

# An Impedance Study about the Effect of *pH* on the Electron Transport Rate at Poly(*o*-aminophenol) Film Electrodes

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**Abstract:** Impedance measurements on poly(*o*-aminophenol) (POAP) film electrodes in contact with solutions of different *pH* were carried out. Impedance spectra were interpreted in terms of the modified electron hopping model described in F.J. Rodríguez Nieto, R. Tucceri, J. Electroanal. Chem., 416(1996), 1. An increase of the metal/POAP interfacial resistance with the increase of *pH* was obtained. With regard to the bulk charge-transport process, a decrease of the electron diffusion coefficient with the increase of *pH* was extracted from the fitting procedure. The change of the charge-transport and charge-transfer parameters with the increase of *pH* was attributed to an increase in electron hopping distance between adjacent redox sites at POAP films. Impedance results seem to be in agreement with potentiodynamic surface resistance measurements carried out in R. Tucceri, J. Electroanal. Chem., 543(2003), 61-71.

**Keywords:** Electron diffusion coefficient, *pH* effect, Poly(*o*-aminophenol)film electrodes, redox site distribution.

## 1. INTRODUCTION

The current interest in poly(*o*-aminophenol) (POAP) is well documented by the growing literature data, recently reviewed [1]. POAP shows the peculiarity of having properties depending on the *pH*, showing either conducting or passivating behaviours if synthesized in acidic and neutral/basic media, respectively. Accordingly, possible applications of such a material range from electrocatalyst, cation capturing film, up to being a permselective layer to use as amperometric biosensors [2].

POAP synthesized in acidic medium exhibits a one-step redox process [3]. Parameters characterizing the charge transfer and charge transport processes at POAP films, and their dependence on the external electrolyte contacting the polymer, have been estimated using different techniques [4-8]. In both practical applications and active research on thermodynamic and kinetic properties of POAP synthesized in acid medium, the redox process of the polymer and its dependence on the external solution *pH* play an important role because at *pH* values higher than 4, the polymer becomes nonelectroactive [9]. It is well-known that in POAP a redox mechanism operates involving addition/elimination of protons coupled to a reversible one-electron transfer process at the metal/polymer interface [7]. Thus, the decrease of the proton concentration makes the redox process more difficult and this is reflected in the interfacial resistance response of a POAP-coated gold film electrode [10]. As the surface resistance changes on metal film surfaces not only depend on the number of scattering centres but also on their distribution over the surface, it was concluded in [10] that the compactness of the redox site

distribution of a POAP film deposited on a gold film surface decreases as the *pH* increases. The objective of the present work is to confirm the information obtained previously by means of the surface resistance technique with respect to a change in the redox site distribution at a POAP film as the solution *pH* increases [10], by employing an alternative technique, that is, Electrochemical Impedance Spectroscopy (EIS).

## 2. EXPERIMENTAL

The experimental arrangement employed to perform EIS experiments is one in which a POAP film is supported on a rectangular thin gold film. Eight gold thin film electrodes of constant thickness  $\phi_m \sim 30$  nm are prepared by vacuum evaporation as was previously described [11]. The electrode area was 1 cm<sup>2</sup>. POAP films were grown on these base electrodes following the procedure described in [3,9]. That is, polymer films were obtained by immersing the base electrodes in a 10<sup>-3</sup> M *ortho*aminophenol + 0.4 M NaClO<sub>4</sub> + 0.1 M HClO<sub>4</sub> solution and cycling the potential between -0.25 and 0.8 V (*versus* SCE) at a scan rate  $\nu = 0.05$  V s<sup>-1</sup>. POAP films were grown up to an approximate thickness of  $\phi_p \sim 60$  nm by using a reduction charge ( $Q_{Red,T} = 2.8$  mC cm<sup>-2</sup>) *versus* the ellipsometric thickness working curve [12]. Each one of the eight POAP-coated gold film electrodes was then rinsed and transferred to a supporting electrolyte solution (NaClO<sub>4</sub> + HClO<sub>4</sub>) of different *pH* between 1 and 6.5 (Table 1). A large-area gold grid was used as counterelectrode. All the potentials reported in this work are referred to the Saturated Calomel Electrode (SCE).

Impedance spectra for each one of the POAP-coated gold film electrodes in contact with NaClO<sub>4</sub> + HClO<sub>4</sub> solutions of different *pH* were obtained in the frequency range 0.01 Hz and 10 kHz by following a 30-min application of the steady-state potential value of  $E = -0.3$  V (reduced state of POAP).

