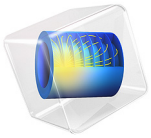


Model created in COMSOL Multiphysics 6.4

Crevice Corrosion of Iron in an Acetic Acid/Sodium Acetate Solution

Introduction

Mass transport limitations within thin crevices can often result in significant concentration differences between the crevice opening (mouth) and end (tip). As a result of this differences in the local electrochemical environment, corrosion may occur.

This example models crevice corrosion of iron in an acetic acid/sodium acetate solution. The model reproduces the results of Walton (Ref. 1).

Model Definition

The crevice investigated is 10 mm deep and 0.5 mm wide. Due to the high aspect ratio of the crevice a 1D model geometry is used, in which concentration variations along the width of the crevice are neglected.

Due to the absence of a supporting electrolyte the transport of all charged species need to be accounted for. All species are considered to be diluted in water. The **Aqueous Electrolyte Transport** interface is used to model the electrolyte potential and the transport of the species in the electrolyte. The modeled species, together with their respective diffusion coefficients in water, are listed in Table 1.

TABLE 1: MODELED SPECIES WITH THEIR RESPECTIVE DIFFUSION COEFFICIENTS.

SPECIES	D (dm^2/s)·10^7
Fe^{2+}	0.7
$FeOH^+$	1
Na^+	1.3
CH3COOH	1.1
$CH3COO^-$	1.1
$CH3COOFe^+$	1.1

The modeled electrolyte has a higher viscosity than pure water. Thus, the diffusion coefficients listed in Table 1 are altered to account for this. Furthermore, the mobilities $u_{m,i}$ (m^2·mol/(J·s)) are calculated using the Nernst–Einstein relation:

$$u_{m,i} = \frac{D_i}{RT}$$

The conditions at the mouth of the crevice are set to measured values for the electrolyte potential and to the bulk concentrations. No Flux / Insulation conditions are applied to the crevice tip.

EQUILIBRIUM REACTIONS

The following equilibrium reactions occur in the electrolyte:

$$H_2O + Fe^{2+}(aq) \Leftrightarrow FeOH^{+}(aq) + H^{+}(aq) \qquad K_1 = 1.63 \cdot 10^{-7}$$

$$CH_3COOH(aq) \Leftrightarrow H^{+}(aq) + CH_3COO^{-}(aq) \qquad K_2 = 1.75 \cdot 10^{-5}$$

$$CH_3COO^{-}(aq) + Fe^{2+}(aq) \Leftrightarrow CH_3COOFe^{+}(aq) \qquad K_3 = 25.1$$

where K_1 through K_3 are the equilibrium constants.

These reactions are modeled using the **Equilibrium Reaction** domain node; one for each reaction. The **Equilibrium Reaction** nodes solve for one additional degree of freedom each, where the additional degree of freedom represents the local reaction rate required in order to fulfill the equilibrium expression. The equilibrium expressions are based on the reaction stoichiometry and equilibrium constant K_k according to

$$K_k = \prod_i \left(\frac{c_i}{c_{a0}}\right)^{\upsilon_{ik}}$$

where c_i (mol/m^3) is the concentration of species i, c_{a0} (mol/m^3) is the unit activity concentration and υ_{ik} is the stoichiometric coefficient of species i in reaction k.

The water dissociation equilibrium reaction is built-in for the **Aqueous Electrolyte Transport** interface.

ELECTROCHEMICAL REACTIONS

Iron dissolution occurs in the crevice according to

$$Fe^{2+}(aq) + 2e^{-} \Leftrightarrow Fe(s)$$

Experimental polarization data available in corrosion material library is used for this reaction according to Figure 1, where the local current density (A/m^2) of the reaction is evaluated as

$$i_{Fe} = f(\phi_s - \phi_l)$$

The whole crevice is modeled as a porous electrode (with a single pore), with the specific surface area $2/w$ (1/m).

