

Atmospheric Corrosion

Introduction

Atmospheric corrosion may occur when thin films of liquid water, in the range of up to hundreds of micrometers, forms on metal surfaces in contact with humidified air. The thickness of the film depends on the relative humidity of the surrounding air, but also on factors such as surface roughness and the presence of particles, especially salt crystals. The thin film of moisture acts as electrolyte, and may cause various corrosion phenomena, such as galvanic corrosion of a bimetallic element or crevice corrosion.

This tutorial model studies atmospheric galvanic corrosion as a function of the relative humidity of the surrounding air and salt load (NaCl) on a bimetallic aluminum alloy – steel surface. It is assumed that the electrolyte film solution is in equilibrium with solid salt particles, distributed uniformly over the surface at a given load.

The example uses parameter data from [Ref. 1,](#page-10-0) [Ref. 2](#page-10-1), and [Ref. 3](#page-11-0).

Model Definition

The model set-up is shown in [Figure 1](#page-1-0).

Figure 1: Model set-up. Each metal surface is 12 mm wide.

The thickness of the electrolyte film depends on both the salt load density and the relative humidity, see [Figure 2.](#page-2-0) The film grows significantly toward 100% relative humidity.

Figure 2: Thickness of the electrolyte for different relative humidities and salt load densities. The conductivity varies linearly with the salt load density. ([Ref. 1](#page-10-0)*)*

The oxygen solubility, oxygen diffusivity, and the electrolyte conductivity also depend on the relative humidity, see [Figure 3](#page-3-0), [Figure 4,](#page-4-0) and [Figure 5.](#page-5-0)

Figure 3: Oxygen solubility vs relative humidity.([Ref. 1](#page-10-0)*)*

Figure 4: Oxygen diffusivity vs relative humidity.([Ref. 2](#page-10-1)*)*

Figure 5: Electrolyte conductivity vs relative humidity. ([Ref. 1](#page-10-0)*)*

ELECTROCHEMICAL REACTIONS

The less nobler aluminum alloy is oxidized in the cell, with the electrode reaction kinetics described in terms of experimental polarization data from the corrosion material library.

On the steel surface, oxygen reduction occurs. The oxygen reduction reaction is limited by oxygen transport through the film. The limiting current density, *i*lim, O2 (SI unit: A/ $m²$), depends on the film thickness, the oxygen solubility and the oxygen diffusivity according to:

$$
i_{\lim, O_2} = \frac{4FDc_{\text{sol}}}{d_{\text{film}}}
$$

where F (96485 C/mol) is Faraday's constant, D (SI unit: m^2/s) is the diffusivity of oxygen in the film, c_{sol} (SI unit: mol/m³) is the solubility of oxygen, and d_{film} (SI unit: m) is the film thickness.

By assuming a first order dependency of the oxygen reduction kinetics on the local current density of the oxygen concentration, the following expression for the current density, i_{lim} $_{\text{O2}}$ (SI unit: A/m²), can be derived:

$$
i_{\text{loc, O}_2} = \frac{i_{\text{expr}}}{1 + \left|\frac{i_{\text{expr}}}{i_{\text{lim, O}_2}}\right|}
$$

where i_{expr} is the local current density of the electrode reaction in absence of mass transport limitations described in terms of experimental polarization data from the corrosion material library.

Results and Discussion

[Figure 6](#page-7-0) shows the local current density of the electrode reactions for a salt load of 0.5 g/ $m²$ and various relative humidities. The cathodic currents reach a plateau close to $x = 0$ at a magnitude that is significantly affected by the relative humidity. This is due to a changing limiting current density for oxygen reduction. As the film thickness grows, the electrolyte

transport length for oxygen increases, in combination with an increased oxygen solubility and diffusivity for higher relative humidities.

*Figure 6: Local current densities along the metal surface at a salt loading of 0.5 g/m*2 *and relative humidities (RH) spanning from 80% to 98%.*

[Figure 7](#page-8-0) shows the maximum anodic currents for various salt load densities and relative humidities. For all salt loads, a maximum current density is seen around a relative humidity of 90%.

Figure 7: Maximum metal oxidation anodic current density on the aluminum alloy metal surface for varied relative humidities and salt load densities (LD).

