Modeling current density distribution in electrochemical systems

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Abstract

A numerical method was developed for predicting current density distribution in electrochemical systems of several species at steady-state. The fundamental transport equation consisted a partial differential equation (PDE) involving linear terms of diffusion and laminar convection, and nonlinear terms of ionic migration. The boundary conditions (BCs) consisted also PDEs including flux conditions and involving nonlinear terms associated with exponential kinetics of heterogeneous electrode reactions. The method of finite-difference (FD) was used to approximate solution of the global PDE system in two dimensions using a nonuniform rectangular mesh of fine size near electrode edges where boundary layers and steeper gradients were developed. Diffusion and migration terms were discretized by central finite differences, while the convective term was discretized using an upwind differencing scheme in conjunction with introduction of a 'minimal artificial viscosity' to ensure convergence and prevent anomalies in solution at high velocities. The false boundaries technique treated flux BCs. The method was tested by application to a model and an experimental system placed between two equal size parallel-plate electrodes fixed in a channel’s walls under laminar parabolic flow. Numerical results for local cathodic current density were compared to experimental measurements and analytical predictions for limiting conditions. Excellent agreement was demonstrated thus verifying applicability of this FD method to real situations.

Keywords: Current density; Modeling; Electrochemical; Convection; Parallel-plate reactor

1. Introduction

The prediction of current density is an essential step in the rational design and scale-up of electrochemical reactors and in engineering analysis of electrochemical processes. A numerical method for predicting current density distribution in multi-ion electrolytes was developed, assuming steady-state, 2D, dilute solution theory and constant properties. The parallel-plate electrochemical reactor (PPER) geometry was used. The calculation of current density for the PPER has been a frequent subject of study but reported mathematical models exist only for limited cases. For example, the models by Parrish and Newman [1] and by Caban and Chapman [2] were based on the thin diffusion layer approach, that by Pickett [3] on the mass transfer control assumption, and those by White, Bain and Raible [4] and by Nguyen, Walton and White [5] ignore axial diffusion and axial migration and do not account for high velocities. Our previous works [6,7] on pattern etching addresses modeling issues related to the present study, which illustrates a complete numerical treatment of phenomena associated with electrochemical processes.

2. Mathematical formulation

Nomenclature for the dimensionless equations is defined in the list of symbols. The governing equations involve a mass transport PDE for species i and the electroneutrality condition

\[ D_i^* \nabla^2 C_i^* + z_i D_i^* ( \nabla V_i^* \nabla \Phi^* + C_i^* \nabla \Phi^* ) - \text{Pe} F^* ( \nabla C_i^* ) = 0 \]

(1)

\[ \sum_j z_j C_j^* = 0 \]

(2)

After numerical solution of Eqs. (1) and (2) the current density is determined by

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\[ i^* = -F \sum_i z_i D_i^* V^* C_i^* - F \sum_i z_i^* D_i^* V^* \phi^* \]  \hspace{1cm} (3)

The boundary conditions (BCs) are the following. On the fluid inlet boundary
\[ C_i^* = C_i^{\text{ref}} \]  \hspace{1cm} (4)
\[ \frac{\partial \phi^*}{\partial n^*} = 0 \]  \hspace{1cm} (5)

On insulating walls and fluid outlet boundary
\[ \frac{\partial C_i^*}{\partial n^*} = 0 \]  \hspace{1cm} (6)
\[ \frac{\partial \phi^*}{\partial n^*} = 0 \]  \hspace{1cm} (7)

On a cathode (+) or anode (−) boundary the normal flux of reacting ions is a current sum, whereas of non-reacting is zero
\[ -D_i^* \frac{\partial C_i^*}{\partial n^*} - z_i D_i^* C_i^* \frac{\partial \phi^*}{\partial n^*} = (\pm 1) \sum_k s_{ik} \frac{i_k^*}{n_k} \]  \hspace{1cm} (8)
\[ -D_i^* \frac{\partial C_i^*}{\partial n^*} - z_i D_i^* C_i^* \frac{\partial \phi^*}{\partial n^*} = 0 \]  \hspace{1cm} (9)

Eq. (2) completes the set of electrode BCs. The reaction current density is given by
\[ i_k = i_{ik}^{\text{ref}} \prod_i \left( \frac{C_i}{C_i^{\text{ref}}} \right)^{y_i} \times \left( \exp \left( \frac{z_a n_a F}{RT} (V_M - \phi_0 - E_k^{\infty}) \right) - \exp \left( \frac{-z_a n_a F}{RT} (V_M - \phi_0 - E_k^{\infty}) \right) \right) \]  \hspace{1cm} (10)

