

Non-equilibrium effects in the nickel hydroxide electrode

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The electrochemical reaction



occurring under potentiodynamic conditions in 1 N KOH using complex triangular potential sweep revealed the existence of non-equilibrium effects of both reactant and products which cause the splitting of the anodic current peak already known. By a suitable choice of the perturbation variables, the rate of the chemical change the Ni(OH)₂ species undergoes can be estimated. The reaction presenting the nickel hydroxide electrode is interpreted as two parallel electron transfer steps coupled to two chemical reactions through a square-type reaction model.

1. Introduction

The *E/I* displays corresponding to the electro-oxidation of Ni(OH)₂ under potentiodynamic conditions depend very markedly upon whether the nickel electrode was previously held at a definite anodic or cathodic potential before applying the potential scan [1]. Occasionally double anodic processes are reported under such experimental conditions [2]. Two separate anodic current peaks, one gradually replacing the other in repetitive potential scans, were also described in the literature [3], which were interpreted as the spontaneous change from α -Ni(OH)₂ to β -Ni(OH)₂. The available evidence cannot be considered as sufficient to understand beyond any doubt the cause of the anodic double current peak formation [4].

The existence of a 'fine electrochemical structure' in the *E/I* displays has been more recently described for the reverse electrochemical process, namely the electrochemical conversion of the NiOOH species into nickel hydroxide species [5–7]. The corresponding displays depend on the characteristics of the potential–time perturbation program used. A proper adjustment of the time scale enables one to distinguish between the contributions of the different reactions involved in the overall *E/I* displays.

This paper is devoted to finding the perturbation conditions under which the anodic double current peak related to the electro-oxidation of Ni(OH)₂ is invariably observed, to confirm the occurrence of energetically different species not only for the electroreduction of NiOOH as already reported [5–7] but also for the electro-oxidation process, to establish the chemical transformations undergone by Ni(OH)₂ and, finally, to gain a quantitative description of the variables which are important in the various reactions leading to the more stable compound.

2. Experimental

The experimental set-up is the same as that already described in previous publications [8, 9]. 'Specpure' nickel wires (0.5 mm diameter, 0.25 cm²) were used as working electrodes in 1.0 N KOH, in a N₂ atmosphere at 25°C. The electrode treatment was as follows. After the initial mechanical polishing the electrode was cathodized for 10 min at –0.96 V, then the potential was cycled between –0.96 V and 0.69 V for 1 h. Afterwards the system was left for 1 h at open circuit and finally during 10 min at 0.34 V. One of the potentiodynamic perturbations shown in Fig. 1 was then applied and the *E/I* display recorded.

Most of the experiments were performed using

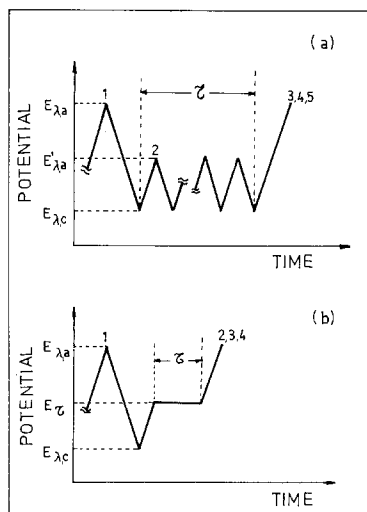


Fig. 1. The potential-time perturbation programs. The numbers correspond to those shown in the following figures. The stabilized triangular potential sweep profile (reference) is indicated by 1.

a constant potential sweep rate but changing either $E_{\lambda,c}$ and $E'_{\lambda,a}$ (for the perturbation program shown in Fig. 1a) or E_{τ} (for the perturbation program shown in Fig. 1b) and τ , within the widest possible range compatible with the reaction response.

Potentials were measured against a saturated calomel electrode but they are all referred to the standard hydrogen electrode in the figures.

