Vanadium Redox Flow Battery

Introduction

Redox flow batteries store the energy in the liquid electrolytes, pumped through the cell and stored in external tanks, rather than in the porous electrodes as for conventional batteries. This approach offers interesting solutions for low cost energy storage, load leveling and power peak shaving.

The vanadium redox flow battery uses two different electrolyte solutions, one for the negative side of the cell and another for the positive side. The two solutions are kept separated in the cell by the use of an ion-exchange membrane that only allows for transport of protons between the two cell compartments.

This example demonstrates how to build a model consisting of two different cell compartments, with different ion compositions and electrode reactions, separated by an ion-exchange membrane. It is a simplified version of a model made by Knehr and others (Ref. 1).

See also the Soluble Lead-Acid Redox Flow Battery model example for how to make a transient flow battery model by coupling the cell model to mass balances for the external storage tanks.

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Model Definition

The cell geometry is shown in Figure 1. The model contains three domains, a negative porous electrode (4 mm thick), an ion-exchange membrane (203 μm thick) and a positive porous electrode (4 mm thick). The cell is 35 mm high.

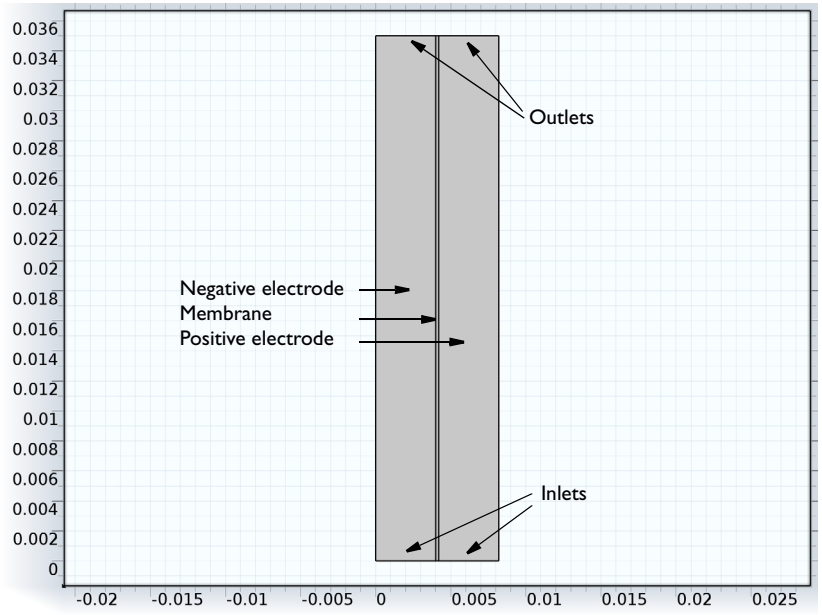

Figure 1: Model geometry. Three domains: negative electrode, membrane, positive electrode.

Each side of the cell is fed with an electrolyte containing sulfuric acid and a vanadium redox couple (see below), flowing through the porous electrodes. The liquid enters the cell from bottom at a constant velocity in the y-direction, corresponding to a flow rate of 30 ml/min at cell depth of 28.5 mm.

The left electrode is grounded, and the current leaves the cell over the right-most boundary at an average current density of 100 mA/cm^2.

The models solves for a stationary case with a given set of inlet concentrations.

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LIQUID ELECTROLYTE SPECIES AND ELECTRODE REACTIONS

The negative electrolyte contains the following ions:

- H^+
- HSO_4^-
- SO_4^{2-}
- V^{3+}
- V^{2+}

The negative electrode reaction is:

$$V^{3+} + e^- = V^{2+}$$

The equilibrium potential for this reaction is calculated using Nernst equation according to

$$E_{\text{eq, neg}} = E_{0,\text{ neg}} + \frac{RT}{F}\ln\left(\frac{a_{V^{3+}}}{a_{V^{2+}}}\right)$$

where $E_{0,\text{ neg}}$ is the reference potential for the electrode reaction (V), a_i is the chemical activity of species i (1), R is the molar gas constant (8.31 J/(mol·K)), T is the cell temperature (K), and F is Faraday's constant (96,485 s·A/mol).

