Passive Behaviour of Nickel in Phosphate Solutions

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Hurlen, T. and Simon, C., 1991. Passive Behaviour of Nickel in Phosphate Solutions. – Acta Chem. Scand. 45: 239–243.

Long-term polarization measurements (20 h stabilization) show that nickel in phosphate solutions of pH 1.9–12.6 exhibits an essentially potential- and pH-independent steady-state passive current, but that the proper passive range shrinks with decreasing pH and disappears at pH below about 2. The pH independence may suggest the transfer of nickel, mainly as neutral complex species at the film/solution interface. Potentiostatic transients yield initial polarization data which suggest $z = 1$ (rather than 2) for the charge number of nickel ions being transferred at the metal/film interface. Galvanostatic transients yield DC capacitance data which at low passive potentials approach expectations from a simple insulator model. These data also help to reveal both the mean dielectric constant of the passive film and the main charge distribution in the passive electrode. Cathodic polarization data suggest that the content of trivalent nickel in the passive film increases with the potential at which the film is formed and stabilized.

The passive behaviour of nickel has been the subject of many investigations, most of which are well reviewed.[1–3] However, studies on well stabilized passive nickel electrodes (stabilization for at least 20 h appears to be needed)[4,5] are scarce. Such steady-state and transient studies have been found quite informative in recent work of ours on passive iron[6,7] and a number of other passive metals (Al,[8] Ti,[9] Zr,[10] Hf,[11] Nb[12] and Ta[13]). These studies generally elucidate the charge-transfer processes occurring at either interface of the passive film, the electric field in this film, its dielectric properties and the charge distribution in the passive metal electrode. This is presently extended to studies on 20 h stabilized passive nickel electrodes in acidic and alkaline phosphate solutions (pH 1.9–12.6) at 25 °C.

From in situ studies by UV–VIS[14–17] and IR[18] spectroscopy, the passive film on nickel is found to consist primarily of $Ni(OH)_2$ which is gradually transformed into $NiOOH$ (or $Ni_2O_3 \cdot H_2O$) at high potentials (mainly in a transpassive range). This transformation is easily reversed, giving a pair of closely connected anodic and cathodic peaks in cyclic voltammograms.[14,19]

From in situ studies by reflectance ellipsometry,[20–24] the passive film on nickel appears to be very thin (often around 1 nm), but possibly increases in thickness almost linearly with the potential of film formation by about 1 nm V^{-1} within the passive range, and this dependence appears to give an extrapolated potential of zero film thickness close to the reversible $Ni(OH)_2/Ni,2OH^-$ potential. These findings are supported by coulometric[20,21,25] and oxygen tracer[26,27] data, but contradictory results[28–30] also exist.

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Experimental

Polycrystalline nickel (99.98 %, Goodfellow) sheet electrodes (4 cm²) were studied at 25 °C in deoxygenated (N_2) solution portions (100 ml) of the following compositions:

0.03 M H_3PO_4	(pH 1.9)
0.05 M NaH_2PO_4	(pH 4.5)
0.1 M NaH_2PO_4 + 0.1 M Na_2HPO_4	(pH 6.7)
0.1 M Na_2HPO_4	(pH 9.2)
0.1 M Na_3PO_4	(pH 12.6)

All the solutions were made from A.R. quality chemicals and water twice distilled in a quartz apparatus. Prior to use, the nickel electrodes were mechanically polished (1200 mesh SiC), thoroughly rinsed in distilled water, dried and degreased in acetone and chloroform, and cathodically treated in a preportion of test solution to destroy their air-formed oxide film.

