



Surface resistance change during nickel hydroxide phase transformations



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ABSTRACT

Nickel hydroxide undergoes profound structural transformations under prolonged potential cycling in alkaline solutions. In this work, gold film electrodes modified with different nickel hydroxide coverages were subjected to continuous potentiodynamic cycling in alkaline medium, while the simultaneous evolution of voltammetric and surface resistance records was monitored until stable responses were obtained. A surface resistance (SR) increase proportional to the nickel hydroxide coverage was observed at potential values more negative than -0.3 V (vs. SCE), which was attributed to the deposition of nickel adatoms from the reduction of nickel hydroxide layers. This SR change was analysed on the basis of the electron scattering theory, considering that nickel adatoms act as scatterers for the reflection of gold conduction electrons. The nickel adatom layer produced from the reduction of the nickel hydroxide structure formed during the first voltammetric scan potential cycles (<40) exhibits a more specular reflection than that generated after a larger number of potential cycles (>140). As the specularity of a layer for electron scattering can be associated with scatterer compactness, the distance between nickel atoms in the former nickel adatom structure is shorter than that in the last one.

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1. Introduction

Surface resistance (SR) refers to changes in resistivity (or conductivity) of thin metal films (thickness, $\phi_m < 30$ nm) brought about by defects, impurities and carrier concentration in the interfacial region of the exposed face of the material sample, assuming all the bulk effects and other conditions remain unaltered. The use of the SR changes as an alternative method to study the electrochemical interface was reviewed considering both experimental and theoretical aspects [1]. The most important contributions to electrode resistance changes in electrochemistry are: (i) the field effect, related to the application of an electric field that modifies the electrode conductivity; (ii) the size effect, which refers to conductivity changes brought about by changes of the film thickness; and (iii) adsorption effects. With regard to adsorption effects, it has been considered that the resistance of a thin metal film is sensitive to surface processes that affect the specular reflection of conduction electrons at the metal film surface.

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 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 [2] and Sondheimer [3]. 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 $\phi_m/l_m \geq 1$:

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

In Eq. (1), p is the specularity parameter [3]. This parameter represents the probability of an electron being reflected specularly or diffusely at the film surface. The p 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 [4]. 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 p values lower than 1. Besides the size effect, 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 centres for the surface reflection of electrons from the inside of the metal, has been analysed on

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the basis of Eq. (1). Assuming that the specularity, p , is the main parameter influenced by the surface concentration of foreign scattering centres at the film surface, Γ_{surf} , differentiation of Eq. (1) leads to the relationship:

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

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

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

In Eq. (3), $G (= l/w)$ is the relationship between the length, l , and the width, w , of the metal film electrode. Usually, the relative resistance change as a function of potential ($\Delta R/R-E$) is recorded in SR experiments, where R is the initial resistance value of the gold film and depends on the film thickness. $\Delta R/R$ changes around 10^{-5} could be measured (see the [Experimental](#) section).

1.1. Application of the surface resistance technique to study the nickel hydroxide-gold modified electrode

Eq. (3) was employed in previous work [5] to interpret the SR response of a gold film electrode modified with different nickel hydroxide coverages. As a SR increase in going towards the negative potential direction from -0.3 V to -0.5 V proportional to the nickel hydroxide surface coverage, Γ_{Ni} , was observed, the change of the specularity parameter in Eq. (3) was expressed as $\Delta p = -k_0 \Gamma_{\text{Ni}}$, and Eq. (4) (below) was applied.

$$\Delta R = 3/8 G (\rho_m l_m / \phi_m^2) k_0 \Gamma_{\text{Ni}} \quad (4)$$

The parameter k_0 in Eq. (4) is a constant independent of Γ_{Ni} . The surface coverage of the different Au/Ni(OH)₂ modified electrodes was estimated from the stabilized voltammetric responses (>150 potential cycles at 10 mV s^{-1}). The linear dependence of the $\Delta R/\Gamma_{\text{Ni}}$ slope on ϕ_m^{-2} , according to Eq. (4), was also verified. The ΔR increase within the potential region $-0.3 > E > -0.5$ V expressed by Eq. (4) was attributed to the deposition of nickel adatoms from the reduction of nickel hydroxide layers. Although only stabilized voltammetric and resistance responses were analysed in [5], it was observed that both records gradually change with the number of potential cycles before stable profiles are reached. In this work, we analyse the simultaneous evolution of voltammetric and surface resistance records of a nickel hydroxide-gold film modified electrode subjected to prolonged potential cycling with the twofold purpose of extending the application of the SR technique to the study of the structural transformation of an adsorbed layer on gold and obtaining some complementary information to that reported in the literature about the electrochemical modifications of a nickel hydroxide layer during potential cycling by employing a non-traditional technique. To our knowledge, the SR technique has never before been employed to study a structural transformation [1].

