Blocking Effect of Poly(*o*-aminophenol) Towards Adsorption Processes at a Gold Film Surface. A Comparison with its Performance as Biosensor and Electrocatalyst Material

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Abstract: The aim of this work was to qualitatively analyze how the electrochemical response of a metal surface is modified when it is gradually coated by poly(*o*-aminophenol) (POAP). To this end the electrochemical response of a thin gold film electrode was firstly studied in the presence of different adsorbates (perchlorate, sulfate and benzenesulfonate anions and the macromolecule poly(vinyl imidazole)). Then, the gold film electrode was gradually coated by POAP films of different thicknesses and again, its electrochemical response in the presence of the same adsorbates was recorded. Cyclic Voltammetry and the Surface Resistance technique were employed in this study. Also, SEM images on the gold film surface coated by POAP films of different thicknesses are shown. Dependence of the resistance change of the gold film on the external electrolyte composition at POAP thicknesses lower than 0.4 mC cm^{-2} was attributed to the discontinuous character of the polymer thickness on the gold surface. For polymer thicknesses higher than 0.4 mC cm^{-2}, the resistance response of the gold film becomes independent of both the external electrolyte composition and POAP thickness. Thus, POAP thicknesses higher than 0.4 mC cm^{-2} seem to be compact enough at the metal|polymer interface to prevent the interaction of the species contained in the supporting electrolyte with the gold film surface. This conclusion seems to be in agreement with SEM images. Although the SR technique does not detect changes at the metal film|POAP interface for POAP thicknesses within the range 0.4 mC cm^{-2} to 1.5 mC cm^{-2}, SEM images show that the external morphology of POAP becomes porous for film thicknesses higher than 0.8 mC cm^{-2}. The observations reported in this work could be useful for understanding more clearly the electrochemical performance of sensors and catalysts based on poly(*o*-aminophenol).

Keywords: Poly(*o*-aminophenol) films, gold film electrode, surface resistance.

1. INTRODUCTION

Poly(*o*-aminophenol) (POAP) is a ladder polymer [1-5] whose parameters characterizing charge-transfer and charge-transport processes have been obtained by employing different electrochemical techniques. Besides, dependences of these transport parameters on external variables, such as electrolyte concentration and polymer thickness, have been extensively investigated [6-12]. With regard to practical applications of POAP, the membrane properties exhibited by the polymer have been tested in sensors [13-15], and also its catalytic activity towards the electro-oxidation of methanol has been exploited successfully [16]. However, it was observed that the POAP thickness plays an important role in its different practical applications. It was found that the anodic peak current for the methanol oxidation process on Pt microparticles decreases as the POAP film thickness increases [16]. On the other hand, a gradual increase in the response current with the increase of POAP thickness was observed in the horseradish peroxidase (HRP)-ferrocene modified carbon paste biosensor that employs an electrochemically generated POAP membrane for the determination of hydrogen perox-

ide [13]. These facts demonstrate that the film thickness is a critical parameter in the practical uses of POAP. The aim of the present work was to study how the electrochemical response of a metal surface electrode changes when it is gradually coated with POAP. To this end, a thin gold film was employed as base metal electrode. The electrochemical response of this gold film electrode towards the adsorption of ion and molecular species was monitored at different POAP coverages. In this regard, anions, such as perchlorate, sulfate and benzenesulfonate, and the macromolecule poly(vinyl imidazole) were considered as adsorbates in this study. Cyclic voltammetry (CV) and the Surface Resistance (SR) technique [17] were employed in this analysis. Also, SEM images of the thin gold film electrode coated by different POAP film thicknesses were obtained. In this way interesting conclusions about a metal surface coated by POAP were drawn, which could help understand more clearly the POAP behavior in some of its practical uses.

2. EXPERIMENTAL

2.1. The Gold Film Electrodes

Gold thin film electrodes of constant thickness $\phi_m \sim 30$ nm were prepared by vacuum evaporation as was previously described [18]. These gold films are polycrystalline with crystallite sizes between 0.01 and 0.1 μm [19]. The samples were inserted into an electrochemical cell similar to that

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shown in a previous paper [20] and employed as working electrodes. An electrode area of 0.56 cm^2 was exposed to the solution. These electrodes exhibit initial resistance values $R \sim 10$ ohms. The relationship between the length l and the width w of these gold film electrodes was $G = l/w = 2$. A gold grid of large area was used as counter electrode. All the potentials reported in this work are referred to the SCE.

The gold film conductivity was measured by circulating a *dc* current (1 mA) between the extreme contacts while polarizing the electrode ensemble through the central contact [21]. The resistance change obtained in this way [20] was recorded as a function of the potential ($\Delta R/R$-E), together with the voltammetric response (j-E). The experimental setup for simultaneous voltammetric and surface conductivity measurements on thin film electrodes has previously been described in detail [21]. These measurements were used to study the effect of ion adsorption on gold. To this end, 0.4 M NaClO$_4$ + 0.1 M HClO$_4$, 0.4 M Na$_2$SO$_4$ + 0.1 M H$_2$SO$_4$ and 0.4 M sodium benzenesulfonate + 0.1 M benzenesulfonic acid solutions were employed. Admittance measurements as a function of potential were performed to study the adsorption of poly(vinyl imidazole) on gold. In this case the capacitance change as a function of potential (C-E) was recorded together the surface resistance change ($\Delta R/R$-E). The admittance was measured at different frequencies (f) in the range $10 < f < 80$ Hz and then extrapolated to zero, f. The sweep rate was 1×10^{-2} V s^{-1}. In this case a 0.04 M NaF + 1.4 x 10^{-6} M poly(vinyl imidazole) solution was used.

