

REAL SURFACE DETERMINATION OF OXIDE THIN FILMS: THE  $\text{Co}_3\text{O}_4$  AND  $\text{NiCo}_2\text{O}_4$   
ELECTROCATALYSTS

J. Douch<sup>1</sup>, M. Hamdani<sup>1\*</sup>, M.I. da Silva Pereira<sup>2</sup>

*1- Laboratoire de Chimie Physique, Faculté des Sciences, Université Ibnou Zohr, B.P. 28 / S Agadir, Maroc.*

*2- CITECMAT, Departamento de Química e Bioquímica da Faculdade de Ciências de Lisboa, Campo Grande, 1700  
Lisbon, Portugal*

**Abstract**

Extensive quantities, like electrode reaction rates and double layer parameters, have to be referred to the unit real surface of the electrode, in order to compare the activity of different electrode materials and / or different preparation methods for the same material. The purpose of this paper is to review three methods usually used for the estimation of the real surface of  $\text{Co}_3\text{O}_4$  and  $\text{NiCo}_2\text{O}_4$  thin film electrodes. Two of them, capacitance ratio and voltammetric charge, are based on the voltammetric technique whereas the third one,  $\text{Zn}^{2+}$  ion adsorption (ZIA), is based on the ionic interaction at the solid-liquid interface. The applicability, advantages and limitations of the three methods are compared.

**Keywords:** real surface area, roughness factor, spinel oxide electrode, oxygen, electrocatalysis.

**1. Introduction**

One of the most important problems encountered in electrocatalysis by oxides is to compare the reactivity of electrode materials and assess their intrinsic electrocatalytic activity. It is well known that the oxide preparation method, conditions and precursors as well as the electrode form (pressed powder or thin films) affect their physicochemical properties and hence their catalytic activity [1-5]. The oxide preparation temperature influences considerably their catalytic activity and has antagonistic effects. An increase in synthesis temperature decreases the real or true surface area (RSA) and the non-stoichiometry of the oxide and consequently the number of surface sites (sites  $\text{cm}^{-2}$ ) [6], leading to a decrease on activity. It is worthy of note that, Nikolov et al. [7] have reported that the specific site electrocatalytic activity ( $\text{A site}^{-1}$ ) increases with increasing the temperature. The parameters, which directly influence the electrocatalytic properties of the electrode material, must be known in order to discriminate between geometric and electronic factors.

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Corresponding author. Fax 00212 4 8 22 01 00  
E- mail adress: mohamed.hamdani@caramail.com

The reaction rates, like most double layer parameters, have to be referred to the unit area of the electrode surface. Generally, comparing the current measured at a constant potential, which is an extensive quantity and consequently undergoes geometric effects, assesses the activity of an electrode. The real surface of porous electrodes, which will be dealt with in this paper, is estimated by taking into account the surface roughness factor,  $R$ , defined by the ratio of the real,  $S_r$ , and the geometric,  $S_a$ , surface areas. Thus, real surface, and apparent or geometrical surface, are related to one another by the relationship  $S_r = S_a \times R$ . Unless  $S_r$  is known, it will be impossible to relate different published information, or even to compare the data obtained using different preparation methods, on the same electrode.

Several electrochemical, chemical and physical methods exist for real surface area determinations and lead themselves readily to in situ measurements, while others are totally unsuited for that. It should be emphasized that the real surface area should be estimated, using a method, which best approaches the experimental situation to which the surface area is to be applied. An excellent paper "The surface area and roughness of electrodes" by Kuhn [8] covers all aspects of the problem with an interesting relevant bibliography. More recently, Trasatti and Petrii [9] scrutinize the basis on which fifteen methods rest, to evaluate their relevance on the determination of the real surface area. The latter work, which also cites other reviews, is especially recommended.

The present paper is concerned with the discussion of three popular methods used for the RSA determination of  $\text{Co}_3\text{O}_4$  and  $\text{NiCo}_2\text{O}_4$  thin films, the most investigated oxides as electrocatalysts for the oxygen reduction and evolution reactions, in spite of the sparse literature data of the latter oxide.

## 2. Electrochemical methods

The most accepted electrochemical methodologies to evaluate in situ, the real surface area of thin  $\text{Co}_3\text{O}_4$  and  $\text{NiCo}_2\text{O}_4$  films, the capacitance ratio and charge measurements, uses the cyclic voltammetry technique [1,9]. The results are more accurate insofar as they give an estimate of the active surface and in all cases allow data comparison. It must be said that a relative measure is always achieved and not an absolute value.

