Oxygen evolution on $NiCo_2O_4$ electrodes

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$NiCo_2O_4$ was investigated as anode material for alkaline water electrolysis. This catalyst was prepared by thermal decomposition of metal salts and this rapid and simple technique gives reproducible results. A study of the preparation parameters shows that factors such as decomposition temperature, duration of the heat treatment and catalyst loading, determine the morphology of the oxide layer and so influence the performance of the catalyst. The conductivity of the oxide layer was found to change markedly with the final heat treatment.

It is shown that alternative Teflon-bonded $NiCo_2O_4$ electrode structures give approximately the same activity.

1. Introduction

The oxygen evolution reaction during water electrolysis is of special interest, because of its high anodic overvoltage. The main cause of efficiency losses is the low electrocatalytic properties of the present anode materials. A good anode material should have a high exchange current density (i_0) and a low Tafel slope (b).

Recent research into developing new anode materials has been mainly directed to the use of transition metal oxides. One of the most promising materials in an alkaline electrolyte is the spinel oxide $NiCo_2O_4$ which is, moreover, a cheap electrode material. A review of $NiCo_2O_4$ and other spinels has been given by Trasatti and Lodi [1]. Many papers have been devoted to a study of the kinetics of these materials [2–7] and different preparation techniques have been used, e.g. thermal decomposition [5, 8], cryochemical synthesis [3, 4, 8] and coprecipitation [4, 8]. Sometimes an effect of the substrate (Pt or Ni) has been noticed [2]. Tseung *et al.* [3] have investigated the use of Teflon-bonded $NiCo_2O_4$ electrodes and found an increased electrochemical activity. Singh *et al.* [5], on the other hand, noticed that non Teflon-bonded electrodes have higher activity and stability than Teflon-bonded systems; moreover, the Teflon incorporation influences the gas bubble evolution and this also affects the anodic behaviour.

Comparison of the results of various authors is difficult because of different preparation techniques which result in differences in porosity and hence surface area. Furthermore, the various conditions for the deposition of the $NiCo_2O_4$ layer on the substrate appear to have a large influence on its activity and, moreover, discrepancies are evident in the way the iR-drop is corrected. Therefore a systematic study was carried out to establish the kinetic parameters of the oxygen evolution reaction at $NiCo_2O_4$ electrodes with the emphasis on the preparation technique. The thermal decomposition method was chosen because it results in electrodes of high mechanical stability and this preparation technique is an easy and rapid one. Furthermore, with this technique both Teflon- and nonTeflon-bonded electrodes can be prepared, whereas with $NiCo_2O_4$ prepared via cryochemical synthesis (freeze drying followed by decomposition in vacuum) or coprecipitation, only Teflon-bonded electrodes can be made. In this work the optimum deposition conditions for thermal decomposition were determined and the anodic performance of Teflon-bonded and nonTeflon-bonded $NiCo_2O_4$ electrodes were compared.

2. Experimental details

2.1. *Electrode preparation*

2.1.1. Preparation of porous NiCo₂O₄ electrodes.
All porous $NiCo_2O_4$ electrodes used in this study
were prepared by thermal decomposition on a
substrate. In principle, the preparation method
was as follows. $Ni(NO_3)_2 \cdot 6H_2O$ and $Co(NO_3)_2 \cdot$
$6H_2O$, mixed in stoichiometric amounts, were
dissolved in water or alcohol. A nickel screen of
30 mesh was spot-welded to a nickel wire. After
cleaning it was preheated for 3–5 min in an oven
at T_F° C (T_F = temperature of the final heat
treatment). The nickel screen was dipped into the
solution of the nitrates, dried in hot air to remove
the solvent before decomposition, and heated in
the oven at T_F° C for 3–5 min to decompose the
nitrates. This process was repeated until the
desired loading had been reached. The electrode
was then finally cured at T_F° C for t h to complete
the thermal decomposition.

2.1.2. Preparation of Teflon-bonded NiCo₂O₄
electrodes. In order to compare the Teflon-bonded
and nonTeflon-bonded electrode structure, the
same preparation method as that for the $NiCo_2O_4$
catalyst, namely, thermal decomposition, was used
for both electrode structures.

The Teflon-bonded electrodes were prepared
by mixing the appropriate amounts of Teflon
(Teflon 30 N Dupont or Teflon powder 0.3–
0.5 μ) and $NiCo_2O_4$ catalyst in a small bottle,
and dispersing in an ultrasonic bath. The resulting
mixture was painted onto the nickel gauze. The
electrode was then dried in hot air and finally
cured in air in an oven at 300° C for 1 h.

