Created in COMSOL Multiphysics 6.2

Alternating Current-Induced Corrosion

Introduction

Corrosion induced by alternating currents (AC) is evident in the oil and gas industry, particularly when a pipeline is in close proximity to high power transmission lines.

The model presented here first evaluates the effect of a direct current (DC) applied potential on corrosion using a stationary analysis, and then evaluates the effect of AC on corrosion using a transient analysis. The model is subsequently extended to investigate the effect of frequency on the AC corrosion rate, thereby demonstrating the role of the capacitive double-layer at higher frequencies.

The model is based on a paper by Ghanbari and others (Ref. 1).

Model Definition

The model geometry is defined in 1D, where the length is set to equal to the diffusion layer thickness. A steel electrode surface is assumed to be located at the left-hand side, with the bulk electrolyte boundary placed at the right, as shown in Figure 1.

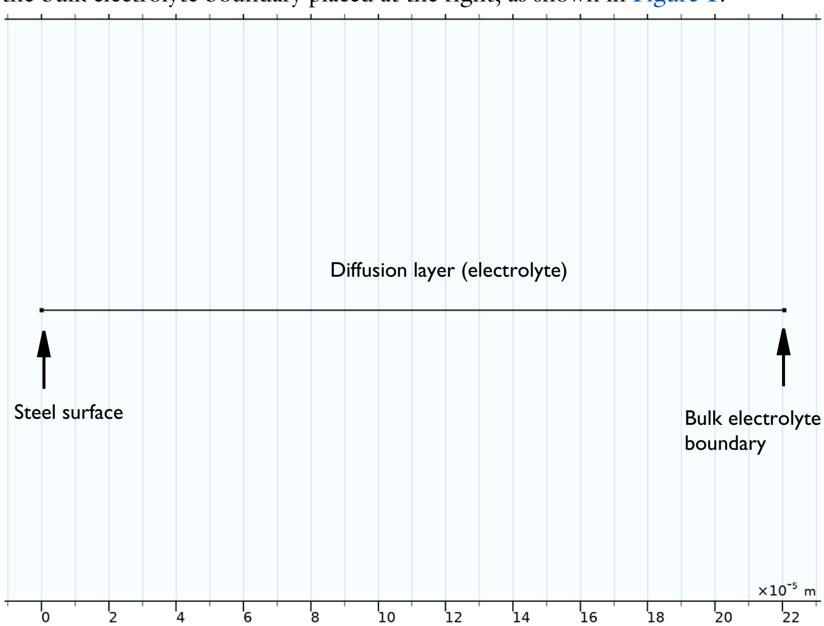

Figure 1: Model geometry.

The concentration of dissolved oxygen is solved for across the diffusion layer thickness, with the transport equation defined according Fick's law:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (-D_i \nabla c_i) = 0 \tag{1}$$

Here, c_i is the dissolved oxygen concentration in the electrolyte (mol/m^3) and D_i is diffusion coefficient of dissolved oxygen in the electrolyte (m^2/s).

The diffusion layer thickness is set based on the limiting current density for the oxygen reduction reaction, i_{lim}, across the diffusion layer:

$$L = \frac{4FDc_{\mathrm{sat}}}{i_{\mathrm{lim}}} \tag{2}$$

The oxygen concentration is set equal to the saturated concentration for dissolved oxygen when in equilibrium with air, c_{sat}, at the right boundary. At the electrode surface on the left, the flux of oxygen is defined based on the local current density for oxygen reduction in combination with Faraday's law.

The Electrode Surface boundary node is used to calculate the total current density, i_T, which includes contributions from the metal dissolution (anodic), oxygen reduction (cathodic) and hydrogen evolution (cathodic) electrochemical reactions, as well as the double layer capacitance.

The electrode potential is assumed to be measured versus a reference electrode located outside the diffusion layer. The electrode potential versus the reference, E_T, is hence the sum of the potential drop across the electrochemical interface, E, and the potential drop across the solution resistance, R_s:

$$E_T = E + i_T R_s \tag{3}$$

The potential drop across the electrochemical interface, E, is solved using a Global Equations node.

