LIBERATION AND IONIZATION OF CHLORINE ON RUTHENIUM-TITANIUM OXIDE ELECTRODES AT INCREASED CURRENT DENSITIES.

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Earlier [1, 2] we suggested a mechanism of the chlorine reaction on a ruthenium-titanium oxide electrode (RTOA). According to this mechanism the kinetic principles of the reaction, in particular, the low Tafel slope of the anodic branch of the polarization curve, equal to 30 mV [3], are explained by barrierless occurrence of the slow electrochemical oxidation of atomic chlorine in the sequence of steps:

$$Cl^{-}{}_{aq}-e\rightleftarrows Cl_{ad};\ Cl_{ad}-e\rightarrow Cl^{(+I)};\ Cl^{(+I)}+Cl^{-}{}_{aq}\rightleftarrows Cl_2.$$

In accord with this mechanism, the Tafel slope of the anodic branch of the polarization curve in general is expressed in the form $b = 2.3RT/(1 + \alpha)$ [1]. In the case of barrierless discharging, $\alpha = 1$ and $b = 30$ mV.

As is well known, when the anodic overvoltage is increased, the barrierless process should give way to a normal process [4], to which $\alpha = 0.5$ corresponds, and, consequently, $b = 40$ mV. To verify this conclusion, it was necessary to achieve overvoltages at which a change in α occurs, i.e., we have to increase the true-current density, while avoiding diffusion limitations and ohmic potential drops. For this purpose we prepared RTOA with an extremely thin oxide layer – several hundredths of a gram of Ru_{met} per m^2 of electrode surface.

The polarization curves, taken on such electrodes (Fig. 1) actually consist of two Tafel portions. The slope of the upper portion is equal to 40 mV. The fractional value $\alpha \approx 1.5$ confirms a three-step mechanism with an electrochemical (one-electron) slow step, which proceeds barrierlessly in the region of the lower portion.* The orders of the reaction with respect to Cl_2 and Cl^- are the same for both portions, as a result of which the value of the potential corresponding to their intersection does not depend on P_{Cl_2} and $[Cl^-]$. This is responsible for the regular shift of the overvoltage, in which case breaks are observed on the polarization curve with increasing reagent concentration, agreeing with the shift of the equilibrium potential. These dependences indicate that the same reaction mechanism corresponds to both Tafel portions. Consequently, the change in the Tafel slope is due to a change in the transport coefficient α, and not replacement of the rate-determining step. Moreover, this conclusion follows from the low value of the slope of the upper portion (40 mV). Actually, if there were a replacement of the rate-determining step with increasing potential, then at more-positive potentials the first electrochemical step of the anodic process – the step of discharging of the Cl^- ion – should have become the rate-determining step. However, then the Tafel slope could not be less than 60 mV (a substantiation of this was cited in [1]).

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*The Tafel slope of the lower portion (30 mV) and other kinetic principles can also be explained on the basis of the two-step scheme of the mechanism with a slow first two-electron step $Cl^{-}{}_{aq} - 2e \rightarrow Cl^{(+I)}$. In this case the Tafel coefficient $b = 2.3RT/2\alpha F$. Without barrierless discharging $\alpha = 1$ and $b = 30$ mV. Generally speaking, the two-electron mechanism is less probable than a one-electron mechanism and does not describe the experimental data as well, since for it the transition to a normal process with $\alpha = 0.5$ leads to a slope of 60 mV, and not 40 mV.

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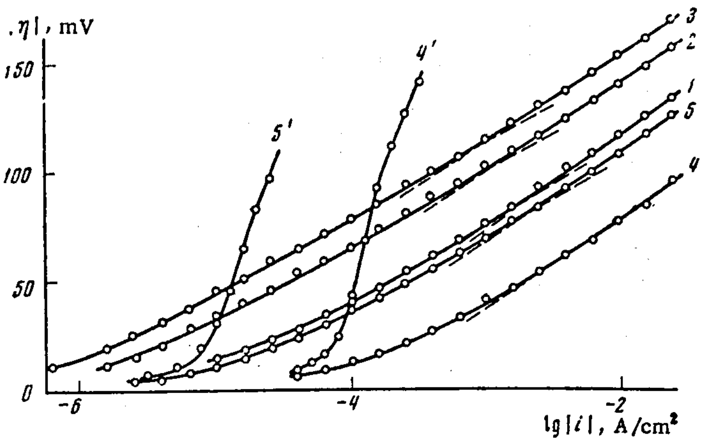

