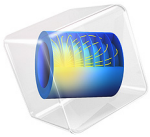


Atmospheric Corrosion with Mass Transport

Introduction

When a metal surface is in contact with humidified air, a thin film of liquid water may form, which in turn may result in atmospheric corrosion. This tutorial model simulates atmospheric corrosion of a galvanic couple comprising of an aluminum alloy and steel, in contact with a 50 μm thick electrolyte film. The model accounts for charge and mass transport of 10 species, involving 6 homogeneous reactions. The model simulates the transient and spatial distribution of the species in the electrolyte film, including corrosion products.

The example is based on a paper by Ruiz-Garcia and others (Ref. 1).

Model Definition

The model defines a galvanic couple in contact with an electrolyte (0.6 M NaCl) film of 50 μm thickness.

The model geometry consists of two linear segments, each 5 cm wide, representing the thin electrolyte film located above the aluminum alloy (AA5083-H131) and the steel (AISI 4340) parts of the surface, as shown in Figure 1.

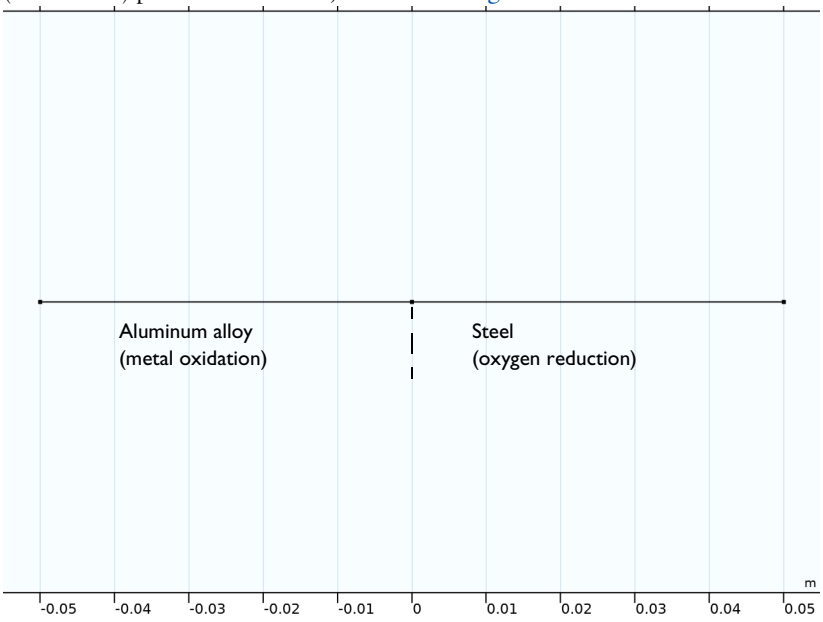


Figure 1: Model set-up. Each metal surface is 5 cm wide.

Note that the model is defined in 1D, assuming homogeneous properties of the electrolyte in the thickness direction of the film.

ELECTROCHEMICAL REACTIONS

Aluminum dissolution occurs at aluminum surface according to

$$\mathrm{Al} \Leftrightarrow \mathrm{Al}^{3+} + 3e^-$$

Oxygen reduction reaction occurs at steel surface according to

$$\mathrm{O_2} + 2\mathrm{H_2O} + 4e^- \Leftrightarrow 4\mathrm{OH}^-$$

The local current density, i_{loc} ($\mathrm{A/m^2}$), for the above electrode reactions is described in terms of experimental polarization data from the Corrosion Material Library (Ref. 2).

In the model, the local current density is homogenized in the film thickness direction into a volumetric electrode reaction source, i_v ($\mathrm{A/m^3}$), by multiplying by the active specific surface area, a_v ($\mathrm{m^2/m^3}$), according to

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

where the active specific surface area is described in terms of the electrolyte film thickness, δ (m), according to

$$a_v = \frac{1}{\delta}$$

HOMOGENEOUS REACTIONS

Six homogeneous reactions are considered in the model. The reactions, together with their respective forward and reverse rate constants, are listed in Table 1.

