

VOLTAMMETRIC DISCHARGE EFFICIENCY OF NICKEL HYDROXIDE ELECTRODES CHEMICALLY PRECIPITATED ON A PLATINUM SUBSTRATE

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Summary

The discharge and deposition efficiencies of nickel hydroxide electrodes chemically precipitated on platinum substrates were measured using cyclic voltammetry. These efficiencies depend on the concentration of the precipitating solutions, the thickness of the film, and the concentration of the electrolyte. The temperature of the precipitating solutions has a significant influence on the deposition efficiency but not on the discharge efficiency. Changes in the discharge efficiency are mainly analyzed in terms of changes in the morphology and physical structure of the nickel hydroxide film at the substrate/nickel hydroxide interphase. Discharge efficiencies, based on one electron per nickel ion, as large as 130% are obtained at very low concentrations of precipitating solutions. On the other hand, extremely low discharge efficiencies are obtained with highly concentrated precipitating solutions.

Introduction

The nickel hydroxide electrode is of high technological importance as the positive electrode in nickel/cadmium, nickel/hydrogen, and other alkaline battery cells [1 - 3]. There are several significant processes in the electrode performance and degradation, such as the buildup of residual capacity and changes in the resistance and structure of the active material, that will affect the discharge and recharge efficiencies. All these processes are determined, in principle, by the preparation conditions of the nickel hydroxide film as well as by the conditions used during the electrochemical perturbations.

Nickel hydroxide electrodes are produced by electrochemical impregnation (cathodic deposition in concentrated $\text{Ni}(\text{NO}_3)_2$ solutions) [4 - 6] or

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by chemical deposition of Ni(OH)_2 on inert substrates. This has been shown to be a suitable method of obtaining the reversible $\text{Ni(OH)}_2/\text{NiOOH}$ electrode when the electrochemical interphase is properly polarized [7 - 11]. The influence of the precipitating conditions on the crystalline structure has been investigated previously [9], but there is no information about the effect of these conditions on the discharge efficiency.

The discharge efficiency, or electrode utilisation as referred to by some authors [12], is usually less than the theoretical 100% based on the one electron transfer per nickel ion necessary for the $\text{Ni(III)} \rightarrow \text{Ni(II)}$ redox reaction. Although one electron transfer per nickel ion is not necessarily the maximum amount possible, since oxidation states ranging from 2+ to 4+ are, in principle, found in nickel hydroxide for nickel ions [1], the maximum discharge efficiency experimentally observed is of the order of 80% [12 - 14]. Zimmerman [2] has recently reported that one of the most important factors in determining the recharge and discharge efficiencies of nickel hydroxide electrodes is the morphology and the physical structure of the substrate/nickel hydroxide interphase, the contact area between the active material and the substrate being the main reason for this. This contact area determines the electrical resistance of the interphase. Another reason for changes in recharge and discharge efficiencies could be the textural characteristics of the material. Figlarz *et al.* [14] have recently reported that certain crystallized nickel hydroxides are inactive for electrochemical cycling due to their textural characteristics.

Taking into account the advantage of a completely inert substrate in relation to the redox reactions involved in the charge/discharge processes of the $\text{Ni(OH)}_2/\text{NiOOH}$ couple, we have undertaken the present study with the aim of investigating systematically the influence of the preparation conditions (number of immersions, concentration and temperature of the precipitating solutions) and the concentration of the electrolyte on the voltammetric discharge efficiency of nickel hydroxide electrodes chemically precipitated on Pt substrates.

Experimental

The preparation of the Ni(OH)_2 film used as the working electrode was made by chemical precipitation on a platinum wire (area = 0.48 cm^2) through N alternate immersions of 5 s in $y \text{ M NiSO}_4$ ($y = 0.001, 0.01, 0.1$ and 1) and in $x \text{ M NaOH}$ ($x = 0.001, 0.01, 0.1$ and 1) following the procedure already described [7 - 11]. The precipitation of the Ni(OH)_2 film was performed in the temperature range $20 \text{ }^\circ\text{C} - 100 \text{ }^\circ\text{C}$. Unless otherwise stated in the Figure captions, the precipitation was performed at $20 \text{ }^\circ\text{C}$. The substrate was cleaned with a 15 s immersion in a 2:1 $\text{H}_2\text{SO}_4:\text{HNO}_3$ mixture, followed by a careful rinse for 1 min with purified H_2O in order to obtain reproducible results.

