus, the counter-ion is able to cross the film|solution interface to retain the bulk film electroneutrality. The second part deals with the transport properties of POAP films contacting redox active solutions. In this last case, redox species inside the electrolyte solution participate in an interfacial electron exchange with the polymer at the polymer|solution boundary.

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The review is interesting due to the wide range of practical applications of poly(*o*-aminophenol). In this connection, the polymer has been employed in the construction of sensors for the amperometric detection of glucose, uric acid, lactate, nicotine and hydrogen peroxide. Also, poly(*o*-aminophenol) has been used as a potentiometric ferric cation sensor in solution and in the development of a sensor to determine the concentration of NO in solution. Furthermore, the crucial effect of the polymer on the enhancement of platinum microparticle efficiency towards the catalytic oxidation of methanol has been reported. In these practical applications, it is necessary to maintain the conducting properties of the polymer unaltered. However, in some of them the polymer is subjected to extreme conditions that can cause its partial deactivation. In this regard, it seems to be important to know the fundamental nature of the charge propagation in poly(*o*-aminophenol) film electrodes.

## 2. POLY(O-AMINOPHENOL) (POAP) FILM ELECTRODES IN CONTACT WITH INACTIVE ELECTROLYTES

### 2.1. The Charge Conduction Process at Poly(*o*-aminophenol) Films. Values of Charge Transfer and Transport Parameters

Cyclic Voltammetry (CV) is one of the major techniques for experimental study of electroactive polymers. The method uses an electrochemical cell with three electrodes; a reference electrode, working electrode and counter electrode. CV is a type of potentiodynamic electrochemical measurement in which the working electrode potential is ramped linearly *versus* time. This ramping is known as the potential scan rate ( $V s^{-1}$ ). The potential is measured between the reference electrode and the working electrode and the current is measured between the working electrode and the counter electrode. Experimental data are plotted as current (*i*) *versus* potential (*E*). The electrochemical behaviour of POAP films contacting a 0.1 M HClO<sub>4</sub> + 0.4 M NaClO<sub>4</sub> solution was studied by CV in [1]. A plot of  $\ln i_{pa}$  *versus*  $\ln v$  (where  $i_{pa}$  is the anodic peak current and  $v$  is the potential scan rate) showed, for values of  $v$  less than  $0.5 V s^{-1}$ , a slope that approaches unity as predicted theoretically for an adsorbed species of film-modified electrodes with thin-layer behaviour. For values of  $v$  greater than 2.5, the slope was 0.5, which indicates semi-infinite diffusion behaviour. The intermediate zone, between  $0.5$  and  $2.5 V s^{-1}$ , was shown to correspond to finite diffusion behaviour. Similar results were obtained for the cathodic peak but with the difference that the thin-layer behaviour was restricted to values of  $v$  lower than  $0.3 V s^{-1}$ , revealing that the cathodic process is slower than the anodic one. Plots of  $i_{pa}$  *versus*  $v^{1/2}$  were linear for values of  $v$  as high as  $10 V s^{-1}$ . By assuming that these plots follow the Randles-Sevcik or the equivalent Nicholson and Shain equation, the slope was proportional to  $cD^{1/2}$ . The concentration of active sites,  $c$ , was calculated for a homogeneous film considering the film thickness known from ellipsometric data [2] ( $c = 4.7 M$ ). Then, an apparent diffusion coefficient for the anodic process  $D$  was calculated from the  $cD^{1/2}$  slope. A  $D$  value of  $4.0 \times 10^{-11} cm^2 s^{-1}$  was obtained in [1]. The close fit to the  $i_{pa}$  *versus*  $v^{1/2}$  plot with the Randles-Sevcik equation suggested that the anodic charge transport within the film might be by electron hopping with the necessarily charge-compensating counter-ion motion. Since the

reduction peak was affected by kinetic effects, this invalidates the previous calculation on the basis of CV in the reduction process. A value of the conductivity of POAP was calculated in [1] by using the formalism of Nicholson [3]. The value obtained, with the assumption of fast charge transfer at the electrode/film and film/solution interfaces, was  $1.34 \times 10^{-4} S cm^{-1}$ .

A comparative study of the conduction properties of polyaminoarene films by employing CV was presented in [4]. It was demonstrated that in the case of POAP, the charge transport is diffusion-limited and a linear dependence of peak current on the square root of the sweep rate ( $i_p v^{1/2}$ ) was observed. From this feature the authors of [4] calculated an effective diffusion coefficient,  $D_{ef}$ , using a model of semi-infinite diffusion [5]. The calculated values of  $D_{ef}$  for polyaminophenol films in acid electrolytes are shown in [4]. The strong difference between diffusion coefficient values of polyaminophenols and PANI films was attributed to the different molecular structure and segment mobility of polymer chains. The presence of electron-donor substituents in the benzene rings should cause some loss of conductivity and electron-transport rate [6]. For the rigid ladder polymer structure of POAP the values of  $D_{ef}$  are 2-3 orders lower as compared to PANI, indicating a low rate of charge transport in POAP films. Similar trends were found between the absolute mobilities of anions in the electrolyte solutions in which  $D_{ef}$  values were calculated [7].

CV was also employed in [8] to study POAP film electrodes. Measurements were performed in LiClO<sub>4</sub> and HClO<sub>4</sub> solutions at different pH values and constant ionic strength (1M). In [8] it was considered that CV curves for POAP films result from two different processes. The former corresponds to a background film conduction, similar to that observed for the unmodified base electrode, while the latter is determined only by redox activity of the film. In order to separate the contributions of such processes, to the total CV trace, subtraction of a base current  $I_f(E)$ , from the total one  $I(E)$ , was performed. Anodic and cathodic peak currents ( $I^{(p)}$ ), as computed by the background subtraction, were not proportional to  $v^{1/2}$ . Also, the slope of  $\ln I^{(p)}$  *versus*  $\ln v$  was 0.9. This was attributed to the fact that injection of one or two types of charge carriers into the film was a limiting step of the total charge-transfer process under the conditions of the CV measurements.

Kinetic and transport parameters for POAP (the standard rate constant,  $k^0$ , the transfer coefficient,  $\alpha$ , and the apparent diffusion coefficient,  $D_{app}$ ) were obtained in [9] by employing different electrochemical techniques, such as CV (Cyclic Voltammetry), PSCA (potential-step chronoamperometry), PSCC (potential-step chronocoulometry) and NPV (normal pulse voltammetry). Anodic and cathodic peak currents of the voltammetric response were found to scale linearly with the square root of the potential scan rate within the range 5-200  $mV s^{-1}$ . This indicated that both anodic and cathodic charge-transport processes within POAP films are diffusion-controlled. Potential Step Chronoamperometric and Chronocoulometric responses for the oxidation and reduction of POAP films were employed in [9] to obtain Cottrell plots ( $i-t^{-0.5}$  and  $Q-t^{-0.5}$ ). These plots were found to be linear, indicating that, in agreement with CV results, the charge-transport processes within POAP films follow Fickian diffu-

sion laws [10]. The slopes of the linear chronoamperometric and chronocoulometric Cottrell plots allowed the authors to obtain  $D_{app}$  values. With regard to NPV, normal pulse voltammograms for the oxidation and reduction of a POAP film were recorded at various sampling times. Plots of the cathodic and anodic limiting currents ( $i_{lim}$ ) of normal pulse voltammograms against the inverse of the square root of the sampling time ( $\tau$ ) were found to be linear, as expected for a diffusion-controlled limiting current. Thus,  $D_{app}$  values were also obtained from the slope of  $i_{lim}$  versus  $\tau^{-0.5}$  plots by using the normal pulse voltammetric Cottrell equation. The kinetic parameters ( $k^0$  and  $\alpha$ ) of the heterogeneous electron-transfer reaction were extracted from the rising part of the normal pulse voltammograms [10].

Transient currents for POAP-modified electrodes as a function of the reciprocal of the square root of time were also recorded in [8]. According to the authors, the current relaxation for POAP films does not satisfy the Cottrell equation. It was indicated that the main part of the recorded current responses well fits a two-exponential time dependence, which most likely indicates a limiting influence of the charge carrier injection processes at both interfaces of POAP films. Then, results presented in [8] seem to indicate that charge transfer through POAP films is complicated by irreversible injection processes at the film interfaces.

In [11], EIS was employed to obtain transfer and transport parameters of POAP films in contact with a 0.1 M  $HCO_4^-$  + 0.4 M  $NaClO_4$  (pH1) solution. Impedance measurements were made within the potential range  $0.125 < E < 0.7$  V (versus NHE). Impedance diagrams were interpreted through a simple charge-transfer resistance in parallel with a constant capacity at high frequencies and the redox capacity ( $C_{if}$ ) in series with the film resistance at low frequencies. The electrochemical rate constant ( $k_{s,h}$ ), the concentration of redox centres ( $C_T$ ), the film conductivity ( $\sigma_{if}$ ) and the diffusion coefficient of electrons ( $D_e$ ) were determined in [11]. A maximum conductivity ( $\sigma_{if}$ ) value of  $(4.55 \pm 0.2) \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$  was obtained from the minimum low-frequency resistance value,  $R_{if}$ , at  $E = 0.3$  V (NHE). According to the  $\sigma_{if}$  value obtained in [11], POAP exhibits a lower conductivity as compared with PANI. An electron-diffusion coefficient value  $D_e$  of about  $1.3 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$  was obtained by employing the formalism of Chidsey and Murray ( $D_e = \sigma_{if}/C_{if}$ ) [12]. With the values of  $C_T$  known from previous measurements [13] and assuming the charge-transfer coefficients are equal for the anodic and cathodic partial processes,  $\alpha = \beta = 0.5$ , a  $k_{s,h}$  value of about  $2.3 \times 10^6 \text{ cm s}^{-1}$  was extracted from the fitting performed in [11].

Impedance measurements were also performed in [14] to study POAP behaviour. Impedance data of POAP given in [14] were interpreted in terms of the diffusion-migration transport of the two charge carriers within the film. It was assumed that electron transport is ensured by interchain electron hopping. Thus, the general expression of the faradaic impedance of redox polymers derived by Mathias and Haas [15] was employed. The low-frequency capacitance,  $C_L$ , and the low-frequency resistance,  $R_L$ , were expressed in terms of the coupled diffusion coefficient  $D$  ( $=D_i t_e + D_e t_i$ , where  $D_e$  and  $D_i$  are the electron and ion diffusion coefficients, and  $t_e$  and  $t_i$ , are the transference numbers for electrons and ions, respectively). As the behaviour of the low-frequency resis-

tance,  $R_L$ , (relative to potential), was basically similar to that of the charge-transfer resistance,  $R_c$ , this implies that charge transport in the polymer occurs by a diffusion-like process due to molecular electron exchange, as suggested by Gabrielli *et al.* [16]. On the basis of relationships between  $R_L$  and the polymer resistance,  $R_p$ , a rate-determining step in charge transport through POAP films was discussed in [14]. In this connection, the authors of [14] show the two combinations of transport parameters in the extreme cases of ion-transport control, electron-transport control and mixed control. The ohmic resistance  $R(\infty)$  of the electrode system was determined from the high-frequency intercept of impedance plots with the real axis. A value of about 24 ohm was obtained in 0.2 M HCl, which was independent of the potential within the range -0.2 to 0.2 V (versus Ag/AgCl).  $R_p$  was very small (less than 2 ohms) irrespective of the oxidation level. Thus  $R_p/R_L$  was very low, since  $R_L$  values were within the range 0.2 - 2 k  $\Omega$  at a thickness film of  $d = 0.1 \mu\text{m}$ . Then, it was deduced that  $t_e \gg t_i$  or  $t_e \ll t_i$ . Then, at POAP one of the two carriers moves much faster than the other. In order to shed light on this point, the authors of [14] calculated the  $D$  versus  $E$  dependence from experimental  $R_L$  and  $C_L$  values. In spite of the error in the  $D$  values (near 50%), it was found that  $D$  depends on  $E$ , that is, on the oxidation level of the polymer. The calculated  $D$  versus  $E$  dependence shows a maximum near the formal potential of POAP. By comparing the  $D$  versus  $E$  dependence extracted from experimental  $R_L$  and  $C_L$  values with the  $D$  versus  $E$  dependence extracted from models [17], the existence of an electron-transport control in POAP was established. Thus, under electron-transport control, the  $D_e$  value was found to be around  $6 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$  (0.2 M HCl) from the estimated  $D$  maximum. This  $D_e$  value is very small as compared with the  $D_i$  value of PANI ( $0.9\text{-}5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  [18]). This was explained considering that in swollen films electron hopping is slow in comparison with ion transport.

