JOURNAL OF APPLIED ELECTROCHEMISTRY **21** (1991) 6–10

Local current densities in a two rotating disc electrode system with an axial electrolyte inlet measured by an autoradiographic method

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Received 24 November 1989; revised 20 February 1990

The distribution of local current densities in a rotating electrolyser with axial electrolyte inlet in a laminar flow regime was studied by the autoradiographic method. With all systems studied, the local current density decreased monotonically from a maximum value at the inner to a minimum at the outer boundary of the electrode. Experimental results are compared with the numerical solution of the convective diffusion equation by the finite element method.

Nomenclature

a, b	constants
c	concentration
c_0	concentration in the bulk phase
d	optical density
D	diffusion coefficient
F	Faraday constant, 96 487 C mol^{-1}
h	interelectrode distance
j	local current density
$J_{n,\text{dif}}$	density of diffusion flux in outer normal direction
n	number of electrons transferred in the elementary step
$\dot{n}_{\text{dif}}$	diffusion flux
Q	volume rate of flow
r	radial coordinate
r_0	inner electrode radius
r_1	outer electrode radius
r_v	radius of inlet orifice
r_d	outer disc radius
t	time
v_r	radial velocity component of liquid
v_z	normal velocity component of liquid
z	normal coordinate
γ	thickness of the layer in which the equation of convective diffusion is solved
ν	kinematic viscocity
ω	angular velocity

1. Introduction

An electrolyser with two rotating parallel discs with an axial inlet of electrolyte is denoted in the literature as a rotating electrolyser. This system has been studied both theoretically and practically by a number of authors [1–5]; its description and a survey of results were given in our earlier work [6]. However, the distribution of local current densities on the disc electrodes has not been studied as yet. The mean current densities were measured in various model systems [3, 5, 6]; the following analytical expression was derived for the local current density in a rotating electrolyser with electrodes located far from the rotation axis [6]:

$$j = 0.363\, nFD^{\frac{2}{3}} c_0 (\omega Q/r)^{\frac{1}{3}} (r^2 - r_0^2)^{-\frac{1}{3}} \qquad (1)$$

For electrodes located closer to the rotation axis, the mean current densities are approximated by numerical solution of the convective diffusion equation by the finite-element method [6, 7].

Our aim was to determine the local current densities in a model rotating electrolyser and to compare them with Equation 1 and with the results of numerical solution of the convective diffusion equation by the finite-element method.

2. Theoretical

It was found [7] that the mean current densities in a rotating electrolyser are well approximated (± 10%) by numerical solution of the convective diffusion equation. This was achieved by the finite-element method; the structure of the program for the calculation of the local current densities was the same as in our earlier work [6]. It turned out that it is not suitable to calculate the local current densities (or the local

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intensities of the diffusion flux $J_{n,\mathrm{dif}}$) form the derivative of the concentration with respect to the normal

$$J_{n,\mathrm{dif}} = -D\left(\frac{\partial c}{\partial z}\right)_{z=0} \tag{2}$$

and it is preferable to proceed analogously as in the calculation of the mean current densities [6]. We assume that if the division into elements is sufficiently fine in the radial direction (19 elements), then the mean intensity of the diffusion flux in a given element is approximately equal to the local intensity in the centre of this element. Then

$$\begin{aligned} J_{n,\mathrm{dif}} &= \dot{n}_{\mathrm{dif}}/\pi\,(r_i^2 - r_{i-1}^2) \\ &= 2\Big[r_{i-1}\int_0^{\gamma} c(r_{i-1})v_{\mathrm{r}}(r_{i-1})\,\mathrm{d}z \\ &\quad - \int_{r_{i-1}}^{r_i} c(\gamma)rv_z(\gamma)\mathrm{d}r \\ &\quad - r_i\int_0^{\gamma} v_{\mathrm{r}}(r_i)c(r_i)\mathrm{d}z\Big]\Big/(r_i^2 - r_{i-1}^2) \end{aligned} \tag{3}$$

Here, r_{i-1} denotes inner radius and r_{i} outer radius of an element of the integration domain (electrode area), c concentration, v_{r} radial velocity, v_z normal velocity, γ thickness of the domain in which the equation of convective diffusion is solved. Equation 3 is valid for systems with fast electrochemical reaction in the presence of an excess of supporting electrolyte where the migration term can be neglected.

