The calculation was carried out while using for function G*, both the expressions (4) and (6) and the result obtained previously in [6] in the context of Eq. (5). Over the range of parameters examined for the model used to describe the dielectric nonuniformity, both of the above definitions of function G* gave results which had a very weak effect on the shape of function $\chi_a^{(1)}(x)$.

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INVESTIGATION OF THE ADSORPTION OF IONS AND THE STRUCTURE OF THE ELECTRICAL DOUBLE LAYER ON RUTHENIUM – TITANIUM OXIDE ANODES

INFLUENCE OF THE COMPOSITION OF THE OXIDE COATING ON THE ADSORPTION OF ANIONS

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The electrochemical properties of ruthenium-titanium oxide anodes (RTOA), produced by thermal decomposition of solutions applied on a titanium base, are largely determined by the amount and ratio of ruthenium and titanium oxides contained in the coating [1-10]. The electrochemical activity of oxidized alloys of titanium and ruthenium is also determined by the ruthenium concentration in them [11, 12]. A change in the oxide coating of RTOA leads to a change in the conductivity and microstructure of the coating [1, 9, 13, 14]. An important source of information permitting the establishment of the interrelationship between the physicochemical properties of RTOA of various compositions and their electrochemical properties, is provided by investigations of the adsorption capacity of RTOA. The study of adsorption on RTOA with various amounts of the oxides RuO_2 and TiO_2 also permits a determination of the role of each of the oxides contained in the coating. There is no such information in the literature.

The method of preparation of the RTOA electrodes, the radioisotopic method for measuring the adsorption, and the radioactive preparations were the same as in [15]. Electrodes annealed at 480°C contained 0, 10, 30, 50, 70, and 100 mole % RuO_2 (remainder TiO_2). In the preparation of the electrodes, to vary the percent content of the coating, the amount of the oxide TiO_2 in the coating was varied, while the amount of the oxide RuO_2 was left constant (7.1 g/m^2 of visible surface); thus, electrodes with a smaller fraction of ruthenium oxide in the coating were characterized by a larger total amount of mass of the coating per unit visible surface. Summary data on electrodes of various compositions are presented in Table 1 (the data are cited calculated for titanium and ruthenium dioxides). As can be seen from the table, the roughness factor is high and varies within wide limits.

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TABLE 1. Summary Data on Electrodes of Various Compositions

Amount of oxides in the coating			Total amount of oxides,* g/m²	Roughness factor of electrodes according to BET	Amount of oxides in the coating			Total amount of oxides,* g/m²	Roughness factor of electrodes according to BET
RuO_2, mole %	RuO_2,* g/m²	TiO_2,* g/m²			RuO_2, mole %	RuO_2,* g/m²	TiO_2,* g/m²		
0	–	24,2	24,0	670	50	7,1	4,2	11,3	300
10	7,1	38,4	45,5	1800	70	7,1	1,8	8,9	120
30	7,1	9,6	16,7	700	100	7,1	–	7,1	160

* Calculated per m^2 of visible surface.

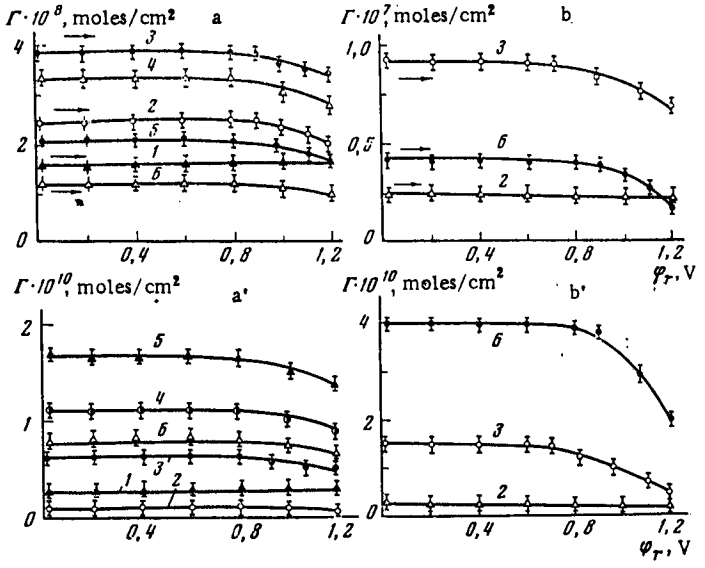

Fig. 1. Dependence of the values of the adsorption of anions of sulfuric (a, a') and hydrochloric (b, b') acids on the potential of the RTOA calculated for the visible (a, b) and true (a', b') surface of the electrodes in solutions of 10^{-3} M H_2SO_4 + 0.1 M $HClO_4$ (a, a') and 10^{-2} M NaCl + 0.1 M $HClO_4$ (b, b') at various ratios of the oxides RuO_2 and TiO_2 in the coating. Content of RuO_2 in the coating, mole %: 1) 0, 2) 10, 3) 30, 4) 50, 5) 70, 6) 100. The arrows indicate the direction of variation of the electrode potential.

