Created in COMSOL Multiphysics 6.2

Secondary Current Distribution in a Zinc Electrowinning Cell

Introduction

In a zinc electrowinning cell, zinc deposition is the desired main reaction at the cathode, whereas oxygen is evolved at the anode. A good alignment of the electrodes is required to achieve a uniform current distribution. Even small spatial deviations of the electrode placement in the cell may increase the tendency for short circuits and loss of current efficiency.

This model, which reproduces the results of Bouzek and others (Ref. 1), investigates the effect of the cathode alignment in a zinc electrowinning cell.

Model Definition

The model geometry is shown in Figure 1.

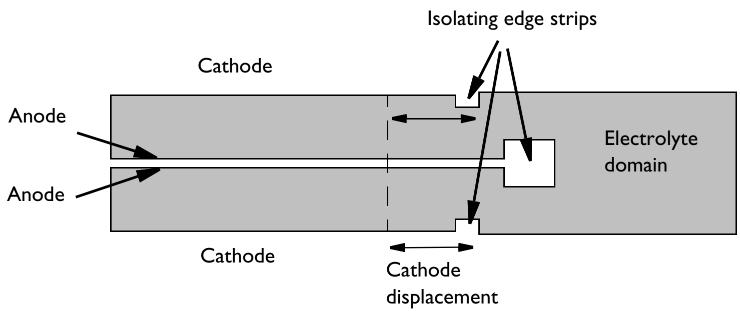


Figure 1: Modeled geometry.

The geometry is a unit cell containing a single electrolyte domain where the anodes and cathodes are modeled as electrode surfaces on the boundaries. The end of the electrodes are isolated using edge strips of isolating material. The stationary problem is solved using a parametric study, investigating the impact of displacing the cathode in the horizontal direction for a range of different values between –60 mm to +40 mm.

Concentration gradients in the electrolyte are neglected. This implies that a secondary current distribution is assumed. The model is set up using the Secondary Current Distribution interface using a constant conductivity of 36.2 S/m in the electrolyte.

At the cathode, zinc ions are reduced according to

$$\mathrm{Zn}^{2+} + 2e^{-} \Leftrightarrow \mathrm{Zn}(s)$$

Hydrogen evolution may also occur at the cathode according to

$$\mathrm{H}^{+} + e^{-} \Leftrightarrow \frac{1}{2}\mathrm{H}_2$$

On the anode, oxygen is evolved:

$$\mathrm{H_2O} \Leftrightarrow \frac{1}{2}\mathrm{O}_2 + 2\mathrm{H}^{+} + 2e^{-}$$

Butler–Volmer expressions are used to describe the electrode reaction kinetics for all electrode reactions:

$$i = i_0\left(\exp\left(\frac{\alpha_a F\eta}{RT}\right) - \exp\left(\frac{-\alpha_c F\eta}{RT}\right)\right)$$

where the overpotentials for the electrode reactions, η, are defined by

$$\eta = \phi_s - \phi_l - E_{\mathrm{eq}}$$

Using the Nernst equation, the equilibrium potentials, E_{eq}, are calculated according to

$$E_{\mathrm{eq}}(\mathrm{Zn}^{2+}/\mathrm{Zn}) = E^0(\mathrm{Zn}^{2+}/\mathrm{Zn}) - \frac{RT}{2F}\ln\frac{a_{\mathrm{Zn}}}{a_{\mathrm{Zn}^{2+}}} = -0.797\ \mathrm{V}$$

$$E_{\mathrm{eq}}\left(\mathrm{H}^{+}/\frac{1}{2}\mathrm{H}_2\right) = 0 - \frac{RT}{F}\ln\frac{a_{\mathrm{H_2}}^{0.5}}{a_{\mathrm{H}^{+}}} = 0.016\ V$$

$$E_{\mathrm{eq}}(\mathrm{O_2/H_2O}) = E^0(\mathrm{O_2/H_2O}) - \frac{RT}{2F}\ln\frac{a_{\mathrm{H_2O}}}{a_{\mathrm{O_2}}^{0.5}a_{\mathrm{H}^{+}}^{2}} = 1.247\ V$$

where E^0 is the standard electrode potential for the respective reactions, and a_i denotes the species activity.