TABLE 1: HOMOGENEOUS REACTIONS WITH THEIR RESPECTIVE RATE CONSTANTS.

Reactions	k_f	k_r
$\mathrm{H_2O} \Leftrightarrow \mathrm{H}^+ + \mathrm{OH}^-$	1×10^{-8} (1/s)	1 ($\mathrm{m^3}$/mol/s)
$\mathrm{Al}^{3+} + \mathrm{OH}^- \Leftrightarrow \mathrm{AlOH}^{2+}$	1×10^{3} ($\mathrm{m^3}$/mol/s)	1.05×10^{-4} (1/s)
$\mathrm{AlOH}^{2+} + \mathrm{OH}^- \Leftrightarrow \mathrm{Al(OH)_2^+}$	1×10^{3} ($\mathrm{m^3}$/mol/s)	8.58×10^{-4} (1/s)
$\mathrm{Al(OH)_2^+} + \mathrm{OH}^- \Leftrightarrow \mathrm{Al(OH)_3}$	1×10^{3} ($\mathrm{m^3}$/mol/s)	5.02×10^{-4} (1/s)

TABLE 1: HOMOGENEOUS REACTIONS WITH THEIR RESPECTIVE RATE CONSTANTS.

Reactions	k_f	k_r
$Al^{3+} + Cl^- \Leftrightarrow AlCl^{2+}$	0.226 (m^3/mol/s)	75.27 (1/s)
$AlOH^{2+} + Cl^- \Leftrightarrow AlOHCl^+$	19 (m^3/mol/s)	5.7 x 10^3(1/s)

SPECIES TRANSPORT

The flux for each of the species (ions) in the electrolyte is given by the Nernst-Planck equations according to

$$\mathbf{N}_i = -D_i \nabla c_i - z_i u_i F c_i \nabla \phi_l,$$

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, $u_{i,\text{eff}}$ 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 modeled species, together with their respective diffusion coefficients in the electrolyte solution, are listed in Table 2.

TABLE 2: MODELED SPECIES WITH THEIR RESPECTIVE DIFFUSION COEFFICIENTS.

Species	D (m^2/s)·10^9
Na^+	1.334
Cl^-	2.032
H^+	9.311
OH^-	5.273
Al^{3+}	0.541
$AlOH^{2+}$	0.541
$Al(OH)_2^+$	0.541
$Al(OH)_3$	0.541
$AlCl^{2+}$	0.541
$AlOHCl^+$	0.541

The mobilities are calculated using the Nernst-Einstein relation:

$$u_i = \frac{D_i}{RT}$$

The rate of electrochemical reaction for each species $R_{i,\text{echem}}$ (mol/m^3/s) is based on the volumetric current density according to Faraday's law

$$R_{i,\,\text{echem}} = -\frac{\nu_i i_v}{nF}$$

where ν_i is a stoichiometric coefficient for the species i in the reaction and n the number of electrons.

The material balances are then expressed through

$$\frac{\partial \varepsilon_l c_i}{\partial t} + \nabla \cdot \mathbf{N}_i = R_{i,\,\text{chem}} + R_{i,\,\text{echem}}$$

using one material balance per species. $R_{i,\text{chem}}$ is the volumetric rates of the homogeneous reactions occurring in the electrolyte film as described above.

The governing equation for the electrolyte potential is based on the sum of all mass balances and the electroneutrality condition, given by the following expression:

$$\sum_i z_i c_i = 0$$

Results and Discussion

Figure 2 shows the change in OH^- ion concentration along the electrode surfaces at different times. It can be seen that OH^- ion concentration increases with time at the steel surface due to the cathodic reaction. The peak in OH^- ion concentration is shifted away from the junction with time. This is attributed to the consumption of OH^- ions due to

homogeneous reactions considered in the model, which involve Al^{3+} ions generated at the aluminum surface and transported toward the steel surface due to diffusion and migration.