2. Experimental

Five gold film electrodes of different thicknesses ($\phi_m = 30$ nm; 24 nm; 18 nm; 14 nm and 10 nm) were synthesized. Rectangular gold films were prepared by vacuum evaporation, as was previously described [5]. The relationship between the length, l , and the width, w , ($G = l/w$) of these gold film electrodes was 25. The electrode area was 0.69 cm^2 . It is well-known that thin metal films obtained by evaporation (low rate of evaporation) exhibit specular surfaces with a relatively low number of defects as compared with a massive metal surface (see

Introduction). Our gold films were prepared at low evaporation rates and they show a specularity parameter (p) near 0.91. Each gold film electrode was conditioned electrochemically by cycling the potential between -0.5 V and 0.6 V for 160 cycles, at a scan rate of 10 mV s^{-1} , in a deoxygenated 0.2 M Na(OH) solution.

Nickel hydroxide was deposited on the gold film electrodes employing the procedure described elsewhere [6], that is, after being subjected, for a different time periods, to a constant potential of -0.5 V in a deoxygenated $0.5 \text{ M Ni(NO}_3)_2$ solution, each one of the gold films was transferred to a deoxygenated 0.2 M Na(OH) solution and cycled between -0.5 V and 0.6 V (vs. SCE) at 10 mV s^{-1} , while both $i-E$ and $\Delta R/R-E$ responses were continuously recorded until stable profiles were achieved (160 cycles). The surface coverage (Γ_{Ni}) of the different Au/Ni(OH)₂ modified electrodes was estimated from the stabilized voltammetric oxidation (or reduction) charge ($Q_{\text{Ni(OH)}_2}$) evaluated in the supporting electrolyte solution (0.2 M NaOH) by using the equation $\Gamma_{\text{Ni}} = Q_{\text{Ni}} / nFA$, where Q_{Ni} is the anodic (or cathodic) voltammetric charge corresponding to the oxidation (or reduction) process, assuming that all the nickel redox sites are electroactive on the voltammetric time scale; F is the Faraday's constant; A is the geometric surface area of the gold electrode; and n is the number of electrons transferred in the Ni (II) \leftrightarrow Ni (III) oxidation (reduction) reaction.

Thus, five series of six nickel hydroxide-coated gold film electrodes each were prepared (see columns 2 to 6 in [Table 1](#)) to study the evolution of CV and SR responses under prolonged potential cycling. The thickness of the five gold films of each series is indicated in the heading of columns 2 to 6 in [Table 1](#). The sequence of the nickel hydroxide surface coverage of each one of the five gold films of each series is listed in column 1 of [Table 1](#). As can be seen, the sequence of Γ_{Ni} values was always the same for each one of the five series. A large-area gold grid was used as counter-electrode in all experiments. All the potentials reported in this work are referred to the SCE. All measurements were performed employing electrolyte solutions previously deoxygenated by N₂ bubbling for 5 h. The reduction of the oxygen content in the electrolyte solution is necessary in order to avoid the interference of the O₂ reduction process in the CV and SR responses at potential values more negative than -0.3 V (SCE).

