Investigation of thin-film alpha- and beta-Ni(OH)₂ electrodes in alkaline solutions

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INVESTIGATION OF THIN-FILM α - AND β -Ni(OH)₂ ELECTRODES IN ALKALINE SOLUTIONS

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ABSTRACT

Thin films of α - and β -Ni(OH)₂ were investigated on Pt, C and Ni substrates. The growth of α -Ni(OH)₂ during cathodic deposition from Ni(NO₃)₂ electrolyte was followed ellipsometrically; a transparent film is formed with refractive index $n - ki = 1.41 \pm 0.03 - 0i$ ($\lambda = 546.1$ nm). For β -Ni(OH)₂, prepared by conversion of α -Ni(OH)₂ in strong alkaline solution, the refractive index was found to be $1.46 \pm 0.03 - 0i$.

In the cyclic voltammograms of α - and β -Ni(OH)₂ the anodic oxidation peak for β -Ni(OH)₂ is about 70 mV higher than for α -Ni(OH)₂. The characteristic peaks of both α - and β -Ni(OH)₂ are observed at film electrodes that were deposited at very low cd.

For γ -NiOOH a refractive index $1.54 - 0.39i$ is obtained (if no change in thickness during oxidation is assumed), or $1.74 - 0.51i$ if a thickness change on the basis of the ratio of the densities is assumed. The optical transients during oxidation- and reduction-cycling indicate a different behaviour of α - and β -Ni(OH)₂.

INTRODUCTION

The nickel hydroxide electrode has been studied extensively because of its application in alkaline batteries [1,2]. Two modifications of Ni(OH)₂ are known; their preparation and identification was established by Bode [3,4]. The α -species is known to be unstable in alkaline solution and converts to β -Ni(OH)₂. Electrodes of Ni(OH)₂ are prepared by electrochemical or chemical deposition on to a conducting substrate; also colloidal films of Ni(OH)₂ in inert substrates have been studied [5–7]. Barnard et al. [8] distinguish four types of active material designated as activated α , activated β and deactivated α and β . The oxidation of α - and β -Ni(OH)₂ leads to oxides with Ni³⁺ and Ni⁴⁺ valencies and several oxide compositions have been detected by X-ray investigations. Ageing of sintered nickel hydroxide plates results in a decrease in charge acceptance, caused by changes in the crystal structure [9].

Here, α - and β -Ni(OH)₂ are electronic insulators or low conductivity p-type semiconductors [10]. The oxidation is accompanied by an increase in the conductivity of the film. Little is known about the optical properties of nickel hydroxide and higher oxides. In this paper the electrodeposition of Ni(OH)₂ from Ni(NO₃)₂

electrolyte and its oxidation in KOH solutions are investigated by ellipsometry and cyclic voltammetry.

EXPERIMENTAL

The α - and β -Ni(OH)₂ electrodes were prepared following the method of Bode [3]: α -Ni(OH)₂ was cathodically deposited on to Pt, Ni or glassy carbon substrates from 0.1 M Ni(NO₃)₂; β -Ni(OH)₂ was prepared from α -Ni(OH)₂ by keeping the freshly prepared α -electrode for 2 h in 7 M KOH at 70°C. Before deposition of the nickel hydroxide film, the substrates were thoroughly cleaned and then dipped in 6 M HCl to improve the adhesion of the film.

Films of different thickness were prepared ranging from 1 to 2000 mC cm⁻² at cathodic cds between 8 and 2000 μ A cm⁻². After deposition, the electrode was transferred to a cell filled with 0.1 M KOH electrolyte. The cyclic voltammetry experiments were carried out in a three-compartment cell with a Pt counterelectrode and a Pt hydrogen reference electrode. All potentials are referred to this RHE. The potential sweep was applied by means of a P.A.R. Model 175 universal programmer in conjunction with a Wenking potentiostat. For cathodic deposition of Ni(OH)₂, a Bruker E-350 polarograph was used.

The optical measurements were conducted with a Rudolph Model RR 2200 automatic ellipsometer, equipped with a tungsten iodine light source and monochromatic filter for 546.1 nm. For these experiments a Ni substrate was used, which was polished with alumina down to 0.05 μ m and then cathodically reduced in 1 M H₂SO₄.

