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## POLY (O-AMINOPHENOL) A POLYMER EMPLOYED AS MATERIAL OF BIOSENSORS. ITS DEACTIVATION. A REVIEW ARTICLE

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### ABSTRACT

Electrochemical and chemical treatments, such as, storage time without use (STWU), prolonged potential cycling (PPC), high positive potential limits (HPPL) and soaking in a ferric ion solution (SFeIS), affect the conduction properties of poly (o-aminophenol) (POAP). The effect of these treatments on the conducting properties of POAP was studied employing cyclic voltammetry (CV), rotating disc electrode voltammetry (RDEV), electrochemical impedance spectroscopy (EIS) and surface resistance (SR). A review of these studies is presented in this work.

### KEYWORDS

Poly (o-aminophenol) film electrodes, Deactivation, Storage time without use, Prolonged potential cycling, High positive potential limits and Soaking in a ferric ion solution.

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### INTRODUCTION

*Ortho*-aminophenol (*O*-AP) can be polymerized electrochemically in acidic, neutral and alkaline solutions to produce poly (*o*-aminophenol) (POAP)<sup>1,2,3</sup>. While a conducting film is only formed in acidic media, POAP synthesized in neutral and alkaline media leads to a nonconducting film<sup>4</sup>. The properties of POAP synthesized in basic medium are favorable to applications in the field of bioelectrochemistry and electrocatalysis<sup>5</sup>. The charge-transport process at POAP films synthesized in acid medium was mainly studied from the basic research viewpoint employing different electrochemical techniques<sup>1,3,6,7</sup>. POAP synthesized in acidic medium is also found to be a useful material to

build electrochemical sensors and electrocatalysts<sup>8-11</sup>. It is often indicated that POAP films have good properties in terms of conductivity and ion-permeability and also that they present good durability and long-term stability under different electrochemical conditions (*i.e.*, storage and potential cycling during several weeks). The aim of the present work was show that charge-transport and charge-transfer parameters of POAP change with storage without use for prolonged time periods, prolonged potential cycling (PPC), application of high positive potential limits (HPPL) and soaking in a ferric ion solution (SFeIS). Different techniques were employed in these studies. RDEV data were analyzed in terms of a spreading of the POAP redox site configuration as the polymer gradually becomes deactivated. Impedance diagrams of POAP films after deactivation were interpreted by employing two theoretical models: the first was used to obtain transport parameters when POAP contacts an electro active solution and the second one was employed to analyze the impedance behavior of POAP films in the sole presence of the supporting electrolyte solution. Interfacial resistance (SR) measurements were also performed<sup>12,13</sup>. SR measurements demonstrate the existence of different distributions of redox sites at deactivated POAP film electrodes as compared with nondeactivated ones. Changes of the redox site configuration after POAP deactivation monitored by SR were associated to changes of the charge-transfer and charge-transport parameters obtained by employing RDEV and EIE. Besides, charge-transfer and charge-transport parameters obtained after POAP deactivation by STWU, prolonged electrode potential cycling (PPC)<sup>14</sup>, application of high positive potentials limits (HPPL)<sup>15</sup> and soaking a ferric ion solution (SFeIS)<sup>16,17</sup> are compared. It is expected that the present work will shed light on the limits of stability and durability of POAP, particularly when it is proposed as material to develop sensors and electro catalysts.

## MATERIAL AND METHODS

### The electrochemical techniques employed to study POAP deactivation

A gold rotating disc electrode (RDE) was used as base electrode to deposit POAP films<sup>1,2</sup>. In order to obtain a more specular gold surface to deposit POAP films, a gold film about 50 nm in thickness was deposited by vacuum evaporation<sup>12</sup> ( $\sim 10^{-7}$  Torr) on the gold disc. POAP films were grown up to an approximate thickness of  $\phi_p \sim 60$  nm by using a reduction charge *versus* the ellipsometric thickness working curve<sup>6,18</sup>. A typical voltammetric response of these films is shown in Figure No.1 (plot (a)). The POAP films maintain this response on potential cycling within the potential range  $-0.2 \text{ V} < E < 0.5 \text{ V}$  up to 500 cycles. These POAP films are herein called non-deactivated films. A large-area gold grid was used as counter electrode. All the potentials reported in this work are referred to the SCE. Different POAP-coated RDE was prepared and deactivated by employing the different electrochemical treatments above indicated (see for instance first column in Table No.1 for deactivation by STWU). Each POAP film was stored without use in a deoxygenated supporting electrolyte solution for a given time period (see second column in Table No.1) and then, it was cycled within the potential region  $-0.2 < E < 0.5 \text{ V}$  to obtain a stable voltammetric response. Then, the corresponding *j-E* responses for each one of the eight POAP films were compared. An attenuation of the voltammetric response was observed (Figure No.1). These POAP films are herein called deactivated films. Then, with both nondeactivated and deactivated by storage POAP films, RDEV and *ac* impedance experiments were performed in the presence of a solution containing equimolar concentrations of *p*-benzoquinone (Q) and hydroquinone (HQ) species ( $0.1 \text{ M HClO}_4 + 0.4 \text{ M NaClO}_4 + 2 \times 10^{-3} \text{ M Q/HQ}$ ). Stationary current-potential curves (*I-E*) at different electrode rotation rates,  $\Omega$ , were recorded. From these curves, cathodic and anodic limiting current *versus* electrode rotation rate ( $I_{\text{lim}}$  *versus*  $\Omega^{1/2}$ ) dependences were obtained. Also, with nondeactivated and deactivated POAP films, *ac*

impedance diagrams at the cathodic current plateaux were obtained for different electrode rotation rates. Impedance spectra of nondeactivated and deactivated POAP-coated electrodes in the sole presence of the supporting electrolyte solution (0.4 M NaClO<sub>4</sub> + 0.1 M HClO<sub>4</sub>) solution were also recorded.