The potential of the steel electrode is defined to be the sum of a DC potential, E_{DC}, and an AC potential perturbation, and is set according to

$$E_T = E_{\mathrm{DC}} + E_{\mathrm{RMS}} \sin(\omega t) \tag{4}$$

Here, E_{RMS} is the amplitude of the AC potential; ω is the angular frequency, which is equal to $2\pi f$, where f is the frequency of the AC potential; and t is time.

Tafel kinetics are used to define all faradaic reactions. For the oxygen reduction reaction, the kinetics expression is concentration dependent according to

$$i_{O2} = -\frac{c}{c_{sat}} i_{0,\,O2} 10^{\eta/A_c} \tag{5}$$

where A_c is the Tafel slope and $\eta = E - E_{eq}$ is the overpotential.

The nonfaradaic double layer capacitance current density is defined as

$$i_{dl} = C_{dl} \frac{dE}{dt} \tag{6}$$

where C_{dl} is considered to be a combination of double layer and oxide capacitances. Different C_{dl} values are used in the model for different DC applied potentials, which are taken from Ref. 1.

The model is solved in two steps. In the first step, a stationary solution for the pure DC problem is computed. In the second time-dependent step, the solution of the stationary step is used as initial values, and the simulation is performed for multiple consecutive periods. In order to compare the AC to the DC solution, the corrosion rate is calculated as an average for the last period of the simulation.

Results and Discussion

Figure 2 shows the anodic (metal dissolution) current density for different applied DC potentials with and without AC. It can be seen that the anodic current density in both cases (with and without AC) increases with an increase in applied DC potential. Adding the AC contribution generally increases the corrosion rate, with the effect of AC being most dominant near the open circuit potential of -0.67 V/SCE.

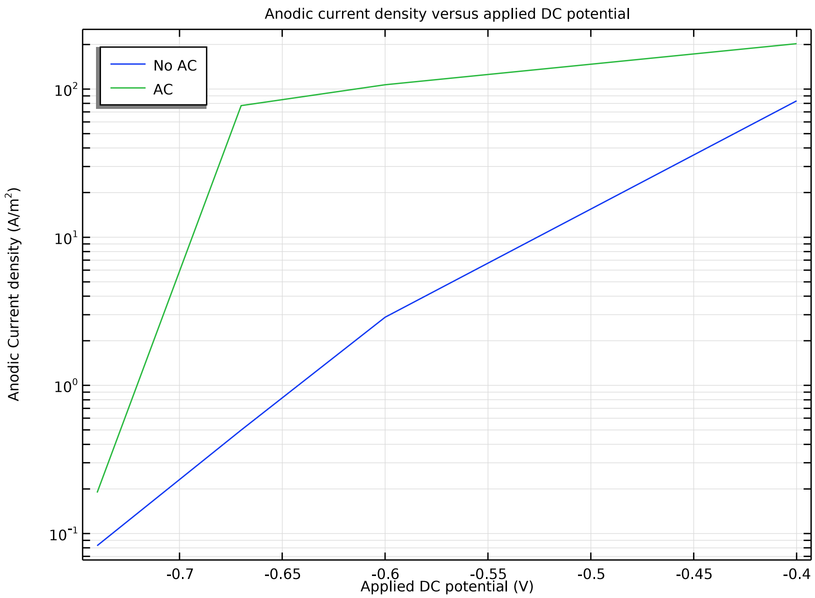

Figure 2: Anodic current density with and without AC for different applied DC potentials.

Figure 3 and Figure 4 show the change in total current density against time along with contributions from anodic, cathodic and double layer for frequencies 60 Hz and 0.01 Hz, respectively. It can be seen that double layer (nonfaradaic) contribution to the total current density is quite significant at frequency of 60 Hz (Figure 3), whereas at lower frequency of 0.01 Hz the total current density is mainly constituted of anodic current density (faradaic).