Looking at the maximum cathodic currents in [Figure 8,](#page-9-0) it is seen that the maximum oxygen currents are about one order of magnitude smaller than the anodic currents, but that they follow the same trend with a maximum around a relative humidity of 90%. These currents are very close to the limiting current densities for oxygen reduction.

Figure 8: Maximum oxygen reduction cathodic current densities on the steel metal surface for varied relative humidities and salt load densities (LD).

Finally, [Figure 9](#page-10-2) shows the average anode current density, which gives us a measure of the total corrosion rate of the sample, for various relative humidities and salt load densities. The maximum is found for a salt load density of 3.5 g/m^2 and a relative humidity of 95%.

Figure 9: Average current densities on the aluminum alloy metal surface for varied relative humidities and salt load densities (LD).

Notes About the COMSOL Implementation

The model is implemented using the Current Distribution, Shell interface with two Parametric Sweeps to study the impact of a range of different relative humidities and salt load densities.

References

1. Z.Y. Chen, F. Cui, and R.G. Kelly, "Calculations of the Cathodic Current Delivery Capacity and Stability of Crevice Corrosion under Atmospheric Environments," *J. Electrochemical Society*, vol. 155, no. 7, pp. C360–368, 2008.

2. D. Mizuno and R.G. Kelly "Galvanically Induced Intergranular Corrosion of AA5083- H131 Under Atmospheric Exposure Conditions — Part II — Modeling of the Damage Distribution," *Corrosion*, vol. 69, no. 6, pp. 580–592, 2013.

3. D. Mizuno, Y. Shi, and R.G. Kelly, "Modeling of Galvanic Interactions between AA5083 and Steel under Atmospheric Conditions," *Excerpt from the Proceedings of the 2011 COMSOL Conference in Boston*.

Application Library path: Corrosion_Module/Atmospheric_Corrosion/ atmospheric_corrosion

Modeling Instructions

From the **File** menu, choose **New**.

NEW

In the **New** window, click \bigotimes **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>Current Distribution, Shell (cdsh).

- **3** Click **Add**.
- **4** Click \ominus Study.
- **5** In the **Select Study** tree, select **General Studies>Stationary**.
- **6** Click **Done**.

GEOMETRY 1

Draw the geometry as two adjacent linear polygon segments, each 12 mm wide.

Polygon 1 (pol1)

- **1** In the **Geometry** toolbar, click **Polygon**.
- **2** In the **Settings** window for **Polygon**, locate the **Object Type** section.
- **3** From the **Type** list, choose **Open curve**.
- **4** Locate the **Coordinates** section. From the **Data source** list, choose **Vectors**.
- **5** In the **x** text field, type -12[mm] 0 0 12[mm].
- **6** In the **y** text field, type 0 0 0 0.
- **7** Click **Build All Objects**.

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 atmospheric_corrosion_parameters.txt.

DEFINITIONS

Now create some average and maximum operators. These will be used later on when postprocessing the simulation results.

Average 1 (aveop1)

- **1** In the **Definitions** toolbar, click **Nonlocal Couplings** and choose **Average**.
- **2** In the **Settings** window for **Average**, locate the **Source Selection** section.
- **3** From the **Geometric entity level** list, choose **Boundary**.
- **4** Select Boundary 1 only.

Maximum 1 (maxop1)

- **1** In the **Definitions** toolbar, click **Nonlocal Couplings** and choose **Maximum**.
- **2** In the **Settings** window for **Maximum**, locate the **Source Selection** section.
- **3** From the **Geometric entity level** list, choose **Boundary**.
- **4** Select Boundary 1 only.

Maximum 2 (maxop2)

- **1** Right-click **Maximum 1 (maxop1)** and choose **Duplicate**.
- **2** In the **Settings** window for **Maximum**, locate the **Source Selection** section.
- **3** Click **Clear Selection**.
- **4** Select Boundary 2 only.

MATERIALS

Use the Corrosion Material Library to set up the material properties for the electrode kinetics at the aluminum and steel electrode surfaces.

ADD MATERIAL

1 In the **Home** toolbar, click **Add Material** to open the **Add Material** window.

- **2** Go to the **Add Material** window.
- **3** In the tree, select **Corrosion>Iron Alloys (Steels)>AISI 4340 steel in 0.6M NaCl at pH = 8.3**.
- **4** Click **Add to Component** in the window toolbar.

