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ELECTROCHIMICA

Electrochimica Acta 52 (2006) 658-664

www.elsevier.com/locate/electacta

# Growth of passive layers on nickel during their voltammetric anodic dissolution in a weakly acid medium

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Available online 10 July 2006

#### Abstract

Quartz crystal microbalance in combination with voltammetry has been used for studying the electrochemical oxidation behaviour of a nickel deposit in a weakly acid medium. The instantaneous mass/charge ratio (Fdm/dQ) analysis allows to obtain the fraction of charge consumed in the passivation process, and, that way, the experimental kinetic equation of the passive layer growth. This experimental law has been fitted to the theoretical equation derived from the point defect model theory under voltammetric conditions.

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Keywords: EQCM; Instantaneous mass charge analysis; Point defect model

## 1. Introduction

Nickel is a very important element from a technological point of view. It takes part in many alloys thus increasing their corrosion resistance [1-3]. This is because nickel has been the subject of many researches related with dissolution and passivation mechanisms in acid and basic medium by means of different electrochemical techniques [4–12]. However, several points are yet unclear because of the strong tendency for self-passivation of nickel and, that way, the process of active dissolution, passive layer formation and chemical dissolution cannot be well separated in the obtained experimental results. This tendency should prove more pronounced in weakly acid or alkaline media [10–12] and is drastically affected to a great extent by the anions [13] and other experimental conditions [6,7]. Passive layers on nickel have a great importance because of their use in rechargeable alkaline batteries [14], cathodes in fuel cells [15] and electrocatalysts for oxygen evolution [16].

When a passive layer completely covers all the electrode surface, the processes which take place at the metal/passive layer/solution interfaces can be schematized, according to the

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point defect model (PDM) theory [17–19] as follows:

$$m + V_{\rm M}^{\chi'} \xrightarrow{k_1} M_{\rm M} + v_{\rm m} + \chi e^-$$
 (1)

$$M_{\rm M} \xrightarrow{k_3} M^{\delta +}({\rm aq}) + V_{\rm M}^{\chi'} + (\delta - \chi) e^-$$
 (2)

$$m \xrightarrow{k_2} M_{\rm M} + \left(\frac{\chi}{2}\right) V_{\rm O^{2-}} + v_{\rm m} + \chi e^-$$
 (3)

$$V_{\mathrm{O}^{2-}} + \mathrm{H}_2\mathrm{O} \xrightarrow{k_4} \mathrm{O}_\mathrm{O} + 2\mathrm{H}^+ \tag{4}$$

$$MO_{\chi/2} + \chi H^+ \xrightarrow{k_5} M^{\delta +} + \frac{\chi}{2} H_2 O + (\delta - \chi) e^-$$
(5)

$$m \xrightarrow{k_6} M_i^{\chi +} + v_{\rm m} + \chi e^- \tag{6}$$

$$M_i^{\chi + k_7} \xrightarrow{k_7} M^{\delta +} (\mathrm{aq}) + (\delta - \chi) \mathrm{e}^-$$
(7)

where the symbols are defined as follows: *m* (metal atom),  $M_i^{\chi^+}$  (metal cation interstitial), O<sub>O</sub> (oxygen anion in anion site),  $M^{\delta'}(aq)$  (metal cation in solution),  $v_m$  (vacancy in metal phase),  $M_M$  (metal cation in cation site),  $V_M^{\chi'}$  (cation vacancy) and  $V_O^{2-}$ (anion vacancy). In the case of nickel  $\chi = 2$  and  $\delta = 2$ . Eqs. (1) and (2) are responsible for metal electrodissolution, whereas Eqs. (3) and (4) are responsible for metal passivation (passive film growth) when the electrode surface is fully covered by a passive film [18,19]. Processes (1), (3) and (6) take place at the metal/film interface, whereas processes (2), (4), (5), and (7) take

