Model created in COMSOL Multiphysics 6.4

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 $L = 60\ \mu\text{m}$, 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):

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

in which D represents the diffusion coefficient and c the species concentration.
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).

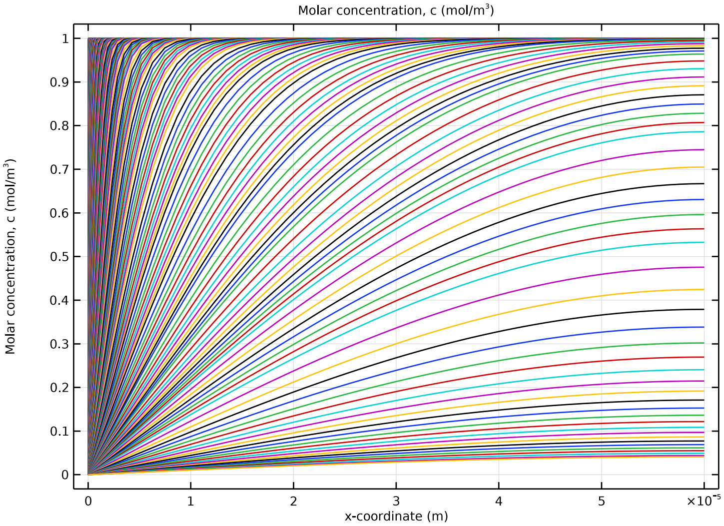


Figure 1: Concentration profiles of the analyte across the thickness of the cell, as the experiment proceeds (from upper left to lower right).

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).

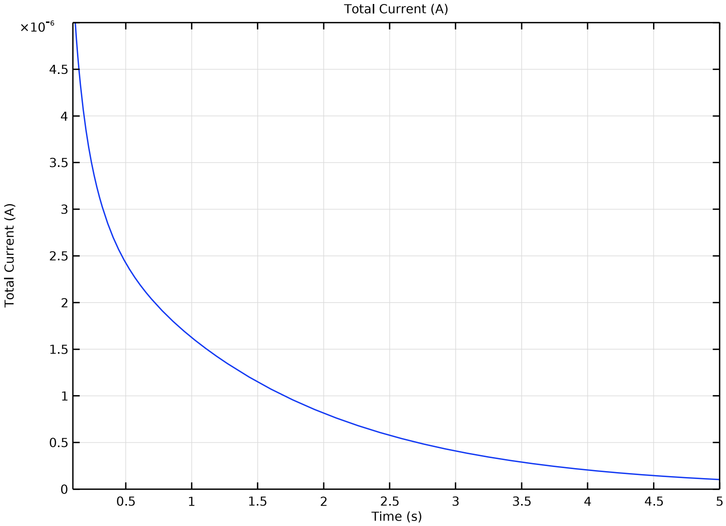


Figure 2: Measured chronoamperogram for the thin-layer cell.

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:

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

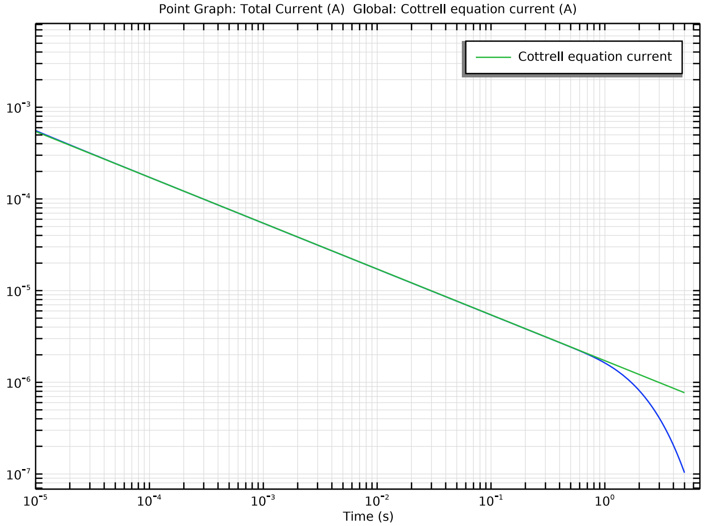


Figure 3: Simulated chronoamperogram (blue line) compared on a logarithmic scale to the Cottrell equation for chronoamperometry with unlimited available analyte (green line). The deviation at long times is caused by the finite quantity of analyte the cell.

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.

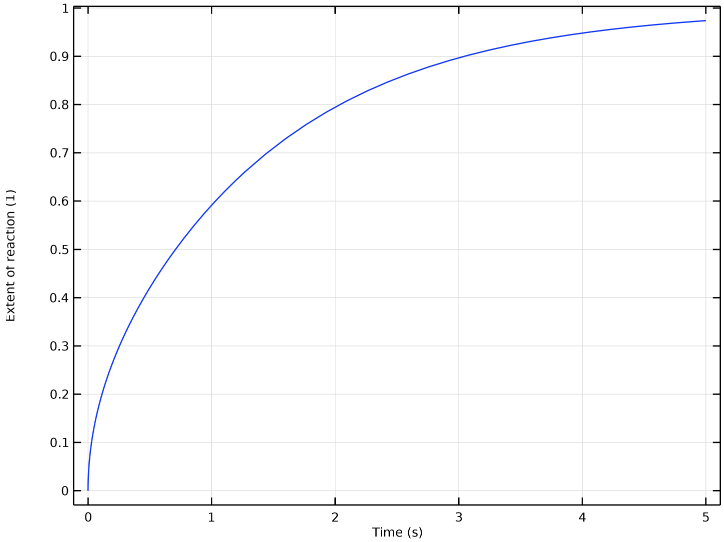


Figure 4: Proportion of the initial quantity of analyte that is consumed through the experiment.

