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ANNULAR THIN-LAYER CONCENTRATION PROFILE DURING BULK ELECTROLYSIS

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ABSTRACT

Thin-layer electrodes hold a narrow (<100 μm) layer of solution so close to the electrode surface that they allow for a bulk measurement or complete conversion of material within the thin-layer within seconds. During measurements, concentration profiles are often presumed to be flat, but there are, of course, limits to this assumption. Here, the finite Hankel transform is used to reach an analytical solution for the radial mass transfer equations. We find that the assumption of flat concentration profiles is not reasonable, that thinner layers are converted more quickly, and that the width of the thin-layer does not strongly influence the slope of the concentration profile.

NOMENCLATURE

r	Distance from center of annulus (m)
t	Time since the initiation of current (s)
C	Concentration of the analyte ($mol\ L^{-1}$)
r_1	Distance from the center to the electrode surface (m)
L	Distance from the center to the thin-layer boundary (m)
C^*	Initial concentration of the analyte ($mol\ m^{-3}$)
D	Diffusion coefficient ($m^2\ s^{-1}$)

INTRODUCTION

High-temperature processes using molten salts, such as electrorefining and molten salt reactors, involve many different products, byproducts, and impurities that need to be known. Currently, there is no well-established method to measure high concentrations (>10wt%) in molten salts during process operation [1]. It is hypothesized that thin-layer electrodes could measure very high concentrations because of their ability to completely convert or measure a thin layer of solution in seconds (see Figure 1). This ability is why thin-layer electrolysis is classified as a bulk electrolysis method. Thin-layer electrodes have only been used in molten salts a handful of times, and always with dilute concentrations [2-3].

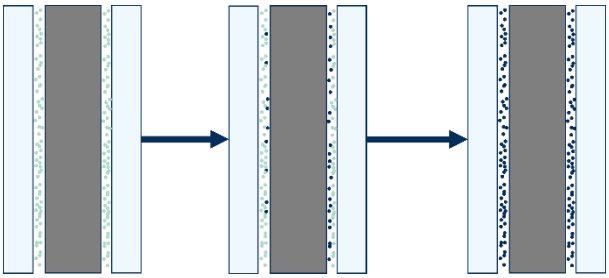

Figure 1. Graphic demonstrating the bulk conversion of one species (light green) to another (dark blue) inside the thin layer between an electrode (grey) and an insulating capillary of glass (light blue).

In this paper we solve the transient concentration profile of a singular analyte in an annular thin-layer during bulk electrolysis to evaluate the commonly held assumption of a flat concentration profile during electrolysis (i.e., C is not a function of r). This solution was done in the annular domain, a departure from the typical cartesian solutions [2,4].

METHODS

To model the concentration profile in the annular domain, we solved the following equation:

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right)=\frac{1}{D}\frac{\partial C}{\partial t} \qquad r_1 < r < L, t > 0 \qquad (1)$$

Assumptions and Boundary Conditions:

To solve this problem, we assumed that there are no noticeable effects due to radial position or z position. For the boundaries, we assumed the reaction of the analyte at the electrode was diffusion limited and that at the edge of the thin layer the concentration gradient is constant. Also, we assumed the initial concentration to be constant over the system. This led to the following boundary conditions:

$$C(r_1,t)=0 \qquad C'(L,t)=0 \qquad C(r,0)=C^* \tag{2}$$

Solution Method:

Equation (1) along with the boundary conditions in (2) is in the correct form to be solved using a finite Hankel transform of type I-II. [5]. The kernel for this transform and its squared norm are shown below in (3):

$$X_n=\frac{J_0(\lambda_n r)}{J_0(\lambda_n r_1)}-\frac{Y_0(\lambda_n r)}{Y_0(\lambda_n r_1)} \qquad \|X_n\|^2=\int_{r_1}^{L}X_n^2 r\,dr \tag{3}$$

where J_0 is the Bessel function of the first kind, zero order, and $Y_0$is the Bessel function of the second kind, zero order. Eigenvalues (λ_n) are roots of the equation (4):

$$0=-J_0(\lambda_n r_1)Y_1(\lambda_n L)+J_1(\lambda_n L)Y_0(\lambda_n r_1) \tag{4}$$

Where subscript *1* denotes the first order of the respective Bessel function. The operational property with homogeneous conditions is (5):

$$\mathcal{H}\left\{\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right)\right\}=-\lambda_n^2\overline{C_n} \tag{5}$$

Where $\overline{C_n}=\mathcal{H}\{C\}$. Once the Hankel transform was applied, we applied a Laplace transform to solve the linear equation and then applied the reverse Laplace and Hankel transforms to receive an analytical solution of the problem.