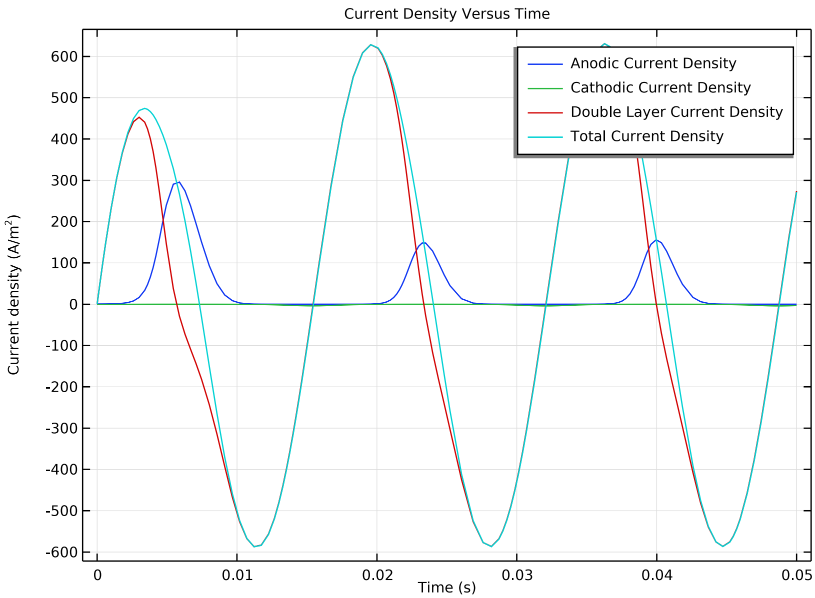

Figure 3: Transient distribution of the total current density along with anodic, cathodic and double layer contributions at frequency of 60 Hz.

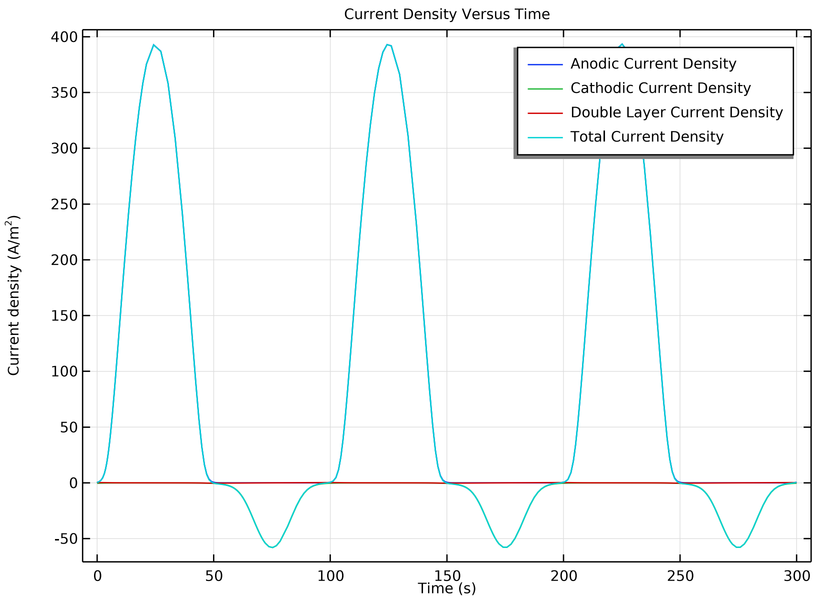

Figure 4: Transient distribution of the total current density along with anodic, cathodic and double layer contributions at frequency of 0.01 Hz.

References

1. E. Ghanbari, M. Iannuzzi, and R.S. Lillard, "The mechanism of alternating current corrosion of API grade X65 pipeline steel," Corrosion, vol. 72, no. 9, pp. 1196–1210, 2016.

Application Library path: `Corrosion_Module/General_Corrosion/ac_corrosion`

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>Electroanalysis (tcd)**.
3 Click **Add**.
4 In the **Number of species** text field, type `1`.
5 In the **Concentrations (mol/m³)** table, enter the following settings:

c02

6 In the **Select Physics** tree, select **Mathematics>ODE and DAE Interfaces>Global ODEs and DAEs (ge)**.
7 Click **Add**.
8 Click **Study**.
9 In the **Select Study** tree, select **General Studies>Stationary**.
10 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 `ac_corrosion_parameters.txt`.

GEOMETRY 1

Draw a 1D geometry representing the diffusion layer thickness.

1 From the **Geometry** menu, choose **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**.

DEFINITIONS

Variables 1

Load the model variables from a text file.

