

# Gas-Generating Porous Electrodes: The Nature of the Low-Polarizability Portion in the Polarization Curves

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**Abstract**—The phenomenon of a low-polarizability portion (LPP) is discussed in the paper. The phenomenon is responsible for the possible rapid increase in the current in polarization curves (PC) for the gas generation in gas-generating porous electrodes (GGPE). A fresh viewpoint on the nature of LPP is propounded. The inflection in PC, which follows the linear Tafel portion, owes its inception to the emergence, in the electrode pores, of a network of gas pores that are freed of electrolyte and are connected with each other. The effective diffusion coefficient for gas molecules in gas pores filled with water vapor is larger than the effective diffusion coefficient for the same gas molecules in liquid pores filled with an electrolyte solution by several orders of magnitude. The emergence of a gas phase in a GGPE leads to a rapid increase in the effective diffusion coefficient. This circumstance in turn is capable of rapidly intensifying processes of the formation and removal of gas, which leads to a considerable increase in the overall current. A method for obtaining an approximate solution of the problem (the notion on ideal porous electrode) is suggested. A system of equations is derived, which can sufficiently accurately, qualitatively and quantitatively describe the character of variations in a polarization curve in the initial part of a low-polarizability portion. Theoretical and experimental polarization curves for the chlorine evolution on a dimensionally stable anode are compared quantitatively.

## 1. THE FORMULATION OF THE PROBLEM

When experimentally studying the process of the formation of chlorine in dimensionally stable anodes [1–8], which are denoted here as ORTA, and the process of evolution of hydrogen in gas-generating porous electrodes (GGPE) that were prepared from the platinum group metals [9–14], in the polarization curves (PC), which were presented in the  $E, \log I$  coordinates, after the Tafel portion that had a linear character, there was discovered a special portion of the polarization curve that was called a low-polarizability portion (LPP) in [1]. At a certain critical overvoltage, a polarization curve began to sharply deviate to the right. Thus, in this narrow range of overvoltages, one observed an anomalously rapid increase in the overall current. One could find several explanations for the LPP phenomenon in the literature. For example, Losev [15] had believed that the point, at which a low-polarizability portion originated, was the point where the formation of a gas phase commenced. The oversaturation of the near-electrode layer of solution with chlorine reached a limiting level, which substantially facilitated an external gas removal. Now, the removal of the product of the electrochemical reaction began to be realized predominantly through the formation of gas bubbles, rather than by means of the diffusion of chlorine molecules in electrolyte. The outer-diffusion limitations, according to Losev, were removed to a considerable extent, and that was why the overall current began to rise. The weakness of the Losev hypothesis is, to our minds, two-pronged. First, he performed his deliberations using a

smooth electrode, rather than a porous electrode, as an example. Second, his arguments were of a qualitative, rather than a quantitative character.

Erenburg and Krishtalik [16] had given a different interpretation to the nature of the low-polarizability portion for the process of chlorine evolution on ORTA. They believed that, in the region of small overvoltages (region of PC before LPP), i.e. in the region where no gas evolved in the pores yet, and the entire porous space of the electrode was still filled with electrolyte solution, the gas generation zone encompassed only a small fraction of the inner porous space, specifically, a narrow region that was localized near the front surface of the electrode. This zone gradually extended in LPP and, finally, the zone began to encompass the entire thickness of an ORTA of a standard size (5  $\mu\text{m}$ ). That was why a considerable increase in the overall current occurred in LPP. Sadly enough, the deliberations aired in [16] had the character of a hypothesis; the authors of [16] substantiated them with neither calculations nor experiments.

Müller and Heidrich [10] studied hydrogen evolution in GGPE prepared from the platinum metals. They believed that the growth of gas bubbles at the front surface of a porous electrode and their floating up lead to a strong agitation of electrolyte in the interelectrode space. This accelerates the removal of the reaction product from the electrode surface in view of the emergence of the process of convective diffusion. In fact, Müller and Heidrich were developing the Losev hypothesis. Evdokimov [17] considered the gas evolu-

tion in GGPE as a self-accelerating process. He believed that the formation of a gas phase in the electrode pores is capable of giving rise to a general macroscopic motion of the gas-liquid mixture in the electrode pores. If this is true, then the slow molecular diffusion, which facilitates the gas removal from the electrode pores into the interelectrode space, is complemented by a rather effective convective transfer of gas molecules, which explains, according to Evdokimov, the rapid increase in the overall current in LPP. However, in our viewpoint, the assumption of the Evdokimov hypothesis that the velocity of the electrolyte motion in the electrode pores is proportional to the overall current seems rather doubtful. This condition fails to satisfy the obvious requirement. The point is that, in the course of formation of first gas bubbles (when the overall current is already perceptibly other than zero), the rate of filtration of liquid in the electrode pores is still equal to zero, because the liquid in the electrode pores was quiescent before LPP.

To our minds, the fallacy of all the above attempts to explain the nature of LPP lies in the fact that, although the majority of the authors had inclined to the viewpoint that the emergence of gas pores in a porous electrode plays a crucial role, no one had made an attempt to take into account the effect the structural characteristics of GGPE (distribution of the electrode pores by size, the type and structure of the electrode pores) have on the processes that lead to the emergence of a gas phase in the electrode and thus exerting an influence on the character of polarization curves. Which was for the first time unequivocally stated in [18].

## 2. THE HYPOTHESIS OF THE AUTHORS OF THIS WORK

In general terms, the nature of a low-polarizability portion may be explained in the following manner. The substantial increase in the magnitude of the overall current of GGPE in a low-polarizability portion is the result of the formation of gas pores in the porous electrode.

