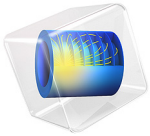

Localized Corrosion

Introduction

A metallic alloy with two constituent phases of different equilibrium potentials is susceptible to corrosion when it is exposed to an electrolyte solution. The constituent phase with a lower potential acts as an anode and preferentially corrodes whereas the other phase with a positive potential acts as a cathode. In order to capture the preferential dissolution of the anode phase, an explicit tracking of the dissolving interface is required which makes it a moving boundary problem.

In this model formulation, the electrode kinetics at both the anode and cathode phases are implemented in a unique way in terms of the level set function. Similarly, movement of the anode surface is implemented using the level set function and the in-built moving mesh formulation.

This model example simulates the cross-sectional microstructure evolution during a corrosion event and 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. The cross-sectional microstructure shown in Figure 1 is represented in terms of the level set function using an interpolation function called "micro". It has width of 200 μm and depth of 25 μm and the maximum depth of the alpha phase is 10 μm. The alpha and beta phases at the electrode boundary are identified when the interpolated level set function, `micro`, has a value of 0 and 1, respectively.

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

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

where $\mathbf{i}_l$ (SI unit: A/m^2) is the electrolyte current density vector and σ_l (SI unit: S/m) is the electrolyte conductivity which is assumed to be a constant of 2.5 S/m.

Use the default Insulation condition for all boundaries except the electrode surface:

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

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

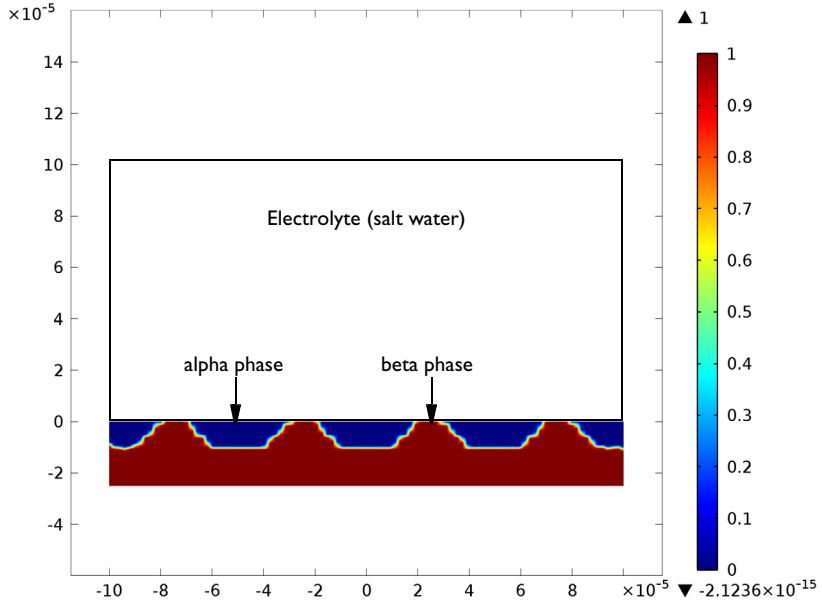

Figure 1: Model geometry along with cross-sectional microstructure comprising the alpha and beta phases and exposed to the electrolyte solution.

Use an Electrode Surface boundary node, with an added Dissolving-Depositing Species, at the electrode surface. This will set the boundary condition for the electrolyte potential to

$$\mathbf{n} \cdot \mathbf{i}_l = \sum_m i_{\text{loc},\,m} + i_{\text{dl}}$$

where $i_{\text{loc},m}$ (SI unit: A/m^2) is the local individual electrode reaction current density.

The dissolution at the electrode surface with a velocity in the normal direction is evaluated according to

$$\mathbf{n} \cdot \frac{\partial x}{\partial t} = \sum_i \frac{R_{\text{dep},\,i,\,m} M_i}{\rho_i}$$

where M_i is the molar mass (23.98 g/mol) and ρ_i is the density (1770 kg/m^3) of the corroding species i.

$R_{\text{dep},i,m}$ is evaluated using the following equation:

$$R_{\text{dep},\,i,\,m} = -\frac{\upsilon_{\text{dep},\,i,\,m} i_{\text{loc,m}}}{n_{\text{m}} F}$$

where $\upsilon_{\text{dep},\,i,\,m}$ is the stoichiometric coefficient and $n_m$is the number of electrons participating in the electrode reaction.

