Model created in COMSOL Multiphysics 6.4

Cyclic Voltammetry at a Macroelectrode in 1D

Introduction

Cyclic voltammetry is a common analytical technique for investigating electrochemical systems. In this method, the potential difference between a working electrode and a reference electrode is swept linearly in time from a start potential to a vertex potential, and back again (see Figure 1). The resulting current at the working electrode is recorded and is plotted against the applied electrode potential in a *voltammogram*.

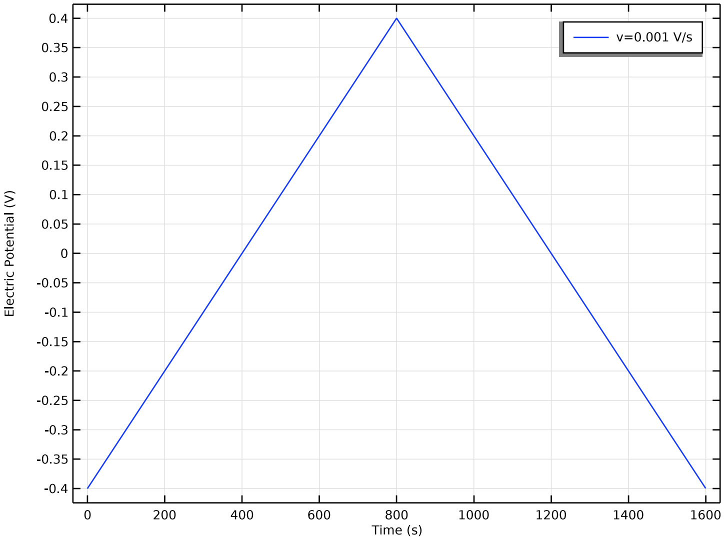


Figure 1: Potential of the working electrode during one voltammetric cycle. The potential is cycled between the vertex potentials 0.4 V and −0.4 V. The scan rate is 1 mV/s.

Voltammetry is a valuable technique because information about both the electrochemical reactivity and the transport properties of a system can be extracted simultaneously. For quantitative interpretation of voltammetry, however, we must use numerical methods to solve the physical equations that describe voltammetry. Then, unknown physical quantities in the system can be inferred by “fitting” to experimental data.

This example demonstrates the use of a common approximation in which a large electrode (macroelectrode) is assumed to have uniform transport behavior across its surface, so only physics occurring normal to the surface need to be considered. By simplifying the model to 1D, an efficient time-dependent analysis is possible.

In this model, a Parametric Sweep is used to compare voltammetry recorded at different voltammetric scan rates.

Model Definition

The model contains a single 1D domain of length L, which is the maximum extent of the diffusion layer over the duration of the voltammetry experiment. A conservative setting for L is set to greatly exceed the mean diffusion layer thickness:

$$L = 6\sqrt{Dt_{\max}}$$

Here, D is the diffusion coefficient of the reactant and $t_{\max}$ is the duration of the cyclic voltammogram.

DOMAIN EQUATIONS

We assume the presence of a large quantity of supporting electrolyte. This is inert salt that is added in electroanalytical experiments to increase the conductivity of the electrolyte without otherwise interfering with the reaction chemistry. Under these conditions, the resistance of the solution is sufficiently low that the electric field is negligible, and we can assume $\phi_l = 0$.

The Electroanalysis interface implements chemical transport equations for the reactant and product species of the redox couple subject to this assumption. The domain equation is the diffusion equation (also known as Fick's second law) to describe the chemical transport of the electroactive species A and B:

$$\frac{\partial c_i}{\partial t} = \nabla \cdot (D_i \nabla c_i)$$

BOUNDARY EQUATIONS

At the bulk boundary ($x = L$), we assume a uniform concentration equal to the bulk concentration for the reactant. The product has zero concentration here, as in bulk.

At the electrode boundary ($x = 0$), the reactant species A oxidizes (loses one electron) to form the product B. By convention, electrochemical reactions are written in the reductive direction:

$$\mathrm{B} + \mathrm{e}^- \leftrightarrow \mathrm{A}$$

The stoichiometric coefficient is –1 for B, the "reactant" in the reductive direction, and + 1 for A, the "product" in the reductive direction. This formulation is consistent even in examples such as this model where at certain applied potentials, the reaction proceeds favorably to convert A to B. The number of electrons transferred, n, equals one.

