

Voltammetry and anodic stability of a hydrous oxide film on a nickel electrode in alkaline solution

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A hydrous oxide film on a nickel electrode was formed electrolytically by square-wave cycling in 1 mol dm^{-3} NaOH solution. The reproducibility of a second scan in a voltammetric experiment depended on holding the potential at a negative value (-1.1 V vs SCE) and on the positive potential limit. The hydrous oxide film, with a charge enhancement factor of 19, exhibited two stages of oxide reduction. Coulometric data showed that the majority of the oxide (80–90%) was reduced in Ni(III)/Ni(II) transition almost reversibly at potentials where the higher oxide was formed while, depending on the potential of formation, about 10–20% of the NiOOH was irreversibly reduced in the potential region of the hydrogen evolution reaction. An anodic stability test in the oxygen evolution reaction was carried out at 0.1 A cm^{-2} . The hydrous oxide layer was stable over 14 days of electrolysis with an unchanged charge enhancement factor. The electrocatalytic activity of the electrode, however, expressed through the overpotential at the same current density, was not maintained.

1. Introduction

The use of nickel in electrochemistry is longstanding; nickel, as a relatively cheap material, has been used as anode in batteries and alkaline water electrolyzers [1, 2]. In alkaline solution the metal surface is covered with a film of nickel hydroxide. Continuous potentiodynamic cycling in alkaline solution induced both oxide growth [3, 4], and an enhancement of the oxygen evolution reaction on a grown oxide [5, 6]. The experimental conditions of oxide growth with respect to potential limits, frequency, sweep rate, symmetry of the signal, pH and hydroxide concentration have been described [7, 8]. However, there is a lack of anodic stability data for such electrolytically grown oxide. It is generally accepted that hydrous oxide films exhibit better electrocatalytic but inferior stability performances [9], nevertheless, the anodically formed oxide films of platinum group metals (Ru, Ir and Rh), which are hydrous in nature at anodic potentials, exhibit various degrees of anodic stability. For example, electrodeposited rhodium exhibited about three orders of magnitude better stability than ruthenium in the oxygen evolution reaction from acidic solution [10]. Therefore, each material is a specific case and it is of interest to examine the anodic stability of a hydrous oxide film on a nickel electrode, particularly in the light of enhanced oxygen evolution on a grown hydrous oxide [5, 6].

2. Experimental details

The nickel electrode was a wire of 0.05 cm diam., 0.25 cm^2 area, 99.99% purity (Goodfellow Metals) fixed by epoxy resin into a glass tube. It was polished

by emery paper and $0.05 \mu\text{m}$ alumina powder, and washed by quadruply distilled water. The polishing procedure was repeated before each new preparation of a hydrous oxide film in order to remove unreduced nickel oxide [11].

Electrochemical experiments were carried out using an EG&G 273/97 potentiostat/galvanostat. A sodium hydroxide solution (Fluka p.a.) was prepared with quadruply distilled water. A three compartment electrochemical cell thermostatted at $298 \pm 0.1 \text{ K}$, with a platinum foil as a counter electrode was used. The counter electrode compartment was separated via a stopcock from the working electrode compartment. A thin layer of electrolyte provided electrical contact. On the other hand, it isolated the working electrode from possible contamination with platinum species that might be dissolved during the cyclic procedure. A type K-701 (Radiometer) saturated calomel electrode (SCE), was used as reference electrode. This had a fine glass frit, and was connected via another glass tube, which also ended with a glass frit, to the Luggin capillary. These precautions were undertaken in order to prevent contamination of the working electrode compartment with chloride ions.

The oxide was grown by SQW pulses between -1.3 and 0.7 V vs SCE .