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**Table 1. Standard electrochemical rate constant and diffusion coefficient values at different pH extracted from the impedance model given in [14].**

<sup>a</sup> pH	<sup>b</sup> 10 <sup>5</sup> <i>k</i> <sub>sh</sub> /cm s <sup>-1</sup>	<sup>c</sup> 10 <sup>10</sup> <i>D</i> <sub>e</sub> /cm <sup>2</sup> s <sup>-1</sup>
1	13.6	2.23
2.4	4.11	1.64
3.01	3.14	1.35
3.7	2.16	0.84
4.02	1.03	0.54
5.03	1.63	0.41
6.02	0.81	0.34
6.5	0.77	0.29

<sup>a</sup>pH values; <sup>b</sup>Values of the standard electrochemical rate constant, *k*<sub>sh</sub> and diffusion coefficient values.

The solution *pH* was varied between 1 and 6.5 while the ionic strength remained constant at 0.5 M. The *pH* of the solution was measured “in situ” with a glass electrode. Impedance values were determined at seven discrete frequencies per decade with a signal amplitude of 5 mV. The validation of the impedance spectra was done by using Kramers-Kronig transformations [13].

Impedance measurements were performed with a PAR 309 system. Analyte reagent grade chemicals were used throughout. *O*-aminophenol (Fluka) was purified as described elsewhere [3,9]. HClO<sub>4</sub> and NaClO<sub>4</sub> (Merck) were used without further purification. The solutions were prepared with water purified using a Millipore Milli-Q system, *i.e.* RODI water.

### 3. RESULTS AND DISCUSSION

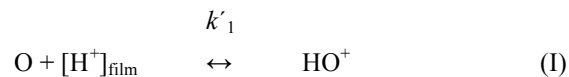
Dynamic voltammetric and Surface Resistance (SR) responses of POAP films in solution of different *pH* are shown in Figs. (10 and 11), respectively, of Ref. [10]. Starting at a potential value of 0.5 V towards the negative potential direction, that is, going from the reduced to the oxidized state of POAP, an attenuation of the surface resistance response with the increase of the solution *pH* was observed (see Fig. 11 in [10]). This effect was explained in terms of the lower number of reduced sites formed as the *pH* increases, which leads to distributions of redox sites with mutual distances between them that are larger as higher is the *pH* of the external solution. That is, reduced sites at the gold/POAP interface should form progressively less compact distributions on the gold film surface as *pH* increases [10].

The electron diffusion coefficient, *D*<sub>e</sub>, in electroactive materials has been expressed in terms of the mean distance between adjacent active redox sites [14], according to *D*<sub>e</sub> = (*a*<sup>2</sup>*k*<sub>o</sub>), where *k*<sub>o</sub> is the intermolecular electron-transfer rate constant and *a* is the mean distance between two adjacent redox sites. The hopping rate, *k*<sub>o</sub>, exhibits an exponential dependence on *a*, through the energy  $-U(x+a)$  of a state with an electron in the position *x* along the current direction (see eq. (23) in Ref. [14]). In this respect, a *k*<sub>o</sub> decrease should be

expected as the hopping distance *a* increases. Then, as the hopping distance should be related to the mean distance between redox sites, and it was demonstrated from Surface Resistance measurements that the mutual distances between redox sites increase as the solution *pH* increases, then, a decrease in the electron diffusion coefficient should be expected with increasing the solution *pH*. The aim of the present work is to obtain the change of the electron transport rate at POAP films as function of the solution *pH* employing EIS.

Nyquist diagrams [15] at the reduced state (*E* = -0.3 V) for POAP films at different solution *pH* values are shown in Fig. (1) (discrete points). The early increase in the imaginary component of the impedance and the absence of any semicircle at high frequency for a POAP film at pH 1 are indicative of a fast interfacial charge-transfer process (plot (a) in Fig. 1). However, a well-defined high-frequency semicircle is observed in the impedance diagrams of POAP films in contact with solutions of *pH* values higher than 1. As the *pH* increases the high-frequency semicircle is more pronounced. The increase in the size of the high-frequency semicircle in Nyquist plots is indicative of a restriction in the charge-propagation process across the gold/POAP/solution system.

