

Calculation of mean current densities in a two rotating disc electrodes system

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A theoretical relationship for mass transfer in the laminar flow region of streaming in a rotating electrolyser was derived by the method of similarity of the diffusion layer for electrodes placed sufficiently far from the rotation axis. The obtained relationship was compared with the known equations valid for systems with axial symmetry. The mean current densities were found from the numerical solution of the convective diffusion equation by the finite-element method and were compared with experimental results.

Nomenclature

a	constant, exponent	v_z	normal velocity component
c	concentration	z	normal coordinate
c_0	concentration in the bulk phase	γ	thickness of the layer in which the equation of convective diffusion is solved
C_{ij}	matrix coefficient	Γ	boundary of the integration domain
D	diffusion coefficient	δ	thickness of the diffusion layer
F	Faraday constant, 96487 C mol^{-1}	δ_N	thickness of the Nernst diffusion layer
h	interelectrode distance	ν	kinematic viscosity
j	current density	ω	angular velocity
\bar{j}	mean current density	Ω	surface
J	mass flux density	<i>Criteria</i>	
L_j	base function	Re_{chan}	channel Reynolds number $Q/h\nu$
n	number of transferred electrons in electrode reaction	Re_{loc}	local Reynolds number, $Q/\pi\nu(r + r_0)$
n_{Γ}	outer normal to the boundary	\bar{Re}_{loc}	local Reynolds number at mean electrode radius, $Q/\pi\nu(r_1 + r_0)$
\dot{n}	mass flux	Re_{rot}	rotation Reynolds number, $\omega r_d^2/\nu$
N	number of nodal points in an element	\bar{Re}_{rot}	modified rotation Reynolds number at mean electrode radius, $\omega(r_1 + r_0)^2/4\nu$
Q	volume rate of flow	Re'_{rot}	modified rotation Reynolds number, $\omega(r + r_0)^2/4\nu$
\bar{Q}	mean volume rate of flow	Sc	Schmidt number, ν/D
r	radial coordinate	$Sh_{\Delta r}$	local Sherwood number, $j(r - r_0)/nFDc_0$
r_0	inner electrode radius	$\bar{Sh}_{\Delta r}$	mean Sherwood number, $\bar{j}(r_1 - r_0)/nFDc_0$
r_1	outer electrode radius	Ta	Taylor number, $h(\omega/\nu)^{1/2}$
r_v	radius of inlet orifice		
r_d	outer disc radius		
v_r	radial velocity component		

1. Introduction

A system of two rotating parallel disc electrodes with axial inlet of electrolyte is denoted in the literature as a rotating electrolyser [1]. One of the disc electrodes is provided with a central hole for the electrolyte inlet [2]; the electrodes are electrically insulated and fixed to a common axis, around which they rotate at an angular velocity, ω , (Fig. 1). Interaction between radial flow of

electrolyte and rotation of the disc brings about a strong streaming in their proximity, so that the anolyte and catholyte are hydrodynamically separated from each other if the flow is laminar and the rotation speed is sufficiently high [3]. It is also possible to use this equipment as a diaphragmless electrolyser [1, 4].

A survey of results from the solution of a system of Navier–Stokes equations and the continuity equation

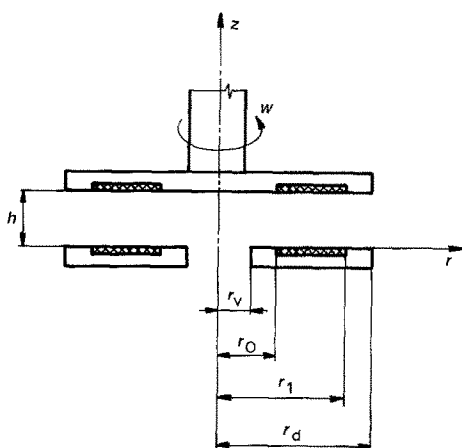


Fig. 1. Rotating electrolyser. (Symbols: as denoted in nomenclature listing).

and analysis of the course of the velocity components and of the static pressure in a rotating electrolyser was given by Jansson [1]. The velocity field and the static pressure were approximated by functions of first and third order [1] and later by functions of fifth order [5]. Analysis of the velocity field showed that for higher values of the Taylor number ($Ta = h(\omega/\nu)^{1/2} \geq 14$) and of the channel Reynolds number ($Re_{\text{chan}} = Q/h\nu \geq 1500$) the functions of third and higher orders oscillate, impairing the accuracy of the description of the velocity field close to the inlet [5].