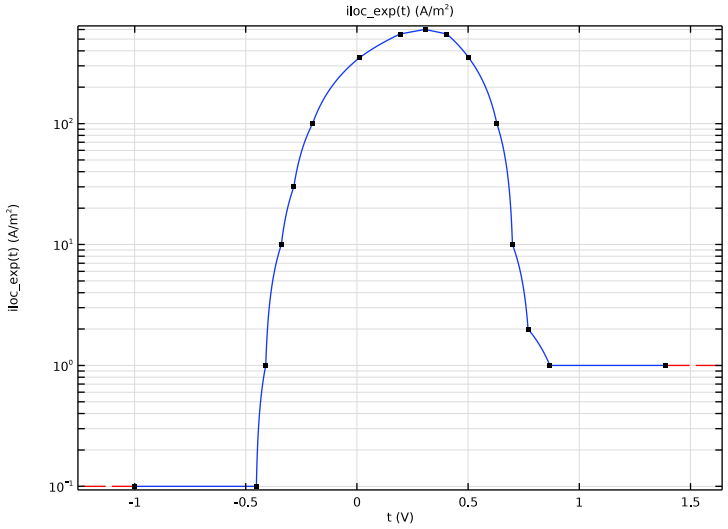


Figure 1: Polarization curve (anodic) for iron.

STUDY SETTINGS

The problem is solved using an Auxiliary Sweep on a stationary solver, sweeping the potential in the electrode phase, $V_{\text{pol}} = \phi_s$, from –0.6 V to 0.844 V (SHE). The sweep is needed to ensure that the intended active-to-passive polarization behavior is captured in the simulation, since due to the nonmonotonic shape of the polarization curve the problem may have more than one solution. (When there are multiple roots to a problem, the initial values will determine to which root COMSOL Multiphysics will converge.)

Results and Discussion

Figure 2 shows the concentration distribution of the different species in the crevice. The sodium concentration is significantly lower in the crevice, compared to the bulk, whereas

the iron, which is dissolved in the crevice, and the iron complexes have higher concentrations toward the tip.

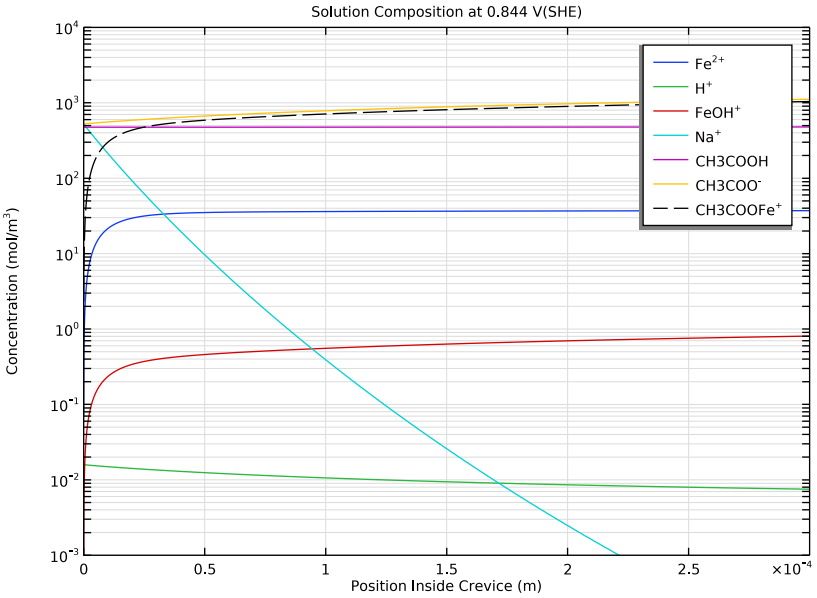


Figure 2: Concentration distribution in the crevice at 0.844 V(SHE).

