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Parallel Plate Electrochemical Reactor Model

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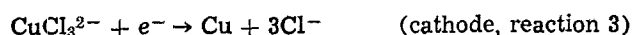
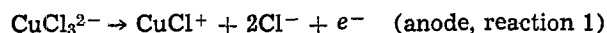
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ABSTRACT

A model is presented for a parallel plate electrochemical reactor which has electrodes that are the same size and are close together. That is, the distance between the electrodes (S) is much smaller than the length (L) or width (W) of the electrodes. Consideration of the material balance equations in light of this small aspect ratio (S/L) condition leads to predictions of derived quantities of interest (e.g., current efficiency) that depend on the product of the aspect ratio and the Peclet number, where $Pe = 2v_{avg}S/D_R$. Predictions of such derived quantities are made for electrolysis of an aqueous, hydrochloric acid solution containing copper in a cell with no separator.

The design of a parallel plate electrochemical reactor (see Fig. 1) often requires predicting such quantities as the current and energy efficiency for multiple electrode reactions, the conversion per pass of a reactant or product, and the selectivity of a desired product. For example, in a cell with no separator, the electrode reactions for electrowinning of copper from a chloride solution might be



Note that CuCl_3^{2-} , or Cu(I) reacts at both electrodes and CuCl^+ , or Cu(II), is a product at the anode and a reactant at the cathode. This scheme is presented here as a hypothetical illustration of a complex system. The possibility of Cu(II) reacting with copper deposited on the cathode was ignored for convenience. Many, if not most, electrochemical processes of interest are similarly complicated and often it is some aspect of the complexity that dictates the performance of the system.

The design of an electrochemical cell based on the above reactions should include predictions of the current and energy efficiency for copper deposition, the conversion per pass of both Cu(I) and Cu(II), and the selectivity of copper deposition. These predictions would be expected to depend on, among other things, the cell potential, the flow rate of the electrolyte through the cell, and the length of the electrodes at a fixed separation. Classical design techniques [see Ref. (1), e.g.] cannot be used to make these predictions because they do not include the capabilities to handle the complexities due to the above reactions.

Pickett (1), for example, presents models for parallel plate cells which are based on the assumption that only one electrode reaction is important and that it is mass transfer controlled. He does present a method for including an undesired side reaction, but it is cumbersome to use. In a different work, he and Stanmore (2) do present a model for the case where different electrode reactions occur at the anode and cathode but do not include multiple electrode reactions.

Other more complicated (3-10) models have been presented for parallel plate cells, but they are also not suitable here for one reason or another. Sakellaropoulos and Francis (3-5) present a model for a parallel plate cell which does include both series and parallel elec-

trode reactions at one electrode, but does not include the reaction at the other electrode nor the effect of the separation of the electrodes. Parrish and Newman (6) present a model for a parallel plate cell which includes the electrode separation and the kinetics of the electrode reactions (same reaction at both electrodes), but does not include multiple electrode reactions. Caban and Chapman (7) present essentially the same model as Parrish and Newman, but set the cell potential instead of the cell current. Caban (8) extends their model to include multiple electrode reactions (and, consequently, the ability to predict current efficiencies), but not the conversion per pass of a reactant or product. Lee and Selman (9) extend Caban and Chapman's work to include a separator in the cell and nonisopotential electrodes, but do not include the conversion per pass. Lee (10) extends their work to include multiple electrode reactions and a heterogeneous reaction at one of the electrodes and a method for predicting ap-

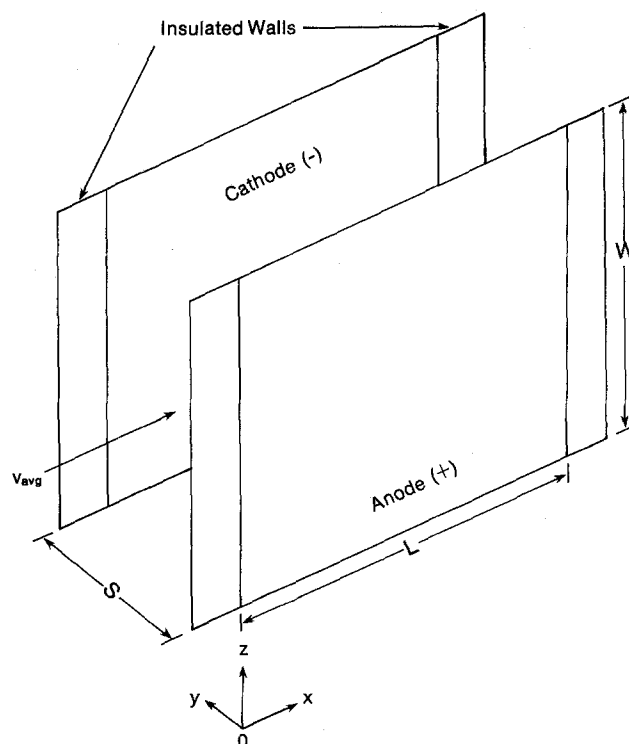


Fig. 1. Schematic of a parallel plate electrochemical reactor

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Key words: metals, cell, current efficiency, mass transport.