The $NiCo_2O_4$ catalyst was prepared according
to two variants. In the first [9, 10], the two
nitrates, $Ni(NO_3)_2 \cdot 6H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$
were weighed in the exact proportion Ni:Co =
1:2 and dissolved in water. The solution was
evaporated to dryness until there were no more
NO_2 fumes. The black powder was heated in an
electric furnace in air for t h at temperature T_F.
In the second variant, the $NiCo_2O_4$ catalyst
material was scraped from the nickel carrier of
porous $NiCo_2O_4$ electrodes, prepared as given in
Section 2.1.1.

2.2. *Physical characterization*

An X-ray pattern of the samples was obtained
using Mo$K\alpha$ or Fe$K\alpha$ radiation and compared
with ASTM data for nickel cobalt oxide. Thermo-
gravimetric analysis was applied to study the
course of the decomposition as a function of
temperature with a Mettler Thermoanalyzer 2.

2.3. *Electrochemical characterization*

All experiments were performed in a thermo-
statted (25° C), three-compartment Pyrex glass
cell containing 5 M KOH, prepared from Merck
potassium hydroxide PA and double distilled
H_2O. A piece of 7 × 2.5 cm platinum foil was
used as the counter electrode and the potential
of the working electrode was measured against
the reversible hydrogen electrode (RHE) or the
mercury(II) oxide electrode (Hg/HgO, 5 M KOH;
0.926 V vs. RHE, 25° C), via a Luggin capillary
close to the working electrode.

To determine the electrocatalytic activity
steady-state galvanostatic measurements were
carried out. The electrodes were firstly subjected
to anodic polarization for 30 min to 2 h at the
highest current densities to be studied, to ensure
the presence of higher oxides on the surface.
The potentials were measured with decreasing
current densities. The time between each reading
was 5 min. The time required to reach steady-
state was in all cases within 2 min, and usually
within 1 min. The ohmic potential drop between
the tip of the Luggin capillary and the working
electrode was measured by the current interruptor
technique [11].

3. Results and discussion

3.1. *Preparation parameters*

The following parameters were investigated:
temperature of the thermal decomposition,
duration of the final heat treatment, catalyst
loading, number of coatings, type of anion in the
metal salts, solvent and support material.

3.1.1. Influence of the decomposition temperature
and duration of the heat treatment. In order to
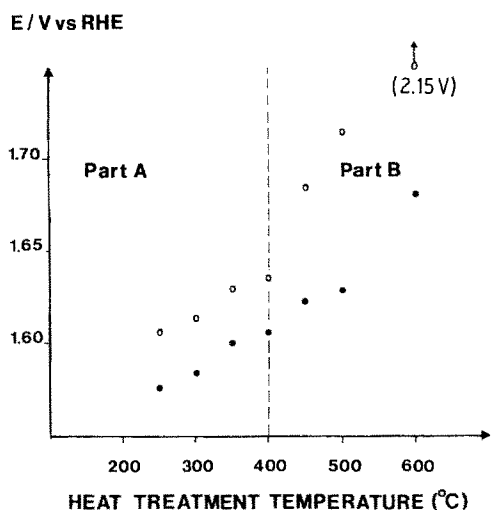investigate the effect of the heat treatment on

E / V vs RHE

Fig. 1. Effect of the temperature of the final heat treatment on the anodic performance of NiCo$_2$O$_4$ electrodes for oxygen evolution at 200 mA cm^{-2} in 5 M KOH, 25°C. ● – 200 mA cm^{-2} (iR-corrected); ○ – 200 mA cm^{-2} (not iR-corrected).

Heat treatment T_F (°C)/t (h)	Catalyst loading (mg cm^{-2})
250/1	20.85
300/1	18.65
350/1	20.40
400/1	17.70
450/1	14.20
500/1	18.95
600/1	17.35

both the electrocatalytic activity and the mechanical stability of the deposit, the temperature and duration of heat treatment was studied. The temperature range between 250 and 600° C was examined whilst the time of heat treatment was varied between 15 min and 100 h. Although there is a possibility of segregation of the individual oxides NiO and CoO during decomposition, the spinel structure could be confirmed for all the electrodes by X-ray analysis in the temperature range 250–400° C. With temperatures above 400° C and longer time of heat treatment, lines corresponding to a cubic phase, presumably NiO, appeared. The thermogravimetric diagram for NiCo$_2$O$_4$ is in agreement with X-ray analysis for NiCo$_2$O$_4$ and reveals furthermore that the decomposition of the

NiCo$_2$O$_4$ spinel sets in at temperatures above 400° C. These results are in agreement with those obtained by other authors [8, 12, 13].

