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$V_a$	anode potential, V
$v_{avg}$	average velocity of the electrode, cm/s
$V_c$	cathode potential, V
$v_x$	velocity component of the electrolyte in the $x$ -direction, cm/s
$W$	width of the electrode, cm
$x$	axial coordinate, cm
$y$	radial coordinate, cm
$z_i$	charge number of species $i$

## Greek

$\alpha$	aspect ratio, $S/L$
$\beta_{ij}$	dimensionless residence time
$\Delta x$	axial step size, cm
$\zeta$	dimensionless axial coordinate ( $x/L$ )
$\eta$	dimensionless axial coordinate ( $y/S$ )
$\theta_i$	dimensionless concentration of species $i$ ( $c_i/c_{i,ref}$ )
$\theta_{i,avg}$	dimensionless average concentration of species $i$
$\theta_{i,feed}$	dimensionless feed concentration of species $i$
$\theta_{i,o}$	dimensionless concentration of species $i$ at the electrode surface
$\lambda_{j,avg}$	the ratio of average current density for reaction $j$ to the average limiting current density ( $i_{nj,avg}/i_{lim,avg}$ )
$\xi_{ij}$	dimensionless formulation of the electrode gap
$\Phi$	solution potential, V

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## A Mathematical Model for a Parallel Plate Electrochemical Reactor, CSTR, and Associated Recirculation System

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### ABSTRACT

A mathematical model is presented for a system comprised of a parallel plate electrochemical reactor (PPER) and a continuous, stirred-tank reactor (CSTR) under both total and partial recycle. The model is used to predict the time dependent behavior of the electrowinning of copper from an aqueous, hydrochloric acid solution. The model includes many important aspects of a PPER/CSTR system which have been neglected previously. These aspects are the kinetics of electrode reactions, the electroneutrality condition, three mass transfer processes for ionic species in the electrolyte (diffusion, ionic migration, and convection) and the electrode gap in the PPER, and the inclusion of a true CSTR in the recycle stream.

Parallel plate electrochemical reactors have been used in many industrial electrochemical processes: chlor-alkali production, metal extraction and refining, and electro-organic synthesis, as well as in batteries and fuel cells (1, 2). In some of these processes, the system consists of a parallel plate electrochemical reactor (PPER), a continuous, stirred-tank reactor (CSTR), and an associated recirculation system, as shown in Fig. 1 and 2. The CSTR plays a very important role in some electrochemical processes in which the electrochemical reactor is used mainly to generate the necessary reactants that produce the final product through homogeneous chemical reactions in the CSTR. An example of such a process is the electrogeneration of hypochlorite and chlorate (3-8). There have been several models developed for a PPER in total recycle with a well-mixed reservoir in which the PPER was treated as a plug flow reactor (9, 10) or a plug flow reactor with axial diffusion (11). No model for a batch PPER system was found which includes in the PPER the effects of the separation of the electrodes, applied cell potential, ionic migration, and the kinetics of the electrode reactions, and in the well-mixed reservoir, the capability of handling chemical reactions.

Pickett (9, 12) presented simple approximate models in which the electrochemical reactor is considered to be an ideal plug flow reactor operating at limiting current con-

ditions for a single reaction. To obtain his analytical solutions, Pickett decoupled the governing equations for the PPER from those of the reservoir by assuming that the residence time in the reservoir is large enough to ignore the time dependence of the outlet concentration of the reservoir (which, of course, is the same as the feed concentration to the electrochemical reactor). Thus, his models are applicable only to a process with a very large residence time in the reservoir. Mustoe and Wragg (11) presented an approximate model similar to those of Pickett, but extended the transport equation for the

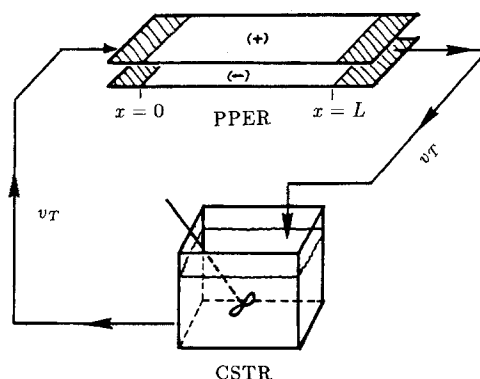


Fig. 1. Schematic of a batch PPER/CSTR or reservoir system

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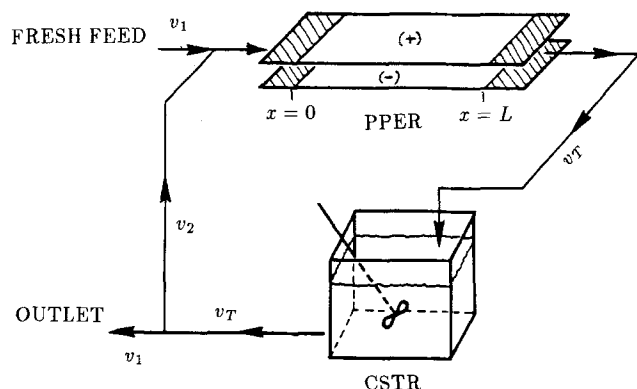
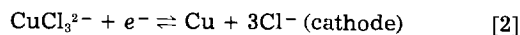
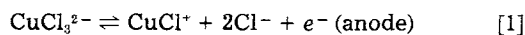


Fig. 2. Schematic of a PPER/CSTR or reservoir system with partial recycle.

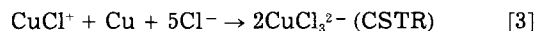
PPER to include the effects of axial diffusion. Unfortunately, Mustoe and Wragg's model is also restricted to large residence times in the reservoir. Walker and Wragg (10) published a more rigorous model for a batch PPER system in which the PPER was treated as a plug flow reactor or a perfectly mixed reactor, both operating under total recirculation with a perfectly mixed reservoir. Each model was solved analytically without decoupling the system of equations. However, these authors assumed that only one electrode reaction occurs and that it occurs under convective mass transfer control. Unfortunately, their model is limited because it neglects the effects of the electrode gap, applied cell potential, and ionic migration.

It is important to recognize that the modeling of a batch PPER system, with or without a chemical reaction occurring in the associated recirculation tank, should include important features which have not been included in models presented previously. These features are the electrode gap, the kinetics of the electrode reactions that occur on each electrode and in many cases, multiple electrode reactions at one electrode (13), homogeneous reactions (14), and the applied cell potential (or set average current density). These features are, or could be, included in the model presented here. Also, in this model a chemical reaction is included in the well-mixed reservoir, as shown below. (Unfortunately, some authors have referred to a well-mixed reservoir as a CSTR, even though no chemical reactions occur there in their models).

In order to gain a better understanding of the dynamic behavior of this PPER/CSTR system, a detailed mathematical model is presented here and applied to the electro-winning of copper from an aqueous, hydrochloric acid solution, which could alternatively be considered to be the regeneration of a copper leachant ( $\text{CuCl}^+$ ). The electrochemical reactions that are assumed to occur are



During the actual operation of the copper electro-winning process, reaction [1] would proceed from left to right at the anode and from right to left at the cathode; however, for simplicity and for ease of comparison to other simpler models, the complexity of reaction [1] occurring in reverse at the cathode is ignored but could be included easily (13). The model is developed first for a batch system consisting of a parallel plate electrochemical reactor, a well-mixed reservoir, and a recirculation system (see Fig. 1), and then extended later to include an inlet and outlet stream to treat partial recycle cases (Fig. 2). Finally, the capability of handling a CSTR (i.e., including a simultaneous chemical reaction in the well-mixed reservoir) is demonstrated by including the following copper-leaching reaction in the CSTR



Note that reaction [3] would also proceed at the cathode of an actual electro-winning process with no separator, but this complexity is also ignored here for simplicity.

### Model Development

The batch PPER/CSTR model is developed by extending the time-dependent parallel plate electrochemical reactor model by Nguyen *et al.* (15) to include a well-mixed reservoir and associated recirculation system. This model is then expanded to include partial recycle and a simultaneous chemical reaction occurring in the well-mixed reservoir (i.e., CSTR).

The following assumptions apply to the batch PPER/CSTR system

1. Isothermal operation.
2. Gas generation effects are ignored.
3. Newtonian electrolyte.
4. Constant physical and transport properties.
5. Nernst-Einstein equation ( $u_i = D_i/RT$ ) applies.
6. Dilute solution theory (16) applies.
7. Well-developed laminar flow in the PPER.
8. Electrode reactions follow Butler-Volmer kinetic expressions.
9. No heterogeneous or homogeneous chemical reactions occur in the PPER.
10. The time delays of the fluid moving in the pipes from the PPER to the CSTR and from the CSTR to the PPER are assumed to be negligible.
11. The CSTR is operating at the same temperature as the PPER.

If needed, the model could be modified to include a chemical reaction occurring in the PPER [as done by Mader (14)] and the time delays of the fluid moving in the pipes between the PPER and the CSTR (by treating the volume of the pipes as part of the CSTR or by treating the pipes as tubular reactors). The governing equations for the concentration of species  $i$  and the potential in the solution ( $\Phi$ ) in the PPER are reviewed first, followed by the equation for the concentration of species  $i$  in the reservoir. Finally, a discussion of how these equations are coupled is presented.

