Chemistry for Sustainable Development **13** (2005) 587–598

Theory of Porous Hydrophobized Electrodes Applied in Electrosynthesis (Review)

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(Received June 15, 2004)

Abstract

Results of the researches on the new branch in the theory of porous hydrophobized electrodes, in particular, hydrophobized electrodes that are applied in electrosynthesis, have been systematized. An attempt has been made to comprehend the experimental results, which have been obtained during electrosynthesis of inorganic and organic substances inside the porous hydrophobized electrodes in the intrakinetic mode. The role of a porous hydrophobized electrode in the processes of indirect electrochemical synthesis has been revealed as promising and ecologically safe method of producing the chemicals.

INTRODUCTION

At present, great attention is given to electrochemical methods of producing chemicals, which is related primarily to environmental problems [1]. It is common knowledge that the electric current can be considered a pure reagent from the ecological point of view and, during electrosynthesis, it acts as an oxidizer in anodic processes and as a reducer, in cathodic ones [1–4]. To intensify electrochemical processes, various types of porous electrodes with highly developed surfaces are applied [1–4]. In technology of fuel cells (FC), porous hydrophobized electrodes (HPE) with gaseous (HEGR) and liquid reagents (HELR) have found a wide application. The theory of HEGR is summarized in [5, 6] and that of HELR in [7].

During the last 20 years, HPE have found application in the processes of direct and indirect electrosynthesis with involvement of the sparingly water-soluble inorganic and organic substances [8–13]. Thus far, the large experimental material concerning these questions has been accumulated, which needs a systematization and theoretical understanding. The known theory of HPE for FC is insufficient to describe the processes of electrosynthesis in HPE and thus it is to be refined and added.

The basic difference lies in the different approaches when considering a stage of removal of termination products from a pore space of an electrode. For an instance of HPE for H_2/O_2 FC, the termination product is the solvent itself (H_2O) and typically, its removal stage is not discussed. In the case of electrosynthesis in HPE, a new substance is always formed that is the target product, which exerts a great influence on the HPE functioning both at the micro- and at the macrokinetic levels. Heavy demands regarding the mechanical strength are imposed on the HPE for electrosynthesis, as they are functioning in FC under more severe conditions and an issue of their optimum thickness becomes important. In addition, the overwhelming majority of the processes of electrosynthesis proceeds with the current efficiency that is other than 100 % and the theory of HPE for electrosynthesis cannot answer to many questions, which were insignificant for FC. In the present review, we mount the first attempt of that kind. Prominence is given to an intrakinetic operating mode of HPE, because the majority of experimental results we know have been obtained in this mode.

PROPERTIES AND FEATURES OF HYDROPHOBIZED ELECTRODES

The hydrophobized electrode represents a porous electrode, which is made up of hydrophilic and hydrophobic material. There are three kinds of pores inside the HPE: hydrophilic (CC) pores that are wetted with water solution of electrolyte, hydrophobic (FF) ones that are filled with a liquid or gaseous reagent and pores with the hydrophobic-hydrophilic walls (CF) whose role depends on the operating conditions of HPE. Owing to these pores (channels), a steady capillary equilibrium is established in HPE and a highly developed boundary of three-phase contact, namely, electrolyte–electrocatalyst–reagent (ECR) is formed and this ensures an effective work of HPE [5–7, 14, 15].

It must be emphasized that HPE plays the part of hydrophobic-hydrophilic membrane that separates the electrolyte chamber and the reagent chamber of an electrolytic cell.

Hydrophobized electrodes have found application not only in electrosynthesis with the sparingly water-soluble substances involved. It has been found that they are also effective when using the readily soluble reagents, for example, such as SO_2 [16] and methanol [17–19].

The detailed description of the HPE designs, the questions concerning an application of various materials for their manufacturing, technological features and the fields of their application for electrosynthesis are described in [9, 10].

Dependence of HPE activity on the content of water repelling agent

A variation in the content of a water repelling agent (usually fluoroplastic material) in HPE leads to changing its activity because of the varying HPE characteristics, which have an influence on the HPE functioning, in particular the electrolyte pore space and the reagent pore space, as well as the length of the boundary of three-phase contact.

Effect of concentration C_{fl} of water repelling agent on the activity of HPE during its work in the intrakinetic regime has received little attention. It is usually believed [6] that

$$S_{\text{ef}} = (1 - C_{\text{fl}})S_0 \qquad (1)$$

where S_{ef} is the effective wetted surface of the electrocatalyst, S_0 is the effective wetted surface at zero content of the water repelling agent.

Authors of [20] have found that the dependence of the activity of sooty HPE on C_{fl} in the course of electrosynthesis is a complicated one and it cannot be explained by means of the equation (1).

In work [21], authors made a thorough investigation of the dependence of HPE activity on C_{fl} under the intrakinetic regime of its work with allowance for an effect of pores of CF, if it is assumed a priori that the effective electroconductivity κ_{ef} depends on C_{fl}.

The derivation of the dependences was based on the fact that the wettability of HPE with an electrolyte solution was influenced only by CC and CF pores with the wettability of CF pores being significant. Two extreme cases are possible. In the first case, the CF pores are completely unwetted and the effective wetted surface appears less than the surface determined from the equation (1). In the case when CF pores are completely wetted, S_{ef} becomes greater.

Obtained dependencies for some particular cases are listed below.

