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http://www.electrochem.org/  
Publisher's Version: [http://dx.doi.org/10.1149/1.2108798](http://dx.doi.org/10.1149/1.2108798)  
DOI: 10.1149/1.2108798

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Parallel Plate Electrochemical Reactor Model: Material Balance Closure and a Simplification

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ABSTRACT

A material balance closure calculation is presented to test the consistency of a previously published model of a parallel plate electrochemical reactor. New expressions are used in this procedure to calculate the average concentration of species \( i \) and the average current density for reaction \( j \) from the predicted concentration and potential distributions. Also, the previously presented model equations are simplified by assuming that the axial concentration gradient for species \( i \) can be approximated by a step change from the known feed concentration to the unknown outlet concentration. This one-step model provides a qualitative evaluation of cell performance and adds insight into understanding of the previous model, while providing substantial savings in computer time. The models are compared using a hypothetical case of the electrowinning of copper from a chloride solution. For a small aspect ratio \( S/L \), the models show that a set of independent variables consists of the cell potential \( (E_{cell}) \), the surface area of an electrode per unit of cell volume \((A/L)\), and the residence time \((L/v_{avg})\) when the feed concentrations \((c_{i,feed})\) are fixed.

Developments

White et al. (1) describe a two-dimensional model of a parallel plate electrochemical reactor with multiple electrode reactions which can be used to predict such quantities as current efficiencies and conversion per pass under various cell conditions. This information is valuable in the design of both bench and production scale parallel plate cells and in the selection of operating conditions to use for optimum performance. The model of White et al. (1) is a "complete" model in the sense that the interaction between closely spaced electrodes is included in the model equations, multiple electrode reactions can occur, and predictions of cell performance such as the conversion per pass are made. Their model is an alternative to the less complete models of Sakellaropolous and Francis (2-4), Parrish and Newman (5), Caban and Chapman (6), and Lee and Selman (7). Sakellaropolous and Francis (2-4) presented a model for a parallel plate cell which has multiple reactions at one electrode but, their model does not include the effect of the cell gap (S). Parrish and Newman (5) presented a model which takes the interaction of closely spaced electrodes into account, but they did not include multiple electrode reactions. Caban and Chapman (6) presented essentially the same model as Parrish and Newman (5) except that they set the cell potential instead of the cell current. Lee and Selman (7) presented a model of the Zn/Br\(_2\) cell, but did not include multiple electrode reactions. This paper presents corrections to the previously presented model equations and boundary conditions are solved using an implicit stepping technique (8) in the axial direction and Newman's BAND algorithm (9, 10) in the radial direction. The BAND algorithm is used to determine \( c \) and \( \Phi \) at a specific value of \( x \), then, a step of size \( \Delta x \) is taken in the axial direction and the set of variables is calculated again using the BAND algorithm. This stepwise procedure is repeated until \( x = L \).

The mathematical definition of what White et al. (1) call bulk average concentration, \( c_{avg}(x) \), is improper if one wishes to determine a conversion per pass of a particular species and thus causes problems in achieving a material balance using the model's predicted concentration profile. The definition used by White et al. (1) for \( c_{avg} \) [see Eq. [32] of Ref. (1)] is incorrect because the velocity profile between the plates is laminar and not plug flow. Thus, it is appropriate to calculate what might best be termed a local average concentration by beginning with a radial average of the molar flux of a species at a particular value of \( x \). This is given by

\[
N_{avg}(x) = \frac{1}{S} \int_0^S N_{i}(x, y) \, dy \tag{1}
\]

where \( N_{i}(x, y) \) is the molar flux in the flow direction and is expressed as

\[
N_{i}(x, y) = -D_i \frac{\partial c_{i}}{\partial x} - \frac{zD_iF}{RT} c_i \frac{\partial \Phi}{\partial x} + \nu_{i}c_i \tag{2}
\]

