Lecture 4

Electrochemical methods. Chronoamperometry. Mass transfer kinetics.

Chronoamperometry is a technique in electroanalysis in which current drawn at an electrode is measured after a rapid step in the applied voltage.

In a thin-layer cell, the anode and cathode are separated by a microscale distance. This means that chemical species transport across the cell is fast, so an analyte in the cell can be consumed exhaustively after only a few seconds. By integrating the current transient (chronoamperogram), the initial concentration of analyte can be determined.

If the kinetics of the electrochemical reaction are always fast, there is no need to resolve the current density as a function of applied potential. Instead, the concentration of the analyte can be assumed to be driven to zero at the working electrode surface. Under this approximation, only the chemical species transport needs to be resolved [1].

Model Definition

This model contains a single 1D domain of length *L* = 60 μm, which is the thickness of the thin layer. Transport in plane with the anode and cathode is ignored; only normal transport is considered, which is assumed to be uniform across the cell.

Domain equation

The transport of the analyte obeys the diffusion equation (Fick's 2nd Law) [2-3]:

$$\frac{\partial c}{\partial t} = \nabla \cdot (D\nabla c)$$

The solution is assumed to be static ("quiescent") so there is no mass transport by convection. A supporting electrolyte is present in high concentration, so the electric field is also taken to be zero. We do not model the product species as its concentration does not influence the current density.

Boundary equation

A high overpotential is applied so that the analyte undergoes a very fast electrochemical reaction at the working electrode surface (*x* = 0). To model this, the analyte concentration here is rapidly stepped to zero. The facing surface (*x* = L), is impermeable to the analyte—no flux is passed. We assume the counter reaction of the electrochemical cell to either take place at a physically separate counter electrode, or to involve a distinct chemical species, present in excess, which we ignore in this model.

Time dependent study

The Einstein equation gives the time for the mean position of a diffusion layer to cross a distance *L*, as a function of the diffusion coefficient *D*:

$$t = \frac{L^2}{4D}$$

In the thin layer, the Einstein time is 0.9 s. After a few Einstein times, the analyte reacts to near exhaustion, and so the duration of the simulation is set to 5 s.

Results and discussion

The concentration profiles through time demonstrate the growth of the diffusion layer across the cell (**Figure 1**).

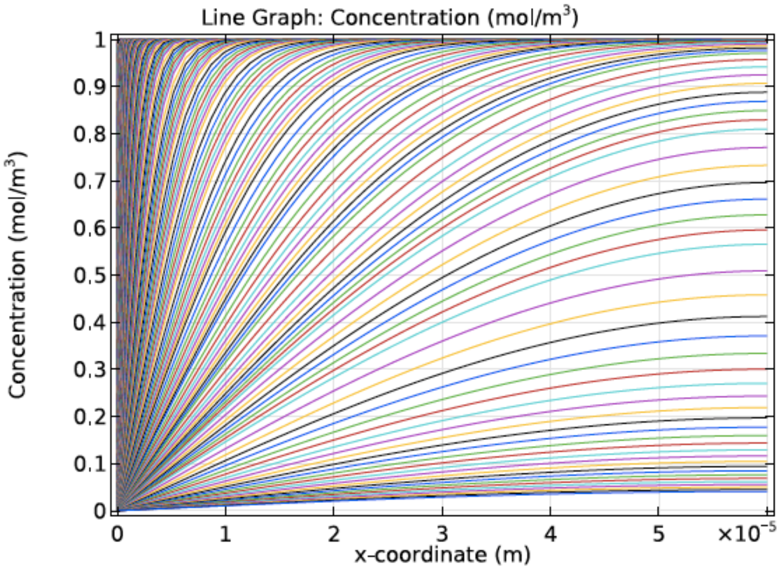

Figure 1. Concentration profiles of the analyte across the thickness of the cell, as the experiment proceeds (top-left to bottom-right)

Once the diffusion layer encounters the outer boundary of the cell, the concentration here begins to diminish as the continuing electrochemical reaction exhausts the available analyte.

As the diffusion layer expands, the flux at the working electrode becomes smaller. Correspondingly the current also decreases (**Figure 2**).

From transport theory, the chronoamperometric current for an infinite expanse of bulk solution falls off inversely proportionally to the square root of time, as given by the Cottrell equation, where i is the current density, n is the number of electrons transferred per molecule of analyte, c is the bulk concentration of analyte and D is its diffusion coefficient [4]:

