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Porous Flow Electrodes for Solving Ecological Problems

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Abstract

Publications dealing with theory and practice of harnessing porous flow electrodes (PEs) for electrochemical processing of dilute solutions (extraction of metals, disposal of processing media, electrosynthesis) are reviewed. Peculiarities of this type of PE and brief history of their studies and applications, including research at the Institute of Solid State Chemistry and Mechanochemistry, SB RAS, are considered. It is demonstrated that significant progress has been achieved after 30 years of work; this primarily manifests itself in the development of a wide range of efficient porous materials based on fine carbon and metallic fibers, promoting diffusion controlled electrochemical processes several hundreds (and even thousands) fold. Seeking conditions that ensure the efficient use of the entire surface of a PE available for electrolysis turned out to be a more complicated problem. It is stressed that inhomogeneous porous matrices should be studied from the viewpoint of prospects to substantially increase the effective working depth of the PE (using the variable conductivity of the solid phase) and for better insight into the dynamics of changes in the properties of porous matrices in the course of metal incorporation.

INTRODUCTION

A new field of application of porous flow electrodes (PEs) appeared in the 1970s due to environmental problems and dissemination of electrochemical methods in hydrometallurgy. Unlike current supplies and fuel cells generally employing small volumes of concentrated electrolytes with the electrode process occurring within the limits of a single kinetically controlled and current-creating reaction, the new problems necessitate processing large volumes of dilute solutions and predominantly diffusion kinetics (in the target process). This is done for extracting technically valuable and ecologically dangerous components (mainly heavy metals), or for fulfilling redox processes: reduction of the dissolved oxygen or chlorine in the boiler-water conditioning, reduction of iron or hexavalent chromium ions during decontamination and regeneration of pickling and galvanic solutions, preparative organic electrosynthesis, *etc*. In addition, along with the target process, at least a single side process usually proceeds inside the PE (for cathodic processes this is more often evolution of hydrogen). Thus analysis of the behavior of PEs under these new conditions is of substantial interest and is important for macrokinetics studies of electrode processes.

CLASSIFICATION OF POROUS ELECTRODES

Works on non-flow PEs typical of chemical current sources and of corrosion problems are reviewed in monograph [1]. Although the results cannot be directly transferred to flow PEs, Daniel-Beck [2], Frumkin [3], Ksenzhek and Stender [4–6] have laid the groundwork for a quantitative way of looking at the problem of calculating current distribution in PEs. We will dwell upon these results partially when discussing PE simulation.

Performance characteristics of liquid flow fuel cells for a single electrode reaction proceeding on the PE surface are overviewed in [7]. In a series of works by V. S. Bagotzky *et al.* [8–10], various modes and directions of reagent delivery in PE, as well as current, potential, and reagent concentration distributions down the whole electrode, were considered in detail. The extreme cases of low and high polarizations have been analyzed, and problems of optimization of fuel cell operation have been discussed. Because of distinctions in operating conditions, the results obtained cannot be directly applied to processing of dilute solutions. At the same time, a number of inferences obtained in analysis of liquid fuel cell operation, for example, the inference about the displacement of the electrode process (limited by the slow charge transfer for increased overall current density) from the bulk of PE onto its frontal surface, are important for understanding the behavior of PEs during processing of dilute solutions.

Ample literature is available on liquid-gas PEs. Study of the latter is directly related to the design of the most promising sources of electric energy, air-metallic batteries, and fuel cells with gaseous fuel. This is the most complicated type of PE with coexisting systems of liquid and gas pores. Works on fuel cells published before 1971 are summarized in the monograph [1], in collection issues [11, 12], and also in later reviews [13–16].