2.2. The POAP-Coated Gold Film Electrodes

POAP-coated gold film electrodes were obtained by immersing the gold films described in the previous section in a 10^{-3} M *ortho*-aminophenol + 0.4 M NaClO$_4$ + 0.1 M HClO$_4$ solution and cycling the potential between - 0.25 V and 0.8 V at a scan rate $v = 0.05$ V s^{-1}. These experimental conditions lead to adherent POAP films on the gold film surface, which are mechanically stable and with a very reproducible electrochemical response [1, 22]. The POAP thickness was increased by increasing the number of potential cycles in the solution containing the monomer. In order to measure the polymer thickness, these POAP-coated gold film electrodes were then rinsed and transferred to the supporting electrolyte solution (0.4 M NaClO$_4$ + 0.1 M HClO$_4$). Then, the voltammetric reduction charge Q_{Red} in this solution was determined by integrating the cathodic current of the voltammetric response between -0.25 V and 0.5 V ($v = 0.05$ V s^{-1}) [23]. Thus, Q_{Red} was considered as representative of the polymer thickness. Several POAP films with Q_{Red} values ranging between 0.06 mC cm^{-2} and 1.5 mC cm^{-2} were employed in this work. For this type of polymer, many researchers have correlated the charge obtained from the integration of the voltammetric profile with the ellipsometric thickness [23-26]. Although this procedure is reasonable within an order of magnitude, the ellipsometric thickness is usually obtained under the assumption of a homogeneous film, that is, by averaging the optical film properties across its thickness. As our SEM images evidence heterogeneity of thin POAP films, in this work the voltammetric charge is quoted, which should be related, although not directly, to the polymer film thickness. Despite this consideration and according to previous work [23], the Q_{Red} values indicated above would correspond to polymer thickness (ϕ_p) within the range around 2 nm < ϕ_p

< 70 nm. With these POAP-coated gold film electrodes, resistance responses were recorded (separately for each ϕ_p value) within the potential range -0.2 V and 0.5 V at a scan rate $v = 0.01$ V s^{-1} in solutions containing ClO$_4^-$, SO$_4^{2-}$ and benzenesulfonate (C$_6$H$_5$SO$_3^-$ = BS) anions, and poly(vinyl imidazole) (PVI), respectively. Before recording these responses, POAP-coated gold electrodes were cycled in the different electrolytes for at least 1 h.

2.3. Apparatus, Chemicals and Solutions

A PAR Model 173 potentiostat together with a PAR Model 175 function generator were used. The potential drop at the extremes of the film was measured with a Keithley Model 160 voltmeter during the resistance measurements. An X-Y$_1$-Y$_2$ Hewlett Packard Model 7046 B plotter was used for simultaneous recordings of $\Delta R/R$-E and j-E responses. The equipment for admittance measurements comprised the above-mentioned potentiostat and function generator, together with a lock-in amplifier PAR model 5204 and an oscillator Level Model TG 200DM. The in-phase and quadrature admittance components were plotted on the X-Y$_1$-Y$_2$ Hewlett Packard Model 7046 B plotter together with the $\Delta R/R$-E change. The *ac* current was taken in differential mode from a 10.02 ohm resistor placed in the auxiliary electrode circuit. The amplitude of the *ac* voltage was 4.81 x 10^{-3}V. The admittance values were converted to differential capacitance and solution resistance (series circuit) in the usual way.

AR grade chemicals were used throughout. *o*-Aminophenol (Fluka) was purified as described elsewhere [1]. The solutions were prepared with water purified using a Millipore Milli-Q system. NaClO$_4$, HClO$_4$, H$_2$SO$_4$, Na$_2$SO$_4$, benzenesulfonic acid and sodium benzenesulfonate were employed to prepare the corresponding solutions. The synthesis of PVI was performed as described in [27].

3. RESULTS AND DISCUSSION

3.1. Electronic Transport in Thin Metal Films

The experimental arrangement in this investigation was one in which a poly(*o*-aminophenol) film was supported on a thin gold film whose thickness was of the order of the mean free path of conduction electrons of gold. This arrangement allows one to apply the surface resistance technique to study the electrochemical processes occurring on these modified electrodes. As Surface Resistance (SR) is a nontraditional technique in Electrochemistry, a brief explanation about the electronic transport in thin metal films will be given.

Electronic transport in thin metal films (thickness comparable to the mean free path of conduction electrons) is strongly affected by interfacial phenomena. For example, the scattering of conduction electrons at planar interfaces defined by the top and bottom surfaces of the film under study can contribute significantly to the resistivity. In the case of thin metal films, the electrical resistivity ρ_f is higher than the bulk resistivity ρ_m of the massive metal with the same structure as the metal film, and the ρ_f/ρ_m ratio decreases with increasing film thickness, ϕ_m. This "Size Effect" becomes evident when ϕ_m is comparable with the mean free path, l_m, of the conduction electrons. The theory to account for the size effect was postulated by Fuchs [28] and Sondheimer [29]. The exact expression for the dependence of the film resistiv-

ity, ρ_f, as a function of ϕ_m is complicated. However, it can be reduced to a limiting form when $\phi_m/l_m \geq 1$

$$\rho_f /\rho_m = 1 + (3/8)\,(1\text{-}r)\,l_m/\phi_m \qquad (1)$$

In Eq. (1), r is the specularity parameter [29]. This parameter represents the probability of an electron being reflected specularly or diffusely at the film surface. The r value ranges from 0 for complete diffuse scattering to 1 for complete specular scattering. At first, it should be considered that thin metal films can be prepared to satisfy the Fuch's model in a sufficient way to exhibit a specularity parameter near 1 (a surface with a smooth mirrorlike finish that is free of defects). However, this parameter, which is also interpreted as the fraction of the surface that specularly reflects electrons, depends on the quality of the metal film surface, that is, on the method of preparation of the metal film [30]. In this sense, an appreciable fraction of the conduction electrons can be scattered diffusely and give rise to an additional resistance, which correlates with the roughness of surface topography and the presence of surface defects. All these imperfections should lead to experimental r values lower than 1.

