INTRODUCTION

Dimensionally stable anodes (DSA) have found wide application in the industrial production of chlorine and sodium chlorate. The latter is usually produced by electrolyzing aqueous NaCl solutions of pH 6 to 7 at 60—80°C and 0.2 A cm⁻² in cells with common anodic and cathodic spaces, with DSA as the anodes. The cathodes are usually made of steel or titanium.

In a chlorate electrolysis, the fast primary process of formation of chlorine molecules occurs at the porous anode. The molecules then undergo hydrolysis with the subsequent slow homogeneous chemical reaction of the sodium chlorate formation [1–3]:

\[
\begin{align*}
2\text{Cl}^- & = \text{Cl}_2 + 2e, \\
\text{Cl}_2 + \text{H}_2\text{O} & = \text{HClO} + \text{Cl}^- + \text{H}^+, \\
\text{HClO} & = \text{H}^+ + \text{ClO}^-, \\
2\text{HClO} + \text{ClO}^- & = \text{ClO}_3^- + 2\text{H}^+ + 2\text{Cl}^-.
\end{align*}
\]

In scheme I, the formation of chlorine molecules involves several stages. This process can involve four successive stages [4]:

\[
\begin{align*}
\text{S} + \text{H}_2\text{O} & = \text{SOH} + \text{H}^+ + e, \\
\text{SOH} + \text{Cl}^- & = \text{SOH}^+ + \text{Cl}^- + e, \\
\text{SOH}^+ & = \text{HCIO}, \\
\text{SHClO} + \text{H}^+ + \text{Cl}^- & = \text{S} + \text{H}_2\text{O} + \text{Cl}_2,
\end{align*}
\]

where S denotes an active center on the DSA surface. Scheme I reflects the basic, chemical mechanism of the sodium chlorate formation with a high current efficiency (CE) of about 90%. An electrochemical mechanism of the sodium chlorate formation is also possible. In this case, the chlorate forms directly on the anode in the overall reaction

\[
6\text{HClO} + 3\text{H}_2\text{O} = 2\text{ClO}_3^- + 12\text{H}^+ + 4\text{Cl}^- + 3/2\text{O}_2 + 6\text{e}^- \tag{III}
\]

with a simultaneous evolution of oxygen.

A comparison of processes of the chlorine and chlorate formation suggests that the kinetics of reactions occurring on DSA in the chlorine and chlorate electrolyses have much in common. Indeed, in either case, the target reactions on DSA are accompanied by side reactions of oxygen evolution and anodic dissolution of RuO₂. The distribution of rates of side reactions over the DSA depth depends on the distribution of the pH-determining reaction of the formation and ionization of chlorine molecules, which is accompanied by hydrolysis of chlorine and acidification of solution in the DSA pores [5, 6].

Effect of porosity on the chlorine formation in DSA was analyzed in [5, 6], with allowance made for the equilibrium reaction of the chlorine hydrolysis in a chlorine and chlorate electrolysis performed at 90°C. The kinetics of the target and side reactions in a chlorine and chlorate electrolysis at \(i \leq 0.2\) A cm⁻² and a high NaCl concentration had some specific features [5, 6]. Under these conditions, the porous coating of DSA worked for the formation of chlorine molecules to a limited depth that was smaller than the overall coating thickness, because the rest of the porous coating sustained an electrochemical equilibrium between the processes of formation and ionization of chlorine molecules. The hydrolysis of chlorine molecules evolved in DSA pores acidified the solution in the pores to pH of about unity in a chlorine electrolysis and to pH of approximately four in a chlorate electrolysis. The presence of a negative order by H⁺ ions forced both side
reactions towards the external DSA side. This conclusion, made in [5, 6], conformed to the results that had been obtained in [7], whose author had studied the way the Ru dissolution rate depended on the Ru content in DSA during the polarization of DSA in a 5 M NaCl solution of pH 6.5–7, at 0.2 A cm\(^{-2}\) and 80°C. According to the results, the DSA corrosion rate was independent of the active-coating thickness at Ru contents above 1.35 g m\(^{-2}\). A substantial corrosion deceleration at smaller Ru contents was explained by a change in the Ru content in the active coating, which occurred during the production of thin coatings.