3. Results

The conventional E/I display obtained under a single triangular potential sweep [3, 5] contains a broad anodic current peak located at about 0.64 V and two well-defined cathodic current peaks. The more symmetrical one involving the largest charge is at about 0.56 V and the smaller one, which is more ill-defined, appears at about 0.49 V. These characteristics are changed when the potential perturbation program of Fig. 1a is employed, particularly in the anodic current region. These changes depend both on $E'_{\lambda,a}$ and on τ and are clearly depicted in a series of E/I displays obtained between $E_{\lambda,c} = 0.34$ V and $E_{\lambda,a} = 0.68$ V at $v = 0.1$ V s⁻¹ with different $E'_{\lambda,a}$ values and $0.5 \text{ min} \leq \tau \leq 5 \text{ min}$ (Fig. 2).

Thus, when $E'_{\lambda,a} < 0.62$ V, only a broad anodic current peak is recorded even with τ as large as

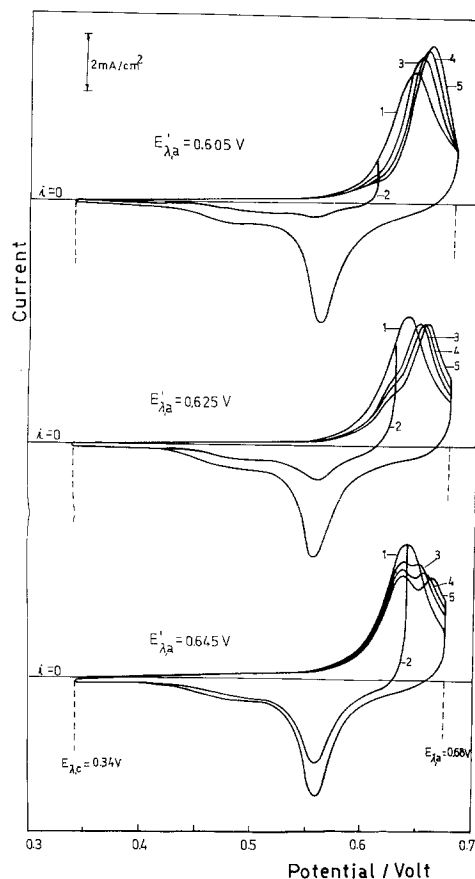


Fig. 2. Potentiodynamic E/I displays obtained with the perturbation program (a). Influence of $E'_{\lambda,a}$. $v = 0.1$ V s⁻¹; $\tau = 0.5$ min (3), $\tau = 2$ min (4), and $\tau = 5$ min (5).

5 min, but the shift of the current peak towards anodic potentials, at a constant τ , is definitely more marked as $E'_{\lambda,a}$ decreases. Then, the anodic current peak, although always involving the same charge, becomes progressively thinner. For a fixed $E'_{\lambda,a}$ the shift of the anodic peak towards the anodic potential side is more noticeable as τ increases. This occurs simultaneously with the slight shift of the main cathodic peak towards more anodic potentials.

On the other hand, when $E'_{\lambda,a} > 0.62$ V, so that through the intermediate potential sweep nearly one-half of the total charge involved is periodically formed and removed, the double peak is progressively recorded as τ increases. The effect is more remarkable when $E'_{\lambda,a}$ increases to a value where the E/I display encloses a charge value closer to one-half of the total charge. Under these circumstances, for instance for $E'_{\lambda,a} = 0.64$ V and

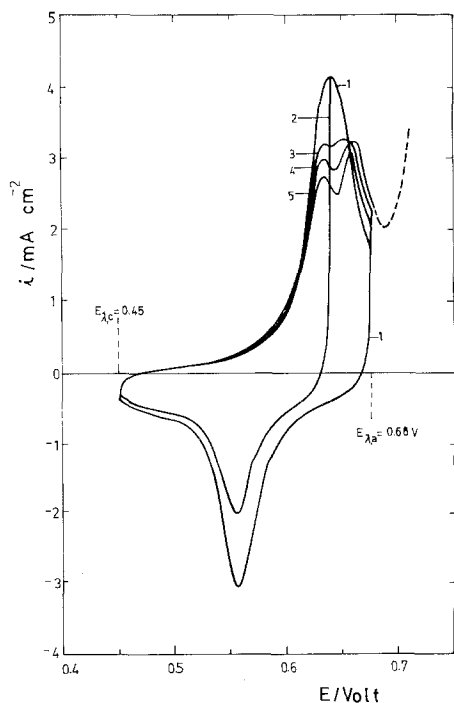


Fig. 3. Potentiodynamic E/I displays obtained with the perturbation program (a). Influence of τ . $v = 0.1 \text{ V s}^{-1}$; $E'_{\lambda,a} = 0.64 \text{ V}$; $\tau = 0.5 \text{ min}$ (2), 2 min (3) and 5 min (4).

