Orange Battery

Introduction

This tutorial example serves as an introduction to electrochemistry modeling in COMSOL, and models the currents and the concentration of dissolved metal ions in a battery (corrosion cell) made from an orange and two metal nails.

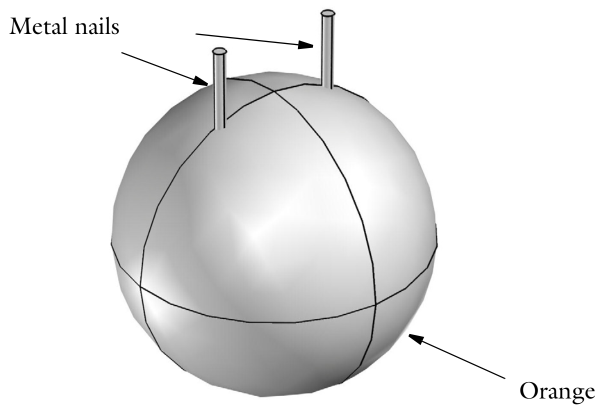

Figure 1: Modeled geometry. Orange and two metal nails.

This type of battery is commonly used in chemistry class tuition. Instead of an orange, also lemons or potatoes can be used.

Model Definition

The citric acid and various other ions in the orange serves as electrolyte, and using nails of different metals as electrodes creates a galvanic potential over the cell.

In this example a zinc nail is used as one of the electrodes, giving rise to the following electrode reaction:

$$\mathrm{Zn}(s) \rightarrow \mathrm{Zn}^{2+} + 2e^{-} \qquad E_0 = -0.82\,V \tag{1}$$

The other nail consists of copper, and here hydrogen evolution is assumed to take place:

$$2H^{+} + 2e^{-} \rightarrow H_2(g) \qquad E_0 = 0\,V \tag{2}$$

The model for the currents in the orange and electrodes is set up using the Secondary Current Distribution interface. The electric currents in the nails, and the electrolyte current in the orange is thereby solved for by Ohms law. One nail is grounded and the other one is set to a cell potential of 0.5 V. Butler-Volmer type expressions are used for the electrode kinetics on the surface of the nails within the orange.

The initial values for the electric potential in the electrodes is set to the values at the end terminals; ground (0 V) for the zinc electrode, and the cell potential for the copper electrode. For the electrolyte potential the initial value is set to correspond to the potential of a cell at open circuit (i.e. no activation potential). Following the definition of the overpotential:

$$\eta = \phi_s - \phi_l - E_0 \tag{3}$$

the initial value becomes:

$$\phi_{l,\,\mathrm{init}} = \phi_s - E_0 - \eta = 0 - E_{0,\,\mathrm{Zn}} - 0 = -E_{0,\,\mathrm{Zn}} \tag{4}$$

In an extension of the model the diffusion and migration of the dissolved zinc ions in the orange from the zinc electrode reaction is modeled by the Transport of Diluted Species interface in a time-dependent simulation. This assumes that the zinc ion transport can be described by the Nernst-Planck equations (without an electroneutrality condition due to a supporting electrolyte). Also the zinc electrode kinetics are modified to be dependent on the zinc concentration, which increases in the orange as more and more zinc is dissolved.

The zinc concentration is set to 0.01 mol/m^3 at the start of the simulation. All boundaries except the zinc electrode are isolated.

Results and Discussion

Figure 2 shows the potential field in the orange. The potential decreases as the current flows from the zinc electrode (left) to the upper electrode (right). The main part of the cell voltage loss is due to Ohmic losses in the electrolyte.

The performance of the battery could probably be increased by using an electrolyte of higher conductivity (for example, a lemon instead of an orange) or by decreasing the distance between the nails.

