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Origin of ohmic losses at Co_3O_4/Ti electrodes

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Co_3O_4/Ti and $NiCo_2O_4$/Ti electrodes were prepared in different ways to investigate the origin of the ohmic losses observed experimentally. In particular, titanium was pretreated in various ways including etching with a HF mixture, and reduction by cathodic hydrogen discharge prior to coating. Different types of commercial titanium and different concentrations of the precursors in solution were also tried. Some electrodes were prepared with a RuO_2 interlayer. Nickel and mild steel were also used as supports. Parameters to quantify the ohmic losses were the peak distance in voltammetric curves, and the initial slope and the deviation from linearity of current vs sweep rate plots. The experimental picture corroborates the view that the main component of the ohmic drop comes from the insulating barrier which forms at the support/oxide layer interface. The intrinsic conductivity of spinels does not appear to represent the main problem for thermal layers as usually prepared.

1. Introduction

Substantial ohmic losses may develop at oxide/Ti interfaces, a feature of DSA electrodes [1]. The measurable ohmic component of overpotential can be resolved [2] into three subcomponents:

$$\Delta V_\Omega = \Delta\phi_1 + \Delta\phi_2 + \Delta\phi_3 \qquad (1)$$

$\Delta\phi_1$ is the uncompensated ohmic drop between the electrode surface and the Luggin capillary tip, $\Delta\phi_2$ is the ohmic drop across the oxide overlayer, and $\Delta\phi_3$ is the ohmic barrier which can onset at the Ti/coating boundary.

In previous work from this laboratory on Ti-supported Co_3O_4 electrodes [3–5], it has been shown that the uncompensated ohmic losses substantially higher than with RuO_2/Ti electrodes are responsible for anticipated deviations of Tafel lines from linearity, as well as for separation of the coupled voltammetric peaks located just prior to oxygen evolution. In particular, it has been pointed out that the observed ohmic losses are related to the formation of an insulating TiO_2 interlayer which is not doped by Co_3O_4 as it is in contrast by RuO_2. Thus, the distance between the coupled peaks at about 1.40 V vs RHE has been proposed as a parameter to monitor the conducting properties of the Ti/Co_3O_4 interface.

A different view has recently been taken by Burke and McCarthy [6]. Following these authors, the observed ohmic losses are essentially related to the intrinsic poor conductivity of Co_3O_4 which is therefore unsuitable, as such, for the manufacture of technological electrodes. The same authors have maintained that it is necessary to dope Co_3O_4 with a small amount of RuO_2 to increase substantially its conductivity so as to make its performances suitable for applications. However, as Co_3O_4 is doped with RuO_2, the simultaneous doping of the TiO_2 interlayer cannot be avoided [7] so that the two effects cannot be disentangled. Moreover, RuO_2 brings about its own electrocatalytic activity which has nothing to do with the improved conductivity.

Several papers in the literature corroborate the explanation in terms of an insulating TiO_2 interlayer. Iwakura *et al.* [8] have studied the effect of the support on the activity of Co_3O_4 for oxygen evolution. From their plots, it is easy to see a much higher ohmic loss effect with Ti, Nb and Ta than with Ni, Co, Fe and Pt. Spynu *et al.* [9] have compared Co_3O_4 electrodes obtained by thermal decomposition of $Co(NO_3)_2$ on etched titanium, with electrodes obtained by thermal oxidation of electrodeposited $Co(OH)_2$. The higher ohmic losses with the former electrodes (with substantially the same structure and composition of the latter) have been interpreted in terms of a more efficient screening of the support by $Co(OH)_2$ during calcination. Konovalov *et al.* [2] have measured the overpotential of oxygen evolution on Co_3O_4/Pt electrodes with and without metallic probes introduced into the oxide layer. The absence of any detectable effects proves that the ohmic drop along the oxide layer is negligible. On the contrary, with Co_3O_4/Ti electrodes high ohmic losses have been observed without metallic probes. Hamdani *et al.* [10] have reported that the separation of the peaks is negligibly affected by the correction for the ohmic drop across the oxide layer if a conducting support is used.

