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Effect of distortions in the ideal profile of solid phase conductivity on performance efficiency of porous electrodes

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The effect of distortions in the ideal profile of the solid phase conductivity $\chi_s(x)$ on porous electrode (PE) performance efficiency has been analysed using a one-dimensional model and an overall polarization curve involving both main and side reactions. Although an ideal electrically equally accessible PE is provided only by a hyperbolic profile $\chi_s(x)$ passing through the middle of the electrode (the point $\chi_s = \chi_L$), it has been shown that a noticeable improvement in performance can be obtained using a rough approximation with any monotonic function providing a decrease in conductivity in the direction from the back current supply to the front plane of the PE, including functions not necessarily passing through the point $\chi_s = \chi_L$ in the middle of the electrode. This permits less rigid requirements for the $\chi_s(x)$ profile reproduction accuracy and simplification of experimental data acquisition.

Keywords: *porous electrodes*, *solid phase conductivity*, *efficiency*

List of symbols

χ_s, χ_L	solid and liquid phase conductivities (Ω^{-1} cm^{-1})
L	thickness of PE (cm)
L_{eff}	effective thickness of PE layer operating at the limiting diffusion current (cm)
i, i_1, i_2	current densities of the overall, main and side cathode reactions (A cm^{-2})
i_{1l}	the limiting current density of the main reaction (A cm^{-2})
c_{01}	inlet concentration of electroactive component of the main reaction (mol cm^{-3})
i_{01}, i_{02}	exchange current densities of main and side reactions (A cm^{-2})
z_1	number of electrons transferred per ion discharged in the main reaction
u	linear rate of the solution flow (cm s^{-1})
k_m	mass transfer coefficient (cm s^{-1})
a, b	coefficients controlling the shift of an ideal $\chi_s(x)$ profile

Greek letters

α_1, α_2	transfer coefficients of the main and side reaction
$\varphi_{r1}, \varphi_{r2}$	equilibrium potentials of the main and side reactions (V)

1. Introduction

The use of nonhomogeneous porous matrices with definite solid phase conductivity profiles $\chi_s(x)$ is a promising way of elevating PE efficiency [1, 2]. We have demonstrated [2, 3] that an electrically equally accessible PE with ideally uniform distribution of polarization over the whole thickness may be achieved if $\chi_s(x)$ corresponds to the equation:

$$\chi_s(x) = \chi_L\left(\frac{L}{x} - 1\right) \tag{1}$$

where x is an arbitrary point ($0 < x < L$) at the x-axis, the zero point of this axis being the position of the back current supply. Unfortunately, the profile $\chi_s(x)$ has not yet been precisely reproduced experimentally in the form described by Equation 1. Eforts of researches have been directed at approximations of this profile.

It was shown in the studies of multilayered PE [4] that even a rough approximation of the profile (Equation 1) by a three-layered electrode with different conductivities and layer thickness caused a 2–3-fold increase in the working surface. The scale of this effect was confirmed experimentally [5]. However, due to the limited number of porous matrices differing only in conductivity, the possibilities of this approach are reduced and continuous approximations of the profile (1) must be used. We demonstrated [6] the possibility of introducing limitations at the edges of the profile (1) without any noticeable worsening of PE performance. The regions $\chi_s \to \infty$ and $\chi_s \to 0$ could be substituted by layers exhibiting constant conductivity. In the present work we analyse a possibility of simplifying the profile (1). We also attempt to reveal the extent to which the requirement concerning equal conductivities of solid and liquid phases at the middle point of the profile is rigid. We also consider the possibility of replacing hyperbola with other functions.

2. Calculation procedure

The effect of the solid phase conductivity profile on PE performance efficiency was analysed through calculations. The hyperbolic profile (Equation 1) with the limitations at the ends (0.3 Ω^{-1} cm^{-1} at the back end and 0.02 Ω^{-1} cm^{-1} at the front end) was chosen as the basis. Modelling of the distortion variants was carried out. The hyperbolic character of the profile was conserved in the first set of calculations. The effect of the profile shift along the horizontal or vertical axis was investigated. In the second set of calculations we studied the possibility of displacing the hyperbola with other functions for the case of fixed ends of the variable profile region.

