



Corrosion Inhibitor Transport

Introduction

The model simulates the resulting atmospheric corrosion due to a scratch in a metallic coating. The scratch results in a galvanic couple, comprising of an Al-Co-Ce metallic coating and an aluminum alloy, in contact with a thin electrolyte film.

Corrosion inhibitors are released from the metallic coating and are transported to the aluminum scratch surface by diffusion and migration. The model accounts for charge and mass transport of 11 species, including 5 homogeneous reactions.

The model computes the transient and spatial distribution of species in the film, estimating the time required for accumulation of critical inhibitor concentration over the aluminum scratch surface, in order to protect it from corrosion. As the scratch size and initial pH of the electrolyte are varied, the accumulation time changes.

The example is based on a paper by Presuel-Moreno and others ([Ref. 1](#)).

Model Definition

The model defines a galvanic couple in contact with an electrolyte (0.05 M NaCl) film of 100 μm thickness.

The model geometry is defined in 1D and consists of two domains representing the thin electrolyte film located above the Al-Co-Ce metallic coating and the aluminum alloy (AA2024) surfaces, as shown in [Figure 1](#).

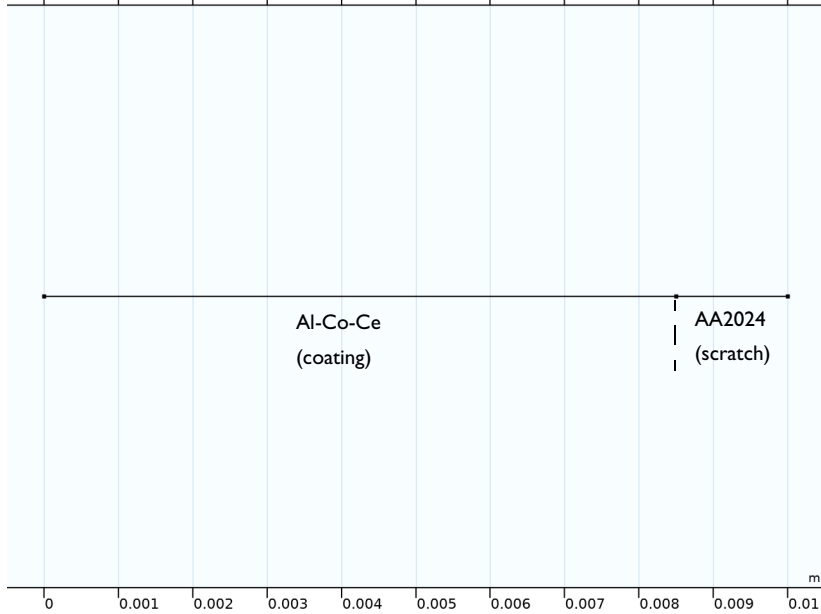


Figure 1: Model geometry.

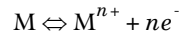
The AA2024 surface represents the scratch where the metallic coating is compromised, exposing the underneath aluminum surface. Two scratch widths are considered in this model: 750 μm and 1500 μm . The total width of the coating, including the scratch width, is 1 cm.

Note that by defining the model in 1D, homogeneous properties of the electrolyte in the thickness direction of the film are assumed.

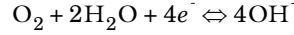
ELECTROCHEMICAL REACTIONS

Metal dissolution and oxygen reduction are two electrochemical reactions that occur at both the Al-Co-Ce metallic coating as well as AA2024 scratch surfaces.

Metal dissolution occurs according to



Oxygen reduction reaction occurs according to



The local current density for metal dissolution, $i_{\text{loc, Me}}$ (A/m²), and oxygen reduction, $i_{\text{loc, O}_2}$ (A/m²), generally depend both on potential and the pH.

At the open circuit potential, the passivation current density i_{pass} (A/m²), relates to the metal dissolution and oxygen reduction current densities as

$$i_{\text{pass}} = i_{\text{loc, Me}} = -i_{\text{loc, O}_2}$$

so that

$$i_{\text{loc, Me}} + i_{\text{loc, O}_2} = 0$$

In this tutorial, experimental data for the passivation current density and corresponding open circuit potentials as functions of pH, using interpolation functions ([Ref. 1](#)), are used to define the local current densities.

For metal dissolution, the local current density is approximated to equal the corresponding passivation current density at all potentials for both the Al-Co-Ce metallic coating and AA2024 scratch surfaces. The Al³⁺, Co²⁺, and Ce³⁺ ions are assumed to dissolve congruently at the metallic coating surface in proportion to their composition in the alloy (Al₈₇Co_{8.7}Ce_{4.3}).

