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 for the cell in order 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.

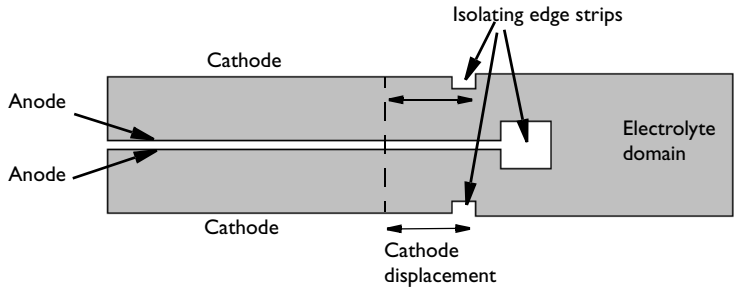


Figure 1: Modeled geometry.

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

$$\mathrm{Zn}^{2+} + 2e^- \Leftrightarrow \mathrm{Zn}(s) \tag{1}$$

Hydrogen evolution may also occur at the cathode according to

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

On the anode, oxygen is evolved:

$$\mathrm{H}_2\mathrm{O} \Leftrightarrow \frac{1}{2}\mathrm{O}_2 + 2\mathrm{H}^+ + 2e^- \tag{3}$$

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

$$i = i_0\left(\exp\left(\frac{\alpha_a F\eta}{RT}\right) - \exp\left(\frac{-\alpha_c F\eta}{RT}\right)\right) \tag{4}$$

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

$$\eta = \phi_s - \phi_l - E_{\mathrm{eq}} \tag{5}$$

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

$$\begin{aligned} E_{\mathrm{eq}}(\mathrm{Zn}^{2+}/\mathrm{Zn}) &= E^0(\mathrm{Zn}^{2+}/\mathrm{Zn}) - \frac{RT}{2F}\ln\frac{a_{\mathrm{Zn}}}{a_{\mathrm{Zn}^{2+}}} = -0{,}797\ \mathrm{V} \\ E_{\mathrm{eq}}\left(\mathrm{H}^+/\frac{1}{2}\mathrm{H}_2\right) &= 0 - \frac{RT}{F}\ln\frac{a_{\mathrm{H}_2}^{0,5}}{a_{\mathrm{H}^+}} = 0{,}016\ V \\ E_{\mathrm{eq}}(\mathrm{O}_2/\mathrm{H}_2\mathrm{O}) &= E^0(\mathrm{O}_2/\mathrm{H}_2\mathrm{O}) - \frac{RT}{2F}\ln\frac{a_{\mathrm{H}_2\mathrm{O}}}{a_{\mathrm{O}_2}^{0,5}a_{\mathrm{H}^+}^2} = 1{,}247\ V \end{aligned} \tag{6}$$

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 a Electrolyte-Electrode Boundary interface and the above electrode reactions, setting the electric potential to 0 V at the anode and a cell voltage of 3.597 V at the cathode. All other boundaries are isolated.

Results and Discussion

Figures 2 and 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.

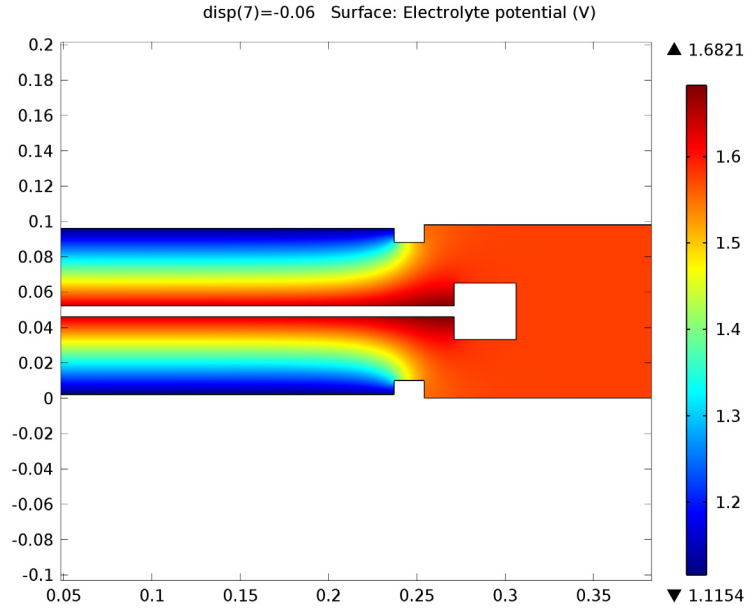


Figure 2: Electrolyte potential distribution for a cathode displacement of -60 mm.