The distribution of electroactive component concentration, polarization and current density inside the PE were calculated according to a one-dimensional quasi-homogeneous model for constant liquid phase conductivity and variable solid phase conductivity. The mathematical formulation of the corresponding boundary problem and the computational technique were described earlier [1, 2, 7]. Back current supply and back reagent inflow were employed. The overall cathode polarization curve accounted for both the main and the side reaction (hydrogen evolution). Both the charge transfer and concentration polarization were taken into account for the partial polarization curve of the main process, while only charge transfer was considered for the side reaction. We restrict the analysis to the condition involving low depletion of the solution with respect to the main component during a single pass through the PE. This assumption simplifies the problem and makes the direction in which the solution is fed unimportant.

The main subject of the present study involves the regularities of the influence of distortions in the profile of solid phase conductivity. Kinetic characteristics of the electrochemical system are considered as constant parameters and are auxiliary in character. Particular values of electrode parameters and polarization curve characteristics are presented in the captions to Figs 1 and 2.

Since the penetration depth depends on the geometric current density, the latter increasing to some limit [8], to achieve the comparability all the calculations were carried out at a fixed geometric current density, which was 10% higher than the limiting geometric current density at which the whole PE surface operated in conditions of limiting diffusion current.

The current efficiency (CE) of the main process and the effective penetration depth were taken as indices of PE operation efficiency:

$$L_{\text{eff}} = \int_0^L \frac{i_1(x)}{i_{1l}(x)} \mathrm{d}x \qquad (2)$$

As Equation 2 suggests, L_{eff} takes into account the PE regions where the current density is as high as the limiting value, as well as the regions with lower current density [1].

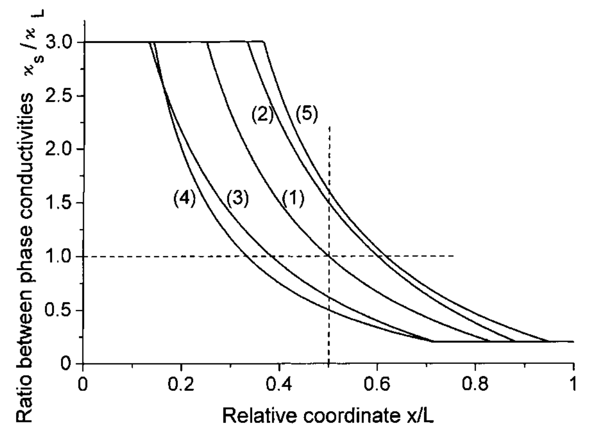

Fig. 1. Set of hyperbolic profiles $\chi_s(x)$ with fixed upper ($\chi_s = 0.3\ \Omega^{-1}$ cm^{-1}) and lower ($\chi_s = 0.02\ \Omega^{-1}$ cm^{-1}) limits calculated from Equation 2 using the following coefficients: (1) $a = 1$, $b = 0$; (2) $a = 1$, $b = 0.07$; (3) $a = 1$, $b = -0.07$; (4) $a = 0.5$, $b = 0$; (5) $a = 1.5$, $b = 0$. Parameters of PE: $L = 0.6$ cm, $S_v = 150$ cm^{-1}, $\chi_L = 0.1\ \Omega^{-1}$ cm^{-1}.

3. Results and discussion

The set of hyperbolic functions (Fig. 1) was calculated according to the modified equation obtained from Equation 1:

$$\chi_s(x) = a\chi_L\left(\frac{L}{(x-b)} - 1\right) \qquad (3)$$

This equation gives various horizontal and vertical shifts of the nonlinear profile region by varying the

