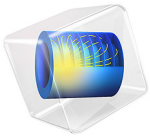

Crevice Corrosion of Iron in an Acetic Acid/Sodium Acetate Solution

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 Nernst–Planck equations, together with an electroneutrality condition, are used to describe the transport of the species in the electrolyte. A Tertiary Current Distribution Nernst–Planck interface is used to model the electrolyte potential and the transport of the species.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 divided by a factor of four. Furthermore, the mobilities 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 a measured value 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. The self-ionization constant of water (K_w) is defined in the parameter file.

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

ELECTROCHEMICAL REACTIONS

Iron dissolution occurs in the crevice according to

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

Experimental polarization data available in corrosion material library is used for this reaction according to Figure 1, where the local current density (SI unit: 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 $2/w$ (SI unit: $1/\mathrm{m}$).

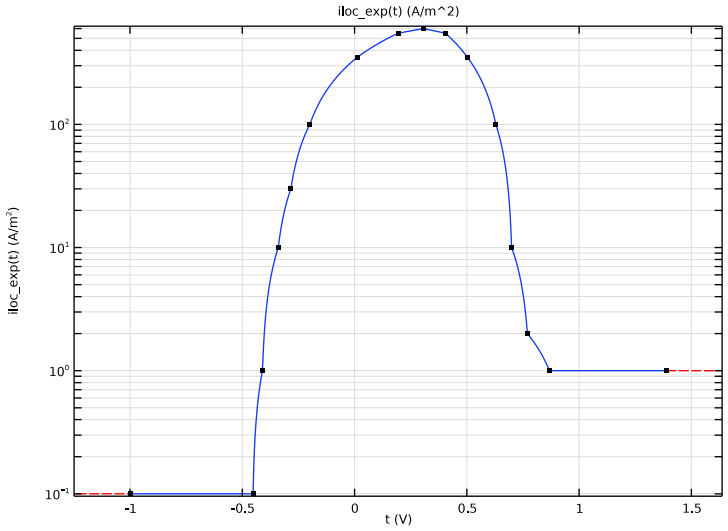

Figure 1: Polarization curve (anodic) for uncreviced iron.

STUDY SETTINGS

Since the conductivity of the metal phase is very high, the electric potential is assumed to be constant over the crevice. Therefore, solving for ϕ_s is disabled in the solver.

The problem is solved using an Auxiliary Sweep on a stationary solver, sweeping the potential in the electrode phase, $V_{\mathrm{pol}} = \phi_s$, 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.

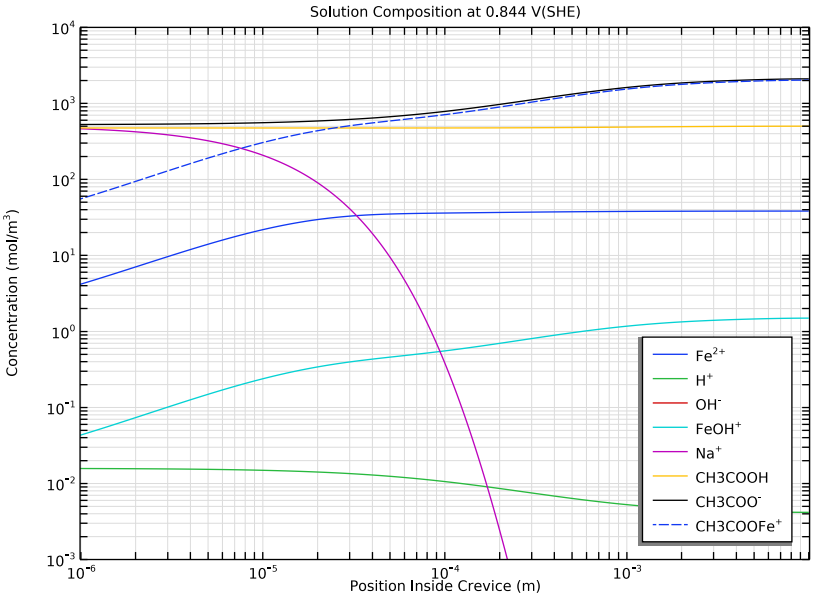

Figure 2: Concentration distribution in the crevice at 0.844 V(SHE).

