MECHANISM OF CHLORINE EVOLUTION AT A RUTHENIUM – TITANIUM OXIDE ELECTRODE

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A previous communication [1] dealt with the evolution and ionization of chlorine at a ruthenium–titanium oxide electrode (RTOE). This communication gives new data which agree entirely with the previous results but require reappraisal of the process mechanism.

The measurement procedure was the same as in [1]. During the experiments the electrolyte was mixed by a magnetic stirrer. An S1-19A oscillograph was used to measure the fall in potential when the circuit was broken.

Figures 1 and 2 show the polarization curves recorded on an RTOE of the composition RuO_2 30 mole % + TiO_2 70 mole % (~1 g Ru_{met} per square meter of electrode surface) in solutions with different chloride concentrations. The strong dependence of the overpotential (η) on the solution composition is incompatible with slow recombination, as we postulated in [2]. The dependence of the reaction rate on the chloride concentration is very unusual: at constant η the reaction rate increases with a decrease in $[Cl^-]$ in both the anode and cathode regions. The order of the anode reaction with respect to the Cl^- ion at constant potential $(\partial \log i/\partial \log [Cl^-])_\varphi$, determined in solutions containing 2 moles/liter H_2SO_4, is +1.*

The differential capacitance of the electrode was measured from the initial slope of the potential–time curve, using the potential drop method; it was found to be ~3 $\mu F/cm^2$ of visible surface, which corresponds to an electrode capacitance of ~30 $\mu F/cm^2$ expressed in terms of the true surface.†

An experimental value of the capacitance close to the usual double electric layer capacitance may be observed when the degree of surface coverage by intermediate electroactive particles is roughly equal to zero ($\theta \ll 1$) or unity ($\theta \approx 1$). An anode Tafel slope of ~30 mV and a zero anode reaction order with respect to molecular chlorine [1] are together incompatible with the condition $\theta \approx 1$. In fact, if we had a slow stage supplying the intermediate reaction product at $\theta \approx 1$, and if the subsequent stages of removal of this product were equilibrial, the value of $1-\theta$ must inevitably decrease with an increase in the chlorine pressure. The velocity of the slow stage in the anode direction $\overrightarrow{v_r} \propto (1-\theta)$ would have a negative (not zero) order with respect to Cl_2. In nonequilibrial stages of product removal the Tafel slope would be ≥ 60 mV.

The condition $\theta \approx 1$ does actually signify the independence of θ on the electrode potential φ. Therefore if the stage involved in removal of the intermediate product is the slow one, the dependence of its velocity on the potential‡ $\overrightarrow{v_r} \propto \theta e^{\alpha_r \varphi}$ would correspond to the experimental Tafel slope $b = 2.3\ RT/\alpha_r F$, where α_r is the true transfer coefficient of the slow stage. For the stage due to charge transfer $0 \leq \alpha_r \leq 1$ and the value of b cannot be less than 60 mV ($\alpha_r = 1$). With a purely chemical slow stage (or with $\alpha_r = 0$) $b \approx \infty$, i.e., we would observe an anode limiting current.

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*A high sulfuric acid concentration is added to suppress secondary effects due to a change in the structure of the double electric layer on the electrode and in the surface state, which may be induced by a change in the chloride concentration.

†The true electrode surface was determined by T. V. Ivanova and D. V. Kokoulina by comparing the charging curves with the data obtained by the BET method.

‡Here and below, in the formulas the potential φ and the overpotential η are expressed in RT/F units.

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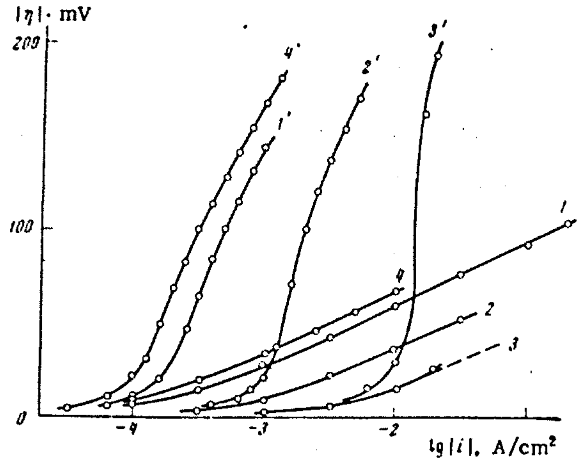

Fig. 1. Anode (1-4) and cathode (1'-4') polarization curves recorded on 30% RTOE (roasting temperature 420°C) at P_{Cl_2} = 1 atm in solutions of the composition: 1) 1.5 N HCl + 2.5 N NaCl; 2) 1.5 N HCl; 3) 0.5 N HCl; 4) 0.5 N NaCl + 2 N H_2SO_4. t^0 = 30°C.

