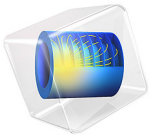

An Application that Demonstrates Cyclic Voltammetry

About the Application that Demonstrates Cyclic Voltammetry

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. The resulting current at the working electrode is recorded and plotted against the applied electrode potential in a *voltammogram*.

The purpose of the application is to demonstrate the use of cyclic voltammetry for studying an electrochemical reaction according to the following chemical equation:

$$\mathrm{Ox} + e^{-} = \mathrm{Red} \tag{1}$$

Since the reaction is simple, studying it gives a good understanding of the method of cyclic voltammetry, which can then be applied to more complex reactions. In addition to the simple reaction, the electrode used in the application is assumed to have a uniform current distribution, which simplifies the interpretation of the results even more. This is a valid assumption for well-designed cells, for example, a cell using a spherical working electrode with cylindrical counter electrodes placed relatively far away from the working electrodes.

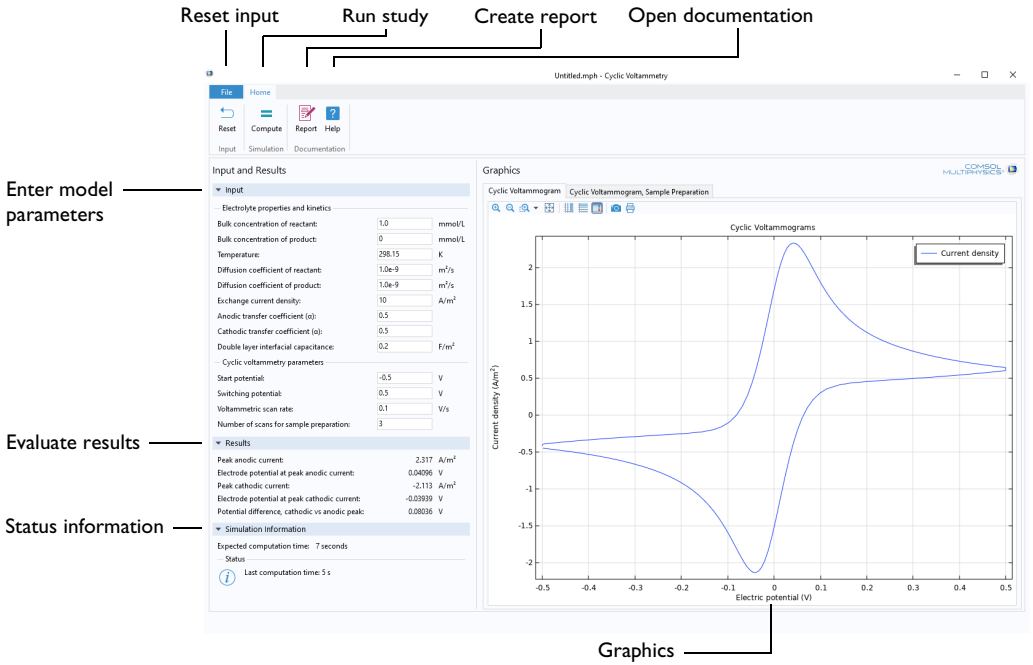

Figure 1: Graphical user interface of the Cyclic Voltammetry application.

In the application, a cyclic voltammogram is simulated for a cell consisting of a redox couple in a large quantity of supporting electrolyte. The following parameters can be varied:

- The bulk concentration of both species (Ox and Red).
- Temperature.
- Transport properties (diffusivity) and kinetic parameters (exchange current density and double layer capacitance).
- Cyclic voltammetry parameters such as start potential, switching potential, and voltammetric scan rate.

The shape of the cyclic voltammogram shows the relation between electrode kinetics and chemical species transport (diffusion). Additionally, the app evaluates the following parameters:

- Peak anodic and cathodic currents.
- Electrode potential at peak anodic and cathodic currents.
- Potential difference between the anodic and cathodic peaks.

The Embedded Model

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 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 so 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 2nd 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:

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

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 for this reaction is given by the Butler-Volmer equation for a one-electron transfer reaction:

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

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:

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

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*, on 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:

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

CYCLIC VOLTAMMETRY STUDY

In the cyclic voltammetry experiment, the potential applied to the working electrode surface is varied linearly as a function of time and the voltammetry is recorded for a particular scan rate. The shape of the cyclic voltammogram (Figure 2) shows the relation between electrode kinetics and chemical species transport (diffusion).

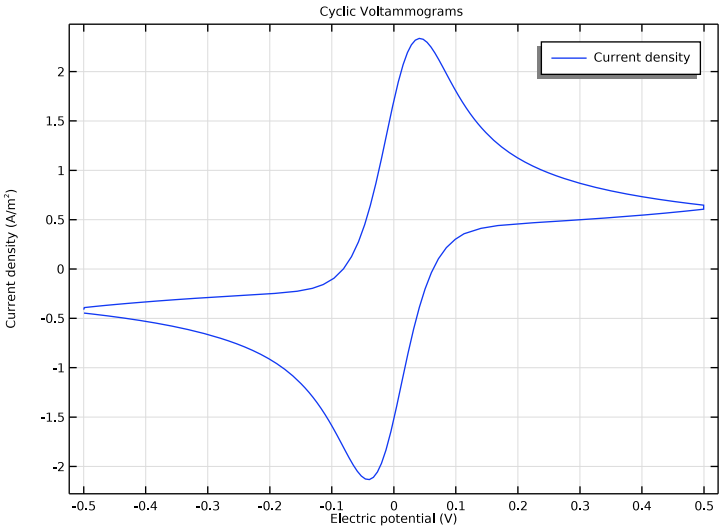

Figure 2: Cyclic voltammetry recorded at a macroelectrode.

Initially, at reducing potentials, the oxidation reaction is not driven and negligible current is drawn. As the potential moves towards 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 towards 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 towards 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.

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: `Electrochemistry_Module/Applications/cyclic_voltammetry`