The experimental set-up for simultaneous voltammetric and SR measurements on thin film electrodes has previously been described in detail [4,7,8]. The electrochemical cell was also the same as that described in [7]. The electrode resistance change was measured employing the three-contact method described earlier [8]. Then, the potential drop along the resistive electrode, together with the polarization current, is measured as a function of the applied potential E . The voltage difference at the extremes of the film is directly proportional to the resistance, and thus to the resistivity of the electrode. The potential drop ΔV was measured with a voltmeter. The output of the voltmeter was compensated for by employing a reference tension. In this way only resistance variations, ΔR (or ΔV potential variations), as a function of the electrode potential, E , are measured. ΔR changes around $10^{-4} \Omega$ could be measured. Usually, the relative resistance change as a function of potential ($\Delta R/R-E$) is recorded in SR experiments, where R is the initial resistance value of the gold film and depends on the film thickness. The R value of the five films of each series is indicated in the heading of columns 2 to 6 of [Table 1](#). The possibility of coupling between the faradaic and measuring currents inside the electrode was taken into account in [8]. It was demonstrated that side effects of the faradaic current passing through the electrode can be neglected when the contacts at the ends of the electrode are symmetrically placed with respect to the central one. Let the distances from the end contacts to the central one be l_1 and l_2 , then, the factor h can be defined as $h = (l_1 - l_2) / l_1$, which takes into account the symmetry of the electrical contacts in a rectangular film. In the present electrode design, $h = 0.003$ results from the l_1 and l_2 values measured with a travelling microscope with a precision of 10^{-4} cm . Thus, despite the high faradaic current passing through the resistive gold film electrode within the potential region

Table 1
Stabilized $\Delta R/R$ value at $E = -0.5$ V of different gold film electrodes modified with different nickel hydroxide surface coverages.

$^a \Gamma_{\text{Ni}}/\text{nmol cm}^{-2}$	$^b 10^3 \Delta R/R$ ($R = 20 \Omega$) Thickness $\phi_m = 30$ nm (Series 1)	$^b 10^3 \Delta R/R$ ($R = 25 \Omega$) Thickness $\phi_m = 24$ nm (Series 2)	$^b 10^3 \Delta R/R$ ($R = 33 \Omega$) Thickness $\phi_m = 18$ nm (Series 3)	$^b 10^3 \Delta R/R$ ($R = 43 \Omega$) Thickness $\phi_m = 14$ nm (Series 4)	$^b 10^3 \Delta R/R$ ($R = 60 \Omega$) Thickness $\phi_m = 10$ nm (Series 5)
0.7	1.53	1.97	2.16	3.21	5.95
1.2	2.65	3.33	4.01	5.67	9.12
1.8	3.74	4.63	5.87	8.14	13.51
2.5	5.53	6.90	9.32	11.87	16.60
3.1	6.01	8.19	10.31	12.81	23.32
6.2	6.23	8.98	10.98	13.50	23.12

^a Different nickel hydroxide surface coverage. The surface coverage was estimated from the stabilized (after 140 cycles) voltammetric oxidation (or reduction) charge (Q) evaluated in the supporting electrolyte solution (0.2 M NaOH) by using the equation $\Gamma_{\text{Ni}} = Q/nFA$, where Q is the anodic (or cathodic) voltammetric charge of the wave centred at about 0.35 V corresponding to the Ni(III) \leftrightarrow Ni(II) oxidation (reduction) process.

^b Stabilized $\Delta R/R$ value (after 140 cycles) at $E = -0.5$ V (SCE) of the gold film electrode whose thickness is indicated in the headings of columns 2 to 6, for each nickel hydroxide surface coverage indicated in column 1. R is the initial resistance value of the gold film free of nickel hydroxide coverage, which depends on the film thickness, ϕ_m .

corresponding to the Ni(II) \leftrightarrow Ni(III) redox process ($0.35 < E < 0.6$ V), simultaneous CV and SR measurements could be taken within the electrode potential range -0.5 V $< E < 0.6$ V.

Voltammetric experiments were performed using a measurement system comprising a PAR model 175 universal programmer, a PAR model 173 potentiostat-galvanostat, and a Philips model 8134 x-y1-y2 recorder. AR grade chemicals were employed throughout. Ni(NO₃)₂ (Fluka) was employed. NaOH (Merck) was used without purification. The solutions were prepared with water purified using a Millipore Milli-Q system. The potential drop at the extremes of the film was measured with a Keithley Model 160 voltmeter.