Experiments on adsorption were conducted at 22°C. The supporting electrolyte used was 0.1 M $HClO_4$, "special purity." The results of a measurement of the adsorption in solutions of hydrochloric and sulfuric acids are presented in Figs. 1 and 2.* The measurements were performed in precisely the same way as in [15].

In Fig. 1a and b, the values of the adsorption of anions are cited calculated per visible surface of the electrodes, while in Fig. 1 (a', b') and Fig. 2 they are cited calculated for the true surface.

From Figs. 1 and 2 it can be seen that at all compositions of the coating there is a specific adsorption of anions, and that the amounts of adsorbed anions at all potentials and concentrations depend on the composition of the coating calculated both for the visible and for the true surface of the RTOA. From Fig. 1 it is evident that for anions of sulfuric and hydrochloric acids, for all compositions of the coating, the value of the

* Figures 1 and 2 present the static values of the adsorption of anions. We did not specially study the kinetics of the adsorption of anions. The time of reaching of the static values of the adsorption was equal to an average of 5 min.

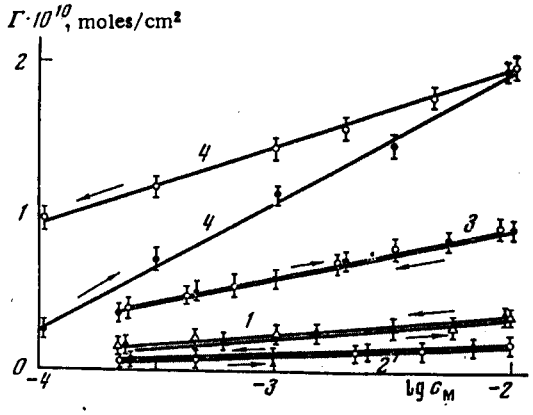

Fig. 2. Dependence of the adsorption of sulfuric acid anions on their concentration in a solution with composition x M H_2SO_4 + 0.1 M $HClO_4$ at the potential 0.4 V on TiO_2 (1) and on RTOA of various compositions of the coating (2-4). Content of RuO_2 in the coating, mole %: 2) 10, 3) 30, 4) 100. The arrows indicate the direction of variation of the concentration of anions in solution.

adsorption of anions is independent of the RTOA potential within the limits of the experimental error in the region of φ_r* from 0 to 0.8 V. The analogous nature of the dependences obtained indicates the same nature of the adsorption of anions on RTOA with different compositions of the coating. When the composition of the coating is varied, differences are observed in the behavior of the anions at $\varphi_r > 0.8$ V (Fig. 1), which may be associated with the different absorbability of oxygen on these coatings [7].

From Fig. 2 it can be seen that the dependences of the values of the adsorption of anions on their concentration in solution, obtained when the concentration is increased from 10^{-4} to 10^{-2} M, entirely coincide with those obtained when the concentration is varied from 10^{-2} to 10^{-4} M. This conclusion is correct for coatings containing 0, 10, and 30 mole % RuO_2 (curves 1-3). If, however, the measurements were performed on coatings consisting of 100% RuO_2, there is a hysteresis (curve 4, Fig. 2).

The experimental data described above permit us to assert that changes in the composition of the coating of the RTOA are not accompanied by any change in the basic principles and nature of the adsorption of anions, but cause chiefly a change in the absolute amount of adsorbed anions.

It is known that the working substance of the RTOA is a metastable, defective, and incompletely crystallinely ordered phase of rutile solid solutions; free RuO_2 is also present in the film, and at low concentrations of RuO_2, solid solutions with an anatase structure are also present [1, 9, 13, 14]. Therefore, it might be expected that the film is also inhomogeneous in adsorption capacity.

The opinion is expressed in the literature [4, 7, 12] that the adsorption on mixed RuO_2-TiO_2 coatings occurs chiefly on centers of the surface containing ruthenium atoms. From an examination of Fig. 1a and b it follows that at a constant amount of Ru in the coating, with increasing mole fraction of Ru in it, the adsorption of anions passes through a maximum. This dependence in the case of the adsorption of the anion of sulfuric acid (according to the data of Fig. 1a) is represented by curve 1 of Fig. 3. If adsorption were determined only by Ru atoms, its value would not depend on the composition, since the absolute amount of Ru per unit visible surface in coatings of all compositions was the same.

In the case of oxygen [7], the differences in the values of its adsorption at various compositions of the coating are no more than 30% of the value of its adsorption on the individual oxide RuO_2, i.e., the values of the adsorption on different compositions are comparatively close, while the dependences of the adsorption on the composition themselves have not a maximum, but a minimum. In the case of adsorption of anions, the differences in the values of the adsorption are significantly greater (for ions of hydrochloric acid approximately twice as great, for anions of sulfuric acid more than twice as great). It might have been assumed that for

*φ_r is the electrode potential relative to the reversible hydrogen electrode in the same solution.