The electrochemical measurements were performed in a three-compartment electrolysis cell using a large area platinum counter-electrode and an Hg/HgO/1 M NaOH reference electrode (+0.098 V *versus* NHE).

The following solutions were used as electrolyte:

1 M NaOH, (pH = 14)

0.1 M NaOH + 0.3 M Na₂SO₄, (pH = 13)

0.01 M NaOH + 0.33 M Na₂SO₄, (pH = 12)

All solutions were prepared from AR chemicals and water purified by Milli Ro and Milli Q systems and were de-aerated with purified nitrogen.

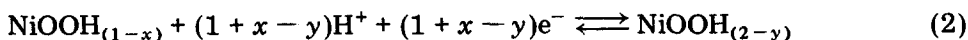
The working electrode was perturbed with repetitive triangular potential sweeps at $v = 0.2; 0.1; 0.05; 0.025; 0.01$ and 0.005 V s^{-1} between preset cathodic ($E_{s,c}$) and anodic ($E_{s,a}$) switching potentials. All the electrochemical experiments were made at 20°C .

The experimental set-up for the electrochemical measurements was the same as already described in previous publications [9 - 11].

Because the use of the discharge efficiency concept requires the definition of a 100% value, which is usually taken as the value for a one electron transfer per nickel ion, we used the average number of electrons transferred in the cathodic reaction during the potential cycling per nickel ion present in the electrode as a measurement of the discharge efficiency. This number was experimentally determined from the ratio of the charge associated with the cathodic current peak to the number of moles of nickel (determined by chemical analysis) precipitated on the substrate:

$$\eta = \frac{q_c}{nF} \quad (1)$$

where η is the average number of electrons transferred per nickel ion, F is the Faraday constant, n is the amount of moles of nickel precipitated per square centimeter of electrode and q_c is the reduction charge density in C cm^{-2} corresponding to the general reaction:



where $-1 < x < 1$ and $0 < y < 1$ with the restriction $1+x \geq y$. Thus, the oxidation state of nickel after charging (oxidation) is $(3+x)$ and the oxidation state after discharging (reduction) is $(2+y)$ [11].

The charge density q_c was evaluated as follows: once a stabilized j/E profile is obtained after 10 min of cycling at 0.1 V s^{-1} , a run is performed at 0.005 V s^{-1} and q_c is measured, since at 0.005 V s^{-1} the electrochemical process is under kinetic control [9] and the charge involved is independent of the sweep rate.

The number of moles of nickel per square centimeter of electrode (n) was measured according to the method already described in the literature [15, 16]. The Ni(OH)₂ films were dissolved with a 2 min immersion of the electrode in a 0.5 wt.% KCN solution under ultrasonic stirring, and the absorbance was determined at 267 nm in a Shimadzu recording UV-260 spectrophotometer. The complete dissolution of the Ni(OH)₂ film was

verified by running a voltammogram of the Pt substrate after the dissolution. No charge associated with reaction (2) was observed after this procedure.

