Potentiodynamic response of the Ni (OH)₂ /NiOOH redox couple at the inner layer of the complex interface

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Received 28 April 1981

The electrochemical response of the Pt/Ni(OH)₂ interface subjected to potentiodynamic sweeps shows the contribution of the Ni(OH)₂/Ni(OOH) redox couple immediately attached to the Pt(O) surface, when the substrate surface to Ni(OH)₂ layer volume ratio is varied. A comparison with previously published results shows that the response of the innermost portion of the Ni(OH)₂/NiOOH layer depends on the characteristic of the substrate, the temperature, the electrolyte concentration, the degree of hydration of the Ni(OH)₂ film and the hydrophobicity of the substrate. The results indicate that the water content of the inner film is probably lower than that of the bulk, the Ni(III) species probably approaching the O-octahedral co-ordination corresponding to γ_1-NiOOH.

1. Introduction

The overall reaction related to the Ni(OH)₂/NiOOH redox couple in alkaline electrolytes is

$$Ni(OH)_2 = NiOOH + H^+ + e. \qquad (1)$$
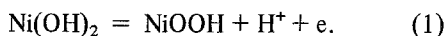
It exhibits a complex behaviour, which, for thin films (< 100 Å thickness), was interpreted through a reaction pathway involving the participation of chemical reactions of both reactants and products coupled with the electron and proton transfer processes [1–3]. For thicker films mass transport processes in the film contribute to the kinetics of the overall reaction. The transition from surface reaction control to mass transport control was discussed recently [4].

For thin films the potentiodynamic electroreduction (E/I) profile of the NiOOH species run with the Ni(polycrystalline)/Ni(OH)₂/0.01 N NaOH + 0.66 N Na₂SO₄ interface under triangular potential sweeps (TPS) at a scan rate of $v = 0.1\,V\,s^{-1}$ between $E_{s,c} = -0.77\,V$ and $E_{s,a} = 0.72\,V$ (versus Hg/HgO/1 M NaOH scale) depicts two cathodic current peaks at *ca.* 0.6 V (peak III)

and *ca.* 0.45 V (peak IV) (Fig. 1). Under properly adjusted potentiodynamic ageing perturbations the main cathodic peak (peak III) splits into two current peaks [5], so that the whole cathodic E/I curve can be resolved into at least three current peaks (IIIA, IIIB and IV), drawn in terms of three distribution functions [6]. At low temperature the charges corresponding to peaks IIIA and IIIB are relatively much larger than that involved in peak IV, but the reverse effect is observed when the temperature increases [3]. However, the charge of peak IV appears to attain a maximal value which should be of the order of a few monolayers of active material compared with the Ni(OH)₂ monolayer charge [7, 8]. The charge of peak IV was attributed to the electroreduction of the NiOOH species in direct contact with the Ni electrode [1]. However, the relative contribution of current peak IV also depends on the perturbation conditions (switching potentials $E_{s,a}$ and $E_{s,c}$ potential scanning rate v and time of holding the potential at either $E_{s,c}$, $E_{s,a}$ or any intermediate potential value) the composition of the electrolyte solution and the temperature.
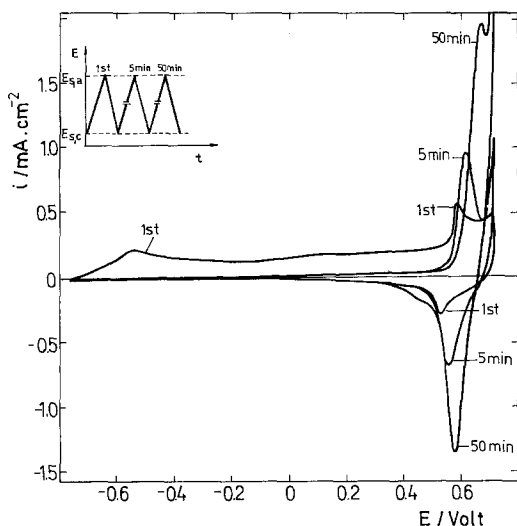
Fig. 1. Potentiodynamic E/I curves run with the Ni/10^{-2} N NaOH + 0.66 N Na$_2$SO$_4$ interface. The perturbation programme is indicated in the figure. Other experimental details are referred to in the text. The first E/I display and those obtained after 5 and 50 min potential cycling are shown.

