To selection of low-wear anode coatings based on iridium, ruthenium, titanium and tantalum oxides for direct electrolysis of natural waters

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Abstract. Selection of anode coatings to obtain low-concentration sodium hypochlorite by direct electrolysis of natural waters is considered. The corrosion resistance of anodes with different packing of ruthenium, iridium and tantalum oxides, as well as their characteristics have been determined: chlorine current output, cell voltage, dynamics of growth of active chlorine concentration in solution. It is shown that when tantalum is added to the OIRTA system composition, the solid solution system turns from the three-component one into the four-component one, which adds certain advantages to the metal oxide coating of the anode: increased anode service life, reduction of the specific packing of precious metal (cost reduction), reduction of energy costs, which allows to conclude that it is expedient to use an OIRTA-Ta coating.

1. Introduction
The annual demand for sodium hypochlorite (HCS) is constantly growing. This reagent is widely used as a disinfectant, for cleaning the surface, bleaching fabrics, removing odor [1,2], anodic oxidation of dye molecules [3-6], phenols in wastewater [7], etc. Hypochlorite has many advantages: ease of dosing, monitoring and determining safe storage and transportation, the possibility of obtaining at the place of consumption, and the relative cheapness of raw materials.

As a rule, sodium hypochlorite is generated by electrolysis of aqueous solutions of edible salt (NaCl). Among the operating costs for the production of sodium hypochlorite, along with the cost of electricity, the cost of salt used as a source of chloride ions has the greatest effect [8]. Therefore, one of the most promising and less costly methods of chemical and biocidal water treatment is the production of HCS by the electrolysis of chloride-containing solutions, which can be sea water, groundwater and surface water [8-10].

Natural waters used for drinking purposes have low mineralization (up to 1 g/l). The electrolysis of such water proceeds with a high voltage (6-8 V) on the electrolyzer cell. It is very important to reduce the voltage on the electrolyzer to reduce power consumption while maintaining the same performance as active chlorine.
The efficiency of electrochemical disinfection depends on the device of the cell, the electrode material, the composition of the solution, the conditions of mass transfer, the current density and the potential of the electrode [11]. The most significant, determining electrical and electrochemical parameters of electrolysis, its efficiency and operational regulations, the design of the apparatus and their durability is the material of the anode [12-17].

The electrode material is one of the factors that determine the direction of the electrode reaction, the reaction rate, the performance and the quality of the product. Electrodes shall meet the requirements of: high electrical conductivity, effective electrochemical catalysis for desired reactions, chemical corrosion resistance, mechanical strength, reasonable price [18,19].

Selection of electrodes should be carefully considered, since the electrode material and its surface treatment or modification can completely change the mechanism of the reaction process, the formation of by-products and, thus, change the characteristics of the final product [20-22].

The most optimal from the point of view of corrosion resistance and selectivity of electrochemical processes are multicomponent systems. These systems are called a mixture of solid solutions consisting of two or more components that are in a solid state.

One of the relatively new materials used to coat the anode electrodes is boron doped diamond electrodes (BDD). BDD are being actively studied both in Russia and abroad, however, such coatings have not yet found wide application in industry, in particular, in the production of low-concentrated sodium hypochlorite by direct electrolysis due to its high cost and the probability of formation of by-products during electrolysis [23-28].

Results of the studies of HCS electrosynthesis on electrodes made of graphite, platinum, manganese oxides, lead, cobalt, cobalt aluminate and ruthenium oxide led to the conclusion that oxide-ruthenium-titanium anodes (ORTA) and OIRTA (oxide-iridium-ruthenium-titanium are most effective anodes). However, along with the advantages (high selective and electrocatalytic properties, mechanical and corrosion resistance) ORTA and OIRTA, like other anodes, are not without drawbacks, the main of which is the limited service life associated with the continuous reduction of the active coating thickness during electrolysis and, as a result, irreversible loss of ruthenium and iridium oxide [29, 30]. This problem is particularly acute with the use of reverse polarity technology (reverse) - periodic switching of the electrode operating mode from anodic polarization “+” to cathodic “−” and back. Re-polarity is used as a way to combat the formation of hardness salt deposits on cathodes, which, when not properly removed (prevented), disrupt the operation of the electrolyzer, which leads to rapid destruction of the electrodes, especially during the electrolysis of natural hard waters.

