Characterization of NiCo2O4 electrodes for O2 evolution. Part III. Ageing phenomena of NiCo2O4 electrodes

Citation for published version (APA):

DOI:
10.1016/0022-0728(86)80541-1

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.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.
CHARACTERIZATION OF NiCo₂O₄ ELECTRODES FOR O₂ EVOLUTION

PART III. AGEING PHENOMENA OF NiCo₂O₄ ELECTRODES

J. HAENEN *, W. VISSCHER and E. BARENDRECHT

Laboratory for Electrochemistry, Department of Chemical Technology, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven (The Netherlands)

(Received 18th October 1985; accepted 24th March 1986)

ABSTRACT

During ageing, the cyclic voltammetric behaviour of freshly prepared NiCo₂O₄ electrodes shows a characteristic change. This is influenced not only by the lower and upper switching potentials of the scan range, but also, in a different way, by potentiostatic or potentiodynamic treatment. These ageing phenomena were interpreted in terms of partial decomposition of the NiCo₂O₄ surface layer.

On the basis of electrochemical and non-electrochemical characterizations, the following general cation distribution was proposed for NiCo₂O₄ spinel: \( \text{Co}^{2+}_{1-x} \text{Co}^{3+}_x [\text{Ni}^{2+}_{1-y} \text{Ni}^{3+}_{y-x} \text{Co}^{3+}_{x+y}] \text{O}_{4+y/2} \), with two valence states on the sublattices and the possibility of excess oxygen.

1) INTRODUCTION

The stability of spinel oxides is influenced by the polarization conditions. Bagotzky [1] found that the reduction of spinel oxides formed on nickel–cobalt alloys starts at 0.6 V. Likewise, Singh et al. [2] reported that porous NiCo₂O₄ electrodes appear to be unstable in the region of potential where oxygen reduction occurs at appreciable rates. NiCo₂O₄ has been shown to undergo complete decomposition at potentials below 0.1 V [3,4]. However, the influence of the lower limit potential and positive polarization on the cyclic voltammetric behaviour was not reported.

In part I [5], it was reported that the voltammetric behaviour of a freshly prepared NiCo₂O₄ electrode was found to differ remarkably from that of an aged one. The ageing process introduces an irreversible transformation in the potentiodynamic response.

It will be shown in this part that the voltammetric behaviour of a fresh NiCo₂O₄ electrode is not only influenced by the lower and upper switching potentials of the...
scan range, but that the voltammetric response is also influenced, in a different way, by potentiostatic or potentiodynamic treatment. Finally, the results of Parts I [5], II [6] and III are correlated.

(II) EXPERIMENTAL

See Part I [5].

(III) RESULTS

(III.1) Influence of the lower limit potential

The time of residence of the freshly prepared electrode at the rest potential, i.e. 1.1 V, in alkaline solution was varied between 5 min and 65 h and did not influence

![Graph of cyclic voltammetry](image)

Fig. 1. Cyclic voltammetric behaviour of a freshly prepared NiCo$_2$O$_4$ electrode previously polarized negatively in the $E$ range 0.9–0.7 V. Experimental conditions: oxygen-free 5 M KOH, 25°C; $v = 25$ mV s$^{-1}$; $T_p = 400$°C and $t_p = 1$ h; catalyst loading = 22.60 mg cm$^{-2}$. $E_{pol} = 1.1$ V for 15 min (curve I); 0.9 V for 15 min (II) and for 1 h (III); 0.8 V for 15 min (IV), for 1 h (V), for 2 h (VI) and for 3 h (VII); 0.7 V for 15 min (VIII) and for 4 h (IX).
Fig. 1 (continued).

the voltammetric response. Also, keeping the NiCo$_2$O$_4$ electrode in air for 6–12 months before the measurements were started did not affect the results.

Figure 1 presents the potentiodynamic response of a freshly prepared NiCo$_2$O$_4$ electrode which was previously subjected to a potential in the range 0.9–0.7 V. The voltammogram was recorded, starting from the rest potential, in the $E$ range 0.9–1.45 V at a sweep rate of 25 mV s$^{-1}$. Curve I presents the cyclic voltammogram of the fresh NiCo$_2$O$_4$ electrode. Previously holding the fresh NiCo$_2$O$_4$ electrode at a potential of 0.9 V for different periods did not influence the voltammetric response, as shown by curve II, which was held for 15 min at 0.9 V, and curve III, for 60 min. Thereafter the electrode was held at a potential of 0.8 V for different periods. The voltammetric behaviour started to change as shown in curves IV and VI: a sharp new cathodic peak, at about 1.3 V, and an increase in the second anodic peak $E_{a2}$ is observed, both increasing continuously with increasing time of arrest at 0.8 V. The increase in the second anodic peak $E_{a2}$ is correlated with the new cathodic peak, as is indicated by the ratio of the respective charges which approaches unity. Further lowering of the arrest potential to 0.7 V did not give rise to new peaks, as
From the voltammetric charge of the new cathodic peak, the net mean potentiostatic reduction current at 0.8 V was calculated as a function of the polarization time; this is shown in Fig. 2. The figure indicates that the decomposition process in the $E$ range 0.9–0.7 V is slow and probably limited to the surface of the catalyst. This is also illustrated in the next experiment.