In an attempt to confirm and extend the above interpretation, especially the electrochemical and possible structural characteristics of the species involved in the reaction related to peak IV, the reaction was investigated on conducting substrates other than Ni. For this purpose polycrystalline Pt and vitreous carbon electrodes were used [9, 10]. This also avoids the roughness uncertainty of the Ni substrate.

2. Experimental procedure

The preparation of the Pt/Ni(OH)$_2$ interface was made through colloidal precipitation of Ni(OH)$_2$ on a polycrystalline Pt wire (specpure) following the same technique previously described [9, 10]. The Ni(OH)$_2$ precipitation on the two different substrates was made at room temperature from ten alternative immersions in 10^{-2} N NaOH + 0.66 N Na$_2$SO$_4$ (Solution I) and 4×10^{-3} N NiSO$_4$ (Solution II). In each solution the immersion time was fixed at 5 s. The treatment of the substrate has a considerable influence on the potentio-dynamic response of the electrochemical reaction. Thus, to obtain reproducible results the Pt electrode was immersed in the 1 : 1 H$_2$SO$_4$: HNO$_3$ mixture (acid mixture) for a period of time t_{imm}, where $0 \leqslant t_{imm} \leqslant 30$ min, to produce different

surface conditions. Then, by varying both the time t_{imm} and the amount of Ni(OH)$_2$ on the substrate the charge of peak IV to the charge of the overall electroreduction ratio could be changed. Occasion-ally other Pt electrode surface treatments such as cathodization and chemical reduction were made. The roughness of the working Pt electrode was determined by evaluation of the hydrogen elec-trosorption charge in the potentiodynamic E/I profile run in 0.5 M H$_2$SO$_4$ [11].

Occasionally vitreous carbon electrodes were also employed. These electrodes were first im-mersed in dilute H$_2$SO$_4$, then they were success-ively polished with the finest grade emergy paper and alumina 400 grit and finally they were rinsed in thrice-distilled water.

A conventional three compartment electrolytic cell was used. The potential of the working elec-trode was measured against the Hg/HgO/1 M NaOH electrode. The counterelectrode was a Pt sheet. The electrolyte was 10^{-2} N NaOH + 0.66 N Na$_2$SO$_4$ which was prepared from thrice-distilled water and analytical reagent chemicals. The electrolyte in the cell was maintained under a purified N$_2$ atmosphere. Runs were made at 25° C using the simple and combined potential sweep techniques at 0.1 V s^{-1} referred to in previous works [1, 6, 12].

