THE KINETICS AND MECHANISM OF THE NICKEL ELECTRODE—III. THE POTENTIODYNAMIC RESPONSE OF NICKEL ELECTRODES IN ALKALINE SOLUTIONS IN THE POTENTIAL REGION OF Ni(OH)₂ FORMATION*

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Abstract—The electrochemical behaviour of nickel in alkaline aqueous solutions within the anodic potential range yielding Ni(OH)₂ and under different potentiodynamic perturbations profiles has been investigated. The formation of Ni(OH)₂ is characterized by an irreversible anodic current peak which is quantitatively interpreted in terms of a complex reaction pathway involving different hydroxo-adsorbed species.

INTRODUCTION

THERE IS clear evidence that nickel in contact with an alkaline hydroxide aqueous solution is spontaneously covered by a layer of Ni(OH)₂.[1-7] The study of the electrochemical behaviour of nickel in that medium, particularly under stationary conditions, indicates that the metal behaves like a hydrated nickel hydroxide electrode. This sort of electrode is widely used in different batteries. Many authors have conducted detailed and careful investigations to understand the possible reactions related to these electrodes as well as their kinetics and probable mechanisms,[8-12] but in spite of them the subject still deserves further study.

The first potentiodynamic anodization of Ni in 0.2N KOH shows that different reactions take place within relatively well defined potential ranges.[2,4,7] The electrochemical anodization can be separated into at least three main processes. The first one involves the formation of Ni(OH)₂, the second one corresponds to the β-NiOOH formation and finally, at higher anodic potentials, oxygen evolution takes place as well as the probable formation of other nickel compounds of higher oxidation states. Recent ellipsometric results show that Ni(OH)₂ and NiOOH are present within the potential range preceding oxygen evolution[13] in agreement with preceding studies.[14] The literature on the anodization of nickel has paid particular attention to the various processes, including the influence of the crystallographic structure of the surface,[2,4] the degree of reversibility of the various processes under different conditions,[8-12] the electrochemical characteristics of the hydrated nickel hydroxide electrodes,[11,12] the influence of hydrogen and oxygen adsorption,[15,16] the growth and resistance of nickel oxide films,[6,17,18] the effect of anions[19] and cations,[20] the participation of proton diffusion through the nickel hydroxide lattice,[11,21,22] the ageing of the solid phases electrochemically formed[11,23] and the electrochemical response and

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conversion of the various hydrated forms of $Ni(OH)_2$ and $NiOOH$.[14] Most of these results, however, are still a matter of considerable controversy and the kinetics and mechanisms of the corresponding reactions are far from proven.

The present report furnishes quantitative kinetic information about the anodization process yielding $Ni(OH)_2$. Under a linear potentiodynamic perturbation the formation of $Ni(OH)_2$ is characterized by an irreversible anodic current peak which under certain circumstances has been assigned to a hydrogen electro-oxidation current.[24] As $Ni(OH)_2$ is gradually built up as a non-conducting layer, a sort of pre-passivation of the metal is observed prior to a further oxidation of $Ni(OH)_2$ to β-$NiOOH$.[25–27] As far as the $Ni(OH)_2$ formation is concerned, the results of the present work in comparison with those reported in previous papers[29,30] support the idea that the type of reaction yielding $Ni(OH)_2$ is, either in acid or alkaline solutions, scarcely dependent on SO_4^{2-} ions concentration.[30] The present results render possible the presentation of a probable reaction pathway involving a composite pattern related to the $Ni(OH)_2$ formation.

EXPERIMENTAL METHOD

The experimental set-up and the technical procedures employed in the present work were the same as already described in previous publications.[28–30] Johnson Matthey "Specpure" nickel wires (0.5 mm dia., 0.25 cm²) were used as working electrodes. The counter electrode was a large area Pt sheet previously cleaned with the usual procedures. Potentials were experimentally measured vs a saturated calomel electrode but they are quoted here with respect to the standard hydrogen electrode scale.

The following electrolytic solutions were employed: 1.00 N KOH (solution A); 0.10 N KOH (solution B); 0.10 N KOH + 0.10 N K_2SO_4 (solution C); 0.01 N KOH + 0.66 N K_2SO_4 (solution D). They were prepared from triple distilled water and analytical grade reagents. Experiments were made under nitrogen gas saturation at 20°C using different programmed potential perturbation techniques. Occasionally H_2 gas saturated electrolytic solutions were employed.

