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Ionic mass transfer in parallel plate electrochemical cells

D. J. PICKETT and B. R. STANMORE

Department of Chemical Engineering, University of Manchester Institute of Science and Technology, Manchester U.K.

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Experimental investigations have been made of ionic mass transfer in a parallel plate electrochemical cell under both laminar and turbulent flow. The results obtained in the laminar flow region were found to be well represented by a Leveque-type equation modified to include the cell aspect ratio as an additional parameter. The influence of decreased mass transfer at the edges of the electrodes due to changes in the velocity profile was found to be small. For the turbulent region, there is a correlation of the mass transfer coefficient with Reynolds number to an exponent of 0·875 and Schmidt number to exponent of 0·21. This is in accord with existing correlations for heat and mass transfer in similar geometries over the range studied.

Introduction

Increasing interest in industrial electrochemical processes has stimulated investigations into the performance of process cells especially in the field of organic syntheses. Design and operation of cells for organic materials is often complicated by low reactant solubilities and small current densities. Often these small current densities are due to the slowness of one of the electrochemical steps but, in the case where mass transfer is limiting, the use of high electrolyte velocities will increase the mass transfer coefficient and help to offset the effects of low solubilities.

From an industrial point of view a favoured cell geometry is one in which the electrodes form opposite sides of a rectangular duct and this system has been studied by a number of workers [1–3]. Most interest has been shown in the mass transfer due to laminar flow and in the development of the mass transfer boundary layer with theoretical comparison provided by the Leveque–Graetz treatment [4, 5]. On the other hand little attempt has been made to extend knowledge to the turbulent regions which are potentially important.

This paper reports data obtained with a parallel plate cell, without a diaphragm, using both laminar and turbulent electrolyte flows under developing and fully developed mass transfer conditions.

Experimental

The cell and flow circuit are shown schematically in Fig. 1 and are fully described elsewhere [6]. The cell was made of Perspex with an integral rectangular cross-section 0·5 cm × 3·00 cm, the total length being 130 cm between inlet and outlet. A hydrodynamic entry length of 78 cm and exit length of 22 cm were included. The anode was a piece of 3·2 mm thick copper 30 cm × 3 cm cemented on to one wall. The cathode was removable and mounted on a Perspex plate which, when bolted down, located its surface flush with the wall. It was constructed from three strips of 1·6 mm in copper 30 cm long, the centre piece being 1·00 cm wide and the edges 0·885 cm wide, the pieces were insulated from each other by strips of 0·007 in thick polythene. This insulation and the Perspex lips remaining at the edges meant that 7·8% of the wall area was not a working electrode.

The electrolyte consisted of acidified copper sulphate solutions of different concentrations and was circulated by a small stainless steel pump from a 20 l reservoir. The flow was metered by two rotameters, specially calibrated, and regulated by a bypass and two Saunders valves. Flow direction was always upwards except for a few runs to check natural convection. Nitrogen was sparged into the electrolyte periodically to remove oxygen and a vent fitted to purge air. Temperature control was achieved using a QVF glass heat exchanger mounted in the bypass. This also enabled runs above ambient temperatures by circulation of hot water through the exchanger.

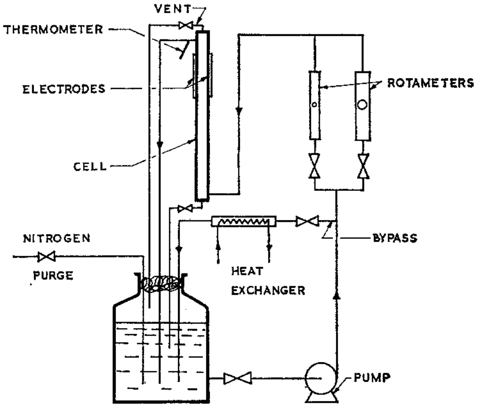

Fig. 1. Flow system.

Electrical power was supplied by a Coutant LP power unit with a maximum capacity of 2 A. Current flow was measured by two Avometers Model 8 Mark 3 with a guaranteed accuracy of 1% of full scale. These were arranged so that one measured the current from the centre electrode and the other the current from either one of the edge electrodes, via a double pole throw switch. On switching, a variable resistor was switched into the circuit; this maintained a constant resistance in the edge circuits whether they were being metered or not. The variable resistors were adjusted to give zero potential difference between centre and edge electrodes. The potential was measured using an EIL electronic voltmeter model 23 A range 0–800 mV which was either connected across the cell or between the centre and either of the edge cathodes, to give a uniform cathode potential.