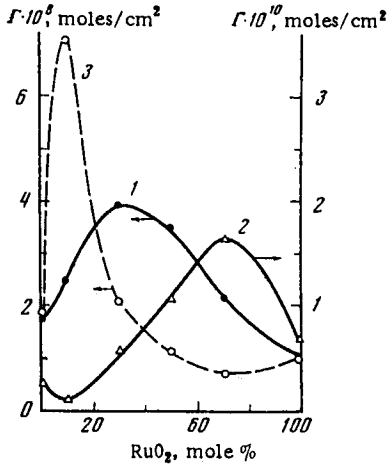

Fig. 3. Dependence of the adsorption of anions of sulfuric acid on the composition of the coating at a potential 0.4 V from a solution of 10^{-3} M H_2SO_4 + 0.1 M $HClO_4$ per unit visible surface (1) and per unit true surface (2) and dependence of the adsorption calculated according to the data of curve 1 on the assumption that the adsorption on the mixed oxide is an additive sum of the adsorption on the individual oxides RuO_2 and TiO_2 (3). Remaining explanations in text.

anions this is associated with supplementary adsorption on active sites containing TiO_2, since there is a substantial adsorption of anions on the individual oxide TiO_2.

The dependence of the adsorption of anions on the composition of the coating per unit true surface can be calculated according to the data of curve 1 of Fig. 3. Such a dependence, represented in Fig. 3 by curve 2, is also complex.

Curve 3 in Fig. 3 represents the calculated curve of the dependence of the adsorption of anions on a unit visible surface on the composition of the coating, obtained on the assumption that adsorption is made up of adsorption on the oxide RuO_2 and on the oxide TiO_2, occupying the fraction of the total surface that corresponds to a set composition of the mixed phase. Calculation was performed considering the change in the mass of the coating (see Table 1). From Fig. 3 it is evident that as a result of calculation, a curve with a maximum was obtained. But curve 3 differs substantially from the experimental data (Fig. 3, curve 1), both in absolute value of the adsorption and in the position of the maximum, which indicates the impossibility of describing the adsorption properties of the coatings of the RTOA with the aid of a model of simple additivity. The absence of simple additivity is also indicated by the nonlinearity of the dependence of the degree of coating of the surface with oxygen on the composition of the coating, found in [7]. Thus, the data cited in this work can be explained, on the one hand, by the fact that the composition of the surface does not correspond to the volume composition of the phase, and on the other hand, by the fact that there is an appreciable mutual influence of Ru and Ti atoms, so that their properties in the mixed oxide differ from their properties in the pure phases.

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EFFECT OF THE ANION ON THE SINTERING RATES OF ELECTROLYTIC PLATINUM DEPOSITS APPLIED TO PLATINUM AND TANTALUM

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Work has been published in recent years concerning the sintering of disperse structures of platinum-group metals in aqueous electrolyte solutions [1-5]. Factors such as the potential [1, 3-5], gas adsorption (H_2 [4-7], O_2 [3-7], and CO [1]) and the adsorption of various impurities present in the electrolyte [1, 3] influence the surface changes occurring in these structures during sintering. It was shown in [5] that the influence of potential on the sintering rate of electrolytic platinum and rhodium deposits in sulfate and fluoride electrolytes is governed by the variation of the reversible surface work of formation of unit surface area, σ (or the associated value of surface tension, γ) with potential. The specific adsorption of anions is known to produce a significant decrease in σ [8]. It is the principal task of the present work to examine the effect of the anion (with SO_4^{2-}, Cl^-, and Br^- ions as examples) on the sintering rate of electrolytic platinum deposits at different potentials. Also touched upon in the present work are some aspects of the sintering mechanism of the electrolytic platinum deposits.

Test samples were electrolytic platinum deposits applied to platinum or tantalum sheets with S_{app} = 1 cm^2 from 4% aqueous H_2PtCl_6 solution at 20°C under potentiostatic conditions: to Pt at φ_r = 250 mV [9], and to Ta at φ_r = 150 mV [10]. The surface areas were calculated from the hydrogen sections of the charging curves [11] measured in 1 N H_2SO_4 at 20°C before (S_{in}) and after (S_f) sintering, Sintering of the electrolytic deposits was conducted by the procedure reported in [5]; the solutions: 1 N H_2SO_4, 1 N Na_2SO_4 + 0.01 N H_2SO_4, 1 N KCl + 0.01 N HCl, and 1 N KBr + 0.01 N HBr were used, the temperature limits were 40 and 80°C. Kinetic curves of the degree of sintering, A ($A = (S_{in} - S_f)/S_{in} \cdot 100\%$) were recorded as functions of time, τ, at constant φ_r, and A vs φ_r curves were recorded at constant τ (τ = 2 h). The reproducibility of the A values was ±5%.

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