A Butler-Volmer type of kinetics expression is used for the negative electrode reaction according to:

$$i_{\text{neg}} = Ai_{0,\text{ neg}}\left(\exp\left(\left(\frac{(1-\alpha_{\text{neg}})F\eta_{\text{neg}}}{RT}\right) - \exp\left(\frac{-\alpha_{\text{neg}}F\eta_{\text{neg}}}{RT}\right)\right)\right)$$

$$i_{0,\text{ neg}} = Fk_{\text{neg}}(a_{V^{2+}})^{1-\alpha_{\text{neg}}}(a_{V^{3+}})^{\alpha_{\text{neg}}}$$

where A is the specific surface area (m^3/m^2) of the porous electrode, α_{neg} the transfer coefficient (1), k_{neg} the rate constant.

The overpotential, η_{neg} (V), is defined as

$$\eta = \phi_s - \phi_l - E_{\text{eq}}$$

where ϕ_s is the electric potential of the solid phase of the electrode (V) and ϕ_l the electrolyte potential (V).

The positive electrolyte contains the following ions:

- H^+
- HSO_4^-
- SO_4^{2-}
- VO^{2+}
- VO_2^+

The positive electrode reaction is:

$$VO_2^+ + e^- + 2H^+ = VO^{2+} + H_2O$$

with the equilibrium potential calculated according to:

$$E_{\text{eq, pos}} = E_{0,\text{ pos}} + \frac{RT}{F}\ln\left(\frac{a_{VO_2^+}(a_{H^+})^2}{a_{VO^{2+}}}\right)$$

$$i_{\text{pos}} = Ai_{0,\text{ pos}}\left(\exp\left(\left(\frac{(1-\alpha_{\text{pos}})F\eta_{\text{pos}}}{RT}\right) - \exp\left(\frac{-\alpha_{\text{pos}}F\eta_{\text{pos}}}{RT}\right)\right)\right)$$

$$i_{0,\text{ pos}} = Fk_{\text{pos}}(a_{VO^{2+}})^{1-\alpha_{\text{pos}}}(a_{VO_2^+})^{\alpha_{\text{pos}}}$$

SULFURIC ACID DISSOCIATION

The first dissociation step of sulfuric acid is assumed to be complete

$$H_2SO_4 \rightarrow H^+ + HSO_4^-$$

whereas the second step

$$HSO_4^- \rightarrow H^+ + SO_4^{2-}$$

is described using a dissociation source term, r_d:

$$r_d = k_d\left(\frac{a_{H^+}a_{HSO_4^-}}{a_{H^+} + a_{HSO_4^-}} - \beta\right)$$

where k_d is a rate parameter, and β the degree of dissociation.

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CHOICE OF CURRENT DISTRIBUTION INTERFACE

In this model we will make use of the Nernst-Planck equations for ion flux and charge transport by which the following equation describes the molar flux of species i, $\mathbf{N}_i$, due to diffusion, migration and convection:

$$\mathbf{N}_i = -D_i\nabla c_i - z_i u_{\text{mob},i} F c_i \nabla\phi_l + c_i\mathbf{u}$$

The first term is the diffusion flux, D_i is the diffusion coefficient (m^2/s). The migration term consists of the species charge number z_i, the species mobility $u_{\text{mob},i}$ ($\text{s}\cdot\text{mol}/\text{kg}$) and the electrolyte potential (ϕ_l). In the convection term, $\mathbf{u}$ denotes the fluid velocity vector (m/s).

The electrolyte current density is calculated using Faraday's law by summing up the contributions from the molar fluxes, multiplied by the species charges, with the observation that the convective term vanishes due to the electroneutrality condition (see the Theory for the Tertiary Current Distribution, Nernst-Plank interface):

$$\mathbf{i}_l = F\sum_{i=1}^{n} z_i(-D_i\nabla c_i - z_i u_{\text{m},i} F c_i \nabla\phi_l) \quad (1)$$

The conservation of charge is then used to calculate the electrolyte potential.

$$\nabla\cdot\mathbf{i}_l = F\sum_{i=1}^{n} z_i R_i$$

where the R_i terms are the reaction sources due the porous electrode reactions.

This model uses Equation 1 when solving for the electrolyte potential in the porous electrodes through the Tertiary Current Distribution, Nernst-Planck interface.