Fig. 1

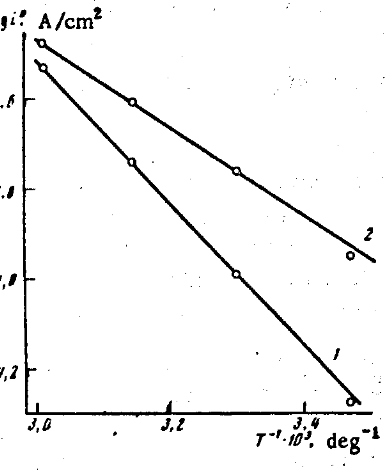

Fig. 2

Fig. 1. Anodic (1-5) and cathodic (4', 5') polarization curves taken on 35% RTOA (0.03 g $\mathrm{Ru_{met}}$ per m^2, temperature of lining 420°C) at P_{Cl_2}: 1, 4) 1; 2) 0.1; 3) 0.0386; 5) 0.0433 atm. Compositions of the solutions: 1, 2, 3) 1.5 N HCl + 2.5 N NaCl; 4, 5) 1.54 N HCl. t° = 30°C.

Fig. 2. Temperature dependence of the rate of the cathodic (1) and anodic (2) process on 30% RTOA in a solution with composition 1.5 N HCl + 2.5 N NaCl (P_{Cl_2} = 1 atm) at an overvoltage η = 0 mV.

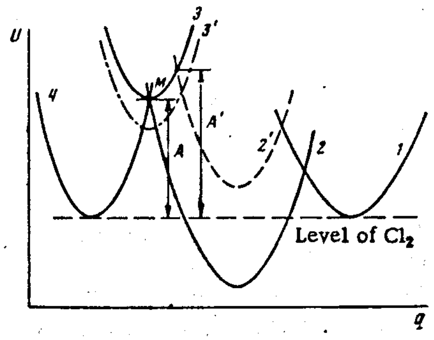

Fig. 3. Energy profile of the reaction of liberation and ionization of chlorine on RTOA at the equilibrium potential q is the polarization of the solvent; U is the potential energy of the system in the states: 1) $2Cl^-$; 2, 2') Cl^- + Cl_{ads} + e; 3,3') $Cl^{(tI)}$ + Cl^-te; 4) Cl_2 + 2e. A,A') Real activation energies according to Temkin [6]; the remaining explanations are given in the text.

The stoichiometric numbers, calculated according to the exchange currents, extrapolated from the lower anodic portion (where b = 30 mV), are less than one, while in the case of extrapolation from the upper portion (b = 40 mV) they are greater than one. This is easy to explain if we consider that the large current of exchange, extrapolated from the region of higher overvoltages η (where α = 0.5), is not realized in the case of small η (α = 1), and, consequently, is not associated with the equilibrium slope $(di/d\eta)_{\eta=0}$ [5]. Therefore, the value of the stoichiometric number ν', calculated according to the exchange current of the upper portion, should be too high. At the same time, the stoichiometric number calculated for the lower Tafel portion, being less than one, is evidence that the equilibrium slope is determined by still another, parallel-reaction pathway [2, 3, 5].

The activation energies were measured for the anodic and upper portions of the cathodic branches of the polarization curves, corresponding to different reaction pathways [2, 3]. They proved equal to ~4 kcal/mole for the barrierless anodic process and ~8 kcal/mole for the normal cathodic process at the equilibrium potential (Fig. 2). The difference between the activation energies confirms the conclusion that the anodic and cathodic branches are determined by different reaction pathways, which are realized on different portions of the electrode surface [2].

