Estimation of Corrosion Kinetics Parameters

Introduction

A common challenge in corrosion modeling is to accurately describe the electrode kinetics as a function of electrode potential. This tutorial shows how to use the Parameter Estimation study node to perform electrode kinetics parameter estimations based on polarization data.

A zero-dimensional electrode polarization model is constructed using an anode Tafel expression for the metal dissolution reaction and a cathode Tafel expression for the oxygen reduction kinetics in combination with an oxygen reduction limiting current density.

Parameter estimation is performed using a global least-squares objective function based on three different sets of polarization data (Ref. 1) recorded for the following metals:

- 70-30 Cu-Ni alloy (SAE/ASTM UNS number CA7150)
- 90-10 Cu-Ni alloy (C70600)
- Ni-Al bronze (C95800)

The experimental data was recorded using potentiodynamic scans at 30 °C for fresh metals in a controlled sea water flow (8.0 ft/s) environment.

To run this tutorial you need the Optimization Module.

Model Definition

The metal dissolution reaction is described by an anodic Tafel expression according to:

$$i_{\mathrm{Me}} = i_{0,\mathrm{Me}} \times 10^{\eta_{\mathrm{Me}}/A_{\mathrm{Me}}} \tag{1}$$

where $i_{0,\mathrm{Me}}$ (A/m^2) is the exchange current density and A_{Me} (V) is the anodic Tafel slope of the metal dissolution reaction, respectively. The overpotential of the metal dissolution reaction, η_{Me} (V), is defined as:

$$\eta_{\mathrm{Me}} = E - E_{\mathrm{eq,Me}} \tag{2}$$

where $E_{\mathrm{eq,Me}}$ is the equilibrium potential of the metal dissolution reaction. Note that the choice of $E_{\mathrm{eq,Me}}$ (which is generally unknown) is arbitrary in this model since the cathodic part of the metal dissolution reaction is neglected. $E_{\mathrm{eq,Me}}=0$ is used in this model.

For the oxygen reduction reaction, the following cathodic Tafel expression is used:

$$i_{\mathrm{O_2,kin}} = -i_{0,\mathrm{O_2}} \times 10^{-\eta_{\mathrm{O_2}}/A_{\mathrm{O_2}}} \tag{3}$$

where $i_{0,\ O2}$(A/m2) is the exchange current density and A_{O2} (V) is the cathodic Tafel slope of the oxygen reduction reaction, respectively. The overpotential of the oxygen reduction reaction, η_{O2} (V), is defined as:

$$\eta_{\mathrm{Me}} = E - E_{\mathrm{eq,\ O_2}} \tag{4}$$

The equilibrium potential for oxygen reduction is defined to be dependent on the pH according to the Nernst equation:

$$E_{\mathrm{eq,\ O_2}} = 1.23\mathrm{V} - \frac{RT}{4F}\ln\left(\frac{1}{0.21 \times 10^{-\mathrm{pH}}}\right) \tag{5}$$

where T (K) is the temperature. (But note that here also the actual choice of $E_{\mathrm{eq,O2}}$ is arbitrary). A pH of 7.7 is used in the model.

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

$$i_{\mathrm{O_2}} = \frac{i_{\mathrm{O_2,\ lim}} i_{\mathrm{O_2,\ kin}}}{i_{\mathrm{O_2,\ lim}} + i_{\mathrm{O_2,\ kin}}} \tag{6}$$

where $i_{\mathrm{O2,lim}}$ (A/m^2) is the limiting current density for oxygen reduction.

Finally, the total current density at the electrode surface, i_{loc} (A/m^2), is:

$$i_{\mathrm{loc}} = i_{\mathrm{Me}} + i_{\mathrm{O_2}} \tag{7}$$

Note that for low potentials one should also consider hydrogen evolution as an additional cathodic reaction. That reaction is however not included in this tutorial.

The model is formulated as a set of parametric expressions in 0D and the Parameter Estimation study node is used to create a least squares objective function used for optimization, based on the experimental data.

Results and Discussion

The experimental polarization curves for the 70-30 Cu-Ni alloy and the corresponding fitted model values are shown in Figure 1 and Figure 2, using a linear or a logarithmic scale for the current density values, respectively.

Figure 3 and Figure 4 show the polarization curves in logarithmic scale for the 90-10 Cu-Ni and the Ni-Al bronze. In all cases, the model seems to be able to capture the salient features of the polarization behavior.