In the three-compartment Pyrex cell used, the pretreated nickel test electrode, after some conditioning at open circuit, was passivated and stabilized by stepping its potential to a chosen value in the passive range and keeping it there for 20 h. Potentiostatic and galvanostatic transients were thereafter recorded on stepping sharply and shortly (5 s) away from the quasi-steady state reached. Between such square single pulses of various amplitudes a return to the stabilized state was awaited. Finally, initial polarization
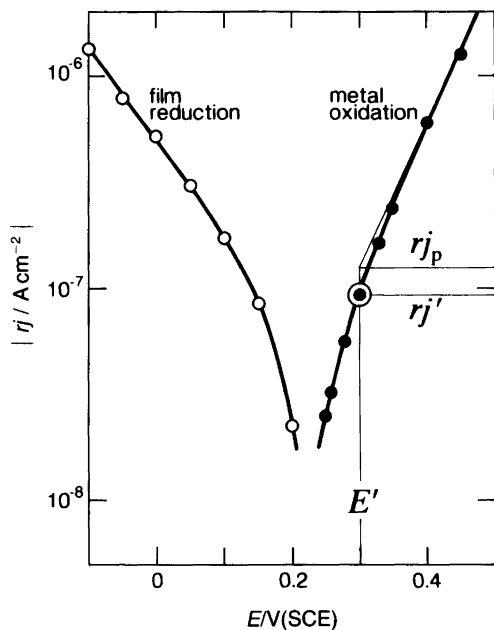
Fig. 1. Initial polarization (E, j) of a passive nickel electrode in single square steps $(E-E')$ from a given 20 h stabilized state (E', j') in a phosphate solution at pH 1.9. (r is the roughness factor.) (●) Anodic and (○) cathodic current.
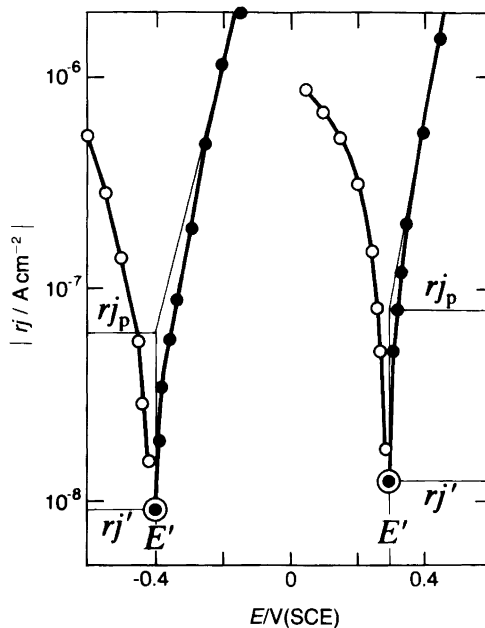

Fig. 2. As in Fig. 1, but two examples in a phosphate solution at pH 12.6.

data and DC capacitance data were extracted by back extrapolation of the potentiostatic transients and from the initial slope of the galvanostatic ones, respectively.[6,7]

The above procedure was repeated with a number of different values for the potential of passivation and stabilization in each of the test solutions noted above. The instruments mainly used were a PAR-173/176 potentiostat/galvanostat and a Goerz-SE-120 recorder. All the potential measurements were made against a saturated calomel electrode (SCE).

Results

In all cases of the present work, on stepping the potential of a nickel electrode to a chosen value for passivation and stabilization, an anodic current rapidly rose to an early value, from which it fell monotonically with time at a decreasing rate. After 20 h it was mostly still falling, but slowly enough to change negligibly over the time needed for a suitable programme of transient studies to be accomplished (2–3 h). This agrees with previous observations.[4,5]

Figs. 1 and 2 give examples of the polarization data obtained in this study on 20 h stabilized passive nickel electrodes in acidic and alkaline phosphate solutions, respectively. For three different cases are shown the quasi-steady polarization point reached (E', j') and initial polarization points obtained (E, j), the latter ones on stepping away from $E = E'$ to various other values of E (on either side of E'). For each case, the initial polarization data separate into an anodic polarization curve, presumably for

metal oxidation, and a cathodic one, presumably for some kind of passive film reduction. In this respect, nickel has much in common with iron.[6,7]

Passive current. The quasi-steady polarization point (E', j') of a 20 h stabilized passive nickel electrode lies on the anodic polarization curve, but not on the anodic Tafel line. It thus does not represent metal oxidation alone, but seems codetermined by some interfering cathodic reduction process. This interference seems to be "dragged" along with the stabilization potential when this potential is
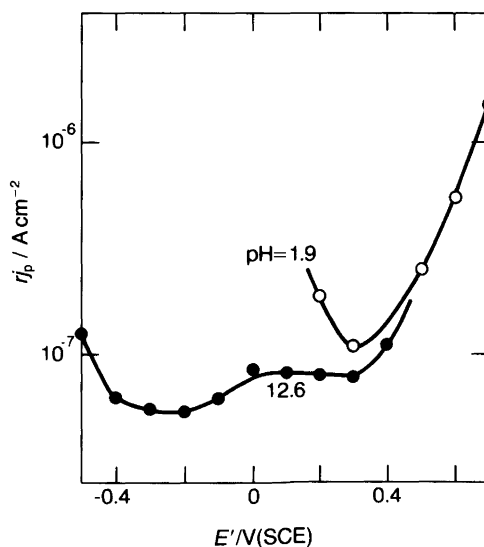

Fig. 3. Quasi-steady passive current (j_p) for nickel electrodes stabilized for 20 h at various potentials (E') in phosphate solutions at pH 1.9 and 12.6. (r is the roughness factor.)

changed (Fig. 2). The quasi-steady passive current (j_p) is then given by the intersection of the anodic Tafel line with the stabilization potential applied. This is illustrated in Figs. 1 and 2.