To calculate the velocity field, not only the kinematic viscosity of the electrolyte, ν , the interelectrode distance, h , and the angular velocity, ω , must be known, but also the volume flow rate, Q . If the electrolyte is forced to flow by means of an external pump, the value of Q is known; if it flows spontaneously, the value of Q is governed by the angular velocity, the geometry of the system, and the physical properties of the electrolyte. Ferreira and Jansson [6] measured the volume rate of flow in a system with an inlet orifice radius $r_v = 13$ mm and a disc radius $r_d = 76$ mm by following the rate of passage of injected CuSO_4 toward a detector electrode. They found that Q ($\text{cm}^3 \text{s}^{-1}$) can be approximated by the empirical equation

$$Q = 4.173 \omega^{0.9737} \quad (1)$$

valid for ω up to 42 s^{-1} and h from 1.7 to 8 mm. Accordingly, the volume rate of flow is independent of the interelectrode distance, h .

Transition from laminar to turbulent flow takes place at $Re_{\text{rot}} = \omega r_d^2/\nu \simeq 1.8 \times 10^5$ [4] in accord with measurements on a free rotating disc [7]. Ferreira and Jansson [6] gave the critical values of the mean Reynolds rotation criterion characterizing the transition to turbulent flow for electrodes at various distances from the disc centre. These critical values depend on the inter-electrode distance.

The convective equation has not been solved for a rotating electrolyser. Measurement of the mass transfer [4] in the limiting current region showed that the Reynolds rotation criterion ($Re_{\text{rot}} = \omega r_d^2/\nu$) rather than the Taylor criterion ($Ta = h(\omega/\nu)^{1/2}$) is suitable

for the calculation of the mean current density, \bar{j} . Thus, for the studied system ($r_v = r_0 = 22$ mm, $r_1 = r_d = 78$ mm, $h = 3.5$ or 6.4 mm) the following equation was found by Jansson [4]:

$$\bar{j} = 0.225 n Re_{\text{rot}}^{0.565} c_0 \quad (2)$$

where \bar{j} is expressed in A cm^{-2} , c_0 (mol cm^{-3}) denotes the concentration of electroactive species and n is the number of transferred electrons.

More accurate measurements [6] on a system with $r_v = 13$ mm and $r_d = 76$ mm and with electrodes located at various distances from the centre in the self-pumping regime led to the conclusion that the rotation Reynolds criterion should involve the mean radius of the disc electrode defined as

$$r_{\text{av}} = [\frac{1}{2}(r_0^2 + r_1^2)]^{1/2} \quad (3)$$

Then the mean current density \bar{j} can be expressed as

$$\bar{j} = a_1 n Re_{\text{rot,av}}^{a_2} c_0 \quad (4)$$

where $Re_{\text{rot,av}} = \omega r_{\text{av}}^2/\nu$, a_1 (in A cm mol^{-1}) and a_2 are constants for the given geometry, $a_2 = 0.43 - 0.58$, c_0 in mol cm^{-3} [6].

The object of the present work was to find a theoretical dependence for the mass transfer in the laminar flow region.

We suppose that the electrode reaction is very fast and the solution contains an excess of supporting electrolyte, so that we may neglect the migration term in the equation of convective diffusion for an electroactive ion (minor species). We used the method of similarity of diffusion layer and numerical solution of the convective diffusion equation by the finite-element method. The results are compared with experimental data from the literature.

2. Method of similarity of the diffusion layer

The assumption of similarity of the diffusion layer profiles [8] implies that the concentration distribution $c(z)$ of the electroactive species in the diffusion layer at any distance, r , from the centre can be described by the same function of the distance, z , from the electrode surface. We assume that $c(z)$ can be expressed by a polynomial of, at most, third order,

$$c(z)/c_0 = a_0 + a_1 z + a_2 z^2 + a_3 z^3 \quad (5)$$

where $a_0 \dots a_3$ are constants and c_0 denotes the bulk concentration. We define the thickness, δ , of the diffusion layer by the conditions that at the electrode surface ($z = 0$) we have $c = 0$, $\partial^2 c/\partial z^2 = 0$, and for $z = \delta$ we have $c = c_0$, $\partial c/\partial z = 0$; the value of δ in the distance r from the rotation axis. The condition $\partial^2 c/\partial z^2 = 0$ for $z = 0$ is exactly valid only for binary electrolytes (e.g. $\text{CuSO}_4\text{-H}_2\text{O}$) [9] and as a good approximation for systems with large excess of the supporting electrolyte (e.g. for $0.001 \text{ M K}_3\text{Fe(CN)}_6$, $0.001 \text{ M K}_4\text{Fe(CN)}_6$, 0.1 M NaOH). These four conditions enable us to determine the constants in