**Parallel plate electrochemical reactor (PPER).**—The material balance equation for species  $i$  in the PPER, with no homogeneous reactions (assumption 9), is given by

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot N_i \quad [4]$$

where  $N_i$  is defined by dilute solution theory (16) to be

$$N_i = -D_i \nabla c_i - z_i u_i F c_i \nabla \Phi + u_i c_i \quad [5]$$

For fully developed laminar flow, the velocity distribution  $u$  is given by

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

and

$$u_y = 0 \quad [7]$$

and the Nernst-Einstein relation for the mobility of species  $i$  gives

$$u_i = \frac{D_i}{RT} \quad [8]$$

Substitution of Eq. [5]–[8] into Eq. [4] gives

$$\begin{aligned} \frac{\partial c_i}{\partial t} = D_i \left[ \frac{\partial^2 c_i}{\partial x^2} + \frac{\partial^2 c_i}{\partial y^2} \right] \\ + \frac{z_i D_i F}{RT} \left[ c_i \frac{\partial^2 \Phi}{\partial x^2} + \frac{\partial c_i}{\partial x} \frac{\partial \Phi}{\partial x} + c_i \frac{\partial^2 \Phi}{\partial y^2} + \frac{\partial c_i}{\partial y} \frac{\partial \Phi}{\partial y} \right] \\ - 6u_{avg} \left[ \frac{y}{S} - \frac{y^2}{S^2} \right] \frac{\partial c_i}{\partial x} \end{aligned} \quad [9]$$

The governing equation for the potential,  $\Phi$ , is the electroneutrality equation

$$\sum_i z_i c_i = 0 \quad [10]$$

Using the dimensionless variables

$$\zeta = \frac{x}{L} \quad [11]$$

$$\eta = \frac{y}{S} \quad [12]$$

$$\theta_i = \frac{c_i}{c_{i,\text{ref}}} \quad [13]$$

to rewrite Eq. [9] and [10] in dimensionless form gives

$$\begin{aligned} \frac{S^2}{D_i} \frac{\partial \theta_i}{\partial t} = & \left[ \alpha^2 \frac{\partial^2 \theta_i}{\partial \zeta^2} + \frac{\partial^2 \theta_i}{\partial \eta^2} \right] \\ & + \frac{z_i F}{RT} \left[ \alpha^2 \left( \theta_i \frac{\partial^2 \Phi}{\partial \zeta^2} + \frac{\partial \theta_i}{\partial \zeta} \frac{\partial \Phi}{\partial \zeta} \right) + \theta_i \frac{\partial^2 \Phi}{\partial \eta^2} \right. \\ & \left. + \frac{\partial \theta_i}{\partial \eta} \frac{\partial \Phi}{\partial \eta} \right] - 3\text{Pe}\alpha \frac{D_R}{D_i} (\eta - \eta^2) \frac{\partial \theta_i}{\partial \zeta} \end{aligned} \quad [14]$$

where

$$\alpha = \frac{S}{L} \quad [15]$$

$$\text{Pe} = \frac{2Su_{\text{avg}}}{D_R} \quad [16]$$

and

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

Equation [14] and [17] are Eq. [I-1] and [I-2], respectively, in Table I, which gives the complete set of model equations for the batch PPER/reservoir system. Equations [I-3] through [I-6] are the same equations used at the anode and cathode in Ref. (13). Equation [I-3] and [I-5] were obtained by relating the molar flux of species  $i$  to the electrode to the rate of electrochemical reaction of species  $i$  occurring at the electrode. Equation [I-4] and [I-6] are the electroneutrality condition in dimensionless form. The sign conventions that positive current leaves the anode and enters the solution and that negative current leaves the solution and enters the cathode have been used as before (13, 15). These equations are written in general for multiple electrode reactions (17) and additional details of their derivation can be found in Ref. (13)-(15), (17), and (19).

In contrast to the boundary conditions at the electrodes, the boundary conditions in the axial direction (Eq. [I-7] and [I-10]) include partial derivatives with respect to time. This is because the conditions at the inlet ( $\zeta = 0$ ) and outlet ( $\zeta = 1$ ) of the PPER are formulated to include the fact that the electrode reactions occur at  $\eta = 0$  and  $\eta = 1$ , which cause the concentrations at the inlet and outlet planes of the reactor to change with time. Equation [I-7] was obtained by writing the following dimensional material balance equation

$$\frac{\partial c_i}{\partial t} \Big|_{x=0} = - \frac{\partial N_{x,i}}{\partial x} \Big|_{x=0} - \frac{\partial N_{y,i}}{\partial y} \Big|_{x=0} \quad [18]$$

and approximating the term  $\partial N_{x,i}/\partial x$  evaluated at  $x = 0$  as follows

$$\frac{\partial N_{x,i}}{\partial x} \Big|_{x=0} = \frac{1}{\Delta x} \left[ N_{x,i} \Big|_{x=0} - N_{x,i} \Big|_{x=-\Delta x} \right] \quad [19]$$

Since the flux of each species  $i$  prior to entering the reactor ( $N_{x,i}|_{x=-\Delta x}$ ) is equal to  $u_x c_{i,\text{feed}}$  (assuming no migration or diffusion in the insulator entrance region), Eq. [19] can be written as

$$\frac{\partial N_{x,i}}{\partial x} \Big|_{x=0} = \frac{1}{\Delta x} \left[ N_{x,i} \Big|_{x=0} - u_x c_{i,\text{feed}}(t) \right] \quad [20]$$

Substituting Eq. [20] into Eq. [18] yields a time-dependent, two-dimensional boundary condition for the inlet of the reactor

$$\frac{\partial c_i}{\partial t} \Big|_{x=0} = - \frac{1}{\Delta x} \left[ N_{x,i} \Big|_{x=0} - u_x c_{i,\text{feed}}(t) \right] - \frac{\partial N_{y,i}}{\partial y} \Big|_{x=0} \quad [21]$$

where  $N_{x,i}$  and  $N_{y,i}$  are the  $x$ -component and  $y$ -component of the flux equation, respectively

$$N_{x,i} = -D_i \frac{\partial c_i}{\partial x} - \frac{z_i F}{RT} D_i c_i \frac{\partial \Phi}{\partial x} + u_x c_i \quad [22]$$

$$N_{y,i} = -D_i \frac{\partial c_i}{\partial y} - \frac{z_i F}{RT} D_i c_i \frac{\partial \Phi}{\partial y} \quad [23]$$

This boundary condition, Eq. [21], accounts for mass transfer in the axial direction across the entrance boundary ( $x = 0$ ), as well as mass transfer in the normal direction ( $y$ ) from one electrode to another. Substituting Eq. [22] and [23] into Eq. [21] and putting the resultant equation in dimensionless form yields

$$\begin{aligned} \frac{S^2}{D_i} \frac{\partial \theta_i}{\partial t} = & \frac{\alpha^2}{\Delta \zeta} \frac{\partial \theta_i}{\partial \zeta} - 3\text{Pe}\alpha \frac{D_R}{D_i} (\eta - \eta^2) \frac{[\theta_i - \theta_{i,\text{feed}}(t)]}{\Delta \zeta} \\ & + \frac{\partial^2 \theta_i}{\partial \eta^2} + \frac{z_i F}{RT} \left[ \frac{\alpha^2}{\Delta \zeta} \theta_i \frac{\partial \Phi}{\partial \zeta} + \theta_i \frac{\partial^2 \Phi}{\partial \eta^2} + \frac{\partial \theta_i}{\partial \eta} \frac{\partial \Phi}{\partial \eta} \right] \end{aligned} \quad [24]$$

where  $\theta_{i,\text{feed}}(t)$  is the time-dependent concentration of species  $i$  in the feed stream. Consideration of Eq. [24] shows that it reduces to the inlet conditions used by White *et al.* (13) when  $c_{i,\text{feed}}$  is a constant,  $\alpha$  is small,  $\partial \theta_i / \partial t = 0$ , and  $N_{y,i} = 0$ .

A boundary condition for the outlet of the reactor can be derived similarly by starting with a material balance on species  $i$  at  $x = L$  which results in the dimensionless equation

$$\begin{aligned} \frac{S^2}{D_i} \frac{\partial \theta_i}{\partial t} = & - \frac{\alpha^2}{\Delta \zeta} \frac{\partial \theta_i}{\partial \zeta} + \frac{\partial^2 \theta_i}{\partial \eta^2} \\ & + \frac{z_i F}{RT} \left[ \frac{-\alpha^2}{\Delta \zeta} \theta_i \frac{\partial \Phi}{\partial \zeta} + \theta_i \frac{\partial^2 \Phi}{\partial \eta^2} + \frac{\partial \theta_i}{\partial \eta} \frac{\partial \Phi}{\partial \eta} \right] \end{aligned} \quad [25]$$

The balance is based on the assumption that there is no axial diffusion and migration involved beyond  $x = L$ . This condition, which is often referred to as the "closed-end" boundary condition (18), is satisfied if the reactor empties into a well-mixed tank, for example. Additional discussion of the inlet and outlet boundary conditions is given by Nguyen (19) and Nguyen *et al.* (15).

