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The rotating electrolyser. II. Transport properties and design equations

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It is shown that mass transfer in the rotating electrolyser is controlled by the rotational Reynolds number (Re_ϕ) and that species electrogenerated at the wall are confined to a thin layer close to the wall. The radial dispersion coefficient is of the same order as that of a non-rotational, capillary gap cell. Criteria for scale-up are discussed briefly.

Symbols

A	electrode area
a	semi-gap
C	concentration
$\bar{D}_r$	radial dispersion coefficient ($cm^2 s^{-1}$)
F	the Faraday
i	current (A)
j	current density ($A cm^{-2}$)
k_m	mass transfer coefficient ($cm s^{-1}$), $k_m = i/nFAC$
$M_1 = \tau$	normalized first moment of response, defined by Equation 3, equivalent to mean residence time of marked material.
M_2	normalized second moment of response, defined by Equation 4
n	number of electrons transferred
r	radius
(Re_ϕ)	rotational Reynolds number, defined by $(Re_\phi) = \omega r_0^2/\nu$
t	transit time of plug flow in a radial diffuser, see Equation 5
u	radial velocity
$\bar{u}$	average (plug flow) radial velocity
$\bar{z}$	distance measured from axial plane
Subscripts	
i	inner (or denotes marker electrode, as appropriate)
m	maximum
o	outer
Greek	
α	Taylor number, defined by $\alpha^2 = a^2 \omega/\nu$
τ	(see M_1)
ν	kinematic viscosity
ω	angular velocity

1. Introduction

In Part I [1] the idea was introduced of employing the double-humped radial velocity distribution predicted by Kreith [2] for rotating source flow to separate anolyte and catholyte layers in a narrow gap electrolyser [3]. Laser–Doppler anemometry showed [1] that in fact the double-humped distribution could be obtained in a practical cell so that there was, in effect, a wall jet close to either electrode with a relatively stagnant zone in between. Doppler measurements also showed that under some conditions there were regions of recirculation in the stagnant zone between the wall jets giving rise to a possible mechanism of anode/cathode transport which would negate the separation of streams produced by the wall jets. The degree of mixing, of course, depends on the distance species, electrogenerated at the surface, diffuse or disperse into the gap so that they ultimately come under the influence of the recirculations. One aim of this paper is to report the results of tracer experiments used to investigate this question and to estimate the degree of dispersion of electrogenerated species.

It was also shown in Part I that with increasing Taylor number, α, both the radial and tangential velocity gradient increase, while the thickness of both velocity boundary layers decrease. Although the tangential (wall) velocity is always higher than the maximum radial velocity, the gradients at the wall are comparable and it is not clear, *ab initio*, which controls the mass transport. Investigations of limiting current mass transport are also reported here together with simple design equations for the electrolyser.

2. Experimental

The design and construction of a trial cell made of nickel has been reported in Part I. This was used under potentiostatic control in a bath of 10^{-3} mol dm^{-3} ferri/ferrocyanide in 0·1 mol dm^{-3} NaOH to measure its mass transfer characteristics with interelectrode distances of 6·4 and 3·5 mm.

A similar cell (Fig. 1) with each plate incorporating a cylindrical copper electrode near the entry and four coaxial nickel strip electrodes at increasing radii was cast in epoxy resin and used for marker experiments in an indifferent electrolyte ($10^{-3\cdot5}$ M H_2SO_4). The interelectrode gap was 4 mm. When a voltage pulse was applied between the copper rings, copper ions entered the solution from whichever was anode and were convected radially outwards by the induced flow. Opposing pairs of nickel rings were kept at a sufficient potential to produce a limiting current and the responses to the pulse stimulus were recorded on a y/t recorder.

In a third cell with copper disc electrodes and a gap of 1·4 mm, a microsampler on a micrometer head was used to take samples of the electrolyte at various stations across the gap at exit. The samples were analysed for copper using atomic absorption spectroscopy. It was necessary to align the needle of the syringe accurately with the local velocity vector to obtain reproducible results.