Since it is assumed that the electrode length \( L \) is much greater than the electrode gap \( S \), the aspect ratio \( \alpha = S/L \) is small and therefore migration and diffusion in the axial (flow) direction are negligible compared to forced convection, as shown in more detail by Nguyen et al. (11). In this case, \( N_{avg} \) may be replaced by \( c_{avg}(x) \) and \( N_{i}(x, y) \) may be replaced by \( \nu_{i}c_i \) in Eq. [1]. Under well-developed laminar flow, the velocity profile is given by

\[
\nu_{i}(y) = \Theta_{avg} \left( \frac{y - y^\prime}{S} \right) \tag{3}
\]

and Eq. [1] can be solved for the local average concentration to give

\[
c_{avg}(x) = \frac{6}{S} \int_0^S \left( \frac{y - y^\prime}{S} \right) c_i(x, y) \, dy \tag{4}
\]

If the dimensionless variables used by White et al. (1) are introduced, Eq. [4] becomes

\[
\Theta_{avg}(\zeta) = \int_0^1 (\eta - \eta^\prime) \Theta(\zeta, \eta) \, d\eta \tag{5}
\]
The integral in Eq. [5] can be evaluated by an appropriate numerical method, such as Simpson's rule, based on the concentrations calculated for each radial step at a fixed axial position.

The consistency of the model can be verified by using the calculated concentration profiles to obtain a material balance closure over the parallel plate reactor for species i. The net rate of consumption by all of the electrochemical reactions occurring on both electrodes for species i in mol/s is

\[
\text{net rate of consumption of species } i = \sum_{j=1}^{n_r} \frac{s_{ij} \Delta n_{j,\text{ave}}}{n_j F} LW \quad \text{by all electrochemical reactions}
\]

where \( s_{ij} \) is the stoichiometric coefficient for species i in electrode reaction j (\( s_{ij} \) is positive if i is an anodic reactant and negative if i is a cathodic reactant), \( LW \) is the area of each electrode, and \( n_r \) is the total number of electrochemical reactions that occur in the cell. The rates of input and output by transport are \( SW N_{f,\text{in}} \) and \( SW N_{f,\text{out}} \), respectively, where \( SW \) is the cross-sectional flow area.

Since the model is for steady-state conditions, no accumulation term is necessary and the final material balance equation is

\[
SW(N_{f,\text{in}} - N_{f,\text{out}}(x = L)) = 0
\]

Again assuming that forced convection is much greater than migration or diffusion in the axial direction, \( N_{f,\text{in}} \) may be simplified so that Eq. [9] becomes

\[
\sum_{j=1}^{n_r} \frac{s_{ij} \Delta n_{j,\text{ave}}}{n_j F} LW = 0
\]

Using the previously given dimensionless variables (Eq. [6]-[8]), Eq. [11] becomes

\[
\frac{\partial c_i}{\partial \xi} = \frac{c_i(x = L, \eta) - c_{i,\text{feed}}}{L}
\]

This approximation of the gradient can be substituted into Eq. [13] of White et al. (1)

\[
\frac{3 D_i}{D_1} \frac{P_e}{(\eta - 1)} \frac{\partial^2 \theta_i}{\partial \eta^2} = \frac{\partial^2 \theta_i}{\partial \xi^2} + \frac{z_i F}{RT} \left[ \frac{\partial^2 \Phi}{\partial \eta^2} + \frac{\partial \theta_i}{\partial \eta} \frac{\partial \Phi}{\partial \eta} \right]
\]

All inlet and boundary conditions, and the electro-neutrality condition as discussed by White et al. (1) are the same for this one-step model. That is, the inlet conditions are

\[
\text{at } \xi = 0: \theta_i = \theta_{i,\text{feed}} \quad \text{and} \quad \sum_{i} z_i c_{i,\text{feed}} \theta_{i,\text{feed}} = 0
\]

and the boundary conditions are

\[
\text{for } \xi > 0
\]
Fig. 2. Schematic of the one-step model

at \( \eta = 0 \) (anode): \[ \sum_j s_i^{\text{inj}} \frac{\Delta x_j}{n_j F} = -N_{i_1} \] \[ 16 \]

at \( \eta = 1 \) (cathode): \[ \sum_j s_i^{\text{outj}} \frac{\Delta x_j}{n_j F} = N_{i_1} \] \[ 17 \]

and

at \( \eta = 0 \) and \( \eta = 1 \): \[ \sum_i z_i c_i \omega_i = 0 \] \[ 18 \]

The governing equations and boundary conditions for the one-step model are solved by the same method as before (1).

