a semiquantitative estimation of the influence of various factors on the selectivity of ion-exchange membranes.

LITERATURE CITED

1. E. Glueckauf and R. E. Watts, Proc. Roy. Soc., 268A, 339 (1962).
2. E. Glueckauf, Proc. Roy. Soc., 268A, 350 (1962).
3. J. M. Grabtree and E. Glueckauf, Trans. Faraday Soc., 59, 2639 (1963).
4. M. V. Pevnitskaya and A. A. Kozine, Paper Deposited at the All-Union Institute of Scientific and Technical Information [VINITI], February 9, 1976, No. 363-76 Dep.
5. B. N. Laskorin, N. M. Smirnova, E. M. Smirnova, T. A. S"yanova, and I. N. Moiseeva, Zh. Prikl. Khim., 47, 2357 (1974).
6. P. V. Kozlov and N. A. Platé (editors), Polyethylene and Other Polyolefins [Russian translation], Mir, Moscow (1964).
7. M. Lopeg, B. Kipling, and H. L. Yeager, Anal. Chem., 49, 629 (1977).
8. N. I. Nikolaev, G. G. Chuvileva, M. D. Kalinina, and V. I. Muromtsev, in: Methods and Instruments for Determination of the Composition and Properties of Matter [in Russian], Ilim, Frunze (1968), p. 82.
9. N. I. Nikolaev, A. M. Filimonova, and N. N. Tunitskii, Zh. Fiz. Khim., 43, 1249 (1969).
10. N. I. Nikolaev, in: Kinetics and Dynamics of Physical Adsorption [in Russian], Nauka, Moscow (1973), p. 32.
11. T. D. Semenovskaya, V. T. Avgul', and K. V. Chmutov, Zh. Fiz. Khim., 43, 778 (1969).
12. R. Robinson and R. Stokes, Electrolytic Solutions, IL, Moscow (1963).
13. P. Mears, Diffusion in Polymers, J. Crank and C. S. Park, eds., Academic Press, London – New York (1968).
14. N. I. Nikolaev, M. D. Kalinina, and G. G. Chuvileva, Zh. Fiz. Khim., 44, 3110 (1970).
15. Kayoko Umezawa and Takeo Yamabe, Bull. Chem. Soc. Jpn., 45, 56 (1972).
16. N. I. Nikolaev and G. G. Chuvileva, Fifth All-Union Conference on Electrochemistry, Summaries of Reports [in Russian], Part 2, VINITI, Moscow (1974), p. 354.

JOINT ISOLATION OF CHLORINE AND OXYGEN ON RUTHENIUM DIOXIDE – TITANIUM DIOXIDE ANODES

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It was shown that the distribution of the potential in a thin (several microns) layer of active mass of anodes is practically uniform. The diffusion of the acid formed in the anodic liberation of oxygen from the pores of the anode is discussed. It was shown that in most of the anode the pH of the solution in the pores is ~1, and only in a thin surface layer does it gradually approach the pH of the anolyte. This pH distribution has a decisive influence on the kinetics of the liberation of oxygen and the nature of the wear of the anode during the electrolysis of chlorides.

For a discussion of the process of joint liberation of chlorine and oxygen, it is necessary to consider the mutual positions of the corresponding polarization curves. The experimental data on the liberation of chlorine (from strongly acid concentrated chloride solutions) and oxygen (from phosphate buffer solutions with various pH), pertaining to electrodes produced according to the same technology and possessing the same basic characteristics, were cited in [1, 2]. A comparison of them shows that in strongly acid solutions (pH ~ 0), at the potential of the liberation of chlorine, the rate of liberation of oxygen is approximately three orders of magnitude lower than for chlorine, i.e., the current yield for oxygen is ~0.1% in this case. With increasing pH of the solution, the polarization curve of the liberation of chlorine is unchanged, whereas the potentials of the liberation of oxygen (according to a normal hydrogen electrode) are shifted by ~60 mV per pH unit in the direction of less positive values [2]. Thus, with increasing pH the mutual arrangement of the polarization curves for the liberation of chlorine and oxygen (in the absence of chloride) indicates an increase in the relative

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rate of liberation of oxygen. In the presence of a sufficient increase in the pH, the process of oxygen formation should have already become dominant in a weakly acid (pH > 3) chloride solution. However, in practice, as is well known, even at pH ~ 7 (i.e., under the conditions of chlorate production), the basic process is the discharging of chloride ions, and not the liberation of oxygen.

