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Electrowinning of Non-Noble Metals with Simultaneous Hydrogen Evolution at Flow-Through Porous Electrodes

I. Theoretical

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ABSTRACT

A mathematical model is developed to simulate the electrowinning of non-noble metals (e.g., Zn, Cr) within flow-through porous electrodes under the conditions of simultaneous evolution of hydrogen gas bubbles. The results of the model are presented as a function of several dimensionless groups representing kinetics, mass transfer, ohmic resistance, and gas bubbles. These coupled, nonlinear effects are investigated by examining the distributions of the metal reduction and hydrogen evolution currents, coulombic efficiency of the metal electrowinning reaction, and gas void fractions under a series of limiting conditions. The gas bubbles accentuate the nonuniform distribution of the potential and the currents of both reactions by increasing the effective resistance of the gas-electrolyte dispersion filling the pore space. This results in a decrease in the limiting current of the metal deposition reaction and an increase in the underutilization of the internal surface area of the porous electrode and accelerates preferential localized plugging of the pores. The model is able to predict the current and potential distributions for the simultaneous deposition of metals from a mixture of their cations (e.g., Cu, Zn or Cr) with simultaneous hydrogen evolution within the pores of the electrode.

The objective of this paper is to present a mathematical model to simulate the electrowinning of a non-noble metal, e.g., Zn or Cr, with simultaneous hydrogen evolution within a flow-through porous electrode. The model treats the effects of the simultaneously generated hydrogen gas bubbles on the distributions of potential, hydrogen evolution, and metal electrowinning reactions, gas void fraction, and coulombic efficiency within the electrode and on its polarization behavior. The equations and analyses presented in this paper enable us to obtain quantitative answers for a given set of structural, transport, and/or kinetic parameters.

Introduction

Flow-through porous electrodes are characterized by both high reaction rates per unit volume and high mass-transfer rates. The theory behind the operation of porous electrodes has been developed to sophisticated levels; several reviews have been published on the theory and applications of these systems.1,2 Flow-through porous electrodes have been used in charging and discharging of redox batteries for load leveling applications,3,4 electrocatalysis,5 water electrolysis,6 destruction and removal of cyanide wastes from electroplating baths7 and recovery of heavy metals from waste streams.8,9 In this latter application, they have been particularly effective in electrowinning of relatively noble metals (e.g., Cu) where no gas bubbles are generated within the electrode.10 The electrowinning of non-noble metals (e.g., Zn or Cr) using porous electrodes requires different design and operating considerations since the inevitable generation of hydrogen gas bubbles within the pores can eventually render the electrode inoperable. The evolving hydrogen gas bubbles accumulate within the pores leading to a significant decrease in the pore electrolyte conductivity.11

Ateya and El-Anadouli12,13 recently modeled the effects of the evolution of hydrogen gas bubbles within the pores on the current and potential distributions within flow-through porous electrodes and on their overall polarization behavior for the case of a single-electrode reaction (i.e., hydrogen evolution reaction). They present here an extension of this model to treat the case of multiple electrochemical reactions (i.e., metal reduction and hydrogen evolution reactions). Alkire and Gould14,15 have earlier treated multiple reactions at flow-through porous electrodes. They predicted the current and potential distributions for the simultaneous deposition of metals from a mixture of their ions, the deposition of a metal in the presence of a redox reaction, and for a multiple step electro-organic synthesis. They assumed that the metal deposition reaction proceeds independently from the other reaction, and that no hydrogen evolution takes place. Experimental results on the electrowinning of zinc from alkaline zincates at a flow-through porous electrode have recently been reported.16 Separating the effects of the hydrogen reaction from the kinetic and mass-transfer limitations of the zincate reduction reaction was not possible. While the effects of evolving gas bubbles on the polarization and current distributions and on the mechanism of mass transfer are well documented on planar electrodes,17,18 they have not been quantified in porous electrodes.