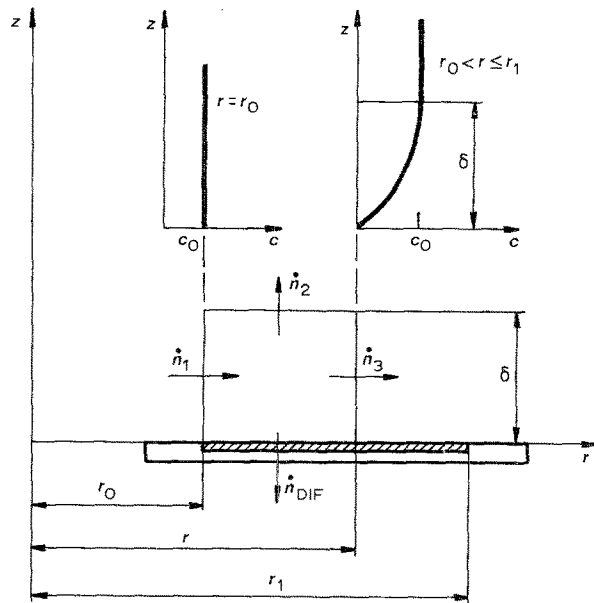


Fig. 2. Mass balance in an element at the lower electrode and concentration profile at points r_0 and r . (Symbols: as denoted in nomenclature listing).

Equation 5, which thus takes the form of

$$c(z)/c_0 = 1.5 z/\delta - 0.5(z/\delta)^3 \quad (6)$$

The thickness δ , thus defined, is related to the Nernst diffusion layer thickness, δ_N , as $\delta = 1.5 \delta_N$ [8].

The dependence of δ on the radius r is obtained from the mass balance in a volume element of thickness δ , which is shown in Fig. 2 together with the concentration profiles at $r = r_0$ and at a distance r from the disc centre. Since we consider the steady state without a source, the mass fluxes \dot{n} satisfy the equation

$$\dot{n}_1 - \dot{n}_2 - \dot{n}_3 = \dot{n}_{\text{dif}} \quad (7)$$

These quantities have the character of convective flows. Analytically expressed, they are of the form:

$$\begin{aligned} c_0 r_0 \int_0^\delta v_r(r_0) dz - c_0 \int_{r_0}^r r v_z(\delta) dr \\ - r \int_0^\delta v_r(r) c(z) dz = D \int_{r_0}^r r \left(\frac{\partial c}{\partial z} \right)_{z=0} dr \end{aligned} \quad (8)$$

The concentration c in the second integral is located in the distance δ from the electrode and is constant $c = c_0$ at boundary δ .

The concentration distribution in the diffusion layer is approximated by Equation 6. Simple relations for the radial, v_r , and normal, v_z , velocity components of the electrolyte can only be obtained if the electrode surface is located sufficiently far from the rotation axis; then the expansions for the velocity components involve only terms inversely proportional to the dimensionless radius [1, 5] and the terms of higher order can be neglected. (See Appendix A)

Accordingly, we may set the normal velocity component equal to zero and the radial velocity at the electrode sufficiently apart from the rotation axis can be estimated from the Taylor theorem [10] as

$$v_r(z) \simeq v_r(0) + \left(\frac{\partial v_r}{\partial z} \right)_{z=0} z \quad (9)$$

where $v_r(0) = 0$ according to the condition of adherence. The final approximate equation for the radial velocity at the wall is

$$v_r(z) \simeq Q\omega z/2\pi\nu r \quad (10)$$

We may assume that this equation holds good up to a distance z from the electrode surface, where the radial velocity attains its maximum value [11].

On introducing equations 6 and 10 into 8 with regard to the condition $v_z(\delta) \simeq 0$ (the terms of third and higher order) we can be neglected in comparison to the term of first order) we obtain

$$\begin{aligned} (Q\omega c_0/\nu) \left\{ \int_0^\delta z dz - \int_0^\delta [1.5(z/\delta) - 0.5(z/\delta)^3] z dz \right\} \\ = 3\pi D c_0 \int_{r_0}^r (r/\delta) dr \end{aligned} \quad (11)$$

and after calculating the integrals

$$Q\omega\delta^2 = 30\pi\nu D \int_{r_0}^r (r/\delta) dr \quad (12)$$

The thickness of the diffusion layer, δ , depends on the distance, r , from the centre, hence the integral in Equation 12 cannot be evaluated in a simple way. However, if $r \simeq r_0$, the value of δ can be considered constant and we obtain

$$\delta = [15\pi\nu(r^2 - r_0^2)D/\omega Q]^{1/3} \quad (13)$$

(See Appendix B)