All solutions were prepared from p.a. chemicals and twice-distilled water.

RESULTS

Cyclic voltammetry

A typical voltammogram of an α -Ni(OH)₂/Pt and a β -Ni(OH)₂/Pt electrode in 0.1 M KOH is given in Fig. 1 for the potential range 1000–1600 mV. The anodic and cathodic peaks are fairly symmetrical for deposited layers up to about 100 mC cm⁻². If thicker films are deposited, the voltammogram begins to show the typical features of an electrode with larger resistance: the potential difference between the anodic and the cathodic peak drastically increases. For a scan rate of 10 mV s⁻¹ the peaks for α -Ni(OH)₂ are: $E_{an} = 1.38 \pm 0.01$ V; $E_{cath} = 1.28 \pm 0.01$ V.

For β -Ni(OH)₂, the anodic peak is shifted with respect to that of α -Ni(OH)₂ in the anodic direction: $E_{an} = 1.46 \pm 0.01$ V; $E_{cath} = 1.27 \pm 0.02$ V. The conversion of α -Ni(OH)₂ into β -Ni(OH)₂ was followed by recording the sweep curves during repeated cycling in 5 M KOH at 55°C. Figure 2 shows that with time the anodic peak shifts to higher potentials.

When very thin films are deposited at low cd, the cyclic voltammogram reveals two pronounced anodic and cathodic peaks, which coincide with respectively the α -

and β -peak (Fig. 3). The relative height of the two peaks changes with cathodic deposition conditions; Fig. 4 shows the effect of cathodic current and deposition time. In some runs only one anodic peak is obtained, while the cathodic voltammo-

Fig. 1. Cyclic voltammogram of α -Ni(OH)₂ (1) and β -Ni(OH)₂ (2) film on Pt substrate in 0.1 M KOH; scan rate 10 mV s⁻¹. Film thickness 192 mC cm⁻².

Fig. 2. Effect of repeated cycling of α -Ni(OH)₂ electrode in 5 M KOH at 55°C; scan rate 10 mV s⁻¹.

Fig. 3. Cyclic voltammogram of very thin (19 mC cm^{-2}) Ni(OH)_2 film on Pt substrate; scan rate 10 mV s^{-1} ; electrolyte 0.1 M KOH .

Fig. 4. Effect of cathodic cd and time upon the deposition of Ni(OH)_2 film on to a Pt substrate; scan rate 10 mV s^{-1} ; electrolyte 0.1 M KOH . (—) $i = 8 \mu\text{A cm}^{-2}$, $t = 600 \text{ s}$; (— — —) $i = 32 \mu\text{A cm}^{-2}$, $t = 600 \text{ s}$; (·····) $i = 8 \mu\text{A cm}^{-2}$, $t = 6000 \text{ s}$.

Fig. 5. Very thin film (1.44 mC cm^{-2}) of Ni(OH)_2 on glassy carbon; scan rate 10 mV s^{-1} .

gram shows two peaks. Similar results are obtained with glassy carbon substrates (Fig. 5).

The open circuit potential of freshly prepared Ni(OH)_2 is lower for thicker films:

$$E_{\text{oc}} \sim -0.115 \log(I t / Q)$$

with I and t current and deposition time respectively, and Q the charge equivalent for a monolayer.

The deposited layers adhere reasonably well to the substrate. This can be concluded from the faradaic efficiency of the deposition. Quantitative measurement of the amount of Ni(OH)_2 on Pt was performed by dissolving the layer in 2 ml 6 *M* HCl and determining the Ni^{2+} concentration polarographically. For a film equivalent to $0.65 \mu\text{mol Ni(OH)}_2$, analysis gave $0.54 \pm 0.07 \mu\text{mol}$ (for both α - and β -electrodes).

