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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Effect of the Composition of Gas-Diffusion Carbon Black Electrodes on Electrosynthesis of Hydrogen Peroxide from Atmospheric Oxygen

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Abstract—Electroreduction of oxygen to H_2O_2 on gas-diffusion air electrodes made of A 437-E acetylene black and its mixture with P 702 and P 268-E furnace blacks with various particle sizes and wettabilities by an alkaline aqueous electrolyte with 8 and 20 wt % polytetrafluoroethylene was studied.

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Air electrodes are widely used in chemical power cells [1]. Studies are underway, intended to enable their application in new areas and, in particular, for electroextraction of oxygen from air [2] and use in hybrid power sources with simultaneous production of H_2O_2 [3].

It is known that air electrodes are less active than oxygen electrodes because the concentration of oxygen in the electrolyte becomes lower via a decrease in its partial pressure and via an increase in the resistance to diffusion of oxygen molecules across a gaseous nitrogen layer formed after atmospheric oxygen contained within electrode pores is consumed. That is inert gases create a diffusion barrier to oxygen transport to the reaction zone. However, an important advantage of air electrodes is the unlimited stock of oxygen in Earth's atmosphere at a place of its consumption without its preliminary recovery from air. This circumstance is also important for developing a process for the extensively studied electrochemical synthesis of H_2O_2 from oxygen [4–7]. In this case, it is required that the electrode structure should provide not only oxygen supply to the reaction zone across the diffusion barrier created by inert gases, but also discharge of the hydrogen peroxide obtained from the electrode volume to prevent its further reduction to water or chemical decomposition. Thus, the structure of an air electrode is even more important than that of an electrode working on pure oxygen.

Porous gas-diffusion electrodes are mostly used as air electrodes. Studies devoted to development and use of air electrodes for manufacture of H_2O_2 are only being commenced and the related published evidence is scarce. For example, an acid solution with a H_2O_2 concentration of 0.03 g l^{-1} has been obtained at a current density of 0.2 mA cm^{-2} [5], and a H_2O_2 solution with a concentration of 0.45 g l^{-1} has been produced with the use of a gas-diffusion air electrode [6].

One of methods affecting the structure of gas-diffusion electrodes is that changing their hydrophobic-hydrophilic properties by varying the content of a waterproofing agent [4, 8–11] or using carbon blacks with different wettabilities by an aqueous electrolyte [12]. For example, the use of a mixture of blacks with various properties for optimizing a gas-diffusion layer with a porosity of 70 vol % for a hydrogen-air fuel cell with a proton-exchange membrane yielded a positive effect in [13]. A mixture of acetylene black with carbon nanotubes as a carbon support for the catalytic layer of a gas-diffusion electrode for metal-air batteries was studied in [14], and the effect of a mixture of blacks on the electrosynthesis of H_2O_2 from oxygen, in [7].

The aim of the present study was to find how changes in the content of a waterproofing agent in a gas-diffusion hydrophobized electrode based on acetylene black and admixtures of a hydrophilic electrocatalyst, furnace blacks with various particle sizes, affect parameters of hydrogen peroxide synthesis from atmospheric oxygen in an aqueous electrolyte: current efficiency, electrode polarization, and kinetics of H_2O_2 accumulation. Also, the in-

Table 1. Physicochemical parameters of carbon blacks

Carbon black brand	Particle size, nm	Specific surface area, $m^2 g^{-1}$		pH of aqueous suspension	Ash content, %
		external	adsorptional		
A 473-E	30–39	101	110	9.2	0.2
P 702	60–100	37	35	8.0	0.5
P 268-E	19–35	158	265	7.8	0.1

fluence exerted by the supply rate of atmospheric oxygen to the electrode surface was analyzed. To elucidate the effect of the electrode structure on the delivery of atmospheric oxygen to the reaction zone, experiments with pure oxygen were carried out.

EXPERIMENTAL

The experimental conditions, electrolyzer design, and electrode fabrication technique are similar to those previously used in electrosynthesis of hydrogen peroxide from oxygen [4, 7, 15].

The following carbon black brands were chosen for the study: hydrophobic acetylene black of A 437-E brand and more hydrophilic furnace blacks of P 702 and P 268-E brands. The physicochemical properties of the blacks are listed in Table 1 [16]. 4D-fluoroplastic (FT-4D) served as a waterproofing agent.