Besides the above-mentioned factors, if foreign entities are present on the film surface, translational symmetry parallel to the interface, changes and additional scattering of the conduction electrons occur. This electron dispersion effect brought about by the presence of entities on the metal surface, thereby acting as dispersion centers for the surface reflection of the electrons from the inside of the metal, has been analyzed on the basis of Eq. (1). Assuming that the specularity, r, is the principal parameter influenced by the surface concentration of foreign scattering centers at the film surface Γ_{surf}, differentiation of Eq. (1) leads to the relationship

$$\Delta\rho_f = -\,3/8\,(\rho_m\,l_m/\phi_m)\,(\Delta r) \qquad (2)$$

On the assumption that the increase of Γ_{Surf} increases the diffuse scattering of the electrons, $\Delta r = -\,k\,\Gamma_{Surf}$, an increase $\Delta\rho_f$ would be expected with increasing Γ_{surf} (Eq. (2)). In terms of the resistance changes ($\Delta R = \Delta\rho_f\,G/\phi_m$), Eq. (2) can be written as

$$\Delta R = -3/8\,G\,(\rho_m\,l_m/\phi^2{}_m)\,\Delta r \qquad (3)$$

In the Wissmann's interpretation [31] the film resistivity change can be expressed in terms of the product of an apparent scattering cross section of the entity, σ_a, and the density of scattering centers at the surface, N_a, as

$$\Delta\rho_f = (\rho_m\,l_m/\phi_m)\,(\sigma_a\,N_a) \qquad (4)$$

By comparing Eqs. (2) and (4), it is evident that a Δr decrease can be associated with an increase in σ_a. From the experimental viewpoint, the relative resistance change, $\Delta R/R$, as a function of potential, E, is recorded during the electrochemical process (adsorption). R is the gold film resistance at a potential value where adsorption on gold is absent (potential region corresponding to the electrical double layer in the presence of the supporting electrolyte).

3.2. The Resistance Change at the Gold Film|Electrolyte Interface

Fig. (**1**) shows $\Delta R/R$-E responses of a 30 nm thick gold film contacting solutions that contain ClO_4^-, SO_4^{-2} and BS

anions, respectively. In this case $\Delta R/R$ changes are referred to the potential value $E = -0.2$ V, where the absence of specific adsorption of anions on gold is assumed. The resistometric change of gold films in the presence of weakly adsorbed anions, such as ClO_4^-, has been ascribed to a surface charge effect rather than to a specific adsorption effect [18]. However, different resistometric changes in the presence of anions able to act as surface impurities (SO_4^{-2} and BS) can be explained in terms of the apparent scattering cross sections of the adsorbates present on the metal film surface [31] (Eq. (4)). In this connection, while the geometrical dimension of the BS anion lying flat on a plane is about 0.54 nm^2 [32], that of sulfate is around 0.18 nm^2 [33]. Besides, aromatic sulfonate anions exhibit distinguishable charged and non-charged parts (the sulfonate group and the benzene ring) as compared with the sulfate anion, which would lead to a stronger interaction of the high electron density of the benzene ring of the BS anion with metal surfaces. A strong adsorbability of (BS) anions on Au(111) single-crystal electrodes, which inhibits the oxidation of the gold surface, was reported by Dutkiewicz and Skoluda [32]. Then, the sequence of $\Delta R/R$ changes ($ClO_4^- < SO_4^{-2} <$ BS) observed in Fig. (**1**) for the three different anions can be considered as representative of a sequence of adsorbabilities of these anions on the gold film electrode [18].
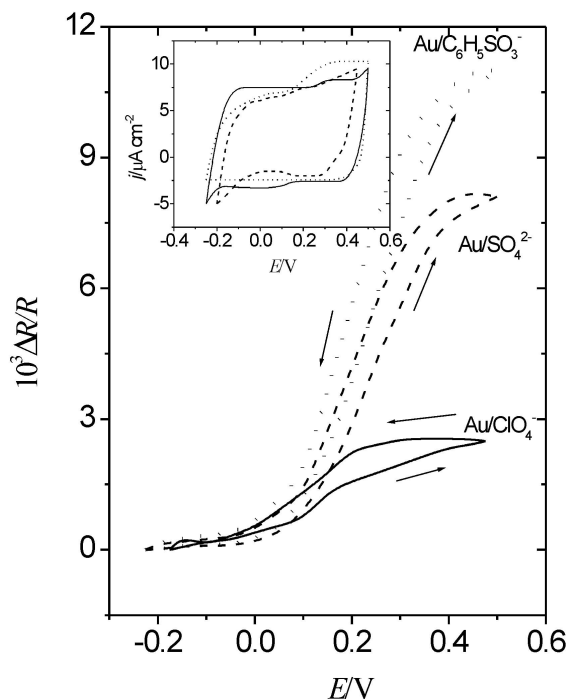

Fig. (1). $\Delta R/R$ *vs.* E responses of a gold film electrode ($\phi_m = 30$ nm) contacting different electrolytes: (——) 0.1 M $HClO_4$ + 0.4 M Na-ClO_4; (- - - -) 0.4 M Na_2SO_4 + 0.1 M H_2SO_4; and (- - - -) 0.4 M sodium benzenesulfonate + 0.1 M benzenesulfonic acid. n = 0.01 v s^{-1}. Inset: the corresponding voltammograms.

