

# DENSITY OF ELECTROCATALYTIC CENTERS ON ELECTRODES WITH NiO, Co<sub>3</sub>O<sub>4</sub> AND NiCo<sub>2</sub>O<sub>4</sub> COATINGS

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Using of oxygen from ambient atmosphere as one of the reagents in metal-air current sources theoretically opens the possibility of a significant increase in their energy capacity. To obtain high efficiency when discharging such current sources at the cathode, there must be a 4-electron oxygen reduction reaction, which can be obtained in the form of a total equation:



Implementation of an oxygen electrode with a low overpotential is possible when using the phenomenon of electrocatalysis. This is achieved by using such cathode materials that have electrocatalytic activity. In practice, electrodes with a highly developed surface are usually used. For comparison of different catalysts, such electrodes are inconvenient, because besides the catalytic properties the speed of the electrode process is affected by the degree of surface development and its availability for diffusion. It is practically impossible to ensure the equality of these factors for different electrodes. Therefore, it is desirable to carry out measurements on flat electrodes on which the catalyst is applied. In order to compare the catalytic properties, it is also important to provide the same treatment of the catalyst surface.

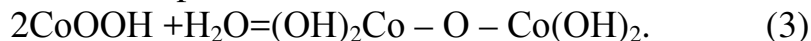
The purpose of this study was to develop a technique and determine the density of the location of the catalytic centers on the electrode surface, which affect the rate of oxygen reduction. The study was carried out on three types of electrodes. As a reference we used nickel with a thickness of 10 μm, applied to a copper plate. Co<sub>3</sub>O<sub>4</sub> and NiCo<sub>2</sub>O<sub>4</sub> were applied for two other electrodes over the Ni layer using hydrothermal method [1,2]. Electrochemical tests were carried out using the cyclic voltammetry at a rate of 1 mV/s. The reference electrode was a saturated silver chloride electrode. All the potentials in the work are referred to a normal hydrogen electrode. The cyclograms were taken in a 1M NaOH solution in the range of potentials from -0.6 to 1.0 V (NHE).

Various mechanisms of oxygen reduction on nickel and cobalt oxides are described in the literature. In this paper we have considered the binuclear mechanism described in [3]. A feature of this mechanism is the presence of two fast electrochemical stages separated by a slow chemical reaction of innercluster reduction of chemisorbed oxygen. This mechanism was considered most thoroughly by Trunov in connection with Co<sub>3</sub>O<sub>4</sub> electrode.

In our work, in order to obtain catalytically active centers, the electrode was polarized by cyclic voltammetry. As a result of cycling in the anodic region, the oxidation of the Co<sub>3</sub>O<sub>4</sub> to CoO<sub>2</sub> takes place. In the cathodic region, a reduction reaction occurs:



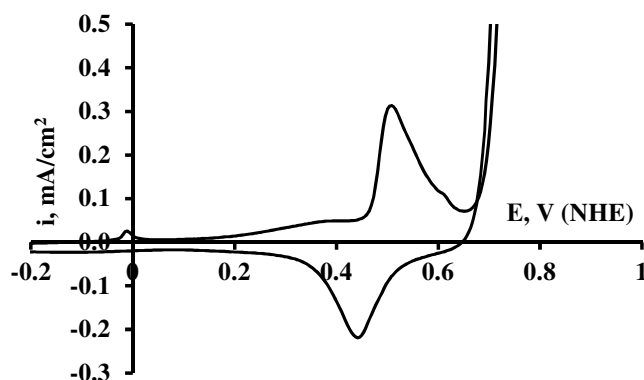
The equilibrium potential of this reaction in a 1M KOH solution was estimated by the authors of [4] as 0.65 V (NHE). In our case, the beginning of the cathodic process is observed approximately at the same potential (figure 1), with the subsequent formation of binuclear complexes:



The reduction rate of reaction (2) depends on the degree of surface coverage  $(1-\theta)$  with cobalt oxide, where  $\theta$  is the fraction of binuclear complexes that varies as the reaction proceeds and can be calculated from the amount of electricity (Q) that passed during the cathodic process:

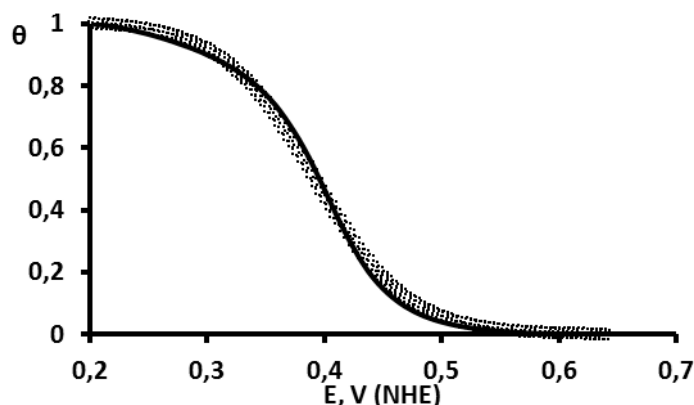
$$\theta = 1 - Q(E)/Q_{\text{sum.}} \quad (4)$$

In this case,  $\theta$  does not in fact mean a portion of the surface, but represents a fraction of the maximum possible number of binuclear complexes that can form on the electrode. Thus, for  $\theta = 1$ , the number of catalytic centers at different electrodes can differ substantially.



**Figure 1.** Cyclic voltammogram at a sweep rate of 20 mV/s of  $\text{Co}_3\text{O}_4$  on nickel in 1M NaOH.

The integration was carried out along the cathode part of the curve to a potential of 0.2 V. The results of the calculation are shown in figure 2.



**Figure 2.** Surface coverage: solid line - experiment, markers - approximation by the Frumkin-Temkin isotherm ( $c = 5.96 \cdot 10^{-5}$ ,  $a = 0.57$ )

The number of binuclear complexes is proportional to the amount of electricity spent on their formation. Expressed in  $\text{mC} / \text{cm}^2$ , it was for pure Ni with a film of

NiO 2.6, for Co<sub>3</sub>O<sub>4</sub> 31.7 and for NiCo<sub>2</sub>O<sub>4</sub> 73.0. The experimental data on the surface coverage  $\theta$  were approximated by the Frumkin-Temkin adsorption isotherm.

$$\theta = \frac{c \cdot \exp\left(a \cdot \frac{F}{RT} E\right)}{1 + c \cdot \exp\left(a \cdot \frac{F}{RT} E\right)}$$

Here  $c$  is a dimensionless adsorption constant, and  $a$  is a lateral attraction constant (at  $a > 0$  there is an attraction between the particles).

To form a binuclear complex according to reaction (3), 2 electrons are consumed, and the density of catalytic centers can be calculated (table).

**Table.** Density of the catalytic centers.

Catalyst	Q, mC/cm <sup>2</sup>	Number of centers, cm <sup>-2</sup>	Average distance, cm
NiO	2.6	$8.07 \cdot 10^{15}$	$1.11 \cdot 10^{-8}$
Co <sub>3</sub> O <sub>4</sub>	31.7	$9.84 \cdot 10^{16}$	$3.19 \cdot 10^{-9}$
NiCo <sub>2</sub> O <sub>4</sub>	73.0	$2.27 \cdot 10^{17}$	$2.10 \cdot 10^{-9}$

As follows from the data of the last column, at such a short distance binuclear complexes cannot be located. Apparently, two factors are decisive: the resulting oxides have a three-dimensional structure with a developed surface, in addition, perhaps their multilayer arrangement. In this case, it is unclear to what extent the high density of catalytic centers will contribute to the increase in the available reaction surface. In further studies it is necessary to determine the fraction of active sites of oxygen available for diffusion.

### References

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