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THE ANODIC OXIDATION OF NICKEL IN ALKALINE SOLUTION

W. VISSCHER and E. BARENDRECHT
Laboratory of Electrochemistry, Eindhoven University of Technology,
P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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Abstract – The anodic oxidation of nickel in alkaline solution was studied by cyclovoltammetric and optical techniques. The range of the scanning potential effects the resulting voltammograms. A constant I–E diagram with anodic peaks at 130 and 270 mV (at scan rate 10 mV · s^{-1}) is obtained after multiple scanning from −800 to +1200 mV. The layer of $Ni(OH)_2$ that is formed in the anodic cycle, is only partially reduced by cathodic polarisation. Growth of the $Ni(OH)_2$ film on Ni occurs by repeated oxidation and reduction. This occurs via oxidation of Ni to α $Ni(OH)_2$ and conversion of α $Ni(OH)_2$ to β $Ni(OH)_2$.

1. INTRODUCTION

The anodic oxidation of nickel in alkaline solution has been the subject of many studies[1]; in particular the reactions that take place in the nickel–alkaline battery. Most of those studies start from the $Ni(OH)_2$-electrode. Cyclic voltammetry on nickel–metal electrodes, to study the oxidation process, shows that the anodic behaviour of nickel is strongly influenced by previous polarisations. The first cyclo voltammogram of a nickel electrode differs from successive voltammograms. This was shown by Weininger and Breiter[2] who attributed these differences to the effect of some oxides remaining on the surface after the pretreatment. Samoilov[3] observed an oxidation and a reduction peak in the voltammogram for potential scans up to 0.3 V *vs rhe*, the reduction peak shifts in cathodic direction for scans up to 0.7 V. This reduction peak is attributed to the reduction of adsorbed oxygen[3–5]. Schrebler Guzman[6] observed an anodic peak at 0.4 V during the first anodic potential sweep on a polished Ni electrode; in the next potential sweep this peak had disappeared. This study reports about the oxidation process of nickel in the potential range 0–1.2 V, with potential scan and optical techniques.

2. EXPERIMENTAL

High purity (99.99%) nickel discs, area 0.66 cm^2, were mounted in perspex matrices. Before each experiment the nickel surface was carefully polished with diamond paste (1 μ) and rinsed thoroughly with distilled water. The experiments were carried out in a cell with separated anodic and cathodic compartments; the reference electrode was a hydrogen electrode in the same electrolyte. A Pt-electrode was used as counter electrode. The electrolyte was aqueous 0.1 M KOH solution prepared from p.a. KOH and distilled water and deaerated by bubbling nitrogen through it. The potential sweep measurements were made with a Wenking potentiostat model 68 FR 0.5 and a scan generator Wenking VSG 72, or with a Bruker polarograph E 350 and a Par Universal Programmer Model 175. The ellipsometric measurements were performed

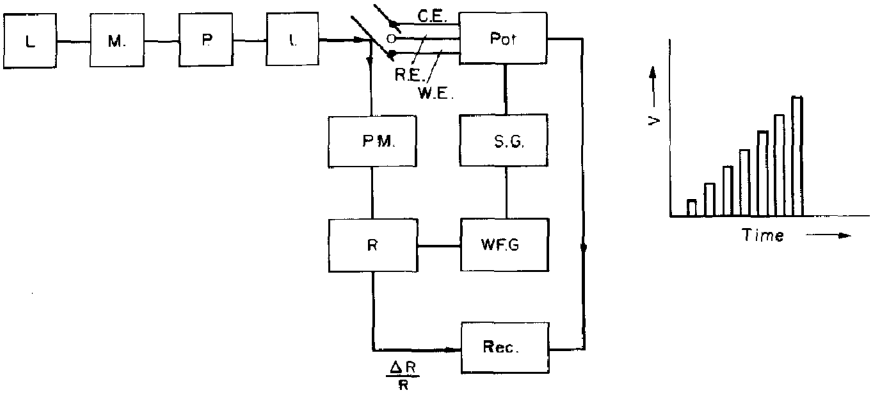

Fig. 1. Schematic diagram of electrochemical spectro-reflectance apparatus. L: Tungsten lamp; M.: monochromator; P.: polariser; L.: lenses; PM.: photomultiplier; Pot: potentiostat; S.G.: scangenerator; Rec.: recorder; WF.G: wavefunction generator; R: measurement of $\Delta R/R$; C.E.: counter electrode; R.E.: reference electrode; W.E.: working electrode (Ni).

with a Rudolph ellipsometer (model 437-200 E) at wavelength 546.1 nm at an angle of incidence 70°.