Fig. 3 gives values obtained accordingly for j_p at the two outermost pH values of the present work (pH 1.9 and 12.6). At the three intermediate pH values applied, intermediate results were obtained. The results show that nickel has a quite broad passive range of essentially potential-independent passive current at high pH, that this range shrinks with decreasing pH (being rather narrow at the lowest pH tested), and that the passive current hardly varies with pH over the pH range tested (pH 1.9–12.6). The apparent passive current density (rj_p where r is the roughness factor) comes out a little below $10^{-7}\,\mathrm{A\ cm^{-2}}$ for our 20 h stabilized electrodes. These results compare reasonably well with previous ones on less stabilized electrodes.[1-3,31]

Initial polarization. In Fig. 4 values obtained in this work for the initial anodic Tafel slope (b) in three of the solutions used are plotted against the stabilization potential (E') to which they apply. Except at high potentials, where transpassive processes may interfere, such data for the present work obey eqn. (1), where E_b is the extrapolated potential

$$b/\mathrm{decade}^{-1} = (0.27 \pm 0.05)\ (E'-E_b) \tag{1a}$$

$$E_b/\mathrm{V(SCE)} = -0.13 - 0.06\ \mathrm{pH} \tag{1b}$$

of zero initial Tafel slope. This potential is found to come close to the reversible $\mathrm{Ni(OH)_2/Ni,2OH^-}$ potential. It also comes close to previous results for the extrapolated poten-

tial of zero steady-state passive film thickness (see Introduction); this is what one should expect in simple case.[32]

Capacitance. In Fig. 5 values presently obtained for the inverse DC capacitance (C^{-1}) of 20 h stabilized passive nickel electrodes in two of the solutions used are plotted against the stabilization potential to which they apply. The determinations have been made from the initial slope ($\mathrm{d}E/\mathrm{d}t$) of galvanostatic transients after various current density steps (Δj) using the relationship $C = \Delta j (\mathrm{d}E/\mathrm{d}t)^{-1}$. Except at high potentials, where trans-passive behaviour may interfere, such data of the present work largely obey eqn. (2),

$$(rC)^{-1} = (E'-E_c)(r\sigma'_m)^{-1} \tag{2a}$$

$$E_c/\mathrm{V(SCE)} = -0.13 - 0.06\ \mathrm{pH} \tag{2b}$$

$$r\sigma'_m/\mu\mathrm{C\ cm^{-2}} = 14 \tag{2c}$$

where E_c is the extrapolated potential of zero inverse capacitance, σ'_m is the surface charge density on the metal (at the metal/film interface) under quasi-steady conditions, and r is the roughness factor which applies. Eqn. (2b) gives the same zero-point potential for C^{-1} as does eqn. (1b) for b (and δ). This equality matches expectations for simple cases in which the electrode capacitance is given by the passive film capacitance ($C = C_f = \varepsilon\varepsilon_0/\delta$).[12,32] The present capacitance data largely agree with previous results on passive nickel electrodes.[23]

Dielectric constant. If space-charge contributions to the electric field in a steady-state passive film are negligible, the field should be given both by $\sigma'_m/\varepsilon\varepsilon_0$ (where ε is the
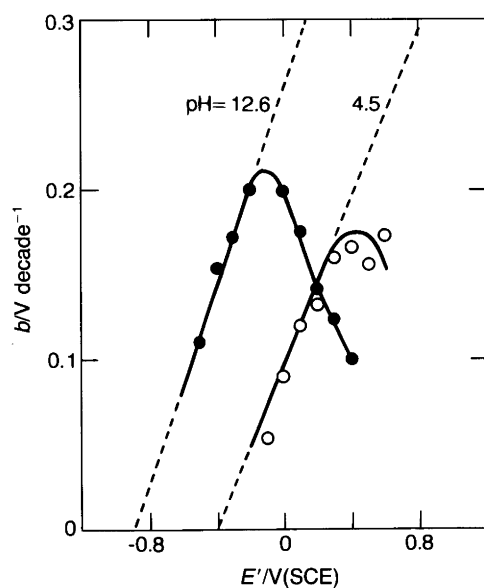
Fig. 4. Initial Tafel slope (b) of metal oxidation (Figs. 1 and 2) for passive nickel electrodes stabilized for 20 h at various potentials (E') in phosphate solutions at pH 4.5 and 12.6.
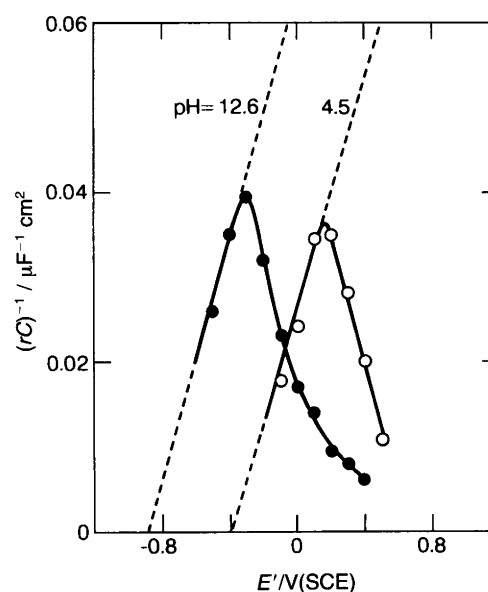
Fig. 5. Inverse DC capacitance (C^{-1}) of passive nickel electrodes stabilized for 20 h at various potentials (E') in phosphate solutions at pH 4.5 and 12.6. (r is the roughness factor.)