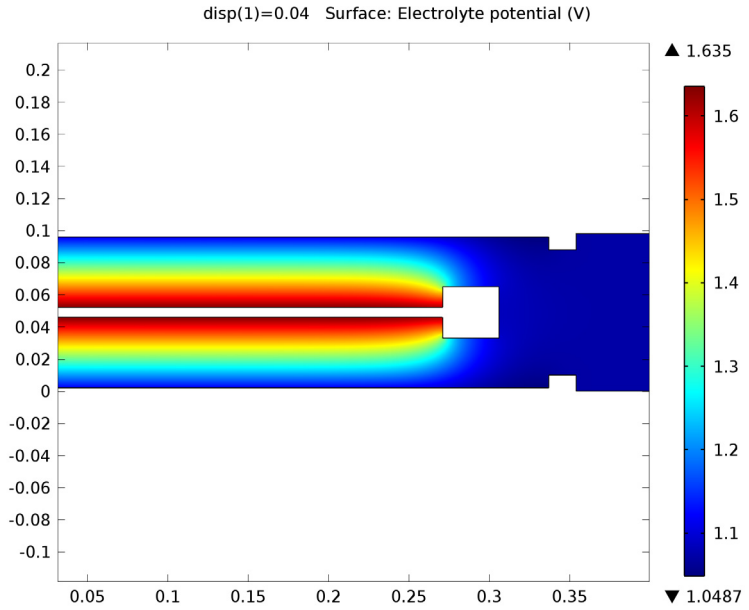


Figure 3: Electrolyte potential distribution for a cathode displacement of +40 mm.

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

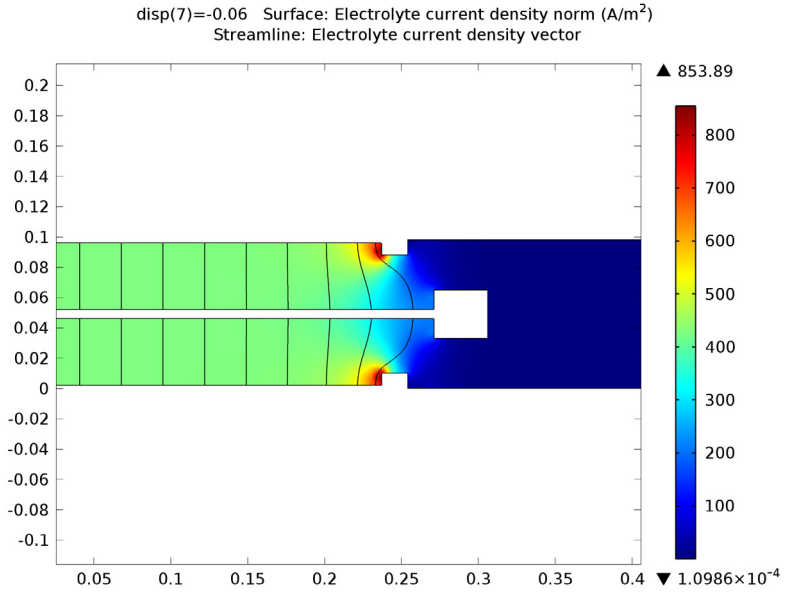


Figure 4: Electrolyte current density distribution for a cathode displacement of -60 mm.