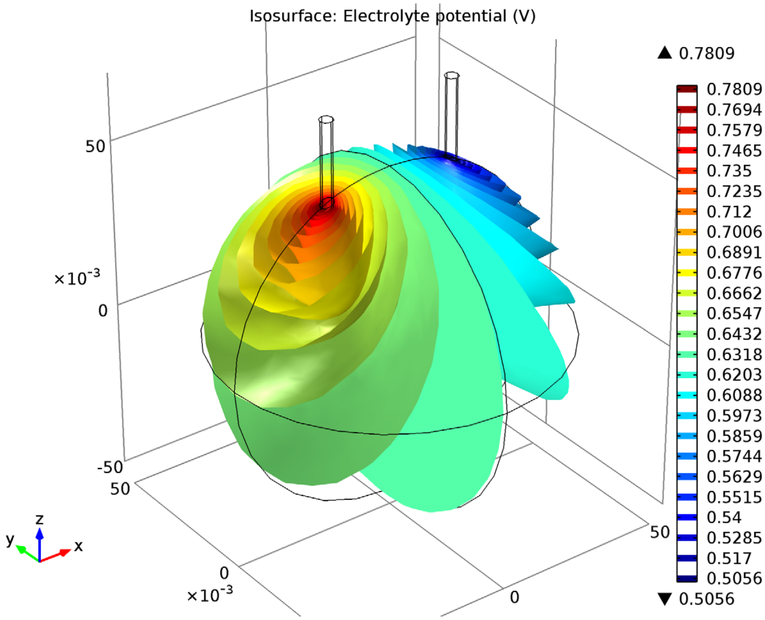

Figure 2: Potential field in the electrolyte.

Figure 3 shows the electric currents in the nails. The current increases along the z-axis as more and more current is transferred from the electrolyte to the electrodes.

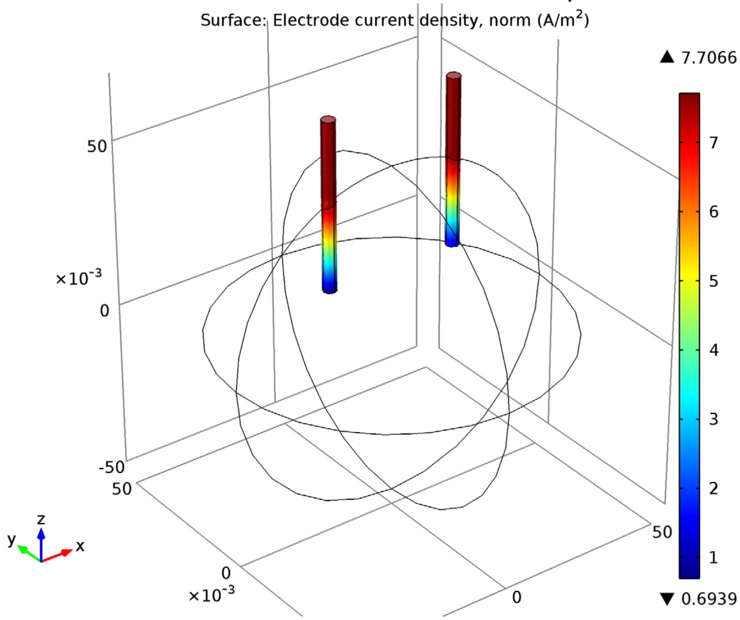

Figure 3: Electric currents in the nails.

Figure 4 shows an isosurface for the 0.2 mol/m^3 concentration level of zinc ions after running the battery for 5 minutes. Figure 5 shows the how far the 0.2 mol/m^3 level has reached after 1 hour.

