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Concentration-time behaviour in a recirculating electrochemical reactor system using a dispersed plug-flow model

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This paper presents a theoretical model which takes account of axial dispersion in the prediction of concentration–time and current–time behaviour of recirculating batches of electrolyte in electrochemical reactor systems. The analysis shows that for a typical laboratory fluidized-bed reactor the error in the predicted time to achieve 90% extraction of copper from a Cu^{2+}-containing batch when a simple plug-flow model is used, is only of the order of 1%.

Nomenclature

A	bed cross-sectional area (cm^2)
a	bed specific surface (cm^{-1})
(Bo)	Bodenstein number, $d_p u/D$
c	concentration ($mol\,cm^{-3}$)
D	axial dispersion coefficient ($cm^2\,s^{-1}$)
d_p	particle diameter (cm)
F	Faraday number ($C\,mol^{-1}$)
I	current (A)
k	mass transfer coefficient ($cm\,s^{-1}$)
L	bed height (cm)
(Pe)	Peclet number
Q	volumetric flow rate ($cm^3\,s^{-1}$)
R	degree of conversion
t	time (s)
u	superficial velocity ($cm\,s^{-1}$)
V	reservoir volume (cm^3)
x	distance along reactor (cm)

Greek

α	defined by Equation 5
Γ	$= (Re)_{mf}/(Re)$
ϵ	voidage
τ	V/Q (s)

Subscripts

i	inlet
o	outlet
mf	minimum fluidization
L	at limiting current

Superscript

0	at $t = 0$

1. Introduction

In a recent paper a rigorous plug-flow model was developed for the prediction of concentration and current histories in electrochemical reactor systems involving batch recirculation of the electrolyte [1]. For many practical purposes a simplified model was shown to give good agreement with the more rigorous approach and the behaviour of a fluidized bed electrochemical reactor (FBER) system has been shown to be well described by the resulting equations [2, 3]. However, the assumption of plug flow in such a reactor is clearly not rigorously correct and it is the purpose of this paper to take account of axial dispersion effects in the formulation of expressions for concentration and current variation with time. The magnitude of the anticipated dispersion effect in an FBER is evaluated and an estimate of the likely error involved in the use of a simple plug-flow model is made.

The following assumptions are made:

(a) The rate of the electrode process is diffusion-controlled.

(b) The particle size in the reactor is constant.

(c) The mass transfer coefficient is uniform throughout the reactor.

(d) Dispersion may be characterised by the axial dispersion coefficient, D.

(e) Temperature and physical properties of the electrolyte are constant.

(f) The reservoir is a perfectly-stirred tank.

(g) The reactor is operated at the limiting current.

2. Concentration–time behaviour

The system under discussion is depicted in Fig. 1. A mass balance on a length element δx of the reactor at any time $t > 0$ may be stated as

$$\epsilon \frac{\partial c}{\partial t}(x,t) + u\frac{\partial c}{\partial x}(x,t) - D\epsilon\frac{\partial^2 c}{\partial x^2}(x,t) + kac(x,t) = 0 \qquad (1)$$

This resultant second-order partial differential equation may be solved rigorously or approximately, the approximate solution adopted here making use of the assumption

$$\frac{\partial c}{\partial t}(x,t)\bigg|_x \ll \frac{\partial c}{\partial x}(x,t) \qquad (2)$$

which is that the change in concentration with time is negligible as compared to its change with length; this is realistic for large reservoir to reactor volume ratios.

The p.d.e. is now reduced to the ordinary differential equation

$$\frac{D\epsilon}{u}\frac{\mathrm{d}^2 c}{\mathrm{d}x^2} - \frac{\mathrm{d}c}{\mathrm{d}x} - \frac{ka}{u}c = 0 \qquad (3)$$

The solution to this equation for boundary conditions appropriate to the present case is [4]

$$c_o = c_i \times \left[\frac{4\alpha\exp\left(\dfrac{uL}{2\epsilon D}\right)}{(1+\alpha)^2\exp\left(\dfrac{\alpha}{2}\dfrac{uL}{\epsilon D}\right) - (1-\alpha)^2\exp\left(-\dfrac{\alpha}{2}\dfrac{uL}{\epsilon D}\right)}\right] \qquad (4)$$

$$\text{where} \quad \alpha = [1 + 4(D\epsilon/uL)(L/u)ka]^{1/2}. \qquad (5)$$

A mass balance on the reservoir which is considered as a perfectly-stirred tank gives