The electrode material was prepared by joint coagulation of an aqueous suspension of fluoroplastic and a suspension of carbon blacks in a vessel equipped with a stirrer [17]. The mixture of carbon blacks was prepared in a 1 : 1 ratio. The material was filtered off, washed with water, dried in a drying box to constant mass at 120°C, ground in a blade mill, and screened through a sieve with 0.25-mm mesh. Further, the material was heated at 300°C for 1 h. The electrodes were formed in a mold with a piston stroke limiter as planar discs 33 mm in diameter and 0.8–0.9 mm thick, with a 0.1-mm-thick nickel grid in the middle of the electrode. The amount of the electrode material necessary for fabricating electrodes of certain porosity was calculated by the known formula [18]. The electrodes were sintered in air at 360°C for 10 min. To diminish limitations on the supply of oxygen into the electrodes, they were fabricated with a high total porosity (65 vol %). The electrolyte porosity of the electrodes was found by hydrostatic weighing [19]. Prior to experiments, the electrodes were impregnated with an electrolyte (0.5 M aqueous solution of NaOH) in the galvanostatic mode at a current density of 40 mA cm^{-2} for 1 h.

The electrolysis was performed in a three-chamber glass electrolyzer-cell [15]. A carbon black electrode (cathode) was placed between the cathode and gas chambers. The catholyte and anolyte (1 M H_2SO_4) were separated by an MF-4SK-100 cation-exchange membrane. A platinum plate served as the anode. The preparative electrolysis was performed in 0.5 M NaOH (~20 ml) at 20°C in the galvanostatic mode at an overall current density of 50 mA cm^{-2} for 5–7 h. The current density was calculated per unit apparent frontal surface area of the electrode (5 cm^2). The electrode potential was measured relative to a saturated silver chloride reference electrode (EVL-1M1). Oxygen and air were continuously fed into the electrode through its backside from the 20-ml gas chamber under atmospheric pressure. Oxygen was delivered in a small excess, discharged into the atmosphere. Air was delivered at flow rates of 0, 20, 50, and 100 ml min^{-1}. The fraction γ of current expended for synthesis of hydrogen peroxide was determined by gasometry in an electrolysis with oxygen. Potentiodynamic polarization curves were measured at a potential sweep rate of 4 mV s^{-1}. The concentration of hydrogen peroxide in solution was determined by permanganatometry. Prior to being sampled, the electrolyte was agitated by bubbling with air. The results obtained are listed in Table 2. It should be noted that by the term hydrogen peroxide are understood all forms of H_2O_2 existence in an alkaline solution, i.e., molecules and ions.

As can be seen in Table 2, a decrease in the fluoroplastic content and introduction of a hydrophilic carbon black make larger the volume of pores filled by the electrolyte. The influence exerted by replacement of oxygen with air and variation of the rate of its delivery into the gas chamber on the polarization dependence is illustrated for electrode no. 2

Table 2. Influence exerted by the electrode composition in reduction of pure oxygen, by atmospheric oxygen, and by the rate of its supply on parameters of H_2O_2 electrosynthesis (electrolysis time 7 h)

Electrode no.	Carbon black	Content of FT-4D, wt %	Electrolyte porosity, vol %	Air supply rate, ml min^{-1}	Potential,* V	Current efficiency by H_2O_2, %	H_2O_2 concentration, g l^{-1}
1	A 437-E	20	8.4	Oxygen**	0.76	70	39
				100	0.85	40	22
2	A 437-E + P 702	20	14	Oxygen**	0.46	67	38
				100	0.48	63	35
				100 + 55 cm of water	0.98	55	31
				20	0.68	55	31
3***	A 437-E + P 268-E	20	32	Oxygen**	0.66	32	13
				100	1.4	14	5.4
4	A 437-E	8	13	Oxygen**	0.52	70	39
				100	0.72	55	31
				20	0.85	40	22

* Electrode potential, current efficiency, and H_2O_2 concentration by the end of electrolysis.

** Results obtained when passing a small excess of pure O_2.

*** Electrolysis duration 5 h.

(Table 2, Figs. 1 and 2). At an air flow rate of 100 ml min^{-1}, the best results were obtained, with the dependence of the current on the air feed rate nearly leveling-off (Fig. 2). Therefore, experiments at higher rates were not performed. Figures 3 and 4 demonstrate for electrode no. 2 the effect of electrolysis duration on the H_2O_2 concentration and current efficiency. The run of these dependences is the same as that in experiments with pure oxygen [4]. The H_2O_2 accumulation curves tend to show a plateau at which the synthesis rate is equal to the decomposition rate of H_2O_2 and the differential current efficiency is zero (Figs. 3 and 4, curve *4*).