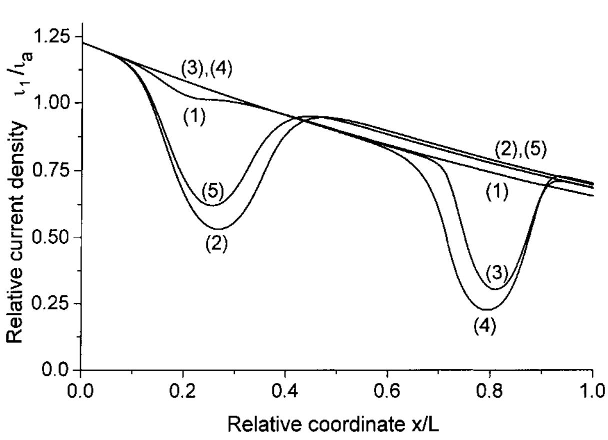

Fig. 2. Profiles of relative current density distribution for the main reaction over the PE depth corresponding to the solid phase conductivity profiles shown in Fig. 1. Here, i_1 is the local current density of the main reaction, i_a is the average current density of the overall cathodic process. Kinetic parameters of overall polarization curve: $i_{01} = 10^{-3}$ A cm^{-2}; $c_{01} = 10^{-5}$ mol cm^{-3}; $z_1 = 1$; $\alpha_1 = 0.5$; $k_m = 0.035$ cm s^{-1}; $u = 5$ cm s^{-1}; $i_{02} = 10^{-6}$ A cm^{-2}; $\alpha_2 = 0.5$; $\varphi_{r2} - \varphi_{r1} = -0.3$ V.

coefficients *a* and *b*. The effects of changes in *a* and *b* are qualitatively similar. In both cases the requirement $\chi_s = \chi_L$ is violated in the middle point of the electrode, and the thickness of the $\chi_s(x)$ profile boundary zones is changed both to the left and to the right. For example, when the nonlinear region is shifted upward or to the left (curves 2 and 5) the relation is $\chi_s(L/2) \approx 1.5\chi_L$. The boundary zone at the back current supply grows, while that at the front end of the PE narrows. When the profile is shifted downward and to the left (curves 3 and 4) opposite changes take place.

The current density distributions (for the main reaction) corresponding to Fig. 1 are shown in Fig. 2. Effective penetration depth and the current efficiency are presented in Table 1. It can be seen that the normal profile (1) corresponds to the most favourable current distribution with the whole PE thickness operating at the limiting current. When the profile is shifted to the right, a parabolic fall of current density is observed in the boundary zone near the back current supply. The shift of the profile to the left is accompanied by the fall in the boundary zone at the front end of the PE. This means that the fall occurs in a boundary zone that increases in thickness with profile shift. It is important to note that worsening of the current distribution is local. The rest of the PE surface operates efficiently in the limiting current regime.

Thus, the data presented in Table 1 suggest the following. Even when the shift of hyperbolic profile causes a 1.5–2-fold derivation of matrix conductivity in the middle of the electrode from the solution conductivity, the effective penetration depth of the main process and the current efficiency remain sufficiently high, the maximum worst change being around 10%. This result is nearly two times better than the maximum penetration depth achieved for a homogeneous porous matrix (at $\chi_s = \chi_L$, $L_{\text{eff}} = 0.27$ cm, CE 48%). The latter means that for conservation of hyperbolic character of $\chi_s(x)$ dependence, its deviation from the optimal value in the middle point is permissible over a rather wide range without any dramatic consequences for the performance efficiency of the PE.

Another variant of the profile distortion is shown in Fig. 3. In this case, the level of restrictions at the upper and lower limits of the profile and boundaries of the zones are fixed. The changes of conductivity between the points A and B are represented by different functions, including straight line and parabolas with various convexity values and directions. The latter was achieved by changing the ordinate of the profile middle point through which (together with the points A and B) the parabola was traced.