Results and discussion

(i) Effect of the number of immersions

The influence of the number of immersions on q_c , n and η was systematically investigated. Results obtained with different concentrations of precipitating solutions are presented in Figs. 1 and 2. For pNi 1 (Fig. 1) q_c increases almost linearly with N at pH 12 and 14, but for pH 13 there is an approximate exponential dependence. A similar result was obtained for the n versus N relationship. For pNi 3 and pH 11 (Fig. 2) there is a linear relation between q_c and N , but not between n and N . In the corresponding η versus N plot it can be observed that for pNi 1 the η values are very low and change slightly with N , particularly for pH 14. Thus, even if n and q_c can be increased with the number of immersions, η cannot be increased by

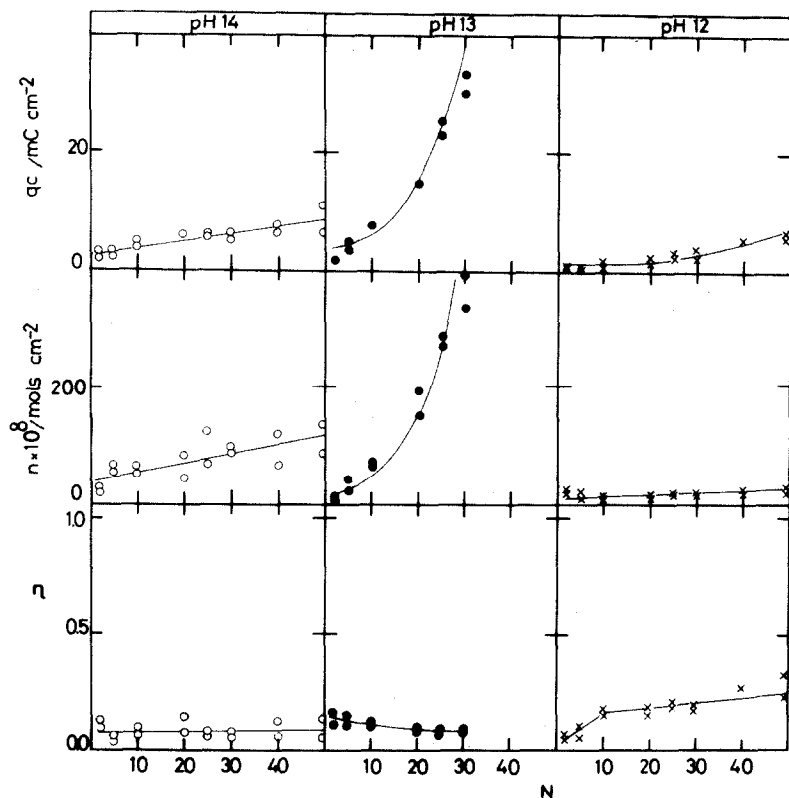


Fig. 1. Dependence of cathodic charge density (q_c), number of moles of nickel per square centimeter (n), and average number of electrons transferred per nickel ion (η) upon the number of immersions (N). Electrolyte: 0.1 M NaOH + 0.30 M Na₂SO₄. Precipitating solutions: pNi 1; ○, pH 14; ●, pH 13; ×, pH 12.

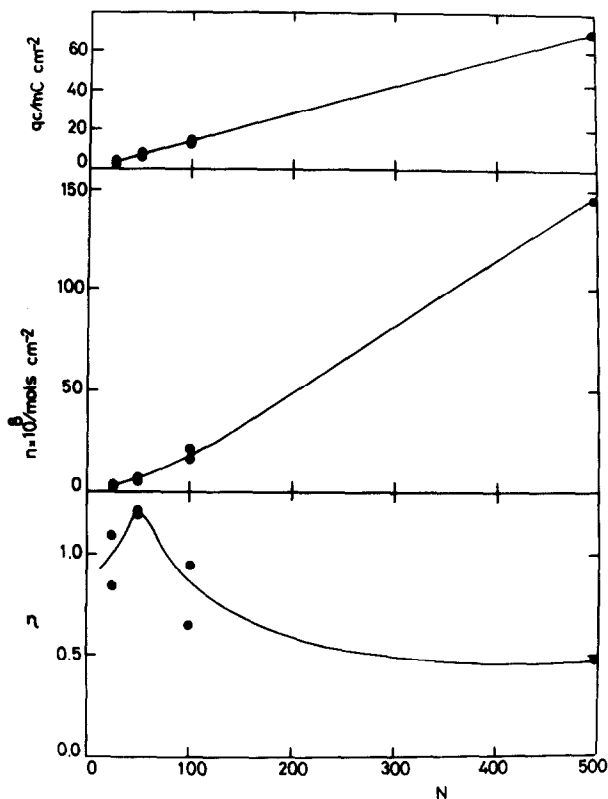


Fig. 2. Dependence of q_c , n and η on N . Electrolyte: 0.1 M NaOH + 0.30 M Na₂SO₄. Precipitating solutions: pNi 3, pH 11.

