

# INTRODUCTION TO Corrosion Module



# Introduction to the Corrosion Module

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# Contents

Introduction
The Applications
The Corrosion Module Physics Interfaces
Physics Interface Guide by Space Dimension and Study Type $\dots$ 13
Cathodic Protection of Steel in Reinforced Concrete17
Model Definition
Results and Discussion
Reference

# Introduction

The Corrosion Module is intended for the modeling and simulation of corrosion and corrosion protection of metal structures.

The module defines components in 1D, 2D, and 3D structures that describe the electrochemical reactions, corrosion reactions, and other surface reactions at the interface between a metal structure and a solution (acting as electrolyte). Also transport of ions and neutral species in the solution, including homogeneous reactions, and current conduction in the metal structure can be included in the models. The simulations can be used to understand and avoid corrosion as well as to design and optimize corrosion protection.

The descriptions in the module allow for the simulation of systems at different scales and at different levels of detail. For example, a model may include a set of geometrically complex structures such as oil rigs or other underwater structures with several hundred sacrificial anodes protecting the structure. Though the structures may be complex, the vigorous mixing in the sea allows for a simpler description of the electrolyte. At the other end of the spectrum, a crevice corrosion model might have a simple geometry, but it requires a more complex solution where all ions and neutral species in the electrolyte are taken into account, as well as including several competing reactions at the metal surface. In terms of size, geometric complexity, and complexity in the described phenomena, the Corrosion Module is able to handle these modeling extremes and anything in between.

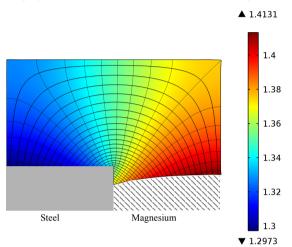
Although most of the tutorials in the Corrosion Module Application Library focus on corrosion phenomena in water (aqueous electrolytes), also other electrolyte systems can be modeled.

# The Applications

The modeling and simulation capabilities of the Corrosion Module cover processes such as galvanic, pitting, and crevice corrosion. The capabilities also include, for example, systems for cathodic protection, sacrificial anode protection, and anodic protection.

Figure 1 is a plot from a tutorial application, which is available in the module's application library. The plot shows the galvanic corrosion of magnesium in electronic contact with steel and an aqueous electrolyte in contact with both metal surfaces. The simulation accounts for the electrode kinetics for the anodic and cathodic reactions on both surfaces. The simulation predicts the change of the shape of the metal surface due to the dissolution of magnesium and dynamically deforms the geometry using moving boundaries. This type of simulation may be relevant in the automotive, shipping, oil and gas, and refinery industries, where

magnesium and aluminum are used together with steel to lower the weight of metal parts. It is then important to estimate life and to access risks that may arise when using different materials in electronic contact that may be subjected to water.



Electrolyte potential [V] and Streamlines of the current density vector

Figure 1: Galvanic corrosion of magnesium in electronic and electrolytic contact with steel. The initial shape of the magnesium and steel surface is planar.

Figure 2 shows the electrolyte potential on the surface of an oil rig steel structure immersed in seawater. The steel structure is protected by 40 sacrificial aluminum anodes. The simulation is able to predict whether all parts of the steel structure are well enough protected by the positioning of the sacrificial anodes. The positioning of the anodes in the model can be optimized to give the best possible protection before the structure and the anodes are deployed in the sea. In addition, the life of the sacrificial anodes can also be predicted for anodes at different positions. This model is also available in the Corrosion Module application library.

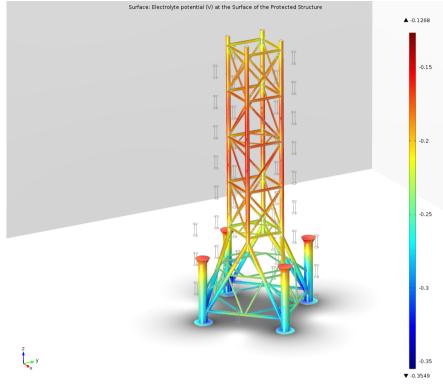


Figure 2: Electrolyte potential at the surface of an oil rig structure.

# The Corrosion Module Physics Interfaces

The module has a number of physics interfaces, which describe the transport and reaction of charged and neutral ions in aqueous electrolytes, surface reactions (electrochemical and chemical) and the formation of adsorbed species or coatings on metal surfaces. It also describes transport of current in electrolytes and metals, transport of current in thin metal structures (treated as shells), fluid flow, and heat transfer.

Figure 3 shows the available physics interfaces as displayed in the Model Wizard for a 3D model.

- 4 👬 Chemical Species Transport
  - 🚽 Transport of Diluted Species (tds)
  - 🛃 Chemistry (chem)
  - Nernst-Planck-Poisson Equations
  - 💀 Transport of Diluted Species in Porous Media (tds)
  - Electrophoretic Transport (el)
  - 🔺 鴍 Reacting Flow
    - 🐋 Laminar Flow, Diluted Species
    - Surface Reactions (sr)
  - 📑 Transport of Diluted Species in Fractures (dsf)
- 4 🔟 Electrochemistry
  - Primary and Secondary Current Distribution
    - 🔰 Primary Current Distribution (cd)
    - 📙 Secondary Current Distribution (cd)
    - 🖳 Current Distribution, Boundary Elements (cdbem)
    - Current Distribution, Shell (cdsh)
    - 🔁 Current Distribution, Pipe (cdpipe)
  - ▲ 🎼 Tertiary Current Distribution, Nernst-Planck
    - 🕌 Tertiary, Electroneutrality (tcd)
    - 🕼 Tertiary, Water-Based with Electroneutrality (tcd)
    - 🕌 Tertiary, Supporting Electrolyte (tcd)
    - 🙋 Electroanalysis (tcd)
    - Electrode, Shell (els)
  - 🔺 😋 Corrosion, Deformed Geometry
    - 😋 Corrosion, Primary
    - 🚽 Corrosion, Secondary
    - 🚔 Corrosion, Tertiary with Electroneutrality
    - 💐 Corrosion, Tertiary with Supporting Electrolyte
- 🔺 测 Fluid Flow
  - 🔺 📚 Single-Phase Flow
    - = Creeping Flow (spf)
    - 📚 Laminar Flow (spf)
  - 4 💽 Porous Media and Subsurface Flow
    - 🔞 Brinkman Equations (br)
    - 🗟 Darcy's Law (dl)
    - 🔚 Free and Porous Media Flow (fp)
  - 🔺 🛬 Nonisothermal Flow
    - 🛬 Laminar Flow
- 🔺 所 Heat Transfer
  - 间 Heat Transfer in Solids (ht)
  - ∣≋ Heat Transfer in Fluids (ht)
  - Heat Transfer in Solids and Fluids (ht)
  - 🔺 🚰 Conjugate Heat Transfer
    - ) 🔁 Laminar Flow
  - 🔺 利 Electromagnetic Heating
    - 혽 Joule Heating
    - 🐚 Heat Transfer in Porous Media (ht)



## THE CURRENT DISTRIBUTION INTERFACES

The Primary Current Distribution (1), Secondary Current Distribution (1), and Tertiary Current Distribution, Nernst Planck (1) interfaces are generic physics interfaces that can be used to model most kinds of electrochemical cells.

