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# *Modelling of a continuous parallel plate plug flow electrochemical reactor: electrowinning of copper*

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On the basis of copper winning in a sulphuric acid medium this paper presents an original calculation method for the design of a continuous parallel plate electrolytic cell consisting of three zones: a turbulent bulk in which convection and migration take place and two thin boundary layers at each electrode where diffusion and migration phenomena are taken into account. Current densities and species concentration profiles may be deduced from this model with the aid of mass transfer and electrochemical kinetic data. For conditions corresponding to industrial applications it can be shown that longitudinal migration in the bulk can be neglected. The validity of the model is successfully proved; in particular, results accounting for the effect of ionic migration on the limiting current density are in a good agreement with previous studies.

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## Nomenclature

| | |
|---|---|
| $A_e$ | electrode area ($m^2$) |
| $a$ | Tafel parameter (V) |
| $b$ | Tafel parameter (V) |
| $C$ | concentration ($mol\,m^{-3}$) |
| $D$ | molecular diffusion coefficient ($m^2\,s^{-1}$) |
| $d_{eq}$ | equivalent diameter (m) |
| $E_0$ | equilibrium potential (V) |
| $E_0^\circ$ | standard equilibrium potential (V) |
| $F$ | Faraday's constant (96487 $C\,mol^{-1}$) |
| $F_i$ | molar flux ($mol\,s^{-1}$) |
| $h$ | cell thickness (m) |
| $i$, $i_x$ | current density ($A\,m^{-2}$) |
| $i_0$ | exchange current densities ;($A\,m^{-2}$) |
| $i_L$, $i_{Lo}$ | limiting current densities ($A\,m^{-2}$) |
| $I$ | overall intensity (A) |
| $I_x$ | longitudinal electrical charge flux (A) |
| $K_x$ | Function defined as $\int_{\delta_c}^{h-\delta_a} (\partial\phi_s/\partial x)\,dy$ (V) |
| $k_d$ | mass transfer coefficient ($m\,s^{-1}$) |
| $l$ | cell width (m) |
| $L$ | cell length (m) |
| $R$ | perfect gas constant ($J\,K^{-1}\,mol^{-1}$) |
| $Re$ | Reynold's number defined on the basis of $d_{eq}$ |
| $r$ | coefficient $C_{H^+}/2C_{SO_4^{2-}}$ |
| $Sc$ | Schmidt number |
| $T$ | temperature (K) |
| $U_c$ | cell voltage (V) |
| $U_{co}$ | minimal cell voltage (V) |
| $\bar{v}$ | velocity ($m\,s^{-1}$) |
| $x$ | longitudinal abscissae |
| $y$ | transverse coordinate |
| $z$ | charge number |
| $\alpha$ | electrochemical kinetics parameter |
| $\gamma$ | electrochemical kinetics parameter |
| $\delta$ | diffusional layer thickness (m) |
| $\eta$ | overpotential (V) |
| $\kappa$ | electrical conductivity ($\Omega^{-1}\,m^{-1}$) |
| $\phi$ | electrical potential (V) |
| $\Omega$ | turbulent bulk section ($m^2$) |

*Subscripts*

| | |
|---|---|
| a | anode |
| c | cathode |
| E | inlet |
| i | compound i |
| M | metal |
| s | solution |
| $\delta$ | at the limit of the diffusion layer |

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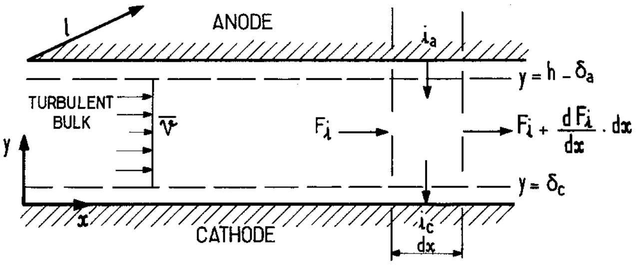


Fig. 1. Schematic view of a parallel plate electrochemical reactor.

## 1. Introduction

Because of its obvious industrial applications the parallel plate cell electrochemical reactor has been the subject of numerous studies. From an electrochemical engineering point of view, models or calculations to predict the performance of such a reactor or to design an electrochemical system have been proposed by several authors. However, it is difficult to solve the full set of equations describing all the phenomena such as fluid hydrodynamic structure, charge and mass transfer and electrochemical kinetics analytically, so that theoretical approaches generally rely upon one or several restrictive assumptions. For instance, mass transfer is often assumed to be a limiting factor in electrochemical reactions [1]; other studies [2] assume kinetic control. Newman [3, 4] has proposed a model of a cell in the laminar flow regime using the approximation of thin diffusion layers at the electrodes; however, the bulk concentrations of the reacting species are assumed to remain constant along the reactor and a multipass process is the only industrial application which could be relevant to these studies. White *et al.* [5] published a more general model taking into account fluid mechanics, ionic and mass transport and electrochemical kinetics for copper winning under the assumption of a well developed laminar flow.

Another approach consists in making use of chemical engineering concepts and models (hydrodynamic behaviour, mass transfer correlations [6, 7] etc). This paper describes a calculation method for the design of a continuous plate cell based on the film model and the assumption of piston flow.

Profiles of current density and of various species concentrations (in the bulk and at the working electrode) can be obtained as a function of the cell voltage. Though the well known example of copper electrowinning from a sulphuric medium is used for the development of the model, the whole methodology remains valid for any anodic or cathodic reaction in an undivided cell.

## 2. Assumptions and principles

In addition to those of constant temperature, constant physical parameters and steady-state conditions, the model is based upon the following assumptions.

(a) Three zones exist inside the reactor (see Fig. 1): a turbulent bulk in which convection and migration phenomena occur and where velocity and concentration profiles are assumed to be flat (plug flow model); and two thin boundary layers at the electrode, where migration and diffusion are taken into account (Nernst film model). The thickness of the anodic and cathodic layers are $\delta_a$ and $\delta_c$ respectively.