We employ a modified electron hopping model developed by us in [16] to interpret impedance spectra at different *pH* values. The model given in [16] considers a protonation reaction (Reaction (I) see below) coupled with a self-exchange process between oxidized and reduced sites (Reaction II, see below)



where  $[H^+]_{\text{film}}$  is the proton concentration inside the film, O is the nonprotonated oxidized form of the polymer, HO<sup>+</sup> and RH are the protonated oxidized and reduced forms of the polymer, respectively, *k*<sub>1</sub> and *k*<sub>-1</sub> are the rate constants involved in chemical step (I) and *k*<sub>f</sub> and *k*<sub>b</sub> are the forward and backward electrochemical rate constants involved in step (II), respectively. Other chemical equilibria following the self-exchange (II) were ignored in [16].

The analytical expression for the impedance derived in [16] is

$$Z(\omega) = R_{Qt} + (RT/nF^2Ac) [k_f + k_b (K+1)/K] A(\omega, D_e, k) \quad (1)$$

where *R*<sub>Qt</sub> is a charge-transfer resistance (see Eq. (32) in [16]), which is given by the expression

$$R_{Qt} = (RT/nF^2Ac) [(k_f + k_b) (k_f k_b)^{-1} + 1/K k_f] \quad (2)$$

where *A* is the electrode area, *c* the volumetric redox site concentration, and *K* an equilibrium constant that can be explicitly written in terms of the solution *pH* as

$$K = (k'_1/k'_{-1}) K_p 10^{-pH} \quad (3)$$

As can be seen from Eq. (3),  $K$  also depends on the  $k'_{-1}$  and  $k'_{-1}$  constants involved in step (I) and a partition coefficient  $K_p$ , which determines the ratio between the proton concentration inside the film ( $[H^+]_{\text{film}}$ ) and the actual proton concentration in solution ( $[H^+]_{\text{sol}}$ ), i.e.,

$$[H^+]_{\text{film}} = K_p [H^+]_{\text{sol}} \quad (4)$$

In Eq. (1),  $A(\omega, D_e, k)$  is a function of the frequency,  $\omega$ , which also contains an effective diffusion coefficient ( $D_e$ ) to describe the charge-transport process within the polymer film and the constant  $k = k'_{-1} + [H^+]_{\text{film}} k'_{-1}$  (see Eq. (33) in Ref. [16]). Concerning step (II), the electroactive centres  $OH^+$  and  $RH$  can exchange electrons with the electrode at the metal/polymer interface following a Butler-Volmer kinetics, with  $k_f$  and  $k_b$  given by the expressions

$$k_f = k_{\text{sh}} \exp [b_f (E - E^0)] \quad (5)$$

$$k_b = k_{\text{sh}} \exp [-b_b (E - E^0)] \quad (6)$$

In Eqs (5) and (6),  $E^0$  is the standard potential of the redox couple,  $b_f$  and  $b_b$  are the Tafel coefficients,  $b_f = \alpha nF/RT$  and  $b_b = (1-\alpha) nF/RT$ , and  $k_{\text{sh}}$  is the electrochemical standard rate constant. The Tafel coefficients are expressed in terms of the number of exchanged electrons during the redox process of the polymer,  $n$ , the gas constant,  $R$ , the absolute temperature,  $T$  and the transfer number,  $\alpha$ .

The redox centres are uniformly distributed throughout the polymer with a total concentration,  $c$ , given by

$$c = [O] + [HO^+] + [RH] \quad (7)$$

Eq. (1) was employed to fit experimental impedance diagrams of POAP films in the presence of the supporting electrolyte solution of different  $pH$  values. As the solution  $pH$  affects the redox process at POAP films, then, an effect of this variable on the charge-transfer process at the metal/polymer interface ( $R_{Qt}$ ) and the electron conduction process ( $D_e$ ) within the polymer film should be expected.

Solid lines on the Nyquist plots shown in Fig. (1) are simulated curves calculated by using Eq. (1). A good fitting was observed for all impedance diagrams. The fitting procedure by using Eq. (1) was based on the CNLS (Complex Nonlinear Squares) method [17]. A rigorous fitting procedure was performed where the error structure was assessed following the reference [18]. Solid lines in Fig. (1) represent the weighted complex nonlinear least-squares fit to the data. Real and imaginary parts versus frequency plots corresponding to each one of the Nyquist representations were also built. One of these representations is shown in Fig. (2).

