

SHORT COMMUNICATION

# The effect of axial dispersion on the concentration distribution in an electrochemical reactor

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Received 5 August 1974

## List of principal symbols

- $c$  electrolyte concentration
- $Fo$  Fourier number
- $L$  length of the electrochemical reactor
- $S$  half-width of the electrochemical reactor
- $x$  coordinate parallel to electrolyte flow
- $y$  coordinate transverse to electrolyte flow, between electrodes
- $v$  electrolyte velocity
- $\alpha$  lateral effective diffusion coefficient
- $\beta$  effective dispersion coefficient

## 1. Introduction

In the mathematical analysis of electrochemical reactors, the usefulness of the stirred tank reactor model [e.g. 1] and the plug-flow model [e.g. 2, 3] for approximate design has been demonstrated. Recent experimental findings by Fleischmann and coworkers [4], who applied short-duration anodic pulses in studying the mixing history of three-dimensional electrodes, indicate, however, that under appropriate circumstances the dispersion coefficient in an electrochemical reactor may be several orders of magnitude higher than the calculated diffusion coefficient; moreover, the importance of the effect increases with increasing Reynolds numbers. The purpose of this communication is to present a mathematical model for an electrochemical reactor, where *both* axial dispersion and lateral diffusion effects are considered in estimating the electrolyte concentration distribution.

## 2. Model development

The fundamental equations of an electrochemical

flow reactor have been previously described [5]. Assuming a flat axial velocity profile in a two-dimensional plane-parallel electrode system, the steady state model can be written as

$$(v) \frac{\partial c}{\partial x} = \alpha \left( \frac{\partial^2 c}{\partial y^2} \right) + \beta \left( \frac{\partial^2 c}{\partial x^2} \right), \quad (1)$$

where  $\alpha$  is the effective *lateral* diffusion coefficient and  $\beta$  is the effective *axial* dispersion coefficient. The following auxiliary conditions are postulated:

- (1) The inlet electrolyte concentration is uniform:  $c(0, y) = c_0$ .
- (2) The concentration distribution is symmetrical about the flow axis, i.e. the distribution of the bulk electrolyte concentration between the axis and either electrode is approximately the same:  $(\partial c / \partial y)(x, 0) = 0$ .
- (3) The electrochemical process (single-step) proceeds at an averaged rate at the electrode surface:  $(\partial c / \partial y)(x, S) = -i / F\alpha$ ;  $i = \text{constant}$ . Diffusion is the only significant process at the electrode surface.
- (4) There is no change in the concentration distribution when the electrolyte leaves the reactor:  $(\partial c / \partial x)(L, y) = 0$ .

Introducing dimensionless variables defined as  $\xi = x/L$ ;  $\eta = y/S$  and  $u = c/c_0$ , the dimensionless form of Equation 1 is

$$\frac{\partial u}{\partial \xi} = Fo \left[ \frac{\partial^2 u}{\partial \eta^2} + f \left( \frac{\partial^2 u}{\partial \xi^2} \right) \right], \quad (2)$$

where  $Fo = \alpha L / \nu S^2$  is the Fourier number of the system and the factor  $f = (\beta/\alpha)(S/L)^2$  expresses the relative importance of the axial dispersion effect. The auxiliary conditions are rewritten, respectively, as (1)  $u(0, \eta) = 1$ ; (2)  $\partial u / \partial \eta(\xi, 0) = 0$ ;

(3)  $\partial u/\partial \eta(\xi, 1) = -ki$ ;  $k = S/c_0 F \alpha$ ; and (4)  $\partial u/\partial \xi(1, \eta) = 0$ . As shown previously in the absence of axial dispersion, i.e. when  $f = 0$  [5], Equation 2 can be solved by the finite cosine transform technique [6]: the transform is defined as

$$\theta(\xi, n) \equiv \int_0^\pi u(\xi, z) \cos nz \, dz; \quad z = \eta\pi, \quad (3)$$

and its essential role is to transform Equation 2 into an appropriate ordinary differential equation whose solution can be written as

$$\theta(\xi, n) = c_1(n) \exp(\gamma_1 \xi) + c_2(n) \exp(\gamma_2 \xi) - \frac{ki \cos n\pi}{n^2}, \quad (4)$$