Ellipsometry

The adherence on optically smooth Pt is poor, therefore Ni was chosen as substrate for the ellipsometric work. The process of deposition of $\alpha\text{-Ni(OH)}_2$ from 0.1 *M* $\text{Ni(NO}_3)_2$ on to a Ni substrate at constant current was followed ellipsometrically. The results are represented in a ψ - Δ diagram (Fig. 6). With increasing deposition time the ψ - Δ values describe an egg-shaped curve. Curve fitting with

Fig. 6. (— —) Experimental ψ - Δ plot during deposition of $\text{Ni}(\text{OH})_2$ on Ni from 0.1 M $\text{Ni}(\text{NO}_3)_2$ at $I = 25 \mu\text{A}$; ($\odot$) starting point, bare surface; (—) calculated ψ - Δ curves for film with increasing thickness at constant refractive index of $n - ki = 1.41 - 0i$ and $1.42 - 0i$. Numbers along the curve indicate thickness values in nm.

Fig. 7. Values of Δ and ψ for $\alpha\text{-Ni}(\text{OH})_2$ during repeated oxidation-reduction cycles in 0.1 M KOH. Upper part: potential scan mode; middle and lower part: Δ , ψ during reduction at 1.0 V ($\cdot$) and during oxidation at 1.40 or 1.45 V ($\odot$).

computed ψ - Δ curves [11] for the growth of a homogeneous transparent film is obtained for a film with refractive index $n - ki = 1.42 - 0i$.

The average value of the refractive index of α -Ni(OH)₂ for 20 runs was

$$n - ki = 1.41 \pm 0.03 - 0i$$

The oxidation of α -film electrodes was investigated in 0.1 M KOH. An α -film was grown on to a Ni substrate in the way described and its thickness was recorded by ellipsometry. The electrolyte was then replaced by 0.1 M KOH and the potential was set at 1.0 V. The electrode was subjected to 10 oxidation–reduction cycles from 1.0 to 1.4 V (sweep rate 10 mV s⁻¹).

Measurement of Δ and ψ at $E = 1.0$ V after this cycling gives the same value, within 0.4°, as before the oxidation–reduction cycles. Figure 7 shows the optical data at 1.0 and 1.4 V for the 10th to the 15th sweep and for two subsequent sweeps to 1.45 V. The data were taken after 10 min hold at the oxidized or reduced potential. Constant values of Δ and ψ were reached, as can also be seen in Fig. 8, for a single oxidation–reduction sweep between 1.0 and 1.4 V.

The properties of β -Ni(OH)₂ were studied at electrodes prepared by conversion of α -Ni(OH)₂ electrodes. After the α -film had been deposited and its thickness measured by ellipsometry, the electrode was converted to β -Ni(OH)₂ by exposure to 7 M KOH at 70°C for 2 h outside the optical cell. Thereafter, the electrode was again transferred to the optical cell. A significant change of Δ and ψ was measured; computation shows for all runs an increase in the real component of the refractive index. If it is assumed that the β -film is also optically transparent ($k = 0$), then the average value for β -Ni(OH)₂ is found to be

$$n - ki = 1.46 \pm 0.03 - 0i$$

Fig. 8. The ψ - and Δ -transient and the current-transient for an oxidation–reduction cycle of α -Ni(OH)₂ in 0.1 M KOH. From left to right: oxidation scan (10 mV s⁻¹) from 1.0 to 1.4 V; 10 min hold of potential at 1.4 V; reduction scan (10 mV s⁻¹) from 1.4 to 1.0 V; 10 min hold of potential at 1.0 V.

The computed value for the thickness of this β -film is about the same as for the original α -film (for most runs within 10%). If the thickness of β -Ni(OH)₂ layer were to be exactly equal to the α -layer, then the corresponding absorption index k becomes 0.02 for some experiments.

The oxidation of β -Ni(OH)₂ was carried out in 0.1 *M* KOH and in 5 *M* KOH. The procedure was as follows: the α -Ni(OH)₂ layer was deposited from 0.1 *M* Ni(NO₃)₂ and then converted to β -Ni(OH)₂ outside the optical cell. The electrode was then replaced in the cell which was now filled with alkaline electrolyte. After measuring Δ and ψ at $E = 1.0$ V, the electrode was oxidized to $E = 1.45$ V. It took much a longer time (30–40 min) before Δ , ψ reached a constant value than during the oxidation of α -Ni(OH)₂. Upon reversal of the potential to 1.0 V, considerable time again elapsed before ψ and Δ became constant. This time effect was not changed when the potential was increased to higher values (1.53 V) or when the oxidation was carried out in 5 *M* KOH instead of 0.1 *M* KOH. Figure 9 shows the optical behaviour during oxidation–reduction cycles with $1.45 \leq E_{\text{OX}} \leq 1.463$ V.