EIS was also employed in [19] to study the effect of the electrolyte solution on the transport properties of POAP. 0.1 M  $HClO_4$  +  $x$  M  $NaClO_4$  solutions were employed, where  $x$  was varied between 0.4 and 2. The dependence of the characteristic impedance quantities at low frequency on the electrolyte concentration was interpreted on the basis of two models: a transmission line [20, 21] and a modified electron-hopping model described in [22]. Analysis of experimental data by means of the transmission line model allowed the authors to separate the charge transport within the film in terms of the electronic and ionic contributions represented by the diffusion constants  $D_e$  and  $D_x$ , respectively. Application of the electron-hopping model developed in [22] only gave an effective diffusion coefficient,  $D_{eff}$ . At the different electrolyte concentrations,  $D_e$  was always two orders of magnitude lower than  $D_x$ . Also, as  $D_{eff}$  was very close to  $D_e$ , this was considered as indicative of a conduction mechanism dominated by electron transport.

## 2.2. Conducting Potential Range of Poly(o-aminophenol)

On the basis of "polaron-bipolaron" model [23, 24] of charging processes at polymer films, Ortega [25] investigated POAP by cyclic voltammetry and ESR measurements to determine the conducting potential range of the polymer. POAP films deposited on a Pt electrode were studied at pH 0.9, where spectra were recorded at different potentials,

scanning forwards and backwards from -0.250 to 0.55 V (versus SCE). The maximum in ESR spectra occurs in the potential range from -0.24 to approximately 0.0 V. The decrease and further absence of a detectable ESR signal at potentials higher than 0.55 V suggests a combination of radicals to give rise to dication species, which are not ESR active because of their paired spin. The determined  $g$  value was 2.00710 for the spectra recorded from -0.2 to 0.05 V and 2.0076 for the one at 0.15 V. A combination of polarons at positive potentials to give rise to dications may produce the slight change in  $g$ , due to the change in the nature of the electrostatic interactions between the charges in the polymer. Thus, in [25] it was concluded that at high positive potential values, the creation of bipolarons by a combination of polarons is possible at POAP films. This conclusion is supported by other spectroscopic studies. In this regard, in [26] Raman spectroscopy and voltammetry were coupled to identify structural changes in POAP during its redox process. Raman spectra of POAP contacting a 1 M HClO<sub>4</sub> solution exhibit bands whose intensities depend on the applied potential. For instance, the band associated with quinoid groups (1474 cm<sup>-1</sup>) and the band assigned to -C=N- in quinoneimine units (1638 cm<sup>-1</sup>) depend on the potential. The behaviour of these bands with the potential shows that when the potential increases, the band at 1474 cm<sup>-1</sup> increases and the band at 1638 cm<sup>-1</sup> also increases until a potential of about 0.2 V and thereafter, it diminishes. The fitting of these bands by employing Lorentz curves allowed the authors of [26] to quantify the evolution with the potential of the species related to these bands. The integrated intensity of the band at 1638 cm<sup>-1</sup> increases until a potential around 0.15 V and then decreases. However, the integrated intensity of the band at 1474 cm<sup>-1</sup> increases until 0.15 V, and then it is maintained. Thus, the behaviour of the band at 1638 cm<sup>-1</sup> corresponds to a typical intermediate species. Since POAP has a conductivity maximum at about 0.04 V versus SCE, the intermediate species was related to the polymer conductivity and then, it was assigned to a charged species. The authors of [26] indicate that the existence of an intermediate species suggests that the oxidation of POAP occurs through two consecutive reactions from the totally reduced phenoxazine form to the completely oxidised one, through a charged species, which could be a cation radical. It is interesting to remark that the behaviour of the integrated Raman intensity of the band at 1638 cm<sup>-1</sup> is similar to that of the band at 750 nm observed in the absorbance versus potential dependence in the UV-Vis region reported in [27]. That is, the maximum of absorbance of both bands (750 nm and 1638 cm<sup>-1</sup>) appears approximately at the same potential. Then, Raman and UV-Vis measurements suggest that the third species could be a cation radical, in agreement with the results obtained by EPR [25].

EIS was employed in [11] to obtain dependences of charge transfer and transport parameters of POAP films on the electrode potential within the range 0.125 V < E < 0.7 V (versus NHE). Impedance measurements were performed with POAP films contacting 0.1 M HCO<sub>4</sub><sup>+</sup> 0.4 M NaClO<sub>4</sub> solutions. Nyquist diagrams at fixed electrode potentials were recorded within the frequency range 0.01-10 kHz. At high frequencies, Nyquist diagrams exhibit a depressed semicircle, which depends on the electrode potential. To determine the charge-transfer resistance, experimental data were fitted to a semicircle. The fit was based on successive

approximations by least square fitting to a linearised equation of a circle. The charge-transfer resistance exhibits a minimum value (500 ohm) at about E = 0.3 V and then it increases strongly at both sides of this minimum value taking high values (> 6000 ohm) for E < 0.1 V and E > 0.5 V, respectively. A high-frequency capacitance (C<sub>dl</sub>) value of 8 x 10<sup>-6</sup> F cm<sup>2</sup> was obtained from the model and it was roughly independent of E. The redox capacity (C<sub>if</sub>) was obtained from -Z'' versus ω<sup>-1</sup> plots at sufficiently low frequencies. The C<sub>if</sub> versus E dependence exhibits a maximum value at E = 0.3 V and then, C<sub>if</sub> decreases strongly at both sides of the maximum value. C<sub>if</sub> becomes nearly zero for potential values E < 0.1 V and E > 0.5 V. The polymer film resistance at low-frequency R<sub>lf</sub>, as a function of E, was also extracted from the model. In a similar way to the charge-transfer resistance, R<sub>lf</sub> exhibits a minimum value at E = 0.3 V and then R<sub>lf</sub> increases strongly at both sides of the minimum value.

With regard to percolation theories [28-30], dynamic Monte-Carlo simulations were employed in [31] in order to find the morphological effect of the insulating-conducting (I-C) transition of POAP on anodic voltammograms. The simulation was based on the theory of the conductive zones under charge-transfer control. In order to verify the simulation results, the chronoamperometric behaviour of electrodeposited POAP films was also studied. With regard to the methodology, the model of the electrochemical system used was a conductive polymer film in a solution containing a large excess of supporting electrolyte and dopant ions. The film was considered as conductive in the oxidised state and non-conductive in the reduced state. Besides, it was assumed that the zone composed of only the conductive species is fully conductive and that the mass transfer of counter or dopant ions associated with the charge transfer has only a mirror effect on the propagation of the conductive zone. A two-dimensional lattice in which each element was a regular rectangle simulated the conductive polymer film. Each element was attributed to a conductive, a non-conductive or an electro-inactive site. A substrate electrode was allocated randomly on the lattice so that the ratio of the area of electro-active sites to that of the lattice was a given value,  $p$ . That is, electro-active sites were assigned to the lattice by the Monte-Carlo method so that the total area of the active sites was  $p$ -times the area of the lattice (where  $p$  is the percolation probability). On the basis of the CV technique and the theory of propagation, the growth rate of the conductive zones was considered to be an exponential function of the electrode potential [32]. Various patterns of the conductive zones were observed at  $p$  ranging from 0.5 to 0.61. From the peak current and the conversion ratio with  $p$ , the voltammogram was classified into the three controlled processes: Nernstian condition control (0 <  $p$  < 0.55), morphological control (0.55 <  $p$  < 0.61) and charge-transfer control at the interface between conductive and non-conductive sites ( $p$  > 0.61). A comparison of the simulated patterns with the corresponding linear sweep voltammogram shows that the peak potential (E = 0.17 V versus Ag, AgCl in SO<sub>4</sub><sup>2-</sup>, pH 5) of linear sweep voltammetry could be considered, as a first approximation, the percolation threshold potential of the electrochemically deposited conductive polymer film. In order to verify this consideration, the authors of [31] performed a chronoamperometric analysis to determine the percolation threshold potential of a conductive POAP film and compare it with the

peak potential of a cyclic sweep voltammogram. Then, a POAP-coated electrode was stepped in the positive potential direction and the growth of the C zone was investigated. It was observed that the electrochemical activity of POAP begins at around 0.11 V (Ag, AgCl), as indicated by the sharply rising initial current ( $I$ ) and its relatively slow decay with time ( $t$ ). Plots of  $I-t^{-1/2}$  and  $I-t^{-1}$  were recorded at various potential step values. Below 0.15 V, a linear dependence of  $I-t^{-1/2}$  was observed, indicating the dominance of the diffusion-controlled processes giving rise to the development of the conducting C zone. Above 0.15 V, no linear dependence of  $I-t^{-1/2}$  was observed. On the other hand, good to fair linear plots of  $I-t^{-1}$  were obtained over a large time period. This linearity was found to be limited to the potential range of 0.15 V <  $E_c$  < 0.17 V. According to the author [31],  $E_c$  is definitely in the range 0.15 V <  $E_c$  < 0.17 V near the peak potential of the corresponding voltammogram. Then, as important conclusion, the percolation threshold during the insulating/conducting transition of electrochemically deposited POAP films was found to lie in the potential range 0.15-0.17 V (Ag, AgCl) [33].

### 2.3. Effect of the Solution pH on the Charge-Transport Process at POAP Films

The electrochemical response of POAP is highly dependent on the solution pH. In this connection, the voltammetric response of thin POAP films (thickness,  $d < 30$  nm) at different pH in HClO<sub>4</sub> solutions of variable concentration and 0.4 M NaClO<sub>4</sub> was studied in [1]. The POAP response was optimal at pH 3. At pH > 7 no response was observed. This indicates that protons and electrons take part in the electrode reaction of POAP. As the pH is increased, the voltammetric peaks maintain their shape, but the peak current decreases, particularly the cathodic peak. At pH close to 5, the cathodic response disappears completely, whereas this occurs for the anodic peak at pH 7. A redox mechanism of POAP films was proposed in [1]. In this mechanism the redox reaction of POAP involves a process of addition/elimination of protons coupled with a reversible electron transfer. The protonation of the oxidised form of POAP was considered as the coupled chemical reaction in the mechanism proposed in [1]. In a polymer film this may be a rate-controlling step due to the restriction of H<sup>+</sup> diffusion through the film matrix. The diffusion of protons across a POAP film was explained in terms of a Grotthus mechanism. The presence of a POAP film does not inhibit proton reduction on the base electrode. In this regard, the negative potential limit for the film depends on the base electrode, being about -0.5 V (SCE) over Pt and Au, and -1.0 V (SCE) over GC. On the other hand, the positive potential limit is about 1.0 V and independent of the bare electrode.