Figure 3 shows the electrode potential of the metal, as compared to a reference electrode placed along the crevice surface in the electrolyte:

$$E_{\text{vs ref}} = \phi_s - \phi_{s,\text{ref}} = V_{\text{pol}} - (\phi_l + E_{\text{eq, ref}}) = V_{\text{pol}} - \phi_l$$

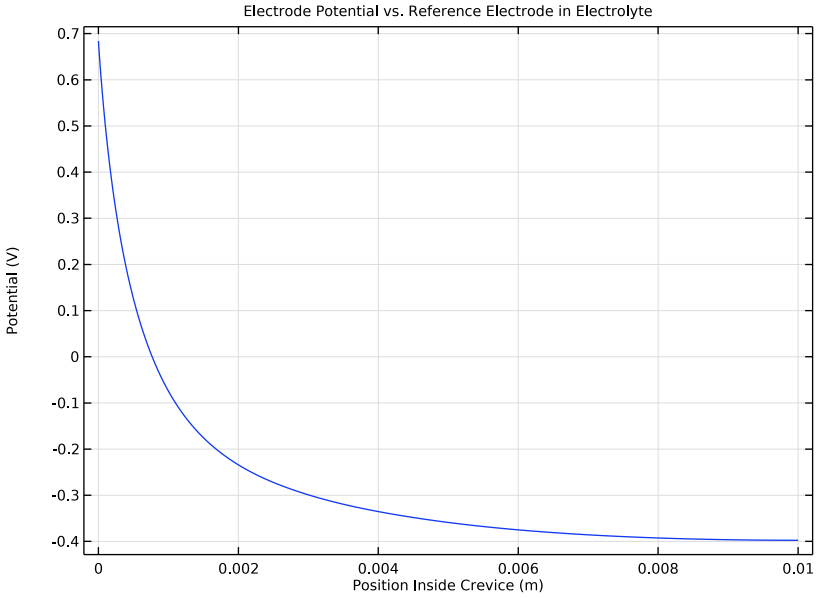


Figure 3: Electrode potential vs. reference placed in electrolyte.

Figure 4 shows the corrosion current density along the crevice. The highest corrosion rate occurs at a crevice depth of about 0.25 mm.

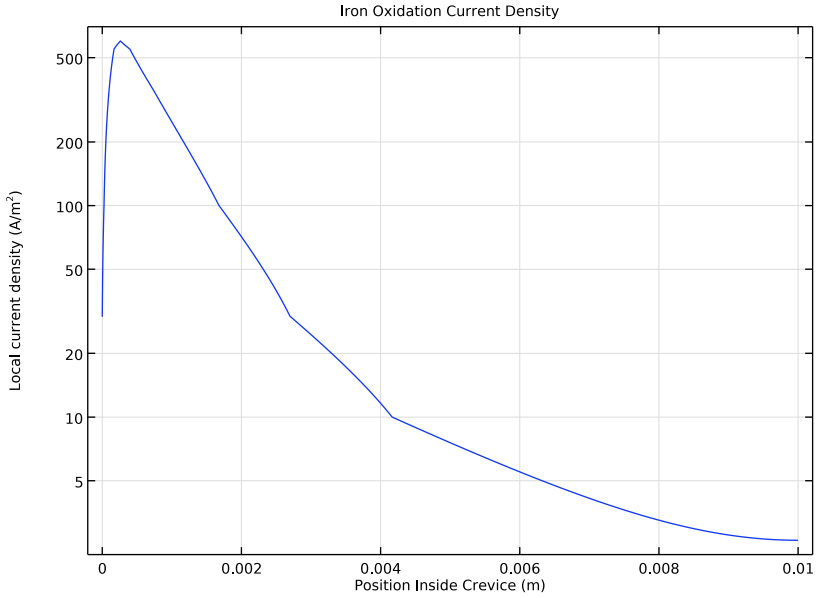


Figure 4: Corrosion current density in crevice.

Reference

1. J.C Walton, "Mathematical Modeling of Mass Transport and Chemical Reaction in Crevice and Pitting Corrosion," *Corrosion Science*, vol. 30, no. 8/9, pp. 915–928, 1990.

Application Library path: `Corrosion_Module/Crevice_and_Pitting_Corrosion/crevice_corrosion_fe`

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 **Electrochemistry** > **Aqueous Electrolyte Transport (aqt)**.

3 Click **Add**.

4 Click **Study**.

5 In the **Select Study** tree, select **General Studies** > **Stationary**.

6 Click **Done**.

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 `crevice_corrosion_fe_parameters.txt`.

GEOMETRY 1

The geometry consists of a single interval.

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
L

4 Click **Build All Objects**.

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

MATERIALS

Use the Corrosion material library to set up the material properties for the electrode kinetics at the iron electrode surface.