The current due to the reduction of the spinel NiCo$_2$O$_4$ was measured in 1 M KOH, oxygen-free, at room temperature, as shown in Fig. 3. A fresh NiCo$_2$O$_4$ electrode was polarized negatively in the potential region of 1.1–0.6 V, with stepwise decrease of the potential (−50 mV). The current started to increase below 0.9 V, but this increase faded with time.

Decreasing the lower limit potential accelerates the irreversible breakdown of NiCo$_2$O$_4$. Below 0.5 V, the cathodic current increases quickly. The NiCo$_2$O$_4$ oxide disintegrates rapidly and fine flakes of oxide can be seen to fall off the electrode. At 0 V, the catalyst loading is almost completely lost.

It appears that the “breakdown” of the NiCo$_2$O$_4$ spinel already starts below 0.9 V. The decomposition of the NiCo$_2$O$_4$ spinel in the $E$ range 0.9–0.7 V, as shown in Fig. 1, resembles that of Co$_2$O$_4$ in which the hydroxide Co(OH)$_2$ appears on the electrode in the same potential region [7,8]. On the basis of the observed potentials at which the decomposition takes place, and the standard potential of the individual nickel and cobalt oxides as given in refs. 9 and 10, it can be suggested that the NiCo$_2$O$_4$ structure initially decomposes with the formation of Ni(OH)$_2$ and that the change in voltammetric response is due to the appearance of the Ni(OH)$_2$/NiOOH
couple. Prolonged negative polarization in the $E$ range below 0.9 V leads to a breakdown of the spinel structure. Thus, a lower limit potential of 0.9 V was chosen in order to prevent spinel decomposition.

**(III.2) Influence of the upper limit potential**

The NiCo$_2$O$_4$ electrode was subjected to stepwise increased positive potentials in order to investigate the dependence of the cyclic voltammetric behaviour on the magnitude of the upper potential limit.

Figure 4 presents the voltammetric curves of a fresh NiCo$_2$O$_4$ electrode, which was each time first polarized at different potentials in the oxygen evolution range for 15 min. The voltammograms were recorded in the potential region 0.9–1.475 V at a sweep rate of 25 mV s$^{-1}$. Curve I presents the voltammogram of the fresh NiCo$_2$O$_4$ electrode. It was found that previously holding NiCo$_2$O$_4$ at positive potentials below 1.4 V did not influence the voltammetric response of curve I. Further polarization of the NiCo$_2$O$_4$ electrode at potentials higher than 1.4 V resulted in a change in the potentiodynamic response, as given in curves II–VI. The

---

Fig. 4. Cyclic voltammetric behaviour of a freshly prepared NiCo$_2$O$_4$ electrode, previously polarized positively in the $E$ range 1.40–1.55 V. Experimental conditions: 5 M KOH, 25°C; $v = 25$ mV s$^{-1}$; $T_F = 400°C$ and $t_F = 1$ h; catalyst loading $= 20.10$ mg cm$^{-2}$. Polarization time was 15 min at $E_{pol} = 1.10$ V (curve I); 1.40 V (II); 1.45 V (III); 1.475 V (IV); 1.50 V (V); 1.55 V (VI).
figure shows that the first anodic peak $E_{a1}$ decreases, while the second one $E_{a2}$ increases. The reduction of the increased peak $E_{a2}$ results in an extra cathodic peak. It thus appears that the change in voltammetric behaviour starts in the oxygen evolution range. Therefore, the influence of the polarization potential and time in the oxygen evolution range was investigated.

Figure 5 shows the progressive change of the voltammetric response of a freshly prepared NiCo$_2$O$_4$ electrode which was previously held at 1.5 V, i.e. just after the oxide formation is completed, before the cyclic voltammogram was recorded. This process was repeated and resulted in the same changes as those observed in Fig. 4. Increasing the polarization time at 1.5 V had no effect on the magnitude of the voltammetric change, as shown by comparing the different curves. It was also

![Figure 5](image)