Electrochemical Impedance Spectroscopy was used in [22] to study the effect of the solution pH on the charge conduction at POAP films. An *a.c.* impedance expression was derived on the basis of a model that considers a chemical reaction influencing the dynamics of the charge-transport process by electron hopping between redox sites. A partition coefficient determines the ratio between the proton concentration inside the film and the actual proton concentration in solution. With regard to chemical step, a pseudo-first-order rate constant and an equilibrium constant were defined in the model. Then, experimental impedance spectra of POAP

films contacting solutions of different pHs were fitted by means of the model. This allowed a comparison between experimental and theoretical impedance quantities. The dependences of impedance quantities on pH were obtained at constant potential within the potential range -0.1 V <  $E$  < 0.1 V (*versus* SCE). It was found that the low-frequency capacitance and the conductivity decrease with pH. A conductivity value of about  $3.2 \times 10^{-6}$  S cm<sup>-1</sup> at pH 0 was reported for POAP in [22]. Also, as the pH affects the dynamics of the electron-hopping process through reduction of the redox centre density, from the fitting it was possible to extract an electron-diffusion coefficient that decreases from  $2.1 \times 10^{-10}$  to  $5 \times 10^{-11}$  cm<sup>2</sup> s<sup>-1</sup> as the pH increases from 0 to 2.

Another *a.c.* impedance study of POAP-coated electrodes was performed in [14] to establish how the kinetic parameters of the charge-transport process are affected by the protonation levels and also by the degree of oxidation of the polymer. Impedance data were analysed on the basis of the electron-hopping transport accompanied with intermolecular proton exchange. From impedance spectra the dependence of the charge-transfer resistance ( $R_c$ ) on the potential ( $E$  *versus* Ag/AgCl) at different pH values was evaluated.  $R_c$  values obtained at a given pH reach a minimum at the formal potential of POAP, which was evaluated as the average of the voltammetric anodic and cathodic peak potentials. The minimum of  $R_c$  considerably increased with increasing pH. Also, the  $R_c$  *versus*  $E$  curve shifts to the negative potential with a rate of -0.06V/pH as pH increases. This effect was considered as indicative of a proton participation in the redox reaction of POAP. With regard to low frequencies of impedance data, the capacitance ( $C_{LF}$ ) was evaluated from the slope of  $Z''$  *versus*  $\omega^{-1}$  plot.  $C_{LF}$  obtained at a given pH shows a maximum near the formal potential. The  $C_{LF}$  *versus*  $E$  curve shifts to the negative potential with increasing pH, whereas the maximum of  $C_{LF}$  was independent of pH ( $17 \pm 1$  mF cm<sup>-2</sup> at a film thickness of 0.14  $\mu$ m). As pH increases, it was also observed that the formal potential of POAP shifts to the negative direction with a rate of -0.06V/pH in the pH range below 6. This shift seems to indicate that one proton is released for each electron transferred in the oxidation process, thus electrochemical oxidation of the polymer was considered equal to its dehydrogenation. With regard to low-frequency capacitance, the calculated  $C_{LF}$  *versus*  $E$  curve shifts to the negative potential with increasing pH. However, the calculated  $C_{LF}$  *versus*  $E$  curve has a smaller width of the capacitance peak as compared with the experimental data. The discrepancy was ascribed to activity effects involving an interaction between electroactive sites of the polymer. The theoretical curve was well fitted to experimental data by using a negative interaction parameter, which means a repulsive interaction between electroactive sites. The charge-transport process in [14] was also expressed in terms of a coupled diffusion coefficient  $D (=D_e \tau_e + D_i \tau_i)$ , where  $D_e$  and  $D_i$  are the electron and ion diffusion coefficients, and  $\tau_e$  and  $\tau_i$  are the transference numbers for electrons and ions, respectively). The  $D$  *versus*  $E$  dependence was calculated from experimental  $R_L$  and  $C_{LF}$  values. It was observed that  $D$  decreases with pH. In order to explain this dependence, it was considered that only protons are the ionic charge carriers in POAP. In this sense, the homogeneous electron transfer in the film should be accompanied with proton transfer from the reduced sites to the oxidised ones. This transport mecha-

nism implies that electronic conductivities ( $\kappa_e$ ) of the polymer probably decrease with its deprotonation. In this regard, authors of [14] measured  $\kappa_e$  of a POAP film at different oxidation levels with a symmetrical cell. It was effectively found that the electronic conductivity decreases with  $pH$ . As  $\kappa_e$  depends on  $D_e$  [15], authors of [14] attributed the  $\kappa_e$  decrease with increasing  $pH$  to the corresponding decrease of  $D_e$ . In this connection, in the electron hopping between adjacent redox sites in different oxidation states,  $D_e$  was expressed as a function of the intermolecular electron-transfer rate constant ( $k$ ) and the mean distance ( $\lambda$ ) between two adjacent redox sites [34]. Then, the  $D_e$  decrease with  $pH$  was attributed to a decrease of  $k$  with the polymer deprotonation.

EIS measurements were also performed in  $\text{LiClO}_4$  and  $\text{HClO}_4$  solutions at different  $pH$  values and constant ionic strength (1M), to elucidate the role of protons in the conduction mechanism of POAP [8]. The simplified theory of polymer film impedances of Mathias and Haas [15] was applied to estimate an effective diffusion coefficient ( $D_{\text{eff}}$ ) value of charge carriers inside POAP films. However, the estimation of  $D_{\text{eff}}$  was hardly possible, because of the absence of a well-defined Warburg region in the impedance spectra. Also, the low-frequency dependences of the imaginary component of POAP impedance spectra at different potentials exhibit curves that consist of two lines and an intermediate region in between. Only the first lines approximately satisfy the impedance theory, since their intercepts are near zero. The second intercepts are non-zero. Also, impedance measurements for POAP became very difficult for frequencies lower than 0.1 Hz due to the noise fluctuations observed in this frequency region. Thus, it was not possible to obtain real low-frequency capacity ( $C_{\text{lf}}$ ) values of the POAP films and then, only estimations were obtained. Apparent capacities  $C_{\text{lf}}^{(\text{ap})}$  were calculated from  $d(-\text{Im}Z)/d(f^{-1})$  slopes and they were compared with the  $C_{\text{lf}}$  values extracted from CV. The latter values are nearly three times higher than the former. Thus, impedance data presented in [8] demonstrate the capacity dispersion in the low-frequency region. Even when this phenomenon at the low-frequency region can be attributed to porosity effects of POAP films, the authors of [8] are rather disposed to explain the observed capacity dispersion as a consequence of the binding of hydrogen ions with polymer nitrogen-containing groups.

Interfacial Resistance measurements [35] were also applied to study the redox mechanism of POAP and its dependence on the solution  $pH$  [36, 37]. The experimental arrangement in these investigations was one in which a POAP film is supported on a thin gold film of thickness 30 nm. Interfacial Resistance is not only sensitive to the presence of scattering centres but also to their distribution at the surface of a metal film. In this connection, it was demonstrated that the oxidation-reduction process of a POAP film, deposited on a thin gold film electrode, has a significant effect on the electronic transport of the base metal film. While Cyclic Voltammetry was used to quantitatively characterise the redox species transformation on the gold film surface contacting the polymer film, the resistance change ( $\Delta R/R$ ) was employed to investigate changes in the electronic properties at the gold|POAP interface during the redox conversion of the polymer [36]. Resistance changes with potential ( $\Delta R/R-E$ ) of a gold film free of and coated with a POAP film, both of them contacting a 0.1 M  $\text{HClO}_4$  + 0.4 M  $\text{NaClO}_4$  solution,

were compared within the potential range  $-0.2 \text{ V} < E < 0.5 \text{ V}$  ( $E$  versus SCE) where POAP exhibits its maximal electroactivity. A  $\Delta R/R$  increase was observed in going from the reduced to the oxidised state of POAP. In this connection, the redox switching of POAP was interpreted in terms of the oxidation of the amino groups to imine [27]. Also, a linear increase of  $\Delta R$  as a function of the degree of oxidation ( $\theta_{\text{ox}}$ ) of the POAP film was observed in [37]. This linear dependence was explained in terms of an interfacial distribution of imine sites in the oxidised state with a spacing among them constant and larger than that corresponding to amine sites in the reduced state. In this regard, it is well known that during POAP oxidation only one in every four or five amine sites is converted to the corresponding imine sites. This gives rise to gaps that would eventually yield a distribution of oxidised sites less compact than the corresponding distribution of reduced ones. It was also observed that the slope of the  $\Delta R-\theta_{\text{ox}}$  dependence increases with increasing the solution  $pH$  [37]. It was considered that as the  $pH$  increases, the lower number of reduced sites of POAP at the metal|POAP interface forms surface distributions that scatter electrons more diffusely than that at  $pH$  1. Thus, reduced sites at the gold|POAP interface should form less compact distributions on the gold film surface as  $pH$  increases. This effect was attributed to a low degree of swelling of a polymer at high  $pH$  values. At high  $pH$  values the ability of the inner solution (incorporated into the polymer matrix) to reduce the electrostatic repulsion of the charged sites is limited. Under these conditions redox sites would adopt an extended configuration so as to minimise the coulombic repulsions.

#### 2.4. Effects of the Type and Concentration of Ions of the External Solution on the Charge-Transport Process at POAP Films

Effects of the type and concentration of ions of the supporting electrolyte on the electrochemical response of POAP films were studied in several papers [1, 8, 19, 26, 38-44]. Some voltammetric experiments were performed in [1] by varying the  $\text{ClO}_4^-$  concentration between 0.1 and 1.7 M. While the anodic peak was not affected, the cathodic peak showed a positive variation. In this sense, a high concentration of perchlorate produces the same effect as a high proton concentration, making POAP more easily reducible. However, no noticeable changes were observed for anions such as  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$  and  $\text{Cl}^-$  or cations such as  $\text{Li}^+$ ,  $\text{K}^+$  and  $\text{Cs}^+$ .

The participation of the supporting electrolyte anions in charge-transfer processes through POAP films was studied in  $\text{LiClO}_4$  and  $\text{HClO}_4$  solutions at different  $pH$  values and constant ionic strength (1M) by employing CV and EQCM [8]. CV experiments with POAP-modified electrodes covered with Nafion thin films were performed. Nafion is known to hinder anionic permeability due to its own negative charge, so the films covered with this polymer should significantly change their electrical properties, as compared to the uncovered ones, when supporting electrolyte anions participate in the redox activity of the films. No significant effects of Nafion were observed for POAP. This allowed the authors of [8] to conclude that no perchlorate anions are involved in the redox reactions of POAP. To confirm this conclusion, the authors of [8] carried out EQCM measurements on POAP films. The microbalance frequency change  $\Delta f_{\text{cm}}$  of the POAP films was measured simultaneously with their

current responses under the electrode potential cycling. The  $\Delta m/\Delta Q(E)$  ratio, where  $\Delta m = \Delta f_{cm}/k$  ( $k$  is the constant of the Sauerbrey law) and  $\Delta Q(E)$  is the charge consumed during the oxidation/reduction process, gave a mass number of about 3-5 in the main range of the cycling potential of 0.0 V to 0.3 V (*versus* Ag/AgCl). Then, even when the authors of [8] consider this mass number low, as compared with the molecular weight of  $\text{ClO}_4^-$  anion, as a consequence of some compensating effect, they recognize that the simplest way is to think about an insignificant insertion of the anions into the POAP films.

