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A note on the effectiveness of fixed bed electrodes

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1. Introduction

Three-dimensional fixed bed electrodes are generally considered for reactions with low operating current densities in order to increase localized mass transfer rates and/or increase overall current per unit cell volume. It is well appreciated, however, that reaction rate distribution may be non-uniform and hence that the surface area of the electrode is not fully utilized. The exception to this is the case of operation at the limiting current throughout the electrode. However, this type of operation requires a large limiting current plateau. With single reactions it is likely that the electrode will operate with local current densities both at and below the limiting current. This type of operation is considered in this paper.

In trying to interpret the non-uniformity of reaction rate and the utilization of the electrode area a convenient and simple concept of effectiveness, E, can be used. This allows the predicted maximum current density, based on a uniform potential distribution in the electrode, to be corrected to give the actual rate. The concept of effectiveness has been used by a number of workers [1, 2] in the analysis of particulate electrodes, but none have considered the influence of mass transport. Alternatively, the utilized (or effective) specific area, a_e, can be assessed and compared to that of equivalent two-dimensional electrodes through the expression $a_e = Ea$.

A previous analysis [3] has considered the effect of mass transport on effectiveness through approximate solutions. These solutions, however, are not generally applicable to all operating ranges. This communication considers the range where approximate solutions are invalid, and describes effectiveness characteristics obtained from numerical solution of the governing differential equation that describes the potential distribution.

2. Particulate bed analysis

The analysis considers a particulate electrode (Fig. 1) of thickness L, bounded on one side by a current feeder ($x = L$) and on the other by a diaphragm or free solution ($x = 0$). Both electrolyte and particulate phases are assumed to be continuous media whose effective conductivities are uniform and in which the electrical potential obeys Ohm's law. The electrode is operated under isothermal steady-state conditions and the bulk electrolyte reactant concentration is assumed constant (in practice the maximum reactant conversion is approximately 5%).

From a previous analysis [3] the differential equation governing potential distribution in the electrode is

$$\frac{d^2\phi}{dy^2} = v^2 \frac{i}{i_0} \tag{1}$$

where the following dimensionless parameters are defined

$$y = \frac{x}{L}; \quad v^2 = \frac{a i_0 L^2 \beta}{\kappa}; \quad \phi = \beta\eta$$

In the above, η is the local overpotential, i is the local current density, a is the specific electrode area, i_0 is the exchange current density, κ is the effective conductivity of the electrolyte and $\beta = nF/RT$.

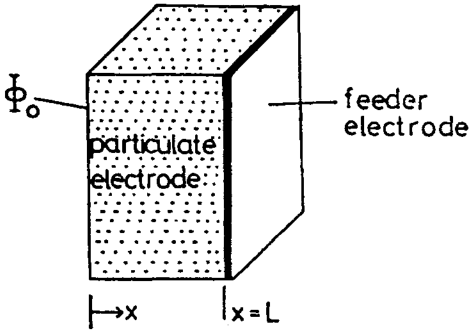

Fig. 1. Diagram of particulate electrode.

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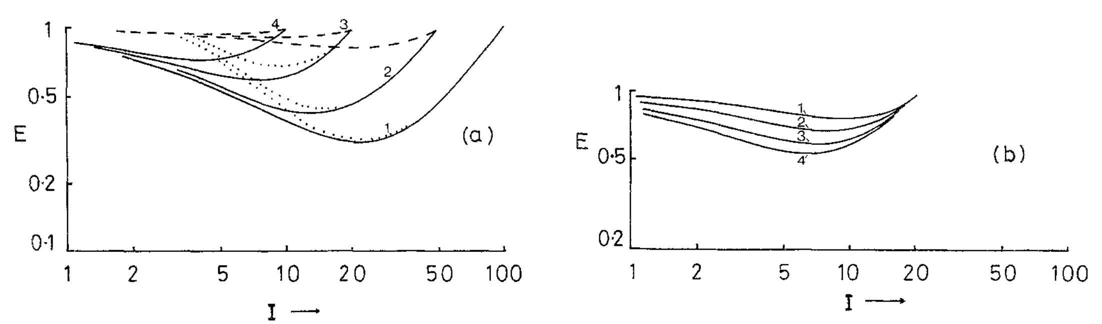

Fig. 2. Effectiveness factors for a Tafel reaction influenced by mass transport. $\alpha = 0.5$. Values of γ: 1, 100; 2, 50; 3, 20; 4, 10. (a) Solid lines, $\nu^2 = 1.0$; dashed lines, $\nu^2 = 0.1$; dotted lines, asymptotic solutions $\nu^2 = 1.0$. (b) Effect of transfer coefficient α on effectiveness. $\nu^2 = 1.0$, $\gamma = 20.0$. Values of α: 1, 0.2; 2, 0.33; 3, 0.5; 4, 0.67.

For a Tafel-type reaction influenced by mass transport (assuming migration is negligible) the local current density can be expressed as

$$\frac{i}{i_0} = \frac{\gamma}{1 + \gamma \exp(-\alpha\phi)} \tag{2}$$

where α is the transfer coefficient and γ is a dimensionless parameter determining the ratio of diffusion-limiting current density i_L to the exchange current density, i.e. $\gamma = i_L/i_0$.