(b) Due to the small values of $\delta_a$ and $\delta_c$ the normal component of the current density is assumed to be constant in the cathodic film at a given position along the cell, i.e. $i_c(x, y = 0) = i_c(x, y = \delta_c) = i_c$. A similar assumption is made at the anode.

(c) In both layers, longitudinal gradients of concentration are negligible compared to transverse gradients ($y$-coordinate).

(d) A single electrochemical reaction occurs at each electrode. For the sake of simplicity, the chosen example is copper electrowinning from an acid solution of copper sulphate. The corresponding reactions are: $Cu^{2+} + 2e^- \longrightarrow Cu$ (at the cathode); $H_2O \longrightarrow 2H^+ + 1/2O_2 + 2e^-$ (at the anode–oxygen evolution). The current efficiency of both reactions is assumed to be 100%.

(e) Ionized species are completely dissociated.

(f) The kinetics of both reactions are based on literature values and take into account diffusional and electrochemical phenomena. In the chosen example Tafel or Butler–Volmer relations may be used:

$$\eta_a = a_a + b_a \log i_a \quad \text{with } i_a = i_a(x) \tag{1}$$

and

$$i_c = i_o \left\{ \exp\left(-\frac{\alpha_c F}{RT}\eta_c\right) - \exp\left(\frac{\alpha_a F}{RT}\eta_c\right)\right\} \tag{2}$$

In Equation 2 the exchange current density $i_o$ depends on the copper concentration $C_{1c}$ at the cathode, i.e. $i_o = kC_{1c}^{\gamma}$. The electrochemical parameters, $k$, $\gamma$, $\alpha_a$ and $\alpha_c$ depend on temperature and on the nature of the electrolytic medium and the cathodic material. Their values are found in the literature [8].

(g) The cell voltage $U_c$ remains constant along the cell and is the sum of several contributions (Fig. 1), namely

$(\phi_{Ma} - \phi_{sa})$, the anodic surface potential

$(\phi_{sa} - \phi_{\delta a})$, the potential difference in the anodic layer

$(\phi_{\delta a} - \phi_{\delta c})$, the ohmic potential drop in the bulk

$(\phi_{\delta c} - \phi_{sc})$, the potential difference in the cathodic layer

$(\phi_{sc} - \phi_{Mc})$, the cathodic surface potential

For given values of the cell voltage, inlet concentrations of the ionic species and hydrodynamic and geometrical parameters (flow velocity, width, length, thickness of the cell), the model allows the profiles of current density and concentration to be obtained.

## 3. Development of the model

In the following developments, indices 1, 2, 3 correspond to species $Cu^{2+}$, $H^+$ and $SO_4^{2-}$ respectively. ($SO_4^{2-}$ does not take part in the electrochemical reactions.)

### 3.1. *Preliminary calculations: magnitude of longitudinal charge flux*

The molar flux $F_i$ of species i at the abscissa $x$ in the turbulent bulk is the sum of the convection and migration terms,

$$F_i = \Omega \bar{v} C_i - z_i F \frac{D_i}{RT} C_i l \int_{\delta_c}^{h-\delta_a} \frac{\partial \phi_s}{\partial x}\, dy \tag{3}$$

where $\Omega$ is the cross-section of the bulk electrolyte, i.e.

$$\Omega = l(h - \delta_a - \delta_c)$$

$$\Omega \simeq lh \text{ if } \delta_a \ll h \text{ and } \delta_c \ll h \tag{4}$$

Mass balance for each chemical species over the length $dx$ of the cell leads to

$$\frac{dF_1}{dx} + \frac{i_c}{z_1 F} l = 0 \tag{5a}$$

$$\frac{dF_2}{dx} - \frac{i_a}{z_2 F} l = 0 \tag{5b}$$

$$\frac{dF_3}{dx} = 0 \tag{5c}$$

Introducing $I_x = \Sigma_{i=1}^{3} z_i F F_i$ in (5) gives

$$\frac{dI_x}{dx} + (i_c - i_a)l = 0 \tag{6}$$

Equation 6 expresses the electrical charge conservation over the element $dx$. Also, $I_x$ physically represents the electrical charge flux flowing longitudinally in the reactor at the $x$ abscissae and expresses the importance of migration phenomena in the bulk.

From Equation 3 written for $i = 1$, 2 and 3 and taking into account the electroneutrality condition, $I_x$ may be expressed as follows:

$$I_x = -\kappa\, l \int_{\delta_c}^{h-\delta_a} \frac{\partial \phi_s}{\partial x}\, dy \tag{7}$$

or

$$I_x = -\kappa\, l\, K_x \tag{7b}$$

in which $\kappa$ is the electrical conductivity,

$$\kappa = \Sigma_i (z_i F)^2 \frac{D_i}{RT} C_i \tag{8a}$$

and

$$K_x = \int_{\delta_c}^{h-\delta_a} \frac{\partial \phi_s}{\partial x}\, dy \tag{8b}$$

Combining Equations 6 and 7 leads to

$$-\kappa \frac{\mathrm{d}K_x}{\mathrm{d}x} = i_a - i_c \tag{9}$$

Though local current densities $i_a$ and $i_c$ may be different, all the overall electrode current crossing the anode reaches the cathode and therefore

$$I = \int_0^L i_a\, l\, \mathrm{d}x = \int_0^L i_c\, l\, \mathrm{d}x \tag{10}$$

Integration of Equation 9 gives the additional condition

$$K_{x=0} = K_{x=L} \tag{11}$$

This result means either that $K_x$ remains constant along the cell or that function $K_x$ presents at least one optimal value. In this case the derived function $\mathrm{d}K_x/\mathrm{d}x$ and the difference $(i_a - i_c)$ may have at least one change of sign. This is in agreement with previous studies [8].

Far upstream from the electroactive zone the molar flux $F_i$ (for $i = 1$–$3$) remains constant:

$$F_i = \Omega\bar{v}C_{iE}\ (x < 0) \tag{12}$$

where subscript E corresponds to the inlet of the cell.

