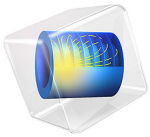

Crevice Corrosion of Nickel with Electrode Deformation

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 Abdulsalam 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.

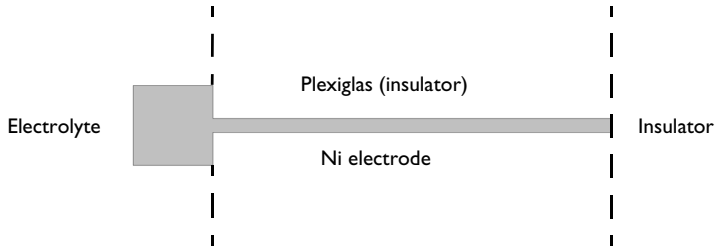

Figure 1: Electrochemical cell for corrosion experiments. The gray area is the modeled geometry.

Polarization data for a planar nickel electrode has been measured separately, with the results shown in Figure 2 is available in corrosion material library. 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 M H_2SO_4.

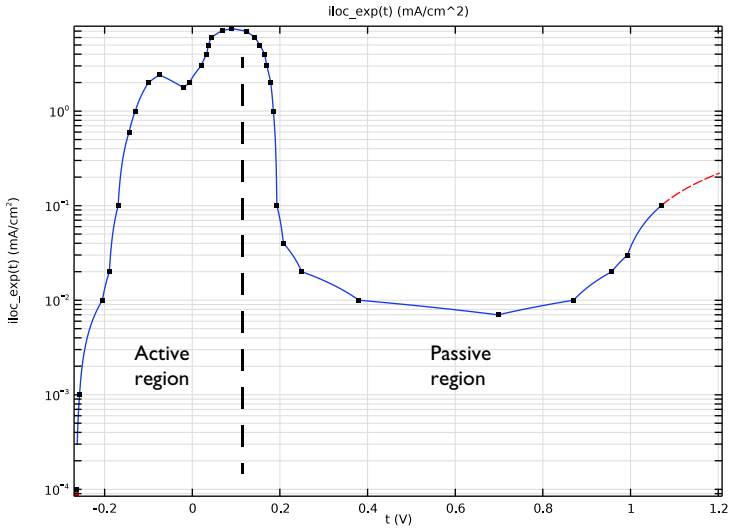

Figure 2: Polarization data for the nickel electrode reaction for a potential scan in the active-to-passive direction.

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 interface 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/cm.

Add an Electrode Surface boundary node 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 nonmoving boundaries, the model is solved with the default Nondeforming Boundary. These boundaries are all straight lines, so to improve the

shape of the deformation in the corners of the geometry, and also to reduce the problem size, change the boundary condition setting of the feature to Zero Normal Displacement.

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 nonmonotonic 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. (When there are multiple roots to a problem, the initial values determine which root COMSOL will converge to. Solving for a high polarization potential directly for this model will result in the solution with an almost uniformly passivated surface, with a low current density). Use an Auxiliary solver in the Current Initialization step to gradually increase the polarization voltage of the electrode. The second, time-dependent study step will then use the last solution of the first step by default.

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.

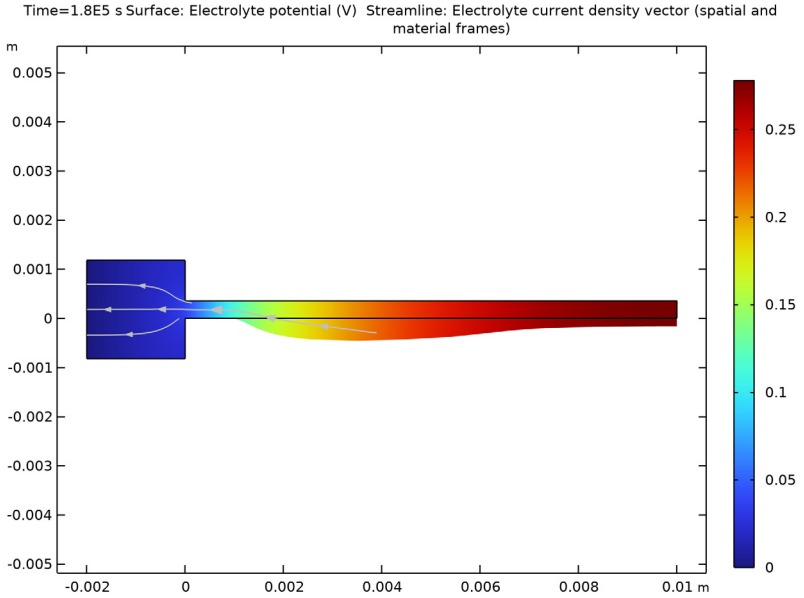

Figure 3: Electrolyte potential and deformed geometry after 50 h.