The anode and cathode surfaces are modeled using two Electrode Surface nodes, where the electrode reactions above are defined. The electric potential is set to 0 V at the anode and to 3.597 V at the cathode. The voltage of the cathode is thus the cell voltage. All other boundaries are isolated.

Results and Discussion

Figure 2 and Figure 3 show the electrolyte potential distribution for a cathode dislocation of -60 mm and +40 mm, respectively. The difference in electrolyte potential between the two plots is due to the change of available electrode surface areas, which causes a difference in the average overpotentials at the electrodes.

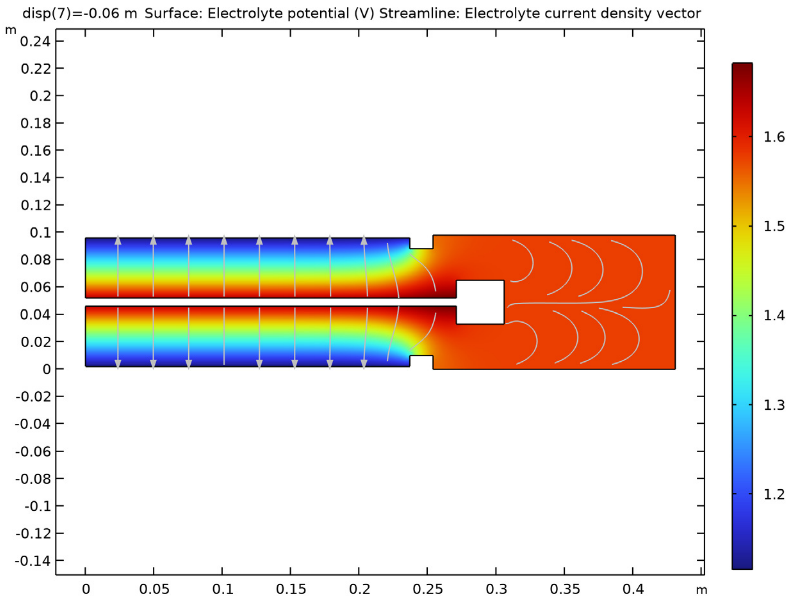


Figure 2: Electrolyte potential distribution for a cathode displacement of -60 mm.

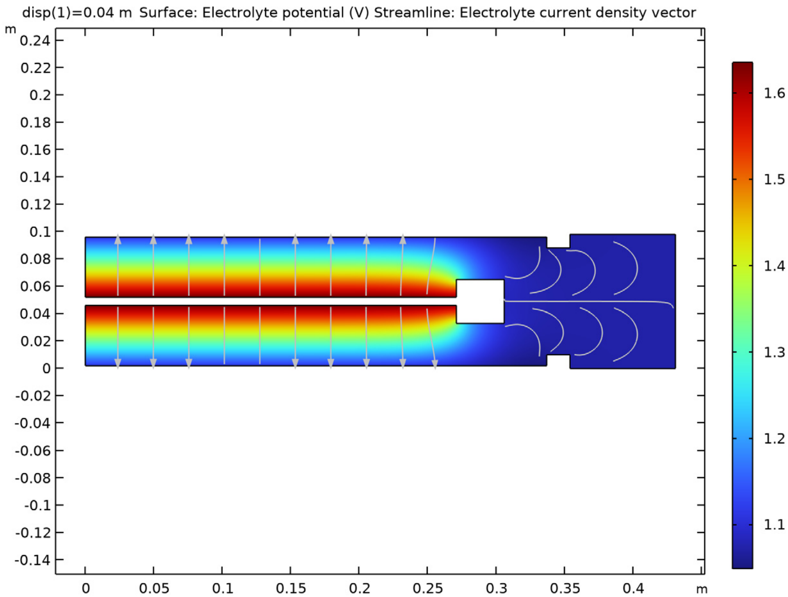


Figure 3: Electrolyte potential distribution for a cathode displacement of +40 mm.

