As might be expected, the proposed method, based on the Enskog–Tarn theory for mixtures of solid spheres, yields more precise results in the case of mixtures of monatomic gases.

NOTATION

ρ, density; m, molecular mass; x_i, mole fraction of i-th component; ν, number of components of mixture; λ, thermal conductivity coefficient; λ^0_{ij}, thermal conductivity coefficient of rarefied gas with molecular mass $2m_i m_j/(m_i + m_j)$. Superscript 0 indicates rarefied gas quantity; subscripts indicate numbering of mixture components.

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COMMENTS ON DESIGNING A DIAPHRAGMLESS REACTOR FOR THE PRODUCTION OF ELECTROLYTIC HYDROGEN

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Criterial relations generalizing the functional interrelationship between a number of dimensionless complexes of hydrodynamics and voltage in a reactor cell are obtained from the differential equations that describe the electrochemical process.

Hydrogen is becoming increasingly important with each year as an energy carrier and a raw material for many branches of industry. A potential demand for it in the near future may come from the microbiological industry, where hydrogen is used as a raw material for the production of feed protein, and in the future will perhaps be used to produce protein for human consumption [1, 2]. Although they are profitable, however, existing methods of producing hydrogen, particularly chemical methods, cannot satisfy the demand of this branch of industry for high-quality hydrogen. In this respect much attention should be focused on the

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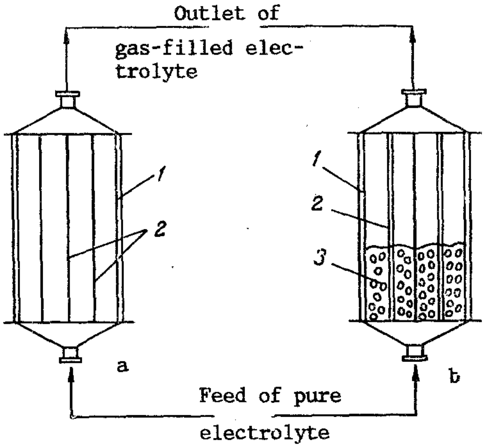

Fig. 1. Diaphragmless electrochemical reactor: a) with plate electrodes; 1) monopolar, 2) bipolar; b) with poured electrodes: 1) monopolar electrode, 2) perforated partition, 3) electrically conducting particles, $d_p = 0.03$ m.

electrochemical method, which ensures ecological clean production as well as producing high-quality hydrogen. In contrast to other chemical methods, this technology is implemented at comparatively low parameters (pressure, temperature) and is easily controlled with a current-voltage load. Because of the high energy content of the process (5-6 kW·h per m^3 of H_2) and low unit output of the electrochemical reactors (electrolyzers) the world production of electrolytic hydrogen still does not exceed 4% [3].

The explanation for the low unit output of diaphragm reactors (electrolyzers) is that while chemical reactions occur in the bulk of the reacting components, the electrochemical reaction occurs only on the surface of the electrode. Their total working area as well as the current density determine the productivity of the electrochemical reactor.

Increasing the reactor productivity through the current density, i.e., intensifying the electrochemical process, does not give any perceptible results since the voltage across the cell increases with the current loading and, therefore, the energy content of the process also increases. If the working area of plate electrodes is increased by using larger electrodes or more of them, the only result is that the diaphragm reactor is larger and heavier and its unit output does not rise appreciably.

At the same time the trend toward bringing the productivity of electrochemical reactors closer to that of chemical reactors, in which the reaction occurs in the entire volume of the solution, has led to the design of reactors with poured electrodes. The main working area of these electrodes is formed by separate electrically conducting particles, which are never linked together mechanically. The working area of poured electrodes and, hence, the reactor productivity are higher when the electrically conducting particles are smaller [4].

Despite the high technical specifications of poured electrodes, the unit output of a diaphragm electrochemical reactor still cannot be increased substantially. In this regard a higher productivity at comparatively low unit energy expenditure is achieved in diaphragmless reactors, especially with poured electrodes.

