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Diffusion-controlled current distributions near cell entries and corners

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This paper reports experimental work undertaken to explore diffusion-controlled current distributions immediately downstream of sudden changes in flow cross-sectional area such as may occur at the entry to electrochemical flow cells. Nozzle flows expanding into an axisymmetric circular duct and into a square duct have been investigated using the reduction of ferricyanide ions on nickel micro-electrodes as the electrode process. The spanwise distribution of current has also been studied for the case of the square cell where secondary corner flows are significant.

Nomenclature

A	electrode area (cm^2)
c_∞	bulk concentration of transferring ions ($mol\ dm^{-3}$)
D	cell diameter (cm)
$\mathfrak{D}$	Diffusion coefficient ($cm^2\ s^{-1}$)
F	Faraday number ($96\,486\ C\ mol^{-1}$)
I	limiting electrolysis current (A)
k	mass transfer coefficient ($cm\ s^{-1}$)
N	nozzle diameter (cm)
u	mean fluid velocity ($cm\ s^{-1}$)
x	distance downstream from point of entry to cell (cm)
z	number of electrons exchanged
μ	electrolyte viscosity ($g\ s^{-1}\ cm^{-1}$)
ρ	electrolyte density ($g\ cm^{-3}$)
$(Re)_D$	duct Reynolds number, $Du\rho/\mu$
$(Re)_N$	nozzle Reynolds number, $Nu\rho/\mu$
(Sc)	Schmidt number, $\mu/\rho\mathfrak{D}$
(Sh)	Sherwood number, $kD/\mathfrak{D}$

1. Introduction

The local distribution of mass transfer and hence current near cell entries and near the corners of plane-sided ducts is known to be strongly influenced by complex flow phenomena especially in diffusion-controlled processes. Downstream of an inlet pipe where the flow suddenly expands into a cell, a region of recirculating flow occurs which is associated with abnormally high wall transfer rates (Fig. 1). A short distance into the cell the flow re-attaches to the wall and begins to develop in the normal manner. Near the corners of rectangular cells secondary flows are known to occur in both laminar and turbulent conditions which may strongly influence the mass transfer distribution and cause currents to be locally higher than those predicted for the plain wall.

The purpose of the work reported here was the exploration of local electrochemical mass transfer rates downstream of circular entry pipes expanding into both axisymmetric circular and square ducts. This work was primarily carried out in order to model important situations involving heat transfer from burner jets and some results have been published elsewhere [1, 2]. The aim of the present note is to emphasize the application of the work to electrochemical reactor design.

Previous similar work is reported by Costello [3] who used 1 : 1.33 and 1 : 2.67 expansions but did not make truly local measurements, and Runchal [4] whose work was limited to a single 1 : 2 expan-

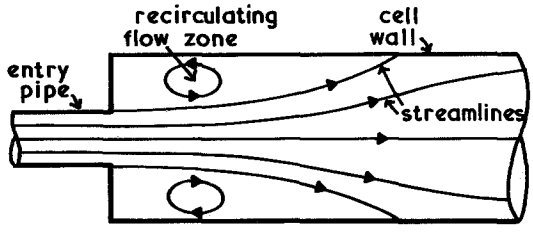

Fig. 1. Flow pattern near a cell entry.

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sion and whose cell design left some uncertainty about mass transfer boundary conditions [2].

2. Experimental

The apparatus and experimental technique have been described elsewhere [1, 2, 6] and only a brief account will be given here. Local nickel electrodes of diameter 1 mm were flush-mounted in a staggered array in the wall of a circular nickel tube of inside diameter 52.2 mm and length 500 mm at intervals of 12.7 mm. Long radius ASME profile nozzle blocks were positioned at the entry to the nickel section so as to give expansion ratios of 1:2, 1:3, 1:4, 1:6 and 1:10. The nickel tube was divided longitudinally into anodic and cathodic sections, the local nickel electrodes being incorporated in the smaller cathode part. Additionally a single local nickel cathode was positioned in the wall of a perspex tube of the same dimensions, the position between this and the inlet nozzle being variable. Thus local mass transfer rates could be determined for two distinct conditions:

(a) with the surrounding wall cathode area also active and

(b) with an inert surrounding area.

A 52.2 mm × 52.2 mm square duct of length 1 m was also constructed from 1.5 mm thick nickel sheet in one wall of which were embedded 140 local nickel cathodes in 35 rows of four. The lateral rows of four electrodes allowed the exploration of the spanwise transfer rate distribution as well as that in the flow direction. One of the four electrodes in each row was situated in a mid-wall position with the others at intervals of 6.35 mm towards the corner.