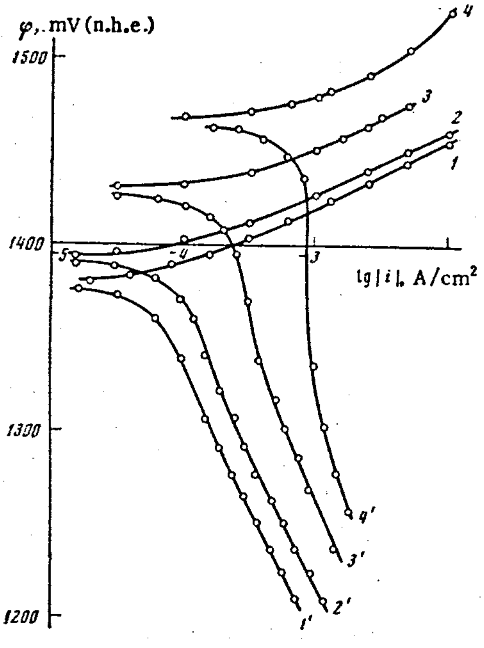

Fig. 2. Anode (1-4) and cathode (1'-4') polarization curves recorded on 30% RTOE (420°C) at P_{Cl_2} = 1 atm and t^0 = 30°C in solutions of the composition xN NaCl + 2 M H_2SO_4 with x equal to: 1) 1.1; 2) 0.56; 3) 0.14; 4) 0.041.

Thus, the assumption at $\theta \approx 1$ must be rejected, and hence $\theta \ll 1$. All the subsequent discussion will therefore be conducted from the viewpoint that Henry's isotherm is applicable. We also postulate that the reaction takes place in stages, not more than one electron being involvable in an event of the slow stage.

Several different mechanisms, to which reaction routes with only one slow stage correspond, can satisfy a first order of the anode reaction with respect to chloride. These mechanisms may be divided into the following three groups.

The first group includes reactions in which the first stage of the anode process is the slow one, one

Cl^- ion participating in one event. It may be a chemical reaction (for example, $Cl_2 + Cl^- \rightarrow Cl_3^-$) followed by rapid electrochemical stages, or it may be electrochemical (slow discharge of the Cl^- ion).

The second group includes reactions in which the second or some later stage of the anode process involving one Cl^- ion is the slow one, no chloride being involved in the preceding fast stages. If the slow stage is due to charge transfer, in the chloride reaction the preceding fast stages must be purely chemical An example of such a reaction is an adsorption-electrochemical mechanism [3, 4] consisting of rapid dissociative adsorption ($Cl_2 \rightleftarrows 2Cl$) followed by slow electrochemical desorption ($Cl^- + Cl - e \rightarrow Cl_2$). On the contrary, a fast electrochemical stage must precede the chemical slow stage. For example, the $Cl_2 - 2e \rightleftarrows 2Cl^{(+I)}$ stage (or the sequence of stages $Cl_2 \rightleftarrows 2Cl$; $Cl - e \rightleftarrows Cl^{(+I)}$ may be the fast stage, and $Cl^{(+I)} + Cl^- \rightarrow Cl_2$ the slow one.

Finally, the third group is comprised by reactions in which the slow stage is the second or a later stage of the anode process in which Cl^- ions are not directly involved. Its initial reagents are particles of the intermediate reaction product formed in the previous fast stages with participation of Cl^-. One run [5] of the slow stage requires the consumption of one chloride ion in the preceding stages. The fast stage may by chemical (for example, $Cl_2 + Cl^- \rightleftarrows Cl_3^-$ and then $Cl_3^- - e \rightarrow Cl_2 + Cl_{ads}$) or electrochemical. The later case is discussed in greater detail below.