3. Results

The evolution of the voltammetric and SR responses with the electrode potential cycling within the potential range -0.5 V $< E < 0.6$ V was studied for the different nickel hydroxide-gold modified electrodes indicated in Table 1. The corresponding responses for the 30 nm gold film modified by a nickel surface coverage of 2.5 nmol cm⁻² are shown in Fig. 1. The voltammetric response is in agreement with that described in previous work [5,6,9]. The i - E response of the Au/Ni(OH)₂ modified electrode is the weighted sum of the activities of gold and nickel hydroxide. Two redox transitions are observed, one of them (a1/c1) is related to gold-oxide formation and reformation of Au⁰, and the other one (a2/c2) is attributed to the Ni(II)/Ni(III) system. While

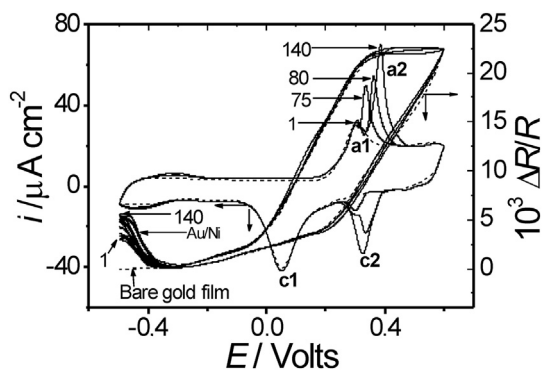


Fig. 1. (—) Evolution of i - E and $\Delta R/R$ - E responses of a 30 nm gold film electrode modified with a nickel hydroxide coverage $\Gamma_{\text{Ni}} = 2.5$ nmol cm⁻² with potential cycling. The number of potential cycles is indicated in the figure. (---) The bare gold film electrode. The (a1/c1) redox transition is related to gold-oxide formation and reformation of Au⁰, and (a2/c2) corresponds to the Ni(II)/Ni(III) system. Electrolyte: a 0.2 M Na(OH) solution. Potential scan rate: 0.010 V s⁻¹.

the SR response of the nickel hydroxide-gold modified electrode and that of the bare gold electrode remain practically equal with potential cycling within the potential range comprised between -0.3 V and 0.6 V, a $\Delta R/R$ increase in going towards the negative potential direction from -0.3 V to -0.5 V is observed for the nickel hydroxide-gold modified electrode as compared with the response of the bare gold film electrode. The $\Delta R/R$ increase becomes more pronounced as the number of potential cycles increases (Fig. 2). However, a stabilized $\Delta R/R$ response is obtained after about 140 cycles for all Γ_{Ni} values (column 1 in Table 1). The stabilized $\Delta R/R$ value at $E = -0.5$ V obtained for different Γ_{Ni} values at constant gold film thickness is shown in columns 2 to 6 of Table 1. As can be seen, the stabilized $\Delta R/R$ value for each Γ_{Ni} value becomes more pronounced as the gold film thickness decreases. This result is consistent with Eq. (4), which indicates a magnification of the ΔR change with the decrease in ϕ_m .

From the evolution of the relative $\Delta R/R$ changes with potential cycling for each gold film thickness (see Fig. 2 for the 30 nm film), ΔR values at $E = -0.5$ V ($\Delta R^E = -0.5$ V) as a function of the potential cycle number for different Γ_{Ni} values were calculated. The corresponding R value for each gold film thickness indicated in the headings of columns 2 to 6 of Table 1 was employed to obtain the ΔR values. The evolution of $\Delta R^E = -0.5$ V with the potential cycle number for the 30 nm and 14 nm gold films modified with different nickel hydroxide surface coverages is shown in Fig. 3(A) and (B), respectively.

In order to analyse the effect of alkali concentration on the evolution of the surface resistance response, we performed an experiment where Na(OH) concentration is increased from 0.2 M to 2 M (see Fig. 4). As can be seen from Fig. 4, the ΔR value at $E = -0.5$ V as a function of the number of potential cycle depends on the alkali concentration.

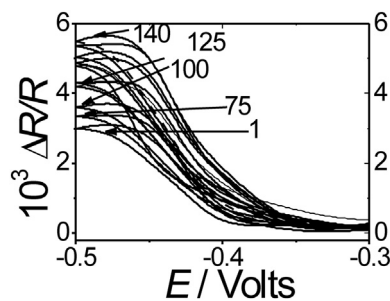


Fig. 2. More detailed evolution of $\Delta R/R$ - E response for the same nickel hydroxide-gold modified electrode indicated in Fig. 1, within the potential range -0.3 V $> E > -0.5$ V. The number of potential cycles is indicated in the figure. Electrolyte: a 0.2 M Na(OH) solution. Potential scan rate: 0.010 V s⁻¹.