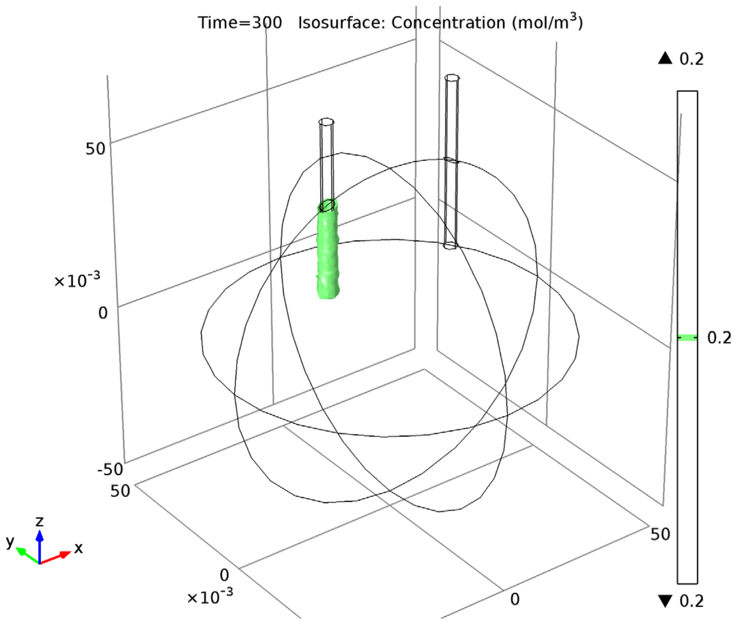

Figure 4: 0.2 mol/m^3 zinc concentration isosurface after 5 minutes.

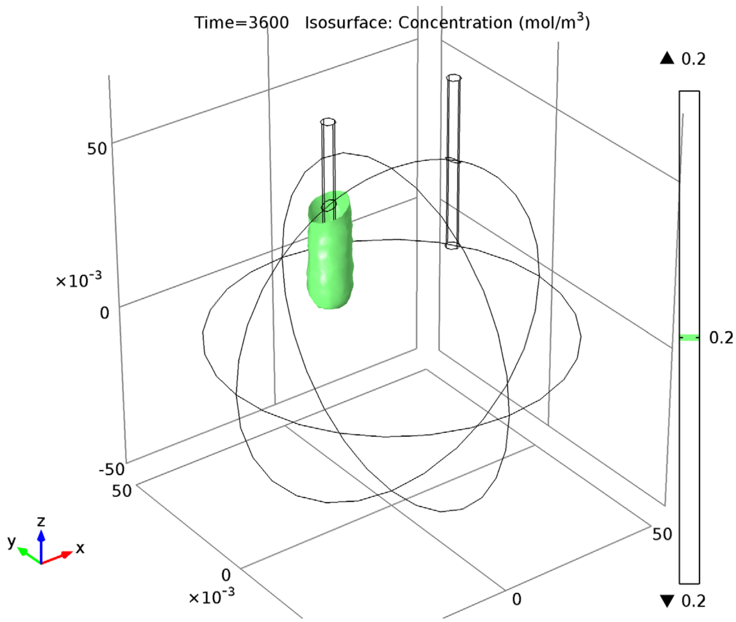

Figure 5: 0.2 mol/m^3 zinc concentration isosurface after 1 hour.

Finally, Figure 6 shows how the cell current evolves with time. Due to the increase of zinc ions at the zinc nail electrode, the battery current decreases for a constant cell voltage.

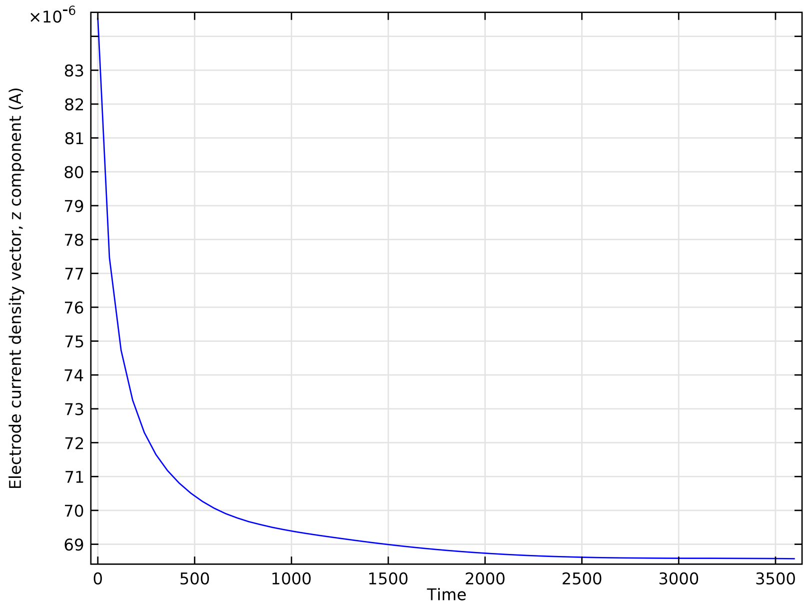

Figure 6: Cell current vs. time.

