

THE INFLUENCE OF MATERIAL DISPERSION ON THE REDOX BEHAVIOUR OF NICKEL OXIDE ELECTRODES

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Summary

The electrochemical behaviour of nickel oxide was investigated using, as a model system, nickel-supported hydrous oxide films produced by potential cycling in base. The potential/pH response of such electrodes was examined under cyclic voltammetry and open-circuit conditions in a range of buffer solutions (pH 7.0 - 13.5). As outlined previously, the cyclic voltammetry data indicated the presence of both anhydrous and hydrous components in the layer - the former giving a potential/pH response of *ca* 59 mV/pH unit and the latter *ca* 88.5 mV/pH unit. Under open-circuit conditions, with relatively thick films in the half-charged state, *i.e.*, $[Ni(II)] = [Ni(III)]$, the observed potential/pH response was *ca* 75 mV/pH unit. With cathodically deposited layers the change from a hydrous to an anhydrous potential/pH response was accompanied by a levelling off of the charge storage capacity - suggesting that the hydrous material is more active with regard to charge acceptance. Along with a thermodynamic interpretation of the unusual potential/pH behaviour of the hydrous material, and relating this to the known structures of these materials, the involvement of hydrous oxide sites in electrocatalytic processes at nickel oxide electrodes was demonstrated.

Introduction

Oxide cathodes are widely used in aqueous battery systems. Such oxides are usually of an attenuated or dispersed character with much of the oxygen present not simply as bridging species between two metal cations (as, for instance, in rutile) but as OH and H₂O ligands. X-ray and electron diffraction patterns for hydrous oxides are frequently difficult or impossible to interpret [1] but some interesting results have been obtained using magnetic susceptibility measurements. According to Selwood [1] the magnetic susceptibility of high surface area chromia (Cr₂O₃) gel is much greater than that of the corresponding crystalline material. Evidently the hydrous oxide exists in a magnetically dilute form which is attributed to the presence of material with a thread-like structure. Heating hydrous oxides generally results in both

a loss of water and conversion of hydroxide to oxide; such reactions are accompanied by a large decrease in magnetic susceptibility.

The influence of hydration on the electrochemical behaviour of hydrous oxides was demonstrated in recent work in this laboratory. It was shown, for instance, that the reversible potentials for redox transitions observed in cyclic voltammograms recorded for hydrous gold [2, 3], iridium [4], rhodium and iron [5] oxides varied with pH, not by the commonly accepted value of 59 mV/pH unit (pH-independent reference electrode) but by *ca* 88.5 mV, *i.e.*, $3/2 (2.303 RT/F)$ V, per pH unit. This behaviour is apparently due to interaction between the acid-base and redox behaviour of these materials. Proton loss, which may be regarded in terms of either an acid dissociation or a hydrolysis reaction, is favoured by the higher positive charge of the central metal ion in the oxidized form of the redox couple — it evidently results in a more anionic form for the oxidized, as compared with the reduced, hydrous oxide species. For the case of gold [3], which was discussed recently in considerable detail, the redox transition giving rise to the 88.5 mV/pH unit shift may be represented for base by the equation



Similar behaviour was described recently for the nickel oxide electrode system by the present authors [6, 7]. It was observed that with films grown on the base metal by potential cycling in base, two redox transitions were observed (particularly on the cathodic sweep) for the Ni(II)/Ni(III) transition in the oxyhydroxide layer at potentials just below that for the onset of oxygen gas evolution. One pair of peaks showed a 59 mV/pH unit shift, characteristic of an anhydrous oxide, whereas the other showed an 88.5 mV/pH unit shift, characteristic of a hydrous oxide. This type of behaviour is of fundamental importance in the electrochemistry of nickel oxide battery systems — the proposed formation of an anionic species in the case of the hydrous material explains, for instance, why the oxidized materials strongly bind alkali metal cations (these are obviously present as counterions).

The potential/pH response of the nickel oxide electrode system has been investigated to date mainly using cyclic voltammetry. In the present work the phenomenon was investigated under open-circuit conditions, *i.e.*, the quasi-steady-state potential of a hydrous oxide-coated nickel electrode was measured in a series of buffer solutions. Once again, an unusual potential/pH response was observed for the system — though the magnitude of the shift under open-circuit conditions is significantly lower than that observed in cyclic voltammetry experiments. Extension of the work to oxygen gas evolution at this type of surface clearly demonstrated the importance of hydrolysis (or acid-base) effects on the electrocatalytic behaviour of hydrous material.

Experimental

The working electrodes used consisted of lengths of nickel wire (99.997% pure, 1.0 mm dia.) sealed directly into glass, leaving an exposed geometric area of *ca* 0.3 cm². Pretreatment before use usually involved abrasion with a fine grade of emery paper followed by washing with triply distilled water. Oxides were grown on the nickel surface by potential cycling in 1.0 mol dm⁻³ NaOH between the limits of -0.5 and +1.55 V (R.H.E.) at a sweep-rate of *ca* 164 mV s⁻¹ [8]. The potential of the working electrode was controlled using a Wenking (Model 68 FR 0 5) potentiostat in conjunction with a Hewlett-Packard function generator (Model 3310A). The oxide growth and cyclic voltammetry experiments were carried out using a conventional three-compartment cell, with a nickel counter electrode and a hydrogen reference electrode in the same solution. Open-circuit potential/pH values were measured with respect to a saturated calomel electrode using a high impedance voltmeter (Exel, Model XL-2000). Buffer solutions were made up using 0.25 mol dm⁻³ H₃BO₃ with addition of either H₂SO₄ or NaOH to adjust the pH; the net ionic strength was maintained at 3.0 mol dm⁻³ by the addition of sodium sulphate.

