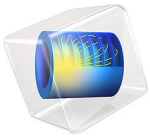


Localized Corrosion Using the Phase Field Method

Introduction

This example models the galvanic corrosion between the two constituent phases of a metallic alloy. Since the two phases have different equilibrium potentials corrosion occurs when the alloy is exposed to an electrolyte solution. The Present model is similar to the Localized Corrosion Using the Level Set Method example, except that the Phase Field method is used here instead of the Level Set method to capture dissolution of a constituent phase.

This model example is based on a paper by Deshpande (Ref. 1).

Model Definition

The model geometry considered in this example is shown in Figure 1, along with a representative cross-sectional microstructure, which consists of the alpha and beta phases exposed to the electrolyte solution.

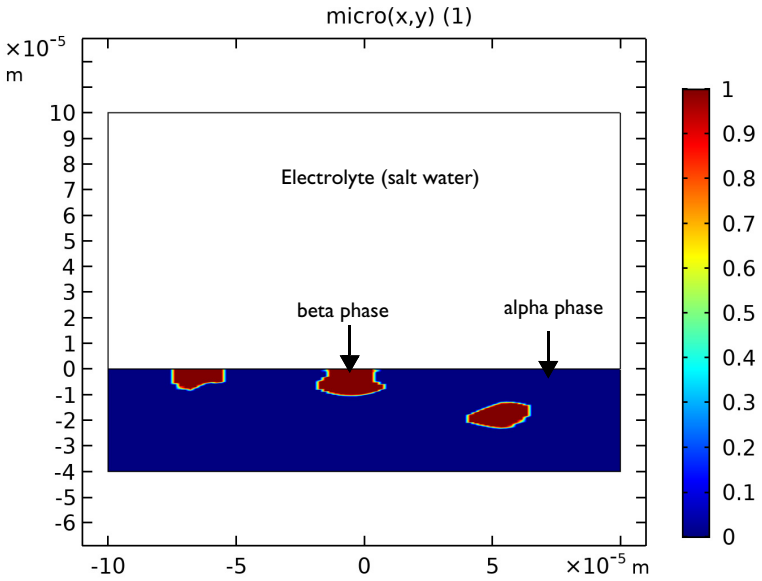


Figure 1: Model geometry along with cross-sectional microstructure comprising of the alpha and beta phases and exposed to the electrolyte solution.

The cross-sectional microstructure shown in Figure 1 is represented in terms of an interpolation function called "micro" which has a value of 0 and 1 for the alpha and beta

phases, respectively. The metal alloy geometry has a width of 200 μm and a depth of 40 μm. The maximum depth of the beta phase is 10 μm.

ELECTROLYTE CHARGE TRANSPORT

Use the Secondary Current Distribution interface to solve for the electrolyte potential, $\phi_l(V)$, over the electrolyte domain according to Ohm's law:

$$\mathbf{i}_l = -\sigma_l \nabla \phi_l$$
$$\nabla \cdot \mathbf{i}_l = 0$$

where $\mathbf{i}_l$ (SI unit: A/m^2) is the electrolyte current density vector.

The electrolyte conductivity, σ_l (SI unit: S/m), is defined for the electrolyte and electrode domains separately using the electrolyte volume fraction defined in terms of phase field variable, ϕ, according to

$$\sigma_l = \sigma_{ed} \times V_{f1} + \sigma_{el} \times V_{f2}$$

where σ_{el} is the electrolyte conductivity in the electrolyte domain and is considered to be equal to 2.5 S/m and σ_{ed} is the electrolyte conductivity in the electrode domain and is considered to be equal to 0.1 S/m. Furthermore, V_{f1} and V_{f2} are the electrolyte volume fractions in electrode and electrolyte domains, respectively. While the electrolyte conductivity in electrolyte domain describes the actual chemistry of the problem, the electrolyte conductivity in the electrode domain is defined only to aid numerical convergence.

Use the default Insulation condition for all exterior boundaries:

$$\mathbf{n} \cdot \mathbf{i}_l = 0$$

where $\mathbf{n}$ is the normal vector, pointing out of the domain.