EXPERIMENTAL RESULTS

The first large potential range E/I display run in the anodic direction from -0.96 up to 0.74 V, with solution A at a linear sweep-rate, $v = 0.1$ V/s, using a freshly polished electrode surface (Fig. 1), shows an anodic current peak at $ca.$ -0.44 V (peak I) with a broad shoulder at the right side and another one (peak II) in the potential range close to the potential region of the oxygen-evolution. The returning cathodic current scan, in principle, exhibits only a single current peak (peak III) which can be related to the complementary cathodic reactions of current peak II. The following successive potential excursions show little variation both in current peaks II and III but current peak I is not observed. The E/I profile can be thus divided into active, prepassive, passive and transpassive potential ranges, although such situation seems to be completely arbitrary after the light shed by recent researches.[23,30]

The simplest and more symmetric E/I profiles of current peak I run from $E_i = -0.96$ V at $v = 0.2$ V/s correspond to those nickel electrodes which have been firstly polished with alumina and cathodically maintained at -0.96 V for 10 min without stirring before the potential excursion. When the mechanical polishing is not used and the electrode is cathodically held for 10 min at -0.96 V under stirring, at least two current peaks whose maxima although poorly defined are located at $ca.$ -0.20 and $ca.$ $+0.15$ V respectively (Fig. 2) are observed. The stirring during
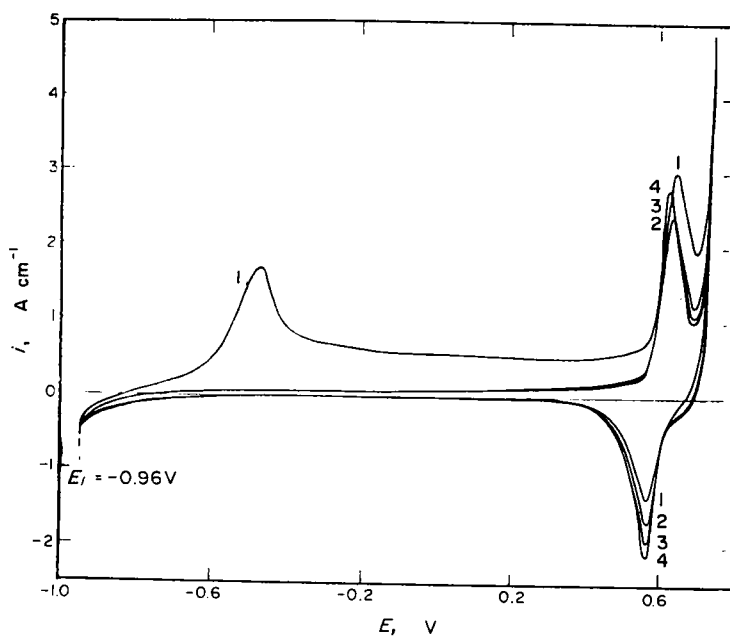
FIG. 1. E/I profiles run with repetitive triangular potential sweeps at 0.1 V/s. Solution A. The numbers correspond to the cycle order.
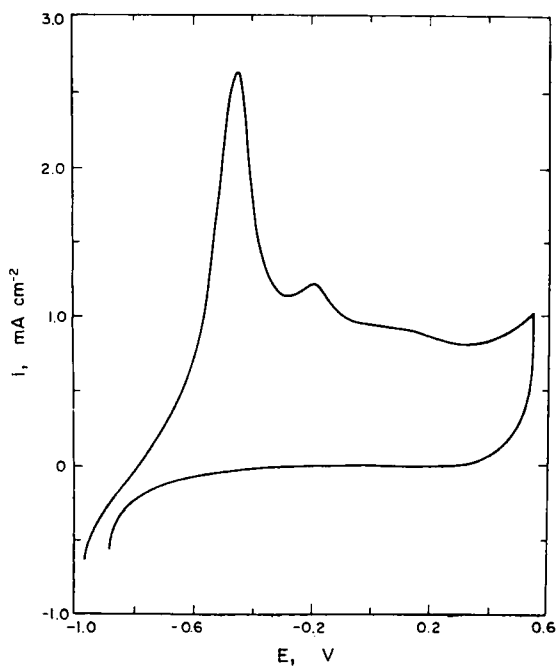

FIG. 2.   Single triangular potential sweep at 0.2 V/s with the conditions described in the text. Solution A.