ADD MATERIAL

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

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

3 In the tree, select **Corrosion** > **Elements** > **Fe in acetic acid/sodium acetate (Anodic)**.

4 Click the **Add to Component** button in the window toolbar.

5 In the **Materials** toolbar, click **Add Material** to close the **Add Material** window.

MATERIALS

Fe in acetic acid/sodium acetate (Anodic) (mat1)

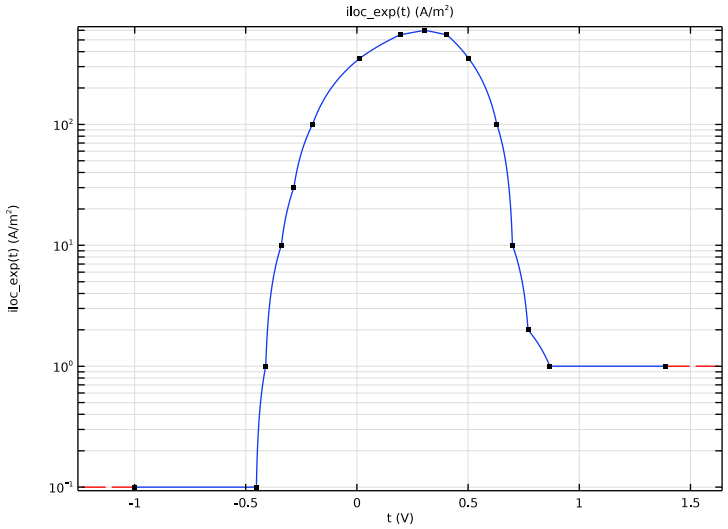
In the **Model Builder** window, expand the **Fe in acetic acid/sodium acetate (Anodic) (mat1)** node.

Interpolation 1 (iloc_exp)

1 In the **Model Builder** window, expand the **Component 1 (comp1)** > **Materials** > **Fe in acetic acid/sodium acetate (Anodic) (mat1)** > **Local current density (lcd)** node, then click **Interpolation 1 (iloc_exp)**.

2 In the **Settings** window for **Interpolation**, click **Plot**.

3 In the **Function Plot** window, click the **y-Axis Log Scale** button in the window toolbar.



Define which species are present in the aqueous electrolyte.

Electrolyte 1

1 In the **Model Builder** window, under **Component 1 (comp1)** > **Aqueous Electrolyte Transport (aqt)** click **Electrolyte 1**.

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

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

Fully Dissociated Species - Fe

1 In the **Physics** toolbar, click **Attributes** and choose **Fully Dissociated Species**.

Define Fe and Na ions in the electrolyte with **Fully Dissociated Species** nodes.

2 In the **Settings** window for **Fully Dissociated Species**, type `Fully Dissociated Species - Fe` in the **Label** text field.

3 Locate the **Fully Dissociated Species** section. In the **Species name** text field, type `Fe`.

4 In the z text field, type `2`.

5 Locate the **Diffusion and Migration** section. In the D text field, type `DFe`.

Electrolyte 1

In the **Physics** toolbar, click **Attributes** and choose **Fully Dissociated Species**.

Fully Dissociated Species - Na

1 In the **Settings** window for **Fully Dissociated Species**, type `Fully Dissociated Species - Na` in the **Label** text field.

2 Locate the **Fully Dissociated Species** section. In the **Species name** text field, type `Na`.

3 In the z text field, type `1`.

4 Locate the **Diffusion and Migration** section. In the D text field, type `DNa`.

Add CH3COOH weak acid as a monoprotic acid using the **Weak Acid** node.

Electrolyte 1

In the **Physics** toolbar, click **Attributes** and choose **Weak Acid**.

Weak Acid - CH3COOH

1 In the **Settings** window for **Weak Acid**, type `Weak Acid - CH3COOH` in the **Label** text field.

2 Locate the **Weak Acid** section. In the **Species name** text field, type `CH3COOH`.

3 In the $\mathrm{p}K_\mathrm{a}$ text field, type `-log10(KCH3COOH)`.

4 Locate the **Diffusion and Migration** section. In the D text field, type `1.1e-7[dm^2/s]/mu_factor`.

Define FeOH and CH3COOFe species forming using **Complex Species** nodes.