MATERIALS

- *AISI 4340 steel in 0.6M NaCl at pH = 8.3 (mat1)*
- **1** Select Boundary 2 only.
- **2** In the **Model Builder** window, expand the **AISI 4340 steel in 0.6M NaCl at pH = 8.3 (mat1)** node.

Interpolation 1 (iloc_exp)

- **1** In the **Model Builder** window, expand the **Component 1 (comp1)>Materials> AISI 4340 steel in 0.6M NaCl at pH = 8.3 (mat1)>Local current density (lcd)** node, then click **Interpolation 1 (iloc_exp)**.
- **2** In the **Settings** window for **Interpolation**, click **Plot**.

The function plot should look like this:

ADD MATERIAL

1 Go to the **Add Material** window.

- **2** In the tree, select **Corrosion>Aluminum Alloys>AA5083-H131 in 0.6 M NaCl**.
- **3** Click **Add to Component** in the window toolbar.
- **4** In the **Home** toolbar, click **Add Material** to close the **Add Material** window.

MATERIALS

AA5083-H131 in 0.6 M NaCl (mat2)

- **1** Select Boundary 1 only.
- **2** In the **Model Builder** window, expand the **AA5083-H131 in 0.6 M NaCl (mat2)** node.

Interpolation 1 (iloc_exp)

- **1** In the **Model Builder** window, expand the **Component 1 (comp1)>Materials>AA5083- H131 in 0.6 M NaCl (mat2)>Local current density (lcd)** node, then click **Interpolation 1 (iloc_exp)**.
- **2** In the **Settings** window for **Interpolation**, click **Plot**.

The function plot should look like this:

CURRENT DISTRIBUTION, SHELL (CDSH)

Now set up the physics for the current distribution. Start with selecting the reference electrode potential.

- **1** In the **Model Builder** window, under **Component 1 (comp1)** click **Current Distribution, Shell (cdsh)**.
- **2** In the **Settings** window for **Current Distribution, Shell**, click to expand the **Physics vs. Materials Reference Electrode Potential** section.
- **3** From the list, choose **0.241 V (SCE vs. SHE)**.

Electrolyte 1

Next, set the electrolyte thickness and electrolyte conductivity.

- **1** In the **Model Builder** window, under **Component 1 (comp1)>Current Distribution, Shell (cdsh)** click **Electrolyte 1**.
- **2** In the **Settings** window for **Electrolyte**, locate the **Electrolyte** section.
- **3** In the *s* text field, type d_film.
- **4** From the σ _l list, choose **User defined**. In the associated text field, type sigma.

Electrode Surface 1

Use Electrode Surface nodes to set up the electrode reactions for the two metallic surfaces.

- **1** In the **Physics** toolbar, click **Boundaries** and choose **Electrode Surface**.
- **2** Select Boundary 1 only.

Electrode Reaction 1

- **1** In the **Model Builder** window, click **Electrode Reaction 1**.
- **2** In the **Settings** window for **Electrode Reaction**, locate the **Electrode Kinetics** section.
- **3** From the *i*loc,expr list, choose **From material**.

Electrode Surface 2

- **1** In the **Physics** toolbar, click **Boundaries** and choose **Electrode Surface**.
- **2** Select Boundary 2 only.

Electrode Reaction 1

- **1** In the **Model Builder** window, click **Electrode Reaction 1**.
- **2** In the **Settings** window for **Electrode Reaction**, locate the **Electrode Kinetics** section.
- **3** From the *i*loc,expr list, choose **From material**.
- **4** Select the **Limiting current density** check box.
- **5** In the i_{lim} text field, type ilim.

MESH 1

Use a finer mesh at the intersection point between the two electrode surfaces for this problem.

Edge 1

- In the **Mesh** toolbar, click **Edge**.
- Click in the **Graphics** window and then press Ctrl+A to select both boundaries.

Distribution 1

- Right-click **Edge 1** and choose **Distribution**.
- In the **Settings** window for **Distribution**, locate the **Distribution** section.
- From the **Distribution type** list, choose **Predefined**.
- In the **Number of elements** text field, type 50.
- In the **Element ratio** text field, type 10.
- Select the **Reverse direction** check box.