In the negative and positive porous electrode domains, where there is free electrolyte present, the concentrations for all the ions are of the same order of magnitude, and the gradients of c_i are not negligible. The membrane, however, consists of a polymer electrolyte, where all the negative ions are fixed in the polymer matrix, implying that the concentration is constant, and the only positive ion present is H^+. Therefore, due to electroneutrality, Equation 1 reduces to

$$\mathbf{i}_l = -u_{\text{m},+} F^2 c_+ \nabla\phi_l = -\sigma_l\nabla\phi_l \quad (2)$$

in the membrane, where σ_l is the electrolyte conductivity. Equation 2 is the equation used in the Secondary Current Distribution interface.

Note that Equation 2 only concerns the governing equation for the electrolyte potential in the membrane. Transport of additional trace species in the membrane, with minor impact on the total charge transport, can be added to the model using the Transport of Diluted Species interface.

MEMBRANE—FREE ELECTROLYTE BOUNDARY CONDITIONS

Set up the boundary conditions at the boundaries between the Secondary Current Distribution interface for the membrane and the Tertiary Current Distribution, Nernst-Planck interfaces in the following way:

First, in the Tertiary Current Distribution, Nernst-Planck interfaces, set the normal electrolyte current density to be equal to the current density in the membrane:

$$\mathbf{n} \cdot \mathbf{i}_{l,e} = \mathbf{n} \cdot \mathbf{i}_{l,m}$$

Also set the proton flux to be proportional to the current, according to Faraday's law

$$\mathbf{n} \cdot \mathbf{N}_{+,e} = \mathbf{n} \cdot \frac{\mathbf{i}_{l,m}}{F}$$

On the membrane side, use electrolyte potential constraints in the Secondary Current Distribution interface according to:

$$\phi_{l,m} = \phi_{l,e} + \frac{RT}{F} \ln\left(\frac{a_{+,m}}{a_{+,e}}\right) \tag{3}$$

where $a_{+,m}$ is the hydrogen activity in the membrane. This potential shift caused by Equation 3 is called a Donnan potential.

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Results and Discussion

Figure 2 shows the concentration of the V^{3+} and the VO^{2+} ions in the cell. The ion concentration for these species is higher towards the current collectors and towards the outlets.

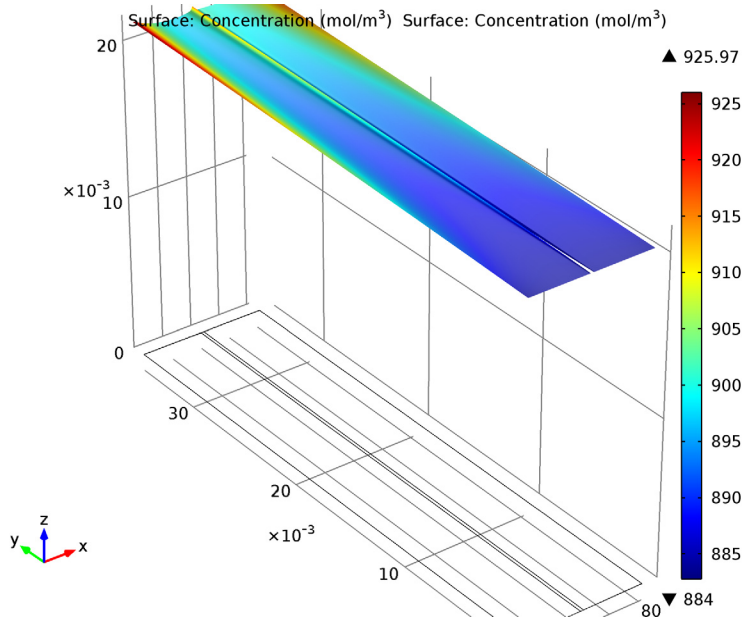

Figure 2: Concentration of the V^{3+} and the VO^{2+} ions

Figure 3 shows the concentration of the V^{2+} and the VO_2^{+} ions. Depletion occurs along the flow direction, and also towards both the current collector and membrane sides of the electrodes.