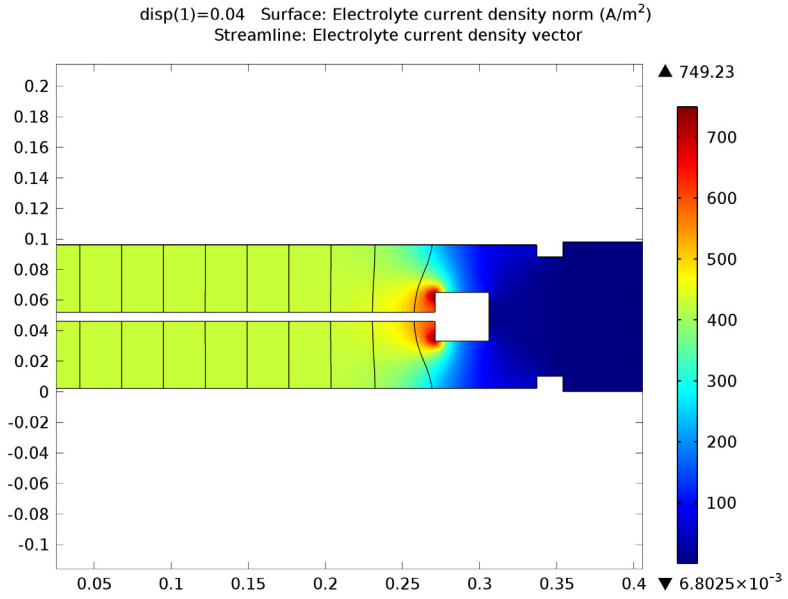


Figure 5: Electrolyte current density distribution for a cathode displacement of +40 mm.

Figure 6 shows 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.

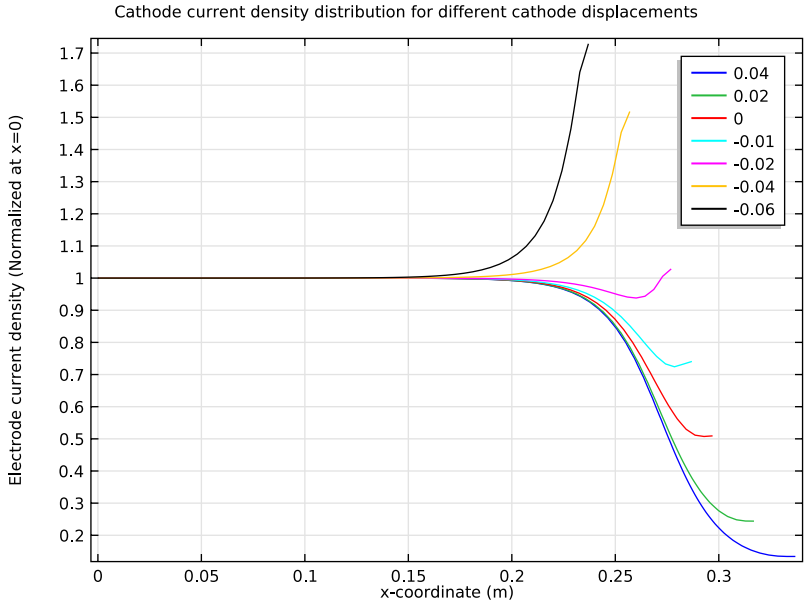


Figure 6: Electrode density at the cathode for different cathode displacements normalized to the electrode density at x = 0.

Reference

1. K. Bouzek and others, "Current Distribution at the Electrodes in Zinc Electrowinning Cells," *Journal of the Electrochemical Society*, vol. 142, no. 1, 1995.

Model Library path: `Electrodeposition_Module/Verification_Models/zn_electrowinning`