Procedure

Copper sulphate solutions were chosen rather than other systems because of their stability. Two solutions were used; 0·067 M $CuSO_4$ and 0·015 M $CuSO_4$ in 1·5 M sulphuric acid (Analar grade chemicals). Dilute solutions were preferred to minimize natural convection, anode dissolution and for small limiting currents. Standardization was by estimating the iodine produced by precipitation of cuprous iodide on addition of excess potassium iodide.

The cathode was prepared by rubbing down with emery paper, degreasing with trichloroethylene and rinsing. Nitrogen was passed through the electrolyte which was circulated for 5 min while a current of 0·5 mA/cm² was applied to produce a uniform surface.

The potential difference across the cell was raised in 50 mV steps until hydrogen evolution began (approximately 600 mV). After an increase in potential, 2 min were allowed for equilibrium to be reached before measurements were made. Sometimes longer was required in the regions of rapidly varying current but around the limiting current far less time was required.

To determine the effect of electrode length, parts of the cathode were insulated from the electrolyte by painting with Lacomit solution. When dry this was smoothed with emery paper to produce a minimum discontinuity at the junction. With the whole electrode insulated it was found that 0·25 mA flowed at the centre strip at the maximum velocity. This was presumably due to imperfect covering and allowance was made for this in all measurements in which part of the surface was insulated. This consisted of an area and flow rate correction, the latter obtained by using the appropriate Reynolds number exponent for the prevalent flow regime. Lengths of electrode used were 16, 8, 4, 2 and 1 cm.

Experiments were performed at ambient temperature (17°C) and 45°C in order to investigate the influence of the Schmidt group on the mass transfer coefficient, using both electrolyte concentrations.

Results and discussion

Typical data for the variation of cell current with cell potential are presented in Fig. 2. Values of the limiting current, I_L, were used to calculate the average mass transfer coefficient, k, and the average Sherwood Number, Sh, over the area, A, from Equations (1) and (2):

$$k = \frac{I_L}{nFAC} \qquad (1)$$

$$Sh = \frac{kd_e}{D} \qquad (2)$$

where C is the concentration of copper sulphate in the electrolyte, nF the number of coulombs required to deposit one gram mole of copper ions, d_e the equivalent diameter of the cell and D the diffusivity of copper sulphate.

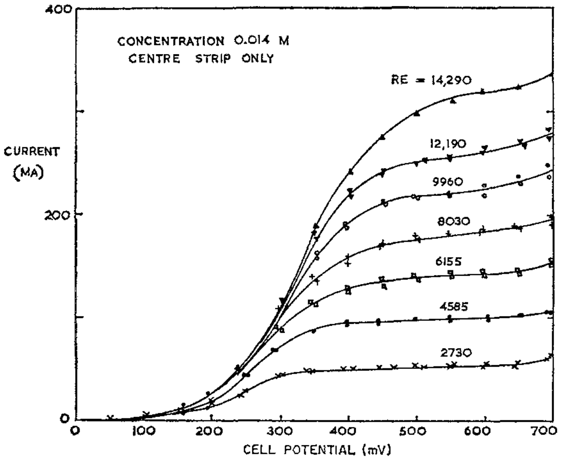

Fig. 2. Current-cell potential curves for acidified copper sulphate solution in turbulent flow.

Values for the physical properties of the electrolyte were obtained from the data of Eisenberg *et al.* [8, 9] and Arvia *et al.* [10].

For the higher flow rates the limiting currents were measured at the points of inflection on the curves. This assumption was consistent with both the potentials and currents at various flow rates.

Current densities for the centre and edge strips were compared to examine the influence of the change in velocity distribution across the channel.

Laminar flow

For established laminar flow the analytical solution for mass transfer to a plane electrode of width B forming one wall of a rectangular channel of cross-section $B \times s$ can be shown by means of the Leveque approximation to be:

$$k = \frac{D}{0{\cdot}893}\left(\frac{\beta}{9Dx}\right)^{\frac{1}{3}}$$

where β is the velocity gradient at the wall. For the parallel plate configuration:

$$\left(\frac{du}{dy}\right)_{y=0} = \beta = \frac{6U}{s}$$

$$\text{Then:}\quad Sh_x = \frac{1}{0{\cdot}893}\left(\frac{2}{3}\right)^{\frac{1}{3}}\left(\frac{d_e^3\,U}{sDx}\right)^{\frac{1}{3}}$$

