

SURFACE RESISTANCE STUDY OF THE DIFFERENT INTERACTIONS OF ClO_4^- , SO_4^{2-} , $\text{C}_6\text{H}_5\text{SO}_3^-$ AND Cu(II) WITH A GOLD SURFACE PARTIALLY BLOCKED WITH POLY(*O*-AMINOPHENOL)

Tucceri, R.

Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA)
Facultad de Ciencias Exactas, Universidad Nacional de La Plata,
Sucursal 4, Casilla de Correo 16, (B1906ZAA), La Plata, Argentina.

Fax: +54 221 425-4642, E-mail: rtuce@inifta.unlp.edu.ar

Received November 8th, 2006. In final form December 28th, 2006

Abstract

In this work is demonstrated that the Surface Resistance (SR) technique can be applied to study the different interactions of anions, such as, perchlorate, sulphate and benzenesulphonate and also a cation as Cu(II), with a gold film surface, even when the metal film surface is partially blocked with an electroactive polymer film. The electroactive polymer poly(o-aminophenol) (POAP) was employed to cover the surface of the gold film electrode. Resistometric changes were detected even after the metal surface was completely covered with the polymer. Dependence of the resistance change on the external electrolyte composition for polymer thicknesses lower than 0.25 mC cm^{-2} was attributed to a competition, at the gold film surface, between the redox process of the polymer and adsorption of different species in the electrolyte. This result points to a discontinuous character of the polymer for thicknesses lower than 0.25 mC cm^{-2} at the metal/polymer interface. For polymer thicknesses higher than 0.8 mC cm^{-2} , the resistometric response becomes independent of both the external electrolyte composition and the polymer thickness. Thus, polymer thicknesses higher than 0.8 mC cm^{-2} seem to be compact enough at the metal/polymer interface to prevent the interaction of species in the supporting electrolyte with the gold film surface. However, the resistometric changes observed, were attributed to the redox conversion of the polymer. In this connection, the redox conversion of POAP from amine to imine groups leads to an increase of the gold film resistance. This increase was explained as a transition from specular to diffuse scattering of the conduction electrons of gold at the gold/POAP interface due to a less compact distribution of oxidised sites (imine) as compared with those of the reduced centers (amine).

Resumen

En este trabajo se demuestra que la técnica de medida de la Resistencia Superficial (RS) puede ser empleada para estudiar los diferentes tipos de interacción de aniones como perclorato, sulfato y bencensulfonato y del catión Cu(II), con la superficie de un film de oro, aún cuando esta superficie esté parcialmente cubierta con una película de un polímero

electroactivo. Poli(o-aminofenol) (POAP) fue empleado como polímero electroactivo para cubrir la superficie de la película de oro. Cambios de resistencia superficial son observados, aún cuando la película de POAP que cubre la película de oro sea altamente compacta. Para espesores de polímero menores que $0,25 \text{ mC cm}^{-2}$, la variación de la resistencia con la composición del electrolito fue atribuida a un proceso competitivo entre la adsorción superficial de especies contenidas en el electrolito y la propia reacción redox del material polimérico. Esto reflejaría el carácter discontinuo de una película polimérica delgada. Para espesores de polímero mayores que $0,8 \text{ mC cm}^{-2}$, la respuesta resistométrica resulta independiente de la composición del electrolito externo y del espesor del polímero. Así, para espesores de polímero mayores que $0,8 \text{ mC cm}^{-2}$, las películas de POAP parecen ser suficientemente compactas como para prevenir la interacción directa de las especies contenidas en el electrolito y la superficie de la película de oro. Sin embargo, la variación resistométrica, aún detectada, fue atribuida a la propia conversión redox del POAP. En este sentido, es sabido que la reacción redox del POAP implica la conversión de grupos amino a imino, lo que conduce a un incremento de la resistencia de la película de oro. Este aumento de resistencia es explicado sobre la base de una transición entre una dispersión electrónica especular a difusa en la interfase oro/POAP, debido a una distribución menos compacta de los sitios redox oxidados (grupos imino) del POAP comparada con la distribución de los centros reducidos (amino).

Introduction

The surface resistance (SR) technique is very sensitive to the surface scattering of the conduction electrons caused by adsorbed species on a thin film electrode [1,2]. The technique was used to study different electrode processes [1]. In [1] is documented the most significant advances that have been made on both, experimental and theoretical aspects of the SR technique applied to electrochemical research until 2003. More recently, measurements of the electrical resistivity of monolayers and bilayers of alkanethiols [3] and the conductance of a single-molecule of a dithiolated aniline trimer [4] have been reported.

In [1] it was reported the ability of the SR technique to detect resistance changes of a gold thin film electrode during the redox conversion of an electroactive polymer deposited on its surface. In this connection, in [5] it was proved that SR can be employed to detect adsorption of species of different charge, positive (Sn(II)) and negative (Fe(CN)_6^{4-}) and the adsorption of neutral species (hydroquinone), on a metal surface covered with poly(o-aminophenol). In the present work, the use of SR was extended to analyse the adsorption of anions of different adsorbability, such as, perchlorate, sulphate and benzenesulphonate and a cation, Cu(II) , on a gold surface partially covered with POAP. The cation seems to be interesting because the ability of POAP to act as sensor of Cu(II) , was recently reported. Poly(o-aminophenol) (POAP) was chosen as the electroactive polymer because it was proved [6] that while thin POAP films only cover partially a gold surface, thick POAP films (thickness $> 50 \text{ nm}$) form a compact polymer layer on a gold surface, in such a way that porosity effects are not too high. By using electrolytes containing species with different degree of adsorbability on the gold surface, in this work is demonstrated that resistometric measurements can be used to detect structural differences at the metal|polymer interface dependent on the polymer thickness. On the basis of well-known redox properties of POAP [7-17], an interpretation of the SR changes, when the gold film is completely covered by a thick POAP films, is suggested. In this sense, as the surface resistance technique may be considered as a non-traditional approach in the study of the electrochemistry of polymers,

important additional information about the redox conversions on POAP at the metal|polymer interface is expected to be given in this work. Also, the study of anion and cation interactions on the gold film surface partially covered by POAP could be important in practical applications of this polymer, because the membrane properties exhibited by POAP have been successfully exploited [18-20] and also, the opportunity to use POAP as a cation sensor was described in recent works [21,22].

