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ELLIPSOMETRY OF NICKEL-OXIDES AND -HYDROXIDES IN ALKALINE ELECTROLYTE

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Résumé

La croissance et l'oxydation de couches minces de $\text{Ni}(\text{OH})_2$ déposées sur Ni ont été étudiées par ellipsométrie. Les indices de réfraction de $\alpha\text{-Ni}(\text{OH})_2$, $\beta\text{-Ni}(\text{OH})_2$ et $\gamma_2\text{-NiOOH}$ ont été obtenus à la longueur d'onde 546,1 nm. On a également étudié l'oxydation anodique de Ni dans 0,1 M KOH. La couche de passivation est initialement $\text{NiO} \cdot x\text{H}_2\text{O}$. Un cyclage répété des potentiels anodique et cathodique modifie les propriétés optiques de cette couche et conduit à la formation d'une couche d'oxyde de faible densité.

Abstract

The growth and oxidation of thin $\text{Ni}(\text{OH})_2$ films deposited on Ni were investigated by ellipsometry. The refractive indices of $\alpha\text{-Ni}(\text{OH})_2$, $\beta\text{-Ni}(\text{OH})_2$ and $\gamma_2\text{-NiOOH}$ were obtained at the wavelength 546.1 nm. Furthermore, the anodic oxidation of Ni in 0.1 M KOH was studied. The passive oxide layer is initially $\text{NiO} \cdot x\text{H}_2\text{O}$. Repeated anodic and cathodic potential cycling change the optical properties of this layer and leads to the growth of a low density oxide layer.

I. INVESTIGATION OF THIN $\text{Ni}(\text{OH})_2$ -ELECTRODES

$\alpha\text{-Ni}(\text{OH})_2$ was formed by cathodic deposition [1] from 0.1 M $\text{Ni}(\text{NO}_3)_2$ on a smooth Ni substrate (0.5 cm^2). The film growth was monitored ellipsometrically at $\lambda = 546.1\text{ nm}$ with a Rudolph Automatic Ellipsometer Model RR 2200. Experimental details are given in [2]. Fig. 1 shows the change of Δ and ψ with time during deposition at $I = 25\text{ }\mu\text{A}$. In a ψ - Δ plot (Fig. 2) these data trace along an egg-shaped curve indicating the formation of a transparent layer. These results are compared with calculated ψ - Δ plots (Fig. 2) for the growth of homogeneous transparent films with refractive index $n = 1.41$ and 1.42 . Optical measurements of $\beta\text{-Ni}(\text{OH})_2$ -films were carried out at electrodes at which first an α -film was deposited of known thickness, usually 50-100 nm; the electrode was then converted to $\beta\text{-Ni}(\text{OH})_2$ by hot alkaline treatment [1] outside the optical cell. The Δ and ψ parameters of the $\beta\text{-Ni}(\text{OH})_2$ electrode were measured in the $\text{Ni}(\text{NO}_3)_2$ -electrolyte. The refractive indices for α - and $\beta\text{-Ni}(\text{OH})_2$ are found to be:

$$n - k i$$

$$\alpha\text{-Ni}(\text{OH})_2 \quad 1.41 \pm 0.03 - 0 i$$

$$\beta\text{-Ni}(\text{OH})_2 \quad 1.46 \pm 0.03 - 0 i$$

For $\alpha\text{-Ni}(\text{OH})_2$ a value of $1.52 - 0 i$ ($\lambda = 632.8\text{ nm}$) has been reported [3]. Density values of $3\text{ Ni}(\text{OH})_2 \cdot 2\text{ H}_2\text{O}$ ($= \alpha\text{-Ni}(\text{OH})_2$) and $\beta\text{-Ni}(\text{OH})_2$ differ considerably: $2.6\text{--}2.8\text{ g.cm}^{-3}$ for $\alpha\text{-Ni}(\text{OH})_2$; 3.9 g.cm^{-3} for $\beta\text{-Ni}(\text{OH})_2$ [1]; so it is concluded that the thin β -films as deposited here, have a higher H_2O -content than bulk $\beta\text{-Ni}(\text{OH})_2$. The $\alpha\text{-Ni}(\text{OH})_2$ to $\beta\text{-Ni}(\text{OH})_2$ conversion is evident from the difference in the cyclic voltammograms in KOH-electrolyte:

At scan rate 0.5 mV.s^{-1} the oxidation peak for $\alpha\text{-Ni}(\text{OH})_2$ is at $E = 1.36\text{ V vs. RHE}$
and for $\beta\text{-Ni}(\text{OH})_2$ at $E = 1.45\text{ V vs. RHE}$.