In the gas phase (more correctly, in the water vapor that fills the space of pores that are freed of electrolyte), the diffusion coefficient for gas molecules that evolved in the course of an electrochemical reaction,  $D_g \approx 0.1-1 \text{ cm}^2 \text{ s}^{-1}$ , exceeds the diffusion coefficient for gas molecules in a liquid,  $D \approx 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , by several orders of magnitude. The number of gas pores starts to rapidly increase in a low-polarizability portion. And finally, chains of gas pores connected with one another and with the front surface of the electrode emerge. This is the way to create a powerful channel—it is capable of removing gas flows from the porous electrode, which are equivalent to currents of hundreds of  $\text{A cm}^{-2}$  without any losses—for collecting, in the porous electrode, the gas from liquid pores (gas evolution occurs at their inner surfaces) and the removal of this gas via gas pores into a space outside the electrode (into the electrolyte

chamber) in the form of gas bubbles. Under these conditions, there is no longer any need for chlorine molecules dissolved in electrolyte to reach the front surface via the diffusion and then, also via the diffusion and collecting molecules into gas bubbles, to reach the chamber of a gas collector. This is exactly what occurs in the region of small overvoltages before the instant when first gas pores begin to form in the porous electrode. In a low-polarizability portion, gas bubbles obtain a chance to directly, without taking part in the inside- and outside-electrode processes of removal of gas molecules, penetrate into the electrolyte chamber from mouths of gas pores that emerge at the front surface of GGPE. In this manner, the possibility emerges for a complete removal of inner- and outer-diffusion limitations and, consequently, for a dramatic intensification of processes of generation and removal of gas in a porous electrode, for a fast increase in the overall current, and for the emergence of a low-polarizability portion in the polarization curve.

The possibility of transition from the ineffective diffusion mechanism of gas removal in GGPE in electrolyzing cells of any type to a highly effective filtration mechanism of the gas removal was already noted in [18]. However, it was not shown how a new channel for the gas removal forms in reality. Now, we will do our best to compensate for this deficiency. At small overvoltages, before the instant when first gas pores begin to form in GGPE (an attempt to estimate the magnitude of the critical overvoltage  $\eta^*$  at which first gas pores begin to form in GGPE was undertaken in [18]), the only mechanism of the gas removal from GGPE is the molecular diffusion in electrolyte solution that fills the electrode pores and the electrolyte chamber. In the region of large overvoltages (portion of a polarization curve following a low-polarizability portion), the gas removal mechanism is the filtration of the gas via gas pores (the behavior of GGPE in the region of large overvoltages was comprehensively described in [19–32]). And in a low-polarizability portion, there occurs a continuous transition from the mechanism of molecular diffusion of the gas in electrolyte solution to the mechanism of filtration of the gas via gas pores. In doing so, the entire mechanism of generation and removal of the gas in GGPE undergoes a fundamental change. What is the manner in which this stupendously complicated transition occurs? What is the stage and what is the overvoltage at which a through channel of gas pores forms? In this particular publication, we will do our utmost to answer, even if approximately, this and other questions.

## 3. THE PHYSICAL GIST OF PROCESSES THAT OCCUR IN A LOW-POLARIZABILITY PORTION

The mechanism that is responsible for the emergence of gas pores in GGPE is as follows. As had been shown in [33] (see also review [34]), in a cylindrical pore of radius  $R$ , which is completely filled with elec-

trolyte, a critical oversaturation  $c^*$  is reached (the source of molecules that enter the electrolyte is the electrochemical process that occurs at the inner surface of the pore). At the critical oversaturation, the pore rids itself of the electrolyte and passes into the class of gas pores. This condition has the form

$$c^* = 1 + r_0/R. \quad (1)$$

Here,  $r_0 = 2\sigma/P_0$  is the characteristic radius of a gas nucleus, where  $\sigma$  is the surface tension, and  $P_0$  is the atmosphere pressure. Under normal conditions,  $r_0 = 1 \mu\text{m}$ . Condition (1) gives us a chance to determine the magnitude of the critical overvoltage at which first gas pores emerge in GGPE. We assume that the limiting stage of the electrochemical formation of gas molecules in GGPE is a slow discharge. Then, the discharge current density  $j$  is connected with the reduced overvoltage  $\eta = FE/RT$  by the relationship

$$j = i_0(e^{\beta\eta} - \zeta e^{-\alpha\eta}), \quad (2)$$

where  $i_0$  is the exchange current of the electrochemical reaction;  $\zeta = c/c_0$  is the oversaturation of electrolyte solution with gas ( $c_0$  is the gas solubility in electrolyte solution); while  $\alpha$  and  $\beta$  are either apparent or true transfer coefficients for, respectively, cathodic or anodic processes, depending on which particular process is considered. Then, as shown in [18], the magnitude of the critical reduced overvoltage  $\eta^*$  is determined by the condition

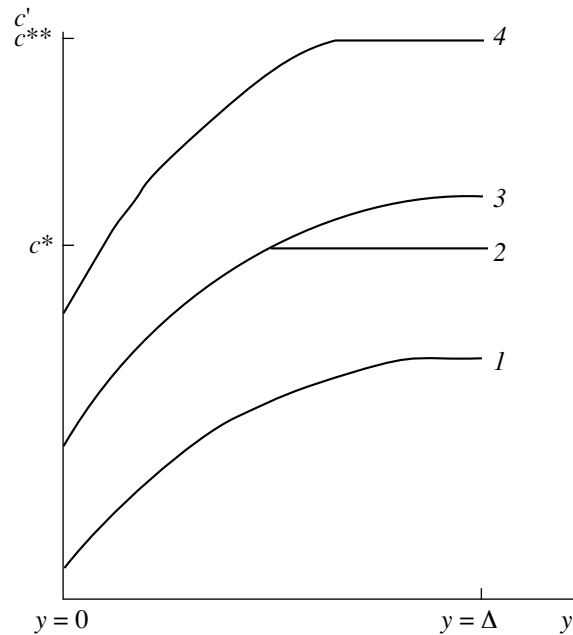
$$e^{(\alpha+\beta)\eta^*} + (c_s - e^{(\alpha+\beta)\eta^*})/\cosh[\Delta e^{-\alpha\eta^*/2}/L_d^0] = c^*. \quad (3)$$