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place at the passive film/solution interface. The global process, which leads to the passive film growth can be schematized as follows:

$$(2/\chi)m + H_2O \rightarrow [(2/\chi)M_M + O_O] + 2H^+ + 2e^-$$
 (8)

For example, in the case of the formation of nickel hydroxide, Eq. (8) can be written the following way:

$$Ni + 2H_2O \rightarrow [Ni_{Ni} + 2OH_{OH}] + 2H^+ + 2e^-$$
 (9)

or, for the formation of nickel oxide:

$$Ni + H_2O \rightarrow [Ni_{Ni} + O_O] + 2H^+ + 2e^-$$
 (10)

In the first case (Eq. (9)) the passive layer contains water molecules and interacts almost with two water molecules at the passive film/solution interface, whereas in the second one (Eq. (10)) only one water molecule interacts at the passive film/solution interface.

In the case of passive layers on nickel, metal interstitials do not play a significant role, and consequently Eqs. (6) and (7) can be disregarded [18,19]. Eq. (5) represents the chemical dissolution of the passive layer. A steady-state for film growth is reached when the rate of two non-conservative processes, Eqs. (5) and (8), are equal [19].

In recent years the use of the mass/charge ratio in the analysis of the electrochemical quartz crystal microbalance (EQCM) experimental results has proved very useful in the field of film modified electrodes [20–29] and metal electrodissolution processes [30–33], when the relation between the changes in the resonance frequency of quartz and mass changes on the electrode surface follows the Sauerbrey equation [34]. Instantaneous mass charge/ratio (Fdm/dQ function) [31] is defined as

$$F\frac{\mathrm{d}m}{\mathrm{d}Q} = \sum_{i} \frac{MW_{i}}{n_{i}} \gamma_{i} \pm \text{ contribution of mass changes due to}$$
  
uncharged species (11)

where  $MW_i$  is the molecular mass of *i* species, which interchanges  $n_i$  electrons,  $\gamma_i$  the charge ratio due to the *i* process and *F* is the Faraday constant.

Recent works of Landolt and co-workers used EQCM measurements in the study of passivation as well as passive state of valve metals [35–37]. In these works, an interesting procedure is developed for obtaining the passive film growth fraction, that is to say, the charge fraction used in the passive film growth [35].

Instantaneous mass/charge analysis proved useful in the characterization of the passive layer growth of Ni(OH)<sub>2</sub> generated at constant potential in a weakly acid sulphate medium [38]. This work is focused on the study of the usefulness of Fdm/dQ function during the active/passive transition observed on the anodic scan of cyclic voltammograms [39].

#### 2. Experimental procedure

All the experiments were carried out in a typical three electrodes cell under these conditions:  $0.32 \text{ M} \text{ H}_3\text{BO}_3$ ,  $0.26 \text{ M} \text{ NH}_4\text{Cl}$ ,  $1.33 \text{ M} \text{ Na}_2\text{SO}_4$ , pH 5.1 and T=298 K. The potential was measured versus the Ag/AgCl/KCl (sat.) reference

electrode. A platinum grid was used as an auxiliary electrode. Solutions were prepared from  $Na_2SO_4$  (Sigma, reagent grade),  $H_3BO_3$  (R.P. Normapur, reagent grade),  $NH_4Cl$  (Panreac, reagent grade), with double deionised water (MilliQ).

For EQCM experiments the working electrodes (supplied by Matel–Fordahl) were made from a quartz sheet embedded between two pieces of gold connected to a resonance circuit. The resonance frequency of the quartz at air was 6 MHz. One of the pieces of gold serves as an electrical surface in contact with the electrolyte. The electrical area was  $0.234 \text{ cm}^2$  and the effective mass area was  $0.196 \text{ cm}^2$ . The microbalance was an UPR15/RT0100 (UPR of the CNRS). The resonance frequency of quartz was measured with a Fluke PM6685. The current in the auxiliary electrode was measured with a Keithley PM2000 multimeter. The potential was applied with a 263A EG&G PAR Potentiostat. The whole system was controlled by a GPIB board. The EQCM was calibrated by means of a galvanostatic Cu deposition [40]. The experimental Sauerbrey constant was  $9.50 \times 10^7 \text{ Hz g}^{-1}$ .

