

# About the Operation of Gas Diffusion Hydrophobized Electrodes Based on Mixtures of Black Species during the Electrosynthesis of Peroxide Ion from Oxygen

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## Abstract

The operation of gas diffusion hydrophobized electrodes (HPE) made of black mixtures (hydrophobic soot A437-E and hydrophilic ones P702 and P805-E) during the electrosynthesis of hydrogen peroxide from oxygen is investigated. Changes in the characteristic length of electrode in the process under investigation depending on the highly developed three-phase boundary electrolyte – catalyst – reagent were used to estimate the stability of operation of gas diffusion HPE. It is concluded that observations of the changes in characteristic length of the operating electrode allow predicting possible resource of its stable operation.

## INTRODUCTION

The electrosynthesis of hydrogen peroxide from oxygen in porous gas diffusion hydrophobized electrodes (HPE) is under rather intensive investigation at present, aiming at indirect electrosynthesis of organic products [1–5] and disinfection of waste water [6–8]. The efficiency of indirect oxidation processes is known to be essentially dependent on the rate of the electrochemical stage of the process, *i. e.*, direct generation of hydrogen peroxide [9]. Intensification of the electrochemical stage of the process is not only connected with the choice of efficient catalysts but also depends on the structural characteristics of HPE.

The operational lifetime of HPE in electrosynthesis of hydrogen peroxide from oxygen in NaOH solutions is known to be yet insufficient for the practical application of these electrodes [1]. The development of HPE with longer operational lifetime is one of complicated

problems in theory and practice of processes realized in porous electrodes. The most probable reason of a decrease in electrochemical activity and small operation lifetime of HPE for obtaining  $H_2O_2$  from  $O_2$  is a change in the state of surface of the graphitized carbon electrocatalyst under the action of oxidizing agent, namely, hydrogen peroxide. This change involves an increase in the concentration of acidic oxygen-containing groups on the surface of the graphitized carbon [10]. Because of this, a solution of the problem of increasing lifetime of HPE for obtaining hydrogen peroxide from oxygen in NaOH solutions is connected first of all with an increase in the efficiency of the removal of the formed peroxide ion from the electrode volume. A solution of the problem is thus formally reduced to stabilization of the contact boundary between electrolyte, electrocatalyst and reagent (ECR) existing in the HPE [11].

The use of mixtures of graphitized carbon materials, characterized by different specific

surface and different hydrophilic or hydrophobic properties, in HPE for fuel elements has lead to an increase in the activity of HPE and to temporal stabilization of the ECR boundary [12]. The direct lifetime tests of HPE are very time- and labour-consuming; however, they can be simplified substantially if one determines criteria directly connected with the operation lifetime of HPE. Previously, we used the slope of polarization curves and the so-called reduced electrode thickness indicating the depth of the process penetration into the electrode [13, 14].

The present paper deals with the investigation of the operation of gas diffusion HPE based on mixtures of hydrophobic (A437-E) and hydrophilic (P702 and P805-E) black in the electrosynthesis of peroxide ions from oxygen.

## EXPERIMENTAL

Electrocatalysts chosen for the present studies were: acetylene black of the A437-E grade with the specific surface of  $101 \text{ m}^2/\text{g}$  exhibiting substantial hydrophobic properties, and hydrophilic carbon-black of P702 grade with the specific surface of  $37 \text{ m}^2/\text{g}$  and P805-E with the specific surface of  $10 \text{ m}^2/\text{g}$  [15]. We investigated electroreduction of  $\text{O}_2$  into  $\text{H}_2\text{O}_2$  in the HPE made of pure acetylene black, pure furnace black P805-E and mixtures of furnace black with the acetylene black containing 70, 50, and 30 % of the latter. We did not investigate the electrodes made of pure carbon-black of the P702 grade because of their rapid wetting which results in a sharp decrease in the activity. The 4D fluoroplastic was used as a hydrophobizing agent. The electrodes were made as discs of 33 mm in diameter and of 0.85 mm thick; total porosity of electrodes was 65 % vol.