The velocity field was approximated by expansions involving functions of up to third order [1, 4], and the volume rate of flow by equations derived experimentally for the same geometry of the set-up [7]. Local current densities, j, at the centre of each element are obtained from Equation 3 and the relation

$$j = nFJ_{n,\mathrm{dif}} \tag{4}$$

where n is the number of electrons transferred in an elementary step.

3. Experimental details

A particularly efficient method for the study of the local current density distribution is the autoradiographic method [8–10]. This is based on detection of the radiation of a galvanically deposited radioactive tracer on the electrode. The silver radioisotope $^{110}_{47}$Ag, a beta-particle/gamma-photon emitter, is most often used for cathodic deposition; the β-radiation serves for the detection since γ-radiation is not absorbed in the photographic film. The quantity of the radioisotope deposited on a given place is proportional to the local current density. After rinsing with water, the deposit is fixed, for example, by application of a 1% solution of polystyrene in chloroform to form a several micrometre-thick film. The autoradiogram was obtained by direct contact with an autoradiographic film ORWO K3, which was then developed by the usual method. The optical density, which is proportional to the number of absorbed β-particles, was measured by a densitometer (JOYCE LOEBEL) using a light beam of 0.25 mm × 2.0 mm cross section. The values of the densities in the radial cross sections were plotted by means of an on-line computer to give a densitogram. Since the optical density is proportional to the local current density, the densitogram also gives the current density distribution.

The experiments were made on a model set-up described in our preceding communication [7]. The electrolyser consisted of two silver disc electrodes whose outer radius was $r_d = 100\,\mathrm{mm}$ and thickness 2 mm, and which could be rotated around a common axis. The mutual distance of the discs was variable, $h = 3.7$, 6.2, or 8.7 mm. The lower disc was provided with a central hole of radius $r_v = 10$ or 20 mm. The free electrode surface area was delimited by circles of radii $r_0 = 35\,\mathrm{mm}$ and $r_1 = 80\,\mathrm{mm}$; the remaining area was insulated by an epoxy resin film.

The electrodes were immersed in a cylindrical vessel of 35 cm diameter filled with a solution of 0.001 mol l^{-1} $AgClO_4$, 0.001 mol l^{-1} $HClO_4$, and 1.0 mol l^{-1} $NaClO_4$. Silver perchlorate was prepared from silver activated by thermal neutrons; its specific activity was 74 MBq(g Ag^{-1}). The solution was used for several measurements, and as soon as its activity decreases to less than 60% of the original, it was replaced by a fresh one.

The electrode reactions at the anode (Ag-dissolution) and at the cathode (Ag-deposition) are rapid, the latter being controlled by convective diffusion. The silver electrode was thoroughly rinsed with toluene and diethyl ether before use to remove residues of polishing pastes.

4. Results

The local current densities at 19 points distributed evenly from r_0 to r_1 were calculated numerically by solving the equation of convective diffusion for different electrolyser geometries and various angular velocities. Their dependence on the distance from certain reference points was sought by the least squares method. Several forms of this dependence were chosen as follows:

$$j = ar^b \tag{5}$$

$$j = a(r - r_0)^b, \tag{6}$$

$$j = a(r^2 - r_0^2)^b \tag{7}$$

$$j = a(r^3 - r_0^3)^b, \tag{8}$$

$$j = a(r^4 - r_0^4)^b \tag{9}$$

Some of these were derived earlier for various axial symmetric systems. The constants a, b, and the correlation coefficient were determined for each relationship. Equation 5, involving the distance from the rotation axis, is not suitable for approximating j since the correlation coefficient is for our systems in the range 0.91–0.97. The other equations have a correlation coefficient higher than 0.99, the highest values applying for Equations 6 and 7. Equation 7 leads to the least dependence of the constant a on the geometry of the system, which is in accord with Equation 1 obtained from the theory of similarity of the diffusion layer, where the velocities were approximated by functions of the first order (electrodes placed sufficiently far from the rotation axis). In this case the exponent b is equal to $-1/3$.