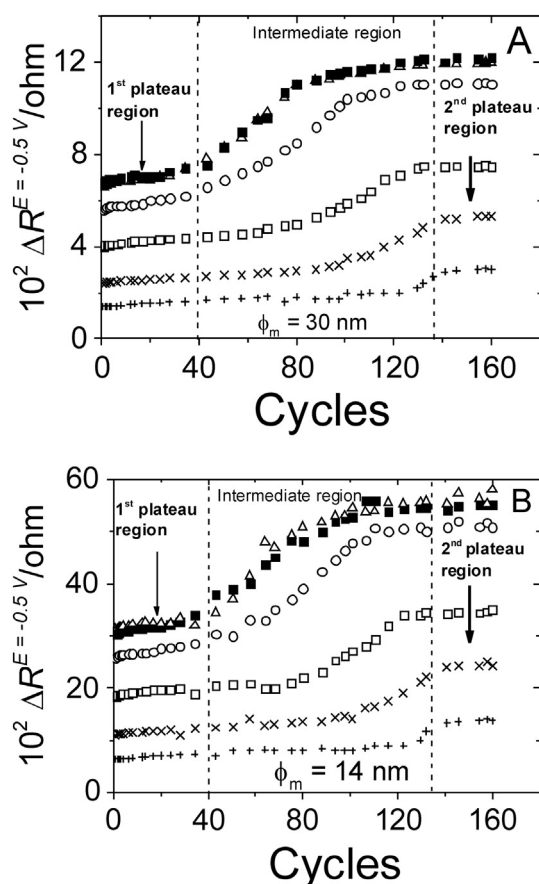


Fig. 3. ΔR value at $E = -0.5$ V as a function of the number of potential cycle for the (A) 30 nm and (B) 14 nm gold film electrodes modified with different Γ_{Ni} values (nmol cm^{-2}): (+) 0.7; (x) 1.2; (□) 1.8; (○) 2.5; (Δ) 3.1; (■) 6.2. Electrolyte: a 0.2 M Na(OH) solution. Potential scan rate: 0.010 V s^{-1} .

4. Discussion

The $\Delta R/R$ increase within the potential range -0.3 V $> E > -0.5$ V shown in Figs. 1 and 2 was attributed to the direct physical interaction of nickel adatom layers with the gold surface after desorption of OH_{ads} and AuO layers [5]. As was indicated, from relative $\Delta R/R$ changes it is possible to calculate ΔR . As can be seen from Fig. 3(A) and (B), the ΔR value at $E = -0.5$ V as a function of the potential cycle number exhibits an S-shape form for each Γ_{Ni} value. Thus, two regimes are clearly differentiated. The first one is represented by a plateau to the left of the S-shaped $\Delta R^E = -0.5$ V change (1st plateau) where the SR remains

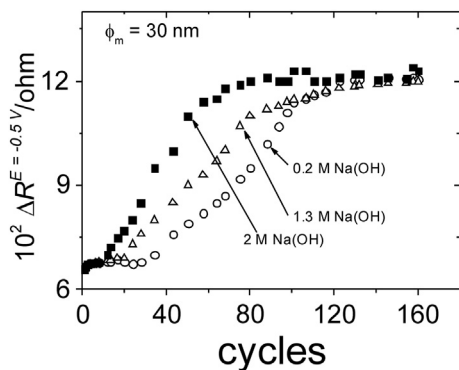


Fig. 4. ΔR value at $E = -0.5$ V as a function of the potential cycle number for the 30 nm gold film electrode modified with a Γ_{Ni} value of 2.5 nmol cm^{-2} . Different electrolyte concentrations are indicated in the figure. Potential scan rate: 0.010 V s^{-1} .