**Batch PPER/well-mixed reservoir system.**—The governing equation used here for species  $i$  in a constant volume, unsteady-state reservoir is

$$\frac{dc_{i,\text{feed}}}{dt} = \frac{v_T}{V} [c_{i,\text{avg}}(t, x = L) - c_{i,\text{feed}}(t)] \quad [26]$$

where  $V$  is the volume of the reservoir,  $v_T$  is the volumetric flow rate through the system, and  $c_{i,\text{feed}}(t)$  is always the inlet concentration to the PPER (which is also the outlet concentration of the reservoir for total recycle, since it has been assumed that no time lags exist). Similarly, it has been assumed that no time lag exists between the outlet of the PPER and the inlet of the reservoir so that  $c_{i,\text{avg}}(t, x = L)$  represents the average concentration of species  $i$  at both the outlet of the PPER and the inlet of the reservoir. The volumetric flow rate through the well-

mixed reservoir ( $v_T$ ) is equal to the volumetric flow rate through the PPER so that

$$v_T = u_{avg}SW \quad [27]$$

where  $W$  is the width of the PPER. Equation [26] can be written in dimensionless form as

$$\frac{V}{v_T} \frac{d\theta_{i,feed}}{dt} = [\theta_{i,avg}(t, \zeta = 1) - \theta_{i,feed}(t)] \quad [28]$$

where (15)

$$\theta_{i,avg}(t, \zeta = 1) = 6 \int_0^1 (\eta - \eta^2) \theta_i(t, \eta, \zeta = 1) d\eta \quad [29]$$

Thus, the complete model for the batch PPER/well-mixed reservoir system consists of the equations for the PPER model and the equations for the reservoir, as shown in Table I. It is worth noting that Eq. [I-11] in Table I (or Eq. [29] above) could be substituted into Eq. [I-8] (or Eq. [28]), thereby eliminating any explicit dependence on  $\theta_{i,avg}(t, \zeta = 1)$ . This would show more clearly the coupling between the equations for the PPER and the reservoir. However, for convenience,  $\theta_{i,avg}(t, \zeta = 1)$  can be treated explicitly as a dependent variable, as was done here.

**PPER/reservoir system with partial recycle.**—The above model for a batch PPER/reservoir system can be extended to include inlet and outlet streams to treat the start-up and steady state with partial recycle case, as shown in Fig. 2. This can be done by modifying the boundary condition used at the inlet of the PPER (Eq. [I-7] in Table I) to account for the fact that the feed stream to the PPER is made up of the mixture of the outlet stream from the reservoir and the fresh feed stream as follows

$$\theta_{i,feed}(t) = \left( \frac{v_2 \theta_{i,out \text{ of reservoir}}(t) + v_1 \theta_{i,fresh \text{ feed}}}{(v_2 + v_1)} \right) \quad [30]$$

where  $v_1$  and  $v_2$  are the volumetric flow rates of the fresh feed stream and the recycled stream from the reservoir, respectively. It is important to point out that in this work the total volumetric flow rate ( $v_T = v_1 + v_2$ ) through the PPER/reservoir system is held constant and the recycle ratio ( $v_2/v_1$ ) is varied without changing the total volumetric flow rate. Replacing the term  $\theta_{i,feed}$  in Eq. [I-7] of Table I with Eq. [30] yields a boundary condition for the inlet of the PPER for this case

$$\begin{aligned} \frac{S^2}{D_i} \frac{\partial \theta_i}{\partial t} = & -3Pe\alpha \frac{D_R}{D_i} \frac{(\eta - \eta^2)}{\Delta \zeta} \\ & \left[ \theta_i - \left( \frac{v_2 \theta_{i,out \text{ of reservoir}}(t) + v_1 \theta_{i,fresh \text{ feed}}}{(v_2 + v_1)} \right) \right] \\ & + \frac{\alpha^2}{\Delta \zeta} \frac{\partial \theta_i}{\partial \zeta} + \frac{\partial^2 \theta_i}{\partial \eta^2} + \frac{z_i \mathbf{F}}{RT} \left[ \frac{\alpha^2}{\Delta \zeta} \theta_i \frac{\partial \Phi}{\partial \zeta} \right. \\ & \left. + \theta_i \frac{\partial^2 \Phi}{\partial \eta^2} + \frac{\partial \theta_i}{\partial \eta} \frac{\partial \Phi}{\partial \eta} \right] \quad [31] \end{aligned}$$

Notice that the term  $\theta_{i,fresh \text{ feed}}$  is equal to one when the fresh feed concentrations are the same as the reference or initial concentrations, as done here.

Next, the material balance equation for the well-mixed reservoir (Eq. [I-8] in Table I) is modified to account for the fact that the outlet stream from the reservoir is no longer fed directly to the PPER, but combines with the fresh feed stream to make up the inlet stream for the PPER. Thus, the material balance equation for the reservoir becomes

$$\frac{V}{v_T} \frac{d\theta_{i,out \text{ of reservoir}}}{dt} = [\theta_{i,avg}(t, \zeta = 1) - \theta_{i,out \text{ of reservoir}}(t)] \quad [32]$$

Table I. Governing equations, boundary, and initial conditions for the batch PPER/reservoir system

$$\begin{aligned} & \text{For } 0 < \eta < 1 \text{ and } 0 < \zeta < 1 \text{ and } t > 0 \\ & \text{(governing equations for the PPER)} \\ & \frac{S^2}{D_i} \frac{\partial \theta_i}{\partial t} = -3Pe\alpha \frac{D_R}{D_i} (\eta - \eta^2) \frac{\partial \theta_i}{\partial \zeta} + \alpha^2 \frac{\partial^2 \theta_i}{\partial \zeta^2} + \frac{\partial^2 \theta_i}{\partial \eta^2} \\ & + \frac{z_i \mathbf{F}}{RT} \left[ \alpha^2 \left( \theta_i \frac{\partial^2 \Phi}{\partial \zeta^2} + \frac{\partial \theta_i}{\partial \zeta} \frac{\partial \Phi}{\partial \zeta} \right) + \theta_i \frac{\partial^2 \Phi}{\partial \eta^2} + \frac{\partial \theta_i}{\partial \eta} \frac{\partial \Phi}{\partial \eta} \right] \quad [I-1] \end{aligned}$$

$$\sum_i z_i c_{i,ref} \theta_i = 0 \quad [I-2]$$

For  $\eta = 0$  and  $0 \leq \zeta \leq 1$  (anode) and  $t > 0$

$$\begin{aligned} \sum_j \frac{s_{ij} S_{i,j,ref}}{D_i c_{i,ref} n_j \mathbf{F}} \left\{ \prod_i (\theta_i)^{v_{ij}} \exp \left[ \frac{\alpha_{aj} \mathbf{F}}{RT} (V_a - \Phi_{oa} - U_{j,ref}) \right] \right. \\ \left. - \prod_i (\theta_i)^{u_{ij}} \exp \left[ \frac{-\alpha_{cj} \mathbf{F}}{RT} (V_a - \Phi_{oa} - U_{j,ref}) \right] \right\} \\ = \frac{\partial \theta_i}{\partial \eta} + \frac{z_i \mathbf{F}}{RT} \theta_i \frac{\partial \Phi}{\partial \eta} \quad [I-3] \end{aligned}$$

$$\sum_i z_i c_{i,ref} \theta_i = 0 \quad [I-4]$$

For  $\eta = 1$  and  $0 \leq \zeta \leq 1$  (cathode) and  $t > 0$

$$\begin{aligned} \sum_j \frac{s_{ij} S_{i,j,ref}}{D_i c_{i,ref} n_j \mathbf{F}} \left\{ \prod_i (\theta_i)^{v_{ij}} \exp \left[ \frac{\alpha_{aj} \mathbf{F}}{RT} (V_c - \Phi_{oc} - U_{j,ref}) \right] \right. \\ \left. - \prod_i (\theta_i)^{u_{ij}} \exp \left[ \frac{-\alpha_{cj} \mathbf{F}}{RT} (V_c - \Phi_{oc} - U_{j,ref}) \right] \right\} \\ = -\frac{\partial \theta_i}{\partial \eta} - \frac{z_i \mathbf{F}}{RT} \theta_i \frac{\partial \Phi}{\partial \eta} \quad [I-5] \end{aligned}$$

$$\sum_i z_i c_{i,ref} \theta_i = 0 \quad [I-6]$$

For  $\zeta = 0$  and  $0 < \eta < 1$  (inlet) and  $t > 0$

$$\begin{aligned} \frac{S^2}{D_i} \frac{\partial \theta_i}{\partial t} = & -3Pe\alpha \frac{D_R}{D_i} (\eta - \eta^2) \frac{[\theta_i - \theta_{i,feed}(t)]}{\Delta \zeta} + \frac{\alpha^2}{\Delta \zeta} \frac{\partial \theta_i}{\partial \zeta} \\ & + \frac{\partial^2 \theta_i}{\partial \eta^2} + \frac{z_i \mathbf{F}}{RT} \left[ \frac{\alpha^2}{\Delta \zeta} \theta_i \frac{\partial \Phi}{\partial \zeta} + \theta_i \frac{\partial^2 \Phi}{\partial \eta^2} + \frac{\partial \theta_i}{\partial \eta} \frac{\partial \Phi}{\partial \eta} \right] \quad [I-7] \end{aligned}$$

$$\frac{V}{v_T} \frac{d\theta_{i,feed}}{dt} = [\theta_{i,avg}(t, \zeta = 1) - \theta_{i,feed}(t)] \quad [I-8]$$