1. If HPE contains no pores of the CF type, $i = i_{\text{fl}=0}(1 - C_{\text{fl}})$.

2. HPE contains the greatest possible proportion of the CF typed pores and they are unwetted, then

$$i = i_{\text{fl}=0}(1 - C_{\text{fl}})\sqrt{(1-2C_{\text{fl}})(1-2pC_{\text{fl}})}$$

3. HPE contains the greatest possible proportion of the CF typed pores and they are completely wetted:

$$i = i_{\text{fl}=0}$$
$$\times\ (1-C_{\text{fl}})\sqrt{[1-2C_{\text{fl}}(1+2C_{\text{fl}})](1+2pC_{\text{fl}})}$$

4. HPE contains the greatest possible proportion of the CF typed pores and they are half-wetted, then $i = i_{\text{fl}=0}(1-C_{\text{fl}})\sqrt{1-2C_{\text{fl}}^2}$

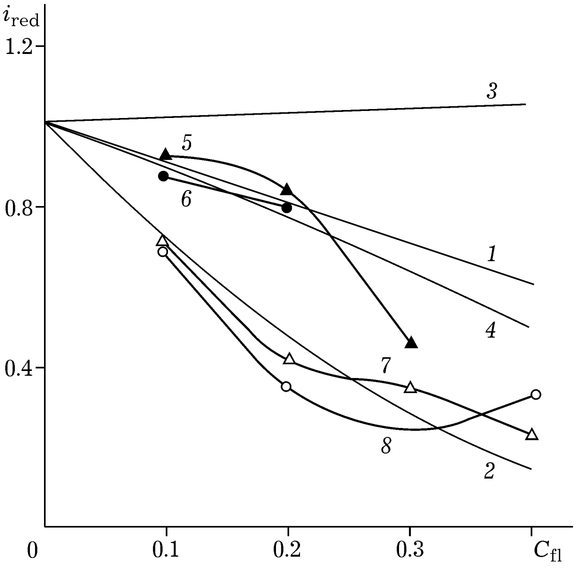

Fig. 1. Dependence of the reduced activity i_{red} of HPE on the content C_{fl} of water repelling agent: *1–4* – theoretical dependences for the cases 1–4, respectively (refer to the text); *5–8* – experimental curves for the case of HO_2^- electrosynthesis from O_2 inside the electrodes from the carbon blacks: A437-E (*5*), P602 (*6*), P702 (*7*), P805-E (*8*).

where i is the overall current density, $i_{fl=0}$ is the overall current density extrapolated to the zero content of water repelling agent, p is an arbitrary coefficient that depends on the electrode structure.

Shown in Fig. 1 are the dependences $i_{red} = i/i_{fl=0}$ on C_{fl}, which were derived starting from the assumption that $p = 1$, for the cases given above. It is evident that up to $C_{fl} = 0.2$, the behaviour of electrodes from A437-E and P602 carbon black corresponds to the case 4. The behaviour of HPE from P702 carbon black is in agreement with the case 2. At greater values of C_{fl}, experimental dependences of HPE activity on C_{fl} differ considerably from the theoretical dependences. Nevertheless, based on the type of the dependence of HPE activity on the content of water repelling agent, one can make an inference about such essential components of HPE structure as a fraction of pores of the CF type and a degree of their wet condition.

Distribution of the polarization inside HPE under the intrakinetic regime and reaction zone thickness

It is generally believed that the polarization in the rear of porous electrodes can be ignored and such electrodes are conventionally referred to as infinitely thick ones [5, 22]. It is known that HPE are of rather small thickness; therefore, a question arises regarding the existence of polarization on their back side. It is important, since the polarization drop for an infinitely thick electrode occurs within a relatively small site that is adjacent to the frontal side. In the case of thin electrodes (when the polarization in the rear of the porous electrode is other than zero), the polarization decreases throughout the whole length of the electrode [23, 24]. Accordingly, the reaction zone for a thick electrode is a small fraction of its thickness, whereas for a thin electrode, the reaction zone is comparable with its thickness.

When choosing an optimum thickness of HPE for electrosynthesis, it is essential that several conflicting requirements be taken into consideration. On the one hand, it is desirable that HPEs show high strength (which can be provided by an increased thickness of the electrode); on the other, it is essential to facilitate the removal of the accumulated product from HPE; therefore, the thickness of the electrode must be minimal.

For a case of intrakinetic HPE operating mode, the differential equation that describes the distribution of polarization inside the electrode takes the form [5, 22, 25]

$$\frac{d^2\psi}{d\chi^2} = \frac{\Delta^2}{L_k^2}\exp\psi \qquad (2)$$

where ψ is the dimensionless reduced polarization that is equal to the ratio of polarization to the slope of the polarization curve b for a smooth electrode in the Tafel coordinates; χ is the reduced electrode thickness that is equal to x/Δ (x is a distance from the frontal surface of the electrode, Δ is the electrode thickness), L_k is the characteristic kinetic length that is equal to $\sqrt{\kappa_{ef} b/(i_0 S_{ef})}$ (κ_{ef} is the effective electroconductivity, i_0 is the exchange current) [5–8, 14].

In the case of infinitely thick electrode, the boundary condition for the equation (2) is of the following form: $\psi = 0$ at $\chi = 1$. If $\psi > 0$ (the case of a thin electrode), then the boundary condition will appear as: $\psi = \psi_\Delta$ at $\chi = 1$ (ψ_Δ is the polarization in the rear of the electrode).