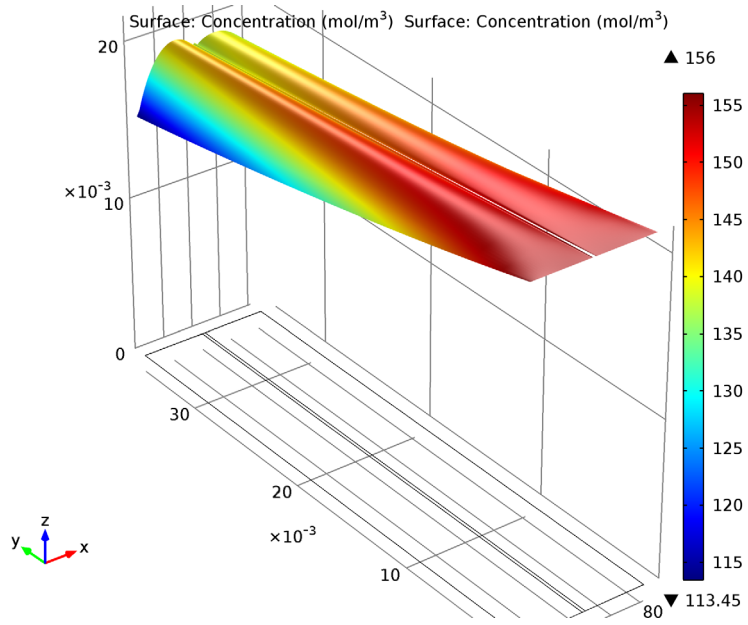

Figure 3: Concentration of the V^{2+} and the VO_2^+ ions

Figure 4 shows the electrolyte potential, which decreases towards the positive current collector.

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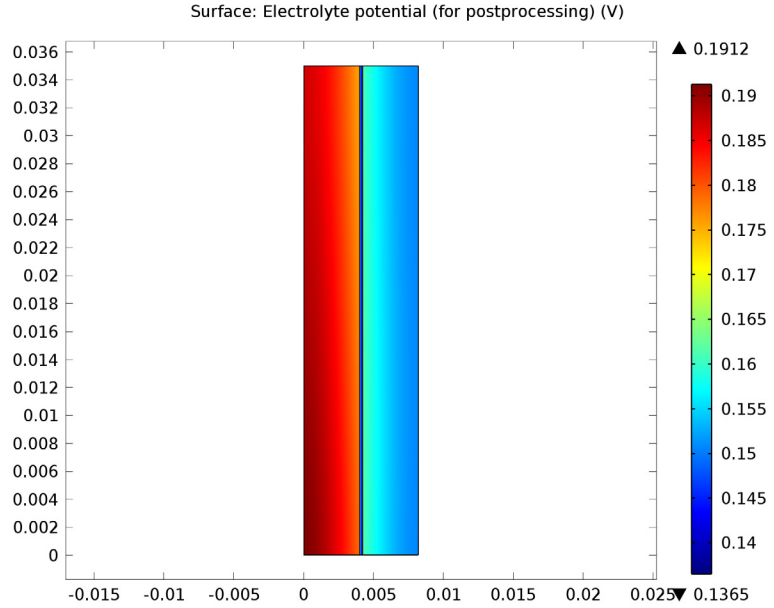

Figure 4: Electrolyte potential.

Figure 5 shows a cut line plot of the electrolyte potential at half the cell height. The Donnan potential shifts at the membrane boundaries are clearly visible in the figure.

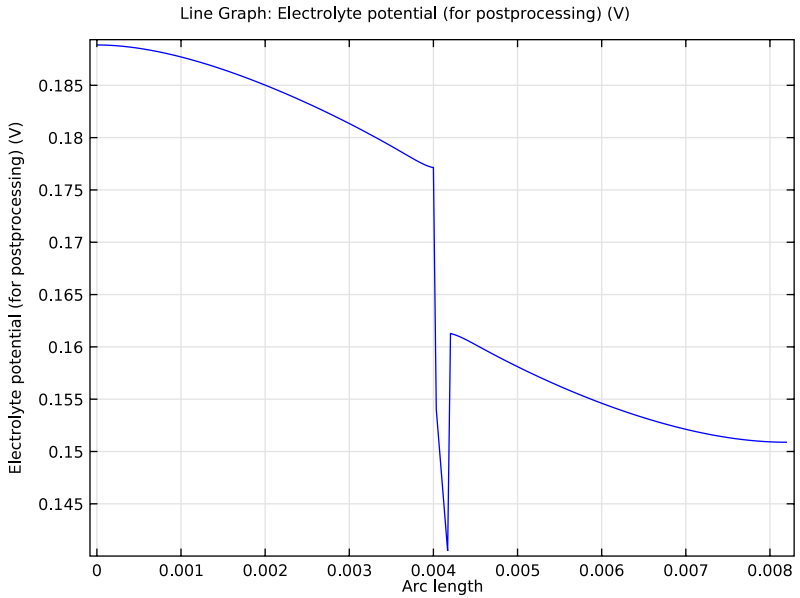

Figure 5: Electrolyte potential along a horizontal line placed at $y = h_{\text{cell}}/2$.