Figure 4 and Figure 5 show the electrolyte current density and streamlines of the electrolyte current for the same cathodes as in Figure 2 and Figure 3. The location of the maximum in electrolyte current is located toward the end of the shorter electrode.

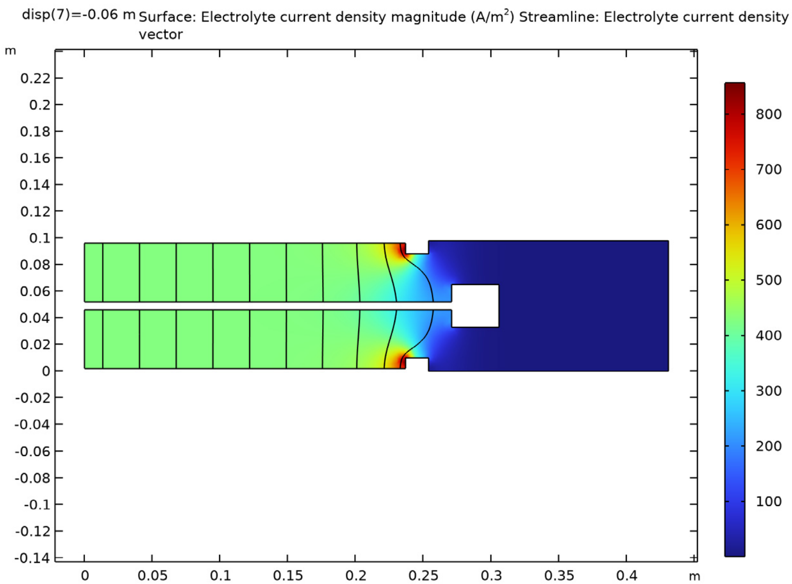


Figure 4: Electrolyte current density distribution for a cathode displacement of -60 mm.

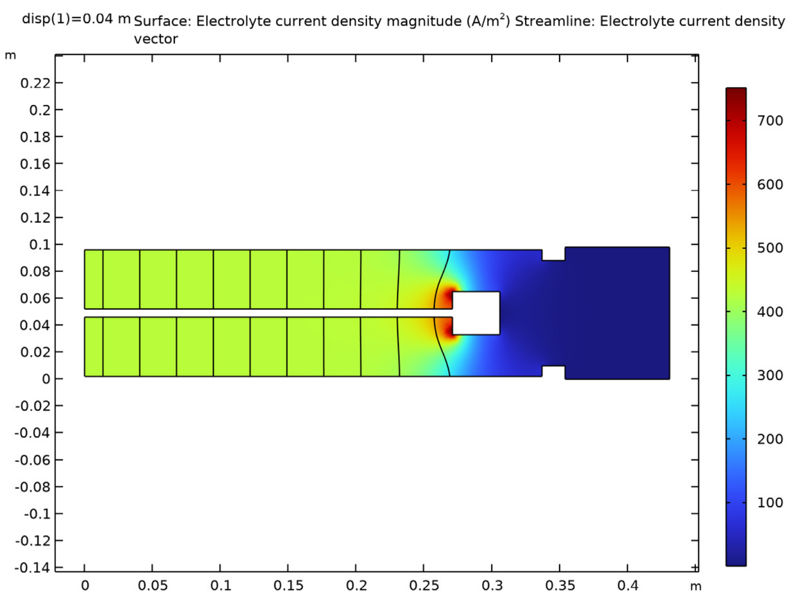


Figure 5: Electrolyte current density distribution for a cathode displacement of +40 mm.

[Figure 6](#) shows a line graph of the total current density at the cathode for different cathode displacements. The most uniform current density is found for a cathode displacement of –20 mm.

