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TECHNICAL NOTE

The potentiodynamic behaviour of nickel in potassium hydroxide solutions

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1. Introduction

The potentiodynamic behaviour of Ni in alkaline solutions has been extensively studied by different authors with particular reference to nickel/alkaline galvanic cells [1, 2], although most of the experimental data imply the formation of a thick solid-phase of nickel-oxo- or nickel-hydroxo- compounds at the electrochemical interface. The mechanisms of the electrochemical processes, however, occurring within the potential range of water electrochemical stability are not yet well established particularly those related to the early stages of the film formation process. Concerning the latter this report shows that processes involved within that potential region, when the solid-phase formed at the metal surface is of the order of a few layers thickness, are more complex than had been thought previously.

2. Experimental

The working electrodes were made from Specpure Ni wire (Johnson Matthey), previously annealed during 16 h at 900° C in an argon atmosphere. The solutions were prepared from KOH analytical grade Merck Reagent and triply distilled water, and they were kept during the experiments under nitrogen gas saturation. The electrochemical cell and general technical procedures were the same as already described [3].

3. Results and discussion

When a polished polycrystalline nickel electrode is anodized in a 1·0 M KOH solution at 25° C, using repetitive triangular potential scans at 100 mV s^{-1} from $E_{\lambda,c} = -0{\cdot}96$ V (versus NHE) up to $E_{\lambda,a} = +0{\cdot}74$ V, the *E–I* plot (Fig. 1) is relatively complex. The initial anodic potential excursion exhibits at first a wide and net anodic current peak at $-0{\cdot}44$ V with a shoulder at the right-hand side followed by an appreciable anodic current over the $-0{\cdot}30$ to $+0{\cdot}40$ V potential range. Then a second net anodic current peak is observed at $+0{\cdot}64$ V which extends over the potential region preceding the evolution of O_2. The reverse scan leads to a net cathodic current peak in the $+0{\cdot}70$ to $+0{\cdot}45$ V potential range, a large cathodic current peak being recorded at $+0{\cdot}56$ V. The following anodic potential excursions exhibit only the second anodic current peak and the current increase due to anodic O_2 evolution but, although most of the cathodic contour reproduces the shape of the former excursion, there is however a net increase of the cathodic current in the 0·4–0·5 V range as the number of cycles increases. This cathodic current approaches a current plateau after about 50 cycles. Furthermore, the overall charge (corresponding to the whole potential excursion) increases with the number of cycles. These successive *E–I* recordings indicate a drastic change of the nature of the electrode surface during these partial excursions.

When the surface has been electroreduced at $E \leqslant -0{\cdot}96$ V for 15 min and the anodic potential excursion starts from $E_{\lambda,c} = -0{\cdot}96$ V, the electrode surface corresponds to a clean Ni surface either partially or completely saturated with H_2, depending on the amount of hydrogen dissolved in the bulk of the metal [4, 5]. However, during the repetitive potential excursion the electrode

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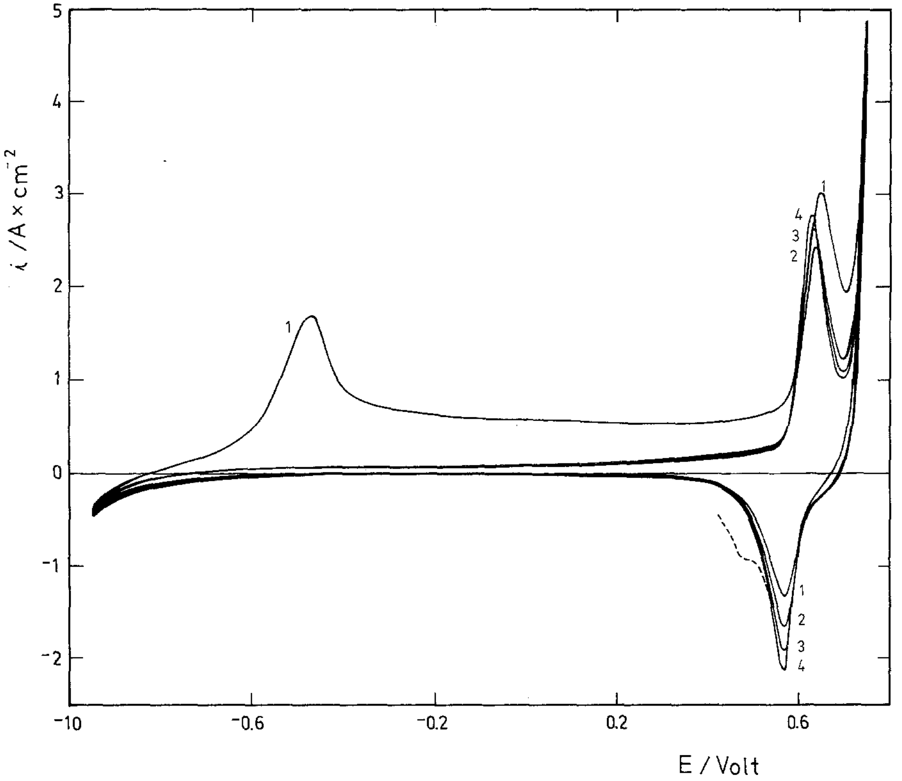