In work [26], a solution of the equation (2) has been found for the case of small electrode thickness. In [25], it has been demonstrated on the basis of this solution that the distribution of polarization throughout the electrode depth is of the form

$$\exp\psi = \exp\psi_\Delta\left[1+\mathrm{tg}^2\left(\mathrm{arctg}\sqrt{\frac{\exp\psi_0-\exp\psi_\Delta}{\exp\psi_\Delta}} - \delta\chi\sqrt{\frac{\exp\psi_\Delta}{2}}\right)\right] \qquad (3)$$

where δ is the relative thickness of an electrode.

Based on the equation (3), it is easy to deduce the dependence between ψ_0 and ψ_Δ:

$$\exp\psi_0 = \exp\psi_\Delta\left[1+\mathrm{tg}^2\left(\delta\sqrt{\frac{\exp\psi_\Delta}{2}}\right)\right] \qquad (4)$$

Work [25] demonstrated that at $\delta < 1.3$, ψ_Δ magnitude is always greater than zero. At $\delta > 1.3$, in case of small ψ_0 values, the polarization in the rear of electrode is practically equal to zero and the polarization gets appreciably larger than zero, as ψ_0 and δ increase. At $\delta < 0.5$ and at small ψ_0 values, ψ_Δ magnitude is great enough and the electrode becomes practically equally accessible, *i.e.* reaction proceeds throughout the whole of the electrode.

Determination of the thickness of the reaction zone in HPE is of practical and theoretical interest.

Work [25] gives an expression for the thickness β of the reaction zone as a layer from 0 to β, wherein 90 % of the product is made [26, 27]:

$$\beta = \frac{L}{\Delta}\sqrt{\frac{2}{\exp\psi_\Delta}} \times \mathrm{arctg}\left(\frac{0.9\sqrt{\exp\psi_0-\exp\psi_\Delta}\sqrt{\exp\psi_\Delta}}{0.9\exp\psi_\Delta+0.1\exp\psi_0}\right) \qquad (5)$$

Figure 2 presents the results of computation of β from the equation (5) for HPE with various δ and ψ_0. It is evident that at $\delta > 1.3$ β sharply decreases with an increase in ψ_0 and $\beta << 0.5$ when the polarization values on the frontal side of the electrode are reasonably great. At $\delta < 1.3$, an equal access area (an interval of polarizations, wherein thickness of the reaction zone is approximately 0.9) is evidenced on the electrodes. Equal access areas considerably differ in their magnitudes for electrodes with the different values of δ. At $\delta \approx 0.1$, electrode can be considered equally accessible for all ψ_0. With an increase in δ, the equal access area decreases and becomes insignificant at $\delta \approx 1$.

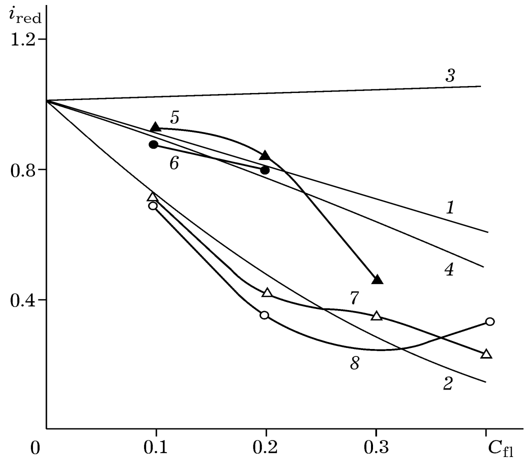

Fig. 2. Dependence of the thickness (Δ) of the reaction zone in a porous electrode on the polarization on the frontal side of electrode (Φ) at various relative thicknesses (δ): 0.1 (*1*), 0.25 (*2*), 0.5 (*3*), 1.3 (*4*), 2.0 (*5*), 3.0 (*6*).

Porous electrodes with relative thickness from 1.30 to 2.18 possess the properties intermediate between the properties of thin (with a finite polarization in their rear) and infinitely thick electrodes. The characteristic property of these electrodes is substantial difference of the β values at small and great ψ_0.

Work [25] suggests referring to these electrodes as “the electrodes of intermediate thickness”.

Distribution of a readily soluble product in the bulk of HPE

It is important to know the concentration of a product in the pore space of HPE and the distribution of concentration during HPE operation. It has been reported the numerical calculation of the distribution of OH_2^- ion concentration inside the HPE from absorbent carbon during electrosynthesis of H_2O_2 from O_2 in the 5 M KOH solution [29]. However, the results of this computation are just arbitrarily applicable to the other cases of electrosynthesis.

In work [30], analytical distribution of the concentration of the accumulated product inside the HPE has been found. It has been established that the concentration C_Δ of the product in the rear of electrode (provided that $\psi_\Delta = 0$) can be determined as $C_\Delta = C_0\psi_0/\lambda + C_0$ (6) where C_0 is the product concentration at the electrode front (in most cases, it is equal to the concentration in the electrolyte chamber), λ is the L_k/L_Δ ratio squared (L_Δ is the characteristic diffusive length that is equal to $\sqrt{nFD_{ef}/(i_0S_{ef})}$ by definition, where D_{ef} is the effective diffusion coefficient) [5, 6, 8, 14]. It follows from the expression that C_Δ is much more than C_0 and increases with ψ_0 and C_0.

