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Approximate evaluation of cell resistance with resistive electrodes

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The resistance of a cell composed of a resistive anode and a conductive cathode has been theoretically calculated by solving the two-dimensional Laplace equation for the solution phase where the anode has an overpotential of a linear type. Conditions were evaluated under which the cell resistance could be obtained on the assumption that the direction of the current flowing in solution was perpendicular to the electrode. These were not strongly dependent on the ratio of the interelectrode distance to the height of the electrodes. The main parameters which determine the conditions were the Wagner number and the ratio of the electrode resistance to the solution resistance.

Nomenclature

a	linear overpotential coefficient
b	linear overpotential coefficient
d	interelectrode distance
h	height of the electrode
i	current density flowing in the solution
i_{av}	average current density
i_{max}	maximum current density
I	current fed to the anode
r	cell resistance
r_{ap}	cell resistance obtained on the assumption that current lines are normal to the electrodes
r_{Lp}	cell resistance calculated from the Laplace equation
t	thickness of the anode
V	cell voltage
V_{eq}	open circuit inner potential difference between the anode and cathode
w	width of the electrodes
Wa	Wagner number given by Equation 12
x	axis normal to the electrode surface
y	axis in the direction to the electrode height
β	ratio of solution resistance to anode resistance
η	overpotential
θ	dimensionless parameter defined by Equation 18
ϱ	resistivity
ϕ	inner potential of the solution
ψ	inner potential of the electrode
ψ^T	inner potential of the electrode at the terminal

Subscripts

a	anode
c	cathode
s	solution

1. Introduction

Electrodes in industrial production-type cells are, in some cases, so poorly conductive that the ohmic drop in the electrodes cannot be neglected. For such resistive electrodes, part of the current fed to the electrode through a bus bar flows immediately to the solution causing electrode reactions, and

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part of the current flows within the resistive electrode and produces heat. Therefore the current density at the electrode surface decreases with increase in distance from the current feeders. Previous papers have discussed such non-uniform current distribution [1–6]. Other work on the resistive electrode problem has been reviewed by Ibl [7].

It is important to examine the relationships between current feeder configurations, cell configurations, overpotential, current distribution, cell voltage, variations of current lines in the solution, and resistance of electrodes and solution. Current in solution flows along a path satisfying the Laplace equation. In order to determine the current line in solution, it is necessary to solve the two- or three-dimensional Laplace equation under given conditions. Since it is difficult to solve rigorously such a problem involving overpotential and complicated cell and electrode geometries as described above, current lines in solution have frequently been approximated as being normal to the electrode [4–6]. This approximation makes the theoretical treatment extremely simple and hence facilitates the introduction of a number of factors into the complicated problem of resistive electrodes. This paper focuses on finding conditions under which the approximation is valid from the viewpoint of the cell resistance.

2. Expressions for cell resistance

The cell treated here consists of two parallel plate electrodes, an anode and a cathode. The anode is resistive whereas the cathode is highly conductive and is regarded as equipotential. It is assumed that the anode is so thin that current flows only in the direction of the y-axis within the anode. It is also assumed that the overpotential at the interface between the solution and the anode is of a linear type. The current is fed to the bottom of the anode. A possible potential variation in the electrodes and in the solution is illustrated schematically in Fig. 1.

2.1. *Rigorous expression (derived from the Laplace equation)*

The boundary value problem for the potential distribution in the cell is given by

$$\partial^2\phi/\partial x^2 + \partial^2\phi/\partial y^2 = 0 \tag{1}$$

when $y = 0$

$$\partial\phi/\partial y = 0 \tag{2}$$

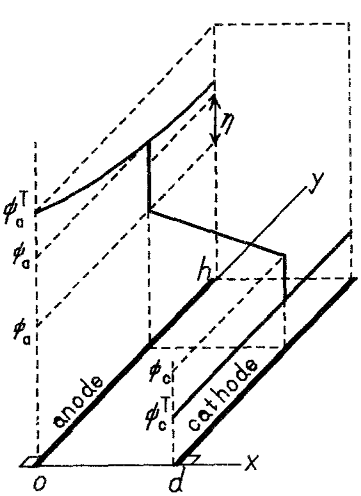

Fig. 1. Schematic diagram of a potential variation in the electrodes and the solution.