Flow PEs intended for processing dilute solutions depending on the type of porous matrix can be divided into two groups: 1) electrodes with a moving porous matrix where the conductive solid particles have just accidental contact with each other and with a current lead, and 2) electrodes with a rigid porous matrix, providing permanent contact between its elements and the current lead. Suspension type and fluidized electrodes belong to the first group. The former are dilute suspensions (volume fraction of solid particles can vary from a few tenths to 2–5 %) of very fine conductive particles (for example, platinum black or absorbent carbon). The particles at first contact with the current lead and are charged to the required potential. Then, under the action of the solution stream, they separate from the current lead. While out of contact with the latter and with other similar particles, they react with the solution components, losing the acquired charge. Suspension electrodes have not yet received wide use, but they are still of interest for researchers [16]. Fluidized PEs have received wider recognition. They have a larger volume fraction of the solid phase (dozens percent) and large enough particles (1 mm and more in diameter) used as conductive elements. Under the action of the solution fed from below, the particles intermittently separate from one another. As a result, the volume of the porous matrix increases, the degree of liquefaction being 5–30 %.

The history of fluidized electrodes probably started 30–35 years ago, when the inventions were patented concurrently [17, 18]. The mathematical model of suspension electrodes was first developed by M. Fleischmann *et al.* [19]. It is similar in many respects to the model of bulk PE with a fixed particle layer [20], but in addition allows for the dependence of the effective resistance of the solid phase on the frequency of particles' collision, which, in turn, is strongly dependent on the degree of liquefaction. Principles of operation of fluidized electrodes are considered in works [21–31] and reviews [32–34]. Possible applications of such electrodes are: fuel cells [35], accumulators [38], electrochemical reactors [39], and metal extraction from dilute solutions [24, 25, 28–31, 33, 34, 36]. It is deemed [37] that fluidized PEs exhibit the same potential with regard to surface development as electrodes with a fixed layer of particles. However, they are inferior in two aspects. First, it is difficult to maintain the stationary mode of liquefaction because of gradual accretion and agglomeration of particles; second, there are anodic zones inside the fluidized electrodes (especially at high degrees of liquefaction), which decrease the operation efficiency dramatically [38]. Anodic zones are usually absent inside bulk electrodes with a squeezed layer of conductive particles; therefore, below we deal with this type of flow PEs. These include bulk PEs of black lead [39, 40], metal granules [30, 41], previously metallized plastic balls [42], and a mixture of conductive and nonconductive particles [43]; other PEs are plate electrodes [44, 45], metal gauzes [46], and foams [47–49]; metal wool [50]; and carbon fibers and felts [51–53].

For any flow PE, two operation modes are possible: 1) flow-through regime with the solution flowing through the current lead so that the vectors of the current and flow velocity are parallel, and 2) flow-by regime with the solution flowing alongside the current lead so that the vectors of the current and flow velocity are perpendicular to each other. The operation of PE with the solution stream alongside the current lead is analyzed in [54–57]. The advantage of this regime lies in the possibility of separately adjusting the thickness of the porous matrix along the current lines and along the streamlines. For example, it is possible to make PE thin along the current lines and thick along the stream of the solution. This will adjust the narrow range of polarization change to the high conversion of the reagent. Current distribution in such PE becomes two-dimensional, because it varies both with the depth and with the height of the PE. A limitation of PE with the solution stream alongside the current lead lies in the fact that it is necessary to complicate the design because of the need to use conductive diaphragms, because of the danger of their intergrowth with the precipitated metal, and also because of the fast clogging by metal of the PE zone at the input point of the fresh solution.

BRIEF HISTORY OF WORKS ON POROUS ELECTRODES FOR SOLVING ECOLOGICAL PROBLEMS

In a number of reviews (see, for example, [58]) the works of R. M. Perskaya and I. A. Zaidenman [59, 60] are considered to be among the first works on PE for solving ecological problems. The authors used a ceramic-metal PE from sintered platinum, and demonstrated its high performance for redox reactions. These and subsequent works [46, 58, 61] can be considered, on the one hand, as transitive from problems on liquid fuel cells to ecological problems, since they neglect side reactions. On the other hand, restriction of the polarization curve to the site of the limiting current of the target reaction is an idealized variation of the general case described above, when the whole PE works with the limiting current. This approach considerably simplifies quantitative analysis of current distribution and makes it possible to obtain a number of useful analytical decisions.