Solution:

Applying the finite Hankel transform of type I-II to Equation (1), we received:

$$-\lambda_n^2\overline{C_n}=\frac{1}{D}\frac{\partial\overline{C_n}}{\partial t} \tag{6}$$

Applying a Laplace transform we received:

$$-\lambda_n^2 U_n=\frac{1}{D}(sU_n-\overline{C^*}_n) \tag{7}$$

Where $U_n=\mathcal{L}\{\overline{C_n}\}$ and $\overline{C^*}_n=\mathcal{H}\{C^*\}$.

$$U_n=\frac{\overline{C^*}_n}{s+D\lambda_n^2} \tag{8}$$

Applying the reverse Laplace transform, we received:

$$\overline{C_n}=\mathcal{L}^{-1}\{U_n\}=\overline{C_n^*}e^{-D\lambda_n^2 t} \tag{9}$$

Applying the reverse finite Hankel transform, we received the solution:

$$C=\sum_{n=0}^{\infty}\frac{\overline{C_n}X_n}{\|X_n\|^2} \tag{10}$$

RESULTS

To evaluate the effect of the thin-layer width on the slope of the concentration profile, the following values were applied to Eq. (10) with three different thin-layer widths of 10 μm, 50 μm, and 100 μm (see Figure 2).

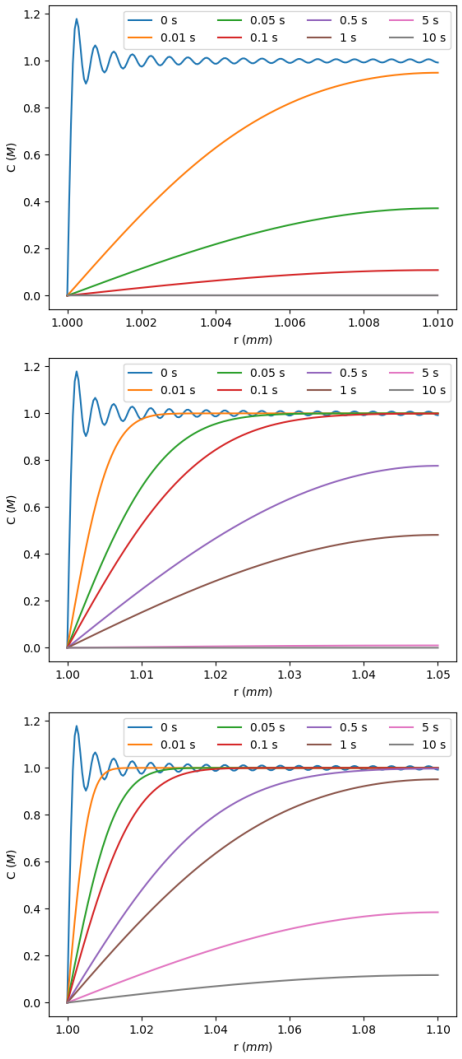

Figure 2. L = 1.01 x 10^{-3} m (top), L = 1.05 x 10^{-3} m (middle), L = 1.10 x 10^{-3} m (bottom). D = 10^{-9} m^2 s^{-1}, C^* = 10^3 mol m^{-3}, r_1 = 10^{-3} m.

Figure 2 clearly shows that the cell is completely converted in much less time for thinner layers of solution. But contrary to our initial instincts, the width of the thin layer did not have a clear effect on the slope of the concentration profile. Indeed, all three thicknesses show that the assumption of a flat concentration profile is fundamentally flawed.

CONCLUSIONS

Here, the mass transfer of concentrated ions within an annular, thin-layer electrode was evaluated using the Hankel and Laplace transforms. The analytical solution was evaluated using three different thicknesses of the thin-layer. We found that the concentration profiles were not flat, that thinner layers were depleted more quickly than thicker layers, and that the thickness of the solution layer did not strongly influence the slope of concentration profiles.

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