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Study of Texture Effect of Gas Diffusion Electrodes Based on A 437-E Acetylene Black on the Efficiency of Electrosynthesis of H_2O_2 from O_2

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Abstract

The paper studied the effect of texture characteristics of gas diffusion electrodes (GDE) based on A 437-E acetylene black for electrosynthesis of H_2O_2 from O_2 in acid solution. Texture characteristics of the initial material (A437-E) and its mixtures with a hydrophobisator fluoroplastic-4D (F-4D) were determined by the low-temperature nitrogen adsorption (LTNA) method. Rate constants for hydrogen peroxide decomposition (K_{chem}) over these materials in acid solution were calculated. The dependence of electrochemical activity of GDE on the quantitative of F-4D content in the working layer was studied and process selectivity (γ) was determined. The effect of the working layer of GDE has a substantial impact on the development of highly developed surface of 3-phase contact and removal efficiency of the target product of electrode pore volume. These conditions were met in electrodes with a low content of a hydrophobisator at comparatively high hydrophilic porosity. Minor microporosity of composites of working layers ensured low losses of the target product due to its heterogeneous decomposition and contributed to its efficient removal from the electrode. The findings on accumulation kinetics of hydrogen peroxide during electrosynthesis from O2 in acid solution at a current density of 150 mA/cm^2 in GDE with different F-4D contents were acquired. Acid solution of 2.43 M hydrogen peroxide with a current efficiency (CE) of 76 % and process selectivity of 0.69 was obtained in GDE using 5 mass % of F-4D for 5.5 h of preparative electrosynthesis.

Keywords: electrosynthesis, hydrogen peroxide, texture of gas diffusion electrodes, process selectivity, current efficiency

INTRODUCTION

Hydrogen peroxide in the development concept of Green Chemistry is regarded as a universal pure redox reagent with a wide application area [1, 2]. However, wider use of H_2O_2 is limited by its comparatively high cost during production by traditional technologies [3]. A new process opened by Berl in 1939 [4] for the preparation of H_2O_2 by cathode reduction of O_2 over a UV cathode is a subject of numerous studies with the aim of developing electrolytic production technology of diluted solutions of hydrogen peroxide from oxygen by reactions in alkaline:

$$O_2 + 2e + H_2O = HO_2^- + OH^- \quad (1)$$

and acid solutions [3, 5–12]:

$$O_2 + 2H+ + 2e = H_2O_2 \quad (2)$$

Hydrogen peroxide accumulation in acid electrolytes depends on oxygen reduction rate constants (2), its further reduction to water (3):

$$H_2O_2 + 2H+ + 2e = 2H_2O \quad (3)$$

and heterogeneous decomposition (4):

$$2H_2O_2 = 2H_2O + O_2 \qquad (4)$$

It is worth noting that this method is waste-free and allows obtaining H_2O_2 at the consumption site as aqueous solutions and using therefrom as a commercial product without pre-isolation of H_2O_2, which significantly reduces its cost [3, 7].

It is known that highly developed 3-phase contact surface, such as gaseous reagent – electrocatalyst – aqueous electrolyte, reliable channels for the supply of the reagent and the electrolyte to this contact border, and product removal from the pore volume of the electrode are formed in gas diffusion electrodes at the optimum quantitative ratio of a hydrophobisator and a hydrophilic electrocatalyst [10]. Proceeding from this, it follows that the texture of the working layer of the electrode should significantly affect the efficiency of electrosynthesis of hydrogen peroxide from oxygen.

A comprehensive study of the effect of texture characteristics of gas diffusion electrodes based on A437-E acetylene black for the efficiency of electrosynthesis of H_2O_2 from O_2 in an acid solution of an electrolyte was the purpose of the present work.

A comprehensive research program includes the following tasks: determination of texture characteristics of the initial material (A437-E) and its mixtures with a hydrophobisator (fluoroplastic-4D), the rate constant of hydrogen peroxide decomposition over these materials, research into the relationship between the electrochemical activity of GDE and the quantitative content of fluoroplastic-4D in the working layer and process selectivity (γ), data acquisition on accumulation kinetics of hydrogen peroxide, current efficiency and a change in γ during electrosynthesis of H_2O_2 from O_2 in an acid solution at the overall current density (150 mA/cm^2) in electrodes with different hydrophobisator contents.