Experimental

With regard to the experimental arrangement used in this work, different POAP films were deposited on a thin gold film whose thickness (ϕ_m) was of the order of the mean free path of the conduction electrons of gold. By employing a thin gold film as base electrode one can apply both, voltammetry and the surface resistance to enquire about changes in the electronic properties at the gold film|polymer film interface during both adsorption and redox conversion of the polymer. Two external variables, the electrolyte composition contacting the polymer film and the polymer thickness, ϕ_p , were changed.

The gold film electrodes

Gold thin film electrodes of constant thickness $\phi_m \sim 30$ nm were prepared by vacuum evaporation as it was described previously [23]. These gold films are polycrystalline with crystallite sizes between 0.01 and 0.1 μm [24]. Samples were inserted into an electrochemical cell similar to that showed in a previous paper [25] and employed as working electrodes. An electrode area of 0.56 cm^2 was exposed to the solution. These electrodes exhibit initial resistance values of $R \sim 10$ 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 polarising the electrode ensemble through the central contact [26]. The resistance change obtained in this way [25] was recorded as a function of the potential ($\Delta R/R-E$) along with the voltammetric response ($j-E$). The experimental set-up for simultaneous voltammetric and surface conductivity measurements on thin film electrodes has been described in detail previously [23,26]. The effect of different anions on the resistometric response of gold was studied from 0.4 M NaClO_4 + 0.1 M HClO_4 , 0.4 M Na_2SO_4 + 0.1 M H_2SO_4 and 0.4 M sodium benzenesulphonate + 0.1 M benzenesulphonic acid solutions, respectively. The effect of a cation such as Cu(II), able to be deposited on gold under *upd* conditions, was studied from a 0.1 M HClO_4 + 10^{-4} M $\text{Cu}(\text{ClO}_4)_2$ solution.

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 orthoaminophenol + 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 $\nu = 0.05$ V s^{-1} . These experimental conditions lead to adherent POAP films on the gold film surface, mechanically stables and with a reproducible electrochemical response [7]. The POAP thickness was increased by increasing the number of potential cycles in the last solution containing the monomer. In order

to obtain a measure of the polymer thickness, these POAP coated gold film electrodes were then rinsed and transferred to the supporting electrolyte solution (0.4 M NaClO₄ + 0.1 M HClO₄). Then, the voltammetric reduction charge Q_{Red} in this last solution was determined by integrating the cathodic current of the voltammetric response between -0.25 V and 0.5 V ($v = 0.05 \text{ V s}^{-1}$) [27]. After this, Q_{Red} was considered as representative of the polymer thickness. Five polymer thickness Q_{Red} ($\sim 0.12, 0.22, 0.42, 0.9$ and 1.5 mC cm^{-2}), respectively, were employed. Many workers have correlated, the charge obtained for this type of polymers from the integration of the voltammetric profile to the ellipsometric thickness [27-30]. Although this procedure is reasonable within an order of magnitude, the ellipsometric thickness is usually obtained under the assumption of an homogeneous film, that is, averaging the optical film properties across its thickness. As our resistometric data evidence heterogeneity of thin POAP films ($Q_{\text{Red}} < 0.25 \text{ mC cm}^{-2}$) in the presence of different electrolytes (see below), in this work the voltammetric charge is quoted, which should be related, although not directly, to the polymer film thickness. According to a previous work [27], the Q_{Red} values above indicated, would correspond to ϕ_p values around 2, 5, 12, 22 and 40 nm, respectively. With these POAP coated gold film electrodes resistometric responses were recorded (separately for each ϕ_p value) within the potential range -0.2 V and 0.5 V at a scan rate $v = 0.01 \text{ V s}^{-1}$ in solutions containing ClO₄⁻, SO₄²⁻, and benzenesulphonate (C₆H₅SO₃⁻ = BS) anions, respectively. $\Delta R/R$ changes were also obtained in the presence of a Cu(II) solution. Before recording these responses, the POAP coated gold electrodes were cycled in the different electrolytes for at least 1 h.

Apparatus, chemical and solutions

APAR 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 resistometric measurements. A X-Y₁-Y₂ Hewlett- Packard Model 7046 B plotter was used for simultaneous records of the $\Delta R/R-E$ and $j-E$ responses.

AR grade chemical were used throughout. *o*-Aminophenol (Fluka) was purified as described elsewhere [7]. The solutions were prepared with purified water using a Millipore Milli-Q system. NaClO₄, HClO₄, H₂SO₄, Na₂SO₄, benzenesulphonic acid, sodium benzenesulphonate and Cu(ClO₄)₂ (Merck, ar grade) were used without further purification.

Results and discussion

Electronic transport in thin metal films

Electronic transport in thin metal films 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 of the same structure as the metal film and the ρ_f/ρ_m ratio decreases with increasing the 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. To account for the size effect a theory was postulated by Fuchs [31] and Sondheimer [32]. The exact expression for the dependence of the film resistivity, ρ_f , as a function of ϕ_m is complicated. However, it can be reduced to a limiting form when $\phi_m/l_m \geq 1$:

$$\rho_f / \rho_m = 1 + (3/8) (1-r) l_m / \phi_m \quad (1)$$

In Eq. (1), r is the specularity parameter [32]. 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 way to exhibit a specularity parameter near 1 (a surface with a smooth mirror-like finish which is free of defects). However, this parameter, which is also interpreted as the fraction of the surface which specularly reflects electrons, depends on the quality of the metal film surface, that is, on the method of preparation of the metal film [33]. 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 the surface topography and the presence of surface defects. All these imperfections should lead to experimental r values lower than 1.

Besides the factors above mentioned, if foreign entities are present on the film surface, the translational symmetry parallel to the interface changes and additional scattering of the conduction electrons occurs. This 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 Eq. (1). Assuming that the specularity, r , is the principal parameter influenced by the surface concentration of foreign scattering centres at the film surface Γ_{surf} , differentiation of Eq. (1) leads to the relationship:

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

On the assumption that the increase of Γ_{surf} increases the diffuse scattering of the electrons, $\Delta r = -k \Gamma_{\text{surf}}$, 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:

$$\Delta R = -3/8 G (\rho_m l_m / \phi_m^2) \Delta r \quad (3)$$

In the Wissmann's interpretation [34] 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 centres at the surface, N_a as:

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

By comparing Eqs (2) and (4), it is evident that a Δr decrease can be associated to an increase in σ_a .