Differential reflectance measurements were carried out, using incident parallel polarised light at 550 nm. Figure 1 gives a schematic diagram of the optical and electrochemical set-up.

The light source is a tungsten lamp; the light passes a monochromator and is incident on the nickel electrode at 45°. The reflected light is detected by a photomultiplier. 30 Hz square wave pulses are combined with a slow scan ($10\,\mathrm{mV \cdot s^{-1}}$), such that the height of the pulse is increased from 0 to 1200 mV (see insert of Fig. 1). The fractional change in reflectance $(\Delta R/R)_p$ is measured using phase compensated synchronic detection.

3. RESULTS

3.1. *Pretreatment*

Different cathodic polarisation procedures were tried out in order to find an appropriate pretreatment that will result in a reproducible voltammogram. A polished nickel electrode was cathodically polarised at −300 mV during 10 min; thereafter a triangular potential sweep (0–1200 mV) was applied at a scan rate of 10 mV/s. The changes in the voltammogram for 5 successive sweeps are shown in Fig. 2. With increasing cycle number a peak at 130 mV (peak 1) begins to grow, before the main peak at 270 mV (peak 2). Cathodic polarisation at −300 mV for 10 min, is applied before each sweep and the curves are recorded after 1 min rest at 0 V. If no waiting time is introduced, both peaks are slightly higher, this effect is more pronounced for peak 1. Both peaks continue to grow with repeated cycling even after 10 sweeps. When the cathodic pretreatment is carried out at −600 mV, the peak current tends to become constant after about 6 sweeps. The time of cathodic polarisation at −300 or −600 mV was not critical. If the cathodic polarisation is not applied between the successive sweeps, no anodic peak is observed in the anodic voltammogram. Excellent reproducibility and a constant diagram was obtained when the electrode was subjected to a potential sweep treatment from −800 mV to 1200 mV (Fig. 3). The diagram is constant after 8–10 sweeps at 10 mV/s. Before the registration of the curves a rest period of 1 min at 0 V was applied.

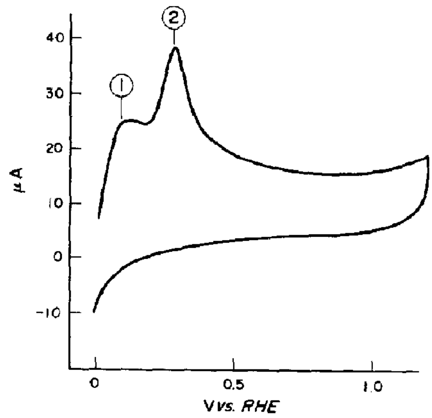

Fig. 3. Voltammogram of Ni in 0.1 M KOH after 11 potential sweeps from −800 to 1200 mV; sweeprate $10\,\mathrm{mV \cdot s^{-1}}$.

This potential sweep treatment appears to be more effective than applying a potential pulse. With a pulse program of 100 s at −600 mV followed by 100 s at 1400 mV, or 500 s at −600 mV and 100 s at 1400 mV a constant voltammogram was not reached after 5 pulses had been applied, even though the total cathodic polarisation time was longer than with the potential sweep treatment. With increasing cathodic potential during the sweep pretreatment, both peaks are slightly shifted into anodic direction and the peak current increases.