In the simulations the following parameter values were considered as known and constants: number of transferred electrons,  $n$  ( $= 0.44$  [8]); polymer thickness,  $\phi_p$  ( $= 60$  nm [12]); total redox site concentration,  $c$  ( $= 4.7 \times 10^{-3}$  mol  $\text{cm}^{-3}$  [8]);  $E^0$  ( $= 0.015$  V versus SCE [8]).  $K$  ( $= 0.085$ ) and  $k$  ( $= 0.18$   $\text{s}^{-1}$ ) values at  $pH$  1 were taken from [16] and considered as reference values in the fitting. Then,  $k_{\text{sh}}$  and  $D_e$ , were calculated from experimental impedance data by the fitting procedure described above. A contribution of the interfacial capacitance,  $C_{\text{H}}$ , considered as a fitting parameter, was included in order to represent the actual impedance diagrams from the calculated ones. Values of  $k_{\text{sh}}$  and  $D_e$ , extracted from the fitting procedure are listed in Table 1.

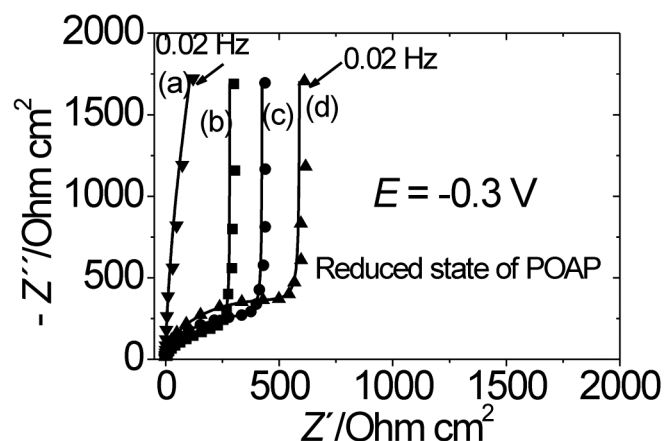


Fig. (1). Nyquist diagrams for POAP films in contact with solutions of different  $pH$  values: (a)  $pH$  1; (b)  $pH$  2.4; (c)  $pH$  3.7; and (d)  $pH$  4.02, respectively.  $E = -0.3$  V. Discrete points are experimental data and continuous lines represent the fitting by using de model described in [14]. Electrolyte:  $\text{HClO}_4 + \text{NaClO}_4$ . Thickness of the POAP film: 60 nm.

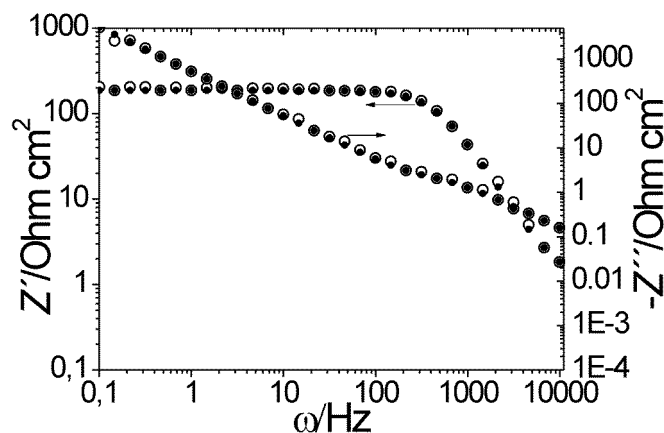


Fig. (2). Real part ( $Z'$ ) and imaginary part ( $-Z''$ ) versus frequency ( $\omega$ ) plots (point to point representations) for a POAP film at  $pH$  1.  $E = -0.3$  V. Electrolyte: 0.1 M  $\text{HClO}_4 + 0.4$  M  $\text{NaClO}_4$ . POAP film thickness: 60 nm. (O) Experimental data; (●) the fitting employing Eq. (1).

Dependences of the gold/POAP interfacial resistance ( $R_{Qt}$ ) calculated from the electrochemical standard rate constant ( $k_{\text{sh}}$ ) values and the electron diffusion coefficient ( $D_e$ ), on the solution  $pH$  are shown in Figs. (3 and 4), respectively. As can be seen from Figs. (3 and 4), while the metal/polymer interfacial resistance increases,  $D_e$  decreases as the solution  $pH$  increases. Low values of  $k_{\text{sh}}$  (high  $R_{Qt}$  values) are indicative of a restriction in the charge-transfer process at the POAP/gold interface. However, a high  $k_{\text{sh}}$  value, such as that obtained from impedance spectra at  $pH$  1 corresponds to a rapid electron-transfer rate across the metal/POAP interface (plot (a) in Fig. 1).