$$= 0{\cdot}978\left(Re\,Sc\,\frac{d_e}{x}\right)^{\frac{1}{3}}\left(\frac{d_e}{s}\right)^{\frac{1}{3}} \qquad (3)$$

with the Reynolds number defined in terms of the equivalent diameter d_e, where:

$$d_e = \frac{4Bs}{2\,(B+s)} \qquad (4)$$

In terms of the aspect ratio γ ($= s/B$):

$$d_e = \frac{2s}{1+\gamma} \qquad (5)$$

so that equation (3) can be rewritten:

$$Sh_x = 0{\cdot}978\left(Re\,Sc\,\frac{d_e}{x}\right)^{\frac{1}{3}}\left(\frac{2}{1+\gamma}\right)^{\frac{1}{3}} \qquad (6)$$

When integrated over the whole electrode of length L this leads to:

$$Sh = 1{\cdot}467\left(Re\,Sc\,\frac{d_e}{L}\right)^{\frac{1}{3}}\left(\frac{2}{1+\gamma}\right)^{\frac{1}{3}} \qquad (7)$$

For infinite parallel plates ($\gamma = 0$) this reduces to the familiar form:

$$Sh = 1{\cdot}85\left(Re\,Sc\,\frac{d_e}{L}\right)^{\frac{1}{3}} \qquad (8)$$

which has been substantiated by Newman [7] as the limiting case for annuli. Rousar *et al.* (16) have produced an analytical expression to take account of the velocity distributions in a duct of finite width:

$$Sh = 1{\cdot}85\,\phi\left(Re\,Sc\,\frac{d_e}{L}\right)^{\frac{1}{3}} \qquad (9)$$

where ϕ is tabulated for various aspect ratios and electrode/duct widths. For electrodes occupying the full channel, substituting values of ϕ leads to Sherwood Numbers which differ by less than 1% from those calculated from Equation (7), providing that γ is in the range 0–0·5. Since operational cells would lie in this range, Equation (7) serves satisfactorily as a design equation.

Comparison of the data with Equation (7) is presented in Figs. 3, 4 and 5 showing the effects of variations of each of the three independent variable groups. For comparison, Equation (8) is also included. Satisfactory agreement regarding the one-third powers for the Reynolds number and d_e/L is apparent. The scattered data are due to Schmidt number variation being produced by both alteration of temperature and concentration, and reflects the disparity between the measured data [8, 9, 10]. With regard to Fig. 5, the results are presented for $Re = 1000$ over the temperature range 17–45°C, corresponding to an apparent Schmidt number variation of 3300 to 960. This produces a Schmidt number exponent of 0·29 which is significantly less than the theoretical value but is probably due to the uncertainty about the diffusion coefficient.

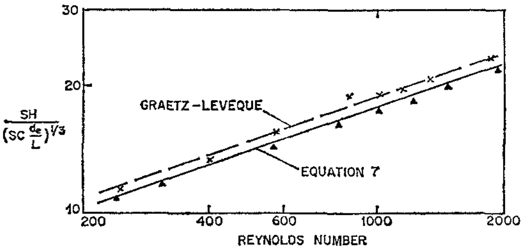

Fig. 3. Influence of Reynolds number, laminar flow.

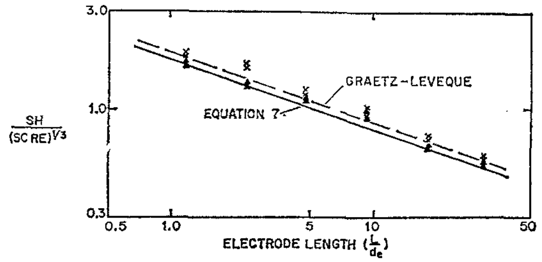

Fig. 4. Influence of electrode length, laminar flow.

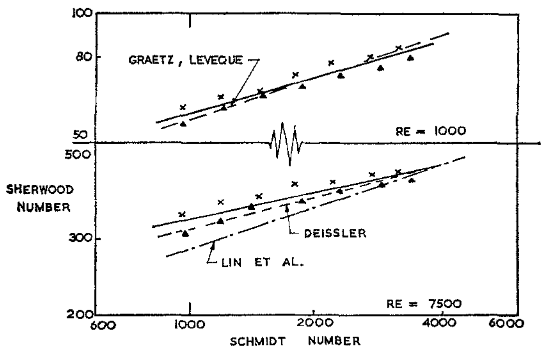

Fig. 5. Influence of Schmidt number, laminar and turbulent flow.