Fig. 5. Cyclic voltammetric behaviour of a NiCo$_2$O$_4$ electrode which was subjected repeatedly to anodic polarization at 1.5 V. Experimental conditions: 5 M KOH, 25°C; $v = 25$ mV s$^{-1}$; $T_P = 400$°C and $t_P = 1$ h; catalyst loading = 26.50 mg cm$^{-2}$. Curve I is the voltammogram of fresh NiCo$_2$O$_4$. Time at $E_{pa} = 1.5$ V: 5 min (II); 10 min (III); each time 15 min (IV–X); each time 30 min (XI–XVI); 15 h (XVII).
noticed that the anodic current at 1.5 V initially decreases rapidly by 50%, on going from curve I to IV, after which it remains nearly constant. Finally, it appeared that anodically and cathodically a single peak voltammogram was obtained. The first anodic oxidation peak $E_{a1}$ had virtually disappeared, while the peak $E_{a2}$ was practically doubled. The cyclic voltammetric response of a fresh NiCo$_2$O$_4$ electrode which was previously subjected to galvanostatic ageing at appreciable oxygen evolution is given in Fig. 6. The voltammograms were recorded in the $E$ range 0.925–1.475 V at a scan rate $v$ of 25 mV s$^{-1}$ in 5 M KOH, 25°C. Curve I presents the cyclic voltammogram of fresh NiCo$_2$O$_4$. The voltammetric response changes into curve II after oxygen evolution at 250 mA cm$^{-2}$ for 1 h. Curve III presents the potentiodynamic response after oxygen evolution overnight at 500 mA cm$^{-2}$ (14 h). It appears that increasing the polarization potential in the oxygen evolution range only initially accelerates the ageing process, i.e. the change in the voltammetric response. This follows by comparing the increase in voltammetric charge (expressed by $i_p$) of curve IV in Fig. 5, i.e. after pre-anodization at 1.5 V for 1 h, and that of curve II in Fig. 6, i.e. after 1 h of oxygen evolution at about 1.62 V. It is found to be nearly equal. After prolonged polarization in the oxygen evolution range, the
NiCo$_2$O$_4$ electrode exhibits a more or less constant voltammogram. No correlation was found between the time or potential of the polarization and the change in voltammetric behaviour.

Galvanostatic rotating ring-disc experiments were also performed, as described earlier in Part I [5]. An anodic charging current $I_D$ of 0.250 mA was applied to the freshly deposited NiCo$_2$O$_4$ layer until steady-state oxygen evolution was attained for 10 min. Curves $I_1$ and $II_1$ in Fig. 7 represent, respectively, the change in disc potential and ring current vs. time. Thereafter, the NiCo$_2$O$_4$ electrode was brought back to the rest potential and the charging experiment was started again. Curves $I_2$ and $II_2$ present the respectively repeated curves. They show that repeating the galvanostatic anodic charging process leads to an increase in overpotential. The difference in overpotential as oxygen evolution is reached is about 30 mV, as seen in Fig. 7 by comparing curves $I_1$ and $I_2$. Next, the disc electrode was subjected to prolonged anodic oxygen evolution at a current density of 10 mA cm$^{-2}$ for 16 h. Then the galvanostatic charging experiment was repeated and resulted in curves $I_3$ and $II_3$. No further increase in overpotential was observed.

The results clearly show that the upper limit potential influences the voltammetric behaviour of NiCo$_2$O$_4$.

The phenomenon of ageing in the oxygen evolution range was studied earlier [11].
in view of its effect on the kinetics of the reaction. An initial decrease in anodic performance of freshly prepared NiCo$_2$O$_4$ was observed and it was mentioned that the rate and extent of ageing varied with different parameters, such as the electrode preparation and the applied current density. It was found that the anodic behaviour remained almost constant after 1 h of pre-anodization. However, it must be noted that the electrocatalytic activity for oxygen evolution was determined at electrodes which were firstly subjected to positive polarization at the highest current densities to be studied, i.e. 1000–1500 mA cm$^{-2}$.

A correlation of the anodic performance with the progressive change in voltammetric behaviour is complicated by the fact that determining the change in activity demands subjecting the electrode to higher positive potentials, where ageing takes place. In fact, only the anodic performance of a freshly prepared and a completely aged electrode can be compared. However, the galvanostatic rotating ring-disc experiment showed that already after one charging experiment an increase in overpotential is observed. When the electrode was subjected to prolonged oxygen evolution, it appeared that there was no further increase in the disc potential $E_D$, although the $E_D$ vs. time curve was changed significantly. The voltammetric charge before oxygen evolution starts was nearly doubled. It also showed that no oxygen evolution was detected before the oxide formation was nearly finished and that the start of it was shifted from 1.40 to 1.44 V, as seen from curves II$_1$ and II$_3$. The results also show that in the case of the ageing process no further oxidation steps take place above 1.55–1.60 V.
Fig. 8. Cyclic voltammetric behaviour of a fresh NiCo$_2$O$_4$ electrode cycled continuously in the $E$ range 0.7–1.5 V. Experimental conditions: 5 M KOH, 25°C; $d = 25$ mV s$^{-1}$; $T_F = 400$°C and $t_F = 1$ h; catalyst loading = 22.50 mg cm$^{-2}$. (a) Cycles 1–150; (b) cycles 150–1500
(III.3) Influence of cycling

The cyclic voltammetric behaviour of NiCo$_2$O$_4$ is also influenced by continuous potentiodynamic scanning.