Electrochemical measurements were performed in a glass cell with the cathode and anode chambers separated with a cation-exchange membrane MK-40 using the procedure described in [16]. Electrosynthesis was carried out in the galvanostatic mode at the current density of  $1500 \text{ A}/\text{m}^2$  in 0.5 M NaOH. The 1 M  $\text{H}_2\text{SO}_4$  solution was used as anolyte. Electrolysis was performed and polarization curves were

recorded with the help of PI-50-1-1 potentiostat. The electrode potential was measured with respect to the reference silver chloride electrode (SCE). Hydrogen peroxide content was determined with potassium permanganate. Electrolysis was performed till the required concentration of  $\text{H}_2\text{O}_2$  in anolyte was achieved; then polarization curves were recorded.

In order to determine the effect of the duration of hydrogen peroxide action on the surface of the electrocatalyst, we also investigated the reference solutions in which the required concentrations of  $\text{H}_2\text{O}_2$  were obtained by adding the known amount of  $\text{H}_2\text{O}_2$  into the anolyte.

## RESULTS AND DISCUSSION

The polarization curves of oxygen electrolytic reduction in HPE in the case of initial absence of  $\text{H}_2\text{O}_2$  in the anolyte volume are shown in Fig. 1. One can see that overvoltage of oxygen reduction to hydrogen peroxide decreases noticeably with the electrodes made of soot mixtures, compared to the electrodes made of pure acetylene black and furnace black of the P805-E grade. The largest decrease in overvoltage is observed for the mixture of

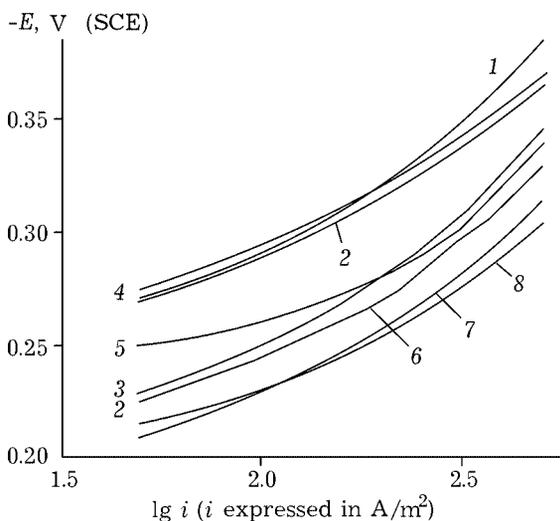


Fig. 1. Polarization curves for electroreduction of  $\text{HO}_2^-$  from  $\text{O}_2$  in the case of initial absence of hydrogen peroxide in the electrolyte; with the electrodes made of A437-E black (1), P805-E (2), their mixtures (3-5) and the mixtures of A437-E and P702 (6-8) with different A437-E black content in mixtures, % mass: 70 (3, 6), 50 (4, 7), 30 (5, 8).

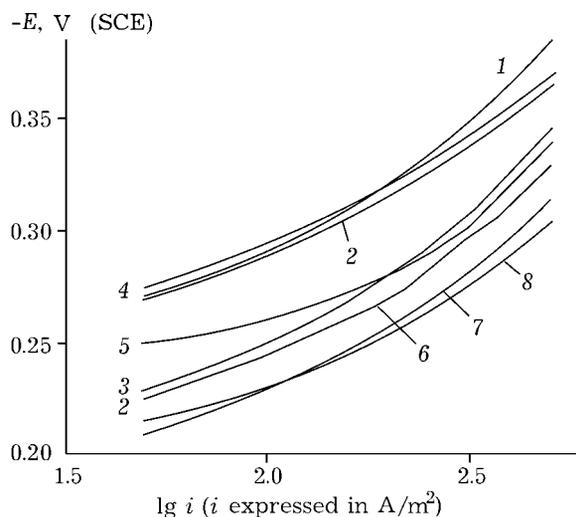


Fig. 2. Polarization curves for electro-synthesis of  $\text{HO}_2^-$  from  $\text{O}_2$  in HPE made of different carbon-black species: 1-3 - A437-E; 4, 5 - 50 % A437-E + 50 % P702; 6, 7 - reference for the electrodes made of 100 % A437-E black. concentration, g/l: 0 (1), 20 (2, 4, 6); 35 (3, 5, 7).