proximately the conversion per pass based on a quasi-steady-state approach. Their method is, however, limited to cases where the conversion per pass is small.

Models based on the Parrish and Newman approach are sometimes referred to as thin diffusion layer models. They are referred to as such because it is assumed in the development of the models that the concentration of a reactant is constant in the bulk solution over the entire length of the reactor and that the reactant concentration differs from its bulk value only within thin diffusion layers on the electrodes. This assumption is reasonable if the conversion per pass of a reactant is small, but this is often not the case. Another assumption used in the thin diffusion layer models is that Laplace's equation governs the potential distribution within the bulk solution and within the thin diffusion layers on the electrodes. This assumption is also questionable because, as shown by White *et al.* (11), the potential at an electrode predicted by Laplace's equation can be different from that predicted by utilizing dilute solution theory, which includes the effect of ionic migration. This difference may be small but important because the predicted current density depends exponentially on the potential difference between the electrode and the adjacent solution. It is worth reiterating, perhaps, that the major limitation of thin diffusion layer models is that they cannot be used to predict the conversion per pass of a reactant because of the requirement that the bulk concentration of a reactant remain the same over the length of the reactor.

To eliminate these assumptions, a model was developed for a parallel plate cell which includes the effect of ionic migration in the flux expression for species *i* and uses the electroneutrality condition as a constraint to determine the potential in the solution. This method was used by Alkire and Ng (12, 13) for a model of a porous, flow-by electrode. The approach removes the limitations of the thin diffusion layer model and provides a method that includes the capability of predicting the quantities mentioned above. Also, the approach could be extended to handle even more complicated cases. The model consists of assumptions, material balance equations, the electroneutrality condition, boundary conditions, and parameters.

Model

The assumptions made in the development of the model are presented first followed by the equations.

Assumptions

The following assumptions apply to the model presented here:

1. Isothermal conditions exist.
2. Gas generation effects are ignored.
3. Newtonian electrolyte.
4. Constant physical and transport parameters.
5. Nernst-Einstein equation ($u_i = D_i/RT$) applies.
6. The length (direction of flow) and width of both electrodes are large relative to the gap between the electrodes.
7. Dilute solution theory (14) applies.
8. Well-developed laminar flow.
9. The Butler-Volmer equation can be used to describe each electrode reaction.
10. No heterogeneous or homogeneous chemical reactions occur.
11. Steady-state conditions exist.

Assumptions 8, 9, 10, and 11 could be modified easily to account for turbulent flow, other types of electrode reactions, heterogeneous or homogeneous (or both) chemical reactions, and dynamic behavior.

Equations

In the absence of homogeneous reactions, the steady-state material balance equation for species *i* is (14)

$$\nabla \cdot \mathbf{N}_i = 0 \quad [1]$$

where

$$\mathbf{N}_i = -D_i \nabla c_i - z_i u_i \mathbf{F} c_i \nabla \Phi + v c_i \quad [2]$$

The velocity distribution within the reactor is assumed to be well-developed laminar flow and is given by (1)

$$v_x = 6v_{avg} \left(\frac{y}{S} - \frac{y^2}{S^2} \right) \quad [3]$$

and

$$v_y = 0 \quad [4]$$

Since the Nernst-Einstein equation

$$u_i = \frac{D_i}{RT} \quad [5]$$

is assumed to be valid, substitution of Eq. [2], [3], [4], and [5] into Eq. [1] yields

$$6v_{avg} \left[\frac{y}{S} - \frac{y^2}{S^2} \right] \frac{\partial c_i}{\partial x} = D_i \left[\frac{\partial^2 c_i}{\partial x^2} + \frac{\partial^2 c_i}{\partial y^2} \right] + \frac{z_i D_i \mathbf{F}}{RT} \left[c_i \frac{\partial^2 \Phi}{\partial x^2} + \frac{\partial c_i}{\partial x} \frac{\partial \Phi}{\partial x} + c_i \frac{\partial^2 \Phi}{\partial y^2} + \frac{\partial c_i}{\partial y} \frac{\partial \Phi}{\partial y} \right] \quad [6]$$

The electroneutrality condition

$$\sum_i z_i c_i = 0 \quad [7]$$

completes the set of $i + 1$ equations needed to determine values for the $i + 1$ unknowns (c_i and Φ) for $x > 0$ and $0 \leq y \leq S$.

