Characterization of NiCo2O4 electrodes for O2 evolution. Part II. Non-electrochemical characterization of NiCo2O4 electrodes

Citation for published version (APA):

DOI:
10.1016/0022-0728(86)80540-X

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:
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CHARACTERIZATION OF NiCo₂O₄ ELECTRODES FOR O₂ EVOLUTION

PART II. NON-ELECTROCHEMICAL CHARACTERIZATION
OF NiCo₂O₄ ELECTRODES

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

ABSTRACT

NiCo₂O₄ spinel oxide was characterized by a number of ex situ non-electrochemical techniques. Thermogravimetric analysis was applied to study the course of the decomposition of the metal nitrates in order to determine the temperature range of the spinel oxide phase. The surface morphology of NiCo₂O₄ was investigated using BET measurements and scanning electron microscopy. X-Ray diffraction, temperature-programmed reduction (TPR) and X-ray and Auger photoelectron spectroscopy (XPS and Auger) were employed to study the surface and bulk composition of NiCo₂O₄. On the basis of the TPR data, NiCo₂O₄ can be presented as M²⁺M³⁺O₄, with an average oxidation state of the metal cation M (M = Ni or Co) equal to 2.67. The presence of divalent nickel is proposed on the basis of the binding energy of the Ni2p 3/2 photoelectron line, and of cobalt as mainly diamagnetic Co³⁺ in a low-spin state, and paramagnetic divalent high-spin cobalt based on the satellite structure in the XPS spectrum.

(1) INTRODUCTION

The influence of the preparation technique and conditions on the anodic performance of NiCo₂O₄ spinel oxide as an electrocatalyst for anodic oxygen evolution has been investigated in ref. 1. In Part I [2], the electrochemical characterization of the NiCo₂O₄ surface features has been given. In this part, a number of ex situ non-electrochemical techniques are used to characterize the nickel–cobalt spinel system in order to provide supplementary information about the surface features of NiCo₂O₄, in particular with reference to heat treatment.

Thermogravimetric analysis was applied to study the course of the decomposition of cobalt nitrate as a function of the temperature. BET measurements and scanning
electron microscopy were used for the investigation of the surface morphology. X-Ray diffraction, temperature-programmed reduction and X-ray and Auger photo-electron spectroscopy were employed to study the surface and bulk composition of NiCo$_2$O$_4$.

(II) THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis (TGA) was carried out using a Mettler thermoanalyzer 2. The heating rate was $3^\circ\text{C} \text{ min}^{-1}$ in the temperature range of 25–1000$^\circ\text{C}$.

Figure 1 shows the thermogravimetric diagram of the decomposition of Co(NO$_3$)$_2$.6 H$_2$O (Merck), and of Ni(NO$_3$)$_2$.6 H$_2$O (Merck) and Co(NO$_3$)$_2$.6 H$_2$O mixed in a stoichiometric ratio of 1:2. The TGA curves are plotted as a fraction of the initial weight $(G_0 - G)/G_0$ vs. the temperature $(G_0$ is the initial weight and $G$ is the weight loss of the sample). It appears that in both cases decomposition occurs below 300$^\circ\text{C}$. It is well known that both decomposition processes give rise to the formation of a spinel oxide, i.e. in the former, Co$_3$O$_4$, and in the latter, NiCo$_2$O$_4$. The TGA curve of cobalt nitrate can be separated into different regions: a major weight loss region below 280$^\circ\text{C}$ which can be divided into two parts, followed by a very small monotonic weight loss up to 500$^\circ\text{C}$. Then no further weight loss takes place in the temperature range of 500–900$^\circ\text{C}$. Finally, a sharp weight loss is observed at 900$^\circ\text{C}$.

Fig. 1. Thermogravimetric curves plotted as a fraction of the initial weight vs. temperature. (---) Co(NO$_3$)$_2$.6 H$_2$O; (-----) Ni(NO$_3$)$_2$.6 H$_2$O·Co(NO$_3$)$_2$.6 H$_2$O = 1 2; (1) part of the solid curve on an expanded real weight scale.
The hydration water molecules are removed in the temperature range below 230°C, as confirmed by calculations of the weight-loss curve. The decomposition of the nitrate, with the evolution of NO, apparently starts as soon as the dehydration is completed. It takes place over a short temperature interval of about 50°C and results in the spinel oxide Co₃O₄. The weight at 280°C does not correspond exactly to that of Co₃O₄. The presence of hydration water in excess over the nominal composition can disturb the calculations based on the TGA curve. Co(NO₃)₂·6 H₂O is known to be extremely deliquescent [3]. The temperature at which the spinel oxide is formed changes with the heating rate. Pope et al. [4] observed that the decomposition was already completed at 200°C when the heating rate was lowered, while Garavaglia et al. [5] reported that at sufficiently long times Co₃O₄ is even formed at 150°C (24 h). The small monotonic weight loss observed in the temperature range of 280–500°C has been related to the progressive loss of excess oxygen in the initially non-stoichiometric oxide [5–8]. Further heating of the sample does not result in any change in weight up to 900°C. This indicates that the spinel-type oxide does not undergo further conversion in this temperature range. At about 900°C, a sharp decrease in the curve is noticed: the spinel oxide Co₃O₄ decomposes to CoO, as indicated by the weight loss.

The TGA curve of the mixed nitrates is initially similar to that obtained for the cobalt nitrate: a sharp weight loss takes place immediately on heating, tapering off above 275°C, at which the processes mentioned earlier take place, i.e. fusion of the salt, dehydration and decomposition of the mixed nitrates. Thereafter, a steady weight loss starting at 275°C up to 800°C is observed, followed by a more pronounced weight loss above 800°C (as shown by curve 1 on an expanded weight scale in Fig. 1).

It can be suggested that NiCo₂O₄ is already formed after the nitrate decomposition is finished (at about 275°C). Further increase in the temperature up to about 400°C causes a weight loss, which can be correlated with the loss of excess oxygen of NiCo₂O₄+ₓ. The weight loss above 400°C can then be interpreted as the thermal decomposition of the spinel oxide NiCo₂O₄. The sharp decrease above 800°C has been attributed to the loss of all spinel phases [9].