Some work was also carried out with electrodeposited nickel oxide films (Ni or Pt electrodes were subjected to cathodic polarization at 12 mA cm⁻² in aqueous 0.1 mol dm⁻³ NiNO₃·6H₂O solution at room temperature for suitable lengths of time, typically 30 min).

Thermally prepared nickel oxide electrodes were produced by pasting an acidified isopropanol suspension of NiNO₃·6H₂O onto platinum or titanium. After drying, these films were fired in air at 420 °C for 2 h to convert the nitrate to oxide. It was generally observed that the hydrous oxide films in particular were not very stable in buffer solutions of pH < 7.0.

Results and discussion

A typical cyclic voltammogram for a nickel electrode, coated with a thick oxide (or hydroxide) layer produced by potential cycling in base, is shown in Fig 1(a). Although usually only one anodic and two cathodic peaks are observed in the region between 1.0 and 1.55 V (R.H.E.), it was recently demonstrated [9] that splitting of the anodic peak may be observed either at slow sweep-rates (less than *ca* 10 mV s⁻¹) or on increasing the number of oxide growth cycles. These peaks above 1.0 V (R.H.E.) are attributed to Ni(II)/Ni(III) transitions; that a lower potential, 0.0 - 0.3 V (R.H.E.), on the anodic sweep in base being attributed to a combination of adsorbed hydrogen oxidation and conversion of Ni(0) to Ni(II). The effect of solution pH on the potential values for the cathodic peaks for the same type of electrode system in various buffer solutions is outlined in Fig. 1(b). One of these peaks remained virtually invariant with respect to pH at a peak maximum value of *ca* 1.28 V (R.H.E.) — the process involved here is

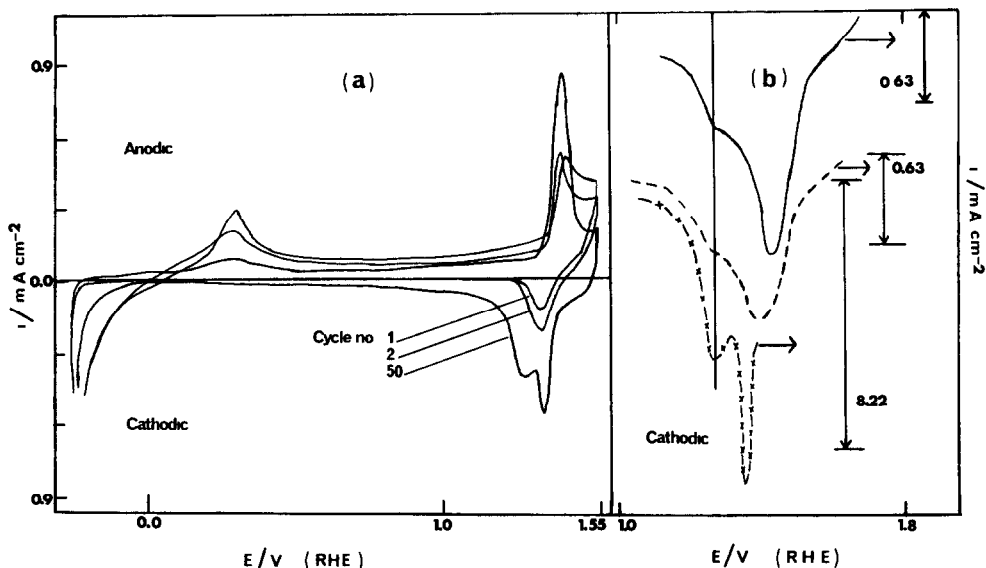


Fig 1 (a) Linear sweep voltammograms (-0.5 to $+1.55$ V, 41 mV s^{-1}) showing the main anodic and cathodic peaks recorded on cycling a bright nickel electrode in 1.0 mol dm^{-3} NaOH at 25°C (b) Effect of solution pH on the cathodic peak profile for hydrous oxide coatings (grown *in situ* in the various solutions) on a nickel substrate, sweep rate = 41 mV s^{-1} , $T = 25^\circ \text{C}$ (the figures on this diagram give the current density values) pH values —, — — —, \times — \times , 13.1

assumed to be reaction of anhydrous, β -type, material according to the equation



The potential of the more anodic peak clearly drifted to more cathodic potentials with increasing solution pH. The reaction involved here is again assumed to be a $\text{Ni}(\text{III})/\text{Ni}(\text{II})$ transition, except that it now occurs in a more hydrated region of the film where, due to hydrolysis phenomena, the oxidized state is more anionic. One equation which would account for the observed 88.5 mV/pH unit variation for the latter peak is



— it should be borne in mind here that the actual reaction occurring in the hydrous region of the film is probably considerably more complex (no attempt is made here, for instance, to include either co-ordinated water molecules or counterions).

For work on open-circuit potential/pH behaviour, oxide films were grown by cycling the potential of a clean nickel electrode in base for various periods of time in order to produce films of different thickness. On transferring such electrodes to buffer solutions, reasonably steady potential values were not readily observed either with very thin films (less than *ca* 20 cycles) or with thick films for which the potential scan was stopped at the lower

region of the oxide growth cycle, *i.e.*, 0 to -0.5 V (R.H.E.). Evidently with electrodes prepared in such a manner there is a major contribution from the $\text{Ni}(0)/\text{Ni}(\text{II})$ reaction.