cathodic polarization tends to increase slightly the appearance of those new current peaks. It is interesting to observe that under these circumstances the height of current peak I decreases although apparently the anodic charge involved remains practically unchanged. In the hydrogen-saturated solution this effect becomes more marked as the contact time between the metal and the electrolyte increases and it is more evident when the cathodic polarization time increases. The spurious current may be attributed to traces of impurities which may act as adsorbed inhibitors on the electrode surface. The behaviour can be compared to that found in the presence of SO_4^{2-} ions that are reduced by hydrogen adatoms to sulphide-type species, which is detected by X-ray photo-electron spectroscopy.[31]

The reproducibility of the results is very satisfactory when the freshly polished electrode is cathodically polarized at $E \leq -0.9$ V for at least 5 min prior to the potentiodynamic sweep. If the cathodic polarization is done with an electrode which has been previously potential cycled, the E/I display reproduces the characteristics just mentioned but the first anodic excursion involves a current peak I more poorly defined. The following experiments are mainly confined to the potential range of current peak I. The latter is from now onwards referred to as the anodic current peak.

At a fixed sweep-rate, v, the height of the anodic current peak referred to the apparent unit area (i_{ap}) and the corresponding current peak potential (E_{ap}) depend on E_i, the cathodic limit of the potential excursion (Fig. 3). When the electrode is held for 10 min at $E_i \leq -0.85$ V, the current peak potential is independent of E_i, but when $E_i > -0.85$ V, it increases with E_i approaching a straight line relationship (Fig. 4) with slope equal to one. A similar behaviour has been observed for iron electrodes in alkaline solutions.[32]

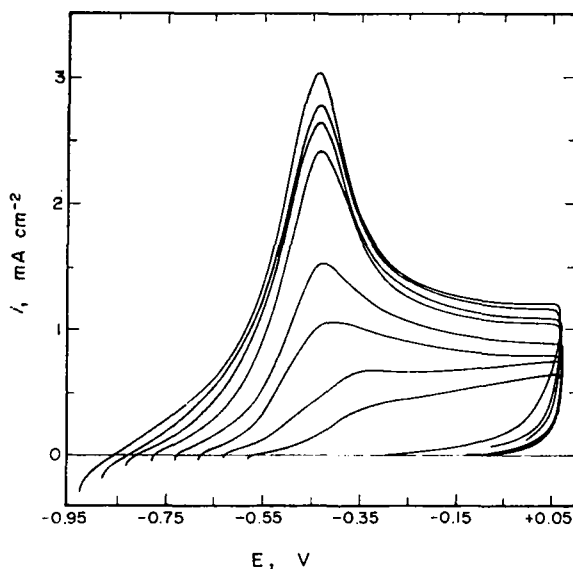Whatever the solution composition the following kinetic relationships are derived

Fig. 3. Single anodic linear potential sweeps at 0.3 V/s. Solution A, starting at different E_i. The nickel electrode is kept at E_i for 10 min before the potential sweep.
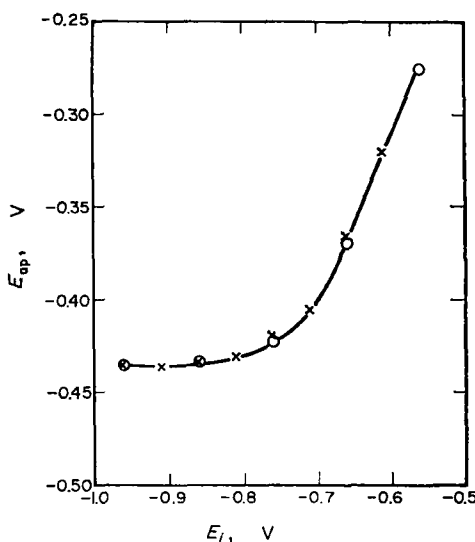
FIG. 4. Dependence of E_{ap} on E_i at 0.3 V/s. ($\circ$) and ($\times$) correspond to two series run under the same conditions.

from the linear potential sweep experiments. There is a linear log i_{ap} vs log v plot with a slope equal to one (Fig. 5). At a constant v the height of current peak I is independent of the solution composition (Fig. 5) within the KOH concentration covered by the present work. The potential of current peak I fits a linear E_{ap} vs log v relationship with a slope equal to the $2.3(RT/F)$ ratio (Fig. 6). At a constant v, there is also a linear E_{ap} vs pH plot involving a slope equal to the $-2.3(RT/F)$ ratio, as can be derived from Fig. 6. The coincidence of the experimental results with the solutions comprising different SO_4^{2-} ion concentrations indicate that the kinetics of the electrode processes is independent of the SO_4^{2-} concentration, at least within the range employed here.