Equation [6] can be simplified since the aspect ratio (α)

$$\alpha = S/L \quad [8]$$

is assumed to be small. This can be seen by substituting the dimensionless variables

$$\xi = x/L \quad [9]$$

$$\eta = y/S \quad [10]$$

$$\theta_i = c_i/c_{i,ref} \quad [11]$$

into Eq. [6] to obtain

$$6Sv_{avg} (\eta - \eta^2) \frac{\partial \theta_i}{\partial \xi} = D_i \left(\alpha^2 \frac{\partial^2 \theta_i}{\partial \xi^2} + \frac{\partial^2 \theta_i}{\partial \eta^2} \right) + \frac{z_i D_i \mathbf{F}}{RT} \left[\alpha^2 \left(\theta_i \frac{\partial^2 \Phi}{\partial \xi^2} + \frac{\partial \theta_i}{\partial \xi} \frac{\partial \Phi}{\partial \xi} \right) + \frac{\partial^2 \Phi}{\partial \eta^2} + \frac{\partial \theta_i}{\partial \eta} \frac{\partial \Phi}{\partial \eta} \right] \quad [12]$$

which shows by inspection that α^2 is a coefficient of the terms that contain derivatives in the axial direction. These terms are negligibly small if α is small and the derivatives in the axial direction are of the same order of magnitude as those in the normal direction.¹ Assuming that these conditions exist reduces Eq. [12] to

$$3 \frac{D_R}{D_i} \text{Pe} \alpha (\eta - \eta^2) \frac{\partial \theta_i}{\partial \xi} = \frac{\partial^2 \theta_i}{\partial \eta^2} + \frac{z_i \mathbf{F}}{RT} \left[\theta_i \frac{\partial^2 \Phi}{\partial \eta^2} + \frac{\partial \theta_i}{\partial \eta} \frac{\partial \Phi}{\partial \eta} \right] \quad [13]$$

where the Peclet number (Pe) is

$$\text{Pe} = \frac{2Sv_{avg}}{D_R} \quad [14]$$

(Equation [14] is reasonable because the Peclet number is defined to be

$$\text{Pe} = \frac{D_e v_{avg}}{D_R} \quad [15]$$

¹ For the case where α is not small, Eq. [12] should be used for the material balance equation for species *i*, the initial conditions replaced by the appropriate boundary conditions, and the IAD-Newman (15) or similar technique used to solve the equations.

and for flow in a rectangular channel

$$D_e = \frac{4SW}{2(S+W)} \quad [16]$$

which, since $W \gg S$, becomes $D_e = 2S$.)

Specification of the initial and boundary conditions completes the system of equations. The initial conditions are simply that

$$\text{at } \zeta = 0 \quad \theta_i = 1 \quad \sum_i z_i c_{i,\text{ref}} \theta_i = 0 \quad [17]$$

and the boundary conditions are

at $\eta = 0$ (anode)

$$\sum_j \frac{s_{ij} i_{nj}}{n_j F} = -N_{ni} \quad [18]$$

at $\eta = 1$ (cathode)

$$\sum_j \frac{s_{ij} i_{nj}}{n_j F} = N_{ni} \quad [19]$$

and at both $\eta = 0$ and $\eta = 1$

$$\sum_i z_i c_i = 0 \quad [20]$$

It should be pointed out that the derivatives in the flux expression for species i (N_{ni}) are defined to be in the positive y direction (from the anode to the cathode), and the signs used for N_{ni} in Eq. [21] and [22] are consistent with the sign convention that positive current leaves the anode and enters the solution and negative current leaves the solution and enters the cathode.