Although electron hopping is believed to be the mechanism for electron transport at polymer materials, it is also possible that ion motions may partially or totally control

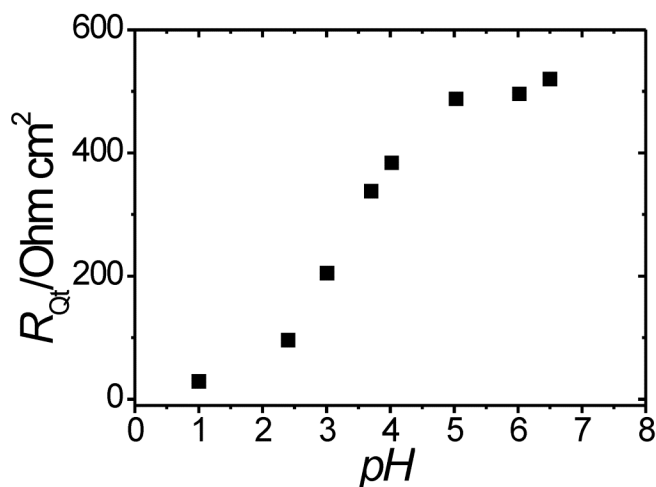


Fig. (3).  $R_{Qt}$  versus pH dependence extracted employing the model described in [14].

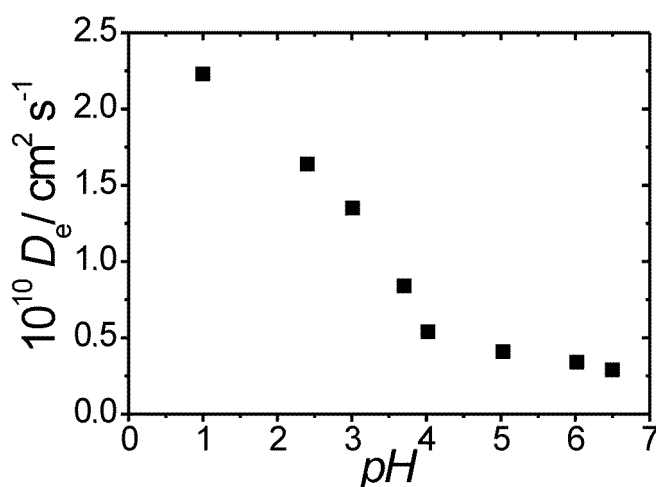


Fig. (4). Electron diffusion coefficient  $D_e$  as a function of pH extracted from the impedance model described in [14].

the rate of charge transport. Then,  $D_e$  obtained with the model derived in [16] (Fig. 4) can be considered as an effective or binary diffusion coefficient value. It should be taken into account that  $D_e$  values obtained in this work correspond to the reduced state of POAP. Electron diffusion coefficient values of the same order were obtained for POAP employing the transmission line model to interpret impedance diagrams [19]. Then, the  $D_e$  decrease can be interpreted in terms as an increase in the electron hopping distance in the redox sites distribution of a POAP film as the solution pH increases. This finding seems to be consistent with the attenuation of the dynamic resistance response at the reduced state of POAP with the increase of the solution pH reported in [10].

#### 4. CONCLUSION

The impedance model [16] used in this work considers a protonation reaction coupled with a self-exchange process between oxidized and reduced sites and then, it seems to be

adequate to explain the dependence of the electrochemical response of poly(o-aminophenol) film electrodes with the solution pH. Conduction parameter values obtained for poly(o-aminophenol) in this work are of the same order of magnitude than those obtained employing traditional models such as the transmission line model [17]. Also, impedance results obtained employing the model described in [16] are consistent with those obtained employing potentiodynamic resistance measurements [10]. In this regard, the decrease of the electron transport rate as the solution pH increases was attributed to an inhibition of the protonation reaction that creates inactive gaps within the redox sites distribution of the polymer. Inactive gaps should cause an increase in the electron hopping distance between adjacent redox sites, which in turn leads to a decrease in the electron diffusion value. More spread redox site configurations with the increase of the solution pH were also invoked to explain the increase in the potentiodynamic interfacial metal/poly(o-aminophenol) film resistance [10]. The modified electron-hopping model used in this work can be employed to monitor bulk and interfacial transport parameters changes of a polymer with the solution pH. In this regard, more work in progress in order to apply the model to other electroactive polymers such as polyaniline, whose electrochemical response also depends on the external solution pH.

#### CONFLICT OF INTEREST

The author(s) confirm that this article content has no conflict of interest.

#### ACKNOWLEDGEMENTS

The author gratefully acknowledges the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) and also the Facultad de Ciencias Exactas, National University of La Plata (UNLP).

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