INTRODUCTION

This work continues the research we initiated into the electrochemical and corrosion processes that occur during chlorate electrolysis with use made of dimensionally stable anodes DSA [1, 2].

In the conditions of chlorate electrolysis on porous DSA, there occurs a fast primary process of the formation of chlorine molecules, which then undergo hydrolysis, with the subsequent slow homogeneous chemical reaction of the NaClO$_3$ formation [3–5]

$$2\text{Cl}^- = \text{Cl}_2 + 2\text{e}^-,$$  \hspace{1cm} (I.1)

$$\text{Cl}_2 + \text{H}_2\text{O} = \text{HClO} + \text{Cl}^- + \text{H}^+,$$  \hspace{1cm} (I.2)

$$\text{HClO} = \text{H}^+ + \text{ClO}^-,$$  \hspace{1cm} (I.3)

$$2\text{HClO} + \text{ClO}^- = \text{ClO}_3^- + 2\text{H}^+ + 2\text{Cl}^-.$$  \hspace{1cm} (I.4) I

According to Ferster, the rate of a homogeneous chemical reaction similar to stage (I.4) is described by the kinetic equation

$$v = k_0[\text{HClO}]^2[\text{ClO}^-].$$  \hspace{1cm} (1)

As follows from (1), the homogeneous reaction of the NaClO$_3$ formation has third order by active chlorine (AC) [3]. The AC concentration [Cl*] is

$$[\text{Cl}^*] = [\text{HClO}] + [\text{ClO}^-].$$  \hspace{1cm} (2)

Formally, the NaClO$_3$ formation can be represented as involving two successive stages. Species of AC form in the first, fast and reversible, electrochemical stage. In the second, slow, homogeneous reaction, these irreversibly convert to NaClO$_3$ via a third order reaction:

$$\text{Cl}^- = \text{Cl}^* + 2\text{e}^-,$$  \hspace{1cm} (II.1)

$$3\text{Cl}^* \rightarrow \text{ClO}_3^-.$$  \hspace{1cm} (II.2) II

Scheme (II) with an irreversible chemical stage formally corresponds to a fast electrochemical process accompanied by a subsequent slow homogeneous chemical reaction of order $p$ (the process was considered in [6–10])

$$\text{Red} = n_\text{M} \text{M} + ne^-,$$  \hspace{1cm} (III.1)

$$p\text{M} = \text{Ox},$$  \hspace{1cm} (III.2) III

provided the rate of the reverse chemical stage of conversion of Ox to M can be ignored in scheme (III), where $v_M$ is a stoichiometric coefficient by component M. As shown in [6–10], sufficiently far from equilibrium, the Tafel slope of a polarization curve (PC) for such an irreversible process in scheme III is

$$b = 2.3 \frac{2v_M RT}{p + 1}$$  \hspace{1cm} (3)

while the reaction’s exchange current is

$$i_0 = \frac{nF}{v_M} \sqrt{\frac{2}{p + 1} v_0 c_0 D},$$  \hspace{1cm} (4)

where $D$ is the diffusion coefficient for substance M in the bulk solution, $v_0$ is the chemical reaction rate under open-circuit conditions, and $c_0$ is the concentration of component M at infinite distance from the electrode.

In view of the above, for conditions of chlorate electrolysis, the Tafel slope must equal $2.3RT/4F$, because $n = 2$, $v_{\text{HClO}} = 1$, and $p = 3$.

THEORETICAL MODEL

When studying the NaClO$_3$ formation kinetics, one can employ not only the method of steady-state PC, but a non-steady-state method as well. The latter involves analysis of relevant kinetic curves, specifically, time dependences of concentrations of AC and NaClO$_3$. Suppose that a “pure” chloride solution is used in experiments. By such a solution we mean an electrolyte...
where initial concentrations of AC and NaClO are zero.

