O2 evolution on nickel-cobalt alloys

Citation for published version (APA):

Haenen, J. G. D., Visscher, W., & Barendrecht, E. (1986). O2 evolution on nickel-cobalt alloys. *Electrochimica Acta*, 31(12), 1541-1551. [https://doi.org/10.1016/0013-4686\(86\)87073-6](https://doi.org/10.1016/0013-4686(86)87073-6)

DOI:

[10.1016/0013-4686\(86\)87073-6](https://doi.org/10.1016/0013-4686(86)87073-6)

Document status and date:

Published: 01/01/1986

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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O₂ EVOLUTION ON NICKEL-COBALT ALLOYS

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(Received 21 October 1985; in revised form 7 April 1986)

Abstract—The electrochemical formation of oxides on nickel-cobalt alloys was investigated with cyclic voltammetry and ellipsometry. The electrocatalytic behaviour for oxygen evolution of the Ni₁Co₂ alloy changes with the pretreatment. After potentiodynamic cycling, a Tafel slope of about 40 mV was found, whereas after preanodization a Tafel slope of 60 mV and an increase in overpotential is observed. The difference in catalytic performance can be explained by the different nature of the electrochemically formed oxides on the Ni₁Co₂ alloy: either by assuming that spinel-like oxides are formed on the Ni₁Co₂ alloy or that, depending on the pretreatment, the alloy electrode behaves predominantly as a nickel or as a cobalt electrode. The two different pretreatments lead optically to the same two-layer film model, *i.e.* a first layer with a refraction index $N = 2.3-0.1i$ and the second with $N = 2.9-2.1i$, but with a difference in thickness of the first layer.

INTRODUCTION

NiCo₂O₄ spinel oxide is well known for its high activity towards oxygen evolution. The electrochemical behaviour of NiCo₂O₄, prepared by thermal decomposition of the metal nitrates, was investigated in previous work[1]. In addition, we studied the electrochemical behaviour of nickel-cobalt alloys in alkaline solution. It is known that, prior to oxygen evolution on a metal electrode, an oxide layer is formed. Therefore, the electrochemical formation of oxides on nickel-cobalt alloys, with emphasis on the Ni₁Co₂ composition, was investigated with cyclic voltammetry and ellipsometry. Steady-state polarization curves were measured to examine the electrocatalytic activity for oxygen evolution.

EXPERIMENTAL

Electrode preparation

Nickel and cobalt are known to exhibit substantial mutual solid solutions[2]. Alloys were made starting from a mixture of nickel (Riedel De Haën 99.8%) and cobalt powder (Ventron 99.99%). Two different compositions were prepared, *i.e.* Ni₁Co₁ and Ni₁Co₂ alloys. The samples were pressed into pellets and melted in a flame arc in argon atmosphere. The resulting buttons were machined into small electrode pieces, which were embedded in Perspex in conical matrices. The electrodes were polished on carborundum 220 and 600 in order to obtain flat electrodes. The electrodes were etched in a solution of HNO₃, HCL, CH₃COOH and water before use.

Electrochemical characterization

All experiments were carried out in a conventional three-compartment cell, and the temperature was kept at 25°C. The potentials were measured against the *rhe* or the Hg/HgO (0.926 V *vs rhe*, KOH 25°C) via a Luggin capillary close to the working electrode; a platinum foil (10 cm²) was used as the counter electrode. All potentials are given against the *rhe*, and the current densities refer to the geometrical surface area (0.40 cm²). The electrolyte solution, 5 M KOH, was prepared from analytical grade chemicals (Merck p.a.) and doubly distilled water.

The cyclic voltammetric measurements were carried out using a Wenking Potentiostat (HP 72), a Universal programmer (PAR 175) and a Data precision 2480 digital multimeter. The current-potential curves were recorded on an XY-recorder (Philips PM 2041).

Steady-state galvanostatic measurements were carried out as follows: the Ni-Co alloys were firstly subjected to anodic polarization for 30 min at the highest current density, thereafter the potentials were measured with decreasing current density, because the method of electrochemical pretreatment was found to affect the Tafel slope. The time between each reading was 5 min. The ohmic potential drop between the tip of the Luggin capillary and the working electrode was measured with the current interruptor technique[3]; *iR*-corrected potential data are given.