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.

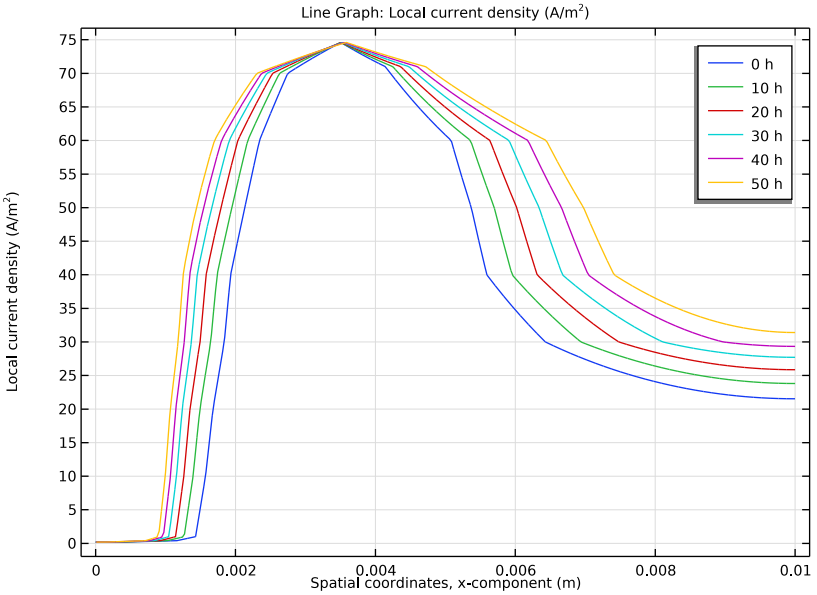

Figure 4: Corrosion current density along the nickel surface.

Figure 3 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 toward higher activity, resulting in higher corrosion currents.

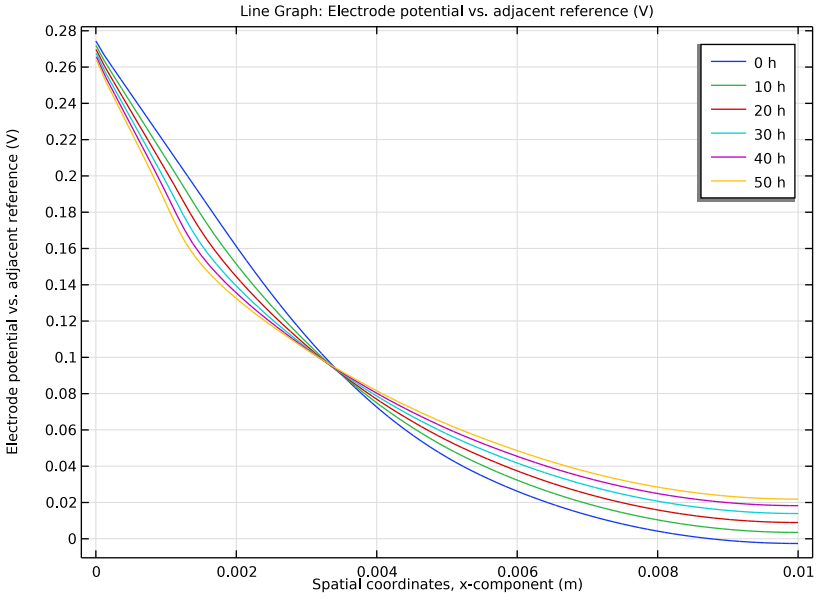

Figure 5: Electrode-electrolyte potential along the nickel surface.