EXPERIMENTAL

Texture properties of initial A437-E carbon black and its mixtures with a hydrophobisator that is a binder were determined by the low-temperature nitrogen adsorption (LTNA) method, as in [13] using ASAP 2420 (Micromeritics, USA). Gas diffusion electrodes were produced as 2-layer flat disks with 30 mm diameter by the technique described in detail in [11]. An aqueous-alcoholic suspension of polytetrafluoroethylene (PFTE, fluoroplastic-4D, F-4D) with the content of dry matter of 62 mass % and stabilizer of 8 mass % was used as binder hydrophobisator. Its content in active masses was varied for the working layer within 0 to 50 mass %. The content of PTFE in the gate layer was 50 mass %. Since the texture of only the working layer of GDE was of interest for us, composites corresponding to the composition of working layers were prepared separately to carry out texture measurements. Measurement

TABLE 1

Physicochemical characteristics of A437-E acetylene black and composites of GDE working layers

Sample number	Content, mass %		S_{BET}, m^2/g	V_{sp}, cm^3/g	μ, cm^3/g	$R(4V/S)$, Å	S/V, m^2/cm^3
	F-4D	A 437-E					
1	0	100	94.5	0.900	0.016	381	105
2	5	95	83.5	0.885	0.001	424	94
3	10	90	65.0	0.840	0.003	517	77
4	20	80	64.0	0.758	–	473	84
5	30	70	53.0	0.702	–	529	75
6	40	60	45.0	0.556	–	494	81
7	50	50	25.0	0.548	–	877	46

Note. S_{BET} – specific surface determined by the BET method; V_{sp} – total specific pore volume; μ – specific micropore volume determined by the method of t-plot; R - maximum position at pore size distribution; S/V – working layer surface normalized by volume.

TABLE 2

Rate constants of chemical decomposition of hydrogen peroxide over A437-E acetylene black and its mixtures with F-4D in acid solution

Electrode composition, mass %		K_{chem}, h^{-1}
A 437-E	F-4D	
100.0	0.0	0.10
95.0	5.0	0.098
90.0	10.0	0.087
80.0	20.0	0.075
70.0	30.0	0.05
60.0	40.0	0.04
50.0	50.0	0.03

results of texture properties of initial carbon black and composites of working layers of GDE are presented in Table 1.

Chemical decomposition constants (Kchem) of H_2O_2 in acid 0.5 M K_2SO_4/0.1 M H_2SO_4 (3 : 1) solution over initial carbon black and its mixtures with F-4D were determined by the technique described in [14]. The initial concentration of H_2O_2 to determine K_{chem} was 1.0 M. The results are presented in Table 2.

Experiments for electrochemical testing of GDE were carried out in a glass thermostated cell with cathode and anode chambers separated by an MF-4SK-100 cation-exchange membrane by the technique described in [11]. A platinum plate with an area of 3 cm^2 was the anode. GDE were placed between the catholyte and gas chambers. Oxygen was fed to the electrode continuously from its rear side *via* the gas chamber at atmospheric pressure. A 2 M H_2SO_4 solution was an anolyte. The potential was measured at the front side of GDE relatively to a reference silver chloride electrode (SCE). IPC-Pro.3A potentiostat was used for electrolysis and polarization curve removal. Electrolyte porosity was determined by the method of hydrostatic weighing in water.

Measurements of a current fraction that goes to oxygen reduction to H_2O_2 (γ) in a 0.5 M H_2SO_4/0.1 M H_2SO_4 solution (3 : 1) were carried out using the electrodes under study. For this purpose, the time required for adsorption of a certain amount of oxygen was determined at the constant current [15]. It is worth noting that the γ value includes not only direct oxygen consumption but also oxygen that appears after heterogeneous decomposition of hydrogen peroxide in the pore volume of the electrode. The current fraction that goes to this or that stage is determined by both electrolysis conditions and the material and electrode texture. Hydrogen peroxide is decomposed in the catholyte volume outside the electrode, as well. Thus, γ characterizes processes occurring in the electrode, and current efficiency demonstrates the efficiency of the entire electrosynthesis process of the target product as a whole. It is natural that γ is one, if the entire oxygen is reduced to H_2O_2 and zero, if it yields water or hydroxide ions.

The results acquired at different overall current densities (50, 100, 150, and 190 mA/cm^2) are presented in Table 3.