3.1.1.1. Decomposition temperature. Fig. 1 shows the effect of the temperature of the heat treatment on the anodic performance of NiCo$_2$O$_4$ for oxygen evolution at 200 mA cm^{-2} (iR-corrected). Lowering the temperature of the final treatment leads to an increase in the electrochemical activity of the catalyst. Actually, the figure can be divided into two parts. In the spinel-only area (Part A: below 400° C), the oxygen overvoltage decreases with decreasing temperature of heat treatment. In Part B (above 400° C), where the decomposition of the spinel structure starts, the oxygen overvoltage increases faster with increasing temperature T_F. From the data without iR-drop correction and with iR-drop correction it appears that the resistance of the oxide layer increases because of the breakdown of the NiCo$_2$O$_4$ spinel structure.

However, the heat treatment temperature of 250° C at a duration of 1 h appears insufficient to complete the decomposition and, consequently, the mechanical stability was not satisfactory since the electrode tends to shed the NiCo$_2$O$_4$ oxide layer: nearly half of the catalyst loading was lost. The stability of the other electrodes was good. No visible damage was observed.

The surface morphology of the NiCo$_2$O$_4$ layer was found to be dependent on the preparation temperature. Visual and microscopic observation of the NiCo$_2$O$_4$ electrodes indicate that the roughness factor increases with decreasing temperature. Our results are in agreement with the work of Tamura et al. [14, 15], who observed the same tendency for Co$_3$O$_4$ electrodes also prepared by thermal decomposition. The difference in oxygen overvoltage can be ascribed partly to the change in the roughness factor. Many authors suggest the existence of a relation between high surface area and low oxygen overvoltage. This is in contradiction with the observation of Tseung et al. [4, 8] who conclude that there is no correlation between the surface area and the electrochemical performance and who suggest that for maximum activity the formation of a meta-stable spinel on the point of losing its oxygen is required.

Table 1. Effect of the duration of the final heat treatment on the magnitude of the iR-drop (at the same Luggin capillary-to-working electrode distance) given as: iR (temperature T_F (°C), duration (h)/iR (300°C, 1 h)

Temperature of the heat treatment (°C)	Duration of the heat treatment (h)				
	1	5	10	24	100
250	1	–	1	–	–
300	1	1	1	1	1
400	1	1.5–2	2	2	> 2
450	2	–	2–3	–	–
500	> 3	–	–	–	–
600	–	20	–	–	–

3.1.1.2. Duration of the heat treatment. The duration of the heat treatment, which was varied between 15 min and 100 h, gave no significant changes in activity for *iR*-corrected results in the temperature range up to 400° C.

However, the conductivity changes with the final heat treatment, as shown in Table 1, for all temperatures from 400° C on. Because the conductivity of the oxide layer seems to decrease with increasing duration of the heat treatment, it is advisable to restrict the duration. It has been established [8, 12, 13] that with an increase in temperature and duration of the heat treatment, above 400° C, a cubic phase, presumably high resistance NiO, appears due to the decomposition of the spinel structure; consequently, we might expect a decrease in conductivity. It is, however, noted here that at the same Luggin capillary-to-working electrode distance the measured *iR*-drop increases for prolonged 400° C heat treatment; the powder X-ray patterns, however, confirmed the spinel structure. The *iR*-drop for the 400° C –

1 h heat treatment is nearly the same as for the $NiCo_2O_4$ electrodes prepared in the temperature range 250–350° C which did not change with increasing duration of heat treatment. The lower limit of detection with the Debye–Scherrer (DS) powder X-ray diffraction method is about 5%, so some NiO might be present in the layer after treatment at 400° C. However, the magnitude of the *iR*-drop for the 450° C treatment is not larger (in which case a cubic phase is definitely detected).

The lack of knowledge of the magnitude of the ohmic drop can give rise to misleading conclusions. The *iR*-corrected results show nearly the same electrocatalytic activity for the 400° C series, but the electrode resistance increases when the duration increases.

3.1.2. Influence of the number of coatings and catalyst loading.

3.1.2.1. Concentration of the dipping solution. Firstly, the concentrations of the mixed nitrates in water was varied, in a constant stoichiometric ratio of Ni: Co = 1:2. Table 2 shows, for the same catalyst loading, the effect of the concentrations of the nickel and cobalt nitrates, the number of coatings and the percentage of the holes per cm^2 gauze which are completely filled up with $NiCo_2O_4$.