These interfaces include functionality to model the current distribution the electrolyte as well as the deposition/dissolution and thickness evolution of thin layers on the electrode surfaces. Note however that if the thickness change of the layers is of the same order of magnitude (or one order lower) compared to the geometrical details of the electrodes, then the one of the Corrosion Deformed Geometry ( ) interfaces may have to be used instead. (See next section).

The Primary Current Distribution  $(\square)$  interface assumes a perfectly mixed electrolyte and neglects the activation losses for the charge transfer reactions and should only be used for relatively fast kinetics, where the activation losses are substantially smaller than the ohmic losses. The assumption of a perfectly mixed electrolyte implies that the electrolyte conductivity is not affected by the magnitude of the currents.

In the Secondary Current Distribution (  $\Box$ ) interface the activation overpotential for the electrochemical reactions, is taken into account in the analysis.

The Primary and Secondary Current Distribution interfaces may be combined with a Chemical Species Transport interface (described below) in order to incorporate kinetics effects of active species in the electrolyte or adsorbed species on an electrode surface.

The Current Distribution, Boundary Elements ( $[\]$ ) interface can be used for solving primary and secondary current distribution problems on geometries based on edge (beam or wire) and surface elements. The interface uses a Boundary Element Method (BEM) formulation to solve for the charge transfer equation in an electrolyte of constant conductivity, where the electrodes are specified on boundaries or as tubes with a given radius around the edges. You typically use this interface in order to reduce the meshing and solver time for large geometries where a significant part of the geometry can be approximated as tubes along edges. The Current Distribution, Shell ( $[\]$ ) interface models ionic current conduction in the tangential direction on a boundary. The physics interface is suitable for modeling thin electrolytes where the potential variation in the normal direction is negligible, for instance in atmospheric corrosion problems. The physics interface is suitable for modeling corrosion phenomena in piping networks where the potential variation in the radial direction of the pipe is negligible.

The Current Distribution, Pipe ( ) interface models ionic current conduction in the tangential direction along an edge in 3D geometries. The physics interface is suitable for modeling corrosion phenomena in piping networks where the potential variation in the radial direction of the pipe is negligible.

The Tertiary Current Distribution, Nernst-Planck ( ) interface accounts for the transport of species through diffusion, migration, and convection and is therefore able to describe the effects of variations in composition on the corrosion process. The kinetics expressions for the electrochemical reactions account for both activation and concentration overpotential. The Electroneutrality and Water-based entries of the physics interface applies the equations of electroneutrality to the set of equations that describe the species and current balances. This also implies that all charged species in the electrolyte have to be defined in the simulations, except those species that are present at very low concentrations and can therefore be neglected in the balance of current.

## THE CORROSION, DEFORMED GEOMETRY INTERFACES

The Corrosion Deformed Geometry( $\searrow$ ) interfaces combine primary, secondary and tertiary current distributions described in the previous section with a Deformed Geometry interface to keep track of the geometrical changes caused by deposition or dissolution reactions on an electrode surface. See Figure 1 for an example. Note however that in the case where the thickness of the dissolving layer at the surface of the anode is negligible for the current distribution in the cell, a generic current distribution interface described in the previous section may also be used.

#### The Electroanalysis Interface

The Electroanalysis interface ( $[\colored]{2}$ ) models mass transport of diluted species in electrolytes using the diffusion-convection equation, solving for electroactive species concentrations. The physics interface is applicable for electrolyte solutions containing a large quantity of inert "supporting" electrolyte. Ohmic losses are assumed to be negligible. The physics interface includes tailor-made functionality for setting up cyclic voltammetry problems.

#### THE CHEMICAL SPECIES TRANSPORT INTERFACES

The Transport of Diluted Species interface (, ) is available under the Chemical Species Transport Branch. In combination with the Secondary Current Distribution interface (), this physics interface can be used to model systems with supporting electrolytes. In these systems, the ions that give the largest contribution to the conduction of current are assumed to be present in uniform concentrations. An example of the use of these physics interfaces is to keep track of the transport of dissolved oxygen in an electrolytic solution while assuming that the concentration of ions is constant over the electrolyte.

The Nernst-Planck-Poisson Equations  $({\bf N}^*)$  interface can be used for investigation of charge and ion distributions within the electrochemical double layer where

charge neutrality cannot be assumed. A requisite when using this interface is that the double layer, which typically is in the range of tens nanometers, is fully resolved in the mesh.

The Transport of Diluted Species in Porous Media interface ( ) is also available and describes species transport between the fluid, solid, and gas phases in saturated and variably saturated porous media. It applies to one or more species that move primarily within a fluid filling (saturated) or partially filling (unsaturated) the voids in a solid porous medium. The pore space not filled with fluid contains an immobile gas phase. Using these, models including a combination of porous media types can be studied. This is suitable for modeling of corrosion and corrosion protections of metal structures in soil or rock, for example in oil and gas and civil engineering applications.

The Electrophoretic Transport ( ) interface can be used to investigate the transport of weak acids, bases, and ampholytes in aqueous solvents. The physics interface is typically used to model various electrophoresis modes, such as zone electrophoresis, isothachophoresis, isoelectric focusing, and moving boundary electrophoresis, but is applicable to any aqueous system involving multiple acid-base equilibria.

The Surface Reactions interface (\*) can be used model reactions and translateral transport of surface (adsorbed) species.

The Chemistry interface (...) can be used to define systems of reacting species, electrode reactions and ordinary chemical reactions. As such, it serves as a reaction kinetics and material property provider to the space dependent transport interfaces, such as the Tertiary Current Distribution, Nernst-Planck interface, or Transport of Diluted Species interface.

## Porous Media Flow

The Fluid Flow interfaces ( $\gg$ ) can be combined with the Corrosion Module interfaces to model free and forced convection in corrosion and corrosion protection.

The Darcy's Law interface ( $\bigotimes$ ) is used to model fluid movement through interstices in a porous medium where a homogenization of the porous and fluid media into a single medium is done. Together with the continuity equation and equation of state for the pore fluid (or gas) this physics interface can be used to model low velocity flows, for which the pressure gradient is the major driving force. The penetration of air through a porous structure is a classic example for the use of Darcy's Law in corrosion and corrosion protection.

Darcy's law can be used in porous media where the fluid is mostly influenced by the frictional resistance within the pores. Its use is within very low flows, or media where the porosity is very small. Where the size of the interstices is larger, and the fluid is also influenced by itself, the gradients in fluid velocity, pressure, and gravity must be considered. This is done in the Brinkman Equations interface.