3.2. *Effect of the range of the potential sweep*

The previous potential sweep effects strongly the subsequent voltammogram. Figure 4 shows the result

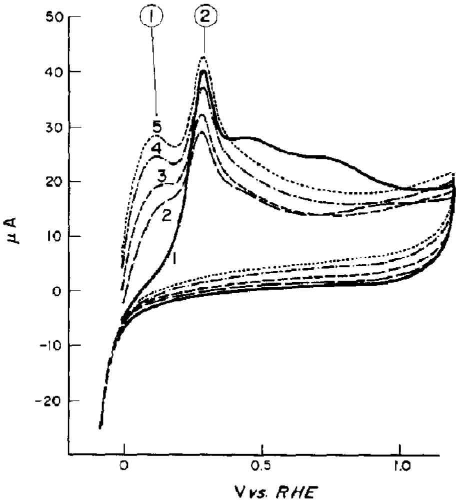

Fig. 2. *i*-*E* diagram of nickel in 0.1 M KOH electrolyte; sweeprate $10\,\mathrm{mV \cdot s^{-1}}$. Before the 1st sweep Ni was polished and cathodically polarised; between each successive recorded sweep, a potential sweep 0–−300 mV was applied.

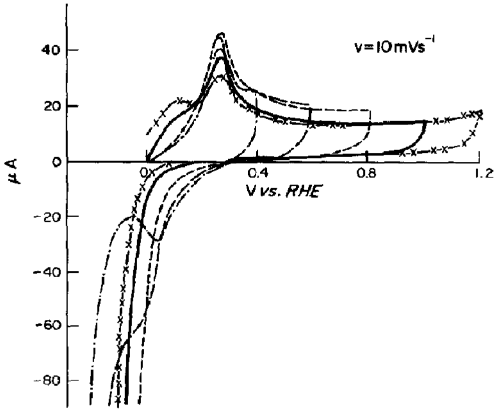

Fig. 4. Effect of increasing anodic return potential; sweeprate $10\,\mathrm{mV \cdot s^{-1}}$. —·— $E_{\mathrm{return}} = 400\,\mathrm{mV}$; ——— $E_{\mathrm{return}} = 600\,\mathrm{mV}$; ---- $E_{\mathrm{return}} = 800\,\mathrm{mV}$; ——— $E_{\mathrm{return}} = 1000\,\mathrm{mV}$; -x-x- $E_{\mathrm{return}} = 1200\,\mathrm{mV}$.

of increasing the anodic return potential of the potential sweep. Peak 1 appears only if the potential is swept to values more anodic than 1 V. It is also seen that the reduction behaviour of nickel is likewise dependent on the anodic return potential. The reduction peak at about 50 mV can only be observed if the anodic limit is not extended beyond 0.8 V.

Next the effect of the potential scan range was investigated for a nickel electrode at which by repeated scanning a constant voltammogram had been obtained as discussed for Fig. 3. This electrode was then subjected to potential sweeps from −800 mV to potentials between 200 and 1200 mV. The results are given in Fig. 5. Lowering the anodic return potential did not affect the length of peak 1 or 2. In the cathodic sweep a reduction peak is observed which shifts into cathodic direction with increasing anodic return potential until the peak finally coïncides with the hydrogen evolution. This shift is a linear function of the anodic potential increase: $\Delta E_{\text{reduction peak 2}} = -0.3\,\Delta E_{\text{anodic return pot}}$ (with E in V). The cathodic peak current increases linearly with increasing anodic return potential (Fig. 5) and increases also with increasing oxidation time at a given anodic return potential, as is shown in Fig. 6.

If the potential scan is restricted to a potential between peak 1 and 2, the voltammogram does not indicate a reduction peak. The reduction peak at 0–50 mV can thus be attributed to the reduction of peak 2.