Model Library path: `Electrochemistry_Module/Tutorial_Models/orange_battery`

Modeling Instructions

MODEL WIZARD

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

2 Click **Next**.

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

4 Click **Add Selected**.

5 Click **Next**.

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

7 Click **Finish**.

GEOMETRY 1

Start by drawing the geometry; one sphere (the orange) and two cylinders (the metal nails).

Sphere 1

1. In the **Model Builder** window, under **Model 1** right-click **Geometry 1** and choose **Sphere**.
2. In the **Sphere** settings window, locate the **Size and Shape** section.
3. In the **Radius** edit field, type `5e-2`.

Cylinder 1

1. In the **Model Builder** window, right-click **Geometry 1** and choose **Cylinder**.
2. In the **Cylinder** settings window, locate the **Size and Shape** section.
3. In the **Radius** edit field, type `2e-3`.
4. In the **Height** edit field, type `5e-2`.
5. Locate the **Position** section. In the **x** edit field, type `-2e-2`.
6. In the **z** edit field, type `2e-2`.

Cylinder 2

1. Right-click **Geometry 1** and choose **Cylinder**.
2. In the **Cylinder** settings window, locate the **Size and Shape** section.
3. In the **Radius** edit field, type `2e-3`.
4. In the **Height** edit field, type `5e-2`.
5. Locate the **Position** section. In the **x** edit field, type `2e-2`.
6. In the **z** edit field, type `2e-2`.

DEFINITIONS

Use selections to group different parts of the geometry together for easier selection when setting up the model.

Explicit 1

1. In the **Model Builder** window, under **Model 1** right-click **Definitions** and choose **Selections>Explicit**.
2. Select Domain 1 only.
3. Right-click **Model 1>Definitions>Explicit 1** and choose **Rename**.
4. Go to the **Rename Explicit** dialog box and type `Orange` in the **New name** edit field.
5. Click **OK**.

Explicit 2

1 Right-click **Definitions** and choose **Selections>Explicit**.

Enabling transparency makes it easier to find and select objects within other objects.

2 Click the **Transparency** button on the Graphics toolbar.

3 Select Domains 2 and 3 only.

4 Right-click **Model 1>Definitions>Explicit 2** and choose **Rename**.

5 Go to the **Rename Explicit** dialog box and type `Zinc nail` in the **New name** edit field.

6 Click **OK**.

Explicit 3

1 Right-click **Definitions** and choose **Selections>Explicit**.

2 Select Domains 4 and 5 only.

3 Right-click **Model 1>Definitions>Explicit 3** and choose **Rename**.

4 Go to the **Rename Explicit** dialog box and type `Copper nail` in the **New name** edit field.

5 Click **OK**.

Explicit 4

1 Right-click **Definitions** and choose **Selections>Explicit**.

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

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

4 Select Boundaries 5–7, 13, and 15 only.

5 Right-click **Model 1>Definitions>Explicit 4** and choose **Rename**.

6 Go to the **Rename Explicit** dialog box and type `Zinc nail active electrode surface` in the **New name** edit field.

7 Click **OK**.

Explicit 5

1 Right-click **Definitions** and choose **Selections>Explicit**.

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

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

4 Select Boundaries 21–23, 29, and 31 only.

5 Right-click **Model 1>Definitions>Explicit 5** and choose **Rename**.

6 Go to the **Rename Explicit** dialog box and type `Copper nail active electrode surface` in the **New name** edit field.

