Model created in COMSOL Multiphysics 6.4

Copper Deposition in a Trench Using the Phase Field Method

Introduction

This model example is based on the Copper Deposition in a Trench Using the Level Set Method model, available in the Electrodeposition Module Application Library, which demonstrates that there is a nonuniform deposition along the trench surface, leading to formation of a cavity or void (Ref. 1). The model example presented here uses the Phase Field interface instead of the Level Set interface and computations are performed for up to 20 s, well beyond the time for cavity formation, similar to the Level Set model.

Model Definition

The deposition process is inherently time-dependent because the cathode boundary moves as the deposition process takes place. The model is defined by the material balances for the involved ions (copper, Cu^{2+}, and sulfate, SO_4^{2-}) and by the electroneutrality condition.

The model geometry is shown in Figure 1. The upper horizontal boundary represents the anode, while the cathode is placed at the bottom. The vertical walls are assumed to be insulating.

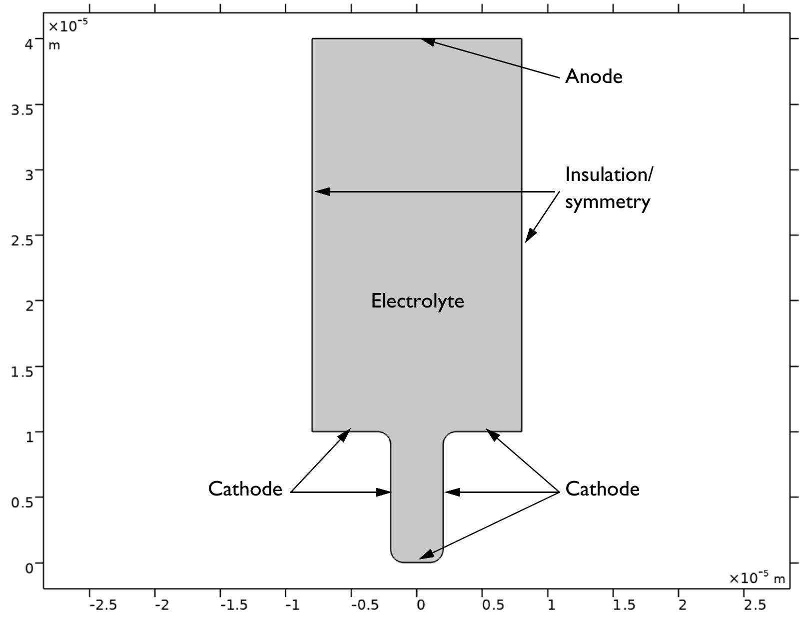


Figure 1: Model domain with boundaries corresponding to the anode, cathode, and vertical symmetry walls.

When using the Phase Field method, both the electrode and the electrolyte are described on the same domain. The Phase Field interface is used to keep track of the deformation at the cathode surface during deposition. For simplicity, the anode position is kept fixed in this model.

In the Phase Field interface the two-phase flow dynamics is governed by a Cahn-Hilliard equation. The equation tracks a diffuse interface separating the immiscible phases. The diffuse interface is defined as the region where the dimensionless phase field variable ϕ goes from -1, in the electrolyte domain, to 1, in the deposited region. to 1. When solved in COMSOL Multiphysics, the Cahn-Hilliard equation is split up into two equations

$$\frac{\partial\phi}{\partial t} + \mathbf{u} \cdot \nabla\phi = \nabla \cdot \frac{\gamma\lambda}{\varepsilon^2}\nabla\psi$$

$$\psi = -\nabla \cdot \varepsilon^2\nabla\phi + (\phi^2 - 1)\phi$$

where $\mathbf{u}$ is the fluid velocity (m/s), γ is the mobility ($\mathrm{m^3{\cdot}s/kg}$), λ is the mixing energy density (N) and ε (m) is the interface thickness parameter. The ψ variable is referred to as the phase field help variable. The following equation relates the mixing energy density and the interface thickness to the surface tension coefficient:

$$\sigma = \frac{2\sqrt{2}}{3}\frac{\lambda}{\varepsilon}$$

In the present model, the interface thickness parameter is set to $\varepsilon = h_{\mathrm{max}}/16$, where h_{max} is the maximum mesh element size in the domain. The mobility parameter γ determines the time scale of the Cahn–Hilliard diffusion and must be chosen judiciously. It must be large enough to retain a constant interfacial thickness but small enough so that the convective terms are not overly damped. A suitable value for γ is the maximum velocity magnitude occurring in the model.