Figure 3 presents a scheme of the energy profile of the reaction at the equilibrium potential. The aggregate of the terms 2 and 3 corresponds to a barrierless course of the slow step. The term 2' corresponds to the active centers of the surface with a lower energy of adsorption of atomic chlorine, on which the normal process occurs. As can be seen from Fig. 3, with such an arrangement of the terms the real activation energy for the normal process is greater than for the barrierless process, A' > A. A relative arrangement of the terms corresponding to the normal process might also have been achieved by a downward shift of term 3 (assuming a large energy of adsorption of the $Cl^{(+I)}$ particle). In this case, however, the activation energy for a normal process will be smaller than for a barrierless process, which contradicts the experiment. Therefore, the larger value of the activation energy of the normal process in comparison with the barrierless process is evidence that the energy of adsorption of atomic chlorine on the active centers of the RTOA, on which the barrierless process occurs, is greater than on the active centers for which $\alpha = 0.5$.

An investigation of the kinetics of equilibrium reactions does not permit an unambiguous judgment of the structure of the quasiequilibrium steps of the process. Thus, the first order of the anodic process with respect to Cl^- at $b \leq 60$ mV can also be satisfied for more-complex reaction schemes, relating to the third group of mechanisms considered in [1], in which the discharging of one Cl^- ion in the preceding rapid step corresponds to one run of the slow step. For example, atomic chlorine might be formed as a result of the occurrence of two successive rapid steps: $2Cl^- - e \rightleftarrows Cl_2^-$; $Cl_2^- \rightleftarrows Cl^- + Cl$, the sum of which is equivalent to the rapid step of discharging $Cl^- - e \rightleftarrows Cl$. An analogous remark can also be made with respect to the rapid step of removal of the $Cl^{(+I)}$ particle.

The available experimental data also do not permit us to draw definite conclusions on the nature of the $Cl^{(+I)}$ particle. It may be, for example, a positively-charged chloride ion Cl^+, adsorbed on the electrode. The possibility also remains that the slow step proceeds with the participation of water: $Cl + H_2O - e \rightarrow HClO + H^+$, i.e., free or adsorbed hypochlorous acid (or some derivatives of it) emerges as $Cl^{(+I)}$. The subsequent rapid step will then be the reverse hydrolysis of chlorine: $HClO + HCl \rightleftarrows Cl_2 + H_2O$.

An analysis of the energy diagram does not contradict this assumption. From Fig. 3 it is evident that the real activation energy of the barrierless process at the equilibrium potential A is equal to the enthalpy change in the first step of the cathodic process $Cl_2 \rightleftarrows Cl_{aq}^- + Cl^{(+I)}$, which actually may be a reaction of hydrolysis of chlorine. The enthalpy change of the hydrolysis reaction, calculated according to the data of [7], is equal to 4 ± 1 kcal/mole, which, within the limits of the experimental accuracy, is sufficiently close to the measured activation energy ~4 kcal/mole. Therefore, the possibility remains that hypochlorous acid or some derivative of it actually plays the role of an intermediate product of the reaction of $Cl^{(+I)}$.

Since the step of discharging of the Cl atom is the slow step, the point of intersection of the terms 2 and 3 should be the highest along the reaction pathway (the point M in Fig. 3). Consequently, the point of intersection of the term 3 with the term 4 can be no higher than the point M. Therefore, the term 4 should be situated with respect to term 3 similarly to what is shown in Fig. 3. As can be seen from Fig. 3, if the energy profile were determined only by the coordinate of the solvent q, then the aggregate of terms 2-3-4 would not differ formally from the single energy barrier corresponding to a single limiting step of electrochemical desorption ($Cl_{aq}^- + Cl_{ad} - e \rightarrow Cl_2$). However, this step requires second order of the anodic reaction with respect to chloride, which does not agree with the experiment [1]. This contradiction can be eliminated if we consider that when the slow step occurs, there should be a change in the steric coordination of the heavy particle, for example, chlorine atom (and possibly the oxygen atom in the formation of HClO). It is therefore most probable that the reaction occurs according to a quasibarrierless pathway [8], when with initially practically-unchanged coordinates of the heavy particles, there is a reorganization of the solvent along the term 2 with jump over of an electron from the Cl atom to the electrode (point M). This leads to the formation of a $Cl^{(+I)}$ particle with nonequilibrium coordinates, which then relax to the equilibrium state, expressed by the term 3'.

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