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

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

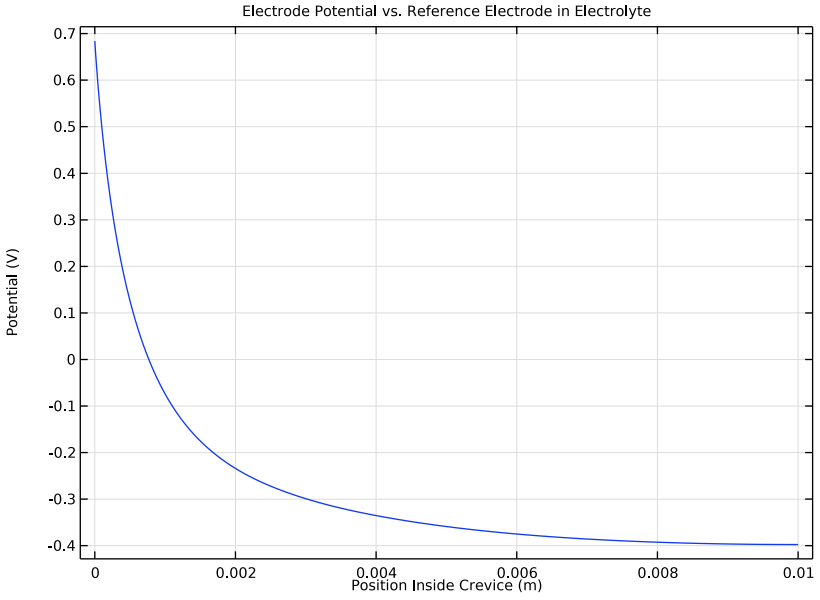

Figure 3: Electrode potential vs. reference placed in electrolyte.

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

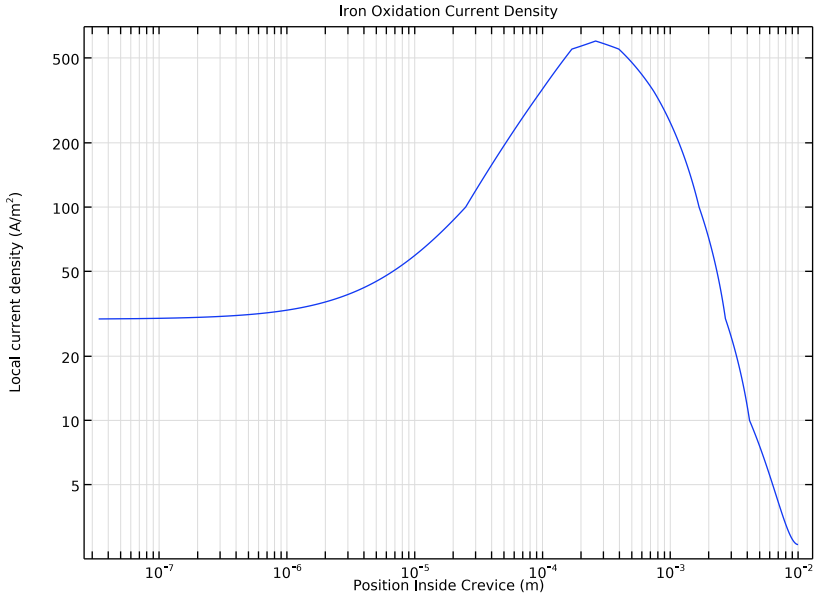

Figure 4: Corrosion current density in crevice.

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>Tertiary Current Distribution, Nernst-Planck>Tertiary, Water-Based with Electroneutrality (tcd)**.

3 Click **Add**.

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

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

cFe
cFeOH
cNa
cCH3COOH
cCH3COO
cCH3COOFe

6 Click **Study**.

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

8 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 **Home** 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 **Add to Component** in the window toolbar.

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 Click **y-Axis Log Scale** in the window toolbar.

The plot should look like Figure 1.

4 In the **Home** toolbar, click **Add Material** to close the **Add Material** window.

TERTIARY CURRENT DISTRIBUTION, NERNST-PLANCK (TCD)

Start defining the physics with charge number at the Species Properties node. The crevice is modeled as a highly conductive porous electrode specifying the polarization potential in the metal phase at the crevice mouth.

Species Charges 1

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_{cFe} text field, type `2`.