$\tau = 5 \text{ min}$, the anodic current shows two current peaks whose contributions are nearly the same. Simultaneously, the main cathodic current peak is permanently located at more anodic potentials covering a relatively wide potential range and presenting a somewhat asymmetric profile. In any case, the final E/I displays obtained after perturbing the system during the lapse τ , involve practically the same amount of charge in either the anodic or the cathodic potential excursions.

The double anodic peak is relatively more easy to define when $E_{\lambda,c}$ increases (Fig. 3) keeping $E'_{\lambda,a}$ constant and correspondingly the contribution of the second anodic current becomes more clearly separated. Once the stable double anodic current peak is set up, the initial single anodic current peak E/I display can be restored by keeping the electrode for 5 min at some $E_{\lambda,c}$, for instance 0.45 V.

The magnitude and distribution of the anodic current peaks forming the doublet are very sensitive to the value of $E'_{\lambda,a}$ as well as to the $E_{\lambda,c}$ value. From these results one deduces that a very important parameter for the definition of the anodic doublet is the relative amount of charge

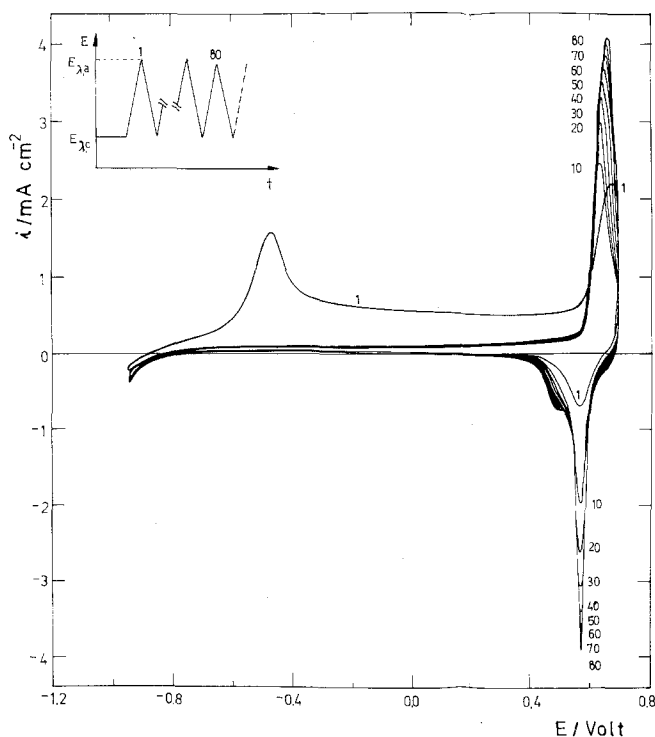


Fig. 4. Repetitive triangular potential cycling at $v = 0.1 \text{ V s}^{-1}$. Influence of cycling to attain a steady E/I profile in the potential range of the nickel hydroxide electrode.

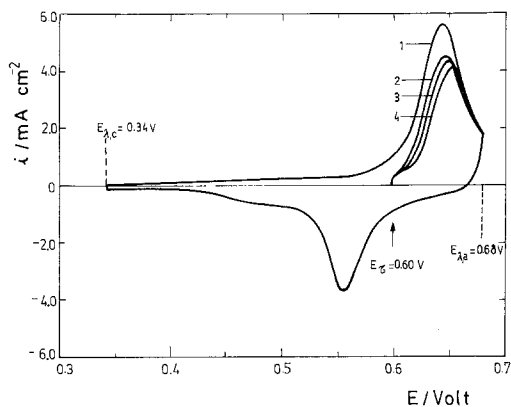


Fig. 5. Potentiodynamic E/I displays obtained with the perturbation program (b). Influence of τ at $E_T = 0.60$ V. $v = 0.1$ V s $^{-1}$; $\tau = 0.5$ min (2), 2 min (3) and 5 min (4).

playing a part during the perturbation period between the switching potentials $E_{\lambda,c}$ and $E'_{\lambda,a}$.