For the oxygen reduction reaction, the following cathodic Tafel kinetics expression is used on both surfaces:

$$i_{\text{O}_2, \text{kin}} = -i_{0, \text{O}_2} \times 10^{-\eta_{\text{O}_2}/A_{\text{O}_2}}$$

where i_{0, O_2} (A/m²) is the exchange current density and A_{O_2} (V) is the cathodic Tafel slope of the oxygen reduction reaction, respectively. The overpotential of the oxygen reduction reaction, η_{O_2} (V), is defined as:

$$\eta_{\text{O}_2} = E - E_{\text{ocp, O}_2}$$

The open circuit potential for oxygen reduction is set to be a constant at the AA2024 scratch surface where as it is defined to be dependent on the pH at the Al-Co-Ce metallic coating surface ([Ref. 1](#)). The Tafel slope is set to be constant for both surfaces.

Furthermore, the local current density of oxygen reduction reaction is assumed to be limited by diffusion, resulting in:

$$i_{\text{loc}, \text{O}_2} = \frac{i_{\text{O}_2, \text{lim}} i_{\text{O}_2, \text{kin}}}{i_{\text{O}_2, \text{lim}} + i_{\text{O}_2, \text{kin}}}$$

where $i_{\text{O}_2, \text{lim}}$ (A/m^2) is the limiting current density for oxygen reduction.

A pH-dependent exchange current density for oxygen reduction may now be derived using the relation

$$i_{\text{pass}} = -i_{\text{loc}, \text{O}_2}$$

resulting in

$$i_{0, \text{O}_2} = \frac{i_{\text{pass}}}{1 - \left| \frac{i_{\text{pass}}}{i_{\text{O}_2, \text{lim}}} \right|}$$

In the model, the local current density for both metal dissolution reaction as well as oxygen reduction reaction is homogenized in the film thickness direction into a volumetric electrode reaction source, i_v (A/m^3), by multiplying by the active specific surface area, a_v (m^2/m^3), according to

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

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

Five homogeneous reactions are considered in the model. The reactions, together with their respective forward and reverse rate constants (Ref. 2), are listed in Table 1.

TABLE 1: HOMOGENEOUS REACTIONS WITH THEIR RESPECTIVE RATE CONSTANTS.

Reactions	k_f	k_r
$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$	$1 \times 10^{-8} (\text{l/s})$	$1 (\text{m}^3/\text{mol/s})$
$\text{Al}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})^{2+} + \text{H}^+$	$4.2 \times 10^4 (\text{m}^3/\text{mol/s})$	$4.6 \times 10^6 (\text{m}^3/\text{mol/s})$
$\text{Al}(\text{OH})^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})_2^+ + \text{H}^+$	$4.2 \times 10^4 (\text{m}^3/\text{mol/s})$	$3.6 \times 10^6 (\text{m}^3/\text{mol/s})$

TABLE 1: HOMOGENEOUS REACTIONS WITH THEIR RESPECTIVE RATE CONSTANTS.

Reactions	k_f	k_r
$\text{Al}(\text{OH})_2^+ + \text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})_3 + \text{H}^+$	$5.6 \times 10^4 \text{ (m}^3/\text{mol/s)}$	$2.8 \times 10^6 \text{ (m}^3/\text{mol/s)}$
$\text{Al}(\text{OH})_3 + \text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})_4^- + \text{H}^+$	$1 \times 10^{-8} \text{ (m}^3/\text{mol/s)}$	$1 \text{ (m}^3/\text{mol/s)}$

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 ($\text{mol}/(\text{m}^2 \cdot \text{s})$), c_i the concentration in the electrolyte (mol/m^3), z_i the charge for the ionic species, u_i the mobility of the charged species ($\text{m}^2/(\text{s} \cdot \text{J} \cdot \text{mole})$), 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 (Ref. 1), are listed in Table 2.

TABLE 2: MODELED SPECIES WITH THEIR RESPECTIVE DIFFUSION COEFFICIENTS.

