

Thin Layer Chronoamperometry

Introduction

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.

Model Definition

This model contains a single 1D domain of length $L = 60\text{ }\mu\text{m}$, 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 EQUATIONS

The transport of the analyte obeys the diffusion equation (Fick's second law):

$$\frac{\partial c}{\partial t} + \nabla \cdot (-D\nabla c) = 0$$

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 EQUATIONS

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 counterreaction 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).

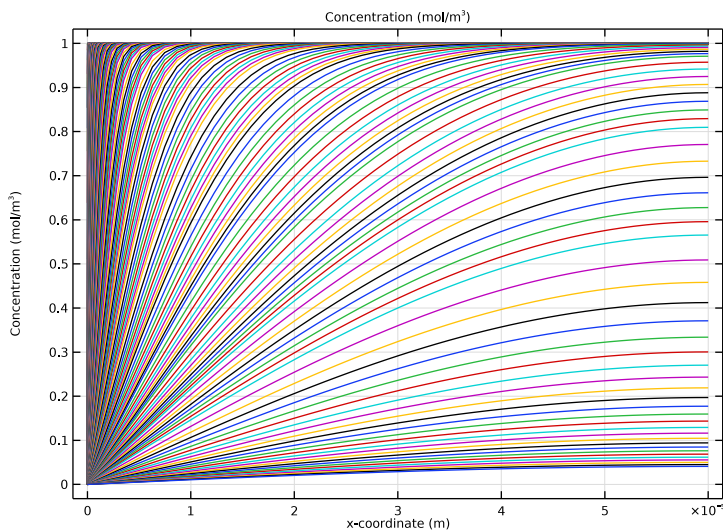


Figure 1: Concentration profiles of the analyte across the thickness of the cell, as the experiment proceeds (from upper left to lower right).

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).

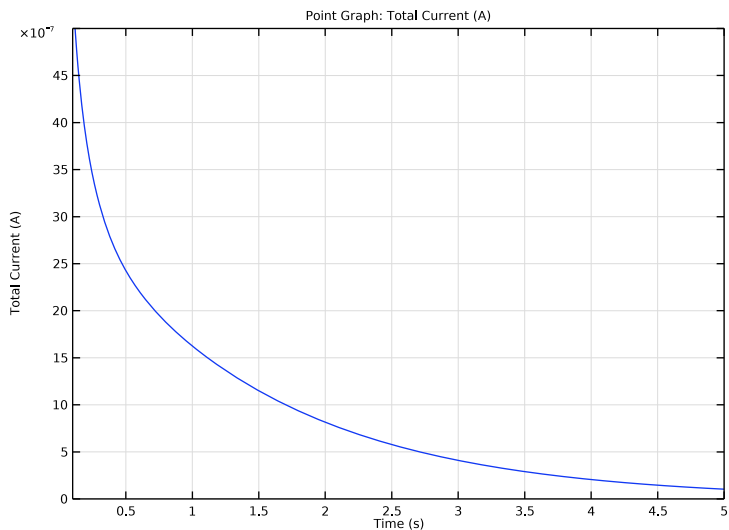


Figure 2: Measured chronoamperogram for the thin-layer cell.

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:

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

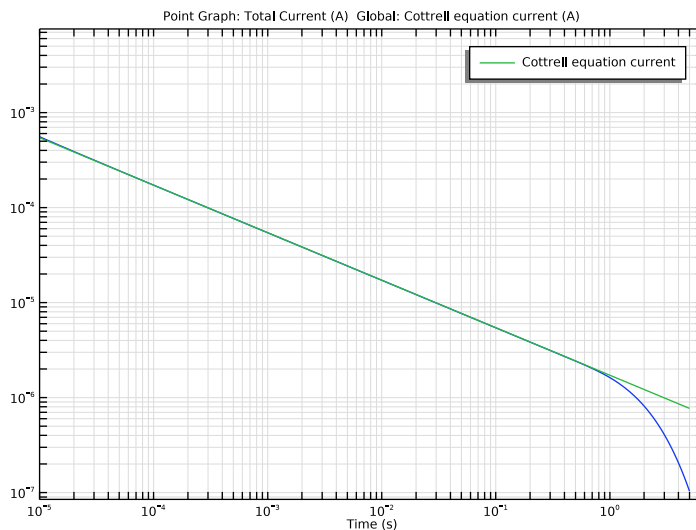


Figure 3: Simulated chronoamperogram compared on a logarithmic scale to the Cottrell equation for chronoamperometry with unlimited available analyte. The deviation at long times is caused by the finite quantity of analyte the cell.

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.

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.