The E/I profile run between -0.96 V and 0.7 V under conventional repetitive triangular potential sweeps (Fig. 4) with an electrode cathodized for only 10 min at -0.96 V, presents a profile which shows a drastic change in shape between the first and the second sweeps. These changes have already been reported and discussed in previous publications. Nevertheless small changes are progressively observed during the successive excursions, so that at $v = 0.1$ V s $^{-1}$,

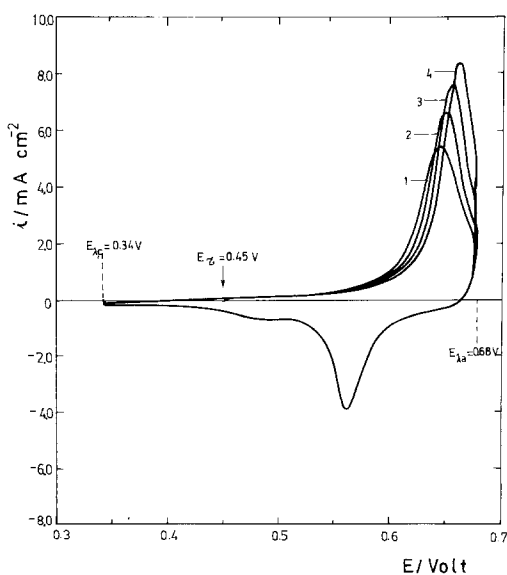


Fig. 6. Potentiodynamic E/I displays obtained with the perturbation program (b). Influence of τ at $E_T = 0.45$ V. $v = 0.1$ V s $^{-1}$. $\tau = 0.5$ min (2), 2 min (3) and 5 min (4).

only after the 10th cycle is the shape kept, although the charge still slightly increases after the 100th cycle.

When the Ni(OH)_2 is aged at a potential E_T located between $E_{\lambda,c}$ and its electro-oxidation potential range (Fig. 5) a clear shift of the anodic current peak is noticed as τ increases. The effect is more remarkable when E_T is more cathodic (Fig. 6). Furthermore, when E_T becomes closer to the anodic current peak potential, although the above-mentioned effect still exists, the amount of charge associated with it decreases to some extent as τ increases.

4. Discussion

The present results definitely establish the occurrence of a double anodic current peak during the potentiodynamic electro-oxidation of Ni(OH)_2 in agreement with previous findings [5–7]. The effect appears more clearly when the electrochemical reaction is perturbed with a potential–time program whose characteristics ($E'_{\lambda,a}$, $E_{\lambda,c}$, τ and v) are within a rather limited range which can be deduced from the results already reported. Then, the overall charge covered by the E/I display is of the order of a few monolayers of product if one assumes a roughness factor equal to one, or what is perhaps more reasonable, the charge may approach that of one or two monolayers, if one admits that the roughness factor is of the order of 3 [10, 11].

The appearance of the doublet is even more remarkable under the perturbation indicated in Fig. 1a. During the lapse the intermediate perturbation restricted between $E_{\lambda,c}$ and $E'_{\lambda,a}$ lasts, only a fraction of the product covering the surface participates in both the anodic and the cathodic reactions. This fraction increases as $E'_{\lambda,a}$ increases rendering the double anodic current peak more easily distinguishable at higher values of τ .

The two anodic current peaks indicate, in principle, that at least two different Ni(OH)_2 species are electro-oxidized. The electro-oxidation of the more unstable species is characterized by the first anodic current peak which is located at 0.61 ± 0.01 V and the one corresponding to the more stable species is found at 0.65 ± 0.01 V. Therefore, the energy difference for electro-oxidation is in the range of 0.5 – 1.0 kcal mol $^{-1}$,