Let us assume that the proportionality between δ and $(r^2 - r_0^2)^{1/3}$ is preserved even for r not close to r_0 ; then Equation 12 gives

$$\delta = [22.5\pi\nu(r^2 - r_0^2)D/\omega Q]^{1/3} \quad (14)$$

This result cannot be used in the region where the radial velocity profile is not fully developed ($Ta \leq 3$) and when δ is larger than the normal distance of the radial velocity maximum from the electrode. (See Appendix C)

Knowledge of the diffusion layer thickness allows calculation of the local diffusion flux intensity to the electrode

$$J_{n,\text{dif}} = -D \left(\frac{\partial c}{\partial z} \right)_{z=0} \quad (15)$$

Equation 6 gives

$$\left(\frac{\partial c}{\partial z} \right)_{z=0} = 1.5c_0/\delta \quad (16)$$

and therefore

$$J_{n,\text{dif}} = -1.5Dc_0/\delta \quad (17)$$

The negative sign means that the intensity of the diffusion flux is directed against the z -axis.

For rapid electrode reactions, the current is controlled by diffusion of electroactive species to the electrode surface and the limiting current density is given as

$$j = nFJ_{n,\text{dif}} \quad (18)$$

which, together with Equations 14 and 17, gives

$$j = 0.363nFD^{2/3} c_0(\omega Q/\nu)^{1/3} (r^2 - r_0^2)^{-1/3} \quad (19)$$

This can be transformed into dimensionless form by introducing the dimensionless criteria; the characteristic length for the Reynolds number is the mean radius $\frac{1}{2}(r + r_0)$ and that for the Sherwood number is the distance from the inner electrode boundary. We set:

the local Sherwood number, $Sh_{\Delta r} = j(r - r_0)/nFDc_0$;

the local Reynolds number, $Re_{loc} = Q/[\pi v(r + r_0)]$;

the modified rotation Reynolds number, $Re'_{rot} = \omega(r + r_0)^2/4v$; and

the Schmidt number, $Sc = v/D$

Thus, Equation 19 takes the form

$$Sh_{\Delta r} = 0.841 [(r - r_0)/(r + r_0)]^{2/3} Sc^{1/3} Re_{loc}^{1/3} Re'_{rot}{}^{1/3} \quad (20)$$

The mean current density to the electrode of inner radius r_0 and outer radius r_1 is calculated as follows:

$$\bar{j} = \int_{r_0}^{r_1} 2\pi jr \, dr / \int_{r_0}^{r_1} 2\pi r \, dr \quad (21)$$

On introducing Equation 19 and rearranging, we obtain

$$\bar{j} = 0.544 nFD^{2/3} c_0 (\omega Q/v)^{1/3} r_1^2 - r_0^2)^{-1/3} \quad (22)$$

By introducing the criteria

$$\bar{Sh}_{\Delta r} = \bar{j}(r_1 - r_0)/nFDc_0 \quad (23a)$$

$$\bar{Re}_{loc} = Q/\pi v(r_0 + r_1) \quad (23b)$$

$$\bar{Re}_{rot} = \omega(r_0 + r_1)^2/4v \quad (23c)$$

Equation 22 can be put into the dimensionless form

$$\bar{Sh}_{\Delta r} = 1.262 [(r_1 - r_0)/(r_1 + r_0)]^{2/3} Sc^{1/3} \bar{Re}_{loc}^{1/3} \bar{Re}_{rot}^{1/3} \quad (24)$$

which can be considered as the basic criterion equation for the mass transfer in a rotating electrolyser with electrodes placed at a sufficient distance from the axis of rotation in the laminar regime.

3. Comparison of equations for mass transfer in a rotating electrolyser with equations for other axial symmetric system

From the practical point of view, the basic axisymmetric system is a rotating disc electrode. The volume rate of flow leaving the disc by centrifugal force, on one side of the disc, at a distance r from the rotation axis is given as [12]

$$Q = 0.886\pi r^2 (\omega v)^{1/2} \quad (25)$$

The mean value of Q at the disc of radius r_d can be calculated as

$$\bar{Q} = \int_0^A Q \, dA / \int_0^A dA = \int_0^{r_d} 2\pi r Q \, dr / \int_0^{r_d} 2\pi r \, dr \quad (26)$$

On introducing Equation 25 we obtain

$$\bar{Q} = 0.443\pi r_d^2 (\omega v)^{1/2} \quad (27)$$

On combining this result with the criterion Equation

24 for a rotating electrolyser, we obtain, for a free disc ($r_0 = 0$),

$$\bar{Sh}_{\Delta r} = 1.215 Sc^{1/3} \bar{Re}_{rot}^{1/2} \quad (28)$$

According to the theory of the rotating disc electrode [7], the criterion (Equation 23 involving the mean Sherwood number) and the rotation Reynolds number has the form

$$\bar{Sh}_{\Delta r} = 1.242 Sc^{1/3} \bar{Re}_{rot}^{1/2} \quad (29)$$

The latter two equations differ merely by the constants of proportionality, their relative difference being 2.2%.