Fig. (**2**) shows capacitance *vs.* potential (C *vs.* E) curves for the gold film electrode in a 0.04 M NaF (pH 3.03) solution in the presence and in the absence of poly(vinyl imidazole). As can be seen from the C *vs.* E curve, in the presence of only the supporting electrolyte (curve (a)), the potential of zero charge is about -0.05 V (*vs.* SCE). However, the pres-

ence of the macromolecule modifies the *C vs. E* curve and displaces the minimum towards the negative potential direction. At the same time, an adsorption-desorption peak system is observed within the potential range $-0.5 \, V < E < 0.5 \, V$. Fig. (**3**) shows the corresponding resistance *vs.* potential (*ΔR/R vs. E*) curves. In the same way as other organic molecules, such as amyl alcohol [34, 35], PVI causes a surface resistance decrease of the gold film electrode. The observed surface resistance decrease can be explained in terms of the field effect and the surface scattering of conduction electrons [17].
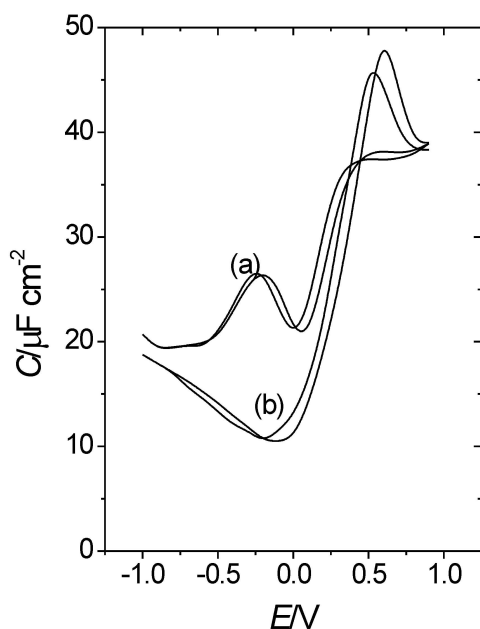
Fig. (2). Capacitance *vs.* potential (*C vs. E*) responses of a gold film electrode ($\phi_m = 30$ nm) in contact with (**a**) a 0.04 M NaF solution and (**b**) a 0.04 M NaF + 1.4 x 10^{-6} M poly(vinyl imidazole) solution. Solution pH, 3.03. Sweep rate, 1×10^{-2} V s^{-1}.

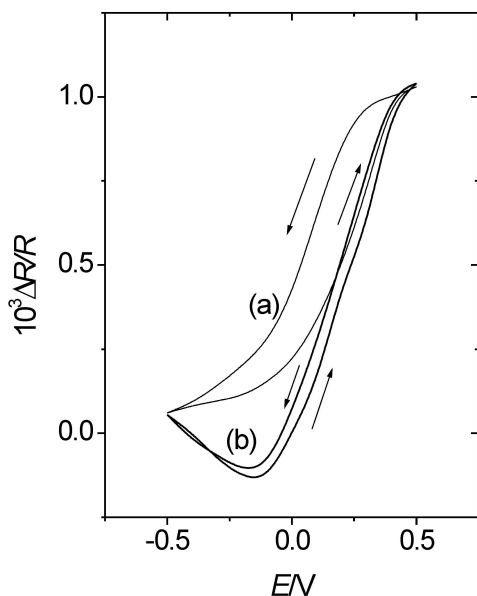**Fig. (3).** *ΔR/R vs. E* responses of a gold film electrode ($\phi_m = 30$ nm) in contact with (**a**) a 0.04 M NaF solution and (**b**) a 0.04 M NaF + 1.4 x 10^{-6} M poly(vinyl imidazole) solution. Solution pH, 3.03. Sweep rate, 1×10^{-2} V s^{-1}.

3.3. The Resistance Change of a Gold Film Electrode Coated by POAP Films of Different Thicknesses

Simultaneous *ΔR/R-E* and *j-E* responses for the 30 nm thick gold film coated with POAP films of different thicknesses were recorded in the same above-mentioned electrolytes containing ClO_4^-, SO_4^{-2}, BS and PVI, respectively. *j-E* responses at a given scan rate (*v*) and POAP thickness in the presence of the different anions do not show big differences. This is shown in Fig. (**4**) for the $Q_{Red} = 1.5$ mC cm^{-2} thick POAP film. In the inset of Fig. (**4**), the corresponding response for a thinner POAP film ($Q_{Red} = 0.22$ mC cm^{-2}) is also shown. Fig. (**5**) shows the resistometric responses corresponding to both POAP thicknesses. That is, curves (a) correspond to the thinner POAP film ($Q_{Red} = 0.22$ mC cm^{-2}) and curves (b) to the 1.5 mC cm^{-2} thick POAP film. In all cases *ΔR/R* changes are referred to the potential value $E = -0.2$ V, where POAP is in its reduced state. Two facts can be noted by comparing the resistance responses of a polymer-free gold film (Fig. **1**) with *ΔR/R* changes of the same gold film coated with different POAP thicknesses (Figs. **4** and **5**). Firstly, the magnitude of the *ΔR/R* change, for a given anion, is strongly attenuated by the presence of the POAP film on the gold surface, as compared with the corresponding *ΔR/R* change of the polymer-free gold film. The attenuation is more pronounced as ϕ_p increases. Secondly, while distinguishable *ΔR/R* changes are obtained even for a thin POAP film ($Q_{Red} = 0.22$ mC cm^{-2}) contacting the different anions, for the 1.5 mC cm^{-2} thick POAP film the *ΔR/R* change becomes independent of the type of anion present in the external solution. Fig. (**6**) shows the *ΔR/R-Q_{Red}* dependence at
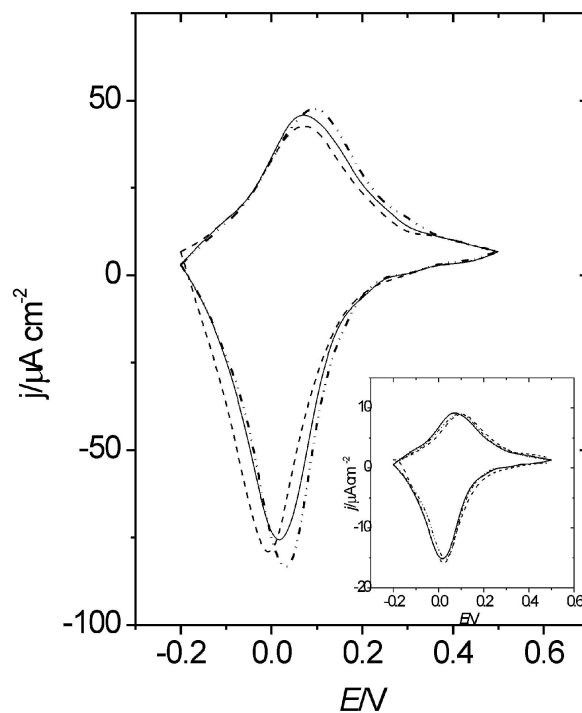