$$V\frac{\mathrm{d}c_i}{\mathrm{d}t} = Q(c_o - c_i) \qquad (6)$$

Letting $\tau = V/Q$ and substituting for c_o from Equation 4 gives

$$\frac{\mathrm{d}c_i}{\mathrm{d}t} = -\frac{c_i}{\tau}\left[1 - \frac{4\alpha\exp\left(\dfrac{uL}{2\epsilon D}\right)}{(1+\alpha)^2\exp\left(\dfrac{\alpha}{2}\dfrac{uL}{\epsilon D}\right) - (1-\alpha)^2\exp\left(-\dfrac{\alpha}{2}\dfrac{uL}{\epsilon D}\right)}\right]. \qquad (7)$$

Upon integration this relates the concentration at any time, t, in the reservoir to the initial concentration c_i^0 as

$$c_i(t) = c_i^0\exp\left\{-\frac{t}{\tau}\left[1 - \frac{4\alpha\exp\left(\dfrac{uL}{2\epsilon D}\right)}{(1+\alpha)^2\exp\left(\dfrac{\alpha}{2}\dfrac{uL}{\epsilon D}\right) - (1-\alpha)^2\exp\left(-\dfrac{\alpha}{2}\dfrac{uL}{\epsilon D}\right)}\right]\right\} \qquad (8)$$

3. Variation of current with time

The current flowing at any point in the reactor is given by

$$\mathrm{d}I = nFkAa\,c(x)\,\mathrm{d}x \qquad (9)$$

where $c(x)$ can be shown [4] to be given by

$$c(x) = c_i \exp\left(\frac{ux}{2\epsilon D}\right)\left\{\frac{2(1+\alpha)\exp\left[\frac{\alpha}{2}\frac{u(L-x)}{\epsilon D}\right] - 2(1-\alpha)\exp\left[-\frac{\alpha}{2}\frac{u(L-x)}{\epsilon D}\right]}{(1+\alpha)^2\exp\left(\frac{\alpha}{2}\frac{uL}{\epsilon D}\right) - (1-\alpha)^2\exp\left(-\frac{\alpha}{2}\frac{uL}{\epsilon D}\right)}\right\} \qquad (10)$$

which reduces to Equation 4 for $x = L$.

The total current along the length L of the reactor is then given by integrating Equation 9 to give

$$I_L = nFQ\,c_i\left[1 - \frac{4\alpha\exp\left(\frac{uL}{2\epsilon D}\right)}{(1+\alpha)^2\exp\left(\frac{\alpha}{2}\frac{uL}{\epsilon D}\right) - (1-\alpha)^2\exp\left(-\frac{\alpha}{2}\frac{uL}{\epsilon D}\right)}\right]. \qquad (11)$$

The term inside the square brackets is equivalent to the steady-state single pass degree of conversion, $R[=(c_i - c_o)/c_i]$. The total current at any time t is now obtained by substituting for $c_i(t)$ from Equation 8 into Equation 11 to give

$$I_L(t) = nFQ\,c_i^0\,R\exp(-tR/\tau). \qquad (12)$$

4. Comparison with PFR and CSTR models

Walker [1] has presented approximate solutions for plug-flow and stirred-tank models of the reactor, the resultant equations being

$$c_i(t) = c_i^0 \exp\left\{-\frac{t}{\tau}\,[1-\exp(-kAaL/Q)]\right\} \qquad (13)$$

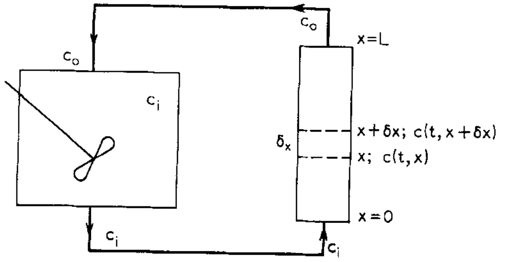

Fig. 1. Schematic representation of the reservoir–reactor system.

and

$$c_i(t) = c_i^0 \exp\left\{-\frac{t}{\tau}\left[1 - \frac{1}{(1+kAaL/Q)}\right]\right\} \qquad (14)$$

respectively. Levenspiel [5] has given a correction factor for small deviations from plug flow and this has been used in analysis of electrochemical reactors by Sioda [6].