As the number of coatings increases, the electrocatalytic activity for oxygen evolution decreases. The $NiCo_2O_4$ layers are prepared by repeated immersion in the mixed nitrate solution. With decreasing concentration of the dipping solution the number of coating layers must be increased, in order to obtain the same catalyst

Table 2. Influence of the number of coatings and concentration ratio of the mixed nitrates on the anodic performance of $NiCo_2O_4$ in 5 M KOH, 25° C (iR-corrected)

$Ni(NO_3)_2 \cdot 6H_2O:Co(NO_3)_2 \cdot 6H_2O$ (M)	Number of coatings	Catalyst loading (mg cm^{-2})	Holes which are completely filled up (%)	Potential (mV) at CD (iR-corrected)	
				200 mA cm^{-2}	100 mA cm^{-2}
1.0:2.0	2	11.80	85	1615	1592
5×10^{-1}:1.0	4	10.00	40	1633	1616
2.5×10^{-1}:5×10^{-1}	8	10.15	0	1651	1629
1×10^{-1}:2×10^{-1}	20	11.35	0	1672	1652
5×10^{-2}:1×10^{-1}	50	10.15	0	1674	1646

loading. If in that case the number of coatings, i.e. immersions, increases, a denser and smoother structure of the NiCo$_2$O$_4$ layer is obtained with mostly open holes of the gauze substrate. If at constant catalyst loading the number of coatings decreases, the resulting NiCo$_2$O$_4$ layer is rougher and the holes nearly all completely filled. In all cases the nickel wires of the screen were completely covered with NiCo$_2$O$_4$ and the gauze profile was maintained.

The morphology of the nickel cobalt layer is influenced by the rate of deposition of the layer. A gradual formation of the NiCo$_2$O$_4$ electrode leads to a denser structure in contrast to a faster deposition which gives a rougher NiCo$_2$O$_4$ surface. Hence, we can conclude that the total top surface area of the NiCo$_2$O$_4$ layer is greater in the case of a highly concentrated solution. The difference in oxygen overpotential is a consequence of the difference in roughness of the electrode surface: the lower the overpotential, the rougher the surface.

3.1.2.2. Catalyst loading.

The variation in anodic performance with the catalyst loading can give an answer to the degree of utilization of the electrocatalyst surface. A visual observation of the course of the catalyst loading process shows that at lower loadings, up to 5 mg cm^{-2}, the nickel wires are not completely covered by the NiCo$_2$O$_4$. As the loading is increased further, the wires become completely covered and subsequently the holes at the centre of each mesh opening become filled, probably then reaching the maximum surface area. Finally, at higher loadings, the coating becomes much denser. The electrode surface is flattened and consequently the roughness decreases.

In the previous section, it has been shown that the number of coatings influences the morphology of the porous layer and hence the electrocatalytic activity.

In the stepwise deposition, which occurs from a more diluted dipping solution (see Fig. 2), the catalyst loading has virtually no influence on the anodic performance, while the percentages of the holes per cm^2 gauze which are filled increases slightly. This indicates that the utilization of the porous NiCo$_2$O$_4$ electrode is limited to the top
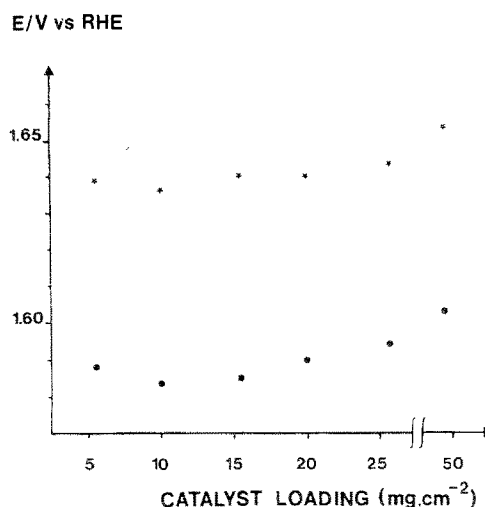

E/V vs RHE

CATALYST LOADING (mg.cm^{-2})

Fig. 2. Influence of the catalyst loading on the anodic performance of NiCo$_2$O$_4$ electrodes in 5 M KOH, 25° C at two current densities (iR-corrected). Stepwise deposition (occurs from a more diluted dipping solution): 0.5 M Ni(NO$_3$)$_2$·6H$_2$O:1.0 M Co(NO$_3$)$_2$·6H$_2$O. Heat treatment: 300° C/1 h. ● – 100 mA cm^{-2}; ★ – 500 mA cm^{-2}.