In the Phase Field interface, the volume fractions of the individual fluids are

$$V_{\mathrm{f1}} = \frac{1-\phi}{2}, \qquad V_{\mathrm{f2}} = \frac{1+\phi}{2}$$

The volume fraction, V_{f1}, varies from 1 in the electrolyte domain to 0 in the deposited region.

The phase field delta function is approximated by:

$$\delta = \frac{3}{4}(1-\phi^2)|\nabla\phi|$$

The velocity field used in the transport equation for phase field variable is evaluated from the copper deposition reaction current density:

$$\mathbf{u} = \mathbf{n}\cdot\left(-\frac{i_{\mathrm{loc}}}{2F}\frac{M_{\mathrm{Cu}}}{\rho_{\mathrm{Cu}}}\right)$$

where i_{loc} is the local current density, M_{Cu} is the molar mass and ρ_{Cu} is the density of copper.

The interface normal $\mathbf{n}$ is calculated as

$$\mathbf{n} = \frac{\nabla\phi}{|\nabla\phi|}$$

The phase field variable of value 1 enters the domain from the bottommost boundaries of the domain, which are prescribed using the Inlet boundary condition. The rest of the boundaries are prescribed using the Outlet boundary condition.

The usage of the Phase Field method means that the balance equations have to be modified in comparison with those used in the Copper Deposition in a Trench model. First, the flux for each of the ions in the electrolyte is given by the Nernst–Planck equation with effective diffusion coefficients and mobilities,

$$\mathbf{N}_i = -D_{i,\,\mathrm{eff}}\nabla c_i - z_i u_{i,\,\mathrm{eff}} F c_i \nabla\phi_l,$$

where $\mathbf{N}_i$ denotes the transport vector (mol/(m^2·s)), c_i the concentration in the electrolyte (mol/m^3), z_i the charge for the ionic species, $u_{i,\mathrm{eff}}$ the mobility of the charged species (m^2/(s·J·mole)), F Faraday's constant (As/mole), and ϕ_l the potential in the electrolyte (V). The effective diffusion coefficients are defined using the electrolyte volume fraction:

$$D_{i,\,\mathrm{eff}} = \varepsilon_l D_i$$

where ε_l is the electrolyte volume fraction; ε_l is defined in terms of the phase field volume fraction, V_{f1}, and varies from 1 in the electrolyte domain to 0 in the deposited region.

Furthermore, the material balances are expressed through

$$\frac{\partial\varepsilon_l c_i}{\partial t} + \nabla\cdot\mathbf{N}_i = R_i$$

one for each species, that is $i = 1, 2$.

The rate of electrochemical reaction is

$$R_i = -\frac{\nu_i i_v}{nF}$$

The electrolyte volume fraction compensation ensures that the electrode will not act as a reservoir for the copper and sulfate ions.

The electroneutrality condition is given by the following expression:

$$\sum_i z_i c_i = 0$$

The deposition process is assumed to take place through the following simplified mechanism:

$$\mathrm{Cu}^{2+} + e^{-} = \mathrm{Cu}^{+}$$

$$\mathrm{Cu}^{+} + e^{-} = \mathrm{Cu}$$

where the first step is rate determining step, RDS, and the second step is assumed to be at equilibrium (Ref. 1). This gives the following the Butler–Volmer equation for the local current density as a function of potential and copper concentration:

$$i_{\mathrm{loc}} = i_0\left(\exp\left(\frac{1.5F\eta}{RT}\right) - \frac{c_{\mathrm{Cu}^{2+}}}{c_{\mathrm{Cu}^{2+},\mathrm{ref}}}\exp\left(-\frac{0.5F\eta}{RT}\right)\right)$$

where η denotes the overpotential defined as

$$\eta = \phi_{\mathrm{s}} - \phi_{\mathrm{l}} - E_{\mathrm{eq}}$$

where ϕ_s denotes the electronic potential of the respective electrode.