### 2.1. Capacitance ratio

Voltammetric curves can, in principle, be used to estimate oxide electrodes surface areas. The method has been proposed [1, 10, 11] as being suitable in the case of high surface area oxide electrode and consists on cycling the electrode in a narrow range of potential (e.g. 50 mV) near its

open circuit potential, where no faradic current is flowing. The double layer charging current must be constant, with the anodic and cathodic currents being equal in magnitude for each sweep rate. The method supposes that the capacitance, measured in a featureless potential range, is sensitive to the extension of the surface area without any sensitivity for its chemical composition and requires the knowledge of a reference electrode capacity.

The double layer capacitance,  $C_{dl}$ , is achieved by using the differential form of the equation  $Q = C_{dl} \times V$  which leads to  $I = C_{dl} \times v$ , where  $v$  is the sweep rate. The slope of the charging current versus the sweep rate plot gives the  $C_{dl}$  value and, an intercept equal to zero indicates absence of faradic processes during the cyclic run. The electrode roughness factor value is determined by assuming a double layer capacitance of  $60 \mu\text{F}/\text{cm}^2$  for a smooth oxide electrode surface. It is noteworthy that this value is proposed by Levine and Smith [12] from theoretical considerations. Other values, namely  $80 \mu\text{F}/\text{cm}^2$ , are used elsewhere [13 -15] and were taken as possible values for the capacitance of the oxide-solution interface.

The method presents some limitations and has undergone some criticism [16,17]. The assumption of  $60 \mu\text{F}/\text{cm}^2$  for the capacitance of the unit true surface area of an oxide, irrespective of its nature, is not established. This value may be accurate to only  $\pm 100\%$  [1]. In addition, the dependence of the oxide capacitance on potential is not considered. Another limitation is related to the presence of ohmic drop effects, that introduces distortion on the current potential curves.

The roughness factor values, collected from the literature for the  $\text{Co}_3\text{O}_4$  and  $\text{NiCo}_2\text{O}_4$  thin films and obtained by this technique, are summarized in Table I. The data analysis shows clearly that roughness factor and, consequently the oxide electrodes RSA, depends strongly on the synthesis temperature and for the same synthesis temperature on the substrate nature, oxide preparation method, electrode type, loading, doping, and sintering temperature. Values ranging from 1 to 200 for  $\text{Co}_3\text{O}_4$  and from 8 to 400 for  $\text{NiCo}_2\text{O}_4$  were found, indicating that in general the  $\text{NiCo}_2\text{O}_4$  electrodes are more porous than the  $\text{Co}_3\text{O}_4$  prepared in the same conditions. It is interesting to note that oxides prepared onto glass or onto others oxides, as sublayers are, generally, more porous than those prepared onto the metallic substrate. Exceptionally a higher value, bigger than 3100, was found by one of us [17] for the roughness factors of  $\text{NiCo}_2\text{O}_4$  electrodes with loadings varying from 8 to 10  $\text{mg cm}^{-2}$ .

Higher values were obtained by Nikolov et al. [7] for pressed Teflon-bonded electrodes using this method. For the  $\text{Co}_3\text{O}_4$  values of 8750 and 4570 were obtained for preparation temperature of  $350^\circ\text{C}$  and  $500^\circ\text{C}$  respectively, while 11500 was obtained for the  $\text{NiCo}_2\text{O}_4$  electrode prepared at  $350^\circ\text{C}$ .

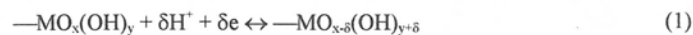
Table I

$\text{Co}_3\text{O}_4$  and  $\text{NiCo}_2\text{O}_4$  thin films roughness factors obtained by voltammetric charging currents