In a chlorate electrolysis, the solution on the anode undergoes acidification. Conversely, at the cathode, there is likely to occur alkalization. Indeed, the rate of formation of an alkali on the cathode (i) must equal the rate of its removal from the cathode through diffusion:

\[
i = -FD_{\text{Oh}} \frac{d[\text{OH}^-]}{dx}.
\]

(1)

Suppose that the distribution of the alkali concentration near the cathode is linear, i.e.

\[
\frac{d[\text{OH}^-]}{dx} = \frac{[\text{OH}^-]_s - [\text{OH}^-]_v}{\delta}.
\]

(2)

Here, [OH\(^-\)]\(_s\) and [OH\(^-\)]\(_v\) represent the near-electrode and bulk alkali concentrations, respectively, and \(\delta\) is the diffusion layer thickness. Then, equations (1) and (2) readily yield the link between the alkalinization magnitude and the current density:

\[
\frac{[\text{OH}^-]_v}{[\text{OH}^-]_s} = 1 + \frac{i}{i_d},
\]

(3)

where

\[
i_d = \frac{FD_{\text{Oh}} [\text{OH}^-]}{\delta}.
\]

(4)

is the limiting diffusion current by the OH\(^-\) ions. Assuming that \(F = 10^3\) A mol\(^{-1}\), \(D_{\text{OH}^-} = 10^{-5}\) cm\(^2\) s\(^{-1}\), [OH\(^-\)]\(_s\) = 10\(^{-10}\) M, and \(\delta = 0.001\) cm, we obtain \(i_d = 10^-7\) A cm\(^{-2}\) in a chlorate electrolysis. The working current density in (3) is about 0.1 A cm\(^{-2}\). Hence, the alkali concentration in the near-electrode solution layer increases by six orders of magnitude.

The main distinguishing feature of the chlorate electrolysiss, which determines the behavior of anodes, is a successive passing of electrolyte through a cascade of electrolyzing cells or the cells of a multisection electrolyzing cell, with its gradual depletion by chloride, specifically, from 180–280 to 40–60 g l\(^{-1}\) NaCl, and a corresponding enrichment in chlorate. According to the authors of [8], low chloride concentrations at the final stage of the electrolysis, combined with relatively high current densities reaching 0.6 A cm\(^{-2}\), elevated electrolysis temperatures, and the presence of an admixture of anions, which make the anodic potential increase, may increase the probability of exceeding the so-called critical anodic potential at which the destruction rate of the anode’s active mass sharply increases.

By recording polarization curves (PC) in chloride–chlorate solutions of different composition at different values of pH and temperature, the authors of [8] demonstrated that, at current densities below 0.7 A cm\(^{-2}\), the critical anodic potential occurs in solutions with a NaCl concentration of 50 g l\(^{-1}\) and lower. The fact that the critical anodic potential was reached was indicated by a sharp increase in the slope of galvanostatic PC. The same authors, by comparing PC recorded on anodes covered with a RuO\(_2–TiO_2\) coating (DSA) and an IrO\(_2–RuO_2–TiO_2\) coating (DSA-I) under conditions of electrolysis in chloride–chlorate solutions, discovered that the increase in the slope of PC corresponding to transition into the region of potentials exceeding the critical anodic potential on DSA-I was less pronounced than that on DSA [9]. However, it should be noted that reaching the critical anodic potential at a low chloride concentration is, most likely, associated with the presence of outer-diffusion and inner-diffusion limitations on the chloride supply to the external side of the anode and in pores of its active coating, rather than with a sharp increase in the destruction rate of the anode’s active mass. The former probably favors oxidation of the titanium support and the formation of a barrier layer, especially at a high electrolysis temperature.

According to the authors of [10], at low chloride concentrations, the Cl\(^-\) ions are likely to penetrate into the anode’s porous coating to a limited depth that is smaller than the overall thickness of the porous coating, which leads to doubling the Tafel slope of an anodic PC. Additional outer-diffusion limitations by chloride are likely to increase the slope of PC even more, with its subsequent transition into the region of the limiting diffusion current. Under these conditions, the chloride concentration tends to zero, and the anode works in this part of the coating predominantly for oxygen evolution [10].

Indeed, let us assume, as we did in [5, 6], that the effective diffusion coefficient for the Cl\(^-\) ions in anode pores is \(D = 10^{-6}\) cm\(^2\) s\(^{-1}\) and the specific surface area of the porous coating of a DSA is \(S = k/l\) (cm\(^{-1}\)), where \(k = 700\) is the effective roughness factor at the porous coating’s thickness \(l = 5 \times 10^{-4}\) cm, the exchange current of the chlorine reaction \(i_{0,\text{Cl}} = 10^{-4}\) A cm\(^{-2}\), apparent anodic transfer coefficient \(\beta = 2\), overvoltage \(\eta = 50\) mV, and temperature 90°C. Then, we can estimate the characteristic diffusion length by chloride, \(l_{\text{d, CT}}\), i.e. the region of the DSA’s porous coating where the chloride concentration changes the most in a chlorate electrolysis. Specifically,

\[
l_{\text{d, CT}} = \sqrt{\frac{FD_{\text{Cl}}}{S i_{0,\text{Cl}} \exp(\beta F \eta /RT)}}.
\]

(5)