Instead of hydrogen and oxygen separately, a hydrogen—oxygen gas mixture in the stoichiometric ratio ($H_2:O_2 = 2:1$) is obtained in these reactors. If necessary the separation of the gas mixture into its components can be carried out in gas separators [5]. If the gas mixture is to be used as a raw material for the production of microbic biomass, separation becomes unnecessary since hydrogen and oxygen are fed together into the biochemical reactor.

The design features of diaphragmless reactors with plate and poured electrodes (Fig. 1) allow the electrochemical process to be carried out with forced electrolyte circulation, thus ensuring that more concentrated solution is fed continuously into the reaction zone. This ensures a continuous inflow of electrically active particles (H^+, OH^-) to the surface of the electrodes; hence, the particle density (C') near the surface and the density (C^0) in the core of the cell will tend to even out ($C' \leq C^0$). In this case the electrochemical reaction occurs at a lower current density.

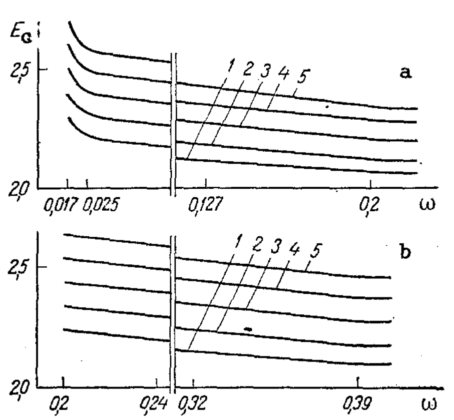

Fig. 2

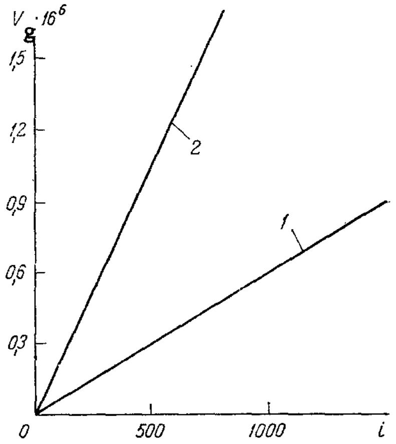

Fig. 3

Fig. 2. Voltage (E_c) of the cell of a diaphragmless electrochemical reactor as a function of the hydrodynamics of the process: a) plate electrodes: 1) at I = 2A, 2) 3A, 3) 4A, 5) 6A; b) poured electrodes: 1) at I = 2A, 2) 3A, 4) 5A, 5) 6A. ω, $m \cdot sec^{-1}$.

Fig. 3. Productivity of an electrochemical diaphragmless reactor versus the design parameters of the electrode: 1) plate electrodes, 2) poured electrodes. V_g, $m^3 \cdot sec^{-1}$ and i, $a \cdot m^{-2}$.

$$i = ZFD\frac{C^0 - C'}{\delta}, \ A \cdot m^{-2}. \tag{1}$$

Mass transfer in a reactor cell is characterized by a combination of molecular and convective transport of electrically active particles (H^+ and OH^-) between the working surfaces of the electrodes. Other conditions being equal, this process is more intensive when the electrolyte resistivity is lower, which is due primarily to the absence of extraneous inclusions, dielectrics, in the electrolyte. The gas fraction in the volume of the cell, consisting of hydrogen and oxygen bubbles, constitutes such inclusions. The larger the volume occupied by the gas fraction, i.e., the higher the gas filling of the electrolyte, the higher the resistivity (r_g) of the electrolyte.

The gas filling of the electrolyte (in %) is determined by the ratio of the rates of two processes: the rate of gas liberation, i.e., the current density ($i = 1/S \ A \cdot m^{-2}$) and the rate of removal of the gas fraction from the zone of the electrochemical reaction and the volume of the cell.