Reasonably reproducible results were obtained with thicker films (200 - 700 oxide growth cycles) when the oxide growth sweep was stopped either at the anodic end of the sweep (*i.e.*, at 1.55 V) or at the maximum of the anodic peak at *ca.* 1.40 V — the latter procedure was regarded as being more suitable as the system was then buffered by having an approximately equal quantity of $\text{Ni}(\text{II})$ and $\text{Ni}(\text{III})$ species in the surface layer. There is also less likelihood of complications due both to the presence of $\text{Ni}(\text{IV})$ species in the surface layer and depolarization effects associated with oxygen gas evolution [10]. On transferring such an electrode to a buffer solution there was some initial drift in potential (Fig. 2), especially over a period of *ca.* 5 min. In most cases the potential reading in a given buffer solution was taken after an immersion period of 20 min.

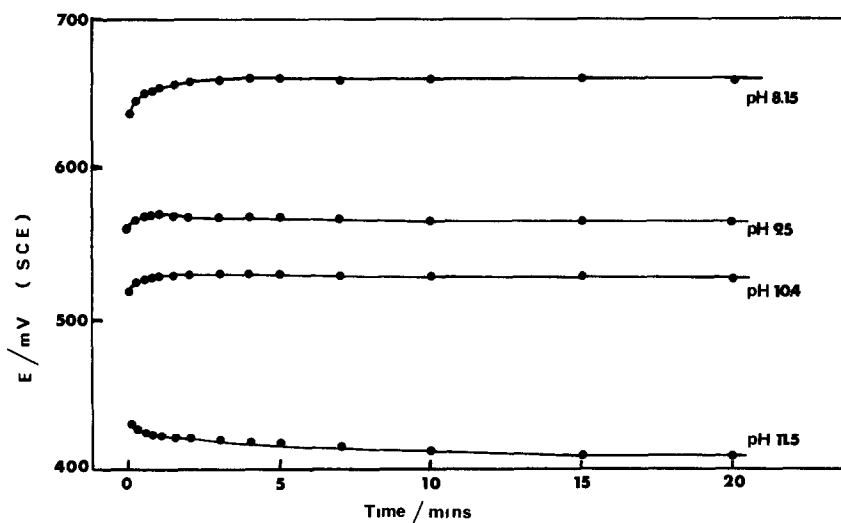


Fig 2 Variation of the open-circuit potential with time for a hydrous oxide-coated nickel electrode (prepared by cycling bare nickel, -0.5 to 1.55 V at 64 mV s^{-1} for 320 cycles in 1.0 mol dm^{-3} NaOH ($T = 25^\circ\text{C}$)) on transfer in the half-charged state (see text) to various buffer solutions.

Some typical potential/pH variations are shown in Fig. 3. For films grown for 200 - 700 cycles a constant potential/pH variation of *ca.* 78 mV/pH values was observed. As is clear from Fig. 4, lower potential/pH values were observed for thinner films. In fact, with very thin films, the observed value was less than the 59 mV/pH unit expected for anhydrous oxide behaviour. Mixed potential processes are probably involved here, *i.e.*, with thin films there may well be a significant contribution due to the $\text{Ni}(\text{II})/\text{Ni}(0)$ reaction at the underlying metal. With increasing number of oxide growth cycles (especially above *ca.* 100 cycles [8]) the rate of increase

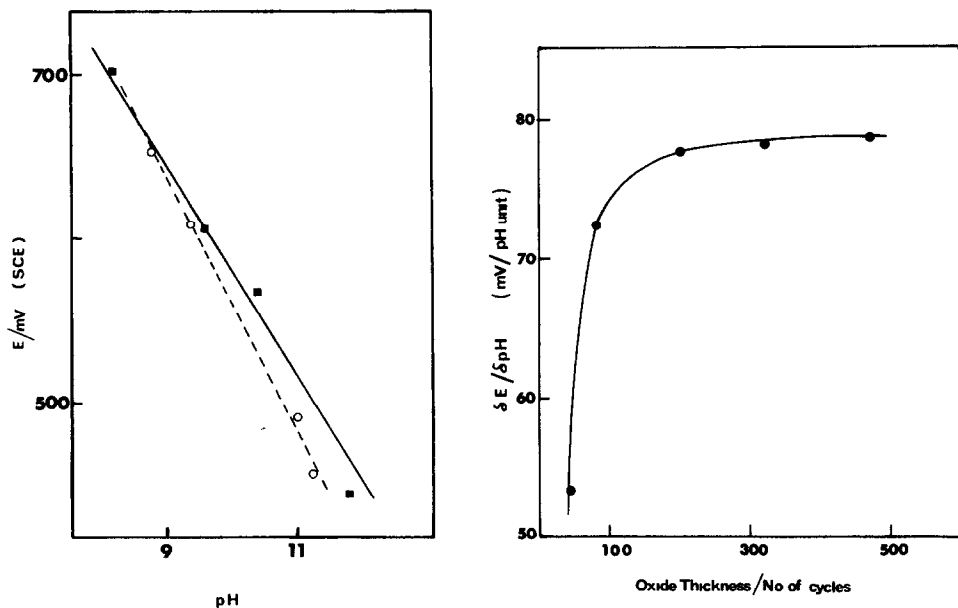


Fig 3 Typical potential/pH variations for hydrous oxide coated nickel electrodes in the half-charged state prepared as outlined in Fig 2 ■ and ○ represent oxides grown for 200 and 340 cycles, respectively

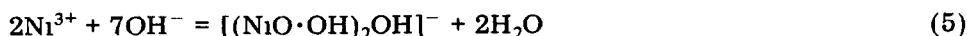
Fig 4 Potential/pH variation for a hydrous oxide-coated nickel electrode in the half-charged state (potentials measured with respect to sat calomel) as a function of the number of cycles used to grow the hydrous film in base, $T = 25^\circ\text{C}$

in oxide charge capacity, and presumably the film thickness, decreases. This may be attributed to inhibition of both water molecule and hydroxide ion transfer to the inner region of the surface layer, *i.e.*, with increasing film thickness the metal surface is more effectively passivated and the Ni(II)/Ni(0) contribution to the open-circuit potential behaviour is effectively eliminated.