Use an Electrolyte Current Source domain node to define the electrode kinetics at the corroding boundary:

$$Q_l = i_{loc}\delta$$

where i_{loc} (SI unit: A/m^2) is the local electrode reaction current density and δ (SI unit: 1/m) is the phase field delta function.

Use a user-defined electrode kinetics expression to model the electrode reaction at the alpha and beta phases on the electrode surface.

Set the local current density for the alpha phase at the electrode surface to

$$i_{\text{alpha}} = f(\phi_{s,\,\text{ext}} - \phi_l) \times (1 - \text{micro}(x, y))$$

The `1-micro(x,y)` factor ensures that the local current density is applied only at the alpha phase on the electrode surface.

Similarly, use the following expression for the local current density at the beta phase:

$$i_{\text{beta}} = f(\phi_{s,\,\text{ext}} - \phi_l) \times \text{micro}(x, y)$$

The interpolation function `micro(x,y)` ensures that the local current density is applied only at the beta phase on the electrode surface.

A relationship between the local current density and the electrolyte potential, $f(\phi_{s,\text{ext}} - \phi_l)$, is incorporated in the model using a piecewise cubic interpolation function for the experimental polarization data. The same polarization data as used in the Localized Corrosion example is used here for the alpha and beta phases.

Set the local current density for the alpha and beta phases at the electrode surface according to

$$i_{\text{loc}} = i_{\text{alpha}} + i_{\text{beta}}$$

CORROSION INTERFACE TRACKING

Use the Phase Field interface to keep track of dissolution of the alpha phase. 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 electrode domain to 1 in the electrolyte domain. 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 interface velocity (m/s), γ is the mobility ($\text{m}^3 \cdot \text{s/kg}$), 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 $\varepsilon = h_{\max}/32$, 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 this model formulation, it is assumed that the anodic dissolution reaction takes place at the alpha phase surface, and that the cathodic hydrogen evolution reaction (which is not associated with any loss of material) takes place at the beta phase surface. Hence, the alpha phase surface will move (dissolve) whereas the beta phase surface remains intact. This is achieved in the model by setting the alpha phase dissolution velocity in normal direction according to

$$\mathbf{u} = \mathbf{n} \cdot \left(\frac{i_{\text{loc}} M_{\text{Mg}}}{2F} \frac{}{\rho_{\text{Mg}}} \times (1 - \text{micro}(x, y)) \right)$$

where M_{Mg} is the mean molar mass (23.98 g/mol) and ρ_{Mg} is the density (1770 kg/m^3) of the magnesium alloy.

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

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

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

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

In the present model, the electrode domain is defined as Fluid 1 and the electrolyte domain as Fluid 2.

The phase field delta function is approximated by:

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

Use the Inlet boundary node for the exterior boundaries of the electrolyte domain and set the phase field variable to 1 at those boundaries.

Use the Outlet boundary node for the exterior boundaries of the electrode domain.

To set the initial interface position, use the Initial Interface boundary node for the interior boundary between the electrolyte and electrode domains.

Results and Discussion

Figure 2 shows a surface plot of the electrolyte potential at time t = 300 h. It can be seen that the alpha phase, being electrochemically more active, is dissolving from the electrode surface whereas the beta phase, being relatively nobler, remains intact. With the preferential dissolution of the alpha phase, the underlying beta phase gets exposed to the electrolyte solution, resulting in an increase in the surface beta phase fraction at the electrode surface. It can be seen in Figure 2 that the alpha phase in the electrode domain, as shown in Figure 1, is dissolved in the electrolyte solution. The dissolved alpha phase and intact beta phase are highlighted in Figure 2 at time t = 300 h.