nearly constant during the first cycles, and a second one at the end of the S-shaped $\Delta R^E = -0.5$ V variation observed at a potential cycle number higher than 140 (2nd plateau), where again $\Delta R^E = -0.5$ V takes a constant value but higher than that obtained at the beginning of potential cycling. It is interesting to notice from Fig. 3(A) and (B) that while the first plateau shrinks, the second one extends as Γ_{Ni} increases. The same feature is observed for the other film thicknesses. In order to establish the common existence of two plateaux for all Γ_{Ni} values, we consider ΔR values within the range 1 to 40 potential cycles and beyond 140 cycles to define the first and second plateaux, respectively (see Fig. 3A and B). An intermediate zone is also defined between the two plateaux. The comparison of Fig. 3(A) and (B) shows that: (i) at fixed Γ_{Ni} value, the $\Delta R^E = -0.5$ V is magnified as the gold film thickness decreases. This fact is in agreement with Eqs. (3) and (4), which show the ΔR vs. ϕ_m^{-2} dependence. (ii) A saturation in the S-shape form is observed at $\Gamma_{Ni} > 3$ nmol cm^{-2} for all gold film thicknesses (see dependences for Γ_{Ni} values of 3.1 and 6.2 nmol cm^{-2} , respectively, in Fig. 3(A) and (B)). (iii) Linear $\Delta R^E = -0.5$ V vs. Γ_{Ni} dependences are obtained up to $\Gamma_{Ni} = 3$ nmol cm^{-2} when $\Delta R^E = -0.5$ V values corresponding to the first and the second plateaux are considered, respectively (Fig. 5). By comparing $\Delta R^E = -0.5$ V/ Γ_{Ni} slopes extracted from both plateaux at fixed gold film thickness, a lower value is obtained from the former as compared with the latter (Fig. 5). Again, as can be seen from Fig. 5, ΔR is magnified as ϕ_m decreases.

The ΔR increase with Γ_{Ni} shown in Fig. 5 can be interpreted, from the electron scattering point of view, in terms of the specularity parameter change ($\Delta p = -k_0 \Gamma_{Ni}$) (see Eq. (3)), and considering that the more dense the surface layer is, the more specularly the electrons are reflected [1]. The Δp difference between the specularity parameter at $E = -0.5$ V ($p(E = -0.5$ V)) and that at $E = -0.3$ V ($p(E = -0.3$ V)) is a negative number, that is, $\Delta p = p(E = -0.5$ V) $- p(E = -0.3$ V) < 0 because always $p(E = -0.5$ V) $< p(E = -0.3$ V). That is, the electron reflection is more diffuse at $E = -0.5$ V than at $E = -0.3$ V (see Fig. 2). Thus, as Γ_{Ni} increases, Δp decreases because $p(E = -0.5$ V) decreases while $p(E = -0.3$ V) remains constant. Although absolute values of $p(E = -0.5$ V) and $p(E = -0.3$ V) are unknown, the ΔR saturation is indicative of a $p(E = 0.5$ V) limiting value at a given Γ_{Ni} value. Then, in terms of the electron conduction scattering at a gold film surface coated with nickel adatoms, the initial linear resistance increase observed in Fig. 5 would mean that scatterer centres (nickel adatoms) for the gold conduction electrons are far apart from one another, forming part of a surface structure in which the nearest scatterer distances are constant and higher than the Fermi wavelength [10] of the conduction electrons of the substrate (gold). The latter would correspond to an island growth mechanism, as proposed by several authors for explaining SR data of different adsorbates on thin metal films [1]. As nickel adatom surface coverage increases further ($\Gamma_{Ni} > 3$ nmol cm^{-2}), more compact structures that reflect electrons more specularly are formed, leading in these regions to no change or a decrease in SR. The appearance of these structures makes, on average, $\Delta R^E = -0.5$ V depart from the initial straight line, leading to a smaller slope and eventually to a constant

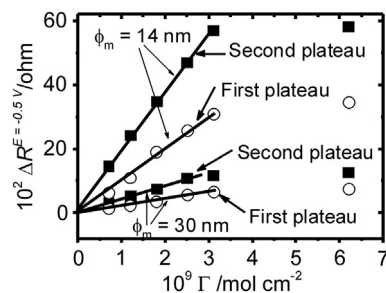


Fig. 5. ΔR vs. Γ_{Ni} dependence for two gold film thicknesses: 14 nm and 30 nm. (○) First and (■) second plateaux, respectively.

