Electrochemical chromic acid regeneration process: fitting of membrane transport properties

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Abstract

A mathematical model was developed to predict changes in contaminant concentrations with time, and to estimate contaminant fluxes due to migration, diffusion, and convection in a laboratory-scale batch electrolysis cell for the regeneration of contaminated hard-chrome plating baths. The feed and extract compartments of the batch-cell were separated by a Nafion-117 diaphragm. The mathematical model was used to estimate process parameters and physical properties of Nafion-117 membrane from experimental results, assuming quasi-stationary operation. Best-fit ionic mobilities of Cu, Fe, and Ni through the Nafion-117 membrane were found to be 5.4, 1.7, and $5.2 \times 10^{-10}$ cm$^2$/Vs, respectively. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Solutions of hexavalent chromium are used in a number of industrial processes, most commonly in etching plastics prior to metallizing and decorative and hard chrome plating. A common problem in regenerating these solutions is the removal of contaminant cations such as Fe$^{3+}$, Cu$^{2+}$, and Ni$^{2+}$. In the ongoing work, we have shown that Nafion as a separator allows the removal by electrodialysis of these non-oxidizable cations to the cathode compartment of an auxiliary separation cell immersed in, or adjacent to, the plating bath [8–10]. A particular advantage of Nafion in this process is the exceptional chemical inertness, thermal stability, and mechanical strength, coupled with favorable electrical conductivity [1,11]. Another feature of this process is the use of a fuel-cell type cathode to achieve separation at lower energy costs. The anode was a lead oxide plate to reoxidize trivalent chromium to hexavalent chromium and the cathode was a fuel cell cathode, which is platinum catalyst supported on carbon and interfaced via a Nafion-117 membrane [12,13]. In this work, a model is developed to simulate the operation of the laboratory-cell and to estimate effective Nafion-117 properties by fitting. This paper emphasizes the effect of the Nafion-117 separator. Other aspects of the fuel-cell cathode operation will be reported on in a later paper.

A comprehensive description of membrane processes is given by Mason [14]. Verbrugge and Hill [15] have developed a macro-homogeneous mathematical model for the transport of sulfuric acid through Nafion-117 membrane. This model takes
into account transport due to concentration, electric potential, and momentum gradients, and it assumes Donnan exclusion. Recently, Guzman-Garcia et al. [16] have developed a comprehensive molecular-level pore-transport model to study the cation uptake of Nafion for a variety of cations in single, binary, and ternary solutions of monovalent or divalent cations, as well as a combination of monovalent and divalent cations. In their model, they considered the change of the ion’s solvation energy as it moves from the bulk liquid to the Nafion membrane environment, its transport due to concentration and electric potential gradients radially as well as axially, and the effect of variable pore geometry.

Rather than aiming at a comprehensive description, another goal of this paper is a practically useful (though perhaps incomplete) description of the transport of metal cations through Nafion-117 membrane in concentrated chromic acid. The model equations were solved using the orthogonal collocation method (OCM).

2. Model development

2.1. Physical system description

The chromic acid regeneration and purification process is assumed to be a batch process occurring in two compartments separated by a membrane (see Fig. 1). The left compartment contains the plating bath solution, from which a small concentration of contaminant metal is removed. In this study, the left compartment contains a finite quantity of plating bath solution, and the process is modeled as a transient process (batch reactor).
On the right is a catholyte compartment where the metal will be concentrated and where, to some extent, may be plated out at the cathode located at the far end of the compartment. Contaminant metal ions move from the left compartment through the membrane into the catholyte, and are thereby removed from the plating bath. As is usual in macrohomogeneous models, we distinguish three mechanisms underlying transport in the membrane, diffusion, migration, and convection.

At the membrane/electrolyte interface, an adsorption/partitioning process takes place that brings the ion to the membrane surface. From there, the ion moves under the driving forces of electric potential, pressure, and concentration gradients to the other side of the membrane. The anode, is a source of Cr(VI) due to reoxidation of Cr(III), while at the far end of the catholyte there exists the cathode at which several species (H\(^+\), O\(_2\), metal ions) are consumed. In other words, metals may be plated out and Cr(VI) may be reduced to Cr(III) at the cathode, however, the major cathode reaction is oxygen reduction.