A freshly prepared NiCo$_2$O$_4$ electrode was cycled continuously in the potential range of 0.7–1.5 V for about 1500 cycles at a sweep rate of 25 mV s$^{-1}$ in 5 M KOH, 25°C, as shown in Fig. 8. Both switching potentials exceed the limit potentials which were determined earlier. A fast change of the cyclic voltammogram of the NiCo$_2$O$_4$ electrode is obtained. At first, the second anodic peak $E_{a2}$, at 1.40 V, increases and a shoulder on the cathodic peak $E_{c1}$, at 1.175 V, is observed. No decrease in the first anodic peak $E_{a1}$, at 1.225 V, takes place. After 50 scans, a shoulder $E_{a2}$ is clearly observed. With further increase of cycle number a new anodic peak, at 1.35 V, increases quickly and dominates $E_{a2}$. At the same time, a new cathodic peak grows and shifts to more negative potentials. Finally, after 1500 scans, the voltammogram results in one broad anodic peak, at 1.39 V, and a cathodic peak, at 1.04 V. The total voltammetric charge increased by a factor of 3.0, and the ratio of the anodic vs. cathodic charge approached unity.

The electrode was then subjected to oxygen evolution at a current density of 500 mA cm$^{-2}$ for 24 h. Thereafter the voltammogram exhibited the same features and the charge increase was less than 5%.

The voltammogram of the cycled NiCo$_2$O$_4$ electrode recorded at a sweep rate of 2.5 mV s$^{-1}$ is given in Fig. 9. Lowering the scan rate results in a deconvolution of the broad peaks, an anodic peak at 1.275 V, with a shoulder at 1.355 V corresponding to $E_{a2}$. The observed peak potentials for the fresh NiCo$_2$O$_4$ electrode at a scan rate of 2.5 mV s$^{-1}$ were $E_{a1}$ at 1.20 V, $E_{a2}$ at 1.35 V, and $E_{c1}$ at 1.19 V. The $E_{a1}$ peak can no longer be distinguished. Cathodically, the new anodic peak is reduced at 1.115 V. The shoulders at higher potentials corresponds to the reduction of $E_{a2}$.

This experiment was repeated with switching potentials which did not exceed the (lower) limit potential, i.e. in the potential range 0.9–1.45 V, as shown in Fig. 10a. In contrast with Fig. 9, the cyclic voltammetric behaviour of the fresh NiCo$_2$O$_4$ electrode is much more stable. The voltammetric charge increase was less than 5% in the first 100 scans. The changing profile in the first 500 cycles resembles that of potentiostatic or galvanostatic ageing in the oxygen evolution range. Anodically, only an increase in the second anodic peak $E_{a2}$ is observed, which is reduced in the shoulder at about 1.25 V. Also, a slight decrease in the first anodic peak $E_{a1}$ is noticed. Between scan numbers 500 and 1725 as presented in Fig. 10b, similar behaviour is observed, as seen before in Fig. 8. The new anodic peak is distinctly observed as a shoulder of $E_{a2}$ and its increase is high compared to that of $E_{a2}$. However, the change in voltammetric charge over 1800 cycles is only a factor of 0.5 and the observed peaks are $E_{a1}$ at 1.22 V, the new anodic peak at 1.325 V, and $E_{a2}$ at 1.39 V. Cathodically, a broad peak is observed at 1.17 V with a shoulder at 1.35 V. Thereafter, the electrode was subjected to oxygen evolution potentials, and again one broad peak was obtained (the dashed curve in Fig. 10a).
Table 1 gives the anodic performance for oxygen evolution at two current densities, i.e. 200 and 500 mA cm$^{-2}$, for the prolonged scanned electrodes and for a fresh NiCo$_2$O$_4$ electrode which was only pre-anodized at 1.5 A cm$^{-2}$ for 1 h.

<table>
<thead>
<tr>
<th>Electrode treatment</th>
<th>$E$/V at 200 mA cm$^{-2}$</th>
<th>$E$/V at 500 mA cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cycled from 0.9 to 1.45 V</td>
<td>1.60</td>
<td>1.63</td>
</tr>
<tr>
<td>Cycled from 0.7 to 1.5 V</td>
<td>1.63</td>
<td>1.66</td>
</tr>
<tr>
<td>Fresh$^b$</td>
<td>1.60</td>
<td>1.635</td>
</tr>
</tbody>
</table>

$^a$ $T_e = 400^\circ$C and $t_e = 1$ h.

