

# Absorption of hydrogen in reduced nickel oxide

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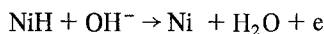
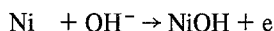
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By repeated oxidation and reduction of nickel in alkaline solution an oxide film is formed on nickel which cannot be reduced further. In this film hydrogen is absorbed during cathodic polarization. The absorbed hydrogen is manifest in the voltammogram as an anodic peak before the Ni(OH)<sub>2</sub> peak. This was proved by H-diffusion experiments through nickel foils. From experiments with Ni electrodes covered with  $\alpha$ - or  $\beta$ -Ni(OH)<sub>2</sub> films, it can be concluded that the reduced nickel oxide layer on nickel is most likely a  $\beta$ -Ni(OH)<sub>2</sub> layer.

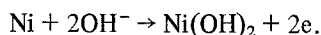
## 1. Introduction

With cyclic voltammetry the oxidation processes of nickel in alkaline solution can be studied. With increasing anodic potential the voltammogram shows first the Ni-Ni(OH)<sub>2</sub> peak at 0.27 V and at 1.4 V the Ni(II)/Ni(III) peak. During multiple scanning of the electrode a peak at about 0.1 V appears. The occurrence of this peak is not always recognized in the literature.

For the reactions that take place in the potential region 0-0.5 V, Weininger and Breiter [1] have suggested NiH oxidation and NiOH formation. For potentials  $-0.1 \text{ V} < E < +0.1 \text{ V}$  they give



this NiH being formed during cathodic polarization ( $E < -0.1 \text{ V}$ ); and for potentials  $E > +0.1 \text{ V}$



Their experimental data do not reveal this first peak. Others [2, 3] attribute the first peak (peak 1) to oxygen adsorption. Burgal'tseva [4, 5] argues that the maximum in the potential scan 0-0.5 V is solely due to oxidation of absorbed hydrogen. Franklin [6] observed four peaks in the voltammogram of a nickel electrode after cathodic polarization and attributes these peaks to respectively adsorbed H, absorbed H and NiOH, Ni(OH)<sub>2</sub> and NiOOH formation. The observed

peak potentials however do not agree with other nickel data [7].

Hydrogen can penetrate interstitially into the nickel crystals during cathodic polarization in 0.5 M H<sub>2</sub>SO<sub>4</sub> at a sufficiently high current density [8]. This can ultimately lead to nickel hydride formation. In acid electrolyte the formation of an  $\alpha$ - and a  $\beta$ -phase for H in Ni was observed; in alkaline solution only the  $\alpha$ -phase was obtained [9]. Also trapping of hydrogen in nickel can occur as was observed by Louthan *et al.* [10]. Hydrogen permeation experiments through nickel foils were carried out by Bockris *et al.* [11] using an electrochemical technique.

This study was carried out to get more insight into the first stages of the nickel oxidation process and the possible role of H-absorption by using cyclic voltammetry at nickel electrodes and at the bipolar nickel electrodes through which hydrogen was diffusing. The results were compared with the Ni(OH)<sub>2</sub> electrode prepared by deposition of Ni(OH)<sub>2</sub> on nickel.

## 2. Experimental

### 2.1. Electrochemical measurements

High purity (99.99%) nickel disc electrodes were embedded in a perspex holder (exposed area: 0.66 cm<sup>2</sup>). The Ni-electrode was placed in an electrochemical cell with two compartments. A Pt electrode was used as the counter electrode and a Pt-hydrogen electrode in the same electrolyte as

the reference electrode. The potential sweep experiments were carried out by means of a Wenking potentiostat (model 68 FR 0.5) with a voltage scan generator VSG 72 or with a Bruker polarograph E 350 and a PAR model 175 universal programmer. The electrolyte was a 0.1 M KOH solution for most experiments.