Nickel electrodeposits on the microbalance electrodes were obtained by means of a potentiostatic method in a 0.245 M K<sub>2</sub>SO<sub>4</sub> (Probus, reagent grade), 0.005 M H<sub>2</sub>SO<sub>4</sub> (Merk, reagent grade) and 0.001 M NiSO<sub>4</sub>·6H<sub>2</sub>O (Scharlau, reagent grade) solution prepared with double deionised water (MilliQ). In this case, pH 2.7 and the temperature cell was T = 298 K. The reference electrode used in the electrodeposition process was an SSE electrode (Saturate Sulphate Electrode). A potential E = -1450 mV (versus SSE) was applied for 5 min. This process was repeated several times at the same potential, and finally, the calculated mass density for the nickel deposit on the electrode surface was about 23.7  $\mu$ g cm<sup>-2</sup>. From this value and the nickel density value, the nickel deposit thickness can be estimated,  $\delta = 0.027 \,\mu\text{m}$ . This thickness is small enough and then no non-ideal contributions are expected and Sauerbrey equation applies [34,40]. The surface of nickel deposits obtained by this procedure shows a well homogeneous aspect when observed by SEM.

The voltammetric sweep was carried out in the [-500, 500] mV (versus Ag/AgCl/KCl (sat.)) potential interval at 20 mV/s. The electrolyte was bubbled for 5 min with Ar (Air Liquide) so as to remove the dissolved oxygen before the electrochemical experiment, and all the measurements were made under inert atmosphere and at constant and controlled temperature T = 298 K.

The applicability of Fdm/dQ analysis according to Eq. (11) is based on the assumption that all electrogenerated films are perfectly rigid, and therefore all changes of the resonant frequency are due to mass changes of the films. For thin films (thickness  $\delta < 0.1 \,\mu$ m) Sauerbrey equation [34] can be used without limitation coming from viscoelastic properties of the film [41,42] or other non-ideal contributions, which could cause frequency shifts, like roughness [43]. In all cases films were thin enough (less than  $0.1 \,\mu$ m) and then no non-ideal contributions are expected and Sauerbrey equation becomes applicable.

For the impedance measurements the potential was controlled by means of a 273A EG&G PAR Potentiostat–Galvanostat and the impedance spectra was recorded with the help of a 5210 EG&G PAR Lock-in Amplifier. The working electrodes were made from a nickel sheet (99.9%, Johnson&Matthey). The geometrical area was  $0.25 \text{ cm}^2$ . The impedance spectra were recorded at different stabilization potentials,  $E_0$ , in the [-0.125, 0] V potential range (versus Ag/AgCl/KCl (sat.)). The stabilization potential E<sub>0</sub> (versus Ag/AgCl/KCl (sat.)) was applied for 5 min before recording the impedance spectrum. The impedance measurements were carried out from  $10^4$  to  $5 \times 10^{-2}$  Hz frequency range and the amplitude of the harmonic potential perturbation was 5 mV r.m.s. The impedance measurements from 10 kHz to 5 Hz were performed in a single-sine type of experiment, and from 5 Hz to 50 mHz in a multi-sine type experiment. The fitting of the experimental impedance data to the proposed equivalent circuit was carried out by means of a non-linear least squares procedure based on the Marquardt algorithm for function optimisation [44,45]. According to Boukamp [46], following the idea of "measurement models" of Agarval et al. [47], the condition sufficient for immittance data to be valid and KKT (Kramers Kronig transformation) transformable is their compliance with any passive equivalent circuit used as a measurement model. The equivalent circuit used for this purpose is nothing more than a number of adjustable real parameters, which do not have any direct physical meaning. The measurement model involves as many R and C elements as needed to get a close enough fit of relevant linear function to experimental data. No restriction is imposed on signs of  $R_i$  and  $C_i$  parameters, except that their products, or time constants  $\tau_i = R_i C_i$ , should be real and positive numbers [46–48]. In this case, two parallel R#C combinations are sufficient for obtaining a very good fitting of the measured impedance spectra. The addition of more time constants does not appreciably improve the fitting. Two time constants can be well defined in the obtained impedance results [47]. This shows the compliance of the measured impedance spectra with the constraints of the linear system theory [48].