The laminar, parabolic flow field is described by
\[ u^* = -y^*(v^* - 1), \hspace{1cm} v^* = 0 \]  \hspace{1cm} (11)

The set of Eqs. (1) and (2) with the velocity substituted by Eq. (11) and BCs given by Eqs. (4)–(9) and Eq. (2) form a system of nonlinear, coupled partial differential equations (PDEs) which was solved simultaneously for the concentration and potential fields; then the current density was determined from equation Eq. (3). The electrode BCs associated with Eq. (10) is an example of boundary nonlinearity.

3. Method of solution

The FD method was used to approximate the numerical solution of the PDE global system in 2D. The computational domain was discretized by unequally spaced nodes along both directions resulting in a nonuniform rectangular mesh of fine size near electrodes where boundary layers are developed and steeper gradients are expected, in order to achieve the desired resolution while minimize computational time and memory needs. The FD form for partial derivatives was derived from partial Taylor series expansion. For any continuously differentiable function \( f \), the centered difference analogue of its first and second partial derivatives at node \((i, j)\) are:
\[ \frac{\partial f}{\partial x}_{ij} = \frac{f_{i+1,j} - f_{i-1,j}}{2(h_i + h_{i-1})} \]  \hspace{1cm} (12)
\[ \frac{\partial^2 f}{\partial x^2}_{ij} = \frac{2h_i f_{i+1,j} + 2h_{i-1} f_{i-1,j} - 2(h_i + h_{i-1}) f_{i,j}}{h_i h_{i-1}(h_i + h_{i-1})} \]  \hspace{1cm} (13)

Both the diffusion and migration terms in Eq. (1) were discretized by central FD, the difference analogue of diffusion and the migration terms for ion \( m \) are given by
\[ T_d = D_m \left( \frac{\partial^2 C_m}{\partial x^2}_{ij} + \frac{\partial^2 C_m}{\partial y^2}_{ij} \right) \]  \hspace{1cm} (14)
\[ T_m = z_m D_m C_m^{\text{ref}} \left( \frac{\partial \phi}{\partial x}_{ij} + \frac{\partial \phi}{\partial y}_{ij} \right) + z_m D_m \left( \frac{\partial C_m}{\partial x}_{ij} \frac{\partial \phi}{\partial x}_{ij} + \frac{\partial C_m}{\partial y}_{ij} \frac{\partial \phi}{\partial y}_{ij} \right) \]  \hspace{1cm} (15)

where the first and second order derivatives in Eqs. (14) and (15) are approximated by Eqs. (12) and (13). However, the convective term was discretized using an upwind differencing scheme in conjunction with the introduction of a ‘minimal artificial viscosity’ described in detail by Roache [8], in order to maintain the diagonal dominance of the matrix associated with the governing equations, which is lost when Peclet number is too high compared to the in all other terms. Hence, numerical solution was ensured at high velocities as well. The half nodes \( i-1/2, j, i+1/2, j, i, j-1/2 \) and \( i, j+1/2 \) were introduced as shown in Fig. 1 and the difference expression for the convective term of Eq. (1) was obtained for the interior node \((i, j)\)
\[ T_c = \frac{Pe(h_i - h_{i-1}) u_{i,j} + Pe(k_{j-1} - k_{j-1}) c_{i,j}}{h_i h_{i-1}} C_{i,j} + \frac{Pe h_{i,j} u_E}{h_i(h_i + h_{i-1})} C_{i,j}^{\text{ref}} - \frac{Pe h_{i,j} u_W}{h_{i-1}(h_i + h_{i-1})} C_{i-1,j}^{\text{ref}} + \frac{Pe k_{j-1} v_N}{k_j(k_j + k_{j-1})} C_{i,j+1}^{\text{ref}} - \frac{Pe k_j v_S}{k_{j-1}(k_j + k_{j-1})} C_{i,j-1}^{\text{ref}} \]  \hspace{1cm} (16)