The gold film|electrolyte interface

Fig. 1 shows $\Delta R/R-E$ responses of a 30 nm thick gold film contacting solutions which contain ClO_4^- , SO_4^{2-} and BS anions. 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 [35]. However, different resistometric changes in the presence of anions capable of acting 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 (Eq. (4)). In this connection, while the geometrical dimension of the BS anion lying flat on a plane is about 0.54 nm^2 [36] that of sulphate is around 0.18 nm^2 [37]. Besides, aromatic sulphonate anions exhibit distinguishable charged and non-charged parts (the sulphonate group and the benzene ring) as compared with the sulphate 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 [36]. Then, the sequence of $\Delta R/R$ changes ($\text{ClO}_4^- < \text{SO}_4^{2-} < \text{BS}$) observed in Fig. 1 for the three different anions can be considered as representative of a sequence of adsorabilities of these anions on the gold film electrode [23].

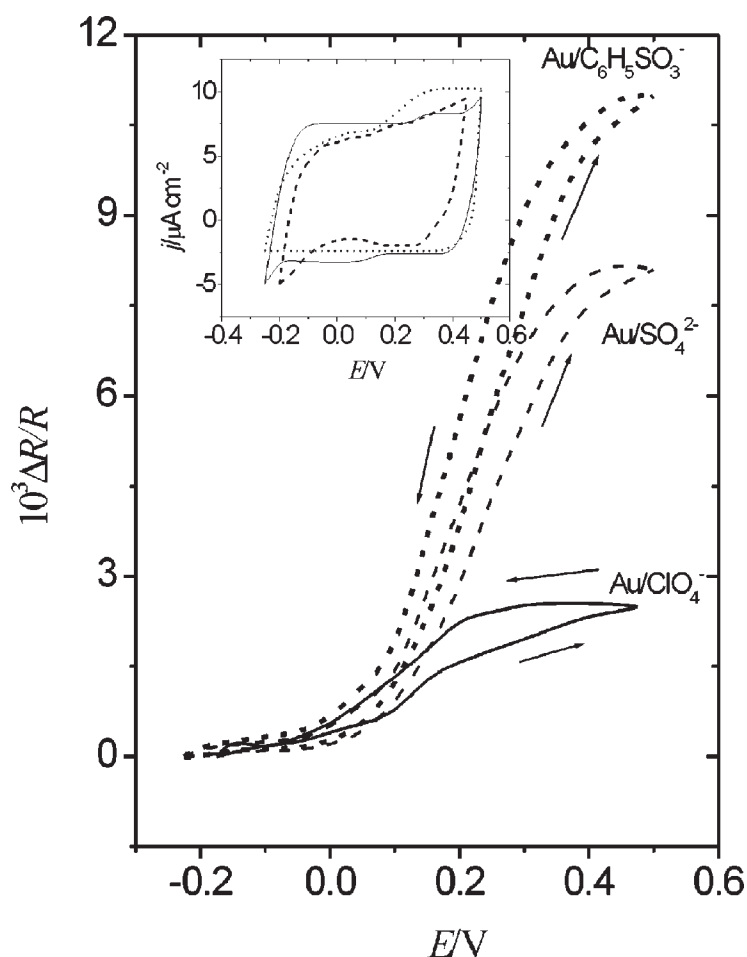


Figure 1. $\Delta R/R$ vs. E responses of a gold film electrode ($\phi_m = 30 \text{ nm}$) contacting different electrolytes: (—) $0.1 \text{ M HClO}_4 + 0.4 \text{ M NaClO}_4$; (---) $0.4 \text{ M Na}_2\text{SO}_4 + 0.1 \text{ M H}_2\text{SO}_4$; and (- - -) 0.4 M sodium benzenesulphonate + 0.1 M benzenesulphonic acid. $\nu = 0.01 \text{ V s}^{-1}$.
Inset: the corresponding voltammograms.

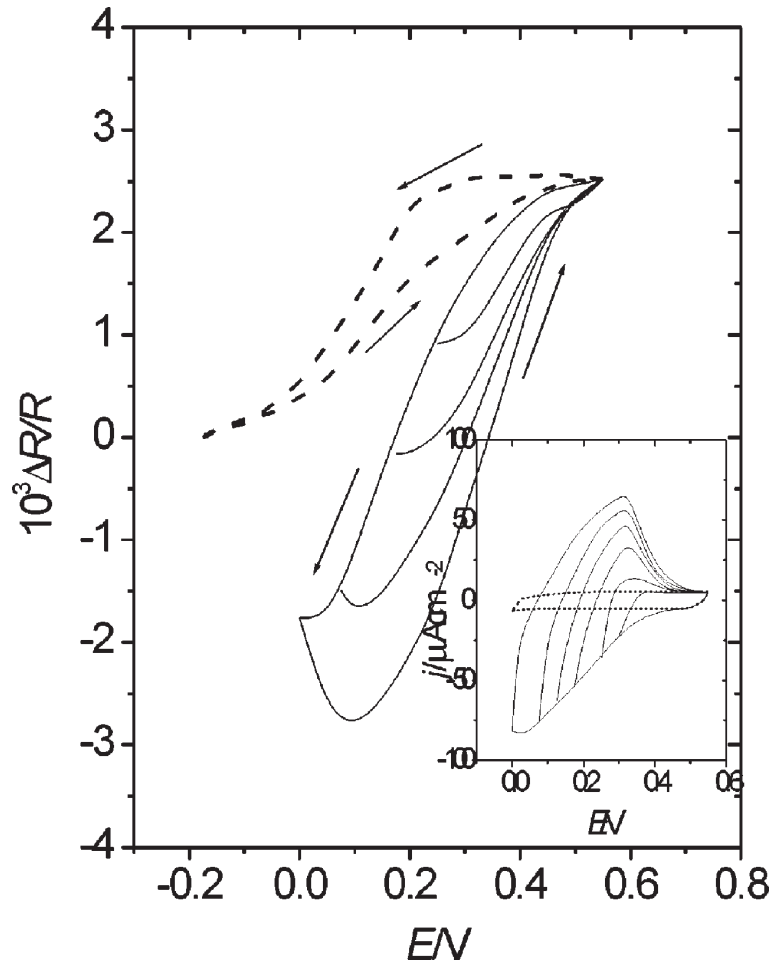


Figure 2. (—) $\Delta R/R$ vs. E response of a gold film electrode ($\phi_m = 30$ nm) contacting a 0.1 M $\text{HClO}_4 + 10^{-4}$ M $\text{Cu}(\text{ClO}_4)_2$ solution; (---) $\Delta R/R$ vs. E response for the same gold film in the sole presence of the supporting electrolyte: 0.1 M HClO_4 , $\nu = 0.01$ V s $^{-1}$.

Inset: the corresponding voltammetric responses. In the presence of $\text{Cu}(\text{II})$ the potential limit was gradually extended from $E = 0.5$ V to $E = 0.0$ V.