1 In the **Home** toolbar, click **Variables** and choose **Local Variables**.

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

3 Click **Load from File**.

4 Browse to the model's Application Libraries folder and double-click the file `ac_corrosion_variables.txt`.

Integration 1 (intop1)

Add an integration operator.

1 In the **Definitions** toolbar, click **Nonlocal Couplings** and choose **Integration**.

2 In the **Settings** window for **Integration**, locate the **Source Selection** section.

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

4 Select Boundary 1 only.

ELECTROANALYSIS (TCD)

Set up the physics of the model.

Electrolyte 1

1 In the **Model Builder** window, under **Component 1 (comp1)>Electroanalysis (tcd)** click **Electrolyte 1**.

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

3 In the D_{cO2} text field, type `D_O2`.

Initial Values 1

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 $cO2$ text field, type `c_O2_sat`.

Concentration 1

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

2 Select Boundary 2 only.

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

4 Select the **Species cO2** check box.

5 In the $c_{0,\mathrm{cO2}}$ text field, type `c_O2_sat`.

Electrode Surface 1

Next, set up the Electrode Surface node to describe the anodic, cathodic, and double-layer contributions to the total current density.

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

2 Select Boundary 1 only.

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

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

Electrode Reaction: Anodic Reaction

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

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

3 From the E_{eq} list, choose **User defined**. In the associated text field, type `Ecorr`.

4 Locate the **Electrode Kinetics** section. From the **Kinetics expression type** list, choose **Anodic Tafel equation**.

5 In the i_0 text field, type `icorr`.

6 In the A_{a} text field, type `ba`.

7 In the **Label** text field, type `Electrode Reaction: Anodic Reaction`.

Electrode Surface 1

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

Electrode Reaction: Oxygen reduction cathodic reaction

1 In the **Physics** toolbar, click **Attributes** and choose **Electrode Reaction**.

2 In the **Settings** window for **Electrode Reaction**, type `Electrode Reaction: Oxygen reduction cathodic reaction` in the **Label** text field.

3 Locate the **Stoichiometric Coefficients** section. In the n text field, type `4`.

4 In the ν_{cO2} text field, type `-1`.

5 Locate the **Equilibrium Potential** section. From the E_{eq} list, choose **User defined**. In the associated text field, type `Ecorr`.

6 Locate the **Electrode Kinetics** section. From the **Kinetics expression type** list, choose **Cathodic Tafel equation**.

7 In the i_0 text field, type `icorr*cO2/ c_O2_sat`.

8 In the A_c text field, type `bc`.

Electrode Surface 1

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

Electrode Reaction: Hydrogen evolution cathodic reaction

1 In the **Physics** toolbar, click **Attributes** and choose **Electrode Reaction**.

2 In the **Settings** window for **Electrode Reaction**, type `Electrode Reaction: Hydrogen evolution cathodic reaction` in the **Label** text field.

3 Locate the **Equilibrium Potential** section. From the E_{eq} list, choose **User defined**. In the associated text field, type `E_H2`.

4 Locate the **Electrode Kinetics** section. From the **Kinetics expression type** list, choose **Cathodic Tafel equation**.

5 In the i_0 text field, type `i0_H2`.

6 In the A_c text field, type `b_H2`.

Electrode Surface 1

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

Double-Layer Capacitance 1

1 In the **Physics** toolbar, click **Attributes** and choose **Double-Layer Capacitance**.

2 In the **Settings** window for **Double-Layer Capacitance**, locate the **Double-Layer Capacitance** section.

3 In the C_{dl} text field, type `C`.

GLOBAL ODES AND DAES (GE)

Add a Global Equation to solve for electric potential, E.