# 3. EQCM measurements

Mass changes were followed on a nickel deposit in a voltammetry experiment at an scan rate of  $20 \text{ mV s}^{-1}$ , as represented in Fig. 1.

Between -0.05 and 0.5 V measured mass loss is  $\Delta m = -1.49 \ \mu \text{g cm}^{-2}$ , and the calculated anodic charge is  $\Delta Q = 9.5 \text{ mC cm}^{-2}$ . This anodic charge was calculated by means of the integration of the intensity curve between -0.2 and 0.5 V. This potential range included anodic peak I which is associated to nickel oxidation. From these values, the averaged mass/charge ratio could be calculated as  $F\Delta m/\Delta Q = -15 \text{ g mol}^{-1}$ . Based on previous results obtained by other workers [49–51], this value is consistent with a simultaneous nickel electrodissolution/nickel passivation taking place at the explored potential interval. According to our previous obtained results, chemical dissolution of the electrogenerated passive layer does not play a significant role in these experimental conditions [33]. Moreover, according to our recent results in a similar pH, passive layer chemical dissolution begins to become important after 30 s of a



Fig. 1. Voltammogram (solid line) and mass variations during the voltammetric cyle for a nickel deposit. [-500, 500] mV, scan rate 20 mV/s, 0.32 M H<sub>3</sub>BO<sub>3</sub>, 0.26 M NH<sub>4</sub>Cl, 1.33 M Na<sub>2</sub>SO<sub>4</sub>, pH 5.1, T = 298 K.

potentiostatic transient [38], since Eq. (5) will not be considered from now on, since, by considering a scan rate of  $20 \text{ mV s}^{-1}$ , passive layer chemical dissolution will not have any influence in the explored potential interval.

In order to check the relative contribution of both nickel electrodissolution/nickel passivation to the overall anodic process at each applied potential the analysis of the instantaneous mass/charge ratio, Fdm/dQ function, as defined in Eq. (11), was performed in the potential interval [-0.05, 0.5] V.

Calculated Fdm/dQ values are represented in Fig. 2 as a function of the electrode potential between 0 and 0.5 V. In this potential range the signal to noise ratio is high enough to make Fdm/dQ values affected by a low uncertainty. The experimental calculated values show variations between -12 and -17 g cm<sup>-2</sup> at all the explored potential range.



Fig. 2. Voltammogram (solid line) and instantaneous mass/charge ratio function (circles) during the anodic scan for a nickel deposit. [-500, 500] mV, scan rate 20 mV/s, 0.32 M H<sub>3</sub>BO<sub>3</sub>, 0.26 M NH<sub>4</sub>Cl, 1.33 M Na<sub>2</sub>SO<sub>4</sub>, pH 5.1, *T* = 298 K.

For the analysis of the Fdm/dQ behaviour it is considered that for the electrodissolution process:

$$Ni \rightarrow Ni_{aq}^{2+} + 2e^{-}, \qquad Fdm/dQ|_{diss} = -29 \,\mathrm{g \, mol^{-1}}$$
 (12)