3. Results

3.1. *Mass transfer*

The distribution of radial velocity is determined [1, 2, 3] by the Taylor number, $\alpha = (a^2\omega/\nu)^{1/2}$. In Part I it was shown that the distribution of tangential velocity was also determined by α, the gradient at the wall becoming steeper as α increased. Fig. 2 shows plots of the logarithm of current density versus ln α for two different gaps. The slopes in the laminar range are similar, but the plots cannot be collapsed. Fig. 3, however, shows that the data can be collapsed if the rotational Reynolds number $(Re_\phi) = \omega r_0^2/\nu$, is used as the correlating parameter, demonstrating that it is the relative tangential motion which controls mass transfer, i.e. the mass transfer at the surface is independent of the gap.

Transition is indicated at $(Re_\phi) \cong 1{\cdot}8 \times 10^5$, which is consistent with observations in other rotational cells [4, 5, 6]. In the laminar region the mass-transfer coefficient, k_m, is given by

$$k_m = 2{\cdot}337 \times 10^{-6} (Re_\phi)^{0{\cdot}565} \qquad (1)$$

The exponent is slightly higher than for a free disc or shear flow cell [4] and is half the value obtain-

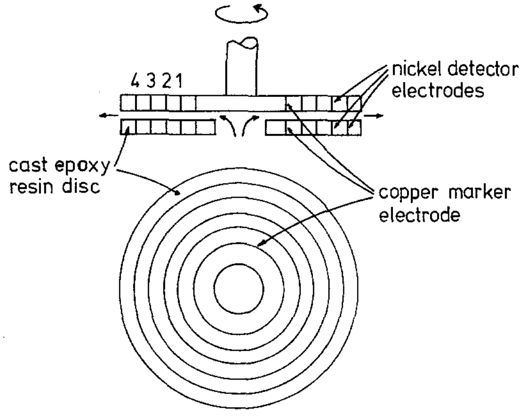

Fig. 1. Schematic diagram of rotating electrolyser showing marker and detector electrodes.

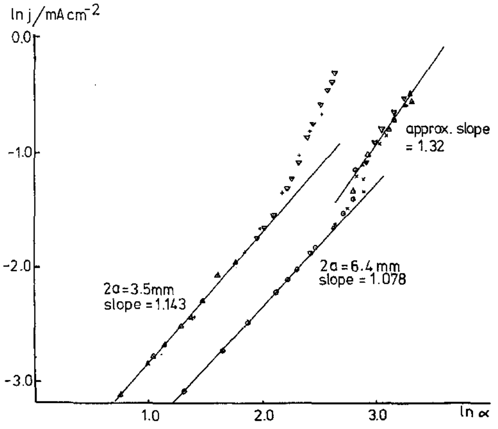

Fig. 2. Log current density versus log Taylor number for two different gap widths.

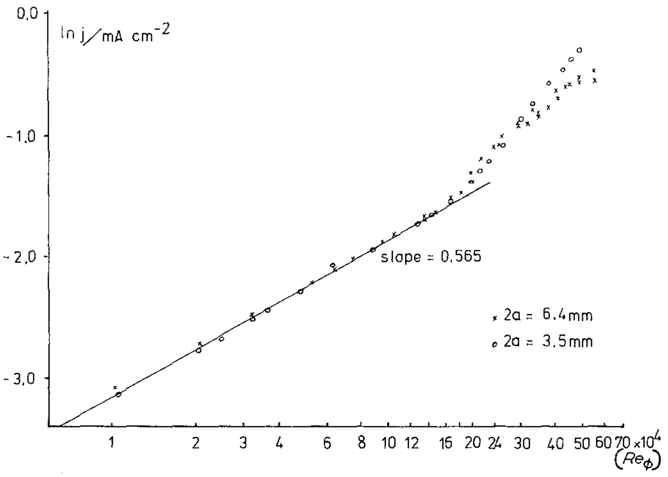

Fig. 3. Log current density versus log rotational Reynolds number for two gap widths.

able from Fig. 2, which is understandable since

$$\alpha^2 = a^2\omega/\nu = (a/r_o)^2\omega r_o^2/\nu = (a/r_o)^2(Re_\phi) \quad (2)$$

Above $(Re_\phi) \cong 1{\cdot}8 \times 10^5$, k_m increases more rapidly but the flow within the gap is turbulent, hence highly dispersive.