From the weight loss in the range 300–400°C the excess oxygen, i.e. the value of x in NiCo₂O₄+ₓ, can be calculated from the thermogram using the equation

\[ x = \frac{(G_T - G_S)}{G_S} \times \frac{240.56}{16} \]  

where \( G_T \) is the weight of the sample at temperature \( T \), \( G_S \) is the weight expected for the stoichiometric compound formed and the constants in the numerator and denominator are the molecular mass of NiCo₂O₄ and the atomic mass of oxygen, respectively. The results are shown in Table 1. It appears that the stoichiometric composition is reached at about 360°C. At 400°C, a negative value of \( x \) is found, which indicates the decomposition of the spinel structure. This number has no physical meaning above 400°C, i.e. in the two-phase region.

However, the restrictions of the calculation based on a simple weight-loss curve
must be borne in mind. The values were derived from TGA, which gives non-equilibrium data. It was also found that when the TGA curve is interrupted and held constant, the weight loss still changes considerably. The calcination time is important here, especially at lower temperatures \((\leq 300^\circ C)\). Further, the presence of excess hydration water can disturb the calculation. The thermogravimetric analysis of the cobalt nitrate and the mixed cobalt nitrate is in agreement with the results obtained by other authors [3–12].

(III) BET SURFACE AREA

Surface areas were measured using the BET method. The pore size distribution was also determined. The NiCo\(_2\)O\(_4\) powder samples were prepared by thermal decomposition as described earlier [1].

Figure 2 illustrates the effect of the temperature \(T_F\) and duration time \(t_F\) of the heat treatment on the BET surface area of the NiCo\(_2\)O\(_4\) powders. The specific surface areas decrease with increase of \(T_F\) and with \(t_F\). At each temperature \(T_F\), the surface area of NiCo\(_2\)O\(_4\) reaches a constant value as the duration time \(t_F\) is increased. So, at each temperature \(T_F\), a duration time \(t_F\) exists beyond which no

![Fig. 2. BET surface area of NiCo\(_2\)O\(_4\) powders as a function of the temperature \(T_F\). (\(\bigcirc\)) \(t_F = 1\) h; (\(\bigstar\)) \(t_F = 5\) h; (\(\bullet\)) \(t_F = 10\) h; (\(\bigcirc\)) \(t_F = 24\) h]
TABLE 2
BET surface areas of NiCo$_2$O$_4$ powders and apparent electrochemical surface areas of NiCo$_2$O$_4$ electrodes as a function of $T_F$ and $t_F$.

<table>
<thead>
<tr>
<th>Heat treatment</th>
<th>BET surface area of NiCo$_2$O$_4$ powders $/m^2$ g$^{-1}$</th>
<th>Apparent electrochemical surface area of NiCo$_2$O$_4$ electrodes $/m^2$ g$^{-1}$ [2]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_F/°C$</td>
<td>$t_F/h$</td>
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</tr>
<tr>
<td>250</td>
<td>10</td>
<td>39.9</td>
</tr>
<tr>
<td>300</td>
<td>1</td>
<td>32.0</td>
</tr>
<tr>
<td>300</td>
<td>10</td>
<td>16.0</td>
</tr>
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<td>4.5</td>
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<tr>
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</tbody>
</table>

significant changes in surface area are observed; this value is, of course, reached faster at higher $T_F$. The difference in surface area in this limit, i.e. $t_F = 24$ h, between the heat treatment of 300 and 400°C is 25%. This differs from the cyclic voltammetric results [2], where the charge was proposed to be a measure of the surface area of the NiCo$_2$O$_4$ electrode. The voltammetric charge depends strongly on $T_F$, but only slightly on $t_F$. Virtually no further change in surface area after a heat treatment of 1 h was observed. It was found that the difference in surface area between the heat treatment at 300 and 400°C was about 100%.

The BET surface areas of the NiCo$_2$O$_4$ powder materials and the apparent electrochemical surface areas of the NiCo$_2$O$_4$ electrodes [2] are compared in Table 2. They show the same dependence with respect to temperature $T_F$: a decrease of the surface area with increasing $T_F$.

The dependence of the surface area on the duration time $t_F$ shows that when a voltammetric technique is used, an approximately constant surface area is reached faster. Apparently, no further sintering takes place after a heat treatment of 1 h, while in the case of powder material at least a thermal treatment of 10 h at 300°C or 5 h at 400°C is required. The discrepancies in the magnitude of the surface area as a function of $T_F$ and $t_F$ between the powder and electrodes can be explained by a difference in the morphology of the NiCo$_2$O$_4$ oxide due to the slightly different preparation conditions. Unfortunately, it was not possible to subject the NiCo$_2$O$_4$ electrodes as such to a BET examination.

A pore size distribution was carried out on NiCo$_2$O$_4$ powder samples, prepared (a) at a temperature $T_F$ of 300°C and for a duration time of 1 h, (b) at 400°C for 1 h and (c) at 400°C for 24 h. In describing pore size, the notation of Dubinin [13] is commonly adopted: micropores are pores with a diameter of less than 2 nm, mesopores have diameters in the range of 2–30 nm and macropores are those larger than 30 nm. The samples showed no distinct mean pore diameter; they were spread in the mesopore range. It appeared that there were no micropores. In sample (a) most pore diameters are situated in the range 2–5 nm, in sample (b) 5–15 nm, and in sample (c) from 7 to 20 nm.
TABLE 3
Values of the interplanar d-spacing (in Å = 0.1 nm), the Miller indices and the relative intensities of the NiCo$_2$O$_4$ electrodes as a function of $T_F$ and $t_F$

<table>
<thead>
<tr>
<th>$T_F/$°C</th>
<th>$t_F$/h</th>
<th>hkl</th>
<th>d</th>
<th>l/l₁</th>
<th>l/l₂</th>
<th>l/l₃</th>
<th>d</th>
<th>l/l₁</th>
<th>l/l₂</th>
<th>l/l₃</th>
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<th>l/l₁</th>
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</table>

NiCo$_2$O$_4$: ASTM 20.781
NiO: ASTM 4-0835
Fig 3. SEM micrographs of the surfaces of NiCo$_2$O$_4$ electrodes prepared at different temperatures $T_F$. (a) 300°C for 1 h; (b) 400°C for 1 h. Magnification factor = 120.