The measurements were taken after 30–40 min hold of the potential at the oxidized or reduced value. After oxidation, the Δ and ψ values at 1.0 V do not return exactly to the values before the oxidation but seem to drift to higher Δ , ψ values after each cycle. Longer waiting times (20 h) did not alter this behaviour.

Fig. 9. Values of ψ and Δ for β -Ni(OH)₂ in 5 *M* KOH during oxidation at $1.45 \leq E \leq 1.463$ V and during reduction at 1.40 V. E_{OX} : (○) 1.45 V; (Δ) 1.459 V; (◻) 1.461 V; (⊗) 1.463 V.

DISCUSSION

The oxidation of α - and β -Ni(OH)₂ is given by [4,12]

The nickel valency in γ_2 -NiOOH is 3 and 4, usually equivalent to NiO_{1.75}. Reduction of γ_2 -NiOOH gives α -Ni(OH)₂.

This reaction takes place in dilute alkaline solution; in concentrated alkaline electrolyte

β -NiOOH (equivalent to NiO_{1.50}) gives γ -NiOOH during prolonged oxidation. Reduction of this γ -NiOOH gives β -Ni(OH)₂ directly.

The Gibbs energy of the conversion

is $-14.3 \text{ kJ mol}^{-1}$, so that the reverse conversion $\beta \rightarrow \alpha$ does not occur. The observed oxidation potentials of $E = 1.38 \text{ V}$ for α -Ni(OH)₂ and of $E = 1.45 \text{ V}$ for β -Ni(OH)₂ correspond to reactions (1) and (2).

The different behaviour of α - and β -hydroxide films is demonstrated by the higher oxidation potential of β and also in the later onset of the O₂ evolution on α -film electrodes, which implies that oxidized β -Ni(OH)₂ is a better catalyst for the H₂O oxidation than α . At both electrodes a Tafel slope of 38–40 mV is found.

The reduction peak potentials for oxidized α - and β -Ni(OH)₂ are found at about the same potential: 1.28 V (cf. Fig. 1); however, in the cyclic voltammogram of the film electrode at which both α - and β -Ni(OH)₂ are deposited, reduction peaks at 1.31 and 1.38 V are observed. Hence, the reduction peak at $E = 1.31 \text{ V}$ corresponds to the reduction peak of reaction (1) while $E = 1.38 \text{ V}$ corresponds to that of reaction (2). The lower reduction potential of pure β -Ni(OH)₂ then signifies that during the positive sweep the oxidation has proceeded further to γ -NiOOH which is subsequently reduced (directly) to β -Ni(OH)₂, so $E = 1.27 \text{ V}$ is attributed to the reduction γ -NiOOH/ β -Ni(OH)₂. These values are in accordance with sweep data at film electrodes [4,5,13]. Studies carried out at sintered Ni(OH)₂ electrodes have shown [8] the necessity of careful preparation of such electrodes in order to obtain the reversible potentials of partially charged α - and β -Ni(OH)₂. In both electrode systems transition from single homogeneous phase to two phases takes place above a nickel oxidation state of 2.25. The potential is then constant and appears at $E = 1.296 \text{ V}$ for α -Ni(OH)₂/ γ -NiOOH and $E = 1.357 \text{ V}$ for β -Ni(OH)₂/ β -NiOOH in 3 M KOH.

Simultaneous deposition of α - and β -Ni(OH)₂ appears to occur if cd is suitably low. At sufficiently low cd either deposited α -Ni(OH)₂ is restructured to β -Ni(OH)₂ or β is directly deposited. This can occur if both c_{OH^-} and $c_{\text{Ni}^{2+}}$ have reached a critical value: for example, at the same cd two peaks are observed in 0.1 M

$\text{Ni}(\text{NO}_3)_2$ but only one peak in 0.01 M $\text{Ni}(\text{NO}_3)_2$.