The normal component of the current density for reaction j (i_{nj}) is assumed to be given by the Butler-Volmer equation and is shown here for reaction j at the anode

$$i_{nj} = i_{oj,\text{ref}} \left\{ \pi_i \left(\frac{c_{i,o}}{c_{i,\text{ref}}} \right)^{p_{1i}} \exp \left[\frac{\alpha_{aj} F}{RT} (V_a - \Phi_{oa} - U_{j,\text{ref}}) \right] - \pi_i \left(\frac{c_{i,o}}{c_{i,\text{ref}}} \right)^{q_{1i}} \exp \left[\frac{-\alpha_{cj} F}{RT} (V_a - \Phi_{oa} - U_{j,\text{ref}}) \right] \right\} \quad [21]$$

where

$$U_{j,\text{ref}} = U_j^\theta - U_{re}^\theta - \frac{RT}{n_j F} \sum_i s_{ij} \ln \left(\frac{c_{i,\text{ref}}}{\rho_o} \right) + \frac{RT}{n_{re} F} \sum_i s_{i,re} \ln \left(\frac{c_{i,re}}{\rho_o} \right) \quad [22]$$

Equation [21] can be used for the cathode reactions by changing V_a and Φ_{oa} to V_c and Φ_{oc} , respectively. Substitution of Eq. [21] and its counterpart for the reactions at the cathode into Eq. [18] and [19] yields a system of equations for the dependent variables θ_i and $F\Phi/RT$ in terms of the independent variables ζ and η and parameters (kinetic, geometric, physical, thermodynamic, transport, reference concentrations, and the cell potential).

Parameter Values

The utility of the model can be demonstrated by calculating the potential and concentration distributions within the reactor for the hypothetical case given above with HCl included as a supporting electrolyte.

The fixed parameter values used here are given in Table I for this system of species and reactions. The variable parameter values are the average velocity of the electrolyte (v_{avg}), the length of the reactor (L), and the potential of the anode (V_a) relative to the half-cell potential of reaction 1 evaluated at the appropriate reference concentrations. Note, however, that according to Eq. [13], Pe_α is the important indepen-

Table I. Fixed parameter values

Kinetic and thermodynamic						
Reaction (j)	$10^{10} i_{oj,\text{ref}}$ (A/cm ²) ^a	α_{aj}	α_{cj}	n_j	U_j^θ (V) ^b	$U_{j,\text{ref}}$ (V) ^c
1	1.0	0.5	0.5	1	0.438	0
2	1.0	0.5	0.5	1	0.438	0
3	100.0	0.5	0.5	1	0.233	0.1143
$T = 298.15 \text{ K}$						
Component (i)	Reactions 1 and 2 (j = 1, 2)					
	s_{1j}	p_{1j}	q_{1j}			
H ⁺	0	0	0			
Cl ⁻	-2	0	2			
Cu(I)	1	1	0			
Cu(II)	-1	0	1			
Component (i)	Reaction 3 (j = 3)					
	s_{1j}	p_{1j}	q_{1j}			
H ⁺	0	0	0			
Cl ⁻	3	3	0			
Cu(I) [†]	-1	0	1			
Cu(II)	0	0	0			
$V_{\text{cathode}}^d = 0.0V$						
Geometric						
$S = 0.1 \text{ cm}$						
Transport and reference concentrations						
Component (i)	z_i	$10^8 D_i^e$ (cm ² /sec)	$10^8 c_{i,\text{ref}}$ (mol/cm ³)			
H ⁺	1	9.312	1.000			
Cl ⁻	-1	2.032	1.000			
Cu(I) [†]	-2	0.720	0.500			
Cu(II)	1	0.720	0.100			

^a Chosen arbitrarily.

^b See Ref. (11, 16).

^c The open-current potential of reaction j at the reference concentrations ($U_{j,\text{ref}}$) was chosen for convenience to be relative to reaction 1 (i.e., $re = 1$ in Eq. [22]).

^d Relative to the half-cell potential of reaction 1 evaluated at the reference concentrations of Cl⁻, CuCl₂²⁻, and CuCl⁺ (i.e. an imaginary reference electrode at which reaction 1 occurs and the reactants that participate in reaction 1 are at their reference concentrations).

^e Taken from Ref. (14, 11).

[†] Designated as the limiting reactant.

dent variable and not S , v_{avg} , or L separately. Thus, for the case where S and D_R are constants, v_{avg} and L can be replaced by Pe_α . Also, note that the cell potential ($E_{\text{cell}} = V_a - V_c$) is actually the independent variable, not V_a . That is, even though V_a and V_c can be varied independently within the model, the results depend only on their difference, not their individual values.

Consideration of the above boundary conditions written in dimensionless form gives rise to the following fixed dimensionless parameters

$$\xi_{ij} = \left| \frac{s_{ij} i_{oj,\text{ref}} S}{n_j c_{i,\text{ref}} D_i F} \right| \quad [23]$$

The magnitudes of these dimensionless parameters provide a qualitative guide to the relative rates of charge transfer to mass transfer as shown in Table II. (Note that both ξ_{ij} and Pe_α depend on S .)