Work [30] suggests an approximate expression for the distribution of the product concentration across the thickness of an electrode:

$$\omega = 1 + \frac{2}{\lambda}\ln\left(\frac{\Delta}{\sqrt{2}L_k}\lambda\exp\frac{\psi_0}{2} + 1\right) \tag{7}$$

where ω is the relative concentration of the product that is equal to C/C_0 (C is the concentration of the product in a given point of the electrode).

Based on the analysis of expressions (6) and (7), the following conclusions have been made in [30]:

1. Maximum concentration of a product in the bulk of the electrode is practically independent of the structural parameters of the electrode and is controlled by the parameters ψ_0, C_0, D_{ef} and κ_{ef}.
2. Distribution of the concentration of a product in the pore space of HPE at a constant ψ_0 is controlled by the magnitude λ and by the relative thickness δ of electrode. At great values of δ, the concentration of the product is in agreement with C_Δ throughout practically the whole of electrode and at reasonably small C_Δ, it varies throughout practically the whole of electrode.

POLARIZATION DEPENDENCE OF HPE FOR ELECTROSYNTHESIS

It is known that the polarization dependences for porous and smooth electrodes differ considerably [5, 6, 14]. The basic difference is that a slope in the Tafel coordinates for porous electrodes is much greater as compared to smooth electrodes. It is believed that to a first approximation, an intrakinetic regime of the process in point is matched by double slope and an intradiffusive regime, by quad-ruple slope [5, 6, 14, 22]. These conclusions have been made by consideration of the processes that occur in FC, whose work is practically unaffected by a removal of termination products from the pore space of an electrode. Polarization dependence of HPE for electrosynthesis should be considered in intimate association with the removal of the accumulated product.

Electrosynthesis of a readily soluble product

Combined consideration of the distributions of potential and concentration of the accumulated product in HPE is given in [30]. For this case, the following system of the differential equations is suggested:

$$\begin{cases} \dfrac{d^2\psi}{d\chi^2} = \dfrac{\Delta^2}{L_k^2}\exp\psi \\ \dfrac{d^2\omega}{d\chi^2} = \dfrac{\Delta^2}{L_\Delta^2}\exp\psi \end{cases} \tag{8}$$

where χ is the reduced coordinate that is equal to the ratio between the coordinate reckoned from the frontal surface of the electrode and its thickness.

On the basis of the solution of the system (8) in [30], the distribution of the reduced concentration of a soluble product inside a porous electrode was derived:

$$\frac{d\omega}{d\chi} = \frac{\Delta L_k\sqrt{2}}{(L_\Delta)^2}\sqrt{\exp\left(\psi_0 - \lambda\omega + \lambda\right) - 1} \tag{9}$$

On the basis of the equation (9) in [30], the known expression for the polarization behaviour for the intrakinetic regime was derived [5, 6, 8, 14]:

$$i = \sqrt{\frac{RT\kappa_{ef}i_0S_{ef}}{\alpha nF}\left(\exp\psi_0 - 1\right)} \tag{10}$$

Electrosynthesis whereby the target product current efficiency is less than 100 %

Work [31] considers the polarization dependence of HPE for electrosynthesis, whereby the current efficiency (CE) for a target product is less than 100 %. The conclusion was based on the principle of the independence for the concurrent reactions (PICR) [32, 33], by which these concurrent electrode reactions each proceed independently of the others.

In the case of a great enough CE for a target product and a small difference between the equilibrium potential of the target reaction and the steady-state potential, which is evidenced on HPE, the following expression is derived:

$$i = \left[1 + \sqrt{\frac{b_2 i_{02}}{b_1 i_{02}} \exp\left[\left(\frac{b_2}{b} - 1\right)\psi + \psi_{\Delta 2}\right]}\right] \times \sqrt{2 b_1 i_{01} \kappa_{ef} S_{ef} \left(\exp \psi - 1\right)} \quad (11)$$

where b_1 and b_2 are the Tafel (partial) slopes of polarization curves for the smooth electrodes in the target and side reactions respectively, i_{01} and i_{02} are the exchange currents of the target and side reactions, $\psi_{\Delta 2}$ is the difference between the equilibrium potential of the side reaction and the steady-state potential for the side reaction in terms of the reduced polarization.

It is evident from the equation (11) that the polarization behaviour of HPE with the CE for a target product of less than 100 % depends on the ratio between partial slopes of polarization curves for the side and target reactions, on the ratio between the exchange current and the difference between the steady-state potential of HPE and the equilibrium potential for the side reaction.

Electrosynthesis of a soluble electroactive product

The difference of CE from 100 % for a target product may be attributable to the formation of electroactive substance, for example, during electrosynthesis of methyl hydroxylamine from nitromethane [8, 9] and hydrogen peroxide from oxygen [9, 11]. Work [34] considers the polarization behaviour of HPE with allowance made for the presence of an electroactive product in the solution.

Equation for the polarization curve in the case of accumulation of the electroactive product is of the form

$$i = \left[\sqrt[4]{\frac{C_0}{C}}\left(1 - \sqrt{\frac{b_2 i_{02}}{b_1 i_{01}}}\right) + \sqrt{\frac{b_2 i_{02}}{b_1 i_{01}}}\sqrt[4]{\frac{C}{C_0}}\right] \times \sqrt{2 b_1 i_{01} \kappa_{ef} S_{ef} \left(\exp \psi - 1\right)} \quad (12)$$

where C is the current concentration of the produced substance, C_0 is the initial concentration of the produced substance that corresponds to the moment when the variations of the polarization on the electrode, which are related to the changing concentration of the product, are rather small.