Distribution 2

- Right-click **Distribution 1** and choose **Duplicate**.
- Select Boundary 2 only.
- In the **Settings** window for **Distribution**, locate the **Distribution** section.
- Clear the **Reverse direction** check box.

5 Click **Build All.**

Your finished mesh should now look like this:

STUDY 1

The problem is now ready for solving. Use a Parametric Sweep to study the corrosion currents for a range of different relative humidities and salt load densities.

Parametric Sweep

- **1** In the **Study** toolbar, click $\frac{1}{2}$ **Parametric Sweep**.
- **2** In the **Settings** window for **Parametric Sweep**, locate the **Study Settings** section.
- **3** From the **Sweep type** list, choose **All combinations**.
- **4** Click $+$ **Add**.
- **5** In the table, enter the following settings:

6 Click $+$ **Add**.

In the table, enter the following settings:

Solution 1 (sol1)

Decrease the solver tolerance to improve the accuracy of the solutions.

- **1** In the Study toolbar, click $\frac{1}{\sqrt{2}}$ Show Default Solver.
- In the **Model Builder** window, expand the **Solution 1 (sol1)** node, then click **Stationary Solver 1**.
- In the **Settings** window for **Stationary Solver**, locate the **General** section.
- In the **Relative tolerance** text field, type 0.00001.
- In the **Study** toolbar, click **Compute**.

RESULTS

Reproduce the plots from the [Results and Discussion](#page-6-0) section in the following way:

1D Plot Group 5

- In the **Home** toolbar, click **Add Plot Group** and choose **1D Plot Group**.
- In the **Settings** window for **1D Plot Group**, locate the **Axis** section.
- Select the **y-axis log scale** check box.

Line Graph 1

- In the **1D Plot Group 5** toolbar, click **Line Graph**.
- In the **Settings** window for **Line Graph**, locate the **Data** section.
- From the **Dataset** list, choose **Study 1/Solution 1 (sol1)**.
- From the **Parameter selection (LD)** list, choose **First**.
- Click in the **Graphics** window and then press Ctrl+A to select both boundaries.
- Locate the **y-Axis Data** section. In the **Expression** text field, type abs(cdsh.iloc_er1).
- Select the **Description** check box. In the associated text field, type Local current density.
- Locate the **x-Axis Data** section. From the **Parameter** list, choose **Expression**.
- In the **Expression** text field, type x.
- Click to expand the **Legends** section. Select the **Show legends** check box.
- In the **1D Plot Group 5** toolbar, click **Plot**.

1D Plot Group 6

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

Global 1

- **1** In the **1D Plot Group 6** toolbar, click $\left(\frac{1}{2}\right)$ Global.
- **2** In the **Settings** window for **Global**, locate the **y-Axis Data** section.
- **3** In the table, enter the following settings:

1D Plot Group 6

- **1** In the **Model Builder** window, click **1D Plot Group 6**.
- **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 Maximum Anode Current Density.
- **5** Locate the **Plot Settings** section.
- **6** Select the **x-axis label** check box. In the associated text field, type Relative Humidity (1).
- **7** Select the **y-axis label** check box. In the associated text field, type Current Density (A/m²sup>2²/sup>).
- **8** Locate the **Legend** section. From the **Position** list, choose **Upper left**.
- **9** In the **1D Plot Group 6** toolbar, click **Plot**.

1D Plot Group 7

Right-click **Results>1D Plot Group 6** and choose **Duplicate**.

Global 1

- **1** In the **Model Builder** window, expand the **1D Plot Group 7** 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:

1D Plot Group 7

- **1** In the **Model Builder** window, click **1D Plot Group 7**.
- **2** In the **Settings** window for **1D Plot Group**, locate the **Title** section.

3 In the **Title** text area, type Maximum Cathode Current Density.

4 In the **1D Plot Group 7** toolbar, click **Plot**.

1D Plot Group 8

In the **Model Builder** window, under **Results** right-click **1D Plot Group 6** and choose **Duplicate**.

Global 1

- **1** In the **Model Builder** window, expand the **1D Plot Group 8** 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:

1D Plot Group 8

1 In the **Model Builder** window, click **1D Plot Group 8**.

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

3 In the **Title** text area, type Average Anode Current Density.

4 In the **1D Plot Group 8** toolbar, click **Plot**.