The experimental arrangement employed to perform surface resistance (SR) 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 were prepared by vacuum evaporation as was previously described<sup>12</sup>. All these electrodes exhibit initial resistance ( $R$ ) values of about 20.02 ohm. The electrode area was 1 cm<sup>2</sup>. POAP films of 60 nm were grown on these base electrodes following the procedure previously described. Also, different POAP-coated gold film electrodes (eight) were prepared for SR measurements and each one of them was stored without use in a deoxygenated supporting electrolyte solution for the time periods indicated in Table No.1. Then, the corresponding  $j$ - $E$  and  $\Delta R/R$ - $E$  responses for each one of the eight POAP films were recorded. The experimental setup for simultaneous voltammetric and SR measurements on thin film electrodes has previously been described in detail elsewhere<sup>12,19</sup>.

In the other deactivation procedures, PPC, HPPL, and SFeIS, POAP films were respectively, cycled within the potential region  $-0.2 \text{ V} < E < 0.5 \text{ V}$  (SCE), subjected to electrode potential limits beyond 0.5 V (SCE) and soaked in a ferricitation solution for different time periods as indicated in Table No.1.

## RESULTS AND DISCUSSION

### Voltammetric responses of nondeactivated and deactivated POAP films

The voltammetric response corresponding to a non deactivated POAP film within the potential range comprised between -0.2 V and 0.5 V is shown in Figure No.1 (plot (a)). With regard to STWU, the voltammetric response of POAP starts to change beyond 30 h. Figure No.1 compares the  $j$ - $E$  responses of a nondeactivated POAP film (plots (a))

with those of the films (1), (2), (4), (5), (6) and (8) (see first column of Table No.1) that were stored without use in the supporting electrolyte for the time periods listed in column 2 of Table No.1. The more attenuated voltammetric response observed in Figure No.1, as the storage time increases allows one to calculate a degree of deactivation,  $\theta_c^d$  on the basis of the different charge values of nondeactivated and deactivated films<sup>17</sup>.

### Rotating disc electrode voltammetry and ac impedance measurements in the presence of an electroactive solution

Nondeactivated and deactivated POAP films in contact with an electroactive solution containing the hydroquinone/*p*-benzoquinone redox couple were studied by employing RDEV and EIE. Steady-state current-potential curves were interpreted on the basis of the traditional electron hopping model<sup>20,21</sup> and impedance spectra were analyzed employing the general theory of *ac* impedance described in previous work<sup>22</sup>, which allows one to obtain electron and ion diffusion coefficients and different interfacial (metal/polymer and polymer/solution) resistances and capacitances of an electroactive material. In previous work<sup>23</sup> RDEV experiments at gold electrodes coated with POAP films were carried out to study the diffusion processes of benzoquinone ( $Q$ ) and hydroquinone ( $HQ$ ) species through nondeactivated films. Diffusion-limited currents at  $E < 0.0 \text{ V}$  for  $Q$  reduction and at  $E > 0.8 \text{ V}$  for  $HQ$  oxidation were observed. While the anodic limiting current corresponds to the oxidation of  $HQ$  species that penetrate through the polymer film to reach the metal surface, cathodic limiting currents for  $Q$  reduction are related to a rapid electron-transfer mediation at the POAP| redox active solution interface, which occurs without significant penetration of  $Q$  into the polymer layer. Figure No.2 shows stationary current-potential curves ( $I$ - $E$ ) at different electrode rotation rates,  $\Omega$ , for a deactivated POAP film contacting a 0.1 M HClO<sub>4</sub> + 0.4 M NaClO<sub>4</sub> +  $2 \times 10^{-3} \text{ M}$  Q/HQ solution. ( $I$ - $E$ ) curves at different  $\Omega$  values were also obtained for each one of the deactivated POAP films indicated in Table No.1. As can be seen from

Figure No.2, after a given electrode rotation rate, which depends on the degree of deactivation, the cathodic limiting current for a deactivated film becomes independent of this variable.  $I_{lim,c}$  versus  $\Omega^{1/2}$  dependences at potential values  $E < 0.0$  V for both nondeactivated and deactivated POAP films are shown in Figure No.3. For a nondeactivated POAP film a linear  $I_{lim,c}$  versus  $\Omega^{1/2}$  dependence, which follows the Levich equation, is obtained within a wide range of  $\Omega$  values (empty circles). However, for POAP films that have been deactivated by storage without use for different time periods, after a certain  $\Omega$  value, a constant cathodic limiting current value,  $I_{lim,c}$ , independent of  $\Omega$  is achieved (black triangles). Also, it is observed that the transition at which the cathodic limiting current becomes independent of  $\Omega$  occurs at lower  $\Omega$  values as the degree of deactivation increases. The explanation of this effect can be given in terms of the electron hopping model<sup>20,21</sup>. Limiting current values at which  $I_{lim,c}$  ( $= I_e$ ) becomes constant were considered as a representation of the maximum flux of electrons confined in the polymer, according to Eq. (2)<sup>21</sup>

$$I_e = n F A D_e c / \phi_p \quad (1)$$

In Eq. (1),  $c$  is the concentration of redox sites of the polymer and  $\phi_p$  the polymer film thickness.  $D_e$  represents a measure of the electron hopping rate and  $n$  expresses the numbers (fractions) of unit charges per monomer unit of the polymer.  $A$  is the electrode area and  $F$  the Faraday's constant. Experimental  $I_e$  values, corresponding to each one of the eight deactivated POAP films contacting a  $2 \times 10^{-3}$  M HQ/Q solution, were extracted from the cathodic plateau and they are listed in Table No.2 (Third column). As can be seen from Table No.2,  $I_e$  (and then  $D_e$  obtained from Eq. (1)) decreases with increasing  $\theta_a$ . By employing the  $I_e$  values shown in Table No.2 and using the parameter values  $c = 4.7$  M<sup>1</sup>,  $A = 1$  cm<sup>2</sup>,  $n = 0.44$ <sup>24</sup> and  $\phi_p = 60$  nm in Eq. (1), one obtains a decrease of  $D_e$  from  $2.00 \times 10^{-11}$  to  $0.5 \times 10^{-11}$  cm<sup>2</sup> s<sup>-1</sup> for a relative increase of  $\theta_c$  from 0.05 to 0.77. As can be seen from the inset in Figure No.3, the electron diffusion rate extracted from RDEV measurements decreases linearly with the