The anodic charge involved up to the current peak potential also depends on E_i. Thus, within the sweep rate range 0.01 V/s $\leq V \leq 0.3$ V/s, and for -0.96 V $\leq E_c \leq -0.86$ V, $(Q_a)_p = 1.1 \pm 0.1$ mC/cm². The initial portion of the potentiodynamic E/I profile at any value of v when $i < 0.7(i_{ap})$, fits a sigmoid E vs log i relationship whose asymptotic initial slope, although somewhat uncertain, apparently approaches the $2.3(RT/F)$ ratio, and after the inflexion point, corresponds to values which are in the range of the $2.3(3RT/F)$ to $2.3(4RT/F)$ ratio, depending on v.

When E_a, the anodic potential limit, lies at potentials close to the potential of the anodic current peak, the returning cathodic potential excursion exhibits a clear cathodic current peak (Fig. 7), whose potential is more anodic than that corresponding to the hydrogen evolution reaction. The cathodic current peak potential at a constant v shifts to the cathodic potential side when E_a increases. Otherwise, at a constant E_a the cathodic current peak becomes better defined and its maximum is located at more anodic potentials as v increases. Both effects, which are bound to the same charge, indicate that the species anodically formed undergoes a chemical change to a more stable configuration. During the triangular potential cycling keeping
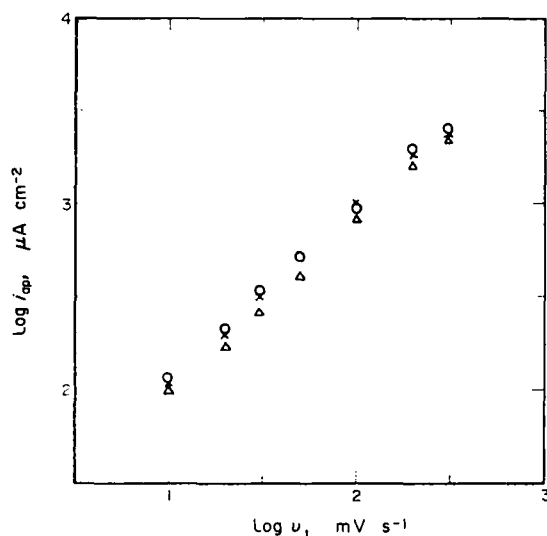
FIG. 5. Dependence of i_{ap} on v from the first potential scan after keeping the electrode at $E_i = -0.96$ V during 10 min: (○) solution A; (×) solution C; (△) solution D.

both E_a and E_i constants, both the anodic and cathodic current peak potentials shift simultaneously as if the overall electrochemical reaction attained an apparently more reversible kinetic behaviour after the nth cycle (Fig. 8).
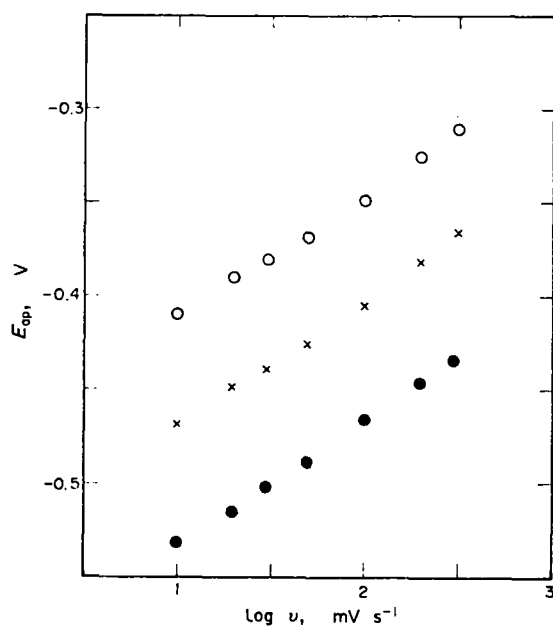