Modeling Instructions

MODEL WIZARD

1 Go to the **Model Wizard** window.

2 Click the **2D** button.

3 Click **Next**.

4 In the **Add physics** tree, select **Electrochemistry>Secondary Current Distribution (siec)**.

5 Click **Add Selected**.

6 Click **Next**.

7 Find the **Studies** subsection. In the tree, select **Preset Studies>Stationary**.

8 Click **Finish**.

GLOBAL DEFINITIONS

Parameters

1 In the **Model Builder** window, right-click **Global Definitions** and choose **Parameters**.

2 In the **Parameters** settings window, locate the **Parameters** section.

3 Click **Load from File**.

4 Browse to the model's Model Library folder and double-click the file `zn_electrowinning_parameters.txt`.

GEOMETRY 1

Rectangle 1

1 In the **Model Builder** window, under **Model 1** right-click **Geometry 1** and choose **Rectangle**.

2 In the **Rectangle** settings window, locate the **Size** section.

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

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

5 Click the **Build Selected** button.

Rectangle 2

1 In the **Model Builder** window, right-click **Geometry 1** and choose **Rectangle**.

2 In the **Rectangle** settings window, locate the **Size** section.

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

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

5 Click the **Build Selected** button.

Rectangle 3

1 Right-click **Geometry 1** and choose **Rectangle**.

2 In the **Rectangle** settings window, locate the **Size** section.

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

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

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

6 Click the **Build Selected** button.

Rectangle 4

1 Right-click **Geometry 1** and choose **Rectangle**.

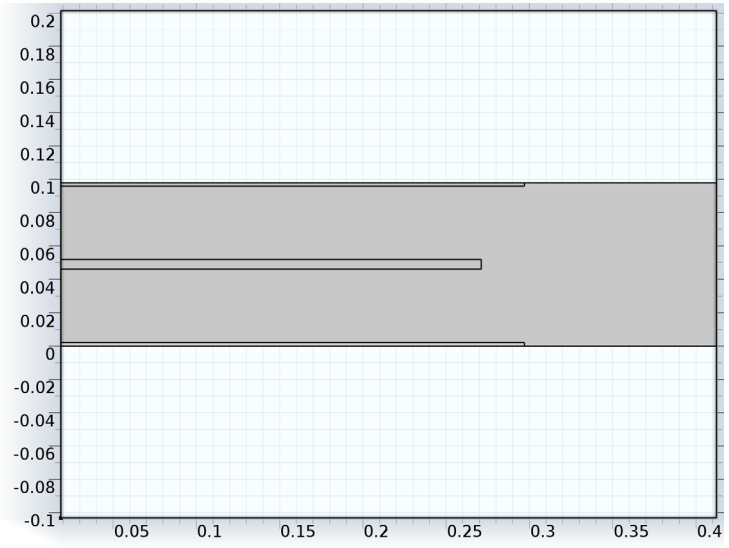
2 In the **Rectangle** settings window, locate the **Size** section.

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

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

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

6 Click the **Build Selected** button.



Rectangle 5

1 Right-click **Geometry 1** and choose **Rectangle**.

2 In the **Rectangle** settings window, locate the **Size** section.

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

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

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

6 Click the **Build Selected** button.

Rectangle 6

1 Right-click **Geometry 1** and choose **Rectangle**.

2 In the **Rectangle** settings window, locate the **Size** section.

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

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

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

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

7 Click the **Build Selected** button.

Rectangle 7

1 Right-click **Geometry 1** and choose **Rectangle**.

2 In the **Rectangle** settings window, locate the **Size** section.

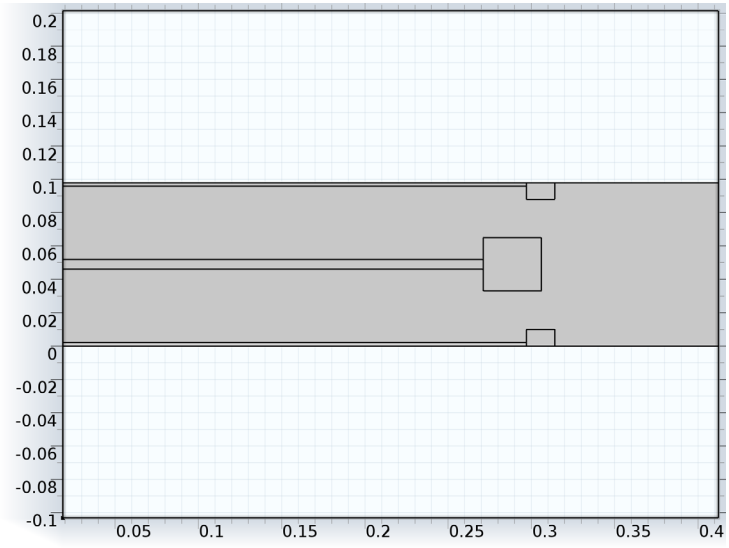
3 In the **Width** edit field, type `l2`.

