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Nickel hydroxide film electroformation in alkaline chloride solutions

M. R. GENNERO DE CHIALVO, A. C. CHIALVO

Programa de Electroquímica Aplicada e Ingeniería Electroquímica (PRELINE), Facultad de Ingeniería Química (UNL), Santiago del Estero 2829, (3000) Santa Fe, Argentina

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The electroformation of thick hydrous nickel hydroxide films on polycrystalline nickel electrodes in alkaline chloride solutions has been investigated. The films were obtained through the application of repetitive square-wave potential signals (RSWPS). A significant increase in the charge storage capacity of this kind of electrode with respect to those obtained by the same method in chloride-free solutions was found. It has been concluded that the halide ions do not participate directly in the metallic dissolution process which takes place at the metal–hydroxide interface, but they affect some superficial phenomena at the hydroxide–solution interface during the RSWPS treatment.

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1. Introduction

Nickel and its oxides are used extensively as anode materials in alkaline water electrolysis [1–3]. The results obtained by the application of a repetitive square-wave potential signal (RSWPS) to a nickel electrode in alkaline media have been reported recently [4]. Through this method, a thick hydrous nickel hydroxide film was produced with a relatively large charge storage capacity. The electrocatalytic characteristics of this kind of electrode for the oxygen evolution reaction in alkaline solutions were also studied [5]. It was demonstrated that there is a linear dependence of the apparent electrocatalytic activity upon the amount of nickel hydroxide present in the film. Therefore, the present paper is a report of further work in this area dealing with the improvement of the method mentioned above in order to obtain larger amounts of active material.

Dyer has reported a procedure to yield a nickel hydroxide layer within a porous nickel structure using alternating current and dilute aqueous solutions of KCl and KBr [6]. It would be of interest to examine the effect of adding a halide anion to the alkaline solution in which the nickel hydroxide film is formed. Consequently, the RSWPS technique was applied to nickel electrodes in alkaline solutions containing different concentrations of sodium chloride at constant ionic strength.

2. Experimental details

Runs were carried out in a three-electrode, two-compartment Pyrex glass cell. Nickel electrodes were obtained by electrodeposition on stainless steel wires (0.4–0.7 cm^2 geometric area). A Watts-type nickel plating bath was used, working at a constant current of $5\,mA\,cm^{-2}$, at room temperature. Before each run, these electrodes were dipped in 1 : 1 H_2SO_4 solution for about 3 min and rinsed in triply distilled water. A helical-shaped nickel counterelectrode (10 cm^2 geometric area) concentric to the working electrode was used. A Hg/HgO/0.5 M NaOH reference electrode was employed. Special attention was paid to the construction and location of the Luggin–Haber tip, which consisted of a capillary tube (0.2 mm external diameter) placed at ca. 0.1 mm from the electrode surface, so as to ensure negligible ohmic drop in the solution.

The following electrolyte solutions were used: 0.5 M NaOH (solution A), 0.49 M NaOH + 0.01 M NaCl (solution B), 0.45 M NaOH + 0.05 M NaCl (solution C), 0.4 M NaOH + 0.1 M NaCl (solution D) and 0.3 M NaOH + 0.2 M NaCl (solution E). All were prepared from triply distilled water and analytical grade reagents. Experiments were performed under nitrogen gas saturation at 30 ± 0.1° C.

The anodization procedure consisted of applying a repetitive square-wave potential signal (RSWPS) to the working electrode between lower ($-2.6\,V \leqslant E_l \leqslant -1.4\,V$) and upper ($-0.5\,V \leqslant E_u \leqslant 1.2\,V$) potential values at a certain frequency ($1.0\,kHz \leqslant f \leqslant 5.0\,kHz$) for a certain time ($1\,s \leqslant t \leqslant 90\,s$). The duration of each potential step τ_u and τ_l, respectively, was adjusted at convenience. Most of the results reported in this paper correspond to the application of a symmetric wave ($\tau_l = \tau_u$), except where otherwise stated. Before and after the RSWPS treatment, the electrode was subjected to a repetitive triangular potential sweep (RTPS) at $0.1\,V\,s^{-1}$ between -0.5 and 0.65 V for 5 min and then the corresponding voltammograms were recorded. The amount of nickel hydroxide present in the film was determined through the difference between the voltammetric electroreduction charge for the Ni(III) species obtained after the application of the RSWPS and the charge obtained before it, both referred to the geometric electrode area. Other details of the experimental set-up are as previously described [4].