Table 1. *Effective penetration depth, L_{eff}, and the current efficiency of the main reaction (CE) for different shapes of the profile $\chi_s(x)$ shown in Figs 1 and 3*

Curve	*Fig. 1*		*Fig. 3*	
	L_{eff}/cm	*CE*/%	L_{eff}/cm	*CE*/%
1	0.595	90.4	0.529	82.9
2	0.538	83.9	0.586	89.4
3	0.554	85.8	0.567	87.3
4	0.530	83.1	0.498	79.3
5	0.553	85.6	0.470	75.8

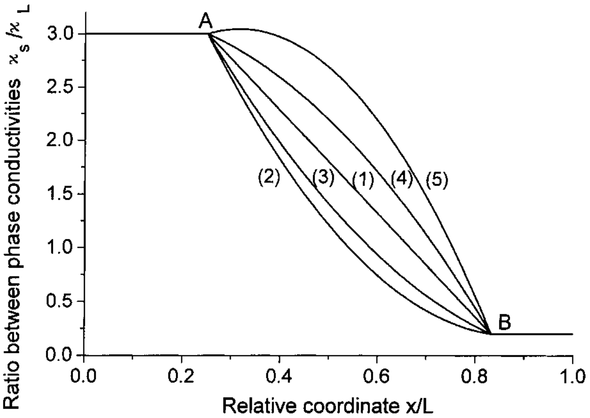

Fig. 3. A set of nonhyperbolic profiles $\chi_s(x)$ between the points A and B. Linear (1) and parabolic profiles with different values of the middle point ordinate: (2) $y = 1$; (3) $y = 1.2$; (4) $y = 2$; (5) $y = 2.5$.

Corresponding profiles of the current density distribution over the PE thickness are shown in Fig. 4 for the main reaction. The electrode performance efficiency is characterized in Table 1. It can be seen from Fig. 4 that all the functions give a similar current distribution: the front half of the electrode operates at the limiting current while a current fall is observed at the back half. The differences between the profiles are quantitative, namely, in the depth and width of the fall. A linear profile (curve 1) occupies an intermediate position. Parabolic profiles, with the convexity directed upwards, produce a worse current distribution and over larger thickness of the electrode. In contrast, the profiles with the convexity directed downwards provide a better current distribution approaching an ideal hyperbolic profile with minor deviations from limiting current in a more narrow layer (see Fig. 2). This is also depicted in

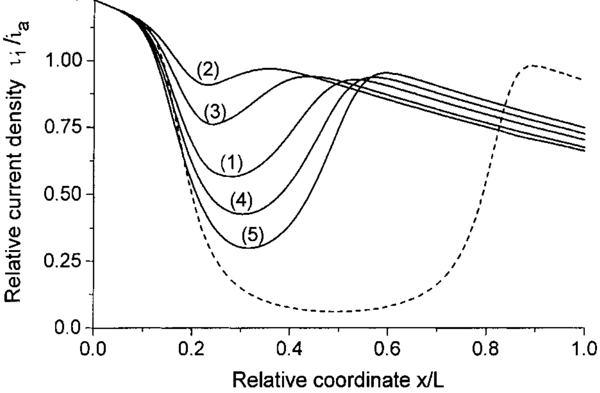

Fig. 4. Profiles of relative current density distribution for the main reaction corresponding to nonhyperbolic profiles $\chi_s(x)$ shown in Fig. 3 (curves are numbered similarly). For comparison the current distribution profile at $\chi_s = \chi_L = \text{const}$ is shown using a dashed line.

integral characteristics of the PE performance. Comparison suggests that even the essential deviations from the hyperbolic profile provide high efficiency of the PE surface usage. For example, decrease in L_{eff} for the linear profile, compared to the hyperbolic profile, is about 11%. Even for the profile with an opposite convexity (curve 5) this parameter is about 21%. As a result, even a PE with strongly distorted $\chi_s(x)$ profile exhibits much better performance than an electrode of the same thickness with constant solid phase conductivity (dashed line).

Thus, although an ideal distribution of the polarization over the PE thickness is provided only by a hyperbolic conductivity profile of the porous matrix for equal conductivities of the phases at the midpoint of the electrode, a rough approximation of the profile is sufficient to achieve a notable improvement in the electrode performance efficiency, compared to the variant involving a homogeneous matrix. In fact, any monotonic profile providing conductivity decrease from the current supply to the counter electrode will be appropriate in this case, including profiles with a pronounced discrepancy from the equality of phase conductivities in the middle of the PE. This allows substantial lowering of the demands on the accuracy at which the ideal $\chi_s(x)$ profile is reproduced and makes the possibility of its experimental realization more likely.

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