Electrolyte 1

In the **Model Builder** window, click **Electrolyte 1**.

Complex Species - FeOH

1 In the **Physics** toolbar, click **Attributes** and choose **Complex Species**.

2 In the **Settings** window for **Complex Species**, type `Complex Species - FeOH` in the **Label** text field.

3 Locate the **Equilibrium Constant** section. In the K_{eq} text field, type `KFeOH`.

4 Locate the **Stoichiometric Coefficients** section. Select the **Fe** checkbox.

5 In the $\nu_{Fe^{2+}}$ text field, type `-1`.

6 Select the **OH** checkbox.

7 In the ν_{OH^-} text field, type `-1`.

8 Locate the **Diffusion** section. In the D text field, type `DFeOH`.

Electrolyte 1

In the **Model Builder** window, click **Electrolyte 1**.

Complex Species - CH3COOFe

1 In the **Physics** toolbar, click **Attributes** and choose **Complex Species**.

2 In the **Settings** window for **Complex Species**, type `Complex Species - CH3COOFe` in the **Label** text field.

3 Locate the **Equilibrium Constant** section. In the K_{eq} text field, type `KCH3COOFe`.

4 Locate the **Stoichiometric Coefficients** section. Select the **Fe** checkbox.

5 In the $\nu_{Fe^{2+}}$ text field, type `-1`.

6 Select the **CH3COOH (-1)** checkbox.

7 In the ν_{CH3COO^-} text field, type `-1`.

8 Locate the **Diffusion** section. In the D text field, type `DCH3COOFe`.

Set the initial potential and concentrations. For weak acid, weak base, and ampholyte, only total concentrations are required. In this case that is applicable for CH3COOH.

Initial Values 1

1 In the **Model Builder** window, under **Component 1 (comp1)** > **Aqueous Electrolyte Transport (aqt)** click **Initial Values 1**.

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

3 In the $\phi_{l,0}$ text field, type `phil_mouth`.

4 Locate the **Concentration** section. In the $c_{Fe,0}$ text field, type `cFe0`.

5 In the $c_{Na,0}$ text field, type `cNa0`.

6 In the $c_{CH3COOH,0}$ text field, type `cCH3COOH_tot0`.

Define the crevice as a highly conductive porous electrode that specifies the polarization potential in the metal phase at the crevice mouth.

Highly Conductive Porous Electrode 1

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

2 In the **Settings** window for **Highly Conductive Porous Electrode**, locate the **Domain Selection** section.

3 From the **Selection** list, choose **All domains**.

Leave the **Electrolyte volume fraction** as it is (1) to define that the entire domain contains electrolyte solution only.

4 Locate the **Effective Transport Parameter Correction** section. From the list, choose **No correction**.

5 Locate the **Electrode Phase Potential Condition** section. In the ϕ_s text field, type `V_pol`.

Porous Electrode Reaction 1

1 In the **Model Builder** window, expand the **Highly Conductive Porous Electrode 1** node, then click **Porous Electrode Reaction 1**.

2 In the **Settings** window for **Porous Electrode Reaction**, locate the **Model Input** section.

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

4 Locate the **Stoichiometric Coefficients** section. In the $\nu_{Fe^{2+}}$ text field, type `-1`.

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

Set the **Active Species Surface Area** to double the inverse of the crevice width to define the **Highly Conductive Porous Electrode** as a crevice (or a single pore) with electrode walls.

6 Locate the **Active Specific Surface Area** section. In the a_v text field, type `2/w`.

At the crevice mouth set an electrolyte and concentrations representing just outside of the crevice. This is done using the **Reservoir** boundary feature.

Reservoir 1

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

2 Select Boundary 1 only.

3 In the **Settings** window for **Reservoir**, locate the **Concentration** section.

4 In the $c_{0,\mathrm{Fe}}$ text field, type `cFe0`.

5 In the $c_{0,\mathrm{Na}}$ text field, type `cNa0`.

6 In the $c_{0,\mathrm{CH3COOH}}$ text field, type `cCH3COOH_tot0`.

7 Locate the **Electrolyte Potential** section. From the **Potential condition** list, choose **Potential**.

8 In the $\phi_{\mathrm{l,bnd}}$ text field, type `phil_mouth`.

MESH 1

Build a mesh with a finer resolution at the mouth.