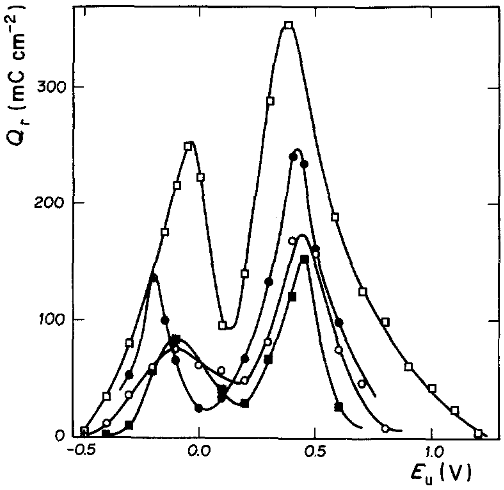

Fig. 1. Dependence of Q_r on E_u at different electrolyte concentrations: (○) solution A, (●) solution B, (□) solution D and (■) solution E. RSWPS characteristics: $E_l = -1.74$ V, $f = 2.5$ kHz, $t = 1$ min, 30° C.

SEM micrographs of nickel hydroxide films resulting from different treatments were obtained. An EDAX analysis technique was applied in order to determine the presence of chlorine in the film.

3. Results

3.1. *Voltammetric characteristics of nickel hydroxide films*

The voltammetric response of polycrystalline nickel electrodes in alkaline solutions before and after the application of the RSWPS treatment was described in a previous publication [4]. Potential cycling between -0.5 and 0.65 V yielded current peaks related to the Ni(II)/Ni(III) reversible couple in the nickel hydroxide film. After the application of the RSWPS, a significant increase in the voltammetric charge was observed. Differences in the shape of the voltammograms and in the potentials of both the oxidation and reduction peaks of the nickel hydroxide redox couple when different concentrations of sodium chloride were added to the electrolyte solution were not found.

3.2. *Dependence of the electroreduction charge of the nickel hydroxide on the characteristics of the RSWPS*

For constant E_l, f and t the electroreduction charge (Q_r) of the nickel hydroxide depends on E_u (Fig. 1). The Q_r vs E_u plots show that Q_r attains two maximum values for all the solutions investigated. One of them is in the potential range $-0.05\,\text{V} \leqslant E_{u1} \leqslant -0.20\,\text{V}$ (Q_{r1}) and the other in the potential range $0.35\,\text{V} \leqslant E_{u2} \leqslant 0.40\,\text{V}$ (Q_{r2}), when $E_l = -1.74$ V, $f = 2.5$ kHz and $t = 1$ min. The largest charge value corresponds to the solution D. On the other hand, the solution most concentrated in chloride anions (solution E) presents a charge lower than that of the blank. However, in this case a greater mechanical detachment of the film layer was observed. It may be considered that, within the experimental error, the potentials of the maximum Q_r values are the same for all the sodium chloride concentrations. Nevertheless, it must be noted that, in the case of the first maximum, there is a greater dispersion of these values. In the present case, for all the solutions studied, the maximum Q_r value corresponding to E_{u2} is larger than that of E_{u1}. When the solution is more concentrated in NaOH this behaviour is reversed [4].

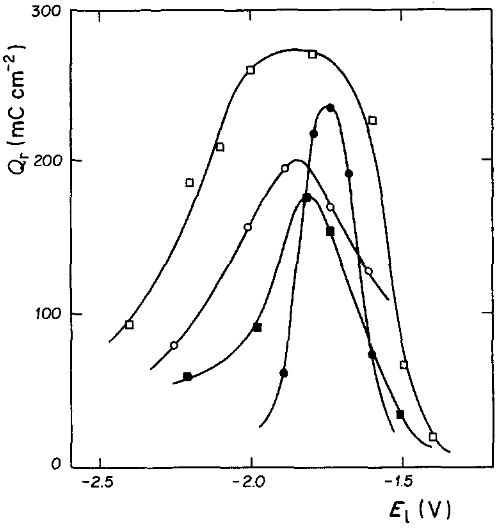

Fig. 2. Dependence of Q_r on E_l at different electrolyte concentrations: (○) solution A, (●) solution B, (□) solution D and (■) solution E. RSWPS characteristics: $E_u = 0.45$ V for solutions A, B and E and $E_u = 0.5$ V for solution D, $f = 2.5$ kHz, $t = 1$ min, 30° C.