The Brinkman Equations interface ( **Constant**) is used to model compressible flow at speeds of less than Mach 0.3, but control over the density and any of the mass balances that are deployed must be maintained to help with this.

The Free and Porous Media Flow interface ( ) is useful for equipment that contain domains where free flow is connected to porous media, such as concrete structures immersed in water.

#### HEAT TRANSFER

The Heat Transfer interfaces (  $\iiint$ ) have ready-made formulations for the contribution of Joule heating, and other electrochemical losses, to the thermal balance in corrosion and corrosion protection.

The features of the various Heat Transfer interfaces include Heat Transfer in Fluids ( $j \approx$ ), Heat Transfer in Solids ( $j \approx$ ), and Heat Transfer in Porous Media ( $j \approx$ ), and account for conductive and convective heat transfer. These features interact seamlessly and can be used in combination in a single model.

The detailed equations and assumptions that are defined by the physics interfaces are formulated in the *Corrosion Module User's Guide* and the *COMSOL Multiphysics Reference Manual*.

#### MATHEMATICS - MOVING INTERFACE

The Level Set  $(\mathbb{N})$  interface can be used in problems including deforming electrodes, subject to topological changes.

# Physics Interface Guide by Space Dimension and Study Type

The table lists the physics interfaces available with this module in addition to those included with the COMSOL basic license.

PHYSICS INTERFACE	ICON	TAG	SPACE DIMENSION	AVAILABLE STUDY TYPE
🛟 Chemical Species Tr	anspor	t		
Surface Reactions	•	sr	all dimensions	stationary (3D, 2D, and 2D axisymmetric models only); time dependent

PHYSICS INTERFACE	ICON	TAG	space Dimension	AVAILABLE STUDY TYPE	
Transport of Diluted Species	;=*	tds	all dimensions	stationary; time dependent	
Transport of Diluted Species in Porous Media	<b>1</b>	tds	all dimensions	stationary; time dependent	
Transport of Diluted Species in Fractures	<b>7</b>	dsf	3D, 2D, 2D axisymmetric	stationary; time dependent	
Electrophoretic Transport		el	all dimensions	stationary; stationary with initialization; time dependent; time dependent with initialization	
Chemistry	<b>:</b> :-	chem	all dimensions	stationary; time dependent	
Nernst-Planck-Poisson Equations	;	tds+es	all dimensions	stationary; time dependent; stationary source sweep; small-signal analysis, frequency domain	
Reacting Flow					
Laminar Flow, Diluted Species	///		3D, 2D, 2D axisymmetric	stationary; time dependent	
Electrochemistry			·		
Primary Current Distribution	IJ	cd	all dimensions	stationary; stationary with initialization; time dependent; time dependent	
Secondary Current Distribution	<u>Г</u>			with initialization; AC impedance, initial values; AC impedance, stationary; AC impedance, time dependent	
Tertiary Current Distribution, Nernst-Planck (Electroneutrality, Water-Based with Electroneutrality, Supporting Electrolyte)	1 L	tcd	all dimensions	stationary; stationary with initialization; time dependent; time dependent with initialization; AC impedance, initial values; AC impedance, stationary; AC impedance, time dependent	

PHYSICS INTERFACE	ICON	TAG	SPACE DIMENSION	AVAILABLE STUDY TYPE	
Current Distribution, Boundary Element	□ <mark>+</mark>	cdbem	3D, 2D	stationary; stationary with initialization; time dependent; time dependent with initialization; AC impedance, initial values; AC impedance, stationary; AC impedance, time dependent	
Current Distribution, Shell	• 🗍 -	cdsh	3D, 2D, 2D axisymmetric	stationary; stationary with initialization; time dependent; time dependent with initialization; AC impedance, initial values; AC impedance, stationary; AC impedance, time dependent	
Current Distribution, Pipe		cdpipe	3D	stationary; stationary with initialization; time dependent; time dependent with initialization; AC impedance, initial values; AC impedance, stationary; AC impedance, time dependent	
Electroanalysis		tcd	all dimensions	stationary; time dependent; AC impedance, initial values; AC impedance, stationary; AC impedance, time dependent; cyclic voltammetry	
Electrode, Shell	¥\$	els	3D, 2D, 2D axisymmetric	stationary; time dependent	
Corrosion, Deformed Geometry					
Corrosion, Primary Corrosion, Secondary	1	cd + dg	all dimensions	stationary; stationary with initialization; time dependent; time dependent with initialization; AC impedance, initial values; AC impedance, stationary; AC impedance, time dependent	

PHYSICS INTERFACE	ICON	TAG	SPACE DIMENSION	AVAILABLE STUDY TYPE		
Corrosion, Tertiary with (Electroneutrality, Supporting Electrolyte)	1. J.	tcd + dg	all dimensions	stationary; stationary with initialization; time dependent; time dependent with initialization; AC impedance, initial values; AC impedance, stationary; AC impedance, time dependent		
Fluid Flow						
🐚 Porous Media and	l Subsu	Irface Flo	w			
Brinkman Equations	Ø	br	3D, 2D, 2D axisymmetric	stationary; time dependent		
Darcy's Law	\$	dl	all dimensions	stationary; time dependent		
Free and Porous Media Flow		fp	3D, 2D, 2D axisymmetric	stationary; time dependent		
∭ Heat Transfer						
Heat Transfer in Porous Media	<b>)</b>	ht	all dimensions	stationary; time dependent		
Moving Interface	Moving Interface					
Level Set	<u>}</u>	ls	all dimensions	time dependent with phase initialization		

# Cathodic Protection of Steel in Reinforced Concrete

Cathodic protection (CP) is a common strategy for retarding the corrosion of reinforcing steel in concrete structures, such as bridges and parking garages. By the use of CP the potential of the corroding surface is lowered, thereby decreasing the rate of undesired anodic corrosion reaction.

This example models the cathodic protection of a steel reinforcing bar (rebar) in concrete. The corrosion cell consists of a zinc anode, the concrete, acting as electrolyte, and the steel surface. Iron oxidation, water reduction (hydrogen evolution), and oxygen reduction are considered on the steel surface, whereas oxygen and charge transport are accounted for in the concrete electrolyte.

The anode and the steel surface are connected electrically via a potentiostat that controls the cell voltage.

Concrete is a porous material, and hence its transport properties for ions and gases vary with the moisture content. Therefore the electrolyte conductivity and oxygen diffusion coefficient are modeled to vary with the concrete pore saturation level using empirical data. The corrosion rate for various moisture contents is investigated in this model. The model example is based on a paper by Muehlenkamp and others. (Ref. 1).

# Model Definition

## GEOMETRY

Figure 4 shows the model geometry. The geometry represents a two dimensional cross section of a repeating unit cell in a larger structure where three symmetry planes (top, bottom, and right) have been used to reduce the model geometry.

The zinc anode has been coated onto the concrete by thermal spraying and is assumed to be permeable to air.