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

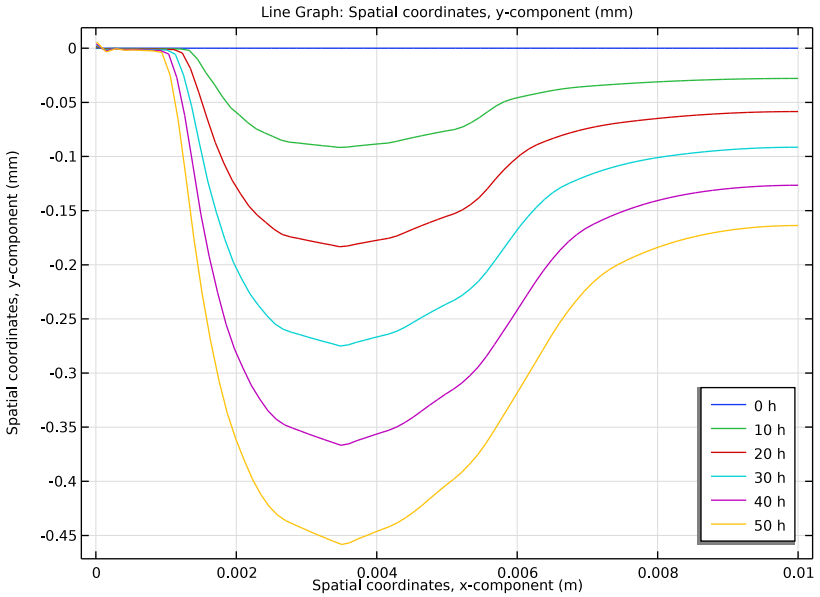

Figure 6: Electrode deformation at various times.

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, pp. 2276–2284, 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.

Application Library path: `Corrosion_Module/Crevice_and_Pitting_Corrosion/crevice_corrosion_with_deformation`

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 **2D**.

2 In the **Select Physics** tree, select **Electrochemistry>Corrosion, Deformed Geometry> Corrosion, Secondary**.

3 Click **Add**.

4 Click **Study**.

5 In the **Select Study** tree, select **Preset Studies for Selected Physics Interfaces> Time Dependent with Initialization**.

6 Click **Done**.

GLOBAL DEFINITIONS

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

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 In the table, enter the following settings:

Name	Expression	Value	Description
V_pol	0.3[V]	0.3 V	Polarization potential vs SCE
w	0.35[mm]	3.5E-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 **Geometry** toolbar, click **Rectangle**.

2 In the **Settings** window for **Rectangle**, locate the **Size and Shape** section.

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

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

5 Click **Build Selected**.

Square 1 (sq1)

1 In the **Geometry** toolbar, click **Square**.

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

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

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

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

6 Click **Build Selected**.

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

Union 1 (uni1)

1 In the **Geometry** toolbar, click **Booleans and Partitions** and choose **Union**.

2 Select both objects (**sq1** and **r1**).

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

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

5 Click **Build Selected**.

MATERIALS

Use the Corrosion Material Library to set up the electrode kinetics at the Nickel 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>Ni in 1M H2SO4 (Anodic)**.

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

MATERIALS

Ni in 1M H2SO4 (Anodic) (mat1)

1 In the **Settings** window for **Material**, locate the **Geometric Entity Selection** section.

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

3 Select Boundaries 4 and 5 only.

4 In the **Model Builder** window, expand the **Ni in 1M H2SO4 (Anodic) (mat1)** node.

Interpolation 1 (iloc_exp)

1 In the **Model Builder** window, expand the **Component 1 (comp1)>Materials> Ni in 1M H2SO4 (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 2.

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

SECONDARY CURRENT DISTRIBUTION (CD)

Now set up the electrochemistry. Start with selecting the reference electrode.

1 In the **Settings** window for **Secondary Current Distribution**, click to expand the **Physics vs. Materials Reference Electrode Potential** section.

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

Electrolyte 1

Set the user defined electrolyte conductivity.

1 In the **Model Builder** window, under **Component 1 (comp1)> Secondary Current Distribution (cd)** click **Electrolyte 1**.

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

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

Electrode Surface 1

Now set up the corroding electrode using Electrode Surface node.

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

2 Select Boundaries 4 and 5 only.

3 In the **Settings** window for **Electrode Surface**, locate the **Electrode Phase Potential Condition** section.

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

5 Click to expand the **Dissolving-Depositing Species** section. Click **Add**.

6 In the table, enter the following settings:

Species	Density (kg/m^3)	Molar mass (kg/mol)
s1	8900[kg/m^3]	0.05869[kg/mol]

Electrode Reaction 1

Set the local current density of the electrode reaction to a From material which uses the built-in polarization data for the interpolation polynomial.