Use a User Defined electrode kinetics expression type to model the electrode reaction at the alpha phase on the electrode surface.

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

$$i_{\text{alpha}} = f(\phi_{s,\,\text{ext}} - \phi_1) \times (1 - \text{micro}(x, y)) \tag{1}$$

A relationship between the local current density and the electrolyte potential for the alpha phase at the electrode surface is incorporated in the model using a piecewise cubic interpolation function for the experimental polarization data as shown in Figure 2.

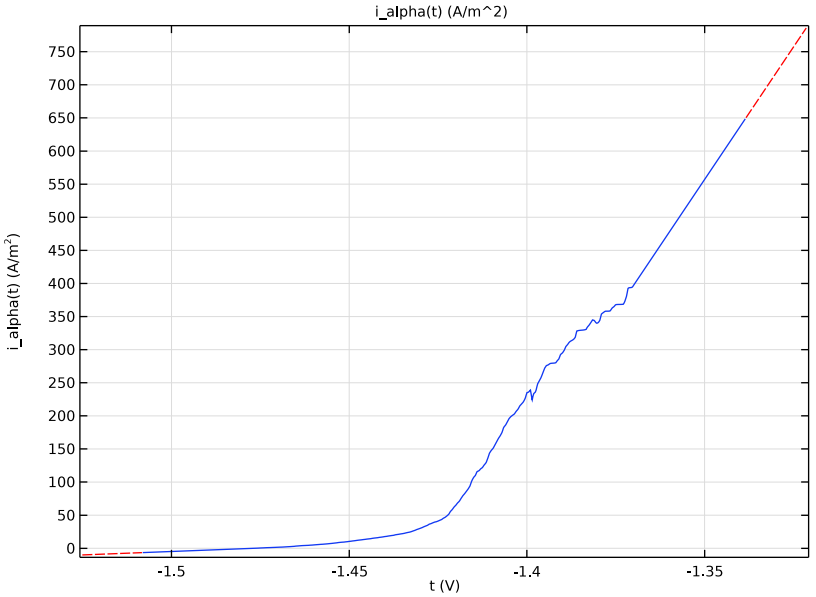

Figure 2: Anodic polarization data for the alpha phase.

It should be noted that the expression, `1-micro(x,y)`, ensures that the local current density is applied only at the alpha phase on the electrode surface.

Similarly, set the electrode kinetics to model the electrode reaction at the beta phase on the electrode surface using the following expression for the local current density:

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

A relationship between the local current density and the electrolyte potential for the beta phase at the electrode surface is incorporated in the model using a piecewise cubic interpolation function for the experimental polarization data as shown in Figure 3. The level set function `micro(x,y)` ensures that the local current density is applied only at the beta phase on the electrode surface.

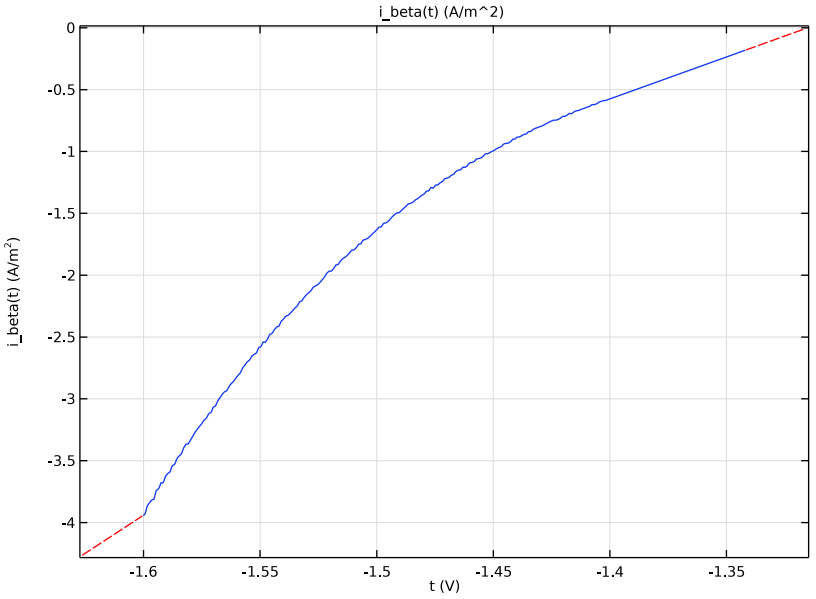

Figure 3: Cathodic polarization data for the beta phase.