$$\sum_i z_i c_{i,ref} \theta_i = 0 \quad [I-9]$$

For  $\zeta = 1$  and  $0 < \eta < 1$  (outlet) and  $t > 0$

$$\begin{aligned} \frac{S^2}{D_i} \frac{\partial \theta_i}{\partial t} = & -\frac{\alpha^2}{\Delta \zeta} \frac{\partial \theta_i}{\partial \zeta} + \frac{\partial^2 \theta_i}{\partial \eta^2} \\ & + \frac{z_i \mathbf{F}}{RT} \left[ \frac{-\alpha^2}{\Delta \zeta} \theta_i \frac{\partial \Phi}{\partial \zeta} + \theta_i \frac{\partial^2 \Phi}{\partial \eta^2} + \frac{\partial \theta_i}{\partial \eta} \frac{\partial \Phi}{\partial \eta} \right] \quad [I-10] \end{aligned}$$

$$\theta_{i,avg}(t, \zeta = 1) = 6 \int_0^1 (\eta - \eta^2) \theta_i(t, \eta, \zeta = 1) d\eta \quad [I-11]$$

$$\sum_i z_i c_{i,ref} \theta_i = 0 \quad [I-12]$$

For  $0 \leq \eta \leq 1$  and  $0 \leq \zeta \leq 1$  for  $t \leq 0$  (initial conditions)

$$\begin{aligned} \theta_i = 1 \quad \theta_{i,feed} = 1 \quad \sum_i z_i c_{i,ref} \theta_i = 0 \\ \sum_i z_i c_{i,ref} \theta_{i,feed} = 0 \quad \theta_{i,avg}(\zeta = 1) = 1 \quad [I-13] \end{aligned}$$

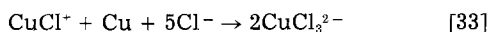
$\Phi$  No initial condition is needed

$$(\text{arbitrarily set equal to } 0.0V) \quad [I-14]$$

The total number of unknowns for the PPER/reservoir system with partial recycle remains the same as in the batch PPER and reservoir model; but the unknown  $\theta_{i,feed}$  is replaced by  $\theta_{i,out \text{ of reservoir}}$ .

**Batch PPER/CSTR system.**—The batch PPER/reservoir model developed above can be extended to include the

following copper-leaching reaction in the well-mixed reservoir, which is now referred to as a CSTR



This chemical reaction is assumed to be irreversible and pseudo-homogeneous. That is, even though copper is usually present as a solid either in the form of copper sheets or circuit boards placed in the CSTR to be leached, it is assumed here that the copper exists as particles suspended in the solution, and consequently the CSTR reaction can be treated as a single phase mixture, so that the reaction rate expression can be written as a pseudo-first-order reaction rate. The material balance equation for the CSTR can be written in dimensionless form as follows

$$\frac{V}{v_T} \frac{d\theta_{i,\text{feed}}}{dt} = [\theta_{i,\text{avg}}(t, \zeta = 1) - \theta_{i,\text{feed}}(t)] + \frac{V}{v_T} \frac{R_{\text{CSTR},i,\text{feed}}}{C_{i,\text{ref}}} \quad [34]$$

Table II. Implementation of the IAD-Newman technique for the batch PPER/reservoir system

First half-time step (implicit in axial ( $\zeta$ ) direction)	
[1] $\longrightarrow$ [1]	$\eta = 0$ (anode)
⋮	
[2] $\longrightarrow$ [3] $\longrightarrow$ [4]	$0 < \eta < 1$ (channel)
⋮	
[1] $\longrightarrow$ [1]	$\eta = 1$ (cathode)
$(\zeta = 0) \longrightarrow (\zeta = 1)$	
$\theta_i^* = \theta_i \quad \theta_{i,\text{avg}}^* = \theta_{i,\text{avg}} \quad \theta_{i,\text{feed}}^* = \theta_{i,\text{feed}} \quad \text{and} \quad \Phi^* = \Phi$	
$\theta_i^* = \theta_i \quad \theta_{i,\text{avg}}^* = \theta_{i,\text{avg}} \quad \theta_{i,\text{feed}}^* = \theta_{i,\text{feed}} \quad \text{and} \quad \Phi^* = \Phi$	
$\frac{S^2}{D_i} \frac{(\theta_i^* - \theta_i)}{\Delta t/2} = -3\text{Pe}\alpha \frac{D_R}{D_i} (\eta - \eta^2) \frac{(\theta_i^* - \theta_{i,\text{feed}}^*(t))}{\Delta \zeta} + \frac{\alpha^2}{\Delta \zeta} \frac{\partial \theta_i^*}{\partial \zeta}$	
$+ \frac{\partial^2 \theta_i}{\partial \eta^2} + \frac{z_i F}{RT} \left[ \frac{\alpha^2}{\Delta \zeta} \theta_i^* \frac{\partial \Phi^*}{\partial \zeta} + \theta_i^* \frac{\partial^2 \Phi^*}{\partial \eta^2} + \frac{\partial \theta_i}{\partial \eta} \frac{\partial \Phi^*}{\partial \eta} \right]$	
$\frac{V}{v_T} \frac{(\theta_{i,\text{feed}}^* - \theta_{i,\text{feed}})}{\Delta t/2} = [\theta_{i,\text{avg}}^*(\zeta = 1) - \theta_{i,\text{feed}}^*]$	
$\frac{\partial \theta_{i,\text{avg}}^*}{\partial \zeta} \Big _{0 \leq \zeta < 1, 0 < \eta < 1, t > 0} = 0, \quad \sum_i z_i C_{i,\text{ref}} \theta_i^* = 0$	
$\frac{S^2}{D_i} \frac{(\theta_i^* - \theta_i)}{\Delta t/2} = -3\text{Pe}\alpha \frac{D_R}{D_i} (\eta - \eta^2) \frac{\partial \theta_i^*}{\partial \zeta} + \alpha^2 \frac{\partial^2 \theta_i^*}{\partial \zeta^2} + \frac{\partial^2 \theta_i^*}{\partial \eta^2}$	
$+ \frac{z_i F}{RT} \left[ \alpha^2 \left( \theta_i^* \frac{\partial^2 \Phi^*}{\partial \zeta^2} + \frac{\partial \theta_i^*}{\partial \zeta} \frac{\partial \Phi^*}{\partial \zeta} \right) + \theta_i^* \frac{\partial^2 \Phi^*}{\partial \eta^2} + \frac{\partial \theta_i}{\partial \eta} \frac{\partial \Phi^*}{\partial \eta} \right]$	
$\frac{\partial \theta_{i,\text{avg}}^*}{\partial \zeta} \Big _{0 \leq \zeta < 1, 0 < \eta < 1, t > 0} = 0$	
$\frac{\partial \theta_{i,\text{feed}}^*}{\partial \zeta} \Big _{0 \leq \zeta < 1, 0 < \eta < 1, t > 0} = 0$	
$\sum_i z_i C_{i,\text{ref}} \theta_i^* = 0$	
$\frac{S^2}{D_i} \frac{(\theta_i^* - \theta_i)}{\Delta t/2} = -\frac{\alpha^2}{\Delta \zeta} \frac{\partial^2 \theta_i^*}{\partial \zeta^2}$	
$+ \frac{z_i F}{RT} \left[ \frac{-\alpha^2}{\Delta \zeta} \theta_i^* \frac{\partial \Phi^*}{\partial \zeta} + \theta_i^* \frac{\partial^2 \Phi^*}{\partial \eta^2} + \frac{\partial \theta_i}{\partial \eta} \frac{\partial \Phi^*}{\partial \eta} \right]$	
$\theta_{i,\text{avg}}^* = 6 \int_0^1 (\eta - \eta^2) \theta_i^*(t, \eta, \zeta = 1) d\eta$	
$\frac{\partial \theta_{i,\text{feed}}^*}{\partial \zeta} \Big _{0 < \zeta \leq 1, 0 < \eta < 1, t > 0} = 0 \quad \sum_i z_i C_{i,\text{ref}} \theta_i^* = 0$	
Second half-time step (implicit in normal ( $\eta$ ) direction)	
[5] $\longrightarrow$ [5] $\longrightarrow$ [5]	$\eta = 0$ (anode)
[6] $\cdots$ [8] $\cdots$ [9]	$0 < \eta < 1$ (channel)
[7] $\longrightarrow$ [7] $\longrightarrow$ [7]	$\eta = 1$ (anode)
$(\zeta = 0) \longrightarrow (\zeta = 1)$	

where  $R_{\text{CSTR},i,\text{feed}}$  represents the production rate of species  $i$  in the CSTR due to homogeneous or pseudo-homogeneous reactions. The subscript feed is used to emphasize that the production rate is based on the outlet concentration of the CSTR (which is the concentration in the CSTR since it is well mixed), which is also the feed to the PPER when there is total recycle. According to the stoichiometry of the reaction shown in Eq. [33], the production rates of each species can be written in terms of  $\text{CuCl}^+$

$$R_{\text{CSTR},\text{CuCl}^+,\text{feed}} = -kc_{\text{CuCl}^+,\text{feed}} \quad [35]$$

$$R_{\text{CSTR},\text{Cl}^-,\text{feed}} = 5R_{\text{CSTR},\text{CuCl}^+,\text{feed}} = -5kc_{\text{CuCl}^+,\text{feed}} \quad [36]$$

$$R_{\text{CSTR},\text{CuCl}_3^{2-},\text{feed}} = -2R_{\text{CSTR},\text{CuCl}^+,\text{feed}} = 2kc_{\text{CuCl}^+,\text{feed}} \quad [37]$$