The difference analogue of Eq. (1) was obtained for ion
m at node \((i, j)\), after introduction of the ‘minimal artificial viscosity’

\[
\begin{align*}
(2\mu_t h_{i-1} + 2\mu_w h_i + P e u_z (h_i^2 - h_{i-1}^2)) & + \frac{2\mu_N k_{i-1} + 2\mu_N k_i + P e u_z (k_i^2 - k_{i-1}^2)}{h_i (h_i + h_{i-1})} \, C_{i+1,j}^m + \\
& \left(-2\mu_t h_{i-1} + P e h_{i-1} u_E \right) \frac{C_{i+1,j}^m}{h_i (h_i + h_{i-1})} + \\
& \left(-2\mu_N k_{i-1} + P e k_{i-1} v_N \right) \frac{C_{i,j+1}^m}{k_i (k_i + k_{i-1})} C_{i,j+1}^m + \\
& \left(-2\mu_N k_j - P e k_j v_N \right) \frac{C_{i,j-1}^m}{k_j (k_j + k_{j-1})} C_{i,j-1}^m - T_m = 0
\end{align*}
\]

4. Results and discussion

The method was applied to a model and two experimental systems. Input parameters are summarized in Tables 1 and 2. Table 3 relates experimental Reynolds number and Peclet number used here.

4.1. 1 M CuSO\(_4\) binary electrolyte

The method was implemented into a model system in order to be tested in terms of producing reliable results. The 1 M CuSO\(_4\) binary electrolyte in a PPER with aspect ratio (electrode length:gap) 1:1 under hydrodynamic conditions of a laminar parabolic flow crossing the electrodes was considered. This electrolyte system was selected as a model system because it combined...
transport by diffusion, migration and convection and heterogeneous electrode reactions with exponential kinetics. Concentration contours are displayed in Fig. 2 for Pe/C30 = 1, 10² and 10⁴ and applied voltage of 40 mV versus a saturated mercurous sulfate electrode (MSE). Concentration values are dimensionless; however they can be regarded as having units of mol l⁻¹ since concentration was nondimensionalized by 10⁻³ mol cm⁻³.

It is observed from Fig. 2 that the contours are smooth and even at the high Peclet number of 10⁴ no anomalies are present (neither convergence problems in the solution appeared at such Peclet values). In addition, the development of the concentration profile with increasing Peclet number was as expected. At the low Peclet number of 1, the concentration changes in the electrodes realm were mainly due to diffusion. At Peclet numbers 10² to 10⁴ the convection effect dominated and concentration changes were confined in to a smaller distance from the electrode surfaces, since the thickness of the mass transfer boundary layer was progressively reduced.

Potential contours and current lines are displayed in Fig. 3 for Pe = 10⁶ and V_app = 40 mV and are typical for the flow range 1 ≤ Pe ≤ 10⁶. The equipotential surfaces are represented by solid plain curves and the current lines by solid arrowed curves. Potential values are dimensionless. These two sets of curves being perpendicular to each other.

### Table 2
Input parameters for reactions 1, Cu → Cu²⁺ + 2e⁻; 2, Cu²⁺ + e⁻ → Cu

<table>
<thead>
<tr>
<th>Reaction</th>
<th>E_k/C1 [mV]</th>
<th>h_k/A cm⁻²</th>
<th>h_k/A cm⁻²</th>
<th>x_k</th>
<th>y_k</th>
<th>s₁,k</th>
<th>γ₁,k</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 and 2</td>
<td>– 403</td>
<td>0.56 × 10⁻³</td>
<td>4.07 × 10⁻³</td>
<td>0.5</td>
<td>0.21</td>
<td>–1</td>
<td>0.75</td>
</tr>
</tbody>
</table>

Experimentally determined [14].

### Table 3
Correlation between Re and Pe

<table>
<thead>
<tr>
<th>Re</th>
<th>230</th>
<th>1200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pe</td>
<td>1239447</td>
<td>6466680</td>
</tr>
</tbody>
</table>

Fig. 2. Iso-concentration contours of 1 M CuSO₄ in a PPER with aspect ratio 1:1 under laminar channel flow for Pe = 1, 10² and 10⁴ at V_app = 40 mV (MSE).
cular to each other as shown in Fig. 3, are characteristic of the potential and current distribution between two planar electrodes when electrode kinetics are taken into account. The current distribution between the two electrodes is alternatively displayed in the vector plot of Fig. 4 and is typical for the same flow range. The vector lengths are proportional to the dimensionless current values, and the vector arrows point to the current direction through the domain. It is observed from Fig. 4 that current flows from the anode through the solution to the cathode as expected, while it is nearly zero everywhere else. The ‘streamtraces’ which are actually the paths of ions moving in the current field within the solution correspond to the current lines shown in Fig. 3.

