

Equivalent electrical circuits of impedances of Pt, Ir and Ni electrodes under anodic polarization

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Nano-structured and bulk Pt, Ir, Ni electrodes as well as their alloys are widely used as electrocatalysts in the anodic oxidation of various organic and inorganic substances: methanol, ethanol, ammonia and urea oxidation, and oxygen evolution reaction. In the study of these processes by means of electrochemical impedance spectroscopy (EIS) there is the problem of modeling of the electrical circuit equivalent to the impedance of the electrocatalyst under its anode polarization. Currently, this problem is not entirely solved for both micro- and nano-structured electrodes [1-4].

The aim of this work is the modeling of the electrical circuits equivalent to the respective impedances of polycrystalline Pt, Ir, and Ni electrodes based on the experimental EIS data obtained in 0.5 M H<sub>2</sub>SO<sub>4</sub> under anodic polarization.

The anodic current is observed on cyclic voltammograms in the "electrical double layer" region for both Pt and Ir, and in the passivation region of Ni electrode. At the same time, the impedance spectra at these potentials deviate from the shape characteristic of impedance spectrum of an ideally polarized electrode, which is a serial connection of a resistor and a capacitance. Therefore, in the proposed equivalent impedance circuit (Figure 1) we incorporated a branch containing a resistor. The resistor is connected in parallel to a branch, which has a capacitor corresponding to a capacitance of the electrical double layer. Since the experimental spectrum differs significantly from a semicircle with a center on the abscissa axis, which is characteristic of the parallel connection of a capacitance and a resistance, another branch is added to the electrical circuit. The additional branch has at least two elements (Figure 1).

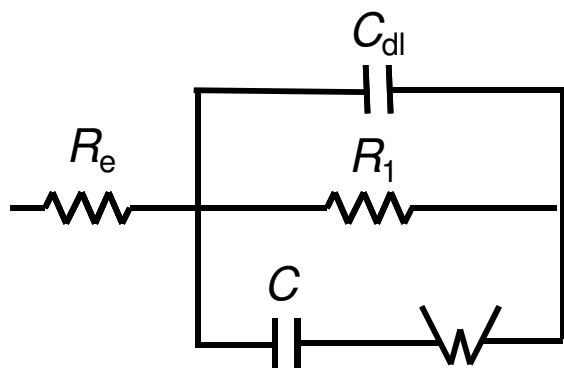


Figure 1: Equivalent electrical circuit

Recently [5], the diagnostic coordinates were proposed for some of these combinations of elements. In these coordinates one obtains a straight line if the experiment corresponds to the theoretical model and therefore to the proposed electrical circuit.

For branches with a series connection of Warburg impedance and a capacitance, the total impedance is:

$$Z = (1 - j)\omega^{-1/2}A + (j\omega)^{-1}C^{-1} \quad (1)$$

where  $A$  is the Warburg constant. After minor transformations we obtain:

$$Z' - jZ'' = (j\omega)^{-1}C^{-1} \quad (2)$$

Figure 2 shows in logarithmic coordinates the results of processing the residual experimental impedance components of Pt, Ir and Ni electrodes after the preliminary determination of  $C_{dl}$  and  $R_1$ .

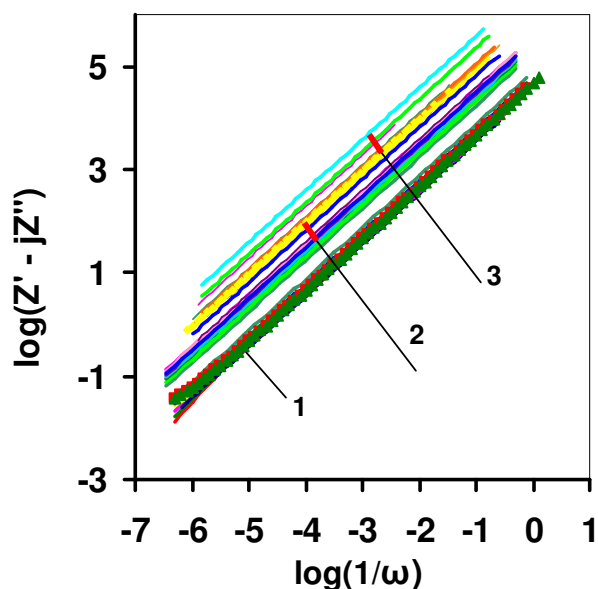


Figure 2: Relevance of the theory to experiment. Groups of lines: (1) Pt ( $E = 0 - 1200$ ) (2) Ni ( $E = -50 - 1000$ ) (3) Ir ( $E = -100 - 800$ ) ( $E$  vs. RHE, mV)

As it can be seen from Figure 2 there is an excellent agreement between the synthesized equivalent electrical circuit and the experimental impedance spectra of Pt, Ir and Ni electrode in 0.5 H<sub>2</sub>SO<sub>4</sub> in the proposed diagnostic coordinates.

#### References:

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