Works on metal extraction from dilute solutions by means of flow PEs have emerged concurrently in the early 1970s in the USA [39, 42], England [18, 62], France [17], Germany [37, 63], and USSR [44]. Later, similar studies were started in Italy, Japan, and China. The overwhelming majority of foreign (especially English-language) publications before 1977 are overviewed in [64], and later works, in reviews [13, 58, 65]. Literature data on the effective parameters (porosity, specific surface) and on the dependence of mass transfer coefficients on the flow rate for various types of PE are collected in [66]. From these data it follows that a wide set of PEs is now available with porosity varying from 0.4 to 0.96 and with specific surface S_{sp} varying from unity to hundreds inverse centimetres.

In the USSR, works aimed at using PEs for metal extraction were initiated in 1968 at the Electrochemistry Laboratory of the Institute of Solid State Chemistry and Mineral Raw Processing, SB AS USSR (Novosibirsk). At the first stage, a particular practical problem was formulated by the “Glavzoloto” organization of the USSR Ministry of Non-Ferrous Metallurgy and to develop an electrochemical method of gold extraction from thiourea processing media instead of gold cementation using zinc dust. Analysis performed on cathodic and anodic processes in thiourea solutions revealed two basic problems of the electrolysis of these solutions: firstly, separation of electrode spaces to prevent anodic decomposition of thiourea, and secondly, application of the flow PEs to drastically promote the cathodic process [67–69].

Within a short period of time, a process has been designed [70] together with two types of the flow PE, namely, titanium plate electrodes [44] and fibrous electrodes of carbon felt [51]. It was the first time that carbon fibers were used for this purpose. A similar invention [52] was patented in England a few months later. Pilot trials of both types of PE have demonstrated that titanium plate cathodes promote gold extraction by a factor of ~20 [71], and PEs of carbon felt, by a factor of 120 [72].

Later, the designed process and instrumentation were modified and used for solving other problems of gold-mining industry [73–77]. The Laboratory started investigations aimed at clarifying the operation of PEs. Taking into account experience with PEs of fibrous carbon materials (FCMs) and their great potential, main efforts were concentrated on these types of porous matrices.

R. Yu. Beck and A. P. Zamyatin [78] studied the dependence of the mass transfer coefficient $k_m = f(u)$ for carbon felt and provided an answer to the important question regarding the surface of this type of fibrous material that is accessible to electrolysis with the limiting current. Having measured the limiting current with good conduction carbon felt and with a single filament placed into the same nonconductive felt to retain the hydrodynamic properties, the authors found the value of the effective surface of good conduction carbon felt (3700 cm^2/g), which appeared to be approximately equal to the lateral surface of filaments (2700 cm^2/g) provided these are smooth cylinders. Similar results with close values of k_m for other FCM were published later [79, 80]. R. Yu. Beck [81] expanded the range of the flow rate (0.05–5 cm/s) and demonstrated that the relationship $k_m = 1.9 \cdot 10^{-2}\ u^{0.352}$ is retained, including the case with another test system (extraction of copper from sulphate solutions).

This approach to studies of the electrode properties of PE from FCM was considerably expanded later by V. K. Varentsov and A. F. Zherebilov [82, 83]. Practically the whole assortment of FCM samples produced in the USSR has been investigated. Some characteristics of nonwoven FCM cited in [82] are listed in Table 1.

From the results presented and also from correlation with data for other porous materials (see [66]) it follows that the FCMs are characterized by the highest values of specific surface (160–280 cm^{-1} for the noncompressed state) and porosity (0.92–0.98). This means that if layers' thickness is taken into account, even a single FCM layer provides growth of the electrode surface by a factor of approximately two orders of magnitude (by a factor of 40–112). If we also take into account that k_m increases by a factor of more than 10, then the possible net effect of the increased reaction rate of the diffusion controlled electrode process will comprise about three orders of magnitude.