Table 1 shows the fitted parameter values for the polarization data for the three different metals. The two Cu-Ni alloys exhibit fairly similar values, whereas the values for the Ni-Al bronze are more different. The limiting current density for oxygen reduction are similar for all cases. This is expected since the experiments where conducted for fresh metals in a controlled flow environment.

TABLE 1: OPTIMIZATION PARAMETERS AND CORRESPONDING ESTIMATED VALUES FOR THE THREE DIFFERENT ALLOYS.

Parameter	**Unit**	**70-30 Cu-Ni**	**90-10 Cu-Ni**	**Ni-Al bronze**
A_{Me}	mV	63	68	70
A_{O2}	mV	-170	-166	-125
$i_{0,Me}$	A/m^2	$10^{3.3}$	$10^{2.8}$	$10^{3.5}$
$i_{0,O2}$	A/m^2	$10^{-7.1}$	$10^{-7.3}$	10^{-10}
$i_{O2,lim}$	A/m^2	-13	-15	-15

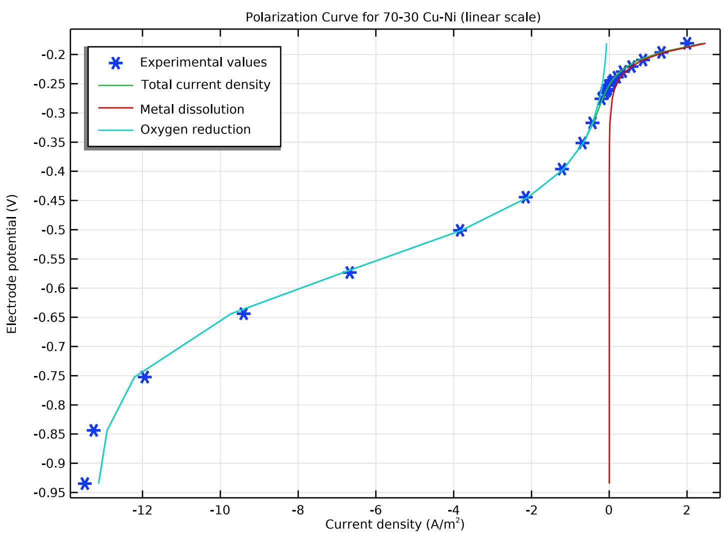

Figure 1: Polarization curve (linear scale) for the 70-30 Cu-Ni alloy.

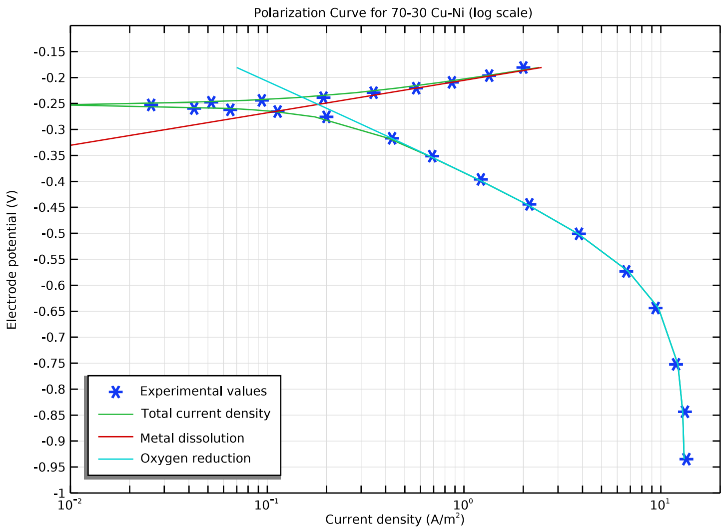

Figure 2: Polarization curve (log scale) for the 70-30 Cu-Ni alloy.

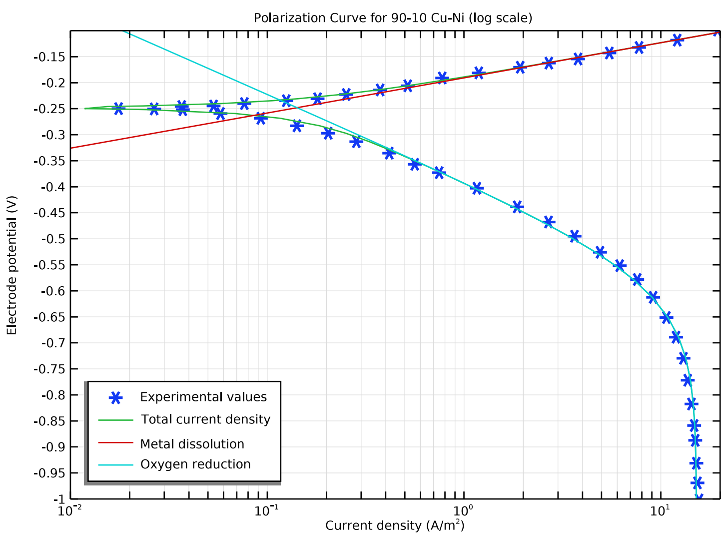

Figure 3: Polarization curve (log scale) for the 90-10 Cu-Ni alloy.