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

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

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

7 Click the **Build Selected** button.



Difference 1

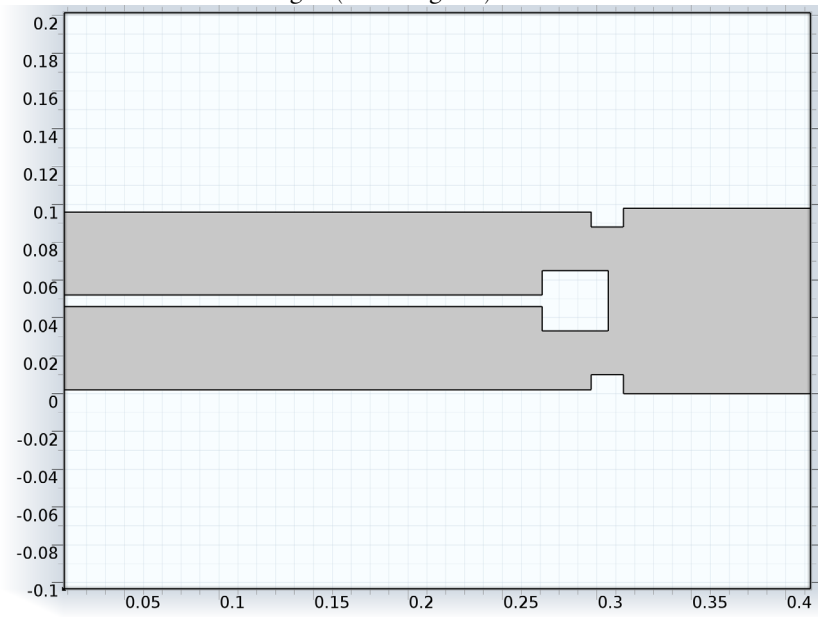
1 Right-click **Geometry 1** and choose **Boolean Operations>Difference**.

2 Select the object **r1** only.

3 In the **Difference** settings window, locate the **Difference** section.

4 Under **Objects to subtract**, click **Activate Selection**.

5 Select the other six rectangles (**r2** through **r7**).



DEFINITIONS

Explicit 1

1 In the **Model Builder** window, under **Model 1** right-click **Definitions** and choose **Selections>Explicit**.

2 Right-click **Explicit 1** and choose **Rename**.

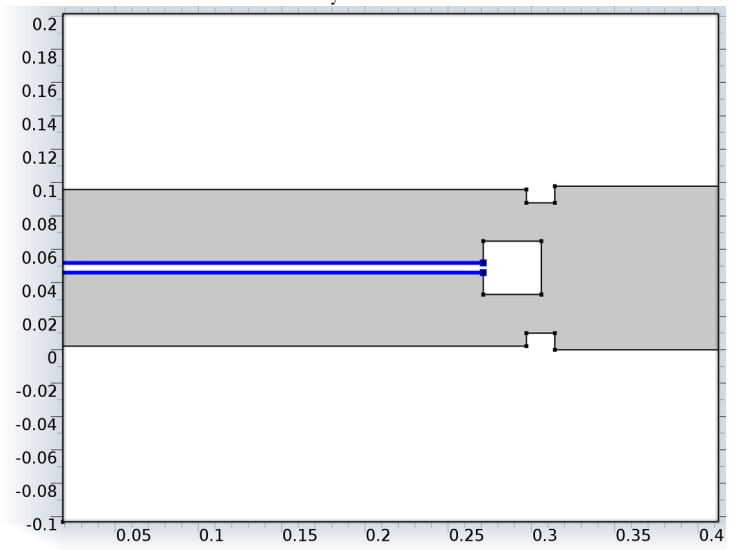
3 Go to the **Rename Explicit** dialog box and type `Anode` in the **New name** edit field.

4 Click **OK**.

5 In the **Explicit** settings window, locate the **Input Entities** section.

6 From the **Geometric entity level** list, choose **Boundary**.

7 Select Boundaries 3 and 5 only.



Explicit 2

1 In the **Model Builder** window, right-click **Definitions** and choose **Selections>Explicit**.

2 Right-click **Explicit 2** and choose **Rename**.

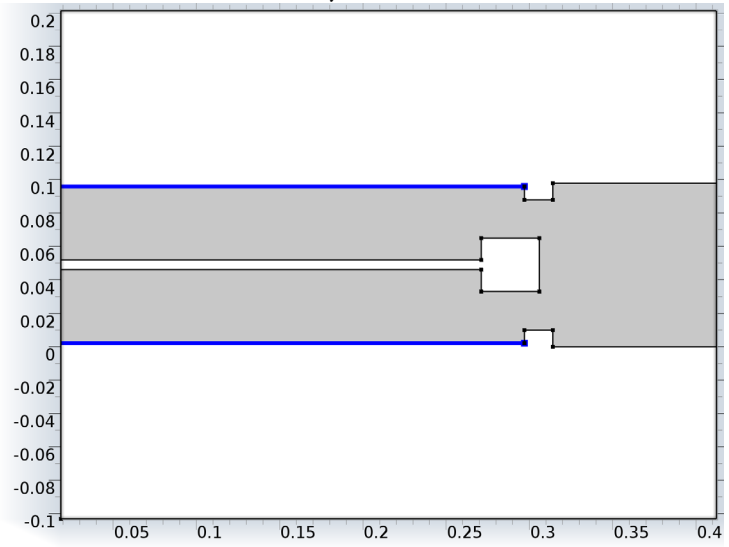
3 Go to the **Rename Explicit** dialog box and type `Cathode` in the **New name** edit field.