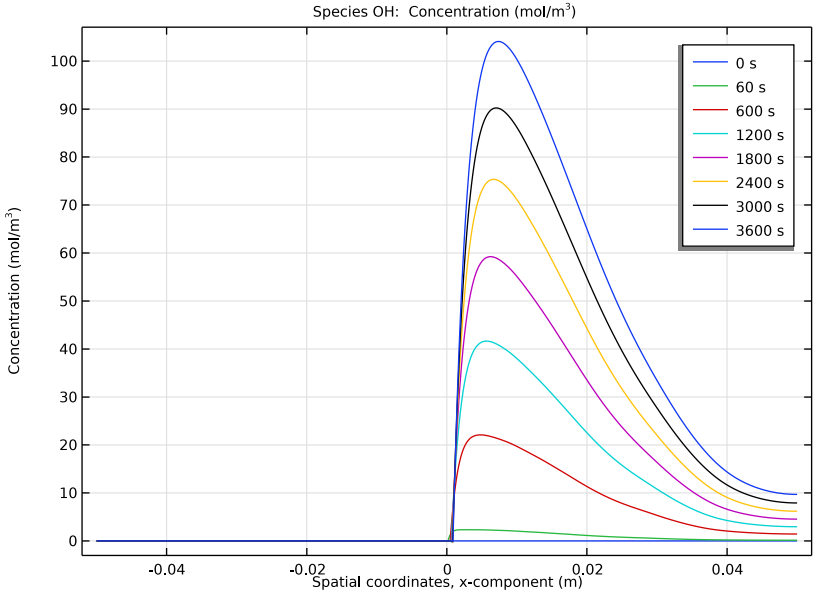


Figure 2: The change in OH^- ion concentration along the electrode surfaces at different times.

Figure 3 shows the change in Al^{3+} ion concentration along the electrode surfaces at different times. It can be seen that Al^{3+} ion concentration increases with time at the aluminum surface due to the anodic reaction. The peak in Al^{3+} ion concentration is shifted away from the junction with time. This is attributed to the consumption of Al^{3+} ions due to homogeneous reactions considered in the model, which involve OH^- ions generated at the steel surface and transported toward the aluminum surface due to diffusion and migration.

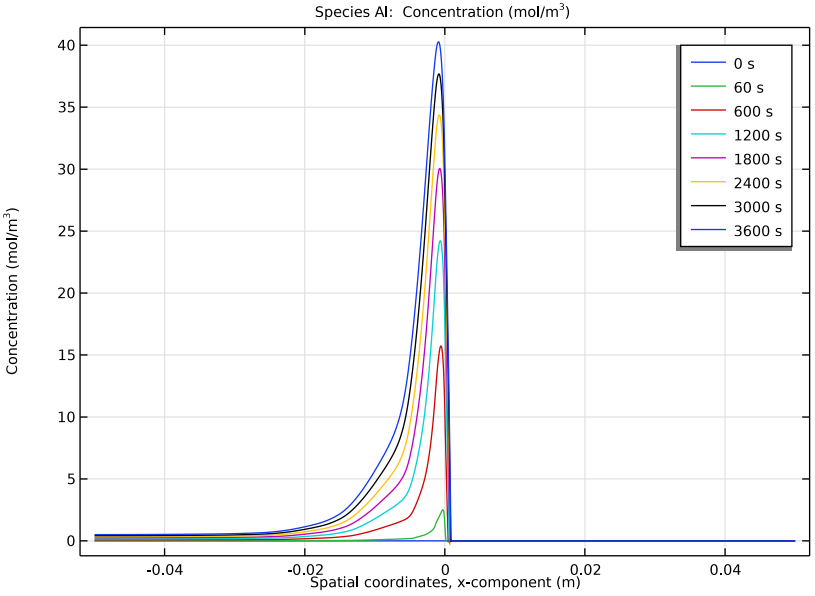


Figure 3: The change in Al^{3+} ion concentration along the electrode surfaces at different times.

Figure 4 shows the change in concentration of corrosion product, $Al(OH)_3$, along the electrode surfaces at different times. It can be seen that $Al(OH)_3$ concentration increases with time in the vicinity of the joint due to the homogeneous reaction.