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Evidence for the presence of a barrier interlayer has always been deduced indirectly. The purpose of this work has been to obtain a more direct proof of the substantial effect of the insulating interlayer in determining the properties of Co_3O_4/Ti electrodes.

2. Experimental details

2.1. *Generalities*

Experiments carried out with Co_3O_4 electrodes were devised specifically for this study, while occasional observations with $NiCo_2O_4$ electrodes during the course of another work are also reported.

Spinel electrodes were prepared by thermal decomposition at 400° C of solutions in isopropanol of $Co(NO_3)_2 \cdot 6H_2O$ alone or mixed with $Ni(NO_3)_2 \cdot 6H_2O$. With the purpose of investigating the effect of the concentration of the precursor solution, 0.2 and 1.0 M solutions were used. A 0.3 M solution of $RuCl_3 \cdot xH_2O$ was used in the case of RuO_2 interlayers. The support consisted of 10 mm × 10 mm × 0.2 mm titanium platelets. To investigate the different tendency to passivate of differently produced titanium samples, two different types of commercial titanium were used: Strem Chemicals (hereafter denoted A) and Contimet (denoted B) both of first grade purity degree. Nickel (Goodfellow) platelets of the same size were also used with Co_3O_4.

The support was treated with emery paper and etched with boiling 10 wt % oxalic acid for 30 min. It was then coated as such, or after further pretreatment as specified below. Nickel was etched with boiling 20% HCl. The loading with spinel was normally $4.0 \pm 0.4\,\mathrm{mg\,cm^{-2}}$. Where an interlayer of RuO_2 was present, its loading was about $0.6 \pm 0.1\,\mathrm{mg\,cm^{-2}}$. The number of layers were normally one for RuO_2 and about 30 with the more dilute solution of spinel precursors.

2.2. *Special pretreatments*

The depassivating power of a pretreatment depends on many factors but mainly on the composition of the bath. An etching bath based [11] on $HF + HNO_3 + H_2O$ in the proportion 1 : 1 : 4 was also used after the common treatment described in 2.1. Further, it is known [12] that TiO_2 cannot be easily reduced to metallic titanium by cathodic treatment, but it can be reduced to highly conducting suboxide phases. Therefore, a few samples were subjected to cathodic hydrogen discharge at $10\,\mathrm{mA\,cm^{-2}}$ for 30 min prior to depositing the coating.

2.3. *Electrochemical techniques*

The open circuit potential (E_{oc}) of fresh electrodes did not show any clear, systematic dependence on the electrode preparation. E_{oc} was around -0.09 ± 0.04 V vs SCE for $NiCo_2O_4$/Ti, -0.28 ± 0.04 V vs SCE for Co_3O_4/Ti and about -0.21 V for Co_3O_4/Ni. The less negative potential of the nickel-supported layers is outside the range of experimental uncertainty and might be associated with some intermixing at the oxide/support boundary. If so, the solution must reach the bottom of the layers to be sensitive to the composition of the interlayer. Actually, Co_3O_4 electrodes prepared from the 1 M solution of the precursors systematically showed a slightly more negative value of the open circuit potential (-0.31 V and -0.25 V, respectively) which suggests that the above general uncertainty cannot be attributed to unspecific experimental scatter. In the presence of a RuO_2 interlayer the difference amounts to only 10 mV and the value is close to -0.30 V. This suggests that the difference is probably due to the passive properties of the titanium surface at the bottom of open pores through the coating, with the porosity being higher as the more concentrated solution of precursors is used.

Electrodes were tested by cyclic voltammetry in 1 M NaOH solutions. The general 'electrochemical spectrum' was recorded at $20\,\mathrm{mV\,s^{-1}}$ in a potential range of 600 mV just prior to oxygen evolution. The total voltammetric charge was determined by graphical integration using an appropriate device.

