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Analysis of the distribution of geometrical current density along the direction of solution flow inside flow-by porous electrodes

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ABSTRACT

Calculations of electric field inside a flow-by porous electrode usually involve the assumption that the distribution of geometrical current density along the direction of solution flow inside the electrode is uniform. In the present work we propose the version of its successive refinement without using *a priori* assumptions. It is demonstrated that the assumption of the uniform current distribution along solution flow is quite acceptable under the conditions of the small changes of polarization resistance at the boundary between the porous electrode and the solution (small current density, high flow rate or prevalence of the side reaction of hydrogen evolution). Quite contrary, in the case of a sharp change of polarization resistance along solution flow this assumption is not fulfilled and causes quantitative distinctions of the spatial distribution of potential, current and concentration inside this electrode. An increase in non-uniformity of overall current distribution with an increase in solution depletion degree inside the porous electrode was confirmed experimentally for copper electrodeposition as an example.

1. Introduction

Flow porous electrodes (PE) possessing developed surface and at the same time high mass transfer rate provide one of the most promising directions to intensify electrochemical processes involved in the treatment of diluted solutions [1–3]. Two versions of these electrodes, differing from each other by the mutual positions of the vectors of electric current and solution flow, were proposed almost simultaneously during their development [4]. These vectors are parallel in the first version (flow-through porous electrode, FTPE) while they are mutually perpendicular in the second version (flow-by porous electrode, FBPE). Brief reviews of the studies dealing with FBPE are presented in [5–8].

The approaches used at the early stage of FBPE studies were mainly approximate, for example, the assumption of the limiting diffusion current mode [7,9–11]. In this case, a two-dimensional electric field inside the PE was not considered, while the distribution of current density was reduced to the distribution of reagent concentration. In later works [5–8,12–18] more complicated mathematical models taking into account two-dimensional distribution of current and concentration were used to simulate FBPE. In this situation, the constancy of potential at the boundary between the PE and the membrane was used in many works as the boundary condition for Poisson equation describing the distribution of potential and current inside FBPE. The data on the validity of this boundary condition are contradictory in the general case: from good compliance with this condition for the cylindrical version of FBPE operating in the limiting current mode [9], to noticeable deviation of the experimental values of the potential at the boundary with the membrane from E = const [8]. Later works on FBPE simulation [5,16,17] specify current distribution at the boundary of PE with current feeder as the boundary condition of the two-dimensional Poisson equation; so far all the authors accepted this distribution to be uniform. In our opinion, the correctness of this assumption for arbitrary PE operation conditions is not evident.

As shown schematically for FBPE operation in Fig. 1, electric current from the anode enters the porous electrode through the liquid phase from the membrane side and passes out from the electrode through the solid phase and the contact with current feeder. In each electrode layer perpendicular to solution flow direction, the current on this way surmounts total resistance composed of the ohmic resistance of the solution, polarization resistance at the boundary between the solution and electrode surface, and the ohmic resistance of electrode material. The change of this total resistance will most likely define the distribution of geometrical current density in FBPE along the solution flow direction. For the system of parallel auxiliary electrode and FBPE, one may expect that the sum of ohmic resistances of the liquid and solid phases in the direction of solution flow changes insignificantly. In turn, polarization resistance at the interface for the nonlinear polarization curve depends on the local polarization and concentration of the electroactive component. Polarization distribution inside FBPE is unknown in advance, so it is difficult to estimate reliably its effect on the changes of polarization resistance along solution flow direction. However, because of the nonmonotonic effect of polarization change on the local value of polarization resistance and the necessity to average these values over PE thickness, the contribution from this factor into the change of current distribution along the solution flow direction may

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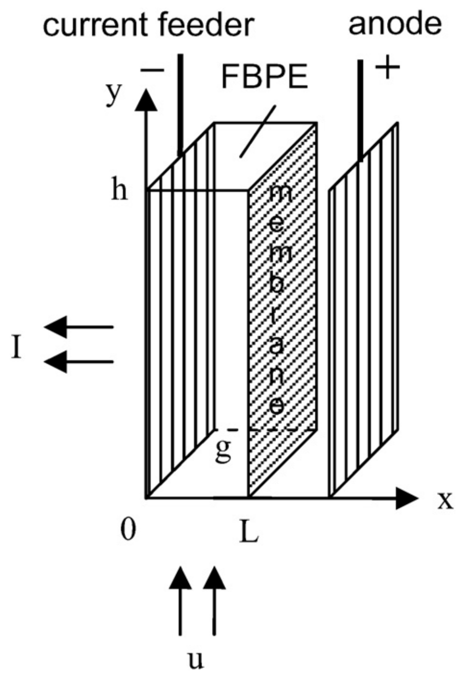

Fig. 1. Scheme of FBPE under consideration.

also be considered to be limited. Quite contrary, the effect of the concentration of electroactive component on polarization resistance is known and rather substantial. Because of this, according to this logic, sharp depletion of the solution inside PE should lead to an increase in polarization resistance from the point of solution input into PE to its outlet, and to the corresponding decrease in geometrical current density along solution flow direction. So, the problem of actual current distribution along the current feeder inside FBPE requires further studies without using *a priori* assumptions. This is the goal of the present work.