These three groups exhaust all possible types of chloride reaction mechanisms satisfying a first order of the anode reaction with respect to chloride.*

With $\theta \ll 1$ the observed anode slope, less than 60 mV, signifies that the first electrochemical stage of the anode process cannot be the limiting stage. The slow stage must at very least be the second stage due to electron transfer; transfer of one electron must occur in the preceding fast stages. We can therefore reject the first two groups of mechanisms and those of the third group in which all the fast stages preceding the slow one are chemical.†

Therefore a low slope of 30 mV may be observed only in the case of mechanisms of the third group. These include mechanisms with two successive electrochemical stages, followed by the chemical stage, the first electrochemical stage being fast. The most probable slow stage is the second electrochemical stage, since we cannot readily suppose that a chemical reaction involving an active Cl^+ particle will be slow (see below).

Thus the experimental data correspond to the following fundamental reaction scheme.

In actual fact, in the case of mechanisms belonging to the first group, with $\theta \ll 1$ the rate of the process $\vec{i} \propto (1-\theta) e^{\alpha_r n_r \varphi} \propto e^{\alpha_r n_r \varphi}$, where n_r is the number of electrons involved in an event of the slow stage, which may be equal to 0 or 1 (the chemical or electrochemical stage, respectively). Hence it follows that the Tafel slope cannot be less than 60 mV ($b = 60$ mV when $\alpha_r n_r = 1$). Nor can low slopes be observed for those mechanisms of the second or third groups in which fast chemical stages precede the slow stage. In view of the fact that in this case θ is governed by their equilibrium and is therefore independent of φ, then $\vec{i} \propto \theta e^{\alpha_r n_r \varphi} \propto e^{\alpha_r n_r \varphi}$. Similarly, if the chemical stage is the slow one and is not preceded by more than one electrochemical stage, then $\theta \propto e^{\varphi}$ and $\vec{i} \propto \theta \propto e^{\varphi}$, hence $b = 60$ mV. These alternative versions exhaust the mechanisms of the first and second groups and part of the mechanisms of the third group in which the slow stage or its preceding fast stages are chemical.

At first we have fast discharge of a Cl^- ion with formation of adsorbed atomic chlorine: $Cl_{aq}^- - e \rightleftarrows Cl_{ads}$. As a consequence of discharge equilibrium we have an exponential dependence of surface coverage by atomic chlorine on θ: $\theta \propto e^{\varphi}$. In the next, slow stage the chlorine atom undergoes further oxidation to a state with valence +I: $Cl_{ads} - e \rightarrow Cl^{(+I)}$. In the third, fast stage the $Cl^{(+I)}$ particle reacts with Cl^- from the solution with formation of molecular chlorine: $Cl^{(+I)} + Cl^- \rightleftarrows Cl_2$. Thus according to the postulated mechanism formation of positive monovalent chlorine on an RTOE is a primary process and formation of

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*The previously postulated reaction schemes with slow stages of recombination and electrochemical desorption, preceded by an equilibrial discharge stage [1, 2], are inapplicable because in them one run of the slow stage requires a total discharge of two Cl^- ions as the initial reagents; in such a case the order of the anode reaction with respect to chloride is 2.

†Furthermore, for some of the mechanisms in these groups the rate of the anode reaction must depend on P_{Cl_2}, and the stoichiometric number of the slow stage is 2, which does not agree with experiment ($\nu' \leq 1$ [1]).

molecular chlorine is a secondary process. In this scheme one run of the slow stage requires discharge of only one Cl$^-$ ion, and the requirement that the reaction must be of the first order with respect to chloride is satisfied. The rate of the slow stage in the anode direction is proportional to the concentration of its initial reagent, i.e., θ: $\vec{i} \propto \theta e^{\alpha\eta} \propto e^{(1+\alpha)\eta}$. The exponent $1 + \alpha$ ensures a low anode Tafel slope $b_a = 2.3\ RT/(1 + \alpha)F$. The equation of the polarization curve corresponding to this mechanism is written in the form

$$i = k\,[\mathrm{Cl}^-]^{-\alpha} P_{\mathrm{Cl}_2}^{\frac{1+\alpha}{2}} \left[e^{(1+\alpha)\eta} - e^{-\beta\eta}\right] \tag{1}$$

Equation (1) agrees with the experimental data when $\alpha = 1$, which corresponds to barrier-free [3, 6] oxidation of $\mathrm{Cl}_{\mathrm{ads}}$.

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