Crevice Corrosion of Nickel with Electrode Deformation

Introduction

This model exemplifies the basic principles of crevice corrosion and how a time-dependent study can be used to simulate the electrode deformation.
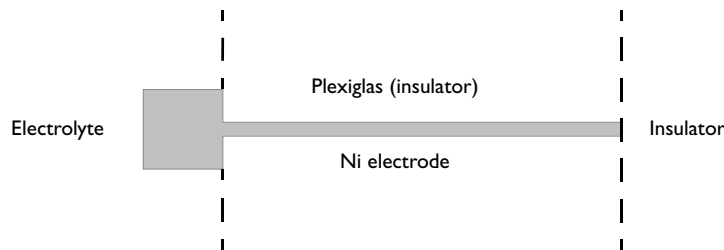
The model is in 2D and the polarization data for the corrosion reaction is taken from a paper by Absulsalam and others (Ref. 1). The model and the results are similar to a 1D model by Brackman and others (Ref. 2).

This model does not account for mass transport effects. For a more detailed treatment of mass transport in a crevice, see the Crevice Corrosion of Iron in an Acetic Acid/ Sodium Acetate Solution model example.

Model Definition

The modeled cell is a laboratory cell (Figure 1), where an open-ended 10 mm crevice, 0.3 mm wide, has been created between a piece of nickel and a sheet of Plexiglas.

Figure 1: Electrochemical cell for corrosion experiments. The gray area is the modeled geometry.

Polarization data for a planar nickel electrode has been measured separately, with the results shown in Figure 2. The polarization curve consists of two parts: the active region, where the current density increases with the increased anodic polarization, and

the passive region, where the current density decreases or remains constant with the increased polarization. The electrolyte used is 1 N H_2SO_4.
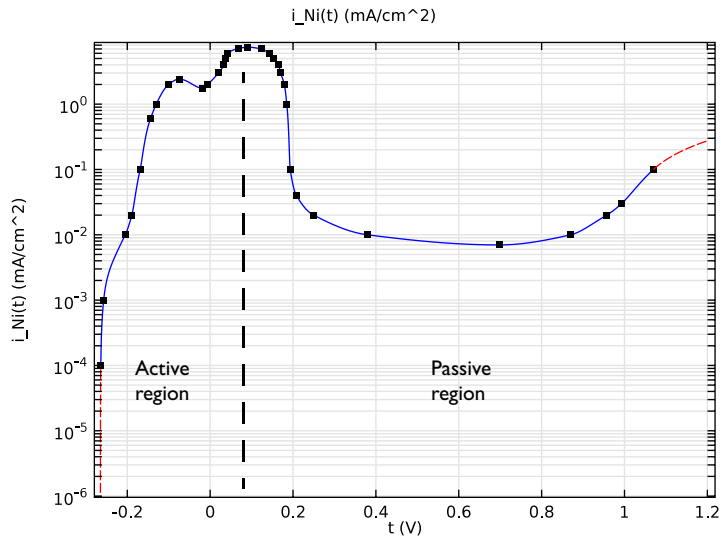

Figure 2: Polarization data for the nickel electrode reaction for a potential scan in the active-to-passive direction.

An electrolyte of high conductivity is used, and the corrosion current densities are expected to be fairly small so that a secondary current distribution can be assumed for this cell (mass transport effects of dissolved nickel and other ions are neglected). Use a Corrosion, Secondary physics to model the problem.

Model the cell geometry by including the crevice and a 2 mm square outside the mouth of the crevice. Use one Electrolyte domain to model the electrolyte charge transport, with a constant conductivity of 0.184 S/m.

Add an External Corroding Electrode boundary condition to model the nickel surface deformation. Use the experimental polarization data for the electrode reaction kinetics as an interpolation polynomial. Set the potential of the electrode to 0.3 V.

Use an Electrolyte Potential boundary condition to apply a 0 V electrolyte potential along the leftmost boundary.

Use the default Insulation condition for all other boundaries.