Results obtained for the binary electrolyte in the PPER at the range $1 \leq Pe \leq 10^6$ are normal and demonstrate that the method is a working technique capable of predicting the current density distribution also at high velocities.

4.2. 0.002 M CuSO$_4$+0.1 M H$_2$SO$_4$ electrolyte

The method was also applied to the experimental tertiary acidic copper sulfate electrolyte in a PPER with copper electrodes and aspect ratio 35:1 under laminar parabolic flow, and tested by comparison with experimental measurements carried out by Gerth [14] and with the Leveque analytical solution for limiting current.

Fig. 3. Iso-potential dimensionless contours and current lines of 1 M CuSO$_4$ in a PPER with aspect ratio 1:1 under laminar channel flow for $Pe = 10^6$ at $V_{app} = 40$ mV (MSE).

Fig. 4. Distribution of dimensionless current density for 1 M CuSO$_4$ in a PPER with aspect ratio 1:1 under laminar channel flow typical for the range $1 \leq Pe \leq 10^6$ at $V_{app} = 40$ mV (MSE).

Fig. 5. Comparison of local cathodic current density between FD method (solid curve), Leveque analytical solution (dashed curve) and experimental data (circles) at $Re = 1200$, $V_{app} = -100$ mV (MSE) for 0.002 M CuSO$_4$+0.1 M H$_2$SO$_4$. 
conditions described in the book by Newman [15]. This system combined transport by diffusion, migration, convection, electrode reactions with nonlinear kinetics, and multiple ions. The low dissociation of the acidic bath was not included into the model since the diffusivities of HSO₄⁻ and SO₄²⁻ ions in dilute media are almost identical and the solution was considered electrochemically neutral. In Fig. 5 the cathodic current density is plotted along the cathode length. Fig. 5 illustrates the comparison of local cathodic current density predicted by the FD method (solid curve) with experimental measurements (circles), and Leveque analytical solution (dashed curve) for \( Re = 1200 \) and \( V_{\text{app}} = -100 \text{ mV (MSE)} \) corresponding to limiting current conditions. It may be seen in Fig. 5 that both predicted and measured current density sharply decreased from its upstream infinite value due to a steep concentration gradient developed by depletion of Cu²⁺ on the cathode. Agreement between FD and Leveque predictions is excellent as shown in Fig. 5 for \( Re = 1200 \); in addition agreement with experimental measurements is excellent. A similar behaviour is shown in Fig. 6 which illustrates the comparison of local cathodic current density predicted by the FD method (solid lines) with experimental measurements at applied voltage of \(-200\) mV (diamonds), corresponding also to limiting current conditions, and the Leveque analytical solution (dashed line), for \( Re = 230 \). The limitations of the Leveque analytical solution at lower velocities where other transport mechanisms besides mass transport would be important are apparent in Fig. 6. It should be noted that the Leveque analytical solution includes several simplifications of the general equations, does not account for migration, and is valid at limiting current conditions where mass transport controls the deposition process. Besides, the very good agreement between the numerical predictions and the experimental measurements supports all assumptions included in the model.

The present method can address any number and type of electrochemical reactions at the electrodes, including gas evolution, without any further modification, on the condition that the reaction kinetics are available. Then the related partial current density can be computed. Interesting results occur however when part of the gas is re-dissolved into the electrolytic solution and may react with other reaction products resulting in bath regeneration. Modeling of a reaction plane which is formed in an unknown position within the diffusion layer due to an instantaneous reaction between dissolved gas and reaction products has been reported by the author before [16].

5. Conclusions

A numerical method based on finite-differences was developed for modeling the current density distribution in electrochemical systems. The method provided a unified treatment of multi-ion electrolytes behaviour in 2D rectangular geometries with respect to diffusion, migration, and laminar convection including high velocities and electrochemical reactions of exponential kinetics. All input parameters were experimentally determined; no adjustable parameters were used. The FD method was tested by application to model and experimental systems and comparison with the Leveque analytical solution and experimental measurements. Excellent agreement was demonstrated, thus lending credence to validity of involved assumptions and verifying applicability of the method as a solid numerical approach which treats the exact general form of transport equations with no simplifications and is also effective at high velocities, to real situations, at least for simple geometries (PPER). In the future, the method may be used to predict the current density distribution in other electrochemical systems or geometries, and further in the design and scale-up of electrochemical reactors as well as chemical reactors described by similar sets of equations excluding migration. Furthermore, the method developed here may undoubtedly serve as the basis on which powerful industrial software could be built.