Monitoring of the substrate by ellipsometry during deposition at this low cd did not reveal a change in Δ and ψ .

The ellipsometric measurements during $\alpha\text{-Ni}(\text{OH})_2$ deposition give a $\psi\text{-}\Delta$ plot which can be fitted with a computed curve calculated for a homogeneous transparent film. Since these optical investigations must be performed on very smooth substrates, this causes sometimes poor adherence; optically this results in a flattened $\psi\text{-}\Delta$ curve. Most runs, however, give $\psi\text{-}\Delta$ curves which can be matched with constant refractive index curves; some deviation begins at ca. 150 nm, which is probably caused by variations in water uptake during the deposition.

The refractive indices for $\alpha\text{-Ni}(\text{OH})_2$, $1.41 - 0i$, and for $\beta\text{-Ni}(\text{OH})_2$, $1.46 - 0i$, do not differ much, but measurements show a distinct change after conversion of α into β .

In $\alpha\text{-Ni}(\text{OH})_2$ ($3 \text{ Ni}(\text{OH})_2 \cdot 2 \text{ H}_2\text{O}$) the water molecules form an interlaminar layer [4] or are arranged in a disordered fashion [14] in the interlayer space. During conversion to $\beta\text{-Ni}(\text{OH})_2$ the H_2O molecules leave this position and move to the vacancies of the main cell [4]. Therefore, $\beta\text{-Ni}(\text{OH})_2$ has still a high water content equivalent to that of α .

The optical results indicate that $\beta\text{-Ni}(\text{OH})_2$ is also transparent; no significant change in thickness is observed after conversion of an α -film. The small increase in refractive index for $\beta\text{-Ni}(\text{OH})_2$ is explained by an alteration in the nickel hydroxide structure.

The value $\hat{n} = 1.41 - 0i$ for $\alpha\text{-Ni}(\text{OH})_2$ is somewhat lower than reported by Hopper and Ord: $\hat{n} = 1.52 - 0i$ for α -film on Ni [15] and $\hat{n} = 1.502 - 0i$ for α -film on Pt [16] ($\lambda = 632.8 \text{ nm}$). However, Hopper and Ord [15] observed for the reduced film (i.e. after oxidation of $\alpha\text{-Ni}(\text{OH})_2$) $\hat{n} = 1.43 - 0i$, which is then attributed to $\beta\text{-Ni}(\text{OH})_2$ because of the difference with the original value. Our results show that after oxidation and reduction of $\alpha\text{-Ni}(\text{OH})_2$, Δ and ψ return to about the same values as before, so that we conclude that the α -film is not changed by oxidation and reduction. This could then imply that $n = 1.43$ also refers to $\alpha\text{-Ni}(\text{OH})_2$. This might be attributed to differences in morphology; however, we found for $\alpha\text{-Ni}(\text{OH})_2$ deposited on Pt the same value as for Ni substrate. No data can be found for freshly prepared β -hydroxide.

The oxidation of $\alpha\text{-Ni}(\text{OH})_2$ to $\gamma_2\text{-NiOOH}$ is reversible as is evident from cyclic voltammograms; repeated cycling does not change the diagram. Also, the optical results do not show significant changes in ψ and Δ after oxidation and reduction. With repeated cycling one or two shoulders can appear on the reduction peak, but this is not seen in the optical measurements, possibly because the ellipsometric changes during reduction are large and occur over a small potential range.