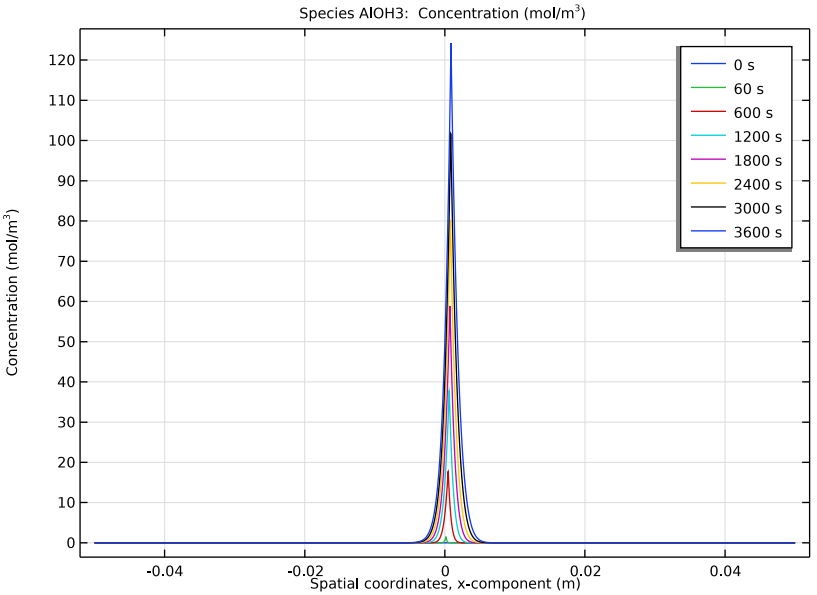


Figure 4: The change in concentration of corrosion product, $Al(OH)_3$, along the electrode surfaces at different times.

Figure 5 shows the change in concentration of corrosion product, $AlCl^{2+}$, along the electrode surfaces at different times. It can be seen that $AlCl^{2+}$ concentration increases with time at the aluminum surface due to the homogeneous reaction. The peak in $AlCl^{2+}$ concentration is shifted away from the junction with time.

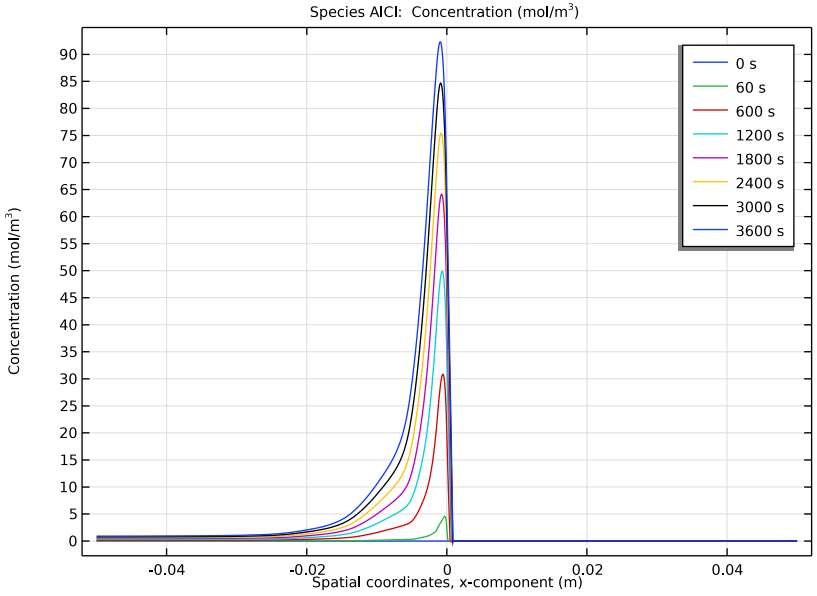


Figure 5: The change in concentration of corrosion product, $AlCl^{2+}$, along the electrode surfaces at different times.

Notes About the COMSOL Implementation

The **Tertiary Current Distribution, Nernst-Planck** interface is used to model the electrolyte potential and the transport of the species. The **Highly Conductive Porous Electrode** node is used for facilitating setting up electrochemical reactions, and the corresponding species source/sink terms. The electrolyte volume fraction ε_l is set to 1 to define that the entire domain contains electrolyte solution only.