Obviously, anions present in the solution may participate during the electrodissolution process, but taking into account that there is an adsorption followed by a desorption process, their influence may be neglected in the Fdm/dQ function if these processes take place fast enough. On the other hand, according to recent spectroscopic and electrochemical measurements, it can be considered that at the early stages of nickel passivation the passive layer is mainly formed by Ni(OH)<sub>2</sub>, without any other anion incorporation in the passive film structure [51,52]. When time elapses, *i.e.* for successive voltammetric cycles, a bilayer structure is developed for the passive layer consisting in an inner more crystalline layer and an outer more amorphous one [18,19,33]. Then, the passivation process may be written such as

$$Ni + 2OH^{-} \rightarrow Ni(OH)_{2} + 2e^{-},$$
  

$$Fdm/dQ|_{pass} = 17 \text{ g mol}^{-1}$$
(13)

This Eq. (13) is equivalent to Eq. (8) when written for the case of the formation of nickel hydroxide, as indicated in Eq. (9). Then, in this case:

$$Fdm/dQ|_{exp} = -29\gamma_1 + 17\gamma_2 \tag{14}$$

$$\gamma_1 + \gamma_2 = 1 \tag{15}$$

where  $\gamma_1$  and  $\gamma_2$  are the charge fractions due to reactions (12) and (13), respectively.  $\gamma_2$  values define the growth fraction as defined by Landolt and co-workers [35–37] as the fraction of charge consumed in passive layer thickening.  $\gamma_2$  can be calculated by solving the system of equation defined by (14) and (15). This allows to calculate the current component exclusively due to passivation process as  $i_2 = i\gamma_2$ .  $\gamma_2$  obtained values are between 0.38 and 0.28. Therefore, only a minor part of the total current leads to passive layer formation as observed in other experimental conditions [38,49,50]. The fact that only a minor part of the total current leads to passive layer formation is in agreement with the fact that the main charge carriers within passive layers on nickel are cation vacancies (see Eqs. (1) and (2)) [53]. This is because passive layers on nickel show p-type semiconductor behaviour in passivity potential range [53].

 $i_2$  values are represented in Fig. 3 together with the total measured current, *i*, for comparison. That way, by considering valid the above hypotheses, the kinetics of the passive layer growth can be really followed. In Fig. 3 the passive layer thickness is also represented as a function of the applied potential. Passive layer thickness,  $\delta$ , is calculated as  $\delta = \Delta Q_{\text{pass}} V_f$ , where  $V_f = 1.848 \times 10^{-4} \text{ cm}^3 \text{ C}^{-1}$  is the volume per unit charge for the Ni(OH)<sub>2</sub> [11,54], and  $\Delta Q_{\text{pass}}$  calculated as  $\Delta Q_{2\text{pass}}(t) = \int_{t=0}^{t} i_2 dt$  is the charge consumed in the passivation process from t = 0 until each measured time, *t*. Initially, a non-linear and quick increase in thickness was observed followed by a linear variation region in passivity potential range. An inflexion point is defined at E = 0.068 V, which corresponds to the peak potential for  $i_2$  values.

Fig. 3. Total intensity current (solid line), intensity current due to passivation process (dashed line) and layer thickness variation curves during the anodic scan for a nickel deposit. Same experimental conditions as in Fig. 1.

According with the results represented in Fig. 2, nickel deposit becomes readily passive in these experimental conditions. Moreover, according with the results presented in Fig. 3, passive layer thickness at E = 0 mV is about 0.6 nm. Considering that for crystalline nickel hydroxide the distance between monolayers is about 0.3 nm [51], then, at E = 0 V approximately two monolayers of Ni(OH)2 are electrogenerated, if the passive layer generated during the first anodic scan is mainly formed by Ni(OH)2 and a bilayer structure is not formed (as occurs for greater times of anodic polarization [33]). This implies that all the electrode surface is covered by a passive layer at the beginning of the anodic peak, and, consequently, the PDM is applicable. From a general point of view, the point defect model theory is applicable for metal surfaces fully covered by a passive layer, independently of their composition (oxide or hydroxide), when the inherent hypothesis of the theory are fulfilled [19], as discussed below. Within this context, Eq. (12) represents the global process, which leads to nickel dissolution according to Eqs. (1) and (2), whereas Eq. (13) represents the global process which leads to nickel passivation according to Eqs. (3) and (4), or Eq. (8), within the framework of the PDM.