The corrected form of Equation 13 would be

$$c_i(t) = c_i^0 \exp\left(-\frac{t}{\tau}\left\{1 - \left[1 + \left(\frac{kAaL}{Q}\right)^2\frac{D\epsilon}{uL}\right]\exp\left(\frac{-kAaL}{Q}\right)\right\}\right). \qquad (15)$$

It is of interest to compare the results given by Equations 8, 13, 14 and 15 when applied to a fluidized-bed reactor system as used in earlier experimental work for which the operating conditions are summarized in Table 1.

It should be noted that for the purpose of comparison, the same value of the mass transfer coefficient is employed in all four cases and dispersion coefficient values of 0·1, 1·0, 10 and 100 $\mathrm{cm^2\,s^{-1}}$ are used. Results are shown in Table 2 and in Fig. 2. From the table it can be seen that Levenspiel's correction becomes inaccurate

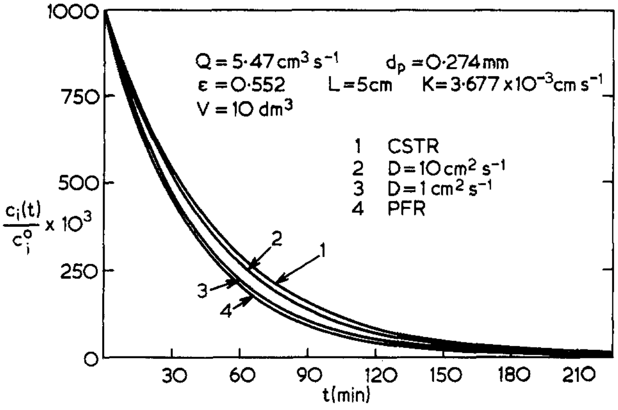

Fig. 2. Comparison of concentration–time behaviour as predicted by Equations 8, 13, 14 and 15.

Table 1. Fluidized-bed operating conditions

Flow rate	Q	$5{\cdot}347\ \mathrm{cm^3\ s^{-1}}$
Area cross-section	A	$5\ \mathrm{cm^2}$
Bed height	L	$5\ \mathrm{cm}$
Voidage	ϵ	$0{\cdot}552$
Particle diameter	d_p	$0{\cdot}0274\ \mathrm{cm}$
Reynolds number	(Re)	$2{\cdot}41$
(Re) (minimum fluidization)	$(Re)_{mf}$	$0{\cdot}86$
Mass transfer coefficient	k_L	$3{\cdot}67 \times 10^{-3}\ \mathrm{cm\ s^{-1}}$
Reservoir volume	V	$10\ \mathrm{dm^3}$

for $D = 1\ \mathrm{cm^2\ s^{-1}}$ (and in fact became unstable for $D = 10\ \mathrm{cm^2\ s^{-1}}$). The present DPFR model lies between the extremes of PFR and CSTR and shows the expected progression with the value of the dispersion coefficient. Fig. 2 shows the DPFR model with $D = 1$ and $10\ \mathrm{cm^2\ s^{-1}}$ only for clarity.

Values available in the literature for dispersion coefficients are varied, especially for fluidized beds. For liquid–solid systems Kramers *et al.* [7] have obtained values of D in the range 1–$10\ \mathrm{cm^2\ s^{-1}}$ using a DPFR model whilst Trawinski [8] and Wicke and Trawinski [9] quote values of the order of $1\ \mathrm{cm^2\ s^{-1}}$ in studies of liquid mixing patterns. Chung and Wen [10] have correlated liquid-phase axial dispersion coefficients via the equation

$$\frac{\epsilon(Bo)}{\Gamma} = 0{\cdot}20 + 0{\cdot}011\,(Re)^{0{\cdot}48} \tag{16}$$

where $(Bo) = d_p u/D$
and $\Gamma = (Re)_{mf}/(Re)$ (= 1 for packed beds)
and $0{\cdot}4 \leqslant \epsilon \leqslant 0{\cdot}8$, $10^{-3} \leqslant (Re) \leqslant 10^3$.

Although the Chung and Wen data are rather scattered this equation gives an estimate of the likely value of D for the operating conditions for an FBER indicated in Table 1. The result gives