The use of specially profiled nozzles creates a flat velocity profile [7] at the cell entry, this rather idealized situation being convenient in the present work in order to match a parallel programme of mathematical modelling [8, 9].

Conventional limiting current determinations were carried out using an electrolyte of composition 0.005 M $K_3Fe(CN)_6$, 0.005 M $K_4Fe(CN)_6$ and 0.5 M NaOH. Experiments were conducted at 20° C (± 1° C) at which temperature the mass transfer property number (Schmidt number) had a value of 1450.

Mass transfer coefficients are directly related to measured limiting currents by the equation

$$k = I/(zFAc_\infty). \tag{1}$$

3. Results

3.1. *Circular cross-section cell*

A set of results for local mass transfer coefficients at a single turbulent flow Reynolds number for all five nozzle sizes for the circular cell geometry is shown in Fig. 2. These data are for a local cathode with the surrounding main cathode active, a complete set of these results having been published

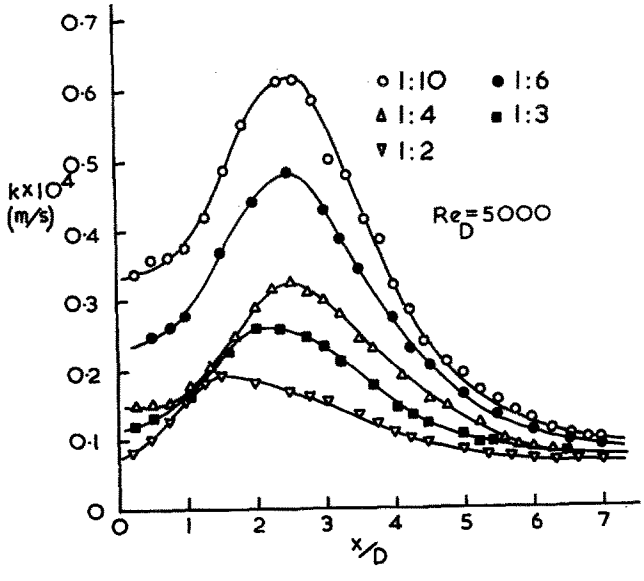

Fig. 2. Variation of local wall mass transfer coefficient with downstream distance from the circular cell entry.

over the full range of Reynolds numbers elsewhere [2]. The pronounced peaks in the mass transfer distributions are characteristic of wall transfer processes in the downstream neighbourhood of sudden enlargements in duct cross-section such as occur at reactor entries. The k values can be seen to be slowly approaching the fully developed turbulent flow predictions of the Dittus–Boelter equation.

$$(Sh) = \frac{kD}{\mathfrak{D}} = 0.023\,(Re)_D^{0.8}(Sc)^{0.33}. \quad (2)$$

The peak k values have been shown [1] to be correlated well by the equation

$$(Sh) = 0.27\,(Re)_D^{0.67}(Sc)^{0.33} \quad (3)$$

which agrees very closely with related work in heat transfer situations.

Fig. 2 shows that the choice of entry port dimensions has a strong influence on the local current distribution in the entry region of a cell for a constant cell Reynolds number. Pickett [5]

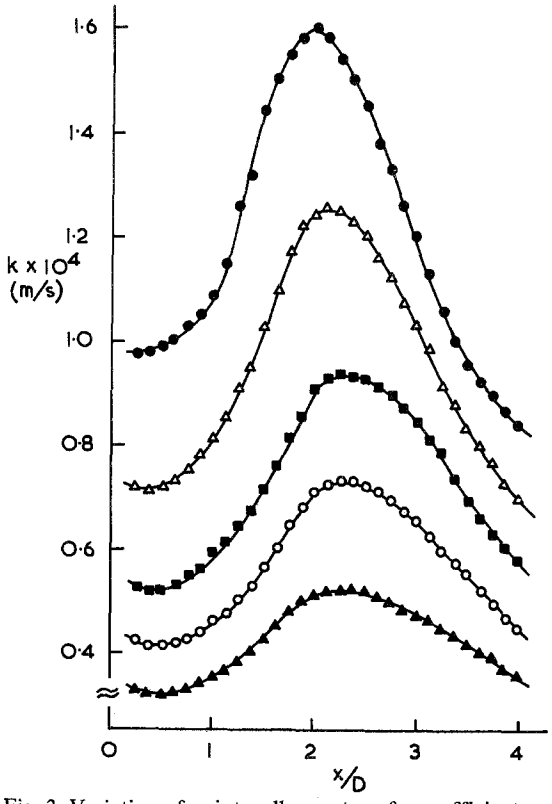

Fig. 3. Variation of point wall mass transfer coefficient downstream of the circular cell entry. Inert surround. 1:6 flow expansion. The values of $(Re)_D$ shown are: •, 15 430; △, 10 125; ■, 6270; ○, 3860; ▲, 1984.

