The theory for the electrochemical behaviour of thin-layer cells is well established [3]. The oxidation and reduction peaks are symmetrical about $E^{\circ\prime}$, the current maximum occurring at E_p, and i_p is directly proportional to scan rate

$$i_p = \frac{n^2F^2VC_R^{\circ}v}{4RT}$$

where v is scan rate, V is the cell's interior volume, C_R° is the initial concentration of R (assuming oxidation) and all the other symbols have the usual significance.

It is intended to apply the cell to *in situ* spectrophotometric monitoring of uv/vis/near-ir absorbance changes due to electrode reactions of biologically electroactive compounds, as well as for the detection of absorbing intermediates. The electrochemical information is a current related to the concentration of species on the electrode surface, while spectroscopy gives the total amount of the absorbing species in the cell. Complementary information from the two techniques should be valuable in elucidation of reaction rates and mechanism.

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ELECTROCHEMICAL BEHAVIOUR OF RHODIUM CONTAINING $NiCo_2O_4$ ELECTRODES

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1. INTRODUCTION

The spinel type oxide $NiCo_2O_4$ is one of the most promising anode materials for oxygen evolution in alkaline solution |1|. Haenen *et al.*|2| have studied the $NiCo_2O_4$ electrocatalytic activity as a function of its structural and physico-chemical properties. It has also been shown that the electrocatalytic activity presented by this oxide is determined not only by the surface area and morphology, but also by the surface composition, since the oxygen evolution reaction occurs *via* the formation of surface higher oxides on the reactive sites |3|. These studies have demonstrated the importance of characterizing the oxide electrode surface.

In the present work, two sets of electrodes were prepared: $NiCo_2O_4$ electrodes and $NiCo_2O_4$ electrodes modified by the presence of Rh^{3+} cations. The partial substitution of cobalt by rhodium was motivated by the high stability of this element in the (+3) oxidation state and also by its preference in occupying the octahedral sites in the spinel structure. Moreover, this substitution may lead to a better understanding of the role of cations located in octahedral sites in the corresponding electrode activities.

Preliminary studies made with $NiCo_2O_4$ electrodes, prepared at 300, 350 and 400°C showed that their behaviour is strongly dependent on the temperature of synthesis, T_s |4|. It has also been observed that the activity, as measured by the current density, increases as T_s decreases.

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However, the electrodes prepared at the lowest temperature showed lack of mechanical and chemical stability. Therefore, the $NiCo_2O_4$ electrode performance was optimized for $T_s = 350^oC$. Hence, the rhodium containing $NiCo_2O_4$ electrodes were also prepared at this temperature.

2. EXPERIMENTAL DETAILS

The electrodes were prepared by coating a nickel foil support with sucessive layers of the oxides.These were optained by thermal decomposition at $T_s = 350^oC$ for 1h of the corresponding nitrates ($Ni(NO_3)_2.6H_2O$, $Co(NO_3)_2.6H_2O$, pro-analyse Merck and $Rh(NO_3)_3.2H_2O$ puriss. Fluka).

All electrochemical experiments were performed in a three compartment glass cell, at room temperature. The electrolytic solution was 5M KOH (pro-analyse Merck) prepared from double destilled water.

The obtained electrodes presented: (i) good mechanical and chemical stability in alkaline solutions, (ii) quite high surface area and (iii) low electrical resistance (0.5 - 1 Ω).

3. RESULTS AND DISCUSSION

The behaviour of the two sets of electrodes is exemplified in fig. 1.

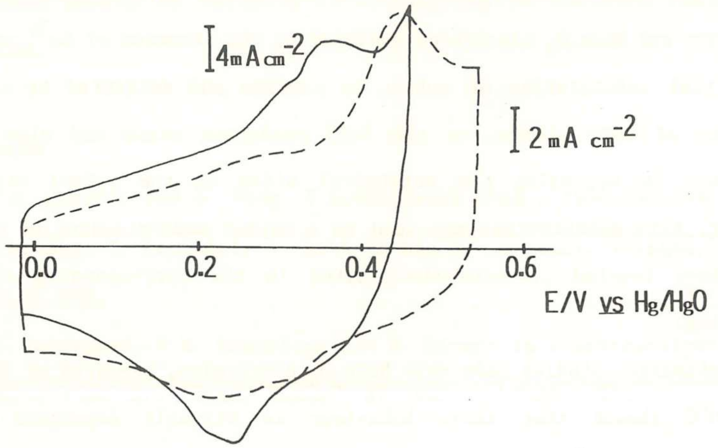


Fig. 1. Cyclic voltammograms of $NiCo_2O_4$ (---) and $NiCo_2O_4$ containing Rh^{3+} (——) electrodes Experimental conditions: 5H KOH, sweep rate: 10 mV s^{-1}.

It is clear that the electrode containing rhodium presents higher current densities, lower overpotential for O_2 evolution and higher charging current than the $NiCo_2O_4$ electrode. Even the surface cationic active composition appears to be distinct for each set of electrodes.