$$D = 0{\cdot}209\ \mathrm{cm^2\ s^{-1}}$$

and

$$D/uL = \frac{1}{(Pe)} = 0{\cdot}039$$

This value of D is small and if plotted using the

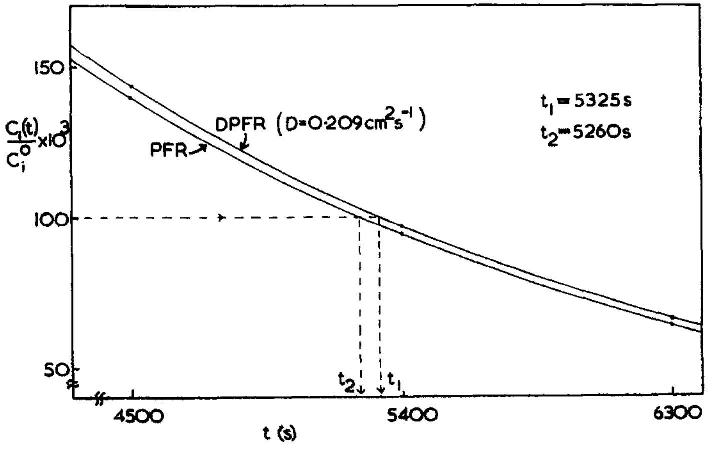

Fig. 3. Comparison of 90% extraction time for a recirculating electrolyte batch as predicted by Equations 8 and 13 with $D = 0{\cdot}209\ \mathrm{cm^2\ s^{-1}}$.

Table 2. Comparison of batch recirculation models. Results are expressed as $c_i(t)/c_i^0$ (× 10^3)

Time (mins)	*PFR*	*PFR corrected* (D = 0·1 cm^2 s^{-1})	*DPFR* (D = 0·1 cm^2 s^{-1})	*PFR corrected* (D = 1·0 cm^2 s^{-1})	*DPFR* (D = 1·0 cm^2 s^{-1})	*DPFR* (D = 10 cm^2 s^{-1})	*DPFR* (D = 100 cm^2 s^{-1})	*CSTR*
0	1000	1000	1000	1000	1000	1000	1000	1000
15	674·5	676·3	676·2	692·4	688·3	721·5	736·1	738·3
30	454·9	457·3	457·3	479·5	473·7	520·5	541·9	545·1
45	306·9	309·3	309·2	332·0	326·1	375·5	398·9	402·5
60	207·0	209·2	209·1	229·9	224·4	270·9	293·6	297·2
75	139·6	141·4	141·4	159·2	154·5	195·5	216·2	219·4
90	94·16	95·65	95·61	110·2	106·3	141·0	159·1	162·0
105	63·51	64·69	64·65	76·32	73·18	101·7	117·1	119·6
120	42·84	43·75	43·72	52·85	50·37	73·40	86·23	88·32
135	28·89	29·58	29·56	36·59	34·67	52·95	63·48	65·21
150	19·49	20·01	19·99	25·34	23·86	38·20	46·73	48·14
165	13·14	13·53	13·52	17·55	16·42	27·56	34·40	35·55
180	8·866	9·150	9·141	12·15	11·30	19·88	25·32	26·25
195	5·980	6·188	6·181	8·413	7·780	14·35	18·64	19·38
210	4·034	4·185	4·180	5·825	5·355	10·35	13·72	14·31
225	2·721	2·830	2·827	4·034	3·685	7·467	10·10	10·56

DPFR model on Fig. 2 would be hardly separable from the plug-flow curve. Levenspiel has argued that a value of the dispersion group D/uL of less than 0·0625 represents little deviation from plug flow and the value obtained here is well within that limit. Results presented by Fleischmann [11] suggest that D is of the correct order for the Reynolds number used. The low value of D, whilst in part attributable to the low Reynolds number, owes more to the small particle diameter indicated in Table 1, which gives a flatter velocity profile across the bed and hence less mixing of fluid elements. It is clear that for fluidized beds of a similar nature little error is introduced by approximating the behaviour using a PFR model and this accounts for the success of such a model in predicting experimental c–t curves for Cu^{2+} deposition in an FBER in a recirculating electrolyte system [2, 3].

However for FBERs where distinct particle circulation patterns are produced by electrolyte inlet design or by using inclined cells as described by Goodridge [12], significant dispersion effects may be encountered.

Finally it is of interest to compare the actual process times required to deplete the Cu^{2+} content of a recirculating electrolyte batch down to a concentration $c(t)/c_{\text{i}}^0$ of 0·1, i.e. an extraction of 90%, as predicted by the plug-flow model and the dispersed plug-flow model with $D = 0{\cdot}209\ \text{cm}^2\,\text{s}^{-1}$. The relevant portion of the concentration–time curve is shown as Fig. 3 where it can be seen that the PFR model underpredicts the treatment time by only 65 seconds in 5325, an error of 1·22%. This error is trivial for a real process when others errors, such as loss of current efficiency and the assumptions involved in the foregoing analysis, are considered.

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