Observation of the samples using scanning electron microscopy (SEM) gives additional evidence that the surface morphology is determined by the preparation temperature $T_F$. SEM micrographs of NiCo$_2$O$_4$ electrodes are shown in Fig. 3. The NiCo$_2$O$_4$ electrode prepared at 400°C exhibits a smooth, circular scaly surface, while the electrode prepared at 300°C shows a rougher and more porous texture. All coatings exhibit some cracks.

(IV) X-RAY DIFFRACTION

X-Ray diffraction analysis of the NiCo$_2$O$_4$ catalyst was carried out using a Philips model PW 1009 Röntgen diffraction spectrometer. FeKα radiation with a Mn filter was used. All diffraction patterns were recorded at room temperature. X-Ray diffraction patterns of the NiCo$_2$O$_4$ electrodes were also obtained using the Philips diffractometer.

The phase composition was identified by comparison with ASTM data [14]. There was little difficulty in identifying the phase present in the Debye–Scherrer powder photographs of freshly prepared NiCo$_2$O$_4$ as a function of $T_F$ and $t_F$. With lower $T_F$ and $t_F$, the diffraction lines became broader and less well defined. X-Ray analysis confirmed the expectations, i.e. the detection of the single-phase NiCo$_2$O$_4$ spinel oxide in the $T_F$ range of 250–400°C. The visually estimated intensities of the Debye–Scherrer diffraction lines were in agreement with the ASTM data of NiCo$_2$O$_4$ [14]. At higher temperatures, lines corresponding to another cubic phase were observed, presumably NiO. NiCo$_2$O$_4$ electrodes at which oxygen had been evolved were analysed by the spectrometric diffraction method.

Table 3 presents the values of the interplanar $d$-spacings, the Miller indices ($hkl$) and the relative intensity (referred to the strongest line $I_1$, i.e. $2\theta = 46.6°$) of the
NiCo₂O₄ coatings as a function of $T_F$ and $t_F$, together with the ASTM data of NiCo₂O₄ and NiO. The X-ray diffraction patterns in the $T_F$ range below 400°C are characteristic of the NiCo₂O₄ spinel. The deviation in the measured relative intensity, which seems to increase with decreasing temperature $T_F$, can be attributed to preferred orientations.

The appearance of NiO at $T_F$ greater than 400°C is confirmed by the detection of the additional reflections at $2\theta$ equal to 49.0° ($d = 2.41$), 55.2° ($d = 2.09$) and 81.8° ($d = 1.48$). The values in parentheses in Table 3 are the relative intensity $I/I_1$ referred to the strongest line $I_1$ of the additional lines, i.e. $2\theta = 55.2°$. The X-ray data analysis is in agreement with the TGA diagram (Section II), and furthermore reveals that the decomposition of the NiCo₂O₄ spinel sets in at temperatures above 400°C, with the appearance of NiO. With Röntgen diffraction, no influence of the oxygen evolution reaction on the NiCo₂O₄ electrodes was detected.

The parameter of the lattice when it corresponds to the closest packing principle is equal to 0.8 nm [15]. The cell parameter of spinels is usually greater than that predicted by the packing density principle. The reported unit cell dimensions of NiCo₂O₄ can be in the range of 0.810–0.812 nm [9,10,16,17]. The lattice parameter or unit cell dimension $a_0$ was simply determined from the observed $d$-spacings for the planes (311) and (440) by making use of the cubic formula for the interplanar spacing $d$,

$$a_0 = d\sqrt{h^2 + k^2 + l^2}$$  \hspace{1cm} (2)

where $h$, $k$ and $l$ represent the Miller indices.

The unit cell dimensions determined from the Debye–Scherrer powder samples show a tendency to increase slightly (0.808–0.810 nm) in the $T_F$ range of 250–400°C. Above 400°C, a decrease in $a_0$ was noticed. No appreciable variation in the lattice constant as a function of $t_F$ was observed.

The lattice parameter of the coatings showed somewhat higher values, i.e. 0.810–0.812 nm, and more discrepancies in the temperature range below 400°C. The decrease in $a_0$ above 400°C was observed more clearly.

The observation of a decrease in $a_0$ values above 400°C in both cases, i.e. powder and coatings, might be related to the spinel decomposition. The difference in $a_0$ values in the $T_F$ range of the spinel-only phase is suggested to be a result of the difference in measuring technique.

(V) TEMPERATURE-PROGRAMMED REDUCTION

(V.1) Experimental

Temperature-programmed reduction (TPR) was applied to investigate the reduction behaviour of the oxide catalyst NiCo₂O₄. In this technique, hydrogen is passed continuously over the catalyst, while the temperature is raised linearly with time. By measuring the consumption of hydrogen, due to the reduction of species in the
catalyst, as a function of the applied temperature, a so-called reduction profile is obtained. The total hydrogen consumption during the reduction enables the stoichiometric composition of the oxide to be determined. The ratio \( \frac{H_2}{M} \) is a measure of the total hydrogen consumption, and expresses the average number of dihydrogen molecules required for the reduction of a metal ion (M) in the oxide. So, TPR allows the determination of the mean valency state of the metal ions in the oxide and, therefore, is of great value in the characterization of the catalyst.

The TPR apparatus has recently been described in detail by Boer et al. [18]; a schematic drawing is presented in Fig. 4. The hydrogen consumption was measured by a thermal conductivity detector (TCD) of the diffusion type. The TCD is very sensitive in detecting small changes in the concentration of \( H_2 \) in Ar because of the differences in thermal conductivity between the active phase, \( H_2 \), and the inert phase, Ar. The heating rate during all TPR experiments was 5 °C min⁻¹.