Catalyst loading (mg cm^{-2})	5.50	10.00	15.50	20.00	25.75	49.50
Number of coatings	3	5	7	9	11	19
Holes per cm^{-2} which are completely filled up (%)	10	20	20	30	35	70

surface. The same effect was observed more clearly for a nickel plate as substrate.

Fig. 3 shows the result when the deposition proceeds from a more concentrated solution: the catalyst now seems to influence the performance. These differences in oxygen overpotentials are due to differences in roughness: in the range 15–20 mg cm^{-2} NiCo$_2$O$_4$ maximum activity coincides with maximum roughness. At extremely high loadings, the electrode resistance increases as a consequence of the denser structure.

3.1.3. Influence of the anion in the metal salts and the solvent.

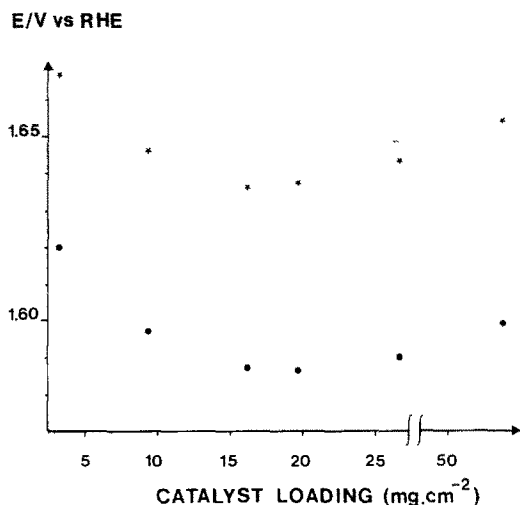3.1.3.1. Effect of the anion of the metal salts. Anions of metal salts other than NO$_3^-$, such as

E/V vs RHE

Fig. 3. Influence of the catalyst loading on the anodic performance of $NiCo_2O_4$ electrodes in 5 M KOH, 25°C at two current densities (iR-corrected). Faster deposition (proceeds from a more concentrated solution): 1.0 M $Ni(NO_3)_2 \cdot 6H_2O : 2.0$ M $Co(NO_3)_2 \cdot 6H_2O$. Heat treatment: 400°C/1 h. ● – 100 mA cm^{-2}; ★ – 500 mA cm^{-2}.

Catalyst (mg cm^{-2})	3.30	9.25	16.15	19.50	26.50	53.50
Number of coatings	1	2	3	4	5	9
Holes per cm^{-2} which are completely filled up (%)	40	85	85	85	95	100

CH_3COO^- and Cl^- have been examined for possible effects on the catalytic activity. The metal salt should be able to decompose in about the same temperature range and produce the $NiCo_2O_4$ spinel only.

The experimental results for electrodes prepared under identical conditions did not show any difference in activity. In the previous section, it has been shown that the concentration of the mixed salt solution influences the morphology of the deposited layer and hence the anodic performance. The solubility of the mixed nitrates in water is the greatest of the various anions investigated; it was therefore decided to use the nitrates in the further study.
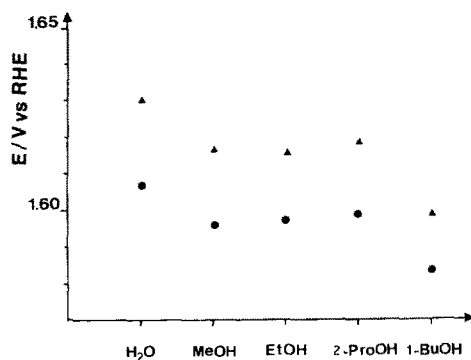

Fig. 4. Influence of the solvent of the dipping solution on the anodic performance of $NiCo_2O_4$ electrodes in 5 M KOH, 25°C (iR-corrected). ● – 100 mA cm^{-2}; ▲ – 200 mA cm^{-2}. Heat treatment: 400°C 1 h. Concentration of the mixed nitrates: 0.4 M Ni^{2+}: 0.8 M Co^{2+}.