For the deformed geometry, on the non-moving boundaries, the model is solved with the default Zero Normal Mesh Velocity boundary condition. However, to improve the

shape of the deformation in the corners of the geometry, and also to reduce the problem size, apply Prescribed Deformation boundary condition to the non-moving boundaries. Assign zero deformation in the x direction for the horizontal boundaries and zero deformation in the y direction for the vertical boundaries.

Solve the problem using a Time Dependent with Initialization study. The study contains two solver steps, a Current Initialization step first solves for the potentials only, using a stationary solver. The second Time Dependent step solves for the full problem for the prescribed 50 hours duration.

Due to the non-monotonic shape of the polarization data there are two possible solutions to the modeled problem: One high current solution with low activation/high ohmic losses, and one low current solution with high activation/low ohmic losses. This case considers the former solution, which can be found by sweeping the voltage from low polarization in the active-to-passive direction. Use a Parametric solver in the Current Initialization step to gradually increase the polarization voltage of the electrode.

Results and Discussion

Figure 3 shows the electrolyte potential and the electrode deformation after 50 hours. The parts of the electrode outside the crevice are hardly deformed. The main

deformation occurs somewhere in the range 2–5 mm into the crevice. Outside the crevice, in the bulk of the electrolyte, the potential drops are small.
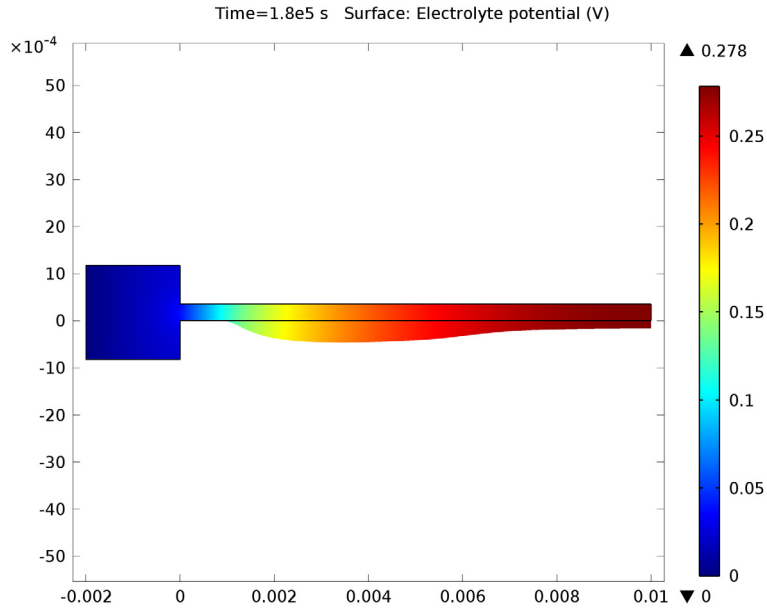

Figure 3: Electrolyte potential and deformed geometry after 50 h.

Figure 4 shows the corrosion current density along the electrode surface for various times. The maximum is found around $x = 3.5$ mm. As time increases, the current peak broadens. Two effects account for the change of the corroding current density profile:

the lowered ohmic drop due to the widening of the crevice, and the increased available surface area due to the changed curvature of the electrode.
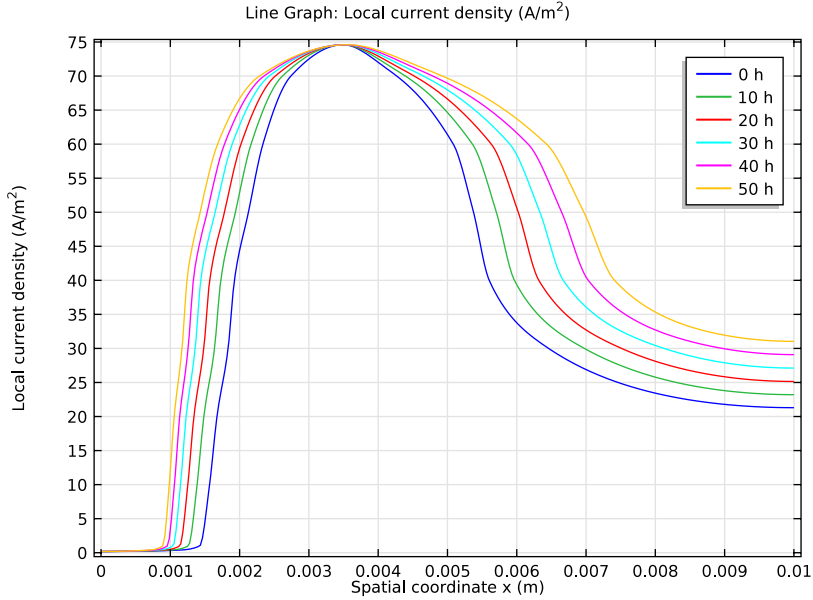
Line Graph: Local current density (A/m²)

Figure 4: Corrosion current density along the nickel surface.

Figure 5 shows the potential difference between the electric potential in the electrode and the electrolyte potential along the nickel surface. The shape of the potential plot, in combination with the polarization data in Figure 2, explains the corrosion current density peak seen in Figure 4. As current enters the crevice, the potential is shifted due to ohmic losses, and the nickel corrosion reaction is thereby shifted from the passive region in the polarization curve towards higher activity, resulting in higher corrosion currents.
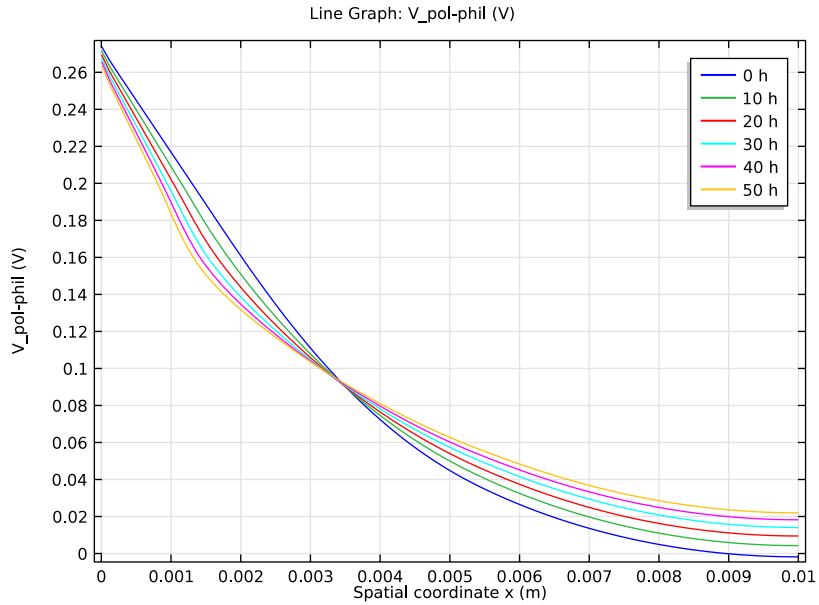
Figure 5: Electrode-electrolyte potential along the nickel surface.

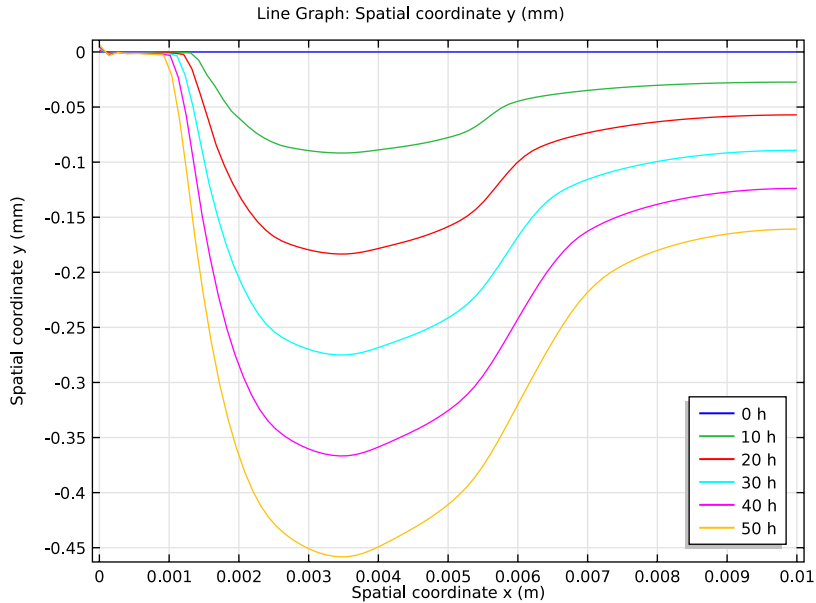Finally, Figure 6 shows the deformation of the electrode at various times.