Species	$D \text{ (m}^2/\text{s)} \cdot 10^9$
Na^+	1.334
Cl^-	2.032
H^+	9.311
OH^-	5.273
Al^{3+}	0.541
AlOH^{2+}	1.185
$\text{Al}(\text{OH})_2^+$	1.185
$\text{Al}(\text{OH})_3$	1.185
Co^{2+}	0.724
Ce^{3+}	0.397

The mobilities are calculated using the Nernst-Einstein relation:

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

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

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

where v_i is a stoichiometric coefficient for the species i in the reaction and n the number of electrons. The stoichiometric coefficient and the number of electrons are set appropriately at the metallic coating surface to capture congruent dissolution Al^{3+} , Co^{2+} , and Ce^{3+} ions in proportion to their composition in the alloy ($\text{Al}_{87}\text{Co}_{8.7}\text{Ce}_{4.3}$).

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

$$\sum_i z_i c_i = 0$$

Results and Discussion

Figure 2 shows the change in Ce^{3+} ion concentration along the electrode surfaces for scratch width of 750 μm and initial pH of 2 at different times. The Ce^{3+} ion concentration is of particular interest, since it is assumed that above a certain critical concentration level, the Ce^{3+} will start to inhibit the metal dissolution of the scratch surface. The critical Ce^{3+} ion concentration, estimated for 0.05 M chloride concentration as reported in Ref. 1, is also plotted as a dashed and dotted line in Figure 2. It can be seen that the critical

concentration of Ce^{3+} ions is reached for the whole of the scratch surface in about 5 h for these conditions.

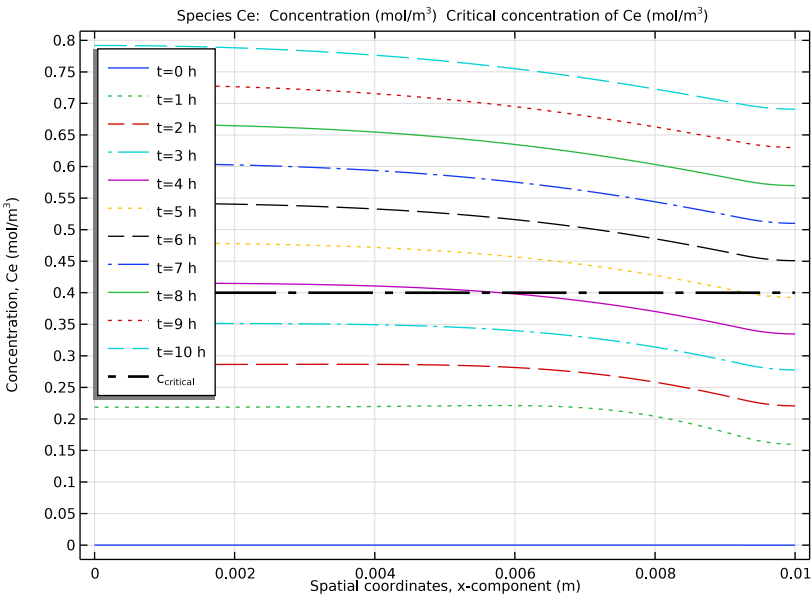


Figure 2: The change in Ce^{3+} ion concentration along the electrode surfaces for scratch width of 750 μm and initial pH of 2 at different times.

Figure 3 shows the change in Ce^{3+} ion concentration along the electrode surfaces when increasing the scratch width to 1500 μm . Now the critical concentration of Ce^{3+} ions is reached after about 7.5 h. Thus, with an increase in the scratch width, the time required

to protect the scratch surface increases, which is expected due to the increased surface area and longer transport length.

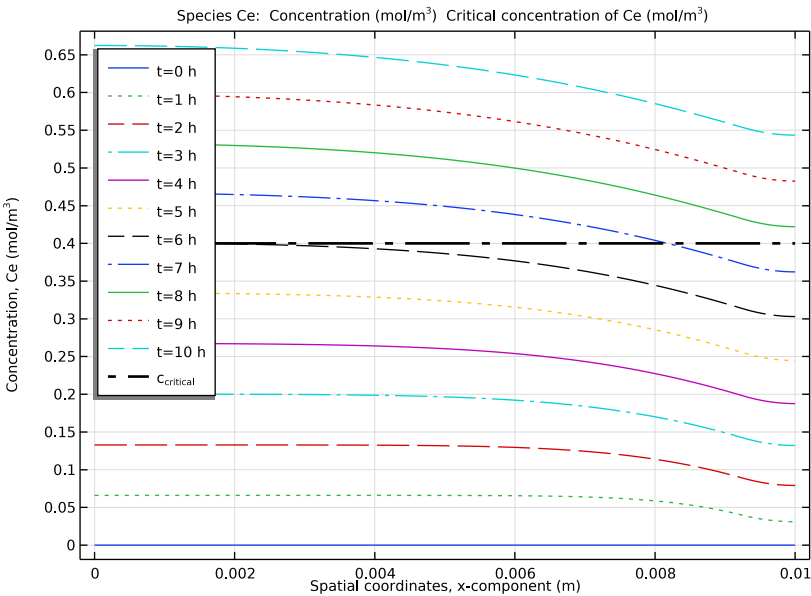


Figure 3: The change in Ce^{3+} ion concentration along the electrode surfaces for scratch width of 1500 μm and initial pH of 2 at different times.