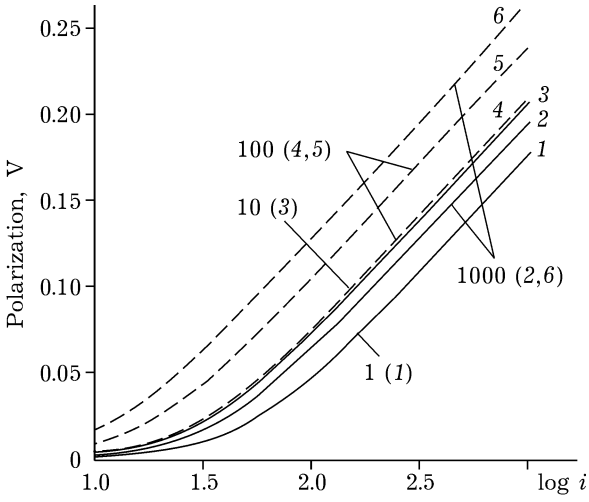

Fig. 3. Polarization dependences for HPE during electrosynthesis of an electroactive product i_{02}/i_{01}: 0.0001 (*1–3*), 0.01 (*4–6*); figures near the curves represent the values C/C_0.

Figure 3 presents the polarization dependences in the Tafel coordinates, which have been calculated by means of the equation (12) at various C/C_0 and $b_2 i_{02}/b_1 i_{01}$ ratios. It is evident that at small magnitude of the ratio of the exchange current intensities, ψ_0 grows with the accumulation of the product and at rather large ratio, the ψ_0 value decreases with an increase in C. Such a behaviour of the polarization curves stems from the fact that the contribution of a side reaction to the combined current increases with a decrease in the magnitude of the ratio of the exchange current intensities.

EXCHANGE CURRENT ESTIMATION OF AN INVESTIGATED REACTION ON HPE

When working out the HPE for electrosynthesis, one needs to choose the most active electrocatalysts. Activity of the electrocatalyst for a reaction under study depends in many respects on the exchange current, the determination of which involves difficulties in the experiments with a smooth electrode (for example, in studies of the reactions that proceed on the carbon black electrodes). In work [35], exchange currents in the reaction of O_2 electroreduction into H_2O_2 in an alkaline electrolyte were measured on the porous HPE that were made from various carbon blacks.

According to HPE polarization behaviour for the intrakinetic regime (10), a curve of dependence of current density on $\sqrt{\exp\psi - 1}$ must be rectilinear and must issue out of the origin of coordinates. It has been demonstrated in work [35] that the ratio of the slope magnitude for a polarization dependence curve (10) in these coordinates $\sqrt{\frac{RT}{\alpha nF}\left(C_{\rm fl} - 1\right)}$ complies with the expression $\sqrt{\kappa_{\rm ef} S_{\rm ef} i_0}$.

Given $\kappa_{\rm ef}$ and $S_{\rm ef}$, the exchange current of an electroreduction on the electrode from the carbon black under investigation can be estimated based on the magnitude of $\kappa_{\rm ef} S_{\rm ef} i_0$ that is extrapolated to zero value of $C_{\rm fl}$. Thus, if one assumes that at $C_{\rm fl} = 0$, carbon black is completely wetted with an electrolyte solution, the exchange current for the electroreduction of oxygen into peroxide ion (electrolyte being the 5 M NaOH solution, a temperature of 15 °C) for various types of carbon black is as follows, A/m^2: P805-9 – 0.14, P602 – 0.0025, P702 – 0.001, A437-E – 0.0007.

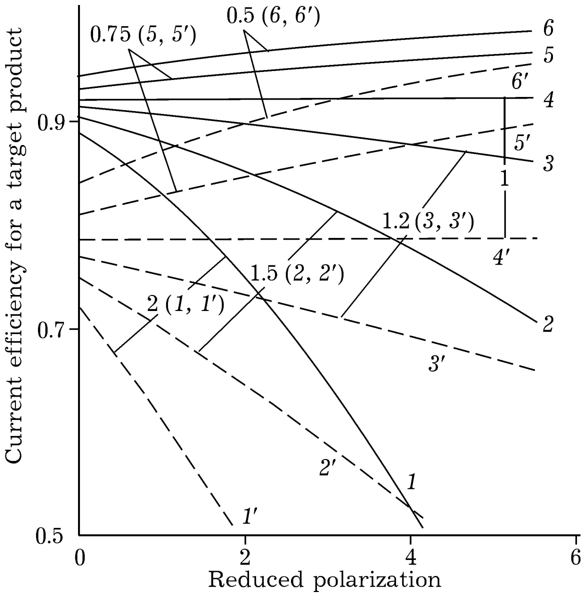

Fig. 4. Current efficiencies of a target product *vs.* the reduced polarization. i_{02}/i_{01}: 0.001 (*1*–*6*), 0.01 (*1*r–*6*r); $\psi_{\Delta 2} = 2$, $\sqrt{2b_1 i_{01} \kappa_{\rm ef} S_{\rm ef}}$; figures near the curves represent the values of the ratios of partial slopes of the polarization curves for the side and target reactions.