7 Click **OK**.

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 In the table, enter the following settings:

Name	**Expression**	**Description**
`E_eq_Zn`	`-0.82[V]`	`Zinc electrode reference potential`
`E_cell`	`0.5[V]`	`Cell voltage`

SECONDARY CURRENT DISTRIBUTION

Now, start setting up the Secondary Current Distribution model. Start with the current conduction in the metal nails.

Electrode 1

1 In the **Model Builder** window, under **Model 1** right-click **Secondary Current Distribution** and choose **Electrode**.

2 In the **Electrode** settings window, locate the **Domain Selection** section.

3 From the **Selection** list, choose **Zinc nail**.

4 Locate the **Electrode** section. From the σ_s list, choose **User defined**. In the associated edit field, type `1e7`.

Electrode 2

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

2 In the **Electrode** settings window, locate the **Domain Selection** section.

3 From the **Selection** list, choose **Copper nail**.

4 Locate the **Electrode** section. From the σ_s list, choose **User defined**. In the associated edit field, type `1e8`.

Electrolyte 1

The Electrolyte is the default domain type, and there is no need to select the domain in this case.

1 In the **Model Builder** window, under **Model 1>Secondary Current Distribution** 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 `0.01`.

The following steps set up the Zn electrode surface and its corresponding electrode reaction:

Electrolyte-Electrode Domain Interface 1

1 In the **Model Builder** window, right-click **Secondary Current Distribution** and choose **Electrolyte>Electrolyte-Electrode Domain Interface**.
2 In the **Electrolyte-Electrode Domain Interface** settings window, locate the **Boundary Selection** section.
3 From the **Selection** list, choose **Zinc nail active electrode surface**.

Electrode Reaction 1

1 In the **Model Builder** window, expand the **Electrolyte-Electrode Domain Interface 1** node, then click **Electrode Reaction 1**.
2 In the **Electrode Reaction** settings window, locate the **Equilibrium Potential** section.
3 In the $E_{\mathrm{eq},ref}$ edit field, type `E_eq_Zn`.
4 Locate the **Electrode Kinetics** section. From the **Kinetics expression type** list, choose **Butler-Volmer**.
5 In the i_0 edit field, type `1e-1`.

The following steps set up the hydrogen evolution reaction on the copper electrode:

Electrolyte-Electrode Domain Interface 2

1 In the **Model Builder** window, right-click **Secondary Current Distribution** and choose **Electrolyte>Electrolyte-Electrode Domain Interface**.
2 In the **Electrolyte-Electrode Domain Interface** settings window, locate the **Boundary Selection** section.
3 From the **Selection** list, choose **Copper nail active electrode surface**.

Electrode Reaction 1

1 In the **Model Builder** window, expand the **Electrolyte-Electrode Domain Interface 2** node, then click **Electrode Reaction 1**.
2 In the **Electrode Reaction** settings window, locate the **Electrode Kinetics** section.
3 In the i_0 edit field, type `10`.

Ground the Zn electrode, set the other electrode to the cell voltage.

Electric Ground 1

1 In the **Model Builder** window, right-click **Secondary Current Distribution** and choose **Electrode>Electric Ground**.

2 Select Boundary 12 only.

Electric Potential 1

1 Right-click **Secondary Current Distribution** and choose **Electrode>Electric Potential**.

2 Select Boundary 28 only.

3 In the **Electric Potential** settings window, locate the **Electric Potential** section.

4 In the $\phi_{s,bnd}$ edit field, type `E_cell`.

Provide as good initial values as possible to shorten the computing time.

Initial Values 2

1 Right-click **Secondary Current Distribution** and choose **Initial Values**.

2 In the **Initial Values** settings window, locate the **Domain Selection** section.

3 From the **Selection** list, choose **Copper nail**.

4 Locate the **Initial Values** section. In the *phis* edit field, type `E_cell`.

Initial Values 1

1 In the **Model Builder** window, under **Model 1>Secondary Current Distribution** click **Initial Values 1**.

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

3 In the *phil* edit field, type `-E_eq_Zn`.

The model is now ready for solving.