The hydrogen diffusion experiments were carried out with Ni-foils diameter 2 cm, 35  $\mu\text{m}$  thick, following the method development by Devanathan, Stachurski and Beck [12]. The electrochemical set-up is given in Fig. 1. The foil is clamped between two compartments A and B. Compartment A is filled with 0.5 M  $\text{H}_2\text{SO}_4$  and compartment B with 4 M KOH. During the experiments side A of the foil is cathodically polarized while to side B a constant potential or a potential sweep is applied, using a PAR model 175 universal programmer. All solutions were prepared from Analar grade chemicals and distilled  $\text{H}_2\text{O}$ .

## 2.2. Preparation of $\alpha$ - and $\beta$ -Ni(OH)<sub>2</sub> electrodes

$\alpha$ - and  $\beta$ -Ni(OH)<sub>2</sub> electrodes were prepared by cathodic deposition on a nickel disc electrode from 0.1 M  $\text{Ni}(\text{NO}_3)_2$  solution, following the method of Bode [13, 14]. The deposited Ni(OH)<sub>2</sub> was analyzed by X-ray and the lines were in agreement with the data of Bode [13, 14].

## 3. Results

### 3.1. Occurrence of Peak 1

A reproducible and characteristic voltammogram is obtained at a nickel disc electrode after polishing and repeated potential scanning from  $-800$  to  $+1200$  mV in 0.1 M KOH. Fig. 2 shows a characteristic diagram recorded with a sweep rate of  $2 \text{ mV s}^{-1}$  in the potential range 0–1200 mV. The peak at 80 mV (peak 1) is only observed if the electrode has been oxidized to 1200 mV and subsequently reduced. The peak at 260 mV (peak 2) is always observed in the anodic voltammogram after a cathodic pre-treatment. The ratio of the heights of peak 1 and peak 2 depends upon the sweep velocity: with increasing velocity peak 1 decreases and at  $50 \text{ mV s}^{-1}$  peak 1 is barely discernible (Fig. 3). The peak potential of peak 1 is 80 mV at  $2 \text{ mV s}^{-1}$  and 130 mV at  $10 \text{ mV s}^{-1}$ .

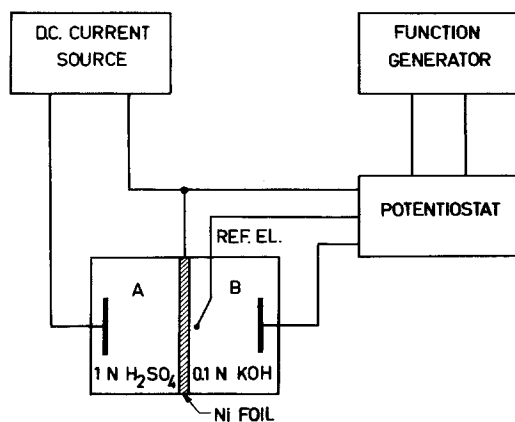


Fig. 1. Diagram of set-up for hydrogen diffusion experiments through Ni-foil.

Both peak 1 and 2 are also observed in  $\text{K}_2\text{CO}_3/\text{KOH}$  electrolytes of different pH. Peak 1 was not seen in electrolytes with  $\text{pH} < 9.7$ .

Cyclic voltammetry was also carried out at foil electrodes where one side of the foil was subjected to potential sweeps of  $-800$  to  $1200$  mV in 0.1 M KOH. As Fig. 4 shows, the voltammogram recorded for the 12th sweep differs somewhat from the disc electrode (Fig. 2): there is a reduction peak at 80 mV and peak 1 is now much larger than peak 2.