TABLE 1

Character of change in current efficiency (CE) of a target product with an increasing polarization (φ) and the ratios of Tafel slopes of polarization curves for the target and side reactions from 1 for some reactions of electrosynthesis inside HPE

Electrosynthesis process	PICR applicability	Assumed magnitude of the ratio of the slopes of the polarization curves for the target and side reactions	Character of change in CE with an increasing φ	References
$CO \to C_2H_6$	+	<1	Grows	[8, 9, 38]
$CO_2 \to HCO_2H$	+	≈1	No appreciable changes	[8]
$RH \to RCl$	+	<1	Grows	[8, 39, 40]
$CH_3NO_2 \to CH_3NHOH$	–	>1	Decreases	[8, 41]
o-nitrophenol → *o*-aminophenol in the alkaline medium	–	not found	No appreciable changes	[8, 42]
The same, in acidic medium	–	not found	≈100 %, decreases	[8, 42]
$RCH_2OH \to RCOOH$	+	<1	Grows	[8, 43]
1,1,2-3Cl_3Fethane → Cl_3Fethylene	–	not found	≈100 %, decreases	[8, 44–46]
$O_2 \to H_2O_2$	+	>1	Decreases	[9, 11]

Obtained values are in reasonably good agreement with the reported literary data [36, 37].

DEPENDENCE OF CURRENT EFFICIENCY FOR A TARGET PRODUCT ON POLARIZATION: COMPARISON OF THE THEORY AND PRACTICE

On the basis of the equation (11), work [31] calculated the dependences of CE of a target reaction on HPE polarization. The computation results with the different ratios of partial slopes for the side and target reactions are presented in Fig. 4. It can be seen that depending on the magnitude of the ratio of partial slopes for the target and side reactions, CE can both rise and decrease with an increased polarization.

Analysis of the established dependences for CE of the target products on the polarization in the electrosynthesis with HPE (Table 1) has demonstrated that when PICR is complied with, an increase or decrease in CE depends on the ratio of Tafel slopes in the target and side reactions that is in accord with the theoretical dependence. In the case that PICR does not hold, a strong suppression of a concurrent reaction may occur and CE of the target product gets close to 100 %.

PREDICTION OF HPE OPERATIONAL LIFE FROM THE BEHAVIOUR OF CHARACTERISTIC KINETIC LENGTH OF THE PROCESS

Works [47–49] deal with the development of methods for prediction of the life-in-service (operational life) of HPE during H_2O_2 electrosynthesis from O_2. It is important since the direct life cycle tests require a lot of time and they are rather labour-consuming.

From the analysis of polarization curves of electrosynthesis with HPE it is possible to find a change in the kinetic length L_k of the process under study on a given electrode. Work [47] demonstrated that on the basis of these data, the prognosis of HPE operational life can be made.

Determination of the absolute value of L_k involves difficulties in view of many discrepancies and uncertainties, which are associated with a sophisticated structure of HPE. However, if not L_k but their ratios are calculated, the problem gets substantially simpler. It has been demonstrated in [49] that the L_k ratio is inversely proportional to the ratio of slopes of polarization curves in the coordinates

$i - \sqrt{\exp\psi_0 - 1}$ for the appropriate HPEs. Therefore, to determine the L_k ratio of the studied process for two different electrodes, it will suffice to find a ratio of slopes of the polarization curves in these coordinates.

To observe the changing L_k during the longterm work of HPE in the process of H_2O_2 electrosynthesis from O_2 in alkaline electrolyte, works [47–49] used the ratio of L_k at certain specified points in time to the initial value of characteristic length L_{0k}. for HPE from A437-E, P702 and P805-E carbon blacks and their mixtures.

It has been demonstrated in work [49] that as the H_2O_2 content increases up to 20 g/l, the L_k/L_{0k} ratio for a HPE from a mixture of carbon blacks drops more sharply than it does for HPE from a pure carbon black, for example A437-E. At higher H_2O_2 content, the decrease of L_k/L_{0k} on the HPE from a mixture of carbon blacks is less sharp. The ratios L_k/L_{0k} for the HPE from a mixture of P702 and A437-E carbon blacks are appreciably higher in comparison with a mixture of carbon blacks typed P805-E and A437-E. For this reason, a conclusion has been made that the boundary of ECR contact in the HPE from a mixture of P702 and A437-E carbon blacks is more stable as compared to the HPE from a mixture of P805-E and A437-E carbon blacks. When the reference solutions are used, the L_k/L_{0k} magnitude varies much less with an increase in H_2O_2 concentration than it does in the case of H_2O_2 production by electrolysis. This may be related to the duration of H_2O_2 action on the electrocatalyst.

The results obtained in works [47–49] derive from the fact that during H_2O_2 electrosynthesis from O_2, as the product accumulation goes on in the pore space of HPE, the ratio L_k/L_{0k} decreases the stronger, the more difficult is a removal of the product from the reaction zone. Application of a mixture of carbon blacks facilitates the removing of the accumulated product. This may be related to their structural changes and, as a consequence, to the improved conditions to pass the process of H_2O_2 electrosynthesis [50].

APPLICATION OF THE CYCLIC VOLTAMPEROMETRY FOR PRODUCT ACCUMULATION LIFE TESTING IN HPE

The products of electrode transformations make an essential effect on HPE functioning during electrosynthesis. To take an illustration, electrosynthesis of H_2O_2 from O_2 is attended by oxidation of the electrocatalyst surface by the accumulated product and by its hydrophylization [11, 47]. In this connection, a practically important problem arises that is to determine experimentally the quantity of a formed product in the pore space of a working electrode.