The copper deposition reaction current density at the cathode surface is added as a source term in the domain, using the phase field delta function to prescribe the deposition reaction along the deforming boundary:

$$i_v = i_{\mathrm{loc}}\delta$$

The boundary condition at the anode surface is:

$$\mathbf{N}_{\mathrm{Cu}^{2+}} \cdot \mathbf{n} = -\frac{i_{\mathrm{loc}}}{2F}$$

where **n** denotes the normal vector to the boundary. For simplicity, the anode surface is not deformed in this model.

All other boundaries are insulating:

$$\mathbf{N}_{\mathrm{Cu}^{2+}} \cdot \mathbf{n} = 0$$

For the sulfate ions, insulating conditions apply everywhere:

$$\mathbf{N}_{\mathrm{SO}_4^{2-}} \cdot \mathbf{n} = 0$$

The initial conditions set the composition of the electrolyte according to

$$c_{\mathrm{Cu}^{2+}} = c_0$$
$$c_{\mathrm{SO}_4^{2-}} = c_0$$

The electrochemical model described above is set up using the Tertiary Current Distribution, Nernst–Planck Equations interface.

Results and Discussion

Figure 2 shows surface plots of the electrolyte potential and the phase field variable after 20 s of deposition operation. The surface plot of the phase field variable, plotted using a gray scale, represents the copper deposition region where its value is greater than 0. It can be seen that there is a nonuniform deposition along the trench (cathode) surface. The deposition rate is higher near mouth of the trench than at the bottom of the trench, leading to formation of a cavity or void. The isolated cavity can be detrimental to the quality of the deposition because a trapped electrolyte can later cause corrosion of components in the circuit board.

The electrolyte potential in the cavity relaxes so that the electrode potential ($\phi_s - \phi_l$) corresponds to the resulting equilibrium potential (E_{eq}) for the concentration in the cavity, leading the local current density value to 0 inside the cavity.

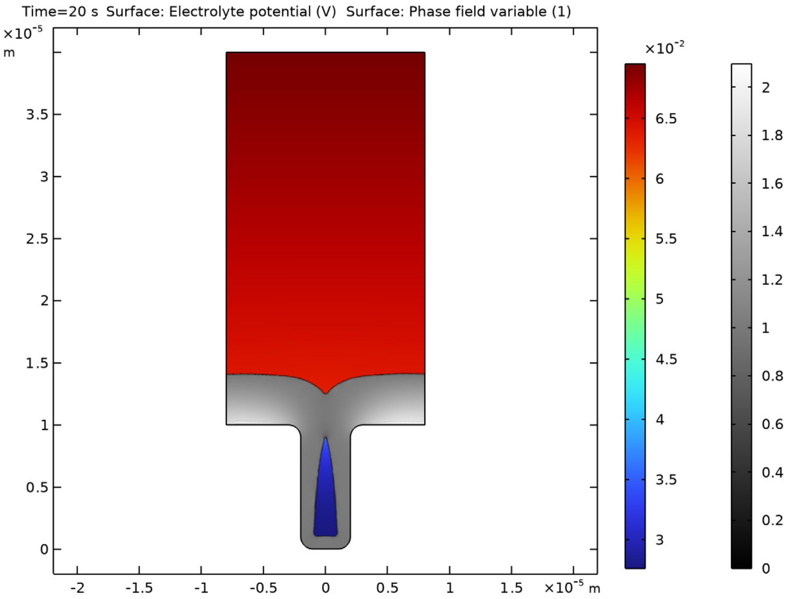


Figure 2: Surface plot of electrolyte potential along with the phase field variable contour of value 0.5 after 20 seconds of deposition operation.

Figure 3 shows the surface plots of the corresponding concentration of copper ions and the phase field variable after 20 s of deposition operation. The simulation shows substantial variations in copper ion concentration in the cell. Such variations eventually cause free convection in the cell. The nonuniform deposition rate at the cathode surface is attributed to nonuniform electrolyte current distribution which is accentuated by the depletion of copper ions at the bottom of the trench.