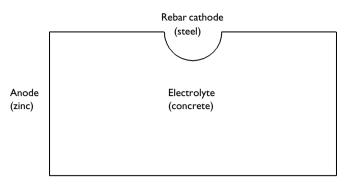


Figure 4: Model geometry. One electrolyte domain and two electrode surfaces.

#### CONCRETE DOMAIN EQUATIONS

A Secondary Current Distribution interface is used to model the electrochemical currents. The electrolyte conductivity depends on the pore saturation level according to Figure 5.

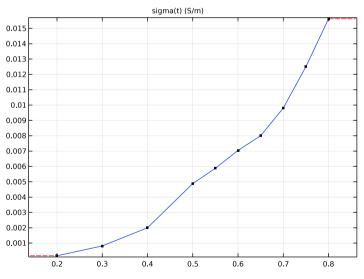


Figure 5: Electrolyte conductivity (S/m) as function of the concrete pore saturation level.

Oxygen transport in the concrete domain is modeled using the Transport of Diluted Species interface. The oxygen diffusivity depends on the pore saturation level according to Figure 6.

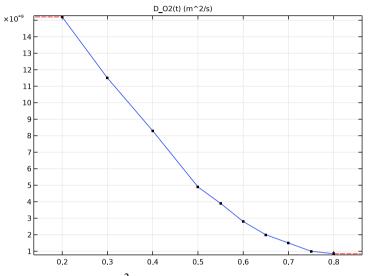


Figure 6: Oxygen diffusivity  $(m^2/s)$  in the concrete as function of pore saturation.

#### **BOUNDARY CONDITIONS**

Choose the electrical potential of the Zn anode as ground for the system. By assuming the kinetics of the Zn anode to be very fast, the polarization is neglected in the model and sets the electrolyte potential to

$$\phi_{\mathrm{l},\,\mathrm{Zn}}\,=\,-E_{\mathrm{eq},\,\mathrm{Zn}}+\phi_{s,\,\mathrm{Zn}}\,=\,-E_{\mathrm{eq},\,\mathrm{Zn}}$$

where  $E_{\rm eq,Zn}$  is an empirically measured equilibrium potential for the thermally sprayed zinc/concrete electrode. In this model  $E_{\rm eq,Zn}$  is set to -0.68 V.

The concentration of oxygen at the Zn anode is set to atmospheric conditions according to

$$c_{O_2, Zn} = c_{O_2, ref}$$

Three different electrode reactions are considered on the steel rebar boundary: iron oxidation, oxygen reduction, and hydrogen evolution:

$$Fe \rightarrow Fe^{2+} + 2e^{-1}$$

$$O_2 + 2H_2O + 4e^{-1} \rightarrow 4OH^{-1}$$

$$2H_2O + 2e^{-1} \rightarrow H_2 + 4OH^{-1}$$

The reaction kinetics for these reactions are modeled with an Electrode Surface node, on which the external electric potential of the steel bar,  $\phi_{s, \text{ steel}}$ , is set to the applied cell potential of -1 V.

The electrode kinetics of the steel bar reactions are described by Tafel expressions according to

$$i_{\text{Fe}} = i_{0, \text{Fe}} \times 10^{A_{\text{Fe}}\eta_{\text{Fe}}}$$
$$i_{\text{O}_2} = -\frac{c_{\text{O}_2}}{c_{\text{O}_2, \text{ref}}} i_{0, \text{O}_2} \times 10^{A_{\text{O}_2}\eta_{\text{O}_2}}$$
$$i_{\text{H}_2} = -i_{0, \text{H}_2} \times 10^{A_{\text{H}_2}\eta_{\text{H}_2}}$$

using the parameters shown in the table, where the overpotential for each reaction is calculated as

$$\eta = \phi_{s, \text{steel}} - \phi_l - E_{eq}$$

PARAMETER	UNIT	Fe	$O_2$	$H_2$
Equilibrium potential, $E_{ m eq}$	V	-0.76	0.189	-1.03
Exchange current density, $i_0$	A/m <sup>2</sup>	7.1·10 <sup>-5</sup>	7.7·10 <sup>-7</sup>	1.1·10 <sup>-2</sup>
Tafel slope, $A$	V/decade	0.41	-0.18	-0.15

The oxygen reduction reaction causes a flux of oxygen at the steel surface according to Faraday's law. The flux is set up using the stoichiometric coefficients entered in the Electrode Reaction node for the oxygen reduction reaction.

Symmetry conditions of the Insulation type apply on all other boundaries.

Atmospheric concentration is used as the initial value for the oxygen concentration variable.

#### Study

The model is solved using a parametric sweep over a stationary study step and solving for a range of pore saturation values from 0.2 to 0.8.

# Results and Discussion

Figure 7 shows the electrolyte potential for a pore saturation level of 0.8. The electrolyte potential is lower towards the back (the right side) of the rebar.

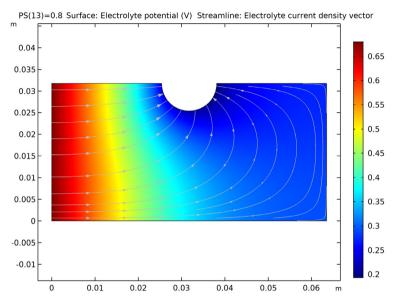


Figure 7: Electrolyte potential for a pore saturation (moisture) level of 0.8

Figure 8 on the next page shows the oxygen concentration in the electrolyte for a pore saturation level of 0.8. The concentration is very low close to the rebar, indicating that the oxygen reduction kinetics should be mass transport limited for this pore saturation level. The concentration is lower toward the back of the rebar.

An important factor for the corrosion rate of the rebar is the operating electrode potential, which is the difference between the electric potential (here the potential applied by the potentiostat) and the electrolyte potential. Figure 9 on the next page shows the operating electrode potential for various pore saturation levels for three different points (front, middle and back) of the rebar surface. The potential drops considerably at a pore saturation level of 0.65.

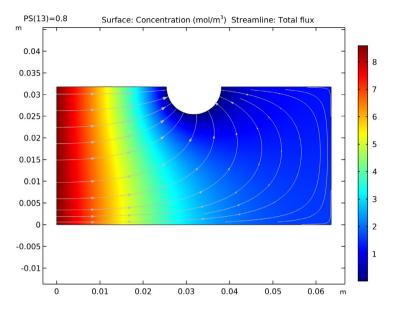


Figure 8: Oxygen concentration for a pore saturation (moisture) level of 0.8.

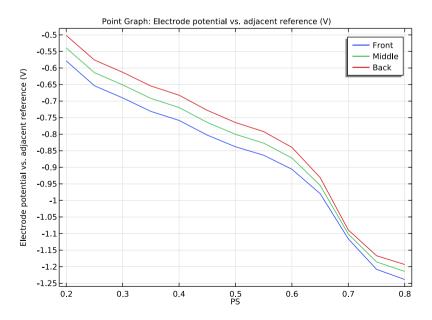


Figure 9: Operating electrode potential for three points at the rebar-concrete interface.