1 In the **Model Builder** window, click **Electrode Reaction 1**.

2 In the **Settings** window for **Electrode Reaction**, locate the **Stoichiometric Coefficients** section.

3 In the n text field, type 2.

4 In the **Stoichiometric coefficients for dissolving-depositing species:** table, enter the following settings:

Species	Stoichiometric coefficient (1)
s1	1

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

Electrolyte Potential 1

Set the electrolyte potential to zero on the leftmost boundary.

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

2 Select Boundary 1 only.

MULTIPHYSICS

Nondeforming Boundary 1 (ndbdg1)

The following applies a stronger constraint (than the default condition) for the planar nondepositing walls in order to enforce a zero boundary movement in the normal direction.

1 In the **Model Builder** window, under **Component 1 (comp1)>Multiphysics** click **Nondeforming Boundary 1 (ndbdg1)**.

2 In the **Settings** window for **Nondeforming Boundary**, locate the **Nondeforming Boundary** section.

3 From the **Boundary condition** list, choose **Zero normal displacement**.

MESH 1

The model is now ready for solving. Use a mesh with an Extremely fine mesh resolution along the crevice electrode surface.

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

Size 1

1 In the **Model Builder** window, right-click **Free Triangular 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 5 only.

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

6 Click **Build All**.

STUDY 1

Due to the nonmonotonic 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 with continuation 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 **Settings** window for **Current Distribution Initialization**, locate the **Study Settings** section.

3 From the **Current distribution type** list, choose **Secondary**.

4 Click to expand the **Study Extensions** section. Select the **Auxiliary sweep** check box.

5 Click **Add**.

6 In the table, enter the following settings:

Parameter name	Parameter value list	Parameter unit
V_pol (Polarization potential vs SCE)	`range(-0.2,0.1,0.3)`	V

Step 2: Time Dependent

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 In the **Output times** text field, type `range(0,10*3600,50*3600)`.

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

RESULTS

A 2D plot of the electrolyte potential and the deformation is created by default (Figure 3). Change the frame of the dataset edges to Geometry in order to show the outline of the original (undeformed) geometry in the figure.

Electrolyte Potential (cd)

1 In the **Model Builder** window, under **Results** click **Electrolyte Potential (cd)**.

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

3 From the **Frame** list, choose **Geometry (Xg, Yg, Zg)**.

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

5 In the **Electrolyte Potential (cd)** toolbar, click  **Plot**.

1D Plot Group 7

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

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

Line Graph 1

1 Right-click **1D Plot Group 7** and choose **Line Graph**.

2 Select Boundary 5 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)> Secondary Current Distribution>Electrode kinetics>cd.iloc_er1 - Local current density - A/m²**.

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

5 In the **Expression** text field, type `x`.

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

7 From the **Legends** list, choose **Evaluated**.

8 In the **Legend** text field, type `eval(t,h) h`.

9 In the **1D Plot Group 7** toolbar, click  **Plot**.

1D Plot Group 7

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

In the **Model Builder** window, right-click **1D Plot Group 7** and choose **Duplicate**.

Line Graph 1

1 In the **Model Builder** window, expand the **1D Plot Group 8** node, then click **Line Graph 1**.

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)> Secondary Current Distribution>cd.Evsref - Electrode potential vs. adjacent reference - V**.

3 In the **1D Plot Group 8** toolbar, click **Plot**.

1D Plot Group 8

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

In the **Model Builder** window, right-click **1D Plot Group 8** and choose **Duplicate**.

Line Graph 1

1 In the **Model Builder** window, expand the **1D Plot Group 9** node, then click **Line Graph 1**.

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

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

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

1D Plot Group 9

1 In the **Model Builder** window, click **1D Plot Group 9**.

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

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

4 In the **1D Plot Group 9** toolbar, click **Plot**.

Corrosion Current Density

Optionally, give the plot group nodes more descriptive names:

1 In the **Model Builder** window, right-click **1D Plot Group 7** and choose **Rename**.

2 In the **Rename 1D Plot Group** dialog box, type `Corrosion Current Density` in the **New label** text field.

3 Click **OK**.

Electrode Potential

1 In the **Model Builder** window, right-click **1D Plot Group 8** and choose **Rename**.

2 In the **Rename 1D Plot Group** dialog box, type `Electrode Potential` in the **New label** text field.

3 Click **OK**.

Electrode Shape

1 In the **Model Builder** window, right-click **1D Plot Group 9** and choose **Rename**.

2 In the **Rename 1D Plot Group** dialog box, type `Electrode Shape` in the **New label** text field.

3 Click **OK**.