Electrodes with a thick oxide coating formed by potential cycling may be regarded as a chemically inert but electronically conducting substrate in contact with an oxide matrix containing, in the half charged state, approximately equal concentrations of Ni(II) and Ni(III) species. Since these species are present in the form of hydroxy complexes, their activities are influenced by the hydroxide ion concentration, and hence the pH, of the surrounding solution. The observed 88.5 mV/pH unit shift in the case of the upper cathodic peak (Fig. 1(b)) may be interpreted in a thermodynamic manner as follows. For the complexes involved in the reaction in question here, eqn. (3), we may define stability constants K_{II} and K_{III} in the form

$$K_{II} = \frac{a_{c(II)}}{a_{Ni^{2+}} a^2_{OH^-}} \quad \text{and} \quad K_{III} = \frac{a_{c(III)}}{a^2_{Ni^{3+}} a^7_{OH^-}} \quad (4)$$

c(II) and c(III) represent the reduced and oxidized form of the surface complex; the chemical formation of the Ni(III) complex in this case is regarded as occurring according to the equation



By analogy with the earlier case of gold [3], the basic electrode reaction is written as



and according to the Nernst equation

$$E = E^0 - \frac{RT}{F} \ln \frac{a_{\text{Ni}^{2+}}}{a_{\text{Ni}^{3+}}} \quad (7)$$

Substitution from eqn (4) yields

$$E = E^0 - \frac{RT}{F} \ln \left(\frac{a_{\text{c(II)}}}{K_{\text{II}} a^2_{\text{OH}^-}} \right) \left(\frac{K_{\text{III}} a^7_{\text{OH}^-}}{a_{\text{c(III)}}} \right)^{1/2} \quad (8)$$

$$= E^0 - K' - \frac{2.303RT}{F} \log a^{1.5}_{\text{OH}^-} \quad (9)$$

$$= E^0 - K - 1.5(0.059)\text{pH}, \quad (T = 25^\circ\text{C}) \quad (10)$$

According to the latter equation the potential/pH variation of the reversible Ni(II)/Ni(III) transition in the hydrous film is, as observed in the cyclic voltammetry experiments, *ca* 88.5 mV/pH unit at 25 °C. It is assumed here that the terms K' and K in eqns (9) and (10), respectively, are pH independent. The results support this conclusion — insofar as the observed potential/pH shift can be fully accounted for in terms of the last term on the right hand side of eqns (9) or (10). Hence, the activities of the oxidized, c(III), and reduced, c(II), form of the redox couple — and therefore the nature of the redox reaction as represented in eqn (3) — do not alter with pH over the range (*ca* 8.0 - 13.0) investigated here. In the case of the hydrous material, the unusual lowering of the redox potential with increasing pH is due to the greater stabilization of the Ni(III) state (in the hydrous, as compared with the anhydrous, hydroxide) with increasing hydroxide ion concentration. This can be clearly seen from expressions for the nickel ion activities:

$$a_{\text{Ni(III)}} = a^{0.5}_{\text{c(III)}}/K^{0.5}_{\text{III}} a^{3.5}_{\text{OH}^-} \quad (\text{hydrous oxide}) \quad (11)$$

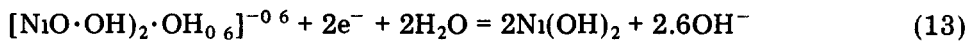
(see eqn (4)), and

$$a_{\text{Ni(III)}} = a_{\text{c(III)}}/K_{\text{III}} a^{3.0}_{\text{OH}^-} \quad (\text{anhydrous hydroxide}) \quad (12)$$

The pH response of the nickel oxide electrode system under open-circuit conditions, *ca* 78 mV/pH unit, is more difficult to interpret. The validity of this result is supported by the fact that similar behaviour is shown by hydrous iridium oxide layers produced on cycling. In the latter case a

shift of *ca* 88.5 mV/pH unit is also observed [6] for the Ir(III)/Ir(IV) transition in cyclic voltammetry experiments — but this drops to *ca* 71 mV/pH unit in open-circuit potential/pH experiments [11] carried out in the same manner, *i.e.*, with the half charged state, as described here for nickel. Even though the redox reactions in these films are relatively rapid, *i.e.*, the system is in an equilibrium state from an electrochemical viewpoint, these hydrous surface layers may be in a rather labile state [12] from a chemical or structural viewpoint.

In order to explain the observed pH dependence it is necessary to assume that interaction between the hydrous regions of the film, and either the solution or the more anhydrous regions of the surface layer (or possibly both), leads to the following type of open-circuit equilibrium reaction



According to the latter equation the active oxynickel (III) species in the film in the open-circuit experiments is somewhat less anionic as compared with the corresponding species in the cyclic voltammetry experiments. There is direct evidence, especially in the work of Arvia *et al* [13, 14], that films formed *in situ* rearrange slowly on cycling — it is suggested here that part of this rearrangement entails transfer of OH^- species either to the solution or to less highly hydrated regions of the oxide (lateral repulsion between OH^- species attached to neighbouring cations in the polymer chains would favour such a process, the counterions present in the hydrous regions of the film would reduce, but not totally eliminate, such repulsion effects).