The morphology of the oxide layer was monitored [5] by recording voltammetric curves in a restricted potential range (50 mV) around the open circuit potential at several sweep rates between 5 and $50\,\mathrm{mV\,s^{-1}}$. The current in the middle of the potential range was plotted as a function of the sweep rate and the (initial) slope measured.

3. Results and discussion

The experiments carried out specifically to elucidate ohmic loss aspects are summarized in Table 1 for Co_3O_4 and Table 2 for $NiCo_2O_4$, although the latter have been less systematic. Besides the details of the preparation procedure, two experimental parameters are reported in the Tables: the initial slope of the current–sweep rate plot, i.e. the capacitance of the surface which is proportional to the working surface area, and ΔE_p for the anodic–cathodic pair of peaks in the case of Co_3O_4, and between the two anodic peaks in the case of $NiCo_2O_4$. This parameter is a measure of the uncompensated ohmic drop [4, 5]. Since $\Delta\phi_1$ in Equation 1 depends essentially on the resistivity of the solution, it should be the same for all electrodes. Therefore, ΔE_p reflects $\Delta\phi_2 + \Delta\phi_3$.

Some of the results are also reported in graphical form. In Fig. 1 voltammetric curves for Co_3O_4 are shown, while those for $NiCo_2O_4$ are displayed in Fig. 2. From the Figures and Tables the following conclusions can be drawn.

3.1. *Effect of concentration*

As the concentration of the precursor is increased the ohmic losses increase. More concentrated solutions give rougher and more porous surfaces. As the

Table 1. Features of Co_3O_4 film electrodes

Support (*a*)	*Further treatment* (*b*)	*Interlayer* (*c*)	$c/mol\,dm^{-3}$ (*d*)	$(\Delta j/\Delta \nu)/mF\,cm^{-2}$ (*e*)	$\Delta E_p/mV$ (*f*)
Ti(A)	–	–	0.2	3.2	65
Ti(A)	–	–	1	6.3	~200
Ti(A)	HF	–	0.2	2.8	35
Ti(A)	HF	–	1	6.0	~200
Ti(B)	–	–	0.2	4.0	120
Ti(B)	–	–	1	10.5	~240
Ti(A)	H_2	–	0.2	5.5	80
Ti(A)	H_2	–	1	10.0	105
Ti(A)	–	RuO_2	0.2	4.0	5
Ti(A)	–	RuO_2	1	8.0	15
Ni	–	–	0.2	6.0	15
Ni	–	–	1	18.0	165

(*a*) A and B distinguish two different commercial titanium foils.
(*b*) HF: etching in $HF + HNO_3 + H_2O$ for a few seconds. H_2: cathodic hydrogen evolution at 10 mA for 30 min before coating.
(*c*) RuO_2 prepared by thermal decomposition of $RuCl_3$ from 0.3 M solution at 400° C. Loading: $0.6\,mg\,cm^{-2}$.
(*d*) Concentration of $Co(NO_3)_2$ in the precursor solution.
(*e*) Slope of the linear portion of the current-sweep rate relationship. Uncertainty: ±0.5.
(*f*) Distance between the anodic–cathodic pair of peaks prior to oxygen evolution. Uncertainty better than ±5 mV.

concentration of the precursor in solution is increased from 0.2 to 1.0 M, the electrode capacitance almost doubles (cf. Table 1). The overlayer protects the support less efficiently so that a TiO_2 interlayer can develop. An alternative explanation is that less dense layers possess a higher resistivity. However, if this were the case the same increase in ΔE_p should be observed irrespective of the pretreatment, which is not the case. In particular, with RuO_2 interlayers (for which the 5 mV of ΔE_p are consistent with the usual 0.5–0.7 Ω giving rise to $\Delta\phi_1$) the very small increase in ΔE_p may be related to porosity in the sense of an increase in $\Delta\phi_1$ due to the electrolyte solution inside the pores. Irrespective of the detailed preparation, an increase in the concentration of the precursor results in an increase of ΔE_p, but the quantitative value depends on the pretreatment. Since the nature of the oxide layer is not expected to be affected by the treatment of the support, these phenomena can consistently be explained by the possibility of formation of an insulating interlayer which is prevented only in the case of RuO_2 being placed between the support and the active layer [7]. Indeed, RuO_2 may diffuse into the oxide layer. However, the magnitude of the observed effect cannot be explained in these terms.