Figure 6: Electrode deformation at various times.

References

1. M. Abdulsalam and H.W. Pickering, "The Effect of Crevice-Opening Dimension on the Stability of Crevice Corrosion for Nickel in Sulfuric Acid," *J. Electrochemical Society*, vol. 145, no. 7, 1998.

2. M. Brackman, C.B. Clemons, D. Golovaty, K.L. Kreider, G.W. Young, R.S. Lillard, and J. Payer, "Modeling and Computational Simulation of Crevice Corrosion Damage Evolution," *NACE Corrosion Conference 2012*.

Model Library path: `Corrosion_Module/Crevice_Corrosion/`
`crevice_corrosion_with_deformation`

Modeling Instructions

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

NEW

1 In the **New** window, click the **Model Wizard** button.

MODEL WIZARD

1 In the **Model Wizard** window, click the **2D** button.

2 In the **Select physics** tree, select **Electrochemistry>Corrosion, Deformed Geometry>Corrosion, Secondary (corrsec)**.

3 Click the **Add** button.

4 Click the **Study** button.

5 In the tree, select **Preset Studies>Time Dependent with Initialization**.

6 Click the **Done** button.

GLOBAL DEFINITIONS

Start by adding values for the parameters that will be used in several places in the model.

Parameters

1 On the **Home** toolbar, click **Parameters**.

2 In the **Parameters** settings window, locate the **Parameters** section.

3 In the table, enter the following settings:

Name	Expression	Value	Description
V_pol	0.3[V]	0.3000 V	Polarization voltage
w	0.35[mm]	3.500E-4 m	Crevice width

GEOMETRY 1

Now build the geometry as a union of a rectangle (the crevice) and a square (part of the electrolyte outside the crevice).

Rectangle 1 (r1)

1 In the **Model Builder** window, under **Component 1** right-click **Geometry 1** and choose **Rectangle**.

2 In the **Rectangle** settings window, locate the **Size** section.

3 In the **Width** edit field, type 10[mm].

4 In the **Height** edit field, type w.

5 Click the **Build Selected** button.

Square 1 (sq1)

1 In the **Model Builder** window, right-click **Geometry 1** and choose **Square**.

2 In the **Square** settings window, locate the **Size** section.

3 In the **Side length** edit field, type 2[mm].

4 Locate the **Position** section. In the **x** edit field, type -2[mm].

5 In the **y** edit field, type -1[mm]+w/2.

6 Click the **Build Selected** button.

7 Click the **Zoom Extents** button on the Graphics toolbar.

Union 1 (uni1)

1 On the **Geometry** toolbar, click **Union**.

2 Select both objects **r1** and **sq1** only.

3 In the **Union** settings window, locate the **Union** section.

4 Clear the **Keep interior boundaries** check box.

5 Click the **Build Selected** button.

DEFINITIONS

Now add the polarization data for the nickel dissolution reaction. Add the data as an interpolation polynomial.