It may be pointed out here that the unusual variation of the rest potential of the nickel oxide electrode system with the hydroxide ion activity of the solution has been noted earlier by Bourgault and Conway [10] who used solutions of different KOH concentration. They also commented on the more acidic properties of the higher oxide and attributed the effect to KOH adsorption. In view of the dispersed nature of the hydrous oxides (particularly the γ -NiO·OH) where individual layers of the oxyhydroxide are separated from one another by sheets of solvent molecules plus electrolyte [15], the distinction between adsorption and total conversion of the hydrous material to an anionic form permeated with counter ions is probably quite tenuous.

It has been reported earlier [7] that thin nickel hydroxide films produced by cathodic deposition differ significantly from those produced by potential cycling in base in that, as illustrated in Fig. 5, the upper cathodic peak, *i.e.*, the one attributed to the Ni(III)/Ni(II) reaction in the hydrous portion of the film, is not usually observed with the former type of deposit. The behaviour of such electrodes is further complicated by the fact that whereas the anodic peak shows an unusual potential/pH variation, that for the reverse reaction is quite regular [7]. Possibly the anodic reaction is controlled by an Ni(II)/Ni(III) conversion in the outer region of the film where hydration can occur at low potentials — this hydration being lost at the anodic end of the sweep, due to oxygen gas evolution or some dissolution,

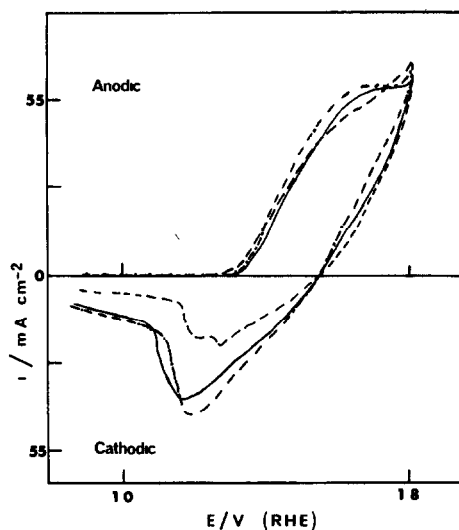
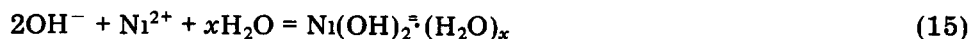
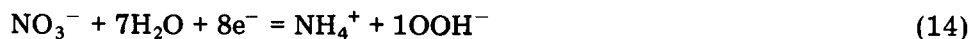


Fig 5 Linear sweep voltammograms showing the main anodic and cathodic peaks observed on cycling (40 mV s^{-1}) cathodically deposited films of various thicknesses in 1.0 mol dm^{-3} NaOH at 25°C . Deposition times: ---, 25 min, —, 30 min, - · -, 60 min

so that the reaction on the subsequent anodic sweep is confined mainly to β -type anhydrous material.

Some results for open-circuit potential/pH measurements for electro-deposited nickel hydroxide with the surface deposit in the half charged state are outlined in Fig. 6. These results, taken from measurements with buffer solutions over the pH range 8.0 - 13.0, show that with thin films the behaviour is typical of hydrous material, whereas with thicker films the pH response is more characteristic of anhydrous layers. These deposits were produced under cathodic conditions in the presence of nitrate ions — the reaction involved may be represented as follows



The initial deposit is evidently highly hydrated, not surprising perhaps as the cathodic deposition technique usually yields dispersed γ -type hydroxide materials [15]. With increasing film thickness, or longer deposition times, however, significant dehydration apparently occurs, possibly due to discharge of coordinated water molecules within the thicker films according to the reaction



It is also assumed that the reaction involved here, *i.e.*, dehydration in the interior of the film, becomes progressively more difficult to reverse with

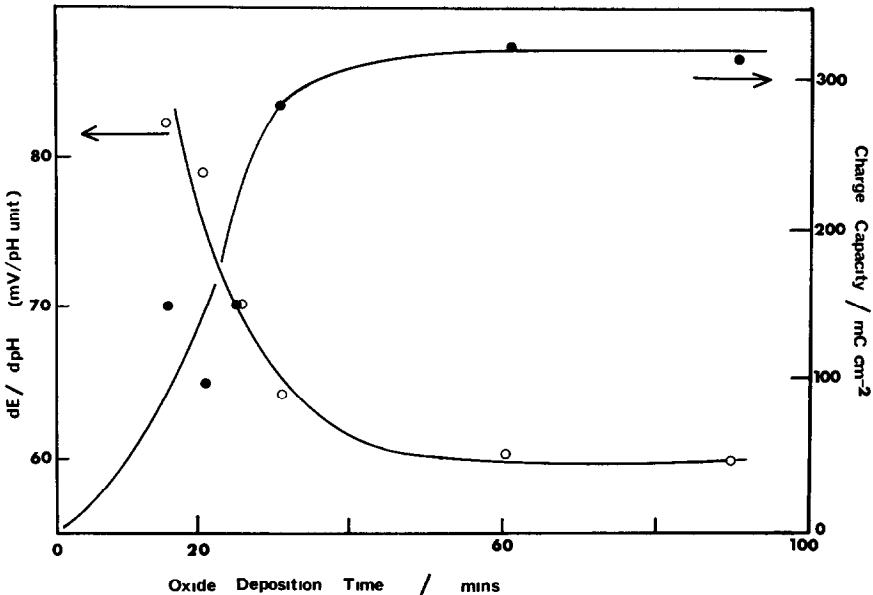


Fig 6 Potential/pH (○) and charge capacity (●) variations for cathodically deposited nickel oxide coatings as a function of the deposition time for the surface layer. The charge capacity values were obtained from the area under the cathodic peak on cycling in $1.0 \text{ mol dm}^{-3} \text{ NaOH}$ (see Fig 5). Open-circuit potential values were recorded with respect to saturated calomel after transferring the half-charged electrodes to a range of buffer solutions.