Fig. 1. (a) Schematic of system boundary and (b) schematic concentration and potential profiles in the system.
2.2. Model assumptions

2.2.1. Model assumptions—transport

For simplicity, the bulk solutions in the anolyte and catholyte are assumed to have uniform concentrations due to complete mixing. The distribution of a solute between two phases (partitioning or, alternatively, adsorption) must be accounted for in our system. Therefore, at the membrane surface we assume a Freundlich isotherm for the adsorption of metal ions onto the membrane. Within the membrane, we assume a constant effective ionic diffusion coefficient and a constant effective ionic mobility. We also assume negligible interaction between the solute species transported within the membrane [17]. Solute–solute interactions are ignored because the concentrations of electro-active species are small. We note, however, that in the case of chromic acid regeneration the solvent is a fairly concentrated chromic acid solution, in which Cr(III) and other metallic contaminants are present in very low concentrations.

2.2.2. Model assumptions—reactions

The electrochemical reactions that may occur during the operation of this process are assumed to be the following.

1. At the anode:
   1.1. oxidation of water under oxygen evolution and
   1.2. reoxidation of trivalent chromium to hexavalent chromium.
2. At the cathode (fuel cell type) electrode:
   2.1. electrochemical reduction of water under hydrogen evolution;
   2.2. electrochemical reduction of oxygen;
   2.3. deposition of iron, copper, and nickel and
   2.4. reduction of hexavalent chromium to trivalent chromium or metallic chromium. No oxidation of Fe^{2+}, Cu^{2+}, or Ni^{2+} to higher valence ions occurs at the anode.

Finally, to simplify the electrochemical description and the material balance equations, the following assumptions are made.

2.2.3. Model assumptions—general simplifications

1. Kinetics of the electrode reactions could be represented by an overall efficiency multiplied by a reaction term, as will be shown in the model equations section. This approximation can be used as long as the characteristic dimension of the pore system, say the mean pore diameter \( \delta_p \), is small compared to a distance over which there is a significant change in potential or concentration [18].

2. The ionic IR drop in the bulk electrolyte is assumed insignificant. Metal ion removal occurs due to a uniform electric field (or potential gradient, \( \nabla \Phi \)) that exists in the membrane.

3. The flux due to convection in the pores of the membrane is negligible (small Peclet number or convection-to-diffusion ratio).

4. The current density \( i \) is constant and uniform over the membrane area as well as the electrodes (leading to a one-dimensional transport model).

3. Flux equations and mass balances

Stefan–Maxwell equations [19,20] are the commonly adopted starting point for a fundamental description of species fluxes. A more experiential alternative is offered by the phenomenological flux equation of Schlägel [21]. However, under the conditions and assumptions stated earlier, i.e. a dilute species in a concentrated multi-component system, the complete equations may be effectively simplified to the Nernst–Planck equation [17]

\[
N_i = -z_i u_i C_i \nabla \Phi - D_i \nabla C_i + C_i v
\]

where \( N_i \) is the flux through the membrane, \( z_i \) the charge on the ion, \( u_i \) the mobility, \( C_i \) the species concentration, \( \nabla \Phi \) the potential gradient, \( D_i \) the diffusivity, and \( v \) is the bulk fluid velocity. The terms on the right side of the above equation represent fluxes resulting from migration, diffusion, and convection, respectively.

3.1. Nafion-117 membrane

The forces acting to transport ions and molecules through a membrane are somewhat more complex than those in the bulk liquid, as discussed by Schlägel [21,22], De Levie and coworkers [23–26], and Buck [27]. The pressure and electric field driven velocity components are significant and are summed as an electro-osmotic flow velocity that depends on the hydrostatic pressure difference \( \Delta P \), and the osmotic
pressure ($\pi$) resulting from differences in concentration. Hydrostatic and osmotic pressure are summed as the modified pressure ($P_{mod}$).