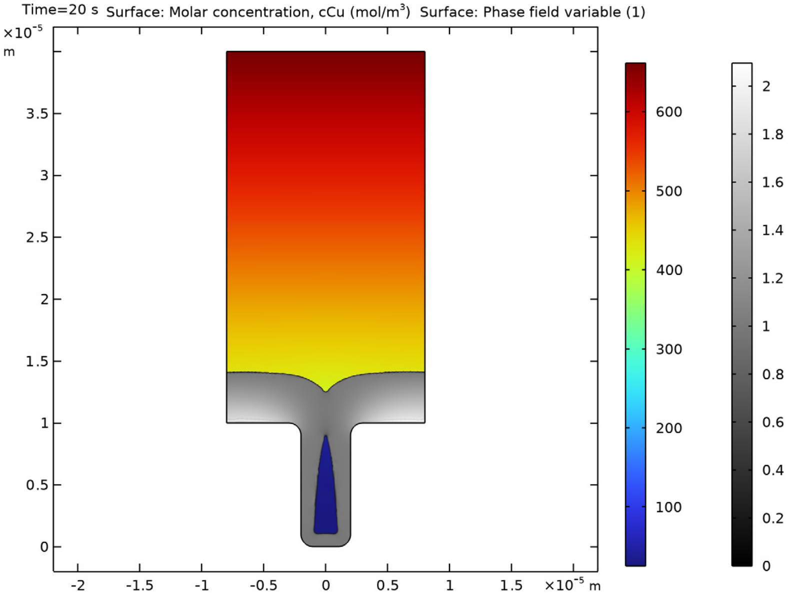


Figure 3: Surface plot of concentration of copper ions along with the phase field variable contour of value 0.5 after 20 seconds of deposition operation.

In Figure 4 and Figure 5 we now compare the results obtained from the Phase Field interface in this model with those obtained from the Deformed Geometry node in the

Copper Deposition in a Trench model, after 14 s of deposition operation (which corresponds to the time close to the cavity formation)

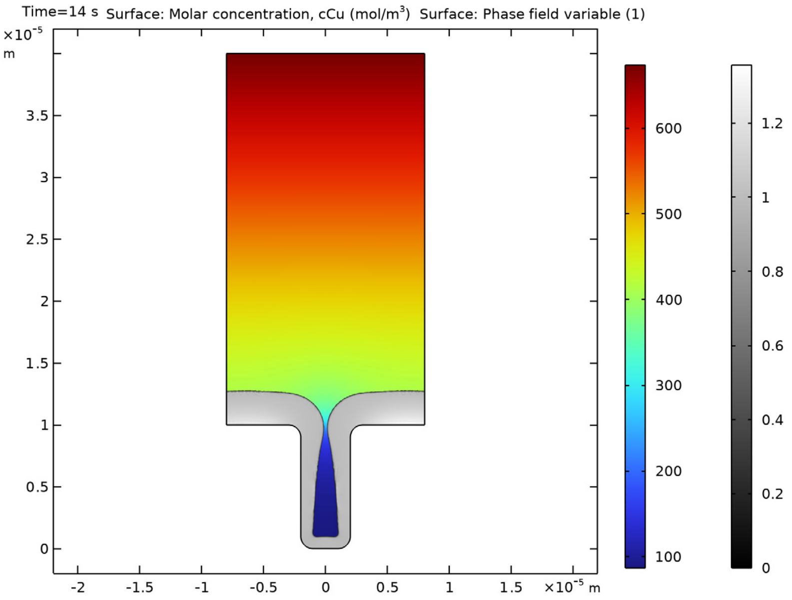


Figure 4: Surface plot of concentration of copper ions along with the phase field variable contour of value 0.5 after 14 seconds of deposition operation using the Phase Field interface.