Fig. 2 shows the resistometric response corresponding to a 30 nm thick gold film electrode contacting a $\text{Cu}(\text{II})$ solution when the potential is negatively decreased from $E = 0.55$ V. The *upd-ups* processes of a copper monolayer on gold [38] occur within the potential range 0.0 V $< E < 0.55$ V/SCE. At $E = 0.55$ V it is assumed that copper monolayer is completely desorbed from the gold surface. Then, in this case a potential positive enough, such as $E = 0.55$ V, was taken as a reference to assess the change of the resistance with increasing the copper coverage. As the potential is decreased towards the negative direction from $E = 0.55$ V, the copper coverage increases and the gold film resistance decreases. For $E < 0.0$ V, bulk copper deposition occurs [38]. Resistance decrease during copper *upd* process on gold was also observed by Hansen [39] and Rath [40]. This decrease suggests that the copper adlayer on the gold surface is more densely packed than the gold surface itself and then it could reflect electrons more specularly than the proper gold film surface.

The gold film surface covered with POAP

Simultaneous $\Delta R/R-E$ and $j-E$ responses for the 30 nm thick gold film coated with POAP films of different thickness were recorded in the electrolytes mentioned (ClO_4^- , SO_4^{2-} , BS and Cu(II)). $j-E$ responses at a given scan rate (ν) and POAP thickness in the presence of the different anions do not show big differences. This is shown in Fig. 3 for $Q_{\text{Red}} = 1.5 \text{ mC cm}^{-2}$ thick POAP film. In the inset to Fig. 3, the corresponding response for a thinner POAP film ($Q_{\text{Red}} = 0.22 \text{ mC cm}^{-2}$) is also shown. $\Delta R/R-E$ responses for the gold film coated with a 0.12 mC cm^{-2} thick POAP film, in the presence of the different electrolytes, are compared in Fig. 4. Fig. 5 shows resistometric responses for other two thicker POAP films deposited on the same gold film (curves (a), $Q_{\text{Red}} = 0.22 \text{ mC cm}^{-2}$ and curves (b), $Q_{\text{Red}} = 1.5 \text{ mC cm}^{-2}$). In all cases $\Delta R/R$ changes were referred to the potential $E = -0.2 \text{ V}$, where POAP is in its reduced state. Two facts can be remarked by comparing resistometric responses of a gold film free of polymer (Fig. 1) with $\Delta R/R$ changes of the same gold film coated with different POAP thicknesses (Figs 4 and 5). Firstly, the magnitude of the $\Delta R/R$ change, for a given anion, is strongly attenuated by the presence of the POAP film on the gold surface, when compared with the corresponding $\Delta R/R$ change of the gold film free of polymer. The attenuation is more pronounced as ϕ_p increases. In this connection, considering the adsorption of BS anions on the gold film surface free of POAP (Fig. 1), the $\Delta R/R$ change decreases nearly 90 per cent by the presence of a 1.5 mC cm^{-2} thick POAP film on the gold surface (Fig. 5). Secondly, while distinguishable $\Delta R/R$ changes are even obtained for thin POAP films ($Q_{\text{Red}} = 0.12$ and 0.22 mC cm^{-2}) contacting the different anions, for the 1.5 mC cm^{-2} thick POAP film the $\Delta R/R$ change becomes independent of the type anion present in the external solution. Both facts are represented in Fig. 6, where $\Delta R/R-Q_{\text{Red}}$ dependence at $E = 0.5 \text{ V}$ (POAP in the oxidised state) is shown. As it can be seen from Fig. 6, for $Q_{\text{Red}} > 0.8 \text{ mC cm}^{-2}$, the $\Delta R/R$ change becomes independent of both the POAP thickness and the anion contacting the polymer. However, it is also interesting to note that for $Q_{\text{Red}} < 0.25 \text{ mC cm}^{-2}$ (see also Figs 4 and 5) even when $\Delta R/R$ changes for the different anions are attenuated as compared with the gold film surface free of polymer, they follow the same trend for anion adsorption on gold, that is, $\text{ClO}_4^- < \text{SO}_4^{2-} < \text{BS}$. Similar effects of the external electrolyte on the resistometric response of gold films coated with very thin POAP films were observed in the presence of the Cu(II) cation. Fig. 7 shows the $\Delta R/R-E$ response (curve (a)) corresponding to a 30 nm thick gold film contacting a Cu(II) solution within the potential range $0.0 \text{ V} < E < 0.55 \text{ V}$ (see also Fig. 2). A strong attenuation of the $\Delta R/R-E$ response for the copper *upd* process on the gold film surface is observed when it is coated with POAP films (curves (b)-(d) in Fig. 7). In this case the oxidised state of POAP ($E = 0.55 \text{ V}$) was taken as reference to assess the resistance decrease in going towards the negative potential direction. As it can be seen, the $\Delta R-E$ response of the 1.5 mC cm^{-2} thick POAP film contacting a Cu(II) solution (curve (d) in Fig. 7) nearly coincides with the curve (e) within the potential range $0.0 \text{ V} < E < 0.5 \text{ V}$. The curve (e) in Fig. 7 is the curve (b) of Fig. 5 corresponding to perchlorate anion. Then, again, it can be conclude that the $\Delta R/R-E$ response of a gold film coated with a thick POAP film is unique and independent of the external solution contacting the polymer film.