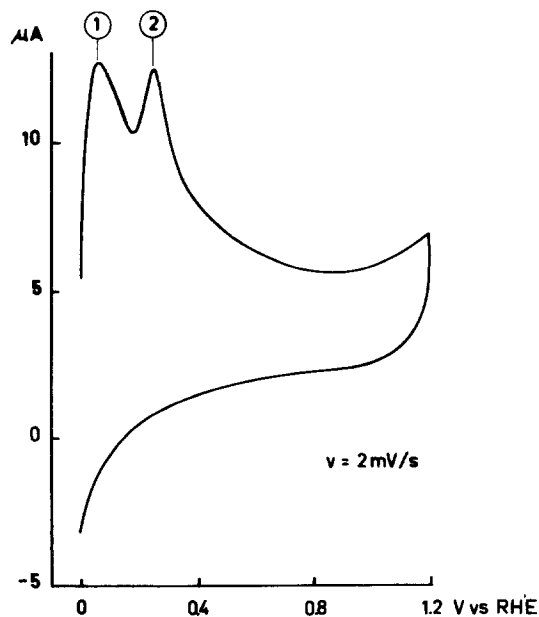


Fig. 2. Voltammogram of Ni in 0.1 M KOH, sweep rate  $v = 2 \text{ mV s}^{-1}$ , recorded after 11 potential sweeps from  $-0.8$  to  $+1.2$  V.

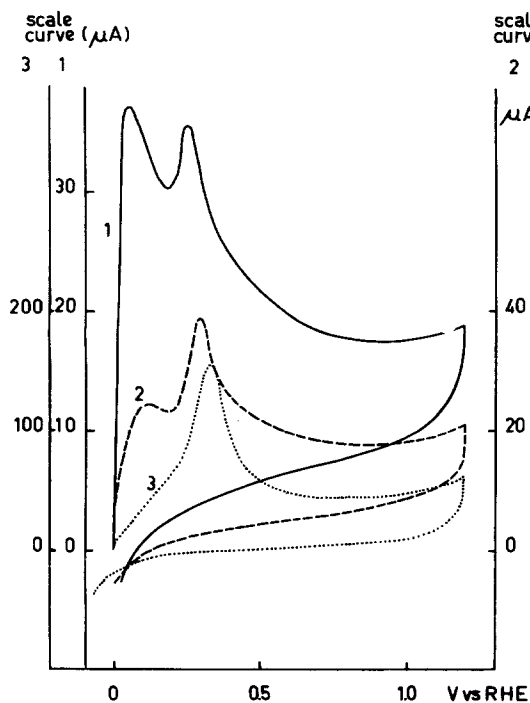


Fig. 3. Effect of sweep rate on voltammogram of Ni in 0.1 M KOH. Pre-treatment of Ni: potential sweeps between  $-0.8$  V and  $+1.2$  V. Curve 1, sweep rate  $v = 2$   $\text{mV s}^{-1}$ ; curve 2,  $v = 10$   $\text{mV s}^{-1}$ ; curve 3,  $v = 50$   $\text{mV s}^{-1}$ .

### 3.2. H-diffusion

For the detection of H diffusing through the foil at side B during cathodic polarization of side A, the potential at side B is held at a relatively high anodic value such that the concentration of H atoms on the surface is maintained essentially at zero. This potential was chosen at  $1.2$  V [15]. Compartment B is filled with  $4$  M NaOH and  $\text{H}_2$  is passed through; in this solution the nickel foil passivates as can be followed by the rise of the open circuit potential to about  $0.5$  V. Thereafter, the potentiostat is connected and the potential is slowly raised to  $1.2$  V. When a constant current had been reached, cell A was filled with  $0.5$  M  $\text{H}_2\text{SO}_4$  and side A of the foil was cathodically polarized. The diffusing H causes the current at side B to increase up to a constant value. Thereafter the potential at side B is swept from  $0$  to  $1.2$  V. This was carried out with H-generating currents at side A from  $2$  to  $200$  mA. A typical voltammogram is given in Fig. 5. If the cathodic current is switched off before applying the poten-