# 4. Discussion

According to the PDM theory, the current consumed in passive film growth can be expressed as [18,35]:

$$i_2 = i_{02} e^{b_2 (E - \varepsilon \delta)} \tag{16}$$

For obtaining a theoretical expression for the passive layer thickness evolution with the applied potential several hypothesis, consistent with the PDM, are made. First, it is considered that the electric field  $\varepsilon$  remains constant within the passive layer almost in the rising part of the anodic peak for  $i_2$  in Fig. 3. It is also considered that the potential drop variations at the film/solution interface can be disregarded when they are compared with potential drops at the metal/film and within the film





Fig. 4. Experimental (circles) and fitted curves (solid lines) for the passive layer thickness variation. Same experimental conditions as in Fig. 1.

[18,35,38]. In a voltammetry experiment  $E = E_{0i} + \nu t$ , where  $\nu$  is the scan rate and  $E_{0i}$  represents the initial potential. Moreover the film growth layer law is [35,55]:

$$\frac{\mathrm{d}\delta}{\mathrm{d}t} = K_{\mathrm{film}}i_2 \tag{17}$$

where  $K_{\text{film}}$  is defined as  $K_{\text{film}} = V_{\text{film}}/(nF)$ , and  $V_{\text{film}}$  is the molar volume of the film. If we consider that the passive film is formed by Ni(OH)<sub>2</sub> then  $V_{\text{Ni(OH)}_2} = 36 \text{ cm}^3 \text{mol}^{-1}$  [10], and  $K_{\text{film}} = 1.9 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . From Eqs. (16) and (17), the following differential equation is obtained:

$$\frac{\mathrm{d}\delta}{\mathrm{d}t} = K_{\mathrm{film}} i_{02} \mathrm{e}^{b_2(E_{0i} + \nu t - \varepsilon \delta)} \to \frac{\mathrm{d}\delta}{\mathrm{e}^{-b_2 \varepsilon \delta}} = K_{\mathrm{film}} i_{02} \mathrm{e}^{b_2(E_{0i} + \nu t)} \,\mathrm{d}t$$
(18)

and if it is considered that at the potential  $E_{0i} = -0.1$  V, the initial film thickness is  $\delta_0 = 0$  nm, the integration of Eq. (18) leads to

$$\delta = \frac{1}{\varepsilon b_2} \ln \left[ \frac{K_{\text{film}} i_{02} \varepsilon}{\nu} (e^{b_2 E_0} - 0.14) + 1 \right]$$
(19)

The experimental passive layer thickness variation with the applied potential has been fitted to the theoretical curve defined by Eq. (19) and the result of the fitting is represented in Fig. 4.

To do this, several initial  $b_2$  values are fixed and proved, finding the best fit for  $b_2 = 20 \text{ V}^{-1}$ . This value is in good agreement with the previously obtained one during nickel deposit potentiostatic passivation [38]. From this fitting procedure the following values for the electric field  $\varepsilon$  is obtained:  $\varepsilon = 2 \times 10^5 \text{ V cm}^{-1}$ . As can be seen in Fig. 4 there is a good agreement between experimental and theoretical curves until the inflexion point in Fig. 3 (or Fig. 4) at E = 0.068 V is reached. From this inflexion point Eq. (19) cannot reproduce the experimental curve.