As for effective electric conductivity of FCM, it varies thousand-fold, changing from 0.001 to 1–2 Ω^{-1}cm^{-1} depending on synthetic conditions. Even for the best conductors of FCM with graphite fibers, conductivity is substantially weaker than, for example, that of metal gauzes or porous graphite: $\approx 10^4\ \Omega^{-1}$cm^{-1} [84]. This means that porous matrices of FCM (without additional metallization) can hardly be considered equipotential.

Subsequent works of V. K. Varentsov *et al.* dealt with various aspects of using PEs of FCMs for solving a broad spectrum of practical problems in hydrometallurgy and engineering industry. The first direction of research is associated with gold and silver extraction from cyanide solutions, which are the products of

TABLE 1

Parameters of nonwoven fibrous carbon materials [82]

FCM grade	Layer thickness, cm	Filament radius, μm	Porosity	S_{sp}^{ef}, cm^{-1}	S_{ef}/S_{geom}	κ_s^*, Ω^{-1}cm^{-1}
VNG-50	0.42	6.0	0.92	265	111.3	1.3/2.6
VNG-30	0.37	5.5	0.96	160	59.2	0.09/0.33
VINN-250	0.45	4.5	0.97	280	126	0.1/0.4
NTM-200	0.38	5.0	0.96	215	81.7	0.07/0.4
NTM-100	0.44	5.4	0.96	220	96.8	0.03/0.12
Mtilon	0.37	5.1	0.94	270	100	0.13/0.5
VVP-66-95	0.44	4.7	0.96	255	112.2	0.006/0.05
FRN	0.48	5.0	0.98	125	60	0.001/0.005
KNM	0.25	6.1	0.98	160	40	0.009/0.03

*FCM conductivity in the free state/conductivity in the twice-compressed state.

leaching of ores and concentrates, and also the products of alkaline desorption of cyanide complexes of these metals from absorbent carbon [85–91]. The second direction is solving ecological problems of electrodeposition and production of printed circuit boards by developing local schemes of washing water decontamination in automated galvanic lines using electrolysis with PE of FCM [92–94].

Analysis of environmental pollution with sewage from electroplating plants and of the potential of electrolysis with flow PEs to abate this pollution is available in [95, 96].

SIMULATION OF POROUS ELECTRODES

In studies of PEs, mathematical simulation methods have received wide acceptance along with experimental methods. This is apparently associated with the complex configurations of electric and concentration fields in PEs, with the diversity of possible versions, large numbers of relevant parameters (two dozen), and complex relations between them. In these situations, mathematical simulation and computer experiment show a number of convincing advantages, which make it possible to investigate separately the effect of each parameter on the outcome, to examine the large number of variations, and to reveal the trends more adequately; situations hardly realizable with physical models can be simulated. Fortunately, mathematical treatment of electrochemical processes in PEs is reasonably well developed. As applied to the flow PEs for processing dilute solutions, the most complete description of the model is given in [97]. It includes a number of components, which we will explain below.

Geometry of porous electrodes

From the geometrical standpoint, all types of PE (except the plate type) are complex three-dimensional ($3D$) structures, for which a detailed description of the shape of a solid porous matrix and fluid channels in it presents difficulties. Therefore, mathematical treatment of PEs generally uses simplified real geometry, and a one-dimensional model is substituted for the $3D$ porous matrix. Two approaches are used for this purpose. In earlier works [3], PE was simulated by a set of pores with certain effective values of length and diameter. As these values did not coincide with the real diameter of pores and with the thickness of PE, Ya. B. Zeldovich [98] suggested another approach. Abstracting from the real structure of the porous matrix, this method considers the matrix to be a quasihomogeneous medium with a uniform distribution of the solid and liquid phases characterized by certain effective parameters. Conditions of applicability of this model to PE are substantiated in [3].