It can be seen that, as it should be, the replacement of oxygen with air makes more pronounced the electrode polarization. Varying the air feed rate has nearly no effect on the electrode polarization up to a current density of 40 mA cm^{-2}, i.e., the electrode structure manages to feed the required amount of oxygen to the reaction zone. However, at higher currents, outer-diffusion limitations become important. The electrode polarization varies in inverse proportion to the air feed rate, and, at zero rate, the polarization curve reaches the limiting current (Fig. 1). Raising the air feed rate from 20 to 100 ml min^{-1} leads to an increase in the current

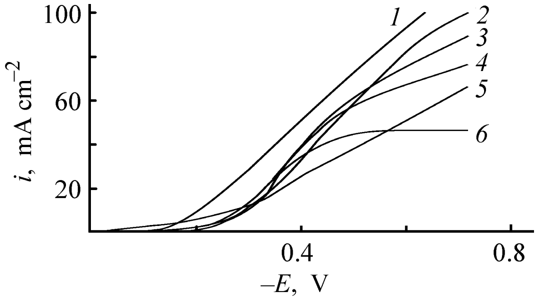

Fig. 1. Polarization curves for electroreduction of (*1*) pure and (*2*–*6*) atmospheric oxygen on an electrode composed of a mixture of carbon blacks: 40 wt % A 437-E + 40 wt % P 702 + 20 wt % FT-4D, in 0.5 M NaOH. (*i*) Overall current density and (E*)* potential. Air feed rate (ml min^{-1}): (*2*) 100, (*3*) 50, (*4*) 20, (*5*) 100 + 55 cm of water, and (*6*) 0.

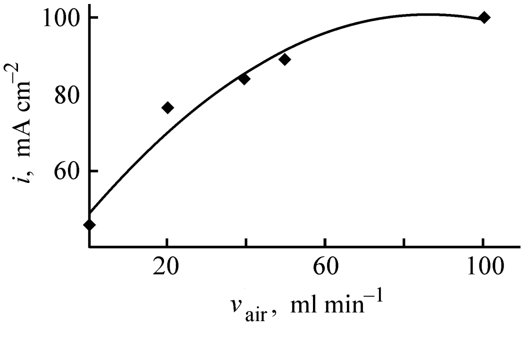

Fig. 2. Effect of the air feed rate v_{air} on the overall current density *i* in electroreduction of atmospheric oxygen at a potential of –0.72 V in 0.5 M NaOH on an electrode composed of a mixture of carbon blacks: 40 wt % A 437-E + 40 wt % P 702 + 20 wt % FT-4D.

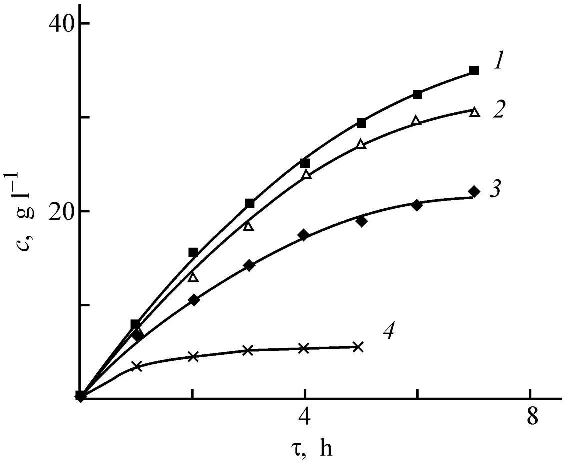

Fig. 3. H_2O_2 accumulation curves measured in electrolysis with gas-diffusion carbon black electrodes in 0.5 M NaOH. Air feed rate 100 ml min^{-1}; the same for Fig. 4. (*c*) H_2O_2 concentration in the electrolyte bulk and (τ) electrolysis duration. Electrode composition (wt %): (*1*) 40 A 437-E + 40 P 702 + 20 FT-4D, (*2*) 92 A 437-E + 8 FT-4D, (*3*) 80 A 437-E + 20 FT-4D, (*4*) 40 A 437-E + 40 P 268-E + 20 FT-4D; the same for Fig. 4.

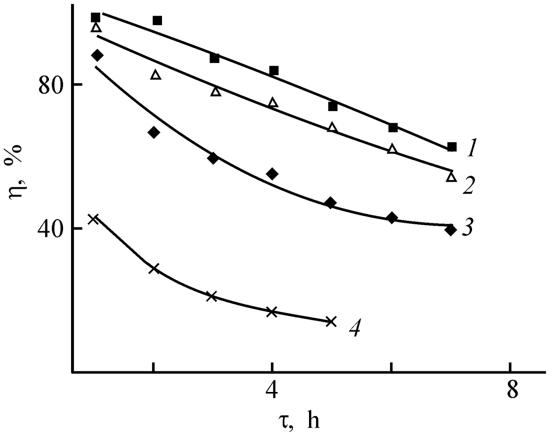

Fig. 4. Current efficiency by H_2O_2, η, vs. the electrolysis duration τ in 0.5 M NaOH for gas-diffusion carbon black electrodes.