TPR experiments of supported and unsupported catalysts were carried out. \( \text{NiCo}_2\text{O}_4 \) and \( \text{Co}_3\text{O}_4 \) spinel oxides were prepared by thermal decomposition [1]. The supports used were \( \text{TiO}_2 \) (Anatase, Tioxide CLDD 1367, 19 m²/g) and Grace SiO₂ (SP 2-324-382, 290 m²/g). The \( \text{NiCo}_2\text{O}_4 \) catalyst was deposited on the supports by means of a standard pore-volume impregnation method: a known amount of an aqueous solution of \( \text{Ni(NO}_3\text{)}_2 \cdot 6 \text{H}_2\text{O} \) and \( \text{Co(NO}_3\text{)}_2 \cdot 6 \text{H}_2\text{O} \), mixed in stoichiometric amounts of 1:2, was added to the support. The samples were dried at a moderate temperature, and finally cured at \( T_F \) for 24 h to form the spinel oxide.

(V.2) Results and discussion

The TPR profiles of the unsupported \( \text{NiCo}_2\text{O}_4 \) (curve a) and \( \text{Co}_3\text{O}_4 \) (curves b and c) are shown in Fig. 5. Curve c is the TPR profile of commercial \( \text{Co}_3\text{O}_4 \) (Merck). The \( \frac{H_2}{M} \) values are given on the curves. The reduction profiles of \( \text{NiCo}_2\text{O}_4 \) and \( \text{Co}_3\text{O}_4 \) are similar. The reduction peaks are asymmetric and broad, indicating that various reducible species are present. It appears that the TPR of \( \text{NiCo}_2\text{O}_4 \) (curve a) takes place at lower temperatures than the reduction of \( \text{Co}_3\text{O}_4 \) (curve b) for both catalysts prepared under identical conditions.
This is most probably due to a difference in stability of the spinel oxides. It has been reported [10,19] that NiCo₂O₄ forms a "metastable" spinel structure, which breaks down already above 400 °C, while Co₃O₄ is stable up to 900 °C, as shown in the TGA curves in Section (II).

Two peak maxima are observed for both spinel oxides and suggest a two-stage process. Also the same stoichiometry is observed. The $H_2/M$ value indicates that the average oxidation state of the metal cation before reduction is 2.67+. Table 4 gives a comparison of the TPR characteristic features of the literature data and this work. Paryjczak et al. [20] have performed a TPR study on Co₃O₄ prepared by coprecipitation and Martens [21] has studied Co₃O₄ supported on TiO₂. Our results are in agreement with the literature data.
TABLE 4

TPR characteristic features of Co$_3$O$_4$ and NiCo$_2$O$_4$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak maxima $/^\circ$C</th>
<th>Peak area ratio</th>
<th>$H_2/M$</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co$_3$O$_4$ $^a$ ($T_F=400^\circ$C; $t_F=1$ h)</td>
<td>347 402</td>
<td>1:3</td>
<td>1.33</td>
<td>This work</td>
</tr>
<tr>
<td>Co$_3$O$_4$ (Merck) $^a$</td>
<td>336 371</td>
<td>1:3</td>
<td>1.33</td>
<td>This work</td>
</tr>
<tr>
<td>Co$_3$O$_4$ (coprecip.) $^a$</td>
<td>320 390</td>
<td>1:3</td>
<td>1.33</td>
<td>19</td>
</tr>
<tr>
<td>Co$_3$O$_4$/TiO$_2$ $^b$</td>
<td>315 413</td>
<td>1:3</td>
<td>1.33</td>
<td>20</td>
</tr>
<tr>
<td>NiCo$_2$O$_4$ $^a$ ($T_F=400^\circ$C; $t_F=1$ h)</td>
<td>288 348</td>
<td>1:3</td>
<td>1.35</td>
<td>This work</td>
</tr>
</tbody>
</table>

$^a$ Unsupported.

$^b$ Supported.

The first step in the TPR of Co$_3$O$_4$, i.e. $\text{Co}^{2+}[\text{Co}^{3+}]_2\text{O}_4$, is the reduction of Co$_3$O$_4$ to CoO and the second step is the reduction of CoO to metallic Co, as follows:

\[
\begin{align*}
\text{Co}_3\text{O}_4 + \text{H}_2 & \rightarrow 3 \text{CoO} + \text{H}_2\text{O} \quad H_2/M = 0.33 \\
3 \text{CoO} + 3 \text{H}_2 & \rightarrow 3 \text{Co} + 3 \text{H}_2\text{O} \quad H_2/M = 1.00 \\
\text{Co}_3\text{O}_4 + 4 \text{H}_2 & \rightarrow 3 \text{Co} + 4 \text{H}_2\text{O} \quad H_2/M = 1.33
\end{align*}
\]

From the observed peak ratio and the $H_2/M$ ratio, a similar course of TPR of NiCo$_2$O$_4$ can be proposed:

\[
\begin{align*}
\text{NiCo}_2\text{O}_4 + \text{H}_2 & \rightarrow \text{NiO} + 2 \text{CoO} + \text{H}_2\text{O} \quad H_2/M = 0.33 \\
\text{NiO} + 2 \text{CoO} + 3 \text{H}_2 & \rightarrow \text{Ni} + 2 \text{Co} + 3 \text{H}_2\text{O} \quad H_2/M = 1.00 \\
\text{NiCo}_2\text{O}_4 + 4 \text{H}_2 & \rightarrow \text{Ni} + 2 \text{Co} + 4 \text{H}_2\text{O} \quad H_2/M = 1.33
\end{align*}
\]

The reduction of the unsupported Co$_3$O$_4$ and NiCo$_2$O$_4$ takes place in two not clearly separated peaks. However, in the case of Co$_3$O$_4$ supported on TiO$_2$ [21], two clearly separated peaks were observed with $H_2/M$ ratios of 0.33 vs. 1.00, which led to the two-step reduction model. Figure 6 presents the TPR profile of 7.15 wt% NiCo$_2$O$_4$/TiO$_2$ for different calcination temperatures $T_F$, i.e. 300 and 400°C.