Global Equations 1

1 In the **Model Builder** window, under **Component 1 (comp1)>Global ODEs and DAEs (ge)** click **Global Equations 1**.

2 In the **Settings** window for **Global Equations**, locate the **Global Equations** section.

3 In the table, enter the following settings:

Name	f(u,ut,utt,t) (1)	Initial value (u_0) (1)	Initial value (u_t0) (1/s)	Description
`E`	`E_app-tcd.itotavg_es1*Rs-E`	`E0`	`0`	`Electric potential`

4 Locate the **Units** section. Click **Define Dependent Variable Unit**.

5 In the **Dependent variable quantity** table, enter the following settings:

Dependent variable quantity	Unit
Custom unit	V

6 Click **Define Source Term Unit**.

7 In the **Source term quantity** table, enter the following settings:

Source term quantity	Unit
Custom unit	V

STUDY : AC EFFECT

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

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

3 Clear the **Generate default plots** check box.

4 In the **Label** text field, type `Study : AC Effect`.

Parametric Sweep

Use the parametric sweep to investigate the effect of applied DC potential along with the respective double layer capacitance values.

1 In the **Study** toolbar, click **Parametric Sweep**.

2 In the **Settings** window for **Parametric Sweep**, locate the **Study Settings** section.

3 Click **Add**.

4 In the table, enter the following settings:

Parameter name	Parameter value list	Parameter unit
E_DC (Applied DC potential)	`-0.74[V] -0.67[V] -0.6[V] -0.4[V]`	V

5 Click Add.

6 In the table, enter the following settings:

Parameter name	Parameter value list	Parameter unit
C (Double layer capacitance)	35[F/m^2] 2.61[F/m^2] 2.57[F/m^2] 3.09[F/m^2]	F/m^2

Now solve the stationary study step to get results without AC effect first.

7 In the **Study** toolbar, click **Compute**.

Solver Configurations

Store a copy of the solution for comparison purposes.

Solution 1 (sol1)

1 In the **Model Builder** window, expand the **Study : AC Effect>Solver Configurations** node.

2 Right-click **Solution 1 (sol1)** and choose **Solution>Copy**.

Solution 1 - No AC

1 In the **Model Builder** window, under **Study : AC Effect>Solver Configurations** click **Solution 1 - Copy 1 (sol2)**.

2 In the **Settings** window for **Solution**, type `Solution 1 - No AC` in the **Label** text field.

Step 2: Time Dependent

Now add a Time Dependent study node to investigate the effect of AC.

1 In the **Study** toolbar, click **Study Steps** and choose **Time Dependent>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,tf/10,tf)`.

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

RESULTS

Plot the anodic current density to compare the effect of AC.

Effect of AC

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

2 In the **Settings** window for **1D Plot Group**, type `Effect of AC` in the **Label** text field.

3 Locate the **Data** section. From the **Dataset** list, choose **None**.

4 Click to expand the **Title** section. From the **Title type** list, choose **Manual**.

5 In the **Title** text area, type Anodic current density versus applied DC potential.

6 Locate the **Plot Settings** section.

7 Select the **y-axis label** check box. In the associated text field, type Anodic Current density (A/m²).

8 Locate the **Axis** section. Select the **y-axis log scale** check box.

9 Locate the **Legend** section. From the **Position** list, choose **Upper left**.

Global 1

1 In the **Effect of AC** toolbar, click **Global**.

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

3 From the **Dataset** list, choose **Study : AC Effect/Solution 1 - No AC (sol2)**.

4 Locate the **y-Axis Data** section. In the table, enter the following settings:

Expression	Unit	Description
ia	A/m^2	Anodic current density

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

6 In the **Expression** text field, type E_DC.

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

8 In the table, enter the following settings:

Legends
No AC

Effect of AC

In the **Model Builder** window, click **Effect of AC**.

Global 2

1 In the **Effect of AC** toolbar, click **Global**.

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

3 From the **Dataset** list, choose **Study : AC Effect/Parametric Solutions 1 (sol4)**.

4 From the **Time selection** list, choose **Last**.

5 Locate the **y-Axis Data** section. In the table, enter the following settings:

Expression	Unit	Description
`timeint(tf-1/f,tf,ia)/(1/f)`	`A/m^2`	`Time averaged anodic current density`

6 Locate the **x-Axis Data** section. From the **Axis source data** list, choose **Outer solutions**.

7 From the **Parameter** list, choose **Expression**.

8 In the **Expression** text field, type `E_DC`.

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

10 In the table, enter the following settings:

Legends
AC

11 In the **Effect of AC** toolbar, click **Plot**.

The plot should look like Figure 2.