### 3.1.1. Concentration profile

Using the approach of a differential slice [20], and assuming dilute-solution formulation, the following one-dimensional equations may be written for the time-dependent concentration profile within the membrane:

$$\frac{\partial C_i}{\partial t} = -\frac{\partial N_i}{\partial x} \pm R_i, \quad 0 < x < 1$$

(2)

In the absence of a chemical reaction $R_i$, this equation may be written as follows:

$$\frac{\partial C_i}{\partial t} = z_i u_i F \left( \frac{\partial C_i}{\partial x} \frac{\partial \Phi}{\partial x} \right) + D_i \frac{\partial^2 C_i}{\partial x^2} + v \frac{\partial C_i}{\partial x}, \quad 0 < x < 1$$

(3)

This second order partial differential equation requires two boundary conditions and one initial condition. These are given as:

- **I.C.1**: $C_i = C_{i0}$, for $0 < x < 1$, $t < 0$
- **B.C.1**: $C_i|_{x=0} = C_i^0$
- **B.C.2**: $C_i|_{x=1} = C_i^1$

### 3.1.2. Potential profile

Since the flow of electric charge is related to the current density in the pores of the membrane by

$$i = F \sum_i z_i N_i$$

(7)

We may then write for the electric potential

$$\frac{\partial \Phi}{\partial x} = \frac{i}{F} \left( \sum_i z_i D_i \frac{\partial C_i}{\partial x} \right) + \frac{E}{F} \left( \sum_i N_i C_i \right) v$$

(8)

Here, the ionic conductivity $k$ is defined as

$$k = \frac{F^2}{RT} \sum_i D_i z_i^2 C_i$$

(9)

The first term on the right-hand side of Eq. (8) may be viewed as an Ohmic contribution, the second is referred to as the diffusion potential, and the last term represents the effect of a flowing liquid having a net electric charge (electro-kinetic or electro-osmotic potential) on the potential gradient. Since we assume electro-neutrality in all parts of our system (except in the electric double layer at each electrode), i.e. $\sum z_i C_i = 0$, so the third term of Eq. (8) becomes 0.

### 3.1.3. Solvent velocity profile

In order to obtain values of interest such as the concentration and component flux at a certain point, we must know the velocity field. This field can be obtained by integrating the continuity equation (Eq. (11)) and the Navier–Stokes equations [20]. Because of the dilute solution assumption, the bulk (hydrodynamic) velocity equals the solvent velocity.

$$\nabla v = \frac{\partial \Phi}{\partial x} = 0$$

(10)

For the velocity of the solvent, we may use the modified Schlogl equation [21]

$$v = \kappa \left( \frac{z_m c_m + \sum_i z_i C_{i,ads}}{F \sum_i z_i C_i} \right) \frac{\partial \Phi}{\partial x} = \frac{\partial P}{\partial x}$$

(12)

where $\kappa$ is a "hydrodynamic permeability". Eq. (12) is a general equation describing the so-called ‘pressure diffusion’ of solute across the membrane. Notice that here $P$ is the modified pressure that accounts for both hydrostatic and osmotic pressure [14].

### 3.1.4. Pressure profile

Combining the continuity equation (Eq. (11)) and the velocity equation (Eq. (12)) yields the following equation for the pressure profile:

$$0 = \left( z_m c_m + \sum_i z_i C_{i,ads} \right) \frac{\partial^2 \Phi}{\partial x^2} + \frac{\partial P}{\partial x}$$

(13)
This equation requires two boundary conditions for the hydrostatic pressure

\[ P|_{x=0} = P^a \]  

\[ P|_{x=\delta_m} = P^c \]  

We assume constant current density along the thickness of the membrane, which implies from Eq. (8) that Eq. (13) becomes \( \nabla P = \int_0^{\delta_0} z \text{ci,ads} \nabla \Phi \). This reveals the dependence of pressure on the concentration of adsorbed species. However, since the concentration of cationic impurities within the Nafion-117 membrane (measured total of \( 1.23 \times 10^{-4} \text{ mol/cm}^3 \) for Fe, Ni, and Cu [10]) is small, the pressure gradient is also negligible. In addition, the hydrostatic pressure difference is negligible in our geometry. Overall, we conclude that the pressure in the membrane may be assumed uniform.