Since the one-step model is essentially a one-dimensional model, it is a less accurate solution than the continuous model for systems with a high conversion per pass. However, it is reasonably accurate for low conversions per pass (12, 13) and its development is useful in understanding the continuous model better. Figure 3 shows schematically how the continuous model may be thought of as a series of one-step models in which concentration, potential, and, consequently, the current density of reaction \( j \) are functions of an increment of size \( \Delta x \), the size of one step. Thus, the continuous model consists of a large number of one-step models using the radial concentration profile from the previous one-step model segment as the feed to the next one-step model segment with a step size \( \Delta x \) small enough to give results to a desired accuracy.

The calculation of the average current density of reaction \( j \), \( i_{\text{inj}} \), is a good example of the importance of the conceptualization of the continuous model as a series of one-step models. White et al. (1) give the following formula for \( i_{\text{inj}} \) for the continuous model

\[ i_{\text{inj}} = \frac{1}{L} \int_0^L i_{\text{inj}}(x) \, dx \] \[ 19 \]

The correct value for \( i_{\text{inj}} \) for use in the material balance closure equation (Eq. [10]) could be obtained from Eq. [19] by using Simpson's rule, e.g., if a large number of steps were used to obtain \( i_{\text{inj}}(x) \). However, since the solution method used here treats the concentration and potential distributions and, therefore, \( i_{\text{inj}}(x) \) as constants over the previous axial step, a simple average of the \( i_{\text{inj}}(x) \) values over the length \( L \) of the reactor yields an average current density that is consistent with the solutions obtained for the average exit concentrations from each step. That is, the proper expression to use to calculate the average current density to be used in the material balance closure equation (Eq. [10]) is

\[ i_{\text{inj}} = \frac{1}{L} \sum_{k=1}^{nk} i_{\text{inj}}(k)(\Delta x)_k \] \[ 20 \]

where \( i_{\text{inj}}(k) \) is the current density of reaction \( j \) over the \( k \)th interval. A comparison of the two methods is presented below.

Finally, for both the continuous and one-step models, it is important to identify a set of independent variables which can be used to describe the behavior of the electrochemical reactor. The variable parameters in these models are \( v_{\text{avg}} \), \( S \), \( L \), and \( E_{\text{cell}} \) with the values of \( c_{\text{feed}} \) set equal...
to \( c_{\text{lim}} \). Nguyen et al. (11) showed that \( v_{\text{avg}} \), \( S \), and \( L \) are not all independent variables. They did this by showing that for small values of the aspect ratio \( \alpha = S/L \) these variables can be combined into two dimensionless groups

\[
P_{\text{ea}} = \frac{2Sv_{\text{avg}}}{D_{\text{e}}S}
\]  

and

\[
\xi_j = \frac{s_{\text{i,j,avg}}}{n_{\text{i,C,CuCl}}} D_{\text{i}} F
\]  

with \( i \) and \( j \) specified appropriately (e.g., the limiting reactant in a particular reaction). These two dimensionless groups can be combined to form a different dimensionless group as follows

\[
\beta_j = \frac{\xi_j}{P_{\text{ea}}} = \frac{2Sv_{\text{avg}}}{D_{\text{e}}S}
\]

\[
\beta_j = \frac{s_{\text{i,j,avg}} D_{\text{i}} L}{2n_{\text{i,C,CuCl}} D_{\text{i}} F v_{\text{avg}}}
\]

Only two of these three dimensionless groups \( (P_{\text{ea}}, \xi_j, \text{and } \beta_j \) for \( i \) and \( j \) specified properly) are independent. Consideration of \( \xi_j \) and \( \beta_j \) reveals that \( 1/\beta_j \) could be considered to be a dimensionless surface area of an electrode per unit volume \((1/S)\) and \( \beta_j \) a dimensionless residence time \((L/v_{\text{avg}})\) since all of the other quantities in the expressions for \( \xi_j \) and \( \beta_j \) are considered here to be fixed. Consequently, \( 1/S \) and \( L/v_{\text{avg}} \) can be used as dimensional independent variables, as done here.