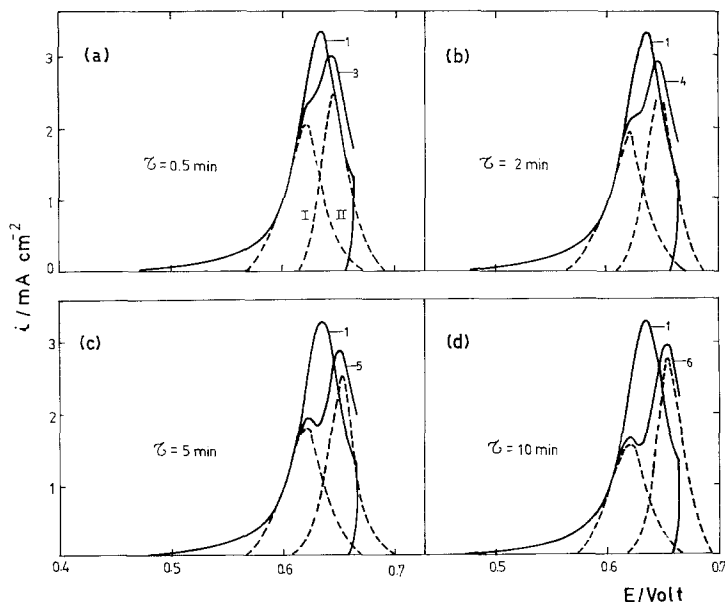


Fig. 7. Separation of the double E/I profiles obtained at different τ in terms of two single anodic E/I profiles. $v = 0.1 \text{ V s}^{-1}$; $E'_{\lambda,a} = 0.62 \text{ V}$. The reference E/I display and the final one are shown as full traces. $\tau = 0.5 \text{ min}$ (a) 2 min (b); 5 min (c) and 10 min (d).

a figure which is too small for structural rearrangements involving bond breaks of any type. This energy difference is believed to correspond to a stretching of the hydroxide lattice structure. The two $\text{Ni}(\text{OH})_2$ species are probably related to those reported in the literature as $\alpha\text{-Ni}(\text{OH})_2$ and $\beta\text{-Ni}(\text{OH})_2$, the former corresponding to a more open structure [4, 12–16]. There is also ellipsometric evidence of two forms of nickel hydroxide [16]. Accordingly, each of these species undergoes its proper anodic reaction, their corresponding reaction products also probably being different [11, 16]. Both anodic reactions, as further described, are coupled through chemical reactions. The nickel hydroxide interconversion explains the ageing effects on its electrochemical properties reported earlier [17] as well as that in the oxidation and reduction of nickel hydroxide at constant potentials. Although the composition of the material was not particularly affected by layer thickness, it was sensitive to previous ageing of the $\alpha\text{-Ni}(\text{OH})_2$ [18].

The present results, on the other hand, clearly indicate a chemical interconversion between the two hydroxide species.

A further insight into the characteristics of these reactions is obtained when the experimental E/I profiles are interpreted in terms of those corresponding to the individual reactions. For the pres-

ent case it is assumed that the potentiodynamic profile of each electrochemical reaction is represented by a Gaussian function whose maximum coincides with the corresponding peak potential derived from the experiments (Fig. 7). Under these circumstances one can estimate Q_I and Q_{II} , the charges of both anodic current peaks, as a function of the time during which the system is held either under the intermediate perturbation or at the switching potential limit, E_τ . The charge Q_I , assigned to the first anodic reaction product is taken to a first approximation as proportional to the amount of reactant $\alpha\text{-Ni}(\text{OH})_2$, while the charge Q_{II} is related to the amount of $\beta\text{-Ni}(\text{OH})_2$. For any E_τ , the Q_I/Q_{II} ratio decreases as τ increases. From this dependence, at least within the $0 \leq \tau \leq 10 \text{ min}$ range, for experiments run at any $E'_{\lambda,a}$ one can roughly estimate that $(Q_I/Q_{II}) = 0$ at $\tau_0 = 18 \pm 3 \text{ min}$. The latter figure suggests that the first anodic current peak can be practically ignored when the interface is perturbed at sweep rates lower than 1 mV s^{-1} .