The values of a and b were obtained by numerical correlation of the j values by Equation 7 for various geometries and angular velocities and for various approximations of the volume rate of flow. The values of a and b corresponding to the analytical expression of Equation 3 are also given. It can be seen that for an electrode sufficiently far from the axis of rotation ($r_0 = 100\,\mathrm{mm}$) the finite-element method Equation 1 give similar results: the difference between the values of constant a does not exceed 5% and the difference between the values of b 3%. With electrodes located nearer to the centre, $r_0 = 35$–$50\,\mathrm{mm}$, the exponent b varies from -0.34 to -0.21.

The numerical calculations by the finite-element method yielded the concentration distribution in the whole integration domain and the mean local current densities at the centres of the elements. Lines of constant concentration in the diffusion layer are shown in Fig. 1a and the current density distribution on the electrode is shown in Fig. 1b.

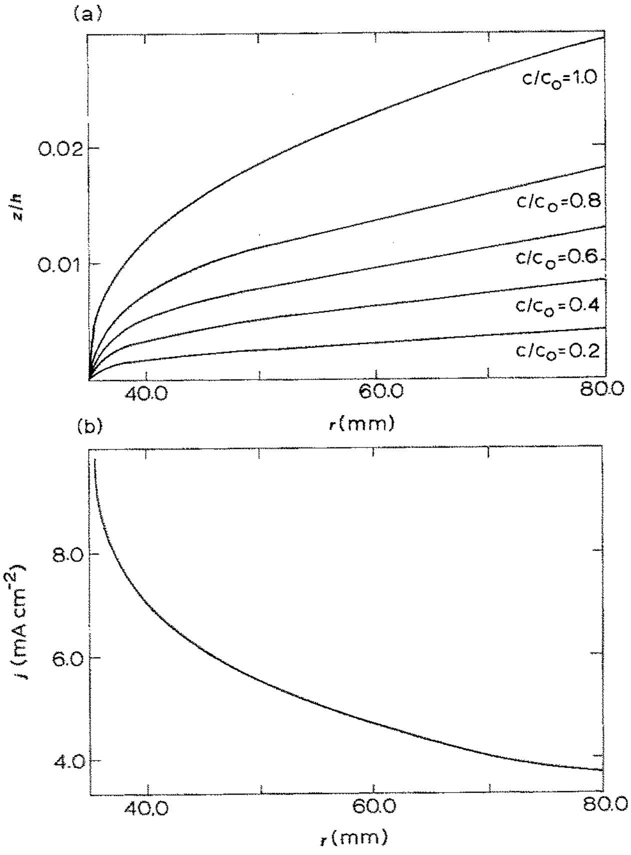

Fig. 1. Lines of constant concentration, c/c_0, at the electrode surface in the diffusion layer, (a). These lines are located in the 2D-space with a normal coordinate, z/h, and radial coordinate, r. Distribution of local current densities, j, on the radial coordinate, r, along the electrode, (b). Results obtained by numerical solution using the finite-element method; grid of 20×20 points, $h = 3.7\,\mathrm{mm}$, $r_0 = 35\,\mathrm{mm}$, $r_1 = 80\,\mathrm{mm}$, $\omega = 9.33\,\mathrm{s}^{-1}$, $Q = 77.1\,\mathrm{cm}^3\,\mathrm{s}^{-1}$, $D = 6.58 \times 10^{-6}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$, $\nu = 1.08 \times 10^{-2}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$, $c_0 = 0.03$ $\mathrm{mol\,l}^{-1}$, $n = 1$.