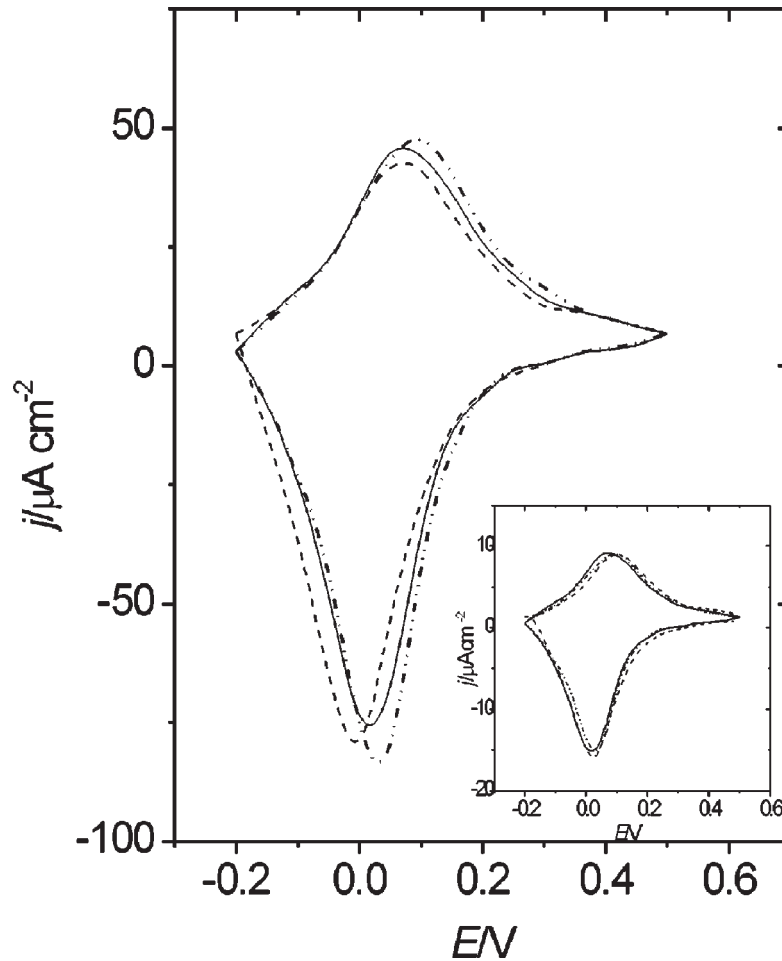


Figure 3. j vs. E responses for a gold film ($\phi_m = 30$ nm) coated with a 1.5 mC cm^{-2} thick POAP film. Electrolytes: (—) $0.1 \text{ M HClO}_4 + 0.4 \text{ M NaClO}_4$; (- - -) $0.4 \text{ M Na}_2\text{SO}_4 + 0.1 \text{ M H}_2\text{SO}_4$; and (- .. - ..) 0.4 M sodium benzenesulphonate + 0.1 M benzenesulphonic acid. $\nu = 0.01 \text{ V s}^{-1}$.

Inset: j vs. E responses for the same gold film coated with a 0.22 mC cm^{-2} POAP film.

It is established, in accordance with the theory [41], that the density of the polymer layer decreases with film thickness, *i.e.*, from the metal surface to the polymer|solution interface. Inner parts of polymer films could have a different structure than their external counterparts. In this connection, during the synthesis of polymer films [42], two or more stages of the polymerisation process are usually distinguished: first, islands of the polymer are formed at the substrate surface, then a continuous film, compact (non-porous), is formed by fusion of these islands, and then further growth takes place above this compact layer giving rise to the external, porous part, of the film.

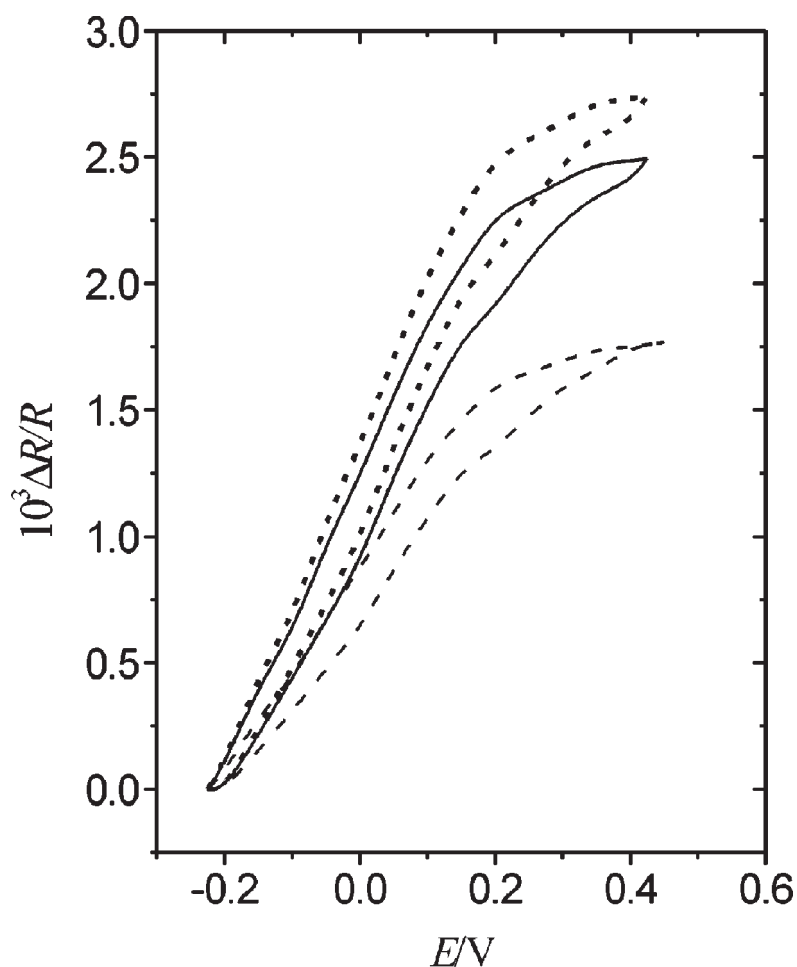


Figure 4. $\Delta R/R$ vs. E responses of a gold film electrode ($\phi_m = 30$ nm) coated with a 0.12 mC cm^{-2} thick POAP film in the presence of different electrolytes: (---) 0.1 M HClO_4 + 0.4 M NaClO_4 ; (—) 0.4 M Na_2SO_4 + 0.1 M H_2SO_4 ; and (- - -) 0.4 M sodium benzenesulphonate + 0.1 M benzenesulphonic acid. $\nu = 0.01$ Vs^{-1} .

Under these considerations, a continuous polymer film should only be formed after the end of the first stage of the polymerisation process. As was indicated, the measuring of the surface resistance only detects processes occurring at the metal film surface, which cause electron scattering. Resistance measurements applied to gold film coated with different POAP films seem to indicate that polymer coverages lower than 0.25 mC cm^{-2} are not sufficiently compact at the metallpolymer interface to prevent the specific adsorption of anions and cations proceeding from the external electrolyte on the gold film surface (Figs 4-7). It is possible that at low POAP thickness (< 0.25 mC cm^{-2}) either polymer islands or polymer layers with imperfections exist on the gold surface.

