



Model created in COMSOL Multiphysics 6.4

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.

Model Definition

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

$$i_{\text{Me}} = i_{0, \text{Me}} \times 10^{\eta_{\text{Me}}/A_{\text{Me}}} \quad (1)$$

where $i_{0, \text{Me}}$ (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:

$$\eta_{\text{Me}} = E - E_{\text{eq}, \text{Me}} \quad (2)$$

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

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

$$i_{\text{O}_2, \text{kin}} = -i_{0, \text{O}_2} \times 10^{-\eta_{\text{O}_2}/A_{\text{O}_2}} \quad (3)$$

where i_{0,O_2} (A/m²) is the exchange current density and A_{O_2} (V) is the cathodic Tafel slope of the oxygen reduction reaction, respectively. The overpotential of the oxygen reduction reaction, η_{O_2} (V), is defined as:

$$\eta_{Me} = E - E_{eq, O_2} \quad (4)$$

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

$$E_{eq, O_2} = 1,23V - \frac{RT}{4F} \ln\left(\frac{1}{0,21 \times 10^{-pH}}\right) \quad (5)$$

where T (K) is the temperature. (But note that here also the actual choice of E_{eq,O_2} 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:

$$i_{O_2} = \frac{i_{O_2, \lim} i_{O_2, \text{kin}}}{i_{O_2, \lim} + i_{O_2, \text{kin}}} \quad (6)$$

where $i_{O_2, \lim}$ (A/m²) is the limiting current density for oxygen reduction.

Finally, the total current density at the electrode surface, i_{loc} (A/m²), is:

$$i_{loc} = i_{Me} + i_{O_2} \quad (7)$$

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 were 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_{O_2}	mV	-170	-166	-125
$i_{0,Me}$	A/m ²	$10^{3.3}$	$10^{2.8}$	$10^{3.5}$
i_{0,O_2}	A/m ²	$10^{-7.1}$	$10^{-7.3}$	10^{-10}
$i_{O_2,lim}$	A/m ²	-13	-15	-15

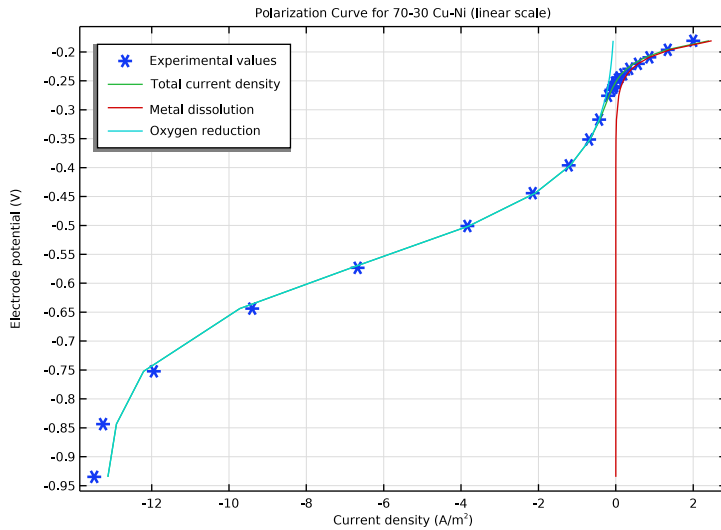


Figure 1: Polarization curve (linear scale) for the 70-30 Cu-Ni alloy.