4 In the z_{cFeOH} text field, type `1`.

5 In the z_{cNa} text field, type `1`.

In the zcCH3COOH text field, keep the default setting 0.

6 In the $z_{cCH3COO}$ text field, type `-1`.

7 In the $z_{cCH3COOFe}$ text field, type `1`.

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**.

4 Locate the **Model Input** section. From the T list, choose **User defined**. In the associated text field, type `T`.

5 Locate the **Diffusion** section. In the D_{cFe} text field, type `DFe`.

6 In the D_{cFeOH} text field, type `DFeOH`.

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

8 In the $D_{cCH3COOH}$ text field, type `DCH3COOH`.

9 In the $D_{cCH3COO}$ text field, type `DCH3COO`.

10 In the $D_{cCH3COOFe}$ text field, type `DCH3COOFe`.

Set the porosity to unity. This implies that all the volume of the modeled domain belongs to the electrolyte phase.

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

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

13 Locate the **Electrode Phase Potential Condition** section. In the $\phi_{s,ext}$ text field, type `V_pol`.

Porous Electrode Reaction 1

Set up the iron oxidation electrode reaction using From material option for the local current density expression, which uses in-built interpolation polynomial.

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 `2`.
4. In the ν_{cFe} text field, type `-1`.
5. Locate the **Electrode Kinetics** section. From the $i_{loc,expr}$ list, choose **From material**.
6. Locate the **Active Specific Surface Area** section. In the a_v text field, type `2/w`.

Equilibrium Reaction 1

Add the three homogeneous equilibrium reactions. Note that the water auto-ionization equilibrium reaction is inherently included in the mathematical formulation of the water-based with electroneutrality charge transport model, selected at the physics top node. It should hence not be included here.

1. In the **Physics** toolbar, click **Domains** and choose **Equilibrium Reaction**.
2. In the **Settings** window for **Equilibrium Reaction**, locate the **Domain Selection** section.
3. From the **Selection** list, choose **All domains**.
4. Locate the **Equilibrium Condition** section. In the K_{eq} text field, type `K1`.
5. Locate the **Stoichiometric Coefficients** section. In the ν_{cFe} text field, type `-1`.
6. In the ν_{cFeOH} text field, type `1`.
7. In the ν_{cH} text field, type `1`.
8. Right-click **Equilibrium Reaction 1** and choose **Duplicate**.

Equilibrium Reaction 2

1. In the **Model Builder** window, expand the **Component 1 (comp1)> Tertiary Current Distribution, Nernst-Planck (tcd)>Equilibrium Reaction 2** node, then click **Equilibrium Reaction 2**.
2. In the **Settings** window for **Equilibrium Reaction**, locate the **Equilibrium Condition** section.
3. In the K_{eq} text field, type `K2`.
4. Locate the **Stoichiometric Coefficients** section. In the ν_{cFe} text field, type `0`.
5. In the ν_{cFeOH} text field, type `0`.
6. In the $\nu_{cCH3COOH}$ text field, type `-1`.

7 In the $\nu_{cCH3COO}$ text field, type `1`.

8 Right-click **Equilibrium Reaction 2** and choose **Duplicate**.

Equilibrium Reaction 3

1 In the **Model Builder** window, click **Equilibrium Reaction 3**.

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

3 In the K_{eq} text field, type `K3`.

4 Locate the **Stoichiometric Coefficients** section. In the ν_{cFe} text field, type `-1`.

5 In the $\nu_{cCH3COOH}$ text field, type `0`.

6 In the $\nu_{cCH3COO}$ text field, type `-1`.

7 In the $\nu_{cCH3COOFe}$ text field, type `1`.

8 In the ν_{cH} text field, type `0`.

Initial Values 1

Set the initial values to the values at the crevice mouth.

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 *cFe* text field, type `cFe0`.

4 In the *cFeOH* text field, type `cFeOH0`.

5 In the *cNa* text field, type `cNa0`.

6 In the *cCH3COOH* text field, type `cCH3COOH0`.

7 In the *cCH3COO* text field, type `cCH3COO0`.

8 In the *cCH3COOFe* text field, type `cCH3COOFe0`.

9 In the *phil* text field, type `phil_mouth`.

Concentration 1

Set the concentrations at the crevice mouth to the bulk.