Ellipsometry

Simultaneous electrochemical and ellipsometric measurements were made in a Teflon cylindrical vessel with quartz windows, fixed for an angle of incidence of 70° at the mounted working electrode. The optical cell contains a platinum counter electrode (1 cm²), and a Luggin capillary placed close to the working electrode and connected to the Hg/HgO reference electrode. All potentials are referred to the *rhe*. The optical measure-

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ments were conducted with a Rudolph automatic ellipsometer model RR 2200, equipped with a tungsten iodine light source and a monochromatic filter for 5461 Å. In some experiments, intensity measurements were also carried out with the polarizer at 0 and 90°, in order to obtain the reflection coefficients R_p and R_s . Before each experiment, the electrodes were carefully polished with alumina, down to finally 0.3 μm .

RESULTS AND DISCUSSION

Electrochemical characterization

Figure 1 presents the initial cyclic voltammetric behaviour of a Ni_1Co_2 alloy recorded in N_2 -saturated 5 M KOH at a potential scan rate of 20 mV s^{-1} . Before cycling, the Ni_1Co_2 electrode was maintained at -0.5 V for 10 min, and the voltammogram was recorded in the E range -0.1 to 1.55 V , starting from the lower limit potential. The voltammogram exhibits in the first scan an anodic doublet peak with the peak potentials at 0.11 and 0.33 V , where the latter appears to be most pronounced. This doublet peak decreases fast with further scanning. In addition to these peaks, initially a broad anodic peak is observed in the E range 1.05 to 1.30 V . The following anodic potential scans exhibit a decreasing peak at about 1.1 V , and an increasing sharp anodic peak at about 1.38 V , which slightly shifts to more cathodic values. The reverse cathodic sweep shows three peaks: two increasing with scanning, at about 1.30 and 1.175 V , and a decreasing peak at about 0.15 V . Figure 2 shows the initial voltammetric behaviour of the Ni_1Co_1 alloy recorded in N_2 -saturated 5 M KOH at scan rate of 20 mV s^{-1} . The Ni_1Co_1 electrode was prereduced at -0.5 V for 30

min, and recorded in the E range -0.275 to 1.525 V . Similarly, an anodic doublet peak is initially observed with peak potentials 0.115 and 0.295 V , but in contrast to Ni_1Co_2 , the first peak appears to be more pronounced. Further, another doublet peak is observed with peak potentials 1.39 and 1.435 V , which increases with cycling. These peaks are preceded by very weak peaks at about 0.9 and 1.1 V . The reverse cathodic sweep shows an increasing asymmetrical peak (probably a shoulder) at 1.285 V , and also a broad decreasing peak at about 0.1 V . It appears that the cyclic voltammograms of the two nickel-cobalt alloys are very similar, and the successive $E-i$ recordings indicate a drastic change of the electrode surface. These initial voltammograms can be compared with the ones of pure nickel and cobalt. Both the voltammograms of Ni [4, 5] (prereduced at vigorous hydrogen evolution potential) and Co [6–8] are characterized by two anodic peaks in the E range 0.05 to 0.40 V in alkaline solution.

From the comparison of the voltammetric behaviour of the nickel-cobalt alloys and of the individual metals, it follows that the initial anodic doublet peak of the alloys, observed below 0.5 V can be correlated to the $\text{M}^{0/2+}$ conversion (M is either Ni or Co): the peak at about 0.11 V can be due to the oxidation of absorbed hydrogen[4, 9] or to $\text{Co}(\text{OH})_2$ formation[6–8], whereas the peak at about 0.30 V can be correlated with the Co^{2+} oxide formation[5–7] or the Ni^{2+} hydroxide or oxide formation[4, 5, 10–12]. The stronger presence of the peak at 0.11 V on Ni_1Co_1 vs Ni_1Co_2 indicates that it is mainly due to nickel oxidation. The appearance of the anodic peak at about 1.1 V , more distinctly noticed in the Ni_1Co_2 alloy, is also observed on pure Co [6, 7], but not on Ni [4, 5, 9], therefore it can be attributed to a $\text{Co}^{2+/3+}$ conversion.

Fig. 1. Initial cyclic voltammetric behaviour of a Ni_1Co_2 alloy in O_2 -free 5 M KOH, 25°C at a scan rate of 20 mV s^{-1} .

Fig. 2. Initial cyclic voltammetric behaviour of a Ni₁Co₁ alloy in O₂-free 5 M KOH, 25°C at a scan rate of 20 mV s⁻¹.