Fig. (4). *j vs. E* responses for a gold film ($\phi_m = 30$ nm) coated with a 1.5 mC cm^{-2} thick POAP film. Electrolytes: (—) 0.1 M HClO$_4$ + 0.4 M NaClO$_4$; (----) 0.4 M Na$_2$SO$_4$ + 0.1 M H$_2$SO$_4$; and (- .. - .. -) 0.4 M sodium benzenesulfonate + 0.1 M benzenesulfonic acid. *v* = 0.01 V s^{-1}. Inset: *j vs. E* responses for the same gold film coated with a 0.22 mC cm^{-2} POAP film.
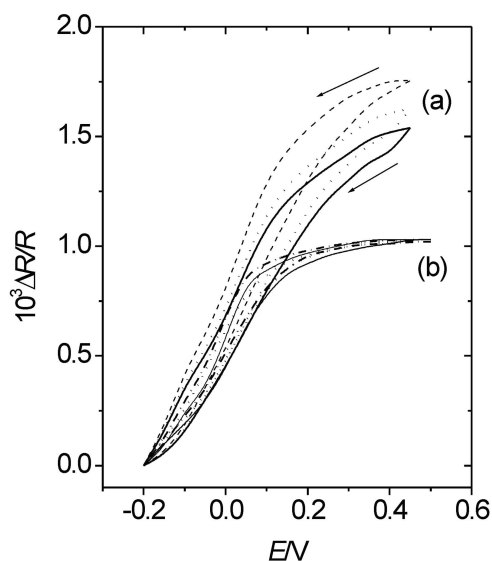
Fig. (5). *ΔR/R vs. E* responses of a gold film electrode ($\phi_m = 30$ nm) coated with (**a**) a 0.22 mC cm^{-2} thick POAP film and (**b**) a 1.5 mC cm^{-2} thick POAP film, in the presence of the same electrolytes indicated in Fig. (**4**): (-.-.-.) 0.1 M HClO$_4$ + 0.4 M NaClO$_4$; (—) 0.4 M Na$_2$SO$_4$ + 0.1 M H$_2$SO$_4$; and (- - -) 0.4 M sodium benzenesulfonate + 0.1 M benzenesulfonic acid. $v = 0.01$ V s^{-1}.

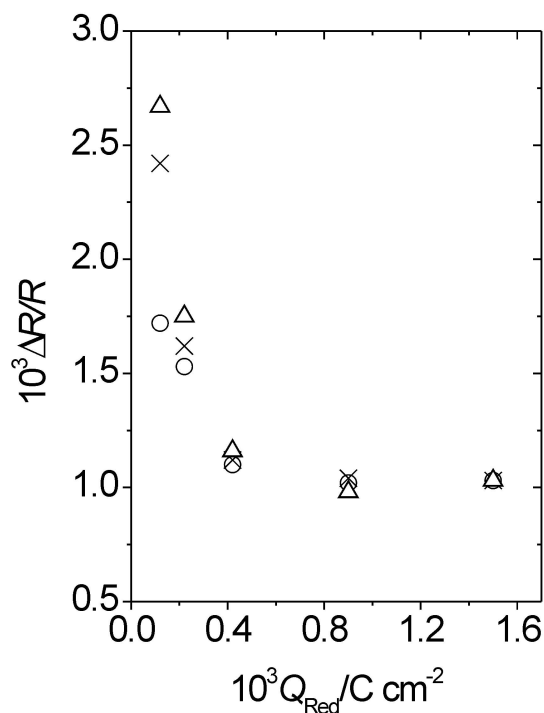**Fig. (6).** *ΔR/R vs. Q*Red dependence at *E* = 0.5 V (POAP in the oxidized state). Symbols represent different anions: (Δ) BS; (X) Sulfate; (O) perchlorate.

E = 0.5 V (POAP in the oxidized state). As can be seen from Fig. (**6**), for $Q_{Red} > 0.4$ mC cm^{-2}, the *ΔR/R* change becomes independent of both the POAP thickness and the anion contacting the polymer. Fig. (**7**) shows the different *ΔR/R-E* responses of the gold film towards the adsorption of PVI, as it is gradually coated by different POAP film thicknesses. Again, it was found that the *ΔR/R-E* response becomes inde-

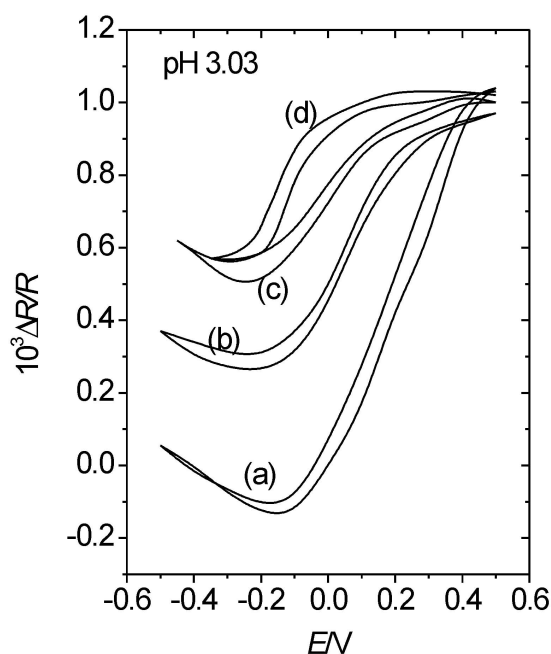pendent of the POAP thickness for charge values higher than 0.4 mC cm^{-2}.