1 In the **Model Builder** window, under **Component 1 (comp1)** right-click **Mesh 1** and choose **Edit Physics-Induced Sequence**.

Size

1 In the **Model Builder** window, under **Component 1 (comp1)** > **Mesh 1** click **Size**.

2 In the **Settings** window for **Size**, locate the **Element Size** section.

3 Click the **Custom** button.

4 Locate the **Element Size Parameters** section. In the **Maximum element size** text field, type `1e-5`.

5 In the **Maximum element growth rate** text field, type `1.1`.

Size 1

1 In the **Model Builder** window, right-click **Edge 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 1 only.

5 Locate the **Element Size** section. Click the **Custom** button.

6 Locate the **Element Size Parameters** section.

7 Select the **Maximum element size** checkbox. In the associated text field, type `1e-7`.

STUDY 1

Use an auxiliary sweep with continuation to gradually increase the polarization potential.

Step 1: Stationary

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

2 In the **Settings** window for **Stationary**, click to expand the **Study Extensions** section.

3 Select the **Auxiliary sweep** checkbox.

4 Click + **Add**.

5 In the table, enter the following settings:

Parameter name	Parameter value list	Parameter unit
V_pol (Polarization potential vs. SHE)	`range(-0.6, 0.2, 0.8)` `0.844`	V

6 In the **Model Builder** window, click **Study 1**.

7 In the **Settings** window for **Study**, locate the **Study Settings** section.

8 Clear the **Generate default plots** checkbox.

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

RESULTS

The following steps reproduce the plots from the Results and Discussion section. First create a plot that shows all concentrations.

Solution Composition at 0.844 V(SHE)

1 In the **Results** toolbar, click ~ **1D Plot Group**.

2 In the **Settings** window for **1D Plot Group**, type `Solution Composition at 0.844 V(SHE)` in the **Label** text field.

3 Locate the **Data** section. From the **Parameter selection (V_pol)** list, choose **Last**.

4 Click to expand the **Title** section. From the **Title type** list, choose **Label**.

5 Locate the **Plot Settings** section.

6 Select the **x-axis label** checkbox. In the associated text field, type `Position Inside Crevice (m)`.

7 Select the **y-axis label** checkbox. In the associated text field, type `Concentration (mol/m<sup>3</sup>)`.

Line Graph 1

1 Right-click **Solution Composition at 0.844 V(SHE)** and choose **Line Graph**.

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

3 From the **Selection** list, choose **All domains**.

4 Click **Replace Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Component 1 (comp1)** > **Aqueous Electrolyte Transport** > **Fully Dissociated Species - Fe** > **aqt.c_Fe - Concentration, Fe species - mol/m³**.

5 Click to expand the **Legends** section. Select the **Show legends** checkbox.

6 From the **Legends** list, choose **Manual**.

7 In the table, enter the following settings:

Legends
Fe²⁺

Line Graph 2

1 Right-click **Line Graph 1** and choose **Duplicate**.

2 In the **Settings** window for **Line Graph**, click **Replace Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Component 1 (comp1)** > **Aqueous Electrolyte Transport** > **Electrolyte 1** > **aqt.cH - Proton concentration - mol/m³**.

3 Locate the **Legends** section. In the table, enter the following settings:

Legends
H⁺

Line Graph 3

1 Right-click **Line Graph 2** and choose **Duplicate**.

2 In the **Settings** window for **Line Graph**, click **Replace Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Component 1 (comp1)** > **Aqueous Electrolyte Transport** > **Complex Species - FeOH** > **aqt.el1.coms1.c_comp - Complex species concentration - mol/m³**.

3 Locate the **Legends** section. In the table, enter the following settings:

Legends
FeOH⁺

Line Graph 4

1 Right-click **Line Graph 3** and choose **Duplicate**.

2 In the **Settings** window for **Line Graph**, click **Replace Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Component 1 (comp1)** > **Aqueous Electrolyte Transport** > **Fully Dissociated Species - Na** > **aqt.c_Na - Concentration, Na species - mol/m³**.