Here,  $c_s$  is the oversaturation at the front surface of GGPE,  $\Delta$  is the electrode thickness, and

$$L_d^0 = (nFD^*c_0/Si_0)^{1/2} \quad (4)$$

is a characteristic diffusion length. In formula (4),  $D^*$  is the effective diffusion coefficient for gas molecules in GGPE when the electrode pores are completely filled with electrolyte, and  $S$  is the overall specific surface area of pores in GGPE. And critical oversaturation  $c^*$  in condition (3) may be estimated with the aid of equation (1), under the assumption that  $R$  in the equation is equal to  $r_{\text{max}}$ , where  $r_{\text{max}}$  denotes the radius of the largest pores in GGPE.

The largest pores in GGPE are those that have the maximum radius  $R$ . As follows from condition (1), following an increase in the overvoltage and, correspondingly, in the oversaturation of electrolyte solution with gas, the largest pores are the first to fall into the class of gas pores. Moreover, gas pores must, naturally, emerge first of all in the GGPE part where the oversaturation is maximum. Thus, to determine the magnitude of reduced overvoltage  $\eta^*$ , it is necessary to calculate the distribution of the oversaturation of electrolyte solution with gas throughout the entire thickness of the porous



**Fig. 1.** Distribution of oversaturation over the GGPE thickness in the presence of substantial limitation on the gas removal in the electrolyte chamber:  $c^*$  is oversaturation, at which first gas pores form in GGPE;  $c^{**}$  is oversaturation, at which a network of interconnected gas pores emerges in GGPE and which is capable of leveling oversaturation in the region adjacent to the rear surface of GGPE; (1)  $\eta < \eta^*$ ; (2)  $\eta > \eta^*$ , for ideal GGPE; (3)  $\eta > \eta^*$ , for a real GGPE; and (4)  $\eta^* < \eta < \eta^{**}$ , this is an effective curve which makes it possible to fit the theory and experiment; see text for other explanations.

electrode. In the region of small overvoltages, i.e. at  $\eta \leq \eta^*$ , such calculations were performed in [18].

A typical dependence of  $\zeta$  on  $y$  in the region of small overvoltages is represented by curve 1 in Fig. 1. All the curves in Fig. 1 are shown under the assumption that there exist considerable complications in the removal of gas in the electrolyte chamber: then the oversaturation of gas at the front surface will rise with overvoltage. The oversaturation is minimum at the front surface of GGPE and maximum, at its rear side. Once the critical overvoltage  $\eta^*$  is reached, the formation of a gas phase begins first of all at the rear surface of the porous electrode, where oversaturation  $\zeta = c^*$ . If the overvoltage is increased further, then at  $\eta > \eta^*$ , gas pores begin to form in a certain region adjacent to the rear side of the porous electrode (Fig. 1; curves 2, 3). The instant when the first gas pores emerge, signifies the beginning of the region of a low-polarizability portion. Now, pores of GGPE, which in the region of small overvoltages, before the low-polarizability portion, were filled, all of them, without a single exception, the radius notwithstanding, with electrolyte, are divided in the low-polarizability portion into two classes. One class comprises pores of small radii; these are liquid pores. The other class includes pores with large radii,

which are large enough for the pores to fall, at a given oversaturation, into the class of gas pores.

As we have repeatedly stated, the emergence of gas pores in GGPE fundamentally alters the general pattern of the gas formation in GGPE. The rate of diffusion of gas molecules in the gas phase (in gas pores) exceeds the magnitude of the diffusion coefficient for gas molecules in liquid (in liquid pores) by four to five orders of magnitude. Thus, processes of gas transfer in the electrode pores considerably accelerate with the emergence of gas pores in GGPE. After the emergence of gas pores in GGPE, portions of GGPE adjacent to the front and rear sides of GGPE find themselves in different conditions. Now, we can isolate two qualitatively different regions in GGPE, i.e. region I and region II.

**Region I.** This is the region that is adjacent to the front surface of GGPE. The region's coordinates are  $0 < y < y^*$  ( $y = 0$  is the coordinate of the front surface). According to (1), only pores with the largest radii turn into gas pores at point  $y^*$ ; all the other pores of the porous electrode are here completely filled with electrolyte solution, as before, and are liquid pores. In these pores, and throughout the entire region I, processes of the generation and removal of gas occur in exactly the same manner as this had occurred throughout the entire porous electrode before the instant when the critical overvoltage  $\eta^*$  was reached. The obvious condition

$$\hat{c}(y = y^*) = c^* \quad (5)$$

is satisfied at point  $y^*$ .