# 22 |

Figure 10 shows the local oxygen concentration at the rebar for various pore saturation levels. The concentration drops significantly towards higher saturation levels. This is an effect of the decreasing diffusivity of oxygen in the concrete for higher saturation levels.

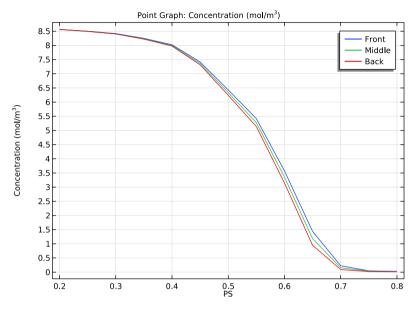


Figure 10: Local oxygen concentration at the rebar-concrete interface.

The local oxygen reduction current densities at the rebar are shown in Figure 11 on the next page. The magnitude of the reduction current is highest around a pore saturation level of 0.6–0.65. Up to this point the current densities are increasing due to increased electrolyte conductivity, but for higher pore saturation levels the current densities decrease due to decreased oxygen diffusivity.

The hydrogen evolution currents are shown in Figure 12 on the next page. Hydrogen evolution is very limited below a PS level of 0.65, which is the saturation level at which the electrode potential gets below the equilibrium potential (1.03 V) for the hydrogen evolution reaction, see Figure 9.

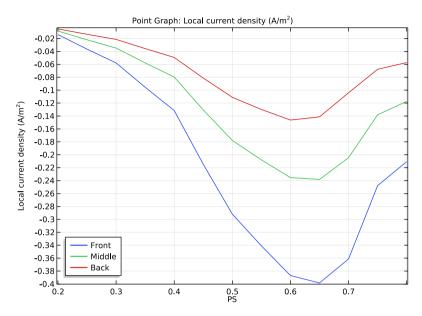


Figure 11: Local oxygen reduction current densities at the rebar-concrete interface.

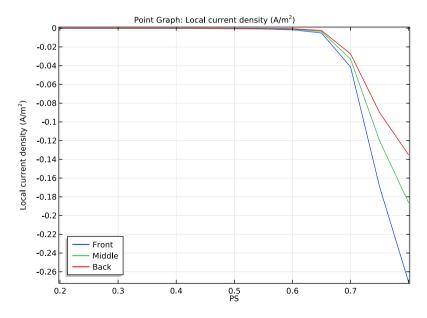


Figure 12: Local hydrogen evolution current densities at the rebar-concrete interface.

Finally, the iron oxidation currents are shown in Figure 13. Corrosion current densities are higher for low PS levels, which is in line with the higher electrode potential for low PS levels (Figure 9). In general, iron oxidation currents are low, indicating that the rebar is well protected.

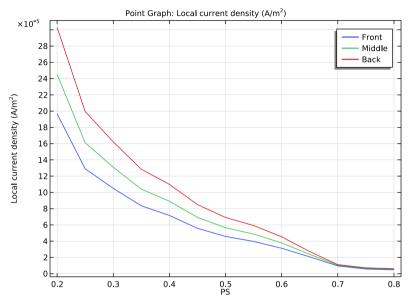


Figure 13: Iron corrosion current densities at the rebar-concrete interface.

## Reference

1. E.B. Muehlenkamp, M.D. Koretsky, and J.C. Westall, "Effect of Moisture on the Spatial Uniformity of Cathodic Protection of Steel in Reinforced Concrete", *Corrosion*, vol. 61, no 6. pp. 519–533, 2005.

# Model Wizard

**Note:** These instructions are for the user interface on Windows but apply, with minor differences, also to Linux and Mac.

I To start the software, double-click the COMSOL Multiphysics icon on the desktop. When the software opens, you can choose to use the Model Wizard to

create a new COMSOL Multiphysics model or Blank Model to create one manually. For this tutorial, click the Model Wizard button.

If COMSOL Multiphysics is already open, you can start the Model Wizard by selecting New 🗋 from the File menu and then click Model Wizard 🧟.

The Model Wizard guides you through the first steps of setting up a model. The next window lets you select the dimension of the modeling space.

- 2 In the Space Dimension window click the 2D button 🧠.

Select Physics	Review Physics Interface
Search	Tertiary Current Distribution, Nernst-Planck (tcd)
<ul> <li>C Recently Used</li> <li>AC/DC</li> <li>Acoustics</li> <li>Chemical Species Transport</li> <li>Electrochemistry</li> <li>Fertiary Current Distribution</li> <li>Tertiary, Current Distribution, Nemst-Planck</li> <li>Tertiary, Electroneutrality (tcd)</li> <li>Tertiary, Supporting Electrolyte (tcd)</li> <li>Electronelysis (elan)</li> <li>Electrode, Shell (els)</li> <li>Battery Interfaces</li> <li>Corrosion, Deformed Geometry</li> <li>Electroneutry</li> </ul>	Dependent Variables         Number of species:         1         Concentrations:         c         +         Electrolyte potential:         phil         Electric potential:         phis
Added physics interfaces:         Image: Contract of the second	

- 4 Click Add.
- 5 In the Number of Species text field, type 1.
- 6 In the Concentrations table, enter c.
- 7 Click Study 🚭 button.
- 8 In the tree under General Studies, click Stationary 🚬 .
- 9 Click Done 🗹.

# **Global Definitions**

Load the model parameters from a text file.

**Note:** The location of the files used in this exercise may vary based on the installation. For example, if the installation is on your hard drive, the file path might be similar to C:\Program Files\COMSOL55\applications\.

#### Parameters

I On the Home toolbar click Parameters  $\ P_i$  and select Parameters 1  $\ P_i$  .

**Note:** On Linux and Mac, the Home toolbar refers to the specific set of controls near the top of the Desktop.

- 2 In the Settings window for Parameters click the Load from File button 📂.
- 3 Browse to the application library folder, Corrosion Module>Cathodic Protection, and double-click the file cathodic\_protection\_in\_concrete\_parameters.txt.