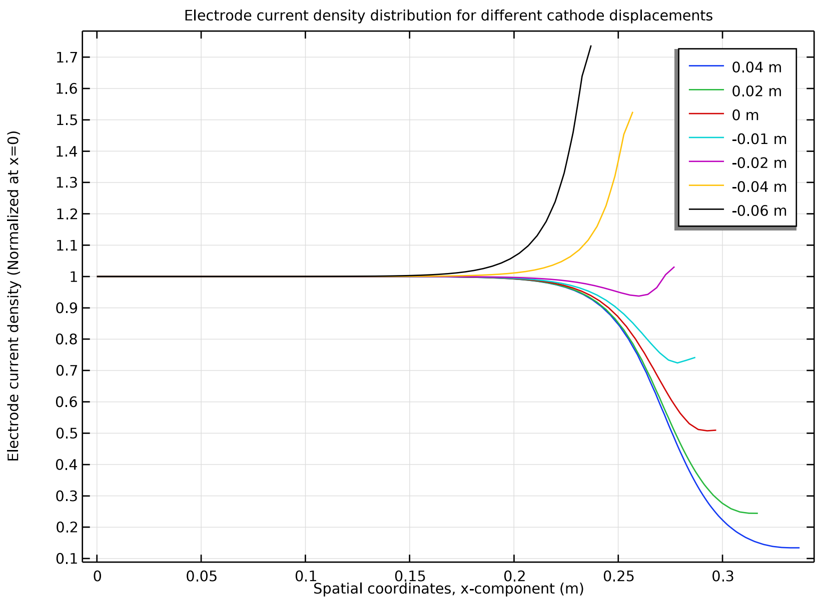


Figure 6: Electrode density at the cathode for different cathode displacements normalized to the electrode density at x = 0.

Reference

1. K. Bouzek, K. Korve, O.A. Lorentsen, K. Osmundsen, I. Rousar, and J. Thonstad, "Current Distribution at the Electrodes in Zinc Electrowinning Cells," *J. Electrochemical Society*, vol. 142, no. 1, 1995.

Application Library path: `Electrodeposition_Module/Verification_Examples/zn_electrowinning`

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 **2D**.

2 In the **Select Physics** tree, select **Electrochemistry>Primary and Secondary Current Distribution>Secondary Current Distribution (cd)**.

3 Click **Add**.

4 Click **Study**.

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

6 Click **Done**.

GLOBAL DEFINITIONS

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 `zn_electrowinning_parameters.txt`.

GEOMETRY 1

Rectangle 1 (r1)

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

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

3 In the **Width** text field, type `l6+l2+l3`.

4 In the **Height** text field, type `2*d4+d1+d5+d2`.

5 Click **Build Selected**.

Rectangle 2 (r2)

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

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

3 In the **Width** text field, type `l6+disp`.

4 In the **Height** text field, type `d4`.

5 Click **Build Selected**.

Rectangle 3 (r3)

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

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

3 In the **Width** text field, type `l5`.

4 In the **Height** text field, type `d5`.

5 Locate the **Position** section. In the **y** text field, type `d2+d4`.

6 Click **Build Selected**.

Rectangle 4 (r4)

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

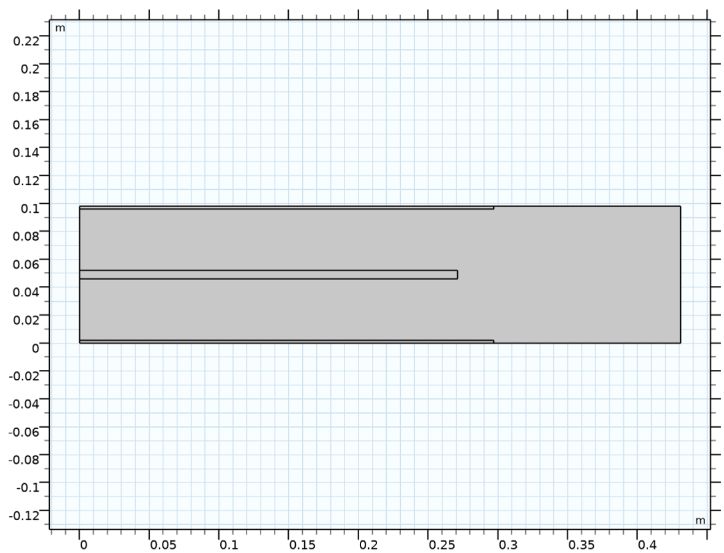
2 In the **Settings** window for **Rectangle**, locate the **Size and Shape** section.