Oxides	Preparation method	Synthesis temperature °C	Roughness factor	References
Ti/ $\text{Co}_3\text{O}_4$	Spray pyrolysis	400	9	18
CdO/ $\text{Co}_3\text{O}_4$	Spray pyrolysis	350	6 to 28	19
CdO/ $\text{Co}_3\text{O}_4$	Spray pyrolysis	400	5	20
Glass/ $\text{Co}_3\text{O}_4$	Spray pyrolysis	400	3	21
$\text{SnO}_2$ / $\text{Co}_3\text{O}_4$	Spray pyrolysis	150	65 to 200	22
Pt/ $\text{Co}_3\text{O}_4$	Nitrates decomposition	350	77	23
NiCr/ $\text{Co}_3\text{O}_4$	Sputtering	-	1	24
Ti/ $\text{NiCo}_2\text{O}_4$	Spray pyrolysis	400	58	18
CdO/ $\text{NiCo}_2\text{O}_4$	Spray pyrolysis	350	8 to 114	19
CdO/ $\text{NiCo}_2\text{O}_4$	Spray pyrolysis	400	65	20
Ni/ $\text{NiCo}_2\text{O}_4$	Spray pyrolysis	400	25	25
Ni/ $\text{NiCo}_2\text{O}_4$	Spray pyrolysis	350	62	26
Pt/ $\text{NiCo}_2\text{O}_4$	Nitrates decomposition	325-350	400	11
Ni/ $\text{NiCo}_2\text{O}_4$	Nitrates decomposition	350	650 to 3188	17

## 2.2. Voltammetric charge

Trasatti and coworkers [14, 27-30] propose the voltammetric charge as a measure of oxide electrodes active surface area. The charge is obtained by integrating the voltammetric peaks just prior to oxygen evolution, providing the surface charge  $q$  transferred under these peaks during the potential scan, and it is generally related to the following redox reaction in acidic medium



According to this process, the local pH increases cathodically and decreases anodically due to the injecting or ejecting of protons into the oxide electrode. In alkaline solution, exchange of  $\text{OH}^-$  takes place at the oxide surface. The application of this method requires reproducible voltammetric curves with well-defined and non-distorted peaks.

The  $q$  value is very sensitive to the oxide surface composition and turns out to be proportional to the

concentration of the active sites undergoing redox reactions.

Charge measurements have been already used to elucidate the surface behaviour of oxide electrodes such as  $\text{Co}_3\text{O}_4$ , and  $\text{NiCo}_2\text{O}_4$  prepared at different temperatures and procedures [31-33]. The referred materials present reversible redox transitions in a potential range where the solvent is not electrochemically decomposed, what make them suitable for the application of the method.

The surface charge  $q$  depends on sweep rate, oxide loading, decomposition temperature, preparation procedure and used electrolyte. The decrease on the voltammetric charge  $q$ , with the increasing on sweep rate, is a recurring observation with oxide electrodes, and can be explained by the exclusion of the inner electrode surface (pores, cracks, grains boundaries, etc.) as the sweep rate increases. The extrapolation of the voltammetric charge to  $v = 0$  and  $v = \infty$  gives, respectively, the total,  $q_t$  and outer,  $q_0$ , surface charges. These values are related by:  $q_t = q_i + q_0$  with  $q_i$  being the inner surface charge [34,35]. The ratio  $q_i/q_t$  is accepted as an electrochemical measure of porosity.

Boggio et al. [16] found for  $\text{Co}_3\text{O}_4$  layers, deposited on titanium substrates by thermal decomposition of nitrate, and with nominal thickness of  $3\mu\text{m}$ , variations on the roughness factor from approximately 10 at  $500^\circ\text{C}$  up to 1000 at  $200^\circ\text{C}$ , assuming a value of  $0.1\text{ mC cm}^{-2}$  (i.e.  $6.2 \cdot 10^{14}$  sites  $\text{cm}^{-2}$ ) for the charge associated with a monolayer of monovalente substance [29].

The same group [36] also reported a value of  $100\text{ mC cm}^{-2}$  for the total surface charge, obtained for freshly prepared  $\text{NiCo}_2\text{O}_4$  layers on titanium at  $450^\circ\text{C}$  and with a thickness of 1-2  $\mu\text{m}$ . This value leads, to a roughness factor of 1000, taking into account the assumed value of  $0.1\text{ mC cm}^{-2}$  for the monolayer charge of a monovalente transition.

It should be referred that the effects of the uncompensated ohmic drop and surface heterogeneity on the integrated charge are neglected in this method. However Baronetto et al. [37] showed that for the  $\text{Co}_3\text{O}_4/\text{Ti}$  electrodes, the voltammetric curves, are affected by a meaningful component of the ohmic drop that comes from the insulating barrier localized at the support/oxide layer interface. In addition, the method cannot be generalized for all the oxides unless they possess redox transition in the appropriate electrolyte. Considerations of confined redox species at the surface without referring to the whole layer thickness are not justified.