Multiplying Equation 12 by $z_iF$ and summing the $i$ equations leads to

$$K_x = 0 \text{ for } x < 0$$

Assuming that $K_x$ is a continuous function at the entrance of the active zone one obtains

$$K_{x=0} = K_{x=L} = 0$$

As the molar flux $F_3$ is constant all along the reactor,

$$\Omega\bar{v}C_3 - z_3F\frac{D_3}{RT}C_3\, l\, K_x = \Omega\bar{v}C_{3E} \tag{13}$$

After dividing this relation by $C_3$, it is possible to express the difference $(i_a - i_c)$ as a function of concentrations $C_3$ and $C_{3E}$ and the gradient $\mathrm{d}C_3/\mathrm{d}x$ with the aid of Equation 9.

It can be seen from Equation 13 that if $C_3$ remains constant along the cell, the anodic current density $i_a$ is equal to the corresponding cathodic value $i_c$. Therefore two different solution methods have been considered:

(i) $C_3$ remains constant. Under these conditions $K_x$ is zero for all positions in the cell; the longitudinal charge flux $I_x$ is considered negligible.

(ii) $C_3$ may vary and the contribution of $I_x$ has to be taken into account. Calculations are then much more complex and require a numerical integration.

For the sake of simplicity only the first case will be presented. (The more rigorous model is developed in the Appendix where the validity of this assumption is shown for industrial processes involving current densities larger than 1 A m$^{-2}$.)

In the following, the current density $i_x$ is assumed to be only a function of the variable $x$.

### 3.2. *Calculations of the components of the cell voltage*

*3.2.1. Potential drop in the bulk.* Applying Ohm's law in the bulk and assuming that $\delta_a$ and $\delta_c$ are small compared to the channel thickness $h$ gives

$$\phi_{\delta a} - \phi_{\delta c} = \frac{h}{\kappa} i_x \tag{14}$$

*3.2.2. Potential drop in the cathodic diffusion layer.* Taking into account the previous assumptions, the three mass balances in the cathodic layer are written

$$\frac{\partial C_1}{\partial y} + \frac{z_1F}{RT}C_1\frac{\partial \phi_s}{\partial y} = \frac{i_x}{z_1FD_1} \tag{15a}$$

$$\frac{\partial C_2}{\partial y} + \frac{z_2F}{RT}C_2\frac{\partial \phi_s}{\partial y} = 0 \tag{15b}$$

$$\frac{\partial C_3}{\partial y} + \frac{z_3F}{RT}C_3\frac{\partial \phi_s}{\partial y} = 0 \tag{15c}$$

Summing these equations and integrating the relation obtained between 0 and $\delta_c$ leads to

$$i_x = z_1Fk_{dc}\left[(C_1 + C_2 + C_3) - (C_{1c} + C_{2c} + C_{3c})\right] \tag{16}$$

where $k_{dc} = D_1/\delta_c$ is the mass transfer coefficient between the cathode and electrolyte.

Additionally, an integration of the mass balances for ionic species 2 and 3 provides the following relations:

$$\frac{C_2}{C_{2c}} = \exp\left[-\frac{z_2F}{RT}(\phi_{\delta c} - \phi_{sc})\right] \tag{17a}$$

$$\frac{C_3}{C_{3c}} = \exp\left[-\frac{z_3F}{RT}(\phi_{\delta c} - \phi_{sc})\right] \quad (17b)$$

and also

$$\left(\frac{C_2}{C_{2c}}\right)^{1/z_2} = \left(\frac{C_3}{C_{3c}}\right)^{1/z_3} \quad (18)$$

Let us consider the abscissa $x$ inside the reactor corresponding to a given value of $C_1$ in the bulk. As concentration $C_3$ is assumed to be constant in the bulk, concentration $C_2$ can be obtained through the electroneutrality equation. Then Equation 18, associated with the electroneutrality equation, makes it possible to obtain $C_{1c}$, $C_{2c}$ and $i_x$ as a function $C_1$ and $C_{3c}$.

In the example of copper electrowinning,

$$z_1 = 2,\ z_2 = 1 \text{ and } z_3 = -2$$

$$C_2 = 2C_{3E} - 2C_1$$

$$C_{1c} = (2C_{3c} - C_{2c})/2 \text{ and } C_{2c} = C_2\left(\frac{C_{3E}}{C_{3c}}\right)^{1/2}$$

Finally the potential drop in the cathodic layer is provided by Equation 17,

$$\phi_{\delta c} - \phi_{sc} = -\frac{RT}{z_2F}\ln\frac{C_2}{C_{2c}} \quad (19)$$

*3.2.3. Potential drop in the anodic diffusion layer.* Similar considerations to those described above can be made, starting from mass balances in the anodic layer:

$$\frac{\partial C_1}{\partial y} + \frac{z_1F}{RT}C_1\frac{\partial \phi_s}{\partial y} = 0 \quad (20a)$$

$$\frac{\partial C_2}{\partial y} + \frac{z_2F}{RT}C_2\frac{\partial \phi_s}{\partial y} = \frac{i_x}{z_2FD_2} \quad (20b)$$

$$\frac{\partial C_3}{\partial y} + \frac{z_3F}{RT}C_3\frac{\partial \phi_s}{\partial y} = 0 \quad (20c)$$

These lead to

$$C_1 = C_{1a}\exp\left[-\frac{z_1F}{RT}(\phi_{\delta a} - \phi_{sa})\right] \quad (21a)$$

$$C_3 = C_{3a}\exp\left[-\frac{z_3F}{RT}(\phi_{\delta a} - \phi_{sa})\right] \quad (21b)$$

which can also be expressed as

$$\left(\frac{C_1}{C_{1a}}\right)^{1/z_1} = \left(\frac{C_3}{C_{3a}}\right)^{1/z_3} \quad (22)$$

Summing Equations 20a–c and integration of the relation obtained gives

$$(C_{1a} + C_{2a} + C_{3a}) = (C_1 + C_2 + C_3) + (i_x/z_2Fk_{da}) \quad (23)$$

in which $k_{da}$, the ratio of the diffusion coefficient $D_2$ and the layer thickness $\delta_a$, is the mass transfer coefficient at the anode.