more than a limiting value which for pNi 1 is of the order of 0.35. However, for dilute precipitating solutions (pNi 3, pH 11) a limiting value of *ca.* 1.3 is reached as N decreases, being more than the theoretical 100% efficiency for a one electron transfer per nickel ion in reaction (2). At high N values η decreases, and simultaneously it is observed that after the first oxidation cycle the film remains black (not fully reduced) even under high cathodic polarization, providing a clear indication that for these conditions the relatively low values of η are due to high γ values in reaction (2).

In addition to the wide differences in the η values between electrodes prepared with pNi 1 and pNi 3 (*i.e.*, for pNi 1, $\eta < 0.35$ while for pNi 3 $\eta > 0.5$ for the N values used in the present work), the dependence of η on N is larger when the precipitating solutions are more dilute. This dependence could be associated with changes in the film conductivity as its thickness changes. Thus, the conductivity of the film would be influenced by the concentrations of the precipitating solutions, probably due to changes in the morphology of the precipitated hydroxide. However, no simple, direct correlation was found between η and the film thickness because the plot of η versus n (not shown) yielded a scattering of points.

Under the conditions used in the present work, films with average thicknesses up to 10^4 \AA (estimated using the n values and assuming $\delta = 2.5 \text{ g cm}^{-3}$ and $\text{MW} = 104.7 \text{ g mol}^{-1}$) can be obtained. These thicknesses are of the same order of magnitude as those of practical nickel electrodes [17].

(ii) *Effect of the concentration of the precipitating solutions*

The effects of pNi and pH of the precipitating solutions on q_c , n and η are shown in Fig. 3 for $N = 10$ and 25 at constant electrolyte concentration. This Figure reveals some interesting points. It should be noted that for q_c a maximum is observed when $[\text{Ni}^{2+}] = [\text{OH}^-]$ (pNi = pOH), and on the other hand, q_c seems to be dependent on both, pNi and pH. A similar behaviour is observed in general for n , showing practically the same tendency in the 0 - 2 pNi range. Nevertheless, the situation is different for the η versus pH plots at different pNi values. For each pNi, the maximum values in η are obtained when $[\text{Ni}^{2+}] > [\text{OH}^-]$ (pNi < pOH). The η values obtained when the lowest pNi is used represent a particular case for $\text{Ni}(\text{OH})_2$ colloidal electrodes since the values are very low whatever the OH^- concentration of the alkaline precipitating solution.

It is useful at this point to consider the important role played by the stoichiometry of the $\text{Ni}(\text{OH})_2$ film [18]. In fact, under the conditions used here, the maximum amount of material is obtained when the concentrations of both precipitating solutions are the same. This seems reasonable since, for this particular case, it is supposed that in each immersion all the precipitating