In this model formulation, it is assumed that the anodic dissolution reaction takes place at the alpha phase surface and the cathodic hydrogen evolution reaction, where there is no material loss, takes place at the beta phase surface. Hence, the alpha phase surface is considered to be moving (dissolving) whereas the beta phase surface is considered to remain intact. This is achieved in the model by setting the value of stoichiometric coefficient to 1 and 0 for the alpha phase and beta phase electrode reactions, respectively.

The mesh used in the model is shown in Figure 4.

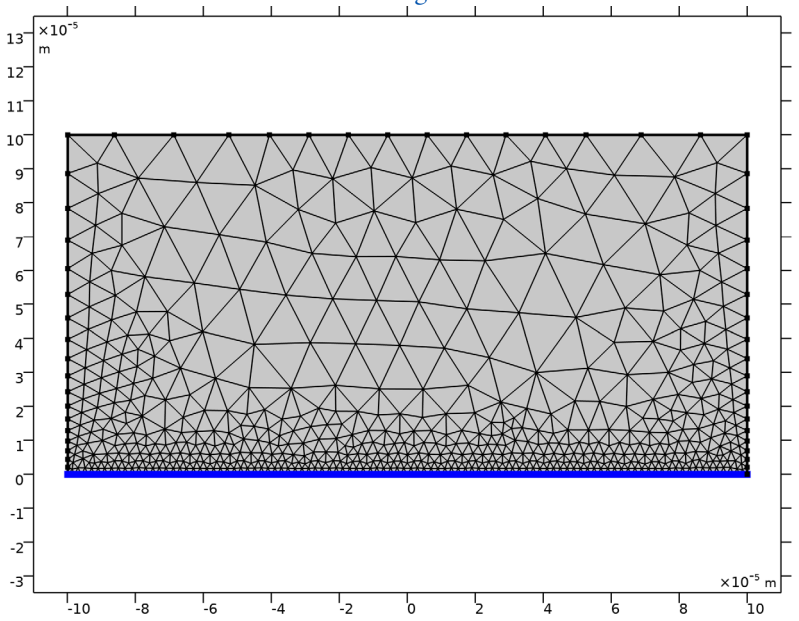

Figure 4: The mesh used in the model.

Results and Discussion

Figure 5 shows a surface plot of the electrolyte potential at time t = 59 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 underneath beta phase gets exposed to the electrolyte solution resulting in an increase in the surface beta phase fraction at the electrode surface. The computations are stopped when the surface beta phase fraction reaches a value of 0.95 which happens at time t = 59 h in this case. It can be seen in Figure 5 that most of the alpha phase shown in Figure 1 is dissolved in the electrolyte solution at time t = 59 h.