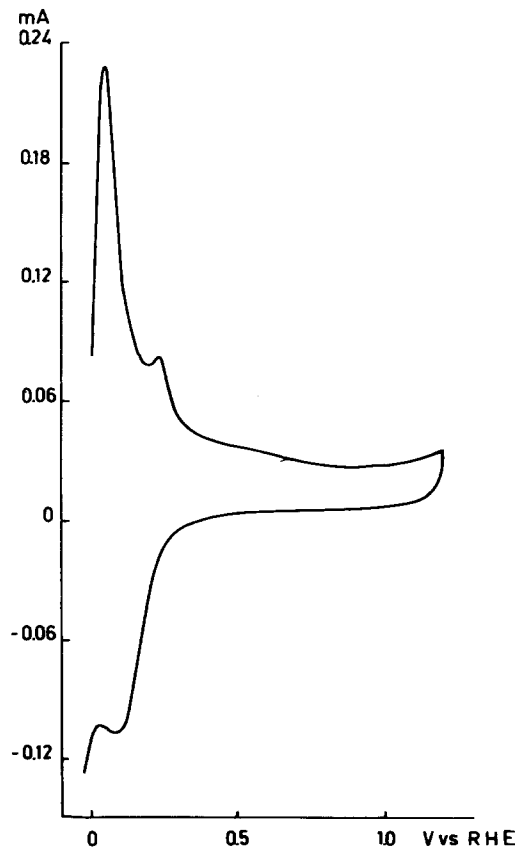


Fig. 4. Voltammogram of Ni-foil electrode in  $0.1$  M KOH, sweep rate  $2$   $\text{mV s}^{-1}$ , recorded after 11 potential sweeps from  $-0.8$  V to  $1.2$  V.

tial sweep, the voltammogram shows a rapidly decreasing anodic peak (Fig. 5, curve B) the height of it gradually decreases with longer waiting times. In a further experiment, side B was again set at a potential of  $1200$  mV ( $\text{N}_2$  atmosphere), while side A was cathodically polarized with  $i = 20$  mA. After reaching a steady state, side B was first subjected to cathodic polarization with a potential sweep from  $1200$  to  $-800$  mV, sweep rate  $10$   $\text{mV s}^{-1}$ , before the potential sweep of  $0$ – $1200$  mV was applied. The result is shown in Fig. 6, curve 1. In order to decrease the contribution from the H-diffusion from side A, the cathodic current at A was then switched off and again a potential sweep was recorded (curve 2 in Fig. 6). This results in two anodic peaks in the voltammogram.

Passivation of the nickel appears to be an essential condition for the H-absorption. This follows from experiments carried out at foils which were

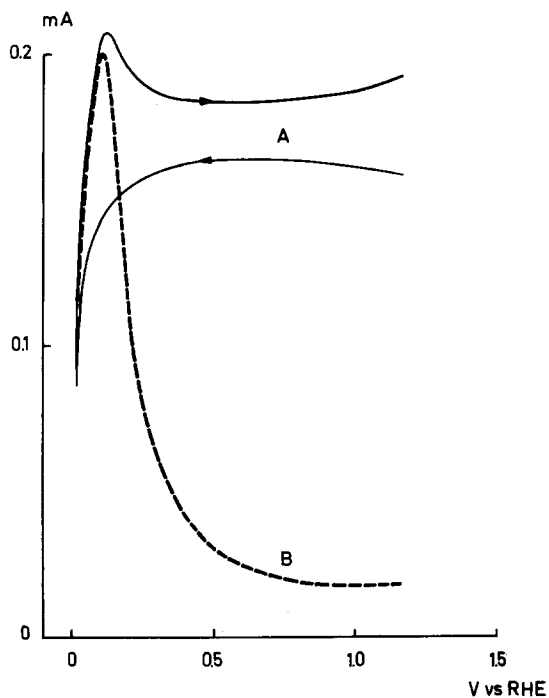


Fig. 5. Voltammogram of Ni foil during (curve A) and after (curve B) hydrogen diffusion through Ni-foil, sweep rate  $2 \text{ mV s}^{-1}$ .