FIG. 6. Dependence of E_{ap} on v from the first potential scan after keeping the electrode at $E_i = -0.96$ V during 10 min: (●) solution A; (×) solution C; (○) solution D.
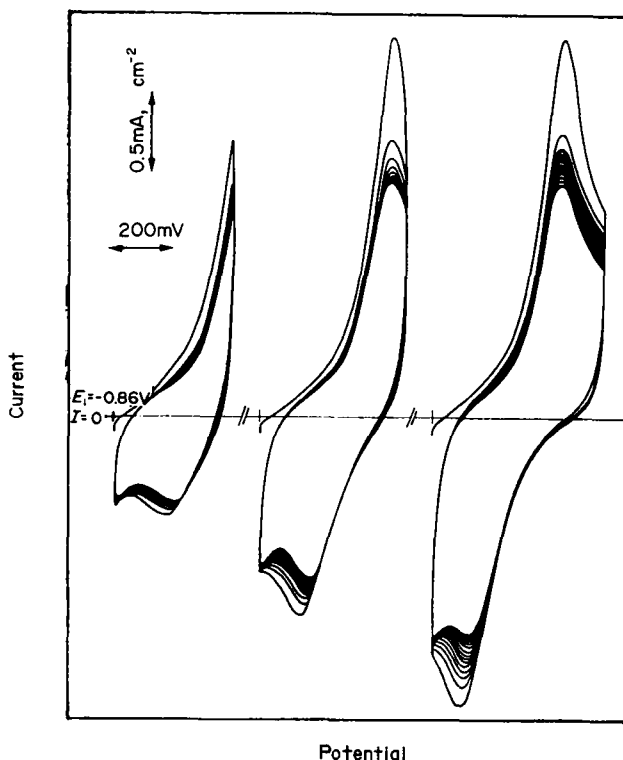
FIG. 7. E/I profiles run with repetitive triangular potential sweeps at 0.3 V/s, starting from constant potential $E_i = -0.86$ V and reaching different E_a. Solution B.

The probable influence of the hydrogen kept either on the metal surface or on the bulk of the metal can be visualized through E/I profiles run from different E_i with previous cathodic polarization at this potential for a certain time, without flushing out the hydrogen gas before the potentiodynamic run. It is observed that the hydrogen influence is apparently only related to a small current hump located at *ca.* -0.65 V which distorts the symmetry characteristics of the E/I display. Moreover, the latter is more evident when the 5 min cathodization occurs at $E_i \leq -0.75$ V. These experiments confirm that the characteristics of the anodic current peak are definitely different from those of the hydrogen electro-oxidation on Ni.

The charge playing part from E_i up to the current peak potential decreases when $E_i > -0.85$ V. On the other hand, $(Q_a)_p \approx 1.1$ mC/cm^2 when $E_i < -0.85$ V. These results are valid whatever the composition of the solution employed. In any case $(Q_a)_p$ increases slightly with v, an effect which might be attributed to the contribution of the double layer charge during the potentiodynamic runs. The charge is also, having regard to the scatter of the results, independent of either pH or SO_4^{2-} ion concentration.

The fact that $(Q_a)_p$ decreases when E_i increases indicates that the compound that passivates the electrode is also produced spontaneously on the nickel surface in contact with the alkaline solution. The cathodic polarization of the surface at $E_i < -0.85$ V
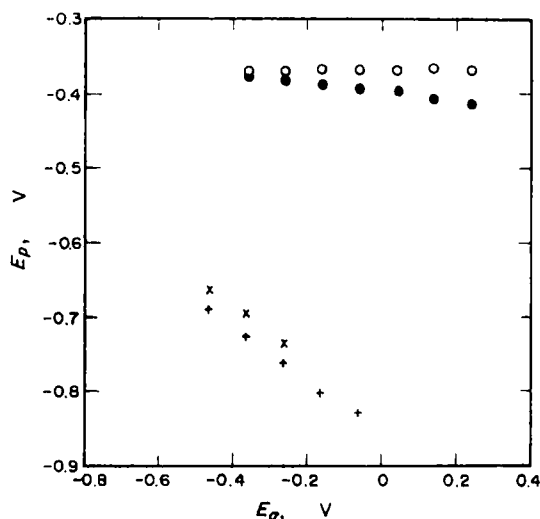
FIG. 8. Dependence of E_p on E_a from repetitive triangular potential sweeps recorded at 0.3 V/s, $E_i = -0.86$ V. Solution B. (○) and (●), E_{ap} read at the first and the nth cycles respectively; (+) and (×), E_{cp} read at the first and the nth cycles respectively.

is required to "clean" it from the passivating species.

Once the passivating species is allowed to stand for a relatively long time, its electro-reduction takes place only at cathodic potentials as high as those where an abundant hydrogen evolution takes place.