$$R_{\text{CSTR},\text{H}^+,\text{feed}} = 0 \quad [38]$$

where  $k$  is the reaction rate constant and  $R_{\text{CSTR},\text{H}^+,\text{feed}}$  has been included for completeness. Replacing the reaction

$$\sum_j \frac{S_j S_{i,j,\text{ref}}}{D_i C_{i,\text{ref}} n_j F} \left\{ \prod_i (\theta_i^{**})^{n_{ij}} \exp \left[ \frac{\alpha_j F}{RT} (V_a - \Phi_{\text{oc}}^{**} - U_{j,\text{ref}}) \right] - \prod_i (\theta_i^{**})^{n_{ij}} \exp \left[ \frac{-\alpha_j F}{RT} (V_a - \Phi_{\text{oc}}^{**} - U_{j,\text{ref}}) \right] \right\} = \frac{\partial \theta_i^{**}}{\partial \eta} + \frac{z_i F}{RT} \theta_i^{**} \frac{\partial \Phi^{**}}{\partial \eta} \quad [\text{II-5}]$$

$$\theta_{i,\text{avg}}^{**} = \theta_{i,\text{avg}}^*, \quad \theta_{i,\text{feed}}^{**} = \theta_{i,\text{feed}}^*,$$

$$\sum_i z_i C_{i,\text{ref}} \theta_i^{**} = 0$$

$$\frac{S^2}{D_i} \frac{(\theta_i^{**} - \theta_i^*)}{\Delta t/2} = -3\text{Pe}\alpha \frac{D_R}{D_i} (\eta - \eta^2) \frac{(\theta_i^* - \theta_{i,\text{feed}}^*(t))}{\Delta \zeta} + \frac{\alpha^2}{\Delta \zeta} \frac{\partial \theta_i^*}{\partial \zeta} + \frac{\partial^2 \theta_i^{**}}{\partial \eta^2} + \frac{z_i F}{RT} \left[ \frac{\alpha^2}{\Delta \zeta} \theta_i^{**} \frac{\partial \Phi^*}{\partial \zeta} + \theta_i^{**} \frac{\partial^2 \Phi^{**}}{\partial \eta^2} + \frac{\partial \theta_i^{**}}{\partial \eta} \frac{\partial \Phi^{**}}{\partial \eta} \right] \quad [\text{II-6}]$$

$$\frac{V}{v_T} \frac{(\theta_{i,\text{feed}}^{**} - \theta_{i,\text{feed}}^*)}{\Delta t/2} = [\theta_{i,\text{avg}}^{**}(\zeta = 1) - \theta_{i,\text{feed}}^{**}]$$

$$\theta_{i,\text{avg}}^{**} = \theta_{i,\text{avg}}^{**} \quad (\text{calculated at } \zeta = 1)$$

obtained from previous iteration in this half-time step

$$\sum_i z_i C_{i,\text{ref}} \theta_i^{**} = 0$$

$$\sum_j \frac{S_j S_{i,j,\text{ref}}}{D_i C_{i,\text{ref}} n_j F} \left\{ \prod_i (\theta_i^{**})^{n_{ij}} \exp \left[ \frac{\alpha_j F}{RT} (V_c - \Phi_{\text{oc}}^{**} - U_{j,\text{ref}}) \right] - \prod_i (\theta_i^{**})^{n_{ij}} \exp \left[ \frac{-\alpha_j F}{RT} (V_c - \Phi_{\text{oc}}^{**} - U_{j,\text{ref}}) \right] \right\} = -\frac{\partial \theta_i^{**}}{\partial \eta} + \frac{z_i F}{RT} \theta_i^{**} \frac{\partial \Phi^{**}}{\partial \eta} \quad [\text{II-7}]$$

$$\theta_{i,\text{avg}}^{**} = \theta_{i,\text{avg}}^*, \quad \theta_{i,\text{feed}}^{**} = \theta_{i,\text{feed}}^*,$$

$$\sum_i z_i C_{i,\text{ref}} \theta_i^{**} = 0$$

$$\frac{S^2}{D_i} \frac{(\theta_i^{**} - \theta_i^*)}{\Delta t/2} = -3\text{Pe}\alpha \frac{D_R}{D_i} (\eta - \eta^2) \frac{\partial \theta_i^*}{\partial \zeta} + \alpha^2 \frac{\partial^2 \theta_i^*}{\partial \zeta^2} + \frac{\partial^2 \theta_i^{**}}{\partial \eta^2} + \frac{z_i F}{RT} \left[ \alpha^2 \left( \theta_i^* \frac{\partial^2 \Phi^*}{\partial \zeta^2} + \frac{\partial \theta_i^*}{\partial \zeta} \frac{\partial \Phi^*}{\partial \zeta} \right) + \theta_i^{**} \frac{\partial^2 \Phi^{**}}{\partial \eta^2} + \frac{\partial \theta_i^{**}}{\partial \eta} \frac{\partial \Phi^{**}}{\partial \eta} \right] \quad [\text{II-8}]$$

$$\theta_{i,\text{avg}}^{**} = \theta_{i,\text{avg}}^*, \quad \theta_{i,\text{feed}}^{**} = \theta_{i,\text{feed}}^*,$$

$$\sum_i z_i C_{i,\text{ref}} \theta_i^{**} = 0$$

$$\frac{S^2}{D_i} \frac{(\theta_i^{**} - \theta_i^*)}{\Delta t/2} = -\frac{\alpha^2}{\Delta \zeta} \frac{\partial \theta_i^*}{\partial \zeta} + \frac{\partial^2 \theta_i^{**}}{\partial \eta^2} + \frac{z_i F}{RT} \left[ \frac{-\alpha^2}{\Delta \zeta} \theta_i^* \frac{\partial \Phi^*}{\partial \zeta} + \theta_i^{**} \frac{\partial^2 \Phi^{**}}{\partial \eta^2} + \frac{\partial \theta_i^{**}}{\partial \eta} \frac{\partial \Phi^{**}}{\partial \eta} \right]$$

$$\theta_{i,\text{avg}}^{**} = 6 \int_0^1 (\eta - \eta^2) \theta_i^{**}(t, \eta, \zeta = 1) d\eta \quad [\text{II-9}]$$

$$\theta_{i,\text{feed}}^{**} = \theta_{i,\text{feed}}^*, \quad \sum_i z_i C_{i,\text{ref}} \theta_i^{**} = 0$$

term,  $R_{\text{CSTR},i,\text{feed}}$ , in Eq. [34] for each species involved with its appropriate definition (Eq. [35]–[38]) completes the model development of the batch PPER/CSTR system with a simultaneous chemical reaction.

### Solution Technique

The set of parabolic differential equations in Table I can be solved using a numerical method referred to as the IAD-Newman technique (15, 19–21). The method provides a means of solving simultaneously the entire system of equations in Table I by solving for values at an intermediate pseudo-time step. The implementation of the IAD-Newman technique requires two difference equations for each differential equation which are used in turn over successive half-time steps. During the first half-time step, the first equation is implicit in one direction ( $\zeta$ , the axial direction) and during the second half-time step the second equation is implicit in the other direction ( $\eta$ , the normal direction). Table II gives a full implementation of the solution method for the PPER/reservoir system, and the Appendix gives a detailed description of the technique, as used here.

### Fixed and Variable Parameters

Values for the dependent variables ( $\theta_{i,\text{feed}}$ ,  $\theta_i$ ,  $\theta_{i,\text{avg}}$  ( $\zeta = 1$ ), and  $\Phi$ ) can be obtained by using the IAD-Newman technique to solve the equations presented in Table I once values have been set for the parameters of the system. For simplicity, most of the parameters for the models presented here have been fixed and are presented in Table III. The remaining parameters that have been treated here as variables are:  $E_a$ ,  $V$ ,  $v_2/v_1$ , and  $k$ . Since  $E_c$  is fixed, the variation of  $E_a$  results in the variation of the cell

Table III. Values for fixed parameters used in the model

Kinetic and thermodynamic						
Reaction (j)	$10^4 \theta_{i,\text{ref}} (A/\text{cm}^2)^a$	$\alpha_{aj}$	$\alpha_{cj}$	$n_j$	$U_j^b (V)$	$U_{j,\text{ref}}^c (V)$
1	1.0	0.5	0.5	1	0.438	0
2	1.0	0.5	0.5	1	0.233	0.1144
$T = 298.15 \text{ K}$						
Component (i)	Reaction 1 (j = 1)			Reaction 2 (j = 2)		
	$s_{ij}$	$p_{ij}$	$q_{ij}$	$s_{ij}$	$p_{ij}$	$q_{ij}$
$\text{H}^+$	0	0	0	0	0	0
$\text{Cl}^-$	-2	0	2	3	3	0
$\text{CuCl}_3^{2-}$	1	1	0	-1	0	1
$\text{CuCl}^+$	-1	0	1	0	0	0
$u_{\text{avg}} = 3.6 \times 10^{-2} \text{ cm/s}$						
$E_c = 0 \text{ V}$ $S = 0.1 \text{ cm}$ $W = 10 \text{ cm}$ $L = 10 \text{ cm}$						
$\alpha^e = \frac{s}{L} = 0.01$						
$\text{Pe}\alpha^e = \frac{2s^2 u_{\text{avg}}}{D_R L} = 10$						
Transport and reference concentrations						
Component (i)	$z_i$	$10^5 D_i (\text{cm}^2/\text{s})$	$10^3 c_{i,\text{ref}} (\text{mol}/\text{cm}^3)$			
$\text{H}^+$	1	9.312	1.00			
$\text{Cl}^-$	-1	2.032	0.10			
$\text{CuCl}_3^{2-}$	-2	0.720	0.50			
$\text{CuCl}^+$	1	0.720	0.10			

<sup>a</sup> Chosen arbitrarily.