With constant E_u, f and t ($E_u = 0.45$ V for the solution A, B and E and $E_u = 0.5$ V for the solution D; $f = 2.5$ kHz and $t = 1$ min), Q_r depend on E_l (Fig 2). There is a maximum value of E_l which lies between -1.90 and -1.75 V. The largest charge value corresponds again to solution D and the smallest to solution E.

For preset E_l, E_u and t ($E_l = -1.74$ V, $E_u = 0.32$ V, $t = 1$ min) and solution D, the Q_r vs f plot exhibits a maximum Q_r value at 1.8 kHz (Fig. 3). Approximately the same results were obtained for other solutions investigated, including the blank. When these experiments were performed at an E_u value in the potential range of Q_{r1}, the same maximum value for the frequency was found.

For $E_l = -1.74$ V, $E_u = 0.4$ V, $f = 2.5$ kHz the charge Q_r increases according to the duration of the RSWPS (Fig. 4), approaching a limiting value after approximately 20 s for all the solutions studied. It should be noted that the initial oxide growth rate is nearly the same for the different solutions, but the limiting charge value is greatly influenced by the sodium chloride concentration. Similar results were obtained when the experiments were carried out at E_{u1} rather than E_{u2}.

At constant E_l, E_u, f and t, the increase of Q_r depends on the symmetry of the RSWPS, i.e. on both τ_l and τ_u. Thus, for $E_l = -1.74$ V, $E_u = 0.32$ V,

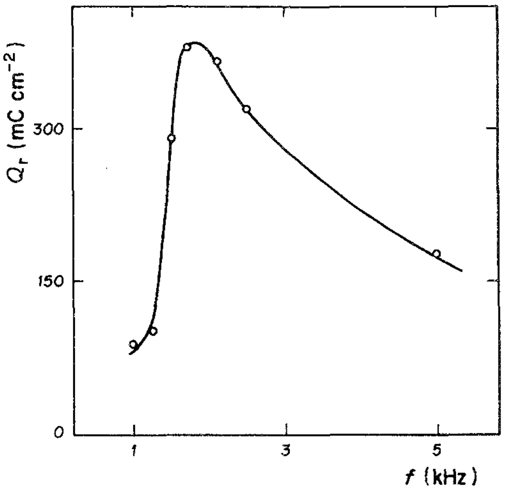

Fig. 3. Dependence of Q_r on f. RSWPS characteristics: E_u = 0.32 V, E_l = −1.74 V, t = 1 min, solution D, 30° C.

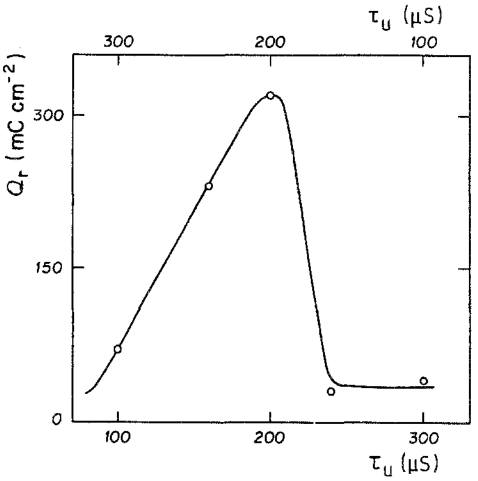

Fig. 5. Dependence of Q_r on τ. RSWPS characteristics: E_u = 0.32 V, E_l = −1.74 V, f = 2.5 kHz, t = 1 min, solution D, 30° C.

f = 2.5 kHz and t = 1 min, Q_r reaches a maximum at $\tau_l = \tau_u = 200\,\mu s$ (Fig. 5).

3.3. *Influence of the sodium chloride concentration on the nickel hydroxide film formation*

From Figs 1 and 2, the amount of hydrated nickel hydroxide produced by the RSWPS treatment, as measured through the Q_r values, depends on the sodium chloride concentration. Figure 6 shows the variation of the maximum Q_r values for both E_{u1} and E_{u2} as a function of the halide concentration, at constant ionic strength. There is an optimum concentration ranging between 0.05 and 0.1 M and for higher concentrations the effect is reversed.