value of $\Delta R^E = -0.5 \text{ V}$. In the present case, no $\Delta R^E = -0.5 \text{ V}$ change is observed for $\Gamma_{\text{Ni}} > 3 \text{ nmol cm}^{-2}$ (see Fig. 5). The coverage $\Gamma_{\text{Ni}} = 3$ would be the point where areas occupied by surface structures reflecting diffusely are, on average, compensated by those reflecting specularly. A similar explanation has been proposed in gas phase studies to interpret oxygen adsorption layers on Cu (001) surfaces [11]. On the basis of these considerations related to the free electron scattering model [1], the lower $\Delta R^E = -0.5 \text{ V}/\Gamma_{\text{Ni}}$ slope value obtained from the first plateau, as compared with that extracted from the second one, would mean that the nickel adatom structures formed at the beginning of potential cycling (first plateau) are more compact, that is, they reflect conduction electrons more specularly than structures stabilized after a high number of voltammetric scan cycles (>140). In other words (see Fig. 5), at a fixed Γ_{Ni} value, the distance between nickel islands in structures corresponding to the first plateau is shorter than that in structures corresponding to the second one. As was indicated, this effect is observed for all gold film thicknesses. The different specularity of nickel adlayers for the gold conduction electrons at these two different stabilization steps is shown in Table 2, where k_0 values were calculated from experimental $\Delta R^E = -0.5 \text{ V}/\Gamma_{\text{Ni}}$ slopes for the different gold film thicknesses by employing Eq. (4).

As can be seen in column 4 of Table 2, the ($k_0^{2\text{nd}}/k_0^{1\text{st}}$) relationship is almost 2 for the different gold film thicknesses. According to the $\Delta p = p(E = -0.5 \text{ V}) - p(E = -0.3 \text{ V}) = -k_0 \Gamma_{\text{Ni}}$ dependence, one can conclude that nickel adlayers formed at a low number of voltammetric scan cycles exhibit a reflectance for the gold conduction electrons that is nearly twofold (compact nickel adatom distribution) compared to that of nickel adlayers formed after a large number of voltammetric scan cycles (spread nickel adatom distribution).

With regard to $\text{Ni(II)} \leftrightarrow \text{Ni(III)}$ transition, the evolution of the voltammetric response with potential cycling shown in Fig. 1 shows that the peak currents increase with the number of potential cycles. Also, the anodic peak a2 is shifted in the positive potential direction with the increase in the number of potential cycles. Besides, two cathodic peaks are observed after a few voltammetric scan cycles. The same characteristics are observed for other Γ_{Ni} values. The evolution of the i - E response with potential cycling of the Au/nickel hydroxide electrode was discussed elsewhere [6] and it was associated to phase transformations. As has been reported, nickel hydroxide can exist at least in four different phases [12–15], which are designed as β - Ni(OH)_2 , β - NiOOH , γ - NiOOH and α - NiOOH , respectively. Voltammetric and XPS investigations carried out with nickel hydroxide electrochemically deposited on gold indicate that α - Ni(OH)_2 is the initial phase of nickel hydroxide formed by cathodic deposition on gold [6]. However, the α - Ni(OH)_2 phase is very unstable in the presence of water and alkali, and it is converted to β - Ni(OH)_2 . The conversion seems to be faster as the alkali concentration increases [16]. The oxidation of the β - Ni(OH)_2 phase gives two varieties of oxyhydroxides, β - NiOOH and γ - NiOOH , which could explain the existence of two cathodic peaks during the