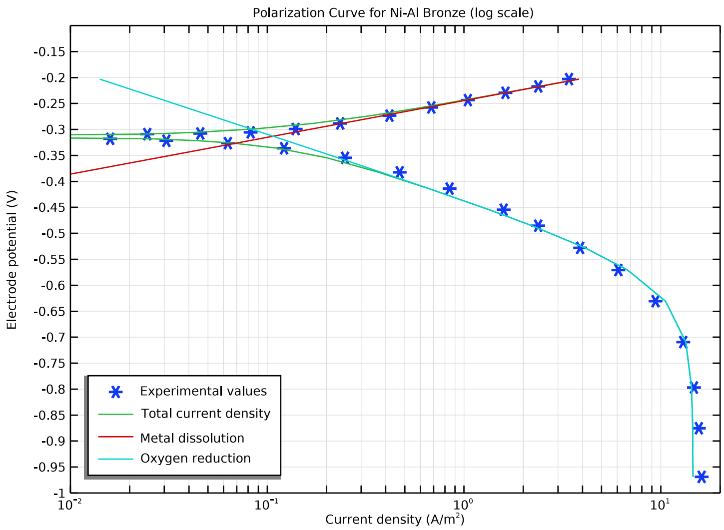

Figure 4: Polarization curve (log scale) for the Ni-Al bronze.

Reference

1. *Atlas of Polarization Diagrams for Naval Materials in Seawater*. Harvey P Hack. Carderock Division, Naval Surface Warfare Center, CARDIVNSWC-TR-61 -94/44, April 1995.

Application Library path: `Corrosion_Module/General_Corrosion/corrosion_parameter_estimation`

Modeling Instructions

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

NEW

In the **New** window, click **Blank Model**.

ADD COMPONENT

In the **Home** toolbar, click **Add Component** and choose **0D**.

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 `corrosion_parameter_estimation_parameters.txt`.

DEFINITIONS

Interpolation 1 (int1)

1 In the **Home** toolbar, click f(X) **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 In the **Filename** text field, type `7030CuNi_pol.csv`.
5 Click **Import**.

Interpolation 2 (int2)

1 Right-click **Interpolation 1 (int1)** and choose **Duplicate**.
2 In the **Settings** window for **Interpolation**, locate the **Definition** section.
3 From the **Data source** list, choose **File**.
4 In the **Filename** text field, type `9010CuNi_pol.csv`.
5 Click **Import**.
6 In the **Function name** text field, type `int2`.

Interpolation 3 (int3)

1 Right-click **Interpolation 2 (int2)** and choose **Duplicate**.
2 In the **Settings** window for **Interpolation**, locate the **Definition** section.
3 From the **Data source** list, choose **File**.
4 In the **Filename** text field, type `NiAlBronze_pol.csv`.
5 Click **Import**.
6 In the **Function name** text field, type `int3`.

ADD STUDY

1 In the **Home** toolbar, click **Add Study** to open the **Add Study** window.

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

3 Find the **Studies** subsection. In the **Select Study** tree, select **Preset Studies for Selected Physics Interfaces>Stationary**.

4 Click **Add Study** in the window toolbar three times.

5 In the **Home** toolbar, click **Add Study** to close the **Add Study** window.

STUDY 1

Use the **Parameter Estimation** study step to specify the polarization data (70-30 Cu-Ni) used by the optimization solver. The objective function will be created automatically by the study step.