when $y = h$

$$\partial\phi/\partial y = 0 \tag{3a}$$

$$\mathrm{d}\psi_{\mathrm{a}}/\mathrm{d}y = 0 \tag{3b}$$

when $x = 0$, $y = 0$

$$\psi_{\mathrm{a}} = \psi_{\mathrm{a}}^{\mathrm{T}} \tag{4}$$

when $x = d$

$$\psi_{\mathrm{c}} = \psi_{\mathrm{c}}^{\mathrm{T}} \tag{5}$$

Taking into account the current balance at the anode,

$$I = -(wt/\varrho_{\mathrm{a}})(\partial\psi_{\mathrm{a}}/\partial y) + w\int_0^y i\,\mathrm{d}y \tag{6}$$

The difference in the inner potentials of both of the electrodes can be connected with the difference in those of the solution on both sides of the electrodes through the following relation:

$$\psi_{\mathrm{a}} - \psi_{\mathrm{c}}^{\mathrm{T}} = V_{\mathrm{eq}} + \eta + (\phi_{\mathrm{a}} - \phi_{\mathrm{c}}) \tag{7}$$

where η is overpotential of a linear type

$$\eta = a + bi \tag{8}$$

The boundary value problem similar to the above has been solved by the Fourier expansion technique by Ishizaka and Matsuda [3]. According to this, ψ_{a} is expressed by

$$\psi_{\mathrm{a}} = \psi_{\mathrm{c}}^{\mathrm{T}} + a + V_{\mathrm{eq}} + [I/(wh)]\left\{b\left[1 + \sum_{n=1}^{\infty} A_{\mathrm{n}}\cos(n\pi y/h)\right]\right.$$
$$\left. + \varrho_{\mathrm{s}}d + \varrho_{\mathrm{s}}h\sum_{n=1}^{\infty}(A_{\mathrm{n}}/n\pi)\tanh(n\pi d/h)\cos(n\pi y/h)\right\} \tag{9}$$

with

$$A_{\mathrm{n}} = 2[(n\pi)^2(Wa)\beta(d/h) + 1 + n\pi\beta\tanh(n\pi d/h)]^{-1} \tag{10}$$

where

$$\beta = \varrho_{\mathrm{s}}t/(\varrho_{\mathrm{a}}h) \tag{11}$$

$$Wa = b/(\varrho_{\mathrm{s}}d) \tag{12}$$

The cell resistance is given by

$$r = (\psi_{\mathrm{a}}^{\mathrm{T}} - \psi_{\mathrm{c}}^{\mathrm{T}} - V_{\mathrm{eq}} - a)/I \tag{13}$$

Taking y to be zero in Equation 9 and eliminating $\psi_{\mathrm{a}}^{\mathrm{T}}$ from Equations 9 and 13, the rigorous expression for the cell resistance is obtained in the following form:

$$r_{\mathrm{Lp}} = [(\varrho_{\mathrm{s}}d + b)/(wh)]\left\{1 + [Wa/(1 + Wa)]\sum_{n=1}^{\infty} A_{\mathrm{n}}\right.$$
$$\left. + \left[[(h/d)/(1 + Wa)]\sum_{n=1}^{\infty}(A_{\mathrm{n}}/n\pi)\tanh(n\pi d/h)\right]\right\} \tag{14}$$

This is a function of Wa, β and d/h.

2.2. *Approximation (current lines normal to the electrodes)*

When current lines in the solution are normal to the electrodes it is not necessary to solve the Laplace equation. Instead of Equation 1,

$$i = (\phi_a - \phi_c)/\varrho_s d \tag{15}$$

is used. Substituting Equation 15 into Equations 6 and 8, eliminating η from Equations 7 and 8, differentiating Equation 6 with respect to y and eliminating $(\phi_a - \phi_c)$ from the resulting equations yields [6]

$$d^2\psi_a/dy^2 = (\varrho_a/t)(\psi_a - \psi_c^T - V_{eq} - a)/(\varrho_s d + b) \tag{16}$$

Solving Equation 16 under the conditions of Equations 3 and 4, gives

$$\psi_a = \psi_c^T + V_{eq} + a + (\psi_a^T - \psi_c^T - V_{eq} - a)[e^{\theta y/h}/(1 + e^{2\theta}) + e^{-\theta y/h}/(1 + e^{-2\theta})] \tag{17}$$

with

$$\theta = [(\varrho_a/t)/(\varrho_s d + b)]^{1/2} h = [(1 + Wa)\beta(d/h)]^{-1/2} \tag{18}$$

Inserting Equation 17 into Equation 6 for $y = 0$ and eliminating I by use of Equation 13, gives [6]

$$r_{ap} = [(\varrho_s d + b)/(wh)]\theta/\tanh(\theta) \tag{19}$$

3. Discussion

The quantity to be discussed here is the ratio of r_{ap} to r_{Lp}, given by

$$r_{ap}/r_{Lp} = \left\{(1 + Wa)\beta(d/h)^{-1/2}/\tanh[(1 + Wa)\beta(d/h)^{-1/2}]\right\}\left\{1 + [Wa/(1 + Wa)]\sum_{n=1}^{\infty} A_n + [(h/d)/(1 + Wa)]\sum_{n=1}^{\infty}(A_n/n\pi)\tanh(n\pi d/h)\right\}^{-1} \tag{20}$$