3. Results and discussion

3.1. Voltammetric measurements

Figure 1 shows a typical voltammetric curve of nickel in 1 mol dm^{-3} NaOH. The electrochemical process between -1.1 and -0.6 V is due to Ni/Ni(OH)₂ transition [12]. The second part of the voltammogram

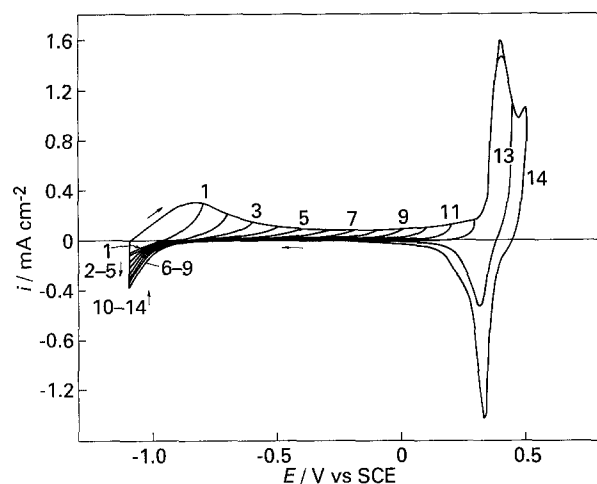


Fig. 1. Cyclic voltammogram at a sweep rate of 50 mV s^{-1} of a clean (without grown oxide) nickel electrode in 1 mol dm^{-3} NaOH recorded with 100 mV increments in positive direction. The potential before each subsequent cycle was held for 60 s at -1.1 V .

in the positive direction from -0.6 to 0.3 V is due to transformation of $\alpha\text{Ni}(\text{OH})_2$ to $\beta\text{Ni}(\text{OH})_2$. The pair of peaks at 0.4 V corresponds to the $\text{NiOOH}/\text{Ni}(\text{OH})_2$ process, while the shoulder at 0.2 V in the oxide reduction is due to the presence of a second crystallographic form of NiOOH . Figure 1 shows that the reproducibility of the second, as well as of subsequent scans, can be achieved by holding the potential at negative values for some time. In the experiment, as shown in Fig. 1, the potential was held at -1.1 V for 60 s . The minimum time was not investigated, it probably depends on the positive limit of potential excursion. However, 60 s was sufficient to reduce the majority of oxide formed at positive potential.

Figure 2 shows how various degrees of irrepro-

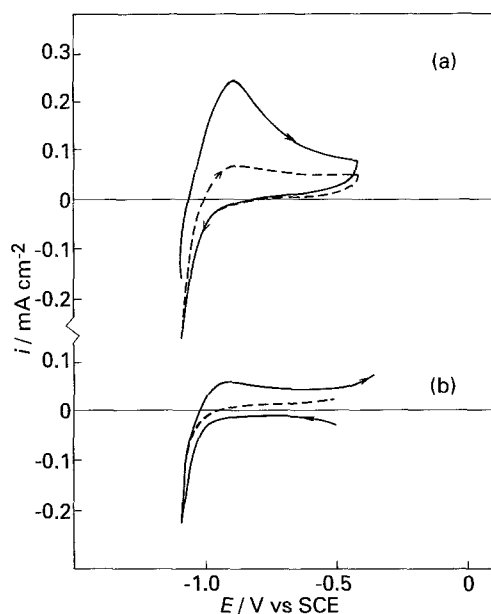


Fig. 2. Cyclic voltammograms at a sweep rate of 50 mV s^{-1} of a clean nickel electrode with and without holding at -1.1 V . (a) 60 s holding time, positive potential limit -0.2 V (—); without holding at -1.1 V , positive potential limit -0.2 V (---); (b) without holding, positive potential limit 0.5 V (—); positive scan only, without holding at -1.1 V and after potential excursion to 0.5 V (---).

ducibility of the second scan can be obtained. The full line in Fig. 2(a) in the positive direction was recorded as the first scan after holding the potential at -1.1 V . The positive limit of potential was up to -0.2 V . When the potential scan after the first cycle was immediately switched in the positive direction without holding at -1.1 V , the current was not reproducible with the first sweep. The potential limit was again -0.2 V . When the positive potential limit was extended to 0.5 V and the subsequent cycle recorded again without holding at -1.1 V , the full line in Fig. 2(b) was obtained accompanied by a further decrease of anodic charge in the subsequent cycle. The current in this scan almost disappeared, as also observed by other authors. Burke and Twomey [7] were able to restore the initial peak by shifting the lower limit towards more negative values into the region of the hydrogen evolution reaction. Therefore, various degrees of irreversibility and reducibility of nickel oxides/hydroxides exist, depending on whether the potential excursion is extended only to $\text{Ni}(\text{OH})_2$ formation or more positive values where NiOOH is formed.