Solvent	H_2O	MeOH	EtOH	2 PrOH	1-BuOH
Catalyst loading (mg cm^{-2})	13.60	12.40	13.45	15.90	14.75
Holes per cm^{-2} which are filled up (%)	25	70	45	45	70

3.1.3.2. Solvent effect. Different solvents, i.e. water and alcohols, were examined for the best deposition conditions. Non-aqueous solvents spread out better on the surface and evaporated at lower temperatures. The $NiCo_2O_4$ layer deposited from an alcohol solution has a lower oxygen overvoltage than the same electrode obtained from an aqueous solution (see Fig. 4). (The other preparation parameters were the same.) The percentage of the holes per cm^2 gauze which are filled shows the influence on the surface morphology.

Though there is a decrease in oxygen overpotential as a result of the use of an alcohol as solvent which spreads out better, there is a negative aspect: because of the smaller solubility of the mixed nitrates in alcohol as compared with water, a greater number of dips is required to obtain the same loading. This also affects the morphology. Under similar preparation conditions, the more interesting solvent appears to be BuOH (see Fig. 4). But there are no significant differences in overpotential if, for each solvent, the more concentrated dipping solution is used for both water and BuOH.
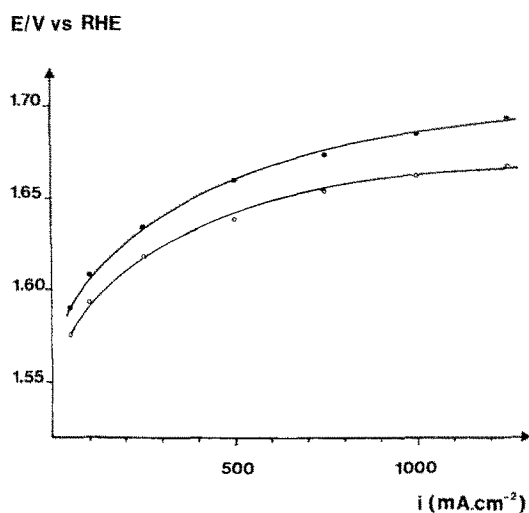
E/V vs RHE

Fig. 5. Initial decrease in performance of a $NiCo_2O_4$ electrode for oxygen evolution in 5 M KOH, 25° C (iR-corrected). o – measurements taken immediately at freshly prepared electrode; ● – after 1 h polarization at the highest current density.

E/V vs RHE

Fig. 6. Performance at 500 mA cm⁻² (iR-corrected) during a 24 h run of $NiCo_2O_4$ electrodes in 5 M KOH, 25° C prepared at different decomposition temperatures and durations of heat treatment.

Symbol	Heat treatment		Catalyst loading (mg cm⁻²)
	T_F (° C)	t (h)	
★	400	1	18.15
△	350	1	19.45
+	300	10	17.30
▲	300	1	20.60
●	250	10	19.70

3.1.4. Ageing phenomena and long-term performance.

The effect of ageing was studied in order to compare our results with those of Tseung and King [16] and Davidson [7]. An initial decrease in performance of freshly prepared $NiCo_2O_4$ electrodes at constant current density can mostly be observed, see Fig. 5. After 1 h, the anodic behaviour remains almost constant. Fig. 6 shows the performance of $NiCo_2O_4$ electrodes prepared at different temperatures and durations of heat treatment at 500 mA cm⁻² during a 24 h run in 5 M KOH. The rate and magnitude of ageing is not always the same and varies with different parameters such as the electrode preparation and the applied current density. The increase in overpotential takes place only if the electrode is submerged in the electrolyte. If a porous $NiCo_2O_4$ electrode is kept in air, even for several months, no change in the activity occurs. Study of the ageing phenomenon is continuing. The decline in performance may be due to a surface transformation such as silting up of surface pores which results in a decrease in the roughness of the electrode surface, or to a chemical transformation by a change in valency states. Other authors [16] have mentioned partial charge compensation in the oxide surface by hydroxyl ions from the electrolyte.

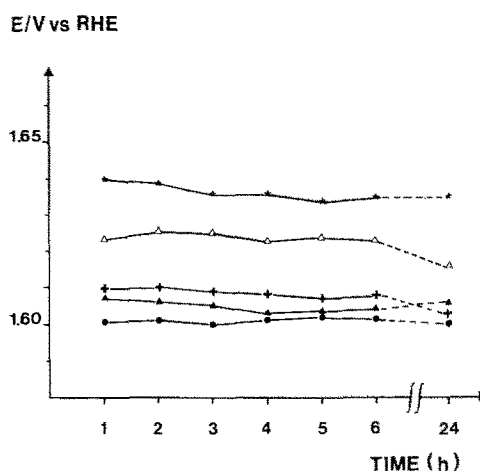In view of possible practical applications long-term stability tests were carried out for up to 350 h continuous operation. It was noticed that after the earlier mentioned initial rapid decrease in anodic performance, only a small increase in oxygen overpotential was found. Table 3 shows data at 1, 250 or 350 h (Column 2). At the end of this long-term performance, the KOH solution was renewed and the potential was measured again, as shown in Table 3 (see Column 3); the values were found to be only slightly higher than the 1 h data. The change of electrolyte is necessary because of the excessive water loss by evaporation and possible CO_2 uptake. The porous electrodes were mechanically stable. This was checked by determining the loss of $NiCo_2O_4$ particles by weighing before and after the long-term performance and was less than 3% after 300–600 h.