**Region II.** This is the region that is adjacent to the rear surface of GGPE. The region's coordinates are  $y^* < y < \Delta$ . Here, the situation with the filling of pores by electrolyte and gas is more complicated. To find the distribution of the electrolyte oversaturation with gas throughout the GGPE thickness in this region, it is necessary to solve a self-consistent problem about how the distribution of the electrolyte oversaturation with gas affects the number of gas pores and, vice versa, how the distribution of gas pores in this region of porous electrode increases the effective diffusion coefficient and accelerates diffusion processes, thus influencing the distribution of the electrolyte oversaturation with gas in this region. The approaches to solving this rather complicated problem and to a conjugation of the curves calculated for regions I and II, at their common boundary, in a plane with the coordinate  $y^*$ —all these questions will come to our attention below. However, even now we can make an important qualitative conclusion: with the emergence of gas pores in GGPE and with the emergence of region II in GGPE, the character of pores in GGPE must undergo qualitative changes. The overall current must begin to rise at rates that are higher than those that took place in the region of small overvoltages (at  $0 < \eta < \eta^*$ ). That the size of region II begins to gradually increase after reaching the critical overvoltage  $\eta^*$  is obvious, as does the fact that the value of coordinate  $y^*$ , which falls within the range  $0 < y^* < \Delta$ , begins to

diminish. And, at a certain new critical overvoltage  $\eta^{**}$ , the coordinate  $y^*$  drops to zero. And this is precisely what means the formation of chains of interconnected gas pores in GGPE. Such chains extend throughout the entire thickness of GGPE. It is precisely these phenomena that explain the emergence of an inflection in the polarization curves observed in experiments performed on GGPE: a decrease in the slope of polarization curves in the low-polarizability portion, as compared with the portion of the polarization curve preceding it, where there takes place a linear Tafel slope.

#### 4. POROUS ELECTRODE: REGION I

Let us now pass to a quantitative calculation of a polarization curve in a low-polarizability portion. There are no gas pores in region I with the coordinates  $0 < y < y^*$ , with the exception of the region's ultimate right-hand point  $y^*$ . Therefore, all the relationships [18] that took place throughout the entire porous electrode in the region of small overvoltages at  $0 < \eta < \eta^*$  remain valid here. As far as estimates show, in the region of small overvoltages and in a low-polarizability portion, we can assume that the overvoltage is constant throughout the entire electrode thickness

$$\eta \equiv \text{const.} \quad (6)$$

Thus, in reality, we have to determine only the nature of the distribution of the electrolyte oversaturation with gas,  $\hat{c}$ , over the GGPE thickness. In region I, the equation for the distribution of the oversaturation over the thickness of GGPE has the form

$$d^2 \hat{c} / d\hat{y}^2 = \hat{c} - e^{(\alpha+\beta)}, \quad (7)$$

where  $\hat{y} = y/L_d$  is a reduced coordinate, which is referred to the front surface of GGPE, and  $L_d = L_d^0 e^{\alpha\eta/2}$ .

The effective diffusion coefficient  $D^*$  in relationship (4) may be estimated with the aid of the equation

$$D^* = Dg_1/\nu = D_{\max}/\nu, \quad (8)$$

where  $D$  is the true diffusion coefficient for gas in electrolyte solution;  $g_1$  is the electrode's liquid porosity, which coincides with the electrode's porosity  $g$  in region I; and  $\nu \geq 1$  is a quantity that has no definite physical meaning. The last parameter shows how many times the true effective diffusion coefficient differs from the maximum possible diffusion coefficient  $D_{\max}$ . Its magnitude is defined by specific features of the structure of a porous space. There are two polar types of porous media: some may be modeled as lattices of sites, others, as lattices of bonds [35, 36]. Calculations showed that parameter  $\nu \approx 1$  in lattices of sites and  $\nu \gg 1$  in lattices of bonds. Equation (7) must be supplemented by two boundary conditions. For the front surface, we have

$$y = 0 \quad \hat{c} = c_s. \quad (9)$$

And at point  $y = y^*$ , condition (5) must be satisfied. The solution of equation (7) has the general form

$$\dot{c} = e^{(\alpha+\beta)\eta} + Ae^{\gamma} + Be^{-\gamma}. \quad (10)$$

With boundary conditions (5) and (9), we obtain the set of two equations

$$c^* = e^{(\alpha+\beta)\eta} + Ae^{\gamma^*} + Be^{-\gamma^*}, \quad (11)$$

$$c_s = e^{(\alpha+\beta)\eta} + A + B. \quad (12)$$

## 5. POROUS ELECTRODE: REGION II

In region II, where there are gas pores in existence, the effective molecular diffusion coefficient for gas in the electrolyte pores stops being a constant, as was the case in region I. Therefore, the finding of the distribution of the electrolyte oversaturation with gas is a complicated task here. It is obvious that, with increasing overvoltage in a low-polarizability portion, at  $\eta \geq \eta^*$ , the number of gas pores in GGPE increases. At the beginning, gas pores are prevented from contact with each other by smaller liquid pores, and the effective diffusion coefficient is still on the order of  $D^*$  (see (8)). But, gradually, pores with radii more shallow than  $r_{\max}$  are included in the number of gas pores as well. And all the gas pores, no matter the radius, start to join, first into clusters, and then into a unified combined network of gas pores (provided a percolation threshold is reached [37–42]). The effective molecular diffusion coefficient, which is contributed to by both liquid pores and gas pores, starts to rapidly rise and is now determined predominantly by its gas component. Then, in the parts of GGPE where the union of gas pores is reached, we can, to a large degree of accuracy, adopt a trivial solution of the problem, specifically, we can assume that here there occurs a leveling of the electrolyte oversaturation with gas, which does not depend on coordinate:

$$\dot{c} \equiv \text{const}. \quad (13)$$

The problem that we are considering is that of calculation of the GGPE characteristics in a low-polarizability portion. This problem is absolutely new for the theory of porous electrodes. And that is barely surprising: now it is necessary to solve a percolation problem ([37–42]; see also monograph [43] and reviews [44–46]) of an entirely new type. Now, the probability for a wide pore to be filled with gas depends not on one but on two parameters, specifically, on the pore radius and the electrolyte oversaturation with gas at a given point in the porous medium. Now, the affiliation of a given pore with either the class of gas pores or the class of liquid pores must be determined as a result of a calculation of a certain equation of the diffusion type with coefficients whose magnitude is, in turn, determined by the distribution of gas and electrolyte in the porous space. The development of procedures for solving such a self-consistent problem, is still a good distance in the future. In

this particular communication, we will strive to find a sufficiently simple, approximate solution for the problem. Specifically, we assume that we are dealing with an ideal GGPE. What this means is that we adopt the following two simplifying assumptions.

