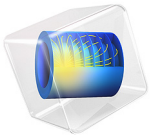


Model created in COMSOL Multiphysics 6.4

Voltammetry at a Microdisk Electrode

Introduction

Cyclic voltammetry is a common electroanalytical technique. Since the 1980s, it has been common in *voltammetry* to use a *microdisk* electrode as the working electrode (Ref. 1). This is a disk electrode with a radius on the order of micrometers, embedded in an insulator whose surface is flush with the electrode.

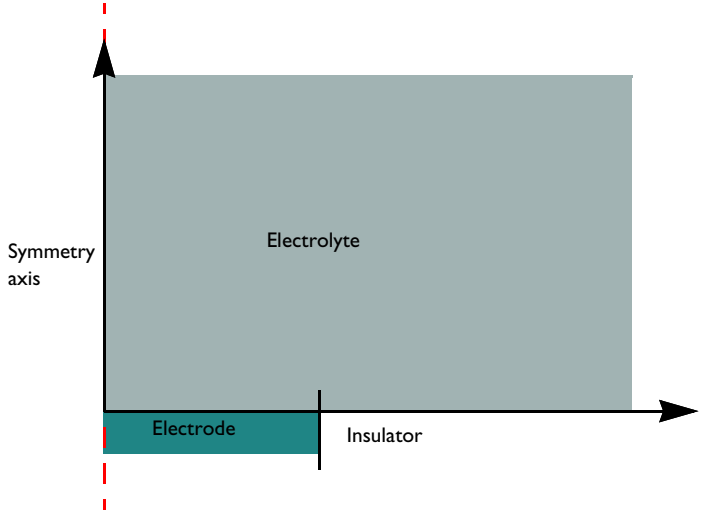


Figure 1: Schematic of the simulation geometry for a microdisk electrode.

These very small electrodes have advantageous mass transport properties that can maximize the measured current density, and so enable the study of electrochemical behavior that would not be observable by conventional voltammetry as performed on a large macroelectrode. (See the model Cyclic Voltammetry at a Macroelectrode in 1D.)

This example demonstrates the use of a common approximation in which an electrode with microscale dimensions is assumed to have stationary (equilibrium) diffusion properties on the time scale of a voltammetry study. This simplifies the analysis because a time-dependent model is not required. Instead, a Parametric Sweep is used to assemble a voltammogram under a quasistatic approximation.

Model Definition

The model contains a 2D axisymmetric domain surrounded by a concentric region in which Infinite Elements are used to extend the bulk solution in the model to 'infinity'. The

approximation that the bulk solution is infinitely distant is suitable if the electrochemical cell is several orders of magnitude larger than the electrode.

The x-axis is divided by a point at the electrode radius, r_e, which equals 10 µm. At $r < r_e$, this axis represents the working electrode (microdisk) where the electrochemical reaction takes place. At $r > r_e$, this axis represents the surrounding insulator in-plane with the disk electrode.

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 that the electrolyte potential $\phi_l = 0$ (Ref. 2).

The Electroanalysis interface implements chemical species 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), which describes the chemical transport of the electroactive species A and B. At steady-state, this reduces to:

$$\nabla \cdot (D_i \nabla c_i) = 0$$

Here D_i represents the diffusion coefficient and c_i the concentration of a species.

BOUNDARY EQUATIONS

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

At the insulating (inert) surface, the normal flux of both species A and B equals zero, since this surface is impermeable and neither species reacts there.

At the electrode boundary, 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 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 i_{loc} is the local current density, 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. Additionally, F, R, T, represent Faraday's constant, the ideal gas constant and the temperature, respectively.

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

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

Here $\mathbf{n}$ is the normal vector of the boundary, $\mathbf{J}_i$ the molar flux, and the product $-\mathbf{n}\cdot\mathbf{J}_i$ the molar flux across the boundary. Additionally, ν_i represents the stoichiometric factor and n the number of electrons transferred.

This is expressed in the Electrode Surface boundary condition.