The ionic exchange of POAP in the presence of perchlorate anions was studied by using Probe Beam Deflection (PBD) in [26]. During the reduction scan only a positive deflection of the PBD signal was observed, which was indicative of a simultaneous expulsion of perchlorate and insertion of protons, the latter process being dominant. To check this, a PBD profile was simulated by convolution of the current response using parameters reported in the literature [38] and considering that only protons are exchanged between the solution and POAP. The simulated profile fits reasonably well the negative scan but differs significantly in the positive direction, suggesting that not only protons but also perchlorate anions are exchanged during the positive scan.

EIS was employed in [19] to study the effect of the ionic strength ( $\mu$ ) of the solution on the transport properties of POAP. To this end 0.1 M  $\text{HClO}_4 + x$  M  $\text{NaClO}_4$  solutions were employed, where the concentration of perchlorate anions,  $x$ , was varied in order to change the ionic strength. Experimental complex impedance plots of POAP at constant potential and different ionic strengths were recorded. It was observed that when POAP is in its oxidised state, impedance diagrams depend strongly on the electrolyte concentration. However, when POAP is in its reduced state ( $E = -0.1$  V *versus* SCE), the impedance response does not exhibit a significant dependence on the bathing electrolyte concentration. Dependences of the characteristic impedance quantities, at low frequency, on  $\mu$  were interpreted on the basis of two models: a transmission line model [20,21] and a modified electron-hopping model [22]. From the former model it was possible to separately extract an electron ( $D_e$ ) and an anion ( $D_x$ ) diffusion coefficient. From the latter [22] only an effective diffusion coefficient,  $D_{\text{eff}}$ , was obtained. It was observed that the low-frequency capacitance  $C_{\text{LF}}$  does not depend much on the ionic strength. However, the low-frequency resistance,  $R_{\text{LF}}$ , depends markedly on  $\mu$ , at constant  $E$ .  $R_{\text{LF}}$  *versus*  $E$  curves pass through a minimum value, which depends on the electrolyte concentration. From the fitting of experimental low-frequency resistance curves as a function of the degree of oxidation ( $\theta_{\text{ox}}$ ) by employing the transmission line model,  $D_e$  and  $D_x$  *versus*  $\theta_{\text{ox}}$  dependences were extracted. Application of the electron-hopping model described in [22] allowed obtaining the  $D_{\text{eff}}$  *versus*  $\theta_{\text{ox}}$  dependence for different  $\mu$  values. The authors of [19] show the dependences of the respective diffusion coefficients on the ionic strength. Several explanations have been given to account for the dependence of the transport process at POAP films on external electrolyte concentration. It has been suggested that an excess of supporting electrolyte can be incorporated into the polymer phase during the redox process. If the incorporated ions act as counterions, an increase in their concentrations

within the film would cause a decrease in the resistance of charge transport through it or an equivalent increase in the diffusion coefficient. Another explanation invokes reduction of the electrostatic repulsion between redox centres as the electrolyte concentration increases, which allows a sufficiently facile ion transport.

Another study about the effects of the electrolyte concentration and degree of oxidation on the conduction properties of POAP films by employing EIS is reported in [39].

Participation of anions in the charge-transport process of POAP films was also analysed through fractal dimensions [40]. To this end, POAP films were deposited on glassy carbon in acidic media and in the presence of different anions, and then, fractal dimensions of the films were determined by CV. Correlations were observed between the size of the anions, the length scales and the yardstick for scaling of the fractal surfaces with the fractal dimensions of the surfaces. The formalism developed by Stromme *et al.* [41] was employed to obtain the fractal dimensions. In the presence of different anions,  $\text{ClO}_4^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$ , the fractal dimensions of the films were 2.46, 2.46, 2.46 and 2.32, respectively. The fractal dimension in the presence of chloride differs from the others. To shed light on the physical significance of fractal dimension values, diffusion layer widths were employed as a yardstick to estimate the length scales traversed by anions on the surface at the condition of the maximum currents. According to the Fick's first law, the diffusion-limited current is proportional to the magnitude of the concentration gradient of the electroactive species. Accordingly, the width of the diffusion layer was considered proportional to the difference between bulk concentration of the anions inside the polymeric film and that of its surface, at the time the peak current is reached. The diffusion coefficient value,  $D$ , was estimated using the Randles-Sevcik equation. The authors of [40] show the diffusion coefficient values of POAP films in the presence of different anions.

Fractal dimensions in [40] were also obtained from EIS by employing the  $Z$  *versus*  $\omega$  dependence. A constant phase element (CPE) was considered in the electrical characteristics of the system. From the impedance response and equivalent circuits, the fractal dimensions derived were 2.45, 2.43, 2.41 and 2.33, for  $\text{ClO}_4^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$ , respectively. To determine the length scales used in the fractal scaling, an equation relating the electrode capacitance,  $C_o$ , the film resistance,  $R$ , and the frequency  $f$  of measurement to the length scale,  $\lambda$ , was employed in [40]. The capacitance  $C_o$ , at the frequency of  $f$ , was obtained from  $C$  *versus*  $\log f$  plots. The length scale lay in the range 1.43-7.3 Å. According to the authors of [40], the smaller fractal dimension obtained in the presence of chloride is due to its smaller size and then leads to a larger yardstick for scaling the surface.

In [42] the processes of doping of electrodeposited POAP films with different anions under the regime of CV were analysed by the application of "Chaotic Logistic Map". The electrochemical data were fitted to a quadratic Logistic Map [43,44]. It was found that the system is more complicated than a simple non-linear system with a feedback to withstand a perfect fit to the quadratic logistic equation. Thus, other contributions such as charge/discharge of the double layer capacitance complicate the behaviour and cause deviation from a perfect fit. During the anodic sweep, where participa-

tion of anions is the main phenomenon (which consequently gives rise to a better fit), the increase of the potential sweep rate is accompanied by a decrease in anion insertion in the polymer matrix (anion insertion/movement cannot respond quickly enough to the increasing field). Thus, the doping process is no longer a dissipative one and a feedback-controlled phenomenon appears in the form of a more poor fit to the Logistic Map. The fitting of current *versus* charge to quadratic logistic equation for different anion-doped POAP in the anodic half cycle of a voltammogram shows that the chloride/POAP system exhibits the less satisfactory fit. The authors of [42] rationalize this on the basis of topological structural differences in a film doped with Cl<sup>-</sup> compared to that doped with the other anions, as revealed by the differences in their fractal dimensions. On the basis of fractal dimension values for chloride, it was considered that the Cl<sup>-</sup>-doped film possesses a self-affine structure with less available regions in the film capable of being involved in the transport process. So, in the Cl<sup>-</sup>-doped films, dissipative processes occur less favourably with the consequent breakdown of the applicability of the logistic equation and poorer fit, especially in the region of higher charges.

### 2.5. Effect of the Film Thickness on the Charge Conduction Process of POAP

While in some papers it was reported that only thin POAP films could be synthesised to perform electrochemical measurements [8,11,19,22], in other ones it was indicated that thick films could be manufactured [14]. In this connection, in [8] it is reported that POAP film thickness did not exceed 50 nm due to the self-limiting effect, caused by the low polymer film conductivity. While in some studies voltammetric charge values were employed for film thickness estimation [8,45], in other ones the ellipsometric thickness was considered [19]. In this regard, the Surface Resistance technique was applied in [45] to study the interaction of different anions, such as perchlorate, sulphate and benzene sulphonate, and also a cation such as Cu(II), with a gold film surface when it is blocked with a POAP film. The dependence of the resistance change on the external electrolyte composition for POAP thickness lower than 0.25 mC cm<sup>-2</sup> was attributed to a competition at the gold film surface, between the proper redox process of the polymer and the adsorption of the different species contained in the electrolyte solution on the gold surface. This result points to a discontinuous character of POAP for thicknesses lower than 0.25 mC cm<sup>-2</sup>. For POAP thicknesses higher than 0.8 mC cm<sup>-2</sup> the resistance response becomes independent of both the film thickness and electrolyte composition. This result is indicative of the presence of a compact polymer layer at film thicknesses higher than 0.8 mC cm<sup>-2</sup>.

The effect of the film thickness on the POAP charge-transport process was treated in several papers. EIS was employed in [11] to obtain different transport parameters of POAP. Impedance measurements were performed in the frequency range 0.01-10 kHz and at two different film thicknesses ( $d = 30$  and 300 nm). At high frequencies Nyquist diagrams exhibit a depressed semicircle. It was observed that the change of the film thickness does not affect the size of the semicircle. Thus, this was considered as indicative of the existence of an interfacial charge-transfer process at the metal|polymer interface. However, the pseudo-capacitive rise

of  $Z''$  at low frequencies occurs at larger  $Z'$  values for thicker films. This means that the film resistance at low frequencies depends on the film thickness,  $d$ . The redox capacity was obtained from  $-Z''$  *versus*  $\omega^{-1}$  plots at sufficiently low frequencies. Despite the redox capacity increases with  $d$ , the dependence was not linear. On the contrary, in [14] the low-frequency capacity, at a given potential and  $pH$ , was proportional to the film thickness in the range 0.05-0.5  $\mu\text{m}$ .

Dependences of different characteristic impedance quantities on film thickness were studied in [19]. Results were interpreted on the basis of two models, a modified electron-hopping model and a transmission line one. While the former only allowed obtaining an effective diffusion coefficient,  $D_{\text{eff}}$ , the latter allowed obtaining electron ( $D_e$ ) and ion ( $D_x$ ) diffusion coefficient values. The authors of [19] show the dependences of the respective diffusion coefficients on film thickness for POAP. The low conductivity of thin POAP films seems to be anomalous. This was explained in terms of a structure that changes as the film thickness increases. In this connection, during the synthesis of a polymer film, two or more stages of the polymerisation process are usually distinguished: first, islands of the polymer are formed at the substrate surface, then a continuous film, compact (non-porous), is formed by fusion of these islands, and then, further growth takes place above this compact layer giving rise to the external, porous part of the film. In this regard, a high permeability of thick films, as compared with thin ones, should allow the incorporation of electrolyte solution into the polymer matrix. Electrolyte incorporated into the film should affect the polymer conduction, increasing the rate of the charge-transport process.