3.2. *Effect of etching*

HF is shown to be especially aggressive towards TiO_2. Its action is expected to be particularly efficient in removing the titanium passive layer. This is evident from the results, although the effect is quantitatively small only because the pretreatment has not been optimized. However, with both electrodes the HF treatment can be seen to reduce the ohmic drop. In the particular case of Co_3O_4 from dilute precursor, the result is not far from that with RuO_2. This observation is difficult to explain in terms of intrinsic Co_3O_4 conductivity rather than of the presence of an insulating barrier.

3.3. *Effect of the support*

Different qualitites of titanium show different tendencies to passivation and, therefore, to depassivation. Commercial Ti(A) consisted of foils apparently prepared from sintered powder. Commercial Ti(B)

Table 2. Features of $NiCo_2O_4$ film electrodes

Support (*a*)	*Further treatment* (*b*)	*Interlayer* (*c*)	$c/mol\,dm^{-3}$ (*d*)	$(\Delta j/\Delta \nu)/mF\,cm^{-2}$ (*e*)	$\Delta E_p/mV$ (*f*)
Ti(B)	–	RuO_2	1	69.5	155
Ti(B)	–	RuO_2	0.2	40	140
Ti(B)	–	–	1	nonlinear	distorted
Ti(A)	–	–	1	nonlinear	distorted
Ti(A)	HF	–	1	57.5	155
Ti(A)	HF	–	0.2	36	155
Ti(B)	–	–	0.2	20	160
Ti(A)	H_2	–	0.2	24	145

(*a–e*) See footnote of Table 1.
(*f*) Distance of the pair of anodic peaks before oxygen evolution.