The current density, i_{loc}, for this reaction is given by the electroanalytical Butler–Volmer equation for an oxidation:

$$i_{\mathrm{loc}} = nFk_0\left(c_{\mathrm{A}}\exp\left(\frac{(n-\alpha_{\mathrm{c}})F\eta}{RT}\right) - c_{\mathrm{B}}\exp\left(\frac{-\alpha_{\mathrm{c}}F\eta}{RT}\right)\right)$$

in which k_0 is the *heterogeneous rate constant* of the reaction, α_{c} is the cathodic *transfer coefficient*, and η is the overpotential at the working electrode. This overpotential is the difference between the applied potential and the *equilibrium potential* (formal reduction potential) of the redox couple of species A and B.

According to Faraday's laws of electrolysis, the flux of the reactant and product species are proportional to the current density drawn:

$$-\mathbf{n}\cdot\mathbf{N}_i = -\frac{\nu_i i_{\mathrm{loc}}}{nF}$$

Here $-\mathbf{n}\cdot\mathbf{N}_i$ is the molar flux normal to the electrode surface and ν_i is the stoichiometric coefficient. This is expressed in the Electrode Surface boundary condition.

The applied triangular waveform for the cyclic voltammetry study is specified in the Electrode Surface boundary condition according to two vertex potentials — forming a *potential window* between –0.4 V and +0.4 V, either side of the equilibrium reduction potential — and a *voltammetric scan rate*, v (SI unit: V/s), which is the rate at which the applied potential is changed.

In the 1D approximation, the total current is related to the current density simply by multiplying by the electrode area A:

$$I_{\mathrm{el}} = i_{\mathrm{loc}}A$$

CYCLIC VOLTAMMETRY STUDY

In the cyclic voltammetry experiment, the potential applied to the working electrode surface is varied linearly as a function of time. A Parametric Sweep is used to compare the voltammetry recorded at different scan rates.

Results and Discussion

The shape of the cyclic voltammogram (Figure 2) shows the relation between electrode kinetics and chemical species transport (diffusion).

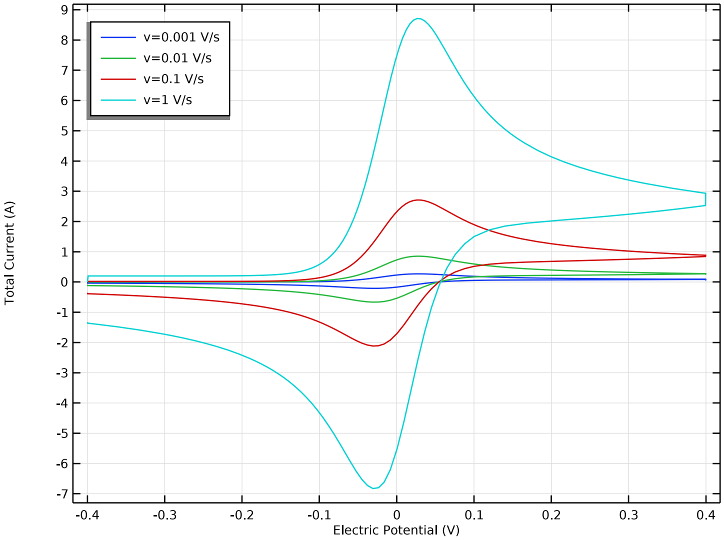


Figure 2: Cyclic voltammetry recorded at a macroelectrode.

Initially, at reducing potentials, the oxidation reaction is not driven and negligible current is drawn. As the potential moves toward the reduction potential of the redox couple, the oxidation reaction is accelerated and the current increases. Once the oxidation reaction has consumed the reactant at the electrode surface, the current becomes limited by the rate of transport of A toward the working electrode. Therefore, a peak current is observed, and at higher potentials, the voltammetric current falls off at a potential-independent rate; this region is termed "diffusion-controlled" or "transport-controlled".