dielectric constant of the film, and ε_0 is the permittivity of free space) and by $1/a'$ (where a' is the steady-state anodization ratio, defined as $a' = d\delta'/dE'$). For the passive film on nickel, this yields eqn. (3), when use is made of

$$\varepsilon = a'\sigma'_m/\varepsilon_0 = 16/r \qquad (3)$$

the relationship $a' = 1$ nm V^{-1} (see Introduction) and of eqn. (2c). This is not far from previously determined values for ε in passive films on nickel at low passive potentials.[23]

Discussion

The present work shows that the primary passive range of well stabilized nickel electrodes shrinks with decreasing pH and essentially disappears at pH values below about 2 (Fig. 3). At lower pH, a direct transition from passivation to trans-passive behaviour seems to occur without any intermediate proper passive range appearing. This may perhaps be the reason for rather strange ellipsometric thickness data[30] for passive films on nickel at low pH, but more normal ones[23] at higher pH.

The present work further shows that the essentially potential-independent passive current of well stabilized nickel electrodes in proper passive states (pH above about 2) is also pH-independent (Fig. 3). From the general theory of passive metal behaviour given by Vetter,[33] this pH independence may reflect rate control by transfer of some uncharged nickel species at the film/solution interface. This may be species such as $Ni(OH)_2$, $NiHPO_4$ or similar ones. It has previously been found that the steady-state passive current on nickel mainly produces divalent nickel species in solution.[1-3,20]

The initial anodic Tafel slope of eqn. (1a) is believed to represent the metal oxidation process at the metal/film interface of the passive nickel electrode. A theoretical expression for this slope is given by eqn. (4),[8,9,12] where z is

$$b = 2.303\ (RT/F)a'(z\lambda fg)^{-1}(E'-E_b) \qquad (4)$$

the charge number for ions being transferred at the metal/film interface, λ is their activation (half-jump) distance, f and g are a transient field and site factor, respectively, and other symbols have their usual meaning. Comparing this with the empirical eqn. (1a) on using $\lambda = 0.15$ nm (Ref. 34) and $a' = 1$ nm V^{-1} (see above), one obtains eqn. (5) for the

$$z\,f\,g = 1.5 \pm 0.3 \qquad (5)$$

dimensionless triple product noted.

For cases as in the present work, where $E_b = E_c$ and $C = C_f = \varepsilon\varepsilon_0/\delta$, one should expect f to be unity.[32] Moreover, since values of g normally are in the range 1–2,[12] eqn. (5) suggests $z = 1$ (rather than 2) for the ion-transfer process at the metal/film interface of the passive nickel electrode. To satisfy our knowledge of the composition of the film (see

Introduction), this ion-transfer process must be succeeded by a fast process of electron transfer back to the metal from Ni(I) species in the film, making these species rather short-lived intermediate ones. This corresponds well with previous findings on the anodic dissolution of active nickel in aqueous solutions.[35-37]

In DC capacitance behaviour (Fig. 5) passive nickel groups with passive aluminium,[8] niobium[12] and tantalum[13] by showing $E_c = E_b$ $(= E_d)$ and $C = C_f$ $(= \varepsilon\varepsilon_0/\delta)$ at low passive potentials. Passive iron,[6,7] titanium,[9] zirconium[10] and hafnium[11] behave differently in this respect. This has been discussed to some extent previously.[12,32]

For passive nickel, both b (Fig. 4) and C^{-1} (Fig. 5) go through a maximum and subsequently fall with increasing stabilization potential. This is as if δ decreases and ε increases with increasing potential in the trans-peak range, an assumption which agrees with previous results obtained by ellipsometry and impedance spectroscopy.[23] Moreover, the cathodic observations of the present work (Figs. 1 and 2) suggest that the passive film on nickel has a Ni(III) content which increases with increasing passivation potential. The cathodic response is most likely one leading to the reduction of Ni(III) to Ni(II) in the film.

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