Distribution of Polarization and Thickness of Reaction Region in Porous Water-Proofed Electrodes in the Intrakinetic Mode

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Abstract

The analysis of the solution of the differential equation for a porous electrode operating in the intrakinetic mode under exponential kinetics is carried out. The distribution of polarization and thickness of the reaction region in porous water-proofed electrodes of different thickness operating under the same conditions is considered. A more accurate formulation of the intermediate-thickness electrode is presented; its specific features in comparison with a thick and a thin electrode are analyzed.

INTRODUCTION

Development of ecologically safe and economically efficient processes in chemistry is possible only with a wide use of ecologically safe reagents, such as electric current. It is known that it acts as electron donor in reductive (cathode) processes and as electron acceptor in oxidative (anode) ones. In addition, the price of an equivalent amount of electricity as a chemical reagent is comparable with the price of such a widespread oxidizer as nitric acid [1]. Because of this, electrochemical methods of obtaining chemical products are very promising at present and will be so in future both from the ecological and the economical viewpoint.

However, a substantial shortcoming of electrochemical processes in comparison with catalytic ones is lower productivity of the former. The reason is a limited surface of contact between the reagent and electrocatalyst within the electrolyte volume [2]. Because of this, much attention has been paid during the recent 30 years to the development of various electrodes with highly developed surface and creation of the theory describing their behaviour [2–4].

A complex solution of the problem connected with an increase in the rates and selectivity of electrosynthesis processes during the electrolysis of gaseous and liquid reagents poorly soluble in aqueous electrolytes can be provided by the porous water-proofed electrodes (WPE) which are now widely used in hydrogen-oxygen fuel elements [2, 5]. These electrodes allow one to use poorly soluble substrates without dissolution mediators, to create a highly developed a reagent – electrocatalyst – electrolyte contact surface at almost zero change of pressure, and to provide reliable channels of reagent and electrolyte supply to the boundaries of this contact [5, 6].

The theory of WPE for fuel elements was developed by Yu. G. Chirkov and generalized in [5, 6]. However, it cannot be transferred in full to the WPE operating in electrosynthesis [4].

For electrosynthesis, the strength of WPE should be much higher than that for the fuel elements [4]. Mechanical strength of WPE is usually achieved by an increase in their thickness; however, in order to provide effective removal of the formed product, the electrode thickness should be small.

So, a choice of an optimal thickness of WPE for electrosynthesis is determined by the distribution of polarization inside the WPE and with the related thickness of the reaction region.

It is known that the distribution of polarization in the electrodes of different thickness is not identical [2, 7–9]. In rather thick electrodes (as a rule, hydrophilic ones), polarization from the electrode front decreases sharply and is equal to zero in the rear of the electrode. These electrodes are considered as infinitely thick [2, 7].

In a thin porous electrode, polarization slowly decreases from the front toward the depth of the electrode, while in its rear it is rather large. These electrodes are usually called thin ones [8, 9].

The authors of [10] proposed to refer the electrodes with the intermediate characteristics between infinitely thick and thin ones as the electrodes of intermediate thickness.

The goal of the present paper is to consider the distribution of polarization and thickness of the reaction region in porous water-proofed electrodes of different thickness for electrosynthesis operating in the intrakinetic mode.

STATUS OF THE PROBLEM

For the case of intrakinetic mode of WPE operation in electrosynthesis, a differential equation describing the distribution of polarization inside the porous electrode can be written down as [2, 7]

$$\frac{d^2\phi}{d\chi^2} = \frac{\Delta^2}{L^2} f(\phi) \quad (1)$$

where ϕ is the dimensionless reduced polarization which is equal to $(E - E_0)/b$ (b is the slope of polarization curve in the Tafel coordinates for a smooth electrode); χ is the reduced electrode thickness, which is equal to x/Δ (x is the distance from the frontal surface of the electrode, Δ is its thickness); L is the characteristic length, which is equal to , where κ_{eff} is the effective electric conductance, S is the specific wetted surface of the porous electrode, i_o is the exchange current).

From the formal point of view, a notion of infinitely thick electrode means that there is the boundary condition for eqn. (1): $\phi = 0$ for $\chi = 1$. If polarization in the rear of the electrode cannot be neglected, the boundary condition becomes as follows: $\phi = \phi_\Delta$ for $\chi = 1$.