$$i = nFc\sqrt{\frac{D}{\pi t}}$$

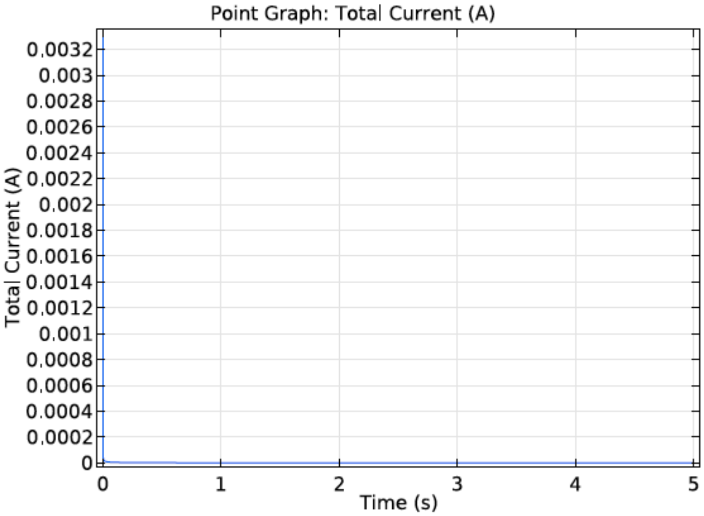

Figure 2. Measured chronoamperogram for the thin-layer cell

By comparing the simulated results with the Cottrell equation, plotted on a logarithmic scale (**Figure 3**), good agreement is observed until roughly *t* = 1 s. At this time—which is approximately the Einstein time noted above—the diffusion layer encounters the wall of the cell.

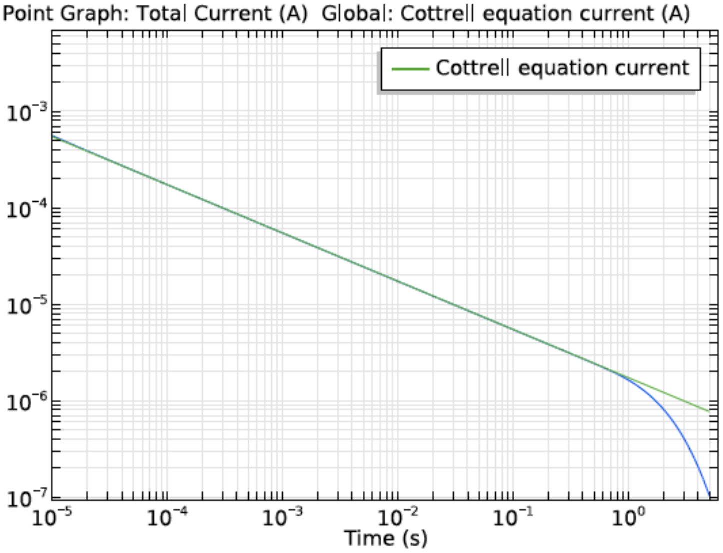

Figure 3. Simulated chronoamperogram compared on a logarithmic scale to the Cottrell equation for chronoamperometry with unlimited available analyte. The deviation at long times is caused by the finite quantity of analyte the cell.

After this point, the current diminishes more quickly due to the exhaustion of available electroactive material for reaction. Under these conditions, the Cottrell equation no longer applies—the simulated current deviates negatively.

By integrating the concentration across the cell, we can calculate the proportion of the initial amount of analyte that has been consumed (**Figure 4**). After 5 seconds, 99% of the analyte has undergone an electrochemical reaction.

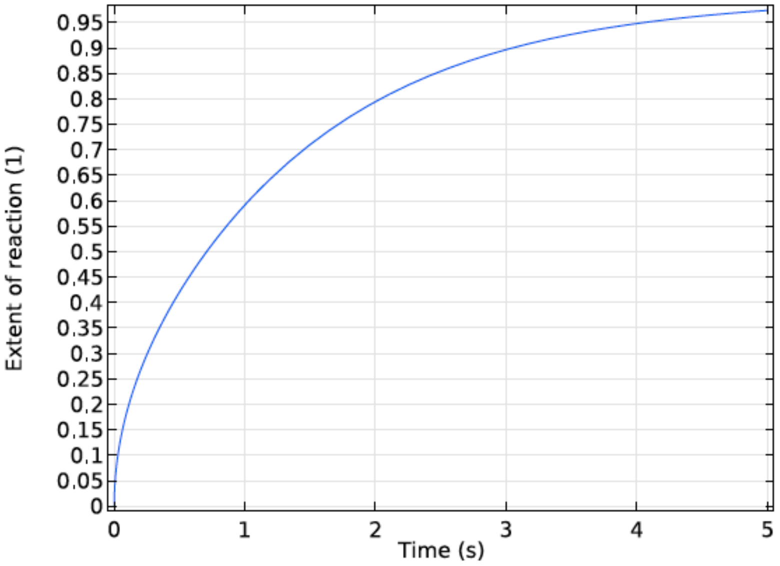

Figure 4. Proportion of the initial quantity of analyte that is consumed through the experiment

References

1. https://www.comsol.com/model/thin-layer-chronoamperometry-14423

2. R.G. Compton and C.E. Banks, Understanding Voltammetry, 2nd ed., World Scientific Publishing Co. Pte. Ltd, London, 2011.

3. A.J. Bard and L.R. Faulkner, Electrochemical Methods, Fundamentals and Applications, 2nd ed., Wiley, Hoboken, 2001.

4. F.G. Cottrell, Zeitschrift für Physikalische Chemie, vol. 42, pp. 385–431, 1903.