4 Click **OK**.

5 In the **Explicit** settings window, locate the **Input Entities** section.

6 From the **Geometric entity level** list, choose **Boundary**.

7 Select Boundaries 2 and 6 only.



Integration 1

1 In the **Model Builder** window, right-click **Definitions** and choose **Model Couplings>Integration**.

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

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

4 Select Point 4 only.

SECONDARY CURRENT DISTRIBUTION

Electrolyte 1

1 In the **Model Builder** window, expand the **Model 1>Secondary Current Distribution** node, then click **Electrolyte 1**.

2 In the **Electrolyte** settings window, locate the **Electrolyte** section.

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

Electrolyte-Electrode Boundary Interface 1

1 In the **Model Builder** window, right-click **Secondary Current Distribution** and choose **Electrolyte>Electrolyte-Electrode Boundary Interface**.

2 In the **Electrolyte-Electrode Boundary Interface** settings window, locate the **Boundary Selection** section.

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

4 Locate the **Boundary Condition** section. In the $\phi_{s,ext}$ edit field, type `3.597`.

Electrode Reaction 1

1 In the **Model Builder** window, expand the **Electrolyte-Electrode Boundary Interface 1** node.

2 Right-click **Electrode Reaction 1** and choose **Rename**.

3 Go to the **Rename Electrode Reaction** dialog box and type `Oxygen evolution` in the **New name** edit field.

4 Click **OK**.

5 In the **Electrode Reaction** settings window, locate the **Model Inputs** section.

6 In the T edit field, type `T`.

7 Locate the **Equilibrium Potential** section. In the $E_{eq,ref}$ edit field, type `E_02`.

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

9 In the i_0 edit field, type `0.0089[A/m^2]`.

10 In the α_a edit field, type `0.4`.

11 In the α_c edit field, type `1.6`.

Electrolyte-Electrode Boundary Interface 2

1 In the **Model Builder** window, right-click **Secondary Current Distribution** and choose **Electrolyte>Electrolyte-Electrode Boundary Interface**.

2 In the **Electrolyte-Electrode Boundary Interface** settings window, locate the **Boundary Selection** section.

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

Electrode Reaction 1

1 In the **Model Builder** window, expand the **Electrolyte-Electrode Boundary Interface 2** node.

2 Right-click **Electrode Reaction 1** and choose **Rename**.

3 Go to the **Rename Electrode Reaction** dialog box and type `Zinc reaction` in the **New name** edit field.

4 Click **OK**.

5 In the **Electrode Reaction** settings window, locate the **Model Inputs** section.

6 In the T edit field, type `T`.

7 Locate the **Equilibrium Potential** section. In the $E_{\mathrm{eq},ref}$ edit field, type `E_Zn`.

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

9 In the i_0 edit field, type `0.0291[A/m^2]`.

10 In the α_a edit field, type `1.2`.

11 In the α_c edit field, type `0.8`.

Electrode Reaction 2

1 In the **Model Builder** window, under **Model 1>Secondary Current Distribution** right-click **Electrolyte-Electrode Boundary Interface 2** and choose **Electrode Reaction**.