The total current, I_{el}, recorded at the disk electrode can be extracted by integrating the local current density across the electrode surface. For this purpose, the Electroanalysis interface defines an electrode current variable according to

$$I_{\mathrm{el}} = \int_S i_{\mathrm{loc}}\,dA$$

Note that it is not sufficient to simply multiply by the area of the electrode, because the current density may be nonuniform.

STATIONARY STUDY

In contrast to macroelectrode voltammetry, a voltammogram recorded at a microdisk does not exhibit hysteresis. Diffusion is so fast on the time scale of the experiment that a stationary approximation is suitable. A quasistatic approximation applies when:

$$\frac{r_{\mathrm{e}}^2}{D} \ll \frac{RT}{Fv}$$

where v is the voltammetric scan rate (SI unit: V/s). The two terms in this inequality are respectively the *diffusive* and *voltammetric time scales* of the system.

Within the Stationary study, a parametric sweep is used to study the range of applied potentials achieved in the voltammogram.

Results and Discussion

The stationary concentration profile around a microdisk electrode (Figure 2) has a distinct shape. At large distances from the electrode, the concentration profile is roughly hemispherical, but close to the disk edge the flux is elevated. For fast kinetics the concentrations on the electrode surface are roughly equilibrated and so are uniform. This leads to unequal flux over the surface of the electrode — it is *nonuniformly accessible*.

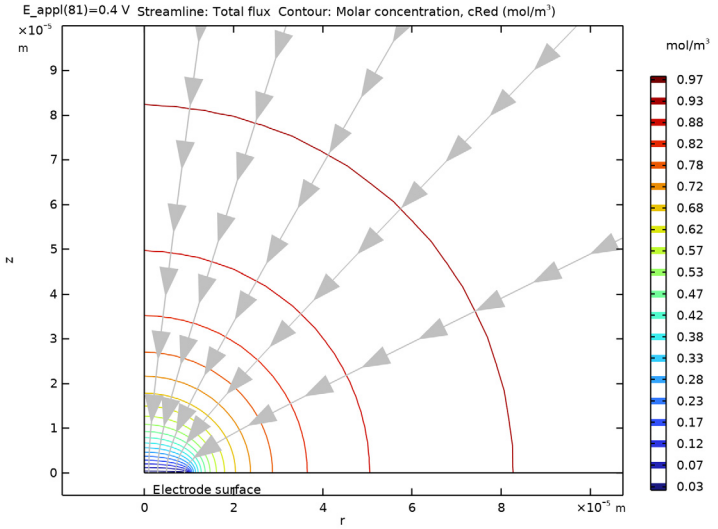


Figure 2: Characteristic concentration profile and mass flux streamlines for transport-controlled oxidation of species A at a microdisk electrode (2D cross section).

The shape of the cyclic voltammogram (Figure 3) illustrates the relation between electrode kinetics and chemical species transport (diffusion).

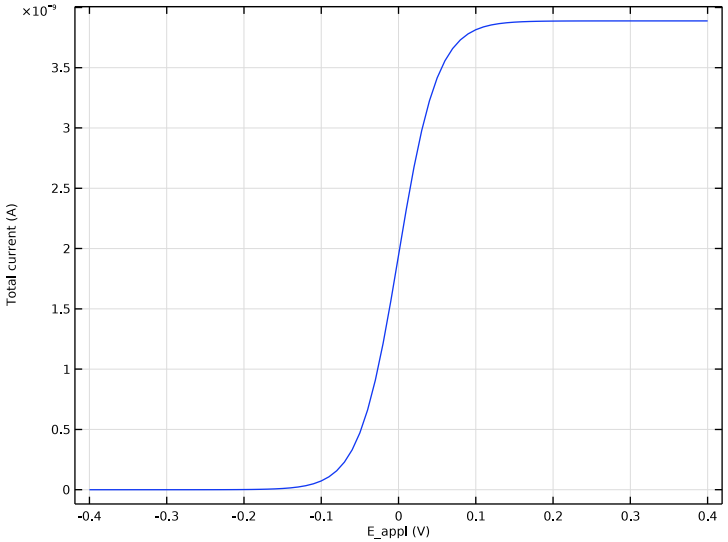


Figure 3: Quasistatic (steady-state) cyclic voltammetry recorded at a microdisk electrode. We can here see the limiting current density as explained below.