The rate of chemical reactions for 6 homogeneous reactions considered in the model are set up using the **Chemistry** interface.

References

1. A. Ruiz-Garcia, E. Jimenez-Gonzalez, E. Cano, R. Mayen-Mondragon, J. Genesca, and R. Montoya, "The corrosion products in a carbon steel/aluminum alloy galvanic couple under thin electrolyte films: An efficient model," *Electrochemistry Communications*, vol. 104, article 106485, pp. 1–6, 2019.

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.

Application Library path: `Corrosion_Module/Atmospheric_Corrosion/atmospheric_corrosion_mass_transport`

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 **1D**.

2 In the **Select Physics** tree, select **Chemical Species Transport>Chemistry (chem)**.

3 Click **Add**.

4 In the **Select Physics** tree, select **Electrochemistry>Tertiary Current Distribution, Nernst-Planck>Tertiary, Electroneutrality (tcd)**.

5 Click **Add**.

6 In the **Number of species** text field, type 10.

7 In the **Concentrations (mol/m³)** table, enter the following settings:

cNa
cCl
cH
cOH
cAl
cAlOH
cAlOH2
cAlOH3
cAlCl
cAlOHCl

8 Click **Study**.

9 In the **Select Study** tree, select **Preset Studies for Selected Physics Interfaces> Tertiary Current Distribution, Nernst-Planck>Time Dependent with Initialization**.

10 Click **Done**.

GEOMETRY 1

Draw the geometry comprising of two adjacent linear segments, each 5 cm wide.

Interval 1 (i1)

1 In the **Model Builder** window, under **Component 1 (comp1)** right-click **Geometry 1** and choose **Interval**.

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

3 In the table, enter the following settings:

Coordinates (m)
-5[cm]
0
5[cm]

4 Click **Build All Objects**.

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

GLOBAL DEFINITIONS

Parameters 1

Load the model parameters from a text file.

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_mass_transport_parameters.txt`.

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 Domain 2 only.

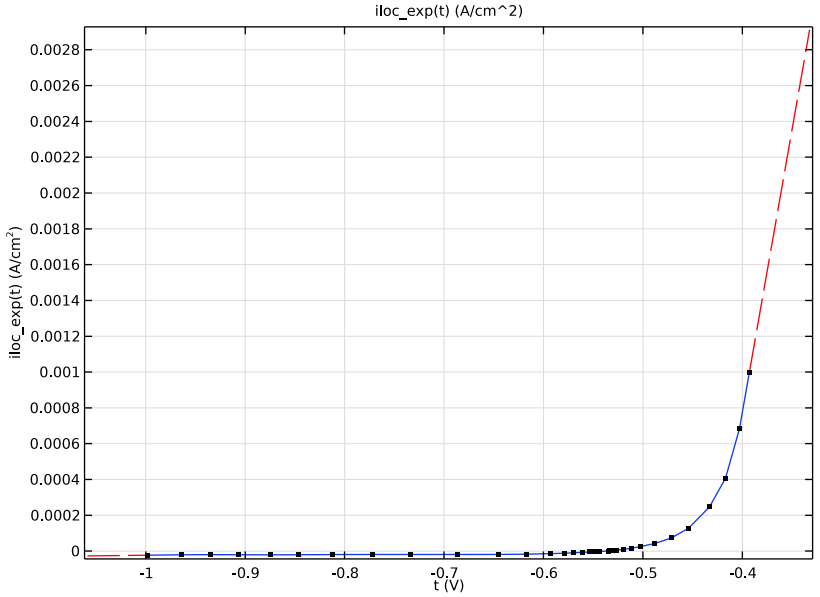
2 In the **Model Builder** window, expand the **AISI 4340 steel in 0.6M NaCl at pH = 8.3 (mat1)** node.

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 Domain 1 only.