Interpolation 1 (int1)

1 On the **Home** toolbar, click **Functions** and choose **Global>Interpolation**.

2 In the **Interpolation** settings window, locate the **Definition** section.

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

4 Find the **Functions** subsection. Click the **Browse** button.

5 Browse to the model's Model Library folder and double-click the file
crevice_corrosion_with_deformation_i_Ni.txt.

6 Click the **Import** button.

7 In the **Function name** edit field, type i_Ni.

8 Locate the **Interpolation and Extrapolation** section. From the **Interpolation** list, choose **Piecewise cubic**.

9 From the **Extrapolation** list, choose **Linear**.

10 Locate the **Units** section. In the **Arguments** edit field, type V.

11 In the **Function** edit field, type mA/cm^2.

12 Click the **Plot** button.

13 Click the **y-Axis Log Scale** button on the Graphics toolbar. (see Figure 2)

CORROSION, SECONDARY (CORRSEC)

Now set up the electrochemistry. Start with the electrolyte conductivity.

Electrolyte 1

1 In the **Model Builder** window, under **Component 1 >Corrosion, Secondary (corrsec)** click **Electrolyte 1**.

2 In the **Electrolyte** settings window, locate the **Electrolyte** section.

3 From the σ_l list, choose **User defined**. In the associated edit field, type 0.184[S/cm].

External Corroding Electrode 1

Now set up the corroding electrode.

1 On the **Physics** toolbar, click **Boundaries** and choose **External Corroding Electrode**.

2 Select Boundaries 4 and 5 only.

3 In the **External Corroding Electrode** settings window, locate the **Boundary Condition** section.

4 In the $\phi_{s,ext}$ edit field, type V_pol.

Surface Properties 1

1 In the **Model Builder** window, under **Component 1 >Corrosion, Secondary (corrsec)>External Corroding Electrode 1** click **Surface Properties 1**.

2 In the **Surface Properties** settings window, locate the **Corroding Species** section.

3 In the M_{ccorr} edit field, type 0.05869[kg/mol].

4 In the ρ_{ccorr} edit field, type 8900[kg/m^3].

Electrode Reaction 1

1 In the **Model Builder** window, expand the **Component 1 >Corrosion, Secondary (corrsec)>External Corroding Electrode 1** node, then click **Electrode Reaction 1**.

2 In the **Electrode Reaction** settings window, locate the **Electrode Kinetics** section.

3 From the **Kinetics expression type** list, choose **User defined**. Set the local current density of the electrode reaction to a user-defined expression using the polarization data of the interpolation polynomial. The corrsec.phisext variable is the potential in the metal phase of the electrode surface.

4 In the i_{loc} edit field, type i_Ni(corrsec.phisext-phil).

5 Locate the **Stoichiometric Coefficients** section. In the ν_{ccorr} edit field, type 1.

6 In the n_m edit field, type 2.

Electrolyte Potential 1

Set the electrolyte potential to zero on the leftmost boundary.

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

2 Select Boundary 1 only.

Prescribed Mesh Displacement 1

The model is now ready for solving. However, to improve the deformed geometry results in some corners, and to reduce the number of degrees of freedom, add Prescribed Displacement conditions to all non-moving boundaries.

1 On the **Physics** toolbar, click **Boundaries** and choose **Prescribed Mesh Displacement**.

2 Select Boundaries 2, 3, and 7 only.

3 In the **Prescribed Mesh Displacement** settings window, locate the **Prescribed Mesh Displacement** section.

4 Clear the **Prescribed x displacement** check box.

Prescribed Mesh Displacement 2

1 On the **Physics** toolbar, click **Boundaries** and choose **Prescribed Mesh Displacement**.

2 Select Boundaries 1, 6, and 8 only.

3 In the **Prescribed Mesh Displacement** settings window, locate the **Prescribed Mesh Displacement** section.

4 Clear the **Prescribed y displacement** check box.

MESH 1

Use a mesh with an Extremely fine mesh resolution along the crevice electrode surface.