increase of  $\theta_a$ . It is interesting to remark that a constant current  $I_e$  independent of  $\Omega$  is also obtained for a nondeactivated POAP film in contact with a 0.1 M HClO<sub>4</sub> + 0.4 M NaClO<sub>4</sub> +  $2 \times 10^{-3}$  M Q/HQ solution. However, in this case the constant current is obtained at very high electrode rotation rates and HQ/Q concentrations. A constant current  $I_e$  ( $\approx 15$  mA cm<sup>-2</sup>) is observed for a nondeactivated film. Considering the constant current value obtained for high HQ/Q concentrations, a  $D_e$  about  $1.22 \times 10^{-10}$  cm<sup>2</sup> s<sup>-1</sup> is obtained for a nondeactivated POAP film. On the basis of these data one can assess the efficiency of POAP to act as mediator in the 0.1 M HClO<sub>4</sub> + 0.4 M NaClO<sub>4</sub> +  $2 \times 10^{-3}$  M Q/HQ solution. In this regard, one can calculate the ( $I_e/I_o \times 100$ ) ratio, where  $I_e$  are the different constant current values for the different deactivated films (see Table No.2) and  $I_o$  is the current value (3.2 mA cm<sup>-2</sup>) corresponding to the non-deactivated film. In Table No.2, ( $I_e/I_o \times 100$ ) represents the efficiency of POAP to act as mediator in the HQ/Q redox reaction. For a non-deactivated film,  $I_o = I_e = 3.2$  mA cm<sup>-2</sup>, then,  $I_e/I_o = 1$  and ( $I_e/I_o \times 100$ ) = 100, which corresponds to the maximal efficiency. As can be seen from the Table No.2, the efficiency of a POAP film is reduced to about 16 per cent for a storage time without use of 120 h. Nyquist diagrams at different electrode rotation rates for a nondeactivated and of each one of the eight deactivated POAP films at potential values within the range  $-0.30$  V  $< E < 0.0$  V (*versus* SCE) were also recorded<sup>24</sup>. The  $D_e$  decrease can be attributed to a more spread redox site configuration in a deactivated POAP film as compared with a nondeactivated one<sup>25</sup>.

### Interpretation of *ac* impedance data

As was indicated, the general theory of *ac* impedance described by Vorotyntsev *et al.*<sup>22</sup> was employed to interpret experimental impedance data. As in the present case one has the modified electrode geometry with a redox active electrolyte solution (m|film|es), Eq. (41) of the Vorotyntsev model<sup>22</sup> must be applied in this work. Impedance diagrams were simulated with the Vorotyntsev model<sup>22</sup> and then the different impedance quantities

( $R_{m|f}$ ,  $R_i^{fls}$ ,  $R_e^{fls}$ ,  $C_p$ ,  $D_e$  and  $D_i$ ) as a function of the degree of deactivation were extracted.  $R_{m|f}$  is the metal|film interfacial electron-transfer resistance,  $R_i^{fls}$  is the film|solution interfacial ion-transfer resistance,  $R_e^{fls}$  is the interfacial electron-transfer resistance at the film|solution interface,  $D_e$  and  $D_i$  are the diffusion coefficients for the electrons and ion species, respectively and  $C_p$  is the redox capacitance. A good fitting was observed for the different impedance diagrams. The fitting procedure was based on the CNLS (Complex Nonlinear Squares) method<sup>26,27</sup>. The  $D_i$  and  $D_e$  versus  $\theta_d$  dependences are shown in Figure No.4 and 5, respectively. While  $D_e$  decreases almost linearly with the increase of  $\theta_d$ ,  $D_i$  versus  $\theta_d$  exhibits a break at about  $\theta_d = 0.3$ . The break observed in the  $D_i$  versus  $\theta_d$  dependence at about  $\theta_d \sim 0.3$  was also observed in the  $R_i^{fls}$  versus  $\theta_d$  dependence (not shown). The decrease of  $D_e$  with the increase of  $\theta_d$  could be attributed to an increase of the hopping distance between remnant redox active sites after polymer deactivation. Impedance measurements reported in reference<sup>7</sup> indicate that POAP is only doped with hydrogen ions and the effect of anions is negligible. Then, it is possible that both parameters  $R_i^{fls}$  and  $D_i$  are related to proton movements across the POAP|solution interface and inside the polymer film, respectively, rather than to anion transport. Concerning the proton movement into POAP films, the existence of two forms (mobile and bound) of hydrogen ions in the bulk film has been proposed in reference<sup>7</sup>. It was suggested that in polymers derived from aromatic amines, hydrogen ions could be constrained by nitrogen atoms of polymer chains and do not contribute to the electrical conductance of the film, and another part of such constrained groups is able to dissociate producing the mobile form of hydrogen, which provides the film conductance.  $R_{m|f}$  increases almost linearly within the whole  $\theta_d$ . The  $R_e^{fls}$  values are around one order of magnitude lower than  $R_{m|f}$  values. The storage time without use seems to affect more strongly the polymer|solution interfacial ion-transfer resistance  $R_i^{fls}$  than the polymer|solution interfacial electron-transfer resistance,  $R_e^{fls}$ .

### Impedance measurements in the sole presence of the supporting electrolyte

The aim of this part of the work was to study the charge conduction process at POAP films employing a different impedance model to that described by Vorotyntsev *et al.*<sup>22</sup> and then, compare charge-transport parameters obtained from both models. To this end we employ the impedance model given in reference<sup>28</sup> which considers a protonation reaction coupled with a self-exchange process between oxidized and reduced sites. This model allows one to obtain a charge-transfer resistance  $R_{Qt}$ , which contains an equilibrium constant,  $K$ , for the polymer protonation reaction and also the electrochemical standard rate constant ( $k_{sh}$ ) for the electron charge-transfer process across the metal-polymer interface. The model also gives an effective diffusion coefficient,  $D_e$  which involves electron and ion movements. A good fitting with this model was observed for all impedance diagrams<sup>26,27</sup>. Table No.3 shows that  $k_{sh}$  decreases as the POAP film becomes more deactivated with the storage time. The  $R_{Qt}$  versus  $\theta_d$  dependence (not shown) extracted from the model given in reference<sup>28</sup> is in good coincidence with the  $R_{m|f}$  versus  $\theta_d$  dependence obtained from the model described in reference<sup>22</sup>. As can be seen by comparing  $D_e$  versus  $\theta_d$  dependence extracted employing the model described in paper<sup>28</sup> (inset in Figure No.5) with  $D_i$  and  $D_e$  values extracted from Vorotyntsev's model (Figure No.4 and 5, respectively), the order of magnitude of  $D_e$  obtained from the model developed in pervious work<sup>28</sup> is closer to that of  $D_i$  than to that of  $D_e$  extracted from the model given in reference<sup>22</sup>. This observation seems to be consistent with the assumption that ion transport controls the whole charge-transport process at POAP.