A numerical evaluation of r_{ap}/r_{Lp} was made for three-dimensional combinations of values of Wa, β and d/h, in the ranges $0.001 \leqq \beta \leqq 100$, $0.001 \leqq Wa \leqq 100$ and $0.001 \leqq d/h \leqq 1$, which are expected to cover most of the conditions employed in practical electrolysis. Some examples are shown in Figs 2–4, in which values of r_{ap}/r_{Lp} have been plotted against β, Wa and d/h, respectively. The departure of r_{ap}/r_{Lp} from unity in these curves is associated with the approximation that current lines in solution could be regarded as normal to the electrodes. When values of β and Wa increase, the degree of the approximation becomes better, as shown in Figs 2 and 3. For such large values

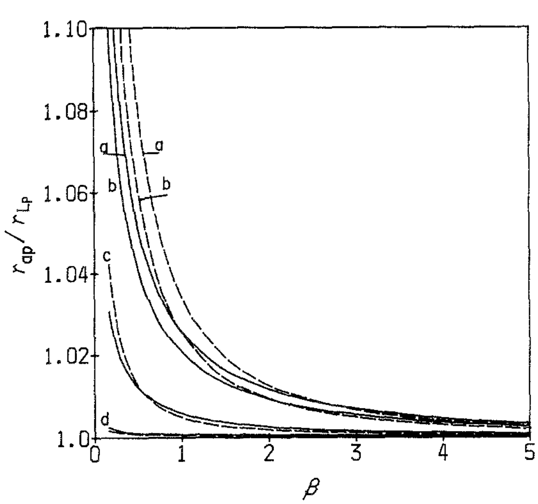

Fig. 2. Variations of r_{ap}/r_{Lp} with β for Wa equal to: (a) 0.01; (b) 0.1; (c) 1; (d) 10, when values of d/h are 0.2 (solid curves) and 0.5 (dashed curves).

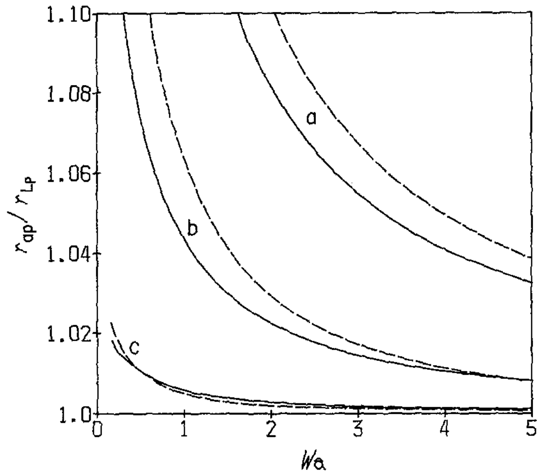

Fig. 3. Variations of r_{ap}/r_{Lp} with Wa for β equal to (a) 0.01; (b) 0.1; (c) 1, when values of d/h are 0.2 (solid curves) and 0.5 (dashed curves).

of β the anode is so conductive that it can be regarded as equipotential. Consequently, current in solution flows normal to the electrode. When values of Wa are large the contribution of overpotential to the cell voltage is predominant and hence variations of current lines in solution have minor effects on the cell resistance.

On the contrary, variations of r_{ap}/r_{Lp} with d/h are not so marked as those with β or Wa, as shown in Fig. 4. This is an interesting result because it has been reported [1] that the current distribution largely depends on d/h (see curves in Figs 9 and 10 of [1]). For example, values of the electrode utilization factor [4], which is a measure of the effective utilization of the electrodes defined by i_{max}/i_{av}, are 4.0, 2.8, 1.8 and 1.4 at $d/h = 0.5$ for curves a, b, c and d, respectively, when calculated from Equation 22 of [1] which was derived from the Laplace equation [1]. On the other hand, values of i_{max}/i_{av} calculated from Equation 30 of [1] are 3.2, 2.3, 1.6 and 1.3. Comparison of these values indicates that variations of current distribution are sensitive to those of the cell resistance [8, 9]. As d/h increases from zero, the curves in Fig. 4 gradually increase and then take a peaked shape. The increase in r_{ap}/r_{Lp} is obviously due to deviation of current lines in solution from the direction normal to the electrode. The decrease in r_{ap}/r_{Lp} beyond the peak may be explained by the fact that current lines in solution smooth with an increase in d/h.