Figure 6 shows the electrode reaction source at half the cell height. The maximum is located towards the current collectors, with a minimum located in the middle of the electrodes. The reason for this phenomena is the similar conductivities of both phases (electrolyte and electrode) of the porous electrodes.

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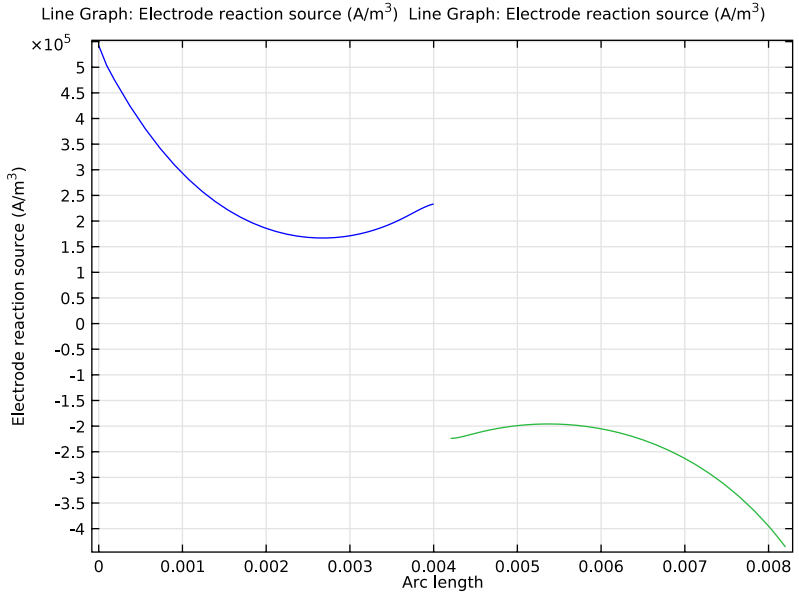

Figure 6: Electrode reaction source in the porous electrodes along a horizontal line placed at $y = h_{\text{cell}}/2$.

Figure 7 shows the rate of the dissociation reaction. Except from very close to the boundaries, the rates are generally very low, indicating that equilibrium is reached swiftly.

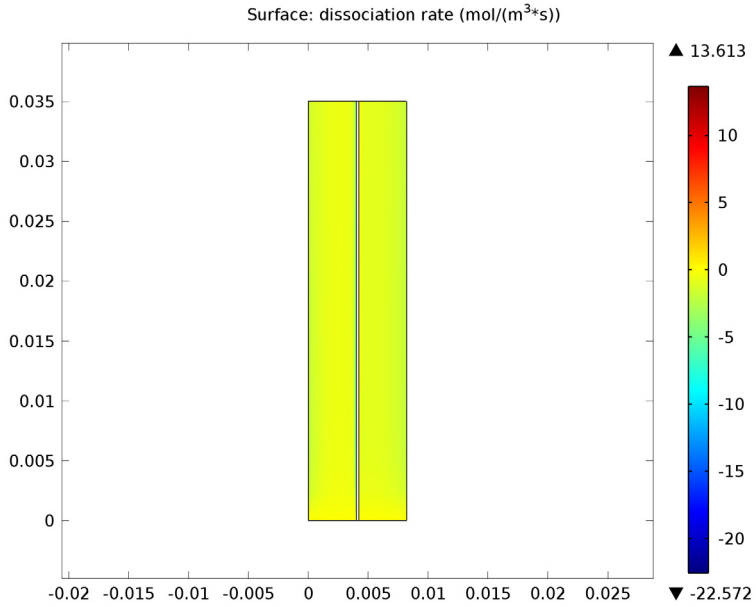

Figure 7: Sulfuric acid dissociation rate.