### Results and Discussion

The developments presented above have been evaluated by using the same hypothetical case of the electro-winning of copper from a chloride solution used by White et al. (1), which should be consulted for values of the fixed parameters. The reactions considered are

\[
\text{CuCl}_2^- \rightarrow \text{CuCl}^- + 2\text{Cl}^- + e^- \quad \text{(anode, reaction } j = 1) \\
\text{CuCl}^- + 2\text{Cl}^- + e^- \rightarrow \text{CuCl}_2^- \\
\text{CuCl}_2^- + e^- \rightarrow \text{Cu} + 3\text{Cl}^- \quad \text{(cathode, } j = 3) 
\]

Case studies have been used to test the consistency of the models by material balance closure, to compare the one-step and continuous models, and to illustrate the importance of the three independent variables \((1/S, L/v_{\text{avg}}, \text{and } E_{\text{cell}})\).

### Table I. Comparison of one-step and continuous models

<table>
<thead>
<tr>
<th>Input parameters</th>
<th>( E_{\text{cell}} )</th>
<th>( 1/S - 10 \text{ cm}^{-1} )</th>
<th>( L/v_{\text{avg}} - 277.8 \text{ s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>One-step</td>
<td>Continuous (120 steps)</td>
<td>% difference from continuous</td>
</tr>
<tr>
<td>( \Delta x ) (cm)</td>
<td>10.0</td>
<td>0.9833</td>
<td>—</td>
</tr>
<tr>
<td>( \lambda_{1,\text{avg}} )</td>
<td>—</td>
<td>0.9833</td>
<td>16.1</td>
</tr>
<tr>
<td>( \lambda_{2,\text{avg}} )</td>
<td>0.245</td>
<td>0.230</td>
<td>6.5</td>
</tr>
<tr>
<td>( \theta_{\text{avg}}(\xi = 1) )</td>
<td>0.538</td>
<td>0.703</td>
<td>—23.5</td>
</tr>
<tr>
<td>( \Theta_{\text{avg}} )</td>
<td>7.748</td>
<td>9.320</td>
<td>—21.1</td>
</tr>
<tr>
<td>** ( \Theta_{\text{avg}}(\xi = 1) ) **</td>
<td>0.5398</td>
<td>0.7056</td>
<td>—23.5</td>
</tr>
<tr>
<td>** ( \Theta_{\text{avg}} ) **</td>
<td>2.345</td>
<td>2.764</td>
<td>15.0</td>
</tr>
</tbody>
</table>

### Computation time on CDC CYBER 170/852 (CPU s)

\[
21.0 \\
892.0
\]

* See White et al. (1) for the other parameters used in the model.

\( \lambda_{\text{avg}} \) obtained using \( \Theta_{\text{avg}} \) obtained by using Eq. [20].

\( \lambda_{\text{avg}} \) obtained using \( \Theta_{\text{avg}} \) obtained by using Simpson’s rule on Eq. [20].

\( \Theta_{\text{avg}}(\xi = 1) \) obtained by calculating \( \Theta_{\text{avg}}(\xi = 1) \) by Eq. [20].

The consistency of the models is verified by use of the material balance closure relation given by Eq. [10]. The Appendix gives the details of a sample calculation based on \( \text{CuCl}_2^- \) for the continuous model, where each side of Eq. [10] is evaluated separately. In this example, the concentration related terms \((L/v_{\text{avg}})\) give a value of \( 1.2701 \times 10^{-7} \) mol/cm\(^2\)-s, while the current density related term \((E_{\text{cell}})\) gives a value of \( 1.2707 \times 10^{-7} \) mol/cm\(^2\)-s, when \( \lambda_{\text{avg}} \) is calculated by Eq. [20]. An incorrect value of \( 1.2851 \times 10^{-7} \) mol/cm\(^2\)-s is obtained when \( \lambda_{\text{avg}} \) is calculated by using Simpson’s rule applied to Eq. [19].