STUDY 1

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

RESULTS

Use an isosurface for visualizing the potential field in the electrolyte.

1 Click the **Transparency** button on the Graphics toolbar.

3D Plot Group 3

1 In the **Model Builder** window, right-click **Results** and choose **3D Plot Group**.

2 Right-click **3D Plot Group 3** and choose **Rename**.

3 Go to the **Rename 3D Plot Group** dialog box and type `Potential Isosurface` in the **New name** edit field.

4 Click **OK**.

Potential Isosurface

1 Right-click **Results>3D Plot Group 3** and choose **Isosurface**.
2 In the **Isosurface** settings window, locate the **Levels** section.
3 In the **Total levels** edit field, type `25`.
4 Click the **Plot** button.
5 Click the **Zoom Extents** button on the Graphics toolbar.

The following steps create a plot of the norm of the current density that is suitable here to visualize the currents within the metal nails.

3D Plot Group 4

1 In the **Model Builder** window, right-click **Results** and choose **3D Plot Group**.
2 Right-click **3D Plot Group 4** and choose **Rename**.
3 Go to the **Rename 3D Plot Group** dialog box and type `Electrode Current` in the **New name** edit field.
4 Click **OK**.

Electrode Current

1 Right-click **Results>3D Plot Group 4** and choose **Surface**.
2 In the **Surface** settings window, click **Replace Expression** in the upper-right corner of the **Expression** section. From the menu, choose **Secondary Current Distribution>Electrode current density, norm (siec.NormIs)**.
3 Click the **Plot** button.
4 Click the **Zoom Extents** button on the Graphics toolbar.

MODEL 1

Now, extend the model to investigate the concentration of the dissolved zinc ions in the orange over time. Start by adding an interface to handle the mass transport.

1 In the **Model Builder** window, right-click **Model 1** and choose **Add Physics**.

MODEL WIZARD

1 Go to the **Model Wizard** window.
2 In the **Add physics** tree, select **Chemical Species Transport>Transport of Diluted Species (chds)**.
3 Click **Add Selected**.

4 Click **Finish**.

TRANSPORT OF DILUTED SPECIES

1 In the **Model Builder** window, under **Model 1** click **Transport of Diluted Species**.

2 In the **Transport of Diluted Species** settings window, locate the **Domain Selection** section.

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

4 Locate the **Transport Mechanisms** section. Clear the **Convection** check box.

5 Select the **Migration in electric field** check box.

Diffusion and Migration

1 In the **Model Builder** window, expand the **Transport of Diluted Species** node, then click **Diffusion and Migration**.

2 In the **Diffusion and Migration** settings window, locate the **Model Inputs** section.

3 In the V edit field, type `phil`.

4 Locate the **Migration in Electric Field** section. In the z_c edit field, type `2`.

The following steps couples the electrochemical reaction currents to the ion flux at the electrode surface.

Electrode-Electrolyte Interface Coupling 1

1 In the **Model Builder** window, right-click **Transport of Diluted Species** and choose **Electrode-Electrolyte Interface Coupling**.

2 Click the **Transparency** button on the Graphics toolbar.

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

4 From the **Selection** list, choose **Zinc nail active electrode surface**.

Reaction Coefficients 1

1 In the **Model Builder** window, under **Model 1>Transport of Diluted Species>Electrode-Electrolyte Interface Coupling 1** click **Reaction Coefficients 1**.

2 In the **Reaction Coefficients** settings window, locate the **Model Inputs** section.

3 From the i_{loc} list, choose **Local current density (siec)**.

4 Locate the **Stoichiometric Coefficients** section. In the n_m edit field, type `2`.

5 In the ν_c edit field, type `-1`.

Initial Values 1

1 In the **Model Builder** window, under **Model 1>Transport of Diluted Species** click **Initial Values 1**.

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

3 In the c edit field, type `c_ref`.

Note that `c_ref` is colored orange, this is because the parameter is not yet defined. Define it now.