Selection of electrodes with small, medium, and high hydrophobisator contents, namely 5, 20, and 50 mass % was made on the ground of potentiometric curves of oxygen reduction over GDE with different contents of F-4D in an acid electrolyte (not given in the paper text). The accumulation kinetics of the target product for 5.5 h was studied on their ground. Figure 1

TABLE 3

Characteristics of electrodes of acetylene black with different contents of F-4D in 0.5 M K_2SO_4/0.1 M H_2SO_4 solution (3 : 1)

Content of F-4D, mass %	Electrolyte porosity, vol. %	Overall current density, mA/cm^2							
		50		100		150		190	
		γ	*E*, V	γ	*E*, V	γ	*E*, V	γ	*E*, V
5	16.1–19.2	0.88	0.28	0.92	0.32	0.92	0.36	0.90	0.39
20	7.3	0.89	0.31	0.86	0.36	0.86	0.42	0.76	0.43
50	7.5	0.99	0.55	0.95	0.81	0.94	0.9.0	0.87	1.15

Note. γ is current fraction that that goes oxygen reduction to H_2O_2 (share of units), *E* is the electrode potential on the front side when determining γ.

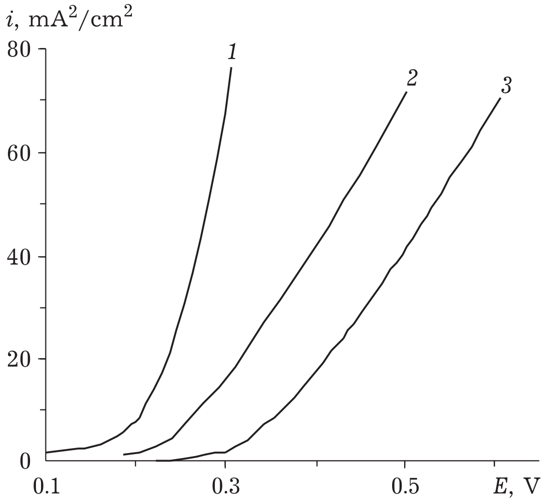

Fig. 1. Polarization curves of oxygen reduction on GDE with different content of F-4D, mass %: 5 (*1*), 20 (*2*), 50 (*3*). i is overall current density , E is the electrode potential on the front side of the electrode.

presents the polarization curves of oxygen reduction over these electrodes.

The accumulation kinetics of H_2O_2 was studied *via* preparative electrosynthesis in galvanostatic mode at an overall current density of 150 mA/cm^2 in 0.5 M H_2SO_4/0.1 M H_2SO_4 (3 : 1) at 20–22 °C. Current efficiency of H_2O_2 and γ were determined for each hour of electrolysis during 5.5 h. The quantitative content of hydrogen peroxide in the catholyte was determined by the method of permanganatometry [16].

RESULLTS AND DISCUSSION

As it follows from the data of Table 1, the initial material of A437-E carbon black almost does not have the true porosity. Micropores have been detected in trace amounts and are probably attributable to slot-like pores, *i.e.* cracks in carbon black species. The calculated value of pore diameter (passage diameter) from the approximation of their cylindrical structure ($4V/S$) yields a value of 38.1 nm. Consider that this size is comparable to the distance between the species and confirm the thesis about the absence of the true porosity. Working layers characteristics are monotonically decreasing with increasing hydrophobisator contents. There is a high correlation when comparing carbon black mass fraction in the GDE working layer normalized to the surface volume (S/V, m^2/cm^3). At the same time, the surface decreases in four times at the transition from the initial material to sample 7, and the volume – only twice. The described dynamics of changing the properties allows suggesting a significant excess of particle size of fluoroplastic relatively to carbon black species. In fact, the passage diameter of pores of GDE increases from 38.1 to 87.7 nm for sample 7 (more than twice). Apparently, spherical species of fluoroplastic serve as carrier matrix, ensuring relatively high indicators of porous space volume of the GDE and partially occluding carbon black species. In this regard, the fact of the disappearance of micropores in working layers, beginning with sample 4 (20 mass % of F-4D), appears to be natural due to dilution of carbon black with fluoroplastic.

The rate constant value of chemical heterogeneous decomposition of H_2O_2 monotonically decreases with increasing the hydrophobisator amount in the composite: in the studied range, by 3.3 times with decreasing the BET surface area in 3.8 times, as established by the results of Table 2. This finding should have a positive effect on the accumulation kinetics of the target product in GDE with high hydrophobisator contents, *i.e.* reduce product losses due to its heterogeneous decomposition.