As mentioned above, there is a linear variation of the passive layer thickness in passivity potential range (between 0.2 and 0.4 V), where the intensity current  $i_2$  is quite potential independent (see Fig. 3). Then Eqs. (16) and (17) imply that the passive layer thickness is proportional to the applied potential. This linear relationship is also represented in Fig. 4. Consequently, in this potential range the calculated electric field is  $\varepsilon = 1.6 \times 10^6 \,\mathrm{V \, cm^{-1}}$ . Then, the electric field does not remain constant within the passive layer during a voltammetric experiment. This electric field variation has been already observed at more basic pH [11], and it is produced at the potential range of negative slope of the voltammetric peak for  $i_2$  in Fig. 3. Therefore, the  $\varepsilon$  variation is the cause for the deviation between experimental and theoretical growth behaviour for the passive layer under voltammetric conditions, since the hypothesis of  $\varepsilon$ constant inherent to the PDM is no longer fulfilled. According to previously published results, the  $\varepsilon$  variation is produced by changes in the crystalline structure of the passive layer, which becomes more protective with potential [11]. This more protective character implies a decrease in the slope of mass loss, as can be seen in Fig. 1. However, this increase in the electric field value causes a change in  $\gamma_1$  (charge fraction associated to nickel electrodissolution process) and  $\gamma_2$  (charge fraction associated to passive film growth) values, as can be deduced from Fig. 2. It is observed in Fig. 2 that  $\gamma_1$  values increase (Fdm/dQ evolves form -12 to  $-17 \text{ g mol}^{-1}$ ) during the potential range of negative slope of the voltammetric peak I. This increase can be due to an enhanced metal vacancies migration due to higher  $\varepsilon$  values. This enhanced metal vacancy migration could be the origin of the anodic shoulder defined between 0.15 and 0.25 V in Fig. 1, since this anodic shoulder does not appear in  $i_2$  values potential evolution in Fig. 3. This enhanced metal vacancy migration has associated another interesting effect: an increase in vacancy recombination, which implies a greater degree of crystalline structure of the electrogenerated passive layer enhancing the passivation efficiency, in accordance with previous works [11].

According to the above discussion, nickel surface becomes readily covered by a 3D passive layer in a weakly acid medium under voltammetric conditions. In the following it is discussed if the same is true under impedance measurements experimental conditions for a polycrystalline nickel electrode. It must to be considered in the following that the impedance study has been performed for a metallic nickel electrode, whereas the above discussed voltammetric and EQCM results concerned a nickel deposit. In Fig. 5 the anodic scan of the cyclic voltammogram recorded at a low scan rate of 0.5 mV s<sup>-1</sup> for a polycrystalline nickel electrode is represented. Anodic peak I marks the active/passive transition of the nickel surface, but in passivity potential range II, an upper rise in current is clearly observed. The presence of chloride ions in the acid medium causes a local attack of the electrogenerated passive layer and an enhanced metal electrodissolution is produced [13]. After a complete cycle in these experimental conditions pitting on electrode surface is clearly observed.

Several impedance spectra have been recorded at stabilization potentials located in the descending part of the anodic peak I in Fig. 5, as are represented in Fig. 6.

In Table 1 intensities values, which correspond at each stabilization potential are listed as a function of the applied potential.



Fig. 5. Voltammetric curve recorded at 0.5 mV/s in the [-940, 860] mV potential interval. 0.32 M H<sub>3</sub>BO<sub>3</sub>, 0.26 M NH<sub>4</sub>Cl, 1.33 M Na<sub>2</sub>SO<sub>4</sub>, pH 5.1, *T* = 298 K.



Fig. 6. Experimental impedance spectra at  $E_0 = -75 \text{ mV}$  (circles),  $E_0 = -50 \text{ mV}$  (up triangles) and  $E_0 = -25 \text{ mV}$  (diamonds). 0.32 M H<sub>3</sub>BO<sub>3</sub>, 0.26 M NH<sub>4</sub>Cl, 1.33 M Na<sub>2</sub>SO<sub>4</sub>, pH 5.1, T = 298 K.