The objective of this paper is to present a mathematical model to simulate the electrowinning of a non-noble metal, e.g., Zn or Cr, with simultaneous hydrogen evolution within a flow-through porous electrode. The model treats the effects of the simultaneously generated hydrogen gas bubbles on the distributions of potential, hydrogen evolution, and metal electrowinning reactions, gas void fraction, and coulombic efficiency within the electrode and on its polarization behavior. The equations and analyses presented in this paper enable us to obtain quantitative answers for a given set of structural, transport, and/or kinetic parame-

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The conservation of charge along with assumptions 4 and 5 relates the reaction current to the metal solution current (see Appendix A)

\[
di_s(x) = -j_H(x) = -\frac{\pi_{s,m} i_{M,L}}{i_{H_2}} \exp \left[ \alpha \eta_{H_2}(x)/b \right]
\]

where \(j_H(x)\) and \(j_M(x)\) refer to the metal solution and reaction currents, respectively, and the rest of the variables are defined in the List of Symbols. The local limiting current density of the metal deposition reaction, \(i_{H_2}\), is based on the internal (true) area of the pore space and is related to the local mass-transfer coefficient and the bulk concentration by

\[
i_{H_2} = \frac{F}{r_m} C_m
\]

Expressions for the local mass-transfer coefficient, \(k_m\), can be obtained from empirical correlations.\(^{28,29}\)

For the hydrogen evolution reaction, the relationship between the hydrogen solution current, \(i_{H_2}(x)\), and the reaction rate, \(j_{H_2}(x)\), is given by

\[
di_{H_2}(x) = -j_{H_2}(x) = -\frac{\pi_{H_2,m} i_{M,L}}{i_{H_2}} \exp \left[ -\alpha \eta_{H_2}(x)/b \right]
\]

Note that the solution current densities, \(i_{H_2}(x)\) and \(i_{M,L}(x)\), are calculated on the basis of the geometrical cross-sectional area of the packed bed electrode. The flux overpotential is taken to be negative and the solution current positive for a cathodic reaction. The overpotentials operating on the individual reactions are related through the difference between their equilibrium potentials, i.e.

\[
\eta_{H_2} = \eta_{H_2} + \Delta E
\]

where \(\Delta E = E_{H_2} - E_{H_2}^\text{eq}\). The total solution current is the algebraic sum of the two individual currents, i.e.

\[
i(x) = i_{H_2}(x) + i_M(x)
\]

Assumption 1, in conjunction with Ohm's law applied to the electrolyte, governs the variation in overpotential as the solution current travels through the gas–electrolyte dispersion filling the pore space. Thus

\[
i(x) = \kappa(x) \frac{d\eta(x)}{dx}
\]

The conductivity of the gas-electrolyte dispersion within the pores, \(\kappa(x)\), is a complex function involving the nature and concentration of the electrolyte, the porosity of the bed, and the void fraction of the gas filling the pore electrolyte, \(\varepsilon\). The gas void fraction varies with distance within the electrode following the variation of \(i_{H_2}(x)\) which generates the gas bubbles. There are various correlations for the conductivity of such multiphase media.\(^{20}\) For the purpose of the present work, we use the Bruggeman's equation as an expression for the conductivity of the gas-electrolyte dispersion which fills the pore space, i.e.

\[
\kappa(x) = \kappa' \left[ \left( 1 - \varepsilon(x) \right)^{1/3} \right]
\]

where \(\kappa'\) is the bulk electrolyte conductivity. The gas void fraction \(\varepsilon(x)\) is related to the hydrogen current by\(^{31}\)

\[
\varepsilon(x) = \frac{\theta_{H_2}(x)}{\sigma(x)} + \frac{\theta_{H_2}(x)}{\sigma(x)}
\]

where \(\sigma\) is a factor which converts the hydrogen current to the volume of gas generated. Assuming ideal gas behavior, \(\sigma\) is given by\(^{31}\)

\[
\sigma = \frac{RT}{2FP}
\]

where \(P\) equals 0.127 cm\(^3\)/C for the hydrogen evolution reaction at standard pressure and temperature.
Table I. The dimensionless groups and parameters.