3.2. Anolyte

The material balance in the anolyte compartment may be expressed as

\[ V_a \frac{\partial C_a}{\partial t} = -A_m N_i|_0 + A_c R_a \]  

where \( R_a \) represents the rate of electrochemical reaction occurring in the anolyte compartment for species \( 'i' \). In this case, only \( \text{Cr}^{3+} \) and \( \text{H}_2\text{O} \) (oxidized to \( \text{O}_2 \)) would be reacting species. The reaction rate term \( R_a \) is the product of the current efficiency \( \epsilon_i \) and the total reaction rate \( R_a \) as

\[ R_a = \frac{\epsilon_i s_i nF}{\delta \mu} \]  

where \( s_i \) represents the stoichiometric coefficient of any reaction that involves species \( 'i' \). The stoichiometric coefficients are 2 for both water and \( \text{Cr}^{3+} \) [28].

The initial condition of Eq. (16) is

\[ C_{a_i} = C_{a_i}^0 \]  

3.3. Catholyte

The material balance in the catholyte compartment may be expressed as

\[ V_c \frac{\partial C_c}{\partial t} = -A_m N_i|_{\delta_m} + A_c R_c \]  

At low pH, no bulk chemical reaction will take place for any species, however, a bulk reaction term might be of importance if the pH in the catholyte rises after very long operation, since in this case metal hydroxides will precipitate. However, in our design this condition is preferably avoided and therefore will be disregarded. In any case, the electrochemical reactions (Section 2.2.2) are important. They are represented by the second term on the right side of Eq. (19).

The initial condition for Eq. (19) is

\[ C_{c_i} = C_{c_i}^0 \]  

4. Dimensionless representation of model equations

Dimensionless representation is useful to identify dimensionless numbers, reduce the computation time and to eliminate the floating-point error in computers adopting the floating point system of calculation. Also, a normalized physical domain is a requirement for the use of the orthogonal collocation technique [29–31]. The dimensionless variables and parameters are defined in Table 1.

The dimensionless equations are given as follows.

Table 1

<table>
<thead>
<tr>
<th>Dimensionless parameters and variables</th>
<th>Relationship</th>
</tr>
</thead>
<tbody>
<tr>
<td>Independent variables</td>
<td></td>
</tr>
<tr>
<td>( x ) (m)</td>
<td>( \tilde{x} ) = ( \frac{x}{\delta} )</td>
</tr>
<tr>
<td>( t ) (s)</td>
<td>( \tilde{t} ) = ( \frac{t}{D} )</td>
</tr>
<tr>
<td>Dependent variables</td>
<td></td>
</tr>
<tr>
<td>( \tilde{C}_i ) (mol/m^3)</td>
<td>( \tilde{C}<em>i ) = ( \frac{C_i}{C</em>{i_0}} )</td>
</tr>
<tr>
<td>( \tilde{\Phi} ) (V)</td>
<td>( \tilde{\Phi} ) = ( \frac{\Phi}{F \tilde{\Phi} R} )</td>
</tr>
<tr>
<td>( \tilde{P} ) (atm)</td>
<td>( \tilde{P} ) = ( \frac{P}{P_{c_i}} )</td>
</tr>
<tr>
<td>( \tilde{v} ) (m/s)</td>
<td>( \tilde{v} ) = ( \frac{v}{D} )</td>
</tr>
<tr>
<td>Control parameters</td>
<td></td>
</tr>
<tr>
<td>( \tilde{i} ) (A/m^2)</td>
<td>( \tilde{i} ) = ( \frac{i}{\delta} )</td>
</tr>
<tr>
<td>( \tilde{V} ) (m^3)</td>
<td>( \tilde{V} ) = ( \frac{V}{D} )</td>
</tr>
<tr>
<td>Dimensionless number</td>
<td>( \tilde{P}<em>{ij} ) = ( \frac{-\sigma_i \tilde{v} R \tilde{F}}{P</em>{c_i}} )</td>
</tr>
</tbody>
</table>
4.1. Membrane region