For high polarization in the intrakinetic mode, eqn. (1) can be written down as [11]

$$\frac{d^2\phi}{d\chi^2} = \frac{\Delta^2}{L^2} \exp(\phi) \quad (2)$$

The appearance of the function in the right-hand part of eqn. (2) is due to the fact that electrosynthesis processes often occur at rather high potential, with a Tafel-type dependence of current on potential. We call eqn. (2) an equation with exponential kinetics.

When solving eqn. (2), exp ϕ is often replaced by 2sh ϕ [2, 7, 9]. In our opinion, this approximation is poorly suitable for the case of electrosynthesis in water-proofed electrode because of rather high polarization observed during electrosynthesis in WPE. Moreover, the solutions of this equation, which we are aware of, are mainly related to the case of infinitely thick electrode. Nevertheless, the main conclusions arising from the solution based on this approximation can be spread to the case of exponential kinetics. The main conclusion is that in the case of infinitely thick electrode the polarization inside it decreases sharply at short distances from the frontal surface of the electrode. It is demonstrated in [9] with the analysis of the solution of this equation that the condition of infinitely thick electrode is fulfilled at the relative thickness $\delta > 3$ (δ is the ratio of electrode thickness Δ to the characteristic length L) independently of polarization at its front. For high polarization, electrode can be considered to be infinitely thick at smaller δ. According to [9], for very small δ (≈ 0.1), the porous electrode becomes equally accessible in the sense that polarization decreases in it relatively slowly.

The authors of [8] found an approximate distribution of polarization Ψ inside the electrode using eqn. (2):

(3)

where x is the distance from the frontal surface of the electrode, w is the parameter determined by equation $\omega \operatorname{tg} \omega = i/(2 b a_s S L)$ (i is the overall current density). The analysis of this equation allows concluding that in case of large polarization at the front, the uniformity of its distribution in the electrode increases with a decrease in total current density and in electrode thickness.

Almost no cases of exponential kinetics were considered in the literature which we are aware of. Noteworthy is a solution of eqn. (2) for polarization distribution inside a porous electrode of small thickness reported in [12]:

$$\delta\chi = \frac{2}{\sqrt{\exp\phi_\Delta}}\left(\sqrt{\frac{\exp\phi_0 - \exp\phi_\Delta}{\exp\phi_\Delta}} - \sqrt{\frac{\exp\phi - \exp\phi_\Delta}{\exp\phi_\Delta}}\right) \quad (4)$$

where ϕ_0, ϕ_Δ are the polarization at the front and at the rear of the electrode, respectively.

ANALYSIS OF THE EQUATION FOR THE DISTRIBUTION OF POLARIZATION IN POROUS ELECTRODE WITH EXPONENTIAL KINETICS

Solution (4) of the differential eqn. (2) can be written down as

$$\exp\phi = \exp\phi_\Delta\left[1 + \operatorname{tg}^2\left(\operatorname{arctg}\sqrt{\frac{\exp\phi_0 - \exp\phi_\Delta}{\exp\phi_\Delta}} - \delta\chi\sqrt{\frac{\exp\phi_\Delta}{2}}\right)\right] \quad (5)$$

In the case when polarization at the rear of the electrode is equal to zero, this equation is transformed into

$$\exp\phi = 1 + \operatorname{tg}^2\left(\operatorname{arctg}\sqrt{\exp\phi_0 - 1} - \frac{\delta\chi}{\sqrt{2}}\right) \quad (6)$$

One can see in eqn. (6) that it has physical sense only in the case when $\delta\chi < \pi\sqrt{2}$, that is, for electrodes with rather large relative thickness, polarization can be calculated using equation (6) not for all distances from the electrode front. The physical sense of this equation for the rear of the electrode is conserved for $\delta > 2.18$. If $\delta > 2.18$, polarization at the rear of the electrode will never be larger than zero, and such an electrode should be considered to be infinitely thick.

If $\delta < 2.18$, one should use equation (5) to calculate the distribution of polarization at the front of the electrode.