3 In the **Width** text field, type `l6+disp`.

4 In the **Height** text field, type `d4`.

5 Locate the **Position** section. In the **y** text field, type `d4+d1+d5+d2`.

6 Click **Build Selected**.



Rectangle 5 (r5)

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

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

3 In the **Width** text field, type `l2`.

4 In the **Height** text field, type `d3+d4`.

5 Locate the **Position** section. In the **x** text field, type `l6+disp`.

6 Click **Build Selected**.

Rectangle 6 (r6)

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

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

3 In the **Width** text field, type `l4`.

4 In the **Height** text field, type `d5+2*d6`.

5 Locate the **Position** section. In the **x** text field, type `l5`.

6 In the **y** text field, type `d2+d4-d6`.

7 Click **Build Selected**.

Rectangle 7 (r7)

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

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

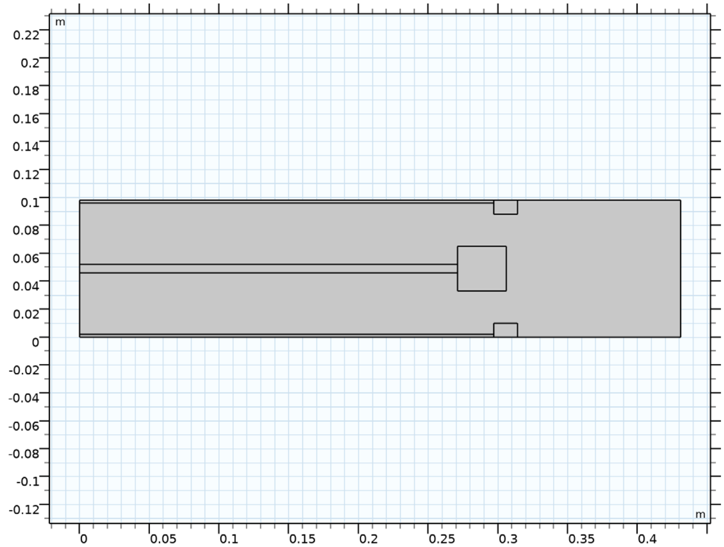
3 In the **Width** text field, type `l2`.

4 In the **Height** text field, type `d3+d4`.

5 Locate the **Position** section. In the **x** text field, type `l6+disp`.

6 In the **y** text field, type `d4+d1+d5+d2-d3`.

7 Click Build Selected.



Difference 1 (dif1)

1 In the **Geometry** toolbar, click **Booleans and Partitions** and choose **Difference**.

2 Select the object **r1** only.

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

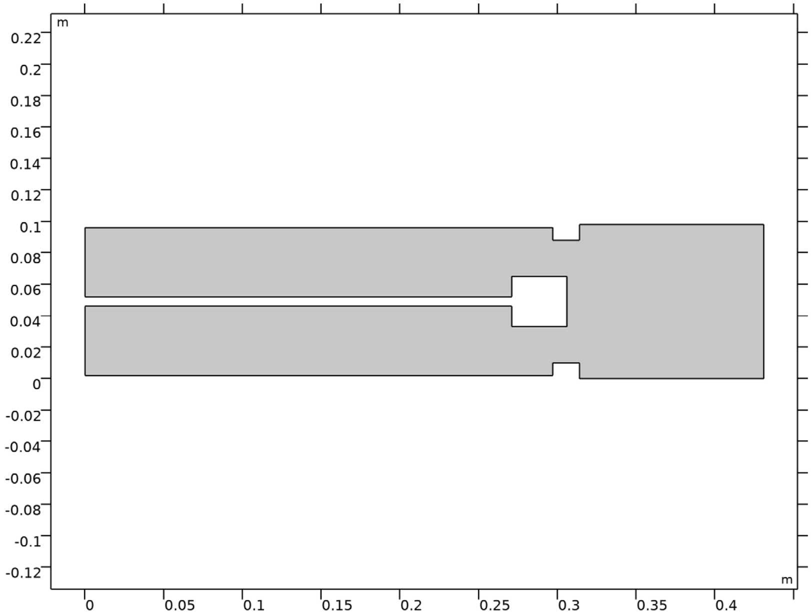
4 Click to select the **Activate Selection** toggle button for **Objects to subtract**.