While the capillary and quasihomogeneous models are equivalent (both are one-dimensional and involve "effective" parameters), the second model is simpler and more adequate, since it does not create an illusion that a complex $3D$ structure of the real PEs can be reflected exactly and replaced with a system of capillaries. Therefore, the one-dimensional macrohomogeneous model of PE is now dominant.

Description of current and potential distributions in porous electrodes

The quantitative approach to description of current distribution in PE was suggested by V. S. Daniel-Beck [2]. The approach is briefly outlined as follows. The total current of electrolysis $I = i_{av} S_{sp} L S_{geom}$ (where i_{av} is the average current density; L is the thickness of PE; and S_{geom} is the overall (geometrical) surface of PE) from an auxiliary electrode enters PE through the liquid phase and gets out of it into the current lead through the solid phase. Inside the electrode, the current gradually passes from liquid to solid phase, and it defines the rate of the heterogeneous electrochemical reaction, which is the purpose of calculation. The local values of current density in each phase are related to the potential gradients in them by Ohm's law:

$$i_l = -\kappa_l \frac{d\varphi}{dx} \qquad (1)$$

$$i_s = -\kappa_s \frac{\mathrm{d}P}{\mathrm{d}x} \tag{2}$$

and their change, by Kirchhoff's law, is exactly equal to the current that passed from one phase into another, *i. e.*, to the local current density i of the electrode process. It is also obvious that, by the conservation law, the loss of current in one phase is equal to its incremental value in another:

$$\frac{\mathrm{d}i_l}{\mathrm{d}x} = -S_{sp} i(\eta, c) \tag{3}$$

$$\frac{\mathrm{d}i_s}{\mathrm{d}x} = S_{sp} i(\eta, c) \tag{4}$$

Substituting (1) and (2) into (3) and (4), respectively, we obtain differential equations describing current and potential distributions in each phase of PE:

$$\frac{\mathrm{d}^2\varphi}{\mathrm{d}x^2} = \frac{S_{sp}}{\kappa_l} i(\eta, c) \tag{5}$$

$$\frac{\mathrm{d}^2 P}{\mathrm{d}x^2} = \frac{S_{sp}}{\kappa_s} i(\eta, c) \tag{6}$$

where φ, P are the potentials; and i (η, c) is the equation of the polarization curve describing the dependence of current density i on concentration c and overvoltage η.

Equations (5) and (6) can be reduced to one equation relative to the potential jump on the interface ($P - \varphi$) or (which is even better) relative to the potential difference $\eta = P - \varphi - \varphi_r$, which takes into account the equilibrium potential φ_r of the target electrode reaction:

$$\frac{\mathrm{d}^2\eta}{\mathrm{d}x^2} = \left(\frac{1}{\kappa_s} + \frac{1}{\kappa_l}\right) i(\eta, c) \tag{7}$$

Although Eq. (7) was derived [2] for PEs with phases of constant conductivity, this restriction is not implied by the logic of the derivation; therefore, the same approach may also be applied to the case when the conductivities of PE phases are functions of x.

Reagent delivery

To adequately describe the operation of PEs, Eq. (7) needs to be complemented with the equation of reagent transport, with the particular formula of the polarization curve $i = f(\eta, c)$, and with boundary conditions. Typically, two variations of delivering are considered: diffusive (for non-flow PEs) and convective (for flow PEs). In the latter case, the main flow of substance into PE is connected with the solution's flow rate. The condition of quantitative balance of the reagent delivered by the streamflow and consumed by the electrode reaction gives the following equation:

$$\frac{\mathrm{d}c}{\mathrm{d}x} = \frac{S_{sp} i_1(\eta, c) S_{geom}}{m_{vol} n_1 F} \tag{8}$$

where m_{vol} is the bulk flow rate of the solution; $i_1(\eta, c)$ is current density of the target reaction; n_1 is the number of electrons transferred in the elementary act of this reaction; and F is Faraday constant.