The accumulation of passivating species and the influence of E_a on the potentio-dynamic response during triangular repetitive potential cycling are clearly observed in Figs. 7 and 9. They show that the anodic current drop between the first and the second potential scans is remarkably dependent on those potential limits. The shift
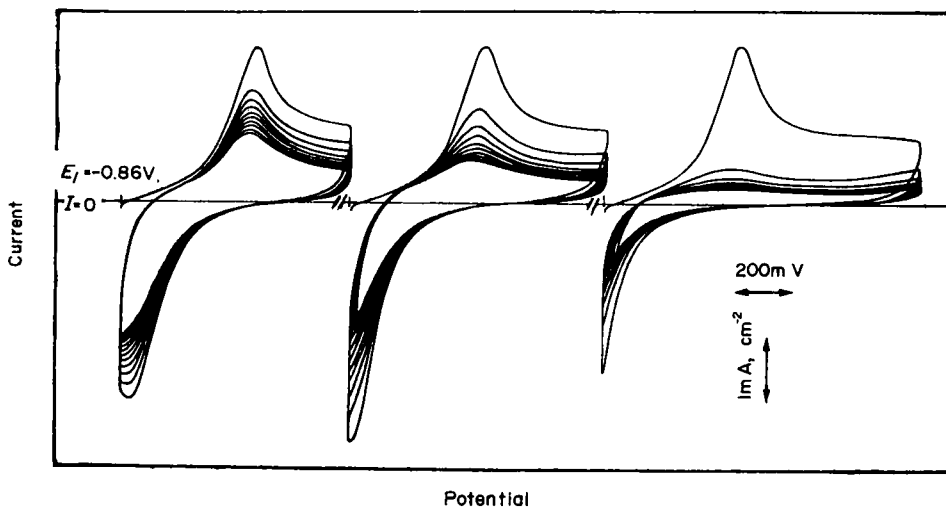

FIG. 9. Same as Fig. 7, but with larger values of E_a.

of the cathodic current profile towards cathodic potentials on increasing E_a agrees with the results already described. Under these circumstances the passivation–depassivation cycle approaches a stable situation which implies a constant charge after a large number of cycles. The charge then involved decreases as E_a increases (Fig. 9).

DISCUSSION

The experimental results clearly reveal that with a clean metal surface, the electrochemical reaction related to the electro-dissolution and prepassivation of nickel in alkaline solutions implies the occurrence of a single although complex reaction. The kinetic results are assembled in Table 1. They are independent of the SO_4^{2-} ion concentration, a fact which had also been established in highly acid aqueous media.[30]

The initial portion of the anodic E/I profile plotted as a Tafel line approaches the RT/F ratio which has been assigned to the steady electro-dissolution of the metal in aqueous solutions,[33] but in the alkaline media the first metal passivation state (prepassivation) depends on the solubility product of $Ni(OH)_2$. There is sufficient evidence concerning the formation of the latter either in acid[26,30] or alkaline solutions[11,14] in the potential range corresponding to the anodic current peak I. The present results indicate that the electro-oxidation of any type of adsorbed hydrogen on nickel should be a negligible contribution to the anodic current peak I. However, the hydrogen electro-oxidation reaction may contribute at the cathodic potential side of the anodic current peak probably at high potential sweep rates if the reaction entails an appreciable irreversibility. The present results, therefore, sustain that neither the hydrogen electro-oxidation processes nor the effect of possible impurity adsorption should be confused with the main $Ni(OH)_2$ formation process which is associated to the anodic current peak.

The charge playing part in the overall $Ni(OH)_2$ film formation process is either of the order of few monolayers if the electrode roughness factor is taken as one, a choice which is rather unlikely for a metal which initially corrodes, or of the order of the $Ni(OH)_2$ monolayer if one admits a roughness factor of 3–4. Nevertheless, part of the anodic charge belongs to the electro-dissolution of nickel as $Ni(II)$.

Taking the latter assumption as the more reasonable one, the reaction pathway can be imagined as being similar to those already discussed for other metals involving

TABLE 1. EXPERIMENTAL KINETICS PARAMETERS AT 25°C

$$\left(\frac{\partial \log i_{ap}}{\partial \log v}\right)_{pH} = 1$$

$$\left(\frac{\partial \log i_{ap}}{\partial pH}\right)_v = 0$$

$$\left(\frac{\partial E_{ap}}{\partial \log v}\right)_{pH} = 0.060 \text{ V}$$

$$\left(\frac{\partial E_{ap}}{\partial pH}\right)_v = -0.060 \text{ V}.$$

surface oxygen-containing species. The overall process consists then of the solvent and the metal electro-oxidation yielding hydroxo-containing species and the deprotonation of the latter in successive steps.