3. Results

The potentiodynamic E/I profiles of the Pt/ Ni(OH)$_2$/0.01 N NaOH + 0.66 N Na$_2$SO$_4$ inter-face, at 25° C, under a TPS with Pt substrates pre-treated for different periods of time in the acid mixture (Figs. 2–4) show that during the first potential scan there is a slight increase in the over-all charge as t_{imm} increases but that the total cathodic to total anodic charge ratio (Q_c/Q_a) remains equal to one. The most notable influence of the immersion time of Pt in the acid mixture appears, however, in the distribution of the elec-troreduction charge (Q_c) among the cathodic current peaks related to the electroreduction of the NiOOH species. Under comparable potential perturbation conditions and in the absence of reduction of the Pt surface either chemically or electrochemically before the colloid precipitation, the charge of current peak IV ($Q_{c,IV}$) increases accordingly with t_{imm}. The $Q_{c,IV}$ charge value can be estimated just by assigning a distribution func-
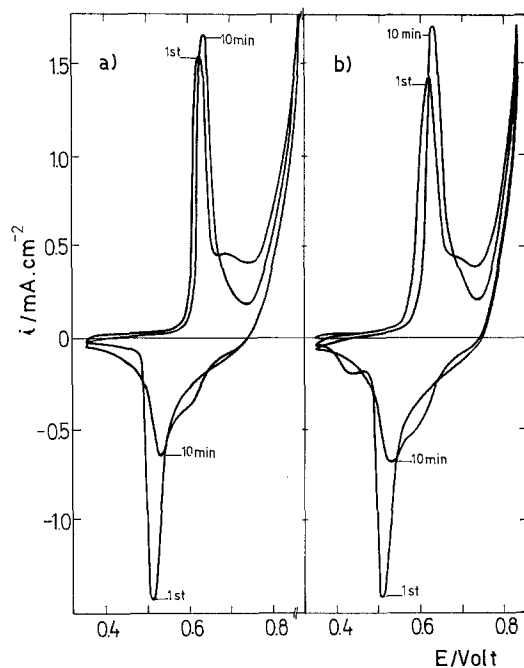
Fig. 2. Potentiodynamic E/I curves run with the Pt/ Ni(OH)$_2$ (colloidal)/10^{-2} N NaOH + 0.66 N Na$_2$SO$_4$ interface showing the influence of the immersion time in the acid mixture. The interface is cathodized at 0.35 V for 30 s before potential cycling. The first triangular potential scan and those resulting after 10 min potential cycling are depicted. (a) t_{imm} = 1 min; (b) t_{imm} = 5 min.

Fig. 3. Potentiodynamic E/I curves run with the Pt/ Ni(OH)$_2$ (colloidal)/10^{-2} N NaOH + 0.66 N Na$_2$SO$_4$ interface showing the influence of the cathodization time at $E_{s,c}$ = − 0.80 V and t = 15 min. Only the first triangular potential scan is shown (a) t_{cat} = 30 s; (b) t_{cat} = 5 min.

tion to it [2, 6]. Then, under the experimental conditions of Fig. 4 the $Q_{c,IV}/Q_c$ charge ratio in the first potential sweep either for Pt or Ni substrates reaches a limiting value equal to 0.20 when t_{imm} = 30 min. This suggests that nearly 20% of the cathodic charge is initially associated with the electroreduction of the apparently most stable NiOOH species. During the following potential cycles the $Q_{c,IV}$ value decreases and the rest of the E/I profile is appreciably modified, to exhibit the type of current peak multiplicity already described [1–6].

For electrodes pretreated in the acid mixture for a constant length of time t_{imm} (Fig. 3), the contribution of peak IV diminishes according to the time the electrode is held at $E_{s,c}$ before running the potentiodynamic cycle. Therefore, cathodization at $E_{s,c}$ produces a decrease of the NiOOH species which is active in the potential range of peak IV.

When the electrodes, which had previously been treated for 10 min in the acid mixture, are thoroughly washed in water, a slight decrease of
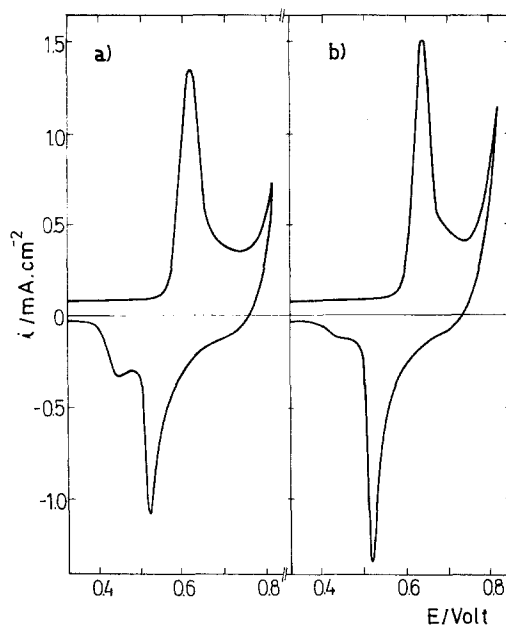
the contribution of current peak IV is observed. Furthermore, the contribution of peak IV disappears when the electrode treated in the acid mixture is immersed for a few minutes in a sodium metabisulphite solution. Then, either by washing or by chemical reduction, the influence of the acid mixture treatment on peak IV is effectively cancelled. Independent of the time during which the Pt is in contact with the acid mixture, the same effect is observed by cathodizing (t_{cat}) the treated surface at − 0.8 V for 1 min before Ni(OH)$_2$ colloid precipitation. The disappearance of peak IV by cathodization at − 0.8 V, is much less effective when the cathodization is made *after* the colloid precipitation. This indicates a partial protective influence of the Ni(OH)$_2$ colloidal layer on the species which is responsible for the enhancement of peak IV (Fig. 3). The relative contribution of peak IV to the overall E/I profile is not noticeable when thick Ni(OH)$_2$ layers are used.