(1) We assume that all the largest pores with a maximum radius ( $r = r_{\max}$ ) are unified into a combined network in the region of  $y^* < y < \Delta$ . Then, following the emergence of first gas pores in GGPE also emerges a unified combined network of gas pores even at  $\eta = \eta^*$ .

(2) We also assume that the diffusion coefficient for molecules that evolve in a gas phase in the course of electrolysis is infinitely large, specifically,  $D_g = \infty$ . With condition 1 satisfied, the necessity to solve percolation problems is completely removed. Once the overvoltage reaches the critical overvoltage  $\eta^*$ , which signifies the formation of first gas pores in GGPE, a gas channel forms in region II of the porous electrode. The channel facilitates an effective leveling of oversaturation with gas throughout the thickness. The number of the widest pores in any cross-section of the porous electrode is infinitesimal. However, the formed channel for the gas removal is nonetheless capable of functioning, provided the condition  $D_g = \infty$  is satisfied. That is why condition 1 must needs be supplemented by condition 2.

Thus, conditions 1 and 2 ensure the constancy of oversaturation throughout the entire region II of GGPE. It is obvious that, in region II,

$$\dot{c} \equiv c^*. \quad (14)$$

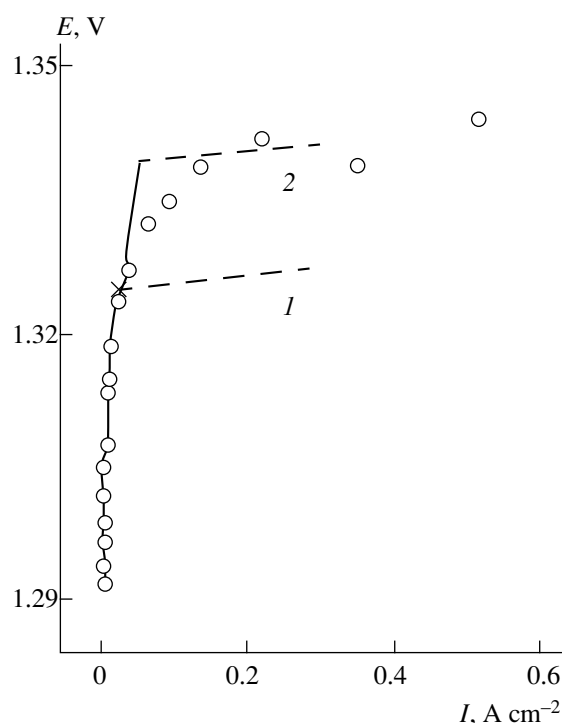
At  $\eta > \eta^*$ , the  $\dot{c}$  vs.  $y$  dependences we obtain for an ideal GGPE are of the type similar to that represented by curve 2 in Fig. 1. We perceive that the oversaturation in region I increases from  $c_s$  to  $c^*$ , while the oversaturation in region II is constant. There is one more circumstance that must be noted. With the exception of the largest pores that have a maximum radius  $r_{\max}$ , all the other pores remain filled with electrolyte solution, exactly as before, and introduce their own contribution to the gas generation process. That is why the following conditions are satisfied in region II:

$$g_1 \equiv g, \quad (15)$$

$$S_1 \equiv S. \quad (16)$$

Then, the contribution into the overall current generated in GGPE throughout the entire region II ( $y^* < y < \Delta$ ) is as follows:

$$\begin{aligned} I^* &= Si_0(e^{\beta\eta} - c^*e^{-\alpha\eta})(\Delta - y^*) \\ &= I_d(e^{\beta\eta} - c^*e^{-\alpha\eta})(\Delta - y^*)/L_d^0, \end{aligned} \quad (17)$$



**Fig. 2.** The link between potential  $E$  and overall current  $I$  in the process of chlorine evolution on ORTA; open circlelets represent experimental data; dashed line 1 represents a calculation of an ideal GGPE at  $c^* = 3.5$ ; dashed line 2 represents a calculation of GGPE at  $c^{**} = 20$ ,  $L_d^0 = 1.27 \mu\text{m}$ ,  $\Delta = 5 \mu\text{m}$ ,  $I_d = 2.13 \times 10^{-2} \text{ A cm}^{-2}$ , and  $\varphi = 7.5$ ; see text for other explanations.

where the characteristic current of diffusion is

$$I_d = (nFD^*c_0Si_0)^{1/2}. \quad (18)$$

## 6. THE ELECTROLYTE CHAMBER

Let us now examine the processes that occur in the space outside the electrode, i.e. in the electrolyte chamber. The coordinates of the electrolyte chamber are  $-\infty < y < 0$ . The ultimate goal of a GGPE is to produce a gaseous product of the electrochemical reaction that proceeds on the inner surface of GGPE. We assume that the total flux of conversions of gas molecules dissolved inside the electrolyte into gas bubbles in a unit volume of an electrolyte solution in the electrolyte chamber in a unit time period is

$$j_g = \psi(\zeta - 1), \quad (19)$$

where the dimensionality of the proportionality factor  $\psi$  is  $\text{g} \cdot \text{mol}^{-1} \text{ cm}^{-3} \text{ s}^{-1}$ . Thus, the equation for the distribution of oversaturation over the thickness of the electrolyte chamber has the form

$$d^2\zeta/dY^2 = \zeta - 1, \quad (20)$$

where  $Y = y/L_g$  is a reduced coordinate referred to the front surface of GGPE, and