<table>
<thead>
<tr>
<th>Group</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimensionless total exchange current</td>
<td>$i_{tot} = \frac{i_{tot} SL}{i_{cell}}$</td>
</tr>
<tr>
<td>Ratio of kinetic resistances</td>
<td>$I_{rel} = \frac{i_{rel}}{i_{cell}} \exp (\alpha \Delta \bar{E})$</td>
</tr>
<tr>
<td>Dimensionless limiting current</td>
<td>$i_{lim} = \frac{i_{lim}}{i_{cell}}$</td>
</tr>
<tr>
<td>Dimensionless conductivity group</td>
<td>$K = \kappa \bar{b} / i_{cell}$</td>
</tr>
<tr>
<td>Dimensionless bubble group</td>
<td>$\Gamma = 2 P \bar{F} / i_{cell} RT$</td>
</tr>
<tr>
<td>Porosity</td>
<td>$\delta$</td>
</tr>
<tr>
<td>Charge-transfer coefficient for the</td>
<td>$\beta$</td>
</tr>
<tr>
<td>hydrogen reaction</td>
<td></td>
</tr>
<tr>
<td>Charge-transfer coefficient for the metal</td>
<td></td>
</tr>
<tr>
<td>reaction</td>
<td></td>
</tr>
</tbody>
</table>

We now have six equations (Eqs. 3, 5, 7–10) describing the distributions of six variables, i.e., $i_{cell}$, $i_{tot}$, $i_{rel}$, $i_{lim}$, $i_{tot}$, and $i_{cell}$. In order to minimize the number of the variables and to obtain results of general applicability, the variables in the governing equations are put in dimensionless forms. The currents are normalized with respect to the cell current, $i_{cell}$, the polarization is presented in multiples of $b$ ($b = RT/F$), the distance is normalized with respect to the bed thickness, $L$, and the pore electrolyte conductivity is normalized with respect to the conductivity of the bulk electrolyte, $\kappa^*$. Thus

$$
\frac{d\bar{i}(y)}{dy} = -\bar{j}_0(y) = -\bar{i}_{lim}(1 - \exp [2\eta_{cell}(y)]) \left(\exp [\beta \eta(y)] + \frac{\bar{i}_{lim}}{I_c}\right)$$

and

$$
\frac{d\bar{j}_0(y)}{dy} = -\bar{j}_0(y) = -\bar{i}_{cell} \exp [-\alpha \eta_{cell}(y)]$$

where $y = x/L$, is the dimensionless distance and the variables with overbars denote normalized variables, i.e., $\bar{i}(y) = i(x)/i_{cell}$, $\eta(y) = \eta(x)/b$, and $\kappa(y) = \kappa(x)/\kappa^*$. The cell current is an important operating parameter, hence it furnishes a more useful basis for normalization. Five dimensionless groups result from this normalization. Table I lists them, along with the porosity of the bed and the charge-transfer coefficients of the reactions in question.

The boundary conditions are

$$y = 0 \quad i = 1$$
$$y = 1 \quad i = i_{cell} = 0 \quad d\bar{i}_{cell}/dy = 0 \quad \kappa = \theta^{1/3} \quad \text{and} \quad \delta = 0$$

In this model, the six variables ($i_{cell}$, $i_{lim}$, $i_{tot}$, $i_{rel}$, $\kappa$, and $\delta$) and the six Eqs. 12–17 were solved using a finite difference algorithm developed by Newman.3 Once the distributions of $i_{cell}$, $i_{lim}$, $i_{tot}$, $\kappa$, and $\delta$ are determined, the local coulombic efficiency, $\xi(y)$, can be calculated from

$$\xi(y) = \frac{\bar{j}_0(y)}{\bar{j}_0(y) + \bar{j}_0(y)}$$

i.e., it is the ratio between the local dimensionless metal reaction current at a particular location to the total dimensionless reaction current at the same location.