Species mass conservation (Eq. (31)):
\[
\frac{\partial \tilde{C}_i}{\partial t} = \frac{z_i u_i RT}{D} \frac{\partial \Phi}{\partial x} + \frac{z_i u_i RT}{D} \frac{\partial^2 \tilde{C}_i}{\partial x^2} + \frac{V}{\Psi_1} \tilde{C}_i \tilde{v},
\]
where \( D \) is a reference diffusion coefficient in the membrane [15]. It is important to note that the Peclet number is the ratio of diffusion resistance to convective mass transfer resistance [15]. For very small values of \( Pe \), the convection term may be neglected (while \( \partial C/\partial x \) and \( \partial \Phi/\partial x \) may become very large). In this work, with estimates for permeability and pore fluid viscosity of \( 10^{-4} \) cm\(^2\)/s, and \( 9 \times 10^{-4} \) kg/m s, respectively [15], \( Pe \) has a small range of \( 10^{-4} \) to \( 10^{-3} \), i.e. convection can be neglected.

Potential gradient contributions (Eqs. (8), (12) and (13)):
\[
\frac{\partial \tilde{C}_i}{\partial x} = \frac{F^2 \tilde{C}_i}{kRT} \left[ -\tilde{\nabla} \Phi - \tilde{\nabla} \tilde{P} \right] = \text{constant}
\]
\[
0 = \tilde{\nabla}^2 \tilde{C}_i + \tilde{\nabla}^2 \tilde{P}
\]

4.2. Anolyte

Species mass conservation (Eq. (16)):
\[
\frac{\partial \tilde{C}_a}{\partial t} = \left( \frac{z_a u_a RT}{D} \tilde{C}_a \tilde{v} - \frac{D_a}{D} \tilde{\nabla} \tilde{C}_a \right) + \frac{V}{\Psi_1} \tilde{C}_a \tilde{v}
\]
\[
\tilde{v} = \left[ -\tilde{\nabla} \Phi - \tilde{\nabla} \tilde{P} \right] = \text{constant}
\]
\[
0 = \tilde{\nabla}^2 \tilde{C}_a + \tilde{\nabla}^2 \tilde{P}
\]

4.3. Catholyte

Species mass conservation (Eq. (19)):
\[
\frac{\partial \tilde{C}_c}{\partial t} = \left( \frac{z_c u_c RT}{D} \tilde{C}_c \tilde{v} - \frac{D_c}{D} \tilde{\nabla} \tilde{C}_c \right) + \frac{V}{\Psi_1} \tilde{C}_c \tilde{v}
\]
\[
\tilde{v} = \left[ -\tilde{\nabla} \Phi - \tilde{\nabla} \tilde{P} \right] = \text{constant}
\]
\[
0 = \tilde{\nabla}^2 \tilde{C}_c + \tilde{\nabla}^2 \tilde{P}
\]

5. Model parameters

It is important to control the number of parameters or transport coefficients needed to solve the model equations or to fit the experimental data. If their number decreases upon manipulation of the equations, an over-constrained problem may result, and some effect has been neglected. In addition, independent determination of parameters requires painstaking experimental work and effort. Therefore, we used experimental data as a basis for input parameters in the following two cases.

Case 1. In this work, diffusion coefficients and partitioning isotherms determined at Clarkson University were used (Table 2) [32].