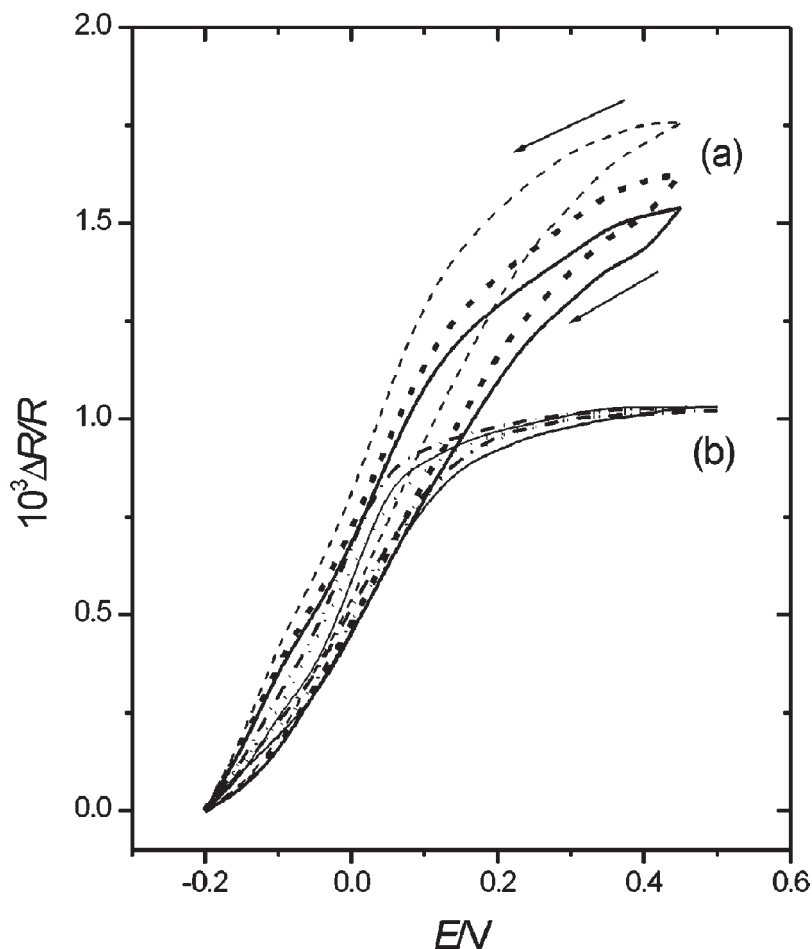


Figure 5. $\Delta R/R$ vs. E responses of a gold film electrode ($\phi_m = 30$ nm) coated with (a) a 0.22 mC cm^{-2} thick POAP film and (b) a 1.5 mC cm^{-2} thick POAP film, in the presence of the same electrolytes indicated in Fig. 4: (—) $0.1 \text{ M HClO}_4 + 0.4 \text{ M NaClO}_4$; (- - -) $0.4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

In this sense, high permeability of some polymer films [43] facilitating the transport of species from the solution in contact with the polymer to the metal substrate have been attributed to dispersed polymer structures with imperfections (*e.g.* pinholes and large channels) with dimensions large compared to those of species present in solution. However, as the amount of polymer increases ($Q_{\text{red}} > 0.8 \text{ mC cm}^{-2}$) the gold surface should be covered by a polymer film compact enough (fusion of islands or absence of imperfections) that the resistometric response (curve (b) in Fig. 5 and curve (e) in Fig. 7) can be considered due to processes at the metal|polymer interface free of effects related to the interaction of species proceeding from the external electrolyte with the metal surface. In the last case (thick POAP films), the change of the gold film resistance in going from the reduced state of POAP to the oxidised one, can be explained only in terms of the generation of electronic entities at the polymer chains near the electrode surface, which occurs by electron transfer across the polymer|metal interface. In this connection, the redox switching of

POAP was interpreted in terms of the oxidation of the amino groups to imine [13]. Thus, it is not unreasonable to expect that the imine sites act themselves as different scattering centres compared with amine sites, increasing in this way the diffuse reflection (increase of $\Delta R/R$) of conduction electrons on the gold surface during POAP oxidation.

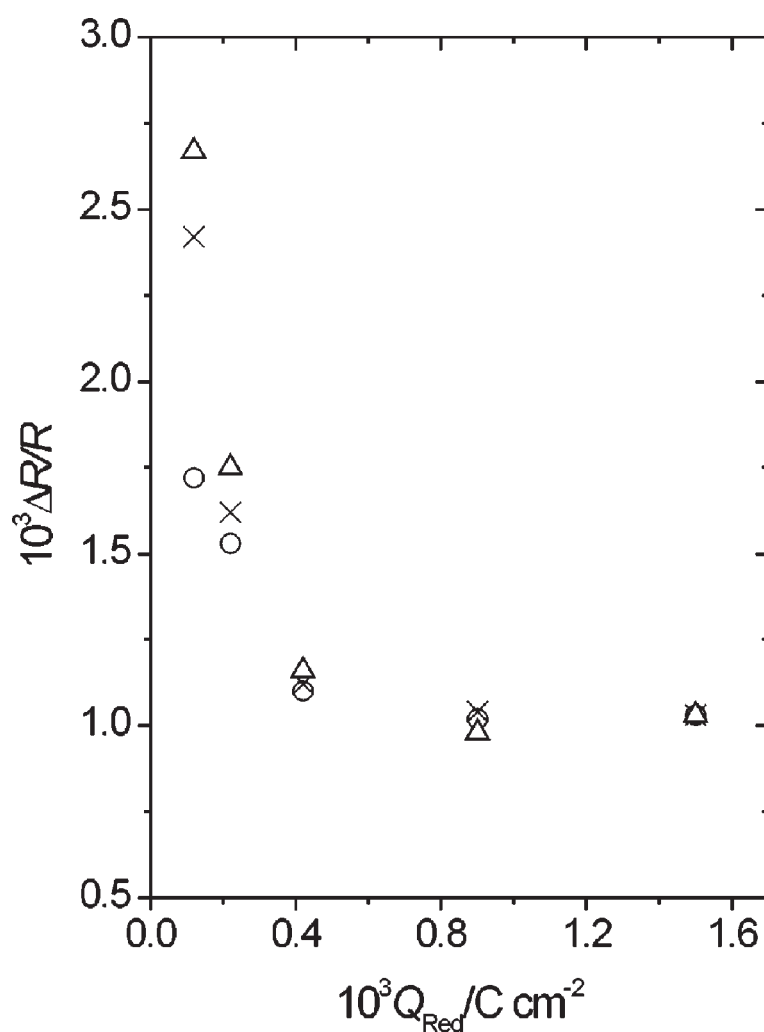


Figure 6. $\Delta R/R$ vs. Q_{Red} dependence at $E = 0.5$ V (POAP in the oxidised state). Symbols represent different anions: (Δ) BS; (X) Sulphate; (O) perchlorate.