Fig. 1. E–I profiles run with repetitive triangular potential sweeps ($v_a = v_c = 0{\cdot}1\ V\,s^{-1}$). Ni (0·25 cm²) in 1 N KOH, 25° C. The successive cycles are numbered. The dashed line corresponds to the 50th cycle.

surface is more complex because, depending on the perturbation conditions, it is likely that in addition to the partial content of hydrogen, the metal becomes partially oxidized.

It is also clear that the products formed in the potential region of the first anodic peak correspond in part to the electro-oxidation of hydrogen and to the formation of a non-conducting layer of $Ni(OH)_2$, the latter participating in the following reactions occurring at more anodic potentials. However, there is no direct evidence either of $Ni(OH)_2$ electroformation or of hydrogen electro-oxidation during the successive potential cycling.

The reactions occurring at potentials in the range of both the second anodic current peak and the cathodic current peak are apparently complementary processes which have been represented by the overall reaction $Ni(OH)_2$ (hydrated) = $NiOOH + H^+ + e^-$. Independently of the number of cycles and at $0{\cdot}03\ V/s \leqslant v \leqslant 0{\cdot}30\ V/s$, the charges playing a part both in the anodic (after correction for the O_2 electroformation) and in the cathodic reactions are equal, although these depend on the potential perturbation conditions. The anodic charge, Q_a, decreases when v_a, the anodic potential sweep rate, increases and the anodic current peak height referred to unit anodic charge increases linearly with v_a.

The overall reactions are linked to Ni → Ni(II) → Ni(III) → Ni(IV) transformations of the surface species during the anodic potential scan, together with the contribution of a direct electro-oxidation of Ni to Ni(III), such as β-NiOOH as already discussed by various authors [6–9]. The cathodic electroreduction yields as a final product Ni(II)-oxygen surface species such as NiO or $Ni(OH)_2$ which can only be electroreduced at high cathodic potentials.

When the electrochemical interface after a certain number of triangular potential scans within $E_{\lambda,c} = 0{\cdot}29$ V and $E_{\lambda,a} = 0{\cdot}67$ V at $100\,mV\,s^{-1}$ is perturbed with a linear potential scan followed by a reverse cathodic excursion which includes the arrest of the potential sweep at a potential close to the $I = 0$ condition, for a certain time τ

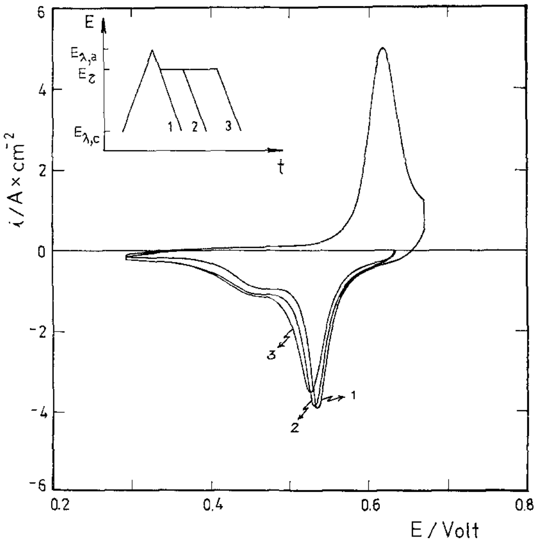

Fig. 2. E–I profiles run with single triangular potential sweeps including variable waiting time at E_τ, after previous cycling to obtain a stable E–I contour ($v_a = v_c$ = 0·1 V s^{-1}). Ni (0·25 cm^2) in 1 N KOH, 25° C. E_τ = 0·63 V; τ = 0(1); τ = 1 min (2) and τ = 5 min (3).