Although the limitations, surface charge measurements are very useful, namely when oxides with different composition and/or different preparation method for the same oxide are being compared.

## 3. Adsorption of $\text{Zn}^{2+}$ from the liquid phase

$\text{Zn}^{2+}$  ion adsorption (ZIA) from aqueous solution, on oxide surface, is another attractive method to determine real surface area. Insofar it is carried out on oxide electrodes as used in electrochemical studies, in contrast to suspended powder forms, it might be expected to give more representative

results of the electrochemical conditions. Originally, this method has been proposed by Kozawa for  $\text{MnO}_2$  [38] and extended later to  $\text{SnO}_2$  and other oxides in powder form [39]. Since then, both stearic acid and peridine have been used to measure  $\text{CuO}$  and  $\text{MgO}$  surface area [40]. O'Grady et al. [41] used ZIA method to measure the surface area of  $\text{RuO}_2$  anode. Nevertheless, the first investigation, on  $\text{RuO}_2$  and  $\text{IrO}_2$  deposited thin films, on titanium substrates, emanates from Savinell et al. [42]. Chartier and coworkers have applied the ZIA method to sprayed films of the spinel series  $\text{Cu}_{1-x}\text{Mn}_x\text{O}_4$  [43, 44] and sprayed films of the title spinel  $\text{Co}_3\text{O}_4$  [45, 46]. An attempt was also made to determine the  $\text{NiCo}_2\text{O}_4$  surface area but without outcome [47]. It was found, in this case, that an ion exchange process occurs between the oxide and the solution. In our knowledge, there is no previous work on the evaluation of this oxide real surface made by the ZIA method.

The principle of the method consists in evaluating the  $\text{Zn}^{2+}$  concentration depletion, after the adsorption equilibrium of these ions on the oxide surface. A  $\text{ZnO} - \text{NH}_4\text{Cl}$  solution and a known mass of oxide (on one side covered substrate) is equilibrated during several hours, being the amount of  $\text{Zn}^{2+}$  obtained by titration with ethylenediamine tetraacetic acid (EDTA), in the presence of a colored indicator, a 0.1% in ethanol Erichrom Black T solution. Titrations, are also carried out with an uncovered substrate presenting similar characteristics to the covered one to take into account  $\text{Zn}^{2+}$  absorption in the oxide absence.

The surface area is then calculated by assigning a cross-section of  $17 \text{ \AA}^2$  to an adsorbed  $\text{Zn}^{2+}$  ion [42] and assuming the formation of a complete adsorbed monolayer on the oxide surface. This value was originally established to bring the calculated area into agreement with the BET (Brunauer, Emmet and Teller) surface area.

The pH of the solution determines the amount of adsorbed adsorbate. Nkeng et al. [46] have adjusted the pH at 9 with a few drops of ammonia in order to stabilize the  $\text{Zn}(\text{EDTA})^{2-}$  complex formed during the titration. In this way, they report roughness factors ranging from 190 to 500 for glass/  $\text{Co}_3\text{O}_4$  films prepared by spray pyrolysis at  $350^\circ\text{C}$ .

This method suffers from some limitations and it is not recommended for routine use [9]. Particularly, the adsorption may not reach the full coverage of the oxide, depending on the nature of adsorption sites. Moreover generally the adsorbate ions may have no access to pores cracks or grain boundaries and the chelation mode of adsorbate ions with OH surface groups are not known.

#### 4. Conclusion

The three analyzed methods have been extensively used to estimate the real surface area of porous electrode oxides as used in electrochemical experiments, namely the  $\text{Co}_3\text{O}_4$  and  $\text{NiCo}_2\text{O}_4$ . Each one has its proper requisites: the capacitance ratio requires a potential range where no Faradaic processes

take place, in contrast the charge measurements requires the occurrence of redox processes, characterized by well defined peaks. These requirements have consequences and draw our attention to the fact that these methods cannot be generalized to all electrode oxides. It is evident that they give essentially relative values and do not lead to the same result, but rather to different quantities that are proportional to the surface area. This complicates the physical meaning of the electrochemically active surface area of an oxide. Nevertheless, a linear relation between the estimated roughness factors and the oxide loading has been established, in the case of the  $\text{Co}_3\text{O}_4$  electrodes.

The reliability of a determination in any case depends on the accuracy of the assuming parameters for each method. It must be said that the use of these methods is strictly valid only for an internal comparison for a given material.

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