The volume of gases liberated increases linearly with the current density while the gas filling increases to a lesser degree, i.e., deviates from the linear. This is attributed to growth of the gas bubbles as they rise in the reactor cell (coalescence). With increasing electrolyte circulation rate, i.e., rate of gas removal, the coalescence decreases appreciably. When gas is liberated and removed at the same rate the electrolyte resistivity due to the presence of the gas fraction stabilizes and a further rise in the electrolyte circulation rate has no effect on reducing the electrolyte resistivity and, hence, on the voltage (Fig. 2). From this follows the conclusion that the voltage across the reactor cell depends in an involved functional manner not only on the physicochemical properties of the electrolyte and cell parameters but also on the hydrodynamics of the electrochemical process. The usual voltage balance equation [3], however, does not adequately take into account the interrelationship between the hydrodynamic and mass-transfer parameters as well as their effect on the voltage:

$$E_c = \eta + E = \eta_a + \eta_c + E_0 + ilr_g B, \tag{2}$$

Mass transfer in relation to the electrochemical process was studied in [6, 7] with allowance for the distinctive features of the motion of viscous liquids, which are described by the Navier–Stokes differential equations [8-10]. These equations, however, cannot be solved by known methods because of the large number of variables characterizing chemical and electrochemical processes. This does not allow them to be used in engineering calculations, including in the design of electrochemical reactors. On the basis of similarity theory, from the differential equations describing the electrochemical process [7] we obtain criterial relations that generalize the functional interrelationship of a number of dimensionless complexes of hydrodynamics, a simplex of geometrical similarity, and for the first time we propose simplexes of the voltage (Se = E_0/E) and the resistivity (Sr = $1/K$) and ascertain the effect of this interrelationship on the voltage balance in the reactor cell.

The criterial relations are given by the following expression:

$$\mathrm{Se} = A(\mathrm{Re})^a(\mathrm{Eu})^b(\mathrm{We})^m(\mathrm{Sr})^c(\mathrm{Gn})^n. \tag{3}$$

Using the familiar method [11], we carried out relevant studies to confirm that the voltage depends on the hydrodynamic conditions of the process. We used a diaphragmless electrochemical reactor with plate and poured electrodes (see Fig. 1). An NaOH aqueous solution (200 g·liter^{-1}) was the electrolyte, the solution temperature was 293.15 K, and the electrodes were made of St3 steel. The results of experimental measurements of the voltage as the electrolyte circulation rate and the current loading were varied are plotted in Fig. 2.

When the results are processed Eq. (3) has the form

$$\frac{E_0}{E} = A\left(\frac{\omega d_{\mathrm{eq}}}{\mu}\right)^{0,03}\left(\frac{H\lambda}{2d_{\mathrm{eq}}}\right)^{-0,05}\left(\frac{\omega^2 d_n\rho}{\sigma}\right)^{0,03}\left(\frac{1}{K}\right)^{0,3}\left(\frac{l}{H}\right)^{0,1}, \tag{4}$$

for a reactor with plate electrodes and

$$\frac{E_0}{E} = A\left(\frac{\omega d_{\mathrm{e}}\rho}{\mu}\,\frac{2\phi}{3(1-\varepsilon)}\right)^{0,03}\left(\frac{H\lambda}{2d_{\mathrm{eq}}}\right)^{-0,15}\left(\frac{\omega^2 d_n\rho}{\sigma}\right)^{0,01}\times \\ \times\left(\frac{1}{K}\right)^{0.1}\left(\frac{d_{\mathrm{e}}}{H}\right)^{0,1} \tag{5}$$

for a reactor with poured electrodes.