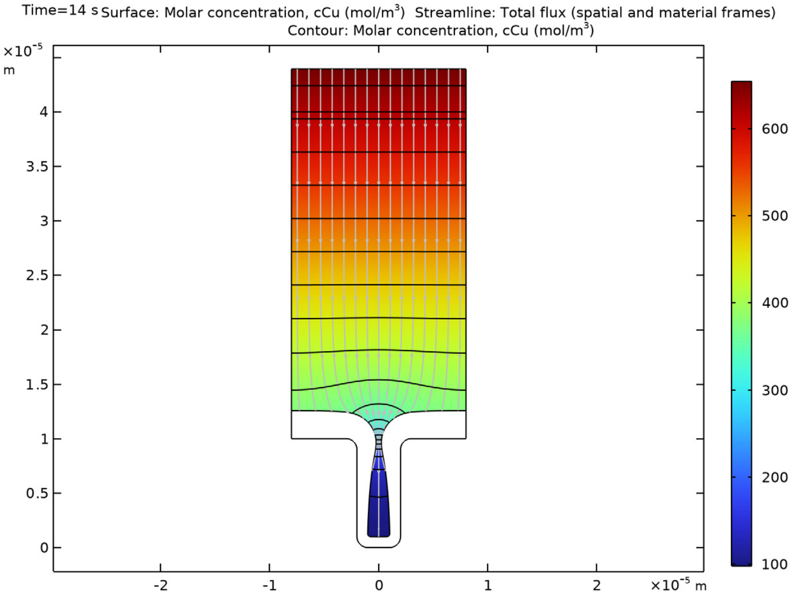


Figure 5: Surface plot of the concentration distribution of copper ions, the isopotential lines, the current density lines, and the displacement of the cathode and anode surfaces after14 seconds of deposition operation using the Deformed Geometry node.

It can be seen from Figure 4 and Figure 5 that the deposition profile and the concentration distribution of copper ions obtained from the Phase Field interface match well with the same obtained from the Deformed Geometry node. Some minor differences can be seen in the plots with regards to concentrations and position of the moving cathode. These can mainly be attributed to the anode position, which is allowed to move in Figure 5, but is fixed in Figure 4.

In conclusion, electrodeposition models using the phase field method can be useful in identifying cavity or void regions formed during a deposition process in complex geometries.

Reference

1. E. Mattsson and J.O'M. Bockris, "Galvanostatic Studies of the Kinetics of Deposition and Dissolution in the Copper + Copper Sulphate System," *Trans. Far. Soc.*, vol. 55, p. 1586, 1959.

Application Library path: `Electrodeposition_Module/Tutorials_with_Deforming_Geometries/cu_trench_deposition_pf`

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** > **Tertiary Current Distribution, Nernst–Planck** > **Tertiary, Electroneutrality (tcd)**.

3 Click **Add**.

4 In the **Concentrations (mol/m^3)** table, enter the following settings:

cCu
cSO4

5 In the **Select Physics** tree, select **Mathematics** > **Moving Interface** > **Phase Field in Fluids (pf)**.

6 Click **Add**.

7 Click **Study**.

8 In the **Select Study** tree, select **Preset Studies for Some Physics Interfaces** > **Time Dependent with Initialization**.

9 Click **Done**.

GEOMETRY 1

Draw the geometry by making a union of two rectangles. Round off the corners of the trench using fillets.

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 `1.6e-5`.
4. In the **Height** text field, type `3e-5`.
5. Locate the **Position** section. In the **x** text field, type `-0.8e-5`.
6. In the **y** text field, type `1e-5`.

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 `0.4e-5`.
4. In the **Height** text field, type `1e-5`.
5. Locate the **Position** section. In the **x** text field, type `-0.2e-5`.
6. Click **Build Selected**.
7. Click the **Zoom Extents** button in the **Graphics** toolbar.

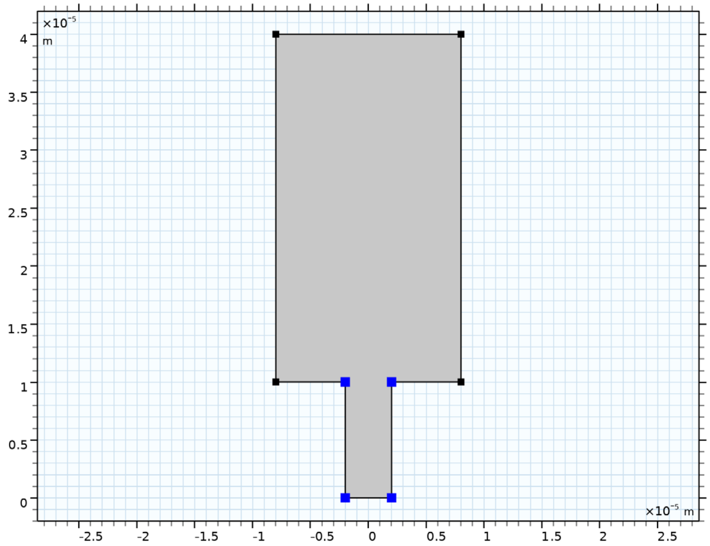
Union 1 (uni1)