3.4. *SEM patterns and EDAX analysis of the film*

Figure 7 shows a scanning electron micrograph of a thick nickel hydroxide film obtained by applying the RSWPS treatment under the following conditions, E_l = −1.74 V, E_u = 0.45 V, t = 1 min, f = 2.5 kHz, in solution E (NaOH 0.3 M + NaCl 0.2 M). Immediately after its preparation, the electrode, which had a light-green colour, was rinsed in triply distilled water, dried under nitrogen atmosphere and then subjected to the SEM observation and the EDAX analysis. The latter detected only the presence of elemental nickel. Therefore, it can be inferred that chlorine and sodium were absent from the nickel hydroxide film, at least within the detection limits of this technique, which is approximately 1%.

4. Discussion

The polarization of a nickel electrode in alkaline solutions by the application of a repetitive square-wave potential signal produces transformation of the superficial layers of the base metal in a nickel hydroxide film, which is highly hydrated and has an amorphous structure. On the other hand, it has been found that the amount of charge accumulated on the film is markedly increased by the presence of chloride ions in the electrolyte solution. This result suggests an analogy with passivity breakdown and the increase in metal

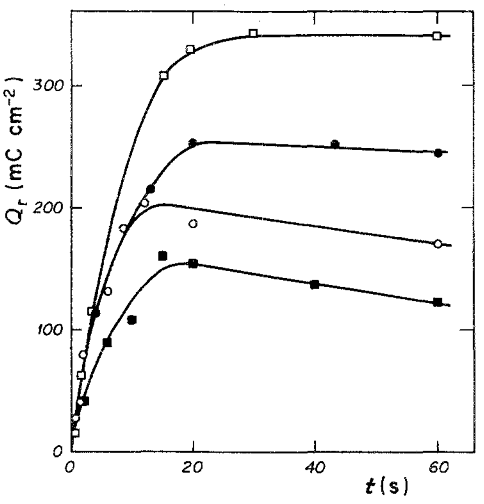

Fig. 4. Dependence of Q_r on t at different electrolyte concentrations: (○) solution A, (●) solution B, (□) solution C and (■) solution E. RSWPS characteristics: E_u = 0.4 V, E_l = −1.74 V, f = 2.5 kHz, 30° C.

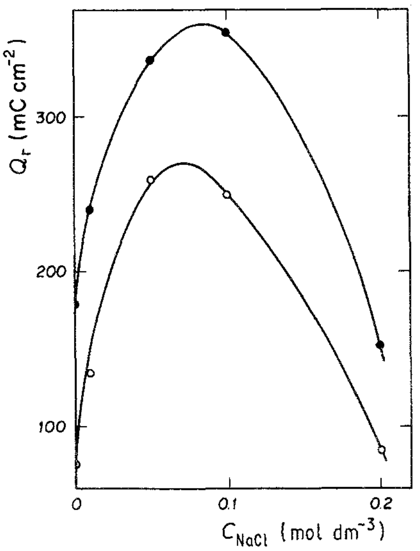

Fig. 6. Dependence of Q_r on the sodium chloride concentration at different E_u values. (○) E_{u1}, (●) E_{u2}.

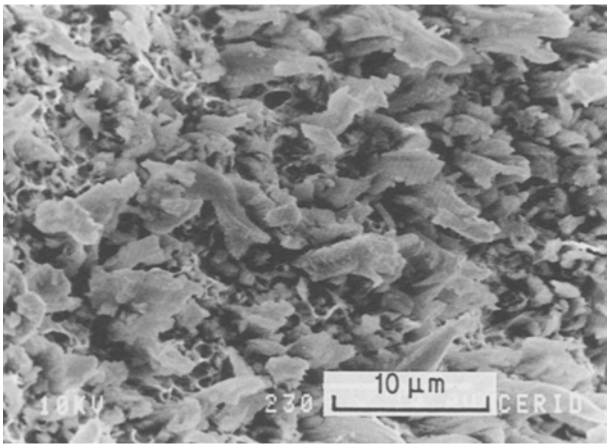

Fig. 7. SEM micrograph of a nickel hydroxide film. RSWPS characteristics: $E_u = 0.45$ V, $E_l = -1.74$ V, $f = 2.5$ kHz, $t = 1$ min, solution E, 30°C. Scale: 10 μm.