From Equations 22 and 23 and the electroneutrality equation, the anodic concentrations $C_{1a}$, $C_{2a}$ and $C_{3a}$ may be expressed as a function of $C_1$ and $i_x$ (or $C_1$ and $C_{3c}$).

As an example, for the case of copper electrowinning, the following expressions are obtained (when $z_1 = +2$; $z_2 = +1$; $z_3 = -2$):

$$C_{3a} = (A + (A^2 + 12C_1C_{3E})^{1/2})/6$$

$$C_{1a} = C_1C_{3E}/C_{3a}$$

and $C_{2a} = 2(C_{3a} - C_{1a})$
with $A = C_1 + C_2 + C_3$

Finally, the potential drop in the anodic layer is written as

$$\phi_{\delta a} - \phi_{sa} = -\frac{RT}{z_1F}\ln\frac{C_1}{C_{1a}} \quad (24)$$

*3.2.4. Electrode potentials.* As has been previously mentioned, the relations between electrode overpotentials $\eta_a$ or $\eta_c$ and the local current density are described by Tafel or Butler–Volmer laws (see Equations 1 and 2).

The anode overpotential $\eta_a$ is defined as

$$\eta_a = (\phi_{Ma} - \phi_{sa}) - E_{oa} \quad (25)$$

where $E_{oa}$ is the equilibrium potential calculated from the standard value $E^{\circ}_{oa}$ and the concentrations $C_2$ and $C_{2a}$. A similar procedure is used for the cathodic contribution $\eta_c$.

It appears therefore that the last two contributions to the overall cell voltage $U_c$, $(\phi_{Ma} - \phi_{sa})$ and $(\phi_{Mc} - \phi_{sc})$ are also functions of the concentrations $C_1$ and $C_{3c}$.

*Table 1. Values of the main geometrical, physicochemical and electrochemical parameters*

Cell parameters: $h = 5 \times 10^{-3}\,\mathrm{m}$; $l = 1\,\mathrm{m}$
Fluid velocity: $\bar{v}$ in the range $10^{-2}$–$10^{-1}\,\mathrm{m\,s^{-1}}$

| Compound | $Cu^{2+}$ | $H^+$ | $SO_4^{2-}$ |
|---|---|---|---|
| Diffusion coefficient $D_i$ ($\mathrm{m^2\,s^{-1}}$) | $0.72 \times 10^{-9}$ | $9.31 \times 10^{-9}$ | $1.06 \times 10^{-9}$ |
| Inlet concentration $C_{iE}$ ($\mathrm{mol\,m^{-3}}$) | 100 | 2–2000 | 101–1100 |

Electrochemical kinetic parameters:

(a) Anode ($O_2$ evolution at a lead electrode)
$\eta_a = 0.303 + 0.12 \log i$ (Tafel's law)

(b) Cathode

$$[i] = i_0\left[\exp\left(-\frac{F}{RT}\eta_c\right) - \exp\left(\frac{F}{RT}\eta_c\right)\right]$$

with

$$i_o = kC_{1c}^{\gamma}$$

and $\gamma = 0.5$, $k = 1\,\mathrm{A\,m^{-2}(m^3 mol^{-1})^{-0.5}}$

## 4. Calculation principles

The various components of $U_c$ are given by Equations 14, 19, 24 and 25 which are described by the concentrations $C_1$ and $C_{3c}$. For a given value of $U_c$, it is possible to express $C_{3c}$ as a function of the local bulk concentration $C_1$.

The general principle of the model consists in considering a chosen value of $C_1$ and in calculating all other unknown concentrations and the current density $i_x$ using the above relations.

As longitudinal migration phenomena in the bulk are neglected in this approach the molar flux $F_1$ is only described by the convection term. Thus the conservation equation of the ionic species 1 is

$$\Omega\bar{v}\frac{\mathrm{d}C_1}{\mathrm{d}x} + \frac{i_x}{z_1 F}l = 0 \qquad (26)$$

which, after integration between 0 and $x$, leads to

$$x = z_1 F\bar{v}h\int_{C_1}^{C_{1E}}\frac{\mathrm{d}C_1}{i_x} \qquad (27)$$

From Equation 27 a graphical or numerical integration leads to the coordinate $x$ corresponding to concentration $C_1$ in the bulk. In addition, other factors such as the electrode area $A_e$ and the residence time $\tau$ inside the cell are given respectively by

$$A_c = lx \quad \text{and } \tau = x/\bar{v}$$

## 5. Results for the case of copper electrowinning

The model has been applied to the example of copper winning inside a parallel plate cell composed of a lead anode and a copper cathode. Table 1 reports the values of the electrochemical, physicochemical and geometrical parameters used. These were obtained from the literature [4, 9, 10]. The cell was provided with S.U. grids [7] giving good mass transfer performance. Under appropriate hydrodynamic conditions the mass transfer coefficient is expressed as

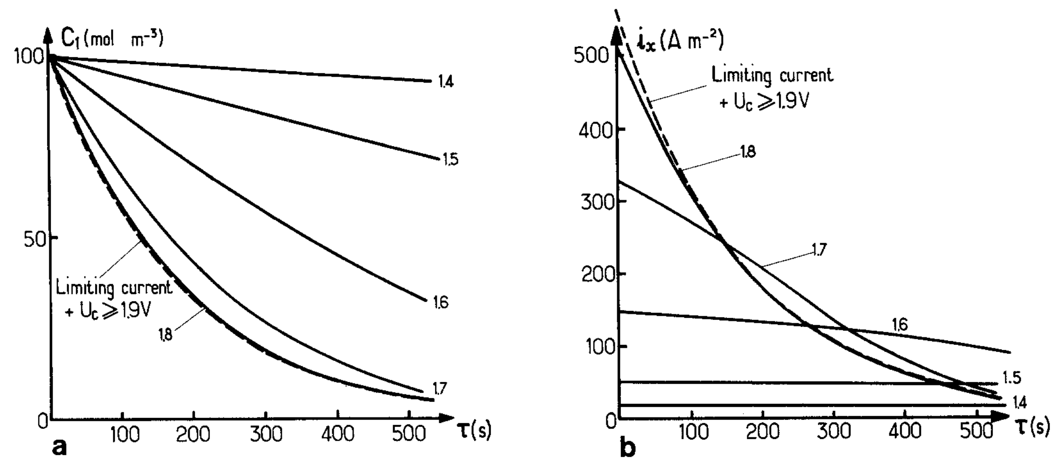
$$k_d = 5.57\,Re^{0.4}Sc^{1/3}\,D/d_{eq} \qquad (28)$$