Figure 3 shows cyclic voltammogram after hydrous oxide growth. The charge enhancement factor (CEF) is often used in defining the increase of the charge storage capacity of grown oxide films [13]. It was defined in this work as the ratio of anodic charge of $\text{Ni}(\text{OH})_2/\text{NiOOH}$ transition before and after cycling the electrode with SQW pulses. More precisely, the voltammetric charge of the anodic peak between 0.32 and 0.47 V was integrated. In the case of experimental conditions given in Fig. 3, the CEF was 19. It should be pointed out that the first anodic peak (not shown in Fig. 3) was of the same height (see Fig. 5) on the originally fresh electrode i.e. without enhancement of charge, as was also observed by Burke and Whelan [3].

3.2. Influence of frequency and symmetry of SQW pulses on the oxide growth

The significance of oxide reduction in the quantity of

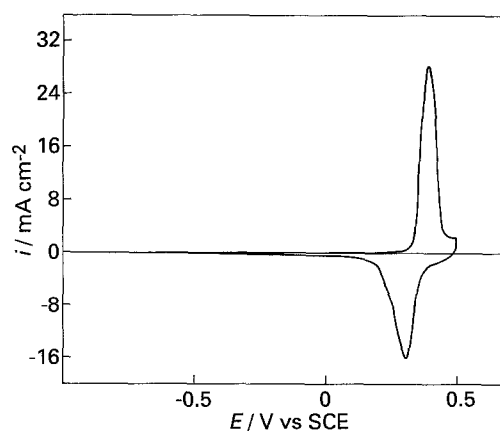


Fig. 3. Cyclic voltammogram at a sweep rate of 50 mV s^{-1} of a nickel electrode subjected to SQW pulses from -1.3 to 0.7 V at 0.1 Hz for 100 min in 1 mol dm^{-3} NaOH solution.

Table 1. CEF values of a hydrous oxide film on a nickel electrode as a function of SQW frequency, f , symmetry of SQW signal and cumulative time of SQW signal, t_{cum}

Time of one halfcycle at -1.3 V/s	Time of one halfcycle at 0.7 V/s	f /Hz	t_{cum} /min	CEF
10	10	0.05	200	26
5	5	0.1	100	19
2.5	2.5	0.2	50	14
1	1	0.5	20	6
0.5	0.5	1	10	4
0.25	0.25	2	5	3
0.25	0.25	2	200	20
9	1	0.1	100	30
1	9	0.1	100	6

hydrous oxide material (CEF values) formed by a cycling procedure is seen in Table 1. It is evident that lower frequencies produced higher CEF values during the same number of SQW pulses. The asymmetric cycling further supports the significance of the oxide reduction. When the holding time of the potential at the negative side was 9 s, CEF was 30, while a signal with opposite symmetry produced CEF of 6. But, it is also evident that if the cumulative time at 2 Hz frequency was extended to 200 min. CEF increased to 19. This means that the oxide need not be reduced completely; the bare nickel atoms react in successive oxidation cycles before complete reduction of compact oxide.