Figure 4 shows the change in Ce^{3+} ion concentration along the electrode surfaces for a scratch width of 750 μm and an increased initial pH of 6. Now 6.5 h are required to reach

the critical concentration. Thus, with an increase in the initial pH, the time required to cover the scratch surface with a critical concentration of Ce^{3+} ions increases.

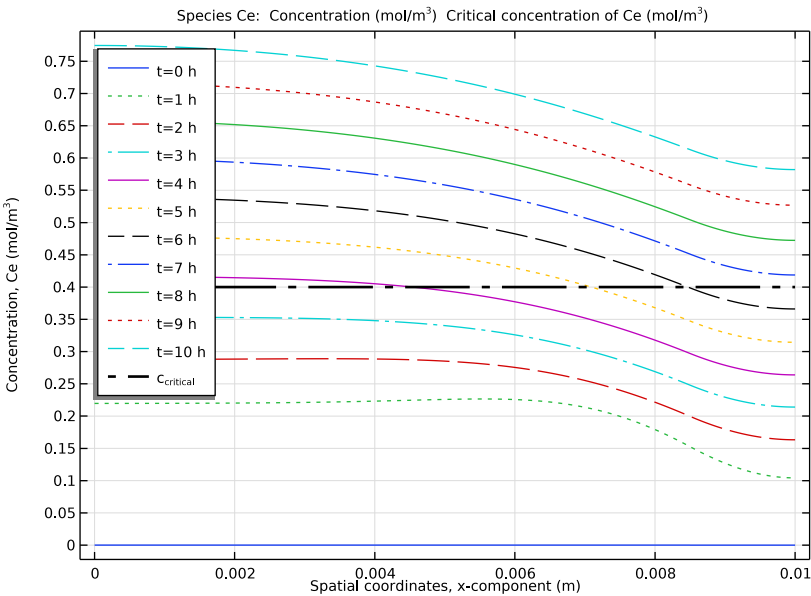


Figure 4: The change in Ce^{3+} ion concentration along the electrode surfaces for scratch width of $750\ \mu m$ and initial pH of 6 at different times.

Figure 5 shows the change in Ce^{3+} ion concentration along the electrode surfaces for both an increased scratch width of $1500\ \mu\text{m}$ and an initial increased pH of 6 at different times. Now 9.5 h are required to reach protecting conditions.

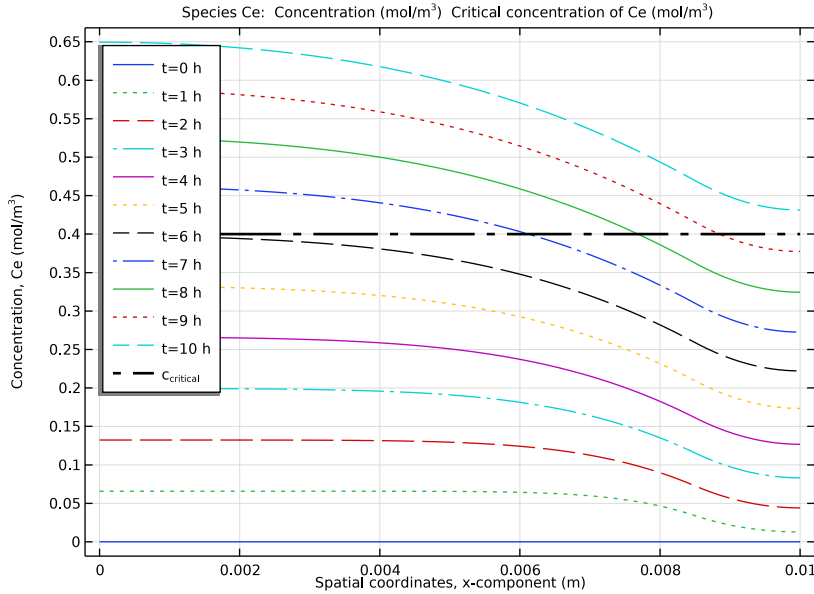


Figure 5: The change in Ce^{3+} ion concentration along the electrode surfaces for scratch width of $1500\ \mu\text{m}$ and initial pH of 6 at different times.