5 Select the objects **r2**, **r3**, **r4**, **r5**, **r6**, and **r7** only (that is, the other six rectangles).

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

The geometry is now complete.

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



DEFINITIONS

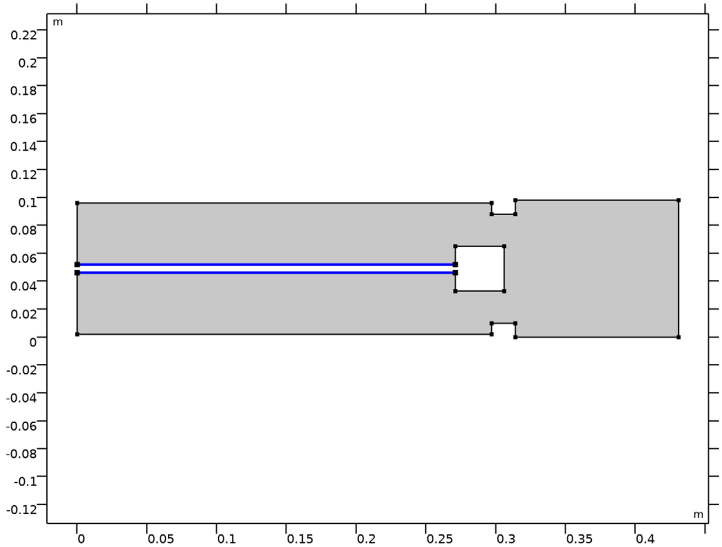
Anode

1 In the **Definitions** toolbar, click  **Explicit**.

2 In the **Settings** window for **Explicit**, type `Anode` in the **Label** text field.

3 Locate the **Input Entities** section. From the **Geometric entity level** list, choose **Boundary**.

4 Select Boundaries 3 and 5 only.



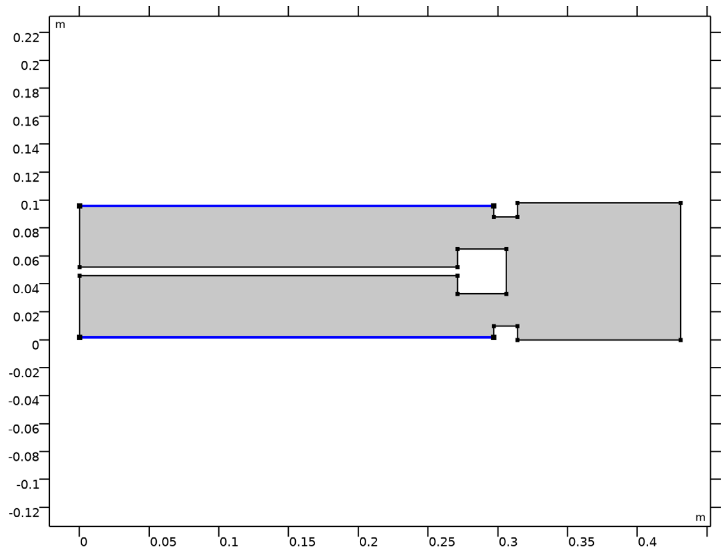
Cathode

1 In the **Definitions** toolbar, click **Explicit**.

2 In the **Settings** window for **Explicit**, type `Cathode` in the **Label** text field.

3 Locate the **Input Entities** section. From the **Geometric entity level** list, choose **Boundary**.

4 Select Boundaries 2 and 6 only.



Integration 1 (intop1)

1 In the **Definitions** toolbar, click **Nonlocal Couplings** and choose **Integration**.

2 In the **Settings** window for **Integration**, locate the **Source Selection** section.

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

4 Select Point 4 only.

SECONDARY CURRENT DISTRIBUTION (CD)

Electrolyte 1

1 In the **Model Builder** window, under **Component 1 (comp1)> Secondary Current Distribution (cd)** click **Electrolyte 1**.