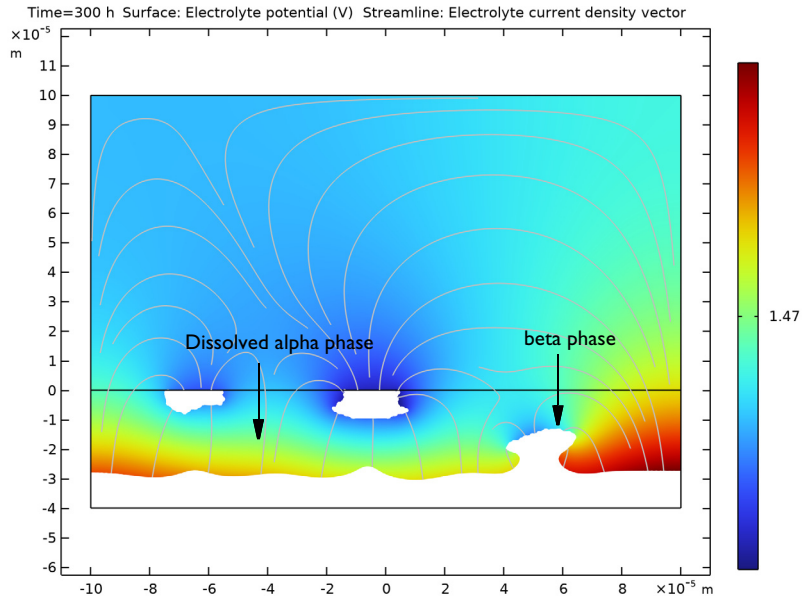


Figure 2: A surface plot of the electrolyte potential at time t = 300 h where the dissolved alpha phase and intact beta phase are highlighted.

Figure 3 shows a surface plot of the volume fraction of fluid 2 at time t = 300 h. The volume fraction of value 1 represents the electrolyte domain and 0 represents the electrode domain. The dissolved alpha phase, undissolved alpha phase and intact beta phase regions

of the electrode domain are highlighted in Figure 3 at time t = 300 h. Since the Phase Field method can handle topological changes, the computations are continued even after the beta phase falls off the electrode surface.

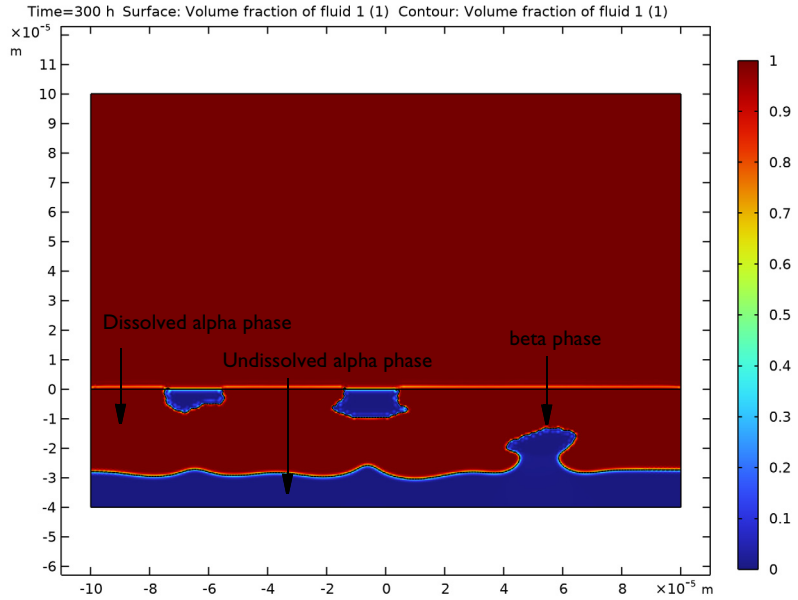


Figure 3: A surface plot of the volume fraction of fluid 2 at time t = 300 h where the value of 1 is the electrolyte domain and 0 is the intact beta phase and the undissolved alpha phase in the electrode domain.

Reference

1. K.B. Deshpande, "Numerical modeling of micro-galvanic corrosion," *Electrochimica Acta*, vol. 56, pp 1737–1745, 2011.

Application Library path: `Corrosion_Module/General_Corrosion/localized_corrosion_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>Primary and Secondary Current Distribution>Secondary Current Distribution (cd)**.

3 Click **Add**.

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

5 Click **Add**.

6 Click **Study**.

7 In the **Select Study** tree, select **Preset Studies for Selected Physics Interfaces>Phase Field in Fluids>Time Dependent with Phase Initialization**.