3.3. Anodic stability of the hydrous oxide film

One of the most important parameters which characterizes the quality of an electrocatalyst is its stability. In the present work the stability of the electrolytically grown hydrous oxide film on a nickel electrode was examined by monitoring the CEF values of the electrode during anodic galvanostatic polarization at 0.1 A cm^{-2} in 1 mol dm^{-3} NaOH solution. It is evident that the electrode remained stable after 14 days of electrolysis (Fig. 4). During

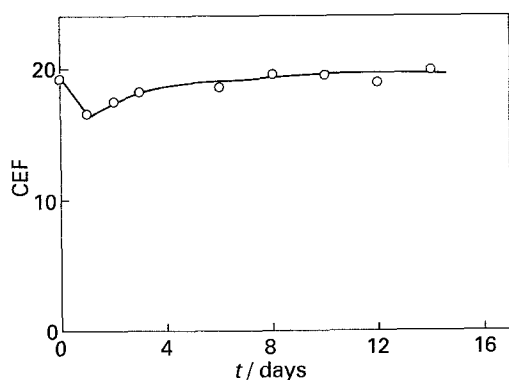


Fig. 4. CEF against time values during anodic galvanostatic polarization at 0.1 A cm^{-2} current density in 1 mol dm^{-3} NaOH solution at 25°C of a hydrous oxide film grown on a nickel electrode. Initial CEF value 19.

this period the process of electrolysis was stopped several times and cyclic voltammograms were recorded from which CEF values were determined. Three questions arise in this connection. First, why CEF was chosen as a measure of stability. CEF is a measure of exchanged electrons in the Ni(II)/Ni(III) transition and, therefore, it is a direct measure of the quantity of an electroactive hydrous material. Second, it is of interest to know, from the electrocatalytic point of view, whether the activity of the electrode was preserved during the stability test. The nickel electrodes, after potentiodynamic treatment and oxide growth, exhibited enhanced oxygen evolution [5, 6] and, therefore were electrocatalytically more active operating at a lower overvoltage. Indeed, the electrode in the present paper, with a CEF value of 19 (Fig. 3), exhibited a decrease of overvoltage for 125 mV at 0.1 A cm^{-2} current density compared to the fresh, uncycled electrode. But, the activity expressed through overvoltage decreased during the stability test. More precisely, the overvoltage at 0.1 A cm^{-2} current density reached the value of the uncycled electrode. In other words, the quantity of electroactive hydrous material was preserved during 14 days of electrolysis; the enhanced activity of the electrode, however, was lost. Third question is whether the oxide growth on a nickel electrode also takes place during anodic polarization without cycling. This phenomenon is well known in the literature. Lu and Srinivasan [11], reported oxide growth and enhanced activity in the oxygen evolution reaction from KOH solution with polarization of the nickel electrode at 1.5 V vs Hg/HgO electrode. A similar experiment was carried out in the present work by polarizing the uncycled nickel electrode galvanostatically at 0.1 A cm^{-2} . CEF was increasing although at a much slower rate than with SQW cycling (CEF was 19 after 100 min at 0.1 Hz ; see Table 1), but, after 6 h at 0.1 A cm^{-2} the CEF was 9. Comparison with some other hydrous metal oxides can be made. For example, the electrolytically grown hydrous oxide film on a rhodium electrode in alkaline

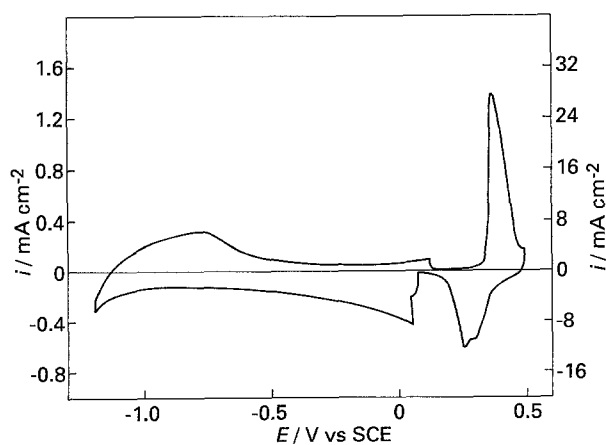


Fig. 5. Cyclic voltammogram recorded at a sweep rate of 50 mV s^{-1} of a hydrous oxide film on a nickel electrode after 12 days of anodic galvanostatic polarization at 0.1 A cm^{-2} current density in 1 mol dm^{-3} NaOH solution. The current sensitivity was switched manually at about 0.1 V .