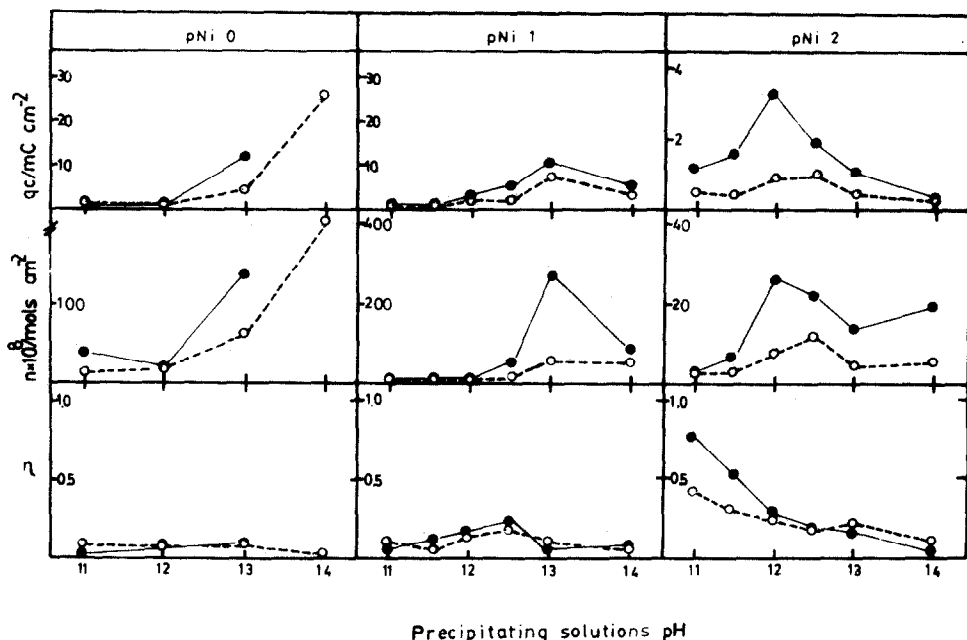


Fig. 3. Dependence of q_c , n and η on the concentration of the precipitating solutions. Electrolyte: 0.1 M NaOH + 0.30 M Na_2SO_4 . \circ , $N = 10$; \bullet , $N = 25$.

solution carried by the electrode on its surface is neutralized by the other one and so on. On the other hand, when one of the precipitating solutions is much more concentrated, a large amount of precipitated nickel hydroxide is formed in the less concentrated solution which falls to the bottom of the container and consequently is not deposited on the substrate. For pNi 0 and pH 14 the obtained film constitutes a particular case, by comparison with the one obtained with other concentrations, since it presents a thickness sufficiently large (even for $N = 1$) for a simple ocular inspection to differentiate between the structural changes occurring when the electrode is subjected to charge/discharge cycles. This has been reported previously by Fleischmann *et al.* [17]. When during the potential sweep an E_{sa} prior to O_2 evolution is reached, the electrode remains green, a clear indication that the outer portion has not been oxidized despite the fact that the potential is sufficiently positive for nickel oxyhydroxide (formally $NiOOH$) to be obtained. This is in accordance with the "two-phases" mechanism proposed by Tye *et al.* for the oxidation process [19]. If the potential is further increased to reach the oxygen evolution region, it is possible to note after several seconds that the green precipitate begins to fall due to the mechanical effects produced by the O_2 bubbles. Furthermore, it can be clearly seen that the O_2 evolution occurs on the inner, black portion of the film, this observation being in good agreement with Tseung *et al.* [20] in the sense that the oxygen evolution always occurs on the higher oxide. The presence of a relatively large amount of unoxidized material (green material) under these precipitating conditions is in agreement with the very low η values observed (Fig. 3), a clear indication that this is due to incomplete oxidation of the $Ni(OH)_2$ film.

The j/E potentiodynamic responses of two typical electrodes with different q_c , n and η are shown in Fig. 4. The electrode with the higher η (pH 11, pNi 2) presents a well-shaped and very sharp anodic current peak, whereas the electrode with lower η (pH 12.5, pNi 2) shows a rather different shape in both the anodic and the cathodic current peaks. The differences are mainly observed in the 0.6 - 0.7 potential range since a larger contribution to the charge in this region is observed for the higher pH (lower η). A similar behaviour is observed when the cationic precipitating solution has pNi 1. Hence, it seems that there could be some relation between η and the j/E potentiodynamic response. For a tentative explanation one could assign the effect of the different charge contributions to the relative amounts of α - and β - $Ni(OH)_2$ structures [21 - 24] which would be oxidized at different potentials and possibly have different η values. This is discussed later.