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

3 From the σ_l list, choose **User defined**. In the associated text field, type `sigma_l`.

Electrode Surface 1

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

2 In the **Settings** window for **Electrode Surface**, locate the **Boundary Selection** section.

3 From the **Selection** list, choose **Anode**.

4 Locate the **Electrode Phase Potential Condition** section. In the $\phi_{s,ext}$ text field, type `phisext`.

Oxygen evolution

1 In the **Model Builder** window, under **Component 1 (comp1)>Secondary Current Distribution (cd)>Electrode Surface 1** click **Electrode Reaction 1**.
2 In the **Settings** window for **Electrode Reaction**, type `Oxygen evolution` in the **Label** text field.
3 Locate the **Equilibrium Potential** section. In the E_{eq} text field, type `E_O2`.
4 Locate the **Electrode Kinetics** section. From the **Kinetics expression type** list, choose **Butler-Volmer**.
5 In the i_0 text field, type `i0_O2`.
6 In the α_a text field, type `alphaa_O2`.
7 In the α_c text field, type `alphac_O2`.

Electrode Surface 2

1 In the **Physics** toolbar, click **Boundaries** and choose **Electrode Surface**.
2 In the **Settings** window for **Electrode Surface**, locate the **Boundary Selection** section.
3 From the **Selection** list, choose **Cathode**.

Zinc reaction

1 In the **Model Builder** window, under **Component 1 (comp1)>Secondary Current Distribution (cd)>Electrode Surface 2** click **Electrode Reaction 1**.
2 In the **Settings** window for **Electrode Reaction**, type `Zinc reaction` in the **Label** text field.
3 Locate the **Equilibrium Potential** section. In the E_{eq} text field, type `E_Zn`.
4 Locate the **Electrode Kinetics** section. From the **Kinetics expression type** list, choose **Butler-Volmer**.
5 In the i_0 text field, type `i0_Zn`.
6 In the α_a text field, type `alphaa_Zn`.
7 In the α_c text field, type `alphac_Zn`.

Electrode Surface 2

In the **Model Builder** window, click **Electrode Surface 2**.

Hydrogen evolution

1 In the **Physics** toolbar, click **Attributes** and choose **Electrode Reaction**.
2 In the **Settings** window for **Electrode Reaction**, type `Hydrogen evolution` in the **Label** text field.

3 Locate the **Equilibrium Potential** section. In the E_{eq} text field, type `E_H`.

4 Locate the **Electrode Kinetics** section. From the **Kinetics expression type** list, choose **Butler-Volmer**.

5 In the i_0 text field, type `i0_H`.

Initial Values 1

1 In the **Model Builder** window, under **Component 1 (comp1)> Secondary Current Distribution (cd)** click **Initial Values 1**.

2 In the **Settings** window for **Initial Values**, locate the **Initial Values** section.

3 In the *phil* text field, type `1`.

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`.