efficiency and H_2O_2 concentration obtained by 13–41%, depending on the electrode composition. The theoretical air flow rate at a current density of 50 mA cm^{-2} and a 100% current efficiency by H_2O_2 is 8.3 ml min^{-1}. As the volume of the gas chamber, and specifically its thickness, decreases, the air flow velocity along the electrode increases, and, consequently, the air feed rate can be lowered to the corresponding extent. Raising the pressure in the gas chamber by 55 cm of water at an air feed rate of 100 ml min^{-1} results in that the electrode polarization becomes stronger and the current efficiency by H_2O_2 and its concentration decrease.

In electrolysis with oxygen, electrode nos. 1, 2, and 4 demonstrated nearly the same current efficiency by H_2O_2. The fraction of current expended for the H_2O_2 electrosynthesis is 95–98% at a concentration of 36–37 g l^{-1}, but the polarization of these electrodes is approximately inversely proportional to their electrolyte porosity and increases in order no. 2 < no.4 < no. 1. The same dependence is observed in electrolysis with air, but the current efficiency by H_2O_2 and its concentration are lower, and this decrease depends on the electrode composition, which indicates that the electrode structure affects just the delivery of atmospheric oxygen. The best results were obtained with electrodes composed of a mixture of carbon blacks A 437-E and P 702. Depending on the electrolysis duration, H_2O_2 solutions with concentrations of 8–35 g l^{-1} were obtained, with the corresponding current efficiencies of 99–63% (Figs. 3, 4). This means that changing the hydrophilic properties and the structure of an electrode by introduction of furnace black with a medium wettability is more effective than making lower the fluoroplastic content. Introduction of a hydrophilic furnace black P 268-E leads to a sharp increase in the hydrophilic porosity and to a decrease in the volume of gas pores. This results in that the inner-diffusion hindrance increases, the area of the three-phase boundary between air, carbon black, and electrolyte becomes smaller, the polarization grows, and the current efficiency by H_2O_2 decreases. The fraction γ of the current is also smaller for this electrode: 50% at a H_2O_2 concentration of 13 g l^{-1}. The size of carbon black particles is also important. Addition of larger particles (P 702) to the electrode material makes it possible to create larger pores, which facilitates oxygen delivery to the reaction zone. By contrast, introduction of a carbon black with smaller particles (P 268-E) hinders this process.

The effect of the electrode composition on the H_2O_2 electrosynthesis from atmospheric oxygen is due to the diffusion hindrance to oxygen delivery into the electrode at a comparatively low content of oxygen in air. Because of this circumstance, the diffusion component of the electrode polarization increases and the zone of H_2O_2 generation shifts to the back (gas) side of the electrode, which is in contact with air. As a result, the way to be traversed by H_2O_2 to leave the electrode volume across the front side of the electrode into the electrolyte and the residence time of H_2O_2 in the electrode become longer, which leads to an increase in its concentration and decomposition rate, with the current efficiency decreasing. This effect becomes more pronounced as the H_2O_2 concentration in the electrolyte increases. This occurs because the rate of H_2O_2 diffusion from the electrode decreases due to the lower H_2O_2 concentration gradient between the pore volume of the electrode and the electrolyte (Fig. 4). Consequently, the farther the H_2O_2 generation zone from the front side of the electrode, the lower the H_2O_2 concentration in the electrolyte and the current efficiency. The reaction zone can also be shifted by varying the air feed rate.

Thus, in the case under consideration, the electrosynthesis parameters are affected both by the electrolyte porosity (via changes in the ohmic polarization) and by the conditions of oxygen delivery to the reaction zone (via changes in the inner- and outer-diffusion components of the electrode polarization).

CONCLUSIONS

(1) Gas-diffusion air electrodes can be successfully used for electrosynthesis of hydrogen peroxide. The best results are obtained on electrodes composed of a 1 : 1 mixture of a hydrophobic acetylene black A 437-E and a semihydrophobic furnace black P 702, with addition of 20 wt % fluoroplastic. Alkaline H_2O_2 solutions are obtained with concentrations of 8–35 g l^{-1} at the corresponding current efficiencies of 99–63%.

(2) Raising the air feed rate into the gas chamber from 20 to 100 ml min^{-1}, which corresponds to a fivefold change of the air volume in the gas chamber in 1 min, makes higher the current efficiency and the H_2O_2 concentration obtained by 13–41%, depending on the electrode composition, and lowers the electrode polarization by 0.07–0.2 V.

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