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APPLIED ELECTROCHEMISTRY
AND CORROSION PROTECTION OF METALS

Effect of the Thickness and Porosity of Carbon-Black Gas-Diffusion Air Electrodes on the Efficiency of Hydrogen Peroxide Synthesis from Atmospheric Oxygen

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Abstract—Effect of the porosity and thickness of hydrophobized gas-diffusion air electrodes composed of A 437-E acetylene black or its mixture with P 702 and P 701 furnace blacks on the efficiency of electroreduction of atmospheric oxygen to H_2O_2 in 0.5 M NaOH was studied.

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Air electrodes are presently used in numerous fields of technology: manufacture of fuel cells and chemical power cells, and electrosynthesis processes, e.g., synthesis of H_2O_2 from O_2, which can be, in particular, used for indirect electrochemical oxidation of organic and inorganic substances [1].

It is known [2, 3] that the electroreduction of O_2 on carbon blacks occurs via formation of the HO_2^- ion, which is a stable product in a wide range of potentials. The use of electrodes fabricated from a mixture of carbon blacks with different physicochemical characteristics [4, 5] as catalysts for electrosynthesis of H_2O_2 from oxygen in gas-diffusion electrodes (GDEs) made it possible to obtain alkaline H_2O_2 solutions with concentrations exceeding 30 g l^{-1} at a current density of 500 A m^{-2}, with a current efficiency by H_2O_2 of 96–98%. The difference in the hydrophilic-hydrophobic properties of the carbon blacks used in the active mass of the working electrode [6, 7] resulted in better conditions of H_2O_2 extraction from the pore space of the electrodes, which created prerequisites for development of electrodes with stable electrochemical characteristics and a prolonged service life.

It is known that the operation efficiency of gas-diffusion air electrodes strongly depends on their structural characteristics, which is primarily due to diffusion limitations on the delivery of oxygen into the reaction zone [8].

The goal of this study was to examine the effect of the porosity and thickness of the working layer of hydrophobized gas-diffusion air electrodes composed of A 437-E acetylene black or its mixture with P 702 and P 701 furnace blacks on characteristics of hydrogen peroxide electrosynthesis from atmospheric oxygen in 0.5 M NaOH: process selectivity and kinetics of H_2O_2 accumulation.

EXPERIMENTAL

The experimental conditions, electrolyzer design, and fabrication conditions of single- and double-layer electrodes were described in [4, 9]. The following brands of carbon blacks were chosen as objects of study: hydrophobic A 437-E acetylene black and hydrophilic P 702 and P 701 furnace blacks. The blacks differ in the specific surface area (37–101 m^2 g^{-1}), particle size (30–100 nm), and ratio between surface groups. The physicochemical characteristics of the blacks are listed in Table 1 [10].

The electrode pastes were prepared from the acetylene black and its mixtures with P 702 and P 701 furnace blacks (A 437-E : P 701, A 437-E : P 702 = 1 : 1)

Table 1. Physicochemical parameters of carbon blacks

Brand of a carbon black	Particle size, nm	Specific surface area, m^2 g^{-1}		pH of aqueous suspension	Ash content, %
		external	adsorption		
A 437-E	30–39	101	ПО	9.2	0.2
P 702	60–100	37	35	8.0	0.5
P 701	60–100	39	70	11	0.35

Table 2. Results of hydrogen peroxide electrosyntheses from atmospheric oxygen on single-layer electrodes

Run no.	Brand of a carbon black	Electrode thickness, mm	Porosity, vol %		Current efficiency by H_2O_2, %	$c_{H_2O_2}$, g l^{-1}
			total	electrolyte		
1	A 437-E	0.40	70	8.3	50	28
2		0.90	70	8.3	40	22
3	A 437-E + P 701	0.40	60	18	35	20
4		0.90	60	10	50	29
5	A 437-E + P 702	0.30	60	14	32	18
6		0.60	60	13	41	23
7		0.70	70	18	46	26
8		0.75	60	14	63	35
9		0.98	60	10	61	34

with a hydrophobizer (FP-4D) content of 20 wt %. The single-layer electrodes had the following parameters: diameter 33 mm, thicknesses 0.3 and 0.8 mm, total porosity 60 and 70 vol %.

In double-layer electrodes with a working layer composed of the mixture (A 437-E : P 701 = 1 : 1), the content of the FP-4D hydrophobizer was also 20 wt %. The blocking layer contained 50 wt % A 437-E and 50 wt % FP-4D. The thickness of the blocking layer was 0.5 mm, and the thicknesses of the working layer, 0.2, 0.3, and 0.4 mm.