 Table 1

 Measured intensity currents as a function of the stabilization potential

$\overline{E_0 (\mathrm{mV})}$	<i>i</i> (µA)	$\Delta E_0 (\mathrm{mV})$	$\Delta \phi_{mlf} (\mathrm{mV})$	$\Delta\delta$ (nm)
-125	31			
-100	14	$-125 \rightarrow -100$	-47	0.8
-75	6	$-100 \rightarrow -75$	-47	0.8
-50	2	$-75 \rightarrow -50$	-65	1.0
-25	1	$-50 \rightarrow -25$	-41	0.7

Calculated and estimated  $\Delta \phi_{mlf}$  and  $\Delta \delta$  values form Eqs. (20) and (21), respectively. A constant electric field of  $E = 9 \times 10^5$  V/cm is considered as a first approach.

A progressive increase in the low frequency limit of the measured impedance is observed in Fig. 6. Moreover, in Table 1 it is observed that the intensity values progressively decrease. Nickel surface becomes more and more passive with the stabilization potential. According to Eqs. (1) and (3), in the case of a nickel electrode fully covered by a passive layer, measured intensity values are determined by the potential drop at the metal/passive layer interface,  $\phi_{m/f}$ . No negative time constant is observed at any stabilization potential at this pH. This fact can be explained by considering that  $\Delta \phi_{m/f} = \phi_{m/fE_1} - \phi_{m/fE_2} < 0$  from the stabilization potential  $E_1$  to the stabilization potential  $E_2$ , this is to say, if there is a decrease in  $\phi_{m/f}$  values with the stabilization potential. Then, the measured current values will also decrease, as is experimentally observed. According to D'Alkaine and Santanna [11],  $\phi_{m/f}$  decrease is due to a progressive increase in electric field values at potentials located at the descending part of the voltammetric peak, in agreement with the EQCM results discussed above. An estimation of  $\Delta \phi_{m/f}$  can be made by the following procedure:

$$\frac{\ln i_2}{\ln i_1} = b\Delta\phi_{m/f} \to \Delta\phi_{m/f} = \frac{\ln i_2 - \ln i_1}{b}$$
(20)

by considering  $b = 20 \text{ V}^{-1}$ . In these conditions, the corresponding thickness increase  $\Delta\delta$  can be calculated if a constant mean electric field of  $\varepsilon = 9 \times 10^5 \text{ V/cm}$  is considered, as a first approximation, since, as indicated above,  $\varepsilon$  values must increase. According to the results discussed above,  $\varepsilon$  goes from  $2 \times 10^5$  to  $1.6 \times 10^6 \text{ V cm}^{-1}$  under voltammetric conditions for a passive layer on a nickel deposit in a EQCM experiment. Then,

$$\Delta \delta = \frac{\Delta E_0 - \Delta \phi_{m/f}}{\varepsilon} \tag{21}$$

The obtained values are listed in Table 1 as a function of the stabilization potential together with the  $\Delta \phi_{m/f}$  calculated ones. As observed in Table 1, at  $E_0 = -25$  mV, passive layer thickness can be estimated as  $\delta = 3.3$  nm. This value is of the same order of magnitude than those measured in EQCM analysis. There exists a good agreement between  $\delta$  values determined by means the two procedures tested.

## 5. Conclusions

Fdm/dQ analysis shows that a passive layer fully covers the electrode surface at the beginning of the recorded anodic oxidation peak. Then, the obtained results are analyzed within the framework of the point defect model theory. Only a minor part of the measured current values are consumed during the passive film growth (nickel passivation). This experimental finding is consistent with cation vacancies being predominant within passive layer. Fdm/dQ analysis allows to obtain the fraction of charge consumed during passivation, and, in this way, following the passive layer thickness variation with the applied potential. It is observed that two monolayers of Ni(OH)<sub>2</sub> fully covers the electrode surface at the beginning of the voltammetric peak.

### Acknowledgements

This work has been supported by Spanish Ministry of Science and Technology (Project CICyT-CTQ2004-08026/BQU). J. Gregori acknowledges a Fellowship from the Spanish Ministry of Education (FPU program). J.J. García-Jareño would also acknowledge the Spanish Ministry of Science and Technology for their position ("Ramón y Cajal" Program).

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