On the basis of the different processes just described, the nickel hydroxide overall reaction becomes even more complex than thought earlier. Therefore, taking into account the previous interpretation it seems reasonable to write the total anodic process occurring under potentiodynamic conditions as follows:

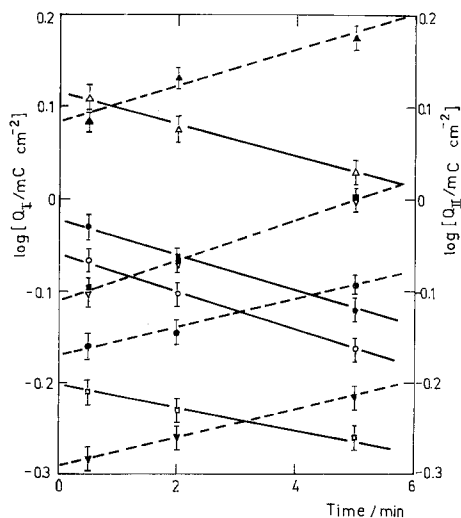
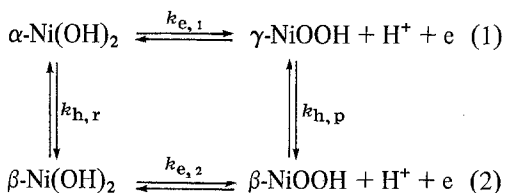


Fig. 8. First order plot for Q_I (full trace) and Q_{II} (dashed trace). $v = 0.1 \text{ V s}^{-1}$. $E_{\lambda,a} = 0.68 \text{ V}$, $0.62 \text{ V} \leq E'_{\lambda,a} \leq 0.64 \text{ V}$, $0.34 \text{ V} \leq E_{\lambda,c} \leq 0.52 \text{ V}$.



where the k s are the corresponding rate constants; e stands for the electrochemical reactions; h, for the chemical reactions; r, for the reactants and p, for the products.

Equations 1 and 2 are written in terms of compounds which are described in the literature [12–15, 17]. Nevertheless, this is perhaps the simplest way to express the electrochemical reactions. The actual situation may be rather more complicated because of the relatively small charge playing a part during the whole electrochemical reaction. This question has already been discussed for the formation and electroreduction of an oxygen-containing monolayer on different metals [19, 20] and the conclusions reached are, in part, also valid in the present case.

Furthermore, if the electrode Reactions 1 and 2 are simply coupled as already indicated above, an estimation of the rate constant $k_{h,r}$ can be attempted by assuming that the $\alpha\text{-Ni(OH)}_2$ to $\beta\text{-Ni(OH)}_2$ transformation follows a first-order law. Thus, by plotting $\log Q_I$ (or $\log Q_{II}$) versus τ acceptable straight lines are obtained (Fig. 8), which exhibit practically the same slope but a

$\log Q_I$ (or $\log Q_{II}$) at $\tau = 0$ which depends on the potential perturbation conditions. The average $k_{h,r}$ value which is derived from those plots is $0.0080 \pm 0.0015 \text{ min}^{-1}$. This apparent first-order rate constant corresponds to a half-life of the chemical transformation equal to $16.3 \pm 2.5 \text{ min}$.

The charge extrapolated at $\tau = 0$ yields the $\alpha\text{-Ni(OH)}_2$ concentration (expressed in terms of charge density) attained at the electrochemical interface after the repetitive potential perturbation between $E_{\lambda,c}$ and $E'_{\lambda,a}$. According to the treatment of the kinetic data, that concentration is taken as the initial concentration of reactant and it depends at a constant v both on the $E_{\lambda,c}$ and $E'_{\lambda,a}$ switching potentials as expected.

The conclusions reached from these results and from previously reported data is that the existence of non-equilibrium effects both in the Ni(OH)_2 -species and in the NiOOH -species, which are clearly detected under appropriate perturbation conditions, is confirmed. Taking into account that nickel hydroxide appears to be a good proton conductor, these effects may result from a change of configuration related to the H atoms in the double layer lattice structure of the nickel hydroxide, probably through the water molecules incorporated between this structure [21] and from a lack of attainment of thermodynamic equilibrium during the normal time of perturbation.

It should be pointed out, however, that the proposed reaction model is an oversimplified reaction scheme which allows a preliminary insight of the complex reaction. A more realistic picture of the reaction probably implies crossed electrochemical reactions as well as more complex chemical reactions involving both reactant and products. Whatever these processes may be they cannot be clearly envisaged from the present results.

Finally, the reported data cast some doubts on previous interpretations of the kinetic measurements on nickel hydroxide electrodes made in terms of the overall anodic current peak recorded under potentiodynamic conditions since the non-equilibrium effects of the species participating in the reaction were overlooked.

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