(iii) Effect of the electrolyte concentration

To investigate the influence of the electrolyte concentration on η , two electrodes with different η values were systematically analyzed (Fig. 5). It can be seen that η has a maximum at $[OH^-]_{elec.}$ 0.1 M (pH 13) for both sets of precipitating conditions and that for all the electrolyte concentrations, the electrode prepared with pH 11.5 and pNi 2 yields an η higher than that

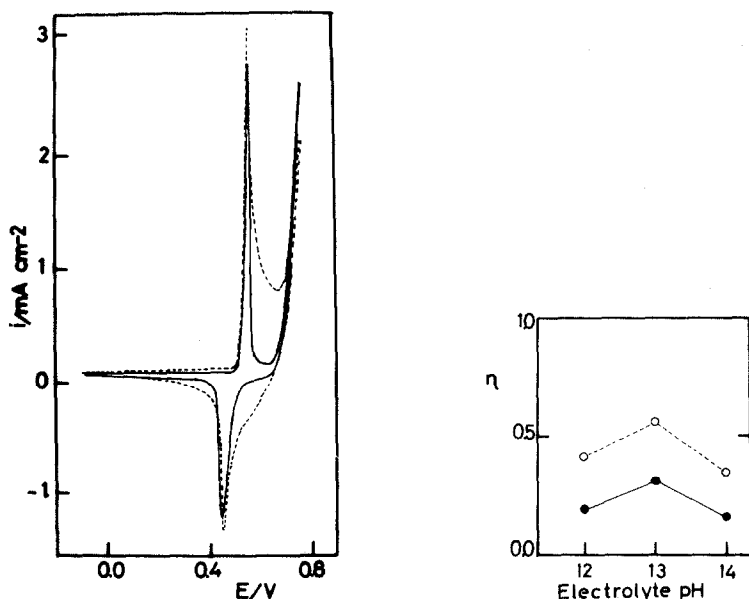


Fig. 4. Potentiodynamic response of the Pt/Ni(OH)₂ electrode for two sets of precipitating conditions. Electrolyte: 0.1 M NaOH + 0.30 M Na₂SO₄. $v = 5 \text{ mV s}^{-1}$; $E_{sc} = -0.10 \text{ V}$; $E_{sa} = 0.75 \text{ V}$; $N = 25$. —, pH 11; pNi 2; - - -, pH 12.5; pNi 2.

Fig. 5. Dependence of η on the electrolyte pH. $N = 25$. Precipitating solutions: pNi 2; ○, pH 11.5; ●, pH 13.

prepared with pH 13 and pNi 2 as was stated above (Fig. 3). It is evident that the relation between η and the OH⁻ concentration of the electrolyte is not simple since, for $[\text{OH}^-]_{\text{elec}} > 10^{-1} \text{ M}$, for example, η probably decreases in consequence of another effect which at this electrolyte concentration becomes predominant. This effect might then be attributed to a competitive effect as a result of the oxygen evolution reaction catalyzed by NiOOH [9, 11, 20]. Thus, if at higher pH, nickel oxyhydroxide becomes more catalytic for O₂ evolution, only part of the anodic charge will be used in the evolution of O₂ instead of oxidizing Ni(OH)₂, resulting in a lower value for η .

From the results of this section, it is possible to assert that η not only depends on the structure of the colloidal Ni(OH)₂ film, but also on parameters which would act indirectly on it by changing the catalytic activity of the nickel hydroxide towards the O₂ evolution reaction, which is a competitive reaction during the charging of the electrode.

(iv) Effect of the temperature of the precipitating solutions

Taking into account recent reports [24, 25] dealing with the relative stability of the α -Ni(OH)₂ and β -Ni(OH)₂ structures, and considering that the intertransformations of these structures are largely influenced by temperature changes, some experiments were undertaken by varying the temperature of the precipitating solutions.

Once the $\text{Ni}(\text{OH})_2$ was chemically precipitated on the Pt substrate at a given temperature, the electrode was immersed in the electrochemical cell at 20 °C and the voltammetric experiments were carried out as described above.