Table II. Fixed dimensionless parameters

Component (i)	ξ_{ij} = $\left \frac{s_{ij} i_{oj,\text{ref}} S}{n_j c_{i,\text{ref}} D_i F} \right $	
	Reactions 1 and 2	Reaction 3
H ⁺	0.0000	0.000
Cl ⁻	0.01020	1.530
CuCl ₂ ²⁻	0.00288	0.288
CuCl ⁺	0.01440	0.000

Results and Discussion

Once the fixed and variable parameters have been set, the above set of equations can be solved for $\theta_1(\zeta, \eta)$ and $\Phi(\zeta, \eta)$ using an implicit stepping technique (17) in the axial (ζ) direction and Newman's technique (14, 18) in the normal (η) direction. The accuracy of the values obtained for θ_1 and Φ depends on the number of mesh points used in both the ζ and η directions. The results reported here are accurate to three significant digits. This accuracy was obtained by adding additional mesh points in both the η and ζ directions until the results no longer changed to within three significant digits. It is worth noting that the potential distribution does not depend on specification of a reference state. That is, it is not necessary to specify the value of Φ at any point. As mentioned above, it is only necessary to fix the potential difference between the anode and the cathode and use the electroneutrality condition at both electrodes (Eq. [20]) to obtain the potential distribution between the electrodes. For the results reported here the values obtained for Φ varied only slightly (approximately 5-10 mV) both across the cell and over the length of the electrodes, as would be expected for well-supported solutions. The concentration and potential distributions obtained can then be used to calculate derived information of interest, such as the current density distribution for each electrode reaction along each electrode.

These current density distributions can be used to obtain another quantity of interest λ which is defined as the ratio of the average current density to the average limiting current density

$$\lambda = \frac{i_{\text{avg}}}{i_{\text{lim,avg}}} \quad [24]$$

where for each electrode

$$i_{\text{avg}} = \sum_j i_{n,j,\text{avg}} \quad [25]$$

with j ranging over the electrode reactions which occur at that particular electrode. The average normal current density of reaction j ($i_{n,j,\text{avg}}$) can be obtained by utilizing the calculated surface concentration and potential distributions and the appropriate Butler-Volmer equation as follows

$$i_{n,j,\text{avg}} = \frac{1}{L} \int_0^L i_{n,j}(x) dx \quad [26]$$

The average limiting current density for the limiting reactant (as designated by the subscript R, Cu(I) here) at the cathode for a one-electron reaction can be obtained from integration of Eq. [26] with $i_{n,j}(x)$ replaced by $i_{\text{lim}}(x)$ (19)

$$i_{\text{lim}}(x) = \frac{-FD_{\text{RCR,ref}}}{(1-t)\Gamma(4/3)} \left(\frac{6v_{\text{avg}}}{9SD_{\text{R}}x} \right)^{1/3} \quad [27]$$

where the transference number (t) for the limiting reactant is assumed to be zero here due to the well-supported solution considered. The result of the integration and this assumption is that

$$i_{\text{lim,avg}} = \frac{-3^{2/3}FD_{\text{RCR,ref}}}{2L\Gamma(4/3)} \left(\frac{Pe}{\alpha^2} \right)^{1/3} \quad [28]$$

Note that the value of $i_{\text{lim,avg}}$ and, consequently, values of λ depend on the choice of the limiting reactant and its reference concentration. Here Cu(I) is chosen to be the limiting reactant and its feed concentration is chosen to be its reference concentration. These choices make $i_{\text{lim,avg}}$ the maximum average current density obtainable for this cell so that λ is always less than or equal to one.

Equation [28] can be used to normalize the predicted current density distributions

$$i_{n,j}^*(x) = \frac{i_{n,j}(x)}{i_{\text{lim,avg}}} \quad [29]$$

as shown in Fig. 2 for a given set of parameter values.² Figure 2 shows that the current density distributions are highly nonuniform for reactions 1 and 3 as expected since the average current density is only slightly less than the average limiting current density ($\lambda = 0.946$).

The predicted current density distributions can also be used to derive local and average current efficiencies which are defined here as follows

$$CE_j(x) = i_{n,j}(x)/i_{\text{avg}} \quad [30]$$

and

$$CE_{j,\text{avg}} = i_{n,j,\text{avg}}/i_{\text{avg}} \quad [31]$$

Figure 3 presents predicted local current efficiencies for copper deposition at a fixed value of $Pe\alpha$ for various cell potentials. The case where the cell potential varies from 0.4 to 0.6V is for a linear change in the anode potential from 0.4V at $\zeta = 0$ to 0.6V at $\zeta = 1$. Note that the 0.4-0.6V case gives a more uniform current efficiency than the 0.6V case. Figure 4 presents the average current efficiency for copper deposition as a function of $Pe\alpha$ for various values of the cell potential. Here the average current efficiency for the 0.4-0.6V case is higher than either the 0.5 or 0.6V case. This means that the current efficiency (or the energy consumption per unit mass of product which is simply related to the current efficiency and cell potential) of a process may be improved by designing the electrodes to have a desired potential drop.