After substituting $\chi = 1$ value (for the rear of the electrode) into eqn. (4), one easily obtains the dependence between polarization at the front and that at the rear of the electrode for different δ:

$$\exp\phi_0 = \exp\phi_\Delta\left[1 + \operatorname{tg}^2\left(\delta\sqrt{\frac{\exp\phi_\Delta}{2}}\right)\right] \quad (7)$$

Polarization in the rear ϕ_Δ can be calculated from eqn. (7) if we know polarization at the front ϕ_0 and relative thickness δ.

DISTRIBUTION OF POLARIZATION INSIDE THE POROUS ELECTRODE

In order to calculate the distribution of polarization inside the porous electrode, one should know polarization at its rear. Assigning polarization at the front ϕ_0 and relative thickness ϕ_Δ, one can easily calculate δ using eqn. (7).

The results of the calculation of ϕ_Δ for $\phi_0 = 1–8$ and $\delta = 0.1–2$ are shown in Fig. 1. One can see that for $\delta < 1.3$ polarization at the rear of the electrode is never equal to zero. For $\delta > 1.3$ in the case of small ϕ_0, polarization is almost zero at the rear of the electrode and becomes larger than zero at a definite polarization at

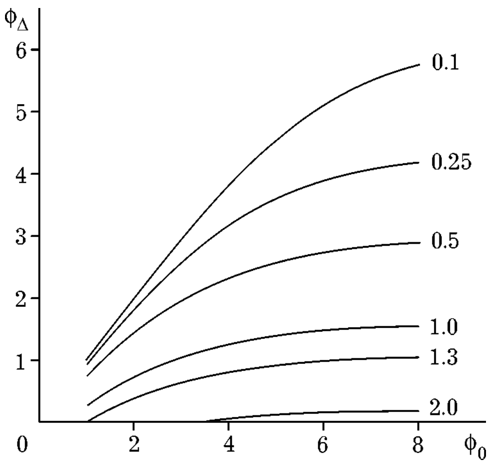

Fig. 1. Dependence of polarization at the rear of a porous electrode on the polarization at the front for different relative thickness of an electrode (thickness values are indicated at the curves).

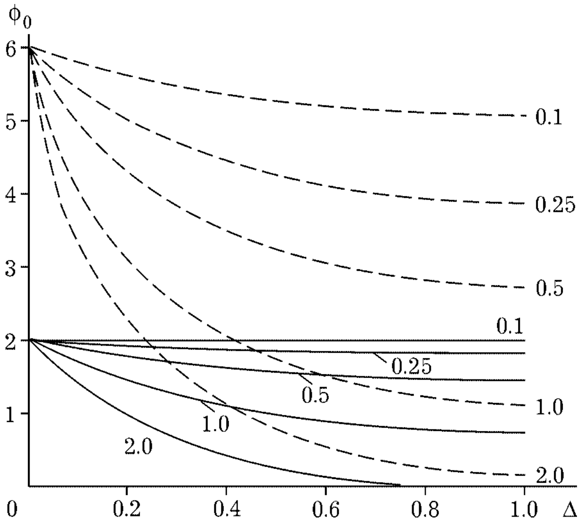

Fig. 2. Distribution of polarization over the thickness of the porous electrode for varied polarization at the front (polarization at the front is indicated at each curve).

the front, depending on the reduced electrode thickness.

For small relative electrode thickness, polarization at its rear is rather large. One can see in Fig. 1 that for reduced thickness less than 0.5 and for small ϕ_0, polarization at the rear is rather large. Under these conditions, the porous electrode becomes almost equally accessible.

The results of calculations of polarization distribution over the depth of the electrode according to eqn. (5) are shown in Fig. 2. One can see that there are two types of electrodes. The first one is observed for rather large relative thickness; in this case, the distribution of potential over the electrode is strongly nonuniform both for high and for low ϕ_0. The second type is observed for small relative thickness. In this case, for small polarization the electrode is almost equally accessible, while for large ϕ_0 the difference between polarization at the front and at the rear is small. The boundary for the electrodes of the first and the second types is found at the reduced thickness $\delta \approx 1$.

REACTION REGION THICKNESS

An equation for the reaction region thickness β (a layer from 0 to β) in which 90 % of the product is formed [13, 14] can be obtained by simple transforms if we accept that 10 % of the product is formed in the layer from β to 1. This equation can be written down as

(7)

The results of calculations of the reaction region thickness for electrodes with different d and ϕ_0 are shown in Fig. 3. One can see that two groups of the electrodes can be distinguished. For relatively large δ (>1.3), the thickness of reaction region always decreases substantially with increasing ϕ_0, while for large polarization it is much less than 0.5.