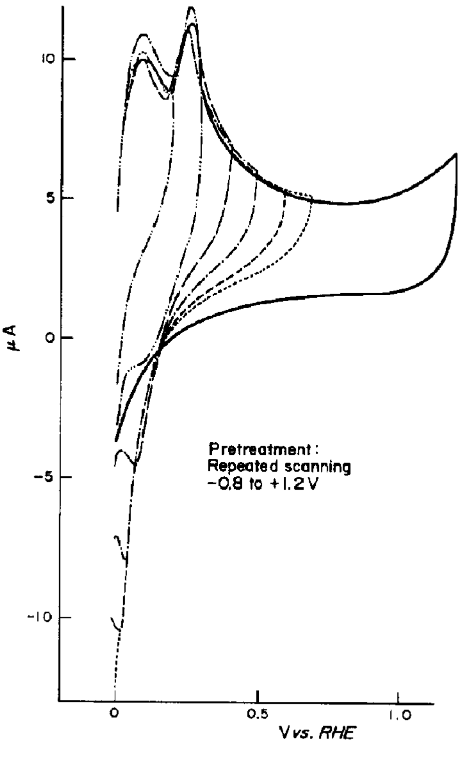

Fig. 5. Effect of increasing anodic returnpotential on a "stabilized" Ni electrode (sweeprate $2\,\text{mV}\cdot\text{s}^{-1}$). —··— $E_{\text{return}} = 160$ mV; —···— $E_{\text{return}} = 300$ mV; ——— $E_{\text{return}} = 400$ mV; —·— $E_{\text{return}} = 500$ mV; ---- $E_{\text{return}} = 600$ mV; ········ $E_{\text{return}} = 700$ mV; ——— $E_{\text{return}} = 1200$ mV.

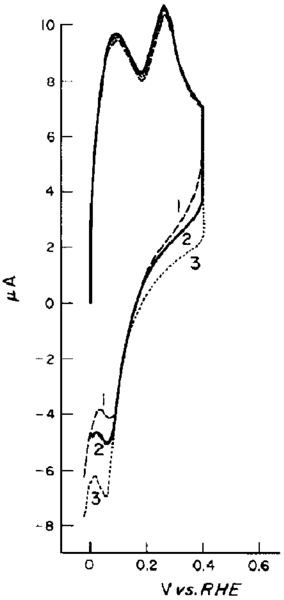

Fig. 6. Effect of oxidation time at $E_{\text{return}} = 400$ mV upon the reduction cycle (sweeprate $2\,\text{mV}\cdot\text{s}^{-1}$).

3.3. *Optical measurements*

Ellipsometric measurements were carried out at an electrode, which after polishing and cathodic pretreatment at −700 mV, was polarised at −100 mV. Repeated cathodic polarisation at −700 mV did not substantially change the ellipsometric parameters Δ and ψ which are therefore considered to represent the clean nickel surface. This is indicated in the Δ, ψ plot of Fig. 7 with "reduced surface". Next, the electrode was oxidized at 400 mV and after 10 min. Δ and ψ were measured (point 1 in Fig. 7). Thereafter the electrode was reduced at −700 mV. The Δ, ψ values subsequently measured at −100 mV (point 2) differ from the values obtained earlier. Repeated and prolonged ca-

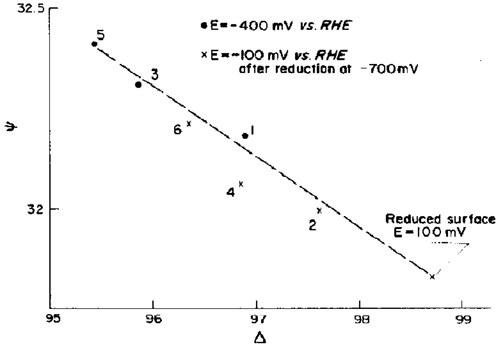

Fig. 7. Change of the ellipsometric parameters with repeated oxidation (at 400 mV) and reduction at −700 mV. After reduction the measurement was carried out at −100 mV. The numbers denote the subsequent processes.