The local coulombic efficiency for the metal deposition reaction, $\xi_{total}$, can be obtained from the normalized metal solution current at $y = 0$ (by virtue of their being equal), or by integrating the metal reaction rate over the thickness of the electrode, i.e.,

$$\xi_{total} = \frac{i_{cell}}{i_{cell}} = \int_{0}^{1} \bar{j}_0(y) \cdot dy$$

where $i_{cell}$ is the dimensionless metal solution current at the front of the electrode.

Significance of the dimensionless groups.—1. The dimensionless exchange current of the metal electrowinning reaction, $I_{rel} = i_{cell} SL/i_{cell}$, is the ratio between the effective exchange current density of the bed for the metal deposition reaction, $i_{cell} SL$, and the cell current, $i_{cell}$. Smaller values of $I_{rel}$ correspond to significant charge-transfer (activation) control on the rate of electrowinning.

2. The dimensionless limiting current of the metal electrowinning reaction, $I_{lim} = i_{cell} SL/i_{cell}$, is the ratio between the effective limiting current supported by the total internal surface area of the bed, $i_{cell} SL$, and the cell current. Smaller values of $I_{lim}$ correspond to significant mass-transfer control on the electrowinning reaction.

3. The kinetic ratio, $I_{rel}/I_{lim} = i_{cell} \exp (\alpha \Delta \bar{E})/i_{cell}$, is the ratio of the exchange current density of the metal deposition reaction (at its equilibrium potential) and the rate of hydrogen evolution at the cell current, $i_{cell} SL/i_{cell}$. It is the more significant group in determining the coulombic efficiencies. Larger values of this ratio favor high coulombic efficiencies.

4. The dimensionless bubble group, $\Gamma = Q/\delta i_{cell}$, it measures the ratio of the electrolyte flow rate to the cell current. It combines the electrolyte flow rate, $Q$, temperature, $T$, the prevailing pressure, $P$ (through $\sigma$, see Eq. 11) and the cell current, $i_{cell}$. Small values of $\Gamma$ indicate more predominant bubble effects. This is obtained under conditions of high cell currents and/or low electrolyte flow rates.

5. The dimensionless conductivity group, $K = \kappa b / (i_{cell} SL)$, is a very significant group with regard to the ohmic potential drop within the pore electrolyte. The reciprocal of this quantity (i.e., $L_{cell} \kappa /b i_{cell}$) has the same form as the index of ohmic effect. It is equal to the maximum ohmic potential drop within the bed (in multiples of $b$). It can be obtained only if the cell current flows through the entire thickness of the bed. Large values of $K$ indicate lower extents of ohmic control. This group also bears strong resemblance to the Wagner's parameterization which determines the potential and current distributions in electrochemical systems.

Results and Discussion

The above system of equations combines the effects of the charge-transfer kinetics, mass transfer, ohmic resistance, and gas bubbles on the distributions of the polarization, the hydrogen evolution and metal electrowinning currents, gas void faction and pore electrolyte conductivity within the porous electrode, and on its overall polarization behavior. The system is quite nonlinear and the variables and parameters are highly interlinked. Hence the equations are solved and the discussion presented for several cases of varying degrees of complexity so that we can better expose the physical significance of the model parameters and its predictions. Table II shows the four different cases with their equations, controlling groups, and the limits of each case.

Case I. Negligible ohmic resistance.—Under the conditions of negligible ohmic resistance, the dimensionless conductivity group is large (i.e., $K \rightarrow \infty$), hence $d\eta_{cell}/dy = 0$, i.e., $\eta_{cell}$ is constant within the bed. This results in completely uniform current distributions and equal local and total coulombic efficiencies. Equations 12, 13, and 15 are sufficient to describe the system. Substituting Eq. 12 and 13 into Eq. 18 gives

$$\xi_{total} = \xi(y) = \frac{i_{cell}}{i_{cell}} \left[1 - \exp [-\alpha \eta_{cell}(y)]\right] \exp \left((-\alpha \eta_{cell}(y)) \right]$$