The two reduction peaks are now completely separated, and the start of the reduction, i.e. the first reduction maximum, takes place at temperatures lower than those in the case of the unsupported catalyst. This can be explained as a consequence of the particle size and distribution. It can be assumed from the properties of the supporting material that the NiCo$_2$O$_4$ particles of the supported catalyst are smaller and more uniform in size, whereas the unsupported particles are greater and have a less uniform particle size distribution. Similar particles have a relatively higher surface area, and thus relatively more surface defects where the reduction can start. The reduction of NiCo$_2$O$_4$ supported on SiO$_2$ also takes place in two separated peaks, and at temperatures lower than those for NiCo$_2$O$_4$/TiO$_2$. This is in accordance with the line of reasoning described above. The expected particle size on SiO$_2$ (290 m$^2$ g$^{-1}$) will be smaller than that on TiO$_2$ (19 m$^2$ g$^{-1}$). However, it was
reported [20] that for Co$_3$O$_4$ supported on silica or alumina, the reduction takes place at higher temperatures. This was ascribed to an interaction between the active phase, the oxide and the support material. Our results indicate that there is no interaction between the NiCo$_2$O$_4$ catalyst, and SiO$_2$ or TiO$_2$. The compounds, i.e. nickel and cobalt titanates or silicates, responsible for the interaction are probably formed only at higher temperatures ($T_F$ was 400°C maximum).

However, complete reduction of the supported NiCo$_2$O$_4$ takes place at higher temperatures than for the unsupported NiCo$_2$O$_4$ powders.

It can be assumed that the second stage in the reduction of the unsupported sample is faster because of the earlier presence of a metallic phase.

The total hydrogen consumption of the first vs. the second reduction peak is in the ratio of 1 to 3. The $H_2/M$ value of 1.33 indicates that the stoichiometric oxide NiCo$_2$O$_4$ is formed and thus can be represented by the general formula $M^{2+}M^{3+}_3O_4$. If, instead of NiCo$_2$O$_4$, NiO and Co$_3$O$_4$ had formed on the support, the $H_2/M$ value would have been 1.22, which is substantially different from the observed value. It is, however, not possible to determine the individual oxidation states of Ni and Co in NiCo$_2$O$_4$.

The ratios of the $H_2/M$ values of both reduction peaks indicate a two-stage reduction. This mechanism assumes that no metallic phase is formed in the first reduction peak. This supposition was investigated in the next experiment. NiCo$_2$O$_4$/TiO$_2$ was reduced in a first TPR (Fig. 7, curve b) until the temperature of this first TPR was 280°C, which is the minimum in the hydrogen consumption between the two peaks (cf. Fig. 7, curve a). At this temperature, the reactor was flushed with argon and cooled down quickly to 25°C. The partly reduced oxide was then reduced in a second TPR run to 600°C (curve c). The reduction peak in the
second TPR coincides with the second peak of a TPR profile without interruption (curve a). It is known that in the presence of a metallic phase the reduction already starts at lower temperatures when the metallic phase is able to absorb hydrogen dissociatively. However, no shift of the second peak towards lower temperatures was observed. This experiment was also carried out for Co$_2$O$_4$ by Paryjczak et al. [20], who found that in the first TPR peak practically no metallic phase was formed (4% metal).

The influence of the temperature $T_F$, and the duration time $t_F$ of the final heat treatment of NiCo$_2$O$_4$ on the TPR profile is shown in Fig. 8. A shift of the reduction peaks towards higher temperatures as a function of increasing $T_F$ and $t_F$ is observed.

For $T_F \geq 300^\circ$C, the $H_2/M$ ratio approaches the value of 1.33. The stoichiometric composition of $M^{2+}M^{3+}O_4$ is reached for NiCo$_2$O$_4$ with a mean cation valency of 2.67+. The increase of the $H_2/M$ ratio at lower $T_F$ is due to the increase in non-stoichiometry of NiCo$_2$O$_4$, as indicated by TGA in Section (II). Although the oxidation state of NiCo$_2$O$_4$ oxide is approximately the same above 300$^\circ$C ($T_F$), the reducibility is different, as shown by the TPR profiles. The TPR curve appears to depend on the heat treatment. The reduction peaks are less separated at higher $T_F$ and $t_F$. The changes in the TPR profiles are attributed to the changes in particle size and stability. The influence of the particle size was discussed above. The temperature at which the reduction starts increases with increasing $T_F$ and $t_F$, and thus with decreasing surface area. This is corroborated by the BET surface area data, as
Fig. 8. TPR profiles of NiCo$_2$O$_4$ catalysts.

<table>
<thead>
<tr>
<th>Curve</th>
<th>Heat treatment</th>
<th>BET surface area /m$^2$ g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>250 $^\circ$C</td>
<td>10/h</td>
</tr>
<tr>
<td>b</td>
<td>300 $^\circ$C</td>
<td>1/h</td>
</tr>
<tr>
<td>c</td>
<td>300 $^\circ$C</td>
<td>24/h</td>
</tr>
<tr>
<td>d</td>
<td>400 $^\circ$C</td>
<td>1/h</td>
</tr>
<tr>
<td>e</td>
<td>400 $^\circ$C</td>
<td>24/h</td>
</tr>
</tbody>
</table>

reported in Fig. 2. On the other hand, it can be assumed that the stability of the NiCo$_2$O$_4$ phase increases with $T_F$, resulting in a decrease in the reducibility. So the reducibility of NiCo$_2$O$_4$ decreases with increasing $T_F$ and $t_F$. 


X-Ray photoelectron spectroscopy (XPS), also referred to as electron spectroscopy for chemical analysis (ESCA), and Auger electron spectroscopy (AES) were used to characterize and determine the composition of the surface of NiCo$_2$O$_4$ anodes as a function of the temperature of the final heat treatment ($T_F$). One of the major problems in the crystal chemistry of mixed oxide spinels is the determination of the valence state and the distribution of the cations among the octahedral and tetrahedral sublattices of the spinel structure, especially if two different metals are present, each of which can adopt more than one valence state. The binding energies and the satellite structure of the XPS photoelectron lines are indicative of the Ni and Co valence states in the charge distribution of NiCo$_2$O$_4$.