When the cathodic switching potential for Ni₁Co₁ is also taken to -0.1 V, as for Ni₁Co₂ in Fig. 1, the anodic and cathodic peak profiles, close to oxygen evolution, show a similar profile as obtained for Ni₁Co₂, Fig. 1. The shape and position of the sharp anodic peak profile and related reduction on both alloys strongly resembles the Ni²⁺/³⁺ oxidation, although other higher oxidation state transitions of Ni and Co cannot be excluded. The cathodic peak at about 0.15 V is characteristic for a reduction to Co metal [6–8].

From the voltammograms of Figs 1 and 2, it can be concluded that initially the nickel–cobalt alloys electrochemically behave as the summation of the two individual metals.

Influence of preanodization

Since the oxygen evolution reaction takes place at an oxide layer, the Ni₁Co₂ alloy was previously subjected to prolonged anodization. Cyclic voltammetry is used to examine the electrochemically formed oxide layer. Figure 3 shows the voltammogram of an aged Ni₁Co₂ alloy (which was previously subjected to oxygen evolution at 1.8 V for 18 h), as a function of the potential scan rate, v , in the E range 0.9–1.5 V. From this figure, it can be seen that after severe oxygen evolution only one large anodic peak remains at about 1.40 V. This was typical for both nickel–cobalt alloys. The position of the anodic peak appears not to depend on the potential scan rate v , which points to a surface redox reaction. The change at 1.8 V was also investigated as a function of time, and it appeared that

after oxygen evolution for 1 h at 1.8 V, no further change in peak profile or current took place. Furthermore, the ageing was also studied as a function of the potential in the oxygen evolution range of 1.50 to 1.80 V, and in time the same stable voltammogram was obtained.

In order to study the effect of the oxide layer on the electrocatalytic activity for oxygen evolution, the E -log i curve is determined on a preanodized Ni₁Co₂ alloy (curve a in Fig. 4), and compared with the Tafel line taken immediately at a freshly polished Ni₁Co₂ alloy (curve b). It appears that an increase in the overpotential with ageing takes place, and a shift of the Tafel slope of about 50 mV for a freshly polished Ni₁Co₂ alloy to a slope of 59 mV. Further preanodization did not alter the Tafel line, nor the voltammetric behaviour.

The influence of cycling

The cyclic voltammetric behaviour of the nickel–cobalt alloy changes with continuous potentiodynamic cycling.

Figure 5 shows the change in the response of the aged Ni₁Co₂ alloy (see Fig. 3) during the first 2 h cycling at a potential scan rate of 20 mV s⁻¹ in the E range -0.2 to 1.475 V. The anodic switching potential of 1.5 V was chosen in order to minimize the oxygen evolution reaction. Previously, it was noticed that with continuous cycling, and with decreasing the cathodic switching potential to at least 0.45 V, a new anodic peak at about 1.28 V is clearly observed as a shoulder on the cathodic side of the large anodic peak, just before oxygen

Fig. 3. Cyclic voltammetric behaviour of a Ni_1Co_2 alloy, previously subjected to oxygen evolution at 1.8 V for 18 h, as a function of the potential scan rate v in 5 M KOH, 25°C.

evolution. At first, the anodic peak profile with shoulder increases with cycling, and evolves to a distinct double peak profile, as seen in Fig. 5. At the same time, both the peak potentials shift to more cathodic values.

Fig. 4. Effect of pretreatment of Tafel lines for a Ni_1Co_2 alloy in 5 M KOH, 25°C. Curve a = preanodized Ni_1Co_2 alloy at 1.8 V for 1 h; curve b = freshly polished Ni_1Co_2 alloy.

Cathodically, the related double peak profile is less distinct, and consists of a sharp peak at 1.27 V with a shoulder at about 1.15 V, which also increases and shifts in cathodic direction, with cycling. Furthermore, a weak broad reduction peak is observed at about 0.55 V. The total voltammetric charge increases continuously with cycling, which indicates that the surface area increases. With further scanning, the doublet peak profile, close to the oxygen evolution potential range, evolves into a single asymmetrical peak, as shown in Fig. 6. This Ni_1Co_2 alloy was cycled for 22 h in the E range -0.05 to 1.475 V at a scan rate of 20 mV s^{-1} . The increase in the peak current, as measured for the voltammetric charge, increases linearly with the cycling time.