Generally, the pH changes in the model, impacting the local kinetics of the electrode reactions are substantial. Figure 6 shows the change in pH along the electrode surfaces for a scratch width of $1500\ \mu\text{m}$ and initial pH 6 at different times. The pH of the electrolyte solution increases with time over the scratch surface which is attributed to the dominant oxygen reduction reaction.

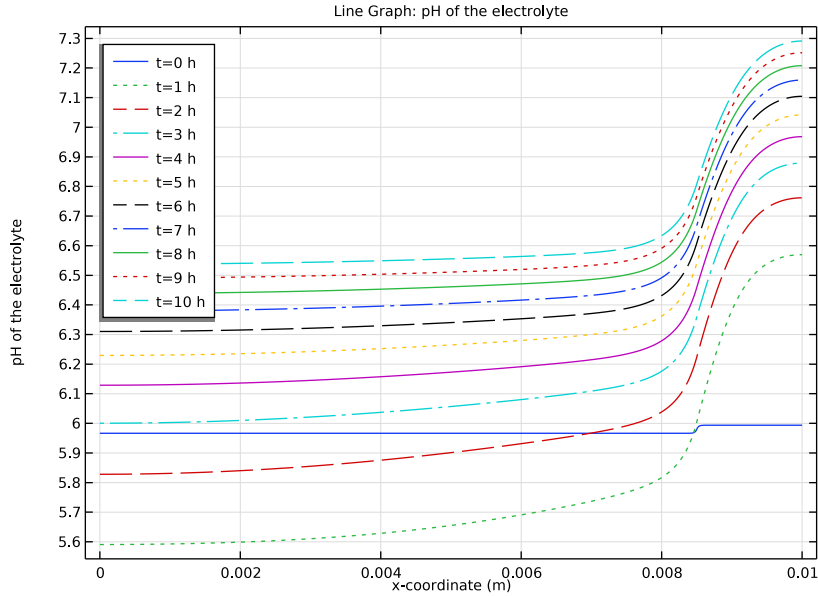


Figure 6: The change in pH along the electrode surfaces at different times for a scratch size of $1500\ \mu\text{m}$ and pH of 6.

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 the five homogeneous reactions considered in the model are set up using the **Chemistry** interface.

References

1. F.J Presuel-Moreno, H. Wang, M.A. Jakob, R.G. Kelly, and J.R. Scully, "Computational modeling of active corrosion inhibitor release from am Al-Co-Ce metallic coating protection of exposed AA2024-T3," *J. Electrochem. Soc.*, vol. 153, no. 11, pp. B486–B498, 2006.


2. C.V. Moraes, R.J. Santucci Jr., J.R. Scully, and R.G. Kelly, “Finite element modeling of chemical and electrochemical protection mechanisms offered by Mg-based organic coatings to AA2024-T351,” *J. Electrochem. Soc.*, vol. 168, no. 051505, 2021.

Application Library path: Corrosion_Module/Atmospheric_Corrosion/
corrosion_inhibitor_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  **ID**.
- 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 11.
- 7 In the **Concentrations (mol/m³)** table, enter the following settings:


cNa
cCl
cH
cOH
cAl
cAlOH
cAlOH2
cAlOH3
cAlOH4
cCe
cCo

- 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**.

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 `corrosion_inhibitor_transport_parameters.txt`.



GEOMETRY 1

Draw the geometry comprising of two adjacent linear segments representing coating and scratch, respectively.

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)
0
1 [cm] -S
1 [cm]

- 4 Click  **Build All Objects**.
- 5 Click the  **Zoom Extents** button in the **Graphics** toolbar.




DEFINITIONS

Load the variables from a text file and create interpolation functions for the passive current density and equilibrium potential as functions of pH for the Al-Co-Ce coating and AA2024 by loading the data from text files.

Variables 1

- 1 In the **Model Builder** window, under **Component 1 (comp1)** right-click **Definitions** and choose **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 `corrosion_inhibitor_transport_variables.txt`.