Auger electron and X-ray photoelectron spectra were recorded on a PHI 550 XPS/AES spectrometer equipped with a magnesium anode ($h\nu = 1253.6$ eV), an electron gun and a double-pass cylindrical mirror analyser. A PDP 11-04 computer interfaced with the spectrometer enabled signal handling to be carried out. The total pressure during the measurements in the spectrometer did not exceed $1 \times 10^{-9}$ Torr. The XPS analyser was calibrated frequently and carefully with a gold sample (Au$_4$f$_{7/2}$ at 83.8 eV). The C1s binding energy of contamination carbon was used for the internal calibration. No shift of the C1s line (284.6 eV) was observed, which indicates that no sample charging occurs. The reproducibility of the binding energy values was within 0.25 eV.

![Fig. 9. XPS spectrum of a freshly prepared NiCo$_2$O$_4$ electrode. $T_F = 300$°C and $t_F = 1$ h.](image)
The XPS survey scan for a freshly prepared NiCo$_2$O$_4$ electrode [1] is shown in Fig. 9. The survey scan is sufficient for the identification of all detectable elements present. Of course, predominantly the Ni$2p$, Co$2p$ and O$1s$ photoelectron lines are observed in this wide range spectrum. The carbon contamination C$1s$ line is also observed.

The XPS concentrations of the various constituents were determined by measuring the peak area of the main photoelectron lines and by utilizing the atomic sensitivity factors, as presented by Wagner et al. [22]. This approach is satisfactory for quantitative work, except in the case of transition metal spectra with prominent shake-up lines. Therefore, the entire $2p$ region of nickel and cobalt, i.e. $2p_{1/2}$ and $2p_{3/2}$, was used when peak areas were measured. A generalized expression for the determination of the atom fraction of any constituent in a sample $C_x$ can be written as

$$C_x = \frac{n_x}{\sum n_i} = \frac{I_x}{\sum I_i}$$

where $n$ is the number of atoms of the element per cm$^3$ of sample. $I$ is the number of photoelectrons per second in a specific spectral peak and $S$ is defined as the atomic sensitivity factor. The use of atomic sensitivity factors will normally furnish semiquantitative results (within 10–20%).

The surface compositions of NiCo$_2$O$_4$ electrodes, determined by XPS measurements as described above, are given in Table 5 for electrodes prepared freshly at temperatures $T_F$ of 300 and 400°C, and for an electrode prepared at $T_F = 300^\circ$C, which was aged by previously subjecting it to oxygen evolution. For freshly prepared NiCo$_2$O$_4$ electrodes, it appears that with lowering $T_F$, the Ni:Co ratio changes: the nickel concentration decreases while the cobalt content increases. Generally, it was found that the measured Ni:Co ratio (vs. nickel) for $T_F$ equal to 400°C varied between the ratios 1.0:1.0 and 1.0:1.4, whereas for $T_F$ equal to 300°C the ratio varied between 1.0:2.0 and 1.0:2.6.

The surface composition of the NiCo$_2$O$_4$ electrode changed after oxygen evolution at 0.5 A cm$^{-2}$ for 24 h, as can be seen in Table 5: the nickel and cobalt concentrations decreased and the oxygen content increased. From this experiment it

<table>
<thead>
<tr>
<th>Materials</th>
<th>Elements/atom %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
</tr>
<tr>
<td>NiCo$_2$O$_4$ (theor.)</td>
<td>14.3</td>
</tr>
<tr>
<td>NiCo$_2$O$_4$ 400°C for 1 h</td>
<td>21.4</td>
</tr>
<tr>
<td>NiCo$_2$O$_4$ 300°C for 1 h</td>
<td>12.3</td>
</tr>
<tr>
<td>NiCo$_2$O$_4$ 300°C for 1 h (after 24 h, 0.5 A cm$^{-2}$)</td>
<td>8.8</td>
</tr>
</tbody>
</table>
is not clear whether the change is due to nickel or cobalt dissolution or whether it has to be attributed to an increase in oxygen species on the surface.

Summarizing, a considerable variation in the composition of the surface of freshly prepared NiCo$_2$O$_4$ electrodes was observed. Also, it was found that with increasing $T_F$, the surface composition deviates more from the theoretically expected one.

However, one must be aware that the experimental conditions of the XPS analysis can influence the quantitative results. Since XPS is a surface-sensitive method, which is performed under vacuum, in situ redox processes and hence surface decomposition of the NiCo$_2$O$_4$ sample can be induced by the X-ray radiation and the low partial oxygen pressure in the spectrometer, resulting in a change of the surface composition. On the one hand, surface enrichment or depletion of certain metal ions can take place, and on the other hand, a reduction of the sample would change the valence state of the metal ions. A study of the influence of the variation of the oxygen pressure in the spectrometer, and of the power of the X-ray source would give more evidence about these phenomena.

In view of the accuracy of the XPS analysis, it is not possible to make accurate quantitative analyses. Therefore, in the case of this study, the approach is useful for obtaining results in terms of orders of magnitudes. It can be concluded that lowering $T_F$ tends to lead to Co enrichment and Ni depletion of the surface.

![Fig. 10. Auger profile distribution of the elements in a fresh NiCo$_2$O$_4$ layer prepared at 300°C ($T_F$) for 1 h ($t_F$).](image)
Furthermore, it confirms that the surface composition is influenced by the temperature $T_F$, as indicated earlier by the voltammetric behaviour (see Part I) [2].

Auger spectroscopy was used to investigate the depth profile of the elements in
Fig. 11. Detailed scan of the XPS spectrum of a NiCo$_2$O$_4$ electrode. $T_F = 400^\circ$C and $t_F = 1$ h. (a) Ni$2p$ spectrum; (b) Co$2p$ spectrum; (c) Ni$3s$ and Co$3s$ spectra; (d) Ni$3p$ and Co$3p$ spectra.
the NiCo$_2$O$_4$ layer. Depth profiling was accomplished by sputtering the surface with argon ions. The distribution of the elements as a function of depth into the specimen (sputtering time) is shown in Fig. 10 for NiCo$_2$O$_4$ prepared at $T_F = 300^\circ$C. It appears that the nickel content increases with increasing sputtering time, whereas the cobalt and oxygen concentrations decrease slightly. However, one must remember that the experimental conditions can influence the AES analysis in a similar way, as mentioned earlier.