<sup>b</sup> See Ref. (11) and (16) of White *et al.* (13).

<sup>c</sup> The open current potential of reaction  $j$  at the reference concentrations relative to reaction 1.

<sup>d</sup> Designated as the limiting reactant.

<sup>e</sup> Included for convenience.

potential

$$E_{\text{cell}} = E_a - E_c \quad [39]$$

The variation of  $V$  with  $u_{\text{avg}}$ ,  $S$ , and  $W$  fixed can be represented conveniently as the residence time in the reservoir or CSTR

$$\tau = \frac{V}{u_{\text{avg}} S W} \quad [40]$$

For the PPER/reservoir system with partial recycle, an additional independent variable is the recycle ratio

$$\text{recycle ratio} = \frac{v_2}{v_1} \quad [41]$$

For the batch PPER/CSTR system, an additional independent variable is the homogeneous chemical reaction rate constant,  $k$ . To study the effects of each of these independent variables on the system, each variable is changed while the other independent variables are held at fixed values.

### Results and Discussion

Various case studies have been selected to illustrate the use of the models presented here. The variation of the feed concentration of  $\text{CuCl}_3^{2-}$  to the PPER with time, for three residence times in the well-mixed reservoir, is shown in Fig. 3. Also shown in Fig. 3 are the predictions obtained from the models given by Pickett (9) and by Walker and Wragg (10). The predictions based on Pickett's model were obtained from this equation

$$\theta_{\text{CuCl}_3^{2-}, \text{feed}, P}(t) = \exp \left\{ -\frac{t}{\tau} \left( 1 - \exp \left[ -2.33 \left( \frac{2A}{\text{ReScSW}} \right)^{2/3} \right] \right) \right\} \quad [42]$$

where  $\text{Re} = v_{\text{avg}} 2S/\nu$ ,  $\text{Sc} = \nu/D_R$ ,  $\tau = V/v_T$ , and  $A$  are the Reynolds number, the Schmidt number, the residence

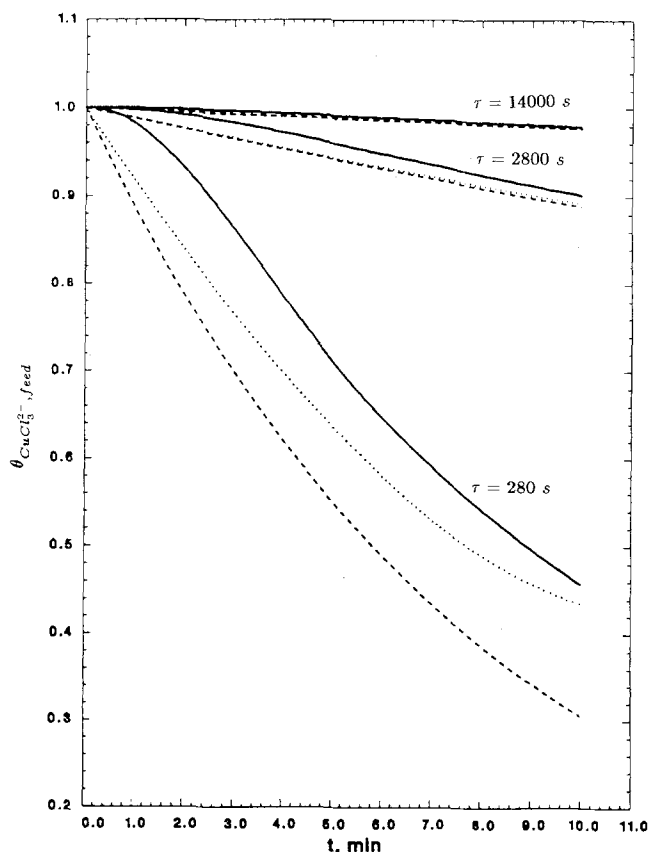


Fig. 3. The effect of residence time on the concentration of  $\text{CuCl}_3^{2-}$  leaving the well-mixed reservoir with  $E_{\text{cell}} = 0.4 \text{ V}$ : --- Pickett (9), ... Walker and Wragg (10), and — this model.

time in the well-mixed reservoir, and the electrode area (both electrodes are included in this study since  $\text{CuCl}_3^{2-}$  reacts on both the anode and the cathode) of the electrochemical reactor, respectively. After substitution of variables, Eq. [42] can be written in dimensionless form as

$$\theta_{\text{CuCl}_3^{2-}, \text{feed}, P}(t) = \exp \left\{ -\frac{t}{\tau} \left( 1 - \exp \left[ -2.33 \left( \frac{\text{Pe}\alpha}{2} \right)^{-2.3} \right] \right) \right\} \quad [43]$$

The predictions in Fig. 3, based on Walker and Wragg's model (10), were obtained by modifying their equation for a packed bed, as presented and discussed by Nguyen (16). The predictions of the three models agree for very large residence times, but disagree significantly for relatively small values of  $\tau$ . As pointed out by Walker and Wragg (10), Pickett's model predicts values for  $\theta_{\text{CuCl}_3^{2-}, \text{feed}}$  that are too low because of his assumption of limiting current conditions. Similarly, Walker and Wragg's model predicts values for  $\theta_{\text{CuCl}_3^{2-}, \text{feed}}$  that are too small because of their assumption that the PPER is an ideal plug flow reactor.

Further consideration of the predicted results in Fig. 3 reveals that, at  $\tau = 280\text{s}$ , a time lag exists according to the model presented here, but not from the models presented by Pickett (9) and Walker and Wragg (10). The reason for this is due to the initial conditions used in their models. That is, the initial conditions used in this work assumes that for  $t \leq 0$  the concentration of each species  $i$  in the reactor is equal to its initial feed concentration, which does not change until the potential is applied to the cell for  $t > 0$ . On the other hand, Pickett (9) and Walker and Wragg (10) assumed that for  $t \leq 0$  a "pre-reacted" steady-state concentration distribution exists in the electrochemical reactor.

Another important feature of the model presented here (not offered in previous models) is the capability to predict the effect of applied cell potential,  $E_{\text{cell}}$ , on the system. The effect of applied potential on the dynamic behavior of the feed concentration of  $\text{CuCl}_3^{2-}$  to the PPER is shown in Fig. 4. As expected, increasing the driving force ( $E_{\text{cell}}$ ) decreases the concentration more rapidly.

An additional independent variable of interest is the recycle ratio ( $v_2/v_1$ ). Figure 5 shows the effect  $v_2/v_1$  has on

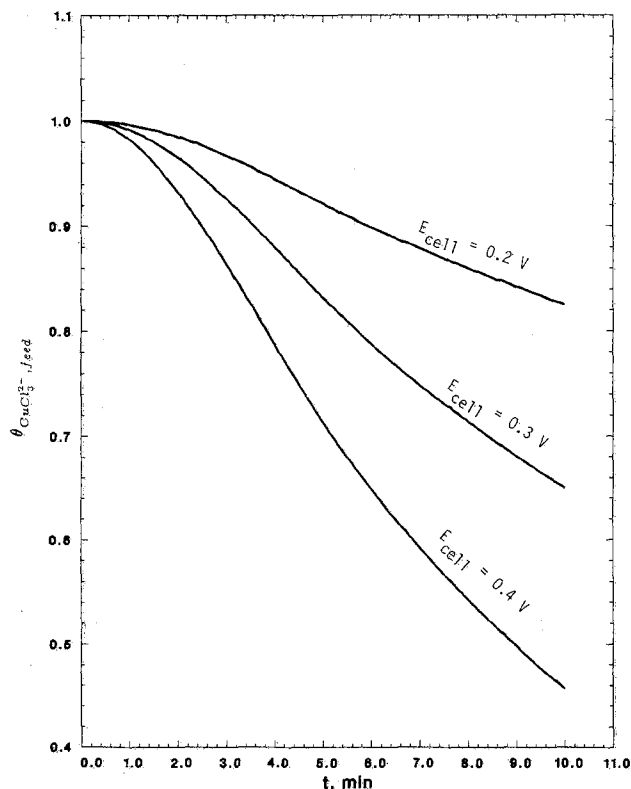


Fig. 4. The effect of cell potential on the concentration of  $\text{CuCl}_3^{2-}$  leaving the well-mixed reservoir with  $\tau = 280\text{s}$ .