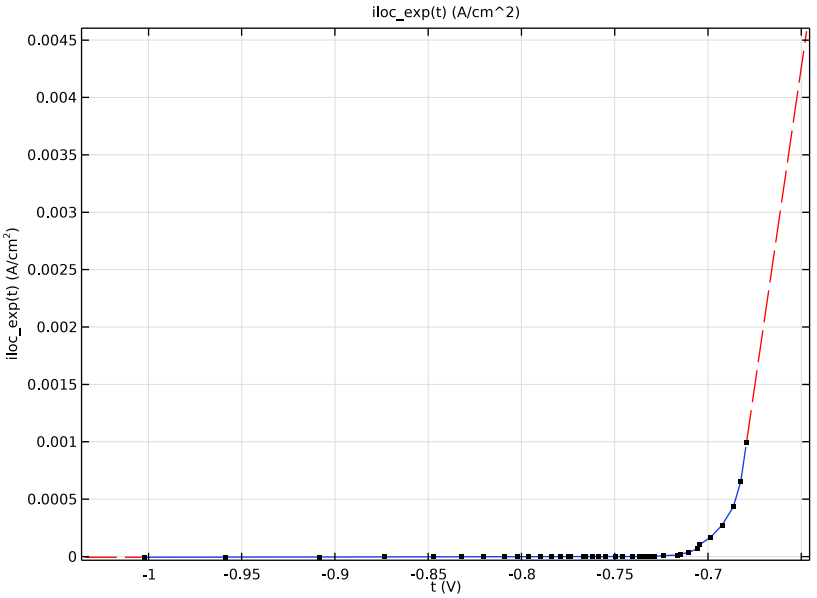
2 In the **Model Builder** window, expand the **AA5083-H131 in 0.6 M NaCl (mat2)** node.

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:



CHEMISTRY (CHEM)

Start setting up the physics by specifying the homogeneous reactions using **Chemistry** interface.

Reaction 1

1 In the **Model Builder** window, under **Component 1 (comp1)** right-click **Chemistry (chem)** and choose **Reaction**.

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

3 In the **Formula** text field, type `H2O<=>H+OH`.

4 Locate the **Rate Constants** section. In the k^{f} text field, type `kfH2O`.

5 In the k^{r} text field, type `krH2O`.

Reaction 2

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

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

3 In the **Formula** text field, type `Al+OH<=>AlOH`.

4 Click **Apply**.

5 Locate the **Rate Constants** section. In the k^{f} text field, type `kfAlOH`.

6 In the k^{r} text field, type `krAlOH`.

Reaction 3

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

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

3 In the **Formula** text field, type `AlOH+OH<=>AlOH2`.

4 Click **Apply**.

5 Locate the **Rate Constants** section. In the k^{f} text field, type `kfAlOH2`.

6 In the k^{r} text field, type `krAlOH2`.

Reaction 4

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

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

3 In the **Formula** text field, type `AlOH2+OH<=>AlOH3`.

4 Click **Apply**.

5 Locate the **Rate Constants** section. In the k^{f} text field, type `kfAlOH3`.

6 In the k^{r} text field, type `krAlOH3`.

Reaction 5

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

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

3 In the **Formula** text field, type `Al+Cl<=>AlCl`.

4 Click **Apply**.

5 Locate the **Rate Constants** section. In the k^{f} text field, type `kfAlCl`.

6 In the k^{r} text field, type `krAlCl`.

Reaction 6

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

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

3 In the **Formula** text field, type `AlOH+Cl<=>AlOHCl`.

4 Click **Apply**.

5 Locate the **Rate Constants** section. In the k^{f} text field, type `kfAlOHCl`.

6 In the k^{r} text field, type `krAlOHCl`.

TERTIARY CURRENT DISTRIBUTION, NERNST-PLANCK (TCD)

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

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

2 In the **Settings** window for **Tertiary Current Distribution, Nernst-Planck**, click to expand the **Physics vs. Materials Reference Electrode Potential** section.

3 From the list, choose **0.241 V (SCE vs. SHE)**.

Species Charges 1

Next set the charge number at **Species Properties** node.

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_{cNa} text field, type `zNa`.