Fig. (7). *ΔR/R vs. E* responses of a gold film electrode ($\phi_m = 30$ nm) coated with POAP films of different thicknesses (ϕ_p): (**a**) $\phi_p = 0$, (**b**) $\phi_p = 0.12$ mC cm^{-2}, (**c**) $\phi_p = 0.32$ mC cm^{-2}, (**d**) $\phi_p = 0.48$ mC cm^{-2}. Electrolyte: 0.04 M NaF + 1.4 x 10^{-6} M poly(vinyl imidazole), pH 3.03. Scan rate, 0.01 V s^{-1}.

3.4. Considerations about Resistance Changes Associated with POAP Film Thickness

It is established, in accordance with the theory [36], that the density of the polymer layer decreases with the film thickness, *i.e.*, from the metal surface to the polymer|solution interface. Internal parts of polymer films could have a different structure than their external parts. In this connection, during the synthesis of polymer films [37], two or more stages of the polymerization process can usually be distinguished: first, islands of the polymer are formed at the substrate surface, then a continuous film, which is compact (nonporous), is formed by fusion of these islands, and further growth takes place above this compact layer giving an external porous part of the film. Fig. (**8**) shows SEM micrographs of POAP films whose thicknesses are 0.12, 0.42 and 1.5 mC cm^{-2}, respectively, deposited on a 30 nm thick gold film electrode. As can be seen, a 0.12 mC cm^{-2} thick POAP film shows a discontinuous structure on the gold substrate (Fig. **8**, upper image). This discontinuous structure was observed within the thickness range 0.06 mC cm^{-2} – 0.37 mC cm^{-2}. Within the thickness range 0.4 mC cm^{-2} – 0.82 mC cm^{-2}, a rather continuous and compact structure was observed. This is shown in Fig. (**8**) (center image) and corresponds to a 0.42 mC cm^{-2} thick POAP film. Then, for a thickness range 0.82 mC cm^{-2} - 1.5 mC cm^{-2}, an external porous structure is observed (Fig. **8**, lower image).

The SR technique only detects processes occurring at the gold film|POAP film interface. Resistance measurements applied to gold films coated with POAP films seem to indi-
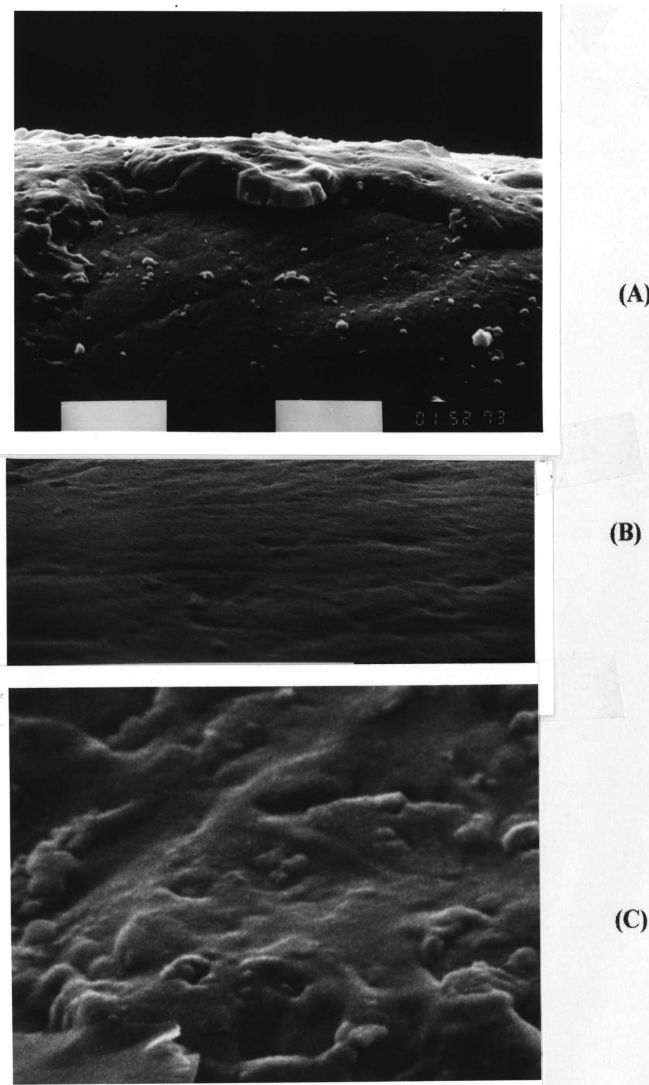
Fig. (8). SEM images of different POAP films deposited on a gold film electrode (ϕ_m = 30 nm). POAP thickness, ϕ_p: (upper image) 0.12 mC cm^{-2}; (center image) 0.42 mC cm^{-2}; (lower image) 1.5 mC cm^{-2}. The white stick below the upper image: 5 μm. The same stick for the three images. Upper image x 7000; center image x 10000, lower image x 7000.

cate that polymer coverages lower than 0.4 mC cm^{-2} are not sufficiently compact at the metal|polymer interface to prevent the specific adsorption of anions and macromolecules, present in the external electrolyte solution, on the gold film surface. However, as the amount of polymer increases (Q_{red} > 0.4 mC cm^{-2}), the gold film surface should be coated by a polymer film compact enough to consider that the resistometric response is due to processes occurring at the gold film|polymer film interface free of effects related to the interaction of species proceeding from the external electrolyte with the gold film surface. In the latter case, the change of the gold film resistance in going from the reduced state of POAP to the oxidized one (plot (b) in Fig. (**5**) and plot (d) in