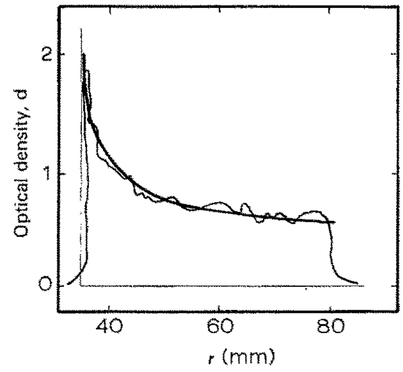

Fig. 2. Distribution of optical density, d, in a radial direction, r, of the measured disc electrode. The origin of coordinates lies at the inner electrode radius, r_0. Parameters: $r_v = 20\,\mathrm{mm}$, $r_0 = 35\,\mathrm{mm}$, $r_1 = 80\,\mathrm{mm}$, $r_d = 100\,\mathrm{mm}$, $h = 3.7\,\mathrm{mm}$, $\omega = 6.49\,\mathrm{s}^{-1}$, $t = 10\,\mathrm{min}$. The measured densities were fitted by equation $d(r) = 1.21(r^2 - r_0^2)^{-0.241}$ using the least squares method.

For the purpose of measurement, it was necessary to determine the duration of silver tracer deposition so that the amount of tracer would be sufficient to expose the photographic film. Thus, for $\omega = 6.49$ and $14.7\,\mathrm{s}^{-1}$ a deposition time of 10 and 4 min, respectively, was sufficient. The optical density was measured on the autoradiograms in several (5–7) radial cross sections. The obtained values, $d(r)$, were treated by the least squares method using the regression equation

$$d(r) = a_1(r^2 - r_0^2)^b \tag{10}$$

corresponding to Equation 7. A typical densitogram is shown in Fig. 2.

To obtain a mean value of b for each experimental arrangement, we found the mean densities from 5–7 radial sections and correlated them by means of Equation 10 using the least squares method. Thus, we obtained mean values of b for each set-up (Table 2). The value of b based on extrapolation of results of the solution of the problem using the finite-element method, given in Table 1 is also given in Table 2. This value of b deviates from the mean exponent b obtained from the mean densities in various sections of the autoradiograms by -7.4% to $+13\%$ for the first, second, third, and fifth measurements, and by $+24\%$ in the fourth measurement.

In all cases we observed a decrease of the local current density with the distance from the inner electrode boundary; no increase was observed, which corresponds to what is known from the electrochemical pump cell [11].

5. Conclusions

Our work showed the advantage of the autoradiographic method in studying the current distribution in a rotating electrolyser, as well as the suitability of the finite-element for theoretical calculations. Exponent b in Equation 7 depends on the geometry of the system and the hydrodynamic conditions, etc. It will probably always lie in the interval between $b = 0$ corresponding to a rotating disc electrode ($r_0 = 0$, $h \to \infty$) and

Table 1. Results of numerical correlation of local current densities with Equation 7. Calculations were carried out by the finite-element method with a 20 × 20 grid; $h = 3.7\,mm$, $D = 6.58 \times 10^{-6}\,cm^2\,s^{-1}$, $\nu = 1.08 \times 10^{-2}\,cm^2\,s^{-1}$, $c_0 = 0.03\,mol\,l^{-1}$, $n = 1$. The velocity field was approximated by an expansion with functions of up to the third order [1, 4]. The values of a *and* b *are also given for the case where Equation 1 for the current density holds good. The relation $Q = 8.1\,\omega$ applies approximately for a system with $r_v = 10\,mm$, $r_d = 100\,mm$, $h = 3.7\,mm$, whereas $Q = 3.7\,\omega$ applies approximately for a system with $r_v = 20\,mm$, $r_d = 60\,mm$, $h = 8.7\,mm$ [7].*