Parameter Estimation

1 In the **Study** toolbar, click **Optimization** and choose **Parameter Estimation**.

2 In the **Settings** window for **Parameter Estimation**, locate the **Experimental Data** section.

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

4 In the **Filename** text field, type `7030CuNi_pol.csv`.

5 Click **Refresh**.

6 Locate the **Column Settings** section. In the table, click to select the cell at row number 1 and column number 2.

7 From the drop-down list, choose **Parameter**.

8 From the **Name** list, choose **E (Electrode potential)**.

9 In the table, click to select the cell at row number 2 and column number 3.

10 In the text fields that appear below the table, enter the following values:

11 In the **Model expression** text field, type `iloc`.

12 In the **Name** text field, type `iloc_exp`.

13 In the **Unit** text field, type `A/m^2`.

14 In the **Weight** text field, type `1/(max(abs(comp1.int1(E)),1e-2))^2`.

15 Locate the **Parameters** section. Click **Add** five times.

16 Row by row, select a parameter name in the first column and set the corresponding initial value and scale as follows:

Parameter name	Initial value	Scale
A_O2 (Cathodic tafel slope for oxygen reduction)	-200[mV]	0.1
A_Me (Anodic tafel slope for metal dissolution)	100[mV]	0.1
i_O2_lim (Limiting current density for oxygen reduction)	-15[A/m^2]	10
log10_i0_O2 (log10 of exchange current density for oxygen reduction)	-9	1
log10_i0_Me (log10 of exchange current density for metal dissolution)	0	1

Since there is no need to constrain the optimization parameters (control variables) for this least-squares problem, the Levenberg–Marquardt method is suitable.

17 Locate the **Parameter Estimation Method** section. From the **Method** list, choose **Levenberg-Marquardt**.

18 In the **Optimality tolerance** text field, type 1e-4.

COMPONENT 1 (COMP1)

By adding global probes for the optimization parameters, one can monitor the progress of the optimization during the computation.

DEFINITIONS

Global Variable Probe 1 (var1)

1 In the **Definitions** toolbar, click **Probes** and choose **Global Variable Probe**.

2 In the **Settings** window for **Global Variable Probe**, locate the **Expression** section.

3 In the **Expression** text field, type A_O2.

Global Variable Probe 2 (var2)

1 In the **Definitions** toolbar, click **Probes** and choose **Global Variable Probe**.

2 In the **Settings** window for **Global Variable Probe**, locate the **Expression** section.

3 In the **Expression** text field, type A_Me.

Global Variable Probe 3 (var3)

1 In the **Definitions** toolbar, click **Probes** and choose **Global Variable Probe**.

2 In the **Settings** window for **Global Variable Probe**, locate the **Expression** section.

3 In the **Expression** text field, type `log10_i0_O2`.

Global Variable Probe 4 (var4)

1 In the **Definitions** toolbar, click **Probes** and choose **Global Variable Probe**.

2 In the **Settings** window for **Global Variable Probe**, locate the **Expression** section.

3 In the **Expression** text field, type `log10_i0_Me`.

Global Variable Probe 5 (var5)

1 In the **Definitions** toolbar, click **Probes** and choose **Global Variable Probe**.

2 In the **Settings** window for **Global Variable Probe**, locate the **Expression** section.

3 In the **Expression** text field, type `i_O2_lim`.

70-30 CU-NI

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

2 In the **Settings** window for **Study**, type `70-30 Cu-Ni` in the **Label** text field.

The model is now ready for solving.

3 Locate the **Study Settings** section. Clear the **Generate default plots** check box.

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

The last row of the probe table now shows the final values of the optimization parameters.

RESULTS

Create polarization plots as follows:

1D Plot Group 2

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

Global 1

1 Right-click **1D Plot Group 2** and choose **Global**.

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

3 In the table, enter the following settings:

Expression	Unit	Description
`E`	`V`	`Electrode potential`

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

5 In the **Expression** text field, type `comp1.int1(E)`.

6 Click to expand the **Coloring and Style** section. Find the **Line style** subsection. From the **Line** list, choose **None**.

7 Find the **Line markers** subsection. From the **Marker** list, choose **Cycle**.

8 Click to expand the **Legends** section. From the **Legends** list, choose **Manual**.

9 In the table, enter the following settings:

Legends
`Experimental values`

Global 2

1 In the **Model Builder** window, right-click **1D Plot Group 2** and choose **Global**.

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

3 In the table, enter the following settings:

Expression	Unit	Description
`E`	`V`	`Electrode potential`

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

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

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

7 In the table, enter the following settings:

Legends
`Total current density`

8 In the **1D Plot Group 2** toolbar, click **Plot**.

Global 3

1 Right-click **Global 2** and choose **Duplicate**.

2 In the **Settings** window for **Global**, locate the **x-Axis Data** section.

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

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

Legends
`Metal dissolution`

5 In the **1D Plot Group 2** toolbar, click **Plot**.

Global 4

1. Right-click **Global 3** and choose **Duplicate**.
2. In the **Settings** window for **Global**, locate the **x-Axis Data** section.
3. In the **Expression** text field, type `i_02`.
4. Locate the **Legends** section. In the table, enter the following settings:

Legends
`Oxygen reduction`

Polarization plot 70-30 Cu-Ni (linear scale)

1. In the **Model Builder** window, under **Results** click **1D Plot Group 2**.
2. In the **Settings** window for **1D Plot Group**, type `Polarization plot 70-30 Cu-Ni (linear scale)` in the **Label** text field.
3. Click to expand the **Title** section. From the **Title type** list, choose **Manual**.
4. In the **Title** text area, type `Polarization Curve for 70-30 Cu-Ni (linear scale)`.
5. Locate the **Plot Settings** section.
6. Select the **x-axis label** check box. In the associated text field, type `Current density (A/m<sup>2</sup>)`.
7. Locate the **Legend** section. From the **Position** list, choose **Upper left**.
8. In the **Polarization plot 70-30 Cu-Ni (linear scale)** toolbar, click **Plot**.

Polarization plot 70-30 Cu-Ni (log scale)

1. Right-click **Polarization plot 70-30 Cu-Ni (linear scale)** and choose **Duplicate**.
2. In the **Settings** window for **1D Plot Group**, type `Polarization plot 70-30 Cu-Ni (log scale)` in the **Label** text field.
3. Locate the **Title** section. In the **Title** text area, type `Polarization Curve for 70-30 Cu-Ni (log scale)`.
4. Click the **x-Axis Log Scale** button in the **Graphics** toolbar.

Global 1

For the log plot, only positive current densities can be plotted.

1. In the **Model Builder** window, expand the **Polarization plot 70-30 Cu-Ni (log scale)** node, then click **Global 1**.
2. In the **Settings** window for **Global**, locate the **x-Axis Data** section.
3. In the **Expression** text field, type `abs(comp1.int1(E))`.

Global 2

1 In the **Model Builder** window, click **Global 2**.
2 In the **Settings** window for **Global**, locate the **x-Axis Data** section.
3 In the **Expression** text field, type abs(iloc).

Global 3

The metal dissolution currents are always positive, so there is no need to modify this expression.

Global 4

1 In the **Model Builder** window, click **Global 4**.
2 In the **Settings** window for **Global**, locate the **x-Axis Data** section.
3 In the **Expression** text field, type abs(i_02).
4 In the **Polarization plot 70-30 Cu-Ni (log scale)** toolbar, click **Plot**.

Polarization plot 70-30 Cu-Ni (log scale)

1 In the **Model Builder** window, click **Polarization plot 70-30 Cu-Ni (log scale)**.
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 1e-2.
5 In the **x maximum** text field, type 20.
6 In the **y minimum** text field, type -1.
7 In the **y maximum** text field, type -0.1.
8 In the **Polarization plot 70-30 Cu-Ni (log scale)** toolbar, click **Plot**.
9 Locate the **Legend** section. From the **Position** list, choose **Lower left**.
10 In the **Polarization plot 70-30 Cu-Ni (log scale)** toolbar, click **Plot**.

Now perform the same optimization for a different dataset (90-10 Cu-Ni).

70-30 CU-NI

Parameter Estimation

In the **Model Builder** window, under **70-30 Cu-Ni** right-click **Parameter Estimation** and choose **Copy**.

STUDY 2

In the **Model Builder** window, right-click **Study 2** and choose **Paste Parameter Estimation**.

Parameter Estimation

1 In the **Settings** window for **Parameter Estimation**, locate the **Experimental Data** section.

2 In the **Filename** text field, type `9010CuNi_pol.csv`.

3 Click **Refresh**.

4 Locate the **Column Settings** section. In the table, click to select the cell at row number 2 and column number 3.

5 Modify the weight:

6 In the **Weight** text field, type `1/(max(abs(comp1.int2(E)),1e-2))^2`.

7 In the **Model Builder** window, click **Study 2**.

8 In the **Settings** window for **Study**, type `90-10 Cu-Ni` in the **Label** text field.

9 Locate the **Study Settings** section. Clear the **Generate default plots** check box.

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

RESULTS

Polarization plot 90-10 Cu-Ni (linear scale)

1 In the **Model Builder** window, right-click **Polarization plot 70-30 Cu-Ni (linear scale)** and choose **Duplicate**.