The results obtained for two electrodes (pNi 2 and pH 11.5 and 13) as a function of the temperature of the precipitating solutions are shown in Fig. 6. It is clearly seen that as the temperature increases, both q_c and n also increase. Nevertheless, η remains practically constant. The effect of the temperature on q_c and n is more pronounced for pH 13 than for pH 11.5. There is an exponential type relationship of q_c and n versus T for pH 13 and a linear one for pH 11.5. However, for both electrodes η remains constant as T changes. This is extremely important from a practical point of view since the increase in temperature is a way of increasing the amount of deposited material without decreasing η , unlike the case when N is increased.

The characteristics of the j/E potentiodynamic response also depend on the temperature at which the chemical precipitation is performed (Fig. 7). These results would indicate that at 20 °C and pH 11.5 only α - $\text{Ni}(\text{OH})_2$ is obtained, whereas at higher T (>70 °C) an important contribution of the β form is observed [24]. With cycling, a continuous transformation of β into the α form seems to occur, so that after 15 min cycling the difference between the different temperatures is less pronounced, an effect that is observed for both pH values. However, even if the temperature of the precipitating solution modifies the j/E profile and the values of q_c and n , it has no influence on η (Fig. 6). These effects could probably be explained as follows. As the temperatures of the precipitating solutions increase, the amount of β - $\text{Ni}(\text{OH})_2$ precipitated on the Pt substrate also increases, but both α and β forms give practically the same η values. The temperature could modify, in great extent, the interlayer water content of the nickel hydroxide structure but not its quality towards the electrochemical reactivity, according to our results.

Even if the phases involved in nickel hydroxide electrodes are difficult to correlate conclusively to α and β forms, the present results seem to indicate that the actual nature of the $\text{Ni}(\text{OH})_2$ obtained by chemical precipitation and, in consequence, its electrochemical response, are markedly dependent on the temperature of the precipitating solutions, revealing at least two main contributions, already described as stable (s) and unstable (u) species [8, 25, 26].

Experiments performed with electrodes that, after precipitation at 20 °C, were immersed for 30 min in 7 M NaOH solution at 70 °C revealed interesting aspects. This pretreatment significantly changes the j/E profile (not shown) by comparison with the profile associated with a similar electrode without pretreatment. The main changes involve an increase in the anodic charge and a shift of the principal current peak towards more positive potentials, as reported previously [10, 26]. In addition, η diminishes considerably. This is not surprising since, as shown previously [26], the immersion of the electrode in concentrated alkaline solution greatly decreases the

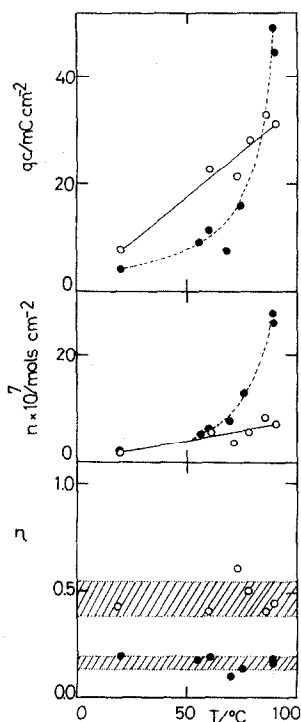


Fig. 6. Dependence of q_c , n and η on the temperature of the precipitating solutions. Electrolyte: 0.01 M NaOH + 0.33 M Na₂SO₄. $N = 25$. Precipitating solutions: pNi 2; ○, pH 11.5; ●, pH 13. The dashed areas in the η vs. T plots correspond to the standard deviations of the experimental points.