Figure 8 shows the local concentrations of the sulfuric acid species at half the cell height. Gradients are only seen close to the membrane, this is due to the influx and outflux of protons at the membrane boundaries in combination with the acid dissociation reaction.

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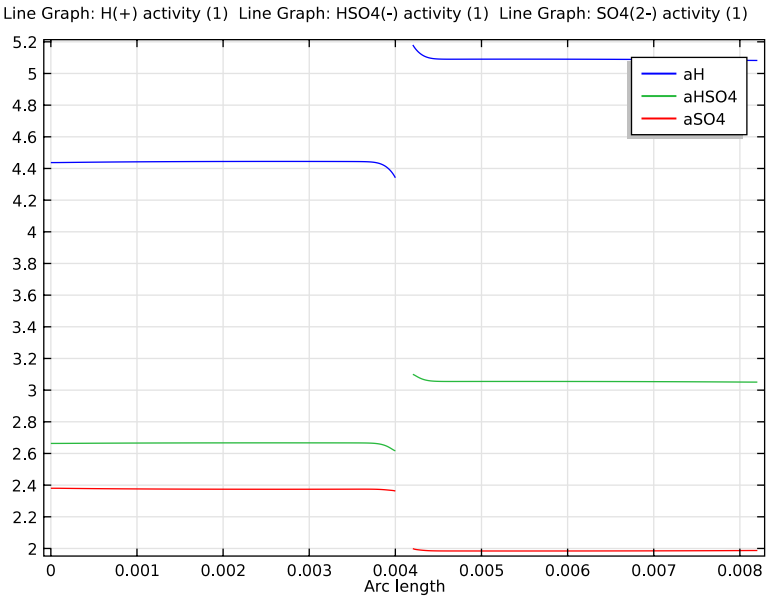

Figure 8: Sulfuric acid species along a horizontal line placed at $y = h_{\text{cell}}/2$.

Notes About the COMSOL Implementation

When setting the **Electrolyte Potential** boundary condition in the **Secondary Current Distribution** interface for the Donnan potential, you need to specify the **Constraint Settings** so that **Apply reaction term forces on** is set to **Individual dependent variables**. The reason for this is that the constraint should be fulfilled by varying the membrane potential only (the default setting would strive to fulfill the constraint by varying the total potential setting expression, which in this case also contains the proton concentration and the free electrolyte potential dependent variables).

To see the **Constraint Settings** section in the **Electrolyte Potential** feature, you need to enable **Advanced Physics Options**.

Reference

1. K. Knehr, E Agar, C. Dennison, A. Kalidindi, and E. Kumbur, "A Transient Vanadium Flow Battery Model Incorporating Vanadium Crossover and Water

Transport through the Membrane," *J. Electrochem. Soc.*, vol. 159, no. 9, pp A1446–A1459, 2012.

Model Library path: `Batteries_and_Fuel_Cells_Module/Batteries/v_flow_battery`

Modeling Instructions

MODEL WIZARD

1 Go to the **Model Wizard** window.

2 Click the **2D** button.

3 Click **Next**.

Add two Tertiary Current Distribution, Nernst Planck and one Secondary Current Distribution interface to your model. They will represent the physics for the two porous electrodes and the membrane, respectively.

4 In the **Add physics** tree, select **Electrochemistry>Tertiary Current Distribution, Nernst-Planck (tcdee)**.

5 Click **Add Selected**.

6 Find the **Dependent variables** subsection. In the **Number of species** edit field, type `5`.

7 In the **Concentrations** table, enter the following settings:

`cSO4_neg`
`cHSO4_neg`
`cH_neg`
`cV2`
`cV3`

8 In the **Electrolyte potential** edit field, type `phil_neg`.

9 In the **Electric potential** edit field, type `phis_neg`.

10 In the **Add physics** tree, select **Electrochemistry>Secondary Current Distribution (siec)**.

11 Click **Add Selected**.

12 In the **Electrolyte potential** edit field, type `phil_m`.

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13 In the **Add physics** tree, select **Electrochemistry>Tertiary Current Distribution, Nernst-Planck (tcdee)**.

14 Click **Add Selected**.

15 In the **Number of species** edit field, type `5`.

16 In the **Concentrations** table, enter the following settings:

cSO4_pos
cHSO4_pos
cH_pos
cV4
cV5

17 In the **Electrolyte potential** edit field, type `phil_pos`.

18 In the **Electric potential** edit field, type `phis_pos`.

19 Click **Next**.

20 Find the **Studies** subsection. In the tree, select **Preset Studies for Selected Physics>Stationary**.

21 Click **Finish**.

GLOBAL DEFINITIONS

Add the model parameters from a text file.