8 Click **Done**.

GEOMETRY 1

Now, create the model geometry by adding two rectangles.

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 `200e-6`.

4 In the **Height** text field, type `100e-6`.

5 Locate the **Position** section. In the **x** text field, type `-100e-6`.

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 `200e-6`.

4 In the **Height** text field, type `40e-6`.

5 Locate the **Position** section. In the **x** text field, type `-100e-6`.

6 In the **y** text field, type `-40e-6`.

7 Click **Build All Objects**.

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

GLOBAL DEFINITIONS

Now, create a predefined cross-sectional microstructure, which gets exposed to the electrolyte solution at the bottom boundary of the electrolyte domain, using an interpolation function. Please note that the interpolation function creates a similar microstructure as reported in Ref. 1.

Interpolation 1 (int1)

1 In the **Home** toolbar, click f(x) **Functions** and choose **Global>Interpolation**.

2 In the **Settings** window for **Interpolation**, locate the **Definition** section.

3 From the **Data source** list, choose **File**.

4 Click **Browse**.

5 Browse to the model's Application Libraries folder and double-click the file `localized_corrosion_ls_microstructure.txt`.

6 Click **Import**.

7 Find the **Functions** subsection. In the table, enter the following settings:

Function name	Position in file
micro	1

8 Locate the **Units** section. In the **Argument** table, enter the following settings:

Argument	Unit
Column 1	m

9 In the **Function** table, enter the following settings:

Function	Unit
micro	1

10 Click **Create Plot**.

RESULTS

2D Plot Group 1

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

2 From the **View** list, choose **View 1**.

3 In the **Model Builder** window, expand the **2D Plot Group 1** node.

Height Expression 1

1 In the **Model Builder** window, expand the **Results>2D Plot Group 1>Function 1** node.

2 Right-click **Height Expression 1** and choose **Disable**.

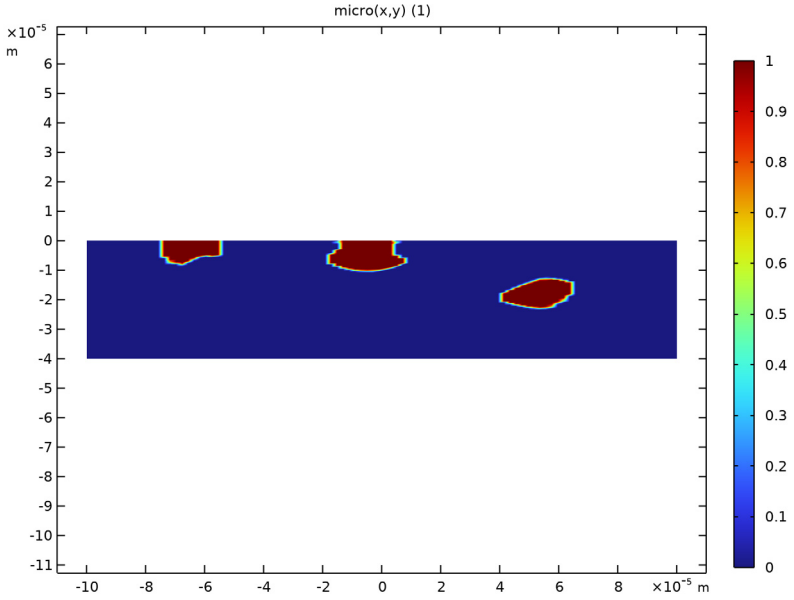
2D Plot Group : Cross-sectional microstructure

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

2 In the **Settings** window for **2D Plot Group**, type `2D Plot Group : Cross-sectional microstructure` in the **Label** text field.

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

The cross-sectional microstructure should look like this:



GLOBAL DEFINITIONS

Load the model parameters.

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 `localized_corrosion_parameters.txt`.

DEFINITIONS

Now, create interpolation functions for the alpha phase and beta phase to prescribe a piecewise cubic relationship between the local current density and the electrolyte potential obtained from the experimental polarization data (Ref. 1).