### 2.6. POAP Degradation and its Effect on the Charge-Transport Process

Partial oxidation (degradation) of POAP films was studied in [46] by employing CV and the EIS technique. The voltammetric response of a fresh POAP film shows one peak at about 0.1 V (*versus* SCE) and its impedance response for a potential corresponding to the peak potential shows a Warburg behaviour at high frequencies and a capacitive increase at low frequencies. POAP gives the same electrochemical response on potential cycling for more than one day provided that the positive potential does not exceed 0.5 V (*versus* SCE). However, after cycling during several days POAP starts to show the characteristics of degradation. Also, as the positive potential limit is increased beyond 0.5 V, the voltammetric response and, more clearly, the impedance response starts to change. In the latter case, a semicircle appears in the Nyquist plot, after degradation. Degradation is accompanied by a decrease in the film conductivity. In this connection in [46] it was observed that the conductivity of a freshly prepared POAP film ( $1 \times 10^{-6} \text{ S cm}^{-1}$ ) decreased up to  $4 \times 10^{-7} \text{ S cm}^{-1}$ , after its degradation.

In [47] the irreversible deterioration suffered by POAP films when the upper positive potential limit ( $E_{\text{upl}}$ ) is extended to values higher than a threshold value of 0.5 V *versus* SCE was studied by using resistance measurements together with Cyclic Voltammetry and Rotating Disc Electrode Voltammetry (RDEV). To this end, POAP films deposited on thin gold films were employed as working electrodes. The deterioration is reflected by a strong reduction in both anodic

and cathodic voltammetric responses of POAP-coated gold film electrodes. Also, a strong attenuation of the gold film resistance within the potential region of maximal electroactivity of POAP was observed after degradation. These last measurements allowed inferring that polymer inactive zones are developed at the POAP|gold interface. In this regard, the distribution of redox sites at the POAP|gold interface, active even after degradation, becomes more expanded than that present on the gold film surface contacting a freshly prepared POAP film. This was inferred from the more diffuse reflection of the conduction electrons from the inside of the gold film at the POAP|gold interface with increasing POAP degradation. RDEV measurements allowed obtaining an electron-diffusion coefficient value, which decreases as the degree of degradation increases. This fact was explained on the assumption of a gradual increase of the hopping distance with increasing polymer degradation. This result is in agreement with that obtained by employing the surface resistance technique.

### 2.7. Insulating POAP Films

Despite numerous papers describing the electropolymerisation of *o*-aminophenol (*o*-AP) in acidic media, in [48] the electropolymerisation of 2-aminophenol was performed in alkaline media ( $pH = 12$ ) to obtain an insulating polymer. The influence of the substrate and the position of the amino group on the electropolymerisation process were investigated. The film composition was also analysed. Electrochemical measurements (Cyclic Voltammetry and Chronoamperometry) were conducted on highly pure vitreous carbon, platinum and copper electrodes, which were employed as substrates to deposit POAP. The electrolyte used was a NaOH hydroalcoholic solution (30 % of methanol) containing 2-aminophenol. Voltammograms in the presence and in the absence of *o*-AP were compared in [48]. Cyclic voltammetry curves ( $30 \text{ mV s}^{-1}$ ) obtained on vitreous carbon (VC), platinum (Pt) and copper in NaOH hydroalcoholic solution (70 vol %  $\text{H}_2\text{O}$ , 30 vol %  $\text{CH}_3\text{OH}$ ) containing 0.3 M NaOH are presented in [48]. The oxidation of these substrates leads to an increase of the current near 0.3 V (SCE). The addition of 0.1 M of 2-aminophenol to the hydroalcoholic solution induced a current peak with a maximum at 0.09 (VC), 0.16 (Pt) and 0.2 V (copper) (*versus* SCE). This peak was attributed to the oxidation of 2-aminophenol that started at -0.2 V. In the case of VC and Pt substrates, current peak was followed by a wide passivity domain, characterised by a very weak current, showing the formation of a very protective layer. After the forward part, the reverse curve with low current confirmed the insulating character of the film and showed the irreversibility of the system.

## 3. POLY(O-AMINOPHENOL) (POAP) FILM ELECTRODES IN CONTACT WITH REDOX ACTIVE SOLUTIONS

The conduction properties of electroactive polymer films are often tested by analysing the electrochemical behaviour of the films contacting different redox active solutions. To this end CV, Rotating Disc Electrode Voltammetry and EIS are employed. Redox mediation and redox solute permeabilities at film-coated rotated-disc electrodes are often determined from the variations of their limiting currents with the electrode rotation rate, film thickness and redox couple con-

centration. Complete mechanism diagnosis criteria from steady-state polarisation curves for redox mediation at electroactive polymers coated electrodes are discussed in [49]. In [50], the same authors of [49], present a review about the theoretical basis for the electrochemical rectification in mediated redox reactions at redox polymer-modified electrodes.

### 3.1. POAP Films in Contact with Redox Active Solutions Containing Negatively Charged Species

Steady-state current-potential curves for the oxidation of  $\text{Fe}(\text{CN})_6^{4-}$  at bare and POAP film-coated rotating BPG (Basal-plane Pyrolytic Graphite) disc electrodes were compared in [9]. The oxidation of  $\text{Fe}(\text{CN})_6^{4-}$  is not thermodynamically mediated by POAP films. This can be seen from the comparison of the formal redox potential ( $E^0$ ) values of POAP (0.044 V *versus* SSCE) with that of  $\text{Fe}(\text{CN})_6^{4-/3-}$  couple (0.350 V *versus* SSCE) in 0.2 M  $\text{NaClO}_4$  aqueous solution ( $pH$  1). Thus, the observed anodic currents in the presence of POAP were assigned to the oxidation of  $\text{Fe}(\text{CN})_6^{4-}$  species that penetrate the POAP film to reach the electrode surface. The quantitative analysis of these experiments was made on the basis of the Koutecky-Levich equation ( $i_{\text{lim}}^{-1}$  *versus*  $\Omega^{1/2}$ , where  $i_{\text{lim}}$  is the limiting current and  $\Omega$  the electrode rotation rate of the disc electrode). Experimental Koutecky-Levich plots of  $i_{\text{lim}}^{-1}$  *versus*  $\Omega^{1/2}$  were linear, and the slopes matched that at the bare electrode. Thus, the diffusion rate of  $\text{Fe}(\text{CN})_6^{4-}$  in POAP films was estimated as  $D_s \kappa = (1.2 \pm 0.3) \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$  (where  $\kappa$  is the partition coefficient of  $\text{Fe}(\text{CN})_6^{4-}$  between the film and the bulk of the solution and  $D_s$  is the diffusion coefficient of  $\text{Fe}(\text{CN})_6^{4-}$  into the polymer film). It was observed that for POAP,  $D_s \kappa > D_{\text{app}}$ , that is, the overall charge-transport within the film is slower than the physical diffusion rate of a dissolved ion ( $\text{Fe}(\text{CN})_6^{4-}$ ) through the film. In [51] the electrochemistry of POAP-modified electrodes in the presence of 0.1 M  $\text{HClO}_4$  + 1.9 M  $\text{NaClO}_4$  +  $3 \times 10^{-3}$  M ( $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ ) solutions was also studied by Rotating Disc Electrode Voltammetry (RDEV). The extrapolated  $\kappa D_s$  value, for high film thickness, by employing the Koutecky-Levich equation resulted in  $\kappa D_s (\text{Fe}(\text{CN})_6^{4-}) = (0.62 \pm 0.2) \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ .

Ortega [25] also analyzed the behaviour of POAP films in contact with the redox active couple  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ . The behaviour of POAP-modified electrodes was studied in 0.4 mol  $\text{dm}^{-3}$   $\text{NaClO}_4$  solutions at  $pH$  9, containing  $10^{-3}$  mol  $\text{dm}^{-3}$   $\text{Fe}(\text{CN})_6^{3-}$ . The redox potential of the  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  couple is strongly dependent on  $pH$ , due to the formation of  $\text{HFe}(\text{CN})_6^{3-}$ . It was observed that the  $E_o$  for  $\text{Fe}(\text{CN})_6^{3-}$ , that is, 0.36 V (*versus* SCE), at  $pH$  9 is located in the region where the applied potential is more positive than the formal potential of POAP. The voltammograms corresponding to the redox process of  $\text{Fe}(\text{CN})_6^{4-}$  at POAP-modified Pt electrode did not show any peak ascribable to hexacyanoferrate ion in the region ranging from 0.0 to 0.75 V (*versus* SCE). Increasing concentrations of  $\text{Fe}(\text{CN})_6^{4-}$  were used as well as different film thicknesses, but no peak was observed. However, a light increase in the cathodic peak current of POAP was observed as the concentration of  $\text{Fe}(\text{CN})_6^{4-}$  increased. It was indicated that it is possible that a very small amount of  $\text{Fe}(\text{CN})_6^{3-}$  was oxidised during the forward scan through pores formed from the swollen reduced form of the film; during the reverse scan, the polymer becomes more compact and the  $\text{Fe}(\text{CN})_6^{3-}$  is reduced when the

polymer becomes conducting. This agrees with a higher conductivity of POAP in the potential range from -0.25 to 0.0 V (*versus* SCE) reported in [25].

In [50] the redox mediation reaction of POAP on the  $\text{Fe}(\text{CN})_6^{3-/4-}$  redox couple in solution was studied by CV and Rotating Disc Electrode Voltammetry.  $\text{Fe}(\text{CN})_6^{3-/4-}$  5 mM, in  $\text{HClO}_4$  0.1 M, was employed as external redox active solution contacting POAP films. At this pH, the formal potential of the couple is  $E_o(\text{Fe}(\text{CN})_6^{3-/4-}) = 0.330$  V (*versus* SCE). The formal redox potential of the quasi-reversible redox couple of POAP was considered to be 0.050 V (*versus* SCE). The *i-E* responses of this couple on both a naked Au and a POAP-coated electrode were compared in [50]. The *i-E* response for POAP-modified electrodes in contact with the couple shows no anodic currents. Also, it was observed by RDEV that the cathodic limiting current was independent of the concentration of  $\text{Fe}(\text{CN})_6^{3+}$  and increases as the POAP film thickness decreases. Furthermore, for relatively high rotation speeds, the cathodic limiting current was independent of this variable. This was taken as an indication of current control by charge transport in the film. It was considered that electronic transport should be responsible for the observed cathodic limiting currents because the permeation of  $\text{Fe}(\text{CN})_6^{3-/4-}$  was ruled out on the basis of the half-wave potential value. Thus, the observed behaviour was explained on the basis of an unfavourable thermodynamic condition for the mediation of the oxidation of  $\text{Fe}(\text{CN})_6^{4-}$  and a slow electronic diffusion in the POAP film.

A voltammetric study of the  $\text{K}_4\text{Fe}(\text{CN})_6$  oxidation on POAP was carried out in [1]. A reversible behaviour at low film thickness was observed. However, with a film thickness greater than 200 nm, quasi-reversible behaviour was observed. This effect was attributed to the film resistance.

### 3.2. POAP Films in Contact with Redox Active Solutions Containing Positively Charged Species

By employing CV in [1] it was demonstrated that positive species that are reduced at potentials lower than the  $E_{pa}$  of POAP, such as  $\text{Cr}^{3+}$ ,  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$ , could not be reduced above such potential, with the exception of protons. Also, couples, which have an  $E^o$  value more positive than the  $E_{pa}$  of the film, could be oxidised easily. According to these observations, the authors of [1] conclude that POAP is conductive in the oxidised state and non-conductive in the reduced one.