2 Right-click **Electrode Reaction 2** and choose **Rename**.

3 Go to the **Rename Electrode Reaction** dialog box and type `Hydrogen evolution` in the **New name** edit field.

4 Click **OK**.

5 In the **Electrode Reaction** settings window, locate the **Model Inputs** section.

6 In the T edit field, type `T`.

7 Locate the **Equilibrium Potential** section. In the $E_{\mathrm{eq},ref}$ edit field, type `E_H`.

8 Locate the **Electrode Kinetics** section. In the i_0 edit field, type `3.72e-10[A/m^2]`.

9 From the **Kinetics expression type** list, choose **Butler-Volmer**.

Initial Values 1

1 In the **Initial Values** settings window, locate the **Initial Values** section.

2 In the *phil* edit field, type `1`.

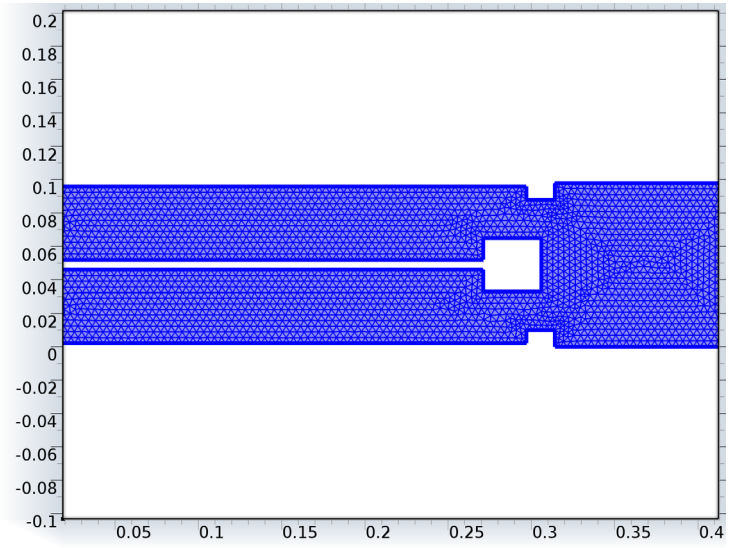
MESH 1

1 In the **Model Builder** window, under **Model 1** click **Mesh 1**.

2 In the **Mesh** settings window, locate the **Mesh Settings** section.

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

4 Click the **Build All** button.



STUDY 1

Parametric Sweep

1 In the **Model Builder** window, right-click **Study 1** and choose **Parametric Sweep**.

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

3 Click **Add**.

4 In the table, enter the following settings:

Parameter names	Parameter value list
disp	0.04 0.02 0 -0.01 -0.02 -0.04 -0.06

5 Right-click **Study 1** and choose **Compute**.

RESULTS

Electrolyte Potential (siec)

- 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 In the **2D Plot Group** settings window, locate the **Data** section.

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

3 Click the **Plot** button.

Compare the result with that in Figure 3.

2D Plot Group 2

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

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

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

3 From the **Data set** list, choose **Solution 2**.

4 Right-click **Results>2D Plot Group 2** and choose **Surface**.

5 In the **Surface** settings window, click **Replace Expression** in the upper-right corner of the **Expression** section. From the menu, choose **Secondary Current Distribution>Electrolyte current density norm (siec.Normll)**.

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

7 In the **Streamline** settings window, click **Replace Expression** in the upper-right corner of the **Expression** section. From the menu, choose **Secondary Current Distribution>Electrolyte current density vector (siec.llx,...,siec.lly)**.

8 Select Boundaries 3 and 5 only.

9 Right-click **2D Plot Group 2** and choose **Plot**.

Compare the resulting plot with that inFigure 4.

10 In the **2D Plot Group** settings window, locate the **Data** section.

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

12 Click the **Plot** button.

Compare the result with the plot in Figure 5.

13 Right-click **2D Plot Group 2** and choose **Rename**.

14 Go to the **Rename 2D Plot Group** dialog box and type `Electrolyte current density` in the **New name** edit field.

15 Click **OK**.

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

1D Plot Group 3

1 Right-click **Results** and choose **1D Plot Group**.

2 In the **1D Plot Group** settings window, locate the **Data** section.

3 From the **Data set** list, choose **Solution 2**.

4 Locate the **Title** section. From the **Title type** list, choose **Manual**.

5 In the **Title** text area, type `Cathode current density distribution for different cathode displacements`.

6 Locate the **Plot Settings** section. Select the **y-axis label** check box.

7 In the associated edit field, type `Electrode current density (Normalized at x=0)`.

8 Right-click **Results>1D Plot Group 3** and choose **Line Graph**.

9 Select Boundary 6 only.

10 In the **Line Graph** settings window, locate the **y-Axis Data** section.

11 In the **Expression** edit field, type `siec.itot/mod1.intop1(siec.itot)`.

12 Locate the **x-Axis Data** section. From the **Parameter** list, choose **Expression**.

13 In the **Expression** edit field, type `x`.

14 Click to expand the **Legends** section. Select the **Show legends** check box.

15 Click the **Plot** button.

16 Right-click **Results>1D Plot Group 3>Line Graph 1** and choose **Rename**.

17 Go to the **Rename Line Graph** dialog box and type `Cathode current distribution` in the **New name** edit field.

18 Click **OK**.