Our previous studies have shown that the inclusion of iridium in anodic ruthenium-titanium oxide coating with a percentage-mass ratio of iridium to ruthenium 80:20 increases the corrosion resistance of anodes by 8 times [31]. Anodic coatings containing iridium in the bulk are operated with less energy, due to the lower voltage on the electrolyzer. The Ti/RuO₂-IrO₂ anode has a low chlorine yield potential and high corrosion resistance with good conductivity.

The annual appreciation of iridium compared to ruthenium has led to research aimed at reducing the cost of anodic coating while simultaneously increasing the service life of the anode. In [32], the possibility of applying a coating with tantalum added to OIRTA was determined, which makes it possible to reduce the cost of coating by partially replacing iridium with tantalum.

The lack of research on the corrosion resistance and energy efficiency of OIRTA and OIRTA + Ta coatings in the production of low-concentrated HCS using diaphragm-free electrolysis determines the need for research on such electrode coatings.

2. Methods

For the manufacture of anodes used titanium brand VT1-0. Anode preform was subjected to sandblasting the surface over the entire area on both sides. The surface of the anode blanks after sandblasting was washed in warm water with detergent. The surface of the metal was degreased with an alkaline solution. Chemical etching was carried out after degreasing the surface in a solution of
sulfuric acid. After degreasing and pickling, the samples were washed. For no more than three hours, the coating was applied to the surface of titanium.

Corrosion resistance was determined on anodes with a different mass ratio of metals (ruthenium, iridium, tantalum) in the coating. A mixture of salts of metals of the platinum group — RuCl₃, IrCl₃, TaCl₅ in combination with TiCl₄ was used as the anodic coating. The total mass of precious metals in the coating varied from 6 to 10 g/m², the mass of TiO₂ in all coatings was 2 g/m².

To test the corrosion resistance of the coating (“lifetime”) and predict its service life compared to the actual operating time of the electrodes, we used an accelerated method for determining the quality of the coating according to the method [33], according to which the onset of coating destruction occurs when the voltage rises from the initial value by 3.5-5.5 V. The corrosion resistance of the anode coating was tested in a 1.5 M H₂SO₄ solution at a current density of 30,000 A/m², with a constant temperature of 30–35°C.

Studies of the ability of coatings to form active chlorine were carried out on an experimental setup presented in Figure 1. Investigations were carried out in an electrochemical cell of a non-diffraction type in a circulation mode of operation using an anodic-cathode coating of 14 cm² each immersed in a solution of sea water, a solution volume of 300 ml, and a current density of 1000 A/m².

The microstructure of the samples was studied on a VEGA II LMU (Tescan) scanning electron microscope equipped with the INCA ENERGY 450/XT energy dispersive microanalysis system (Silicon Drift detector (ADD)). Images were obtained using a scintillator-type ring electron reflection detector (YAG crystal).

100x200 mm samples with a different type of coating and specific packing of precious metal in the amount of 2 pcs. each were made for the research (see Table 1).

3. Results
The results of studies of the corrosion resistance of anodic coatings are presented in Table 3. From the obtained results (Table and Fig. 2), it can be seen that the best performance was shown by the coating of sample No.4, having an Ir/Ru oxide ratio of 50/50% and Ti/Ta 50/50% with a final heat treatment of 550 °C for 1 hour.

In parallel with the studies of the “lifetime” of the samples, studies were conducted to determine the ability of coatings to form active chlorine.