$^b$ Only pre-anodized at 1.5 A cm$^{-2}$ for 1 h.
Fig. 10. Cyclic voltammetric behaviour of a fresh NiCo$_2$O$_4$ electrode cycled continuously in the $E$ range 0.9–1.45 V. Experimental conditions: 5 M KOH, 25°C; $v = 25$ mV s$^{-1}$; $T_F = 400^\circ$C and $t_F = 1$ h; catalyst loading = 26.85 mg cm$^{-2}$. (a) Cycles 1–1800 (dashed curve after oxygen evolution); (b) cycles 500–1725.

The voltammetric behaviour was influenced differently by potentiodynamic cycling or treatment at constant potential or current density. With cycling, a new anodic peak was observed and $E_{a1}$ remained nearly constant. With subsequent cycling, $E_{a1}$ was hidden gradually by the higher anodic peaks, while with potentiostatic or galvanostatic treatment, no similar new anodic peak was observed and $E_{a1}$ in general decreased. It is evident that the switching potentials, i.e. the lower and
upper limit potentials, influence this kind of ageing. Comparison of Figs. 8 and 10 indicates that it is probably the lower limit potential which is responsible for the difference in the rate of changes in the voltammograms.

Table 1 also shows the effect of potentiodynamic cycling on the anodic performance. An increase in overpotential was found for the electrode at which both limit potentials were exceeded, i.e. for the $E$ range 0.7–1.5 V. This increase is not due to a change in surface area because the voltammetric charge increased by a factor of 3, which indicates that the surface area increases. The decrease in activity is probably a result of the spinel decomposition. On the other hand, the anodic performance of the NiCo$_2$O$_4$ electrode scanned in the $E$ range 0.9–1.45 V is still comparable with that of a NiCo$_2$O$_4$ electrode which was only pre-anodized. Apparently, the ageing here has just only started, compared to that in Fig. 8.

(IV) CORRELATION OF THE CHANGE IN VOLTAMMETRIC BEHAVIOUR AND ACTIVITY: INTERPRETATION

An attempt to correlate the change in voltammetric response with the electrocatalytic activity for oxygen evolution was made. The most striking observation was that the cyclic voltammetric behaviour of a freshly prepared NiCo$_2$O$_4$ electrode differs remarkably from that of an aged one. The voltammogram of a freshly prepared NiCo$_2$O$_4$ electrode exhibits two anodic oxidation peaks, while that of an aged one shows only one single peak. The influence of both the limit potentials and of the cycling procedure on the cyclic voltammetric behaviour was considered to be an ageing phenomenon. The shifts in the peak potentials and currents, and the appearance of new anodic and cathodic peaks indicate that it cannot be only an increase in surface area.

In the case of the lower limit potential, it is evident that finally the decomposition leads to loss of activity. The decrease in the electrocatalytic activity is correlated with the rate of decomposition of the spinel NiCo$_2$O$_4$ which depends on the lower limit potential. In the case of the upper limit potential, the anodic performance remains almost constant after an initial decrease in activity, as reported earlier [11].

Continuous cycling also leads to a decrease in anodic performance. Although in all cases the voltammetric charge increased significantly, which indicates an increase in surface area, no increase in anodic performance was observed. If the voltammetric charge is a measure of the number of active sites for oxygen evolution, as concluded for fresh NiCo$_2$O$_4$, we should expect an increase in anodic performance with ageing. However, the anodic performance remained almost constant after ageing in the oxygen evolution range. This implies that the number of active sites on the surface where oxygen evolution takes place is constant. Therefore, it must be concluded that the voltammetric charge of the aged electrodes is no longer a measure of the number of active sites for oxygen evolution. The increase in voltammetric charge indicates that an increasing part of the NiCo$_2$O$_4$ layer becomes involved in the oxidation–reduction process. However, oxygen evolution takes place
only on the top surface of the NiCo$_2$O$_4$ electrode [11], where the number of active sites is apparently constant.

The ageing phenomenon as given here was mainly a phenomenological description of the change in voltammetric behaviour of the freshly prepared NiCo$_2$O$_4$ electrode. The ageing in the oxygen evolution potential range is of special importance in view of the practical application in water electrolysis and will be discussed here.