### Effect of different deactivation procedures on the charge-transport parameters of POAP films

Dependences of the different charge-transport and charge-transfer parameters on the degree of deactivation of POAP films by employing different procedures can be compared. For instance, Figure No.6 compares the electron diffusion coefficient  $D_e$

versus degree of deactivation  $\theta_d$  dependences extracted from EIS for the different deactivation processes of POAP. At each  $\theta_d$  value the sequence  $D_e$  (STWU) >  $D_e$  (PPC) >  $D_e$  (SFeIS) >  $D_e$  (HEPP) is observed. With respect  $R_{mif}$ , while the stronger increase is observed for a POAP films subjected to PPC, the interaction with a ferric ion solution causes the lower effect on the electron transfers across the metal/polymer and polymer/solution interfaces (not shown). The incorporation of ferric ions into the POAP matrix causes a more pronounced decrease in the ion diffusion coefficient value as compared with the other deactivation procedures (not shown).

#### Interpretation of surface resistance measurements

The SR technique is sensitive to the distribution of scatterers at a metal film surface<sup>12,29,30</sup>. In previous works it was proved that SR is a useful technique to detect changes in the redox sites distribution during the redox switching of a POAP film deposited on a thin gold film<sup>31</sup>. Electronic transport in thin metal films is strongly affected by interfacial phenomena. The electron dispersion effect brought about by the presence of entities on the metal surface, thereby acting as dispersion centres for the surface reflection of the electrons from the inside of the metal, has been analysed on the basis of the specularity,  $p$ , which is the principal parameter influenced by the surface concentration of foreign scattering centres at the film surface  $\Gamma_{surf}$ , ( $\Delta p = -k \Gamma_{surf}$ ). In terms of resistance change one can write  $\Delta R \propto (-\Delta p)$ . Then, an increase in the diffuse scattering of the electrons caused by an increase of  $\Gamma_{surf}$  should cause a surface resistance ( $\Delta R$ ) increase. As was described in the experimental section, POAP was deposited on a thin gold film electrode whose thickness was of the order of the mean free path of conduction electrons. Simultaneous voltammetric and SR responses corresponding to a nondeactivated POAP film within the potential range comprised between -0.2 V and 0.5 V are shown in Ref.<sup>12</sup>.

The evolution of the  $\Delta R/R$  vs.  $E$  response for a 60 nm thick POAP film with the storage time is shown in Figure No.7. The redox switching of POAP was interpreted in terms of the oxidation of the amino groups to imine<sup>6</sup>. It is not unreasonable to expect that imine sites act themselves as different scattering centres compared with amine sites, increasing in this way the diffuse reflection of conduction electrons on the gold surface during POAP oxidation (increase of the resistance). That is, the  $\Delta R/R$  increase in going from  $E = -0.2$  V to  $E = 0.5$  V in Figure No.7 can be explained in terms of a  $p$  decrease. The increase of  $\Delta R/R$  during POAP oxidation can be explained in terms of an interfacial distribution of scatterers (imine sites) in the oxidised state with a spacing among them larger than that corresponding to amine sites in the reduced state<sup>6,12</sup>. That is, the distribution of imine species in the oxidized state of POAP should be less compact than the corresponding distribution of amine species in the reduced state, which should lead to a more diffuse reflection of conduction electrons at the gold|POAP interface (lower  $p$  value) at the oxidized state as compared with the value at the reduced one ( $p_{ox} < p_{red}$ )<sup>12</sup>. The change in the redox site distribution with deactivation could explain the change in the electron hopping distance between redox sites, as is proposed in RDEV and EIS measurements to explain the changes of the charge-transport parameters (*i.e.* diffusion coefficients) with the degree of deactivation.

**Table No.1: Effect of the storage time without use in the supporting electrolyte solution on the voltammetric charge of a POAP film**

| <sup>a</sup> POAP films | <sup>b</sup> Storage time/h | <sup>c</sup> $Q_{\text{Red,c}}/\text{mCcm}^{-2}$ | <sup>d</sup> $\theta^d$ |
|-------------------------|-----------------------------|--|-------------------------|
| 1                       | 32                          | 2.65   | 0.05                    |
| 2                       | 45                          | 2.52   | 0.10                    |
| 3                       | 52                          | 2.37   | 0.15                    |
| 4                       | 60                          | 2.10   | 0.25                    |
| 5                       | 72                          | 1.83   | 0.35                    |
| 6                       | 83                          | 1.67   | 0.41                    |
| 7                       | 96                          | 1.12   | 0.62                    |
| 8                       | 120                         | 0.62   | 0.77                    |

<sup>a</sup> Numbers 1 to 8 represent different deactivated POAP films.

<sup>b</sup> Storage time (in hours) of each POAP film in the supporting electrolyte solution.

<sup>c</sup> Voltammetric reduction charge of the different deactivated POAP films after being held without use in the supporting electrolyte solution for the time periods listed in column 2.

<sup>d</sup> Degree of deactivation of each one of the POAP films after being held without use in the supporting electrolyte solution for the time periods listed in column 2. The degree of deactivation achieved by each film after storage was calculated from  $\theta^d = 1 - (Q_{\text{Red,c}}/Q_{\text{Red,T}})$ , where  $Q_{\text{Red,T}} (= 2.8 \text{ mC cm}^{-2})$  is the voltammetric reduction charge of a nondeactivated film.