It can be concluded that prolonged cycling alters the potentiodynamic behaviour, and that a low cathodic switching potential is essential. Curve a in Fig. 7 shows the Tafel line of a Ni_1Co_2 electrode, on which the measurements were taken immediately after polishing, with a slope of 48 mV. After prolonged cycling (22 h), the Tafel line shifts to lower η , and the slope decreases to 42 mV (curve b). However, after ageing in the oxygen evolution range at 1.8 V for 10 h, the Tafel line shifts to

Fig. 5. Change in the voltammetric response of the aged Ni₁Co₂ alloy during the first 2 h cycling in the *E* range -0.02 to 1.50 V at a scan rate of 20 mV s^{-1} .

Fig. 6. Cyclic voltammogram of the Ni₁Co₂ alloy after 22 h cycling in the *E* range -0.050 V to 1.475 V at a scan rate of 20 mV s^{-1} in 5 M KOH , 25°C .

higher overpotentials, and the slope increases to 60 mV (curve c).

Summarizing, it is shown that the electrocatalytic behaviour of the Ni₁Co₂ alloy changes with the pretreatment. At a freshly polished Ni₁Co₂ alloy, a Tafel slope of about 40 mV and a decrease of the overpotential is found after potentiodynamic cycling,

whereas after preanodization a slope of 60 mV and an increase in overpotential is observed. Furthermore, it appears that the Tafel line with a slope of 40 mV changes to a Tafel line with a slope of 60 mV after prolonged oxygen evolution. When the electrode is thereafter continuously cycled for about 20 h, the slope of 40 mV is again obtained. The difference in catalytic

Fig. 7. Tafel lines on a Ni_1Co_2 alloy in 5 M KOH, 25°C as a function of the pretreatment. Curve a = measurements taken immediately at a freshly polished Ni_1Co_2 alloy; curve b = after prolonged cycling in the E range; curve c = after ageing in the oxygen evolution range at 1.8 V for 10 h.

performance must be due to the different nature of the electrochemically formed oxides on the Ni_1Co_2 alloy. This can be explained either by assuming that spinel-like oxides are formed on the Ni_1Co_2 alloy or that, depending on the pretreatment, the alloy electrode behaves predominantly as a nickel or as a cobalt electrode.

A slope of 40 mV is also observed for the NiCo_2O_4 oxide electrode[1], whereas a slope of 60 mV is found for a Co_3O_4 oxide electrode[13], both spinel oxides prepared by thermal decomposition. Therefore, it seems likely that with the multicycling procedure an oxide layer with the spinel structure of NiCo_2O_4 is formed, while prolonged oxygen evolution leads to the formation of a Co_3O_4 spinel-type oxide. Likewise, the change in the voltammogram with cycling resembles that of the NiCo_2O_4 electrode[14], where the voltammogram of a freshly prepared electrode shows two anodic peaks, prior to oxygen evolution, and changes to a single peak profile. However, the voltammogram of a preanodized Ni_1Co_2 alloy as given in Fig. 3 shows also some resemblance with the single peak profile of an aged NiCo_2O_4 oxide electrode. It must be realized that in case of thermally prepared oxides, the spinel is already present, whereas on the Ni_1Co_2 alloy it still must be formed.

However, the behaviour of a cycled Ni_1Co_2 alloy can also be compared with that of a Ni electrode[9], which also shows a 40 mV slope; even so the preanodized Ni_1Co_2 alloy with that of a Co electrode[7], which exhibits a 60 mV slope. Then it must be assumed that cycling of a freshly polished Ni_1Co_2 alloy with a sufficient low cathodic switching potential should give rise mainly to the formation of a $\text{Ni}(\text{OH})_2$ layer, and that Co disappears selectively by dissolution from the surface. The dissolution of $\text{Co}(\text{OH})_2$, formed on Co in alkaline solution during cycling up to a potential of 1.0 V, has been reported by Behl *et al.*[6].