The possibility remains that such a discrepancy may be explained by inhibition of the liberation of oxygen in the presence of chloride. However, as was shown by the experiments of co-workers of our laboratory, D. V. Kokoulina and Yu. I. Krasovitskaya, at increased pH the presence of the chloride ion does not have a sufficiently strong influence on the process of liberation of oxygen.

Thus, we find that in practical electrolysis of a solution of NaCl, the rate of liberation of oxygen on ruthenium dioxide–titanium dioxide anodes (RTOA) is significantly lower, i.e., the polarization curve of the liberation of oxygen lies at higher potentials than corresponds to the pH of the anolyte. The cause of this in weakly acid and neutral solutions may be an acidification of the space near the anode and of the solution in the pores of the anode in the practically unbuffered medium, such as a solution of alkali metal chloride. We reported earlier on acidification of the medium in pores and a substantial influence of increased acidity in the pores in comparison with the acidity in the volume of the anolyte on the course of the oxidation of graphite [3]. However, the kinetic principles both of the chlorine and of the oxygen reaction on graphite and RTOA differ substantially, and therefore a new analysis of this question was required.

Let us consider first the distribution of the current of liberation of chlorine along the depth of the anode. This process, as usual [4], is described by differential equations

$$\frac{d\eta}{dx} = -\rho I, \tag{1}$$

$$\frac{dI}{dx} = -iS, \tag{2}$$

where η is the overvoltage; I is the overall current density (calculated for the visible surface) in the cross section of the electrode at a distance x from its outer surface; ρ is the specific resistance of the electrolyte in the pores; i is the true current density; S is the specific surface of the porous electrode (in cm^2/cm^3). Since we are working in a region of rather high overvoltages and since, as will be seen subsequently, at a small electrode thickness the potential deep within it does not differ greatly from the outer potential, in the entire interval of x we can neglect the current of the reverse reaction in comparison with the direct reaction and can write the dependence of i on η in the form

$$i = i_0 \exp \alpha\eta F/RT. \tag{3}$$

Here α is the formal transport coefficient; the remaining notations are as usual.

The boundary conditions are

$$x=0, \quad I=I_0, \quad \eta=\eta_0, \tag{4}$$

$$x=\delta, \quad I=0, \quad \text{i.e.} \quad \frac{d\eta}{dx}=0. \tag{5}$$

The condition (5) reflects the fact that in the cross section of the porous layer adjoining the substrate, current does not pass through the electrolyte.

The solution of Eqs. (1) and (2), considering (3) with boundary conditions (4) and (5), is

$$\operatorname{arctg}\sqrt{\exp[\alpha(\eta-\eta_0)F/RT]-1} - \operatorname{arctg}\sqrt{\exp[\alpha(\eta_0-\eta_0)F/RT]-1} = -\sqrt{2\frac{F}{RT}\alpha\rho S i_0}\sqrt{\exp(\alpha\eta_0 F/RT)}\,x. \tag{6}$$

If $\eta - \eta_\delta \ll RT/\alpha F$, which, as we shall see later, is fully justified, then considering the equality (at $u \ll 1$) $\arctan\sqrt{\exp u - 1} \simeq \arctan\sqrt{u} \simeq \sqrt{u}$, we can write (6) in the form

$$\sqrt{\alpha(\eta-\eta_0)F/RT} - \sqrt{\alpha(\eta_0-\eta_0)F/RT} = -\sqrt{2\frac{F}{RT}\alpha\rho S i_0 \exp(\alpha\eta_0 F/RT)}\,x. \tag{6a}$$