where the equivalent cell diameter $d_{eq}$ is given by

$$d_{eq} = \frac{4\Omega}{2(1 + h)} \qquad (29)$$

Under the assumption of a negligible longitudinal component of the electric charge flux in the bulk, several numerical examples have been considered.

Fig. 2a–c shows the calculated variations of $C_1$, $i_x$ and $C_{1c}$ with the electrolyte residence time $\tau$ for a fluid velocity of $10^{-2}\,\mathrm{m\,s^{-1}}$ and different



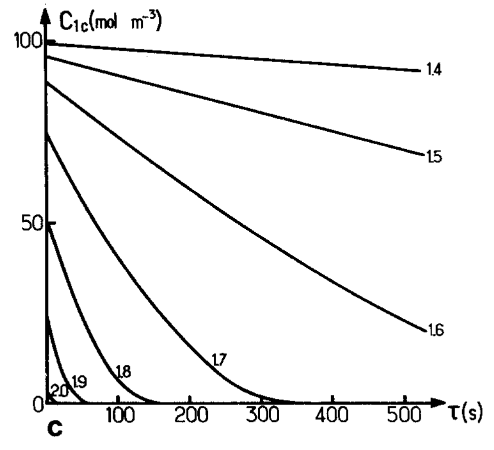


Fig. 2. Current density and copper concentration profiles in the cell $\bar{v} = 10^{-2}\,\mathrm{m\,s^{-1}}$; inlet concentrations, $10^2\,\mathrm{mol\,m^{-3}}$ $CuSO_4$, $10^3\,\mathrm{mol\,m^{-3}}$ $H_2SO_4$. (a) Bulk copper concentration $C_1$; (b) current density $i_x$; (c) copper concentration at the cathode $C_{1c}$.

values of the cell voltage $U_c$. The electrolyte contains $100\,\mathrm{mol\,m^{-3}}$ $CuSO_4$ and $1000\,\mathrm{mol\,m^{-3}}$ $H_2SO_4$, which correspond to typical orders of magnitude in industrial applications.

A large dependance of $U_c$ on the concentration and current density profiles can be observed. The minimum equilibrium cell voltage given by

$$U_{co} = E^{\circ}_{oa} + \frac{RT}{z_2F}\ln(C_{2E}10^{-3}) - E^{\circ}_{oc} - \frac{RT}{z_1F}\ln(C_{1E}10^{-3}) \qquad (30)$$

is close to 0.94 V in the given example. According to Fig. 2b a cell voltage below 1.4 V does not allow current densities larger than $20\,\mathrm{A\,m^{-2}}$. In contrast, for larger cell voltages (1.8–2.0 V), diffusion phenomena play an important role and the copper concentrations $C_{1c}$ at the cathode tend towards zero while the local current density approaches the limiting one. Under these conditions a residence time of 500 s, corresponding in this example to an electrode area of $5\,\mathrm{m^2}$, allows a conversion factor of cupric ions of up to 95%, with a current density close to $500\,\mathrm{A\,m^{-2}}$ at the cell inlet.

For the variations of $C_1$ and $i_x$ with $\tau$ the curves in dotted lines correspond to the case of a pure mass transfer limitation in the presence of an excess of supporting electrolyte. These were deduced from the following classical expressions valid for a piston type flow reactor:

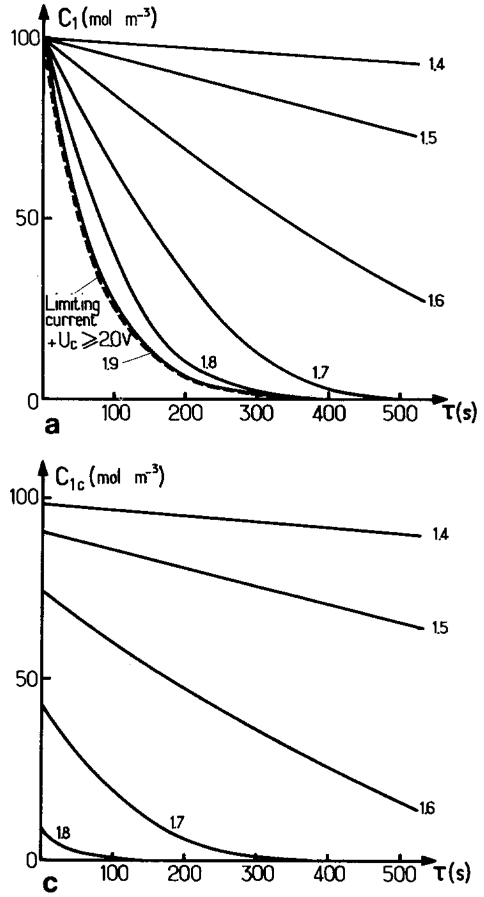
$$C_1 = C_{1E}\exp\left(-k_{dc}\frac{A_e}{V}\tau\right) \qquad (31)$$

and

$$i_x = z_1Fk_{dc}C_1 \qquad (32)$$

where $A_e$ is the electrode area and $V$ the electrolyte volume. There is excellent agreement on the model and these limiting expressions when the cell voltage is sufficiently high ($U_c > 1.9$ V).