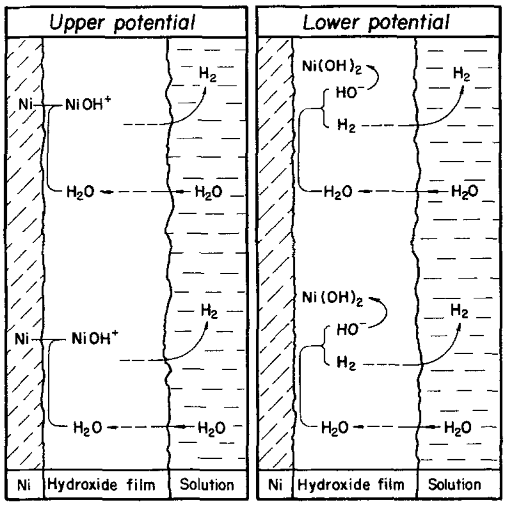

Fig. 8. Reaction schemes showing the flow of the main reactant and product species through the film during the RSWPS treatment.

dissolution produced by aggressive anions, such as halides [7]. This fact has been already reported by Dyer, who developed a method to obtain anode materials using low frequency square-wave current in dilute solutions of potassium chloride [6]. Nevertheless, a better understanding of the role played by the chloride anions in film formation may be inferred from the analysis of the anodizing process.

During the application of the RSWPS treatment, it was observed that part of the nickel hydroxide obtained was detached and dispersed in the bulk solution due to the hydrogen evolution reaction, which occurs simultaneously with the film growth. In spite of this, an appreciable amount of material remained attached to the electrode. This is the part which is electrochemically detected by potentiodynamic sweeps. The charge obtained in this way depends on the parameters of the fast periodic potential signal, such as potential limits, frequency, etc. (Figs 1–5). In order to evaluate the participation of the chloride anions in the dissolution process, it is important to consider the dependence of the initial rate of film growth on the halide concentration. Figure 4 shows that the initial slopes of the curves Q_r vs t are independent of the chloride concentration. Besides, it must be taken into account that in the curves corresponding to the solutions A–C of this figure, the hydroxyl anion concentration can be considered to be approximately constant.

On the basis of the consideration above, it may be concluded that, in the concentration range analysed, the chloride ions do not participate in the reaction in a direct way. Besides, the analysis of the film by the EDAX technique showed the absence of chlorine as well as sodium. Similar results have been obtained by Dyer through the application of the AES technique [6]. On the other hand, the dependence of the detected nickel hydroxide charge upon the different parameters (E_l, E_u, f, t, etc.) of the potential perturbation does not show significant differences in their overall behaviour with respect to the blank solution.

Consequently, as the chloride ions do not take part directly in the dissolution process, it is possible to extend the dissolution–precipitation scheme that has been proposed for pure alkaline solutions and which explains the relationships between the accumulated oxide amounts and the studied parameters [4], to the present case. Thus, dissolution of the superficial atoms of nickel occurs during the anodic half-cycle giving the soluble species $NiOH^+$ [4, 8, 9], which remains surrounding the metal–hydroxide interface (Fig. 8). In the cathodic half-cycle water discharge mainly occurs, causing localized alkalization of the interface. The resulting excess of hydroxyl ions, which are mixed with the $NiOH^+$ species, causes the solubility product of $Ni(OH)_2$ to be reached ($K = C_{NiOH^+} \times C_{OH^-} \cong 10^{13}$) and favours its chemical precipitation. This dissolution–precipitation model is graphically shown in Fig. 8. On this simplified scheme, the main reactions that explain the film formation are shown. Secondary reactions such as hydrogen oxidation are neglected. It must be noticed that the anionic species present in the electrolyte solution do not participate directly as reactants, because the latter are generated *in situ* through the solvent discharge. The diffusional flow of the nonionic species (the inlet of solvent, the outlet of hydrogen) through the film is favoured by the oscillating process due to a decrease on the thickness of the diffusional layer [10]. On the other hand, the migrational flow through the film takes place by a protonic mechanism similar to that described in the Grottus model [11, 12]. Besides, the relation between the nickel hydroxide mass before and after its dehydration at 160°C was about 10. This result shows that the film has a high content of occluded water, apart from that which is bound to the hydroxide [13, 14]. In these conditions, it can be considered that the film is kept in a liquid-like state by the RSWPS treatment.

As was stated above, the chloride ions do not take part directly in the dissolution process, although their presence in the solution allows nickel hydroxide films of greater thickness to be obtained. The steady state attained after about 20 s of application of the RSWPS treatment defines the maximum thickness of the nickel hydroxide film, which is mechanically stable in the presence of the gas flow emerging from the film. These mechanical phenomena are determined principally by the diffusional flows that exist in the film produced by concentration gradients and the interfacial tensions which depend greatly on the potential variations. In this complex system, the chloride ion should principally affect the hydroxide–solution interface due to variations in the relationship between the adsorption and the concentration in solution.

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