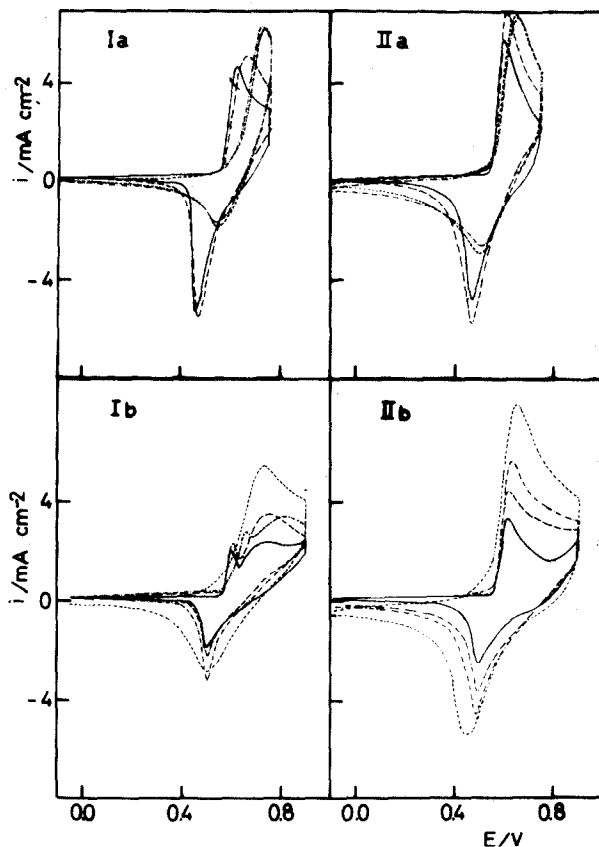


Fig. 7. Influence of the temperature of the precipitating solutions on the potentiodynamic response of the Pt/Ni(OH)₂ electrode. Electrolyte: 0.01 M NaOH + 0.33 M Na₂SO₄. $N = 25$. $v = 0.1$ V s⁻¹; $E_{sc} = -0.1$ V; $E_{sa} = 0.75$ V. I, First cycle; II, after 15 min cycling. (a) Precipitating solutions: pNi 2; pH 11.5. —, 20 °C; ---, 60 °C; -·-, 86 °C; ·····, 90 °C. (b) Precipitating solutions: pNi 2; pH 13. —, 20 °C; ---, 56 °C; -·-, 76 °C; ·····, 90 °C.

overpotential for the oxygen evolution reaction, and this would yield a lower value for η as stated above.

Conclusions

From the results obtained it may be concluded that the changes in the voltammetric discharge efficiency (measured through η) of nickel hydroxide electrodes chemically precipitated on platinum substrates are not related to

the presence of different amounts of α or β structures but to "physical" changes introduced by changes in the preparation conditions. These physical changes should affect the texture and contact area between the film and the substrate (current collector) as well as the water content. The low η values could be due to either incomplete oxidation of the $\text{Ni}(\text{OH})_2$ film (low or negative x values in reaction (2)) since, for example, for pH 14 and pNi 0 (when the lowest η is obtained), the film remains green (unoxidized) even under high anodic polarization, or to incomplete reduction of the NiOOH (high y values in reaction (2)) since, for example, for pNi 3 and pH 11, with $N = 500$, the film remains black (not fully reduced) even under high cathodic polarization. A limiting value for η of ~ 1.30 is reached at very low precipitating solution concentrations. The main effect on η is obtained by varying the precipitating solution concentrations. The temperature, despite its noticeable influence on the deposition efficiency, has apparently no effect on η ; however, an increase in temperature allows an increase in the amount of electrode material without decreasing the η values. Maximum deposition efficiency is obtained when $\text{pNi} = \text{pOH}$ for the precipitating solutions and high η values are obtained when the concentrations of both Ni^{2+} and OH^- in the precipitating solutions are low. The film conductivity could have an influence on η since this depends, under certain preparation conditions, on the number of immersions (thickness of the film).

Preparation conditions could be very important since they can improve the electrode manufacture and performance by increasing the deposition efficiency (η) and power density, as well as decreasing the self discharge [1 - 3]. Experiments are in progress, using different techniques, to investigate the physical changes introduced into the nickel hydroxide films by different preparation conditions.

Acknowledgments

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