However, apart from purely convective transport, other additional channels of reagent transport are also possible in the flow PE. Therefore, with a gradient of concentration at the PE inlet and outlet, transport of substance is possible through axial diffusion. In addition, owing to the nonuniform velocity profile for the streamflow inside the pore (by the wall it is less significant than along the pore axis), the liquid inside a pore may be mixed and the concentration profile may be smeared (axial dispersion). All of this, theoretically, may result in deviation from the simple model of ideal displacement (plug-flow).

The necessity and methods of quantitative calculation of the axial diffusion and dispersion were discussed in a number of works [99, 100]. The outcomes of the discussion and an example of the most correct amendments are given in the review [64]. It has been demonstrated that though the dispersion coefficient increases with the flow rate, its relative role becomes appreciable only at very low flow rates. The effects of axial diffusion and dispersion can be neglected for the majority of significant practised regimes of electrolysis.

Polarization curve

The specific features of the problem solved by using PEs are reflected in the kinetic equation of the electrode process $i = f(\eta)$. Hence, for problems related to chemical current sources, a description of the target reaction kinetics alone is enough. In this case, depending on the range of polarization considered, various forms of the relationship $i = f(\eta)$ are used. When employing PE to treat dilute solutions, a wide range of polarization generally exists inside PE. Thus, besides the full kinetic equation of the target reaction, the polarization curve should include at least a more electronegative side reaction. This natural side reaction is most often evolution of hydrogen [41, 101], but other redox processes are possible as well, for example, reduction of thiosulfate ions in extraction of silver from fixing solutions [102]. The first examples of taking into account the hydrogen-evolving side reaction in the overall polarization curve are cited in [97, 103].

Note that even a single side reaction requires refinement of Eqs. (7) and (8): the first includes the total current density, and the second includes only the current density of the target reaction. In the literature, there are examples describing even more complicated forms of the polarization curve of the total electrode process by including the additional target reactions (for example, discharge of several metals [104, 105]) or additional auxiliary reactions (for example, parallel reduction of the dissolved oxygen or Fe^{3+} [38, 106, 107]). Despite the simplifications made, calculating the potential, current, and concentration distributions inside the PE remains a rather tedious and complicated problem even in the case of the homogeneous porous matrix. Generally, it does not have an analytical solution and is solved exclusively by numerical methods. Several algorithms for solving different versions of this problem are given in [30, 58, 105, 108].

In conclusion, we note that using PE for metal extraction from solutions inevitably results in changes of the parameters of the porous matrix with time. Nevertheless, the dynamics of the process filling the porous matrix with the precipitated metal is virtually uninvestigated.

VARIOUS EFFECTS ON CURRENT DISTRIBUTION IN A POROUS ELECTRODE WITH AN EQUIPOTENTIAL POROUS MATRIX

The direction and scale of the effect on current distribution in PEs is an important part of PE theory, as it defines the possibility to regulate current distribution and to choose optimum conditions of electrolysis. As mentioned above, the problem lies in the large number of these parameters and complex relations between them. Therefore, an attempt to reduce the number of variables, for example, by clustering them into dimensionless groups [64, 109], seems to be reasonable. We used another way of clustering the parameters depending on their relation with definite sections of the current path inside the PE. These sections are 1) current path in the solution, 2) passage through the interface, and 3) passage in the solid phase from the entry point to the current lead.

When current passes in the liquid phase, the conductivity of the solution κ_l is the single relevant parameter. It is common knowledge that with a decrease in κ_l, current distribution becomes less uniform and the operation efficiency of PE decreases. The overwhelming majority of works assumes the solution conductivity to be constant at any point of PE. However, for high current densities with significant amount of gaseous hydrogen evolved, more complicated models that consider changes in κ_l due to gas filling [110, 111] were developed. Note also that for infinite conductivity of the solid phase, the ohmic drop of potential in the solution becomes the reason for the nonuniform distribution of current and polarization throughout the PE. Moreover, as the solution conductivity cannot be physically infinite, the decrease in the potential and irregularity of current distribution cannot be eliminated. Hence it follows that an equipolarized PE (η = const) cannot be created based on a porous matrix with $\kappa_s = \infty$.