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 (0 V), the oxidation reaction is accelerated and the current increases.

Once the oxidation reaction is fast enough that it consumes significant reactant at the electrode surface, the current becomes limited by the rate of transport of A toward the working electrode. Because the diffusion layer is equilibrated, this transport-limited current is constant in time and independent of applied potential. The analytical Saito equation gives this limiting current as (Ref. 3):

$$I_{\mathrm{lim}} = 4nFcDr_{\mathrm{e}}$$

where c is the bulk concentration of reactant.

Negative current is never observed for the "steady-state" voltammetry at a microdisk electrode, since the product species is effectively dispersed to bulk solution. Rapid diffusion on the voltammetric time scale ensures equilibration between the bulk and the electrode surface. Because of the absence of product in bulk, this equilibrium means that the reaction is always oxidative.

Notes About the COMSOL Implementation

A refined mesh is required close to the electrode surface in order to accurately resolve the concentration profile, and hence the current. The mesh is refined further close to the singularity where the electrode and insulator boundaries meet. In the Infinite Element Domain, a Swept mesh is used.

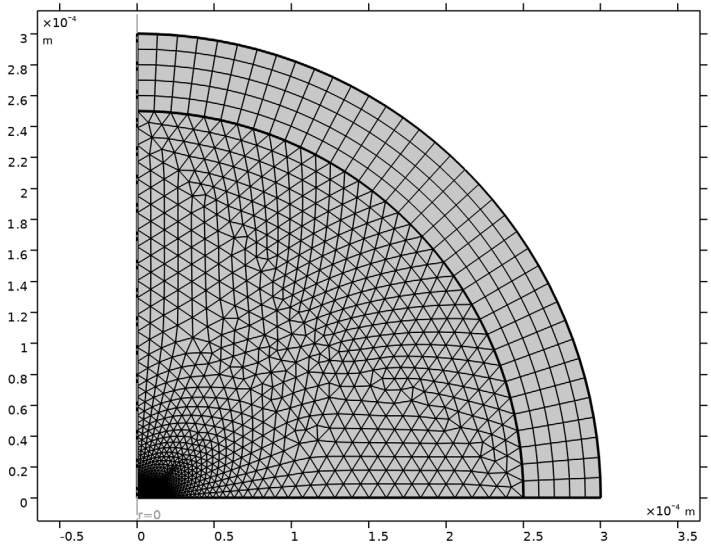


Figure 4: Customized mesh used for the microdisk analysis.

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., Hoboken, 2001.

3. Y. Saito, *Review of Polarography (Japan)*, vol. 15, pp. 177–187, 1968.

Application Library path: `Battery_Design_Module/General_Electrochemistry/microdisk_voltammetry`

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

NEW

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

MODEL WIZARD

1 In the **Model Wizard** window, click **2D Axisymmetric**.

2 In the **Select Physics** tree, select **Electrochemistry** > **Electroanalysis (tcd)**.

3 Click **Add**.

4 In the **Concentrations (mol/m³)** table, enter the following settings:

cRed
cOx

5 Click **Study**.

6 In the **Select Study** tree, select **General Studies** > **Stationary**.

7 Click **Done**.

GLOBAL DEFINITIONS

Load 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 `microdisk_voltammetry_parameters.txt`.

GEOMETRY 1

Draw the model geometry as a quarter circle, and specify the electrode disk radius using a point as follows:

Circle 1 (c1)

1 In the **Geometry** toolbar, click **Circle**.

2 In the **Settings** window for **Circle**, locate the **Size and Shape** section.

3 In the **Radius** text field, type `r_max`.

4 In the **Sector angle** text field, type `90`.

Point 1 (pt1)

1 In the **Geometry** toolbar, click **Point**.

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

3 In the **r** text field, type `re`.

Circle 1 (c1)

Add a second circle that will be used to set up an Infinite Element domain as follows:

Circle 2 (c2)

1 In the **Model Builder** window, under **Component 1 (comp1)** > **Geometry 1** right-click **Circle 1 (c1)** and choose **Duplicate**.