Another derived quantity of interest is the bulk average concentration of species i

$$c_{i,\text{avg}}(x) = \frac{1}{S} \int_0^S c_i(x, y) dy \quad [32]$$

² Again the fixed parameter values are given in Table I and the variable parameter values are given in the figures. Note that S is held fixed. If $Pe\alpha$ is varied by varying S then the figures do not apply unless the ξ_{ij} values are held fixed by changing $i_{0,j,\text{ref}}$.

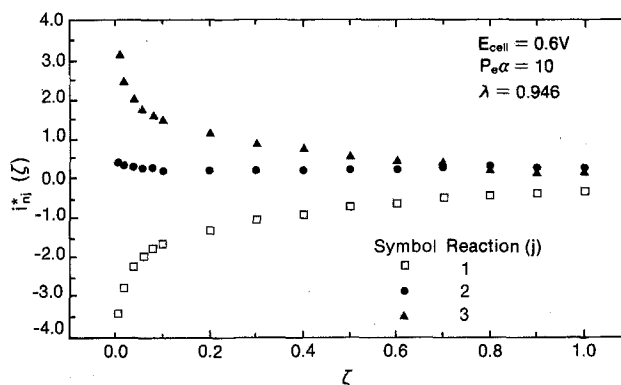


Fig. 2. Normalized current density distributions

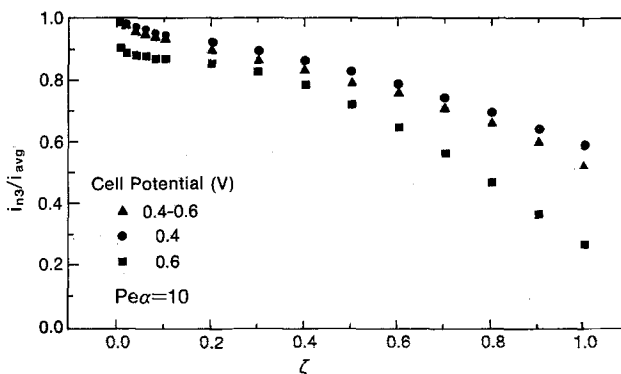


Fig. 3. Local current efficiency for reaction 3

which can be written in dimensionless form as

$$\theta_{i,avg}(\zeta) = \frac{c_{i,avg}(x)}{c_{i,ref}} \quad [33]$$

Figures 5 and 6 present the dimensionless bulk average concentrations of Cu(I) and Cu(II), respectively, as well as their dimensionless concentrations at the electrodes.

These bulk average concentrations can be used to predict the conversion per pass for a particular species which is defined here as

$$CPP_i = |1 - \theta_{i,avg}(\zeta = 1)| \quad [34]$$

Figure 7 shows how the conversion per pass for Cu(I) depends on the values of Pe_α and the cell potential. Note that a mild maximum is predicted for the case where the cell potential is 0.6V.

Finally, the selectivity of copper is defined here as

$$\text{Cu selectivity} = \frac{\text{mols of Cu produced}}{\text{mols of Cu(II) produced}}$$