Electrodes with low hydrophobisator contents (19.2 vol. %) have the highest hydrophilic porosity, as follows from Table 3. Average and high hydrophobisator contents have close hydrophile porosity values – porosity of about 8.0 %. Process selectivity (γ) in the whole studied range of current densities is from 0.76 to 0.99 with different potential values. It is worth noting that there is the lowest polarization in electrodes with low hydrophobisator contents. They have higher hydrophilic porosity. There is a maximum polarization in electrodes with high hydrophobisator contents. These electrodes have relatively low hydrophilic porosities and small surface areas.

The electrochemical activity of GDE substantially depends on quantitative hydrophobisator contents: with increasing F-4D concentration in the working layer, activity is reduced and an electrode with low F-4D contents has the highest activity, as it follows from polarization curves in Fig. 1. This dependence may attest to the intrakinetic operation mode of GDE under these conditions.

Analysis of the results on the kinetics of hydrogen peroxide accumulation presented in Fig. 2 and 3 attests to the fact that electrosynthesis of GDE with 5 mass % of GDE proceeds with higher indicators: target product concentration reaches 2.4 M with a current efficiency of 76.0 % and selectivity of 0.69. The kinetics of H_2O_2 accumulation almost obeys the linear law; this indicates the small proportion of its further reduction to water (3) and heterogeneous decomposition (4) due to its efficient removal from electrode pore volume. It is worth noting that the texture of the working layer of this electrode, in our opinion, is optimum for both hydrogen peroxide generation (accumulation process) and removal therein from electrode pore volume. This is attested (Table 3) by a relatively high hydrophilic porosity (16.1 vol. % in the beginning of electrosynthesis and 19.2 vol. % at the end). Electrodes with average and high F-4D contents demonstrate much lower efficiency: the accumulation kinetics of the target product over them obeys the parabolic law, i.e. processes of heterogeneous decomposition of the target product (4) clearly proceed in electrodes pore volume and possibly its further reduction (3). Noticeably falling curves of current efficiency and selectivity (γ) attest to this. Proceeding from general considerations, it must be said that the efficient GDE operation is probable at a high generation rate of hydrogen peroxide (the presence of a highly developed 3-phase contact, such as O_2 reagent − electrocatalyst − electrolyte) and maximally facile removal of the synthesized product from the pore volume. These conditions are most successfully met in GDE with low hydrophobisator contents (see texture characteristics of sample 2 and Table 1).

The operation of GDE with 50 mass % of F-4D (see Fig. 3, *b*) should be analysed more deeply: CE and process selectivity are relatively high and H_2O_2 concentration reaches 1.1 M for this time, then CE and γ begin to significantly decrease and the former is 60.0 %, and selectivity − 0.2. This sharp decrease of γ may attest to significant losses of the target product due to both its heterogeneous decomposition and further reduction into water

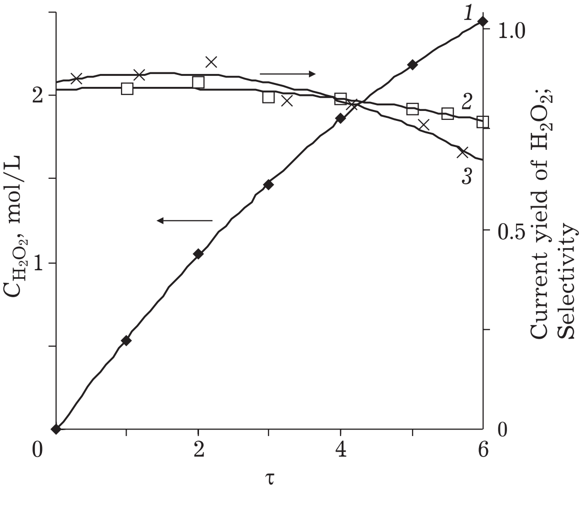

Fig. 2. Kinetics of accumulation of hydrogen peroxide during electrolysis in GDE with 5 mass % F-4D. Here and in Fig. 3: *1* − concentration of H_2O_2, *2* −current yield of H_2O_2, 3 −selectivity g, τ − electrolysis time, h.