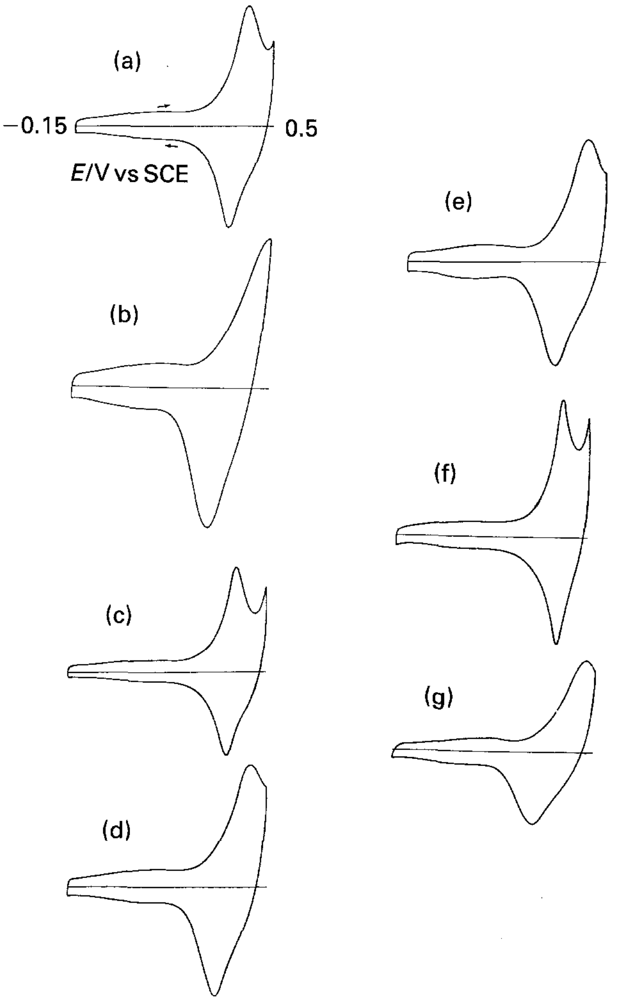

Fig. 1. Typical voltammetric curves of Co_3O_4 layer electrodes showing the effect of various parameters on ΔE_p. (a) Precursor concentration 0.2 M, Ti(B); (b) Precursor concentration 1 M; (c) HF etching; (d) Ti(A); (e) Ti pretreatment by hydrogen discharge; (f) RuO_2 interlayer; (g) nickel support. (a against b) Effect of precursor concentration; (a against c) effect of support etching; (a against d) effect of Ti type; (b against e) effect of hydrogen discharge on support; (a against f) effect of RuO_2 interlayer; (b against g) effect of nickel support.

(Contimet) showed a very uniform and homogeneous texture. Experiments show that Ti(A) is probably more difficult to be etched and depassivated because of the evident grain structure. This is reflected in the different values of ΔE_p which cannot be attributed to experimental scatter or to the features of the oxide layer.

It is interesting to compare titanium with nickel.

Table 3. Co_3O_4 film electrodes. Effect of support and firing atmosphere on $\Delta E_p/mV$

Support	*Firing atmosphere*	
	Air	*Nitrogen*
Steel	–	20, 20, 10, 10
Fe	30, 30	25, 20
Ni	25, 20	10, 10
Ti(A)	distorted	100, 95

Several samples were used. Differently from Tables 1 and 2, the support was here sandblasted as the only pretreatment. The precursor was dissolved in ethanol. Firing temperature: 400° C.

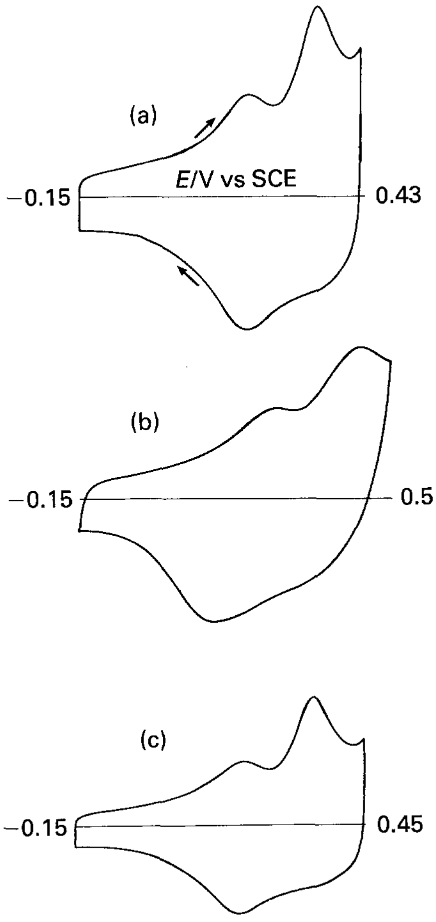

Fig. 2. Typical voltammetric curves of $NiCo_2O_4$ layer electrodes showing the effect of various parameters. (a) RuO_2 interlayer; (b) HF etching of titanium support; and (c) pretreatment of the titanium support by hydrogen discharge.

It is seen that the picture improves with nickel especially at high precursor concentration. However, ohmic losses persist and this is understandable since nickel oxide is not a metallic conductor but basically a p-type semiconductor, even if presumably heavily doped under similar circumstances.

In a different set of experiments, different supports, as well as different firing atmospheres, were compared. The results are summarized in Table 3. The fact that an oxidizing atmosphere (air) results in much higher ohmic drops with titanium supports provides conclusive evidence for the formation of an ohmic barrier at the support/overlayer interface. Actually, the surface properties of Co_3O_4 are not affected by the firing atmosphere [13]. Some effects of an oxidizing atmosphere are visible even with iron and nickel, while no data are available for mild steel. These results indicate that the oxidation of the support is the main reason for ohmic losses even with nonvalve metals. It is interesting to observe that the ohmic losses are minimum with Ni support under inert atmosphere provided the surface is first sandblasted (for the samples in Table 1 and 2 the support was not sandblasted).