The increase of $\Delta R/R$ during POAP oxidation could also be explained in terms of an interfacial distribution of scatterers (imine sites) in the oxidised state with a constant spacing among them and larger than that corresponding to amine sites in the reduced state [44]. In this connection, during POAP oxidation only one in four, or five, amine sites are converted to the corresponding imine sites [13], giving rise to gaps which eventually would yield a distribution of oxidised sites less compact than the corresponding distribution of reduced ones. Thus, a distribution of scatterers (oxidised sites) less compact than the distribution of reduced sites should lead to a

more diffuse reflection of conduction electrons at the gold|POAP interface [44], which in turn yields a resistance increase during POAP oxidation.

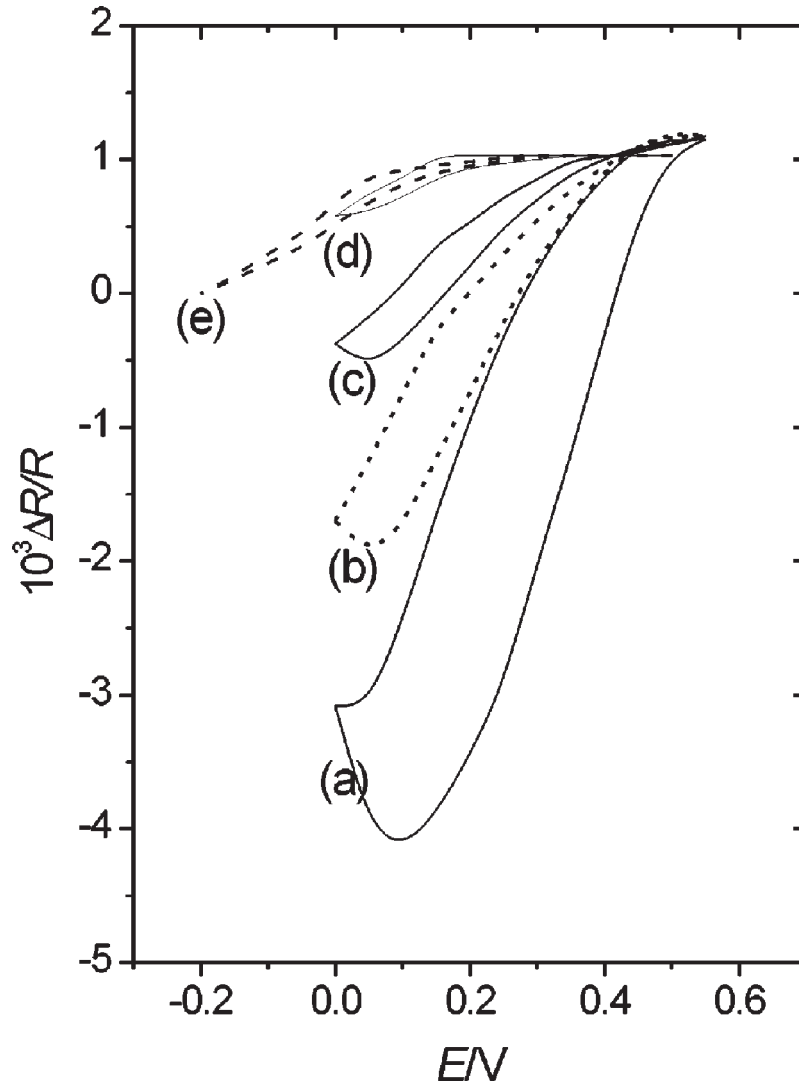


Figure 7. (a) $\Delta R/R$ vs. E response of a gold film electrode ($\phi_m = 30$ nm) contacting a 0.1 M $\text{HClO}_4 + 10^{-4}$ M $\text{Cu}(\text{ClO}_4)_2$ solution; $\Delta R/R$ vs. E responses of the same gold film coated with different thickness of POAP: (b) 0.12 mC cm^{-2} ; (c) 0.22 mC cm^{-2} and (d) 1.5 mC cm^{-2} . Same electrolyte as indicated above. Curve (e) in this figure is curve (b) of Fig. 5 corresponding to perchlorate anion.

Further confirmation about the different reflecting properties of the oxidised 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 [7]. The following values of the anodic and cathodic site interaction parameters were reported for POAP [7], $p_a = -0.55$ M $^{-1}$ and $p_c = -0.18$ M $^{-1}$, respectively. Both are negatives, thus involving a repulsive energy of interaction.

As a higher repulsion is observed between oxidised sites than reduced ones, then a more extended configuration of oxidised sites should be expected than the corresponding distribution of reduced ones. Then, again, it would be expected that the distribution of oxidised 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 for a given thickness (for instance, $R \sim 10$ ohm for $\phi_m = 30$ nm) does not change with POAP deposition, only the relative $\Delta R/R$ value, referred to either the reduced ($E = -0.2$ V) or oxidised ($E = 0.5$ V) state of the polymer, varies with the potential scanning (-0.2 V $< E < 0.5$ V) (see curve (b) in Fig. 5). This should be indicative of a resistometric change only related to an interfacial (metal|polymer) electron dispersion process occurring during oxidation-reduction of the polymer. On the contrary, generation of a non-conducting dead layer (subsurface impurity) during POAP deposition leading to a reduction of the metallic thickness, should lead to an increase of the absolute value of the gold film resistance.

Conclusions

Poly(o-aminophenol) films of different thicknesses between 0.12 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 the conduction electrons of gold. This experimental arrangement allows to study the electrochemical processes occurring on these modified electrodes by employing the surface resistance technique. A dependence of the gold film resistance on the external electrolyte composition was detected during the redox conversion of thin poly(o-aminophenol) films deposited on the gold film surface. This result seems to be indicative of a competition, at the gold film surface, between the redox process of the polymer and the adsorption of different species contained in the electrolyte. This would reflect a discontinuous character of the polymer thickness for values lower than 0.25 mC cm⁻² due to the existence of either polymer islands or polymer layers with imperfections on the gold surface. For polymer thickness higher than 0.8 mC cm⁻², the gold film resistance becomes independent of the external electrolyte composition and only depends on the degree of oxidation of the polymer film. This response of thick polymer films was assigned to the proper redox transformation of the polymer, free of adsorption effects of species proceeding from the electrolyte solution on the gold film surface. Thus, polymer thickness higher than 0.8 mC cm⁻² seem to be compact enough (fusion of islands) at the metal|polymer interface to prevent the interaction of the species contained in the supporting electrolyte with the gold film surface.