negative potential scan (see Fig. 1). The γ - NiOOH phase reduces to form the α - Ni(OH)_2 phase, which, as was indicated, is unstable and converts to the β - Ni(OH)_2 phase. The distance between nickel atoms in the different nickel hydroxide phases is different. EXAFS investigations indicate a contraction in the Ni–Ni distance of 0.05 Å in the lattice of the α - Ni(OH)_2 structure as compared with the Ni–Ni distance in the β - Ni(OH)_2 structure ($d_{\text{Ni-Ni}}^{\beta} = 3.124 \text{ Å}$ and $d_{\text{Ni-Ni}}^{\alpha} = 3.08 \text{ Å}$) [17]. Although one cannot establish that nickel deposits with different reflecting properties for the gold conduction electrons detected by SR measurements at potential values more negative than -0.3 V are directly related to the reduction of different nickel hydroxide phases (α - Ni(OH)_2 and β - Ni(OH)_2), it is interesting to note that structures obtained at a low number of potential cycles seem to be more compact, that is, they exhibit a smaller interatomic distance than those formed at a number of potential cycles higher than 140 (see Table 2). Another interesting observation arises from Fig. 3(A) and (B), where it is noted that while the first plateau shrinks, the second one spreads, as the nickel hydroxide coverage increases. The same effect is observed with the increase of the alkali concentration (Fig. 4). This would mean that the stability range of the more compact nickel structure (higher specularity) decreases as the nickel hydroxide coverage and alkali concentration increase. In other words, spread nickel structures (higher electron diffusivity) are formed early, that is, at a lower number of potential cycles as the nickel hydroxide coverage and alkali concentration increase (see Fig. 3A and B, and Fig. 4). Although we cannot provide a clear explanation for these effects, it is possible that strong repulsion effects between nickel atoms operate at high coverage, reducing the stability range of compact nickel layers. Also, although at potential values more negative than -0.4 V the desorption of OH^- species from the gold surface should be expected, it is possible that in the presence of a high concentration of negatively charged OH^- species in a 2 M Na(OH) solution, the potential cycling will affect atom interactions favouring the formation of more open nickel structures as compared with those formed in a 0.2 M Na(OH) solution.

5. Conclusion

The surface resistance (SR) technique applied to study the behaviour of a nickel hydroxide-gold modified electrode does not allow one to obtain direct evidence about nickel hydroxide structural transformations produced during prolonged potential cycling due to the presence OH_{ads} and AuO layers on the gold substrate within the potential range $-0.3 \text{ V} < E < 0.6 \text{ V}$ (SCE). However, after desorption of OH_{ads} and AuO species at potential values more negative than -0.3 V (vs. SCE), an increase of the surface resistance is observed, which is attributed to nickel layers formed by reduction of nickel hydroxide. Nickel layers formed from the reduction of nickel hydroxide generated after a large number of potential cycles (>140) exhibit an about twofold diffusivity value for the gold conduction electrons as compared with those formed from nickel hydroxide layers generated after a low number of potential cycles (<40). As from the electron scattering model employed to interpret SR changes, electron diffusivity is related to scatterer distribution, it is possible to conclude that nickel adlayers formed by reduction of nickel hydroxide structures generated at a low number of potential cycles are more compact than those formed by reduction of nickel hydroxide structures generated after prolonged potential cycling. The SR also indicates that the relative stability of these nickel layers depends on nickel hydroxide surface coverage and alkali concentration. The higher the alkali concentration and nickel hydroxide surface coverage are, the lower the number of potential cycles at which spread nickel atom layers are obtained.

Conflict of interest

The author declares that he has not conflict of interest.

Table 2

k_0 values for different gold films calculated from experimental $\Delta R/\Gamma_{\text{Ni}}$ slope values by employing Eq. (4). $k_0^{1\text{st}}$ and $k_0^{2\text{st}}$ values correspond to the first and second plateau, respectively. The two plateaux are shown in Figs. 3A and B.

Gold film thickness, $\phi_{\text{m}}/\text{nm}$	^a $10^{-6} k_0^{1\text{st}}/\text{cm}^2 \text{ mol}^{-1}$	^b $10^{-6} k_0^{2\text{nd}}/\text{cm}^2 \text{ mol}^{-1}$	^c $k_0^{2\text{nd}}/k_0^{1\text{st}}$
30	3.70	7.28	1.97
24	3.73	7.17	1.88
18	3.71	7.29	1.96
14	3.72	7.14	1.92
10	3.73	7.22	1.93

^a Values of k_0 extracted from the first plateau employing experimental ($\Delta R^E = -0.5 \text{ V}/\Gamma_{\text{Ni}}$) slope values for each gold film thickness in Eq. (4).

^b Values of k_0 extracted from the second plateau employing experimental ($\Delta R^E = -0.5 \text{ V}/\Gamma_{\text{Ni}}$) slope values for each gold film thickness in Eq. (4).

^c Values of the $k_0^{2\text{nd}}/k_0^{1\text{st}}$ relationship for different gold film thicknesses.

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