$$L_g = (Dc_0/\psi)^{1/2} \quad (21)$$

is a characteristic diffusion length for the electrolyte chamber. Equation (20) must be supplemented by two boundary conditions

$$y = 0 \quad \zeta = c_s, \quad y = -\infty \quad d\zeta/dy = 0. \quad (22)$$

The second boundary condition means that the gas molecules that are dissolved in the electrolyte chamber cannot be removed from it through diffusion. The gas must coalesce into gas bubbles and only in this form leave the electrolyte chamber. By solving equation (20) with boundary conditions (22), we can find the magnitude of the overall current in the electrolyte chamber

$$I = I_g(c_s - 1), \quad (23)$$

where  $I_g$  is a characteristic diffusion current for the electrolyte chamber

$$I_g = nFDc_0/L_g = nF(Dc_0\psi)^{1/2}. \quad (24)$$

## 7. SEWING ALL THE SOLUTIONS

To calculate a polarization curve for GGPE in a low-polarizability portion, it is now necessary to unite individual solutions obtained for the porous electrode in region I (Section 4) and region II (Section 5) and for the electrolyte chamber (Section 6). This means that we must sew together these partial solutions. The aim of the sewing is the determination of a number of unknown quantities that appear in the equations. The quantities in question are constants  $A$  and  $B$  in relationship (10); the oversaturation at the front surface of GGPE,  $c_s$ ; the overall current  $I$ ; and the coordinate, which separates region I in the porous electrode from region II,  $y^*$  (or the ratio  $y^*/L_d^0$ ). Using relationship (10), we can establish one more, in addition to relationship (23), expression for the overall current, namely,

$$I = nFD^*\{dc/dy\}|_{y=0} = [nFD^*c_0/L_d^0]\{d\zeta/d\hat{y}\}|_{y=0} = I_d(A - B). \quad (25)$$

The condition for sewing in the plane  $y = y^*$ , which separates region I in the porous electrode from region II, requires that the currents to the left and right of this plane should be continuous. Therefore, making use of relationships (10), (17), and (18), we have here:

$$A \exp(y^*/L_d^0) - B \exp[-(y^*/L_d^0)] = (e^{\beta\eta} - c^*e^{-\alpha\eta})(\Delta - y^*)/L_d^0. \quad (26)$$

Thus, a set of five equations, specifically, (11), (12), (23), (25), and (26) allows us to determine five unknown parameters, namely,  $A$ ,  $B$ ,  $c_s$ ,  $I$ , and  $y^*/L_d^0$ . In

order to obtain a complete polarization curve, and not only its low-polarizability portion, it is also necessary to use dependences of  $I$  and  $c_s$  on the overvoltage at small overvoltages, i.e. at  $0 \leq \eta \leq \eta^*$ . These functions have the forms [18]

$$I = I_d e^{-\alpha\eta/2} [e^{(\alpha+\beta)\eta} - c_s] \tanh(\Delta e^{-\alpha\eta/2}/L_d^0), \quad (27)$$

$$c_s = [\varphi e^{(\alpha/2+\beta)\eta} \tanh(\Delta e^{-\alpha\eta/2}/L_d^0) + 1] / [\varphi e^{-\alpha\eta/2} \tanh(\Delta e^{-\alpha\eta/2}/L_d^0) + 1], \quad (28)$$

where parameter  $\varphi$  is equal to the ratio between characteristic currents for the porous electrode and the electrolyte chamber

$$\varphi = I_d/I_g = (Si_0g_1/nF\psi v)^{1/2}. \quad (29)$$

One can use the set of equations (11), (12), (23), (25), and (26) only at the terminal segment of overvoltages, specifically, at  $\eta^* \leq \eta \leq \eta^{**}$ , starting with the overvoltage  $\eta^*$ , at which first gas pores emerge in GGPE, to the overvoltage  $\eta^{**}$ , at which region II extends enough to reach the front surface of the porous electrode. The last condition means that

$$y^* = 0 \quad (30)$$

at overvoltage  $\eta^{**}$ . As follows from relationships (11) and (12), upon reaching the overvoltage  $\eta^{**}$ , there takes place the equality

$$c_s = c^*. \quad (31)$$

Thus, in the region of overvoltages  $\eta^* \leq \eta \leq \eta^{**}$ , the oversaturation at the front surface of the porous electrode,  $c_s$ , steadily increases and reaches the quantity  $c^*$ .

## 8. A CALCULATION OF A SET OF EQUATIONS AND A COMPARISON WITH EXPERIMENT

Up to now, we were performing an investigation of GGPE in general terms. Now, for calculations and for comparing their results with experimental data, we select the process of the chlorine generation on ORTA. Let us take a typical anodic branch of PC, which was presented in [1] (Fig. 1, here). When performing estimates, we will assume that the quantities in formulas (11), (12), (23), (25)–(29) are as follows:  $n = 2$ ; liquid porosity of ORTA,  $g_1 = 0.5$ ; the diffusion coefficient for chlorine in electrolyte solution,  $D = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ; the chlorine solubility in electrolyte solution (high NaCl concentrations, temperature  $87^\circ\text{C}$ ),  $c_0 = 2.7 \times 10^{-6} \text{ mol cm}^{-3}$ ; the specific surface area of pores in an ORTA of standard thickness,  $S = f/\Delta = 700/5 \times 10^{-4} = 1.4 \times 10^6 \text{ cm}^{-1}$ , where  $f$  is the roughness factor; and the exchange current  $i_0 = 1.2 \times 10^{-4} \text{ A cm}^{-2}$  [47]. We also assume that the quantity  $v$  in expression (8) for the effective diffusion coefficient is equal to unity. Under these conditions, we have for an ORTA: the characteristic diffusion length of the porous electrode,  $L_d^0 = 1.27 \text{ }\mu\text{m}$ , and its character-