The same type of experiment carried out with the vitreous carbon/Ni(OH)$_2$/0.01 N + 0.66 N Na$_2$SO$_4$ interface (Fig. 5) exhibits the reverse effect already described for Pt after a prolonged immersion in the acid solution, namely, the contribution of $Q_{c,IV}$ increases during the repetitive
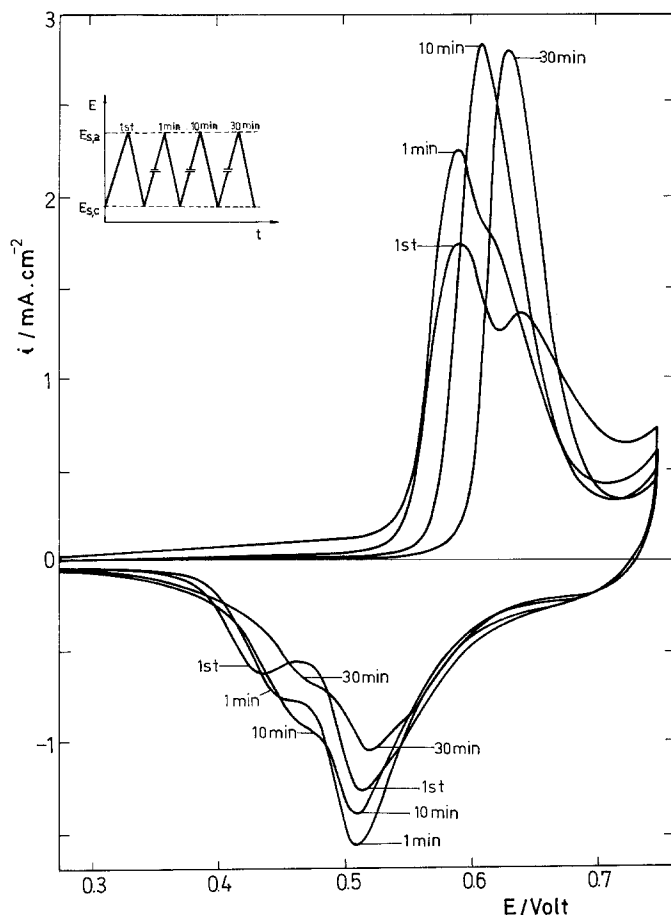
Fig. 4. Potentiodynamic E/I curves run with the Pt/Ni(OH)$_2$ (colloidal)/10^{-2} N NaOH + 0.66N Na$_2$SO$_4$ interface showing the influence of the cathodization time at $E_{s,c} = 0.2$ V with $t_{imm} = 30$ min and $t_{cat} = 30$ s. The first E/I plot and those resulting after 1, 10 and 30 min potential cycling are shown.

potential cycling. In the potential scanning range no O-electrosorption on vitreous carbon is detected. In this sense, the electrochemical behaviour of vitreous carbon is comparable to that reported on Ni, either by repetitive potential cycling [1, 13], or by increasing the SO$_4^{2-}$ ion concentration in solution [5, 6] or by increasing the temperature [3]. The same effect is also observed with Ni in the alkaline borate buffer (pH 9.3) [14].