These results suggest that the electrodes containing rhodium have a higher surface area; this was confirmed by B.E.T. surface area measurements, as show in table I.

TABLE I. B.E.T. surface area for $NiCo_2O_4$ and $NiCo_2O_4$ containing Rh^{3+}.

Material	$A_{B.E.T.}$ / m^2 g^{-1}
$NiCo_2O_4$	18
Rh^{3+} containing $NiCo_2O_4$	74

Scanning Electronic Microscopy (SEM) studies confirmed that the morphology of the two kinds of electrodes is quite different.The electrodes containing rhodium are porous and rougher than $NiCo_2O_4$ ones, indicating a higher surface area (fig. 2).

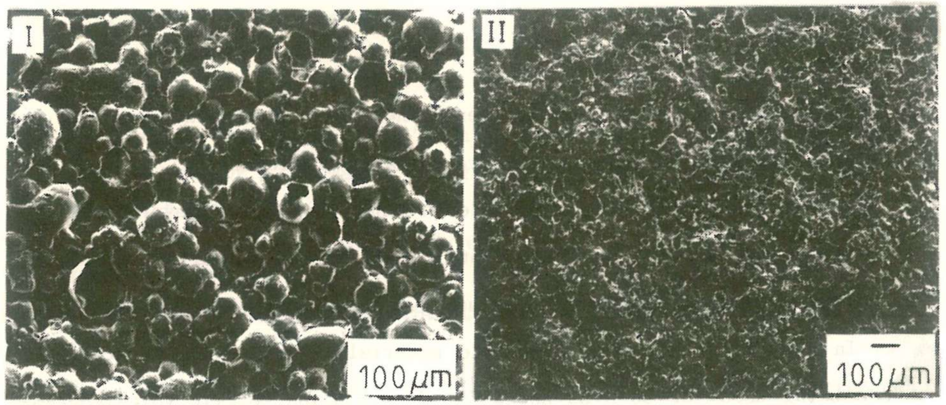
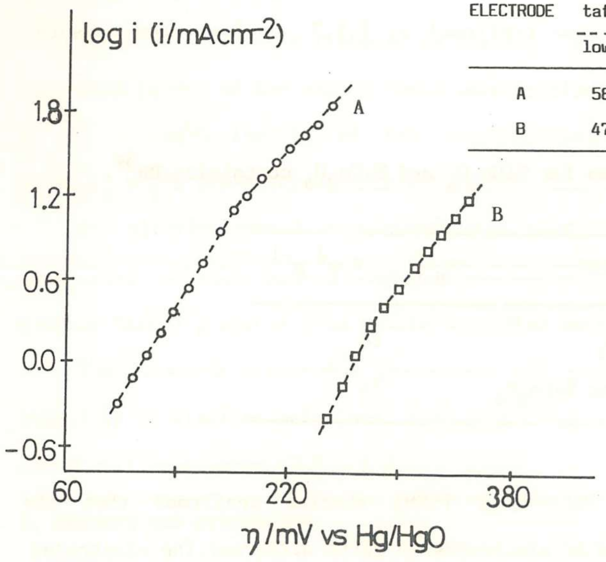


Fig. SEM micrographs of the surface of $NiCo_2O_4$ electrode (I) and $NiCo_2O_4$ electrode containing Rh^{3+} (II) prepared at 350^oC.

Concerning the oxygen evolution reaction, the electrodes containing rhodium showed a much higher catalytic activity in terms of both overpotential and current density as it can be confirmed in fig. 3.



ELECTRODE	tafel slope/mV		$i_o \times 10^7$ / A cm^{-2}	
	low η	high η	low η	high η
A	58	90	9.3×10^{-1}	1.2×10^{3}
B	47	84	2.3×10^{-2}	1.0×10^{1}

Fig. 3. Tafel plots for O_2 evolution reaction in 5N KOH

A - Rh^{3+} containing $NiCo_2O_4$ electrode

B - $NiCo_2O_4$ electrode

This fact is even more evident when the overpotentials for O_2 evolution, obtained at 100 mA cm^{-2}, are compared (table II).

The rhodium containing electrode presents the lowest overpotential, even when compared with the value obtained by Haenen *et al.* |5|, where the $NiCo_2O_4$ performance was optimized by using a nickel screen as a support.

In addition, our novel electrode material revealed a good stability after being used for 30 h as anode for O_2 evolution. Cyclic voltammograms obtained after prolonged use showed similar features to the new ones; according to this, it is reasonable to assume that the state of the surface has not changed significantly.

TABLE II. Overpotential for O_2 evolution, at 100 mA cm^{-2}, for different materials

ELECTRODE	η_{O_2}/mV vs Hg/HgO	REFERENCE
Rh^{3+} containing $NiCo_2O_4$	260	This work
$NiCo_2O_4$	415	This work
$NiCo_2O_4$	360	Haenen *et al* |5|

In conclusion, the present work has shown that both long term stability and electrocatalytic activity of the $NiCo_2O_4$ electrode can be improved by the introduction of Rh^{3+} in the structure.

A structural characterization of this novel material is now in course.

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