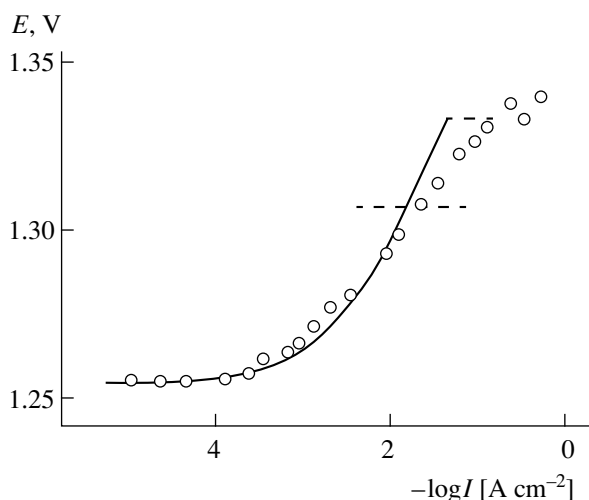
istic diffusion current  $I_d = 21.3 \text{ mA cm}^{-2}$ . Moreover, we assume that there exist considerable complications with the gas removal in the electrolyte chamber: for definiteness sake, we adopt  $\varphi = 7.5$ .

The structure of the porous space in ORTA has not been studied sufficiently enough. And yet, we can glean some information on the characteristics of the porous space. As shown in [48], ORTA contain the pores of two types. One type includes micropores whose radii  $r$  lie in the approximate interval 0.01 to 0.025  $\mu\text{m}$ . The other involves macropores with radii  $r$  in the approximate interval 0.05 to 0.4  $\mu\text{m}$ . Having substituted the value of the maximum pore radius  $R = r_{\text{max}} = 0.4 \text{ }\mu\text{m}$  into equation (1), we obtain the critical oversaturation  $c^*$  at which the first gas pores emerge near the rear surface of the porous electrode:

$$c^* = 1 + 1/0.4 = 1 + 2.5 = 3.5. \quad (32)$$

The reduced critical overvoltage  $\eta^*$ , calculated with equation (3), proved to equal 1.299. Correspondingly, the critical potential  $E^*$  in Fig. 2 is equal to 1.325 V (NHE). This point is marked with a cross in Fig. 2. The reaching of this potential signifies the commencement of the formation of first gas pores in GGPE.

Let us compare experimental and theoretical  $E$  vs.  $I$  and  $E$  vs.  $\log I$  curves (Fig. 2), which were calculated with formulas (11), (12), (23), and (25)–(29) under the assumption that  $c^* = 3.5$ . Open circlets in the figure represent experimental data (Fig. 1 in [1]), and dashed line  $I$  represents a calculated curve. We see a considerable discrepancy between the theory and experiment. The explanation is simple: needless to say, both assumptions that we adopted in Section 5 were far-fetched. The only pores that the gas can in reality reach are the widest pores, which are “diluted” by smaller pores still containing electrolyte. Therefore, the effective diffusion coefficient must not be viewed as infinitely large. The effective diffusion coefficient exceeds the effective diffusion coefficient for a porous electrode whose pores are completely filled with electrolyte solution only a little, if at all. As a result, the distribution of the electrolyte oversaturation with gas over the GGPE thickness is described in Fig. 1 by the real curve 3, rather than by ideal curve 2. With the overvoltage increasing further, at  $\eta > \eta^*$ , the right-hand side of the  $\zeta$  vs.  $y$  curves in Fig. 1, which are adjacent to the rear surface of the porous electrode, cling ever more tightly to a horizontal, because the number of gas pores rapidly rises, and the effective diffusion coefficient increases. In the long run, at a certain critical overvoltage  $\hat{\eta}$ , a network of gas pores connected with one another forms near the rear surface of the porous electrode. The effective diffusion coefficient in this region becomes so large that the  $\zeta$  vs.  $y$  distribution (effective curve 4 in Fig. 1) becomes similar to ideal curve 2 in Fig. 1. In this manner, prerequisites are created for the possibility to again utilize formulas (11), (12), (23), and (25)–(29) in a calculation of all the basic characteristics of GGPE. However, to do

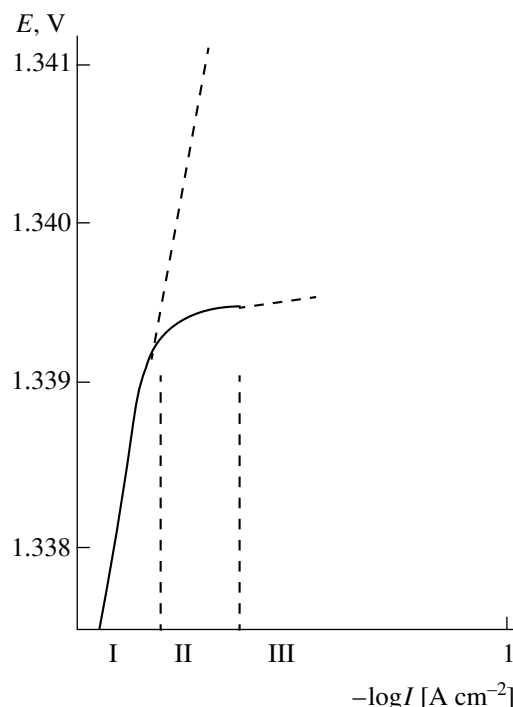


**Fig. 3.** A polarization curve (anodic branch) for the process of chlorine evolution on ORTA; open circlets represent experimental data, and solid line represents a calculation of GGPE at  $c^{**} = 20$ ,  $L_d^0 = 1.27 \mu\text{m}$ ,  $\Delta = 5 \mu\text{m}$ ,  $I_d = 2.13 \times 10^{-2} \text{ A cm}^{-2}$ , and  $\varphi = 7.5$ ; see text for other explanations.

