

# 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):

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

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

- I 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:

С

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

#### GLOBAL DEFINITIONS

Add the model parameters from a text file.

#### Parameters 1

- I In the Model Builder window, under Global Definitions click Parameters I.
- 2 In the Settings window for Parameters, locate the Parameters section.
- **3** Click **b** Load from File.
- **4** Browse to the model's Application Libraries folder and double-click the file thin\_layer\_chronoamperometry\_parameters.txt.

## GEOMETRY I

Create the model geometry as a single interval.

Interval I (i1)

- I In the Model Builder window, under Component I (comp1) right-click Geometry I 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 I (step I)

- I In the Home toolbar, click f(x) 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.

- I In the Home toolbar, click a= 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_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 I

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

- I In the Model Builder window, under Component I (compl)>Electroanalysis (tcd) click Electrolyte I.
- 2 In the Settings window for Electrolyte, locate the Diffusion section.
- **3** In the  $D_{\rm c}$  text field, type D.

#### Initial Values 1

- I In the Model Builder window, click Initial Values I.
- 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.

- I 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<sub>0.c</sub> text field, type c\_bulk\*(1-step1(t/t\_rise)).

#### MESH I

Refine the default mesh.

#### Size

- I In the Model Builder window, under Component I (compl) right-click Mesh I 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

- I In the Model Builder window, right-click Edge I 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 check box. In the associated text field, type x\_step/5.

#### Edge 1

#### I Right-click Edge I and choose Build Selected.

Your finished mesh should now look like this:





#### STUDY I

# Step 1: Time Dependent

The model will be solved for a time range of 5 s.

- I In the Model Builder window, under Study I click Step I: 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).

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  $\mu$ s. 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  $\mu$ s).

# Solution 1 (soll)

- I In the Study toolbar, click **here** Show Default Solver.
- 2 In the Model Builder window, expand the Solution I (soll) node, then click Time-Dependent Solver I.

- **3** In the **Settings** window for **Time-Dependent Solver**, click to expand the **Time Stepping** section.
- 4 Select the Initial step check box. 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:

ID Plot Group 2

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

Point Graph 1

- I 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\_el.

Chronoamperogram

- I 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

- I 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 I

- I 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	А	Cottrell equation current

Comparison to Cottrell equation

- I 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 1e-5.
- **9** In the **Comparison to Cottrell equation** toolbar, click **OM 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 1

- I In the Results toolbar, click <sup>8.85</sup><sub>e-12</sub> 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

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

# RESULTS

Extent of reaction

- I 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.

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