3 Locate the **Legends** section. In the table, enter the following settings:

Legends
Na⁺

Line Graph 5

1 Right-click **Line Graph 4** and choose **Duplicate**.

2 In the **Settings** window for **Line Graph**, click **Replace Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Component 1 (comp1)** > **Aqueous Electrolyte Transport** > **Weak Acid - CH3COOH** > **Dissociated species concentrations - mol/m³** > **aqt.c2_CH3COOH - Concentration, species with 0 charge**.

3 Locate the **Legends** section. In the table, enter the following settings:

Legends
CH3COOH

Line Graph 6

1 Right-click **Line Graph 5** and choose **Duplicate**.

2 In the **Settings** window for **Line Graph**, click **Replace Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Component 1 (comp1)** > **Aqueous Electrolyte Transport** > **Weak Acid - CH3COOH** > **Dissociated species concentrations - mol/m³** > **aqt.c1_CH3COOH - Concentration, species with -1 charge**.

3 Locate the **Legends** section. In the table, enter the following settings:

Legends
CH3COO⁻

Line Graph 7

1 Right-click **Line Graph 6** and choose **Duplicate**.

2 In the **Settings** window for **Line Graph**, click **Replace Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Component 1 (comp1)** > **Aqueous Electrolyte Transport** > **Complex Species - CH3COOFe** > **aqt.el1.coms2.c_comp - Complex species concentration - mol/m³**.

3 Locate the **Legends** section. In the table, enter the following settings:

Legends
CH3COOFe⁺

4 Click to expand the **Coloring and Style** section. Find the **Line style** subsection. From the **Line** list, choose **Dashed**.

Solution Composition at 0.844 V(SHE)

1 In the **Model Builder** window, click **Solution Composition at 0.844 V(SHE)**.

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

3 Select the **y-axis log scale** checkbox.

4 Select the **Manual axis limits** checkbox.

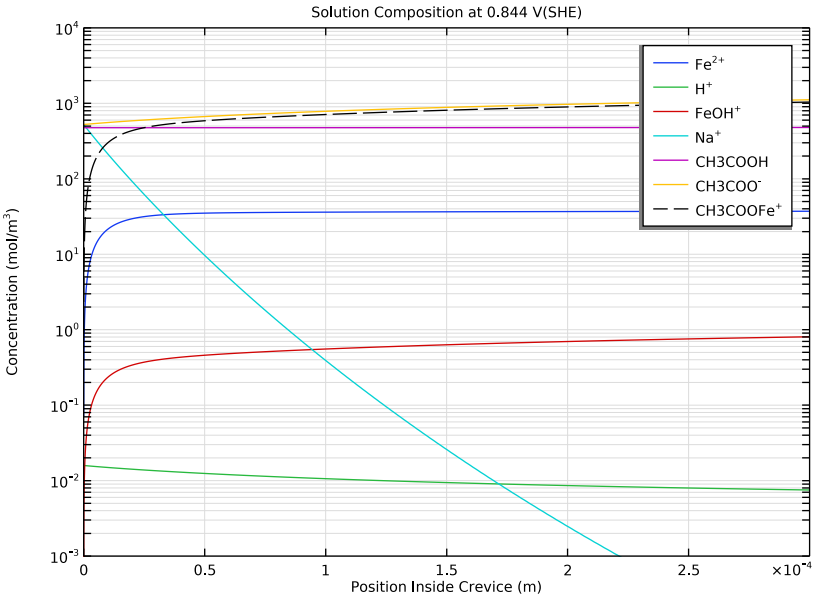
5 In the **x minimum** text field, type `0`.

6 In the **x maximum** text field, type `3e-4`.

7 In the **y minimum** text field, type `1e-3`.

8 In the **y maximum** text field, type `1e4`.

9 In the **Solution Composition at 0.844 V(SHE)** toolbar, click **Plot**.



Electrode Potential vs. Reference Electrode in Electrolyte

The following plots the electrode potential versus a reference electrode in electrolyte at varying positions in the crevice.