Fig. 3a–c shows the effect of a different electrolyte flowrate, $\bar{v} = 0.1\,\mathrm{m\,s^{-1}}$, corresponding to a higher mass transfer coefficient $k_{dc}$. For low values of $U_c$, where the influence of diffusional limitations is weak, the concentration and current density distributions are not modified by an increase in $\bar{v}$ (see for example the curves for



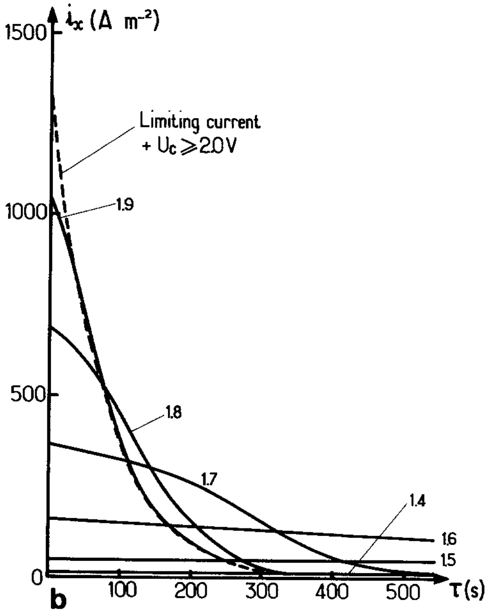


Fig. 3. Current density and copper concentration profiles in the cell: $\bar{v} = 10^{-1}\,\mathrm{m\,s^{-1}}$; inlet concentrations, $10^2\,\mathrm{mol\,m^{-3}}$ $CuSO_4$, $10^3\,\mathrm{mol\,m^{-3}}$ $H_2SO_4$. (a) Bulk copper concentration $C_1$; (b) current density $i_x$; (c) copper concentration at the cathode $C_{1c}$.

$U_c$ = 1.4 and 1.5 V). However, when the cell voltage increases, higher conversion factors may be obtained (for a given residence time $\tau$) and also larger current densities at the cell entrance. Furthermore, by considering lower values of the concentration of sulphuric acid, it is possible to study the effect of ionic migration on the cell performance. As an example, Figs 4a and 4b present the effect of $U_c$ on the current density profiles for the same copper concentration $C_{1E}$ but very different acid inlet concentrations: $1000\,\mathrm{mol\,m^{-3}}$ (Fig. 4a), which corresponds to a large excess of supporting electrolyte, and $1\,\mathrm{mol\,m^{-3}}$ (Fig. 4b). In the latter case very large values of $U_c$ (up to 5 V) are required in order to obtain a good performance due to the low electrolyte conductivity. However, in agreement with previous theoretical studies dealing with copper winning [4, 11], current densities can be larger than the limiting value $i_{L_0}$ obtained with an excess of supporting electrolyte (Equation 32) for the same copper concentration.

Defining $r = C_H^+/C_{SO_4^{2-}}$ [4] in which $C_H^+$ and $C_{SO_4^{2-}}$ are the local concentrations in the bulk, the ratio $i_L/i_{L_0}$ of the limiting current densities obtained either with the effect of ionic migration ($i_L$) or neglecting this effect ($i_{L_0}$) can be calculated.

It is observed that low values of $r$ correspond to low acid concentrations and that $r$ tends to unity in the presence of an excess of supporting electrolyte. Newman [4] used a numerical method to deduce the curve $i_L/i_{L_0}$ vs $r$ for the rotating disk, whereas Hornut *et al.* [11] proposed an original analytical solution,

$$\frac{i_L}{i_{L_0}} = 1 - \frac{z_A}{(z_1 + 2rz_2)} \times \left\{1 + 2r - (2r)^{-z_1/(z_2-z_1)} \times \left[\left(-\frac{z_2}{z_1}\right)^{-z_1/(z_2-z_1)} + \left(-\frac{z_2}{z_1}\right)^{-z_2/(z_2-z_1)}\right]\right\} \qquad (33)$$

where $z_A = 2$ for copper winning.