increasing thickness of the surface layer — hence the anhydrous potential/pH response

In this respect it is interesting that, as also outlined in Fig. 6, the loss of the hydrous potential/pH response coincides roughly with a levelling off of the charge storage capacity of the film despite the increased mass of material deposited at the surface at longer times. The most obvious explanation is that the additional material simply increases the amount of anhydrous, β -type material at the surface. This would account both for the predominance of the anhydrous potential/pH response and, in view of the less open structure of the β -type material, the levelling off of the charge storage capacity. While further work is required here (to check, for instance, the role of electronic conduction in these films) the results suggest that one way to improve the performance of nickel oxide electrodes for use in battery systems is to increase (and stabilize) the percentage of hydrous material present. In earlier work Sugita [16] has suggested that the retention of charge capacity on addition of LiOH to the electrolyte is due to the ability of the lithium ions to retard crystallization of the active (γ -type?) material.

There may be additional complications in the case of electrodeposited layers due to hydroxy-nitrate formation [15] — although precautions were taken in the present work to remove as much nitrate as possible from the deposit by repeated washing with distilled water prior to the rest potential

measurements. Even though an anhydrous-type response, *i.e.*, a potential/pH variation of *ca* 59 mV/pH unit, may be observed with a thick electro-deposited layer (or a thermally prepared oxide deposit formed either by decomposing a nitrate film or heating a film grown by cycling in base to temperatures in excess of 200 °C) evidence was obtained from oxygen gas evolution studies (as outlined in the next section) that the outer layers of such deposits behaved in a hydrated manner.

The behaviour of nickel (or, more precisely, that of the anodically formed oxide layers on this metal) as a substrate for oxygen gas evolution has been reviewed by Hoare [17]. In acid solution the anodic currents recorded below about 1.72 V are largely due to metal dissolution; at higher potentials dissolution becomes inhibited, all the current eventually being accounted for by the oxygen gas evolution reaction. The Tafel plots, especially for low pH values (Fig. 7), show a distinct inflection point which has been attributed [17] to the transition between dissolution and oxygen gas evolution as the main anodic reaction. Similar inflection points were observed at low pH with both thermally prepared and electrodeposited nickel oxide layers on platinum — the effect was not quite as distinct here (and it occurred at significantly lower current density values) as dissolution is less marked with this type of substrate. Since nickel dissolution is less marked at high pH, no distinct inflection point was noted at the onset of oxygen gas evolution on Tafel plots for this reaction at nickel or nickel oxide electrodes in base (Fig. 8). The onset of oxygen gas evolution, however, was clearly marked in this case by the rapid increase in anodic current above about 1.46 V in 1.0 mol dm⁻³ NaOH. The results shown in Fig. 8 are in excellent agreement with the data of Lu and Srinivasan [18] which also show linear Tafel behaviour for oxygen gas evolution on nickel in 1.0 mol dm⁻³ KOH above *ca* 1.45 V.

The most interesting result in the present case is given in Fig. 9. Plotting the potential values for the inflection point for acid (pH values less than 6.0), the potentials for the anodic peak above 1.0 V (R.H.E.) on the cyclic voltammograms for hydrous nickel oxide layers (see Fig. 1(a)) at pH values above 7.0, and the potentials for the onset of oxygen gas evolution at nickel oxide substrates in base — all as a function of solution pH, for the three different types of nickel oxide substrates, yields a single straight line of slope *ca* 29.5 mV/pH unit (or 88.5 mV/pH unit with respect to a pH independent reference electrode). Evidently, the oxygen gas evolution reaction, which occurs at the oxide-solution interface, must involve hydrous nickel oxide sites irrespective of how the oxide layer is formed. The role of the high oxidation states is not totally clear at the present time; while it may be that the oxidation of Ni(II) species leads to the formation of unstable Ni(III) or Ni(IV) complexes which decompose with loss of oxygen (in a manner similar to that described recently for RuO₂ [19]), the formation of the higher oxidation state is also known [20] to substantially increase the electrical conductivity of the poorly conducting Ni(II) surface layer. The resulting reduction of the *iR* drop across the latter on formation of Ni(III)

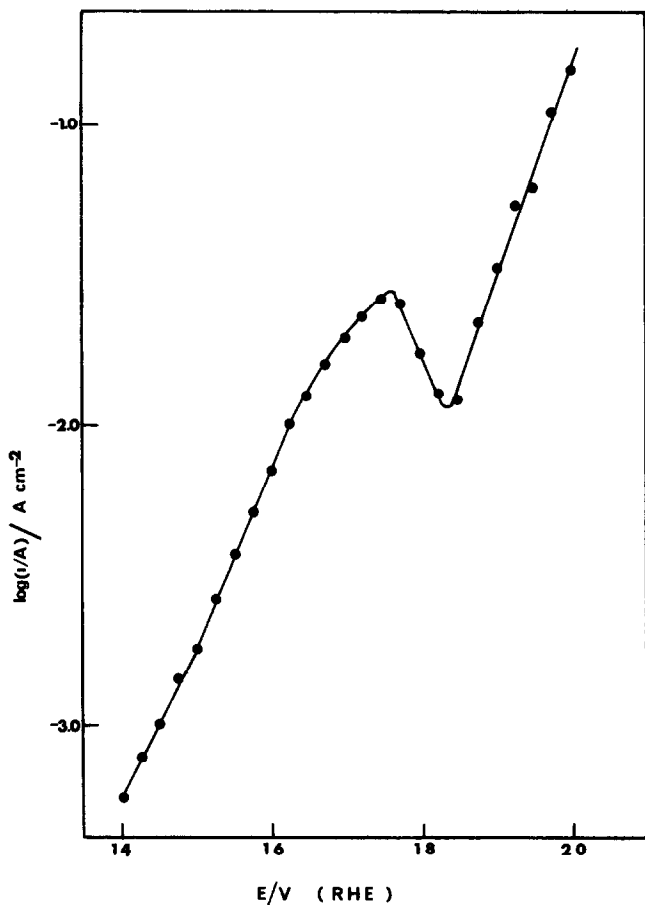
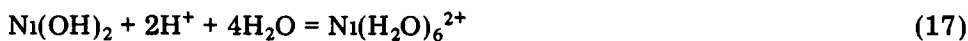