If we apply the same procedure to a rotating disc with a ring, we obtain from Equation 24

$$\bar{Sh}_{\Delta r} = 1.214 \left(\frac{r_1 - r_0}{r_1 + r_0} \right) \left(\frac{r_1^2 + r_0^2}{r_1^2 - r_0^2} \right)^{1/3} Sc^{1/3} \bar{Re}_{rot}^{1/2} \quad (30)$$

According to rotating ring-disc theory [7], the mean Sherwood number is given by

$$\bar{Sh}_{\Delta r} = 1.242 \frac{(r_1^3 - r_0^3)^{2/3}}{r_1^2 + r_0^2} Sc^{1/3} \bar{Re}_{rot}^{1/2} \quad (31)$$

In this case Equation 30 for the rotating electrolyser gives results lower by 2.2 (for $r_0 = 0$) to 6.0 per cent (for $r_0 = 0.9999 r_1$) then Equation 31 for the rotating disc with a ring.

If the discs rotate slowly ($Ta \leq 3$), the system behaviour approaches that of a capillary gap electrolyzer [13]. The criterion equation for this system has the form [8]

$$\bar{Sh}_{\Delta r} = 1.45 [(r_1 - r_0)/h]^{2/3} Sc^{1/3} \bar{Re}_{loc}^{1/3} \quad (32)$$

involving the mean Sherwood number and local Reynolds number (given in Equations 23a, b and c).

4. Calculation of mean current densities by the finite-element method

The finite-element method has become an efficient means for solving differential equations describing various physical problems [14–16]. We therefore used this method in solving the simplified equation of convective diffusion for mass transport to the electrodes of a rotating electrolyzer. In a cylindrical coordinate system, with axial symmetry, this equation reads

$$v_r \frac{\partial c}{\partial r} + v_z \frac{\partial c}{\partial z} = D \left(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial z^2} \right) \quad (33)$$

The integration domain near the electrode is divided into elements and the concentration in each of them is approximated by the expression

$$c = \sum_{j=1}^N L_j c_j \quad (34)$$

where N denotes the number of nodal points in an element and L_j the base function. The weighted residue method and Green's theorem served to derive the statement of the problem [17]. After rearrangement

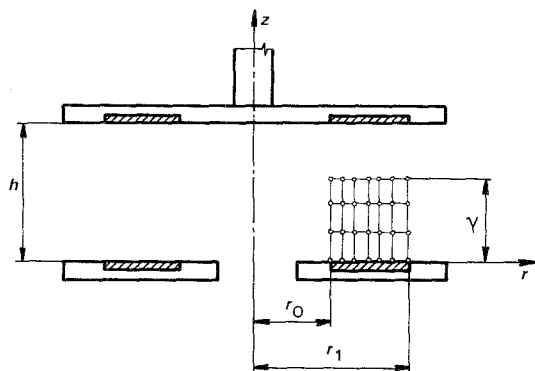


Fig. 3. Division of the integration domain into finite, linear, axial symmetric elements for solving the convective diffusion equation. (Symbols: as denoted in nomenclature listing).

we obtain for each element the system of equations

$$C_{ij}c_j = D \int_{\Gamma} r L_i \frac{\partial c}{\partial n_{\Gamma}} d\Gamma \quad (35)$$

where Γ denotes the boundary of the domain where no stable boundary condition (concentration) is prescribed, and n_{Γ} denotes the outer normal to the boundary. The term C_{ij} is defined as

$$C_{ij} = \iint_{\Omega} r \left(v_r \frac{\partial L_i}{\partial r} L_j + v_z \frac{\partial L_i}{\partial z} L_j + D \frac{\partial L_i}{\partial r} \frac{\partial L_j}{\partial z} + D \frac{\partial L_i}{\partial r} \frac{\partial L_j}{\partial z} \right) dr dz \quad (36)$$

The domain which is divided into elements can be set equal to that part of the interelectrode space in which the concentration rises from zero at the surface to c_0 in the bulk. A section of the space between the disc in the r - z plane with the domain for solving the convective diffusion Equation 33 is shown in Fig. 3. For numerical solution of this equation the simplest linear isoparametric elements with four nodal points ($N = 4$) were used.

Since complications arise in solving problems with dominant convective terms causing oscillations of the solution, we used the Petrov-Galerkin method [18]. Introduction of the boundary conditions presents no problems. The concentration of the electroactive species is assumed to be equal to zero ($c = 0$) at the electrode surface, whereas it is equal to the bulk concentration ($c = c_0$) at the inlet cross-sectional area of flow and at a plane parallel to the electrode at a distance $\gamma > \delta$. We assume that the diffusion flux through the inlet plane is negligible compared to the convective flow, i.e. $\delta c / \partial n_{\Gamma} = 0$.