Evaluation of the optical results for $\gamma_2\text{-NiOOH}$ yields a series of solutions all with $k > 0.2$. If it may be assumed that during the oxidation of $\alpha\text{-Ni}(\text{OH})_2$ to $\gamma_2\text{-NiOOH}$ the thickness remains constant, then the refractive index of $\gamma_2\text{-NiOOH}$ is

$$n - ki = 1.54 - 0.39i$$

For this calculation of the properties of the oxidized layer, assumptions must be made. The value given here is computed with the assumption that no substantial change in thickness takes place during oxidation. A different path was taken by Ord [16]. By setting the real component of the refractive index of oxidized α -Ni(OH)₂ equal to that of α -Ni(OH)₂, he obtained a best fit with $n - ki = 1.502 - 0.27i$. If the same assumption is made for the results presented in this work, a value of $n - ki = 1.41 - 0.31i$ is obtained. However, this also implies an increase of thickness of 35–40%. Such a considerable swelling during oxidation is, however, not expected from consideration of density and X-ray data [4]: $\rho = 2.6\text{--}2.8 \text{ g cm}^{-3}$ for α -Ni(OH)₂; $\rho = 3.79 \text{ g cm}^{-3}$ for γ -NiOOH. The α - and γ -types are hexagonal and monoclinic with axes $a = 0.534 \text{ nm}$; $c = 0.75 \text{ nm}$ (because of the interlaminar water layer) for α -Ni(OH)₂, and $a = 0.490 \text{ nm}$, $c = 0.696 \text{ nm}$ for γ -NiOOH. (In this interlayer alkali and hydroxyl ions can also be incorporated.) Another approach is to assume that the thickness changes in accordance with the ratio of the densities. This results in $n - ki = 1.74 - 0.51i$.

During the oxidation of β -Ni(OH)₂ no constant value seems to be reached. Whether this is caused by more complete oxidation of the layer or by further oxidation to higher valency oxides could not be established, since the reduction also was a slow process.

If it is assumed that the thickness does not change during oxidation, the data for the oxidized β -Ni(OH)₂ film give for the refractive index $n - ki = 1.62 - 0.37i$ in 0.1 M KOH; $n - ki = 1.65 - 0.45i$ in 5 M KOH. If the assumption was made that the real part of the refractive index remains constant, then $n - ki = 1.50 - 0.41i$ would result, with a considerable increase (50%) in thickness.

Now, some increase in thickness might occur: X-ray data of McEwen [14] indicate a small increase in planar separation: for β -Ni(OH)₂ the hexagonal axes are $a = 0.312 \text{ nm}$; $c = 0.460 \text{ nm}$ and for β -NiOOH: $a = 0.282 \text{ nm}$; $c = 0.485 \text{ nm}$; also the density of oxidized β -Ni(OH)₂ is somewhat smaller than that of β -Ni(OH)₂. The data for the refractive index of the oxidized β -Ni(OH)₂ are therefore only tentative.

The oxidation basically involves a transition of Ni^{2+} to Ni^{3+} with proton or hydroxyl ion migration through the film. The process starts at the substrate–film interface and can be regarded as the moving of a phase boundary from the substrate side to the electrolyte side, until finally a homogeneous layer is obtained. The optical transients for the α -Ni(OH)₂ oxidation show an immediate response to the applied potential and Δ and ψ reach a constant value as soon as the oxidation peak is completed. The results for β -Ni(OH)₂ oxidation, however, show a slow response. This seems to point to a phase transition for α -Ni(OH)₂, and for the oxidation of β -Ni(OH)₂ to a layer with mixed composition due to the presence of different oxides, while alkali cations can also be incorporated.

CONCLUSIONS

(1) Measurement of the refractive index of α - and β -Ni(OH)₂ gives $\hat{n} = 1.41 \pm 0.03 - 0i$ (α -Ni(OH)₂) and $\hat{n} = 1.46 \pm 0.03 - 0i$ (β -Ni(OH)₂) at $\lambda = 546.1 \text{ nm}$.

(2) The ellipsometric measurements show that $\alpha\text{-Ni(OH)}_2$ is not changed by oxidation–reduction cycles. For $\gamma_2\text{-NiOOH}$ the refractive index is found to be $n - ki = 1.54 - 0.39i$ if it is assumed that the thickness remains constant during oxidation and $n - ki = 1.74 - 0.51i$ if it is assumed that the thickness changes as given by the density change.

(3) After oxidation and reduction of $\beta\text{-Ni(OH)}_2$ the optical parameters are changed. For the oxidized species a tentative value of $\hat{n} = 1.6 - 0.4i$ is obtained.

(4) Both α - and $\beta\text{-Ni(OH)}_2$ are deposited at very low cd.

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