Furthermore, it seems that after subjecting a freshly polished Ni_1Co_2 alloy to prolonged oxygen evolution, the alloy behaves like a Co electrode. Bagotzky *et al.*[15] reported that, subjecting a cobalt electrode to anodic potentials ≥ 1.45 V, this results in the forma-

tion of a pure Co_3O_4 spinel oxide layer. Behl *et al.*[6] also reported that at about 1.0 V a new "outside" film, i.e. a Co_3O_4 spinel, is formed. They suggested that this film more or less acts as a filter, which blocks the dissolution of $\text{Co}(\text{OH})_2$ and yet allows the transport of OH^- ions for the growth of the $\text{Co}(\text{OH})_2$ film underneath and its subsequent oxidation. Thus, with prolonged oxidation at high anodic potentials (where no Co dissolution can take place), it can be assumed that the Ni_1Co_2 alloy behaves as a Co electrode.

When such a preanodized Ni_1Co_2 electrode is again continuously cycled, Co dissolution will take place again, and consequently the Ni behaviour is again obtained (the behaviour of the Ni_1Co_2 alloy shifts to a Ni one). However, it is not clear why a cycled Ni_1Co_2 alloy electrode, which shows a Ni behaviour, is not stable to prolonged oxygen evolution and changes to a Co behaviour. Therefore, it seems more likely that a metastable NiCo_2O_4 spinel-type oxide is formed with cycling, which is not stable to prolonged oxidation and subsequently decomposes, whereafter the Ni_1Co_2 alloy behaves as a Co_3O_4 electrode. If this electrode is cycled to cathodic return potentials ≤ 0.45 V, the NiCo_2O_4 spinel oxide layer is re-established. Whether or not a NiCo_2O_4 spinel-like oxide is formed on the cycled electrode, it is less suitable for water electrolysis than thermally prepared NiCo_2O_4 oxide electrodes, because the initial catalytic activity decreases with prolonged oxygen evolution: the Tafel slope shifts from 40 to 60 mV and an increase in η takes place.

Ellipsometry

Substrate characterization. In order to establish the value of the refractive index of the Ni_1Co_2 substrate, different pretreatments were carried out: (i) polishing with alumina down to finally 0.3 μm ; (ii) polishing as in (i), followed by reduction under vigorous hydrogen evolution; (iii) polishing as in (i), then dipping in 1 M H_2SO_4 , rinsing thoroughly with distilled H_2O and immediately thereafter transferring to the optical cell; (iv) polishing as in (i), then reducing in 1 M H_2SO_4 under vigorous hydrogen evolution, rinsing with distilled H_2O and immediately thereafter transferring to the cell.

In the cell the potential was held at -0.075 V vs *rhe*, where no hydrogen evolution was observed. Table 1 shows the ellipsometric parameters Δ and ψ , and the refractive index ($n-ik$) taken at this potential for the pretreatments (i), (iii) and (iv).

With method (ii) an anodic current was observed when the potential was brought to -0.075 V after the vigorous hydrogen evolution, which points to anodic film formation. Method (iii) gave poor reproducible results. Pretreatment (iv) gave rise to an extra, inexplicable peak, both in the voltammogram and in the optical curve. Therefore, the ellipsometric readings taken at the potential -0.075 V after pretreatment (i) were assumed to represent the bare substrate of the Ni_1Co_2 alloy electrode. The refractive index of the Ni_1Co_2 alloy, as calculated from Δ and ψ values at $E = -0.075$ V, appears to resemble more that of cobalt than that of nickel metal, as follows from a comparison with the literature data, compiled in Table 2.

Table 1. The ellipsometric parameters Δ and ψ and refractive index ($n-ik$) for the different pretreatments ($\lambda = 5461 \text{ \AA}$)

Pretreatment (see text)	Δ	ψ	n	k
(i)	115.5 ± 0.5	32 ± 0.5	2.6 ± 0.1	4.5 ± 0.1
(iii)	110.5 ± 2.5	32 ± 0.5	2.3 ± 0.2	4.2 ± 0.2
(iv)	115.5 ± 0.5	33 ± 0.5	2.4 ± 0.1	4.7 ± 0.1

Table 2. Refractive index ($n-ik$) for nickel and cobalt ($\lambda = 5461 \text{ \AA}$)

Species	n	k	Medium	Ref.
Ni	1.68	3.63	Phosphate buffer	15
Ni	1.73	3.47	NaOH	11
Ni	1.889	3.449	KOH	4
Co	2.83	3.86	Borate buffer	12
Co	2.39	3.95	Borate buffer	13
Ni ₁ Co ₂	2.6	4.5	KOH	this work