The contradiction of the observed increase in voltammetric charge, which should indicate an increase in surface area, and the observation that the anodic performance remains almost constant, which in turn indicates that the number of active sites is constant, could be interpreted in terms of partial decomposition of the NiCo$_2$O$_4$ surface layer. It seems that some of the surface sites are unstable, probably as a result of the defective nature of NiCo$_2$O$_4$. A chemical decomposition step is not seen in the cyclic voltamogram. However, NiCo$_2$O$_4$ was always under potential control in the alkaline solution. No change in voltammetric behaviour was observed at the rest potential. Thus, polarization is essential to start the ageing phenomenon. These unstable sites will also be oxidized and reduced, and lead to the change in voltammetric behaviour. The initial decrease in anodic performance must be attributed to the loss of some of the active spinel sites, whereafter the number of active sites on the surface is constant. It appeared that the ageing process initially goes rather fast, so the defect sites at the surface are preferentially involved. It was also reported [7] that preliminary anodic oxidation increases the stability of Co$_3$O$_4$ markedly. A similar effect can also explain the decrease in the rate of ageing with time for NiCo$_2$O$_4$. It must be suggested that at least some of the unstable sites dissolve, resulting in a roughening of the NiCo$_2$O$_4$ layer. So, the increasing voltammetric response can be explained by a penetration effect in the NiCo$_2$O$_4$ layer as a result of the “partial decomposition” and “dissolving” process. Consequently, the total area increases, i.e. the number of active and inactive sites. However, this is not expressed in an increase in anodic performance because the oxygen evolution is limited to the surface. A dissolving or leaching process is essential for the roughening process, but it is also limited in depth. This follows from the observation that the increase in the voltammetric charge with ageing in the oxygen evolution range was at most a factor of 3–4.

Complete decomposition, which should result in the formation of individual oxides of nickel and cobalt, must be excluded because then a sharp decrease in anodic performance and an increase in the $iR$ drop would have been observed.

It was also found that the rate of ageing increased with lowering the temperature $T_p$ of the heat treatment, while the magnitude of ageing was nearly equal.

(V) GENERAL CONCLUSIONS

In this section, a correlation of the results of the electrochemical (Part I [5]) and non-electrochemical characterization (Part II [6]), and of the ageing phenomena (Part III) is undertaken.
NiCo$_2$O$_4$ electrodes, prepared by thermal decomposition, are very active for oxygen evolution. It was found that variation of the catalyst loading had virtually no influence on the anodic performance [11], nor on the magnitude of the voltammetric charge of freshly prepared NiCo$_2$O$_4$ electrodes [5]. These results clearly indicate that mainly the top surface layer of the NiCo$_2$O$_4$ electrode is electrochemically active for the oxygen evolution, independent of the electrode structure.

The surface morphology and composition of the NiCo$_2$O$_4$ layer were found to be dependent on the heat treatment, particularly on the temperature $T_F$ of the final heat treatment. The correlation between the increase in activity [11,12] and the increase in cyclic voltammetric charge [5] with decreasing $T_F$ indicates that these effects can be related to a change in surface area. Therefore, the voltammetric charge of freshly prepared NiCo$_2$O$_4$ electrodes can be taken as a measure of the surface concentration of the metal ions participating in the electrochemical processes. These results indicate their number to be 5% at maximum. An apparent electrochemical roughness factor of 500–2000, and an electrochemical surface area of 3–10 m$^2$ g$^{-1}$ can be calculated in the $T_F$ range where only the spinel phase exists. Similarly, the BET surface areas of NiCo$_2$O$_4$ powders show a tendency to increase with decreasing $T_F$ [6].

However, the variation in the ratio of the voltammetric charge of the anodic oxidation peaks as a function of $T_F$ [5] implies that the effect of the heat treatment is not only reflected in an increase of surface area. Both anodic voltammetric peak charges, $Q_{a1}$ and $Q_{a2}$, increase with decreasing $T_F$, but also the ratio $Q_{a2}$ vs. $Q_{a1}$ increases. Therefore, it is conceivable that the difference in anodic performance is only partially a result of the change in surface composition. The XPS measurements [6] revealed for lower $T_F$ an increase of the Co content and a decrease of the Ni content in the NiCo$_2$O$_4$ surface layer with respect to the theoretical NiCo$_2$O$_4$ spinel composition. This confirms that the surface composition is indeed influenced by $T_F$. From a correlation between the charge ratio, and the XPS analysis data, it is conceivable that the increase of the second peak, $E_{a2}$, compared to the first anodic peak, $E_{a1}$, with decreasing $T_F$ [5] is probably due to a higher Co content in the surface region. Thus, irrespective of the increase in surface area, the increase in anodic performance with lowering $T_F$ must apparently be attributed to the increased Co concentration, assuming that Co is the active site. The duration time of the final heat treatment $T_F$ gives no significant changes in activity [11], nor in the magnitude, nor in the ratio of the voltammetric charge [5] of the anodic peaks.

Summarizing, it can be concluded that the surface composition of the NiCo$_2$O$_4$ spinel oxide is affected by the temperature $T_F$, but not by the duration time $t_F$ of the thermal treatment.