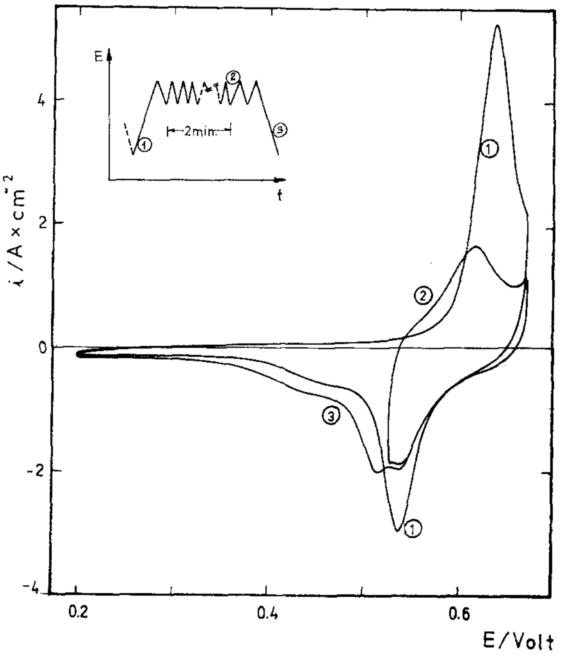

Fig. 3. Potentiodynamic E–I profiles run with an intermediate dynamic ageing at $v_a = v_c$ = 1 V s^{-1} during 2 min between 0·53 V and 0·67 V, as indicated in the figure. Ni (0·25 cm^2) in 1 N KOH, 25° C. (1) $v_a = v_c$ = 0·1 V s^{-1}; (2) E–I trace obtained at $v_a = v_c$ = 0·1 V s^{-1} immediately after the dynamic ageing; (3) E–I trace following (2) at v_c = 0·1 V s^{-1}.

(Fig. 2), the cathodic scan shows a net shift of the cathodic current peak potential towards more cathodic values. Otherwise, no appreciable change of the cathodic current plateau is observed but the current increases due to the baseline shift. This indicates that the electroformed surface species undergoes, either partially or totally, a transformation into another one which is relatively more stable than that initially formed. This chemical change resembles the ageing effect which has been described already for the electroformation of monolayer oxygen containing films on noble metals [10, 11].

A dynamic multiple potential perturbation splits the cathodic current peak into two peaks (Fig. 3). This is further evidence that the anodic process involves a parallel chemical reaction yielding a more stable film-forming species.

The occurrence of different Ni surface species with the same degree of oxidation in the 0·40 V to 0·65 V potential region is also demonstrated by running E–I triangular potential sweep voltamograms with changing $E_{\lambda,a}$. When $E_{\lambda,a}$ decreases to cover a charge just corresponding to a fraction of the maximum surface layer, the contribution of the cathodic current peak located at lower potentials becomes relatively more important. The same effect can be observed by changing the v_a/v_c ratio.

The amount of charge corresponding to the potential range of the cathodic current plateau is of the order of a monolayer of an oxygen-containing species. The location of the E–I profile as well as the charge involved is practically independent of $E_{\lambda,a}$ and of the other perturbation conditions. It is suggested that the cathodic process occurring there involves the electroreduction of the first oxygen-containing monolayer involving the strongest bond with the base oxidized nickel surface.

Therefore, the present results show that in the anodic sweep the E–I trace in the 0·3 V to 0·7 V potential range exhibits similar potentiodynamic profiles either starting with a clean or with an oxidized nickel surface. Both the electrochemical and the chemical processes occurring at the metal/solution interface involve at least three surface compounds having probably the same stoichiometry but different reactivities. The more reactive one may act as a reaction intermediate in the O_2- evolution reaction on the oxidized nickel surface. The structural identification of the surface compounds is difficult using very thin surface films. Nevertheless experiments in progress using different programmed perturbation techniques will probably add information about the kinetics and mechanism of the different processes involved.

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