Equation 20 shows that the coulombic efficiency is a function of the dimensionless polarization, $\eta_{cell}$, $\alpha$, and $\beta$, the kinetic ratio, $I_{rel}/I_{lim}$, and the ratio of kinetics to mass-transfer resistances of the metal reduction reaction, $I_{rel}/I_{lim}$. Figure 2 shows the effect of $\eta_{cell}$ on the $\xi_{total}$ for four different combinations of values of $\alpha$, $\beta$, and $\delta$. When $\eta_{cell}$ is small (i.e., $\eta_{cell} < 1$), the four cases show only a slight difference in behavior. This low polarization is of
only limited practical interest as it supports low reaction rates. Furthermore, the metal reaction is in the near reversible region where metal dissolution seriously affects the coulombic efficiency as shown in Fig. 2. Of more interest is the behavior at higher polarizations (i.e., $\eta_{\text{H}} > -1$), as discussed below.

In case a, Fig. 2, at high polarization, both the metal deposition and hydrogen evolution reactions are equally sensitive to the polarization as $\alpha = \beta$. Hence, Eq. 23 yields

$$\xi_{\text{total}} = \frac{(I_{0,M}/I_{0,H})}{(I_{0,M}/I_{0,H}) + 1}$$

i.e., the coulombic efficiency is independent of the polarization. It depends only on the kinetic ratio ($I_{0,M}/I_{0,H}$). In Fig. 2, $(I_{0,M}/I_{0,H})$ was taken to be equal to 0.84 and hence the limiting value of the coulombic efficiency equals 0.46 at high polarization. Equation 21 shows that as the kinetic ratio increases (i.e., $I_{0,M}/I_{0,H} >> 1$) the limiting value of the coulombic efficiency approaches one. The only design option (when $\alpha = \beta$) is to choose an electrode material which has a sufficiently low exchange current density for the hydrogen evolution reaction so that the rate of this reaction is negligible relative to that of metal deposition. Operating the cell at high currents increases the metal removal rate but it provides no advantage from the standpoint of coulombic efficiency.

In case b, when $\alpha = 2\beta = 0.5$, i.e., the hydrogen reaction is twice as sensitive to the polarization as the metal reduction reaction, the coulombic efficiency is given at high polarization by

$$\xi_{\text{total}} = \frac{(I_{0,M}/I_{0,H})}{(I_{0,M}/I_{0,H}) + \exp[-0.25\eta_{\text{H}}]}$$

Thus, as the polarization becomes more negative (more cathodic), the coulombic efficiency decreases. Therefore, in order to maximize the coulombic efficiency, it is necessary to operate the cell at low overpotentials. However, low overpotentials result in low currents and hence, low removal rates.

Case c, Fig. 2, is the most favorable as the metal reaction is twice as sensitive to the polarization as the hydrogen reaction, since $\alpha = \beta/2 = 0.5$. The coulombic efficiency is given at high polarization by

$$\xi_{\text{total}} = \frac{(I_{0,M}/I_{0,H})}{(I_{0,M}/I_{0,H}) + \exp[0.5\eta_{\text{H}}]}$$

As the polarization becomes more negative, $\xi_{\text{total}}$ increases. This is the most desirable case, since high removal rates and high efficiencies can be achieved simultaneously.

Case d, Fig. 2, is similar to case c except that in case d, the metal reaction is limited by mass transfer at high cathodic polarization, i.e., $\eta_{\text{H}} > -2$. Hence, the coulombic efficiency decreases progressively with increasing cathodic polarizations. As the cathodic polarization increases, the rate of hydrogen evolution increases while that of metal deposition remains constant, at the limiting current, due to mass-transfer limitations. Of the four cases shown in Fig. 2, cases c and d are discussed in further detail here because of their practical significance.