Free Triangular 1

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

Size 1

1 In the **Model Builder** window, under **Component 1 >Mesh 1** right-click **Free Triangular 1** and choose **Size**.

2 In the **Size** settings window, locate the **Geometric Entity Selection** section.

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

4 Select Boundary 5 only.

5 Locate the **Element Size** section. From the **Predefined** list, choose **Extremely fine**.

6 Click the **Build All** button.

STUDY 1

Due to the non-monotonic shape of the polarization data there are two solutions to the problem: One with high activation/low ohmic losses (low currents), and one with low activation/high ohmic losses (high currents). Edit the default solver by adding an auxiliary sweep to the initialization step. This will ensure that the high current solution will be solved for.

Step 1: Current Distribution Initialization

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

2 In the **Current Distribution Initialization** settings window, click to expand the **Study extensions** section.

3 Locate the **Study Extensions** section. Select the **Auxiliary sweep** check box.

4 Click **Add**.

5 In the table, enter the following settings:

Auxiliary parameter	Parameter value list
V_pol	range(-0.2,0.1,V_pol)

Step 2: Time Dependent

1 In the **Model Builder** window, under **Study 1** click **Step 2: Time Dependent**.

2 In the **Time Dependent** settings window, locate the **Study Settings** section.

3 In the **Times** edit field, type range(0,10*3600,50*3600).

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

RESULTS

A 2D plot of the electrolyte potential and the deformation is created by default (Figure 3).

Electrolyte Potential (corrsec)

1 Click the **Zoom Extents** button on the Graphics toolbar.

1D Plot Group 2

Create a plot of the corrosion current density in the following way:

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

2 On the **ID plot group** toolbar, click **Line Graph**.

3 Select Boundary 5 only.

4 In the **Line Graph** settings window, locate the **y-axis data** section.

5 Click **Replace Expression** in the upper-right corner of the section and select **Local current density (corrsec.iloc_er1)**. Locate the **x-Axis Data** section. From the **Parameter** list, choose **Expression**.

6 In the **Expression** edit field, type x.

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

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

9 In the table, enter the following settings:

Legends
0 h
10 h
20 h
30 h
40 h
50 h

I0 On the **ID plot group** toolbar, click **Plot**.

ID Plot Group 3

Duplicate the plot and change the expression in the new plot. This will create a plot of the electrode-electrolyte potential difference:

I In the **Model Builder** window, right-click **ID Plot Group 2** and choose **Duplicate**.

2 In the **Model Builder** window, expand the **ID Plot Group 3** node, then click **Line Graph I**.

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

4 In the **Expression** edit field, type V_pol-phil.

5 On the **ID plot group** toolbar, click **Plot**.

ID Plot Group 4

Finally, duplicate the plot and change the expression again to create a plot of the deformation for various times.

I In the **Model Builder** window, right-click **ID Plot Group 3** and choose **Duplicate**.

2 In the **Model Builder** window, expand the **ID Plot Group 4** node, then click **Line Graph 1**.

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

4 In the **Expression** edit field, type y.

5 From the **Unit** list, choose **mm**.

6 In the **Model Builder** window, click **ID Plot Group 4**.

7 In the **ID Plot Group** settings window, click to expand the **Legend** section.

8 From the **Position** list, choose **Lower right**.

9 On the **ID plot group** toolbar, click **Plot**.

Optionally, give the plot group nodes more descriptive names:

1D Plot Group 2

1 In the **Model Builder** window, under **Results** right-click **ID Plot Group 2** and choose **Rename**.

2 Go to the **Rename ID Plot Group** dialog box and type Corrosion current density in the **New name** edit field.

3 Click **OK**.

1D Plot Group 3

1 In the **Model Builder** window, under **Results** right-click **ID Plot Group 3** and choose **Rename**.

2 Go to the **Rename ID Plot Group** dialog box and type Electrode-Electrolyte Potential in the **New name** edit field.

3 Click **OK**.

1D Plot Group 4

1 In the **Model Builder** window, under **Results** right-click **ID Plot Group 4** and choose **Rename**.

2 Go to the **Rename ID Plot Group** dialog box and type Electrode shape in the **New name** edit field.

3 Click **OK**.