**Table No.2: Efficiency ( $I_e/I_o \times 100$ ) of a POAP film to act as mediator in the HQ/Q redox reaction after to be stored without use in the supporting electrolyte solution for different time periods**

| POAP Film | $\theta^d_c$ | $I_e/\text{mA cm}^{-2}$ | $I_e/I_o \times 100$ |
|-----------|--------------|-------------------------|----------------------|
| 1         | 0, 05        | 3.01                    | 94                   |
| 2         | 0, 10        | 2.75                    | 86                   |
| 3         | 0, 15        | 2.55                    | 79                   |
| 4         | 0, 25        | 2.23                    | 70                   |
| 5         | 0, 35        | 2.02                    | 63                   |
| 6         | 0, 41        | 1.74                    | 54                   |
| 7         | 0, 62        | 1.05                    | 33                   |
| 8         | 0, 77        | 0, 55                   | 16                   |

**Table No.3: Standard electrochemical rate constant ( $k_{\text{sh}}$ ) values for deactivated POAP films extracted from the impedance model given in reference<sup>28</sup>**

| POAP films | <sup>a</sup> $10^5 k_{\text{sh}}/\text{cm s}^{-1}$ | $\theta_i$ |
|------------|--|------------|
| 1          | 10.5   | 0.05       |
| 2          | 3.09   | 0.10       |
| 3          | 3.11   | 0.15       |
| 4          | 2.04   | 0.25       |
| 5          | 1,97   | 0.35       |
| 6          | 1.48   | 0.41       |
| 7          | 0.67   | 0.62       |
| 8          | 0.46   | 0.77       |

<sup>a</sup> Values of the standard electrochemical rate constant,  $k_{\text{sh}}$ , for the different degrees of deactivation given in column 3.

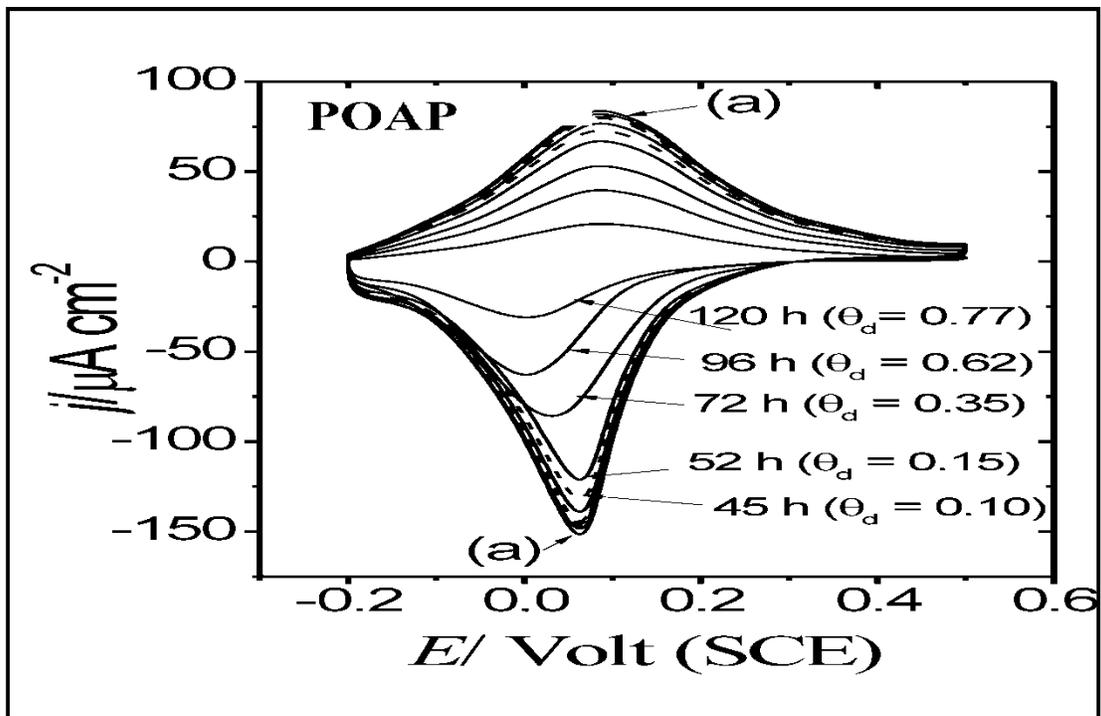


Figure No.1: Voltammetric ( $j$ - $E$ ) responses for a  $2.8 \text{ mC cm}^{-2}$  ( $\phi = 60 \text{ nm}$ ) thick POAP film. (a) A nondeactivated POAP film ( $\theta_d = 0$ ). The other voltammetric responses correspond to POAP films which were held without use in the supporting electrolyte solution for the time periods indicated in the figure. The degrees of deactivation of the films are indicated in Table No.1. Electrolyte:  $0.1 \text{ M HClO}_4 + 0.4 \text{ M NaClO}_4$ . Scan rate:  $\nu = 0.01 \text{ V}$