First oxidation cycle

Firstly, the optical behaviour of a Ni₁Co₂ alloy during the first applied potential scan from -0.075 to 1.425 V is investigated. The limit potentials were chosen in order to minimize the influence of the hydrogen or oxygen evolution. Figure 8 shows the changes in Δ and ψ , and the corresponding anodic

Fig. 8. Plot of the changes in Δ and ψ of a Ni₁Co₂ alloy during the first potential sweep in the E range -0.075 V to 1.425 V in 5 M KOH , 25°C ; scan rate 20 mV s^{-1} . CV = corresponding cyclic voltammogram.

voltammogram. The results can be divided into four regions, as indicated in the figure with A, B, C and D. With increasing anodic potential, initially Δ and ψ remain about constant. At about 0.25 V , Δ begins to decrease while ψ increases (part B), and beyond about 1.05 V , Δ decreases fast and ψ increases further (part C). Finally in part D, ψ starts to decrease and Δ decreases faster. These changes in Δ and ψ correlate with the appearance of different oxidation peaks in the corresponding voltammogram. The optical results of Fig. 8 are replotted in Fig. 9 in a Δ - ψ graph. With increasing anodic potential, up to about 1.25 V , the change of Δ and ψ is such that a linear Δ - ψ relation is obtained, *ie* over part B and C. This implies that in the potential range up to 1.25 V , an oxide layer is formed, which grows with a constant refraction index. At the maximum in the Δ - ψ curve, the optical properties

Fig. 9. Graph of ψ versus Δ for the results of Fig. 8; numbers along the curve refer to potential values. Solid and dashed curves: fitting curves.

change: the decrease in ψ coincides with the onset of a further oxidation process.

From the ellipsometric data and curve fitting using the McCrackin program [16], it appears that in part a of Fig. 9 (which corresponds to parts B and C of Fig. 8), one film is formed. In the figure, several curve fittings (dashed lines) are presented for different n and k values; the best fit corresponds to a layer with a refraction index $N = 2.3 - 0.1i$. At 1.25 V a thickness of 34 Å (film 1) is reached. The low value of the imaginary part of the refraction index, k , points to a poor conductivity. Beyond the potential of 1.25 V, the optical properties change, as seen in Fig. 9. The experimental results in part b (which corresponds to part D of Fig. 8) were fitted according to several models: (1) conversion of film 1 ($N = 2.3 - 0.1i$) to another film, which starts either (a) at the film 1–electrolyte interface or (b) at the substrate–film 1 interface; (2) formation of a new film, either (a) on top of film 1 or (b) on the substrate. By curve fitting of the ellipsometric data, it appears that at higher potentials (> 1.25 V) a conductive oxide (high k value) is formed on top of the first layer. The figure presents some curve fittings for different n and k values (dashed lines); the best fit (solid curve) corresponds to a layer with a refraction index $N = 2.9 - 2.1i$. This layer reaches a final thickness of 24 Å at $E = 1.425$ V. The calculated R_p (perpendicular) and R_s (parallel) values for this model are in agreement with the measured ones at 1.425 V. Summarizing, a two-layer film model can be proposed with refraction indices and thicknesses, as schematically presented in Fig. 10.

Repeated cycling

Figure 11 shows the changes of Δ and ψ in a Δ – ψ plot, when the Ni_1Co_2 alloy is continuously cycled for 80 cycles (about 3.5 h) in the E range -0.075 V to 1.425 V at a scan rate of 20 mV s^{-1} . The first cycle is presented for the complete anodic potential range (part I). Thereafter, the values of Δ and ψ are given at a potential of 1.425 V during successively cycling (part II), indicated with the symbol (●).

The increase in ψ in part II with cycling points to a continuous growth of an oxide layer. It is certainly not the growth of film 2. The best fitting [16] of the experimental curve is obtained with the assumption that the first layer, *ie* film 1 (with $N = 2.3 - 0.1i$), increases in thickness whereas the upper layer, *ie* film 2 (with $N = 2.9 - 2.1i$) remains constant ($d = 24$ Å). The solid curve in part II shows the calculated increase in thickness d of film 1, up to 175 Å, which corresponds to 80 cycles. The accuracy of the fitting is demonstrated by the effect of the change in the value of the real part of the refraction index, n , from 2.2 to 2.4, and of the

imaginary part, k , from 0.0 to 0.2, for $d = 100$ Å, indicated in Fig. 11 with the symbol (*). It appears that the value of $N = 2.3 - 0.1i$ gives the best fit with the experimental results up to 175 Å. Moreover, a further confirmation is given by the calculated R_p and R_s values at these points ($d = 100$ Å), which are in agreement with the experimental ones.