2 In the **Settings** window for **1D Plot Group**, type `Polarization plot 90-10 Cu-Ni (linear scale)` in the **Label** text field.

3 Locate the **Data** section. From the **Dataset** list, choose **90-10 Cu-Ni/Solution 2 (sol2)**.

4 Locate the **Title** section. In the **Title** text area, type `Polarization Curve for 90-10 Cu-Ni (linear scale)`.

Global 1

1 In the **Model Builder** window, expand the **Polarization plot 90-10 Cu-Ni (linear scale)** node, then click **Global 1**.

2 In the **Settings** window for **Global**, locate the **x-Axis Data** section.

3 In the **Expression** text field, type `comp1.int2(E)`.

Polarization plot 90-10 Cu-Ni (log scale)

1 In the **Model Builder** window, right-click **Polarization plot 70-30 Cu-Ni (log scale)** and choose **Duplicate**.

2 In the **Settings** window for **1D Plot Group**, type `Polarization plot 90-10 Cu-Ni (log scale)` in the **Label** text field.

3 Locate the **Data** section. From the **Dataset** list, choose **90-10 Cu-Ni/Solution 2 (sol2)**.

4 Locate the **Title** section. In the **Title** text area, type `Polarization Curve for 90-10 Cu-Ni (log scale)`.

Global 1

1 In the **Model Builder** window, expand the **Polarization plot 90-10 Cu-Ni (log scale)** node, then click **Global 1**.

2 In the **Settings** window for **Global**, locate the **x-Axis Data** section.

3 In the **Expression** text field, type `abs(comp1.int2(E))`.

4 In the **Polarization plot 90-10 Cu-Ni (log scale)** toolbar, click **Plot**.

Finally, also try the optimization on a polarization for a Ni-Al bronze.

70-30 CU-NI

Parameter Estimation

In the **Model Builder** window, under **70-30 Cu-Ni** right-click **Parameter Estimation** and choose **Copy**.

STUDY 3

In the **Model Builder** window, right-click **Study 3** and choose **Paste Parameter Estimation**.

Parameter Estimation

1 In the **Settings** window for **Parameter Estimation**, locate the **Experimental Data** section.

2 In the **Filename** text field, type `NiAlBronze_pol.csv`.

3 Click **Refresh**.

4 Locate the **Column Settings** section. In the table, click to select the cell at row number 2 and column number 3.

5 Again, change the weight:

6 In the **Weight** text field, type `1/(max(abs(comp1.int3(E)),1e-2))^2`.

7 In the **Model Builder** window, click **Study 3**.

8 In the **Settings** window for **Study**, type `Ni-Al Bronze` in the **Label** text field.

9 Locate the **Study Settings** section. Clear the **Generate default plots** check box.

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

RESULTS

Polarization plot Ni-Al (linear scale)

1 In the **Model Builder** window, right-click **Polarization plot 70-30 Cu-Ni (linear scale)** and choose **Duplicate**.

2 In the **Settings** window for **1D Plot Group**, type `Polarization plot Ni-Al (linear scale)` in the **Label** text field.

3 Locate the **Data** section. From the **Dataset** list, choose **Ni-Al Bronze/Solution 3 (sol3)**.

4 Locate the **Title** section. In the **Title** text area, type `Polarization Curve for Ni-Al Bronze (linear scale)`.

Global 1

1 In the **Model Builder** window, expand the **Polarization plot Ni-Al (linear scale)** node, then click **Global 1**.

2 In the **Settings** window for **Global**, locate the **x-Axis Data** section.

3 In the **Expression** text field, type `comp1.int3(E)`.

Polarization plot Ni-Al (log scale)

1 In the **Model Builder** window, right-click **Polarization plot 70-30 Cu-Ni (log scale)** and choose **Duplicate**.

2 In the **Settings** window for **1D Plot Group**, type `Polarization plot Ni-Al (log scale)` in the **Label** text field.

3 Locate the **Data** section. From the **Dataset** list, choose **Ni-Al Bronze/Solution 3 (sol3)**.

4 Locate the **Title** section. In the **Title** text area, type `Polarization Curve for Ni-Al Bronze (log scale)`.

Global 1

1 In the **Model Builder** window, expand the **Polarization plot Ni-Al (log scale)** node, then click **Global 1**.

2 In the **Settings** window for **Global**, locate the **x-Axis Data** section.

3 In the **Expression** text field, type `abs(comp1.int3(E))`.

4 In the **Polarization plot Ni-Al (log scale)** toolbar, click **Plot**.