The expression $i_0 \exp(\alpha\eta_\delta F/RT)$ is none other than i_δ, where i_δ is the true current density at the boundary of the active mass and the substrate. If the overvoltages on the outer part of the surface η_0 and at the boundary with the substrate η_δ differ little, then the true current density can be considered constant in the first approximation and then $S\delta i_\delta \simeq I_0$ is the overall current density on the outer surface of the anode. Considering this

circumstance and assuming $x = \delta$ in (6a), we obtain the following expression for the difference of the overvoltages at the front and rear boundaries of the active layer:

$$\eta_0 - \eta_\delta = 2\rho I_0 \delta. \tag{7}$$

The specific resistance of the electrolyte in the pores $\rho = \rho_0(\gamma^2/v)$, where ρ_0 is the specific resistance of the electrolyte, v is the volume porosity of the active mass, and γ is the coefficient of tortuosity of the pores. Using the usual values for these quantities ($\rho_0 = 2\ \Omega \cdot$ cm, $v \simeq 0.2$, $\gamma \simeq 1.5$), we find that for a layer 5 μ thick at a current density $I_0 = 10^{-1}$ A/cm^2 (the condition of industrial diaphragm electrolysis), $\eta_0 - \eta_\delta =$ 2 mV. Thus, the potential and, consequently, the current density through the entire depth of the active layer are practically constant.*

Let us consider the distribution of the process of liberation of oxygen through the depth of the electrode in an unbuffered chloride solution [5]. The electrode potential is determined by the basic process – the liberation of chlorine – and, as was described above, is practically constant through the thickness of the electrode. Constancy of the potential in the entire layer of active mass still does not mean constancy of the current density of liberation of oxygen, since the latter also depends on the acidity of the solution. As was shown in [2], for RTOA in the region of potentials close to the chlorine potential, the overvoltage of the liberation of oxygen does not depend on the pH, and the lower portion of the polarization curve (before its point of inflection) can be described by the expression

$$i = i_0 \exp(\alpha\eta F/RT) = i_0^0 \exp(\alpha\varphi F/RT)\, c_{H^+}^{-\alpha}, \tag{8}$$

where η is the overvoltage, while φ is the potential relative to a constant reference electrode.

Since the Tafel slope of this portion is close to 30-40 mV, the experimental value of $\alpha \simeq 1.5$-2. To simplify the mathematical computations, it will henceforth be assumed that $\alpha = 2$ (in this case the solution can be obtained in analytical form).

In the liberation of oxygen, an equivalent amount of acid is formed. In a unit volume of the porous electrode in 1 sec, $j = iS/F$ moles of acid is formed. The acid formed diffuses outward from the electrode. Thus, we should solve the problem of diffusion with a distributed source, which is described by the equation

$$-D\frac{\partial^2 c}{\partial x^2} = j. \tag{9}$$

Here the direction of the x axis is taken from the electrode to the solution; D is the effective diffusion coefficient, equal to $(v/\gamma^2)D_0$, where D_0 is the true diffusion coefficient of the H^+ ion.

Substituting (8) into (9) we obtain

$$-D\frac{\partial^2 c}{\partial x^2} = Kc^{-2}, \tag{10}$$

where $K = i_0^0 \exp(\alpha\varphi F/RT)S/F$.

The boundary conditions in our problem will be as follows:

1. $\partial c/\partial x = 0$ when $x = 0$; since x equal to 0 corresponds to the boundary of the layer of active mass and the substrate, the flux of acid through this plane is equal to 0;
2. $c = c_{an}$ when $x = \delta$, where δ is the thickness of the electrode; at the outer boundary the acidity is equal to the acidity of the anolyte.