4 In the z_{cCl} text field, type `zCl`.

5 In the z_{cH} text field, type `zH`.

6 In the z_{cOH} text field, type `zOH`.

7 In the z_{cAl} text field, type `zAl`.

8 In the z_{cAlOH} text field, type `zAlOH`.

9 In the z_{cAlOH2} text field, type `zAlOH2`.

10 In the z_{cAlOH3} text field, type `zAlOH3`.

11 In the z_{cAlCl} text field, type `zAlCl`.

12 In the $z_{cAlOHCl}$ text field, type `zAlOHCl`.

Initial Values 1

Next set the initial values.

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

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

3 In the *cCl* text field, type `cOCl`.

4 In the *cH* text field, type `cOH`.

5 In the *cOH* text field, type `cOOH`.

6 In the *cAl* text field, type `cOAl`.

7 In the *cAlOH* text field, type `cOAlOH`.

8 In the *cAlOH2* text field, type `cOAlOH2`.

9 In the *cAlOH3* text field, type `cOAlOH3`.

10 In the *cAlCl* text field, type `cOAlCl`.

11 In the *cAlOHCl* text field, type `cOAlOHCl`.

Highly Conductive Porous Electrode 1

Next set the charge, mass transport and electrode kinetics at the steel surface using the **Highly Conductive Porous Electrode** node.

1 In the **Physics** toolbar, click — **Domains** and choose **Highly Conductive Porous Electrode**.

2 Select Domain 1 only.

3 In the **Settings** window for **Highly Conductive Porous Electrode**, locate the **Diffusion** section.

4 In the D_{cNa} text field, type `DNa`.

5 In the D_{cCl} text field, type `DCl`.

6 In the D_{cH} text field, type `DH`.

7 In the D_{cOH} text field, type `DOH`.

8 In the D_{cAl} text field, type `DAl`.

9 In the D_{cAlOH} text field, type `DAlOH`.

10 In the D_{cAlOH2} text field, type `DAlOH2`.

11 In the D_{cAlOH3} text field, type `DAlOH3`.

12 In the D_{cAlCl} text field, type `DAlCl`.

13 In the D_{cAlOHCl} text field, type `DAlOHCl`.

14 Locate the **Porous Matrix Properties** section. In the ε_l text field, type `1`.

Porous Electrode Reaction 1

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 `3`.

4 In the ν_{cAl} text field, type `-1`.

5 Locate the **Electrode Kinetics** section. From the $i_{\mathrm{loc,expr}}$ list, choose **From material**.

6 Locate the **Active Specific Surface Area** section. In the a_{v} text field, type `1/d_film`.

Highly Conductive Porous Electrode 1

Next set the charge, mass transport and electrode kinetics at the aluminum surface using duplicate functionality.

In the **Model Builder** window, right-click **Highly Conductive Porous Electrode 1** and choose **Duplicate**.

Highly Conductive Porous Electrode 2

1 In the **Model Builder** window, click **Highly Conductive Porous Electrode 2**.

2 Select Domain 2 only.

Porous Electrode Reaction 1

1 In the **Model Builder** window, expand the **Highly Conductive Porous Electrode 2** node, then 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 `4`.

4 In the ν_{cOH} text field, type `4`.

5 In the ν_{cAl} text field, type `0`.

Reactions 1

Next set the reaction rates for all species using the **Reactions** node which are evaluated in Chemistry interface.