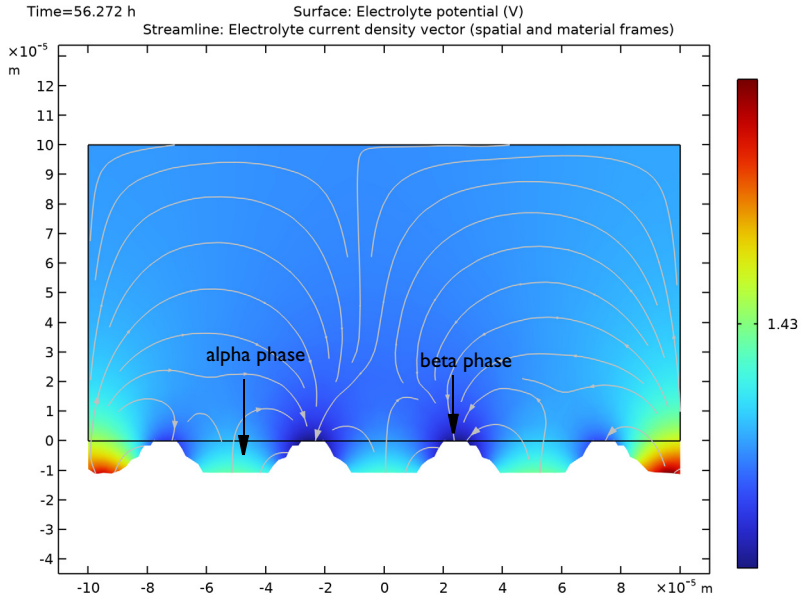

Figure 5: A surface plot of the electrolyte potential at time t = 59 h where the dissolved alpha phase and intact beta phase are highlighted.

The surface beta phase fraction at the electrode surface is evaluated using the following equation:

$$\text{Surface beta phase fraction} = \frac{\int_{\Omega} micro(x,y)d\Omega}{\int_{\Omega} micro(x,y)d\Omega + \int_{\Omega}(1-micro(x,y))d\Omega}$$

It can be seen in Figure 6 that the surface beta phase fraction is around 0.2 at an initial stage and it increases with time due to preferential dissolution of the alpha phase from the electrode surface exposing the underneath beta phase. The change in surface beta phase fraction with time is considerably gradual until time t = 40 h; however, it becomes more rapid for a higher value of surface beta phase fraction.

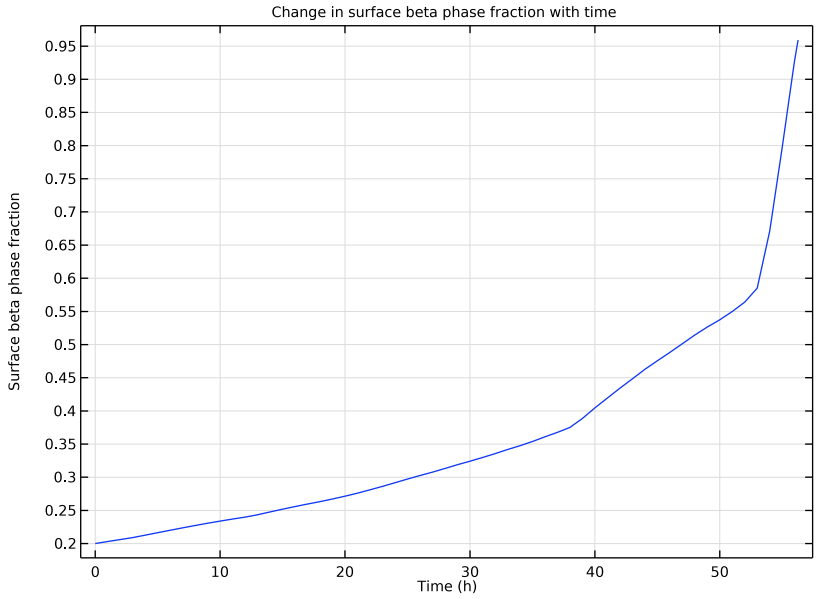

Figure 6: The change in the surface beta phase fraction with time.

The average anode current density at the electrode surface is evaluated using the following equation:

$$\text{Average anode current density} = \frac{\int_{\Omega} i_{\text{alpha}} d\Omega}{\int_{\Omega} (1 - micro(x,y)) d\Omega}$$

where i_{alpha} defined in Equation 1 is used.

Figure 7 shows the change in the average anode current density with time where it is found to be gradual for the lower surface beta phase fraction, similar to the change in surface beta phase fraction. The average anode current density increases very rapidly for the higher surface beta phase fraction which is attributed to a higher cathode to anode area ratio at the electrode surface.