2. Mathematical formulation of the problem and the method to solve it

We will consider a FBPE shaped as a parallelepiped; its width in the direction of current passing is L, its length along the direction of solution flow is h, and its depth is g, accepted to be equal to 1 cm for simplicity (Fig. 1). The current vector is directed along the x-axis, solution is fed from below along the y-axis. A quasi-homogeneous model for PE is used [19,20]. We do not take into account the resistance of membrane, anolyte, and polarization of the anode and allocation of the ohmic losses of the potential in the solid and liquid phases of the PE is also not provided. Because of this, the direct verification of voltage balance equation is neglected. However, these simplifications of the model do not affect the distribution of current and the concentrations of solution components from the cathode to the membrane.

The equal values of the conductivities of solid and liquid phases are taken into account, as well as the overall cathode process including the target redox reaction and the side reaction of hydrogen evolution. Two-dimensional distribution of polarization and current density is described by Poisson equation:

$$\frac{d^2E}{dx^2}+\frac{d^2E}{dy^2}=\left(\frac{1}{\kappa_s}+\frac{1}{\kappa_\ell}\right)\cdot S_v\cdot i(x,y). \tag{1}$$

Expressions for the local current density i(x,y) is determined by the overall cathode polarization curve, which includes (as mentioned above) the current of the target redox reaction i_{or} and the current of the side process of hydrogen evolution i_H at higher values of cathode polarization:

$$i(x,y)=i_{or}(x,y)+i_H(x,y) \tag{2}$$

$$i_{or}=i_{0,or}\left(\frac{c_r}{c_{r,s}}\exp\left(\frac{\alpha zF}{RT}\left(E-E_{eq,or}\right)\right)-\frac{c_{ox}}{c_{ox,s}}\exp\left(-\frac{(1-\alpha)zF}{RT}\left(E-E_{eq,or}\right)\right)\right) \tag{3}$$

$$i_H=i_{0,H}\left(\exp\left(\frac{F}{2RT}\left(E-E_{eq,H}\right)\right)-\exp\left(-\frac{F}{2RT}\left(E-E_{eq,H}\right)\right)\right). \tag{4}$$

In the majority of works on FBPE, metal electrodeposition process was considered as the target cathode reaction (for example, see [5,16,17]), but inevitable change of the parameters of PE with time [21] was not taken into account. From this point of view, the use of redox reaction as the target process allows one to avoid this contradiction. On the other hand, the use of the cathode hydrogen evolution as the side reaction has limitations too. Though hydrogen evolution is indeed the most widespread side process in the electrolysis of aqueous solutions, its specific feature is the formation of the gas phase. Its appearance inside the PE may cause a number of complications connected with the change of the efficient conductivity of solution, the interaction of gas bubbles with electrode surface and change of the hydrodynamics of the gas–liquid flow [22,23]. Though methodical approaches to the estimations of the influence of a number of such effects are known [24,25], however, even for a one-dimensional case for FTPE consideration of gas filling is a very complicated and tedious problem. Because the regimes of flow porous electrodes with high gas filling degree are technologically complicated and economically unprofitable, in our opinion, it is unreasonable to pay special attention to the analysis of such cases and to take into account gas filling effects. So, in the present work, for simplicity, the side reaction of hydrogen evolution will be considered only as an additional source of current without taking into account gas filling effects.

It was accepted for hydrogen evolution that the transfer coefficient is $\alpha_H = 0.5$ and charge change is $z_H = 1$. Because of the large length of FBPE, substantial change of component concentrations along the solution flow direction is possible, so the equilibrium potential $E_{eq,or}$ in Eq. (3) is also the function of the local c_{ox} and c_r values:

$$E_{eq,or}=E_0+\frac{RT}{zF}\ln\frac{c_{ox}(x,y)}{c_r(x,y)}. \tag{5}$$

Here E_0 is the standard value of the equilibrium potential at $c_{ox} = c_r$.

After making replacements $\frac{c_r}{c_{r,s}}=1-\frac{i}{i_{r,\lim}}$ and $\frac{c_{ox}}{c_{ox,s}}=1-\frac{i}{i_{ox,\lim}}$ (6a, 6б), Eq. (3) is transformed to $i_{or}=f(E-E_{eq,or})$. The mass transfer coefficients k_m which are necessary to calculate the limiting diffusion currents $i_{ox,lim}$ and $i_{r,lim}$ were determined from the criterion dependence [26,27]:

$$Sh=a\cdot Re^b. \tag{7}$$

Taking into account expressions for Sherwood and Reynolds criteria, we obtain the following expression for k_m:

$$k_m=\frac{D\cdot a}{d^{1-b}\nu^b}u^b. \tag{8}$$

It follows from (8) that k_m is a power function of flow rate; for the fixed solution composition ($D = \text{const}$, $\nu = \text{const}$) it depends also on filament diameter. Specific values of *a* and *b* constants were taken from experimental data for a PE made of carbon fibers, for which the following dependence was found in [28] for $D = 7\cdot10^{-6}$ cm^2 s^{-1}, $\nu = 0.01$ cm^2 s^{-1} and $d = 10^{-3}$ cm:

$$k_m=0.02\cdot u^{0.35}. \tag{9}$$