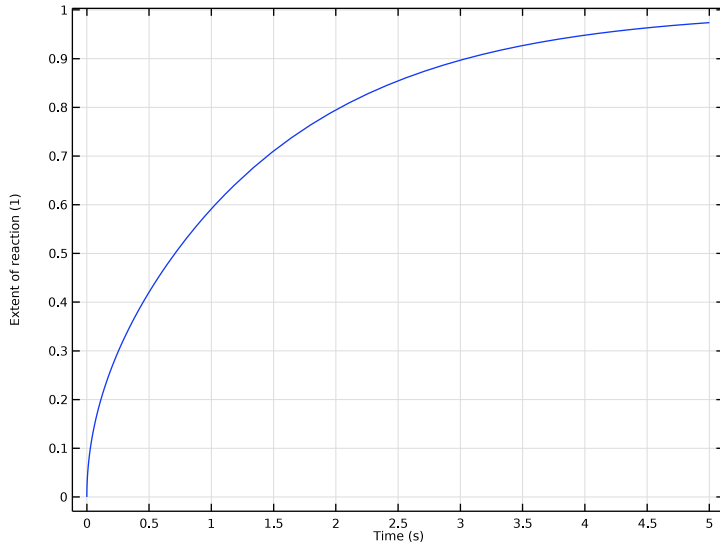


Figure 4: Proportion of the initial quantity of analyte that is consumed through the experiment.

References

1. R.G. Compton and C.E. Banks, *Understanding Voltammetry*, 2nd ed., World Scientific Publishing Co. Pte. Ltd, London, 2011.
2. A.J. Bard and L.R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, 2nd ed., Wiley, Hoboken, 2001.
3. F.G. Cottrell, *Zeitschrift für Physikalische Chemie*, vol. 42, pp. 385–431, 1903.

Application Library path: Electrochemistry_Module/Electroanalysis/
thin_layer_chronoamperometry

Modeling Instructions

From the **File** menu, choose **New**.

NEW

In the **New** window, click  **Model Wizard**.

MODEL WIZARD

- 1 In the **Model Wizard** window, click  **ID**.
- 2 In the **Select Physics** tree, select **Electrochemistry>Electroanalysis (tcd)**.
- 3 Click **Add**.
- 4 In the **Number of species** text field, type 1.
- 5 In the **Concentrations** table, enter the following settings:

c

- 6 Click  **Study**.
- 7 In the **Select Study** tree, select **General Studies>Time Dependent**.
- 8 Click  **Done**.

GLOBAL DEFINITIONS

Add the model parameters from a text file.

Parameters 1

- 1 In the **Model Builder** window, under **Global Definitions** click **Parameters 1**.
- 2 In the **Settings** window for **Parameters**, locate the **Parameters** section.
- 3 Click  **Load from File**.
- 4 Browse to the model's Application Libraries folder and double-click the file `thin_layer_chronoamperometry_parameters.txt`.

GEOMETRY 1

Create the model geometry as a single interval.

Interval 1 (il)

- 1 In the **Model Builder** window, under **Component 1 (comp1)** right-click **Geometry 1** and choose **Interval**.
- 2 In the **Settings** window for **Interval**, locate the **Interval** section.
- 3 In the table, enter the following settings:

Coordinates (m)
0
L

4 In the **Home** toolbar, click  **Build All**.

DEFINITIONS

Add a smoothed step function that will be used to step the concentration at the electrode from initial conditions to zero as a continuous function of time.

Step 1 (step1)

- 1 In the **Home** toolbar, click  **Functions** and choose **Local>Step**.
- 2 In the **Settings** window for **Step**, locate the **Parameters** section.
- 3 In the **Location** text field, type 0.5.
- 4 Click to expand the **Smoothing** section. In the **Size of transition zone** text field, type 1.

Variables 1

Add some variables that will be used during postprocessing for comparing the simulated current with the Cottrell equation.

- 1 In the **Home** toolbar, click  **Variables** and choose **Local Variables**.
- 2 In the **Settings** window for **Variables**, locate the **Variables** section.
- 3 In the table, enter the following settings:

Name	Expression	Unit	Description
i_el	$-F_{\text{const}} \cdot A_{\text{el}} \cdot \text{tcd.tflux_cx}$	A	Total Current
i_Cottrell	$F_{\text{const}} \cdot A_{\text{el}} \cdot c_{\text{bulk}} \cdot \sqrt{D / (\pi \cdot t + \epsilon)}$	A	Cottrell equation current

ELECTROANALYSIS (TCD)

Electrolyte 1

Now start setting up the physics. Start with the domain settings for the diffusion coefficient and the initial concentration.

- 1 In the **Model Builder** window, under **Component 1 (comp1)>Electroanalysis (tcd)** click **Electrolyte 1**.
- 2 In the **Settings** window for **Electrolyte**, locate the **Diffusion** section.
- 3 In the D_c text field, type D.

Initial Values 1

- 1 In the **Model Builder** window, click **Initial Values 1**.
- 2 In the **Settings** window for **Initial Values**, locate the **Initial Values** section.

- 3 In the c text field, type c_{bulk} .

Concentration I

Set up the Concentration condition on the boundary using the step function defined above.

- 1 In the **Physics** toolbar, click  **Boundaries** and choose **Concentration**.
- 2 Select Boundary 1 only.
- 3 In the **Settings** window for **Concentration**, locate the **Concentration** section.
- 4 Select the **Species c** check box.
- 5 In the $c_{0,c}$ text field, type $c_{\text{bulk}}*(1-\text{step1}(t/t_{\text{rise}}))$.