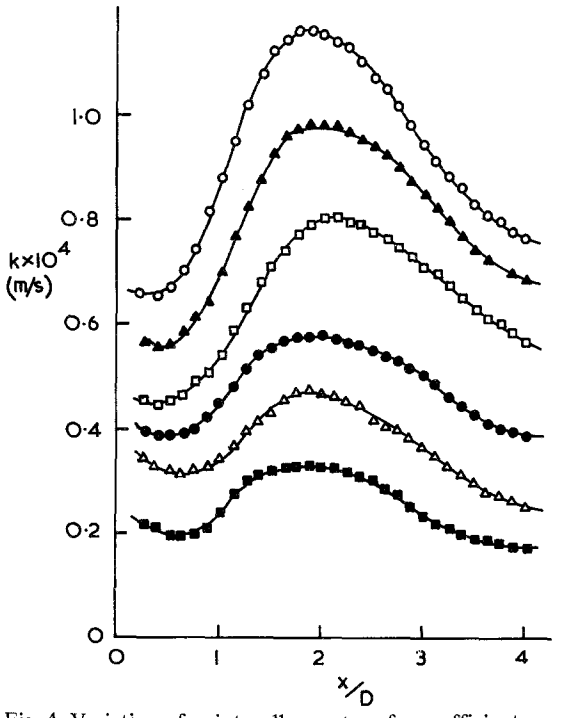

Fig. 4. Variation of point wall mass transfer coefficient downstream of the circular cell entry. Inert surround. 1:3 flow expansion. The values of $(Re)_D$ shown are: ○, 22 182; ▲, 16 400; □, 10 125; •, 6270; △, 3860; ■, 1985.

has made a thorough review of mass transfer in parallel walled and annular cells in laminar and turbulent flow. His treatment has taken account of both hydrodynamic and mass transfer entry effects, but not for cases where flow separation occurs near the cell entry.

Local k values for the other boundary condition studied, that of the test electrode embedded in an inert surrounding surface are shown as Figs. 3 and 4 for the 1:6 and 1:3 expansion ratios respectively, data for the other geometries being available elsewhere [2]. The values shown here are naturally much higher than those for the active cathode case since the test electrode is not situated within a partially developed mass transfer boundary layer, but forms its own leading edge for mass transfer development.

Experiments with a flow-direction sensing electrode have shown that the location of peak mass transfer falls well within the extent of the recirculation zone [1, 2].

3.2. *Square cross-section cell*

Local Sherwood numbers for the square cell

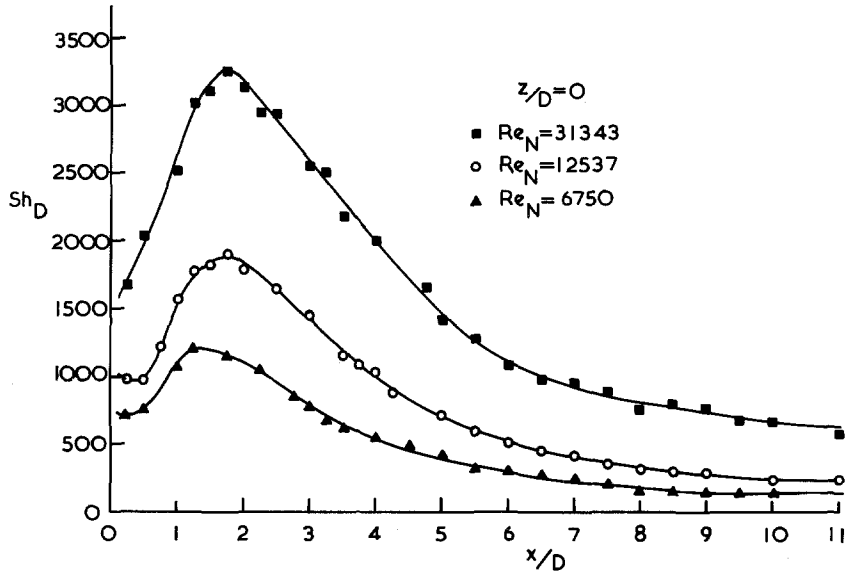

Fig. 5. Variation of local mid-wall Sherwood numbers downstream of a circular entry expanding into a square cell. 1:2 expansion.