1 In the **Results** toolbar, click **1D Plot Group**.

2 In the **Settings** window for **1D Plot Group**, type `Electrode Potential vs. Reference Electrode in Electrolyte` in the **Label** text field.

3 Locate the **Data** section. From the **Parameter selection (V_pol)** list, choose **Last**.

4 Locate the **Title** section. From the **Title type** list, choose **Label**.

5 Locate the **Plot Settings** section.

6 Select the **x-axis label** checkbox. In the associated text field, type `Position Inside Crevice (m)`.

7 Select the **y-axis label** checkbox. In the associated text field, type `Potential (V)`.

Line Graph 1

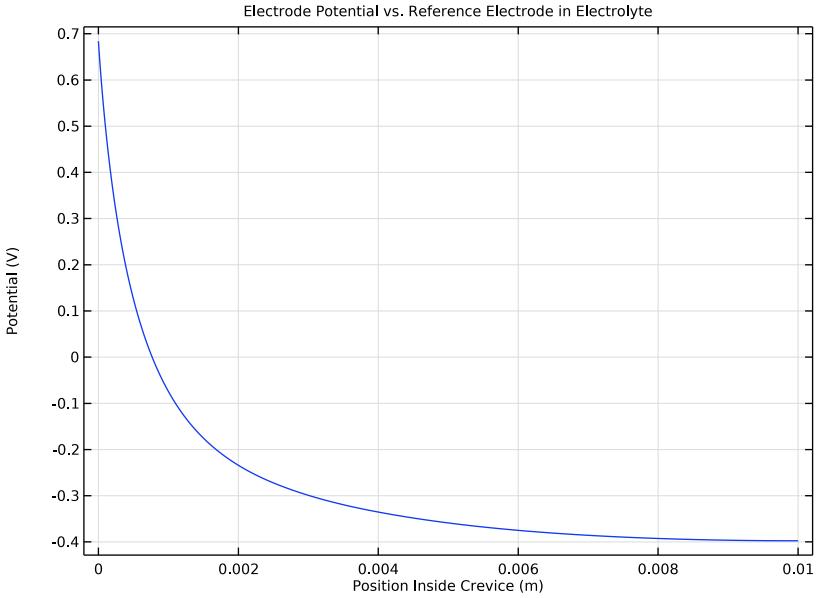
1 Right-click **Electrode Potential vs. Reference Electrode in Electrolyte** and choose **Line Graph**.

2 Select Domain 1 only.

3 In the **Settings** window for **Line Graph**, locate the **y-Axis Data** section.

4 In the **Expression** text field, type `V_pol-aqt.phil`.

5 In the **Electrode Potential vs. Reference Electrode in Electrolyte** toolbar, click **Plot**.



Iron Oxidation Current Density

The following plots the corrosion current density in the crevice.

1 In the **Results** toolbar, click **1D Plot Group**.

2 In the **Settings** window for **1D Plot Group**, type `Iron Oxidation Current Density` in the **Label** text field.

3 Locate the **Data** section. From the **Parameter selection (V_pol)** list, choose **Last**.

4 Locate the **Title** section. From the **Title type** list, choose **Label**.

5 Locate the **Axis** section. Select the **y-axis log scale** checkbox.

Line Graph 1

1 Right-click **Iron Oxidation Current Density** and choose **Line Graph**.

2 Select Domain 1 only.

3 In the **Settings** window for **Line Graph**, click **Replace Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Component 1 (comp1)** > **Aqueous Electrolyte Transport** > **Electrode kinetics** > **aqt.hcpce1.per1.iloc - Local current density - A/m²**.

4 Locate the **x-Axis Data** section. From the **Parameter** list, choose **Expression**.

5 Click **Replace Expression** in the upper-right corner of the **x-Axis Data** section. From the menu, choose **Component 1 (comp1)** > **Geometry** > **Coordinate** > **x - x-coordinate**.

6 Locate the **x-Axis Data** section.

7 Select the **Description** checkbox. In the associated text field, type `Position Inside Crevice`.

8 In the **Iron Oxidation Current Density** toolbar, click **Plot**.