4. Discussion

The contribution of peak IV increases both with the time of immersion in the acid mixture and its relative contribution increases as the thickness of the Ni(OH)$_2$ active material decreases. On the other hand, the maximal value of Q_{IV} is of the order of 360μC cm^{-2}, that is a charge value which is of the order of that of a H-adatom monolayer on polycrystalline Pt (210μF cm^{-2}) with a roughness factor equal to 1.5 or thereabouts [15]. This

fact indicates that the NiOOH species related to peak IV is likely to be located in direct contact with the conducting substrate. Hence, the maximal contribution of $Q_{c,IV}$ can be estimated by considering the ratio of reacting species in contact with the substrate to that in the bulk of the layer.

Let us consider a unit cell of unit base and height equal to the Ni(OH)$_2$ layer thickness (L), where n_b is the number of molecules at the base and n_v the number of molecules in the whole volume, and let us further assume that each PtO surface centre is related to one NiOOH species. Based upon previously reported evidence [16], the oxidized Pt surface is assumed to be a layer of alternating PtO species, which are more difficult to electroreduce than the PtO species electrochemically formed in the O-monolayer potential range. The value of Q_{IV} can be taken as the charge related to a (PtO) dual surface site. Then, after neglecting any influence of the bulk electroactive material:
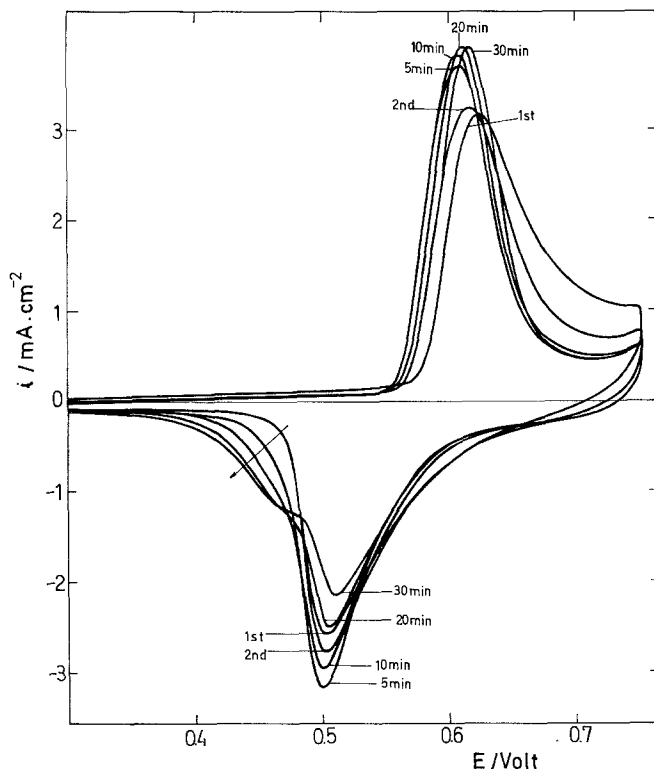
Fig. 5. Potentiodynamic E/I curves run with the C(vitreous)/Ni(OH)$_2$(colloidal)/10^{-2} N NaOH + 0.66 N Na$_2$SO$_4$ interface with $E_{s,c} = 0.2$ V and $t_{cat} = 30$ s. The first and second E/I curves are recorded as well as those resulting after 5, 10, 20 and 30 min potential cycling.

and

$$n_b = L^2 Q N_0 / F \qquad (2)$$

$$n_v = L^3 \delta N_0 \qquad (3)$$

where L is the average film thickness determined through the total electroreduction charge, Q is the charge associated with the Ni(OH)$_2$ layer in direct contact with the substrate, δ is the density of the film, N_0 is Avogadro's number and F is the Faraday. Taking $Q = 210 \, \mu C \, cm^{-2}$ and $\delta = 2.5 \times 10^{-2}$ mol cm^{-3} [17], then $n_b/n_v \approx 9 \, \text{Å} \, L^{-1}$. Therefore, in the limiting case, if the minimum detectable contribution of peak IV in the NiOOH electroreduction profile is fixed at 2%, this is achieved when L exceeds 450 Å. It is reasonable, therefore, to expect that the contribution of peak IV is unnoticed when thick Ni(OH)$_2$ layers are involved in the potentiodynamic electrochemical reaction.