Fig 7 Typical Tafel plot for a bright nickel electrode in $1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ at 25°C , illustrating the distinct break or transition at $\approx 1.8 \text{ V}$, corresponding to the onset of oxygen gas evolution. Current density values were recorded in each case after a constant period of polarization (5 min) at each potential value.

species may also contribute to the marked enhancement of the gas evolution reaction in the region of the surface redox transition. Apart from favouring gas evolution, the onset of the surface transition is accompanied by inhibition of the metal dissolution reaction [17], *i.e.*, surface passivation is observed. Generally the Ni(II) species dissolve readily at low pH values, protonation (or reversal of hydrolysis) under these conditions resulting in the formation of aquo ions, *viz*,



It is possible that the corrosion reaction is enhanced by the strong electric field across the Ni(II) oxide layer, although this may not be of great significance (one could equally well postulate a low field model in which

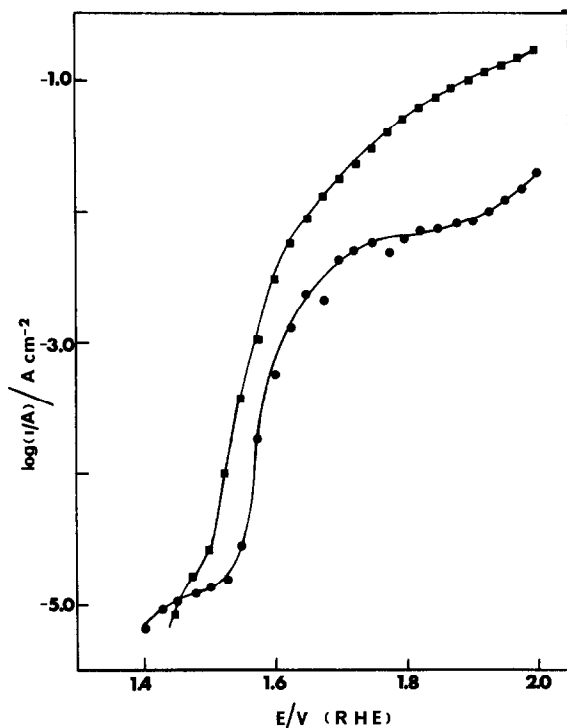


Fig 8 Tafel plots for bright nickel (●) and oxide-coated nickel (■) — coating produced on bright nickel by cycling (50 cycles at 40 mV s^{-1} , -0.5 to 1.55 V) — in 1.0 mol dm^{-3} NaOH at 25°C . Current density values recorded as described in Fig 7

chemical dissolution at the oxide/electrolyte interface is continuously counterbalanced by electrochemical formation of hydroxide at the metal/oxide interface). The rate of dissolution decreases when the film transforms to the Ni(III) state either due to the decrease in the field in the oxide or to the lowering of the reactivity of the Ni(III) oxycations. The stability of the latter will be enhanced not only chemically, due to excess OH^- coordination, but also electrostatically, due to the effect of the positive field at the interface on the anionic species formed on oxidation of hydrous $\text{Ni}(\text{OH})_2$ — see eqn (3). In any event it is now clear that unusual potential/pH effects are important in anodic processes at both metal and oxide surfaces in aqueous media — an effect demonstrated previously in this laboratory for both RuO_2 [19] and Rh_2O_3 [21] anodes prepared by thermal techniques.

The influence of the surface oxide on the electrocatalytic behaviour of nickel as a substrate for oxygen gas evolution has been discussed in some detail by Lu and Srinivasan [18]. They attributed the high activity of the initial film to the presence of $\beta\text{-NiO}\cdot\text{OH}$, and the decay in activity with time above *ca.* 1.56 V to the conversion of Ni(III) to Ni(IV). The present results, however, suggest that the active outer region of these nickel oxide films is hydrated, *i.e.*, the active material is more likely to be a γ -type, rather than a

β -type, material. Furthermore, the decay of oxygen evolution current with time may well be due to structural changes (*e.g.*, conversion of γ to β material, or loss of the outer hydrous coating due to dissolution) rather than to changes in the nickel ion oxidation state

The influence of dispersion on the electrocatalytic behaviour of oxides is now well recognised [22], and conversion from γ to β -nickel oxyhydroxide is expected to decrease the effective area of contact at the oxide/solution interface. While the inflection in the Tafel plots in Fig. 8 may be due to ohmic potential drop across both the oxide film and the layer of electrolyte between the working electrode and the tip of the Luggin capillary, another possibility is that local pH changes due to the reaction



are involved. Proton generation will result not only in OH^- ion neutralization (and, hence, a change in reaction mechanism since H_2O rather than OH^- species will be discharged), but also (if the pH change is substantial — as it may well be in the inner regions of a partially porous film) in a rise in the redox potential for the surface ion transition in accordance with the results shown in Fig. 9. Obviously such electrochemically induced local pH changes could result in deactivation of a significant proportion of the hydrous material — especially at the internal surface of highly dispersed oxide electrocatalysts — and thus contribute to the departure from linear behaviour in the