The detected carbon contamination in Fig. 10 is negligible compared to the values in Table 5. In the XPS experiments the detected carbon content varied significantly for NiCo$_2$O$_4$ electrodes prepared under similar conditions. Since the samples exhibit the carbon 1s peak in different quantities, we are inclined to believe that it is due to experimental conditions, i.e. C contamination in the spectrometer, and not due to the NiCo$_2$O$_4$ oxide sample preparation.

Some detailed spectra of the metal photoelectron lines are given in Fig. 11 and the binding energies (BE) for Co$_2p_{3/2}$, Co$_3p_{3/2}$, Co$_3s$, Ni$_2p$, Ni$_3p_{3/2}$, Ni$_3s$ and O$_{1s}$ are given in Table 6. No influence of the temperature $T_F$, i.e. 300 vs. 400$^\circ$C, on the spectral characteristics is observed. The Ni$_2p$ spectrum (curve a) of NiCo$_2$O$_4$ shows a prominent satellite structure and the Co$_2p$ spectrum (curve b) shows a weak satellite band. No satellite lines are observed in the Ni$_3s$ spectrum (curve c). The Ni$_3p$ spectrum (curve d), consisting of 3$p_{3/2}$ and 3$p_{1/2}$, shows an asymmetrical line with a weak satellite band. No satellite bands can be distinguished in the Co$_3s$ (curve c) and Co$_3p$ spectra (curve d), the adjacent Ni$_3s$ and Ni$_3p$ lines, respectively, can mask them.

XPS provides the ability to obtain information on chemical states from the variation in binding energy or chemical shifts of the photoelectron lines. Since the core levels of atoms may shift because of valence changes and different crystallographic sites, the splitting of core levels is direct proof of the presence of inequivalent atoms [23]. Unfortunately, it is not always possible to find separate peaks if the shifts are too small, as seen, for example, for the Co$^{2+}$ and Co$^{3+}$ states in Co$_3$O$_4$ [24]. In general, the binding energy of core levels shifts about 1 eV, through a change of the ionic charge of an atom by one unit, under the assumption that no other effects, such as covalency, are interfering. As the ligands are oxygen atoms for both lattice sites, covalency effects are supposed to have only a minor effect, and the

TABLE 6

<table>
<thead>
<tr>
<th>Electron binding energies (in eV) for NiCo$_2$O$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$<em>2p</em>{3/2}$</td>
</tr>
<tr>
<td>855.2</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Co$<em>2p</em>{3/2}$</td>
</tr>
<tr>
<td>779.85</td>
</tr>
</tbody>
</table>

* $\Delta$ is the difference in BE of the $(2p_{1/2} - 2p_{3/2})$ lines and gives the position of the $2p_{1/2}$ line.
TABLE 7

Core level energies (in eV) of nickel

<table>
<thead>
<tr>
<th>Compound</th>
<th>$2p_{3/2}$</th>
<th>FWHM</th>
<th>$3p_{3/2}$</th>
<th>FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiCo$_2$O$_4$</td>
<td>855.9</td>
<td></td>
<td>861.3</td>
<td></td>
</tr>
<tr>
<td>Ni$<em>2$0$</em>{3/2}$</td>
<td>862.1</td>
<td></td>
<td>863.0</td>
<td></td>
</tr>
</tbody>
</table>

core levels $M^{2+}$ and $M^{3+}$ ($M = \text{Ni or Co}$) must be distinguishable. Comparison of Ni$_2p_{3/2}$ of NiCo$_2$O$_4$ with those for Ni$^{2+}$ or Ni$^{3+}$ in other oxides [25], as given in Table 7, provides an indication that in NiCo$_2$O$_4$ nickel is present as a divalent ion. The Ni$_2p_{3/2}$ and $3p$ spectrum shows a broadening of the lines as indicated by the full width at half minimum (FWHM) values given in Table 8, compared to that of other spinel oxides. This may be caused by the presence of another valence state. However, the formal oxidation state of cobalt appears to have little influence on the metal binding energies of Co compounds. The absence of any obvious relationship between the formal oxidation state of the Co metal and the metal binding energy has already been noted for Co oxides by McIntyre and Cook [27].

Figure 12 shows the O$_{1s}$ spectrum of a freshly prepared NiCo$_2$O$_4$ electrode and after oxygen evolution. The O$_{1s}$ spectrum for NiCo$_2$O$_4$ exhibits two peaks, one at 529.3 eV and a shoulder at about 530.7 eV.

Contradictory opinions have been reported as to the interpretation of the various O$_{1s}$ peaks which, for example, appear in the Ni–O [28–32] and Co–O [31–34] systems. It may be expected that not only lattice oxygen ions O$^{2-}$, but also chemisorbed species O$_2$, O$_2^-$ and O$^-$ oxygen in other chemisorbed molecules such as $\text{H}_2\text{O}$, $\text{CO}$, $\text{CO}_2$, etc., as well as surface and bulk hydroxides, could appear in the form of separate peaks.

The peak corresponding to the smaller binding energy, i.e. 529.3 eV, can be assigned to lattice oxygen ions O$^{2-}$. It was reported [27] that, in general, oxides of related metals which have identical crystallographic structures have very similar O$_{1s}$ binding energies. It appears that the lattice oxygen O$_{1s}$ binding energy of NiCo$_2$O$_4$ is about 0.6 eV lower with respect to that of the inverse spinel oxides NiFe$_2$O$_4$ and CoFe$_2$O$_4$ [27] and about 0.2 eV lower with respect to that of the normal spinel Co$_3$O$_4$ [32]. An empirical relationship between the O$_{1s}$ binding energy of the lattice oxygen and the valence state of the cation in oxides of the first transition metal.