Work [51] applies the cyclic voltamperometry method (CVA) for these purposes. It has been demonstrated that the quantity of the electroactive product being in the pore space of HPE could be inferred from the area of peaks in the CVA curves.

It has been illustrated that a stationary state comes reasonably quickly during CVA-measurements in HPE. A shape of the steady-state CVA curve depends on the type of carbon black and on the quantity of H_2O_2 that is in the HPE. The peak area for H_2O_2 oxidation is the more, the more difficult is to remove it from HPE.

A conclusion has been drawn that the CVA method is simple and convenient for testing the accumulation of electrode transformation products in a pore space of the electrode.

REMOVAL OF THE ACCUMULATED PRODUCT FROM HPE DURING ELECTROSYNTHESIS

The removal of an accumulated product from the electrode pore space is an important stage in the processes of electrosynthesis in HPE. Depending on the state of aggregation of the produced substance and on its solubility, the removal of the product is effectuated in various ways; therefore, the process of removing a product from HPE should be considered separately in each specific case.

In the case when a readily soluble product is obtained, its transfer from a pore space of the electrode into the electrolyte chamber is described by the initial differential equation. This problem for the intrakinetic regime is dealt with in work [30].

Works [52–54] consider the removal of a gaseous sparingly soluble product from a hydrophilic electrode. It has been demonstrated in [55] that the mechanism of a gaseous product removing from HPE is analogous in many respects; however, HPE specificity leads to some features. They are associated with not a single (as in a hydrophilic electrode) but three types of pores (CC, CF and FF) available in the HPE. Removing an insoluble gaseous product from HPE occurs mostly through the FF channels. Owing to so-called drainage channels (to certain pores with a very big diameter that are expressly created in the electrode [8]), the removal of gaseous product from HPE is substantially facilitated, which leads to a significant decrease in polarization.

In the case when an insoluble liquid product is obtained in HPE, the problem of its removal becomes considerably complicated. For example, process of chloroalkanes production from alkanes at lower is followed by a very fast passivation of HPE and special precautions should be taken to remove the high-boiling product. Carrying out the process of electrochemical chlorination of alkanes at high temperature and at continuously flowing excess of a reagent occurred advantageously due to a significantly facilitated removing of the reaction products from the pore space of electrode [39, 40, 45, 56].

HPE BEHAVIOUR IN THE PROCESSES OF INDIRECT ELECTROSYNTHESIS

At present, much interest is attracted by the processes of indirect electrosynthesis *i.e.* the processes of electrochemical generation of highly reactive intermediates on a cathode or an anode and their subsequent chemical reactions with substrate *in situ* in the bulk of electrolyte [12, 13]. It should be noted that application of HPE in these processes with the aim of intensifying the stage of electrochemical generation of oxygen reduction intermediates is envisioned to hold much promise [13].

Works [57–60] by means of solving the systems of differential equations, which describe the process of indirect electrosynthesis, consider theoretically a possibility for chemical reaction to proceed inside the pore space of an electrode due to diffusion of a substrate into this space. The plausible cases, which happen at various orders of chemical reaction of indirect electrosynthesis, have been considered.

Case of the first order in respect to an intermediate

Based on the solution of system of the differential equations of the second order, which corresponds to this case, works [58, 59] derived an equation for a fraction α of the process of indirect electrosynthesis that runs in the bulk of the electrolyte chamber:

$$\alpha = \frac{D_{\mathrm{ef}}\delta}{\Delta^2 k} \exp \frac{\varphi_0}{2b} \tag{13}$$

where φ_0 is the polarization of HPE, W. It is evident that α depends on parameters of an electrode (D_{ef}, δ, Δ) on the conditions for carrying out the process (polarization of the electrode) and on specific reaction rate k. At certain values of these parameters, the process of indirect electrosynthesis can proceed almost completely in the pore space of the electrode.

Case of the second reaction order in respect to intermediate and substrate

Resulting from the solution of the appropriate system of three equations, the following approximate equation has been found in [58] for a case of the second-order reaction:

$$C_{r0}\alpha + C_0\beta = \frac{D_{\mathrm{ef}}\delta}{\Delta^2 k} \exp \frac{\varphi_0}{2b} \tag{14}$$

where C_{r0} is the reagent concentration at the front of the electrode, C_0 is the concentration of intermediate at the front of the electrode, b is a fraction of the process, which runs inside the pore space of the electrode.

Depending on the kinetic constant of chemical reaction of the second order, different cases can be evidenced.

Very fast chemical reaction:

$$\alpha = \frac{D_{\mathrm{ef}}\delta}{\Delta^2 k C_{r0}} \exp \frac{\varphi_0}{2b} \tag{15}$$

Values of α for some certain conditions are presented in Table 2.

It is evident that the process in the same electrode at various concentrations of a reagent in the electrolyte chamber can proceed, according to the equation (15), virtually completely both in a pore space of an electrode and in the bulk of the electrolyte chamber.

In the case that $kC_{r0} << i_0/(lC_{r0}nF)$, the following expression holds true

$$\alpha = \frac{\delta l C_{r0} n F D_{\mathrm{ef}}}{\Delta^2 i} \exp \frac{\varphi_0}{2b} \tag{16}$$

where l is the parameter equal to the ratio of a volume of the electrolyte chamber to the area of an electrode and i is the current density.