Fig. **7**), can be explained in terms of the generation of electronic entities at the polymer chains near the electrode surface, which occurs by electron transfer across the polymer|gold film interface. In this connection, the redox switching of POAP was interpreted in terms of the oxidation of the amino groups to imine [7]. Thus, it is not unreasonable to expect that imine sites themselves act as different scattering centers compared with amine sites, thereby increasing the diffuse reflection (increase of $\Delta R/R$) of conduction electrons on the gold surface during POAP oxidation. The increase of $\Delta R/R$ during POAP oxidation could be explained in terms of an interfacial distribution of scatterers (imine sites) in the oxidized state with a spacing among them constant and larger than that corresponding to amine sites in the reduced state [38]. In this connection, during POAP oxidation only one in every four or five amine sites is converted to the corresponding imine sites [7], giving rise to gaps that would eventually yield a distribution of oxidized sites less compact than the corresponding distribution of reduced ones. Thus, a distribution of scatterers (oxidized sites) less compact than the distribution of reduced sites should lead to a more diffuse reflection of conduction electrons at the gold film|POAP interface [38], which in turn yields a resistance increase during POAP oxidation. Further confirmation about the different reflecting properties of the oxidized and reduced states of POAP can be found in the different values of the site interaction parameters (p) obtained from the cathodic and anodic voltammetric responses of POAP [1]. The following values of the anodic and cathodic site interaction parameters were reported for POAP, p_a = -0.55 M^{-1} and p_c = -0.18 M^{-1}, respectively. Both are negative, thus involving a repulsive energy of interaction. As a higher repulsion is observed between oxidized sites than between reduced ones, then a more extended configuration of oxidized sites than the corresponding distribution of reduced ones should be expected. Then, again, it would be expected that the distribution of oxidized sites reflects electrons more diffusely than the distribution of reduced ones.

With respect to the polymer redox conversion at the gold film surface, one has to keep in mind that the resistance changes at metal films are not the direct result of the electron transfer between the species on the metal film surface and the metal, but they rather originate from the effect of foreign surface entities on the conduction electrons of the metal itself. At this point it should be pointed out that despite the creation of chemical bonds between the polymer and the metal film, the absolute value of the gold film resistance at a given thickness (for instance, $R \sim 10$ ohm for ϕ_m = 30 nm) does not change with POAP deposition, only the relative $\Delta R/R$ value, referred to either the reduced (E = -0.2 V) or oxidized (E = 0.5 V) state of the polymer, varies with the potential scanning (-0.2 V < E < 0.5 V) (plot (b) in Fig. **5**). This should be indicative of a resistance change only related to an interfacial (gold film|POAP) electron dispersion process occurring during oxidation-reduction of the polymer. On the contrary, generation of a nonconducting dead layer (subsurface impurity) during POAP deposition leading to a reduction of the metal film thickness should increase the absolute value of the gold film resistance.

At this point it should be pointed out that as the resistance response only gives information about the electron dispersion process occurring at the gold film|polymer inter-

face, it is not possible to distinguish electrochemical responses related to different external structures (polymer|solution interface) of POAP (Fig. **8**, center image and lower image). In this connection, a continuous attenuation of the resistance response is only observed as the polymer thickness increases from 0.06 (discontinuous structure at the POAP|gold film interface) to 0.40 mC cm^{-2} (compact structure at the POAP|gold film interface). This was proved by peeling off two POAP films (Fig. **9**, upper image (Q_{red} = 0.4 mC cm^{-2}) and lower image (Q_{red} = 1.5 mC cm^{-2})) from the gold surface. In both cases, the internal surface of the POAP films seems to be compact enough independently of the external surface. This experimental observation seems to justify the fact that the surface resistance response becomes independent of both film thickness and external electrolyte composition, for POAP thicknesses higher than 0.40 mC cm^{-2}.
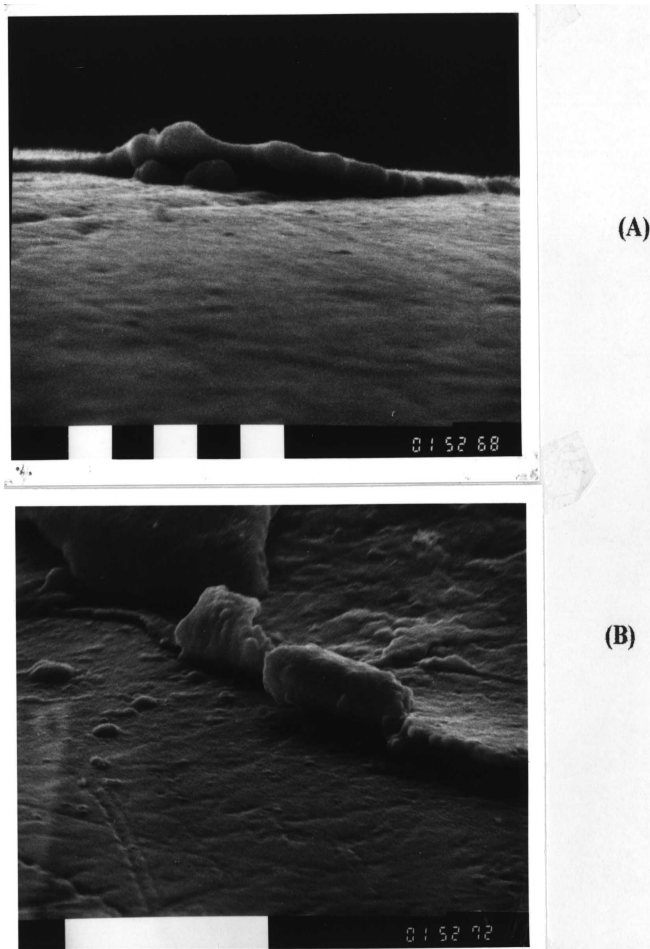
With regard to practical uses of POAP, the crucial effect of the polymer on the enhancement of Pt microparticle efficiency towards the catalytic oxidation of methanol has been reported [16]. It was found that for POAP films that are thick enough (> 0.5 µm), the peak current for the oxidation of methanol becomes independent of the polymer thickness, whereas for lower values, the percent of anodic current decrease is lower as the POAP thickness increases (Fig. **10** was taken from Ref. [16]). This dependence shows the predominant effect of the electrode matrix nature over the effect of the polymer film at low POAP thickness, during the electrocatalytic oxidation of methanol. That is, the effect of the POAP film on the enhancement of the catalytic current appears when the electrode surface is thoroughly covered by POAP, and methanol cannot reach the electrode matrix. Even though we employ neither methanol as adsorbate to study its interaction on a gold surface due to its low adsorbability on gold nor POAP films thick enough as in [16] (0.1 µm - 0.7 µm), our results about POAP thickness seem to be qualitatively in agreement with the observation reported in [16]. That is, we found that specific adsorption of different species at a gold film surface was only possible when the gold surface was partially coated with POAP. However, when the gold film surface was totally coated with POAP, the resistance changes observed seem to be only related to the redox transformation of POAP. On the other hand, it has been suggested that an external electrolyte contacting a polymer film can be incorporated into the polymer phase, thereby influencing the dynamics of the electrochemical process occurring within the film and at the film|electrode interface. Thus, in open structures exhibited by thick POAP films (Fig. **8** (lower image)) that totally cover the gold film surface, there would be enough room for the electrolyte solu-
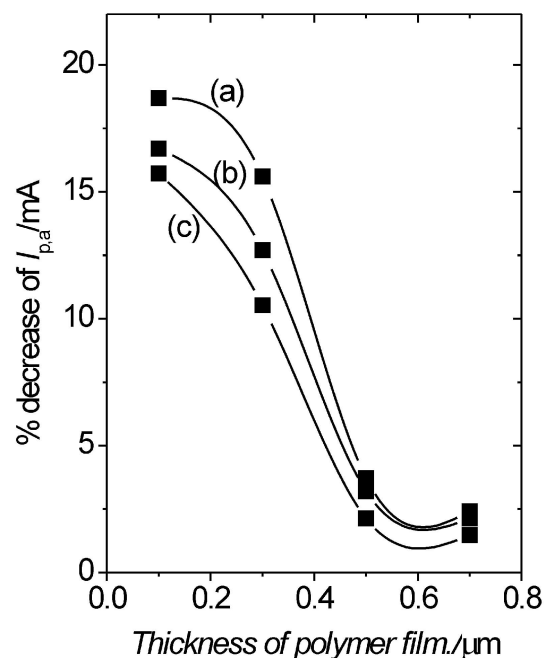