TABLE 8

$\text{Ni}2p_{3/2}$ and $3p_{3/2}$ levels and FWHM for nickel spinels (in eV)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$2p_{3/2}$</th>
<th>FWHM</th>
<th>$3p_{3/2}$</th>
<th>FWHM</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$<em>{0.5}^{2+}$Mn$</em>{0.5}^{4+}$[Ni$<em>{0.2}^{2+}$Mn$</em>{0.8}^{4+}$Mn$_{0.4}^{4+}$]O$_4$</td>
<td>855.0</td>
<td>2.0</td>
<td>67.1</td>
<td>2.5</td>
<td>26</td>
</tr>
<tr>
<td>Zn$^{2+}$[Ni$^{2+}$Mn$^{4+}$]O$_4$</td>
<td>855.1</td>
<td>2.0</td>
<td>66.9</td>
<td>2.0</td>
<td>26</td>
</tr>
<tr>
<td>NiCo$_2$O$_4$</td>
<td>855.0</td>
<td>2.6</td>
<td>67.5</td>
<td>4.0</td>
<td>This work</td>
</tr>
</tbody>
</table>
series has been proposed by Haber et al. [32]. They reported that the O1s binding energy of Co$_3$O$_4$ indicated a mean valence state of the cations of 2.66+. However, it does not predict the expected mean valence state 2.66+ when we apply it to other mixed inverse spinels such as NiFe$_2$O$_4$, CoFe$_2$O$_4$ and NiCo$_2$O$_4$. Thus, no simple relationship exists between the binding energy of the O1s photoelectron line and the chemical state.

The peak at higher binding energy is probably due to surface hydroxyl groups. Figure 12 shows the influence of oxygen evolution at a current density of 0.5 A cm$^{-2}$ for 24 h in 5 M KOH on the O1s photoelectron line. An increase of the O1s peak at higher binding energy is observed, which indicates hydroxyl oxygen. Also, some potassium was detected on the surface by the appearance of the K$_2$P$_{3/2}$ photoelectron line.

Sometimes evidence for certain valencies can be obtained from the presence of satellites, or multiplet splitting in the spectra.

In the Ni2$p$ region of NiCo$_2$O$_4$ a prominent satellite band was observed, as shown in Fig. 11a, like that in NiO, Ni(OH)$_2$ and NiFe$_2$O$_4$ [27]. The satellite shoulder on the 2$P_{3/2}$ line, as seen for NiO, does not occur. The prominent satellite structure in the Ni3$s$ spectral region, which has been observed for NiO and Ni(OH)$_2$, is not seen for NiCo$_2$O$_4$, as for NiFe$_2$O$_4$ [27]. Only weak satellite lines are seen next to the 2$P_{3/2}$ line in the Co2$p$ spectrum.

![Fig. 12. O1s spectrum of NiCo$_2$O$_4$ prepared at $T_f$ = 300°C and $t_f$ = 1 h. Freshly prepared NiCo$_2$O$_4$: (- - -) after oxygen evolution at 0.5 A cm$^{-2}$ for 24 h in 5 M KOH.](image-url)
The appearance of shake-up satellite lines near the M2p core lines (M = Ni or Co) was shown to depend on the paramagnetism or diamagnetism of the compound [35, 37]. Frost et al. [35,36] have shown that high-spin Co^{2+} compounds have intense satellite bands associated with the 3s and 2p lines, while satellite lines for the low-spin Co^{3+} compounds are weak or missing.

The Co2p spectrum of NiCo2O4 shows an intermediate case. The intensity of the satellite structure indicates a mixture of Co^{2+} and mainly Co^{3+}.

Because of the absence of a strong shake-up satellite in the 2p spectrum, cobalt is mainly present as diamagnetic Co^{3+} ions in a low-spin state [38,39]. Furthermore, the Co2p spectrum reveals a weak shake-up satellite due to paramagnetic divalent high-spin cobalt. This is comparable with the mixed valence cobalt spinel oxide, i.e. Co^{2+} [Co^{3+}]_2O_4, which also shows only weak satellite lines in the Co2p spectrum [32]. Thus, it is possible to identify the presence of low-spin Co^{3+} and high-spin Co^{2+} on the basis of the satellite structure. The appearance of Co^{2+} may be caused by the reduction of Co^{3+} ions under the experimental conditions in the spectrometer.

(VII) CONCLUSIONS

From the TGA results, it can be suggested that non-stoichiometric NiCo2O4 spinel oxide is already formed at about 275°C, which is stable up to about 400°C, i.e. the stoichiometric composition. The weight loss above 400°C indicates the start of the breakdown of the NiCo2O4 spinel structure.

The BET experiments show the effect of the temperature T_F and duration time t_F of the final heat treatment on the surface area.

The X-ray data are in agreement with the TGA diagram and furthermore reveal that the decomposition of NiCo2O4 spinel oxide indeed sets in at temperatures above 400°C, with the appearance of NiO.

The TPR data indicate that the average oxidation state of the metal cation in NiCo2O4 before reduction is 2.67+ and that a stoichiometric oxide is formed which can be presented by the general formula M^{2+}M^{3+}_2O_4. Furthermore, at lower T_F an increase in non-stoichiometry of NiCo2O4 takes place, as indicated by TGA.

Summarizing, the NiCo2O4 XPS spectra can be distinguished from the individual nickel and cobalt oxides and they show some resemblance to those of similar mixed-valence spinel oxides, i.e. Co_3O_4, CoFe_2O_4 and NiFe_2O_4. Furthermore, the influence of the temperature T_F on the surface composition has been demonstrated.

The presence of divalent nickel has been proposed on the basis of the binding energy of the Ni2p_3/2 photoelectron line, and of Co as mainly diamagnetic Co^{3+} in a low-spin state and paramagnetic divalent high-spin cobalt, based on the satellite structure.
ACKNOWLEDGEMENTS

The authors are grateful to ir. J. Martens of the Eindhoven University of Technology (THE) for recording the TPR spectra and useful discussions, and to Dr. ir. V.A.M. Brabers (THE) for discussions on the interpretation of the XPS and Auger results. The BET experiments were carried out by the group of Professor J. Scholten at the Department of Chemical Technology, Delft University of Technology. The TPR experiments were carried out by the group of Professor R. Prins at the Department of Inorganic Chemistry, Eindhoven University of Technology.

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