Table I presents a comparison of various derived quantities of interest obtained from the one-step model with those from the continuous model. The percentage difference between the two methods is high, typically 15-25%, since the conversion per pass is high (Table I shows that approximately 70% of the Cu(I) ions are consumed in a single pass). However, the one-step method requires substantially less computer time, being on the order of 40 times faster than the continuous model (which consists of 120 axial steps). In systems in which the conversion per pass is low (about 1%), the two methods compare to within 1-5% [see Ref. (12) and (13)]. In Table I, \( \lambda_{\text{avg}} \) is a dimensionless average current density defined as

\[
\lambda_{\text{avg}} = \frac{i_{\text{avg}}}{i_{\text{lat}}(\xi = 1)}
\]

where \( i_{\text{lat}} \) is the average limiting current density of reaction [3] assuming a thin boundary layer (1, 14), and \( \Theta_{\text{avg}} \) is the fractional conversion per pass of Cu(I) as defined by White et al. (1). That is

\[
\Theta_{\text{avg}} = \frac{\theta_{\text{avg}}(\xi = 1)}{\theta_{\text{avg}}(\xi = 1)}
\]

where \( \theta_{\text{avg}}(\xi = 1) \) is the average concentration leaving the reactor.

Table II presents a comparison of the calculation of \( \lambda_{\text{avg}} \) obtained by calculating \( i_{\text{avg}} \) by Eq. [20] with that obtained by using Simpson’s rule on Eq. [19]. Note that as the number of axial steps \((nk)\) increases, the method based on Simpson’s rule approaches that obtained by using Eq. [20]. Also, at a fixed value of \( nk \), the two methods become equivalent as the driving force \( E_{\text{cell}} \) decreases, and the current distribution becomes more uniform. The large discrepancy between the two methods, especially at small \( nk \) values, is due to the implicit stepping technique itself as well as the assumption in Simpson’s rule case that \( i_{\text{avg}} \) is continuous. In the implicit stepping technique, the first calculated value of \( i_{\text{avg}} \) at \( x = \Delta x \), not at \( x = 0 \), so that the end point value \( \xi = 0 \) of \( i_{\text{avg}}(\xi) \) required in Simpson’s rule must be obtained by an extrapolation, based on the first three calculated values of \( i_{\text{avg}}(\xi) \) (8, 13). Table II also shows that for 30 or 60 axial steps, the continuous model behaves more as a series of one-step models because the values of \( \lambda_{\text{avg}} \) calculated when using Eq. [20] have not reached their actual steady value due to the lower accuracy of taking fewer steps. For \( nk = 120 \) axial steps,

### Table II. Comparison of calculation methods for average current density

<table>
<thead>
<tr>
<th>( nk )</th>
<th>( E_{\text{cell}} ) (V)</th>
<th>( \lambda_{\text{avg}} )</th>
<th>( \lambda_{\text{avg}} )</th>
<th>( \lambda_{\text{avg}} )</th>
<th>( \lambda_{\text{avg}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.6</td>
<td>0.9083</td>
<td>0.950</td>
<td>0.231</td>
<td>0.229</td>
</tr>
<tr>
<td>60</td>
<td>0.6</td>
<td>0.9031</td>
<td>0.945</td>
<td>0.231</td>
<td>0.229</td>
</tr>
<tr>
<td>120</td>
<td>0.6</td>
<td>0.9031</td>
<td>0.941</td>
<td>0.230</td>
<td>0.230</td>
</tr>
<tr>
<td>300</td>
<td>0.6</td>
<td>0.9031</td>
<td>0.938</td>
<td>0.230</td>
<td>0.230</td>
</tr>
<tr>
<td>120</td>
<td>0.5</td>
<td>0.8177</td>
<td>0.821</td>
<td>0.184</td>
<td>0.183</td>
</tr>
<tr>
<td>300</td>
<td>0.5</td>
<td>0.8177</td>
<td>0.821</td>
<td>0.184</td>
<td>0.183</td>
</tr>
</tbody>
</table>

* Same input parameters as those in Table I except for \( E_{\text{cell}} \) as noted.