Interpolation 1 (int1)




- 1 In the **Home** toolbar, click  **Functions** and choose **Local>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 `corrosion_inhibitor_transport_ipass_AlCoCe_pH.txt`.
- 6 Click  **Import**.
- 7 In the **Function name** text field, type `ipass_AlCoCe`.
- 8 Locate the **Units** section. In the **Function** table, enter the following settings:

Function	Unit
<code>ipass_AlCoCe</code>	A/m^2

- 9 In the **Argument** table, enter the following settings:

Argument	Unit
<code>t</code>	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 From the **Data source** list, choose **File**.
- 4 Click  **Browse**.
- 5 Browse to the model's Application Libraries folder and double-click the file `corrosion_inhibitor_transport_ipass_AA2024_pH.txt`.
- 6 Click  **Import**.
- 7 In the **Function name** text field, type `ipass_AA2024`.

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

Function	Unit
ipass_AA2024	A/m ²

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

Argument	Unit
t	1

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

4 Click  **Browse**.

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

6 Click  **Import**.

7 In the **Function name** text field, type Eeq_AlCoCe.

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

Function	Unit
Eeq_AlCoCe	V

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

Argument	Unit
t	1

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. Select the **Specify equilibrium constant** check box.
- 5 In the k^f text field, type k_fH2O .
- 6 Locate the **Equilibrium Settings** section. From the **Equilibrium constant** list, choose **User defined**.
- 7 In the K_j text field, type Kw .


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 $Al+H2O<=>AlOH+H$.
- 4 Click **Apply**.
- 5 Locate the **Rate Constants** section. In the k^f text field, type k_fAlOH .
- 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 $AlOH+H2O<=>AlOH2+H$.
- 4 Click **Apply**.
- 5 Locate the **Rate Constants** section. In the k^f text field, type k_fAlOH2 .
- 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 $AlOH2+H2O<=>AlOH3+H$.
- 4 Click **Apply**.
- 5 Locate the **Rate Constants** section. In the k^f text field, type k_fAlOH3 .
- 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 $AlOH3+H2O<=>AlOH4+H$.
- 4 Click **Apply**.

5 Locate the **Rate Constants** section. In the k^f text field, type kfAlOH4.

6 In the k^r text field, type krAlOH4.

TERTIARY CURRENT DISTRIBUTION, NERNST-PLANCK (TCD)

Now set up the physics for the tertiary current distribution.

Species Charges I

First 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_{cAlOH_2} text field, type zAlOH2.

10 In the z_{cAlOH_3} text field, type zAlOH3.

11 In the z_{cAlOH_4} text field, type zAlOH4.

12 In the z_{cCe} text field, type zCe.

13 In the z_{cCo} text field, type zCo.

Initial Values I

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 c_{Cl} text field, type cOCl.


4 In the c_{H} text field, type cOH.

5 In the c_{OH} text field, type cOOH.

6 In the $phil$ text field, type -Eeq_AA2024.

Highly Conductive Porous Electrode I

Next set the charge, mass transport and electrode kinetics at the Al-Co-Ce coating 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 DA1.
- 9 In the D_{cAlOH} text field, type DA1OH.
- 10 In the D_{cAlOH_2} text field, type DA1OH2.
- 11 In the D_{cAlOH_3} text field, type DA1OH3.
- 12 In the D_{cAlOH_4} text field, type DA1OH4.
- 13 In the D_{cCe} text field, type DCe.
- 14 In the D_{cCo} text field, type DCo.
- 15 Locate the **Porous Matrix Properties** section. In the ε_1 text field, type 1.


Porous Electrode Reaction - Metal dissolution

- 1 In the **Model Builder** window, under **Component 1 (comp1)>Tertiary Current Distribution, Nernst-Planck (tcd)>Highly Conductive Porous Electrode 1** click **Porous Electrode Reaction 1**.
- 2 In the **Settings** window for **Porous Electrode Reaction**, type Porous Electrode Reaction - Metal dissolution in the **Label** text field.
- 3 Locate the **Stoichiometric Coefficients** section. In the n text field, type nAlCoCe.
- 4 In the v_{cAl} text field, type nuAl.
- 5 In the v_{cCe} text field, type nuCe.
- 6 In the v_{cCo} text field, type nuCo.
- 7 Locate the **Electrode Kinetics** section. From the $i_{\text{loc,expr}}$ list, choose **User defined**. In the associated text field, type ipass_AlCoCe (pH).
- 8 Locate the **Active Specific Surface Area** section. In the α_v text field, type 1/d_film.