The aim of this paper is to find domains of β, Wa and d/h in which r_{ap}/r_{Lp} can be regarded as unity.

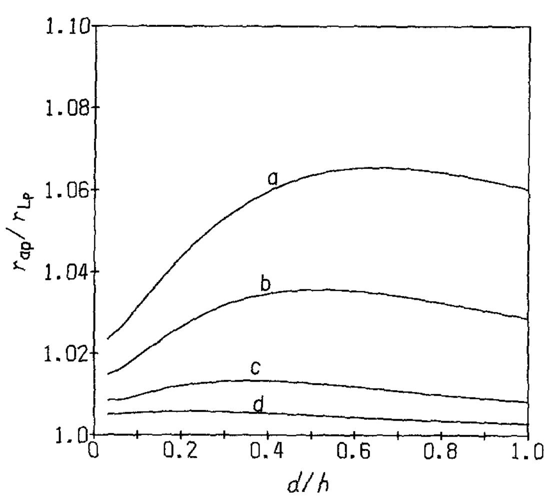

Fig. 4. Dependence of r_{ap}/r_{Lp} on d/h for $Wa = 1$ when values of β are (a) 0.1; (b) 0.2; (c) 0.5; (d) 1.

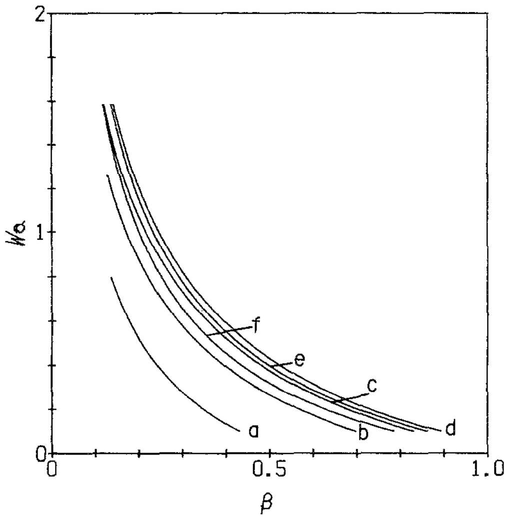

Fig. 5. Domain of β and Wa in which values of r_{ap}/r_{Lp} have less than 3% error for d/h equal to (a) 0.1; (b) 0.2; (c) 0.3; (d) 0.5; (e) 0.7; (f) 1.0.

By computing Equation 20 for various combinations of β, Wa and d/h, three-dimensional data files for β, Wa and d/h were made so that values of r_{ap}/r_{Lp} were 1.01, 1.02, 1.03, 1.04 and 1.05. In Fig. 5, plots of Wa against β for $r_{ap}/r_{Lp} = 1.03$ are shown for several values of d/h. If values of β and Wa fall in the upper right domain of a curve in Fig. 5 for a given value of d/h, the cell resistance corresponding to β, Wa and d/h can be evaluated from the simple approximate Equation 19 within 3% errors. Since the curve for $d/h = 0.5$ in Fig. 5 is in the most upper right location, the approximate Equation 19 holds for any value of d/h as long as β and Wa belong to the upper right domain. It was found that the plot of log $(1 + Wa)$ against log (β) for the curves in Fig. 5 fell on a straight line. From this, the domain of β and Wa in which Equation 19 was valid within z% errors could be formulated:

$$(1 + Wa)\beta^p > q \tag{21}$$

where p and q are constants given in Table 1 for several values of z%. Within a few percentages of z, Equation 21 is roughly reduced to

$$[1 + b/(\varrho_s d)]^2(\varrho_s/h) > \varrho_a/t \tag{22a}$$

or

$$\theta < [\varrho_a h/(\varrho_s t)]^{1/4}(h/d)^{1/2} \tag{22b}$$

For most cases, values of ϱ_a/ϱ_s are less than 10^{-3}. Then, values of θ are less than 5 for $h/d = 3$ and $h/t = 3$. Therefore, all curves in Figs 3 and 4 of [6] are valid.

In conclusion, under the conditions of Equations 21 or 22 and for any value of d/h, the approximation that current lines in solution are normal to the electrode is valid when diagnosed through the cell resistance. Then the cell resistance can be evaluated from Equation 19.

Table 1. Coefficients of p *and* q *in Equation 21*

z(%)	p	q
1	0.58	1.64
2	0.50	1.21
3	0.46	1.04
4	0.42	0.99
5	0.42	0.88

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