Current passage through the interface requires that the additional polarization resistance $R_{pol} = d\eta/di$ should be overcome. The higher the R_{pol} compared to solution's ohmic resistance, the greater the uniformity of distribution for i and η. R_{pol}, in turn, depends on many electrochemical parameters (composition of the solution, kinetic constants, mean current density, flow rate and direction of the solution, *etc.*). Therefore, the possibilities to control current distribution in PE by means of R_{pol} are actually reduced to the dependence on the electrolysis conditions. In this case, the simplest situation for analysis is observed at low conversion of reagent when its concentration, as well as the whole polarization curve, remain virtually constant throughout the PE.

In the region of diffusion control characteristic of operating conditions for PEs with dilute solutions, R_{pol} may be approximately characterized by two parameters: height and width of the limiting current plateau of the target reaction. The smaller the first value and the larger the second, the thicker the electrode layer that works with the limiting current [61, 111]. However, the decreasing reagent concentration also has its limits. This is associated with the fact that reducing the concentration of the target component shifts the equilibrium potential of the target reaction and decreases the exchange current. If the starting potential of hydrogen release remains nearly constant, this can bring about an appreciable reduction of the limiting current plateau and decrease the positive effect of reduced concentration.

The effect of the mean current density on the efficiency of PE was examined in [97]. It was shown, both experimentally and theoretically, that with increased current density, the efficiency at first grows and then flattens to the limiting value. In [112, 113] one can find more complex experimental functions of the degree of extraction $R = f(i)$, passing through a maximum and attributable to deterioration of current distribution owing to increased gas filling, especially in the front area of PE.

The solution flow rate produces a dual effect on the operation of PEs. On the one hand, reduction of the flow rate leads to decreased mass transfer coefficient and volume rate of solution treatment. On the other hand, it brings about a sharper drop of reagent concentration inside the PE, which, in turn, gives rise to growth of polarization resistance and expands the limiting current zone. A comparison between the two operating modes of PE: at a high flow rate and low conversion and, vice versa, at a low flow rate and high conversion [64] showed that the first variant affords about 40 % higher volume rate of solution treatment.

Furthermore, the low flow rate mode of operation during metal extraction from dilute solutions would result in a significantly nonuniform distribution of metal across the electrode, quickly clogging the pores on the side of solution delivery. The suggestion that metal distribution be improved by intermittently changing the direction of solution delivery cannot change the situation drastically [114]. Hence the circulation mode of operation at high flow rates is supposedly the best choice for metal extraction from dilute solutions. Along with the high volume rate of treatment, this mode ensures reasonably uniform distribution of metals across the PE (for $L \cong L_{\text{lim}}$) and, accordingly, substantial clogging of the porous matrix with the precipitated metal (for example, up to 50 kg of gold per 1 kg of the starting FCM in the case of gold extracted on FCM cathodes [72]). Note that this mode of operation was used for gold extraction from thiourea [72] and cyanide [76] solutions.

In conclusion, we estimate the potential of the most efficient porous materials of carbon fibers (see Table 1) as applied to the popular operating conditions: high conductivity of the solid phase and low conversion of the reagent. In this case, the maximum thickness of the limiting current zone can be calculated from the equation

$$L_{\text{lim}} = \sqrt{\frac{2\kappa_l \Delta\eta}{S_{\text{sp}} k_{\text{m}} n_1 F c_0}} \tag{9}$$

It is assumed that the average value of specific surface for FCM in the free state (S_{sp} grows proportionally to the compression degree of the material) is 200 cm^{-1}; the plateau of the limiting current is reasonably wide: $\Delta\eta = 0.5$ V; the solution has reasonably good conduction: $\kappa_l = 0.1\ \Omega^{-1}\text{cm}^{-1}$; the mass transfer coefficient $k_{\text{m}} = 0.019$ cm/s; the corresponding $u = 1$ cm/s; $c_0 = 10^{-5}$ mol/cm^3; $n_1 = 1$. As a result, even with these reasonably favorable operating conditions, we obtain a rather low value of $L_{\text{lim}} = 0.16$ cm.