3.2. Comparison of Teflon-bonded and non Teflon-bonded electrode structures

Some authors [3, 4, 5] have observed differences

Table 3. Long-term performance of NiCo$_2$O$_4$ electrodes for oxygen evolution in 5 M KOH, 25° C (iR-corrected)

Current density (mA cm^{-2})	Potential vs RHE, after X hours (h):(mV)	1 h after changing electrolyte (mV)	Catalyst loading (mg cm^{-2})	Ni^{2+}:Co^{2+} (M)	Heat treatment T_F(° C)/t (h)
200	1:1615 250:1630	1620	17.75	5 X 10^{-1}:1.0	400/1
200	1:1590 350:1635	1600	18.90	1.0:2.0	400/1
500	1:1605 250:1630	1620	23.00	1.0:2.0	320/1

in anodic performance as a consequence of the incorporation of Teflon in the catalyst. Therefore, the Teflon-bonded and non Teflon-bonded electrode structures were compared, with the NiCo$_2$O$_4$ catalyst prepared by thermal decomposition for both electrode structures. The Teflon-bonded electrodes were made as described earlier and the ratio of catalyst:Teflon was varied.

The measured R-values for Teflon-bonded NiCo$_2$O$_4$ electrodes as a function of the Teflon content is shown in Fig. 7 for the same Luggin capillary-to-working electrode distance. It is interesting to note that in the range 0–30% Teflon content the measured iR-drop is nearly the same, and that beyond 30% there appears to be a sharp increase in the electrode resistance (30–40% is a transition range). It is evident that, as long as the volume of the Teflon aggregates are smaller than the volume of the catalyst aggregates, the latter will be in contact with each other.

Fig. 8 demonstrates the effect of the catalyst: Teflon ratio on the anodic behaviour of the
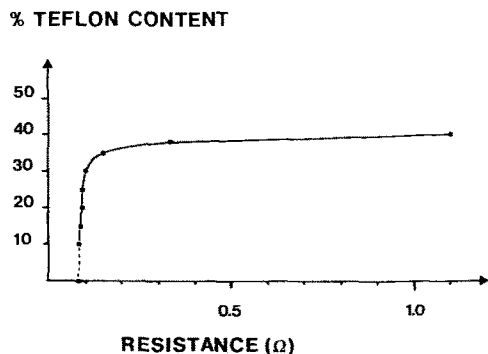
Teflon-bonded NiCo$_2$O$_4$ electrodes by applying the current interruptor technique. The iR-corrected curve also shows a decrease in performance with decreasing catalyst:Teflon ratio.

Oxygen bubbles formed on Teflon-bonded electrodes are larger than those formed on porous non Teflon electrode surfaces. The bubble size increases and the bubbles detach with greater difficulty with increasing Teflon content due to the increasing hydrophobicity of the catalyst surface. The larger bubble formation on the Teflon-bonded electrode surface leads to an increased resistance at higher current densities and also reduces the electrochemically active surface available for oxygen evolution. The irregular detaching of larger bubbles hinders accurate measurements at high current densities during steady-state oxygen evolution.
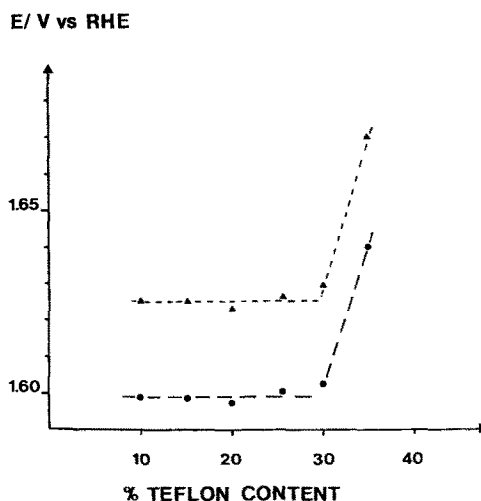

Fig. 7. Influence of the Teflon content (wt %) on the electrode resistance of Teflon-bonded NiCo$_2$O$_4$ electrodes in 5 M KOH, 25° C. Catalyst loading: ± 20 mg cm^{-2}.