Influence of preanodization

The changes in Δ and ψ as functions of the polarization time at 1.8 V for Ni_1Co_2 alloy are shown in Fig. 12. The first cycle (part I) is again completely presented for the anodic potential range. Thereafter, the changes in the ellipsometric parameters Δ and ψ are measured at a potential of 1.425 V (no disturbance by oxygen evolution) with intervals of 30 min oxygen evolution at 1.8 V (part II).

It appears that there is virtually no further change in the optical parameters Δ and ψ after 2 h preanodization. The solid curve in part II shows the best fit with the assumption of the two-layer film model with a growing underlayer (with $N = 2.3 - 0.1i$), whereas the upper layer (with $N = 2.9 - 2.1i$) remains constant in thickness, *ie* $d = 24$ Å.

The calculated thickness of this film 1 is plotted against the polarization time in Fig. 13. It clearly shows that the underlayer grows to a limit of about 75 Å thickness, which is already reached after about 2 h preanodization. This is in contrast with cycling where this underlayer continuously grows. The refraction index of NiCo_2O_4 spinel is not known. In Table 3 some literature data of nickel and cobalt hydroxides and oxides are compiled. A comparison of the refraction index of the two layer film with the published data of Table 3 might suggest that film 1, with $N = 2.3 - 0.1i$, is probably not a Ni or Co hydroxide, but resembles that of CoO , whereas the refraction index of film 2 with $N = 2.9 - 2.1i$ shows some resemblance to that of Co_3O_4 or Co_2O_3 . However, one must bear in mind that this can only give an indication. If indeed a NiCo_2O_4 spinel-type oxide is formed on the Ni_1Co_2 alloy, a large k value (as observed for film 2) is expected, since the conductivity of NiCo_2O_4 is higher than that of Co_3O_4 : a resistivity was reported of approximately $10 \Omega \text{ cm}$ for NiCo_2O_4 and of $10^4 \Omega \text{ cm}$ for Co_3O_4 [21].

Transient measurements

The cyclic voltammogram (Fig. 8) shows that during the first scan in part B–C two oxidation steps are observed. However, it is not clear whether this is an oxidation of two different species or of a further oxidation of one species. From Fig. 9, it appears that the oxides formed in part B and part C are optically identical.

It was tried to distinguish between these two oxidation steps by using a transient technique: a potential step was applied at -0.075 V to a potential in the B–C range, and the resulting changes in the ellipsometric parameters Δ and ψ are recorded as a function of time t . Figure 14 shows the changes in Δ and ψ after a potential pulse to 0.425 V (curve a), 0.725 V (curve b) and 1.025 V (curve c), respectively; the period of time is indicated along the curves. The changes in Δ and ψ are given with respect to their initial

Fig. 10. Schematic representation of the two-layer film model.

Fig. 11. Plot of the changes in Δ and ψ of a Ni_1Co_2 alloy continuously cycled in the E range -0.075 V to 1.425 V at a scan rate of 20 mV s^{-1} . Part I: first cycle for the complete anodic potential range. Part II: with cycling, measured at $E = 1.425$ V ($\bullet$); solid line = fitting curve for the growth of film 1 with $N = 2.3 - 0.1i$; calculated values of Δ and ψ for different refraction indices at a thickness of $100 \text{ \AA}$ ($*$); underlined numbers along the curve refer to cycle numbers, the others to thicknesses. ($\circ$).

Fig. 12. Plot of the changes in Δ and ψ of a Ni_1Co_2 alloy preanodized at 1.8 V. Part I: the first cycle for the complete anodic potential range. Part II: after preanodization, measured at $E = 1.425$ V, numbers along the curve refer to the polarization time in hours.

Fig. 13. Plot of the calculated thickness of film 1 with $N = 2.3 - 0.1i$ against the polarization time.

value at $t = 0$. If there is a difference in the rate of the growth between the different layers (parts B and C), this might be noticeable in the Δ - ψ curve.

