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An approximate design relationship for a fluidized bed electrode operating under conditions of mass transfer control

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1 Introduction

A number of papers in the literature report work both on the modelling of [1–7] and applications of [8–10] fluidized bed electrodes. Potential industrial uses of the electrode at the moment centre around the recovery of copper from dilute solutions and it is generally considered that future applications will be for electrochemical reactions subject to mass transfer control. Bearing this in mind, it would be useful to examine the possibility of applying established mass transfer correlations to the preliminary design and siting of electrodes.

2. Analysis

For a fluidized bed operating under conditions of mass transfer control at a steady state, Fleischmann *et al.* [4,6] have presented the following equation to describe the concentration variation of the reacting species:

$$\frac{u\mathrm{d}c}{\mathrm{d}x} = -\epsilon\frac{DAc}{\delta}\,, \tag{1}$$

where u is the electrolyte velocity in the x direction through the bed, ϵ the voidage, A the electrode area per unit volume and D and δ have their usual significance.

Since D and δ have purely formal significance in this context, the ratio D/δ will be replaced by the mass transfer coefficient k and integration of Equation 1 for a bed of length x gives

$$c = c_\mathrm{o} \exp \frac{-\epsilon kAx}{u}\,, \tag{2}$$

where c_o is the inlet concentration.

The local current density under limiting conditions is

$$i = nFkc \tag{3}$$

Substituting Equation 3 into Equation 2 and integrating over an electrode length L gives the total current I as

$$I = nFc_\mathrm{o}u\left[1-\exp\left(\frac{-\epsilon kAL}{u}\right)\right]. \tag{4}$$

Data obtained from mass transfer studies in liquid fluidized beds have been satisfactorily correlated by semi-empirical equations having the form [11]:

$$\frac{\epsilon k}{u}Sc^{\frac{2}{3}} = \mathrm{m}_1\left(\frac{ud}{\nu}\right)^{-0\cdot5}(1-\epsilon)^{0\cdot5}\,, \tag{5}$$

where m_1 is a numerical constant, d the particle diameter and Sc the Schmidt number $(=\nu/D)$.

Incorporating Equation 5 into Equation 4 and rearranging

$$\log\left(1-\frac{I}{nFc_\mathrm{o}u}\right) = -\mathrm{m}_1\left(\frac{ud}{\nu}\right)^{0\cdot5}(1-\epsilon)^{0\cdot5}\frac{Sc^{-\frac{2}{3}}}{2{\cdot}303}AL\,. \tag{6}$$

For a static bed of length L_o and voidage ϵ_o it is easy to show that, when fluidized to a working length L and voidage ϵ,

$$1-\epsilon = \frac{1-\epsilon_0}{1+\gamma}\ , \tag{7}$$

where γ is the fractional expansion of the bed $(L-L_0)/L_0$.

Similarly the electrode area per unit volume under static conditions A_0 relates to A by

$$A = A_0\frac{(1-\epsilon)}{(1-\epsilon_0)} = \frac{A_0}{(1+\gamma)} \tag{8}$$

Equation 6 can now be modified to include the experimentally measurable quantities γ and ϵ_0 so that

$$\log\left(1-\frac{I}{nFc_0u}\right) = -\mathrm{m}_2\ \frac{L}{u^{0\cdot5}\,(1+\gamma)^{3/2}}, \tag{9}$$

where m_2 is another constant equal to $\mathrm{m}_1\ (\nu/d)^{0\cdot5}\,[(1-\epsilon_0)^{\frac{1}{2}}/2{\cdot}303]\,(A_0Sc^{\frac{2}{3}})$. Thus a plot of fluidized bed experimental data in the form of Equation 9 subject to the limits on L and γ discussed by Backhurst *et al.* [12] should yield a straight line.

3. Application and discussion

The most readily available data for a test of Equation 9 are those obtained by Fleischmann [6] for oxygen reduction in an alkaline electrolyte on silver coated particles and shown in Fig. 7 of that paper.

Fig. 1 presents the above data, covering 5, 10, and 25% expansions of static beds of approximate lengths 4 mm to 25 mm, with $\epsilon_0 = 0{\cdot}42$ and $A_0 = 6500\ \mathrm{m}^{-1}$, as a plot of $\log(1-I/nFc_0u)$ against $L/u^{\frac{1}{2}}(1+\gamma)^{3/2}$; a reasonably good straight line is obtained. The three points which deviate most from the straight line are those for a static bed 25 mm long. This supports the observations of Backhurst *et al.* [12] concerning the maximum effective length of a copper electrode. Under the above conditions, $D = 1{\cdot}42\times10^{-9}\ \mathrm{m}^2\,\mathrm{s}^{-1}$, $\nu = 0{\cdot}95\times10^{-6}\ \mathrm{m}^2\,\mathrm{s}^{-1}$ and $d = 485\ \mu\mathrm{m}$ (average), so that from the slope of Fig. 1, $\mathrm{m}_1 = 1{\cdot}52$, giving the empirical mass transfer relationship for the system as:

$$\left(\frac{k}{u}\right)\epsilon\, Sc^{\frac{2}{3}} = 1{\cdot}52\ (1-\epsilon)^{0\cdot5}\left(\frac{ud}{\nu}\right)^{-0\cdot5}. \tag{10}$$