CONCLUSIONS

From the review of publications presented on the liquid flow PEs, it can be seen that significant progress has been achieved over the past 30 years in the new field of application of these electrodes to processing of dilute multicomponent solutions. First of all, a broad spectrum of flow porous materials with different specific characteristics have been created. Among them, microporous materials based on metal particles of small diameter or fine filament, for example, carbon fibers, may be of special interest from the viewpoint of macrokinetics of electrochemical processes. These materials successfully combine high porosity (up to 96–98 %) and large specific surface (hundreds of square centimetres per cubic centimetre). With the additional effect of reduced effective thickness of the diffusion layer, these flow PEs will enable hundred- and thousand-fold intensification of electrochemical processes.

Significant progress has also been made in understanding of how PEs work in dilute multicomponent solutions with the diffusion control over the target reaction, in studies of various effects (mainly conditions of electrolysis for infinite conductivity of the solid phase), and in practical application of flow PEs to solution of ecological and technological problems. Estimations of the effective working thickness of PEs of carbon fibers have demonstrated that the effective diameter of pores in this case is so small, while the effective length of pores (*i. e.*, PE thickness) is so great that it can be completely accessible to electrolysis only for a narrow range of electrochemical systems. These primarily include the $K_3Fe(CN)_6/K_4Fe(CN)_6$ redox system in alkaline solutions, which is widely used in experimental studies, as well as Cu extraction from sulphate solutions and Hg extraction from chloride solutions. While their solutions are highly conductive, these systems also exhibit a very wide plateau of the limiting current of the target reaction (1–1.5 V).

Mismatch between researchers' recommendations on the use of FCMs and instances of their real application is indicative of the rigid requirements to the parameters of electrochemical systems, which must be satisfied for efficient work of PEs from FCMs. Despite the 30 years of studies of PEs of carbon fibers, as well as their high specific characteristics and availability of patents, only two groups of publications on their practical uses are available in the literature. Among these are primarily works of our laboratory on the application of PEs of carbon fibers to precious metal extraction from the technological solutions of gold-mining plants, washing waters of electroplating shops, and waste photochemical solutions [115, 91, 94]. Second, this is the report of English researchers on FCM application for decontamination of technological solutions from copper at a Scotch whisky plant [108]. Other instances of real application for flow PEs generally refer to porous matrices with a smaller specific surface, for example, the process of NALCO Chemical Corporation to produce tetraalkyl lead using a bulk anode of lead granules [58].

For other electrochemical processes with lower solution conductivity and smaller difference between the equilibrium potentials of the target and side reactions, the efficient use of the entire thickness of the majority of PEs of FCMs is yet impossible, so we are either to give up the application of these most promising porous matrices, or to search for ways of increasing the depth to which electrode processes propagate inside the PE. The first way is obviously undesirable because replacement of FCMs with macroporous matrices will result in a significant loss of reaction rate not only because of the decreased specific surface, but also because of the decreased mass transport velocity for the target reagent. On the other hand, inefficient application of PEs of FCMs with a partial working layer is accompanied not only by overconsumption of FCM, but also by the additional consumption of anodes (which are generally expensive and wear resistant) and of ion-exchange membranes, by increased electrolytic cell size, *etc.* This will result in growth of capital expenditures and working costs, which is also unacceptable. Thus, it is necessary to seek new possibilities to improve the uniformity of current distribution in PEs and to ensure, on this basis, growth of the efficient working thickness of PEs of carbon fibers. Referring to possible ways of solving this problem, it is worth noting that the potential of the currently known electrochemical factors is restricted and already exhausted. Only one factor still remains to be understood, namely, adjusting the potential of the solid phase, which can be done directly (for example, by introducing additional current leads [116, 117]), or by selectively adjusting the conductivity of the solid phase [118, 119].

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