3.2. *Marker experiments*

Fig. 4 shows the responses at four coaxial detector electrodes to anodic pulses at the marker electrode on the same side of the cell. Since they were recorded individually and shot-to-shot reproducibility was not good, the areas under the curves do not show a systematic trend, but Table 1 gives the first and second moments for each response

$$M_1 = \int_0^\infty i(t)t\mathrm{d}t \Big/ \int_0^\infty i(t)\mathrm{d}t = \tau \quad (3)$$

and

$$M_2 = \int_0^\infty i(t)t^2\mathrm{d}t \Big/ \int_0^\infty i(t)\mathrm{d}t \quad (4)$$

where, by definition, τ is the mean residence time of the marked material. It can be seen from Table 1 that $M_1 = \tau$ is of the order of 5–10 s. Since the transit time, t, for plug flow in a radial diffuser of any thickness, h, is

$$t = \frac{\pi(r_o^2 - r_i^2)h}{2\pi h(\bar{u}r)} = \frac{r_o^2 - r_i^2}{2(\bar{u}r)} \quad (5)$$

i.e. independent of the thickness, the transit time should be of the order of a second if the marked fluid moves with the mean velocity of the wall jet. Using laser–Doppler measurements of wall jet velocity, minimum estimates of the mean transit times, t, were calculated and are also shown in Table 1. Clearly plug flow is a poor model in this case, but the ratios τ/t show that the marked material moves at much less than the maximum velocity of the wall jet; in fact t and τ can be reconciled if the marked layer fills about 3% of the semi-gap when $\alpha = 7$. This has been confirmed by photographing the cathodic layer during hydrogen discharge using phenolphthalein to

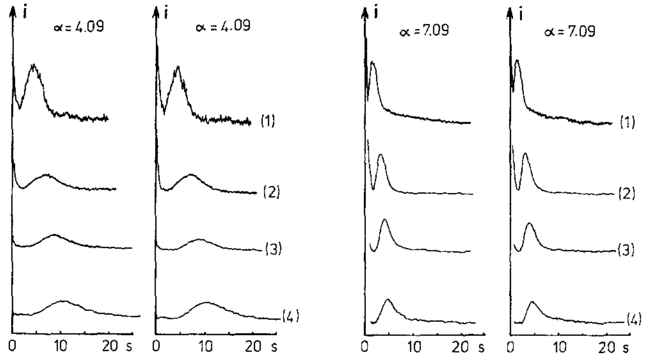

Fig. 4. Response to a marker pulse at four concentric detector electrodes for two different Taylor numbers.

Table 1. Data from marker pulse experiments; gap 4·0 mm, o.d. 134 mm

α	*Microelectrode diameter* (mm)	*First moment* $M_1 = \tau$ (s)	*Second moment* M_2 (s^2)	*Minimum transit time, t* (s)	τ/t	*Approx. dispersion coefficient* $\bar{D}_r$($cm^2\ s^{-1}$)
4·09	60	4·71	26·70	2·0	2·36	0·019
	78	7·22	57·94	2·3	1·90	0·024
	95	9·58	100·62	5·5	1·74	0·031
	113·5	11·38	141·83	7·35	1·55	0·042
7·09	60	3·59	20·98	0·33	10·89	0·068
	78	3·29	13·59	0·63	5·22	0·109
	95	4·59	26·01	0·92	9·99	0·141
	113·5	4·65	25·60	1·23	3·78	0·192

indicate the layer of changed pH. The marked fluid is thus localized between the radial velocity maximum and the adjacent wall, where it is insensitive to recirculations in the interelectrode space (Part I). This is consistent with the observation that no response was ever obtained to an anodic pulse on the opposite electrode. Cross-gap mixing of electrogenerated species is therefore minimal.

Accurately modelling the dispersion in radial, decelerating flow is very difficult, however it has been shown [7, 8] that the reaction environment in most electrochemical cells can be treated as being equivalent to two dispersive plug flows of different speeds, possibly with mass exchange between the two and chemical reaction in one or both. A plug flow model has been devised [9] for radial flow which allows dispersion to be estimated. Application of this theory to shear flow cells of the same nominal geometry as the present case has been successful [9, 10]. Normally the volumetric flow rate is known, but if not, as in this case, the expressions [9] can be rearranged to give

$$\bar{D}_r = \frac{(r^2 - r_i^2)}{4M_1\left[1 + \dfrac{(r^2 + r_i^2)}{(r^2 - r_i^2)}\dfrac{M_1^2}{(M_2 - M_1^2)}\right]} \qquad (6)$$

Estimates of the radial dispersion coefficient, $\bar{D}_r$, based on Equation 6 are shown in Table 1.