1. In the **Geometry** toolbar, click **Booleans and Partitions** and choose **Union**.
2. In the **Settings** window for **Union**, locate the **Union** section.
3. Clear the **Keep interior boundaries** checkbox.
4. Click in the **Graphics** window and then press Ctrl+A to select both objects.

Fillet 1 (fil1)

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

2. On the object **uni1**, select Points 3–6 only.



3. In the **Settings** window for **Fillet**, locate the **Radius** section.
4. In the **Radius** text field, type `1e-6`.

Form Union (fin)

1. In the **Model Builder** window, click **Form Union (fin)**.
2. In the **Settings** window for **Form Union/Assembly**, click **Build Selected**.

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 `cu_trench_deposition_ls_parameters.txt`.

DEFINITIONS

Load the model variables from a text file.

Variables 1

1. In the **Definitions** toolbar, click a= **Local Variables**.
2. In the **Settings** window for **Variables**, locate the **Variables** section.
3. Click **Load from File**.
4. Browse to the model's Application Libraries folder and double-click the file `cu_trench_deposition_pf_variables.txt`.

TERTIARY CURRENT DISTRIBUTION, NERNST–PLANCK (TCD)

Now set up the electrochemical model, consisting of a Highly Conductive Porous Electrode domain and an electrode boundary.

Species Charges 1

1. In the **Model Builder** window, under **Component 1 (comp1)** > **Tertiary Current Distribution, Nernst–Planck (tcd)** click **Species Charges 1**.
2. In the **Settings** window for **Species Charges**, locate the **Charge** section.
3. In the z_{cCu} text field, type `z_Cu`.
4. In the z_{cSO4} text field, type `z_SO4`.

Highly Conductive Porous Electrode 1

1. In the **Physics** toolbar, click **Domains** and choose **Highly Conductive Porous Electrode**.
2. In the **Settings** window for **Highly Conductive Porous Electrode**, locate the **Domain Selection** section.
3. From the **Selection** list, choose **All domains**.
4. Locate the **Diffusion** section. In the D_{cCu} text field, type `D_Cu`.
5. In the D_{cSO4} text field, type `D_SO4`.

   Set the electrolyte volume fraction to `epsl`. This implies that all the volume of the modeled domain belongs to the electrolyte phase.

6. Locate the **Porous Matrix Properties** section. In the ε_{l} text field, type `epsl`.

   Set the effective transport parameter correction for diffusion to user defined and set the correction factor to `epsl` so that the correction is applied only in the electrolyte phase excluding the deposited region.

7. Locate the **Effective Transport Parameter Correction** section. From the **Diffusion** list, choose **User defined**. In the f_{Dl} text field, type `epsl`.
8. Locate the **Electrode Phase Potential Condition** section. In the $\phi_{\mathrm{s,ext}}$ text field, type `phis_cathode`.

Porous Electrode Reaction 1

Set up the copper deposition electrode reaction kinetics parameters.

1 In the **Model Builder** window, click **Porous Electrode Reaction 1**.

2 In the **Settings** window for **Porous Electrode Reaction**, locate the **Stoichiometric Coefficients** section.

3 In the n text field, type `2`.

4 Locate the **Equilibrium Potential** section. From the E_{eq} list, choose **User defined**. In the associated text field, type `Eeq_rel`.

5 Locate the **Electrode Kinetics** section. From the **Kinetics expression type** list, choose **Concentration dependent kinetics**.

6 In the i_0 text field, type `i0`.

7 In the α_{a} text field, type `alpha_a`.

8 In the α_{c} text field, type `alpha_c`.

9 In the C_{O} text field, type `cCu/Cinit`.

10 Locate the **Active Specific Surface Area** section. In the a_{v} text field, type `pf.delta`.

Electrode Surface 1

Define the electrode kinetics at the anode surface.