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 **1D**.

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 (mol/m³)** 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 (i1)

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 as follows:

Step 1 (step1)

1 In the **Definitions** toolbar, click f(X) **More Functions** and choose **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

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

1 In the **Definitions** toolbar, click a= **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_const*A_el*tcd.tflux_cx`	A	`Total Current`
`i_Cottrell`	`F_const*A_el*c_bulk*sqrt(D/(pi*t+eps))`	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 1

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

1 In the **Physics** toolbar, click **Boundaries** and choose **Concentration**.

You can select a boundary by clicking on it in the graphics window.

2 Select Boundary 1 only.

3 In the **Settings** window for **Concentration**, locate the **Concentration** section.

4 Select the **Species c** checkbox.

5 In the $c_{0,\mathrm{c}}$ text field, type `c_bulk*(1-step1(t/t_rise))`.

MESH 1

Refine the default mesh.

1 In the **Model Builder** window, under **Component 1 (comp1)** right-click **Mesh 1** and choose **Edit Physics-Induced Sequence**.

Size

1 In the **Model Builder** window, under **Component 1 (comp1)** > **Mesh 1** click **Size**.

2 In the **Settings** window for **Size**, locate the **Element Size** section.

3 From the **Predefined** list, choose **Extra fine**.

Size 1

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.

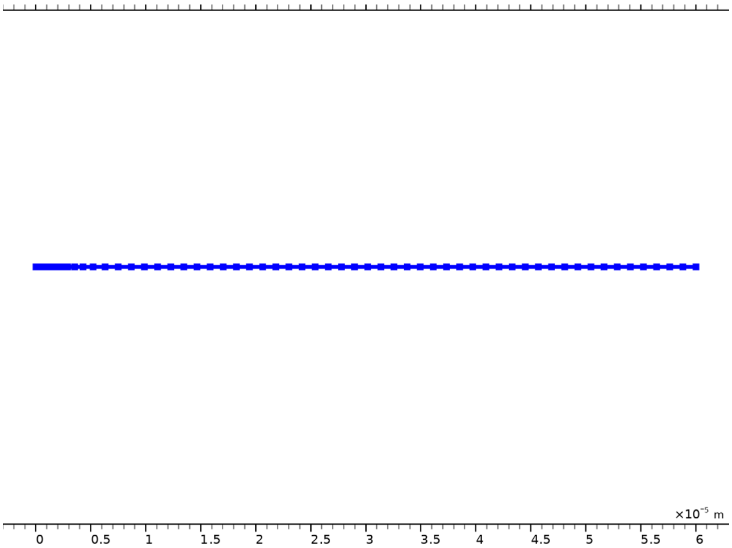
6 Locate the **Element Size Parameters** section.

7 Select the **Maximum element size** checkbox. In the associated text field, type `x_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

The model will be solved 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)`.

Solution 1 (sol1)

With the default solver settings, the solver will not be able to converge the problem. The reason is that the potentiostatic rise time is 1 µs. The default time stepping settings will not resolve the potentiostatic rise. Thus, change the default solver settings so that the initial time step is one tenth of the potentiostatic rise time (0.1 µs).

1 In the **Study** toolbar, click **Show Default Solver**.

2 In the **Model Builder** window, expand the **Solution 1 (sol1)** node, then click **Time-Dependent Solver 1**.

3. In the **Settings** window for **Time-Dependent Solver**, click to expand the **Time Stepping** section.
4. Select the **Initial step** checkbox. In the associated text field, type `1e-7`.
5. In the **Study** toolbar, click **Compute**.

RESULTS

Concentration (tcd)

The first default plot group shows the concentration.

Create the chronoamperogram as follows:

1D Plot Group 2

In the **Results** toolbar, click **1D Plot Group**.

Point Graph 1

1. Right-click **1D 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_el`.

Chronoamperogram

1. In the **Model Builder** window, under **Results** click **1D Plot Group 2**.
2. In the **Settings** window for **1D Plot Group**, type `Chronoamperogram` in the **Label** text field.
3. Locate the **Axis** section. Select the **Manual axis limits** checkbox.
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 as follows:

Comparison to Cottrell equation

1. Right-click **Chronoamperogram** and choose **Duplicate**.
2. In the **Settings** window for **1D 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**
`i_Cottrell`	`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 **1D Plot Group**, locate the **Axis** section.
3. Clear the **Manual axis limits** checkbox.
4. Select the **x-axis log scale** checkbox.
5. Select the **y-axis log scale** checkbox.
6. In the **Comparison to Cottrell equation** toolbar, click **Plot**.
7. Select the **Manual axis limits** checkbox.
8. In the **x minimum** text field, type `1e-5`.
9. In the **Comparison to Cottrell equation** toolbar, click **Plot**.

Line Average 1

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

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_bulk-c)/c_bulk`	`1`	`Extent of reaction`

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

TABLE 1

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

RESULTS

Extent of reaction

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