From the results of testing developed corrosion-resistant coatings, it can be concluded that the maximum concentration of active chlorine is given by ORTA-type coating - 13.8 g/dm³ (Figure 3). At OIRTA 50/50, in which TiCl₄ and TaCl₅ are introduced in equal proportions, the concentration of active chlorine is 12 g/dm³, which gives an increase of 1 g/dm³ with a heat treatment of 450 by 550°C.
When TiCl₄ is completely replaced by TaCl₅, the chlorine yield drops to 7.8 g/dm³. Finishing heat treatment of the coating at 550 °C gives an increase from 7 to 12 g/dm³.

### Table 1. The results of studies of the corrosion resistance of anode coatings.

| Sample No. | Coating type                                      | Number of layers, pieces | Specific packing (by weight), g/m² | Test time, h |
|------------|---------------------------------------------------|--------------------------|-----------------------------------|--------------|
| 1.         | ORTA                                              | 9                        | 8                                 | 1.57/5.04/6.16 |
| 2.         | OIRTA (Ir 50% - Ru 50% - Ti 100%)                 | 9                        | 7.5                               | 18.28/18.45/21.49 |
| 3.         | OIRTA – Ta (Ir 50% - Ru 50% - Ti 50% - Ta 50%), heat treatment at 450°C | 7                        | 5.6                               | 63.59/76.24/82.07 |
| 4.         | OIRTA – Ta (Ir 50% - Ru 50% - Ti 50% - Ta 50%), heat treatment at 550°C | 7                        | 5.6                               | 117.2/123.0/132.1 |
| 5.         | OIRTA – Ta (Ir 50% - Ru 50% - Ti 50% - Ta 100%), heat treatment at 450°C | 9                        | 7.5                               | 33.50/37.22/44.05 |
| 6.         | OIRTA – Ta (Ir 50% - Ru 50% - Ti 50% - Ta 100%), heat treatment at 550°C | 9                        | 7.5                               | 45.57/49.22/53.35 |

![Figure 2](image)

**Figure 2.** Coating time when tested for corrosion resistance: 1 – ORTA; 2 – OIRTA (Ir 50% - Ru 50% - Ti 100%); 3 - OIRTA – Ta (Ir 50% - Ru 50% - Ti 50% - Ta 50%), 450°C; 4 - OIRTA – Ta (Ir 50% - Ru 50% - Ti 50% - Ta 50%), 550°C; 5 - OIRTA – Ta (Ir 50% - Ru 50% - Ti 50% - Ta 100%), 450°C; 6 - OIRTA – Ta (Ir 50% - Ru 50% - Ti 50% - Ta 100%), 550°C.

The minimum indicators of chlorine current yield were observed on the anodes with tantalum, the maximum on the OIRTA 50/50 and ORTA. During the first 60 minutes of electrolysis (Figure 4), the current chlorine output is maximum, then it gradually decreases, which is explained by side reactions at the anode and cathode, which reduce the current output of active chlorine [8, 30].

From figure 5 it follows that the general nature of the dependences of the energy consumption of different coatings is similar, but differs in energy costs. Thus, by spending the same amount of electricity (about 5–6 kW·h/kg), it is possible to obtain oxidant concentrations from 2 to 9 g/dm³. The specific electric power consumption on all investigated coatings was in the range of 4.5-23.0 kW·h/kg. From fig. 5 also shows that coatings containing tantalum with a heat treatment of 450 °C are more energy-intensive (6.0-23.0 kW·h/kg) due to the higher voltage on the electrolysis cell.

The concentration of active chlorine of 8 g/dm³ on coatings with the addition of tantalum during heat treatment of 550 °C, OIRTA and ORTA occurs at the same energy expenditure of about 5-6 kW·h/kg. The ORTA coating showed the best results, the maximum concentration of active chlorine 12.5 g/dm³ was obtained with a minimum energy expenditure of 11 kW·h/kg.
Figure 3. The dependence of the concentration of active chlorine on the operating time of the investigated coatings: 1 – ORTA; 2 – OIRTA (Ir 50% - Ru 50% - Ti 100%); 3 - OIRTA – Ta (Ir 50% - Ru 50% - Ti 50% - Ta 50%), 450°C; 4 - OIRTA – Ta (Ir 50% - Ru 50% - Ti 50% - Ta 50%), 550°C; 5 - OIRTA – Ta (Ir 50% - Ru 50% - Ti 50% - Ta 100%), 450°C; 6 - OIRTA – Ta (Ir 50% - Ru 50% - Ti 50% - Ta 100%), 550°C.