The figure shows what the parameter list should look like after loading the text file. The parameter list can be edited manually and you can also store the parameter list as a text files to reuse it in another model. (To create your own text file, click the Save to File button  $\Box$ .)

abel: Par	ameters 1		
• Parame			
<ul> <li>Parame</li> </ul>	lers		
** Name	Expression	Value	Description
A_Fe	0.41[V]	0.41 V	Tafel slope iron oxidation
A_H2	-0.15[V]	-0.15 V	Tafel slope hydrogen evolution
A_02	-0.18[V]	-0.18 V	Tafel slope oxygen reduction
C_O2_ref	8.6[mol/m^3]	8.6 mol/m <sup>3</sup>	Oxygen reference concentration
Eeq_Fe	-0.76[V]	-0.76 V	Iron oxidation equilibrium potential
Eeq_H2	-1.03[V]	-1.03 V	Hydrogen evolution equilibrium potential
Eeq_O2	0.189[V]	0.189 V	Oxygen reduction equilibrium potential
i0_Fe	7.1e-5[A/m^2]	7.1E-5 A/m <sup>2</sup>	Iron oxidation exchange current density
i0_H2	1.1e-2[A/m^2]	0.011 A/m <sup>2</sup>	Hydrogen evolution current density
i0_02	7.7e-7[A/m^2]	7.7E-7 A/m <sup>2</sup>	Oxygen reduction exchange current density
Eeq_Zn	-0.68[V]	-0.68 V	Zn equilibrium potential
L	3.175e-2[m]	0.03175 m	Concrete section length
R_rebar	0.635e-2[m]	0.00635 m	Reinforcing bar radius
S	2.54e-2[m]	0.0254 m	Concrete thickness
W	6.35e-2[m]	0.0635 m	Width of concrete section
PS	0.6	0.6	Pore saturation
E_app	-1[V]	-1 V	Applied cell potential

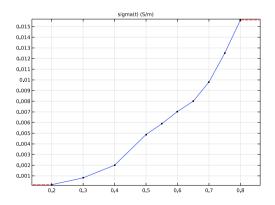
## Definitions

Create interpolation functions for the electrolyte conductivity and oxygen diffusivity as functions of the pore saturation level. Load the data from text files.

Interpolation 1

- I On the Home toolbar click Functions f(x) and choose Interpolation  $\frac{1}{\sqrt{2}}$ .
- 2 In the Model Builder under Definitions, click Interpolation 1 🔬.
- 3 In the Settings window for Interpolation, locate the Definition section and choose File from the Data source list.
- 4 Click Browse and go to the application library folder, Corrosion Module>Cathodic Protection . Double-click the file cathodic\_protection\_in\_concrete\_ sigma.txt.
- 5 Click Import.
- 6 In the Settings window for Interpolation in the Function name text field, enter sigma (replace the default).
- 7 Locate the Units section. In the Function text field, enter S/m.
- 8 Click the Plot button 💿 .

The plot should match this figure:



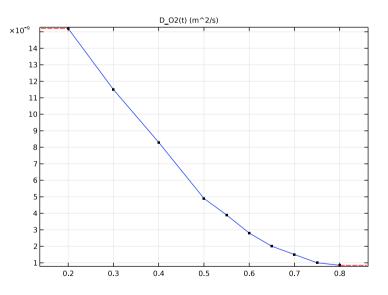
Interpolation 💿 Plot 🛛 Greate P	llot
Label: Interpolation	1
<ul> <li>Definition</li> </ul>	
Data source:	Local table 🔹
Function name:	sigma
* t	f(t)
0.2	0.000175
0.3	0.000815
0.4	0.002
0.5	0.004878
0.55	0.005882
0.6	0.007042
0.65	0.008
0.7	0.009804
0.75	0.0125
0.8	0.015625

#### Interpolation 2

Create a second interpolation function in the same way.

- I On the Home toolbar click Functions f(x) and choose Local Interpolation 🔬.
- **2** In the Model Builder click Interpolation 2 📩.
- **3** In the Settings window for Interpolation locate the Definition section and choose File from the Data source list.
- 4 Click Browse and go to the application library folder, Corrosion Module>Cathodic Protection. Double-click the file cathodic protection in concrete D 02.txt.
- 5 Click Import.
- 6 In the Settings window for Interpolation in the Function name text field, enter D\_02.
- 7 Locate the Units section. In the Function text field, enter m^2/s.
- 8 Click the Plot button 💿 .

The plot should match this figure:



# Geometry I

Now create the geometry by using a rectangle and a circle.

#### Rectangle I

- In the Model Builder right-click Geometry 1  $\land$  and choose Rectangle  $\square$ .
- 2 In the Settings window for Rectangle under Size:
  - In the Width text field, enter W.
  - In the Height text field, enter L.
- 3 Click the Build Selected button and, if required, on the Graphics toolbar the Zoom Extents button .

Settings Rectangle Build Selected  Build All Objects	* #
Label: Rectangle 1	Ē
<ul> <li>Object Type</li> </ul>	
Type: Solid	•
▼ Size and Shape	
Width: W	m
Height: L	m

#### Circle 1

- In the Model Builder right-click Geometry 1  $\land$  and choose Circle  $\bigcirc$ .
  - In the Settings window for Circle, under Size and Shape, enter R\_rebar in the Radius text field.
- 2 Under Position:
  - In the x text field, enter S+R\_rebar.
  - In the y text field, enter L.
- 3 Click the Build Selected button 🖷 .

Settings Circle Build Selec	ted 🔻 📒 Build All Objects 🎴	* #
Label: Circle	1	E
<ul> <li>Object Ty</li> </ul>	pe	
Type: Solid		•
▼ Size and S	Shape	
Radius:	R_rebar	m
Sector angle:	360	deg
<ul> <li>Position</li> </ul>		
Base: Cente	er 🔻	
x: S+R_re	bar	m
y: L		m

#### Difference 1

- I In the Model Builder, right-click Geometry 1 ≯ and choose Booleans and Partitions>Difference .
- 2 Select the object r1 (the rectangle). In the Graphics window, click r1 and Add + to add it to the Objects to add list in the Settings window for Difference.
- 3 In the Settings window for Difference locate the Difference section.
- 4 Under Objects to subtract, click the Active button.
- 5 Select the object cl only (the circle) using the same method as described for the rectangle.
- 6 Click the Build All button 📑 . The geometry should match Figure 4.

Settings	* #
Difference Build Selected 🔻 🟢 Build All Obj	ects 📳
Label: Difference 1	Ę
<ul> <li>Difference</li> </ul>	
Objects to add:	
r1	Ēa +
Active	•‡• 🕅
\$	
Objects to subtract:	
Active	¢⊕• (
Keep input objects	

# Tertiary Current Distribution, Nernst-Planck (TCD)

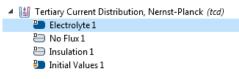
Now set up the physics interface for the tertiary current distribution. Start with the domain transport properties.

Electrolyte I

- I In the Model Builder window, under Component 1 (comp1)>Tertiary Current Distribution, Nernst-Planck (tcd) click Electrolyte 1.
- 2 In the Settings window for Electrolyte, locate the Diffusion section. In the  $D_c$  text field, type D\_02(PS).

<b>-</b> [	Diffusion	
Mate	erial:	
No	one	•
Diffu	ision coefficient:	
Dc	User defined	•
	D_O2(PS)	m²/s
	Isotropic	•

3 In the Model Builder window, click Electrolyte 1.



- I In the Settings window for Electrolyte, locate the Electrolyte Current Conduction section.
- 2 From the  $\sigma_l$  list, choose User defined. In the associated text field, type sigma(PS).

**Note:** The argument PS to the function sigma is the pore saturation parameter defined in the Parameter list in Global Definitions.