The program was compiled by using the published schemes and methods [16]. The diffusion flux was determined from the macroscopic balance in the whole integration domain after calculating the concentrations at the nodal points. The domain was divided by a grid of 20×20 nodal points, i.e. 381 elements. The integral in Equation 36 was calculated by the Legendre-Gauss quadrature formula with a grid of 2×2 integration points [9].

The program for the numerical solution of the convective diffusion equation was used to calculate the mean current densities in a system studied experimentally by Ferreira and Jansson [6] with a solution of $0.001 \text{ M K}_3\text{Fe(CN)}_6 + 0.001 \text{ M K}_4\text{Fe(CN)}_6 + 0.1 \text{ M NaOH}$. The corresponding kinematic viscosity, ν , and the diffusion coefficient were measured [8, 20] as $\nu = 0.01 \text{ cm}^2 \text{ s}^{-1}$ and $D = 6.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at 25° C . The volume rate of flow was approximated by Equation 1 for any geometry, the radial and normal velocity components, v_r and v_z , were approximated by expansions with functions of up to third order [5]. The calculation of the mean current density was repeated for 14–18 values of the angular velocity ($1.6 \text{ s}^{-1} \leq \omega \leq 22.7 \text{ s}^{-1}$); the results were treated by the least squares method for a given geometry with the aid of the regression equation

$$\bar{j} = a_3 \omega^{a_4} \quad (37)$$

The correlation coefficient exceeded 0.99 in all cases; the calculation by the finite-element method lasted for ~ 50 – 60 s on an ICL 4-72 computer for each given angular velocity.

The values of a_3 and a_4 for approximation of the values of \bar{j} obtained experimentally [6], calculated by the finite-element method, calculated from Equation 24, and finally from Equation 31 are given in Table 1. The mean current densities calculated by the finite-element method for $\omega = 20 \text{ s}^{-1}$ differ from the experimental ones [6] by -4 – $+80\%$, those from Equation 24 differ by 48 – 150 and those from Equation 31 by 1 – 154% .

For an electrode with $r_0 = 26.8 \text{ mm}$, $r_1 = 37.5 \text{ mm}$ the relative error of the results calculated by the finite-element method (for $\omega = 20 \text{ s}^{-1}$) ranges from -4 – 11% ; for $r_0 = 38.7 \text{ mm}$ and $r_1 = 70.2 \text{ mm}$ from 18 – 45% ; and for $r_0 = 71.4 \text{ mm}$ and $r_1 = 76.0 \text{ mm}$ from 58 – 80% . In all cases, the error rises from the smallest value at the largest interelectrode distance ($h = 9.0 \text{ mm}$) to the highest value at the smallest distance ($h = 1.6 \text{ mm}$).

The best results were determined for the finite element method calculation although not without considerable errors (up to 80%). The sources of the error are the following. The kinematic viscosity, ν , and the diffusion coefficient, D , were estimated from literature [8, 20]. The error may be up to $\pm 10\%$. The volume flow rate was approximated by the empirical Equation 1, independent of geometric parameters of the system. The error of this equation may be up to $\pm 15\%$. Close to the external border of the electrode with the greatest radius ($r_0 = 71.4 \text{ mm}$, $r_1 = 76.0 \text{ mm}$) the current density may be influenced by effects related with changes of the flow toward the bulk of the solution (the error may be $\pm 30\%$ and more).

5. Conclusions

A relationship was found for the calculation of the mean current density to electrodes located at a sufficient

Table 1. Constants a_3 and a_4 for Equation 37 based on experimental data [6], on the numerical calculation by the finite-element, on Equation 24 for a rotating electrolyzer, and on Equation 31 for a rotating disc electrode with a ring.

r_0 (mm)	r_1 (mm)	h (mm)	Measured [6]		Calculated (FEM)		Equation 24		Equation 31	
			a_3 ($10^{-2} \text{ mA cm}^{-2}$)	a_4	a_3 ($10^{-2} \text{ mA cm}^{-2}$)	a_4	a_3 ($10^{-2} \text{ mA cm}^{-2}$)	a_4	a_3 ($10^{-2} \text{ mA cm}^{-2}$)	a_4
26.8	37.5	1.6	8.58	0.4325	9.12	0.4005	7.47	0.6579	7.06	0.5
		4.5	7.25	0.4758	7.26	0.5039	7.47	0.6579	7.06	0.5
		9.0	7.69	0.4661	7.29	0.5201	7.47	0.6579	7.06	0.5
38.7	70.2	1.6	2.99	0.5880	4.51	0.5776	4.38	0.6579	5.95	0.5
		4.5	3.91	0.5593	4.16	0.6010	4.38	0.6579	5.95	0.5
		9.0	4.10	0.5504	4.16	0.6010	4.38	0.6579	5.95	0.5
71.4	76.0	1.6	4.44	0.5295	7.10	0.5746	7.51	0.6579	12.3	0.5
		4.5	6.44	0.4983	7.07	0.6208	7.51	0.6579	12.3	0.5
		9.0	6.34	0.4818	7.07	0.6208	7.51	0.6579	12.3	0.5