Solving Eqs. (4) and (5) for E and with allowance for Eq. (2), we obtain calculated relations for a reactor with plate and poured electrodes, respectively:

$$E_{\mathrm{c}} = \eta + \frac{E_0(K^{0.3}\mathrm{Gn}^{0.1}\mathrm{Eu}^{0.05})}{0.6(\mathrm{Re}^{0.03}\mathrm{We}^{0.03})},\ \mathrm{V}, \tag{6}$$

$$E_{\mathrm{c}} = \eta + \frac{E_0(K^{0.1}\mathrm{Gn}^{0.1}\mathrm{Eu}^{0.15})}{0.8(\mathrm{Re}^{0.03}\mathrm{We}^{0.01})},\ \mathrm{V}. \tag{7}$$

The criterial relations (6) and (7) obtained above can be used when designing electrochemical diaphragmless reactors. The calculated data do not deviate from the experimental data by more than 11-14%.

Analysis of computational studies on the basis of experimental measurements as well as Eqs. (6) and (7) permits us to make generalizing conclusions about the degree of the effect of hydrodynamic and other factors on the determining parameter of the electrochemical process, viz., the voltage balance in the reactor cell.

One such factor is the electrolyte resistivity, whose effect on the voltage balance with the growth of the current loading is due to the gas content of the electrolyte (through the coefficient K of the increase in electrolyte resistivity because of the gas fraction in it) and the size of the gas bubbles. As shown by calculations for the same percentage content of gas fraction in the electrolyte but with different electrode designs, the gas bubbles differ in size. In a cell with plate electrodes the diameter of the gas bubbles is several times that in a cell with poured electrodes (with a working layer with a porous structure). The explanation for this is that as they rise in the cell with plate electrodes the gas bubbles coalesce (merge or grow). This process occurs only slightly in poured electrodes and as a result the size of the gas bubbles (dielectrics) has a smaller effect on the electrolyte resistivity and, hence, on the voltage. In the criterial relations (6) and (7) this effect is expressed through the exponent of coefficient K.

The gas content of the electrolyte also has other parameters, in particular density and viscosity, which affect how the solution moves in the reactor cell. According to calculations carried out with the results of experimental measurements, the electrolyte motion is turbulent (Re > 9) [10].

The Reynolds number increases with the current density and the circulation rate of the solution as is seen from the graph (Fig. 2), the voltage across the reactor cell decreases with increasing velocity at all values of the current loading. Accordingly, the voltage depends functionally on the Reynolds number, which characterizes the inertial forces (mass velocity) to the viscous forces (friction) in the moving electrolyte stream.

The effect of this dependence on the voltage balance is expressed in terms of the exponent of the Reynolds number, which has the same numerical value for all electrode designs. The explanation for this is that the parameters of a gas-filled electrolyte (viscosity and density) at T = const depend only on the current loading.

The interfacial tension, which depends functionally on the gas bubble size, also has an effect on the voltage balance. The effect of this dependence is expressed in terms of the exponent of the Weber number, which characterizes the ratio of the inertial forces (mass velocity) to the interfacial tension.

We know that the interfacial tension is higher when the diameter of the gas bubble (dielectric) is smaller, which is typical of electrodes with a working surface with a porous structure. Conversely, the interfacial tension decreases with increasing gas-bubble diameter (coalescence).

In view of this, at the same current loading the exponent of the Weber number in the criterial equation for cells with plate electrodes is higher than for cells in which the working surface has a porous structure.

Upon processing the experimental measurements we found that the hydraulic friction decreases with increasing current loading at a constant electrolyte circulation rate. The explanation for this is that the gas fraction forming continuously at the electrode surface during the electrochemical reaction promotes the "destruction" of the hydrodynamic boundary layer, which has the highest hydraulic resistance. The hydrostatic pressure drop in the cell and the Euler number decrease as the coefficient of hydraulic friction decreases. The hydraulic friction, therefore, is found as a functional dependence of the current loading.

This dependence is expressed in terms of the exponent of the Euler number, which characterizes the ratio of the change in the hydrostatic pressure force to the inertial force (mass velocity) of the gas-filled electrolyte during motion in the reactor cell.