Case 2. The plating efficiency was calculated from experimental data [8] according to Eq. (35) and is presented in Table 2.

\[
\epsilon_i = \frac{W_i}{I} \quad \text{eq. (35)}
\]

where \( W \) (mol) is the actual amount of metal plated due to passing current \( I \) (A).
Table 2

<table>
<thead>
<tr>
<th>Cation</th>
<th>Isotherm $K$ (mg/l/m²)</th>
<th>$D_i \times 10^7$ (cm²/s)</th>
<th>Calculated $\varepsilon_i$ percentage during three experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.2 A (3 days)</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>$C_1 = 0.5940C_{01}^{0.5}$</td>
<td>10.10</td>
<td>0.4</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>$C_1 = 0.5173C_{02}^{0.5}$</td>
<td>3.98</td>
<td>0.1</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>$C_1 = 0.5885C_{03}^{0.5}$</td>
<td>7.03</td>
<td>0.1</td>
</tr>
<tr>
<td>$V_a$ (cm³)</td>
<td></td>
<td>300</td>
<td></td>
</tr>
<tr>
<td>$V_c$ (cm³)</td>
<td></td>
<td>900</td>
<td></td>
</tr>
<tr>
<td>$A_{anode}$ (cm²)</td>
<td></td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>$A_{cathode}$ (cm²)</td>
<td></td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>$A_{Nafion}$ (cm²)</td>
<td></td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>$n$</td>
<td>1 for Cu²⁺, Fe³⁺⁺, and Ni²⁺⁺</td>
<td>2, 3, and 2 for Cu²⁺⁺, Fe³⁺⁺,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>for Ni²⁺, respectively.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$K$ is the Freundlich constant.

6. Solution technique and verification

The system of equations (Eqs. (21)–(34)) were solved using the OCM [29–31]. The equations were coded in FORTRAN and a library subroutine LSODE [33] based on Gear’s method for stiff systems, with time step control, was used to solve the system of ODEs.

The verification of this solution can be accomplished only by comparing the results of different methods of numerical solutions, as well as simpler solutions of the integrated equations. In this work, the solution will be verified using experimental data.

7. Model fitting

The model was fitted to the experimental data with the objective of minimizing the difference between experimental and predicted values of concentration of the anolyte versus time according to the least square scheme of minimizing the function $L$ with respect to $u_i$. $L$ is given as [34]

$$L = \sum_{i=1}^{n} \left( C_i^p - C_i^{\text{meas}} \right)^2$$

where $C_i^p$ is the predicted concentration value, and $C_i^{\text{meas}}$ is the measured concentration value in the anolyte at given conditions. The standard deviation of the predicted concentration value and the experimentally determined value is shown in Figs. 2–4.

7.1. Mobilities

The experimental data were fitted to the model equations (Eqs. (21)–(34)) using the parameters listed in Table 2, but treating the ionic mobilities as adjustable parameters. The fit is shown in Figs. 2–4 together with the standard deviation. From this fit, ionic mobilities in the Nafion-117 membrane of 5.4, 5.2, and $1.7 \times 10^{-10}$ cm²/V s for Cu, Ni, and Fe were obtained, respectively. These values for Cu, Ni, and Fe descend in the same order as the diffusion coefficients do (Table 2), and they differ slightly from the ones determined by infinite dilution theory (in water) using the Nernst–Einstein relationship [15,17] (4.1, 2.8, and $1.6 \times 10^{-10}$ cm²/V s for Cu, Ni, and Fe, respectively).

7.2. Tortuosity calculation

The tortuosity factor takes into account the nonlinear path an ion must follow to pass through the membrane, compared to its path in the bulk electrolyte [16,35]. The tortuosity factor is defined by Eq. (37)

$$\tau = \frac{D_i^f}{D_i} = \frac{u_i^f}{u_i}$$

where $\tau$ is the tortuosity factor, $D_i^f$, $D_i$, $u_i^f$, $u_i$ are the electrolyte diffusivity, membrane diffusivity, elec-
trolyte mobility, and membrane mobility of species of species $i$, respectively. The reference diffusivity and mobility (in the electrolyte) are calculated from infinite dilution (in water) equivalent conductance data as

$$D_i \frac{RT}{\lambda_i} = \frac{\lambda_{i0}}{|z_i|F^2}$$

(38)