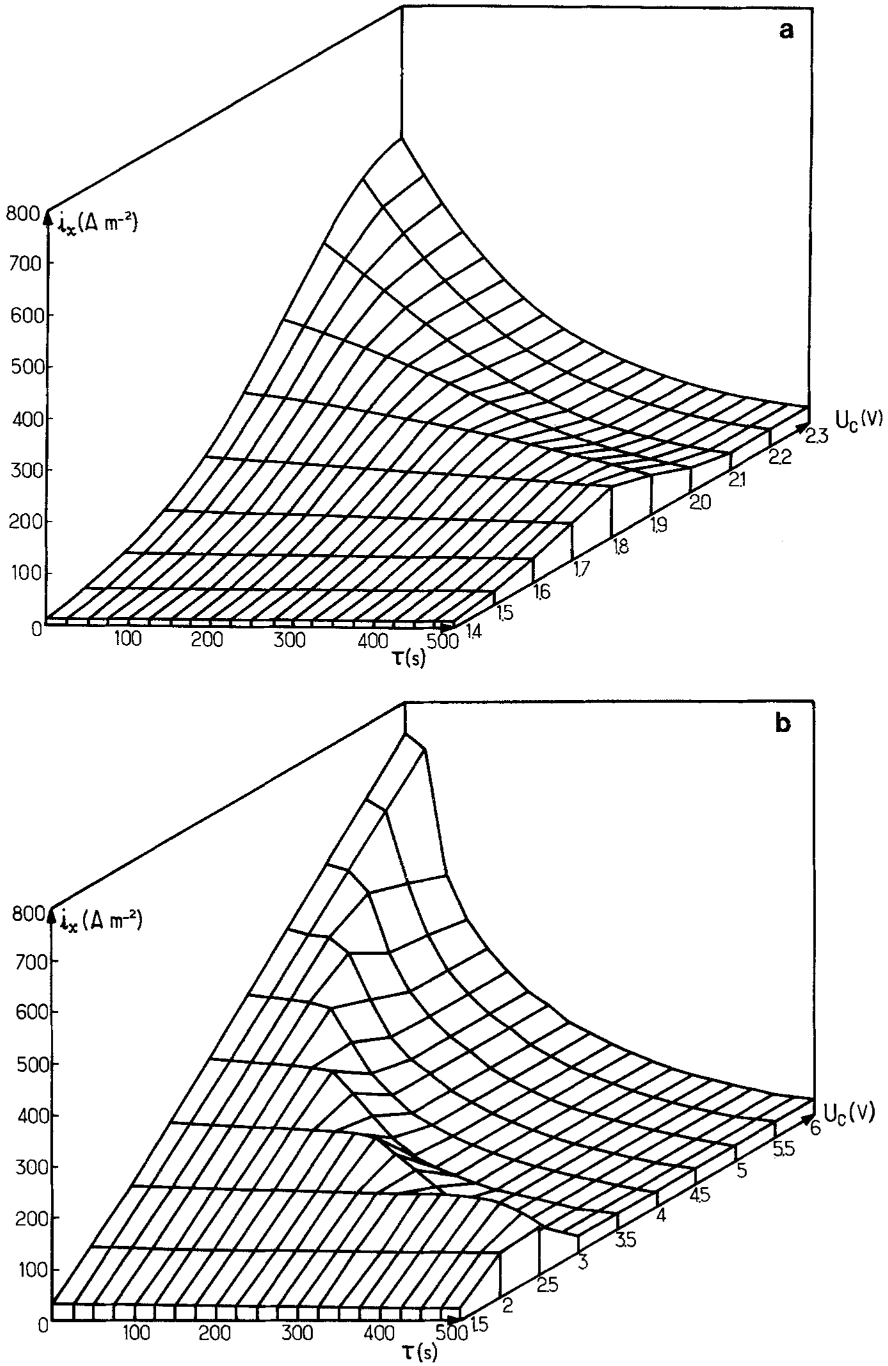


Fig. 4. Variations of the current density $i_x$ vs residence time $\tau$ and cell voltage $U_c$; $\bar{v} = 10^{-2}\,\mathrm{m\,s^{-1}}$; inlet copper sulphate concentration, $10^2\,\mathrm{mol\,m^{-3}}$. (a) inlet $H_2SO_4$ concentration, $10^3\,\mathrm{mol\,m^{-3}}$. (b) inlet $H_2SO_4$ concentration, $1\,\mathrm{mol\,m^{-3}}$.

In the present study the case of an acid inlet concentration of $1\,\mathrm{mol\,m^{-3}}$ was considered. The model provides the values of limiting current densities $i_L$ for which $C_{1c}$ are lower than $10^{-2}\,\mathrm{mol\,m^{-3}}$. Corresponding values of bulk copper concentration $C_1$ lead to limiting current densities $i_{L_0}$ according to Equation 32. By considering cell voltage $U_c$ varying from 2 to 8 V the variations of the ratio $i_L/i_{L_0}$ vs $r$ in the range 0.03–1.0 can be calculated.

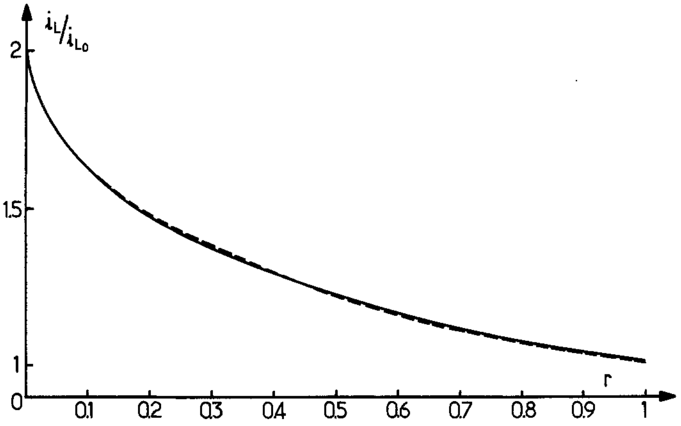


Fig. 5. Calculated variations of $i_L/i_{L_0}$ with $r = C_{H^+}/2C_{SO_4^{2-}}$. ———, present work; ------, equation 33 according to [11].

Fig. 5 shows the good agreement between the results obtained using the present model and the analytical relation (Equation 33) though the approaches to the problem are very different. Both predict a current density $i_L$ twice as large as $i_{L_0}$ for very low concentrations of the supporting electrolyte.

## 6. Conclusion

The present paper describes a simple but general model of a plug flow electrochemical reactor based upon an original electrochemical reaction engineering approach. The model assumes a plate cell consisting of three zones: two boundary layers at the electrodes where diffusion and migration occur and a turbulent bulk in which it has been shown that axial migration can very often be neglected.

The validity of this model has been successfully tested for a few conditions for the case of copper winning. With an excess of supporting electrolyte and for large cell voltages the current densities reach values which are the same as the limits defined by diffusion phenomena. Further, the influence of ionic migration under low values of the electrolyte concentrations can be predicted and is found to be in good agreement with other studies.

## Appendix

The solution procedure of the more general model is presented below. First, the average current density at abscissa $x$ in the bulk can be approximated as the arithmetic mean of $i_a$ and $i_c$ So the ohmic drop in the bulk is given by

$$\phi_{\delta a} - \phi_{\delta c} = \frac{h}{2\kappa}(i_c + i_a) \qquad \text{(A1)}$$

Mass balances in the cathodic layer are similar to Equation 15 in regard to species 1:

$$\frac{\partial C_1}{\partial y} + \frac{z_1 F}{RT} C_1 \frac{\partial \phi_s}{\partial y} = \frac{i_c}{z_1 F D_1} \qquad \text{(A2)}$$

leading to

$$i_c = z_1 F k_{dc}\,[(C_1 + C_2 + C_3) - (C_{1c} + C_{2c} + C_{3c})] \qquad \text{(A3)}$$

Equations 15 and 16 remain valid.

The solution procedure requires a numerical integration vs $x$ and an iterative process has to be used. At the entrance, $C_i = C_{iE}$, and $i = 1$–$3$. Equations A2, A3, 17 and 18 allow expression of $C_{1c}$, $C_{2c}$, $i_c$ and $(\phi_{\delta c} - \phi_{sc})$ at the entrance as functions of $C_{3c}$.