As can be seen from (16), in the case that the rate of chemical reaction is comparatively small, the fraction of the process, which accounts for the electrolyte chamber, is independent of a specific reaction rate.

Slow chemical reaction. On the basis of the solution of an associated set of equations, it has been found in [60] that the fraction β of chemical reaction, which proceeds in the electrode pore space, is equal to $1 - \varphi$, where φ is the polarization of the electrode, V. Thus, in the case of indirect electrosynthesis with a slow chemical reaction, the latter partially

TABLE 2

Values of α at various reagent concentrations and relative electrode thicknesses. $D_{\mathrm{ef}} = 0.5 \cdot 10^{-10}$ s/(mol · m^2), $\exp(\varphi_0/2) = 10$, $\Delta = 10^{-3}$ m, $k = 0.2$ l/(s · mol)

Reagent concentration, mol/l	Relative electrode thickness				
	1	2	5	10	20
0	$2.5 \cdot 10^{-4}$	$5 \cdot 10^{-4}$	$1.2 \cdot 10^{-3}$	$2.5 \cdot 10^{-3}$	$5 \cdot 10^{-3}$
1.0	$2.5 \cdot 10^{-3}$	$5 \cdot 10^{-3}$	$1.2 \cdot 10^{-2}$	$2.5 \cdot 10^{-2}$	0.05
0.5	$1.25 \cdot 10^{-4}$	$2.5 \cdot 10^{-3}$	0.125	0.25	0.5
0.1	$2.5 \cdot 10^{-2}$	0.05	≈1	≈1	≈1

proceeds in the pore space of the electrode and partially, in the bulk of the electrolyte chamber. With an increase in polarization, the fraction of chemical reaction, which proceeds in the pore space of the electrode, is decreased.

Localizations of chemical reaction during indirect electrosynthesis in HPE

Based on the aforesaid, a conclusion can be drawn that during indirect electrosynthesis in HPE, not only electrochemical generation of intermediate, but also its subsequent chemical reaction with substrate occurs under *in situ* conditions. If a kinetic constant of chemical reaction is high enough, the reaction is virtually completely localized in the pore space of an electrode. In the case of slow chemical reaction, it is distributed between the pore space of an electrode and the bulk of the electrolyte chamber.

Distribution of chemical reaction in the process of indirect electrosynthesis between the volume of the electrolyte chamber and the pore space of the electrode depends on the reaction order. At the second order of the reaction, a situation may occur when chemical reaction in the beginning of the process runs almost completely in a pore space of an electrode and in the end, in the bulk of electrolyte chamber. In the case of a slow chemical reaction, it may also be localized in a pore space of an electrode.

The result obtained opens new prospects of HPE application for the processes of indirect electrosynthesis. For example, to perform the effective processes of indirect electrochemical oxidation, an oxidizer content that is higher than the content accumulated in the bulk of electrolyte is often needed. It has been demonstrated by the example of H_2O_2 electrosynthesis from O_2 that the content of H_2O_2 in the pore space of HPE is several times higher than in the bulk of katholyte [29, 30, 61] and thus the chemical reaction as well as its acceleration are possible [59].

CONCLUSIONS

When operating in the intrakinetic mode, the polarization dependences of HPE for electrosynthesis of a readily soluble product (with 100 % CE) and those of HPE for FC are identical.

Polarization dependence of HPE for electrosynthesis, in the case that CE of a target product is less than 100 %, is controlled by the ratios of exchange current intensities for the target and side reactions, by the ratios of slopes of their polarization curves in the Tafel coordinates and by the difference between the steady-state HPE potential and the equilibrium potential for the side reaction.

In the case that a soluble electroactive product is formed, the HPE activity is inversely proportional to the fourth-degree root of concentration of the product.

Electrodes with relative thickness of more than 2.18 are always infinitely thick. When relative thickness is less than 1.3, the electrode may be considered thin.

At the relative thickness of electrodes in the range from 1.3 to 2.18, they differ in their properties both from infinitely thick and from thin electrodes. In our opinion, it is advisable that such electrodes be set off into a separate type of electrodes and be referred to as «electrodes of intermediate thickness”.

Thickness of a reaction zone in HPE depends on the HPE polarization and on its relative thickness. Thin electrodes and electrodes of intermediate thickness under certain conditions are virtually equally accessible.

Under the intrakinetic regime, the rate of removing a readily soluble product from HPE is controlled by its polarization dependence.

Removing a gaseous sparingly soluble product from HPE occurs mostly through the FF channels and it is considerably facilitated if there are so-called drainage channels in the HPE structure.

Removing a high-boiling, slightly soluble product from HPE is considerably hindered. The stable work of HPE in this case is possible only when special steps are taken, which assist the product removal from the HPE pore space.

Temporal stability of a characteristic length of the process under study is intimately connected with the operational stability of HPE for electrosynthesis.

Use of CVA method makes it possible to estimate the efficiency of removing a product from the pore space of HPE.

A possibility was shown to estimate the exchange current of a reaction under investigation from the experiments with HPE.

Under the intrakinetic regime, the dependence of electrochemical activity of HPE on its content of water repelling agent has a more complex nature than the known analogous dependence for FC.

In the processes of indirect electrosynthesis, chemical reaction in HPE occurs both inside the pore space of the electrode and in the bulk of the electrolyte chamber. Distribution of the process between the pore space of the electrode and the bulk of the electrolyte chamber depends on the order of chemical reaction, on its kinetic constant and on the polarization of HPE.

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