Ellipsometrically the oxidation of α - and $\beta\text{-Ni}(\text{OH})_2$ was followed in KOH electrolyte during an applied potential program. The results are shown in Fig. 3 and 4; the changes in Δ and ψ are given with respect to their values at $E = 1.0\text{ V vs. RHE}$.

Fig. 1 - Growth of α -Ni(OH) $_2$ -film on Ni during cathodic deposition.

Fig. 2 - ψ - Δ plot of data of Fig. 1. Numbers along the curves indicate thickness in nm.

Fig. 3

Change in Δ and ψ with respect to the values at $E = 1.0$ V during oxidation and reduction in KOH-electrolyte.

Fig. 3: α -Ni(OH) $_2$ potential range 1.0 to 1.4 V vs. RHE

Fig. 4: β -Ni(OH) $_2$ potential range 1.0 to 1.46 V vs. RHE

Fig. 4

A characteristic feature of the oxidation of α -Ni(OH) $_2$ to γ_2 -NiOOH is that Δ and ψ quickly reach constant values and when the reduction cycle is applied, the original Δ, ψ values of α -Ni(OH) $_2$ are again obtained. The oxidation of β -Ni(OH) $_2$ is a much slower process; moreover, after reduction Δ and ψ differ from the values before the oxidation started. Evaluation of the refractive index of γ_2 -NiOOH yields $n_{\text{ki}} =$

1.74 - 0.51 (calculated assuming a change in thickness proportional to the change in densities; $\gamma_2\text{-NiOOH}$: 3.79 g.cm⁻³) and $n\text{-ki} = 1.54 - 0.39 i$ (calculated assuming no change in thickness).

The oxidation of $\beta\text{-Ni(OH)}_2$ leads to $\beta\text{-NiOOH}$ and then to higher valent oxides. The change in Δ and ψ after cycling indicates change in the thickness of $\beta\text{-Ni(OH)}_2$ or change in the nature of this layer.

II. INVESTIGATION OF ANODICALLY FORMED Ni-OXIDES

When Ni is anodically oxidized in 0.1 M KOH a passive layer is formed. Fig. 5 gives the changes of Δ and ψ during stepwise increase of the potential for a freshly polished, reduced Ni electrode. In the potential range up to ca. 1 V the oxide-layer grows linearly with potential reaching a few monolayers thickness; its refractive index is $n\text{-ki} = 2.45 - 0 i$ and the oxide is considered [4] to be $\text{NiO} \cdot x \text{H}_2\text{O}$.

Fig. 5.
Change in ψ and Δ at
prerduced Ni in 0.1 M KOH
during stepwise increase
and decrease of potential.

With further increase of the potential ψ begins to decrease due to conversion in Ni-III-oxide.

$\text{NiO} \cdot x \text{H}_2\text{O}$ is the initially formed Ni-II-oxide layer. It is changed into a structurally different oxide by repeated potential cycling from -0.8 to +1.2 V vs. RHE. At a freshly polished electrode Δ and ψ , measured at $E = -0.1$ V vs. RHE, give the refractive index of bare Ni; the values of Δ and ψ at $E = -0.1$ V after a complete oxidation-reduction cycle have changed. The difference with respect to the original bare substrate values increases with each cycle and can be interpreted as the growth of an oxide film with $n\text{-ki} = 1.52 - 0 i$; the thickness increase per cycle is ca. 1 nm. This oxide has a much lower density and may be a hydroxide-type layer. The process can be explained by the following scheme in which the growth proceeds via oxidation and (irreversible) conversion into a non-reducible oxide:

REFERENCES

1. Bode H., Dehmelt K. and Witte J., *Electrochim. Acta* 11 (1966) 1079.
Z. Anorg. Allg. Chemie 366 (1969) 1.
2. Visscher W. and Barendrecht E., *J. Electroanal. Chem.*, to be published.
3. Hopper M.A. and Ord J.L., *J. Electrochem. Soc.* 120 (1973) 183.
4. Visscher W. and Barendrecht E., *Surface Sci.*, to be published.