The performance of a NiCo$_2$O$_4$ electrode depends on the valence states of the ions in the surface region in the potential range where the desired reaction takes place. The cyclic voltammogram of a fresh NiCo$_2$O$_4$ electrode represents a surface layer with ions in higher valence states [5]. Both anodic oxidation peaks in the voltammogram indicate one-electron surface-redox reactions, and it was shown that the highest oxidation state up to 1.55 V was 4+ . Furthermore, it was found that the
hydroxyl ion plays an important role in the electrochemical reactions prior to oxygen evolution [5].

On the basis of the cyclic voltammetric behaviour, three different models have been suggested for the conjugated electrochemical processes, before oxygen evolution takes place on the freshly prepared NiCo$_2$O$_4$ electrode. From a correlation of the observed peak potentials with the standard potentials of the individual oxides, and the voltammetric behaviour of Co$_3$O$_4$, the assignment of the first transition $E_{a1}$ to Co$^{2+/3+}$ is justified, whereas the second anodic peak $E_{a2}$ could be a $M^{3+/4+}$ transition, where $M$ is either Ni or Co. However, on the basis of the magnitude of the photoelectron binding energy, it was suggested that nickel in NiCo$_2$O$_4$ is present as divalent ion, and from the satellite structure, that Co is mainly present in the diamagnetic, low-spin Co$^{3+}$ state, and to a lesser extent as paramagnetic, divalent high-spin cobalt.

Therefore, the presence of Co$^{2+}$, from cyclic voltammetry, as well as Ni$^{2+}$, from XPS, has been demonstrated. Both these methods are surface techniques, whereby cyclic voltammetry gives information of the surface features as a function of the potential, whereas XPS of a NiCo$_2$O$_4$ electrode is measured at its rest potential. It is most likely that the voltammetric response reflects the influence of the potential on the valence state of the metal cations already present.

Therefore, it is to be expected that also the Ni$^{2+/3+}$ transition is manifest in the cyclic voltammogram. This must be in $E_{a1}$ or $E_{a2}$, since no other oxidation peaks were observed. In Part I [5], $E_{a1}$ was attributed solely to the Co$^{2+/3+}$ transition; this could explain the difference between the peak potentials of the first transition ($E_{a1}$) on NiCo$_2$O$_4$, i.e. at 1.20 V, and on Co$_3$O$_4$, i.e. at 1.15 V. In this context, it is conceivable that the first anodic peak on NiCo$_2$O$_4$ reflects a $M^{2+/3+}$ conversion, with $M$ = Ni or Co. The other possibility is that the Ni$^{2+/3+}$ transition is masked by processes occurring at $E_{a2}$. A more complex nature of $E_{a2}$ has already been discussed [5].

One of the major problems of the mixed oxide spinels is the cation distribution. The determination of the valences and the distribution of the cation among the tetrahedral and octahedral sites of the spinel structure are tedious, particularly if two different metals are present, each of which can adapt more than one valence state.

A number of different site and charge distributions for NiCo$_2$O$_4$, based on magnetization, X-ray and neutron diffraction and scattering studies, have been proposed in the literature [13–19]. Since many “ferromagnetic” spinels are collinear-spin, Néel ferrimagnets, the spontaneous magnetization at $T = 0 \text{K}$ can generally provide a good indication of the cation distribution and valence states if a localized electron, crystal field model gives the appropriate description of the $d$-electron manifold. More correctly, NiCo$_2$O$_4$ is a ferrimagnetic spinel [18]. Holgersson and Karlsson [13] were the first to report a “ferromagnetic” cubic spinel phase in the system Ni–Co–O, and assigned to it the formula (Ni,Co)O(Ni,Co)$_2$O$_3$, to represent the likely presence of two oxidation states for each cation. Lotgering [14] found a magnetization ($M = (B - H)/4\pi$) of approximately 1.5 $\mu_B$ per for-
Blasse [15], interpreting Lotgering’s magnetization data, proposed the structural formula Co$^{2+}$[Co$^{3+}$Ni$^{3+}$]O$_4^{2-}$. However, the spin-only ferrimagnetic magnetization predicted from this model is 2 $\mu_B$ per formula unit, which is not in agreement with the experimental magnetization data. Knop et al. [16] used X-ray and neutron diffraction, and combined it with magnetization data. Their results show that NiCo$_2$O$_4$ is an inverse spinel. But no reliable determination of the degree of inversion in NiCo$_2$O$_4$ could be made. The authors were unable to distinguish between the magnetic structure proposed by Blasse and the one with the structural formula Co$^{3+}$[Ni$^{2+}$Co$^{3+}$]O$_4^{2-}$. The net magnetic moment derived from the magnetization measurements was only 1.25 $\mu_B$, which is lower than the value of 2 $\mu_B$ expected from either model. Boussart et al. [17] attempted to clarify the ambiguity of the valency assignment by a study of the variation in paramagnetic moment $\mu_{eff}$ with composition in the spinel system Ni$_{1-x}$Co$_{2+x}$O$_4$ (with $x < 1$). They concluded that the more probable valency distribution is Co$^{2+}$Ni$^{2+}$[Ni$^{2+}$Co$^{2+}$]O$_4^{2-}$, which extrapolates to Co$^{3+}$[Ni$^{2+}$Co$^{3+}$]O$_4^{2-}$. However, it predicts a spontaneous magnetization at $T = 0$ K of 2 $\mu_B$ per formula unit, as seen before, which is significantly larger than the observed value. King and Tseung [18] investigated the ferrimagnetic ordering of NiCo$_2$O$_4$ by progressive substitution of foreign ions of precisely known charge and site preference. These authors have rejected Boussart’s model on the basis of the strong octahedral site preference of Co$^{3+}$ ions and suggested the cation distribution Co$^{2+}$Ni$^{2+}$[Ni$^{3+}$Co$^{2+}$]O$_4^{2-}$. However, it predicts a spontaneous magnetization. The considerable concentration of holes in the non-magnetic oxygen 2p bands was adjusted to give the appropriate reduction in spontaneous magnetization. However, Battle et al. [19] rejected such a complex cation distribution because it implies metallic conductivity, which is not in agreement with the conductivity measurements on polycrystalline NiCo$_2$O$_4$ materials [20]. They [19] made a refinement of the nickel atom distribution on the ferrimagnetic NiCo$_2$O$_4$, using neutron diffraction. They suggested the possibility of an inhomogeneous distribution of the nickel and cobalt, and introduced A-site Ni$^{3+}$ (tetrahedral site).