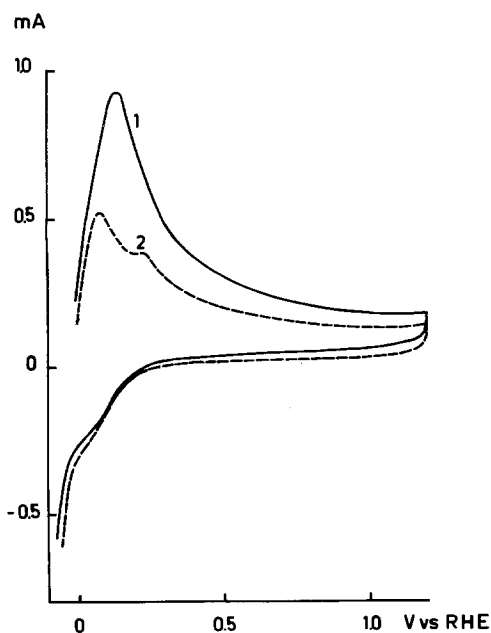


Fig. 6. Effect of cathodic polarization of side B (detection side) of the Ni-foil. Curve 1 is recorded while the polarizing current of 20 mA at the diffusing side A is switched on. Before the curve is registered side B was cathodically polarized. Curve 2 is recorded after switching off the polarizing current at side A.

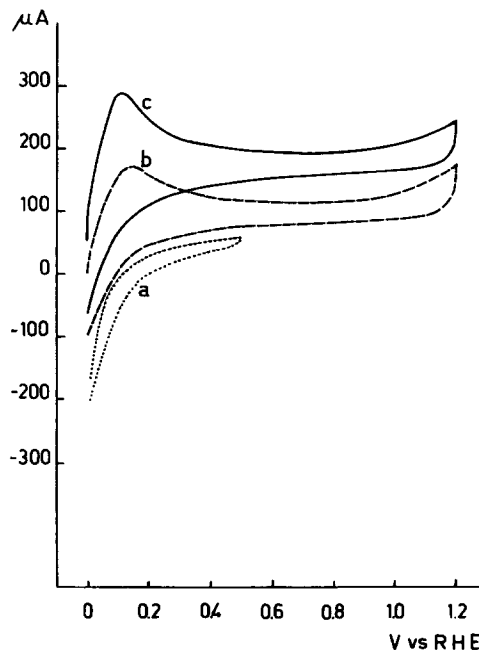


Fig. 7. Voltammograms recorded at side B (0.1 M KOH) of the bipolar nickel foil, sweep rate  $10 \text{ mV s}^{-1}$ . At the polarizing side A (electrolyte 0.5 M  $\text{H}_2\text{SO}_4$ ) the cathodic current is 20 mA for curves a and b, and 50 mA for curve c. Curve a is recorded in the potential range 0–500 mV without any cathodic pre-treatment of side B. Curves b and c, after polarization of side B by potential scanning from  $-800 \text{ mV}$  to  $1200 \text{ mV}$ .

not passivated. A voltammogram, recorded for a potential sweep 0–500 mV applied at side B which was not cathodically polarized, while side A was cathodically polarized, does not show an anodic peak (Fig. 7a). The electrode is then oxidized by changing the potential scan limits to  $-0.8$  and  $1.2 \text{ V}$ . Next, the voltammogram is recorded for an applied potential sweep 0–1.2 V while the cathodic current is maintained at 20 mA. The effect of the increase of the anodic current (curve B) is evident; curve C gives the voltammogram for  $I_{\text{cath}} = 50 \text{ mA}$ .

### 3.3. $\text{Ni}(\text{OH})_2$ electrodes

$\text{Ni}(\text{OH})_2$  electrodes ( $\alpha$  or  $\beta$ ), subjected to potential sweeps 0–0.4 V, do not show any peaks in this potential range. After cathodic polarization the  $\alpha$ -electrode shows one oxidation and one reduction peak and a  $\beta$ -electrode shows two oxidation peaks (Fig. 8). Potential scanning of an  $\alpha$ -electrode in the potential range 0–1.2 V, after cathodic polarization, results in a voltammogram of the same type