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

2 Select Boundary 1 only.

Since three equilibrium reactions are used in the adjacent domain, you may only constrain three (6-3=3) concentrations on the boundary. The three remaining concentration values will be determined by the equilibrium conditions. (If you set more than three concentrations on this boundary, the problem will be over-constrained and will not solve.)

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

4 Select the **Species cFe** check box.

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

6 Select the **Species cNa** check box.

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

8 Select the **Species cCH3COOH** check box.

9 In the $c_{0,\mathrm{cCH3COOH}}$ text field, type `cCH3COOH0`.

Electrolyte Potential 1

Specify the electrolyte potential at the crevice mouth.

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

2 Select Boundary 1 only.

3 In the **Settings** window for **Electrolyte Potential**, locate the **Electrolyte Potential** section.

4 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** check box. 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** check box.

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** check box.

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

RESULTS

The following steps reproduce the plots from the Results and Discussion section. First modify the concentration plot to plot all concentrations.

Concentrations

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

2 In the **Settings** window for **1D Plot Group**, type `Concentrations` 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 **Manual**.

5 In the **Title** text area, type `Solution Composition at 0.844 V(SHE)`.

6 Locate the **Plot Settings** section.

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

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

Line Graph 1

1 Right-click **Concentrations** 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 Locate the **y-Axis Data** section. In the **Expression** text field, type `cFe`.

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

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

7 In the table, enter the following settings:

Legends
Fe²⁺

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

Line Graph 2

1 In the **Model Builder** window, click **Line Graph 2**.

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

3 In the **Expression** text field, type `tcd.cH`.

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

Legends
H⁺

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

Line Graph 3

1 In the **Model Builder** window, click **Line Graph 3**.

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

3 In the **Expression** text field, type `tcd.cOH`.

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

Legends
OH⁻

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

Line Graph 4

1 In the **Model Builder** window, click **Line Graph 4**.

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

3 In the **Expression** text field, type `cFeOH`.

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

Legends
`FeOH<sup>+</sup>`

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

Line Graph 5

1 In the **Model Builder** window, click **Line Graph 5**.

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

3 In the **Expression** text field, type `cNa`.

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

Legends
`Na<sup>+</sup>`

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

Line Graph 6

1 In the **Model Builder** window, click **Line Graph 6**.

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

3 In the **Expression** text field, type `cCH3COOH`.

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

Legends
`CH3COOH`

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

Line Graph 7

1 In the **Model Builder** window, click **Line Graph 7**.

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

3 In the **Expression** text field, type `cCH3COO`.

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

Legends
`CH3COO<sup>-</sup>`

5 Right-click **Line Graph 7** and choose **Duplicate**.

Line Graph 8

1 In the **Model Builder** window, click **Line Graph 8**.

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

3 In the **Expression** text field, type `cCH3COOFe`.

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

Legends
`CH3COOFe<sup>+</sup>`

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

Concentrations

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

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

3 Select the **Manual axis limits** check box.

4 In the **x minimum** text field, type `0.99e-6`.

5 In the **x maximum** text field, type `0.0101`.

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

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

8 Select the **x-axis log scale** check box.

9 Select the **y-axis log scale** check box.

10 Locate the **Legend** section. From the **Position** list, choose **Lower right**.

11 In the **Concentrations** toolbar, click **Plot**.

Electrode potential

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

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

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

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

4 Locate the **Plot Settings** section.

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

6 Select the **y-axis label** check box. In the associated text field, type `Potential (V)`.

7 Locate the **Title** section. From the **Title type** list, choose **Manual**.

8 In the **Title** text area, type `Electrode Potential vs. Reference Electrode in Electrolyte`.

Line Graph 1

1 Right-click **Electrode potential** 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-phil`.

5 In the **Electrode potential** toolbar, click **Plot**.

Corrosion current density

The following plots the corrosion current density in the crevice.

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

2 In the **Settings** window for **1D Plot Group**, type `Corrosion 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 **Manual**.

5 In the **Title** text area, type `Iron Oxidation Current Density`.

6 Locate the **Axis** section. Select the **x-axis log scale** check box.

7 Select the **y-axis log scale** check box.

Line Graph 1

1 Right-click **Corrosion 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)> Tertiary Current Distribution, Nernst-Planck>Electrode kinetics>tcd.iloc_per1 - 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** check box. In the associated text field, type `Position Inside Crevice`.

8 In the **Corrosion current density** toolbar, click  **Plot**.