distance from the axis of rotation. This relationship (Equation 24) takes the form of Equation 29 known from the theory of the rotating disc electrode, if the mean rate of flow at the rotating disc is introduced, within an error of 2.2%.

For a rotating electrolyzer with electrodes located nearer to the axis of rotation, Equation 24 cannot be used and the mean current density must be found from the numerical solution of the convective diffusion equation. However, close to the inlet at a higher rotation speed oscillations take place, making the numerical solution impossible. Equation 31 for the rotating disc with a ring does not involve the volume rate of flow; the relative error of the mean current density \bar{j} from Equation 31 at $\omega = 20 \text{ s}^{-1}$, compared to the experimental values, ranges from 1 to 154% according to the geometry of the electrodes.

Appendix A: Condition of a sufficient distance from the rotation axis

The radial velocity, v_r , in a rotating electrolyzer is approximated by the equation [1, 5]

$$v_r = v \left[\frac{f_1'(\bar{z})}{r} + \frac{v}{\omega} \frac{f_3'(\bar{z})}{r^3} + \left(\frac{v}{\omega} \right)^2 \frac{f_5'(\bar{z})}{r^5} + \dots \right] \quad (\text{A-1})$$

where $\bar{z} = (z - h/2)(\omega/v)^{1/2}$ denotes dimensionless distance. At a sufficient distance from the axis of rotation, we assume that the functions of higher order than one are negligible. Hence,

$$\left| \frac{f_1'(\bar{z})}{r} \right| \gg \left| \frac{v}{\omega} \frac{f_3'(\bar{z})}{r^3} \right| \quad (\text{A-2})$$

Close to the electrode, where the equation of convective diffusion is solved, the functions $f_1'(\bar{z})$ and $f_3'(\bar{z})$ are approximated by using the Taylor theorem in the form

$$\left. \begin{aligned} f_1'(\bar{z}) &= f_1'(\bar{z}_b) + f_1''(\bar{z}_b)(\bar{z} - \bar{z}_b) \\ f_3'(\bar{z}) &= f_3'(\bar{z}_b) + f_3''(\bar{z}_b)(\bar{z} - \bar{z}_b) \end{aligned} \right\} \quad (\text{A-3})$$

where \bar{z}_b denotes the dimensionless normal coordinate of the lower disc ($z = 0$), i.e. $\bar{z}_b = -h/2(\omega/v)^{1/2}$. At the lower disc the functions f_1 and f_3 acquire the values [1, 5]

$$\left. \begin{aligned} f_1'(\bar{z}_b) &= f_3'(\bar{z}_b) = 0 \\ f_1''(\bar{z}_b) &= Q(\omega/v^3)^{1/2}/(2\pi) \\ f_3''(\bar{z}_b) &= -3Q^2\omega/(40\pi^2v^3) \end{aligned} \right\} \quad (\text{A-4})$$

By introducing Equations A-3 and A-4 into A-2 we obtain, after rearrangement,

$$r^2 \gg 3Q/[20\pi(\omega v)^{1/2}] \quad (\text{A-5})$$

The radial velocity must be well described in the whole interelectrode space, i.e. beginning from the inner electrode boundary. Equation A-5 for $r = r_0$ expresses the condition for a sufficient distance from the rotating axis. By introducing the rotation Reynolds number ($Re_{\text{rot},r_0} = \omega r_0^2/v$) and the local Reynolds number ($Re_{\text{loc},r_0} = Q/2\pi v r_0$) at the inner electrode boundary, we obtain from Equation A-5 the condition

$$Re_{\text{rot},r_0}^{1/2}/Re_{\text{loc},r_0} \gg 0.3 \quad (\text{A-6})$$

Appendix B

The thickness of the diffusion layer $\delta = \delta(r)$ can be approximated by means of the thickness of the diffusion layer $\delta(r')$ at the point r' ($r_0 \leq r \leq r_1$) as

$$\delta(r) = \delta(r')[(r^2 - r_0^2)/(r'^2 - r_0^2)]^{1/3} \quad (\text{B-1})$$