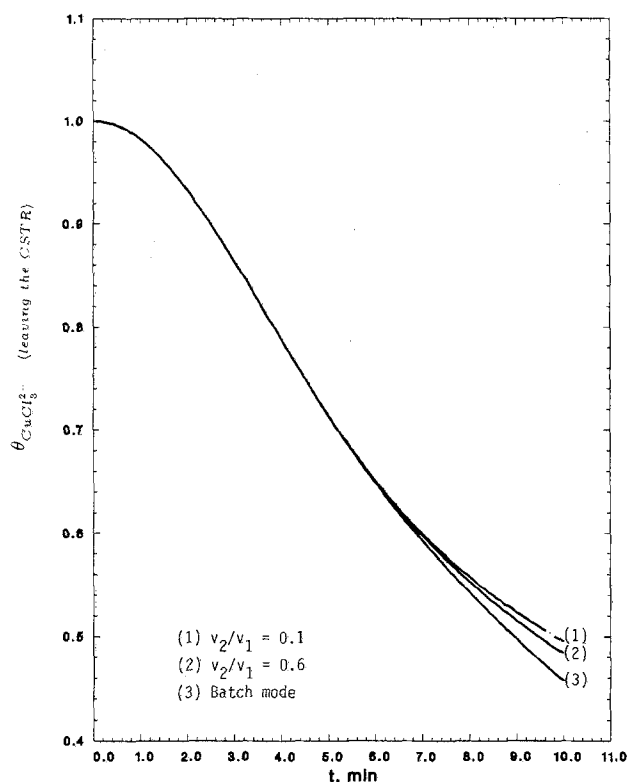


Fig. 5. The effect of recycle ratio on the concentration of  $\text{CuCl}_3^{2-}$  leaving the CSTR with  $E_{\text{cell}} = 0.4\text{V}$  and  $\tau = 280\text{s}$ .

the dimensionless concentration of  $\text{CuCl}_3^{2-}$  leaving the reservoir. Note that as the recycle ratio becomes large,  $\theta_{\text{CuCl}_3^{2-}, \text{out of reservoir}}$  approaches batch mode, as expected. The concentration of  $\text{CuCl}_3^{2-}$  leaving the reservoir, as shown in Fig. 5, will eventually reach a steady-state value; however, due to the limited computer time available, the model was solved for only the first 10 min of elapsed time from startup. The reaction rate in the PPER, on the other hand, can be seen to reach a constant value, as shown in Fig. 6 for a recycle ratio of  $v_2/v_1 = 0.1$ .

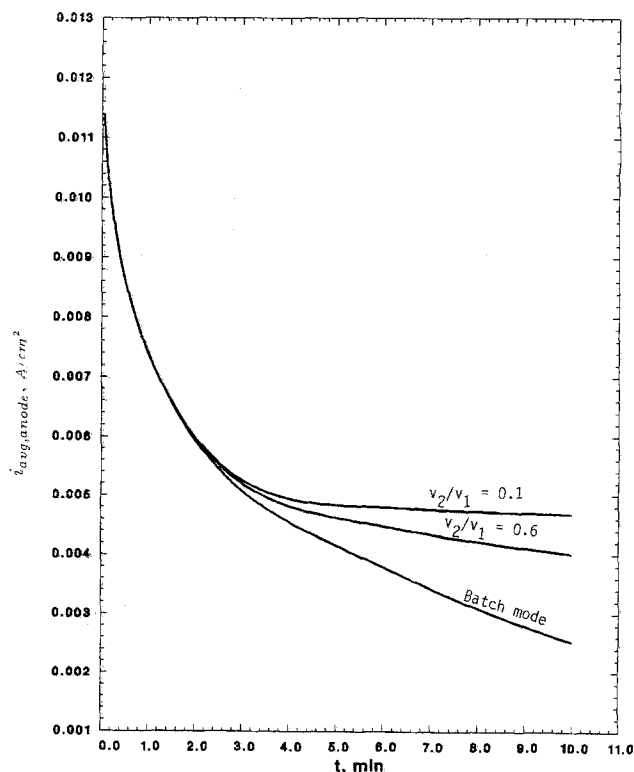


Fig. 6. The effect of recycle ratio on the average current density,  $i_{\text{avg}}$ , with  $E_{\text{cell}} = 0.4\text{V}$  and  $\tau = 280\text{s}$ .



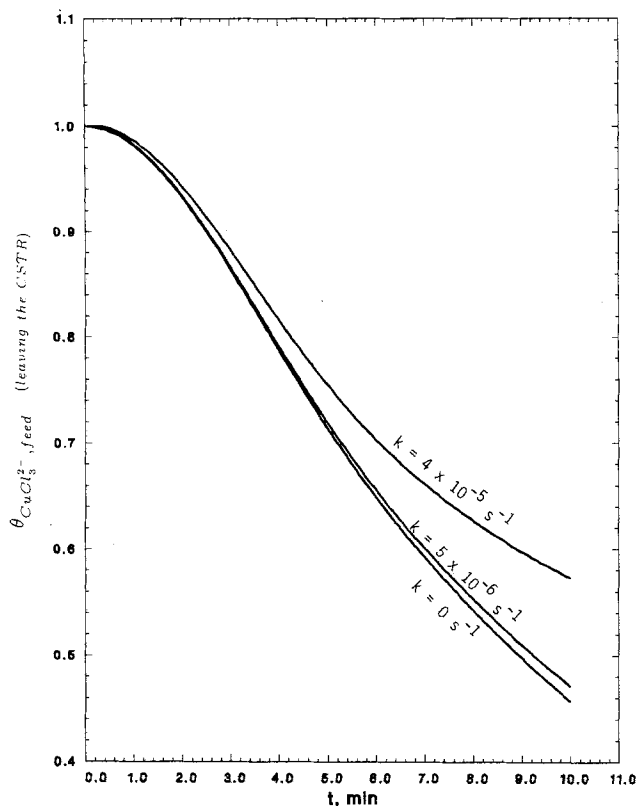


Fig. 7. The effect of simultaneous chemical reaction on the concentration of  $\text{CuCl}_3^{2-}$  leaving the CSTR with  $E_{\text{cell}} = 0.4\text{V}$  and  $\tau = 280\text{s}$ .

Finally, the effect of the chemical leaching reaction (Eq. [33]) on  $\theta_{\text{CuCl}_3^{2-}, \text{feed}}$  in the PPER/CSTR system is shown in Fig. 7 for various values of the chemical reaction rate constant,  $k$ . As expected, increasing the reaction rate constant  $k$  increases the rate of the leaching reaction in the CSTR which thereby yields a large value of  $\theta_{\text{CuCl}_3^{2-}, \text{feed}}$  at a particular time.

### Summary

The models presented here may serve as useful design tools for simulating the behavior of a parallel plate electrochemical reactor operating together with a CSTR under various recirculation modes, particularly during start-up conditions. Also, it may be possible to use the models with experimental data and a parameter estimation technique to determine some of the kinetic or transport parameter values for a system of interest.

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### APPENDIX

#### Application of the IAD-Newman Technique

The models presented here for a PPER, reservoir, and associated recirculation system consists of  $3i + 1$  unknowns ( $\theta_i$ ,  $\theta_{i, \text{feed}}(t)$ ,  $\theta_{i, \text{avg}}(t, \zeta = 1)$ , and  $\Phi$ ). (Again, it is possible to remove the explicit dependence of the system of equations on  $\theta_{i, \text{avg}}(t, \zeta = 1)$  by substituting Eq. [I-11] into [I-8] of Table I. However, this was not done here for the sake of clarity.) Values for these unknowns can be obtained by solving the equations in Table II once values for the parameters are set. Two  $i$  of these unknowns,  $\theta_{i, \text{feed}}(t)$  and  $\theta_{i, \text{avg}}(t, \zeta = 1)$ , depend on time ( $t$ ) only, and  $i + 1$  of these unknowns,  $\theta_i$  and  $\Phi$ , depend on time and the spatial coordinates  $\eta$  and  $\zeta$ . The equations that govern the values for these unknowns are coupled, as shown in Table I, which requires that all of the equations be solved simultaneously. To use the IAD-Newman technique (15, 19-21) to do this, Newman's unknown constant approach (22-24) for the variables  $\theta_{i, \text{feed}}(t)$  and  $\theta_{i, \text{avg}}(t, \zeta = 1)$  can be used. This unknown constant approach consists of utilizing an extra equation to insure that when calculating in the axial ( $\zeta$ ) direction the value of  $\theta_{i, \text{avg}}(t, \zeta = 1)$  depends only on time. The equation in dimensionless form is as follows

$$\frac{\partial \theta_{i, \text{avg}}^*}{\partial \zeta} \bigg|_{0 \leq \zeta < 1, 0 < \eta < 1, t > 0} = 0 \quad [\text{A-1}]$$

Similarly, the unknown constant approach can be applied to  $\theta_{i, \text{feed}}(t)$  (the concentration at the entrance to the PPER). That is

$$\frac{\partial \theta_{i, \text{feed}}^*}{\partial \zeta} \bigg|_{0 < \zeta \leq 1, 0 < \eta < 1, t > 0} = 0 \quad [\text{A-2}]$$

Table II illustrates the implementation of the IAD-Newman technique to the complete set of governing equations shown in Table I. Consideration of the grid equations in Table II shows that during the first implicit half-time step (implicit in the  $\zeta$  direction) the unknowns along the electrodes (grid Eq. [II-1]) are set equal to their values at the beginning of the time step (i.e.,  $\theta_i = \theta_i$ ,  $\theta_{i, \text{avg}} = \theta_{i, \text{avg}}$ ,  $\theta_{i, \text{feed}}^* = \theta_{i, \text{feed}}$ , and  $\Phi^* = \Phi$ ). The unknowns  $\theta_i^*$  and  $\Phi^*$  are treated as shown because the boundary conditions for the electrodes contain derivatives in the  $\eta$  direction only and are satisfied in the next half-time step (implicit in the  $\eta$  direction, grid Eq. [II-5] and [II-7]). The reason for setting  $\theta_{i, \text{avg}}^*$  and  $\theta_{i, \text{feed}}^*$  equal to their previously determined full-time step values is that these unknowns are important only in the bulk of the solution and not at the electrodes. In the bulk of the solution, all of these variables are treated as unknowns, as shown in grid Eq. [II-2], [II-3], and [II-4] in Table II.