3.4. *Effect of an interlayer*

While the presence of RuO_2, a metallic conductor

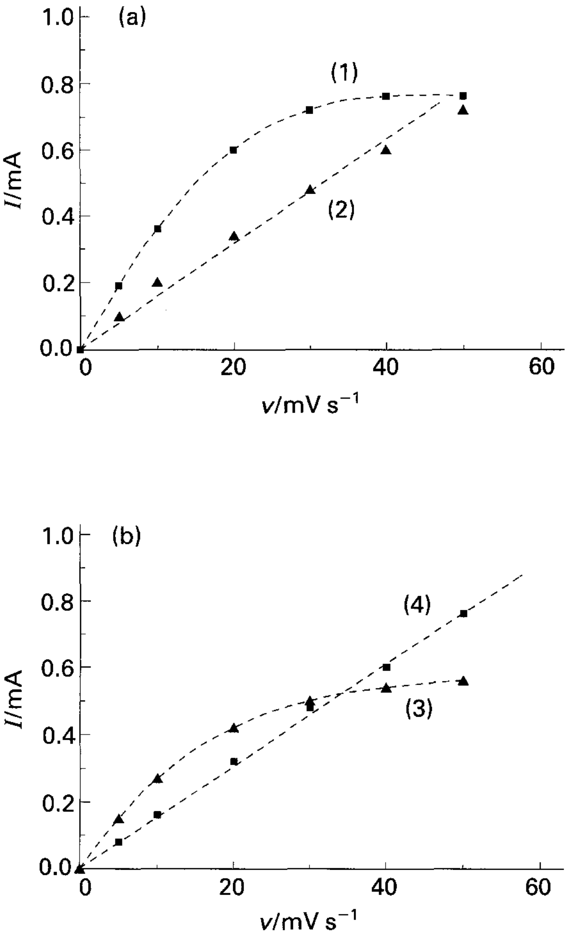

Fig. 3. Variation of current with the potential scan rate for voltammetric curves in a restricted potential range (50 mV) around the open circuit potential: (1) nickel support; (2) titanium pretreatment by hydrogen discharge; (3) Ti(B) 1 M precursor concentration, and (4) RuO_2 interlayer.

able to dope TiO_2 quite efficiently [14], gives self-explanatory results, the prereduction of TiO_2 by means of cathodic hydrogen discharge is the experiment which more directly points to the role of the insulating barrier. Although the effect has not been decisive since in this case also the treatment has not been optimized, it can be seen that the result is especially striking with the porous Co_3O_4 layer, whose ΔE_p is lower than any other case, even the nickel-supported oxide. The same is the case with $NiCo_2O_4$ electrodes, for which a better result than that with HF was observed. This experiment is especially crucial to discriminate between poor conductivity of the oxide layer and an insulating barrier at the interlayer.

3.5. *Effect of morphology*

Figure 3 shows a few specific plots of current against sweep rate to compare various treatments. The initial slope is proportional to the surface area, while the deviation from linearity is indicative of ohmic drops along pores or at the support/oxide boundary. The data show that different surface areas are obtained on different supports. Greater deviations are especially noted with oxides prepared from concentrated solution (porosity is higher) and with untreated titanium.

It may be speculated that the ΔE_p measured voltammetrically can also be related to porosity in that a greater porosity produces a higher ohmic drop in the trapped electrolyte solution, or in the oxide layer itself, as a consequence of the lower density of the layer. However, under similar circumstances, a correlation should be observed between ΔE_p and the surface morphology; i.e. ΔE_p is expected to correspond to a higher surface area.

Figure 4 shows a plot of ΔE_p against the voltammetric charge, which is a measure of the active surface area. The two quantities are totally uncorrelated which rules out that the observed ohmic drops can be related directly to the morphology of the oxide layer, although they are in fact indirectly due to this feature.