On introducing $\delta(r)$ from Equation B-1 into 12, and while rearranging, we obtain

$$Q\omega\delta^2(r) = 30\pi v D \frac{(r'^2 - r_0^2)^{1/3}}{\delta(r')} \int_{r_0}^r \frac{r dr}{(r^2 - r_0^2)} \quad (\text{B-2})$$

After calculation of the integral in Equation B-2 we obtain

$$Q\omega\delta^2(r) = 22.5\pi v D (r'^2 - r_0^2)^{1/3} (r^2 - r_0^2)/\delta(r') \quad (\text{B-3})$$

By eliminating $\delta(r')$ from Equations B-1 and B-3, we receive for $\delta(r)$

$$Q\omega\delta^2(r) = 22.5\pi\nu D(r^2 - r_0^2)/\delta(r) \quad (\text{B-4})$$

and

$$\delta^3(r) = 22.5\pi\nu D(r^2 - r_0^2)/\omega Q \quad (\text{B-5})$$

Equation B-5 is equivalent to Equation 14.

Appendix C: Condition for the diffusion layer not to extend a greater distance from the electrode than would correspond to the radial velocity maximum

The approximation of the radial velocity at a sufficient distance from the rotation axis (Condition A-6) is

$$v_r = \nu \frac{f_1'(\bar{z})}{r} \quad (\text{C-1})$$

That is, in Equation A-1 we neglected the terms of higher order than the first. We assume that the radial velocity maximum lies at a distance d measured from the upper electrode; d corresponds to the dimensionless coordinate $\bar{d} = (h/2 - d)/(\omega/\nu)^{1/2}$. At the local extremum the first derivative is equal to zero: i.e.

$$\frac{\partial v_r}{\partial \bar{z}} = 0 \quad (\text{C-2})$$

which together with Equation (C-1) gives

$$f_1''(\bar{d}) = 0 \quad (\text{C-3})$$

The function $f_1'(\bar{z})$ is given by [1, 5]:

$$f_1'(\bar{z}) = (A_1 + B_1) \sinh \bar{z} \cos \bar{z} + (B_1 - A_1) \cosh \bar{z} \sin \bar{z} \quad (\text{C-4})$$

where

$$A_1 = Q(\omega/\nu^3)^{1/2} \sinh \bar{z}_t \sin \bar{z}_t / [\pi(\sinh 2\bar{z}_t - \sin 2\bar{z}_t)] \quad (\text{C-5a})$$

$$B_1 = -Q(\omega/\nu^3)^{1/2} \cosh \bar{z}_t \cos \bar{z}_t \times [\pi(\sinh 2\bar{z}_t - \sin 2\bar{z}_t)] \quad (\text{C-5b})$$

and \bar{z}_t denotes dimensionless normal distance of the upper electrode ($z = h$), $\bar{z}_t = (h/2)(\omega/\nu)^{1/2}$.

For a well-developed streaming profile ($Ta \gtrsim 5$; and $\sinh \bar{d} \simeq \cosh \bar{d}$) we obtain, by combining Equations C-3 and C-4

$$\frac{A_1 + B_1}{A_1 - B_1} = \frac{\sin \bar{d}}{\cos \bar{d}} \quad (\text{C-6})$$

If the constants A_1 and B_1 are expressed by Equations C-5a and b and using the condition $\sinh \bar{z}_t \simeq \cosh \bar{z}_t$, we obtain

$$\frac{\sin \bar{z}_t - \cos \bar{z}_t}{\sin \bar{z}_t + \cos \bar{z}_t} = \frac{\sin \bar{d}}{\cos \bar{d}} \quad (\text{C-7})$$

and after rearrangement

$$\frac{\cos(-\bar{d} + \pi/4 + \bar{z}_t)}{\sin(\pi/4 + \bar{z}_t) \cos \bar{d}} = 0 \quad (\text{C-8})$$

This relation is satisfied if the numerator is equal to zero, i.e. if

$$-\bar{d} + \pi/4 + \bar{z}_t = \pi/2 + k\pi, \quad k = 0, \pm 1, \pm 2 \dots \quad (\text{C-9})$$

After rearrangement the previously given condition can be written for $k = 0$ as

$$d = 0.25\pi(\nu/\omega)^{1/2} \quad (\text{C-10})$$

For the condition used in deriving Equation 14 to be satisfied, the thickness of the diffusion layer, δ , must not exceed the distance of the radial velocity maximum from the electrode. Thus,

$$\delta < d \quad (\text{C-11})$$

By introducing Equations 14 and C-10 into the inequality C-11 we obtain, after rearrangement, the sought condition in the form

$$\frac{(r_1^2 - r_0^2) D}{Q} (\omega/\nu)^{1/2} < 6.86 \times 10^{-3} \quad (\text{C-12})$$

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