where

$$c_1(n) = -ki \left( \frac{\cos n\pi}{n^2 \pi} \right) \left[ \frac{\gamma_2 [\exp(\gamma_2 - \gamma_1)]}{\gamma_1} \right]$$

$$c_2(n) = ki \frac{\cos n\pi}{n^2 \pi} - c_1(n)$$

and the eigenvalues are

$$\gamma_1 = \frac{1 + \sqrt{(1 + 4\pi^2 F_0^2 f n^2)}}{2F_0 f}$$

and

$$\gamma_2 = \frac{1 - \sqrt{(1 + 4\pi^2 F_0^2 f n^2)}}{2F_0 f}$$

Upon inversion, the solution of Equation 2 can finally be written as

$$u(\xi, \eta) = 1 + \frac{2}{\pi} \sum_{n=1}^{\infty} \theta(\xi, n) \cos n\eta. \quad (5)$$

Equation 5 can be used to estimate local concentrations of the electrolyte in the case of axial dispersion.

### 3. Discussion

Table 1 contains fractional concentration profiles at the reactor exit and selected values of  $\eta$ . The profiles were computed via Equation 5, truncated past the first 25 terms (convergence is slow; for the purpose of numerical illustration in the 25-term expansion is of acceptable accuracy). The entries in the last column correspond to a model with no

axial dispersion and were computed via the corrected\* form of Equation 16 ( $\xi = 1$ ) and Table 1, ref. 5:

$$u(\xi, \eta) = 1 - \frac{2ki}{\pi^2} F(\xi, \eta), \quad (6)$$

Table 1. The effect of axial dispersion of an electrochemical reactor. Binary electrolyte; single electrode reaction involving a univalent ionic species

$\eta$	$u(1, \eta)$ via Equations 4 and 5				$u(1, \eta)$
	$fF_0 = 0.01$	$0.1$	$1.0$	$10.0$	via Equation 6 $fF_0 = 0$
0.2	1.013	1.011	1.005	1.001	1.013
0.4	1.013	1.012	1.005	1.001	1.013
0.5	1.013	1.011	1.005	1.000	1.013
0.7	1.011	1.010	1.005	1.001	1.011
0.9	0.961	0.965	0.989	0.999	0.961
1.0	0.878	0.886	0.931	0.981	0.869

$S = 0.5 \text{ cm}$ ;  $L = 2.5 \text{ m}$ ;  $v = 1 \text{ cm s}^{-1}$ ;  $i = 5 \text{ mA cm}^{-2}$ ;  $\alpha = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ .

where the numerical values of the  $F$  function have been tabulated. It is seen that the concentration gradient toward the electrode becomes smaller, and the concentration at the electrode becomes larger as  $f$  increased. Thus, the practical importance of the dispersion model is in indicating that the actual current flow must be larger than the one predicted via simpler models, in order to counteract the adverse effect of dispersion on reactor performance. Indeed, Equation 5 can be used to estimate such a current flow if  $u(\xi, \eta)$  is specified. It is instructive to interpret these results in terms of the current theory of dispersion in chemical reactors [7, 8]; for the cell parameters in Table 1, the Fourier number is computed as

$$F_0 = \frac{(10^{-5})(250)}{(1)(0.5)^2} = 0.01 \text{ and in the case of } fF_0 =$$

$0.01, f = 1.0$ . In consequence  $\beta = 2.5 \text{ cm}^2 \text{ s}^{-1}$  and the associated reactor dispersion number is

$$\frac{\beta}{vL} = \frac{2.5}{(1.0)(250)} = 0.01. \text{ This could be called a}$$

'small-to-intermediate dispersion' case, and comparison of the second and last columns in Table 1 shows that the dispersion effect on electrolysis can be ignored. On the other hand, as  $f$  is increased,

\* The author is grateful to Dr. D.J. Pickett who has pointed out a missing pi-factor.

$\beta/vL$  becomes progressively larger and the model tends asymptotically toward a perfectly mixed flow reactor model (e.g. at  $f = 1000$ , i.e.  $fFo = 10$ ,  $\beta/vL = 10$  which is very close to the case of 'infinitely' large dispersion number).

### References

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