** \( \lambda_{\text{avg}} \) obtained when \( i_{\text{avg}} \) is calculated using Eq. [20].

*** \( \lambda_{\text{avg}} \) obtained when \( i_{\text{avg}} \) is calculated using Eq. [19].
steps or greater, the model behaves in a more continuous manner because the value of \( \lambda_{\text{avg}} \) remains relatively unchanged as the number of axial steps is increased. Similar results are obtained for species concentrations and potentials.

Finally, the dependence of the performance of the cell on the independent variables is shown in Fig. 4-9 where

\[
CE_{\text{avg}} = \frac{\tilde{i}_{\text{ave}}}{i_{\text{ave}}}
\]  

and \( i_{\text{ave}} \) is obtained according to Eq. [25] of Ref. (1) (here \( i_{\text{ave}} = i_{\text{ave}} \) since only one reaction occurs at the anode). Figures 4-9 illustrate for both models the influence of varying \( 1/S \) or \( L/\nu_{\text{avg}} \) while holding fixed \( E_{\text{cell}} \) and \( L/\nu_{\text{avg}} \) or \( 1/S \), respectively. Figures 4, 5, and 6 present the effect...
ELECTROCHEMICAL REACTOR MODEL

of varying 1/S on \(i_{\text{avg}}\), CPP, \(CE_{\text{avg}}\) and \(CE_{\text{avg}}\) while holding \(L/v_a\) and \(E_{\text{cell}}\) constant. It is interesting to note, as shown in Fig. 4, that a maximum is predicted in the average current density as function of 1/S. This maximum is probably due to an increasing \(i_{\text{avg}}\) due to a lowering of the mass transfer resistance of the cell as 1/S is increased below the maximum and a decrease in \(i_{\text{avg}}\) for values of 1/S larger than the maximum due to increasing consumption of the reactant. For values of 1/S larger than about 7 cm\(^{-1}\), the current density decreases primarily and the conversion per pass of Cu(I) increases (see Fig. 5). The decrease in \(CE_{\text{avg}}\) shown in Fig. 6 is caused by the lower amount of Cu(I) (as \(\text{CuCl}_2\)) available at the cathode due to the high conversion per pass of Cu(I). In addition, the greater amount of CuCl\(^+\) that is produced at the anode causes greater amounts of current at the cathode to be consumed by the undesirable reaction 2. Figures 7, 8, and 9 illustrate reactor performance at fixed 1/S and \(E_{\text{cell}}\) while varying the residence time \(L/v_a\). Note that as the residence time increases, the total reaction rate (shown as \(i_{\text{avg}}\)) decreases rapidly (Fig. 7). Figure 8 shows that as the residence time increases, Cu(I) reacts more completely, as would be expected, though the continuous model shows the conversion relatively constant after a residence time of about 300s in this example. Finally, Fig. 9 again shows that the current efficiency of reaction 3 \(CE_{\text{avg}}\) decreases because of lower concentrations of Cu(I) (as \(\text{CuCl}_2\)) at the cathode while greater amounts of Cu(II) (as CuCl\(^+\)) diffuse and migrate to the cathode and are consumed by reaction 2 [2].

Figures 4-9 give a good visual comparison of the one-step model to the continuous model, showing the ability of the one-step method to duplicate the general trends of the continuous model while saving substantial computational costs. Since the predicted reactor performance is similar (though it may actually deviate by up to 25% for large conversion per pass), the one-step model can be used successfully to identify the regions of independent parameter values that produce optimal performance much more rapidly than the continuous model. Once these regions are identified, the continuous model can be used to obtain the desired accuracy of the predicted reactor performance.