Taking into account that in the alkaline solutions the OH^- ion and the H_2O molecules are in part adsorbed at the electrochemical interface the following equilibria are considered:

$$Ni + H_2O \rightleftharpoons Ni(H_2O)_{ad} \tag{I}$$

$$Ni(H_2O)_{ad} + OH^- \rightleftharpoons Ni(OH)^-_{ad} + H_2O, \tag{II}$$
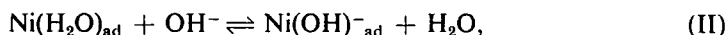
so that the initial step may be given in terms of any of the two adsorbed species. Thus, for a multi-step consecutive mechanism the initial electron transfer step can be put forward either as:

$$Ni(H_2O)_{ad} = Ni(OH)_{ad} + H^+ + e \tag{1}$$

or $$Ni(OH^-)_{ad} = Ni(OH)_{ad} + e, \tag{2}$$
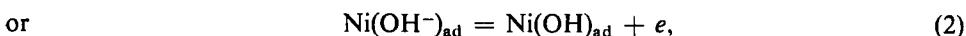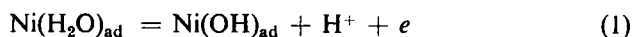
both reactions yielding the hydroxo-surface Ni complex as a reaction intermediate. The following step is a chemical re-accommodation process such as:

$$Ni(OH)_{ad} + H_2O = Ni(OH.H_2O)_{ad}, \tag{3}$$
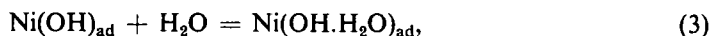
and the intermediate participates in a second electron transfer step:

$$Ni(OH.H_2O)_{ad} = Ni(OH)_2 + H^+ + e. \tag{4}$$
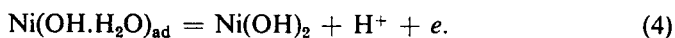
The $Ni(OH)_2$ appears as a hydrated species on the metal surface once the corresponding solubility product is exceeded.

In aqueous solutions $Ni(OH)_2$ is bound to the following well known equilibria in solution:[34,35]

$$Ni(OH)_2 = NiOH^+ + OH^- \tag{5a}$$

$$NiOH^+ = Ni^{2+} + OH^- \tag{5b}$$

$$Ni(OH)_2 = HNiO_2^- + H^+. \tag{5c}$$
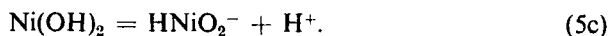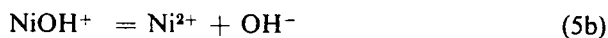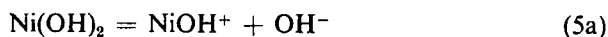
The latter is particularly important in alkaline solution since it entails the anodic dissolution of Ni as a complex anion. As the process advances from step (1) to step (4) a systematic decrease of the metal–metal bond takes place.

Let it be assumed that step (3) is the rate determining step (r.d.s.) and that the formation of the hydrated $Ni(OH)_2$ from the intermediate implies the uniform coverage and passivation of the metal. Under these circumstances, the quasi equili-

brium conditions for step (1), taking into account equilibrium (I), may be expressed as:

$$k_1 (1 - \theta_T) \exp [\alpha_1 FE/RT] = k_{-1} \theta_1 C_{H^+} \exp [- (1 - \alpha_1)FE/RT], \quad (6)$$

where k_1 and k_{-1} are the corresponding specific rate constants of step (1) in both directions, θ_1 is the degree of surface coverage by the intermediate species, θ_T is the degree of surface coverage by the two intermediate species, α_1 is the transfer coefficient assisting the reaction in the anodic direction and E is the applied electrode potential at the electrochemical interface. From (6)

$$\theta_1 = K_1 (1 - \theta_T) C_{H^+}^{-1} \exp [FE/RT], \quad (7)$$

and i_a, the anodic current under quasi-steady conditions is given by:

$$i_a = k' k_3 \theta_1 = k(1 - \theta_T) C_{H^+}^{-1} \exp [FE/RT], \quad (8)$$

where K_1 is the k_1/k_{-1} ratio, k_3 is the specific rate constant of the chemical step (3) and k' is the corresponding proportionality constant. Under a single linear potentiodynamic potential sweep ($E = E_i + vt$, where $v = dE/dt$), the rate of change for i_a is obtained from (8):

$$\frac{di_a}{dt} = k\, c_{H^+}^{-1} \exp [FE/RT] \left\{ (1 - \theta_T)\, \frac{F v}{RT} - \frac{d\theta_T}{dt} \right\}. \quad (9)$$