Mass transfer at the edges became proportionately less than that in the centre as flow rate increased, which is to be expected. The mean difference between the edge third and the centre third over the whole laminar range was found to be about 3%, slightly greater than predicted by Equation (9). There was no interference from natural convection as inverting the flow in the cell did not significantly change the mass transfer rates. Overall the results are best correlated by:

$$Sh = 2{\cdot}54\, Re^{\frac{1}{3}}\, Sc^{0.29} \left(\frac{d_e}{L}\right)^{\frac{1}{3}} \tag{10}$$

Turbulent flow

The dependence of Sherwood number on Reynolds and Schmidt numbers is shown in Figs. 5 and 6. The ordinate $Sh/Sc^{\frac{1}{4}}$ in Fig. 6 was chosen to enable comparison with the correlation of Deissler [11] which is recommended by Sherwood [12] for high Schmidt numbers. The points shown were calculated for $L/d_e = 35$ which was the longest electrode section used. An exponent of 0·875 is indicated for the Reynolds number, except for below $Re = 4000$ where transition

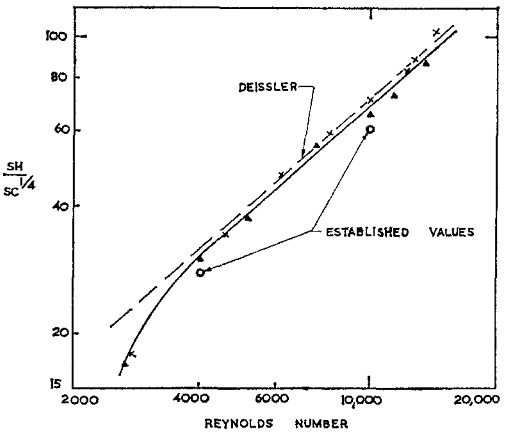

Fig. 6. Influence of Reynolds number, turbulent flow.

flow exists. This exponent verifies many of the commonly used expressions for mass transfer which derive Sh proportional to $\sqrt{f}\,Re$, where f is the friction factor. Good correlation could also be obtained with an equation due to Lin *et al.* [13] by plotting $Sh/Sc^{\frac{1}{3}}$ as ordinate.

A Reynolds number of 7500 was chosen to test dependence of the Sherwood number on the Schmidt number, shown in Fig. 5, where both Lin and Deissler's correlations are given for comparison. A gradient of 0·21 describes the data available better than either 0·25 (Deissler) or 0·33 (Lin). A recent investigation by Mizushina *et al.* [18] has found that Sherwood number varied with about the 0·9 power of Re and with the $\frac{1}{3}$ power of Sc in electrochemical systems operated with Re ranging from 3000 to 80 000.

The variation of average Sherwood number for electrodes of different lengths is shown for Reynolds numbers of 4000 and 10 000 in Fig. 7. These demonstrate that a constant value of mass transfer coefficient is reached at small L/d_e values at higher Reynolds numbers. To obtain local values of Sherwood number, numerical differentiations of the curves were made and presented as broken lines in Fig. 7. The local Sherwood numbers corresponding to the longest electrode are shown as the 'established values' in Fig. 6.

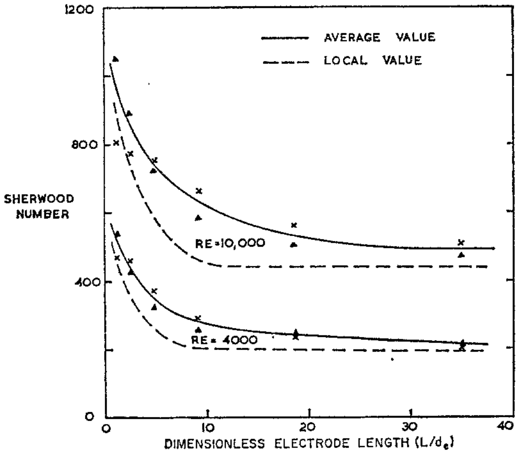

Fig. 7. Effect of dimensionless length (L/d_e), turbulent flow.

Local values of Sh become substantially constant above L/d_e of 10, and for a very long electrode the measured overall values of Sh should approach the local values. Accordingly it is justifiable to use these local values to produce an expression for fully developed mass transfer in turbulent flow.

$$Sh = 0{\cdot}0278\ Re^{0.875}\ Sc^{0.21} \qquad (11)$$

In a practical cell design, Equation (11) would be assumed to predict the mass transfer over the entire electrode length, even though the electrode length might be quite short.