Acknowledgements

The author gratefully acknowledges CONICET, and the Facultad de Ciencias Exactas, La Plata National University, Argentina, for financial support.

References

- [1] Tucceri, R. I., *Surface Science Reports*, **2004**, 56, 85.
- [2] Tucceri, R. I.; Posadas, D., *Curr. Topics Electrochem.* **1994**, 3, 423.
- [3] York, R.L.; Nacionales, D.; Slowinsky, K., *Chemical Physics*, **2005**, 319, 235.
- [4] Chen, F.; Nuckolls, C.; Lindsay, S., *Chemical Physics*, **2006**, 324, 236.
- [5] Tucceri, R.I., *J. Electroanal. Chem.*, **2005**, 505, 72.
- [6] Levin, O.; Kondratiev, V.; Malev, V., *Electrochim. Acta*, **2005**, 50, 1573.
- [7] Barbero, C.; Silber, J. J.; Sereno, L.; *J. Electroanal. Chem.* **1990**, 291, 81.
- [8] Kunimura, S.; Ohsaka, T.; Oyama, N.; *Macromolecules* **1988**, 21, 894.
- [9] Jackowska, K.; Bukowska, J.; Kudelski, A.; *J. Electroanal. Chem.* **1993**, 350, 177.
- [10] Jackowska, K.; Bukowska, J.; Kudelski, A.; *Pol. J. Chem.* **1994**, 68, 141.
- [11] Gonçalves, D.; Faría, R. C.; Yonashiro, M.; Bulhões, L. O. S.; *J. Electroanal. Chem.* **2000**, 487, 90.
- [12] Ohsaka, T.; Kunimura, S.; Oyama, N.; *Electrochim. Acta*, **1988**, 33, 639.
- [13] Tucceri, R.I.; Barbero, C.; Silber, J. J.; Sereno, L.; Posadas, D.; *Electrochim. Acta*, **1997**, 42, 919.
- [14] Barbero, C.; Tucceri, R.I.; Posadas, D.; Silber, J. J.; Sereno, L.; *Electrochim. Acta*, **1995**, 40, 1037.
- [15] Rodríguez Nieto, F.J.; Tucceri, R. I.; *J. Electroanal. Chem.* **1996**, 416, 1.
- [16] Komura, T.; Ito, Y.; Yamaguti, T.; Takahashi, K.; *Electrochim. Acta* **1998**, 43, 723.
- [17] Bonfranceschi, A.; Pérez Córdoba, A.; Keunchkarian, S.; Zapata, S.; Tucceri, R.; *J. Electroanal. Chem.* **1999**, 477, 1.
- [18] Valdés García, M. A.; Tuñón Blanco, P.; Ivaska, A.; *Electrochim. Acta* **1998**, 43, 3533.
- [19] Lobo Castañón, J.; Miranda Ordiers, A. J.; López Fonseca, J. M.; Tuñón Blanco, P.; *Anal. Chim. Acta* **1996**, 325, 33.
- [20] Lobo Castañón, J.; Miranda Ordiers, A. J.; Tuñón Blanco, P.; *Anal. Chim. Acta* **1997**, 346, 165.
- [21] Hernández, N.; Ortega, J. M.; Choy, M.; Ortíz, R.; *J. Electroanal. Chem.* **2001**, 515, 123.
- [22] Yano, J.; Kawakami, H.; Yamasaki, S.; Kanno, Y.; *J. Electrochem. Soc.* **2001**, 148, E61-E65.
- [23] Tucceri, R.I.; Posadas, D.; *J. Electroanal. Chem.* **1985**, 191, 387.
- [24] Romeo, F. M.; Tucceri, R.I.; Posadas, D.; *Surf. Sci.* **1988**, 203, 186.
- [25] Tucceri, R. I.; Posadas, D.; *J. Electrochem. Soc.* **1983**, 130, 104.
- [26] Tucceri, R. I.; Posadas, D.; *J. Electrochem. Soc.* **1981**, 128, 1478.
- [27] Barbero, C.; Zerbino, J.; Sereno, L.; Posadas, D.; *Electrochim. Acta* **1987**, 32, 693.
- [28] Rubinstein, I.; Sabatani, E.; Rishpon, J.; *J. Electrochem. Soc.* **1987**, 134, 3078.
- [29] Greszczuk, M.; Poks, P.; *J. Electroanal. Chem.* **1995**, 387, 79.
- [30] Greef, R.; Kalaji, M.; Peter, L. M.; *Faraday Discuss. Chem. Soc.* **1989**, 88, 277.
- [31] Fuchs, K.; *Proc. Camb., Phyl. Soc. Math. Phys. Sci.* **1938**, 34, 100.
- [32] Sondheimer, E. H.; *Adv. Phys* **1952**, 1, 1.
- [33] Schumacher, D. In *Surface Scattering Experiments with Conducting Electrons*; Hohler, G. ed., Springer Tracts in Modern Physics, Vol. 128, Springer, Berlin, **1992**.

- [34] Wissmann, P.; *Z. Physik. Chem.* **1970**, (NF) 71, 294.
- [35] Tucceri, R. I.; Posadas, D.; *J. Electroanal. Chem.*, **1990**, 283, 159.
- [36] Dutkiewicz, E.; Skoluda, P.; *J. Chem.Soc., Faraday Trans.* **1996**, 92, 3763.
- [37] *Tables of Interatomic Distances and Configurations in Molecules and Ions. The Chemical Society; Burlington House, London, 1958.*
- [38] Aramata, A., in: *Modern Aspects of Electrochemistry*; Bockris, J. O. M.; White, R.E.; Conway, B. E. eds, Vol. 31, Plenum Press, New York, **1997**, Ch.4.
- [39] Hansen, W. N.; *Surf. Sci.* **1980**, 101, 109.
- [40] Rath, D. L.; *J. Electroanal. Chem.* **1983**, 150, 521.
- [41] De Genies, P. G.; *Macromolecules* **1981**, 14, 1637.
- [42] Inzelt, G.; Pineri, M.; Schultze, J. W.; Vorotyntsev, M. A.; *Electrochim. Acta* **2000**, 45, 2403.
- [43] Ikeda, T.; Schmehl, R.; Denisevich, P.; Willman, K.; Murray, R. W.; *J. Am. Chem. Soc.* **1982**, 104, 2683.
- [44] Geus, J. W. In *Chemisorption and Reaction on Metallic Films*, Anderson, J. R. ed., vol. 1, Academic Press, London, p. 388, **1971**.