Once a polarization is imposed, in accordance with scheme (II), AC starts to form in the solution at the rate 
\[ W_0 = \frac{kI}{2VF}, \]
at the expense of electrolysis. Simultaneously, AC will be spent at the rate 
\[ W = 3k[Cl^*]^p, \]
due to the NaClO formation at the rate 
\[ W = k[Cl^*]^p. \]
Quantities \( W_0 \) and \( W \) differ by a factor of three, because three species of AC participate in the formation of one chlorate ion. In these formulas, \( p \) is the reaction order by AC, which can be other than three; \( k = CE/100 \), where CE is the overall current efficiency by AC and NaClO, which can vary with time; \( I \) is the current; \( V \) is the overall electrolyte volume; and \( k \) is an effective rate constant, which can depend on pH. We assume that the chloride concentration and the solution volume undergo no substantial changes during the time period it takes \([Cl^*]\) to reach a steady-state value. The time dependences of volume concentrations of AC and NaClO satisfy the set of differential equations

\[
\frac{d[Cl^*]}{dt} = \frac{kI}{2VF} - 3k[Cl^*]^p, \quad (5)
\]
\[
\frac{d[ClO_3^-]}{dt} = k[Cl^*]^p. \quad (6)
\]

Using the time dependence of CE and concentrations of AC and NaClO, one can determine \( k \) and \( p \) by searching for optimum parameters in (5) and (6). To this end, one has to have an experimental dependence \( v = v([Cl^*]) \) in an explicit form, where \( v \) is the rate of variations in \([Cl^*]\) with time. Such a dependence can be found by differentiating an experimental time dependence of \([Cl^*]\), provided one succeeded in deriving approximating functions for the experimental curves. To the first approximation, one can describe the obtained experimental time dependences by polynomials

\[
[Cl^*] = \sum_{(r)} a_r t^r, \quad [ClO_3^-] = \sum_{(r)} b_r t^r. \quad (7)
\]

According to linear programming (linear regression) calculations, the time dependences of concentrations of AC and NaClO satisfy polynomials of fifth and third order, respectively.

From (7) and the polynomial coefficients, we compute \( v(t) \)

\[
v = \frac{d[Cl^*]}{dt} = \sum_{(r)} a_r r t^{r-1}. \quad (8)
\]

Then we utilize the available time dependences of \([Cl^*]\) and \( v \) to construct an “experimental” dependence of \( v \) on \([Cl^*]\). This dependence is described by the equation

\[
v = \frac{kI}{2VF} - 3k[Cl^*]^p. \quad (9)
\]

The sought-for parameters in (9) are varied until the discrepancy between the theoretical and “experimental” dependences of \( v \) on \([Cl^*]\) is reduced to a minimum.

**EXPERIMENTAL**

The electrochemical behavior of DSA in a chlorate electrolysis was studied in a setup with common anodic and cathodic compartments [11]. The cathode was made of titanium, on which a protective porous film of chromates had been formed, the film substantially diminishing the AC reduction current.

The experiments, in which current efficiencies for AC and NaClO were determined, were carried out in the following manner. Upon pouring 600 ml of a working solution (5 M NaCl + 0.2 g l –1 K2Cr2O7) into the setup, we imposed polarization on the electrolyzing cell \( (I = 4.2 \text{ A}) \) and started supplying an HCl solution diluted in a 1 : 1 ratio. In the course of experiment, solution samples were collected at certain time intervals. To prevent chemical conversion of AC into NaClO3, the samples were rapidly cooled with ice to room temperature. Then the overall content of [HClO] + [NaClO] + [NaClO3], was determined in these solutions by iodometric titration with concentrated hydrochloric acid. The NaClO3 concentration in similar portions of solutions was determined by separate iodometric titration with dilute sulfuric acid.

**RESULTS AND DISCUSSION**

Figure 1 shows a typical anodic PC recorded on standard DSA in a 5 M NaCl + 0.2 g l–1 K2Cr2O7 solution of pH 6 to 7 at 90°C in conditions of chlorate formation at a steady-state concentration of AC in solu-

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1The experimental part of the work was carried out with the participation of V.V. Gorodetskii.