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

2 Select Boundary 3 only.

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

4 In the $\phi_{\mathrm{s,ext}}$ text field, type `phis_anode`.

5 Click to expand the **Dissolving–Depositing Species** section. Click + **Add**.

6 In the table, enter the following settings:

Species	**Density (kg/m^3)**	**Molar mass (kg/mol)**
`cdep_anode`	`8960`	`0.06355`

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 n text field, type `2`.

4 Locate the **Electrode Kinetics** section. In the $i_{0,\mathrm{ref}}(T)$ text field, type `i0`.

5 In the α_a text field, type `alpha_a`.

Initial Values 1

Set the initial concentration of copper and sulfate ions.

1 In the **Model Builder** window, under **Component 1 (comp1)** > **Tertiary Current Distribution, Nernst–Planck (tcd)** click **Initial Values 1**.

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

3 In the $cSO4$ text field, type `Cinit`.

PHASE FIELD IN FLUIDS (PF)

Now, set up the Phase Field model.

1 In the **Model Builder** window, under **Component 1 (comp1)** click **Phase Field in Fluids (pf)**.

2 In the **Settings** window for **Phase Field in Fluids**, click to expand the **Discretization** section.

3 From the **Element order** list, choose **Quadratic**.

Phase Field Model 1

Next, specify the parameter controlling interface thickness, mobility tuning parameter, and velocity field.

1 In the **Model Builder** window, under **Component 1 (comp1)** > **Phase Field in Fluids (pf)** click **Phase Field Model 1**.

2 In the **Settings** window for **Phase Field Model**, locate the **Phase Field Parameters** section.

3 In the ε_{pf} text field, type `pf.hmax/16`.

4 From the **Mobility tuning parameter** list, choose **Calculate from velocity**.

5 In the U text field, type `max(Vn,eps)`.

6 Locate the **Convection** section. Specify the **u** vector as

`-Vn*pf.intnormx`	x
`-Vn*pf.intnormy`	y

Inlet 1

Define inlet and outlet boundaries for the phase field variable.

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

2 Select Boundaries 2, 4–7, and 9–12 only.

3. In the **Settings** window for **Inlet**, locate the **Phase Field Condition** section.
4. From the list, choose **Fluid 2 (φ = 1)**.

Outlet 1

1. In the **Physics** toolbar, click **Boundaries** and choose **Outlet**.
2. Select Boundaries 1, 3, and 8 only.

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 `T0`.

MESH 1

Now make the settings for the mesh.

1. In the **Model Builder** window, under **Component 1 (comp1)** right-click **Mesh 1** and choose **Edit Physics-Induced Sequence**.

Size

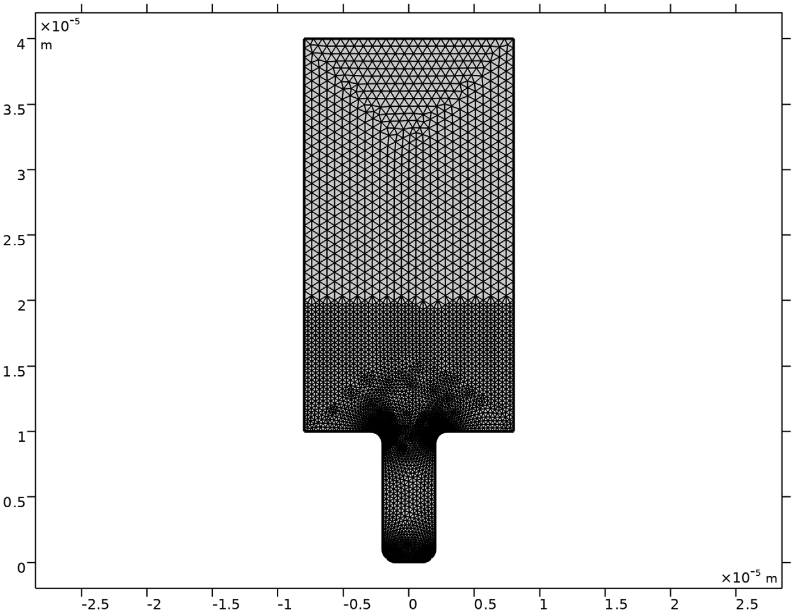
1. In the **Model Builder** window, under **Component 1 (comp1)** > **Mesh 1** click **Size**.
2. In the **Settings** window for **Size**, locate the **Element Size** section.
3. From the **Predefined** list, choose **Normal**.