Highly Conductive Porous Electrode 1

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

Porous Electrode Reaction - Oxygen reduction

- 1 In the **Physics** toolbar, click  **Attributes** and choose **Porous Electrode Reaction**.
- 2 In the **Settings** window for **Porous Electrode Reaction**, type Porous Electrode Reaction - Oxygen reduction in the **Label** text field.
- 3 Locate the **Stoichiometric Coefficients** section. In the n text field, type 4.
- 4 In the v_{cOH} text field, type 4.
- 5 Locate the **Equilibrium Potential** section. From the E_{eq} list, choose **User defined**. In the associated text field, type $E_{\text{eq_AlCoCe}}(\text{pH})$.
- 6 Locate the **Electrode Kinetics** section. From the **Kinetics expression type** list, choose **Cathodic Tafel equation**.
- 7 In the i_0 text field, type i_{0_AlCoCe} .
- 8 In the A_c text field, type $A_{\text{orr_AlCoCe}}$.
- 9 Select the **Limiting current density** check box.
- 10 In the i_{lim} text field, type $i_{\text{dl_AlCoCe}}$.
- 11 Locate the **Active Specific Surface Area** section. In the a_v text field, type $1/d_{\text{film}}$.

Highly Conductive Porous Electrode 1

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

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 - Metal dissolution


- 1 In the **Model Builder** window, expand the **Highly Conductive Porous Electrode 2** node, then click **Porous Electrode Reaction - Metal dissolution**.
- 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 v_{cAl} text field, type -1.
- 5 In the v_{cCe} text field, type 0.
- 6 In the v_{cCo} text field, type 0.
- 7 Locate the **Electrode Kinetics** section. In the $i_{\text{loc,expr}}$ text field, type $i_{\text{pass_AA2024}}(\text{pH})$.

Porous Electrode Reaction - Oxygen reduction

- 1 In the **Model Builder** window, click **Porous Electrode Reaction - Oxygen reduction**.
- 2 In the **Settings** window for **Porous Electrode Reaction**, locate the **Equilibrium Potential** section.
- 3 In the E_{eq} text field, type Eeq_AA2024.
- 4 Locate the **Electrode Kinetics** section. In the i_0 text field, type i0_AA2024.
- 5 In the A_c text field, type A_orr_AA2024.
- 6 In the i_{lim} text field, type id1_AA2024.

Reactions I


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_{cH} list, choose **Reaction rate for species H (chem)**.
- 5 From the R_{cOH} list, choose **Reaction rate for species OH (chem)**.
- 6 From the R_{cAl} list, choose **Reaction rate for species Al (chem)**.
- 7 From the R_{cAlOH} list, choose **Reaction rate for species AlOH (chem)**.
- 8 From the R_{cAlOH2} list, choose **Reaction rate for species AlOH2 (chem)**.
- 9 From the R_{cAlOH3} list, choose **Reaction rate for species AlOH3 (chem)**.
- 10 From the R_{cAlOH4} list, choose **Reaction rate for species AlOH4 (chem)**.

MESH I

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

Edge I


- 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 I

- 1 Right-click **Edge I** 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 1000.
- 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 In the **Number of elements** text field, type 300.
- 5 Clear the **Reverse direction** check box.
- 6 Click  **Build All**.


STUDY 1

Add a Parametric Sweep to study the effect of scratch size and initial pH.

Parametric Sweep

- 1 In the **Study** toolbar, click  **Parametric Sweep**.
- 2 In the **Settings** window for **Parametric Sweep**, locate the **Study Settings** section.
- 3 Click  **Add**.
- 4 In the table, enter the following settings:

Parameter name	Parameter value list	Parameter unit
S (Scratch size)	1500 [um] / 2 1500 [um]	m

- 5 Click  **Add**.
- 6 In the table, enter the following settings:

Parameter name	Parameter value list	Parameter unit
pH0 (Initial bulk pH)	2 6	

- 7 From the **Sweep type** list, choose **All combinations**.


Step 1: Current Distribution Initialization

- 1 In the **Model Builder** window, click **Step 1: Current Distribution Initialization**.

- 2 In the **Settings** window for **Current Distribution Initialization**, locate the **Study Settings** section.
- 3 From the **Current distribution type** list, choose **Secondary**.

Step 2: Time Dependent

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

- 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, 10).
- 5 In the **Study** toolbar, click  **Compute**.

RESULTS

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

Concentration, C_e (tcd)

- 1 In the **Model Builder** window, under **Results** click **Concentration, C_e (tcd)**.
- 2 In the **Settings** window for **ID Plot Group**, locate the **Data** section.
- 3 From the **Parameter selection (S)** list, choose **From list**.
- 4 In the **Parameter values (S (m))** list, select **7.5E-4**.
- 5 From the **Parameter selection (pH0)** list, choose **From list**.
- 6 In the **Parameter values (pH0)** list, select **2**.
- 7 Locate the **Plot Settings** section. Select the **x-axis label** check box.
- 8 Select the **y-axis label** check box. In the associated text field, type Concentration, C_e (mol/m³).
- 9 Locate the **Legend** section. From the **Position** list, choose **Upper left**.