1 In the **Physics** toolbar, click — **Domains** and choose **Reactions**.

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

3 In the **Settings** window for **Reactions**, locate the **Reaction Rates** section.

4 From the R_{cCl} list, choose **Reaction rate for species Cl (chem)**.

5 From the R_{cH} list, choose **Reaction rate for species H (chem)**.

6 From the R_{cOH} list, choose **Reaction rate for species OH (chem)**.

7 From the R_{cAl} list, choose **Reaction rate for species Al (chem)**.

8 From the R_{cAlOH} list, choose **Reaction rate for species AlOH (chem)**.

9 From the R_{cAlOH2} list, choose **Reaction rate for species AlOH2 (chem)**.

10 From the R_{cAlOH3} list, choose **Reaction rate for species AlOH3 (chem)**.

11 From the R_{cAlCl} list, choose **Reaction rate for species AlCl (chem)**.

12 From the $R_{cAlOHCl}$ list, choose **Reaction rate for species AlOHCl (chem)**.

MESH 1

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

Edge 1

1 In the **Mesh** toolbar, click  **Edge**.

2 In the **Settings** window for **Edge**, locate the **Domain Selection** section.

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

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

Distribution 1

1 Right-click **Edge 1** and choose **Distribution**.

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

3 From the **Distribution type** list, choose **Predefined**.

4 In the **Number of elements** text field, type 300.

5 In the **Element ratio** text field, type 10.

6 Select the **Reverse direction** check box.

7 Right-click **Distribution 1** and choose **Duplicate**.

Distribution 2

1 In the **Model Builder** window, click **Distribution 2**.

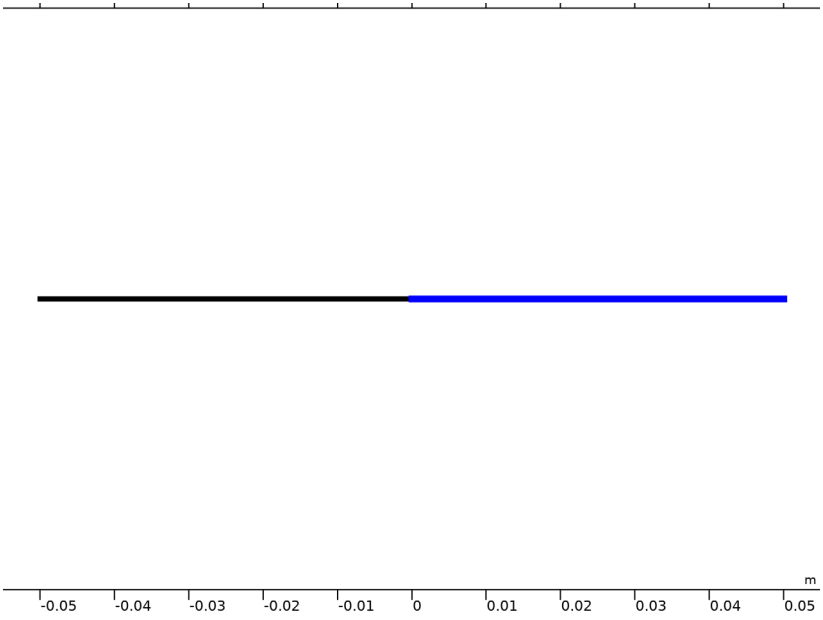
2 Select Domain 2 only.

3 In the **Settings** window for **Distribution**, locate the **Distribution** section.

4 Clear the **Reverse direction** check box.

5 Click **Build All**.

Your finished mesh should now look like this:



STUDY 1

The model is now ready to solved after setting the output times for Time Dependent study step.

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 `0 60 range(600,600,3600)`.

4 In the **Home** toolbar, click **Compute**.

RESULTS

Reproduce the plots from the Results and Discussion section in the following way:

Line Graph 1

1 In the **Model Builder** window, expand the **Concentration, OH (tcd)** node, then click **Line Graph 1**.

2 In the **Settings** window for **Line Graph**, click to expand the **Legends** section.

3 Select the **Show legends** check box.

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

The plot should look like Figure 2.

Line Graph 1

1 In the **Model Builder** window, expand the **Concentration, Al (tcd)** node, then click **Line Graph 1**.

2 In the **Settings** window for **Line Graph**, locate the **Legends** section.

3 Select the **Show legends** check box.

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

The plot should look like Figure 3.

Line Graph 1

1 In the **Model Builder** window, expand the **Concentration, AlOH3 (tcd)** node, then click **Line Graph 1**.

2 In the **Settings** window for **Line Graph**, locate the **Legends** section.

3 Select the **Show legends** check box.

The plot should look likeFigure 4.

Line Graph 1

1 In the **Model Builder** window, expand the **Concentration, AlCl (tcd)** node, then click **Line Graph 1**.

2 In the **Settings** window for **Line Graph**, locate the **Legends** section.

3 Select the **Show legends** check box.

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

The plot should look like Figure 5.