During electrolysis, the efficiency of the investigated coatings can be characterized by comparing the current output of chlorine (Figure 4) and the unit cost of electricity per kilogram of the active chlorine produced (Figure 5).

Figure 4. The dependence of the chlorine current yield on the operating time of the investigated coatings: 1 – ORTA; 2 – OIRTA (Ir 50% - Ru 50% - Ti 100%); 3 - OIRTA – Ta (Ir 50% - Ru 50% - Ti 50% - Ta 50%), 450°C; 4 - OIRTA – Ta (Ir 50% - Ru 50% - Ti 50% - Ta 50%), 550°C; 5 - OIRTA – Ta (Ir 50% - Ru 50% - Ti 50% - Ta 100%), 450°C; 6 - OIRTA – Ta (Ir 50% - Ru 50% - Ti 50% - Ta 100%), 550°C.
Figure 5. The amount of electricity consumed to obtain a kilogram of active chlorine, depending on the concentration of active chlorine: 1 – ORTA; 2 – OIRTA (Ir 50% - Ru 50% - Ti 100%); 3 - OIRTA – Ta (Ir 50% - Ru 50% - Ti 50% - Ta 50%), 450°C; 4 - OIRTA – Ta (Ir 50% - Ru 50% - Ti 50% - Ta 50%), 550°C; 5 - OIRTA – Ta (Ir 50% - Ru 50% - Ti 50% - Ta 100%), 450°C; 6 - OIRTA – Ta (Ir 50% - Ru 50% - Ti 50% - Ta 100%), 550°C

Analyzing the results of experiments "lifetime" of the coating and the release of active chlorine current, it is necessary to take into account not only the ability of the coatings to produce active chlorine, but also to take into account the lifetime of the anode in the electrolyzer.

The results of studies of the structure of materials by the electron probe method are presented in Figure 6 in the form of microphotographs of the surface of the three coatings of the anodes OIRTA + Ta, OIRTA and ORTA, respectively, samples No.4, 2 and 1 table. In all samples, the coating material is homogeneous in terms of structure, phase and chemical composition. From the research results it can be seen that the coating with the addition of tantalum is solid and has many small cracks in the surface layer. OIRTA coating has deep long cracks located on surface irregularities. On the ORTA coating, deep cracks are visible with the simultaneous presence of solid sections. The presence of deep cracks in the coating allows us to conclude that they have a shorter service life due to the fact that the processes of destruction of the oxide layer do not proceed on the surface, but already at the initial stage in its thickness.

4. Conclusion
It is possible to state that the addition of additional components to the anode does not always make it possible to achieve the set result for an increase in the electrochemical characteristics and durability of the coating. However, when the desired result is achieved, it is possible to obtain high performance of the electrode while reducing their cost.

When the fourth oxide – TaO₂ oxide is introduced into the three-component RuO₂ – IrO₂ – TiO₂ system, the anode lifetime increases by no less than two orders of magnitude and is 80–150 hours by the accelerated method. The concentration of active chlorine on the ORTA type coating is maximum and equal to 12.5 g/dm³, but the “lifetime” is 2-10 hours (specific packing 6-10 g/m²) compared to the OIRTA-Ta coating, which has a maximum active chlorine concentration of 12 g/dm³, and a lifetime of 80-150 hours (specific packing 5.6-7.5 g/m²).

When tantalum is added to the OIRTA composition, the system of solid solutions from the three-component one goes into the four-component one, which adds certain advantages to the metal oxide coating of the anode: increased anode service life, reduction of the specific packing of precious metal (cost reduction), reduction of energy costs, which allows to conclude that it is expedient to use an OIRTA-Ta coating.
Figure 6. Microphotographs of OIRTA+Ta, OIRTA and ORTA coatings.

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