MESH I

Refine the default mesh.

Size

- 1 In the **Model Builder** window, under **Component 1 (comp1)** right-click **Mesh 1** and choose **Edit Physics-Induced Sequence**.
- 2 In the **Settings** window for **Size**, locate the **Element Size** section.
- 3 From the **Predefined** list, choose **Extra fine**.

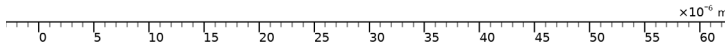
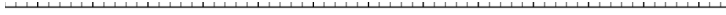
Size I

- 1 In the **Model Builder** window, right-click **Edge 1** and choose **Size**.
- 2 In the **Settings** window for **Size**, locate the **Geometric Entity Selection** section.
- 3 From the **Geometric entity level** list, choose **Boundary**.
- 4 Select Boundary 1 only.
- 5 Locate the **Element Size** section. Click the **Custom** button.
- 6 Locate the **Element Size Parameters** section. Select the **Maximum element size** check box.
- 7 In the associated text field, type $x_{\text{step}}/5$.

Edge 1

1 Right-click **Edge 1** and choose **Build Selected**.

Your finished mesh should now look like this:



STUDY 1

Step 1: Time Dependent

Your model is now ready for solving. Solve for a time range of 5 s.

- 1 In the **Model Builder** window, under **Study 1** click **Step 1: Time Dependent**.
- 2 In the **Settings** window for **Time Dependent**, locate the **Study Settings** section.
- 3 In the **Output times** text field, type range (0,0.1,5).
- 4 In the **Home** toolbar, click  **Compute**.

RESULTS

Concentration (tcd)

The first default plot group shows the concentration.

Create the chronoamperogram as follows:

ID Plot Group 2

In the **Home** toolbar, click  **Add Plot Group** and choose **ID Plot Group**.

Point Graph 1

- 1 Right-click **ID Plot Group 2** and choose **Point Graph**.
- 2 Select Boundary 1 only.
- 3 In the **Settings** window for **Point Graph**, locate the **y-Axis Data** section.
- 4 In the **Expression** text field, type `i_e1`.

Chronoamperogram

- 1 In the **Model Builder** window, under **Results** click **ID Plot Group 2**.
- 2 In the **Settings** window for **ID Plot Group**, type Chronoamperogram in the **Label** text field.
- 3 Locate the **Axis** section. Select the **Manual axis limits** check box.
- 4 In the **x minimum** text field, type 0.1.
- 5 In the **x maximum** text field, type 5.
- 6 In the **y minimum** text field, type 0.
- 7 In the **y maximum** text field, type $5e-6$.
- 8 In the **Chronoamperogram** toolbar, click  **Plot**.

Now, duplicate the chronoamperogram and compare, in log scale, the simulated curve to the Cottrell equation.

Comparison to Cottrell equation

- 1 Right-click **Chronoamperogram** and choose **Duplicate**.
- 2 In the **Settings** window for **ID Plot Group**, type Comparison to Cottrell equation in the **Label** text field.

Global 1

- 1 Right-click **Comparison to Cottrell equation** and choose **Global**.
- 2 In the **Settings** window for **Global**, locate the **y-Axis Data** section.
- 3 In the table, enter the following settings:

Expression	Unit	Description
<code>i_Cottrell</code>	A	Cottrell equation current

Comparison to Cottrell equation

- 1 In the **Model Builder** window, click **Comparison to Cottrell equation**.
- 2 In the **Settings** window for **ID Plot Group**, locate the **Axis** section.
- 3 Clear the **Manual axis limits** check box.

- 4 Select the **x-axis log scale** check box.
- 5 Select the **y-axis log scale** check box.
- 6 In the **Comparison to Cottrell equation** toolbar, click  **Plot**.
- 7 Select the **Manual axis limits** check box.
- 8 In the **x minimum** text field, type $1\text{e-}5$.
- 9 In the **Comparison to Cottrell equation** toolbar, click  **Plot**.

Finally, plot the extent of reaction by calculating the average amount of reacted concentration in a table, and then plotting the table data.

Line Average I

- 1 In the **Results** toolbar, click  **More Derived Values** and choose **Average>Line Average**.
- 2 Select Domain 1 only.
- 3 In the **Settings** window for **Line Average**, locate the **Expressions** section.
- 4 In the table, enter the following settings:

Expression	Unit	Description
$(c_{\text{bulk}} - c) / c_{\text{bulk}}$	1	Extent of reaction

- 5 Click  next to  **Evaluate**, then choose **New Table**.

TABLE

- 1 Go to the **Table** window.
- 2 Click **Table Graph** in the window toolbar.

RESULTS

Extent of reaction

- 1 In the **Model Builder** window, under **Results** click **ID Plot Group 4**.
- 2 In the **Settings** window for **ID Plot Group**, type Extent of reaction in the **Label** text field.