Figure 3 shows the effects of kinetic ratio, $I_{0,M}/I_{0,H}$, on $\xi_{\text{total}}$ at different values of $I_{L}$. As $I_{0,M}/I_{0,H}$ increases, the coulombic efficiency increases until it reaches a limiting value, the magnitude of which is dependent on $I_{L}$. As $I_{0,M}/I_{0,H}$ increases the metal reaction is favored over the hydrogen reaction. However, since the metal reaction is mass-transfer limited, $\xi_{\text{total}}$ reaches a limiting value which corresponds to the mass-transfer limiting current. This limiting value equals the dimensionless limiting current. For example at $I_{L} = 0.5$, the limiting value of the coulombic efficiency equals 0.5. When mass transfer is not limiting (i.e., the limiting current is much greater than the cell current; $I_{L} >> 1$) $\xi_{\text{total}}$ is determined by the kinetic ratio. As the latter increases, the former increases approaching the limiting value of 1 at a kinetic ratio greater than 10.

Case II. Appreciable ohmic resistance; negligible gas bubbles, negligible mass-transfer resistance.—Figures 4 and 5 illustrate the effects of the dimensionless conductivity group, $K$, on the distributions of $\eta_{\text{H}}(y)$ and $I_{D}(y)$, respectively. At very high electrolyte conductivity (e.g., $K > 30$), the distributions of polarization and current are uniform throughout the bed and the behavior of the cell reduces to that given in the previous section. Values of $K > 30$, reveal
a degree of nonuniformity of the distribution of \( \tau_{k} \) and \( j_{k} \). As the conductivity decreases, the polarization and both currents become increasingly nonuniform. At \( K = 5 \times 10^{-2} \), the reactions are localized in a rather thin region near the exit face of the electrode.

Figure 6 shows the effect of the dimensionless conductivity group, \( K \), on \( \xi_{\text{total}} \) at different values of the kinetic ratio. As \( K \) increases, \( \xi_{\text{total}} \) decreases in a nonlinear fashion and approaches a low limiting value at sufficiently high \( K \). This limiting value equals the dimensionless metal reaction current. For example, at \( I_{M}/I_{H} = 0.84 \), \( \xi_{\text{total}} \) approaches 0.69 which is the same value for \( j_{M} \) in Fig. 5 for \( K = 30 \). The limiting values of the total coulombic efficiency (at large values of \( K \)) can be obtained from Fig. 3 for the case at \( I_{L} = 10 \), where mass-transfer limitations are negligible. As \( K \)}
The effects of combined ohmic and mass-transfer resistances can be further explained by studying the local coulombic efficiency. Figure 8 shows the distribution of the local coulombic efficiency at different values of $I_L$. For the case of negligible mass-transfer resistance (i.e., $I_L = 10$), the nonuniformity of the local coulombic efficiency is attributed to ohmic control. At lower values of $I_L$, the metal reaction is under combined mass-transfer and ohmic control. The figure shows low coulombic efficiency at the front of the electrode due to mass-transfer restrictions on the metal reduction reaction in the presence of high hydrogen evolution current due to the high polarization. At relatively small penetrations within the electrode (e.g., $y = 0.2$), the cathodic polarization decreases. However, it is still large enough to support the limiting current of the metal reaction. The hydrogen evolution reaction decreases as a result of the decreases in the cathodic polarization. Consequently, we observe a maximum in the local coulombic efficiency.

**Case IV. Appreciable ohmic resistance: formation of gas bubble with appreciable mass-transfer resistance.**—As hydrogen gas bubbles are generated, the cross-sectional area available for ionic flow decreases, and the effective conductivity of the pore electrolyte decreases (see Eq. 9, 17). As the electrolyte enters the porous electrode at $x = L$, it undergoes a reaction at a low rate, by virtue of the low polarization at $x = L$. This current has two effects: (i) it generates gas bubbles (at a correspondingly low rate) which disperse in the pore electrolyte and increase its resistivity, and (ii) it generates an ohmic potential drop in the pore electrolyte, as is flows up toward the polarized face of the electrode. This results in an increase in polarization at larger distances from $x = L$. As the polarization increases, more current is generated, more bubbles are dispersed in the pore electrolyte producing further increase in its resistivity and a greater potential gradient, and so on.