Conclusions

This paper shows that for a fixed feed concentration, the selection of 1/S, \(L/v_a\), and \(E_{\text{cell}}\) constitute a set of independent parameters which can be used to characterize the performance of a parallel plate electrochemical reactor under laminar flow with a small aspect ratio. The use of these parameters is demonstrated by predicting cell performances by a corrected continuous model and a computationally efficient one-step model.

Acknowledgment

This work was supported in part by the Center for Energy and Minerals Research at Texas A&M University.

Manuscript submitted May 13, 1985; revised manuscript received Dec. 15, 1985.

APPENDIX

Material Balance Closure Example

Reactions

<table>
<thead>
<tr>
<th>Reactions</th>
<th>(\lambda_{\text{avg}})</th>
<th>(s_{\text{CuCl}_2})</th>
<th>(j)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CuCl}_2) + (2\text{Cl}^-) + e(^-) \rightarrow \text{CuCl})</td>
<td>1</td>
<td>0.933 - 0.941</td>
<td>1</td>
</tr>
<tr>
<td>(\text{CuCl}_2) + (2\text{Cl}^-) + e(^-) \rightarrow \text{CuCl}_2)</td>
<td>2</td>
<td>0.230 - 0.230</td>
<td>0.1</td>
</tr>
<tr>
<td>(\text{CuCl}_2) + (\text{Cl}^-) + e(^-) \rightarrow \text{Cu} + \text{Cl}^-)</td>
<td>3</td>
<td>0.703 - 0.711</td>
<td>-1</td>
</tr>
</tbody>
</table>

\(V_0 = 0.6V\)

\(n_k = 120\) steps

\(v_{\text{avg}} = 0.036\) cm/s

\(S = 0.1\) cm

\(L = 10\) cm

\(F = 96,487\) C/mol

\(i_{\text{avg}} = -8.72\times10^{-3}\) A/cm\(^2\)

\(c_{\text{CuCl}_2\text{-feed}} = 0.5\times10^{-3}\) mol/cm\(^3\)

\(c_{\text{CuCl}_2\text{-feed}}(x = L) = 0.1472\times10^{-3}\) mol/cm\(^3\)

\(c_{\text{CuCl}_2\text{-feed}}\) - species i = CuCl\(^2-\)

\(n_k\) - number of electrons passed in reaction j

\(n_k\) - number of steps taken along the electrode length in solution technique

\(P_a\) - anodic reaction order of species i in reaction j, see White et al. (1)

\(P_e\) - Pecket number \((=2Sv_aD_p)\)

\(q_i\) - cathodic reaction order of species i in reaction j, see White et al. (1)

\(R\) - gas law constant, 8.314 J/mol-K

\(S\) - total electrode gap, cm

\(u_S\) - equals surface area of an electrode per unit of cell volume, cm\(^{-1}\)

\(S_0\) - stoichiometric coefficient of species i in reaction j

\(T\) - temperature, K
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 electroorganic 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 the literature. Pickett (9, 12) presented simple approximate models in which 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 conditions 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 electrode gap in the PPER, and the inclusion of a true CSTR in the recycle stream.

Greek

\( \alpha \) aspect ratio, \( S/L \)
\( \beta \) dimensionless residence time
\( \Delta x \) axial step size, cm
\( \eta \) dimensionless axial coordinate (\( x/L \))
\( \theta \) dimensionless concentration of species \( i \) at the electrode surface
\( \theta_{avg} \) dimensionless average concentration of species \( i \)
\( \theta_{feed} \) dimensionless feed concentration of species \( i \)
\( \lambda \) the ratio of average current density for reaction \( j \) to the average limiting current density (\( \theta_{avg}/\theta_{lim,avg} \))
\( \delta \) dimensionless formulation of the electrode gap
\( \Phi \) solution potential, V

\( V \), anode potential, V
\( V_{ave} \) average velocity of the electrode, cm/s
\( V_c \) cathode potential, V
\( v_e \) 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 \( i \)

**Electrochemical Society Active Member.

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