A437-E and P702 (1 : 1). The oxygen reduction overvoltage decreases by a smaller value for the case of mixture of A437-E and P805-E, especially for the mixture containing 30 % of A437-E and 70 % of P805-E.

The difference in the behaviour of polarization curves on HPE made of pure soot and of their mixtures in the presence of hydrogen peroxide is of interest. The polarization curves of  $\text{O}_2$  electrolytic reduction to  $\text{H}_2\text{O}_2$  for the peroxide content in the catholyte volume 0, 20 and 35 g/l are shown in Fig. 2. One can see that for the electrodes made of acetylene black, the slope of polarization curve increases with increased  $\text{H}_2\text{O}_2$  concentration; a noticeable shift toward the cathode region occurs. In our opinion, this shift is connected with instability of the ECR boundary in the HPE made of pure A437-E carbon-black. The potential shift to the cathode region is insignificant in the case of HPE made of a mixture of carbon-black species. We assume that the ECR boundary is more stable in this case. A characteristic feature of all the polarization curves shown in Figs. 1 and 2 is the absence of any clearly expressed linear region. However, only qualitative conclusions can be drawn from the analysis of polarization curves. For a quantitative estimation of the efficiency of HPE operation, it seems reasonable to use the characteristic length of the process ( $L$ ) [17].

For the HPE operating in the internal kinetic mode, the equation is true [17]:

$$(1)$$

where  $\kappa$  is the efficient electric conductance,  $i_0$  is the exchange current,  $S$  is the efficient wetted specific surface of the porous electrode,  $R$  is the universal gas constant,  $T$  is the absolute temperature,  $F$  is Faraday number.

Value of  $L$  can be determined by processing the polarization characteristics of HPE for internal kinetic mode [13, 14, 19]:

$$I = \sqrt{\frac{4 \kappa R T i_0 S}{F}} (\exp \phi - 1) \quad (2)$$

Here  $I$  is the overall current density;  $\phi$  is the reduced polarization, which is equal to  $(E - E_0)/b$ , where  $b$  is the slope of polarization curve of the smooth electrode in  $E - \lg I$  coordinates for the microkinetic polarization dependence of the reaction under investigation. This equation is obtained when the microkinetic dependence of the  $i = i_0 \exp \phi$  kind is used.

In order to determine  $\phi$ , it is necessary to know the elementary slope  $b$ . It is natural that one can rather accurately determine the  $b$  value only from experiments with smooth electrode, which is difficult with graphitized carbon materials because of their very uneven surface. To determine  $b$ , we used (similarly to [14]) the fact that the dependence of current density on  $\phi$  value should be linear and pass through the point of origin. This condition is met assuming that  $b = 0.065 \text{ V}$  [14].

The characteristic length  $L$  includes parameters depending on the structure of electrodes:  $\kappa$  and  $S$ . In this case,  $L$  is closely connected with the ECR boundary.

It is known that one should accept a model of HPE in order to determine  $L$ ; this causes inaccuracy and uncertainty. In order to avoid them, we did not calculate absolute  $L$  values when comparing the results obtained with A437-E + P702 and A437-E + P805-E soot mixtures but only determined their ratios. With such an approach, all uncertainties connected with the differences in HPE structures are mutually eliminated.