To quantify the effects of gas bubbles, Eqs. 12–17 were solved simultaneously, taking account of the dimensionless bubble group, $\Gamma$, which expresses the extent of bubble formation. Figure 9 shows the effect of the dimensionless bubble group, $\Gamma$, on the distribution of gas void fraction. The
The figure reveals that: (i) as the magnitude of $\Gamma$ decreases, the gas void fraction increases, (ii) a significant amount of hydrogen gas can accumulate at the front face of the electrode at values of $\Gamma < 0.5$, and (iii) at sufficiently low $\Gamma$ values (e.g., $\Gamma < 5 \times 10^{-2}$), virtually the entire thickness of the bed is plugged with gas bubbles. This corresponds to low electrolyte flow rates or high cell currents. For example, when the flow rate is 0.012 cm s$^{-1}$ and $i_{\text{cell}} = 0.2$ A cm$^{-2}$, $\Gamma$ equals 0.5 at standard temperature and pressure. Decreasing the flow rate by two orders-of-magnitude, or increasing the cell current by the same order, decreases $\Gamma$ to $5 \times 10^{-2}$. This causes a large increase in the gas void fraction through most of the thickness of the electrode.

The effect of $\Gamma$ on the distribution of the pore electrolyte conductivity, $\kappa(y)$, is shown in Fig. 10. As $\Gamma$ decreases, $\kappa(y)$
Our model is also useful to analyze how the electrolyte conductivity between the pores is affected by the presence of gas bubbles and salt. The model predicts that the electrolyte conductivity between the pores decreases due to the gas bubbles. This decrease in electrolyte conductivity is influenced by the concentration of gas bubbles and salt in the electrolyte. The model also predicts that the electrolyte conductivity decreases as the gas bubbles flow through the electrolyte, and the salt concentration increases. The decrease in electrolyte conductivity is due to the physical properties of the gas bubbles, which change the electrolyte conductivity. The model predicts that the electrolyte conductivity decreases as the gas bubbles flow through the electrolyte, and the salt concentration increases. The decrease in electrolyte conductivity is due to the physical properties of the gas bubbles, which change the electrolyte conductivity. The model predicts that the electrolyte conductivity decreases as the gas bubbles flow through the electrolyte, and the salt concentration increases. The decrease in electrolyte conductivity is due to the physical properties of the gas bubbles, which change the electrolyte conductivity.
i_{cell} \text{ applied cell current per unit cross-sectional area of the packed bed, A cm}^{-2}

i_L \text{ dimensionless total limiting current supported by the packed bed, i_MSL/i_{cell}, Table I }

i_{LM} \text{ metal limiting reaction current per unit reaction area, A cm}^{-2}, \text{Eq. 4}

i_{x}(x) \text{ local metal solution current per unit cross-sectional area, A cm}^{-2}

i_{y}(x) \text{ local hydrogen solution current per unit cross-sectional area, A cm}^{-2}

i_{ex} \text{ exchange current density of species i based on the reaction area, A cm}^{-2}

j(x) \text{ local reaction current per unit volume of the packed bed, A cm}^{-3}

j(y) \text{ dimensionless local reaction current, j/(i_{ex}/L)}

k_D \text{ local mass-transfer coefficient, cm s}^{-1}

k \text{ dimensionless conductivity group, k' b/Li_{cell}, Table I}

L \text{ electrode thickness, cm}

\kappa(x) \text{ pore electrolyte conductivity, O}^{-1} \text{ cm}^{-1}, \text{Eq. 9}

\kappa(y) \text{ dimensionless, pore electrolyte conductivity, Eq. 17}

\kappa \text{ conductivity of the bulk electrolyte, O}^{-1} \text{ cm}^{-1}

\Gamma \text{ dimensionless bubble group, 2 FPQ/RT_i, Table I}

\eta \text{ absolute temperature, K}

\xi \text{ charge-transfer coefficient of metal reduction}

\epsilon \text{ coulombic efficiency}

\eta_m \text{ metal reaction overpotential, V}

\eta_h \text{ hydrogen evolution reaction overpotential, V}

\sigma \text{ const. = RT/2PF, cm}^{-3} \text{ C}^{-1}, \text{ Eq. 11}

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