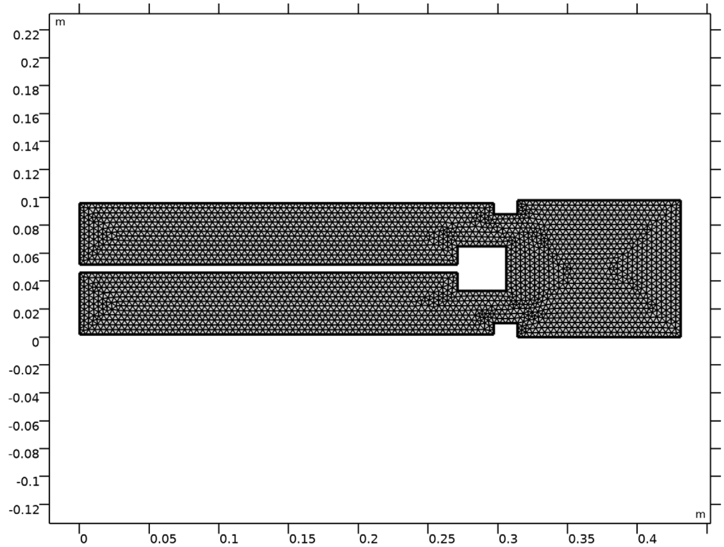
MESH 1

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

2 In the **Settings** window for **Mesh**, locate the **Physics-Controlled Mesh** section.

3 From the **Element size** list, choose **Extremely fine**.

4 Click **Build All**.



STUDY 1

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
disp (Cathode displacement in parametric sweep)	`0.04 0.02 0 -0.01 -0.02 -0.04 -0.06`	`m`

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

RESULTS

Electrolyte Potential (cd)

The default plot shows the electrolyte potential for the last displacement value in the sweep, that is -60 mm. Compare the plot in the **Graphics** window with that in Figure 2. Visualize the potential for the displacement +40 mm as follows:

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

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

3 From the **Parameter value (disp (m))** list, choose **0.04**.

4 In the **Electrolyte Potential (cd)** toolbar, click **Plot**.

Compare the result with that in Figure 3.

2D Plot Group 5

Next, visualize the electrolyte current density field for the same two displacement values in a combined surface and streamline plot.

1 In the **Home** toolbar, click **Add Plot Group** and choose **2D Plot Group**.

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

3 From the **Dataset** list, choose **Study 1/Parametric Solutions 1 (sol2)**.

Surface 1

1 Right-click **2D Plot Group 5** and choose **Surface**.

2 In the **Settings** window for **Surface**, click **Replace Expression** in the upper-right corner of the **Expression** section. From the menu, choose **Component 1 (comp1)> Secondary Current Distribution>cd.IlMag - Electrolyte current density magnitude - A/m²**.

Streamline 1

1 In the **Model Builder** window, right-click **2D Plot Group 5** and choose **Streamline**.

2 In the **Settings** window for **Streamline**, click **Replace Expression** in the upper-right corner of the **Expression** section. From the menu, choose **Component 1 (comp1)> Secondary Current Distribution>cd.Ilx,cd.Ily - Electrolyte current density vector**.

3 Select Boundaries 3 and 5 only.

Electrolyte Current Density

1 In the **Model Builder** window, click **2D Plot Group 5**.

2 In the **2D Plot Group 5** toolbar, click **Plot**.

Compare the resulting plot with that in Figure 4.

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

4 From the **Parameter value (disp (m))** list, choose **0.04**.

5 In the **2D Plot Group 5** toolbar, click **Plot**.

Compare the result with the plot in Figure 5.

6 In the **Label** text field, type `Electrolyte Current Density`.

Electrode Current Density Distribution

Finally, reproduce the plot of the current density distribution at the cathode shown in Figure 6.

1 In the **Home** toolbar, click **Add Plot Group** and choose **1D Plot Group**.
2 In the **Settings** window for **1D Plot Group**, type `Electrode Current Density Distribution` in the **Label** text field.
3 Locate the **Data** section. From the **Dataset** list, choose **Study 1/ Parametric Solutions 1 (sol2)**.
4 Click to expand the **Title** section. From the **Title type** list, choose **Manual**.
5 In the **Title** text area, type `Electrode current density distribution for different cathode displacements`.
6 Locate the **Plot Settings** section.
7 Select the **y-axis label** check box. In the associated text field, type `Electrode current density (Normalized at x=0)`.

Line Graph 1

1 Right-click **Electrode Current Density Distribution** and choose **Line Graph**.
2 Select Boundary 6 only.
3 In the **Settings** window for **Line Graph**, locate the **y-Axis Data** section.
4 In the **Expression** text field, type `cd.itot/comp1.intop1(cd.itot)`.
5 Locate the **x-Axis Data** section. From the **Parameter** list, choose **Expression**.
6 In the **Expression** text field, type `x`.
7 Click to expand the **Legends** section. Select the **Show legends** check box.
8 In the **Electrode Current Density Distribution** toolbar, click **Plot**.