The different electrochemical behaviours of peak IV on the various substrates can be firstly correlated with their surface oxidation states. The enhancement of $Q_{c,IV}$ is also related to the increase of temperature, the increase in electrolyte concentration and the absence of electrochemical reactions at the proper surface substrate. The enhancement of $Q_{c,IV}$ produced by immersion in

the acid mixture can be suppressed simply by cathodizing the electrode at -0.8 V in the same electrolyte. The electrochemical reaction related to peak IV at the pretreated Pt electrode implies a surface which on one side is completely covered by O species and on the other contains another surface species which is removed either electrochemically in the hydrogen evolution potential range or chemically. Nevertheless, the oxidation state of the surface achieved through immersion in the acid mixture is different from the Pt surface oxidized anodically by holding the potential at 1.2 V [18], that is in the potential range where a net O$_2$ evolution occurs. These results are then in agreement with the changes observed in the electrocatalytic properties of Pt according to the previous history of the electrode [19]. In any case they indicate that the contribution of peak IV corresponds to the electroreduction of a Ni(III) species involving the lowest degree of hydration and probably the largest octahedral co-ordination with O atoms. Then, the species in the innermost layer probably approaches a structural configuration of the type of γ_1-NiOOH [20]. The formation of the most stable NiOOH species is thus

favoured on one side by high temperatures and electrolyte concentration and on the other, is favoured at those surfaces where the OH^- ion content at the interface due to the Pt(O) electro-reduction produces an equivalent effect.

It is interesting to note that the potential of current peak III is independent of $Q_{c,IV}$. This suggests that the energy required for electro-reducing the most stable NiOOH species depends principally on the structure and interaction of the Pt(oxidized)/inner NiOOH layer and it is practically independent of any change in the activity of the NiOOH component in the layer, if the latter is conceived as a mixture of at least three NiOOH species.

According to this argument it is reasonable to conclude that the potentiodynamic electro-oxidation of the innermost layer of $Ni(OH)_2$ should be written as

$$Pt(O) \cdot Ni(OH)_2(aq) + OH^- = H_2O$$
$$+ Pt(O) \cdot NiOOH(aq) + e. \qquad (4)$$
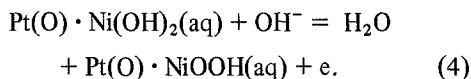
Reaction 4 represents a fraction of the overall process taking place at the $Ni(OH)_2$/NiOOH electrode. Its contribution is magnified during the initial scan because the innermost layer probably requires a longer time to attain quasi-equilibrium hydration conditions. The time required for attaining the stabilized E/I profile during potential cycling should be related to the time needed to achieve the quasi-stationary degree of hydration of the $Ni(OH)_2$/NiOOH film and, for its innermost part, the corresponding O co-ordination of Ni(III). On the basis of this interpretation the relative participation of Reaction 4 in the overall reaction becomes unnoticeable when thick $Ni(OH)_2$ layers are used.

Reaction 4 implies an electrochemical process which, in principle, should occur in both directions. Although these results indicate the type of cathodic reaction the situation for the anodic process is not so well defined. However, previously reported results, derived from the response of the $Ni/Ni(OH)_2$ electrode in the potential range of the Ni(II)/Ni(III) reaction under triangularly modulated triangular potential sweeps [19] and from experiments made with $E_{s,c}$ values located in the potential range of the current peak IV [14], indicate that the complementary anodic current contribution related to Reaction 4 appears from

ca. 0.47 V onwards. In the conventional potentio-dynamic E/I displays this contribution overlaps the main $Ni(OH)_2$ electro-oxidation current peak. The potentiodynamic characteristics of the current contributions related to Reaction 4 correspond to that of an irreversible surface electrochemical reaction, in agreement with previously reported results.

Acknowledgement

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