this, one must substitute  $c^{**}$  for  $c^*$  (Fig. 1) in formulas (11), (26), and (31). Parameter  $c^{**}$  is a certain characteristic oversaturation that defies the theory. It can be established by comparing experimental and theoretical  $E$  vs.  $I$  curves and assuming, in doing so, that it is a free parameter of the problem. By varying parameter  $c^{**}$ , we managed to establish that the best agreement between experiment and the theory can be reached at  $c^{**} = 20$  (Fig. 2, dashed line 2). As opposed to parameter  $c^*$ , which fixes the instant when first gas pores emerge in GGPE, parameter  $c^{**}$  has no definite physical meaning. This is an effective quantity that imbibes the assumption that a gas phase is now present in region I (curve 4 in Fig. 1 intersects the horizontal  $c^* \equiv \text{const}$ : to the left of the intersection point, all the pores in the porous electrode are completely filled with electrolyte solution; to the right, some pores are gas pores). Moreover, this virtual quantity also takes into account the presence, in region II, of a whole spectrum of gas pores with radii extending from a minimum value  $r_{\min}$  to the maximum value  $r_{\max} = 0.4 \mu\text{m}$ . On the whole, the totality of these gas pores in region II may be characterized by a certain effective radius of gas pores  $r_{\text{ef}}$ . Utilizing relationship (1), we can estimate the magnitude of the effective radius of gas pores  $r_{\text{ef}}$  in region II. To do this, it is necessary to substitute  $c^{**} = 20$  for  $c^*$  in relationship (1). Then,

$$r_{\text{ef}} = 1/(c^{**} - 1) = 1/19 = 0.05 \mu\text{m}. \quad (33)$$

Let us now turn our attention to a comparison of experimental and theoretical polarization  $E$  vs.  $\log I$  curves (Fig. 3). We see that, in the portion of low overvoltages, at overvoltages in the interval  $0 < \eta < \eta^*$  (the value of



**Fig. 4.** A calculated polarization curve (anodic branch) for the process of chlorine evolution on ORTA; region I is a Tafel portion; region II is a portion with a network of mutually connected gas pores, which envelops a fraction of the entire thickness of GGPE; and region III is a portion with a network of mutually connected gas pores, which envelops the entire thickness of GGPE;  $c^{**} = 20$ ,  $L_d^0 = 1.27 \mu\text{m}$ ,  $\Delta = 5 \mu\text{m}$ ,  $I_d = 2.13 \times 10^{-2} \text{ A cm}^{-2}$ , and  $\varphi = 7.5$ ; see text for other explanations.

$\eta^*$  in Fig. 3 is marked with a dashed horizontal line), in the region where all the pores of the porous electrode are still completely filled with electrolyte solution, there is observed a satisfactory agreement between experiment (the data taken from Fig. 1 of [1]) and the theory put forth in [18]. The existence of such a satisfactory agreement implies that the basic constants and values of characteristic parameters ( $n$ ,  $g_1$ ,  $D$ ,  $c_0$ ,  $S$ ,  $i_0$ ,  $v$ ,  $L_d^0$ ,  $I_d$ ,  $\varphi$ ) we adopted for the process of chlorine evolution on ORTA are, on the whole, selected correctly. In the same portion of low polarizability, at overvoltages in the interval  $\eta^* \leq \eta \leq \eta'$  (until the instant when curve 4 in Fig. 1 occurs for the first time), after the emergence of gas pores in the porous electrode, there is observed a certain deviation of a theoretical curve (calculated under the assumption that  $c^{**} = 20$ ) from an experimental curve. This is hardly surprising, because we make use of approximate calculations, after all. We have not solved the involved self-consistent problem, specifically, the percolation problem, together with the necessity to calculate a nonlinear diffusion equation with a coordinate-dependent effective diffusion coeffi-



cient, which would have led to a much closer agreement between the theory and experiment.

Let us make one more observation, the final one. It is not by chance that we presented portions of calculated curves in Figs. 2 and 3 as dashed lines. The point here is that the overvoltage  $\eta^{**}$  only marginally differs from the critical overvoltage  $\eta^*$  and the overvoltage  $\eta'$ : after the emergence of first gas pores, there emerges very rapidly a gas channel, which extends from the rear to the front surface of GGPE. At the scale in which Figs. 2 and 3 are performed, this transition, i.e. the transition from  $\eta^{**}$  to  $\eta^*$  or  $\eta'$  is practically indistinguishable. That is why the dashed lines in Figs. 2 and 3 indicate only directions in which a further increase in the overall current is likely to occur. A detailed picture, which reflects variations in the  $E$  vs.  $\log I$  curve for the process of chlorine evolution on ORTA under the adopted assumption that  $c^{**} = 20$ , is presented in Fig. 4. There are three characteristic regions of variations in the current and overvoltage. Region I is a region of small overvoltages, specifically,  $0 < \eta < \eta' \approx 1.34$ . But for the emergence of gas pores in ORTA, the Tafel portion would have continued (dashed straight line in Fig. 4). Region II is the initial portion of the low-polarizability portion, where  $\eta' < \eta < \eta^{**}$ . And finally, region III, where  $\eta > \eta^{**}$  (a dashed-line continuation of the calculated curve) and where the network of mutually connected gas pores extends now throughout the entire thickness of the porous electrode. Region III cannot be calculated with the aid of formulas (11), (12), (23), (25)–(29); other, much more complicated techniques are called for here.

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