Line Graph 1


- 1 In the **Model Builder** window, expand the **Concentration, C_e (tcd)** node, then click **Line Graph 1**.
- 2 In the **Settings** window for **Line Graph**, click to expand the **Coloring and Style** section.
- 3 Find the **Line style** subsection. From the **Line** list, choose **Cycle**.
- 4 Click to expand the **Legends** section. Select the **Show legends** check box.
- 5 From the **Legends** list, choose **Evaluated**.

6 In the **Legend** text field, type $t=\text{eval}(t,h) \cdot h$.


Concentration, C_e (tcd)

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

Line Graph 2



- 1 In the **Concentration, C_e (tcd)** toolbar, click  **Line Graph**.
- 2 In the **Settings** window for **Line Graph**, locate the **Data** section.
- 3 From the **Dataset** list, choose **Study 1/Solution 1 (sol1)**.
- 4 From the **Time selection** list, choose **First**.
- 5 Locate the **Selection** section. From the **Selection** list, choose **All domains**.
- 6 Locate the **y-Axis Data** section. In the **Expression** text field, type $cCeCrit$.
- 7 Locate the **Coloring and Style** section. Find the **Line style** subsection. From the **Line** list, choose **Dash-dot**.
- 8 From the **Color** list, choose **Black**.
- 9 From the **Width** list, choose **2**.
- 10 Locate the **Legends** section. Select the **Show legends** check box.
- 11 From the **Legends** list, choose **Manual**.
- 12 In the table, enter the following settings:

Legends
c_{critical}


- 13 In the **Concentration, C_e (tcd)** toolbar, click  **Plot**.

The plot should look like [Figure 2](#).

Concentration, C_e (tcd)


- 1 In the **Model Builder** window, click **Concentration, C_e (tcd)**.
 - 2 In the **Settings** window for **ID Plot Group**, locate the **Data** section.
 - 3 In the **Parameter values (pH0)** list, select **6**.
 - 4 In the **Concentration, C_e (tcd)** toolbar, click  **Plot**.
- The plot should look like [Figure 3](#).
- 5 In the **Parameter values (pH0)** list, select **2**.
 - 6 In the **Parameter values (S (m))** list, select **0.0015**.
 - 7 In the **Concentration, C_e (tcd)** toolbar, click  **Plot**.

The plot should look like [Figure 4](#).



- 8 In the **Parameter values (pH0)** list, select **6**.
- 9 In the **Concentration, Ce (tcd)** toolbar, click  **Plot**.
The plot should look like [Figure 5](#).

pH

Plot the pH profile for a representative initial pH of 6.

- 1 In the **Home** toolbar, click  **Add Plot Group** and choose **ID Plot Group**.
- 2 In the **Settings** window for **ID Plot Group**, type pH in the **Label** text field.
- 3 Locate the **Data** section. From the **Dataset** list, choose **Study 1/ Parametric Solutions 1 (sol3)**.
- 4 From the **Parameter selection (S)** list, choose **From list**.
- 5 In the **Parameter values (S (m))** list, select **0.0015**.
- 6 From the **Parameter selection (pH0)** list, choose **From list**.
- 7 In the **Parameter values (pH0)** list, select **6**.
- 8 Locate the **Plot Settings** section.
- 9 Select the **x-axis label** check box. In the associated text field, type x-coordinate (m).
- 10 Locate the **Legend** section. From the **Position** list, choose **Upper left**.

Line Graph 1

- 1 In the **pH** toolbar, click  **Line Graph**.
- 2 In the **Settings** window for **Line Graph**, locate the **Selection** section.
- 3 From the **Selection** list, choose **All domains**.
- 4 Locate the **y-Axis Data** section. In the **Expression** text field, type pH.
- 5 Locate the **Coloring and Style** section. Find the **Line style** subsection. From the **Line** list, choose **Cycle**.
- 6 Locate the **Legends** section. Select the **Show legends** check box.
- 7 From the **Legends** list, choose **Evaluated**.
- 8 In the **Legend** text field, type $t=eval(t,h) \quad h$.
- 9 In the **pH** toolbar, click  **Plot**.
The plot should look like [Figure 6](#).