In the same way, in the anodic layer

$$(C_{1a} + C_{2a} + C_{3a}) = (C_1 + C_2 + C_3) + i_a/z_2 F k_{da} \qquad \text{(A4)}$$

At the entrance of the reactor a value of gradient $\mathrm{d}K_x/\mathrm{d}x$, denoted $(\dot{K})_{x=0}$, is arbitrarily chosen, allowing the determination of $i_a$ as a function of $C_{3c}$ from Equation 9. At this abscissa, concentrations $C_{1a}$, $C_{2a}$ and $C_{3a}$ can be obtained vs $C_{3c}$ from Equations 22, A4 and the electroneutrality equation.

Other components of the cell voltage $U_c$ are then expressed versus $C_{3c}$. As explained above, concentration $C_{3\mathrm{c}}$ is calculated from the equation $U_\mathrm{c}$ = Constant, and so every concentration and current density has known values at $x = 0$ for an assumed value of $(\dot{K})_{x=0}$.

Developing Equations 5a–c,

$$\Omega\bar{v}\frac{\mathrm{d}C_1}{\mathrm{d}x} - z_1F\frac{D_1}{RT}l\left[C_1\frac{\mathrm{d}K_x}{\mathrm{d}x} + K_x\frac{\mathrm{d}C_1}{\mathrm{d}x}\right] = -\frac{i_\mathrm{c}}{z_1F}l \qquad \text{(A5a)}$$

$$\Omega\bar{v}\frac{\mathrm{d}C_2}{\mathrm{d}x} - z_2F\frac{D_2}{RT}l\left[C_2\frac{\mathrm{d}K_x}{\mathrm{d}x} + K_x\frac{\mathrm{d}C_2}{\mathrm{d}x}\right] = +\frac{i_\mathrm{a}}{z_2F}l \qquad \text{(A5b)}$$

Values of concentration gradients at the entrance of the reactor can be deduced from Equations A5 and 13. Then, considering the elements $\Delta x$, bulk concentrations at $\Delta x$ are approximated by

$$(C_\mathrm{i})_{x=\Delta x} = (C_\mathrm{i})_{x=0} + \Delta x\left(\frac{\mathrm{d}C_\mathrm{i}}{\mathrm{d}x}\right)_{x=0} \qquad \text{(A6)}$$

The molar flux $F_3$ is constant in the reactor and so

$$\Omega\bar{v}(C_3)_{x=\Delta x} - z_3F\frac{\mathrm{D}_3}{RT}C_3l(K_x)_{x=\Delta x} = \Omega\bar{v}C_{3\mathrm{E}} \qquad \text{(A7)}$$

which leads to the knowledge of $(K_x)_{x=\Delta x}$ and allows the calculations of $C_{\mathrm{ia}}$, $C_{\mathrm{ic}}$, $i_\mathrm{a}$ and $i_\mathrm{c}$ at $\Delta x$.

Function $K_x$ has to be null at the end of the reactor, for $x = L$ which has an imposed value. An optimization procedure is required to find the right value of $(\dot{K})_{x=0}$ in agreement with this constraint.

Various values of the parameters have been used: $C_{1\mathrm{E}}$ and $C_{2\mathrm{E}}$ in the range 1–1000 mol $^{-3}$; $U_\mathrm{c}$ in the range 1.2–5 V, corresponding to current densities larger than $1\,\mathrm{A\,m^{-2}}$; $\bar{v} = 10^{-2}\,\mathrm{m\,s^{-1}}$, and $L = 5\,\mathrm{m}$ (corresponding to $\tau = 500\,\mathrm{s}$ and $A_\mathrm{e} = 5\,\mathrm{m}^2$). $\Delta x$ was chosen equal to $5 \times 10^{-2}\,\mathrm{m}$.

$(\dot{K})_{x=0}$ was optimized in the computer program through a Fibonacci type method and was assumed to be between $-10\,\mathrm{V\,m^{-1}}$ and $+10\,\mathrm{V\,m^{-1}}$. Indeed, function $\mathrm{d}K_x/\mathrm{d}x$ is defined by

$$\frac{\mathrm{d}K_x}{\mathrm{d}x} = \frac{\mathrm{d}}{\mathrm{d}x}\left[\int_{\delta_\mathrm{c}}^{h-\delta_\mathrm{a}}\left(\frac{\partial\phi_\mathrm{s}}{\partial x}\right)\mathrm{d}y\right] \qquad \text{(A8)}$$

It can be assumed that all along the plug flow reactor

$$[\partial\phi_\mathrm{s}/\partial x] < 10\,\mathrm{V\,m^{-1}} \qquad \text{(A9)}$$

Assuming that $\partial\phi_\mathrm{s}/\partial x$ and $K_x$ are continuous functions, $B$, a finite constant can be defined as

$$[K_x] < Bh\;[\,\partial\phi_\mathrm{s}/\partial x]_{\max} \qquad \text{(A10)}$$

Considering a small value of cell thickness, the former relations allow the assumption that $(\dot{K})_{x=0}$ is between $-10\,\mathrm{V\,m^{-1}}$ and $+10\,\mathrm{V\,m^{-1}}$.

Under these conditions it is noticed that whatever the initial value of $(\dot{K})_{x=0}$, function $K_x$ is almost linear and so the constraint $(K_x)_{x=L} = 0$ cannot be satisfied. Optimization of $(\dot{K})_{x=0}$ leads to values lower than $10^{-4}\,\mathrm{V\,m^{-1}}$ and so:

> concentrations $C_3$ are equal $C_{3\mathrm{E}}$ ($\pm 10^{-6}$mol m$^{-3}$); the absolute difference between $i_\mathrm{a}$ and $i_\mathrm{c}$ is lower than $10^{-3}\,\mathrm{A\,m^{-2}}$.

Thus the influence of the migration in the bulk can be neglected thus allowing a much easier calculation of electrochemical functions than that presented above.

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