The second case is observed for small relative thickness δ (<1.3). With these electrodes, the region of equal accessibility is observed for small polarization; the thickness of reaction region is about 0.9 and does not depend on polarization. For electrodes with different δ, the region of equal accessibility accounts for different values. For $\delta \approx 0.1$, the electrode can be considered to be equally accessible within the whole potential range. With increased δ, the region of equal accessibility gets smaller and becomes insignificant for $\delta \sim 1$. For $\delta > 1.3$, equal accessibility region does not exist for porous electrodes.

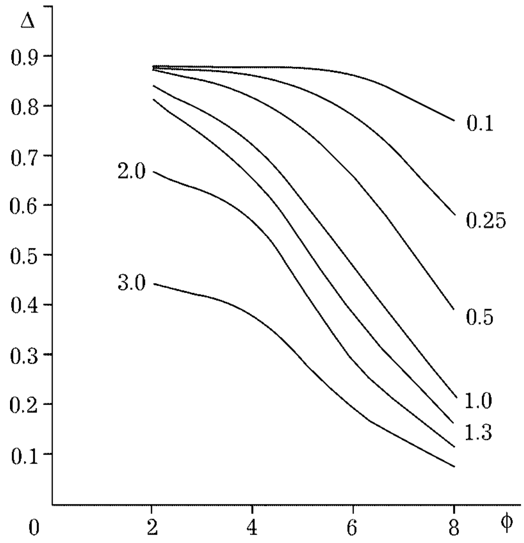

Fig. 3. Dependence of the thickness of reaction region in porous electrode on polarization at the front for different relative thickness values (the reduced thickness values are shown at the curves).

DIFFERENCE IN THE DISTRIBUTION OF POLARIZATION IN POROUS ELECTRODES OF DIFFERENT THICKNESS

On the basis of calculations performed by us, one can see that polarization inside a porous electrode decreases rather sharply for rather large relative thickness (2 and more), as it should be expected. It should be noted that for reduced thickness $\delta < 1.3$ polarization at the rear is never equal to zero for any polarization at the front of the electrode. For relative electrode thickness more than 2.18, polarization at the rear is always zero. Because of this, we propose to consider an electrode with relative thickness more than 2.18 as infinitely thick, while that with the thickness less than 1.3 should be considered as a thin one.

Porous electrodes with relative thickness $\delta = 1.3-2.18$, as one can see in Figs. 1–3, possess characteristics which are intermediate between those of thin and infinitely thick electrodes. For these electrodes, polarization at the rear is insignificant (10 % of that at the front and less). A typical feature of these electrodes is large difference in the thickness of reaction region for small and large polarization at the front of the electrode (see Fig. 3). We propose to refer these electrodes as the electrodes of intermediate thickness and consider the existence of polarization at the rear and impossibility to establish equal accessibility as the criteria to outline the boundaries of the term.

Our proposal concerning the boundary for an infinitely thick electrode $\delta = 2.18$ does not coincide with the conclusion [9] that an electrode can be considered to be infinitely thick if its relative thickness $\delta > 3$, while for large polarization much smaller thickness will suffice (for example, with $\delta = 10$ and $\chi = 0.2$). The difference is that we propose a definition of infinitely thick electrode as an electrode the potential at the rear of which is never larger than zero, while the authors of [9] propose that an infinitely thick electrode is that for which $\beta << 1$.

CONCLUSION

The values describing boundaries for an infinitely thick and a thin electrode, as proposed by us, are important for determining a necessary thickness of an electrode to be manufactured for real process.

For the reduced thickness more than 2.18, the application of thicker electrodes is only reasonable when higher strength characteristics are to be provided.

Our determination of a region in which it is possible to establish equal accessibility with the porous electrode is important for the cases when it is necessary to provide maximal efficiency of the use of electrocatalyst.

It is especially important to take into account the regularities discovered by us in the case when electrosynthesis in WPE is carried out, when the necessity arises to solve a complicated problem of optimizing the design of electrodes focusing on efficient removal of the products from the pore volume.

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