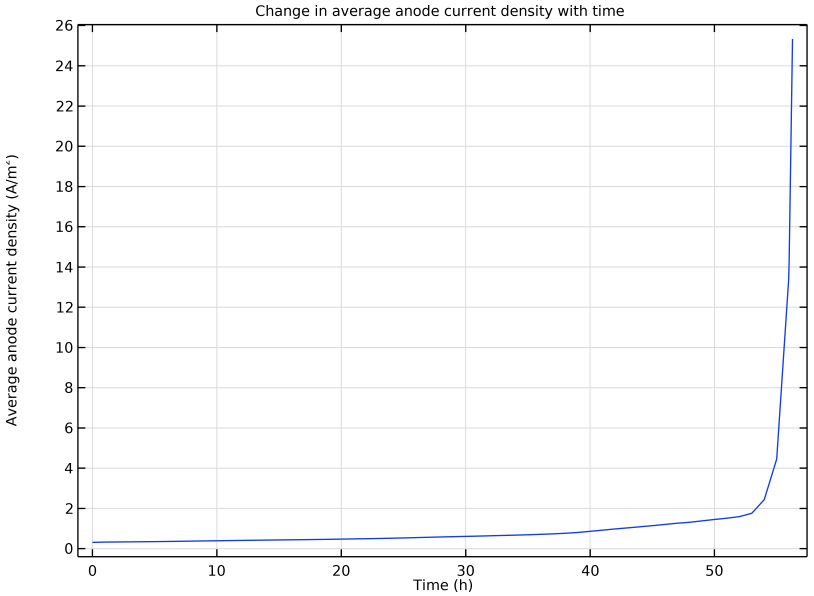

Figure 7: The change in the average anode current density with time.

Notes About the COMSOL Implementation

The Corrosion, Secondary entry from the Model Wizard is used in this model. It is a predefined multiphysics interface that contains a Secondary Current Distribution interface and a Deformed Geometry node. The Deformed Geometry node handles the deformed geometry (moving mesh/ALE) part of the problem.

A cross-sectional microstructure that consists of the alpha and beta phases is prescribed in the model using a level set type of function through interpolation.

The electrode kinetics is incorporated in the model using a piecewise cubic interpolation function for the experimental polarization data obtained separately for the two phases.

A time-dependent study with current distribution initialization is used to solve the model. The use of stop condition to stop the solver is demonstrated here.

A free triangular mesh is used for meshing, with a finer resolution at the electrode surface.

The model also demonstrates utility of an integration operator during computations as well as postprocessing of results.

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`

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>Corrosion, Deformed Geometry> Corrosion, Secondary**.

3 Click **Add**.

4 Click **Study**.

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

6 Click **Done**.

GEOMETRY 1

Now, create the model geometry as a rectangle.

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`.

6 Click **Build All Objects**.

7 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 domain, using an interpolation function. Please note that the interpolation function creates the same microstructure as reported in Ref. 1.

Interpolation 1 (int1)

1 In the **Home** toolbar, click **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_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** right-click **2D Plot Group 1** and choose **Rename**.

2 In the **Rename 2D Plot Group** dialog box, type `2D Plot Group : Cross-sectional microstructure` in the **New label** text field.

3 Click **OK**.

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

The cross-sectional microstructure should now look like Figure 1.

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 **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 Figure 2.

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 Figure 3.

Integration 1 (intop1)

Define a nonlocal integration coupling which would enable integration of several model variables to be used later in representing the model results.

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

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

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

4 Select Boundary 2 only.

Variables 1

Now, load the model variables which are used to evaluate the average surface beta phase fraction and the average anode current density.

1 In the **Definitions** toolbar, click **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_variables.txt`.

SECONDARY CURRENT DISTRIBUTION (CD)

Now set up the physics for the current distribution.

Electrolyte 1

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

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

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

Electrode Surface 1

Now, prescribe the electrode kinetics for both the alpha phase and beta phase at the electrode boundary surface making use of the level set type interpolated function.

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

2 Select Boundary 2 only.

3 In the **Settings** window for **Electrode Surface**, click to expand the **Dissolving-Depositing Species** section.

4 Click **Add**.

5 In the table, enter the following settings:

Species	Density (kg/m^3)	Molar mass (kg/mol)
s1	rho	M

6 Clear the **Solve for surface concentration variables** check box.

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 `z_charge`.

4 In the **Stoichiometric coefficients for dissolving-depositing species:** table, enter the following settings:

Species	Stoichiometric coefficient (1)
sl	1

5 Locate the **Electrode Kinetics** section. From the $i_{\text{loc,expr}}$ list, choose **User defined**. In the associated text field, type `(i_alpha(-phil))*(1-micro(x,y))`.