With the aim of analysing the conducting potential range of POAP, Ortega [25] carried out several experiments with POAP films contacting different redox active solutions, containing  $\text{Fe}(\text{II})/\text{Fe}(\text{III})$ , Paraquat and  $\text{Cu}(\text{II})/\text{Cu}$ . Oxidation of  $\text{Fe}(\text{II})$  to  $\text{Fe}(\text{III})$  is reported to take place at the formal potential of 0.8V (*versus* NHE) in acid medium. However, no peak ascribable to oxidation of  $\text{Fe}(\text{II})$  on POAP was observed in [25]. Thus, POAP does not seem to be conducting in the potential range more positive than the polymer formal potential. Paraquat (1,1'-dimethyl-4,4' bipyridylium or methyl viologen) was also employed in [25] to test the conductivity of POAP at negative potentials. The reversible reduction of Paraquat leads to a violet radical that is stable for nearly 10 minutes. Paraquat was reported to exhibit two reversible peaks at -0.7 V (*versus*  $\text{Ag}/\text{AgCl}$ ) in aqueous solutions at pH 4 [52]. Reduced Paraquat ( $0.5 \times 10^{-3}$  mol  $\text{dm}^{-3}$ )

was obtained and a voltammogram during its redox reaction on bare Pt was recorded in a neutral solution to avoid hydrogen evolution. In the presence of POAP an additional current was observed within the negative potential range, exactly in the region where POAP is in a lower oxidation state. Such additional current was not observed in the absence of radical methyl viologen, which was considered as a signal of the conductivity of the film in that region. Copper was also utilised in [25] to demonstrate the conductivity of POAP at negative potentials. Voltammograms corresponding to copper deposition from an acid solution containing  $\text{Cu}(\text{ClO}_4)_2$  onto bare Pt and POAP-modified electrode were compared in [25]. A voltammogram of POAP-modified electrode submerged in a  $\text{Cu}(\text{II})$  solution clearly shows the oxidation and reduction peaks corresponding to the polymer and  $\text{Cu}(\text{II})/\text{Cu}$  couple. The copper reduction peak appears at more negative potentials, probably due to the resistivity of the film, while the cathodic current does not change significantly. However, the oxidation peak was not significantly affected when the modified electrode was in operation. Voltammograms recorded at different scan rates showed that the reduction peak of copper depends on this parameter in the same way as the POAP reduction peak. That is, it moves to more negative potential as the sweep rate increases. Changes in the scan rates do not affect the oxidation peak potentials of the polymer and copper. Again, according to Ortega [25], the more reasonable explanation for this behaviour is that the film is conductive at negative potentials lower than -0.250 V (*versus* SCE). In this regard, it was assumed that the shift of the reduction peak of copper on a POAP-modified electrode, with respect to the one observed from the naked Pt electrode, originates from the different nature of the substrate, that is, from the potential-dependent resistance of the film. Reduction currents at the modified electrode were also very similar to those recorded when bare Pt electrode was used. These features suggest that the deposition of copper takes place on the polymer/solution interface; otherwise, an appreciable decrease in the current, because of the diffusion of copper through the film, would be observed. In the case of POAP films employed in [25], no pinholes were visible in the scanning electron micrographs, which supports this assumption. Then, the difference between current-potential profiles for the reduction of copper of the POAP-modified electrode and naked Pt was related to the resistance of the polymer film. Voltammograms of modified-rotating disc electrodes were also recorded at different rotation rates. No change was observed in the voltammograms at a rotation rate lower than 50 rad/s because the process is controlled by charge transfer in the polymer matrix. The voltammograms were recorded at low scan rates (3mV/s) so that steady-state conditions were kept during the experiments. Under such conditions, the polymer should also have time to reach its equilibrium conductivity at each potential. Thus, these voltammograms corresponding to the reduction of copper on naked Pt and POAP-modified Pt electrodes were also compared in [25]. In going towards to the negative potential direction, a small hump was observed in the *i-E* curve of the reduction of copper on the modified electrode, which represents the reduction of the polymer. However, a larger one was observed at more negative potential values, which involves the reduction of the metal ion on the polymeric material. Small changes in the potential produce large changes in the current for the

reduction of copper on naked Pt at 0.0 V. However, the curve corresponding to the POAP-modified electrode is less steep, and this was attributed to the potential-dependent resistance of the film that controls copper deposition. As in the experiment described by Ortega an electrode surface area of 0.33 cm<sup>2</sup> and a film thickness of 80 nm, were used, the conductivity ( $\sigma$ ) of the film was determined as a function of the polarisation potential by using the expression  $\sigma = iL/\Delta E A$ , where L is the thickness of the film, A is the area of the electrode, i is the current and  $\Delta E$  is the difference of potential between points with the same magnitude of current for the reduction of copper curves on POAP-modified and naked Pt electrodes. The resulting  $\sigma$ -E plot was compared with the spin intensity-E characteristic also presented in [25]. It was observed that the conductivity increases very sharply at approximately -67 mV (versus SCE), peaks at approximately -120 mV and starts decreasing at more negative potentials. The conductivity and the spin intensity both exhibit a maximum at -0.120 V, which should be indicative of the polaronic nature of the conductivity of the film at that potential range. According to Ortega [25], at more positive potentials the number of polarons decreases, but not so steeply as the conductivity. This was explained assuming that when the concentration of polarons is high, they start to combine to give rise to bipolarons. Some of these bipolarons are converted to a higher oxidised state of the polymer, that is, the ones with opened structure, which decreases the conductivity in the polymer. Some polaron islands surrounded by fully oxidised units can still be present in segments of the chains so that the conductivity of the film is strongly reduced, while ESR spectra still show the presence of radicals. Calculated conductivity values in [25] are in the same order of magnitude as the value reported from four-point probe measurements,  $1.0 \times 10^{-8}$  S/cm.

In [50] the redox mediation reaction of POAP on the Fe(II)/Fe(III) redox couple was studied by CV and Rotating Disc Electrode Voltammetry. Fe(II)/Fe(III) 5 mM, in HClO<sub>4</sub> 0.1 M, was employed as redox active solution contacting POAP films. At this pH, the couple has a formal potential of  $E_o$  (Fe(II)/Fe(III)) = 0.510 V (versus SCE). The formal redox potential of the quasi-reversible redox couple of POAP was considered to be 0.050 V (versus SCE). The *i*-E responses of the couple were studied on both a naked Au and a POAP coated electrode. The *i*-E response for POAP-modified electrodes does not show anodic current. Also, it was observed that in the Fe(II)/Fe(III) system the cathodic limiting current is independent of the film thickness but it depends on the concentration of Fe(III). The fact that for this system the cathodic limiting current was independent of the film thickness was considered as an indication that the electronic transport in the film is not the rate-determining step of the process. On the other hand, the permeation of Fe(III) in the film was ruled out; otherwise, the half-wave potential for the coated electrode should be the same as that for the naked electrode. Then, according to the theoretical basis of the electrochemical rectification given in [50], the cathodic limiting current must be controlled by the kinetics of the electron transfer between the redox species in solution and those from the polymer.

In [51] the electrochemistry of POAP-modified electrodes in the presence of the Sn(II)/Sn(IV) couple was studied by Rotating Disc Electrode Voltammetry (RDEV). Ex-

perimental results relating to the diffusion of these electroactive species through POAP, at potential values  $E > 0.8$  V (SCE), were interpreted on the basis of the membrane-diffusion theory [53]. Extrapolated  $\kappa D_s$  values for high film thickness were considered as true permeation rates for this species through POAP films ( $\kappa$  is the partition coefficient of the species between the film and the bulk of the solution and  $D_s$  is the diffusion coefficient of the species into the polymer film). The resultant extrapolated value was  $\kappa D_s$  (Sn<sup>2+</sup>) =  $(1.42 \pm 0.2) \times 10^{-10}$  cm<sup>2</sup> s<sup>-1</sup>. This value is one order of magnitude lower than that found for a negatively charged species, such as Fe(CN)<sub>6</sub><sup>4-</sup> ( $\kappa D_s$  (Fe(CN)<sub>6</sub><sup>4-</sup>) =  $(0.62 \pm 0.2) \times 10^{-9}$  cm<sup>2</sup> s<sup>-1</sup>).

### 3.3. POAP Films in Contact with Redox Active Solutions Containing Neutral Species

In [51] the electrochemistry of POAP-modified electrodes in the presence of the hydroquinone/benzoquinone (HQ/Q) couple was studied by Rotating Disc Electrode Voltammetry (RDEV). The effects of the electrode rotation rate ( $\Omega$ ), film thickness ( $\phi$ ), charge and concentration (*c*) of the electroactive species and acid concentration (*x*) of the redox active solution on the steady-state current-potential curves (*I*-*E*) were studied. Experimental results relating to the diffusion of these electroactive species through POAP were interpreted on the basis of the membrane-diffusion theory [53]. The electron-hopping model was invoked in order to obtain a diffusion constant for the electron transport [16]. *I*-*E* curves, at different  $\Omega$  values, for a 60 nm thick POAP film contacting a *x* M HClO<sub>4</sub> + (2-*x*) M NaClO<sub>4</sub> + *c* (HQ/Q) solution, where *x* = 0.1 and *c* =  $3 \times 10^{-3}$  M, are shown in [51]. Diffusion-limited currents were observed at  $E > 0.8$  V (versus SCE) for HQ oxidation ( $I_{lim,a}$ ) and at  $E < 0.0$  V (versus SCE) for Q reduction ( $I_{lim,c}$ ). Besides, main anodic and cathodic plateaux, the presence of a pre-plateau ( $0.2 \text{ V} < E < 0.4 \text{ V}$ ) during Q reduction was observed. At  $\Omega$  and *c* fixed, *I*-*E* curves were film thickness and acid concentration dependent. HQ oxidation is not thermodynamically mediated on POAP. Then, the observed anodic currents correspond to the oxidation of HQ species that penetrate through the POAP films to reach the metal surface. Benzoquinone (Q) is reduced in two waves. The first wave originates from the penetration of reactants into the film coupled with their subsequent discharge at the metal|polymer interface. The limiting current for the second wave ( $E < 0.0$  V) was independent of the polymer thickness and follows the Levich equation. This second wave was related to a rapid electron-transfer mediation at the POAP|redox active solution interface. To evaluate the permeation characteristics of POAP films, the expression of Koutecky-Levich was employed. At constant *c*, *x* and ionic strength of the solutions, experimental  $I_{lim,a}^{-1}$  versus  $\Omega^{-1/2}$  representations for different film thicknesses give linear diagrams for the HQ/Q redox couple, with nearly the same slope but different intercepts on the ordinate axis. Thus, for HQ oxidation processes and Q reduction,  $\kappa D_s$  values were obtained in [51] from the Koutecky-Levich equation ( $\kappa = c_{pol}/c$  represents a partition equilibrium at the film|solution interface, where  $c_{pol}$  and *c* are the respective concentrations of the species in the polymer and solution, and  $D_s$  is the diffusion coefficient of the electroactive species in the polymer). It was found that for the oxidation process of HQ,  $\kappa D_s$  decreases with increasing  $\phi$ . The same behaviour was observed

for Q reduction. However, for a film thickness higher than 60 nm,  $\kappa D_s$  becomes independent of  $\phi$ . Thus, extrapolated  $\kappa D_s$  values for high film thicknesses were considered as true permeation rates for the species studied in [51]. The resultant extrapolated values are  $\kappa D_s(\text{HQ}) = (0.92 \pm 0.2) \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  and  $\kappa D_s(\text{Q}) = (0.42 \pm 0.2) \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ . A comparison of these redox solute permeabilities through POAP films with the transport rate of electroinactive anions, such as perchlorate, was made and discussed in [51].