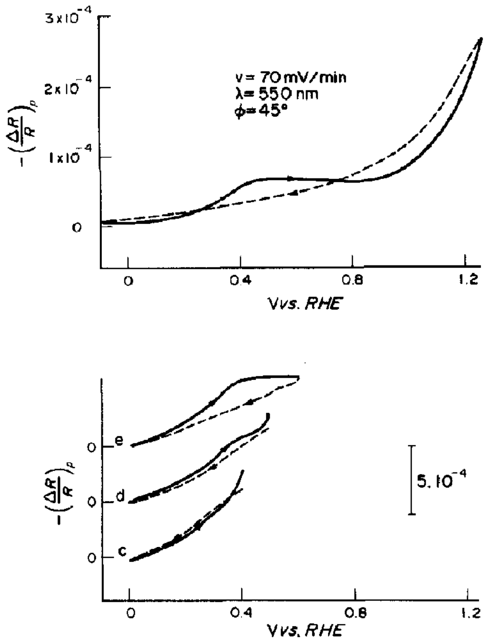

Fig. 8. $(\Delta R/R)_p$ as a function of increasing and decreasing potential for increasing anodic return potentials.

thodic polarisation could not reproduce the Δ and ψ values obtained originally for the reduced surface. This oxidation-reduction cycle was repeated: with the second oxidation $(\Delta, \psi)_3$ was observed and after reduction $(\Delta, \psi)_4$. The next oxidation gave $(\Delta, \psi)_5$ and after reduction $(\Delta, \psi)_6$. Also some reflectivity measurements were carried out for different anodic potential ranges. The measurement of $(\Delta R/R)_p$ as a function of increasing and decreasing potential is given in Fig. 8. With increasing anodic potential limit the hysteresis increases. The data show that from 0 V on a film is formed on the surface which becomes constant in the potential range 400–900 mV.

4. DISCUSSION

After repeated scanning from cathodic potentials to 1.2 V the voltammogram of nickel is characterized by two anodic peaks at 130 and 270 mV respectively (scan rate 10 mV · s^{-1}), while a freshly polished electrode shows only the peak at 270 mV. Cathodic polarisation at hydrogen evolution potentials is required for reappearance of peak 2 in the subsequent voltammograms, whereas for the occurrence of peak 1 the value of the anodic return potential during the previous potential sweep should be $E \geqslant 1.0$ V.

The anodic peak at 270 mV is due to the oxidation of Ni to $Ni(OH)_2$. Its reduction peak is shifted to more negative potentials with increasing anodic return potentials. During the anodic cycle $Ni(OH)_2$ is thus converted or oxidized to an oxide state that is reduced with more difficulty. Some absorbed hydrogen might also be oxidized at this potential. It is however unlikely that this peak is due only to oxidation of absorbed hydrogen as was concluded by Burkalt'seva[7] since the cathodic peaks of Fig. 5 indicate reduction of the species formed during the anodic sweep.

Two anodic peaks, at 50 and 280 mV (v = 100 mV · s^{-1}) were also observed by Shumilova and Bagotsky[4, 5]. They attribute the first peak to oxygen adsorption and possible desorption of hydrogen; this maximum becomes less pronounced after prolonged polarisation. The results as given in Fig. 2 show that peak 1 increases if nickel is subjected to alternate oxidation and strong reduction. If peak 1 is due to O-adsorption the growth of peak 1 during the first number of cycles implies an increasing O adsorption. There is however no increase in the subsequent formation of the phase oxide (peak 2). Experiments with bipolar Ni foils[8] which were cathodically polarised at one side and subjected to cyclic potential sweeps at the other side, have shown that peak 1 should be attributed to oxidation of absorbed hydrogen. It appeared that this absorption of hydrogen takes place on passivated nickel only. The results of Fig. 2 indicate increasing absorption of hydrogen due to growth of the passive layer.

Cathodic reduction does not completely reduce $Ni(OH)_2$ to Ni. This can be deduced from the voltammogram of Fig. 5 and was definitely proved by the ellipsometric data. The Δ, ψ values of Fig. 7 for the reduced surface lie closely at the Δ, ψ line for the surface oxidized at 400 mV. After reduction $Ni(OH)_2$ is still present at the surface. Whether in this change of Δ, ψ also some surface roughening is included, has not yet been verified. For complete removal of the oxide layer mechanical polishing is required.