The electrode paste was prepared by joint coagulation of suspensions of FP-4D and a carbon black under mechanical agitation [11]. The amount of the paste necessary for fabrication of electrodes with certain porosity was calculated by the known formula [12]. The electrodes were sintered in a die mold under a pressure at a temperature of 360°C. The electrolyte porosity of the electrode was determined by hydrostatic weighing [13]. Electrolyses were performed in a three-chamber cell whose design was described in [14]. A gas-diffusion electrode in a fluoroplastic shell was placed between the cathode and gas chambers. The cathode and anode chambers were separated with an MF-4SK-100 cation-exchange membrane.

A 1 M H_2SO_4 solution was used as the anolyte, and a platinum plate, as the anode. The electrolysis was performed in the galvanostatic mode at a current density of 500 A m^{-2} in 0.5 M NaOH at 20°C. The current density was calculated per unit apparent front surface area of the electrode (5 cm^2). The electrode potential was measured relative to a saturated silver chloride electrode. Air was fed into the electrode from its backside via the gas chamber under atmospheric pressure at a rate of 100 ml min^{-1}. The electrodes were tested for selectivity in the reaction of O_2 reduction to the HO_2^- ion by determining by gasometry the current fraction γ expended for synthesis of hydrogen peroxide in electrolyses with oxygen supplied from a cylinder. Potentiometric polarization curves were measured at a potential sweep rate of 10 mV s^{-1}. The concentration of hydrogen peroxide in solution was found using permanganatometry.

The experimental data obtained in electrosynthesis of hydrogen peroxide on single-layer electrodes are listed in Table 2.

It can be seen in Table 2 that 03–0.6-mm single-layer electrodes are less efficient in electrosynthesis

Table 3. Results of hydrogen peroxide electrosyntheses from atmospheric oxygen on double-layer electrodes

Run no.	Brand of a carbon black	Total porosity, vol %	Working layer thickness, mm	Current efficiency by H_2O_2, %	c_{H2O2}, g l^{-1}
1	A 437-E	70	0.2	65	24.3
2	437-E + P 701	70	0.2	63	23.4
3	A 437-E	50	0.3	38	16.0
4	437-E + P 701	50	0.3	68	24.1
5	A 437-E	60	0.3	65	22.0
6	437-E + P 701	60	0.3	70	25.1
7	A 437-E	70	0.3	71	27.2
8	437-E + P 701	70	0.3	80	29.1
9	A 437-E	70	0.4	32	7.5
10	437-E + P 701	70	0.4	30	7.1

of hydrogen peroxide. On thicker electrodes, the efficiency of the process is noticeably higher, the produced concentration of hydrogen peroxide is as high as 35 g l^{-1}, their operation is more stable in the course of time, but the service life is comparatively short. In addition to the lower current efficiencies by H_2O_2 (18–23 g l^{-1}), a phenomenon of electrode "wetting-through" was noticed, i.e., the electrolyte appeared on the electrode backside (Table 2, run nos. 3, 5, and 6). This is presumably due to flooding of gas-supplying pores by the electrolyte, with the result that the stability of the three-phase boundary is disturbed, the efficiency of oxygen supply into the electrode decreases, and the current efficiency by H_2O_2 becomes lower.

It has been noted previously [4] that, in operation of double-layer mixed-carbon-black electrodes on pure O_2, the produced concentration of hydrogen peroxide grows because of the weaker diffusion limitations on the removal of the peroxide from the pore volume of an electrode. Probably, introduction of a more hydrophobic blocking layer into double-layer electrodes operating on atmospheric oxygen must favor solution of several problems. Primarily, the hydrophobic layer not only improves the mechanical stability of electrodes, but also serves as a good transport channel for supply of atmospheric oxygen across the diffusion barrier of inert gases. At the same time, an intermediate layer, more hydrophobic than the working one, is spontaneously created between the blocking and working layers in the stage of electrode fabrication because of the mutual penetration of active masses, which must stabilize the boundary of the three-phase contact. In the process, the thickness of the working layer decreases, and this must affect the efficiency off removal of the produced hydrogen peroxide into the electrolyte bulk. Experimental data on operation of double-layer electrodes are listed in Table 3.

It can be seen in Table 3 that variation of the total porosity within the range under study (50–70 vol%) has no pronounced effect on the efficiency of hydrogen peroxide production, whereas a decrease in the working layer thickness from 0.4 to 0.2–0.3 mm at a 70% total porosity of the electrodes leads to an increase in the concentration of produced hydrogen peroxide to 23.4–29 g l^{-1}.

The electrochemical activity of the electrodes was also determined on the basis of the polarization curves in Fig. 1. The polarization curves of reduction of pure oxygen and atmospheric oxygen in double-layer gas-diffusion cathodes composed of a mixture of carbon blacks show that replacement of oxygen with air noticeably enhances the polarization of the electrode.