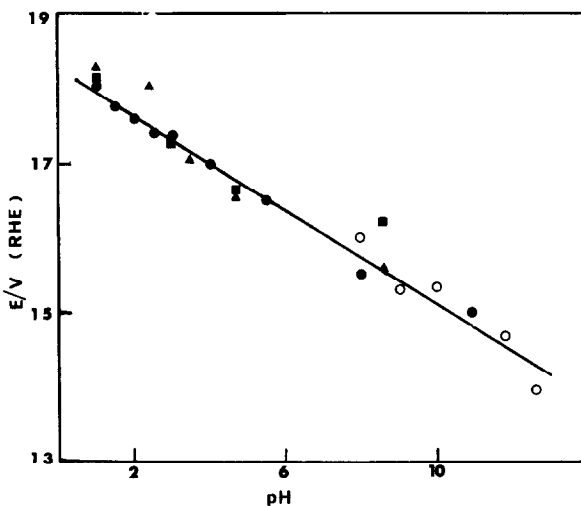


Fig. 9 Potential variation with pH for a variety of interrelated anodic phenomena at anodized nickel/nickel oxide surfaces in aqueous media, $T = 25^\circ\text{C}$. \circ , the anodic peak potential for the main charge storage reaction of a hydrous nickel oxide surface (see Fig. 1(a)), \bullet , \blacksquare and \blacktriangle , potentials for the onset of oxygen gas evolution (or for the mid-point of the break in the Tafel plots at low pH — see Fig. 7 and also ref. 17 for the interpretation of same) for bright nickel, cathodically deposited nickel oxide, and thermally prepared nickel oxide, respectively.

case of Tafel plots for oxygen gas evolution at both nickel and nickel oxide electrodes at high current densities (Fig. 8) in base

Conclusion

The present work confirms the usefulness of pH as a variable in the investigation of the electrochemical behaviour of hydrous oxides in general and nickel oxides in particular. It is possible to give a thermodynamic interpretation of the difference in potential/pH behaviour observed for the peaks recorded in the upper region of the cathodic sweep for the layers formed by potential cycling — this interpretation is in broad agreement with the known structures of the nickel hydroxide and oxyhydroxide systems. There appear, however, to be complications in the system due to interconversion between anhydrous and hydrous phases, coupled with inhibition of the oxidation of the anhydrous phase due to the presence of the outer hydrous phase. Open-circuit e.m.f. and oxygen gas evolution studies support the view that the outer layers of oxide are hydrated and (at least in the oxidized state) anionic. With electrodeposited films the transition from a hydrous to an anhydrous potential/pH response is accompanied by a levelling off of the charge storage capacity, suggesting that the hydrous material is more active with regard to charge storage behaviour.

References

- 1 P W Selwood, *Magnetochemistry*, Interscience, New York, 1964, pp 337 - 341
- 2 L D Burke and M McRann, *J Electrochem Soc*, 125 (1981) 387
- 3 L D Burke, M E Lyons and D P Whelan, *J Electroanal Chem*, 139 (1982) 131
- 4 L D Burke and D P Whelan, *J Electroanal Chem*, 124 (1981) 333.
- 5 L D Burke, M E Lyons, E J M O'Sullivan and D P Whelan, *J Electroanal Chem*, 122 (1981) 403
- 6 L D Burke and T A M Twomey, *J Electroanal Chem*, 134 (1982) 353
- 7 L D Burke and T A M Twomey, in R G Gunther and S Gross (eds), *Proc Symp on the Nickel Electrode*, The Electrochemical Society, Pennington, NJ, 1982, Vol 82-4, pp 75 - 96
- 8 L D Burke and D P Whelan, *J Electroanal Chem*, 109 (1980) 385
- 9 L D Burke and T A M Twomey, *J Electroanal Chem*, submitted for publication
- 10 P L Bourgault and B E Conway, *Can J Chem*, 38 (1960) 1557
- 11 L D Burke, J K Mulcahy and D P Whelan, *J Electroanal Chem*, in press
- 12 S Hackwood, G Beni and P K Gallagher, *Solid State Ionics*, 2 (1981) 297
- 13 R S Schrebler Guzman, J R Vilche and A J Arvia, *J Appl Electrochem*, 9 (1979) 183
- 14 R S Schrebler Guzman, J R Vilche and A J Arvia, *J Electrochem Soc*, 125 (1978) 1578
- 15 P Oliva, J Leonardi, J F Laurent, C Delmas, J J Braconnier, M Figlarz and F Fievet, *J Power Sources*, 8 (1982) 229
- 16 K Sugita, *Denki Kagaku*, 29 (1961) 86
- 17 J P Hoare, *The Electrochemistry of Oxygen*, Interscience, New York, 1968, pp 271 - 293

- 18 P W T Lu and S Srinivasan, *J Electrochem Soc* , 125 (1978) 1416
- 19 L D Burke and J F Healy, *J Electroanal Chem* , 124 (1981) 327
- 20 S H Glarum and J H Marshall, *J Electrochem Soc* , 129 (1982) 535
- 21 E J M O'Sullivan and L D Burke, in W E O'Grady, P N Ross and F G Will (eds), *Proc Symp on Electrocatalysis*, The Electrochemical Society, Pennington, NJ, 1982, Vol 82-4, p 209
- 22 L D Burke and E J M O'Sullivan, *J Electroanal Chem* , 117 (1981) 155