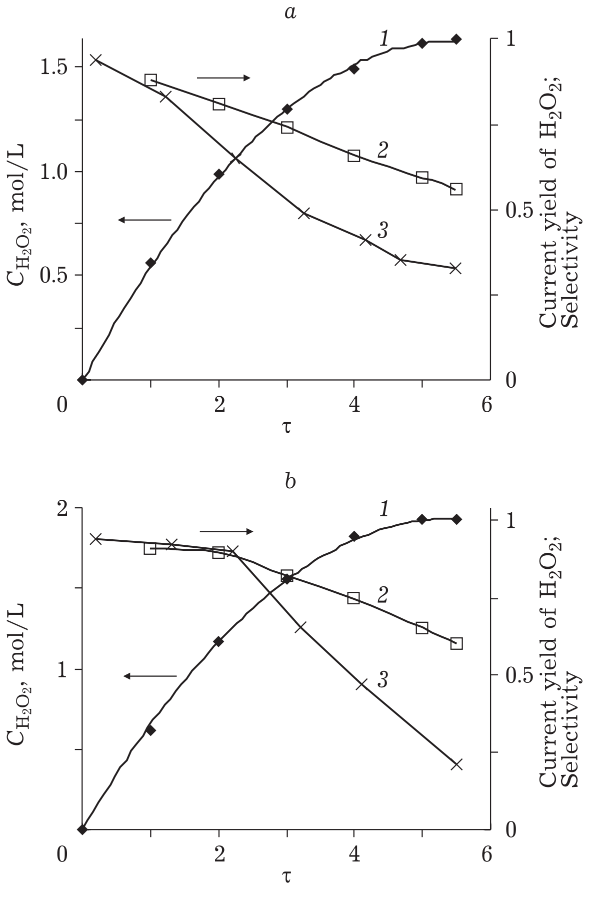

Fig. 3. Kinetics of accumulation of hydrogen peroxide during electrolysis in GDE with 20 (*a*) и 50 mass. % F-4D (*b*). Designations in Fig. 2.

[15]. This is associated by us with its significant accumulation in the pore volume and difficulties in the removal from the electrode.

It is worth comparing our earlier results on preparative synthesis of H_2O_2 from O_2 in GDE based on CH600 carbon black (S_{BET} of about 700 m^2/g, the micropore surface is 306 m^2/g) with the optimum content of F-4D of 60 mass % in similar electrolyte solution: there was accumulated 1.14 M with CE of 62 % for 5 h at overall current density of 100 mA/cm^2. It is possible that low porosity of initial A437-E carbon black and composites based therefrom and actual disappearance at F-4D contents of about 20 mass % (see Table 1, sample 4) contributes to a decrease in target product losses due to its heterogeneous decomposition (4) at difficulties with the removal from electrode pore volume and further reduction (3).

CONCLUSION

A 437-E initial material does not have the true porosity; micropores have been detected in trace amounts and are probably attributable to slot-like pores, i.e. cracks in carbon black species, as demonstrated by the carried-out researches. Working layers characteristics are monotonically decreasing with increasing hydrophobisator contents. Additionally, the fact of the disappearance of micropores in working layers, beginning with sample 4 (20 mass % of F-4D) due to dilution of carbon black with fluoroplastic and their blocking appears to be natural.

The rate constant value of chemical heterogeneous decomposition of hydrogen peroxide is monotonically decreasing with increasing the amount of the hydrophobisator in the composite: in 3.3 times in the studied range at decreasing the BET surface area in 3.8 times.

The texture of the working layer of GDE has a significant effect on process efficiency by formation of the highly developed surface of 3-phase contact and the removal of the target product from electrode pore volume at a relatively high hydrophilic porosity. These conditions are met in electrodes with low hydrophobisator contents. Minor microporosity of composites of working layers ensures small losses of the target product due to its heterogeneous decomposition and contributes to efficient removal from the electrode. Hydrogen peroxide concentration in GDE with 5 mass % of F-4D in the working layer reaches 2.43 M for 5.5 h of preparative electrosynthesis at a current efficiency of 76 % and process selectivity of 0.69, as established.

Based on the totality of the findings, it may be said that texture characteristics of GDE based on A 437-E acetylene black have a significant impact on the efficiency of electrosynthesis of H_2O_2 from O_2, namely, on accumulation kinetics of the target product, current efficiency, selectivity, and polarizability.

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