The solution of the problem is

$$cc_0\sqrt{c^{-1} - c_0^{-1}} + c_0^{3/2} \operatorname{arctg}\sqrt{c_0(c^{-1} - c_0^{-1})} = \sqrt{\frac{2K}{D}}\, x. \tag{11}$$

Here c_0 is the value of c at $x = 0$.

*Under the experimental conditions [1], the difference $\eta_0 - \eta_\delta$ was still approximately an order of magnitude lower. From this, in particular, it follows that the values of the Tafel slope b obtained in these experiments coincide with the true values. An appreciable difference in η (of the order of RT/F) can be achieved under conditions of mercury electrolysis, i.e., using thicker anodes and higher overall current densities. In this case the true current densities on the outer and inner boundaries may differ by an order of magnitude. However, in all cases of practical interest, the current of the reverse reaction can be neglected through the entire thickness of the anode.

The second boundary condition gives us c at $x = \delta$. Substituting the corresponding values into (11), we can find c_0 and then c at any x.

Equation (11) expresses the distribution of concentration in implicit form; therefore numerical calculations were performed on an electronic computer,* making the picture more graphic. The value $D_0 = 4 \cdot 10^{-5}$ $cm^2 \cdot sec^{-1}$ was taken. To estimate the value of K, we proceeded from the experimental value of the apparent current density I in strongly acid solution (1 mole/liter = 10^{-3} mole/cm^3). In such a solution the H^+ ion concentration is so high that no significant variation of it in the pores can be expected, and therefore it can be assumed that the true current density i is distributed uniformly over the thickness of the electrode (a confirmation of the uniformity of the distribution of concentration under these conditions is given below). In this case $I = iS\delta$ and $K = Sic^2/F = Ic^2/F\delta$. On the usual electrode with thickness $\delta = 5 \cdot 10^{-4}$ cm, with a working potential of the chloride electrolyzer, $I \simeq 10^{-3}$ A/cm^2, from which $K = 2 \cdot 10^{-11}$ $(mole/cm^3)^3 \cdot sec^{-1}$.

Calculation gave the following results. At an acidity of the external solution 1 M, the maximum enrichment of the solution in the pores is only 0.07%, and at an acidity 0.2 M it is 0.8%. Thus, in a strongly acid solution the acid concentration in the pores of the electrode is constant with a high degree of accuracy, which justifies the assumption of its uniformity made above in the estimation of K. For lower concentrations of the external solution, the changes in the concentration in the pores become more appreciable. Thus, $c_0 = 0.167$ M at $c_{an} = 0.14$ M and $c_0 = 0.125$ M at $c_{an} = 0.08$ M.

Typical calculation curves for the distribution of pH through the thickness of the electrode are presented in Fig. 1. It is important to emphasize that for these parameters of the anode and conditions of the process, for any acidities of the external solution, no matter how low, the acidity within a large portion of it (~98% of the thickness) is established at the level of 0.01-0.1 M (~80% of the volume works at an acidity ≥ 0.05 M); moreover, the maximum value of the acidity will be $c_0 \gtrsim 0.1$ M. Our calculation cannot be considered accurate for two reasons. In the first place, the estimate of the constants is given approximately. However, this does not introduce any qualitative changes, but leads only to a change of the scale along the x axis without any significant change in the shape of the curve. The second simplification is more important – the curve of liberation of oxygen was described by one Tafel straight line, while actually it consists of two Tafel portions [2]. The potential of transition from the area with low slope to the area with high slope lies above the potential of liberation of chlorine for solutions with pH $\lesssim$ 1.5-2, but at higher pH the process of liberation of oxygen proves to correspond to the upper portion with a larger slope. Thus, in the external layer the liberation of oxygen proceeds at a lower rate than was assumed in our calculation. In view of this, the region with pH > 2 should be somewhat broadened, but its contribution to the total current will be somewhat smaller.