The considerable concentration of holes in the non-magnetic oxygen 2p bands was adjusted to give the appropriate reduction in spontaneous magnetization. However, Battle et al. [19] rejected such a complex cation distribution because it implies metallic conductivity, which is not in agreement with the conductivity measurements on polycrystalline NiCo$_2$O$_4$ materials [20]. They [19] made a refinement of the nickel atom distribution on the ferrimagnetic NiCo$_2$O$_4$, using neutron diffraction. They suggested the possibility of an inhomogeneous distribution of the nickel and cobalt, and introduced A-site Ni$^{3+}$ (tetrahedral site).

The considerable concentration of holes in the non-magnetic oxygen 2p bands was adjusted to give the appropriate reduction in spontaneous magnetization. However, Battle et al. [19] rejected such a complex cation distribution because it implies metallic conductivity, which is not in agreement with the conductivity measurements on polycrystalline NiCo$_2$O$_4$ materials [20]. They [19] made a refinement of the nickel atom distribution on the ferrimagnetic NiCo$_2$O$_4$, using neutron diffraction. They suggested the possibility of an inhomogeneous distribution of the nickel and cobalt, and introduced A-site Ni$^{3+}$ (tetrahedral site).

In Part II [6], the presence of Ni$^{2+}$, high-spin paramagnetic Co$^{2+}$ and low-spin, diamagnetic Co$^{3+}$ was observed by XPS analysis. Since NiCo$_2$O$_4$ is an inverse spinel [16], and low-spin Co$^{3+}$ has a strong octahedral site preference [21,22] (and Ni$^{2+}$), this leads to the preliminary distribution Co$^{2+}$Ni$^{2+}$Co$^{3+}$[Ni$^{2+}$Co$^{3+}$]O$_4^{2-}$. The TPR measurements [6] have shown that NiCo$_2$O$_4$ is formed with an average oxidation state of the metal ions equal to 2.67 + (total valency 8 + ), and that it can be presented by the general formula M$^{2+}$M$^{3+}$O$_4^{2-}$, indicating the presence of di- and trivalent metal ions (Ni or Co) in the ratio 1:2, respectively. The cyclic voltammetric characterization [5] suggested the presence of Co$^{2+}$, and possibly Co$^{3+}$ and Ni$^{3+}$. Therefore, from this correlation exercise the following general distribution can be proposed: Co$^{3+}_{1-x}$Co$^{2+}_x$Ni$^{3+}_{2-x}$Ni$^{2+}_x$Ni$^{1+}_{1-x}$Co$^{3+}_{1-2x}$O$_{4+2x}$, with two valence states on the sublattices.
and the possibility of excess oxygen to maintain the electroneutrality; \(x\), \(y\) and \(z\) are related through \(z = (x - y)/2\).

ACKNOWLEDGEMENT

The authors are grateful to Professor J. Schoonman, Delft University of Technology, for discussions on the cation distribution of NiCo\(_2\)O\(_4\) spinel oxide.

REFERENCES