According to equation (9) an anodic current maximum, i_{ap}, is found at a potential E_{ap}, when

$$\frac{d\theta_T}{dt} = (1 - \theta_T)_p\, \frac{F v}{RT}, \quad (10)$$

and

$$i_{ap} = k\, \frac{d\theta_T}{dt} = k (1 - \theta_T)_p\, \frac{F v}{RT} = k\, c_{H^+}^{-1} (1 - \theta_T)_p \exp [F E_{ap}/RT], \quad (11)$$

which establishes a linear i_{ap} vs v relationship. k corresponds to the charge associated to the total coverage of the surface. Otherwise, from (8) and (11), at $E = E_{ap}$, it results

$$E_{ap} = \frac{2.303\, RT}{F} (\log K - \text{pH} + \log v), \quad (12)$$

yielding at a constant pH an E_{ap} vs log v relationship with a slope $(\partial E_p/\partial \log v)_{\text{pH}} = 2.303\, RT/F$. From equation (11), if θ at i_{ap} is independent of pH as deduced from

the experimental data, i_{ap} must be also independent of pH, at any value of v. Relationships similar to those given by equations (11) and (12) have been earlier obtained for an irreversible anodic monolayer and multilayer formation under Langmuirian conditions.[36,37] Under the same conditions, equation (12) yields $(\partial E_{ap}/\partial$ pH$)_v = - 2.303(RT/F)$, and from (11) it results:

$$(\partial \log i_{ap}/\partial \text{ pH})_v = 1 + (F/2.303 \ RT) \ (\partial E_{ap}/\partial \text{ pH})_v = 0. \tag{13}$$

These results certainly imply that the reaction order with respect to the OH^- ion is one. Therefore, the reaction formalism just discussed takes into account the kinetic response of the electrochemical interface when the $Ni(OH)_2$ film is being formed.

The anodic product at this stage may transform into another compound either chemically or electrochemically, as the anodic potential increases. The electrochemical process are represented by reactions which in part were already indicated to interpret the electrochemical behaviour of nickel in sulphuric acid media. They can be written either in terms of hydrated $Ni(OH)_2$ or $HNiO_2^-$:

$$Ni(OH)_2 = \beta\text{-NiOOH} + H^+ + e \tag{14a}$$

$$HNiO_2^- = \beta\text{-NiOOH} + e, \tag{14b}$$
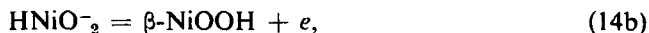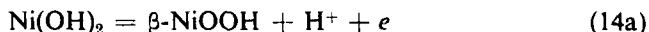
depending on the equilibrium constant of step (5c) and the specific rate constants of step (14). Any of these processes is bound to a potential range more anodic than that of the potential corresponding to the anodic current peak.

The chemical process apparently involves the formation of a more difficult electro-reduced surface species. For a constant amount of anodic product the amount of that species increases with the decrease of the time elapsed between the anodic $Ni(OH)_2$ formation and the initiation of the electro-reduction process, so that the product initially formed, probably $Ni(OH)_{ad}$, can be easily found in the potential region just preceding the hydrogen evolution only if the electro-reduction is conducted rapidly. The corresponding reaction is the reverse of either step (1) or (2). The more stable species may be related either to NiO or β-NiOOH, the former being formed from $Ni(OH)_2$ either by an irreversible chemical reaction:

$$Ni(OH)_2 \rightarrow NiO + H_2O, \tag{15a}$$

or electrochemically:

$$Ni(OH)_2 \rightarrow NiO + 2 \ H^+ + 2e. \tag{15b}$$
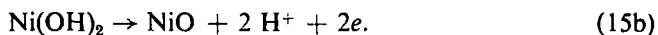
The electro-reduction of NiO hardly takes place in the region of the hydrogen evolution. Recent X-ray photo-electron spectroscopy[31] indicates that the film present on the electrode surface is probably composed of NiO and $Ni(OH)_2$, the former being the passivating species. The present results are in agreement with the spectroscopic conclusion and throw a further insight to understand the mechanism of Ni passivation.

The results also show an effect attributed to some impurity cathodically formed which induces a multiple anodic current peak formation during the anodic linear potential excursion. When this occurs the anodic charge required for passivation is nearly the same, as in its absence. This suggests that the formation of $Ni(OH)_2$ occludes the surface impurity. The film is first formed on the available "clean or bare" metal surface, and when the latter is filled up it continues on the impurity covered centers. The energy required for the process to occur on each type of site should, in principle, be different, causing thus the splitting of the anodic current peak. The appearance of the various current peaks during the potentiodynamic sweep resembles therefore the current/time response associated to a multilayer film formation under a potential step function.[38]

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