2 In the **Settings** window for **Circle**, locate the **Size and Shape** section.

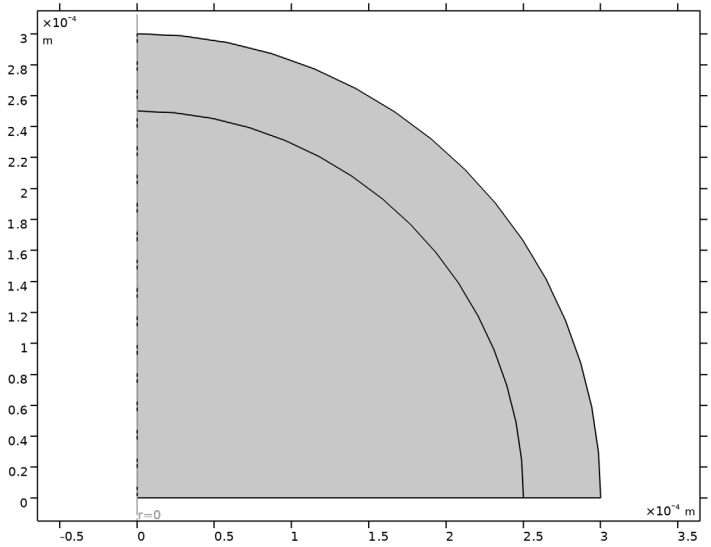
3 In the **Radius** text field, type `r_max*1.2`.

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

5 Click the **Zoom Extents** button in the **Graphics** toolbar.

Your finalized geometry should now like this:

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



DEFINITIONS

Add an Infinite Element domain, and assign it to the outer domain.

Infinite Element Domain 1 (ie1)

1 In the **Definitions** toolbar, click **Infinite Element Domain**.

You can select an element by clicking on it in the graphics window.

2 Select Domain 2 only.

ELECTROANALYSIS (TCD)

Electrolyte 1

Now start setting up the physics. Start with the diffusion coefficients.

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_{cRed} text field, type `D1`.

4 In the D_{cOx} text field, type `D2`.

Electrode Surface 1

Add an Electrode Surface boundary node. Set up the electrode kinetics in the Electrode Reaction subnode as follows:

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

2 In the **Settings** window for **Electrode Surface**, locate the **Electrode Phase Potential Condition** section.

3 From the **Electrode phase potential condition** list, choose **Electrode potential**.

4 In the E_{vsref} text field, type `E_appl`.

5 Select Boundary 2 only.

Electrode Reaction 1

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_{cRed} text field, type `1`.

4 In the ν_{cOx} text field, type `-1`.

5 Locate the **Equilibrium Potential** section. In the $E_{\mathrm{eq,ref}}(T)$ text field, type `Ef`.

6 Locate the **Electrode Kinetics** section. In the $i_{0,\mathrm{ref}}(T)$ text field, type `i0ref`.

Concentration 1

Specify the bulk composition at the outer boundary.

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

2 Select Boundary 7 only.

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

4 Select the **Species cRed** checkbox.

5 In the $c_{0,\mathrm{cRed}}$ text field, type `c_bulk`.

6 Select the **Species cOx** checkbox.

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 *cRed* text field, type `c_bulk`.

MESH 1

Edit the default mesh to ensure good numerical accuracy.

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 **Finer**.

4 Click to expand the **Element Size Parameters** section. In the **Maximum element growth rate** text field, type `1.1`.

Free Triangular 1

1 In the **Model Builder** window, click **Free Triangular 1**.

2 In the **Settings** window for **Free Triangular**, locate the **Domain Selection** section.

3 From the **Geometric entity level** list, choose **Domain**.

4 Select Domain 1 only.

Size 1

1 Right-click **Free Triangular 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 **Point**.

4 Select Point 4 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 `re/100`.

Mapped 1

1 In the **Mesh** toolbar, click **Mapped**.

2 In the **Settings** window for **Mapped**, locate the **Domain Selection** section.

3 From the **Geometric entity level** list, choose **Domain**.

4 Select Domain 2 only.

5 In the **Model Builder** window, right-click **Mesh 1** and choose **Build All**.

STUDY 1

The problem is now ready for solving. Simulate a voltammogram by using a Parametric Sweep for a range of applied potentials.