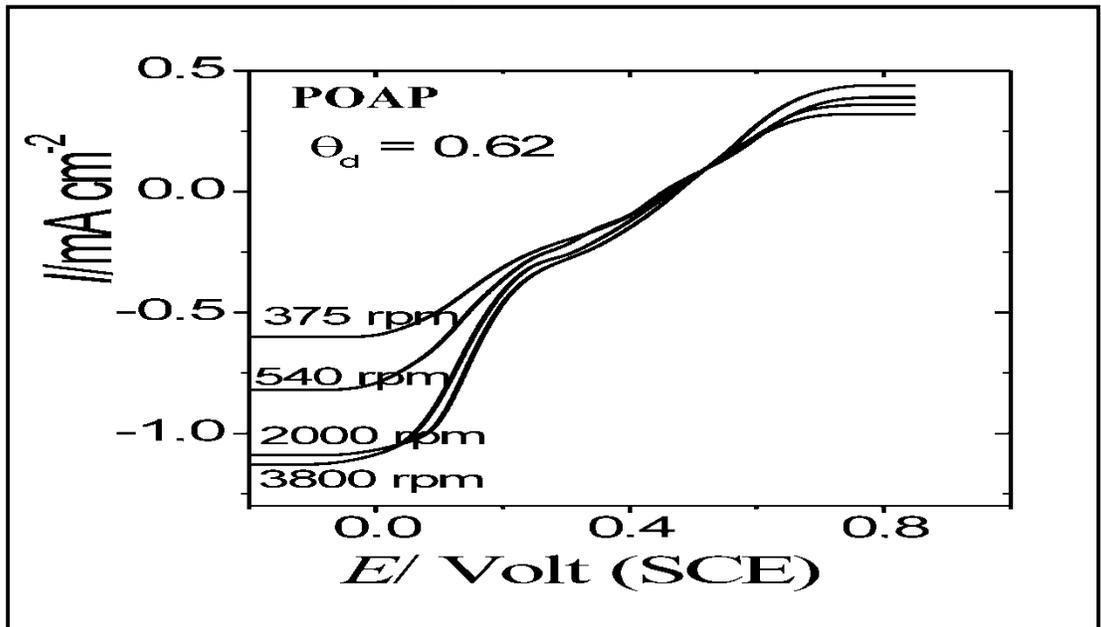


Figure No.2: Steady-state current-potential ( $I$ - $E$ ) curves for different rotation rates ( $\Omega$ ) of the rotating disc electrode. A deactivated POAP film ( $\theta_d = 0.62$ ).  $\Omega$  Values are indicated in the figure. Film thickness:  $60 \text{ nm}$ . Electrolyte:  $0.1 \text{ M HClO}_4 + 0.4 \text{ M NaClO}_4 + 2 \times 10^{-3} \text{ M (HQ/Q)}$

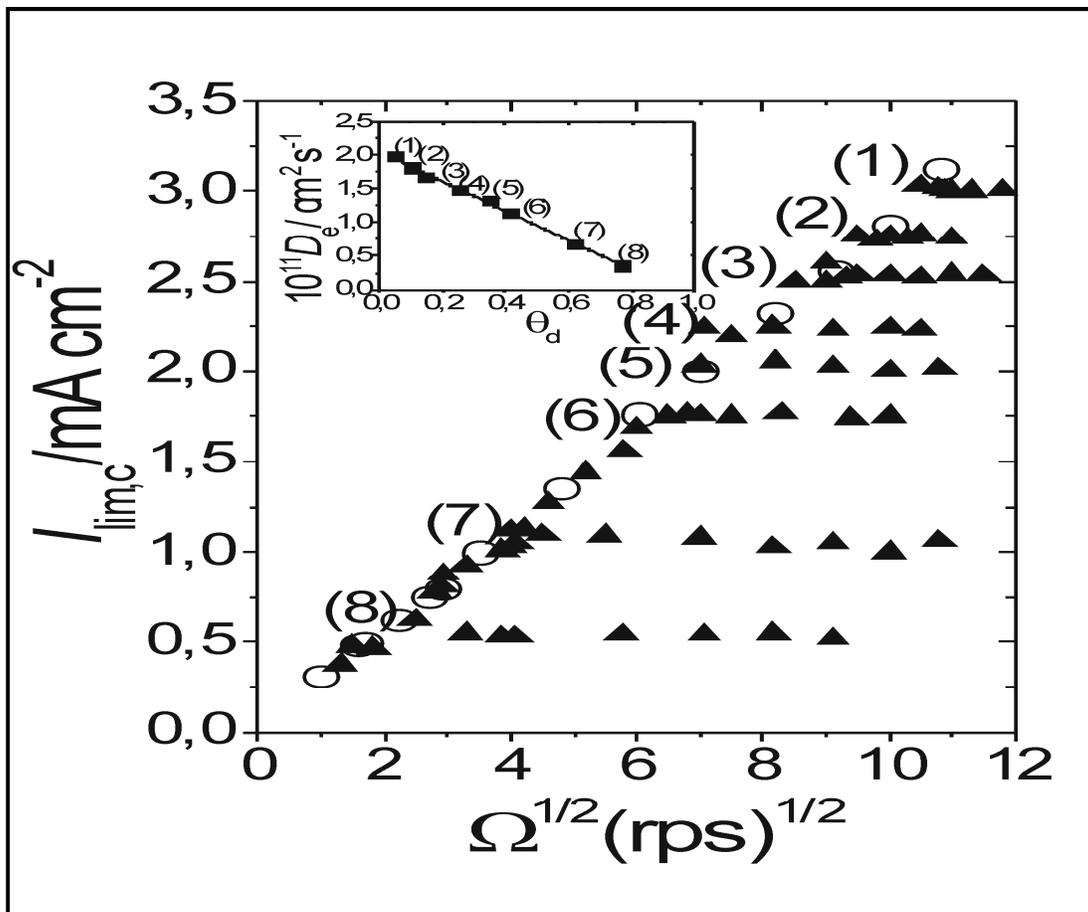


Figure No.3: Levich representations  $I_{lim,c}$  versus  $\Omega^{1/2}$  for POAP films contacting a 0.1 M HClO<sub>4</sub> + 0.4 M NaClO<sub>4</sub> +  $2 \times 10^{-3}$  M (HQ/Q) solution. (O) Empty circles correspond to a nondeactivated POAP film. Black triangles correspond to deactivated films. Numbers from (1) to (8) indicate the different films listed in Table No.1. Inset: Electron diffusion coefficient ( $D_e$ ) (Eq. (2)) as a function of  $\theta_d$ . Numbers (1) to (8) correspond to each one of the deactivated POAP films listed in Table No.1 and 2