Interpolation 2 (int2)

1 In the **Home** toolbar, click f(x) **Functions** and choose **Local>Interpolation**.

2 In the **Settings** window for **Interpolation**, locate the **Definition** section.

3 In the **Function name** text field, type `i_alpha`.

4 Click **Load from File**.

5 Browse to the model's Application Libraries folder and double-click the file `localized_corrosion_i_alpha.txt`.

6 Locate the **Interpolation and Extrapolation** section. From the **Interpolation** list, choose **Piecewise cubic**.

7 From the **Extrapolation** list, choose **Linear**.

8 Locate the **Units** section. In the **Argument** table, enter the following settings:

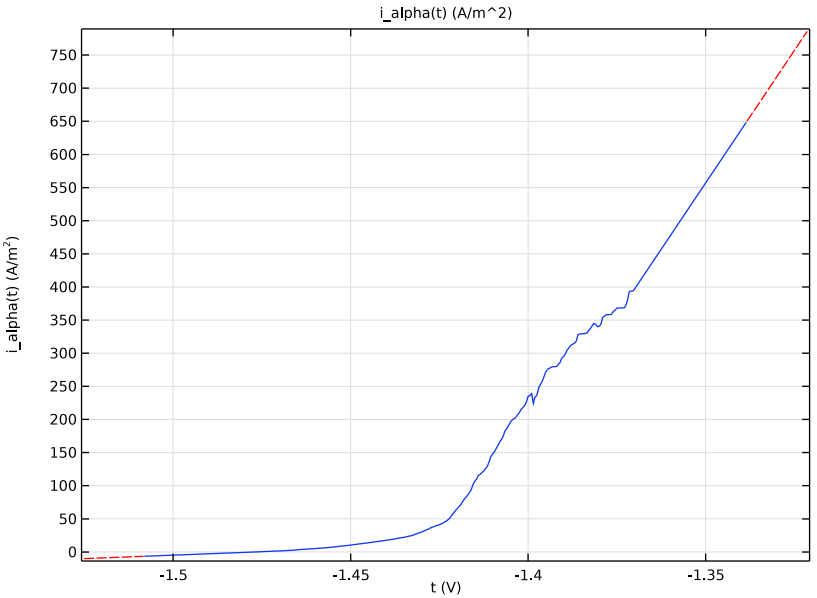
Argument	Unit
t	V

9 In the **Function** table, enter the following settings:

Function	Unit
i_alpha	A/m^2

10 Click **Plot**.

The interpolation plot for the alpha phase should look like this:



Interpolation 3 (int3)