On sweeping back toward more reducing potentials, the reconversion of the product B into the original reactant A gives a negative (cathodic, reductive) current. Depletion of the reacting species B causes a negative peak current and reconversion thereafter proceeds at a diffusion-controlled rate.

The magnitude of the current on the forward peak, I_{pf}, is a common diagnostic variable in voltammetry. For fast electrode kinetics and at a macroelectrode under the 1D approximation, its value is given theoretically by the Randles–Ševcík equation (see Ref. 1 and Ref. 2 for a detailed discussion and derivation):

$$I_{\mathrm{pf}} = 0.446nFAc\sqrt{\frac{nF}{RT}Dv}$$

where A is the electrode area, c is the bulk concentration of the reactant, and D is the diffusion coefficient of the reactant.

The square-root relationship between peak current and scan rate is characteristic of macroelectrode cyclic voltammetry under the above conditions.

References

1. R.G. Compton and C.E. Banks, *Understanding Voltammetry,* 2nd ed., London, 2011.

2. A.J. Bard and L.R. Faulkner, *Electrochemical Methods, Fundamentals and Applications,* 2nd ed., Wiley, New York, 2001.

Application Library path: `Electrodeposition_Module/General_Electrochemistry/cyclic_voltammetry_1d`

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**.

   This model will solve for the two concentrations of a redox couple, change the default concentration variable names to `cA` and `cB`.
4. In the **Concentrations (mol/m³)** table, enter the following settings:

cA
cB

5 Click **Study**.

6 In the **Select Study** tree, select **Preset Studies for Selected Physics Interfaces** > **Cyclic Voltammetry**.

7 Click **Done**.

GLOBAL DEFINITIONS

Parameters 1

Add the model parameters from a text file.

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 `cyclic_voltammetry_1d_parameters.txt`.

GEOMETRY 1

Build the model geometry as a single interval, where the left boundary will later be defined as the electrode surface, and the right boundary will be the boundary toward the bulk.

Interval 1 (i1)

1 In the **Model Builder** window, under **Component 1 (comp1)** right-click **Geometry 1** and choose **Interval**.

Set the interval length to `L`. The value of `L` is defined in the Parameters node. Note that `L` will vary with the Voltammetric scan rate parameter `v`, which is also defined in the Parameters node.

2 In the **Settings** window for **Interval**, locate the **Interval** section.

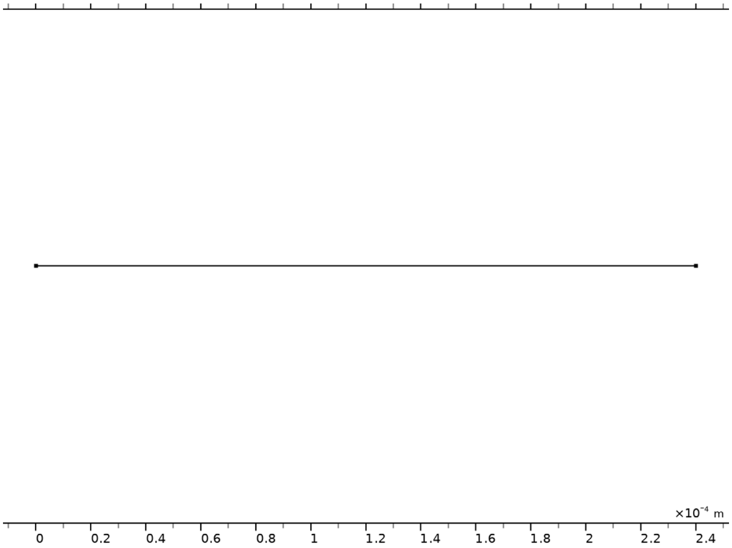
3 In the table, enter the following settings:

Coordinates (m)
0
L

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

The completed geometry should now look like this:

5 In the **Model Builder** window, click **Geometry 1**.



ELECTROANALYSIS (TCD)

Electrolyte 1

Start defining the physics by setting the diffusion coefficients for the two species of the redox couple.

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_{cA} text field, type `DA`.
4. In the D_{cB} text field, type `DB`.

