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Transient Concentration Profile in Electrorefining

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Abstract

The transient concentration profile of Cu^{2+} during the eletrorefining of copper is calculated. Electrorefining is a highly effective and commonly used purification technique for many metals. An approximation for the kinetics of electrodeposition is used. The method of separation of variables is used. The results show a initial transient behavior followed by an eventual steady-state concentration profile.

Nomenclature

$x \rightarrow$ position between cathode and anode in $meters$
$L \rightarrow$ distance between cathode and anode in $meters$
$t \rightarrow$ time in $seconds$
$D \rightarrow$ diffusion coefficient in $\frac{moles}{(meters)^2 \cdot seconds}$
$r \rightarrow$ deposition rate in $\frac{moles}{(meters)^3 \cdot second}$
$k \rightarrow$ rate constant in $(seconds)^{-1}$
$C_0 \rightarrow$ initial concentration in $\frac{moles}{(meters)^3}$
$C_s \rightarrow$ steady state solution
$\tilde{C} \rightarrow$ transient solution

Introduction

Electrorefining is a commonly used separation technique to purify metal products in industry. By controlling the potential and current applied between an impure metal anode and the pure metal cathode, the desired redox couple may be selectively activated allowing the oxidation and later reduction of only the desired metal. The current and potential required in electrorefining are strongly related to the concentration profile of the oxidized species in the solution as a function of time. Thus, being able to model the transient behavior of the concentration profile is imperative to being able to design an effective industrial electrorefining process.

In this paper we model the concentration profile of aqueous Cu^{2+} as a function of time for the electrorefining of copper. An illustration of this system is seen in figure (1). The model presented here assumes an excess of supporting electrolyte and the absence of convection resulting in the form for the Nernst-Planck equation in one dimension [1, 2]:

$$-D\frac{\partial^2 C}{\partial x^2} = \frac{\partial C}{\partial t} \tag{1}$$

The kinetics of electrodeposition are dependent upon the exponential of the overpotential, which is dependent on both the electrical current and concentration of the oxidized species at both electrodes. This makes the boundary

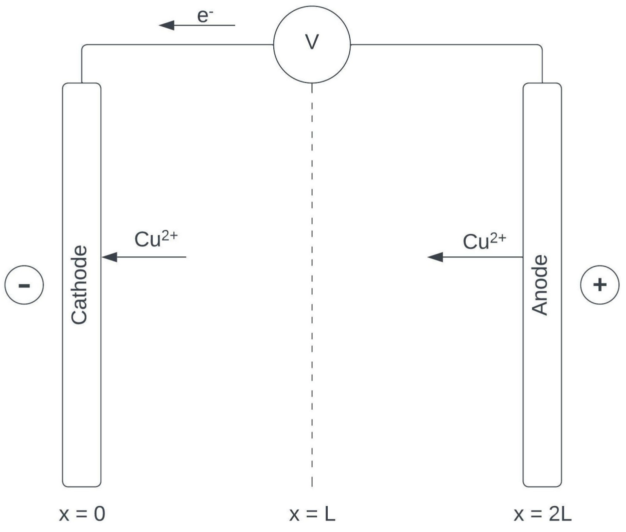

Figure 1: Electrorefining cell diagram.

conditions for this problem extremely complex, making it impossible to be solved analytically. To simplify this problem, we modeled the kinetics according to a simple first-order rate law:

$$r = -kC \tag{2}$$

where r is the rate in units of $\frac{moles}{(meters)^3 \cdot seconds}$.

The values for the constants we used in our solution are:

$$\begin{aligned} L &= 0.025\,meters \\ D &= 0.773 \times 10^{-9}\,\frac{(meters)^2}{second} \\ k &= 2\,(seconds)^{-1} \\ C_0 &= 10\,\frac{moles}{(meters)^3} \end{aligned}$$

For every copper atom deposited at the cathode, one copper atom must be oxidized at the anode. This results in a constant average of the overall concentration. Because of this we can represent the system as having inverse symmetry across the middle of the electrorefining cell. This gives us the boundary condition of a fixed concentration at the middle of the cell $(x = L)$.

Methods

In order to analytically determine the concentration of Cu^{2+} we solve equation (1) subject to the following boundary and initial conditions:

$$\begin{gathered} \frac{\partial C}{\partial x}(0,t) - \frac{k}{D} \cdot C(0,t) = 0 \\ C\left(L,t\right) = C_0 \\ C\left(x,0\right) = C_0 \end{gathered} \tag{3}$$

This equation was solved using separation of variables. Due to the non-zero boundary condition at $(x = L)$, we first solve for the steady state solution. arriving at (4)

$$C_s\left(x\right) = \left(\frac{C_0}{\frac{D}{k} + L}\right) \cdot x + C_0 - \frac{C_0 \cdot L}{\frac{D}{k} + L} \tag{4}$$

Then solving for the transient response via the Sturm-Liouville method and Fourier series we arrive at equation (5)

$$\tilde{C} = \sum_{n=1}^{\infty} a_n \cdot \sin\left(\lambda_n \cdot (x - L)\right) \cdot \mathrm{e}^{-D \cdot \lambda_n^2 \cdot t} \tag{5}$$

$$a_n = \int_0^L \frac{\left[C_0 - C_s\right] \cdot \sin\left(\lambda_n \cdot (X - L)\right)}{\frac{L}{2} - \frac{\sin(2 \cdot \lambda \cdot L)}{4 \cdot \lambda}} dx \tag{6}$$

The total solution is then obtained by combining (4) and (5) giving equation(7)

$$C\left(x,t\right) = C_s + C \tag{7}$$

Plotting this solution over time shows that the Concentration of Cu^{2+} starts out evenly distributed and gradually becomes linear over time. As shown in figure (2).

Conclusions

In this paper we successfully found an analytical solution for the unsteady concentration profile of Cu^{2+} for the aqueous eletrorefining of copper. Several simplifying assumptions were made including:

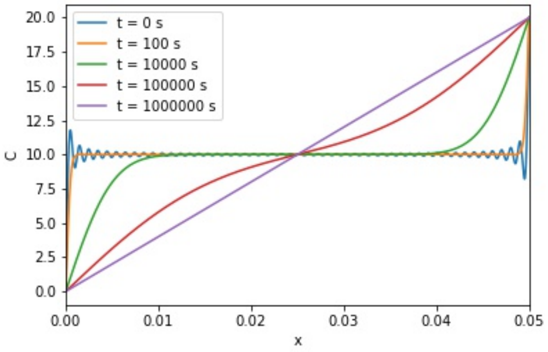

Figure 2: Concentration of Cu^{2+} over the distance between the cathode and anode.

- excess supporting electrolyte
- no convection
- one dimension in x
- electrodeposition kinetics follow a first order rate law
- inverse symmetry across the middle of the electrorefining cell

The concentration profile was plotted as a function of distance x for several times. The expected behavior was observed, including an initial transient state followed by an eventual diffusion-limited steady state.

References

[1] William M. Deen. *Analysis of Transport Phenomena*. 2nd ed. 2012.

[2] Thomas F. Fuller and John N. Harb. *Electrochemical Engineering*. first edition. 2018.