1 In the **Home** toolbar, click **Functions** and choose **Local>Interpolation**.

2 In the **Settings** window for **Interpolation**, locate the **Definition** section.

3 In the **Function name** text field, type `i_beta`.

4 Click **Load from File**.

5 Browse to the model's Application Libraries folder and double-click the file `localized_corrosion_i_beta.txt`.

6 Locate the **Interpolation and Extrapolation** section. From the **Interpolation** list, choose **Piecewise cubic**.

7 From the **Extrapolation** list, choose **Linear**.

8 Locate the **Units** section. In the **Argument** table, enter the following settings:

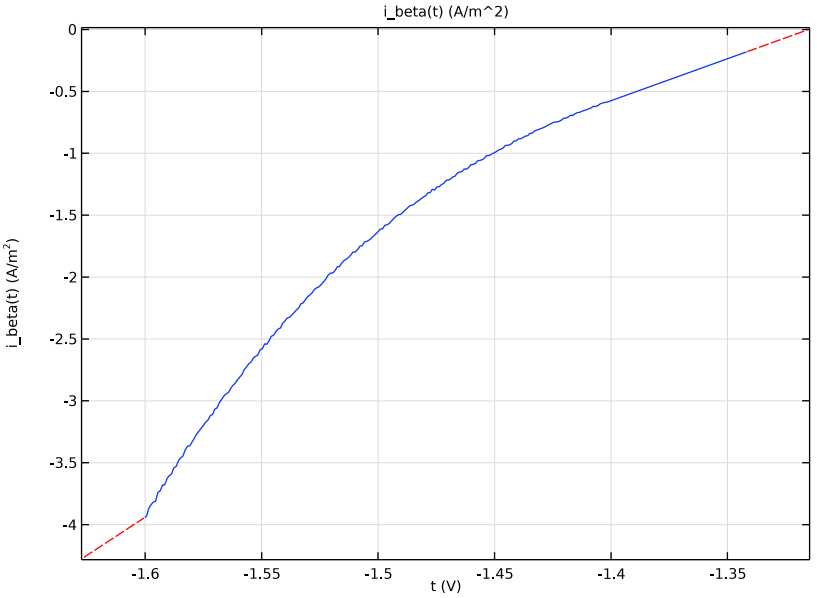
Argument	Unit
t	V

9 In the **Function** table, enter the following settings:

Function	Unit
i_beta	A/m^2

10 Click **Plot**.

The interpolation plot for the beta phase should look like this:



Variables 1

Now, load the model variables.

1 In the **Home** toolbar, click **Variables** and choose **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 `localized_corrosion_pf_variables.txt`.

SECONDARY CURRENT DISTRIBUTION (CD)

Now set up the physics for the current distribution. First, set the electrolyte conductivity and then prescribe the electrode kinetics for both the alpha phase and beta phase making use of the interpolated function, `micro(x,y)`. Also, note that the electrode kinetics is

prescribed as an electrolyte current source term using the phase field delta function, `pf.delta`.

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 `sigmae`.

4 Click the **Show More Options** button in the **Model Builder** toolbar.

5 In the **Show More Options** dialog box, in the tree, select the check box for the node **Physics>Advanced Physics Options**.

6 Click **OK**.

Electrolyte Current Source 1

1 In the **Physics** toolbar, click **Domains** and choose **Electrolyte Current Source**.

2 Click in the **Graphics** window and then press Ctrl+A to select both domains.

3 In the **Settings** window for **Electrolyte Current Source**, locate the **Electrolyte Current Source** section.

4 In the Q_l text field, type `i_loc*pf.delta`.

PHASE FIELD IN FLUIDS (PF)

Now, set up the phase field physics to track the position of dissolving alpha phase interface. Set up the Phase Field model by specifying the parameter controlling interface thickness, mobility tuning parameter, and velocity field.

Phase Field Model 1

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 $\mathbf{u}$ vector as

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

Initial Values 1

Set the initial value of phase field function to -1 for the electrolyte domain and 1 for the electrode domain.

Initial Values, Fluid 2

1 In the **Model Builder** window, click **Initial Values, Fluid 2**.

2 Select Domain 1 only.

Inlet 1

Set the inlet for phase field function.

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

2 Select Boundary 5 only.

Outlet 1

Set the outlet for phase field function.

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

2 Select Boundary 2 only.

MESH 1

Now, mesh a computational domain with a finer resolution at the electrode surface.

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**.

Size 1

1 In the **Model Builder** window, 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 **Domain**.

4 Select Domain 2 only.

5 Locate the **Element Size** section. From the **Calibrate for** list, choose **Fluid dynamics**.

Size 2

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 **Domain**.

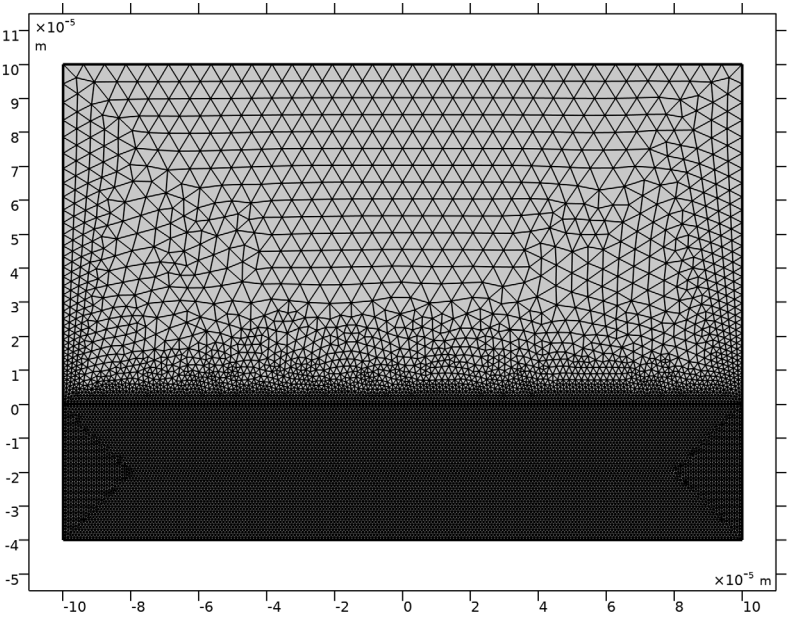
4 Select Domain 1 only.