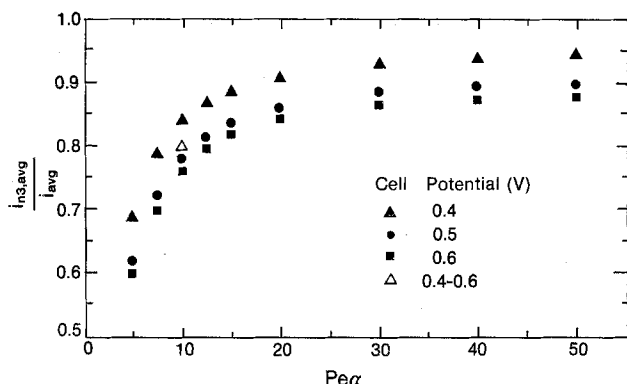


Fig. 4. Average current efficiency for reaction 3

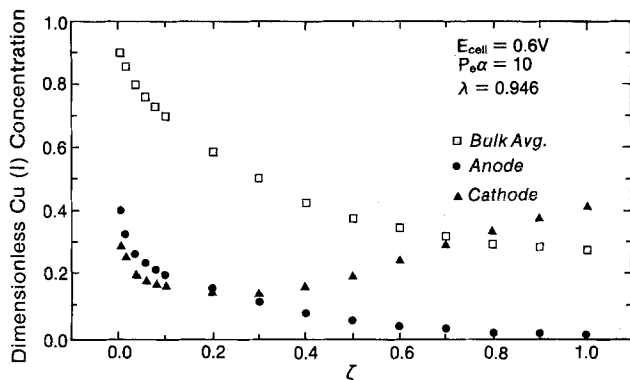


Fig. 5. Dimensionless Cu(I) concentration distribution

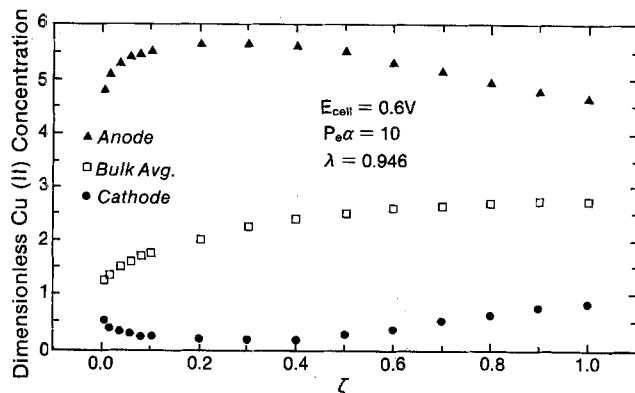


Fig. 6. Dimensionless Cu(II) concentration distribution

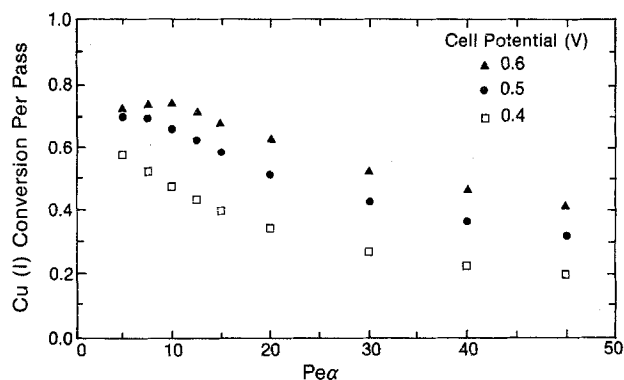


Fig. 7. Cu(I) conversion per pass

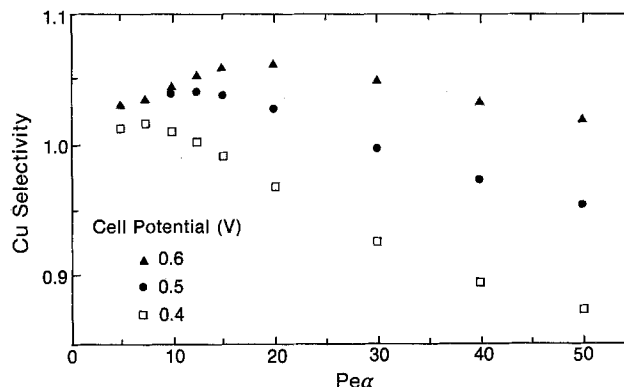


Fig. 8. Copper selectivity

Cu selectivity

$$= \frac{\text{mols of Cu(I) produced} - \text{mols of Cu(II) produced}}{\text{mols of Cu(II) produced}}$$

Cu selectivity

$$= \left| \frac{1 - \theta_{\text{CuCl}_3^{2-},avg}(\zeta = 1)}{\theta_{\text{CuCl}^+,avg}(\zeta = 1) - 1} \right| \left(\frac{c_{\text{CuCl}_3^{2-},ref}}{c_{\text{CuCl}^+,ref}} \right) - 1 \quad [35]$$

and is shown in Fig. 8 as a function of Pe_α for various cell potentials. Note that a mild maximum is predicted for the 0.6V cell potential case at $Pe_\alpha \approx 20$.

Conclusion

The parallel plate electrochemical reactor model presented here may be useful for design purposes if the necessary parameter values are known. Alternatively, the model may be useful for determining some of the unknown kinetic or transport parameter values for a system of interest by using the model, experimental data, and a nonlinear least squares fitting technique; however, it should be pointed out that such a procedure is not well developed.

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Any discussion of this paper will appear in a Discussion Section to be published in the December 1983 JOURNAL. All discussions for the December 1983 Discussion Section should be submitted by Aug. 1, 1983.