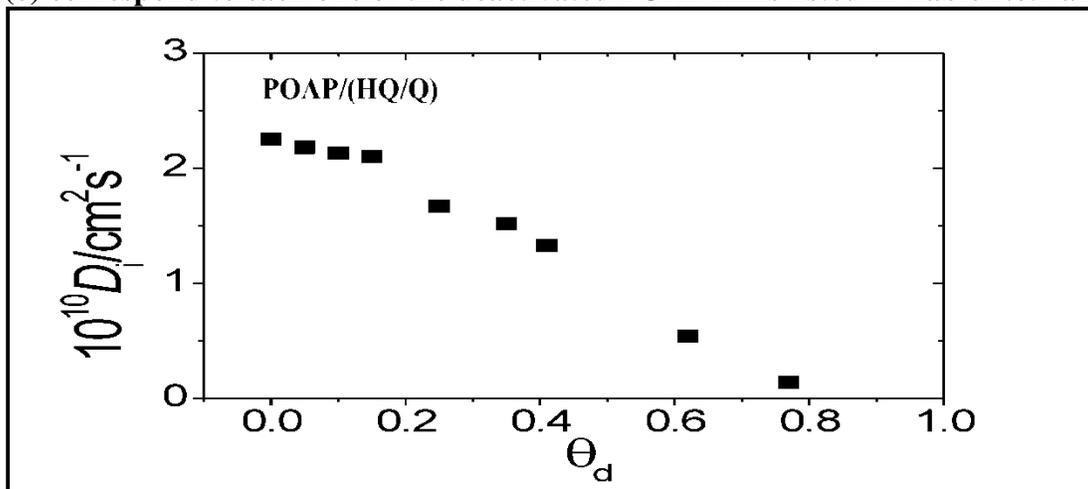


Figure No.4: Ion diffusion coefficient ( $D_i$ ) as a function of  $\theta_d$ . Electrolyte: 0.1 M HClO<sub>4</sub> + 0.4 M NaClO<sub>4</sub> +  $2 \times 10^{-3}$  M (HQ/Q) solution

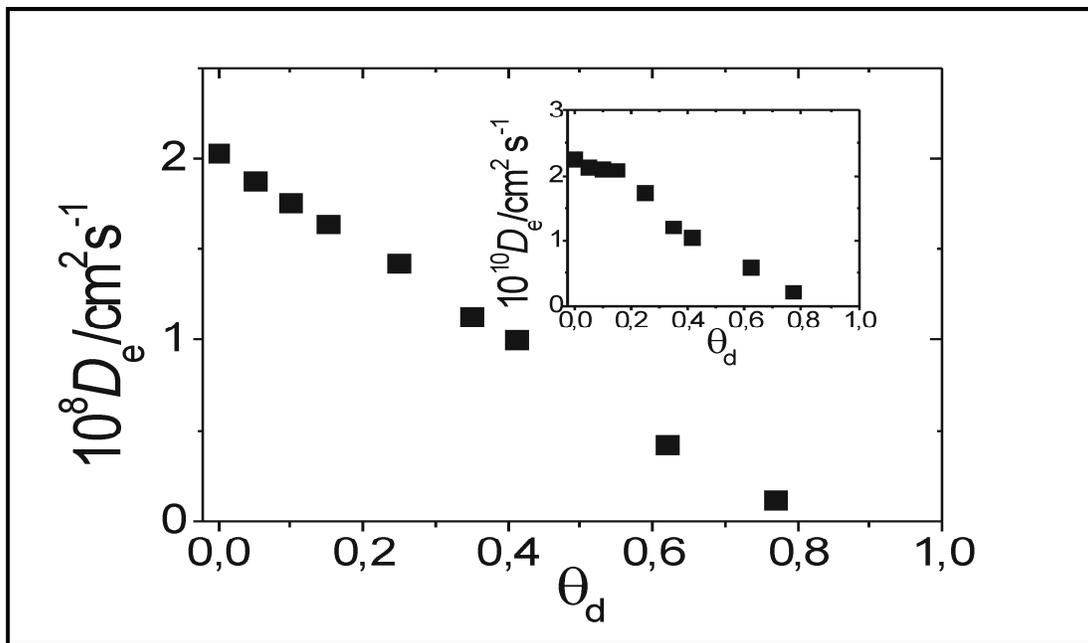


Figure No.5: Electron diffusion coefficient ( $D_e$ ) as a function of  $\theta_a$ . Electrolyte: 0.1 M  $\text{HClO}_4$  + 0.4 M  $\text{NaClO}_4$  +  $2 \times 10^{-3}$  M (HQ/Q) solution. Inset: Diffusion coefficient  $D_e$  versus  $\theta_a$  dependence extracted employing the model described in reference<sup>28</sup>. Electrolyte: 0.1 M  $\text{HClO}_4$  + 0.4 M  $\text{NaClO}_4$  solution