Fig. 8. Influence of the Teflon: catalyst ratio on the anodic behaviour of Teflon-bonded NiCo$_2$O$_4$ electrodes in 5 M KOH, 25° C (iR-corrected). ● – 100 mA cm^{-2}, ▲ – 200 mA cm^{-2}.

Table 4. Comparison of the anodic performance of Teflon-bonded and non Teflon-bonded NiCo$_2$O$_4$ electrodes in 5M KOH, 25° C (iR-corrected). Heat treatment: 400° C/1–2 h

Ratio NiCo$_2$O$_4$: Teflon	Preparation method (1) Evaporation (2) Dipping	Catalyst loading (mg cm^{-2})	Potential (mV) at CD	
			250 mA cm^{-2}	100 mA cm^{-2}
100:0	(2)	23.25	1615	1590
90:10	(1)	~ 24	1612	1585
90:10	(2)	~ 13	1625	1600
85:15	(1)	~ 24	1620	1593
80:20	(1)	~ 24	1613	1583

Table 4 shows a comparison of the anodic performance for Teflon-bonded and non Teflon-bonded NiCo$_2$O$_4$ electrodes in which the NiCo$_2$O$_4$ catalyst material was prepared by thermal decomposition with the same thermal treatment (duration and temperature) and the same catalyst loading. The Teflon content was limited to a maximum of 20%. Beyond 10% Teflon content the structure was friable and the NiCo$_2$O$_4$ layer tended to fall off during oxygen evolution. It is seen that the alternative Teflon-bonded electrode structure gives about the same activity and ohmic potential drop as the porous electrode. Thermal decomposition by evaporation (first method) or by dipping (second method) did not significantly change the anodic performance. The influence of the catalyst loading on the anodic behaviour in the case of the alternative electrode structure shows the same activity for loadings in the range 15–25 mg cm^{-2} NiCo$_2$O$_4$, indicating that only the top surface is active. With respect to the substrate the same tendency was observed with the alternative and the porous electrode: at lower loadings a nickel gauze support material was more favourable than a nickel plate support; at higher loadings the electrode surface was flattened and, consequently, the electrocatalytic activity was the same. After careful examination of the data we conclude that the catalytic activity of porous electrodes is at least comparable with the Teflon-bonded NiCo$_2$O$_4$ electrodes. In no case was superior behaviour in the Teflon-bonded electrodes observed.

In the literature, contradictory results have been reported about the effect of Teflon incorporation: according to Tseung *et al.* [3, 4, 17], the far superior performance of the Teflon-bonded electrode structure is a result of the incorporation of Teflon in the catalyst thus ensuring greater utilization of the available catalyst surface because the interior of the electrode is not completely denuded of electrolyte. This alternative structure is presented as a hydrophobic porous Teflon phase, intertwined with a porous hydrophilic catalyst phase. The comparison of the Teflon-bonded with the non Teflon-bonded electrode structure has been made with electrodes in which the NiCo$_2$O$_4$ catalyst is prepared in the former structure by cryochemical synthesis (freeze drying followed by decomposition in vacuum), and in the latter by thermal decomposition. Results of Singh *et al.* [5] have shown that NiCo$_2$O$_4$ layers prepared by the thermal decomposition method are more active than Teflon-bonded electrodes.

The results of our study indicate that it is mainly the top surface of the NiCo$_2$O$_4$ electrode that is electrochemically active, independently of the electrode structure. It has also been shown that the alternative Teflon-bonded NiCo$_2$O$_4$ electrode gives about the same activity, and no drastic changes with the catalyst loading have been observed for both structures. According to the criterion for the choice of semiconducting oxides for the oxygen evolution reaction, presented by Tseung and Jasem [2, 6], the potential of the metal/metal oxide or the lower metal oxide/higher metal oxide couple must be reached before oxygen evolution takes place. This hypothesis implies that the final step in the irreversible reaction of the oxygen evolution on a metal or metal oxide surface takes place by the breakdown of a species in a high oxidation state, which is formed on the active site. Since our results show that only the top layer is active, it can be said that these active sites must be limited to the surface only. This is in agreement with the work of Rasiyah and Tseung [18] on

Teflon-bonded electrodes, and of Hibbert [19] on porous $NiCo_2O_4$ electrodes.

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