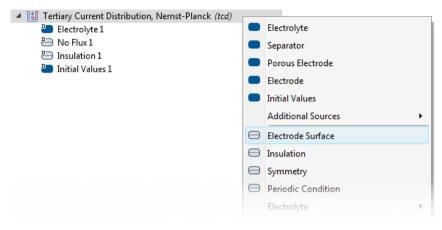
•	Electrolyte Current Conduction	
Elec	ctrolyte conductivity:	
$\sigma_{\rm I}$	User defined	•
	sigma(PS)	S/m
	Isotropic	•

Initial Values 1

- In the Model Builder window, under Component 1 (comp1)>Tertiary Current Distribution, Nernst-Planck (tcd) click Initial Values 1.
- 2 In the Settings window for Initial Values, locate the Initial Values section.
- **3** In the *c* text field, type C\_O2\_ref.

#### Electrode Surface I

I In the Model Builder window, right-click Tertiary Current Distribution, Nernst-Planck (tcd) and choose Electrode Surface.



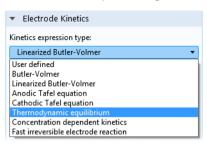
**2** Select Boundary 1 only (the left boundary of the geometry).

#### Electrolyte Reaction I (Zinc oxidation)

Assuming the fast reaction kinetics, a constant potential is set at the anode surface by prescribing an equilibrium potential and using a Primary Condition (Thermodynamic Equilibrium) type of electrode kinetics at the Electrode Reaction child node.

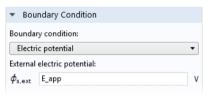
- In the Model Builder window, expand the Electrode Surface 1 node.
- 2 Right-click Electrode Reaction 1 and choose Rename.
- **3** In the Rename Electrode Reaction dialog box, type Zinc oxidation in the New label text field.
- 4 Click OK.
- **5** In the Settings window for Electrode Reaction, locate the Equilibrium Potential section.
- 6 In the  $E_{eq}$  text field, type Eeq\_Zn.

**7** Locate the Electrode Kinetics section. From the Kinetics expression type list, choose Thermodynamic equilibrium.



## Electrode Surface 2

- I On the Physics toolbar click Boundaries  $\bigoplus$  and choose Electrode Surface  $\bigoplus$ .
- **3** Select Boundaries 6 and 7 only (the left and right edges of the rebar).
- **4** In the Settings window for Electrode Surface, locate the Boundary Condition section.



**5** In the  $\phi_{s,ext}$  text field, enter E\_app.

#### Electrode Reaction I (Oxygen reduction)

Three different reactions occur at this electrode surface: oxygen reduction, iron oxidation and hydrogen evolution.

- I In the Model Builder expand the Electrode Surface 2 node and click Electrode Reaction 1.
- 2 Press F2 on the keyboard to rename the node (or right-click the node and choose Rename). Enter Oxygen reduction as the new name.
- Electrode Surface 1
   Electrode Surface 2
   Electrode Reaction 1
- **3** In the Settings window for Electrode Reaction (for the newly named Oxygen reduction node), locate the Stoichiometric Coefficients section.
  - Enter 4 in the Number of participating electrons field.
  - Enter -1 in the Stoichiometric coefficients field.

- 4 In the Settings window for Electrode Reaction, locate the Equilibrium Potential section. In the Equilibrium potential  $E_{eq}$  text field, enter Eeq\_02.
- 5 Under Electrode Kinetics from the Kinetics expression type list, choose Cathodic Tafel equation.
  - In the Exchange current density i<sub>0</sub> text field, enter c/C\_02\_ref\*i0\_02. The exchange current density thus depends on the oxygen concentration.
  - In the Cathodic Tafel slope (<0) A<sub>c</sub> text field, enter A\_02.

•	Electrode Kinetics	
Kine	tics expression type:	
C	athodic Tafel equation	•
Excł	nange current density:	
i <sub>o</sub>	c/C_02_ref*i0_02	A/m²
Cathodic Tafel slope (<0):		
$A_{\rm c}$	A_02	V
iloc	$=-i_0 \times 10^{\eta/A_c}$	
	Limiting current density	

Next add, rename, and define two more Electrode Reaction nodes.

Electrode Reaction 2 (Iron oxidation)

- 2 Press F2 to rename Electrode Reaction 2 to Iron oxidation. Click OK.
- 3 In the Settings window for Electrode Reaction under Equilibrium Potential, enter  $Eeq_Fe$  in the Equilibrium potential  $E_{eq}$  text field.
- 4 Under Electrode Kinetics from the Kinetics expression type list, choose Anodic Tafel equation.
  - In the Exchange current density i<sub>0</sub> text field, enter i0\_Fe.
  - In the Anodic Tafel slope (>0)  $A_{\rm a}$  text field, enter A\_Fe.

•	Electrode Kinetics			
Kine	tics expression type:			
A	nodic Tafel equation	•		
Exch	nange current density:			
i <sub>o</sub>	i0_Fe	A/m²		
Ano	Anodic Tafel slope (>0):			
Aa	A_Fe	V		
iloc	$=i_0 \times 10^{\eta/A_a}$			
	Limiting current density			

## Electrode Reaction 3 (Hydrogen

#### evolution)

- I In the Model Builder window, under Component 1 (comp1)>Tertiary Current Distribution, Nernst-Planck (tcd) right-click Electrode Surface 2 and choose Electrode Reaction.
- 2 Press F2 to rename Electrode Reaction 3 to Hydrogen evolution. Click OK.

- 3 In the Settings window for Electrode Reaction under Equilibrium Potential, enter  $Eeq_H2$  in the Equilibrium potential  $E_{eq}$  text field.
- 4 Under Electrode Kinetics from the Kinetics expression type list, choose Cathodic Tafel equation.

₹ E¢	quilibrium Potential			
Equili	brium potential:			
$E_{eq}$	User defined			
	Eeq_H2	v		

- In the Exchange current density *i*<sub>0</sub> text field, enter i0\_H2.
- In the Cathodic Tafel slope  $(<0)A_{c}$  text field, enter A\_H2.

The concrete is in contact with air at the left, and the concentration is therefore constant at this boundary.

Concentration 1

- I In the Model Builder window, right-click Tertiary Current Distribution, Nernst-Planck (tcd) and choose Electrolyte>Concentration.
- 2 Select Boundary 1 only.
- 3 In the Settings window for Concentration, locate the Concentration section.
- **4** Select the Species c check box.
- 5 In the *c*0, c text field, type C\_O2\_ref.

#### Mesh I

Use the physics-controlled mesh settings with an extra fine mesh size.

- In the Model Builder click Mesh 1  $\triangle$ .
- 2 In the Settings window for Mesh from the Element size list, choose Extra fine.

#### Study |

The problem is now ready for solving. Use an auxiliary sweep to solve for a range of different pore saturation values.

Set up the Stationary study step and Compute

In the Model Builder under Study 1, click Step 1: Stationary 🗁 .