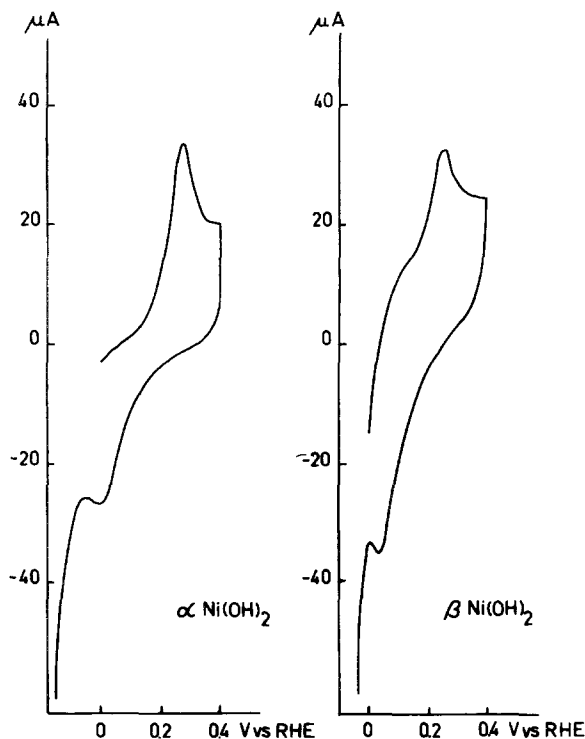


Fig. 8. Voltammogram of  $\alpha$ -Ni(OH)<sub>2</sub> and  $\beta$ -Ni(OH)<sub>2</sub> deposited on nickel, sweep rate 10 mV s<sup>-1</sup>. Electrolyte: 0.1 M KOH. The diagrams are recorded after cathodic polarization for 10 min at -300 mV.

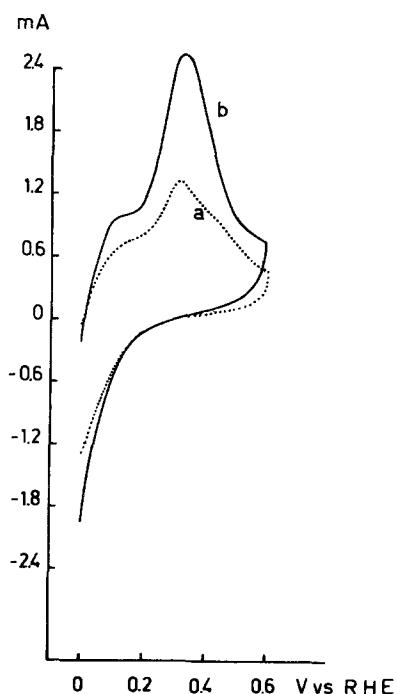


Fig. 9.  $\alpha$ -Ni(OH)<sub>2</sub> on Ni-electrode; electrolyte 0.1 M KOH, sweep rate 10 mV s<sup>-1</sup>. Curve a, after multiple scanning from -600 to 0 mV at  $t = 40^\circ\text{C}$ ; Curve b, after multiple scanning from -600 to 0 mV at  $t = 60^\circ\text{C}$ .

as in Fig. 2, but with much higher current maxima. The effect of temperature on the behaviour of an  $\alpha$ -electrode is shown in Fig. 9. After multiple scanning of an  $\alpha$ -electrode in the potential range -0.6 to +0 V at temperatures of 40°C and 60°C the voltammogram recorded in the potential range 0-600 mV reveals a shoulder before the main peak.

#### 4. Discussion

The results show that the voltammetric behaviour of nickel is affected by diffusing hydrogen. For large H-diffusion currents the voltammogram recorded on the detection side shows only the hydrogen permeation. By decreasing the H-supply, the voltammogram reveals two peaks in which the height of the first peak depends on the amount of permeating hydrogen. It is evident that this first peak is identical with peak 1 of Fig. 2. Therefore it can be concluded that peak 1 is due to the oxidation of absorbed hydrogen.

The relationship between the permeation current  $I_B$  and the polarizing current  $I_A$  was found to be

$$I_B = KI_A^\beta$$

with  $\beta = 0.66$ . This agrees with  $\beta$  measured by Zeilmaker [15].