LIST OF SYMBOLS

- $c_{i,0}$ concentration of species i at the electrode surface, mol/cm³
- $c_{i,ref}$ concentration of species i at the reactor inlet (reference), mol/cm³
- D_i diffusion coefficient of species i , cm²/sec
- D_e equivalent diameter of the reactor (= $2S$ here), cm

D_R	diffusion coefficient of the limiting reactant, cm^2/sec	λ	average current density relative to the average limiting current density ($i_{\text{avg}}/i_{\text{lim,avg}}$)
F	Faraday's constant, 96,487 C/mol	ξ_{ij}	dimensionless parameter (see Eq. [23])
i_{avg}	average current density, A/cm^2	ρ_0	solvent density, kg/cm^3
i_{lim}	limiting current density, A/cm^2	Φ	solution potential, V
$i_{\text{lim,avg}}$	average limiting current density, A/cm^2	Φ_{oa}	solution potential at the anode, V
i_{nj}	normal component of current density due to reaction j, A/cm^2	Φ_{oc}	solution potential at the cathode, V
$i_{\text{nj,avg}}$	average normal current density due to reaction j, A/cm^2		
$i_{\text{oj,ref}}$	exchange current density of reaction j at reference concentrations, A/cm^2		
L	electrode length, cm		
N_i	flux vector of species i, $\text{mol}/\text{cm}^2/\text{sec}$		
N_{ni}	normal component of the flux of species i, $\text{mol}/\text{cm}^2/\text{sec}$		
ρ_{ij}	anodic reaction order of species i in reaction j		
Pe	Peclet number ($= 2Sv_{\text{avg}}/D_R$)		
q_{ij}	cathodic reaction order of species i in reaction j		
R	gas law constant, 8.3143 J/mol K		
s_{ij}	stoichiometric coefficient of species i in reaction j		
S	electrode gap, cm		
T	temperature, K		
u_i	mobility of species i, $\text{cm}^2/\text{mol}/\text{J}\text{-sec}$		
$U_{j,\text{ref}}$	open-circuit potential of reaction j at reference conditions, V		
v	electrolyte velocity vector, cm/sec		
v_{avg}	average velocity of the electrolyte, cm/sec		
v_x	velocity of the electrolyte in the x direction, cm/sec		
v_y	velocity of the electrolyte in the y direction, cm/sec		
V_a	anode potential, V		
V_c	cathode potential, V		
W	electrode width, cm		
x	axial coordinate, cm		
y	normal coordinate, cm		
z_1	charge number of species i		
Greek			
α	S/L		
α_{aj}	anodic transfer coefficient for reaction j		
α_{cj}	cathodic transfer coefficient for reaction j		
$\Gamma(4/3)$	the gamma function of 4/3 = 0.89298		
ξ	dimensionless axial coordinate (x/L)		
η	dimensionless normal coordinate (y/S)		
θ_1	dimensionless concentration		

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Degradation of Sodium β'' -Alumina: Effect of Microstructure

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ABSTRACT

The effect of microstructure on failure initiation of sodium beta''-alumina solid electrolytes have been investigated by acoustic emission detection. Mode I failure initiation follows Weibull statistics with a modulus of about 2.5. The observed average critical current densities were 145 and 640 mA/cm² for large and for small grained electrolytes, respectively. Nonuniform secondary current distributions near the electrode edges were considered and were found to lead to minor corrections to these values. The conditions under which nonuniformity of current would affect failure statistics have been considered in the Appendix. Considerations of failure statistics indicate conditions where proof testing may be necessary to achieve sufficient reliability. These considerations assume complete equivalence between mechanical and electrolytic failure; the indication is, however, that such equivalence is not valid.

When sodium-beta or beta'' alumina solid electrolytes are subjected to ionic charge transfer in sodium/sodium or in sodium/sulfur cells, degradation of the electrolytes may occur. This electrochemical degradation may take different forms, as was recently discussed by De Jonghe *et al.* (1). Mode I degradation involves the cathodic plating of Na into a pre-existing surface flaw on the sodium side of the electrolyte, causing crack extension above some critical value of the current density. This was first discussed by Arm-

strong *et al.* (2) (ADT). Several workers have considered refinements of the ADT treatment, attempting to derive theoretically the critical current density thresholds at which the Mode I crack propagation initiates or propagates (3-6). All calculations, however, lead to predicted current density thresholds that are orders of magnitude higher than the observed ones (6). To fully understand the factors that determine the onset of Mode I degradation, it is first necessary to measure the critical current density thresholds