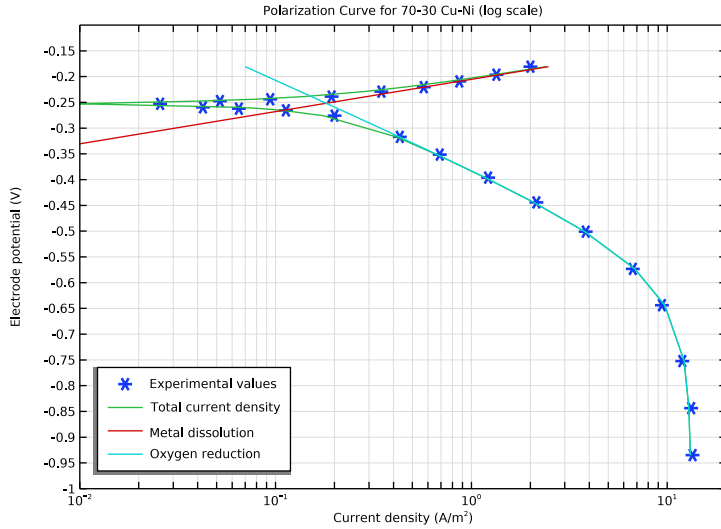


Figure 2: Polarization curve (log scale) for the 70-30 Cu-Ni alloy.

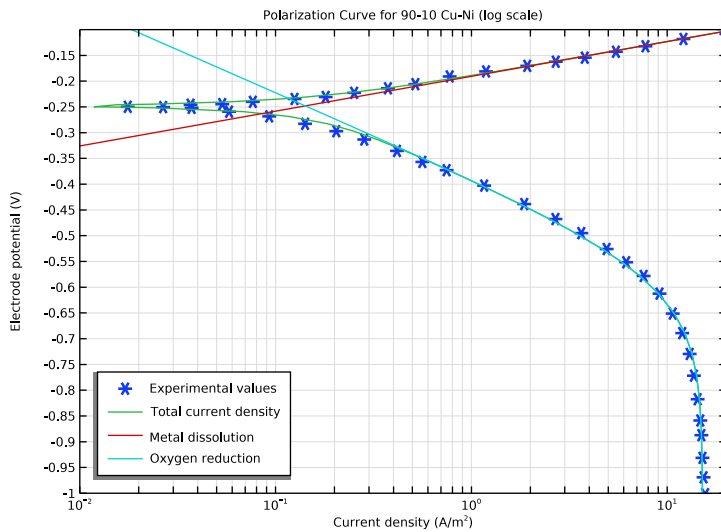


Figure 3: Polarization curve (log scale) for the 90-10 Cu-Ni alloy.

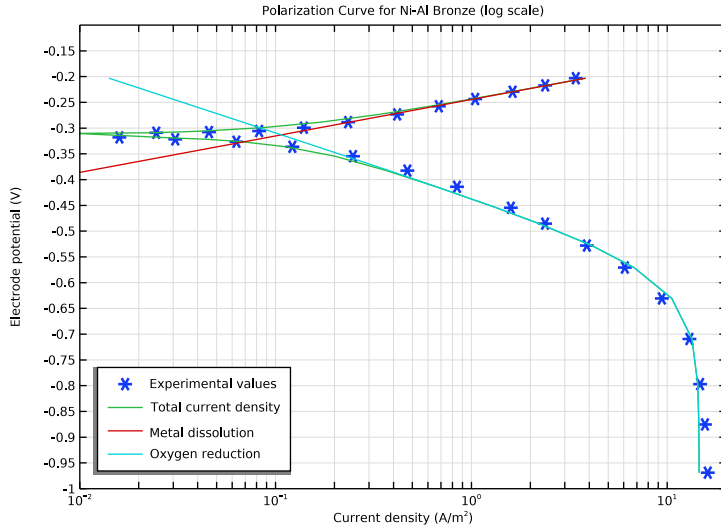


Figure 4: Polarization curve (log scale) for the Ni-Al bronze.

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 **Definitions** toolbar, click  **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_po1.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_po1.csv`.
- 5 Click  **Import**.

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_po1.csv`.
- 5 Click  **Import**.