Refine 1

1. In the **Mesh** toolbar, click **Modify** and choose **Refine**.
2. In the **Settings** window for **Refine**, click to expand the **Refine Elements in Box** section.
3. Select the **Specify bounding box** checkbox.
4. In row **x**, set **Lower bound** to `-1E-5`.
5. In row **x**, set **Upper bound** to `1E-5`.
6. In row **y**, set **Lower bound** to `-8E-7`.
7. In row **y**, set **Upper bound** to `2E-5`.

8 Click **Build All**.

Your finished mesh should now look like this:



STUDY 1

Modify the solver settings to simulate the deposition process during 20 s, storing the solution every 0.5 s. Use the initial valued based scaling and clear generate default plots option and then start the computation.

Step 2: Time Dependent

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

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

3 In the **Output times** text field, type `range(0,0.5,20)`.

Solution 1 (sol1)

1 In the **Study** toolbar, click **Show Default Solver**.

2 In the **Model Builder** window, expand the **Solution 1 (sol1)** node, then click **Dependent Variables 2**.

3 In the **Settings** window for **Dependent Variables**, locate the **Scaling** section.

4 From the **Method** list, choose **Initial-value based**.

5 In the **Model Builder** window, click **Study 1**.

6. In the **Settings** window for **Study**, locate the **Study Settings** section.
7. Clear the **Generate default plots** checkbox.
8. In the **Study** toolbar, click **Compute**.

RESULTS

The following steps reproduce the plots from the Results and Discussion section.

Electrolyte Potential (tcd)

1. In the **Results** toolbar, click **2D Plot Group**.
2. In the **Settings** window for **2D Plot Group**, type `E` in the **Label** text field.
3. In the **Label** text field, type `Electrolyte Potential (tcd)`.

Surface 1

In the **Electrolyte Potential (tcd)** toolbar, click **Surface**.

Filter 1

1. In the **Electrolyte Potential (tcd)** toolbar, click **Filter**.
2. In the **Settings** window for **Filter**, locate the **Element Selection** section.
3. In the **Logical expression for inclusion** text field, type `phipf<0`.

Surface 2

1. In the **Model Builder** window, under **Results** > **Electrolyte Potential (tcd)** right-click **Surface 1** and choose **Duplicate**.
2. In the **Settings** window for **Surface**, locate the **Expression** section.
3. In the **Expression** text field, type `phipf`.
4. Locate the **Coloring and Style** section. From the **Color table** list, choose **GrayScale**.

Filter 1

1. In the **Model Builder** window, expand the **Surface 2** node, then click **Filter 1**.
2. In the **Settings** window for **Filter**, locate the **Element Selection** section.
3. In the **Logical expression for inclusion** text field, type `phipf>0`.
4. In the **Electrolyte Potential (tcd)** toolbar, click **Plot**.

Electrolyte Potential (tcd)

Now, plot the concentration of copper ions by making use of the Duplicate functionality.

Concentration (tcd)

1. In the **Model Builder** window, right-click **Electrolyte Potential (tcd)** and choose **Duplicate**.
2. In the **Model Builder** window, click **Electrolyte Potential (tcd) 1**.

3 In the **Settings** window for **2D Plot Group**, type `Concentration (tcd)` in the **Label** text field.

Surface 1

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

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)** > **Tertiary Current Distribution, Nernst–Planck** > **Species cCu** > **cCu - Molar concentration, cCu - mol/m^3**.

3 In the **Concentration (tcd)** toolbar, click **Plot**.

Concentration (tcd)

Now, plot the concentration of copper ions at 14 s to compare the results with the deformed geometry formulation.

1 In the **Model Builder** window, click **Concentration (tcd)**.

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

3 From the **Time (s)** list, choose **14**.

4 In the **Concentration (tcd)** toolbar, click **Plot**.