Concentration 1

Set the boundary to the right to bulk concentration values.

1. In the **Physics** toolbar, click **Boundaries** and choose **Concentration**.
2. Select Boundary 2 only.
3. In the **Settings** window for **Concentration**, locate the **Concentration** section.
4. Select the **Species cA** checkbox.
5. In the $c_{0,\mathrm{cA}}$ text field, type `c_bulk`.
6. Select the **Species cB** checkbox.

Electrode Surface 1

Set up the electrode surface and the cyclic voltammetry settings on the left boundary.

1. In the **Physics** toolbar, click **Boundaries** and choose **Electrode Surface**.
2. Select Boundary 1 only.
3. In the **Settings** window for **Electrode Surface**, locate the **Electrode Phase Potential Condition** section.
4. From the **Electrode phase potential condition** list, choose **Cyclic voltammetry**.
5. In the **Linear sweep rate** text field, type `v`.

   The voltage will be cycled between the vertex potentials. When the start potential is not specified, the sweep will start at **Vertex potential 2**.
6. In the **Vertex potential 1** text field, type `E_vertex1`.
7. In the **Vertex potential 2** text field, type `E_vertex2`.

Electrode Reaction 1

Specify the electrode reaction as a **Butler-Volmer** reaction, which is concentration dependent as defined by the stoichiometric coefficients.

1. In the **Model Builder** window, click **Electrode Reaction 1**.
2. In the **Settings** window for **Electrode Reaction**, locate the **Stoichiometric Coefficients** section.
3. In the ν_{cA} text field, type `1`.
4. In the ν_{cB} text field, type `-1`.
5. Locate the **Electrode Kinetics** section. In the $i_{0,\mathrm{ref}}(T)$ text field, type `i0ref`.

Double-Layer Capacitance 1

1. In the **Physics** toolbar, click **Attributes** and choose **Double-Layer Capacitance**.
2. In the **Settings** window for **Double-Layer Capacitance**, locate the **Double-Layer Capacitance** section.
3. In the C_{dl} text field, type `Cdl`.

Initial Values 1

Specify the initial concentration values. This will set the concentration values when the simulation starts at $t = 0$.

1. In the **Model Builder** window, under **Component 1 (comp1)** > **Electroanalysis (tcd)** click **Initial Values 1**.
2. In the **Settings** window for **Initial Values**, locate the **Initial Values** section.

3 In the *cA* text field, type `c_bulk-cB0*(1-x/L)`.

4 In the *cB* text field, type `cB0*(1-x/L)`.

GLOBAL DEFINITIONS

Default Model Inputs

Set up the temperature value used in the entire model.

1 In the **Model Builder** window, under **Global Definitions** click **Default Model Inputs**.

2 In the **Settings** window for **Default Model Inputs**, locate the **Browse Model Inputs** section.

3 In the tree, select **General** > **Temperature (K) - minput.T**.

4 Find the **Expression for remaining selection** subsection. In the **Temperature** text field, type `T`.

STUDY 1

Solve the problem for various sweep rates.

Parametric Sweep

1 In the **Study** toolbar, click **Parametric Sweep**.

2 In the **Settings** window for **Parametric Sweep**, locate the **Study Settings** section.

3 Click **Add**.

4 In the table, enter the following settings:

Parameter name	**Parameter value list**	**Parameter unit**
v (Voltammetric scan rate)	`10^range(-3,1,0)`	`V/s`

5 In the **Study** toolbar, click **Compute**.

RESULTS

Cyclic Voltammograms (tcd)

A number of plots are created by default. The first default plot shows the voltammograms created by the **Cyclic Voltammetry** feature in the **Electrode Surface** node.

1 In the **Settings** window for **1D Plot Group**, locate the **Legend** section.

2 From the **Position** list, choose **Upper left**.

Global 1

1 In the **Model Builder** window, expand the **Cyclic Voltammograms (tcd)** node, then click **Global 1**.

2 In the **Settings** window for **Global**, click to expand the **Legends** section.

3 Find the **Include** subsection. Clear the **Description** checkbox.

4 In the **Cyclic Voltammograms (tcd)** toolbar, click **Plot**.