In Fig. 14 several calculated curves are presented for different n and k values, with a thickness which increases with time, up to $50 \text{ \AA}$. It appears that curve c (potential step to 1.025 V) can be fitted by a single layer with a refraction index in the range $2.3 - 0.1i$ to $2.6 - 0.0i$, which is in reasonable agreement with the earlier findings for the first layer. The best fitting of the experimental curve b is obtained with a layer with a refraction index in the range $1.4 - 0.0i$ to $1.8 - 0.0i$. A comparison of this refraction index (range) with the published data of Table 3 might suggest that this film (potential step up to 0.725 V) is probably a Ni or Co hydroxide. No fitting curve was found for curve a in the investigated range of refraction indices. Thus, it might be concluded that in the B-C range indeed more than one oxide is formed.

Table 3. Refraction index ($n-ik$) for nickel and cobalt compounds ($\lambda = 5461 \text{ \AA}$)

Species	n	k	Medium	Ref.
NiO	2.23			19
NiO	1.52	0	KOH	5
α -Ni(OH) ₂	1.41	0	Ni(NO ₃) ₂	17
β -Ni(OH) ₂	1.46	0	Ni(NO ₃) ₂ , KOH	17
γ -NiOOH	1.54	0.39	KOH	17
CoO	2.3	0.1	NaOH	18
Co(OH) ₂	1.4	0	NaOH	20
Co ₃ O ₄	3.2	0.5	NaOH	20
Co ₂ O ₃	3.2	0.95	NaOH	20

Fig. 14. Plot of the changes in Δ and ψ after a potential step from -0.075 V to 0.425 V (curve a), to 0.725 V (curve b) and to 1.025 V (curve c), respectively, the time is given along the curves. $\delta\Delta = \Delta - \Delta_{t=0}$; $\delta\psi = \psi - \psi_{t=0}$.

Finally, it is attempted to correlate the electrochemical and the ellipsometric results. The two different pretreatments lead optically to the same two-layer film model: only it appeared that, with cycling, film 1 grows continuously, whereas with preanodization a maximum thickness of about $75 \text{ \AA}$ is reached.

Firstly, one can try to correlate the ellipsometric two-layer film with the above-mentioned assumption that spinel-like oxides are formed on the Ni_1Co_2 alloy. It is then assumed that film 2 with $N = 2.9-2.1i$ is a spinel-type oxide; it is unlikely that film 1 is spinel-like oxide because of its low k value. However, in order to explain the difference in kinetic behaviour of a cycled (NiCo_2O_4 -like behaviour) or an oxidized Ni_1Co_2 alloy (Co_3O_4 -like behaviour), it is necessary to introduce two forms of film 2, which are optically identical. It must be noticed that the ellipsometric measurements were taken at $E = 1.425 \text{ V}$, prior to oxygen evolution,

whereas the kinetic analysis is carried out at potentials $\geq 1.45 \text{ V}$, *ie* in the oxygen evolution potential range. A schematic representation is given in Fig. 15a, where film 2', formed by cycling, is a NiCo_2O_4 spinel-type oxide and film 2'' is a Co_3O_4 spinel-type oxide formed by oxidation. A cycled Ni_1Co_2 alloy, film 2', converts to film 2'' by oxidation. When it is thereafter continuously cycled, it is again converted to film 2'. In both cases, oxygen evolution takes place at the outer film layer, *ie* film 2' or 2''.

The alternative explanation for the kinetic behaviour was that, depending on the pretreatment, the Ni_1Co_2 alloy behaves predominantly as a Ni or as a Co electrode. The introduction of two forms of film 2, which are optically identical ($N = 2.9-2.1i$), is again required to obtain a correlation between the electrochemical and ellipsometric characterization (Fig. 15b). Here, film 2' exhibits an island structure which

Fig. 15. (a) Schematic representation with assumption of the formation of spinel-type oxides on the Ni_1Co_2 alloy. (b) Schematic representation with the assumption that the Ni_1Co_2 alloy behaves predominantly as a Ni or as a Co electrode.

permits the growth of film 1 with cycling; cobalt disappears selectively by dissolution out of film 1. Consequently, film 1 predominantly consists of nickel oxide and oxygen evolution is supposed to take place at this film. On the other hand, oxidation of the Ni_1Co_2 alloy gives rise to the formation of a compact film 2'', as earlier mentioned, blocking the dissolution. This film prevents the continuous growth of film 1; the evolution of oxygen taken place at film 2'' which shows mainly a cobalt behaviour. Film 2'' is again converted

to film 2' by cycling to low cathodic potentials. However, on the basis of these results, it is difficult to discriminate between these two models.

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