Measurement of the refractive index of the polished and reduced nickel surface gave $n - ik = 1.87 - 3.36\,i$ which is in agreement with literature data[9, 10]. The refractive index of cathodically deposited α-$Ni(OH)_2$ on Pt in 0.1 M $Ni(NO_3)_2$ is $n - ik = 1.502 - 0.0\,i$ (at $\lambda = 632.99$ nm)[11]. According to Ord[11] this film converts to β-$Ni(OH)_2$ ($n - ik = 1.43 - 0.0\,i$) by alternate oxidation and reduction. Hopper and Ord[12] found for the anodic oxide film in the reduced state on Ni in 5 M KOH after oxidation and reduction $n - ik = 1.46 - 0.0\,i$ (= 632.8 nm). For Ni oxidized at 0.5 V in 0.1 M KOH Visscher and Damjanovic (13) measured $n - ik = 1.55 - 0.0\ i$ ($\lambda = 546.1$ nm), whereas Kudryautseva[14] computed a higher value for the anodic film at 0.4 V: $n - ik = (2.8 \pm 0.2) - (0.1 \pm 0.05)\,i$ at $\lambda = 632.8$ nm with an effective thickness of 0.5 nm.

In Fig. 9 Δ, ψ curves are drawn for $n - ik$ values between $n = 1.45$ and 1.55 and $k = 0 - 0.03$.

The Δ, ψ data measured at 400 mV are also plotted. A good fit is obtained for $n - ik = (1.45 - 1.55) - (0.01 - 0.02)\ i$. The thickness at the points 1, 3, 5, calculated with $n - ik = 1.50 - 0.02\,i$; are respectively 3.8; 5.5 and 6.6 nm. From Fig. 7 it can be concluded that after the first oxidation $Ni(OH)_2$ is reduced to about 50 per cent of its thickness (point 3).

Two mechanisms have been proposed (1) for the formation of the $Ni(OH)_2$ layer: a—dissolution precipitation, b—direct surface-oxidation. From the voltammetric data as given here, no definite conclusion with regard to the formation mechanism can be drawn. It was noted that the anodic $Ni(OH)_2$-peak decreases with multiple sweeps if the return potential is 1.2 V. The voltammogram of Fig. 2 does not indicate a

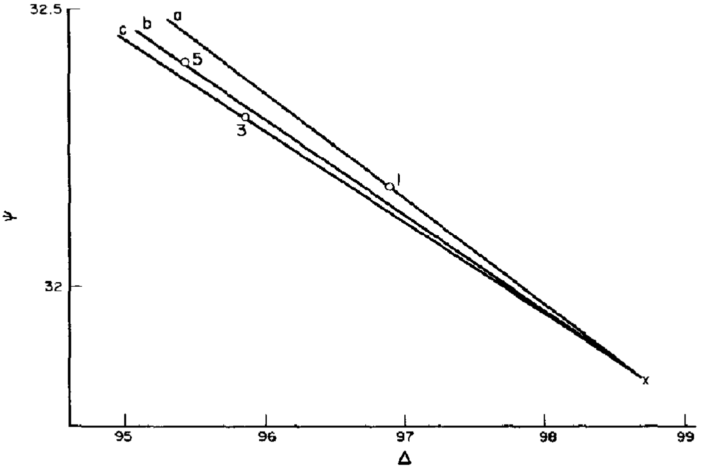

Fig. 9. Calculated Δ, ψ plots for $Ni(OH)_2$ film with refractive indices. curve a: $n\text{-}ik = 1.45 - 0.01\,i$; curve b: $n\text{-}ik = 1.50 - 0.02\,i$; curve c: $n\text{-}ik = 1.55 - 0.03\,i$. The points in the figure are the experimental data of Fig. 7.

further oxidation to higher nickel oxides. Therefore the α-$Ni(OH)_2$ that is formed during the first oxidation stage must be converted to β-$Ni(OH)_2$ in the potential range from 0.4 V up to 1.2 V, which alters the reducibility of the $Ni(OH)_2$ film.

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