Data for Eq. (38), the ionic radii, calculated diffusion coefficients and ionic mobilities at infinite dilution in water are shown in Table 3. Using the measured diffusion coefficients (Table 2) and the mobilities from model fitting the tortuosity factors were calculated from Eq. (37) and shown in Table 3. Apparently, the tortuosity factors under diffusion conditions only are larger than those under electrolysis conditions, which is expected since the applied current overcomes transport resistance and shortens the path an ion has to follow to be transported across the membrane. However, it was found that nickel and copper have the lowest tortuosity (the smallest transport resistance) under electrolysis conditions. This suggests that iron (the smallest ion) may be complexed by sulfate or hydrated within the membrane.

![Fig. 2. Model fit to the Cu concentration in the anolyte at various operating currents.](image)

![Fig. 3. Model fit to the Fe concentration in the anolyte at various operating currents.](image)
Table 3

<table>
<thead>
<tr>
<th>Ion</th>
<th>( r ) (Å)</th>
<th>( \lambda_{i0} ) (m²/S mol)</th>
<th>( u_i ) (cm²/V s)</th>
<th>( D_i ) (cm²/s)</th>
<th>Tortuosity From diffusion measurement</th>
<th>Tortuosity From mobility fitting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu²⁺</td>
<td>0.72</td>
<td>53.60</td>
<td>2.88E−09</td>
<td>7.14E−06</td>
<td>7.0</td>
<td>5.3</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>0.64</td>
<td>46.00</td>
<td>2.43E−09</td>
<td>6.04E−06</td>
<td>15.2</td>
<td>14.3</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>0.69</td>
<td>50.00</td>
<td>2.69E−09</td>
<td>6.66E−06</td>
<td>9.5</td>
<td>5.2</td>
</tr>
<tr>
<td>H⁺</td>
<td>–</td>
<td>349.65</td>
<td>3.76E−08</td>
<td>9.31E−05</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

7.3. Conductivity

The conductivity of Nafion-117 in contaminated chromic acid was determined to be 0.38 \( \Omega^{-1} \text{cm} \) from ac impedance measurements on a specially designed cell. This value was used in the model fitting. It yielded, as shown in Section 7.1, reasonable values for the single ion mobilities (diffusivities) of Cu, Ni, and Fe. However, we note that others have reported that during passage of constant current for prolonged periods of time, sharp concentration gradients develop within the Nafion-117 membrane leading to ion depletion and hence, decreased conductivity [15,36,37]. For this reason, Verbrugge and coworkers [15,36,37] used a conductivity of 0.07 \( \Omega^{-1} \text{cm} \) in fitting their model to the data, which is much lower than the measured value (0.1 \( \Omega^{-1} \text{cm} \)). Patrick and Dexter [7] also reported development of increasing resistance during the operation of a similar process using a Nafion membrane as separator. They recommended operation with an intermittent constant current to reduce the development of this resistance, which they ascribed to depletion of ions in the membrane. The conductivity of their electrolyte was 0.51 \( \Omega^{-1} \text{cm} \) at 25°C (very similar to that of the electrolyte in this work). The relatively low conductivity of the electrolyte used by Verbrugge and Bernardi [37] correctly fits their data, but would be expected to lead to a high Ohmic drop observed across the membrane, which the sharp concentration profiles maintained across the membrane fail to explain, and which result in lower transport rates.

8. Conclusions

1. It is possible to use a mathematical formulation based on dilute solution theory with selected experimentally measured parameters to describe the
2. Plausible mobility values could be derived from fitting a model using such a formulation, and these values are expected to be useful in more detailed design modeling.

3. Using tortuosity factors as a diagnostic for cationic-transport across the membrane suggests that transport across the Nafion-117 membrane is not similar to diffusion (inversely proportional to ionic radius) and smaller ions may be prone to a stronger interaction with sulfonate groups within the Nafion-117 membrane.

4. Also it was found that iron (the cation with the smallest diameter) had the largest tortuosity factor.

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