It may be demonstrated that the ratio of characteristic lengths of different electrodes

TABLE 1  
The  $L/L_0$  ratio for electrodes made of carbon-black mixtures at different  $H_2O_2$  content of catholyte

$H_2O_2$ concentration, g/l	Content of the furnace black in mixture, % mass						
	0	30	50	70	100		
		P702	P805-E	P702	P805-E	P702	P805-E
10	0.99/1	-	0.90/1	-	0.80/1	-	0.78/1
15	0.95/1	0.84/0.89	-	0.74/0.74	-	0.72/0.72	-
20	0.84/0.91	0.89/0.89	0.77/0.72	0.69/0.69	0.52/0.68	0.61/0.63	0.65/0.70
25	0.82/0.90	0.89/0.89	-	0.68/0.84	-	0.72/-	-
30	0.45/0.85	0.79/0.89	0.31/0.56	0.68/-	0.31/0.56	0.66/-	0.44/0.68

Note. Denominator: the  $L/L_0$  value for the case when the required amount of  $H_2O_2$  is added into the catholyte.

$L_1/L_2$  is inversely proportional to the ratio of slopes of their polarization curves in the  $I -$  coordinates. Equation (2) can be easily reduced to the form

$$I = 2i_0SL \tag{3}$$

After equating (2) to (3), we obtain

$$= 2i_0S_{np}L \tag{4}$$

It follows from eqn. (4) that for two different HPE with different  $L$  the following equation is true:

$$\frac{L_1}{L_2} = \sqrt{\frac{\kappa_2 S_2}{\kappa_1 S_1}} \tag{5}$$

Then, we used the ratio of  $L$  under the given conditions to the  $L_0$  of the same HPE in the case of initial absence of  $H_2O_2$  in catholyte as a parameter characterizing the operation of HPE. The  $L/L_0$  ratio was determined using the results of treatment of polarization curves in  $I - \sqrt{\exp \phi - 1}$  coordinates.

The results of calculations are shown in Table 1.

One can see that  $L/L_0$  values decrease more substantially in the case of a mixture of soot species, in comparison with HPE made of pure A437-E soot, for the concentration increased from 10 to 20 g/l. At higher concentration in catholyte, a less sharp decrease in  $L/L_0$  occurs in the catholyte at HPE. The decrease in  $L/L_0$  is substantially smaller when the reference solutions are used. This suggests that the ECR boundary in HPE made of pure A437-E soot at low concentration changes by a smaller value than that observed in the case of mixture of soot species. With further increase in  $H_2O_2$  concentration,  $L/L_0$  sharply decreases in the case of pure acetylene black, while it remains almost unchanged in the case of mixtures of the carbon-black species. With reference solutions, the  $L/L_0$  value changes insignificantly, which can be connected with shorter time of  $H_2O_2$  action on the surface of electrocatalyst. For the 30 and 50 % content of P702 soot in HPE,  $L/L_0$  changes relatively slightly.

This confirms the conclusion that the action of hydrogen peroxide on the surface of electrocatalyst results in worsening of the HPE cha-

characteristics. The  $L/L_0$  values are substantially higher for the HPE made of mixtures of P702 and A437-E soot species than for those made of A437-E and P805-E soot species. These data allow us to conclude that the former electrodes possess more stable ECR boundary than the latter ones. The  $L/L_0$  ratio changes less with an increase in concentration in the case of reference solutions than in the case of liberation during electrosynthesis. This can be explained by the fact that the longer is time of  $H_2O_2$  action on the electrocatalyst surface, the stronger are changes in the ECR boundary. So, one may assume that the smaller are changes in  $L$  with increasing concentration, the more stable is ECR boundary in HPE. Hence, it is promising to perform lifetime tests of HPE made of carbon-black mixtures, in particular of mixtures containing 30 and 50 % of P702 soot and acetylene black.

#### CONCLUSIONS

1. Diffusion restrictions for the removal of hydrogen peroxide from the pore volume of an electrode in case of using a mixture of soot species decrease substantially in comparison with the initial values.

2. As the product is accumulated during electrosynthesis of hydrogen peroxide from oxygen in NaOH medium, the characteristic length of the process increases.

3. Observations of changes in the characteristic length of the electrode allow predicting the operation lifetime of HPE.

4. Among the investigated mixtures of soot species, the best characteristics are exhibited by mixtures composed of P702 carbon-black (30–50 %) and acetylene black of A437-E grade.

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