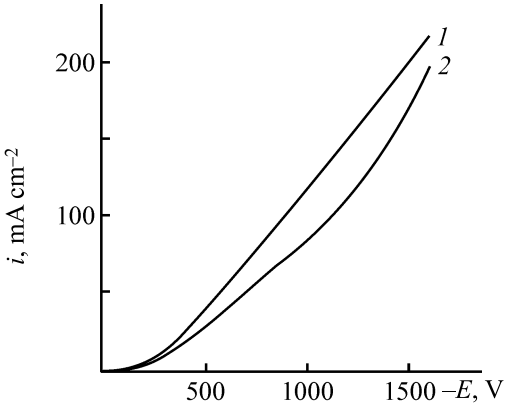

Fig. 1. Polarization curves of electroreduction of (*1*) pure oxygen and (*2*) atmospheric oxygen on double-layer electrodes in 0.5 M NaOH. (*i*) Current density and (*E*) potential.

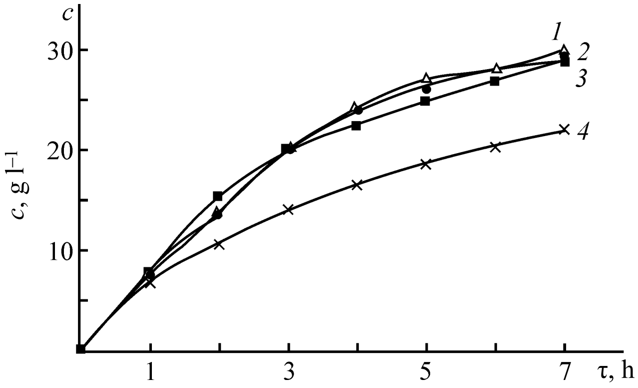

Fig. 2. Curves of hydrogen peroxide accumulation in electrolysis with hydrophobized gas-diffusion carbon-black electrodes in 0.5 M NaOH. (c) H_2O_2 concentration in the electrolyte bulk and (τ) electrolysis duration. Electrodes: (*1, 3*) double-layer and (*2, 4*) single-layer. Electrode composition (wt %): (*1, 2*) mixture of carbon blacks A 437-E + P 701 (1 : 1) and (*3, 4*) A 437-E + 20 FP-4D.

It is known that O_2 is transported by a flowing gas in electrodes operating on pure oxygen and via diffusion in those operating on air, and the transport hindrance to the gas supply to the electrodes becomes more important in air, as also noted in [8]. After electrolyses, the electrochemical activity decreased for all types of electrodes, with a change in the electrocatalytic activity of the working layer also being a possible reason.

Figure 2 shows kinetic curves of hydrogen peroxide accumulation in electrolyses with single- and double-layer electrodes.

The value of γ was determined to be 0.99–0.98 in the reaction of O_2 reduction to H_2O_2 for all the electrodes operating on pure oxygen. For electrodes operating on atmospheric oxygen, γ was calculated from curves of H_2O_2 accumulation, using the equation reported in [15].

It is known that the kinetics of hydrogen peroxide accumulation affects the ratio between the rates of H_2O_2 electrosynthesis and decomposition [15]:

$$V_{acc} = V_s - V_d = A\gamma I/V_{cat} - V_d,$$

where Vacc is the rate of H_2O_2 accumulation (g l^{-1} h^{-1}); V_s, rate of H_2O_2 electrosynthesis; V_d rate of H_2O_2 decomposition; A, electrochemical equivalent of H_2O_2 (g A^{-1} h^{-1}); I, electrolysis current (A); V_{cat}, catholyte volume (l); and γ, fraction of current expended for O_2 reduction to H_2O_2.

The current fraction γ determining the selectivity of hydrogen peroxide synthesis (Fig. 2, curves *1*–*4*) is 0.98–0.95 in the first 2 h of electrolysis. The experimental results of the study and the theoretically calculated points in the H_2O_2 accumulation curves are in good agreement.

It can be seen in Fig. 2 that the process of H_2O_2 accumulation (curve *4*) is less efficient on single-layer electrodes fabricated from A 437-E acetylene black (FP-4D content 20 wt %). The absence of differences in operation between double-layer (curves *1, 3*) and single-layer (curve *2*) electrodes can be attributed to the short operation of the electrodes (7 h).

Naturally, it would be expected that, on passing to prolonged endurance tests, the advantages in operation of double-layer gas-diffusion electrodes fabricated from a mixture of A 437-E and P 701 carbon blacks should become more clearly pronounced. In [4], gas-diffusion electrodes fabricated from a mixture of A 437-E and P 702 operated on pure oxygen for 220 A h without any noticeable decrease in the electrochemical activity.

CONCLUSIONS

(1) It was found that variation of the total porosity of double-layer electrodes within the range under study (50–70 vol %) has no pronounced effect on the efficiency of electrolysis.

(2) The optimal working layer thicknesses (0.2–0.3 mm) at a 70% total porosity of double layer electrodes composed of a mixture of carbon black. At these thicknesses, alkaline hydrogen peroxide solutions with concentrations of 24–29 g l^{-1} can be produced from atmospheric oxygen.

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