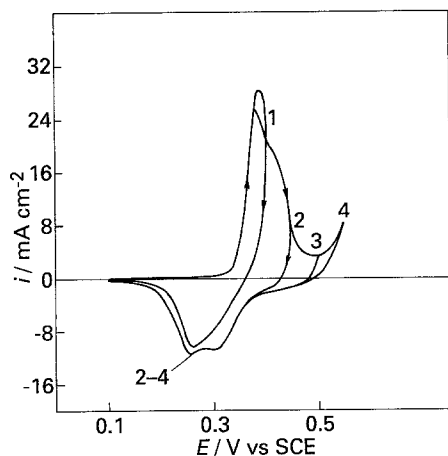


Fig. 6. Cyclic voltammogram of grown hydrous oxide film on a nickel electrode recorded with 50 mV increments in positive direction.

solution by potentiodynamic [14] and/or SQW cycling [15] also exhibited enhanced oxygen evolution [16]. But, when the uncycled rhodium electrode was polarized galvanostatically the oxygen was evolved on a monolayer of the oxide film, i.e. the CEF was 1 [17]. The hydrous oxide film on an iridium electrode grown in acid solution was not stable at the potential of the oxygen evolution reaction [18]. The electrochemical behaviour of a nickel electrode is, therefore, different from these noble metals. The oxide film on a nickel electrode can be grown by either procedure, SQW cycling or galvanostatic (and/or potentiostatic) polarization, but the grown oxide is stable during oxygen evolution. However, due to a loss in activity, this is of marginal practical importance. The reason for the loss in activity was discussed by Lu and Srinivasan [11], who attributed this phenomenon to the formation of Ni(IV) species during oxygen evolution: these species have less active sites than Ni(III) species.

The cyclic voltammogram of the SQW grown nickel oxide polarized galvanostatically for 12 days is shown in Fig. 5. The freshly prepared thick oxide film (Fig. 3) exhibits only shoulder in the anodic peak at 0.2 V; in aged film it splits into a doublet (Fig. 5). A closer look at the Ni(OH)₂/NiOOH transition is presented in Fig. 6, where 50 mV increments in the positive direction were used. It is evident that the majority of NiOOH is reduced almost reversibly. An additional oxide formed between points 2 and 3 is partly reduced at the cathodic side in the same potential

Table 2. Ratio of a cathodic charge Q_c , and anodic charge Q_a of a Ni(OH)₂/NiOOH transition in a nickel hydrous oxide film (CEF 19) as a function of switching potential (see Fig. 6)

Switching potential V	Q_c mC cm ⁻²	Q_a mC cm ⁻²	Q_c/Q_a
0.400	19.6	18.0	1.09
0.450	31.6	35.2	0.90
0.500	34.0	40.0	0.85
0.550	34.4	42.8	0.80

range (reversible oxidation/reduction process). Curves 2–4 in the cathodic side overlap i.e. no further reduction takes place between 0.1 and 0.4 V. Table 2 presents the ratio of anodic and cathodic charge after switching the potential to various values in this potential region.

By current integration it was shown that from 80 to 90% of NiOOH is reduced between 0.5 and 0.1 V, the rest of the oxide is reduced in the hydrogen evolution region together with the Ni(OH)₂ reduction which is evident from Fig. 1 (Curves 10–14). It is also seen from Table 2 that, switching the potential from 0.5 V, 6 mC of the oxide remained unreduced. However, it can not be said conclusively that the rest of the oxide is reduced at -1.1 V. It is difficult to distinguish the contribution of NiOOH reduction from the current of Ni(OH)₂ reduction and hydrogen evolution.

4. Conclusions

Hydrous oxide growth on a nickel electrode in alkaline solution can be achieved by either square-wave cycling or anodic galvanostatic polarization; the first method is significantly faster. As far as the anodic stability of the oxide film is concerned, the oxide is stable during oxygen evolution. The electroactive hydrous layer does not dissolve, but a decrease in electrocatalytic activity of the oxygen evolution reaction takes place.

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