- 2 In the Settings window for Stationary click to expand the Study Extensions section. Click to select the Auxiliary sweep check box.
- 3 Click the Add button + to choose PS (Pore saturation) as the Auxiliary parameter.
- 4 Enter range(0.2, 0.05, 0.8) in the Parameter value list column. This will

weep type:	Specified co	ombinations 🔻
** Parameter	Parameter value list	Parameter ur
PS (Por ▼	range(0.2, 0.05, 0.8)	

compute solutions for pore saturation values from 0.2 to 0.8, with a step length of 0.05.

**5** On the Home toolbar click Compute **=** (or click Study 1 and press F8).

# Results

The model is now solved and default plots are added. Follow the remaining steps below to reproduce the plots from the Results and Discussion section.

ID Plot Group 6 (Rebar Electrode-Electrolyte Potential)

I On the Home toolbar click Add Plot Group  $\[mathbb{m}]$  and choose 1D Plot Group  $\[mathcal{m}]$  .

2 On the 1D Plot Group 6 toolbar click Point Graph  $\succeq$ .

	File 🔻	Home	Definitions	Geometry	Materials	Physics	Mesh	Study	
	€		🔁 Line Graph	🄃 Table Graph	🐺 Annotatio	on or	Ol	or Expressio	
			🔁 Point Graph	լ <mark>լլլ</mark> Histogram		$\sim$		er -	
Plot	Plot In ∙	🕞 Global	📉 Mesh		More Plots •	Exp	ort Expressi		
	PI	ot		Add Plot					

- **3** In the Model Builder click Point Graph 1 📐.
- 4 Select Points 3, 4, and 5 only. These points are on the edge of the rebar.
- 5 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 Model>Component 1> Tertiary Current Distribution, Nernst-Planck>tcd.Evsref Electrode potential vs adjacent reference.
- 6 Click to expand the Legends section. Select the Show legends check box.

7 From the Legends list choose Manual. In each row of the table, enter Front, Middle, and Back as in the figure.

<ul> <li>Legend</li> </ul>	ls			
✓ Show legends				
Legends: [	Manual 👻			
** Legends	5			
Front				
Middle				
Back				
=				

- 8 In the Model Builder click the 1D Plot Group 6  $\sim$  node. Press F2 and rename the node Rebar potential.
- 9 Click the Plot button 🗟 . Your plot should look like the one in Figure 9.

Next, add four more 1D Plot Groups. Except for the Expression selected or entered, the plots are similar. Duplicating the already created nodes reduces the number of required steps.

- ID Plot Group 7(Oxygen Concentration)
- I Right-click Rebar potential  $\sim$  (the third plot group node) and choose Duplicate  $\square$ .
- 2 Click Rebar potential 1  $\sim$  and press F2.
- **3** Go to the Rename 1D Plot Group dialog box and type **Oxygen** concentration in the New name text field. Click OK.
- 4 In the Model Builder expand the Results>Oxygen concentration node then click Point Graph 1 ∼.
- 5 In the Settings window for Point Graph click Replace Expression ↓ (it is in the upper-right corner of the y-axis data section). Choose Model>Component l>Tertiary Current Distribution, Nernst-Planck>c -Concentration.
- 6 Click the Plot button 🗃 . Your plot should look like the one in Figure 10.
- ID Plot Group 8 (Oxygen Reduction Current Density)
- In the Model Builder right-click Oxygen concentration  $\sim$  and choose Duplicate  $\square$ .
- 2 Click Oxygen concentration 1  $\sim$  and press F2.
- **3** Go to the Rename 1D Plot Group dialog box and type **Oxygen Reduction** Current Density in the New name text field and click OK.

4 In the Model Builder expand the Results>Oxygen reduction currents node then click Point Graph 1 ∼.

4	🔎 Re	sults
	Þ 🎆	Data Sets
	8.85 6-12	Derived Values
		Tables
	$\triangleright$	Electrolyte Potential (tcd)
	$\triangleright$	Electrolyte Current Density (tcd)
	$\triangleright$	Electrode Potential vs Ground (tcd)
	$\triangleright$	Electrode Potential vs Adjacent Reference (tcd)
	$\triangleright$	Concentration (tcd)
	$ ightarrow \sim$	Rebar Potential
	$ ightarrow \sim$	Oxygen Concentration
	$\square \sim$	Oxygen Reduction Current Density
		🔁 Point Graph 1

- In the Settings window of the y-axis data section click Replace Expression and choose Model>Component 1>Tertiary Current Distribution, Nernst-Planck>Electrode kinetics>tcd.iloc\_er1 - Local current density.
- 6 Click the Plot button on to update the plot in the Graphics window. Your plot should look like the one in Figure 11.
- ID Plot Group 9 (Iron Oxidation Current Density)
- In the Model Builder right-click Oxygen Reduction Current Density  $\sim$  and choose Duplicate  $\blacksquare$ .
- 2 Click Oxygen Reduction Current Density 1  $\sim$  and press F2
- **3** Go to the Rename 1D Plot Group dialog box and type Iron Oxidation Current Density in the New name text field. Click OK.
- 4 In the Model Builder expand the Results>Iron Oxidation Current Density node, then click Point Graph 1 ≥.
- 5 In the Settings window of the y-axis section click Replace Expression ↓ and choose Model>Component 1>Tertiary Current Distribution, Nernst-Planck>Electrode kinetics>tcd.iloc\_er2 - Local current density.

▼ y-Axis Data	₽.	4	•
Expression:			
comp1.tcd.iloc_er2			
Unit:			
A/m^2			v
Description:			
Local current density			

- 6 Click the Plot button 📷 to update the plot in the Graphics window. Your plot should look like the one in Figure 13.
- ID Plot Group 10 (Hydrogen Evolution Current Density)
- In the Model Builder right-click Iron Oxidation Current Density  $\sim$  and choose Duplicate  $\blacksquare$ .
- 2 Click Iron Oxidation Current Density 1  $\sim$  and press F2.
- **3** Go to the Rename 1D Plot Group dialog box and type Hydrogen Evolution Current Density in the New name text field. Click OK.
- 4 In the Model Builder expand the Results>Hydrogen Evolution Current Density node, then click Point Graph 1 <sup>1</sup>√.
- 5 In the Settings window of the y-axis section click Replace Expression ↓ and choose Model>Component 1>Tertiary Current Distribution, Nernst-Planck>Electrode kinetics>tcd.iloc\_er3 - Local current density from the menu.
- 6 Click the Plot button 📷 to update the plot in the Graphics window. Your plot should look like the one in Figure 12.

The final set of plots under Results should match the following figure.

- Results
   Data Sets
   Derived Values
   Tables
   Electrolyte Potential (tcd)
   Electrolyte Current Density (tcd)
   Electrode Potential vs Ground (tcd)
   Electrode Potential vs Adjacent Reference (tcd)
   Concentration (tcd)
   Concentration
   Oxygen Concentration
   Oxygen Reduction Current Density
   Iron Oxidation Current Density
  - $ho \sim$  Hydrogen Evolution Current Density