GLOBAL DEFINITIONS

Parameters

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

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

3 In the table, enter the following settings:

Name	Expression	Description
c_ref	0.01[mol/m^3]	Reference concentration

SECONDARY CURRENT DISTRIBUTION

Also, modify the electrode kinetics to be dependent on the local concentration of zinc ions.

Electrode Reaction 1

1 In the **Model Builder** window, under **Model 1>Secondary Current Distribution>Electrolyte-Electrode Domain Interface 1** click **Electrode Reaction 1**.

2 In the **Electrode Reaction** settings window, locate the **Electrode Kinetics** section.

3 From the **Kinetics expression type** list, choose **Concentration dependent kinetics**.

4 In the C_O edit field, type `c/c_ref`.

ROOT

Create a new time-dependent study for the concentration simulation.

1 In the **Model Builder** window, right-click the root node and choose **Add Study**.

MODEL WIZARD

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

2 Find the **Studies** subsection. In the tree, select **Preset Studies for Selected Physics>Time Dependent**.

3 Click **Finish**.

STUDY 2

Step 1: Time Dependent

1 In the **Model Builder** window, expand the **Study 2** node, then click **Step 1: Time Dependent**.

2 In the **Time Dependent** settings window, locate the **Study Settings** section.

3 In the **Times** edit field, type `range(0,60,3600)`.

4 In the **Model Builder** window, right-click **Study 2** and choose **Compute**.

RESULTS

3D Plot Group 9

1 In the **Model Builder** window, right-click **Results** and choose **3D Plot Group**.

2 Right-click **3D Plot Group 9** and choose **Rename**.

3 Go to the **Rename 3D Plot Group** dialog box and type `Concentration Isosurface` in the **New name** edit field.

4 Click **OK**.

5 In the **3D Plot Group** settings window, locate the **Data** section.

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

7 From the **Time** list, choose **300**.

Concentration Isosurface

1 Right-click **Results>3D Plot Group 9** and choose **Isosurface**.

2 In the **Isosurface** settings window, click **Replace Expression** in the upper-right corner of the **Expression** section. From the menu, choose **Transport of Diluted Species>Species c>Concentration (c)**.

3 Locate the **Levels** section. From the **Entry method** list, choose **Levels**.

4 In the **Levels** edit field, type `0.2`.

5 Click the **Plot** button.

6 Click the **Zoom Extents** button on the Graphics toolbar.

7 Click the **Transparency** button on the Graphics toolbar.

Export

The following steps create an animation of the zinc ion isosurface during the simulated time:

1 In the **Model Builder** window, under **Results** right-click **Export** and choose **Player**.
2 In the **Player** settings window, locate the **Scene** section.
3 From the **Subject** list, choose **Concentration Isosurface**.
   At t=0 there is no concentration gradient in the orange, de-select the first time-step.
4 Locate the **Animation Editing** section. From the **Time selection** list, choose **From list**.
5 In the **Times** list, choose all time steps except t=0.
6 Right-click **Results>Export>Player 1** and choose **Play**.
7 Click the **Zoom Extents** button on the Graphics toolbar.

Derived Values

Finally, create a plot for how the cell current changes with time. Do this by first integrating the current over the terminal boundary, and then plot that data.

1 In the **Model Builder** window, under **Results** right-click **Derived Values** and choose **Integration>Surface Integration**.
2 In the **Surface Integration** settings window, locate the **Data** section.
3 From the **Data set** list, choose **Solution 2**.
4 Select Boundary 28 only.
5 Click **Replace Expression** in the upper-right corner of the **Expression** section. From the menu, choose **Secondary Current Distribution>Electrode current density vector>Electrode current density vector, z component (siec.Isz)**.
6 Right-click **Results>Derived Values>Surface Integration 1** and choose **Evaluate>New Table**.
7 In the **Table** window, click **Table Graph**.

1D Plot Group 10

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