The H-absorption must take place in, or is catalyzed by, a reduced nickel oxide layer. This follows from (a) the appearance of peak 1 after an oxidation-reduction cycle, (b) the absence of a H-diffusion current through a non-passivated foil. It is to be noted that the hydrogen evolution reaction is also catalysed by the presence of an oxide layer on nickel.

For the nickel oxidation process the following scheme can now be given. During anodic oxidation an oxide film is formed which, during the subsequent reduction cycle, is partially reduced. During the cathodic polarization H is absorbed in this film. The NiH and NiOH species as suggested by Weininger [1] must therefore be considered to be  $\text{Ni}_x\text{O}_y\text{H}$ . Since on reduced  $\beta\text{-Ni(OH)}_2$  both peaks 1 and 2 are observed, while at  $\alpha\text{-Ni(OH)}_2$  only peak 2 is obtained (Fig. 9), the reduced nickel oxide layer is  $\beta\text{-Ni(OH)}_2$  or a reduced form, which could be NiOH. This conclusion is also supported by the results shown in Fig. 9. The H-peak becomes manifest on an  $\alpha\text{-Ni(OH)}_2$  electrode if cycled at higher temperatures. Bode [13, 14] has shown that  $\alpha$  is converted to  $\beta$  if kept for a long time at  $70^\circ\text{C}$  in concentrated KOH solution. This conversion apparently takes place below  $40^\circ\text{C}$ . Comparing the results for electrodes with different thickness of the nickel oxide layer, as is achieved by either repeated oxidation and reduction or by depositing  $\text{Ni(OH)}_2$  layers electrochemically it is seen that H-absorption increases with increasing

thickness of the oxide layer. The growth of the nickel oxide layer by repeated oxidation and reduction proceeds by the growth of the  $\beta\text{-Ni(OH)}_2$  layer. So oxidation takes place via  $\text{Ni} \rightarrow \alpha\text{-Ni(OH)}_2$  which is subsequently converted to  $\beta\text{-Ni(OH)}_2$ .

## References

- [1] J. L. Weininger and M. W. Breiter, *J. Electrochem. Soc.* **111** (1964) 707.
- [2] N. A. Shumilova and V. S. Bagotsky, *Electrochim. Acta* **13** (1968) 285.
- [3] Ku Ling-Ying, N. A. Shumilova and V. S. Bagotsky, *Sov. Electrochem.* **3** (1967) 404.
- [4] L. A. Burkal'tseva and A. G. Pshenichnikov, *ibid* **12** (1976) 40.
- [5] *Idem*, *ibid* **13** (1977) 206.
- [6] Th. C. Franklin and P. E. Hudson, *J. Electrochem. Soc.* **114** (1967) 568.
- [7] A. J. Arvia and D. Pasadas, in 'Encyclopedia of Electrochemistry of the Elements' Vol. 3, (edited by A. J. Bard) Marcel Dekker Inc., New York (1978).
- [8] Z. Szklarska-Smialowska and M. Smialowski, *J. Electrochem. Soc.* **110** (1963) 444.
- [9] B. Baranowski and Z. Szklarska-Smialowski, *Electrochim. Acta* **9** (1964) 1497.
- [10] M. R. Louthan, J. A. Donovan and G. R. Caskey, *Acta Met.* **23** (1975) 745.
- [11] J. O'M Bockris, M. A. Genshaw and M. Fullenwider, *Electrochim. Acta* **15** (1970) 47.
- [12] M. A. V. Devanathan, Z. Stachurski and W. Beck, *J. Electrochem. Soc.* **110** (1963) 886.
- [13] H. Bode, K. Dehmelt and J. Witte, *Electrochim. Acta* **11** (1966) 1079.
- [14] *Idem*, *Z. anorg. allg. Chemie* **366** (1969) 1.
- [15] H. Zeilmaker, *Electrodepos. Surf. Treat.* **1** (1972-73) 109.