4. Conclusions

The experiments carried out in this work, aimed at

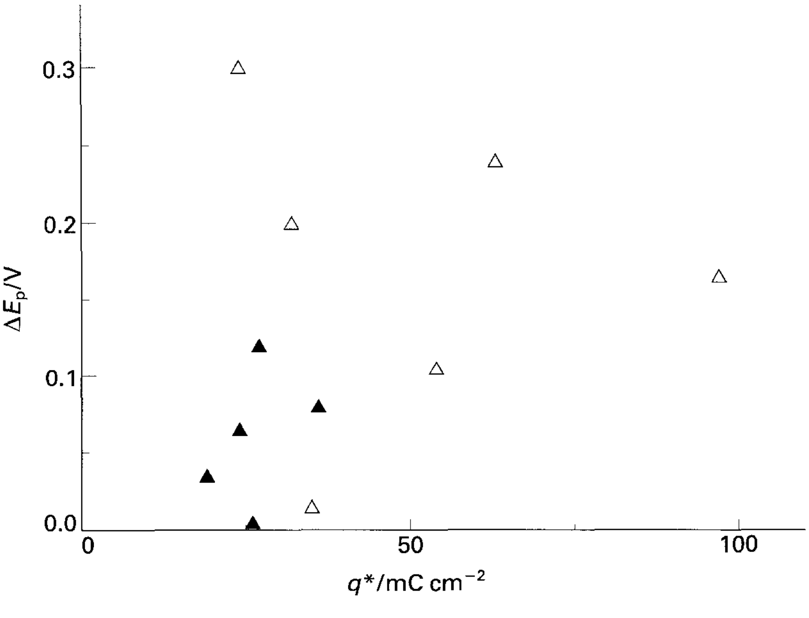

Fig. 4. Plot of ΔE_p for Co_3O_4 layer electrodes against the corresponding voltammetric charge. Concentration of the precursors in solution: (△) 1 M and (▲) 0.2 M.

discriminating between poor conductivity of the active layer and an insulating barrier at the support/electrocatalyst interface in the case of Co_3O_4/Ti and $NiCo_2O_4$/Ti electrodes, have shown that the latter is the main cause for the uncompensated ohmic losses observed in voltammetric or kinetic measurements. Therefore, these materials can be used as such for technological purposes, although special pretreatments of the support are required to minimize the insulating barrier. In the case of a titanium support the problem with spinels ensues from the inability of the oxide to dope TiO_2 [15], which, on the contrary, is readily made by RuO_2.

It is interesting to observe that sandblasting appears to be the most effective procedure to depassivate metal surfaces even in the case of nickel. Under similar conditions a minimum value of ΔE_p (comparable to that obtained with a RuO_2 interlayer) indicates that nickel is specific for Co_3O_4 electrodes, since the probable formation of mixed spinels at the support surface avoids the onset of an ohmic barrier, which is thus a possible source of complications, not only with titanium, though with a different order of magnitude.

In the case of normally sized electrodes, a substantial ohmic drop due to the intrinsic poor conductivity of Co_3O_4 should not be expected. The conductivity of Co_3O_4 can vary greatly depending on the preparation procedure. Results show [16–18] that the conductivity can vary between 1 and $10^{-4}\,\Omega^{-1}\,cm^{-1}$. For layers of 1 μm, the resistance of 1 cm^2 can thus be within 10^{-4} and 1 Ω. Therefore, the ohmic drop across the film can vary between 10^{-5} V and 10^{-1} V at 100 mA cm^{-2}. Also, the conductivity decreases as the calcination temperature is increased, since Co_3O_4 approaches stoichiometry [17]. Under these extreme conditions the intrinsic conductivity can certainly be a problem and doping with Li_2O has been used [19] (Co_3O_4 is a p-type semiconductor). Difficulties increase as bulk form electrodes are used, such as Teflon-bonded structures. However, this is not a general problem and is certainly not the main problem with the thermal electrodes prepared in this, as well as in other, laboratories.

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