are shown in Fig. 5 for the case of the mid-wall electrode with varying (Re) and for the 1:2 expansion. The curves which are for the case of active surrounding surfaces are similar in form to those for the circular cell, but there exists an additional interesting variation of k with spanwise position. This variation with wall position for a single Reynolds number for the 1:3 and 1:6 expansions is shown in Figs. 6 and 7. A notable feature is the fact that in the recirculation zone the mid-wall values are higher than the corner values, whereas in the far downstream region as the primary and secondary corner flows develop, this pattern is reversed and the corner k values are the highest. As shown in Fig. 8, the peak k values for the square cell mid-wall positions coincide very closely with those from the circular cell when plotted as $(Sh)_D$ versus $(Re)_N$.

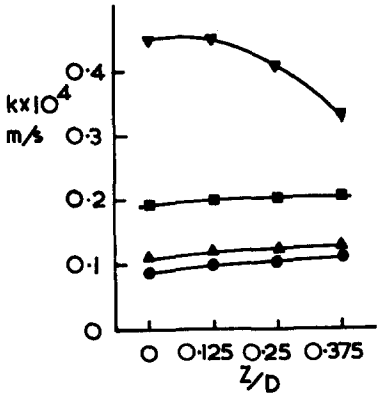

Fig. 6. Spanwise variation of local wall mass transfer coefficient downstream of an expansion into a square cell. 1:3 expansion. $(Re)_D = 15\,670$. The values of x/D shown are: ▼, 1.75; ■, 5.0; ▲, 8.5; ●, 12.0.

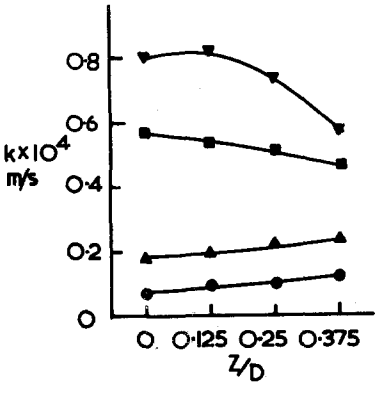

Fig. 7. Spanwise variation of local wall mass transfer coefficient downstream of an expansion into a square cell. 1:6 expansion. $(Re)_D = 13\,260$. The values of x/D shown are: ▼, 2.5; ■, 4; ▲, 6; ●, 12.

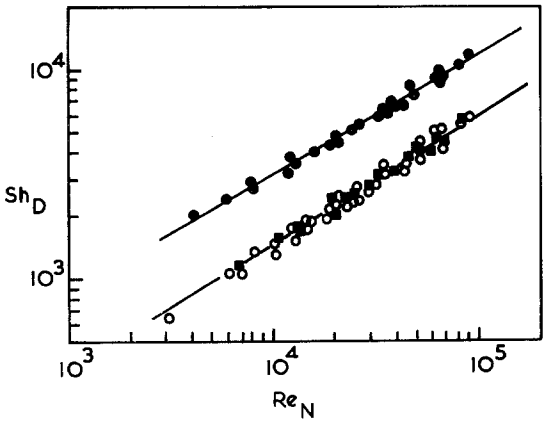

Fig. 8. Correlation of peak mass transfer data as (Sh) against $(Re)_N$ for both the square and circular cells. Active surroundings: ○, circular duct; ▪, square duct. Inert surroundings: ●, circular duct.

4. Discussion

The marked effect of flow separation and recirculation at the entry to cells on the local channel wall mass transfer coefficient and hence current distribution has been clearly demonstrated for diffusion-controlled processes. It is clear that for many cells of short and moderate length the current and mass transfer distributions are dominated by entry effects and classical equations for predicting mass transfer rates at plane walls are of limited use. Where such large variation in current distribution is undesirable careful design of entry port and cell contour is essential, though even so some degree of non-uniform current density is inevitable in all cells at the leading edges of the electrodes. Some types of porous battery and fuel cell electrodes may suffer permanently impaired performance if critical current densities are locally exceeded.

The phenomena observed in this work also have relevance to corrosion situations in pipes and channels especially at changes of cross-section or at changes of direction of flow such as tees and elbows where flow separation occurs. Local regions of high mass transfer may sustain high local corrosion rates where the overall process is, for instance, dictated by a diffusion-controlled step such as the supply of dissolved oxygen.

Finally, it would seem worthwhile to explore this important aspect of cell design more fully with respect to channels having multi-entry ports where the resultant jets and recirculation zones interact with their neighbours thus producing more complex current density distributions at the wall electrodes.

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