As was indicated, in solutions of *pH* 1, a limiting current at  $E < 0.0 \text{ V}$  was observed; it depends linearly on  $\Omega^{1/2}$  and then, this wave was associated with a rapid electron-transfer mediation at the POAP|solution interface where Q diffusion in solution limits the current. However, in solutions where the acid concentration ( $x$ ) was decreased, after a certain  $\Omega$  value, which depends on  $x$ , the limiting current  $I_{\text{lim},c}$  becomes independent of  $\Omega$ . The limiting current at which  $I_{\text{lim},c}$  ( $= I_e$ ) was independent of  $\Omega$ , was considered as a representation of the maximum flux of redox species confined in the polymer, according to  $I_e = nFA D_e c^*/\phi$  [54], where  $c^*$  is the concentration of redox species of the polymer and  $D_e$  represents a measure of the electron-hopping rate.  $n$  Expresses the number (fractions) of unit charges per monomer unit of the polymer,  $A$  is the electrode area and  $F$  the Faraday constant.  $D_e$  values, at different acid concentrations, extracted from experimental  $I_e$  values are shown in [51]. It was observed that the electron-diffusion coefficient decreases as the solution *pH* increases. This is further evidence about the dependence of the charge-transport process at POAP on proton concentration.

A study of the conduction process through POAP films by employing redox species such as ascorbic acid and hydroquinone was carried out in [1]. By employing CV, it was demonstrated that chemical substances that have an  $E^0$  value more positive than the  $E_{\text{pa}}$  of the POAP film could be oxidised easily. In this connection, ascorbic acid suffers irreversible oxidation at a bare and at a POAP electrode, but the latter shows an increase of the total current, which was attributed to a catalytic effect of the film. Hydroquinone oxidises reversibly at the modified electrode showing a negative catalytic effect, which was assigned to the film resistance.

The irreversible deterioration of POAP films when the positive potential limit ( $E_{\text{upl}}$ ) exceeds 0.5 V was studied in [55] by employing CV, Rotating Disc Electrode Voltammetry (RDEV) and EIS. CV was employed to prepare fresh POAP films and also to degrade them quantitatively. Then, the different behaviours of freshly prepared and degraded POAP films contacting the *p*-benzoquinone/hydroquinone redox couple were studied by RDEV and EIS. The resulting experimental impedance diagrams were interpreted on the basis of the homogeneous impedance model described in [56]. The different dependences of the charge-transfer and charge-transport parameters on the degree of degradation of the polymer ( $\theta_{\text{Red,Max}}$ ) are shown in [55]. The different features of some of these dependences (for instance, bulk electronic and ionic transport on  $\theta_{\text{Red,Max}}$ ) were explained in terms of the different mechanisms of electron and ion transport in polymeric materials. The charge-transfer resistance at the metal|polymer interface,  $R_{\text{mjf}}$ , exhibits a strong increase from the beginning of the degradation. At the same  $\theta_{\text{Red,Max}}$  values, the ion-transfer resistance  $R_i^{\text{fis}}$  at the polymer|solution

interface is almost one order of magnitude lower than  $R_{\text{mjf}}$ . Also,  $R_i^{\text{fis}}$  as a function of  $\theta_{\text{Red,Max}}$  exhibits a different feature as compared with  $R_{\text{mjf}}$ . In the same way as  $R_{\text{mjf}}$ , a pronounced increase in the resistance related to the electron interfacial exchange  $R_e^{\text{fis}}$  at the polymer|solution interface was observed from the beginning of the polymer degradation (high  $\theta_{\text{Red,Max}}$  values). However,  $R_e^{\text{fis}}$  values are nearly one order of magnitude lower than  $R_{\text{mjf}}$  values. Then, concerning the polymer|solution interface, a slow ion-transfer process was observed for POAP as compared with the electron-transfer process at this interface. With regard to the high-frequency capacity,  $C_H$ , starting at a value around  $17 \mu\text{F cm}^{-2}$  for a freshly prepared film,  $C_H$  decreased as the degree of degradation of the polymer increased, reaching a value of about  $5 \mu\text{F cm}^{-2}$  for an almost completely degraded POAP film. Electron ( $D_e$ ) and ion ( $D_i$ ) diffusion coefficients changes with  $\theta_{\text{Red,Max}}$  were also extracted from the impedance model described in [56]. While  $D_e$  is strongly affected even at a low degree of degradation ( $0.8 < \theta_{\text{Red,Max}} < 1.0$ ),  $D_i$  changes are more pronounced for  $\theta_{\text{Red,Max}} < 0.6$ . Taking into account that transfer and transport parameters obtained in this work correspond to the reduced state of POAP ( $E < 0.0 \text{ V}$ ), it is possible that  $R_i^{\text{fis}}$  and  $D_i$  only reflect the proton movement through the polymer|electrolyte interface and inside the polymer film, respectively [8,22]. From a quantitative point of view the Voro-tyntsev's model gives  $D_e$  values near two orders of magnitude higher than  $D_i$  for POAP. It is interesting to notice that these relative diffusion coefficient values contrast with those reported in other papers, where electron motion was considered slow relative to the ion motion [14]. In [55] an interesting comparison was established between the transversal charge-transfer resistance at the metal|polymer interface  $R_{\text{mjf}}$  (obtained by impedance spectroscopy) and the lateral resistance  $\Delta R/R$  along the electrode (obtained by Surface Resistance measurements [35,37,47]), as a function of  $\theta_{\text{Red,Max}}$ . In this connection, similar features in  $R_{\text{mjf}}$  versus  $\theta_{\text{Red,Max}}$  and  $\Delta R/R$  versus  $\theta_{\text{Red,Max}}$  dependences were observed, which were explained in terms of two different aspects of the electron motion at metal surfaces contacting a polymeric material. However, while  $R_{\text{mjf}}$  is a transversal resistance at the metal|polymer interface related to the electron-transfer process during the redox reaction of the polymer,  $\Delta R/R$  changes were ascribed to the scattering of conduction electrons from the inside of the metal to the metal|polymer interface, caused by changes in the translational symmetry parallel to the interface due to the presence of different distributions of redox sites at this interface (a more expanded distribution of redox sites as more degraded the polymer becomes) [37]. The results of [55] seem to demonstrate that when POAP films are subjected to rough conditions, as in some of their practical applications, ion and electron diffusion inside the film and rates of interfacial charge transfer processes are strongly reduced. It should be expected that this deterioration process will drastically reduce the efficiency of the material in practical applications.

#### 4. CONCLUDING REMARKS ABOUT THE CHARGE CONDUCTION AT POAP FILMS

Different electrochemical techniques applied to studying the charge conduction through POAP film electrodes indicate the existence of a charge-transport process that is diffusion-limited. It was suggested that this charge transport

might be electron hopping with the necessarily charge-compensating counter-ion motion. In this regard, effective or apparent diffusion coefficient values were extracted from electrochemical measurements. Particularly, from impedance techniques it was possible to separate the charge transport process within POAP films in terms of ion ( $D_i$ ) and electron ( $D_e$ ) contributions.  $D_e$  values are nearly two orders of magnitude lower than  $D_i$  values. This is indicative of a conduction mechanism dominated by electron transport. The conductivity of POAP was also interpreted on the basis of percolation theories. In this connection, a charge-transfer diffusion-controlled process within the potential range 0.11 V to 0.15 V (Ag|Ag/Cl) was observed. Other kinetic parameters, such as the electrochemical standard rate constant,  $k^o$ , and the charge transfer coefficient,  $\alpha$ , were also determined for POAP film electrodes. Values of  $k^o$  within the range  $10^4$  to  $10^6$  cm s<sup>-1</sup> have been reported. In some papers it was indicated that charge transfer through POAP films is complicated by irreversible injection processes at the film interfaces.

The conductivity potential range of POAP was explained on the basis of the polaron-bipolaron model. By employing ESR measurements, the existence of a conductivity maximum within the potential range -0.24 to 0.0 V (SCE) was established. The decrease and further absence of a detectable ESR signal, at potential values above 0.55 V (SCE), was attributed to a combination of radicals to give rise to dication species. EIS measurements also seem to indicate the existence of a conducting potential range between 0.1 V and 0.6 V (NHE). On the basis of percolation theories, the percolation threshold during insulating-conducting transition was found to be in the range 0.15–0.17 V (Ag|Ag/Cl).

Effective diffusion coefficient values for POAP are two or three orders of magnitude lower than those determined for polyaniline. This was attributed to the different molecular structure and segment mobility of polymer chains. The presence of electron-donor substituents in the benzene rings of POAP should cause some loss of conductivity.

Voltammetric and *ac* impedance measurements show that the electrochemical response of POAP depends strongly on the solution *pH*. A redox mechanism was proposed for the polymer, in which the redox reaction involves a process of addition/elimination of protons coupled with a reversible electron transfer. The protonation of the oxidised form of POAP was considered as the coupled chemical reaction. Some impedance measurements seem to indicate that one proton is released for each electron transferred in the oxidation process, thus electrochemical oxidation of the polymer was considered equal to its dehydrogenation. It was suggested that the *pH* affects the dynamics of the electron-hopping process through reduction of the active redox centre density. In this connection, the decreasing electron conductivity observed for POAP as the *pH* increases was explained considering a decrease of the intermolecular electron-transfer rate constant between two adjacent redox sites with the polymer deprotonation.

The participation of supporting electrolyte anions in the charge-transport process of POAP was also studied. While some techniques, such as EQCM, seem to indicate that perchlorate anions do not participate in the redox reaction of the polymer, others, such as PBD, show that even when the in-

sertion of protons is the dominant process during the reduction scan, during the positive direction not only protons but also perchlorate anions are exchanged between the solution and the polymer. By EIS it was observed that electron and ion coefficient values increase as the concentration of perchlorate anions increases.

With regard to the film thickness effect on the charge conduction process of POAP, it was observed that thin films exhibit a lower conductivity as compared with thick ones. This effect is clearly reflected in the ion and electron diffusion coefficient values extracted from EIS. Both parameters increase as the film thickness increases. This effect of the film thickness on the conduction properties was explained in terms of a polymer structure that changes when the film thickness increases. In this connection, while thin films are continuous, compact and non-porous, thick films are porous and more permeable to external electrolyte solution. Thus, electrolyte incorporated into a thick film should give rise to a higher rate of the charge-transport process as compared with that in a thin film.

The redox mediation of POAP on different redox couples in solution was analyzed by employing Cyclic Voltammetry and Rotating Disc Electrode Voltammetry. In some cases cathodic limiting currents, which are independent of the concentration of the redox couple in solution, are observed but they depend on the polymer film thickness. This was considered as an indication of current control by charge transfer across the polymer film. Conversely, in other cases limiting currents independent of the polymer thickness but dependent on the redox substrate concentration in solution were observed. In this latter case limiting currents must be controlled by the kinetics of the electron transfer at the polymer/solution interface. Anodic currents corresponding to oxidation of redox species that penetrate through POAP films to reach the metal surface were also observed. These anodic currents were employed to calculate physical diffusion rates of redox species across POAP films. It was observed that the electron transport through POAP is slower than the physical diffusion of redox species into the polymer. However, the physical diffusion rate of some redox active species across POAP films is comparable with the transport rate of electroinactive ions (perchlorate) into the polymer. The conducting potential range of POAP was analysed in the presence of redox active species. Some authors indicate that positive species that are reduced at potentials lower than the formal potential of POAP could not be reduced above such potential, with the exception of protons. However, species that have formal potential values more positive than the formal potential of POAP could be oxidised easily. Thus, it was concluded that the polymer is conductive in the oxidised state and non-conductive in the reduced one. Other authors have demonstrated that POAP is conductive at negative potentials. In this connection, it was reported that the conductivity of POAP as a function of potential increases sharply at approximately -0.067 V (SCE), peaks at approximately -0.120 V (SCE) and starts to decrease at more negative potential values.