During the second half-time step which is implicit in the normal ( $\eta$ ) direction, the unknowns  $\theta_{i, \text{avg}}^*$  and  $\theta_{i, \text{feed}}^*$  are not needed along the electrodes and are therefore set equal to  $\theta_{i, \text{avg}}^*$  and  $\theta_{i, \text{feed}}^*$ , as shown in grid Eq. [II-5]. Also, note that the same thing is done with these unknowns in the bulk of the solution (i.e., set  $\theta_{i, \text{avg}}^* = \theta_{i, \text{avg}}^*$  in grid Eq. [II-8] and  $\theta_{i, \text{feed}}^* = \theta_{i, \text{feed}}^*$  in grid Eq. [II-8] and [II-9]). This is done because Eq. [A-1] and [A-2] are explicit in the  $\zeta$  direction only.

Additionally, inspection of grid Eq. [II-6] shows that the unknowns  $\theta_{i, \text{avg}}^*$  (calculated at  $\zeta = 1$ ) cannot be determined until grid Eq. [II-5]-[II-9]-[II-7] are solved. There are two ways to handle this case. One way is to set the unknowns  $\theta_{i, \text{avg}}^*$  (calculated at  $\zeta = 1$ ) to some reasonable, but arbitrary, values, solve the system of equations for all  $\zeta$ , and once the unknowns  $\theta_{i, \text{avg}}^*$  at  $\zeta = 1$  are known, substitute them back into grid Eq. [II-6] and solve the grid Eq. [II-5]-[II-6]-[II-7] again. This is done repetitively within the second half-time step, until no change occurs in  $\theta_{i, \text{avg}}^*(\zeta = 1)$ . This step requires only two iterations here. An alternate way to handle this situation would be to solve the grid Eq. [II-5]-[II-9]-[II-7] first and then solve the grid Eq. [II-5]-[II-8]-[II-7] at each  $\zeta$ , and then finally the grid Eq. [II-5]-[II-6]-[II-7]. This alternate approach would be expected to be more efficient, but was not tested.

#### LIST OF SYMBOLS

$A$	electrode area of electrochemical reactor, $\text{cm}^2$
$c_i$	concentration of species $i$ , $\text{mol}/\text{cm}^3$
$c_{i,0}$	concentration of species $i$ at the electrode surface, $\text{mol}/\text{cm}^3$
$c_{i, \text{feed}}$	concentration of species $i$ in the feed stream to the PPER, $\text{mol}/\text{cm}^3$
$c_{i, \text{ref}}$	reference concentration of species $i$ (set equal to the initial feed stream concentrations to the PPER, i.e., at $t = 0$ ), $\text{mol}/\text{cm}^3$
$D_i$	diffusion coefficient of species $i$ , $\text{cm}^2/\text{s}$
$D_R$	diffusion coefficient of limiting reactant, $\text{cm}^2/\text{s}$
$E_a$	anode potential, $\text{V}$
$E_c$	cathode potential, $\text{V}$
$E_{\text{cell}}$	cell potential ( $E_a - E_c$ ), $\text{V}$
$F$	Faraday's constant, $96,487 \text{ C}/\text{mol}$
$i_{\text{avg}}$	average current density, $\text{A}/\text{cm}^2$
$i_{\text{nj}}$	normal component of current density due to reaction $j$ , $\text{A}/\text{cm}^2$
$i_{0j, \text{ref}}$	exchange current density of reaction $j$ at reference concentrations, $\text{A}/\text{cm}^2$
$k$	homogeneous chemical reaction rate constant, $\text{s}^{-1}$
$L$	electrode length, $\text{cm}$
$n_j$	number of electrons involved in reaction $j$
$N_i$	flux vector of species $i$ , $\text{mol}/\text{cm}^2\text{-s}$
$N_{x,i}$	flux of species $i$ in the $x$ -direction, $\text{mol}/\text{cm}^2\text{-s}$
$N_{y,i}$	normal component of the flux ( $y$ -direction) of species $i$ , $\text{mol}/\text{cm}^2\text{-s}$
$p_{ij}$	anodic reaction order of species $i$ in reaction $j$
$Pe$	Peclet number ( $= 2Su_{\text{avg}}/D_R$ )
$Pe_\alpha$	$2S^2u_{\text{avg}}/D_R L$ , dimensionless
$q_i$	cathodic reaction order of species $i$ in reaction $j$

$R$  gas law constant, 8.314 J/mol-K  
 $R_{\text{CSTR},i,\text{feed}}$  production rate of species  $i$  in the CSTR based on the outlet concentration of the CSTR ( $C_{i,\text{feed}}$ ), mol/cm<sup>3</sup>-s  
 $S_{ij}$  stoichiometric coefficient of species  $i$  in reaction  $j$   
 $S$  electrode gap, cm  
 $t$  time, s  
 $T$  temperature, K  
 $u$  velocity vector in the PPER, cm/s  
 $u_{\text{ave}}$  average velocity of the electrolyte, cm/s  
 $u_i$  ionic mobility of species  $i$  ( $= D_i/RT$ , Eq. [8])  
 $u_x$  velocity of the electrolyte in the  $x$ -direction, cm/s  
 $u_y$  velocity of the electrolyte in the  $y$ -direction, cm/s  
 $U_{i,\text{ref}}$  open-circuit potential of reaction  $j$  at reference conditions, V  
 $v_T$  electrolyte flow rate in the system, cm<sup>3</sup>/s  
 $v_1$  volumetric flow rate of fresh feed stream, cm<sup>3</sup>/s  
 $v_2$  volumetric flow rate of recycled stream, cm<sup>3</sup>/s  
 $V$  volume of the well-mixed reservoir or CSTR, cm<sup>3</sup>  
 $W$  electrode width, cm  
 $x$  axial coordinate, cm  
 $y$  normal coordinate, cm  
 $z_i$  charge number of species  $i$

## Greek Symbols

$\alpha$   $S/L$ , dimensionless  
 $\alpha_{aj}$  anodic transfer coefficient for reaction  $j$   
 $\alpha_{cj}$  cathodic transfer coefficient for reaction  $j$   
 $\Delta t$  time step size, s  
 $\zeta$  dimensionless axial coordinate ( $x/L$ )  
 $\eta$  dimensionless normal coordinate ( $y/S$ )  
 $\theta_i$  dimensionless concentration of species  $i$  ( $C_i/C_{i,\text{ref}}$ )  
 $\theta_{i,\text{feed}}$  dimensionless concentration of species  $i$  entering the PPER  
 $\theta_{i,\text{ave}}$  dimensionless average concentration of species  $i$   
 $\theta_{i,\text{ave}}(t, \zeta = 1)$  dimensionless average concentration of species  $i$  leaving the PPER  
 $\theta_{i,\text{out of reservoir}}$  dimensionless concentration of species  $i$  leaving the reservoir  
 $\theta_{\text{CuCl}_2^{2-},\text{feed,P}}$  value obtained from Pickett's model (9), Eq. [21]  
 $\nu$  kinematic viscosity, cm<sup>2</sup>/s  
 $\rho_0$  solvent density, kg/cm<sup>3</sup>  
 $\tau$  residence time in the reservoir/CSTR, s  
 $\Phi$  solution potential, V

$\Phi_{\text{aa}}$  solution potential at the anode, V  
 $\Phi_{\text{oc}}$  solution potential at the cathode, V

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## Piezoelectric Response to Surface Stress Change of Platinum Electrode

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### ABSTRACT

The piezoelectric detection has been proved sensitive to surface stress change of platinum foil electrodes in sulfate solutions of various pH values and sodium hydroxide solution. Electrocapillary-like curves were successfully obtained from the measured piezoelectric signals as a function of potential. The potential of electrocapillary maximum decreases linearly with pH at the rate of  $-40$  mV/pH. The potential of electrocapillary minimum found in the anodic potential scan was  $0.35$  V more positive than the equilibrium potential of PtO/Pt system. It appears that the electrocapillary maximum is connected with a reconstruction or place exchange step of the oxygenated platinum surface corresponding to PtO monolayer.

The measurement of surface stress of solid electrodes, if possible, provides important information concerning the solid/electrolyte interface such as adsorption, potential of zero charge (pzc), electric double layer, and film formation. The technique for surface stress measurement of solid electrodes, however, encounters difficulties compared with that for liquid metal electrodes. Several methods have been employed in literature which are ribbon-extension (1-3), thin film-deflection (4, 5), contact angle (6, 7), and piezoelectric detection (8-15). The piezo-

electric measurement of surface stress of solid electrodes was first developed by Gokhshtein (8-10) and further improved by Malpas *et al.* (11, 12) who employed a simplified electrode for piezoelectric measurement. This technique is highly sensitive to a small change in surface stress and is capable of detecting the derivative of surface stress with electrode potential.

In this study, the piezoelectric detection of surface stress of platinum foil electrodes in sodium sulfate and hydroxide solutions has been conducted to obtain further information on the interfacial properties of solid electrodes.

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