5 Locate the **Element Size** section. From the **Calibrate for** list, choose **Fluid dynamics**.

6 From the **Predefined** list, choose **Extremely fine**.

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

The mesh should look like this:



STUDY 1

Finally, clear solve for check box for Secondary Current Distribution interface in Phase Initialization study node and set the time steps for time dependent solver.

Step 1: Phase Initialization

1 In the **Model Builder** window, under **Study 1** click **Step 1: Phase Initialization**.

2 In the **Settings** window for **Phase Initialization**, locate the **Physics and Variables Selection** section.

3 In the table, clear the **Solve for** check box for **Secondary Current Distribution (cd)**.

Step 2: Time Dependent

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

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

3 From the **Time unit** list, choose **h**.

4 In the **Output times** text field, type `range(0,1,300)`.

Solution 1 (sol1)

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

Store the actual steps taken by the solver to avoid interpolation issues in the stored solution.

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

3 In the **Settings** window for **Time-Dependent Solver**, locate the **General** section.

4 From the **Times to store** list, choose **Steps taken by solver closest to output times**.

The model is now ready to be solved.

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

RESULTS

Surface plots of the electrolyte potential and volume fraction of fluid 1 representing dissolution of alpha phase are plotted by default. Update these default plots by following the below steps to reproduce the plots from the Results and Discussion section.

Surface 1

In the **Model Builder** window, expand the **Electrolyte Potential (cd)** node, then click **Surface 1**.

Filter 1

1 In the **Electrolyte Potential (cd)** 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`.

Streamline 1

1 In the **Model Builder** window, under **Results>Electrolyte Potential (cd)** click **Streamline 1**.

2 In the **Settings** window for **Streamline**, locate the **Coloring and Style** section.

3 Find the **Point style** subsection. From the **Arrow length** list, choose **Normalized**.

4 Select the **Scale factor** check box. In the associated text field, type `2e-6`.

Filter 1

1 Right-click **Streamline 1** and choose **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`.

Electrolyte Potential (cd)

1 In the **Model Builder** window, under **Results** click **Electrolyte Potential (cd)**.

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

The plot should look like Figure 2.

Contour 1

1 In the **Model Builder** window, expand the **Volume Fraction of Fluid 1 (pf)** node, then click **Contour 1**.

2 In the **Settings** window for **Contour**, locate the **Coloring and Style** section.

3 From the **Color** list, choose **Black**.

4 In the **Volume Fraction of Fluid 1 (pf)** toolbar, click **Plot**.

The plot should look like Figure 3.

Animation 1

Plot the animation of volume fraction of fluid 1 to better visualize the evolution of the alpha phase dissolution.

1 In the **Results** toolbar, click **Animation** and choose **File**.

2 In the **Settings** window for **Animation**, locate the **Scene** section.

3 From the **Subject** list, choose **Volume Fraction of Fluid 1 (pf)**.

4 Locate the **Target** section. From the **Target** list, choose **Player**.

5 Locate the **Animation Editing** section. From the **Time selection** list, choose **Interpolated**.

6 In the **Times (h)** text field, type `range(0,1,300)`.

7 Locate the **Frames** section. From the **Frame selection** list, choose **All**.

8 Click the **Play** button in the **Graphics** toolbar.