With regard to the stability POAP film electrodes, they maintain their voltammetric response, at least for a day, provided that the positive potential limit does not exceed 0.5 V (SCE). However, after continuous cycling during several

days, the polymer starts to show the characteristics of degradation. Also, if a freshly prepared film is subjected to a positive potential limit beyond 0.5 V (SCE), the voltammetric response, and more clearly the impedance response, shows a decrease in the film conductivity.

### 5. SOME CRITICAL VIEWPOINTS ABOUT CHARGE TRANSPORT PARAMETER VALUES OF POLY(O-AMINOPHENOL) FILM ELECTRODES

It is evident that application of electrochemical models to interpret experimental results in the field of electroactive polymers is often complicated by concurrent difficulties that are not only theoretical but also experimental. In this connection, most of the impedance models employed to obtain transport parameters of POAP films assume the existence of a homogeneous (uniform) polymer layer on a smooth electrode surface. However, from the theory of porous electrodes and relevant electrochemical studies, it is known that their impedance behaviour differs from that of electrodes with a smooth surface. In some papers as in [36,37,45,47,55] a thin gold film deposited under high vacuum conditions ( $10^{-7}$  Torr) was employed as base metal to deposit POAP films. In this way it was expected to reduce, at atomic scale, surface defects of the base electrode. On studying "size effects" [35] on thin gold films employed in [36,37,45,47,55] a value of the specular parameter,  $p \sim 0.91$ , was estimated. The  $p$  value correlates with the roughness of the metal surface topography and the presence of surface defects. More precisely, this parameter represents the probability of an electron being reflected specularly or diffusely (due to the presence of defects) at the metal film surface. The  $p$  value ranges from 0, for complete diffuse scattering, to 1 for complete specular scattering. Thus, imperfections should lead to experimental  $p$  values much lower than 1. In this connection,  $p$  values of gold films employed in [36,37,45,47,55] are high enough ( $p \sim 0.91$ ) to assume a low amount of surface defects on an atomic scale, as compared with the surface of a bulk electrode mechanically polished to deposit the polymer film. With regard to the structure of the polymer layer, in [36,37] it was proved that when a  $2.8 \text{ mC cm}^{-2}$  thick POAP film covers a metal surface, ions from the electrolyte solution do not interact with the metal electrode, which should be indicative of the existence of a relatively compact polymer layer on the metal surface. Then, some papers as in [55], where a thin gold film deposited by vacuum evaporation was employed as base electrode to deposit a thick POAP film on it, seem to justify the application of a homogeneous electrochemical impedance model to interpret experimental impedance diagrams. However, the thickness of the polymer film is always a critical parameter. In general, thickness is estimated from the charge consumed in reducing the polymer film [14]. In some papers, the films were grown to approximately the desired thickness by employing a reduction charge *versus* ellipsometric thickness working curve [11]. In this connection, it was indicated that voltammetric responses of POAP result from two different processes. The former corresponds to a background film conduction, similar to that observed for the base electrode (unmodified electrode), while the latter is determined by the proper redox process of the film. Charge values corresponding to these different contributions are not always easy to separate in order to estimate film thickness values. It was suggested that the background conductance of

the films most likely results from some residual charge in their bulk and their porosity.

There is evidence about the dependence of transport parameters of POAP on both film thickness and concentration of the external electrolyte solution [19]. This effect was explained considering that the polymer structure changes as the film thickness increases. In this regard, while thick POAP films seem to exhibit open structures that allow incorporation of the electrolyte into the polymer layer, thin films are compact enough to prevent the electrolyte incorporation [19]. In this regard, the high permeability of some polymer films to transport redox species from the solution in contact with the polymer to the metal substrate was attributed to dispersed polymer structures with imperfections (*e.g.* pinholes and large channels) with large dimensions compared to those of species present in solution [53]. This effect should be taken into account when mechanism diagnosis criteria from steady-state polarisation curves for redox mediation at electroactive polymer-coated electrodes are considered, because redox species in solution could reach the metal surface by transport through pores in the polymer layer.

Complex impedance is one of the major techniques for the experimental study of electroactive polymer films. However, it should be taken into account that the estimation of transport parameters values of POAP, such as diffusion coefficient values,  $D$ , is often hardly possible on the basis of impedance spectra, because of the absence of a well-defined Warburg region for this polymer. In this connection,  $D$  values were obtained with an error of 50% [14]. Besides, in some papers it is indicated that impedance measurements cannot be performed for frequencies lower than 0.1 Hz due to the noise fluctuations observed in this frequency region. In this regard, it was indicated that the estimated error in the values of the low-frequency resistance obtained from impedance spectra was around 30 % because of the overlap of the charge-transfer and the diffusion-controlled regions. The observed peculiarities at low-frequency impedance of POAP films were attributed to porosity effects [8].

With regard to impedance models, the general theory of *ac* impedance described by Vorotyntsev [56] was applied in [55] to interpret experimental impedance spectra of POAP in the presence of active redox species in solution. However, this theory was developed within the framework of the assumption that the redox active species is only present in the solution phase but not inside the polymer film, and they participate in the interfacial electron exchange with the polymer at the film|solution boundary. However, it should be taken into account that this theory is strictly valid when charging of the interfacial double layers is negligible, that is, the theory does not account for charging the film|substrate and the film|solution layers in parallel with the process of injection of charge carriers. If this is not the case, a more complete model such as that developed by Vorotyntsev in [57] should be used. In [57], besides the traditional "double layer" capacitance and interfacial charge transfer resistances, two additional parameters for each boundary, "interfacial numbers" for each species and "asymmetry factors", are introduced. However, it should be indicated that even when the authors of [55] attempted to fit experimental impedance spectra by means of the *ac* impedance model presented in [57], the fitting was not much more precise than that ob-

tained by applying the theory given in [56]. Furthermore, the increasing mathematical difficulty of determining the numerous parameters of the model given in [57] from experimental data was remarked. Also, from the physical viewpoint, in some cases diffusion or incorporation of different species into polymer films could alter the molecular structure of the polymeric film, and then, its physical properties. Thus, application of models in these cases should only allow obtaining fitting parameters that do not represent the real physical properties of the system. Even when different authors do not expect a complete coincidence of the electrochemical properties of the polymer film with those predicted by theoretical models, qualitative agreements are often considered satisfactory enough to obtain information about electroactive polymers.

## 6. POLY(O-AMINOPHENOL) AS MATERIAL TO BUILD ELECTROCHEMICAL SENSORS. INFLUENCE OF CHARGE TRANSPORT AND PERMEATION PROCESSES ACROSS POAP FILMS ON THE OPERATING CHARACTERISTICS OF SENSORS

POAP has been used to build different electrochemical sensors. However, in the optimisation of an electrochemical sensor it is important to understand the factors that affect its operating potential, response time, stability, etc. These factors are often determined by the charge conduction process and permeability of the polymer. However, in some cases the stability conditions of other substances incorporated into the sensor also affect its operating characteristics.

In [58] the authors reported the construction and characterisation of a horseradish peroxidase (HRP)-ferrocene-modified carbon paste biosensor, using electrochemically generated POAP films, for the determination of hydrogen peroxide. It was observed that the maximal response (cathodic current) of the sensor was about an operating potential of 0.0 V (*versus* Ag/AgCl). At potential values more negative than -100 mV and more positive than 100 mV, a rapid loss of activity was observed. Also, with regard to the stability of the sensor with storage at room temperature, a *pH* 5 was proved to be optimum because the linear dynamic range remains constant during this period. However, a *pH* 8 was chosen to improve sensitivity during measurements due to the optimum *pH* value of stability of HRP (*pH* 7-8).

With regard to permeability of POAP, experimental conditions related to the preparation and characterisation of an amperometric glucose biosensor based in the immobilisation of glucose oxidase (Gox) in an electrochemically polymerised non-conducting POAP film at a Prussian Blue-modified Pt microelectrode were described in [59]. While Prussian Blue acts as a typical electroactive film that exhibits catalytic properties for H<sub>2</sub>O<sub>2</sub> oxidation, the POAP film functions as a typical non-conducting film acting as an affective barrier to protect the electrode from fouling. Then, the effect of interferences can be decreased significantly due to selective permeability of POAP. The effect of *pH* of the detection solution on the response behaviour of the Prussian Blue/POAP/Gox sensor was also investigated. The maximum of the response current was observed at *pH* 7. This was explained on the basis of the entrapment of Gox in the POAP

film at a PB-modified electrode, making Gox more active at neutral media.

A reagentless uric acid selective biosensor constructed by immobilising uricase and horseradish peroxidase (HRP) in carbon paste, where POAP was deposited at the working surface, was reported in [60]. POAP acts as a conducting polymer layer in this sensor. CV was used to characterise the permselective characteristics of the POAP layer. At an applied potential of 50 mV (*versus* Ag/AgCl) a linear response was obtained up to  $1 \times 10^{-4}$  M with a limit of detection of  $3 \times 10^{-6}$  M. It was observed that the responses to the analyte of interest were *pH* dependent.

An amperometric glucose biosensor based on boron-doped carbon nanotubes (BCNT) and POAP films was reported in [61]. Glucose oxidase (GOx) was employed as the model enzyme and it was immobilised on the BCNT-modified glassy carbon electrode (GC/BCNT) by electrochemical co-polymerisation of GOx and *o*-aminophenol. The impedance spectra of GC/BCNT, GC/BCNT/POAP and GC/BCNT/POAP/GOx electrodes were recorded in the presence of Fe(CN)<sub>6</sub><sup>3-</sup>/Fe(CN)<sub>6</sub><sup>4-</sup> solutions. While a small semicircle followed by a straight line was observed in the case of the GC/BCNT electrode, semicircles of large diameters were observed in the case of GC/BCNT/POAP and GC/BCNT/POAP/GOx electrodes. However, the diameter corresponding to the latter electrode was much larger than that corresponding to the GC/BCNT/POAP electrode. The higher electron-transfer resistance at the GC/BCNT/POAP/GOx electrode was attributed to the entrapment of GOx in the POAP film because GOx is non-conductive.

In [62] the authors reported the fabrication and characterisation of a glucose sensor based on a polypyrrole-platinum composite-modified glassy carbon electrode, which was covered by a layer of POAP-glucose oxidase film (POAP-GOx/PPy-Pt/GCE). In order to obtain a large response current and short-time response, an operational potential of 0.6 V (SCE) was employed. Also, it was observed that the current increased from *pH* 4.5 to 7.0, whereas it decreased sharply above *pH* 7. Despite better conduction characteristics of POAP at low *pH* values, *pH* 7 was chosen due to the better activity of GOx in neutral solutions.

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