Acknowledgements

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Appendix A: List of symbols

\[ C \] characteristic concentration, \( 10^{-3} \) (mol cm\(^{-3}\))

\[ C_i^* \] dimensionless concentration of species \( i \), \( C_i^* = C_i/C \)

\[ C_{i0} \] surface concentration of species \( i \) (mol cm\(^{-3}\))

\[ C_{i,ref} \] reference concentration of species \( i \) (mol cm\(^{-3}\))

\[ C_i^\infty \] dimensionless bulk concentration of species \( i \), \( C_i^\infty = C_i/C \)

\[ D \] characteristic diffusion coefficient (cm\(^2\) s\(^{-1}\))

\[ D_i^* \] dimensionless diffusion coefficient of species \( i \), \( D_i^* = D_i/D \)

\[ E_{E}^c \] equilibrium open-circuit potential of reaction \( k \) (mV)

\[ F \] Faraday constant, 96489.9 C equiv\(^{-1}\)

\[ h \] channel height, 1 cm

\[ h_i, k_j \] steps in \( x \) and \( y \)-direction at node \((i, j)\) respectively

\[ i_k \] dimensionless current density of reaction \( k \), \( i_k^* = i_kh/FDC \)

\[ i_{k0} \] exchange current density of reaction \( k \) at reference concentrations (A cm\(^{-2}\))

\[ n_k^* \] number of electrons transferred in reaction \( k \)

\[ R \] universal gas constant, 8.314 J (mol K\(^{-1}\))

\[ Re \] Reynolds number, \( Re = 4\langle u \rangle w h / 2 \nu (w + h) \)

\[ Pe \] Peclet number, \( Pe = 6\langle u \rangle h / D = 3ScRe \nu (w + h) \)

\[ s_{ik} \] stoichiometric coefficient of species \( i \) in reaction \( k \)

\[ Sc \] Schmidt number, \( Sc = \nu / D \)

\[ \langle u \rangle \] average channel velocity (cm s\(^{-1}\))

\[ u_E \] east horizontal velocity, \( u_E = u_{i,j+1/2,j} = (u_{i,j} + u_{i+1,j})/2 \)

\[ u_W \] west horizontal velocity, \( u_W = u_{i,j-1/2,j} = (u_{i,j} + u_{i-1,j})/2 \)

\[ v_N \] north vertical velocity, \( v_N = v_{i,j+1/2} = (v_{i,j} + v_{i,j+1})/2 \)

\[ v_S \] south vertical velocity, \( v_S = v_{i,j-1/2} = (v_{i,j} + v_{i,j-1})/2 \)

\[ u^* \] dimensionless horizontal velocity, \( u^* = u/6\langle u \rangle \)

\[ V^* \] dimensionless horizontal velocity, \( V^* = V/6\langle u \rangle \)

\[ V_M \] electrode potential (mV)

\[ V_{app} \] applied cell voltage (mV)

\[ x^*, y^* \] dimensionless horizontal and vertical direction, \( x^* = x/h, y^* = y/h \)

\[ z_i \] charge number of species \( i \)

Greek characters

\[ \alpha_{ak} \] anodic transfer coefficient of reaction \( k \)

\[ \alpha_{ck} \] cathodic transfer coefficient of reaction \( k \)

\[ \gamma_{ik} \] constant order of reaction \( k \)

\[ \mu_E \] east artificial viscosity, \( \mu_E = \max(D^m, Peh_{i-1}|u_{Ei}|/2) \)

\[ \mu_W \] west artificial viscosity, \( \mu_W = \max(D^m, Peh_{i}|u_{Wi}|/2) \)

\[ \mu_N \] north artificial viscosity, \( \mu_N = \max(D^m, Pek_{j-1}|v_{Ni}|/2) \)

\[ \mu_S \] south artificial viscosity, \( \mu_S = \max(D^m, Pek_{j}|v_{Si}|/2) \)

\[ \phi^* \] dimensionless viscosity, \( \phi^* = F\phi/RT \)

\[ \phi_0 \] potential in solution adjacent to electrode surface (V)

References