The assumption that k is proportional to $u^{\frac{1}{2}}$ in Equation 10 is admittedly rather tenuous for the range of Reynolds numbers covered by Fleischmann's data $(2 < ud/\nu < 7)$. These are definitely outside the Stokes flow region $(Re < 1)$ where $k \propto u^{\frac{1}{3}}$ but lower than that for the usual correlations [11] which are quoted mostly for $Re > 20$. Data corresponding to fluidized electrode conditions are very fragmentary although an empirical correlation due to Chu [13] for $1 < Re/1-\epsilon < 30$ is

$$\left(\frac{k}{u}\right)Sc^{\frac{2}{3}} = 5{\cdot}7\left(\frac{Re}{1-\epsilon}\right)^{-0\cdot78} \tag{11}$$

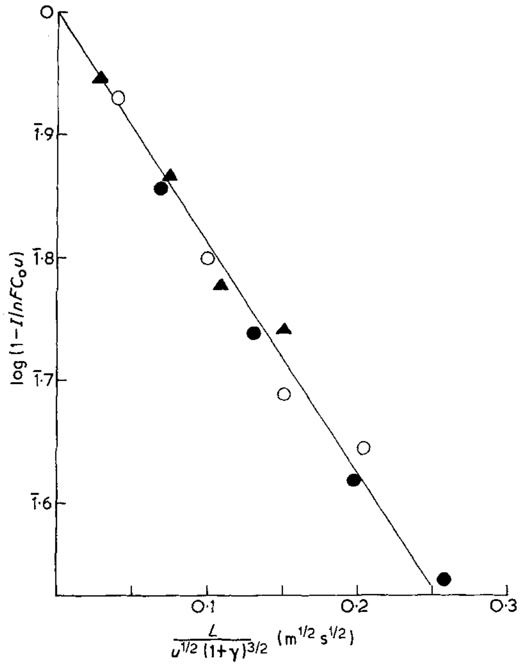

Fig. 1. Plot of data from [6], $u = 5{\cdot}32\ \mathrm{mm\ s}^{-1}$ (5% expansion) (●); $u = 8{\cdot}85\ \mathrm{mm\ s}^{-1}$ (10% expansion) (○); $u = 14{\cdot}2\ \mathrm{mm\ s}^{-1}$ [25% expansion (▲)].

For $Re = 5$ and $\epsilon = 0{\cdot}5$, differences in k values according to Equations 10 and 11 are less than 4%, indicating good agreement in this instance between electrochemical and non-electrochemical mass transfer.

It is not possible to make further effective comparison with published experimental work. Data on a copper bed [7] are not sufficiently detailed although k is quoted as about $1{\cdot}4\times10^{-6}\ \mathrm{m\,s}^{-1}$ with $u = 28\ \mathrm{mm\,s}^{-1}$ for $d \approx 460\ \mu\mathrm{m}$. Approximate calculations of k from Equation 10 gives k ranging between $1{\cdot}05\times10^{-6}\ \mathrm{m\,s}^{-1}$ to

$1{\cdot}44 \times 10^{-6}$ m s^{-1} for $\gamma = 0{\cdot}25$ and $\gamma = 0$ respectively, again indicating quite good agreement with Equation 10. A result quoted by Goodridge and Ismail [1] for the oxidation of ferrocyanide ions on platinised beads is an order of magnitude lower than the prediction of Equation 10, however their data in the absence of the bed also appear to be low in comparison with data on that system with nickel electrodes [14].

It appears reasonable to suggest that for copper deposition when the electrode surface is renewed in a high state of purity and for silver, where any oxide films, if present, would be highly conducting [15], a straightforward mass transfer equation allows a useful approach to cell design. Obviously much more data are desirable to rigorously test the general validity of Equation 10.

References

[1] F. Goodridge and B. M. Ismail, *Proc. Inst. Chem. Engrs. Symp. on Electrochem. Eng.* **1** (1971) 29.

[2] F. Goodridge, D. I. Holden, R. E. Plimley and H. D. Murray, *Trans. Inst. Chem. Engrs.* **49** (1971) 128.

[3] F. Goodridge, D. I. Holden, R. E. Plimley and H. D. Murray, *Trans. Inst. Chem. Engrs.* **49** (1971) 137.

[4] M. Fleischmann and J. W. Oldfield, *J. Electroanal. Chem.* **29** (1971) 211.

[5] M. Fleischmann and J. W. Oldfield, *Ibid.* 231

[6] M. Fleischmann, J. W. Oldfield, and D. F. Porter, *J. Electroanal. Chem.* **29** (1971) 241.

[7] M. Fleischmann, J. W. Oldfield and L. Tennakoon, *J. appl. Electrochem.* **1** (1971) 103.

[8] D. S. Flett, *Chem. Ind.* **13** (1971) 300.

[9] J. A. E. Wilkinson and K. P. Haines, *Trans. Inst. Min. and Metal* **81** (1972) C157.

[10] B. Surfleet and V. A. Crowle, *Trans. Inst. Metal Fin.* **40** (1972) 227.

[11] J. F. Davidison and D. Harrison (eds), 'Fluidisation', Acad. Press. Inc; London (1971).

[12] J. R. Backhurst, J. M. Coulson, F. Goodridge, R. E. Plimley and M. Fleischmann, *J. Electrochem. Soc.* **116** (1969) 1600.

[13] J. C. Chu, J. Kalil and W. A. Wetteroch, *Chem. Eng. Prog.* **49** (1953) 141.

[14] D. J. Pickett, unpublished work (1973).

[15] J. L. Dawson, unpublished data (1973).