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 the **Add Study** button in the window toolbar three times.
- 5 In the **Study** 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 In the **Filename** text field, type 7030CuNi_po1.csv.
- 4 Click  **Refresh**.
- 5 Locate the **Data Column Settings** section. In the table, click to select the cell at row number 1 and column number 2.
- 6 From the list, choose **Parameter**.
- 7 From the **Name** list, choose **E (Electrode potential)**.
- 8 In the table, click to select the cell at row number 2 and column number 3.
In the text fields that appear below the table, enter the following values:
- 9 In the **Model expression** text field, type `i1oc`.
- 10 In the **Column name** text field, type `i1oc_exp`.
- 11 In the **Unit** text field, type `A/m^2`.
- 12 From the **Scale** list, choose **Manual**.
- 13 In the **Scale value** text field, type `max(abs(comp1.int1(E)),1e-2)`.
- 14 Locate the **Estimated Parameters** section. Click  **Add** five times.

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

Parameter	Initial value	Scale	Unit
A_O2 (Cathodic tafel slope for oxygen reduction)	-200 [mV]	0.1	V
A_Me (Anodic tafel slope for metal dissolution)	100 [mV]	0.1	V
i_O2_lim (Limiting current density for oxygen reduction)	-15 [A/m ²]	10	A/m ²
logI0_i0_O2 (logI0 of exchange current density for oxygen reduction)	-9	1	
logI0_i0_Me (logI0 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.

16 Locate the **Parameter Estimation Method** section. From the **Method** list, choose **Levenberg–Marquardt**.

17 From the **Least-squares time/parameter list method** list, choose **Merge within manual range**.


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 $\log_{10} i_{0_02}$.


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 $\log_{10} i_{0_Me}$.

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_{02_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** checkbox.
- 4 In the **Study** 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:

ID Plot Group 2

In the **Results** toolbar, click  **ID Plot Group**.

Global 1

- 1 Right-click **ID 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 **ID 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 `i1oc`.
- 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 **ID 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 **ID 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 **ID Plot Group 2**.
- 2 In the **Settings** window for **ID 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** checkbox. In the associated text field, type Current density (A/m^2).
- 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 **ID 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 **ID Plot Group**, locate the **Axis** section.
- 3** Select the **Manual axis limits** checkbox.
- 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**.

90-10 CU-NI

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

- 1 In the **Settings** window for **Parameter Estimation**, locate the **Experimental Data** section.
- 2 In the **Filename** text field, type 9010CuNi_po1.csv.
- 3 Click  **Refresh**.
- 4 Locate the **Data Column Settings** section. In the table, click to select the cell at row number 2 and column number 3.
- 5 Modify the weight:
- 6 From the **Scale** list, choose **Manual**.
- 7 In the **Scale value** text field, type $\max(\text{abs}(\text{comp1.int2}(E)), 1e-2)$.
- 8 In the **Model Builder** window, click **Study 2**.
- 9 In the **Settings** window for **Study**, type 90-10 Cu-Ni in the **Label** text field.
- 10 Locate the **Study Settings** section. Clear the **Generate default plots** checkbox.
- 11 In the **Study** 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 **ID 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 I


- 1 In the **Model Builder** window, expand the **Polarization plot 90-10 Cu-Ni (linear scale)** node, then click **Global I**.
- 2 In the **Settings** window for **Global**, locate the **x-Axis Data** section.
- 3 In the **Expression** text field, type $\text{comp1.int2}(E)$.

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 **ID 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 I

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

NI-AL BRONZE

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

- 1 In the **Settings** window for **Parameter Estimation**, locate the **Experimental Data** section.
- 2 In the **Filename** text field, type `NiAlBronze_po1.csv`.
- 3 Click  **Refresh**.
- 4 Locate the **Data 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 From the **Scale** list, choose **Manual**.
- 7 In the **Scale value** text field, type `max(abs(comp1.int3(E)), 1e-2)`.
- 8 In the **Model Builder** window, click **Study 3**.
- 9 In the **Settings** window for **Study**, type Ni-Al Bronze in the **Label** text field.
- 10 Locate the **Study Settings** section. Clear the **Generate default plots** checkbox.
- 11 In the **Study** 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 **ID 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 I

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

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