ROOT

Next, add a new study to investigate the effect of the frequency on the corrosion using a Parametric Sweep.

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 **General Studies>Stationary**.

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

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

STUDY : FREQUENCY EFFECT

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

2 In the **Settings** window for **Study**, type `Study : Frequency Effect` in the **Label** text field.

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

Step 2: Time Dependent

In the **Study** toolbar, click **Study Steps** and choose **Time Dependent>Time Dependent**.

Parametric Sweep

Use the parametric sweep to investigate the effect of two frequencies, 60[Hz] and 0.01[Hz].

1. In the **Study** toolbar, click **Parametric Sweep**.
2. In the **Settings** window for **Parametric Sweep**, locate the **Study Settings** section.
3. Click **Add**.
4. In the table, enter the following settings:

Parameter name	Parameter value list	Parameter unit
f (Frequency of AC potential)	60[Hz] 0.01[Hz]	Hz

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,tf/10,tf).
4. In the **Study** toolbar, click **Compute**.

RESULTS

Now, plot the total current density along with different contributions for different frequencies.

Effect of AC Frequency

1. In the **Home** toolbar, click **Add Plot Group** and choose **1D Plot Group**.
2. In the **Settings** window for **1D Plot Group**, type Effect of AC Frequency in the **Label** text field.
3. Locate the **Data** section. From the **Dataset** list, choose **Study : Frequency Effect/ Parametric Solutions 2 (sol11)**.
4. From the **Parameter selection (f)** list, choose **From list**.
5. In the **Parameter values (f (Hz))** list, select **60**.
6. Locate the **Title** section. From the **Title type** list, choose **Manual**.
7. In the **Title** text area, type Current Density Versus Time.
8. Locate the **Plot Settings** section.
9. Select the **y-axis label** check box. In the associated text field, type Current density (A/m²).

Point Graph: Anodic Current Density

1 In the **Effect of AC Frequency** toolbar, click **Point Graph**.

2 In the **Settings** window for **Point Graph**, type `Point Graph: Anodic Current Density` in the **Label** text field.

3 Select Boundary 1 only.

4 Click **Replace Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Component 1 (comp1)>Electroanalysis>Electrode kinetics>tcd.iloc_er1 - Local current density - A/m²**.

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
`Anodic Current Density`

8 Right-click **Point Graph: Anodic Current Density** and choose **Duplicate**.

Point Graph: Cathodic Current Density

1 In the **Model Builder** window, under **Results>Effect of AC Frequency** click **Point Graph: Anodic Current Density 1**.

2 In the **Settings** window for **Point Graph**, type `Point Graph: Cathodic Current Density` in the **Label** text field.

3 Locate the **y-Axis Data** section. In the **Expression** text field, type `tcd.iloc_er2+tcd.iloc_er3`.

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

Legends
`Cathodic Current Density`

5 Right-click **Point Graph: Cathodic Current Density** and choose **Duplicate**.

Point Graph: Double Layer Current Density

1 In the **Model Builder** window, click **Point Graph: Cathodic Current Density 1**.

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

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

4 In the **Label** text field, type `Point Graph: Double Layer Current Density`.

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

Legends
`Double Layer Current Density`

6 Right-click **Point Graph: Double Layer Current Density** and choose **Duplicate**.

Point Graph: Total Current Density

1 In the **Model Builder** window, click **Point Graph: Double Layer Current Density 1**.

2 In the **Settings** window for **Point Graph**, click **Replace Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Component 1 (comp1)> Electroanalysis>Electrode kinetics>tcd.itot - Total interface current density - A/m²**.

3 In the **Label** text field, type `Point Graph: Total Current Density`.

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

Legends
`Total Current Density`

Effect of AC Frequency

1 In the **Model Builder** window, click **Effect of AC Frequency**.

2 In the **Effect of AC Frequency** toolbar, click **Plot**.

The plot should look like Figure 3.

Now plot current density contributions at 0.01 Hz.

3 In the **Settings** window for **1D Plot Group**, locate the **Data** section.

4 In the **Parameter values (f (Hz))** list, select **0.01**.

5 In the **Effect of AC Frequency** toolbar, click **Plot**.

The plot should look like Figure 4.