Electrode Surface 1

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

Electrode Reaction 2

1 In the **Physics** toolbar, click **Attributes** and choose **Electrode Reaction**.

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

3 From the $i_{\text{loc,expr}}$ list, choose **User defined**. In the associated text field, type `(i_beta(-phil))*micro(x,y)`.

MULTIPHYSICS

Nondeforming Boundary 1 (ndbdg1)

The following applies a stronger constraint (than the default condition) for the planar nondepositing walls in order to enforce a zero boundary movement in the normal direction.

1 In the **Model Builder** window, under **Component 1 (comp1)>Multiphysics** click **Nondeforming Boundary 1 (ndbdg1)**.

2 In the **Settings** window for **Nondeforming Boundary**, locate the **Nondeforming Boundary** section.

3 From the **Boundary condition** list, choose **Zero normal displacement**.

MESH 1

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

Free Triangular 1

In the **Mesh** toolbar, click  **Free Triangular**.

Size 1

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 **Predefined** list, choose **Coarse**.

Size 2

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 **Boundary**.

4 Select Boundary 2 only.

5 Locate the **Element Size** section. From the **Predefined** list, choose **Extremely fine**.

6 Click  **Build All**.

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

The mesh should look like Figure 4.

STUDY 1

Finally, set the time steps and a stop condition for time dependent solver.

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

4 In the **Output times** text field, type `range(0,1,24*3)`.

Solution 1 (sol1)

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

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

3 Right-click **Study 1>Solver Configurations>Solution 1 (sol1)>Time-Dependent Solver 1** and choose **Stop Condition**.

4 In the **Settings** window for **Stop Condition**, locate the **Stop Expressions** section.

5 Click **Add**.

6 In the table, enter the following settings:

Stop expression	Stop if	Active	Description
`comp1.beta_phase_fraction> 0.95`	True (>=1)	√	`Stop expression 1`

7 Locate the **Output at Stop** section. From the **Add solution** list, choose **Steps before and after stop**.

8 Clear the **Add warning** check box.

The model is now ready to be solved.

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

RESULTS

A 2D plot of the electrolyte potential and the deformation is created by default. Change the frame of the dataset edges to Geometry in order to show the outline of the original (undeformed) geometry in the figure.

Electrolyte Potential (cd)

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

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

3 From the **Frame** list, choose **Geometry (Xg, Yg, Zg)**.

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

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

1D Plot Group 5

Now, plot the change in the average surface beta phase fraction with time.

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

2 In the **Settings** window for **1D Plot Group**, click to expand the **Title** section.

3 From the **Title type** list, choose **Manual**.

4 In the **Title** text area, type `Change in surface beta phase fraction with time`.

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

6 In the associated text field, type `Surface beta phase fraction`.

Global 1

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

2 In the **Settings** window for **Global**, locate the **y-Axis Data** section.

3 In the table, enter the following settings:

Expression	Unit	Description
`beta_phase_fraction`	1	

4 Click to expand the **Legends** section. Clear the **Show legends** check box.

1D Plot Group : Surface beta phase fraction evolution

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

2 In the **Rename 1D Plot Group** dialog box, type `1D Plot Group : Surface beta phase fraction evolution` in the **New label** text field.

3 Click **OK**.

Finally, plot the change in the average anode current density with time.

1D Plot Group : Surface beta phase fraction evolution 1

1 Right-click **1D Plot Group : Surface beta phase fraction evolution** and choose **Duplicate**.

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

3 In the **Title** text area, type `Change in average anode current density with time`.

4 Locate the **Plot Settings** section. In the **y-axis label** text field, type `Average anode current density (A/m<sup>2</sup>)`.

Global 1

1 In the **Model Builder** window, expand the **1D Plot Group : Surface beta phase fraction evolution 1** node, then click **Global 1**.

2 In the **Settings** window for **Global**, locate the **y-Axis Data** section.

3 In the table, enter the following settings:

Expression	Unit	Description
`i_alpha_phase/alpha_phase`	1	

1D Plot Group : Average anode current density evolution

1 In the **Model Builder** window, right-click **1D Plot Group : Surface beta phase fraction evolution 1** and choose **Rename**.

2 In the **Rename 1D Plot Group** dialog box, type `1D Plot Group : Average anode current density evolution` in the **New label** text field.

3 Click **OK**.