Solutions to Equations 1 and 2 are obtained with the following boundary conditions.

$$y = 0; \quad \frac{d\phi}{dy} = -\nu^2 I; \quad \phi = \phi_0$$

$$y = 1; \quad \frac{d\phi}{dy} = 0; \quad \phi = \phi_1 \tag{3}$$

where $I = i_T/(ai_0L)$ and i_T is the total current density based on the cross-sectional area of the electrode. The solution technique is a shooting method based on Merson's numerical technique and Newton iteration. From this, potential distribution characteristics are determined and thus values of E can be defined:

E = the observed electrolytic current divided by the current obtained if the overpotential at all values of y were equal to its maximum value.

3. Results and discussion

Values of effectiveness are presented in Figs 2 and 3 as a function of total current density, I, for a typical transfer coefficient $\alpha = 0.5$. The range of values of ν^2 covered is from 0.1 to 1.0, i.e. the range where asymptotic solutions tend to be inaccurate. This is seen in Fig. 2 where asymptotic predictions of E (from Equation 28 in [3]) are compared to the exact values. At values of $\nu^2 < 0.1$, effectiveness factors will in most prac-

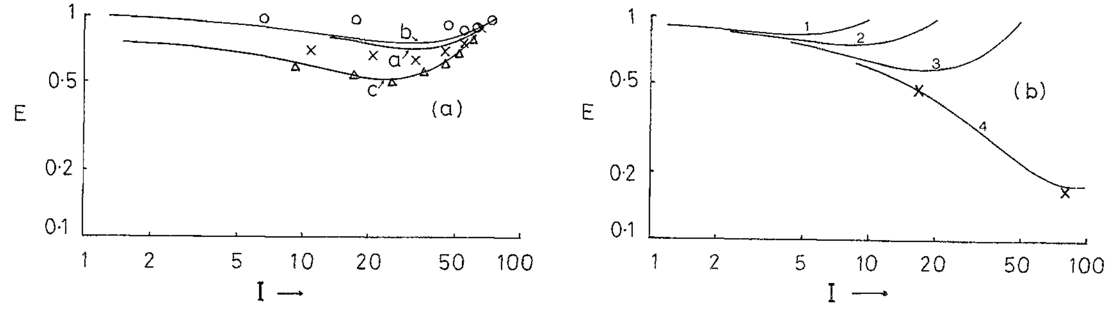

Fig. 3. Comparison of experimental and predicted effectiveness factors. $\alpha = 0.5$. (a) Effectiveness factors for the cathodic reduction of hydroquinone. x: $\gamma = 75$, $\nu^2 = 0.12$, line a shows predicted values. O: $\gamma = 72.5$, $\nu^2 = 0.1$, line b shows predicted values, Δ: $\gamma = 75$, $\nu^2 = 0.25$, line c shows predicted values. (b) Effectiveness factors for the cathodic reduction of nitrobenzene. $\alpha = 0.05$, $\nu^2 = 0.4$. Values of γ: 1, 10; 2, 20; 3, 50; 4, 700. x, experimental data from [5], $\gamma = 700$.

tical systems approach a value of 1.0, i.e. the electrode area is nearly 100% utilized.

The anticipated behaviour of effectiveness, where it passes through a minimum at particular values of I, is seen. This results from a gradual transition from an activation-controlled regime to a mass transport-controlled regime where an increasing proportion of the electrode tends to operate at or near the limiting current. High values of both γ and v^2 tend to give lower values of effectiveness.

The typical effect of variations in transfer coefficient is shown in Fig. 2b. Here high values of α result in lower effectiveness at intermediate values of I.

Fig. 3 shows effectiveness factors determined from experimental data for the cathodic reduction of quinone to hydroquinone on a particulate bed of silver spheres. The general variation of this data concurs with the predicted behaviour, i.e. minima in effectiveness are observed. Disagreement between prediction and experiment can in part be attributed to the values of exchange current density and effective conductivity used in the computation. The values of i_0 used (which varied even with cell length) quoted by Kreysa [4] were obtained by a fit to cell polarization characteristics.

Fig. 3b gives values of effectiveness calculated from the work of Goodridge and Hamilton [5] on the production of *p*-aminophenol on a fixed bed of Monel particles. In the region where mass transport influences behaviour a reasonable agreement between experimental and predicted effectiveness is achieved with a value of $\gamma = 700$ (calculated from the values of i_0 and i_L obtained by Goodridge and Hamilton). For example, at a value of $I = 82$ the experimental value of E is 0.17, compared to the predicted value of 0.185. The predicted value of E in the absence of mass transport limitations is 0.12, indicating the importance of mass transport in estimating particulate bed characteristics.

Overall, for the range of operation considered, this analysis of effectiveness can be used to assess the desirability of a fixed-bed electrode for a particular reaction through, amongst other things, the estimation of the utilized specific area. This, of course, is subject to reliable values of exchange current density being available.

References

[1] B. J. Sabacky and J. W. Evans, *Metallurgical Transactions B* **8B** (1977) 5.

[2] M. Paulin, D. Hutin and F. Coeuret, *J. Electrochem. Soc.* **124** (1977) 180.

[3] K. Scott, *Electrochim. Acta* **28** (1983) 1191.

[4] G. Kreysa, *ibid.* **23** (1978) 1351.

[5] F. Goodridge and M. A. Hamilton, *ibid.* **25** (1980) 481.