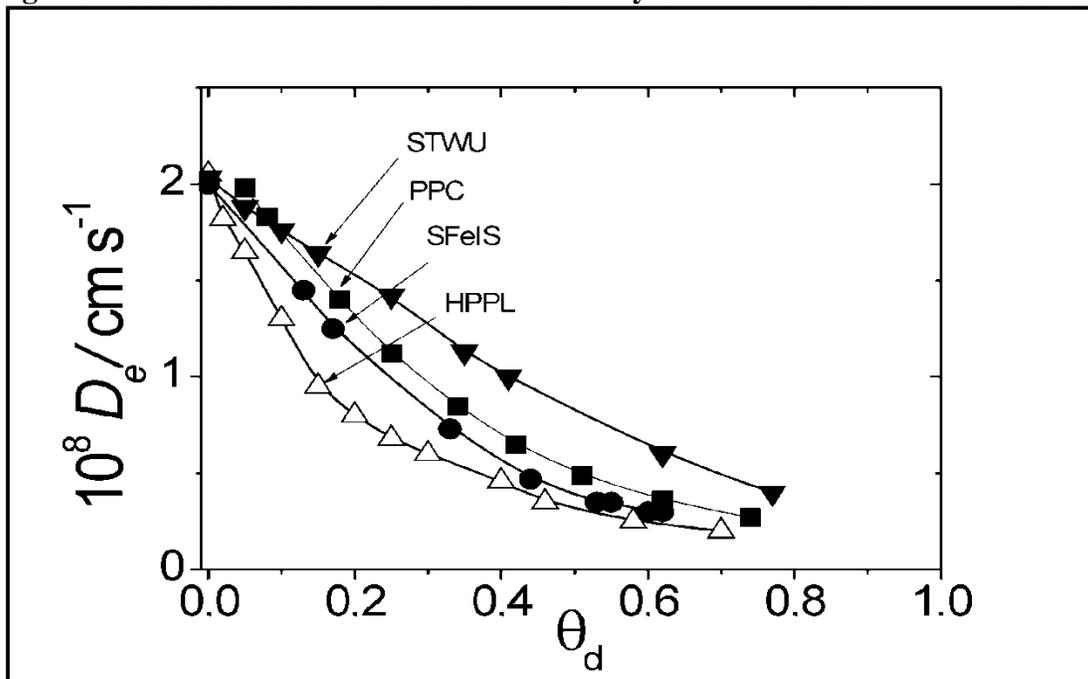


Figure No.6: Comparison of electron diffusion coefficient  $D_e$  versus  $\theta_a$  dependence for different deactivation processes of POAP extracted from EIS. Electrolyte: 0.1 M  $\text{HClO}_4$  + 0.4 M  $\text{NaClO}_4$  +  $2 \times 10^{-3}$  M (HQ/Q) solution. Symbols: ( $\blacktriangledown$ ) STWU (this work); ( $\blacksquare$ ) prolonged potential cycling (values extracted from reference<sup>14</sup>); ( $\bullet$ ) soaking in a ferric ion solution (values extracted from reference<sup>16</sup>); and ( $\Delta$ ) high electrode positive potentials (values extracted from reference<sup>15</sup>). Reduced state of POAP,  $E = -0.2$

V

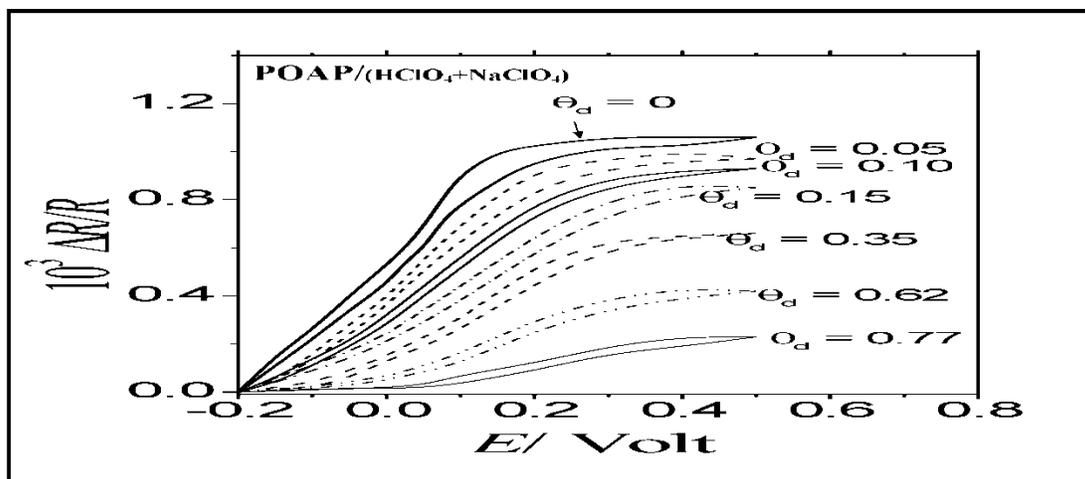


Figure No.7:  $\Delta R/R-E$  responses obtained simultaneously with the  $(j-E)$  responses shown in Figure No.1. The degrees of deactivation are indicated in the figure (see also Table No.1). Thickness of the gold film  $\phi_m = 30$  nm, resistance value of the gold film,  $R = 20.02$  ohm. Thickness of the POAP film,  $\phi = 60$  nm. Electrolyte: 0.1 M  $\text{HClO}_4 + 0.4$  M  $\text{NaClO}_4$ . Scan rate:  $\nu = 0.01\text{V s}^{-1}$

## CONCLUSION

A loss of POAP conductivity was observed as the storage time was extended beyond 30 h. An attenuation of the voltammetric response of POAP with the increase of the storage time is observed. Also, a similar attenuation is observed after PPC, application of positive potential limits beyond  $E = 0.5$  V (SCE) and soaking of a POAP film in a ferric cation solution for different periods. This attenuation allows one to define a degree of deactivation of the polymer. Dependences of conduction parameters on the degree of deactivation were obtained by employing different electrochemical techniques. While electron ( $D_e$ ) and ion ( $D_i$ ) diffusion coefficients decrease, interfacial resistances ( $R_{mf}$ ,  $R_i^{fs}$ ,  $R_e^{fs}$ ) increase as the degree of deactivation of the polymer increases. While parameters representing electron motion extracted from RDEV and impedance measurements seem to change continuously within the whole range of deactivation degree, parameters representing the ion transport show a break at a degree of deactivation of about 0.35. This characteristic of the ion transport at POAP was associated with the existence of two forms of hydrogen ions in the POAP film. The relative surface resistance change of a thin gold film coated with poly (*o*-aminophenol) is gradually

attenuated with the increase of the storage time, PPC, application high positive potential limits and soaking in a ferric cation solution. This effect was attributed to a change in the redox site configuration, that is, to the existence of a more spread redox site configuration in a deactivated film as compared with a nondeactivated one. The dependence of charge-transport and charge-transfer parameters on the degree of deactivation for POAP films deactivated employing different procedures, STWU, PPC, SFeIS and HPPL were compared in this work. While the deactivation of poly (*o*-aminophenol) films by soaking in a ferric ion solution has been attributed to the direct interaction of iron ions with the redox sites of POAP, which impedes the protonation reaction of the polymer, the loss of electroactivity of a polymer film under continuous potential cycling has been associated with the excessive uptake of redox sites by doping anions from the external electrolyte solution. Also, the effect of high positive potential limits on electroactive polymer conductivities has been associated with lateral reactions that could increase the residual saturation in polymeric chains, causing a strong reduction of the electron conduction through conjugated domains in large polymeric chains.

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## DISCLOSURE OF POTENTIAL CONFLICTS OF INTEREST

Conflict of interest: The author declares that he has not conflict of interest.

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