Since the hydraulic resistance in poured electrodes reflects not only the effect of the frictional resistance in the reactor cell, as is observed in the case of plate electrodes, but also the additional local resistances, which arise as the electrolyte moves through the porous structure of the working layer, the exponent of the Euler number for poured electrodes is higher than for plate electrodes.

With allowance for the forced electrolyte circulation the calculation of the energy consumption for these purposes was carried out in accordance with the equation [10]

$$N = \frac{Q \Delta P_n}{1000}, \text{ kW}. \tag{8}$$

The results of the calculations are given in Table 1.

As we see from Table 1, despite the high pressure losses (ΔP_n, $N \cdot m^{-2}$) in poured electrodes, the energy required for feeding the electrolyte, per m^3 of hydrogen, is lower in this

TABLE 1. Electrical Energy Consumption for Electrolyte Circulation per m^3 of Hydrogen

Electrolyte circulation rate, $m \cdot sec^{-1}$	Plate electrodes			Poured electrodes		
	electrolyte flow rate, $m^3 \cdot sec^{-1}$	ΔP_n, $N \cdot m^{-2}$	electrical energy consumption N, kW	electrolyte flow rate, $m^3 \cdot sec^{-1}$	ΔP_n, $N \cdot m^{-2}$	electrical energy consumption N, kW
0,2	25,0	17,3	0,43	0,33	1534,0	0,6
0,24	30,0	28,1	0,84	0,28	2259,0	0,75
0,32	41,0	51,2	2,1	0,51	3818,0	1,9
0,39	50,1	65,3	3,3	0,45	6222,0	2,8

design than with plate electrodes. This is attributable to the higher gas content (V_g, $m^3 \cdot sec^{-1}$) for the same current density at the apparent electrode surface with allowance for the granular structure of its working layer and is several times smaller than the volume of the pumped electrolyte (Q, $m^3 \cdot sec^{-1}$), which is necessary for obtaining 1 m^3 of hydrogen.

At the same specific electrical energy consumptions directly in the electrolysis

$$W = 2.394 E_c \text{ kW} \tag{9}$$

the total energy consumption for obtaining 1 m^3 of hydrogen in a reactor with poured electrodes, with a porous structure of the working layer, is lower than in the reactor with plate electrodes:

$$W_{tot} = W + N = 2.394 E_c + \frac{Q \Delta P_n}{1000}, \text{ kW}. \tag{10}$$

From Eq. (10) we conclude that the electrochemical diaphragmless reactor with poured electrodes has a lower specific energy consumption at a comparatively high productivity than does a reactor with conventional electrodes (Fig. 3).

NOTATION

E_c, total balance of voltages across the reactor cell, V; E, constant part of the total balance of voltages, which depends in a certain way on the physicochemical properties of the electrolyte, the current loading, and the cell parameters, V; I, current loading, A; $\eta = \eta_a + \eta_c$, overvoltage on the electrodes (anode + cathode), V; Re, Reynolds number; Eu, Euler number; We, Weber number; Gn, simplex of geometrical similarity; ΔP_n, voltage drop in the reactor cell, $N \cdot m^{-2}$; S, apparent electrode surface, m^2; r_g, resistivity of the gas-filled electrolyte, $\Omega \cdot m$; E_0, theoretical decomposition potential, due to the physicochemical properties of the electrolyte, V; K, coefficient of the increase caused in electrolyte resistivity by the presence of a gas phase in it; A, coefficient; d_n, average gas-bubble diameter, m, d_{eq}, equivalent cell diameter, m; Φ, form-factor of the electrically conducting particle of the poured electrode, for spherical particles $\Phi = 1$; ω, velocity of the electrolyte motion in the reactor, $m \cdot sec^{-1}$; ℓ, interelectrode distance, m; ρ, density of the gas-filled electrolyte, $kg \cdot m^{-3}$; μ, gas-filled electrolyte, $N \cdot sec \cdot m^{-2}$; λ, coefficient of hydraulic friction during the motion of electrolyte in the reactor cell; and H, height of the cell, m.

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