Mass transfer entry lengths shown in Fig. 7 are significantly longer than those for tubes [14] and annuli [15] under equivalent conditions. This is in accord with a theoretical analysis for heat transfer in turbulent flow through these geometries [17].

With regard to mass transfer variation across the electrode in turbulent flow, there was little difference (*c.* 1·5%) between the current densities on the edge and centre strips. This would be expected due to a more uniform velocity distribution in turbulent flow.

Conclusions

The modified Leveque solution, Equation (7), satisfactorily predicts mass transfer rates in laminar flow to electrodes in the walls of a rectangular duct. However the Leveque solution is itself adequate for small values of aspect ratio.

For turbulent flow the correlation of Deissler which predicts a Schmidt number exponent of $\frac{1}{4}$ agrees well with the experimental data. The recent results of Mizushina appear to be better described by a $\frac{1}{3}$ exponent but, over the range of Schmidt numbers used in this investigation, the correlation of Deissler fits equally as well. This suggests that further experimental work in this system is desirable.

Acknowledgments

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Nomenclature

Symbols

A electrode area (cm^2)

B	width of electrode (cm)
C	concentration (g mol/cm^3)
d_e	equivalent diameter of cell (cm)
D	diffusion coefficient (cm^2/s)
f	friction factor
F	Faraday (A s/g equiv.)
i	current density (A/cm^2)
k	mass transfer coefficient (cm/s)
L	electrode length (cm)
s	distance between anode and cathode (cm).
u	electrolyte velocity (cm/s)
U	mean electrolyte velocity (cm/s)
x	dimension from leading edge of electrode in flow direction (cm)
y	dimension perpendicular to electrode surface (cm)
ρ	density of electrolyte (g/cm^3)
μ	viscosity of electrolyte (g/cm.s)

Dimensionless groups

Re	Reynolds number	$\frac{d_e U \rho}{\mu}$
Sh	Sherwood number	$\frac{k d_e}{D}$
Sc	Schmidt number	$\frac{\mu}{\rho D}$

Subscript

e	equivalent
x	value of variable at position x
L	limiting

References

[1] G. Wranglen and O. Nilsson, *Electrochim. Acta*, **7** (1962) 111.

[2] C. W. Tobias and R. G. Hickman, *Z. Phys. Chem. (Leipzig)*, **299** (1965) 145.

[3] A. Palade de Iribarne, S. L. Marchiano and A. J. Arvia, *Electrochim. Acta*, **15** (1970) 1827.

[4] J. Leveque, *Ann. Mines*, **13** (1928) 201, 305 and 381.

[5] L. Graetz, *Ann. Phys. Chem.*, **25** (1885) 337.

[6] B. R. Stanmore, M.Sc. thesis, University of Manchester (1970).

[7] J. J. Newman, *Ind. Eng. Chem.*, **60** (1968), 12.

[8] C. R. Wilke, M. Eisenberg and C. W. Tobias, *J. Electrochem. Soc.*, **100** (1953), 513.

[9] M. Eisenberg, C. W. Tobias and C. R. Wilke, *J. Electrochem. Soc.*, **103** (1956), 413.

[10] A. J. Arvia, J. C. Bazan and J. S. W. Carrozza, *Electrochim. Acta*, **11** (1966), 881.

[11] R. G. Deissler, *N.A.C.A. Tech. Note* 3145 (1954).

[12] T. K. Sherwood, *Chem. Eng. Prog. Symp. Ser.*, **55** (1959), 71.

[13] C. S. Lin, R. W. Moulton and G. L. Putnam, *Ind. Eng. Chem.*, **45** (1953), 636.

[14] P. Van Shaw, L. P. Reiss and T. J. Hanratty, *Amer. Inst. Chem. Engrs J.*, **9** (1963) 362.

[15] A. A. Wragg, Ph.D. thesis, University of Manchester (1964).

[16] I. Rousar, J. Hostomsky, V. Cezner and B. Stverak, *J. Electrochem. Soc.*, **118** (1971), 881.

[17] A. Quarmby and R. K. Anand, *Inst. J. Heat Mass Transfer*, **13** (1970), 395.

[18] T. Mizushina, F. Ogino, Y. Oka and Y. Fukuda, *Int. J. Heat Mass Transfer*, **14** (1971), 1705.