r_0/r_1 (*mA*)	$\omega = 3.25\,s^{-1}$		$\omega = 6.49\,s^{-1}$		$\omega = 9.33\,s^{-1}$		$\omega = 14.7\,s^{-1}$		$\omega = 21.1\,s^{-1}$		$\omega = 27.7\,s^{-1}$	
	a ($mA\,cm^{-2}$)	b	a ($mA\,cm^{-2}$)	b	a ($mA\,cm^{-2}$)	b	a ($mA\,cm^{-2}$)	b	a ($mA\,cm^{-2}$)	b	a ($mA\,cm^{-2}$)	b
Rate of flow $Q = 8.1\,\omega$												
35.0/50.0	5.87	−0.285	8.26	−0.252	9.21	−0.206	–	–	–	–	–	–
35.0/80.0	6.10	−0.293	8.57	−0.259	9.53	−0.219	–	–	–	–	–	–
50.0/80.0	6.70	−0.323	10.12	−0.314	12.4	−0.306	15.8	−0.295	18.8	−0.280	21.0	−0.262
100.0/120.0	7.13	−0.336	11.2	−0.335	14.0	−0.334	18.8	−0.334	23.6	−0.334	28.0	−0.332
Equation 1	7.23	−0.333	11.4	−0.333	14.4	−0.333	19.3	−0.333	24.5	−0.333	29.3	−0.333
Rate of flow $Q = 3.7\,\omega$												
35.0/50.0	5.31	−0.320	8.10	−0.311	9.97	−0.302	12.8	−0.289	15.2	−0.269	16.9	−0.243
35.0/80.0	5.53	−0.331	8.42	−0.320	10.4	−0.310	13.3	−0.296	15.8	−0.278	17.7	−0.256
50.0/80.0	5.71	−0.340	8.88	−0.336	11.1	−0.331	14.7	−0.328	18.3	−0.323	21.4	−0.317
100.0/120.0	5.84	−0.344	9.23	−0.343	11.7	−0.341	15.8	−0.340	20.1	−0.340	24.0	−0.339
Equation 1	5.77	−0.333	9.14	−0.333	11.7	−0.333	15.7	−0.333	20.0	−0.333	24.1	−0.333

Table 2. Parameters for autoradiographic measurements

Electrode	r_v (*mm*)	r_d (*mm*)	h (*mm*)	ω (s^{-1})	t (*min*)	b* (*radiography*)	b† (*extrapolation*)
lower	20.0	100.0	3.7	6.49	15	-0.27 ± 0.04	-0.25
lower	20.0	100.0	8.7	6.49	10	-0.246 ± 0.007	-0.23
upper	20.0	100.0	3.7	6.49	10	-0.24 ± 0.01	-0.25
lower	10.0	100.0	3.7	9.74	5	-0.17 ± 0.01	-0.21
lower	10.0	100.0	6.2	14.7	4	-0.15 ± 0.01	-0.17

* Values obtained by numerical correlation with Equation 7.

† Values based on extrapolation of the results from Table 1.

The electrode area was eliminated by the radii $r_0 = 35\,\text{mm}$, $r_1 = 80\,\text{mm}$; t denotes the time of deposition.

$b = -1/3$ corresponding to electrodes placed at a sufficient distance from the rotation axis (Equation 1).

The autoradiograms showed that the highest local current density in the laminar regime is at the inner electrode boundary and that it decreases monotonically towards the outer boundary in accord with the numerical solution of the convective diffusion equation. This conclusion is valid for a fast electrochemical reaction governed by the diffusion to the electrode in the presence of an excess of supporting electrolyte for the laminar flow of the electrolyte. In our case see [6] $Re_{\text{rot}} = \omega r_1^2/\nu < 1.7 \times 10^5$ and $Re_{\text{loc}} = Q/(2\pi \nu r_0) < 1300$ fulfilled the condition of laminar flow.

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