Direct measurements by atomic absorption spectroscopy of copper anodically dissolved from an electrolyser with copper electrodes are shown in Fig. 5. The samples were taken just beyond the edges of the discs in the tank, i.e. just at exit, and the values shown have been corrected for the background concentration in the tank, which increased slowly with time. Even though the probe tip (~ 0·35 mm diameter) is equivalent to $\Delta\bar{z}/a \cong 0{\cdot}45$ it is clear that the marked layer is very close to the anode. The high values for $\bar{z}/a > 1$ are caused by the vortex at the edge of the electrode which is caused by interaction of the jet fluid with the external flow, convecting the marked layer around the corner. Such behaviour has been confirmed in flow visualization studies [11].

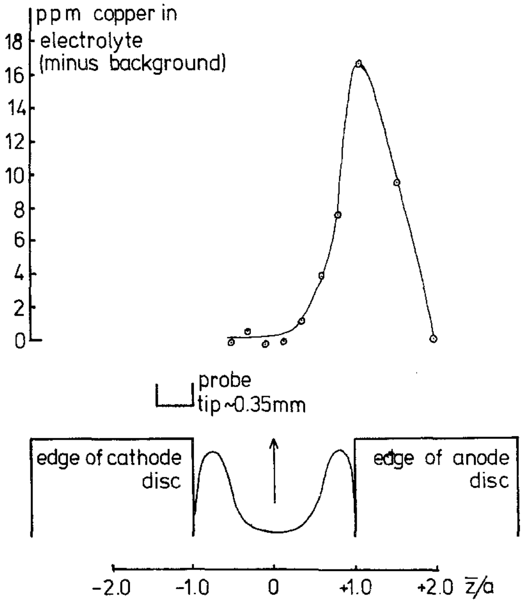

Fig. 5. Concentration of marker copper ions at exit from rotating electrolyser.

4. Discussion

The results reported here and in Part I vindicate the concept of an electrolyser in which anode and cathode streams are separated by hydrodynamics alone. This separation of streams is governed by the dimensionless quantity the Taylor number, α, and even when the cell is made self-pumping the shape of the radial velocity profile close to the wall is preserved, that is it is independent of radius, even though entry effects, exit effects and recirculation in the mid-gap are seen, depending on the value of α (Part I).

On the other hand, the mass transfer rate is governed by the rotational Reynolds number (Re_ϕ), which is a macroscopic parameter grossly characterizing the flow regime [4, 5, 6]. The flow is laminar below $(Re_\phi) \cong 1{\cdot}8 \times 10^5$, which therefore sets an upper bound for the design. It was shown in Equation 2 that α and (Re_ϕ) are related, therefore the bounding condition on α is given by

$$\alpha^2(r_o/a)^2 \lesssim 1{\cdot}8 \times 10^5. \qquad (7)$$

It is the constant aim in applied electrochemistry to reduce the interelectrode gap, $2a$, suggesting that α should have the minimum value which provides effective separation of the streams, say $\alpha = 2$ or 3, when $(r_o/a) \cong 110$–140, or the gap ratio, $G = r_o/2a$, is in the range 70–100. This is rather small for a technical electrolyser, but may be acceptable as the price for having eliminated the diaphragm. If $\alpha = 2$ and $r_o = 250$ mm, then the gap is 2·38 mm and the rotational speed is 27 rev min^{-1} which are easy to achieve; if $\alpha = 3$, the gap is 3·57 mm and again the rotational speed 27 rev min^{-1}. Using Equation 1 it is seen that an electrode 250 mm in radius at 27 rev min^{-1} would have an average mass transfer coefficient k_m, of about $2{\cdot}192 \times 10^{-3}$ cm s^{-1} and would sustain a current density of 21·15 A dm^{-2} at a reactant concentration of 1 mol dm^{-3}, which is sufficient for most organosyntheses. The cell current would be 414 A under these conditions. Table 1 suggests that, for $\alpha = 2$ or 3, the dispersion coefficient is of the order of 10^{-2} cm^2 s^{-1} which is comparable to values found in a capillary gap, parallel channel electrolyser [12] and it has been shown that marked material stays close to the wall so permanent separation of the two streams should be easy; this is being investigated at present [11]. Further, since in many electrolysers the electrogenerated species stay within a short distance of the electrode [7–10, 12] it may be possible to effect a separation even if the flow is macroscopically unsteady or even turbulent. This is also being actively investigated [11].

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