Calculation shows that when the pH of the anolyte is varied within a broad range of values (approximately from 1 to 6), i.e., in the entire region of practical interest, most of the anode works at pH close to 1. A comparison of the rate of liberation of oxygen at this pH with the rate of liberation of chlorine shows that the fraction of current for the liberation of oxygen should be several percent, which approximates the practical data (~1-2%) in order of magnitude [6-9]. Considering the approximate nature of the calculation, the agreement of these values should be considered quite satisfactory.

*The calculations were performed by V. V. Topolev, to whom I should like to express my gratitude.

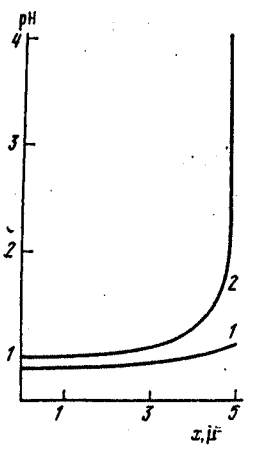

Fig. 1. Calculation curves for the distribution of pH through the thickness of the electrode.

From the picture of the pH distribution through the depth of the anode, two important conclusions follow. In the first place, the current yield for oxygen in work on an RTOA should be relatively insensitive to the pH of the anolyte, especially at pH > 2.

The second conclusion is associated with the fact that at increased pH of the anolyte, a thin surface layer of the anode – of the order of 0.1 μ – works at a relatively higher pH. This means that this layer is under conditions of increased oxygen overvoltage, i.e., in the region of potentials above the point of inflection of the polarization curve. As was shown earlier [2], this potential is critical; above it wear of the anodes is accelerated. Thus, although the entire anode works under a practically uniform distribution of current of liberation of chlorine, the nature of the distribution of acid in the pores leads to a nonuniform wear of the anode – the surface layer wears out more rapidly. Consequently, the thicker the anode, the longer its lifetime. In this the wear of the anode in chlorine electrolysis differs from the wear under conditions of accelerated tests in strongly acid solution, when the stability is unchanged within a definite range of thicknesses.

Thus, although the pH of the anolyte has no sharp influence on the current yield of oxygen and on the deep wear, increasing the pH should greatly affect the wear of the surface layer. In particular, this should lead to a more rapid wear in chlorate electrolysis in comparison with chloride electrolysis. In chloride electrolysis, however, efforts should be made to maintain a low pH of the anolyte. In particular, at pH $\leq$ 2, the electrode still does not exceed the critical value, beginning with which the wear of an RTOA is substantially accelerated.

LITERATURE CITED

1. R. G. Érenburg, L. I. Krishtalik, and I. P. Yaroshevskaya, Élektrokhimiya, 11, No. 1068, 1236 (1975).
2. L. V. Kokoulina, Yu. I. Krasovitskaya, and T. V. Ivanova, Élektrokhimiya, 14, 470 (1978).
3. L. I. Krishtalik, Élektrokhimiya, 2, 393 (1966); L. V. Kokoulina and L. I. Krishtalik, Élektrokhimiya, 3, 848 (1967).
4. O. S. Ksenzhek and V. V. Stender, Dokl. Akad. Nauk SSSR, 106, 487 (1956); 107, 280 (1956).
5. L. I. Krishtalik, D. V. Kokoulina, and Yu. I. Krasovitskaya, Chlorine Industry, Abstracts of Reports [in Russian], No. 11, NIITÉKHIM, Moscow (1976), p. 24.
6. L. M. Yakimenko, Khim. Promst, No. 3, 198 (1973).
7. V. N. Antonov, V. I. Bystrov, V. V. Avksent'ev, L. I. Yurkov, and V. L. Kubasov, Khim. Promst, No. 8, 600 (1974).
8. I. E. Veselovskaya, E. K. Spasskaya, V. A. Sokolov, V. I. Tkachenko, and L. M. Yakimenko, Élektrokhimiya, 10, 70 (1974).
9. N. Ya. Buné, G. A. Shiryaeva, and V. V. Losev, Élektrokhimiya, 13, 1540 (1977).