Fig. (9). SEM images of different POAP films detached from the same gold film indicated in Fig. (**8**). POAP thickness, ϕ_p: (upper image) 0.42 mC cm^{-2}; (lower image) 1.5 mC cm^{-2}. The white stick below the lower image: 5 µm x 5000. The white stick below the upper image: 1 µm x 7000.

Fig. (10). Plot of the anodic peak current decrease as a function of the polymer film thickness for: (**a**) glassy carbon/poly(*o*-aminophenol)/Pt electrode; (**b**) glassy carbon/poly(oaminophenol)/Pt-Ru electrode; (**c**) glassy carbon/poly(*o*-aminophenol)/Pt-Sn electrode. Solution: 0.10 M HClO$_4$ + 0.10 M CH$_4$OH. Pt and Pt alloy loading, 0.1 mg cm^{-2} [16].

tion to be incorporated into the void space of the polymer. Under these conditions, the diffusion of inner electrolyte into the polymer phase would allow an easier transport of electroactive species across the film. On the contrary, compact structures such as those shown by thin films (Fig. **8**, center image) would hinder the incorporation of electrolyte solution into the polymer phase, making the transport of species into the polymer phase more difficult. The effect of incorporating an electrolyte into the open structure of a thick POAP film could explain the higher efficiency of very thick POAP films in the catalytic oxidation of methanol as compared with a thin one.

POAP has also been employed as material to build amperometric glucose biosensors [13]. In this application, POAP acts as a barrier to protect the base electrode from fouling and then, the effects of interferents are decreased significantly due to selective permeability of the polymer film. However, when the influence of experimental variables such as film thickness on the response characteristic of biosensors are analyzed, it is found that thick POAP films show a long response time and low sensitivity. On the contrary, thin POAP films (15 cycles of potential scan during electropolymerization) exhibit maximum values of the current responses but they are not permselective enough to avoid the effect of interferents. Again, in agreement with these observations, our study would indicate that the membrane properties of a POAP film against ion adsorption at a gold surface become/are more effective when a thick POAP is used. However, it is evident that in the construction of a sensor a balance between sensitivity towards the detection substance and blockage towards interferents should be taken into account.

5. CONCLUSIONS

Poly(o-aminophenol) films of different thicknesses between 0.06 and 1.5 mC cm^{-2} were supported on a thin gold film whose thickness was of the order of the mean free path of conduction electrons of gold. This experimental arrangement allows one to study the electrochemical processes occurring on these modified electrodes by simultaneously employing the Surface Resistance technique and Cyclic Voltammetry. For thin poly(o-aminophenol) films a dependence of the gold film resistance on the external electrolyte composition was observed. This observation seems to indicate the existence of a competition, at the gold film surface, between the redox process of the polymer and adsorption of different species contained in the electrolyte. This observation reflects the discontinuous character of polymer thicknesses lower than 0.4 mC cm^{-2}. For polymer thicknesses higher than 0.4 mC cm^{-2}, the gold film resistance becomes independent of both the external electrolyte composition and poly(o-aminophenol) film thickness, and only depends on the redox response of the polymer layer. Thus, a polymer thickness higher than 0.4 mC cm^{-2} seems to be compact enough to prevent the interaction of the species contained in the supporting electrolyte with the gold film surface. Even when in practical applications of poly(o-aminophenol) more complex systems (o-aminophenol copolymerized with other substances on a glassy carbon electrode and further immobilization of macromolecules into the polymer matrix, a glassy carbon electrode modified by a thin poly(o-aminophenol) film containing dispersed platinum and platinum alloy mi-

croparticles, etc.) are employed as compared with that used in this work (poly(o-aminophenol) film gold film interface), the author thinks that the conclusions from this work can be useful for understanding the electrochemical performance of sensors and catalysts based on poly(o-aminophenol).

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