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
E_appl (Applied potential)	`range(E_start,E_step, E_vertex)`	`V`

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

RESULTS

Concentration, Red (tcd)

Two concentration plots are created by default for each species: one in 2D and one revolved 3D plot.

Modify the first default plot as follows:

DEFINITIONS

Change the default 2D view to show the results more clearly. Start by changing the view for the model and its plot. We want to position the view close to the electrode surface.

Axis

1 In the **Model Builder** window, expand the **Component 1 (comp1)** > **Definitions** > **View 1** node, then click **Axis**.

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

3 In the **r minimum** text field, type `-1e-6`.

4 In the **r maximum** text field, type `1e-4`.

5 In the **z minimum** text field, type `-5e-7`.

6 In the **z maximum** text field, type `1e-4`.

7 Click **Update**.

RESULTS

Concentration, Red (tcd)

1 In the **Model Builder** window, expand the **Results** > **Concentration, Red (tcd)** node, then click **Concentration, Red (tcd)**.

2 In the **Settings** window for **2D Plot Group**, locate the **Plot Settings** section.

3 Select the **x-axis label** checkbox. In the associated text field, type `r`.

4 Select the **y-axis label** checkbox. In the associated text field, type `z`.

5 Locate the **Color Legend** section. Select the **Show units** checkbox.

Surface 1

Next, replace the surface plot with a contour plot for the concentration. Keep the streamlines for the total flux that show the increased reaction rate at the electrode edge compared with the center of the electrode.

In the **Model Builder** window, right-click **Surface 1** and choose **Disable**.

Contour 1

1 In the **Model Builder** window, right-click **Concentration, Red (tcd)** and choose **Contour**.

2 In the **Settings** window for **Contour**, locate the **Expression** section.

3 In the **Expression** text field, type `cRed`.

4 Locate the **Coloring and Style** section. From the **Contour type** list, choose **Tube**.

5 Select the **Radius scale factor** checkbox. In the associated text field, type `1.2E-7`.

Streamline 1

Polish the default streamline plot a little.

1 In the **Model Builder** window, click **Streamline 1**.

2 In the **Settings** window for **Streamline**, locate the **Streamline Positioning** section.

3 From the **Positioning** list, choose **On selected boundaries**.

4 In the **Number** text field, type `5`.

5 Locate the **Selection** section. Click to select the  **Activate Selection** toggle button.

6 Select Boundary 2 only.

7 Locate the **Coloring and Style** section. Find the **Point style** subsection. From the **Arrow length** list, choose **Normalized**.

8 Select the **Number of arrows** checkbox. In the associated text field, type `100`.

Annotation 1

1 In the **Model Builder** window, right-click **Concentration, Red (tcd)** and choose **Annotation**.

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

3 In the **Text** text field, type `Electrode surface`.

4 Locate the **Position** section. In the **Z** text field, type `-1.5e-6`.

5 Locate the **Coloring and Style** section. Clear the **Show point** checkbox.

Total current

Create a plot of the voltammogram as follows:

1 In the **Home** toolbar, click  **Add Plot Group** and choose **1D Plot Group**.

2 In the **Settings** window for **1D Plot Group**, type `Total current` in the **Label** text field.

3 Locate the **Legend** section. Clear the **Show legends** checkbox.

4 Click to expand the **Title** section. From the **Title type** list, choose **None**.

Global 1

1 Right-click **Total current** and choose **Global**.

2 In the **Settings** window for **Global**, click **Replace Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Component 1 (comp1)** > **Electroanalysis** > **Electrode kinetics** > **tcd.Itot_es1 - Total current - A**.

3 In the **Total current** toolbar, click  **Plot**.