Parameters

1 In the **Model Builder** window, right-click **Global Definitions** and choose **Parameters**.

2 In the **Parameters** settings window, locate the **Parameters** section.

3 Click **Load from File**.

4 Browse to the model's Model Library folder and double-click the file `v_flow_battery_parameters.txt`.

GEOMETRY 1

Draw the geometry as a union of three rectangles (the two porous electrodes and the membrane domains).

Rectangle 1

1 In the **Model Builder** window, under **Model 1** right-click **Geometry 1** and choose **Rectangle**.

2 In the **Rectangle** settings window, locate the **Size** section.

3 In the **Width** edit field, type `L_e`.

4 In the **Height** edit field, type `H_cell`.

5 Locate the **Selections of Resulting Entities** section. Select the **Create selections** check box.

6 Right-click **Model 1>Geometry 1>Rectangle 1** and choose **Rename**.

7 Go to the **Rename Rectangle** dialog box and type `Negative Electrode` in the **New name** edit field.

8 Click **OK**.

Rectangle 2

1 Right-click **Geometry 1** and choose **Rectangle**.

2 In the **Rectangle** settings window, locate the **Size** section.

3 In the **Width** edit field, type `L_m`.

4 In the **Height** edit field, type `H_cell`.

5 Locate the **Position** section. In the **x** edit field, type `L_e`.

6 Locate the **Selections of Resulting Entities** section. Select the **Create selections** check box.

7 Right-click **Model 1>Geometry 1>Rectangle 2** and choose **Rename**.

8 Go to the **Rename Rectangle** dialog box and type `Membrane` in the **New name** edit field.

9 Click **OK**.

Rectangle 3

1 Right-click **Geometry 1** and choose **Rectangle**.

2 In the **Rectangle** settings window, locate the **Size** section.

3 In the **Width** edit field, type `L_e`.

4 In the **Height** edit field, type `H_cell`.

5 Locate the **Position** section. In the **x** edit field, type `L_e+L_m`.

6 Locate the **Selections of Resulting Entities** section. Select the **Create selections** check box.

7 Right-click **Model 1>Geometry 1>Rectangle 3** and choose **Rename**.

8 Go to the **Rename Rectangle** dialog box and type `Positive Electrode` in the **New name** edit field.

9 Click **OK**.

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10 Click the **Build All** button.

11 Click the **Zoom Extents** button on the Graphics toolbar.

Compare the geometry with Figure 1.

DEFINITIONS

Add an analytic function for the Nernst equation.

Analytic 1

1 In the **Model Builder** window, under **Model 1** right-click **Definitions** and choose **Functions>Analytic**.

2 In the **Analytic** settings window, locate the **Function Name** section.

3 In the **Function name** edit field, type `Nernst`.

4 Locate the **Definition** section. In the **Expression** edit field, type `E0+R_const*T/F_const*log(c_expr)`.

5 In the **Arguments** edit field, type `E0, T, c_expr`.

6 Locate the **Units** section. In the **Arguments** edit field, type `V, K, 1`.

7 In the **Function** edit field, type `V`.

8 Right-click **Model 1>Definitions>Analytic 1** and choose **Rename**.

9 Go to the **Rename Analytic** dialog box and type `Nernst Equation` in the **New name** edit field.

10 Click **OK**.

Variables 1

Add domain specific variables.

1 Right-click **Definitions** and choose **Variables**.

2 In the **Variables** settings window, locate the **Geometric Entity Selection** section.

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

4 From the **Selection** list, choose **Negative Electrode**.

5 Locate the **Variables** section. Click **Load from File**.

6 Browse to the model's Model Library folder and double-click the file `v_flow_battery_negative_variables.txt`.

7 Right-click **Model 1>Definitions>Variables 1** and choose **Rename**.

8 Go to the **Rename Variables** dialog box and type `Negative Electrode Variables` in the **New name** edit field.

9 Click **OK**.

Variables 2

1 Right-click **Definitions** and choose **Variables**.

2 In the **Variables** settings window, locate the **Geometric Entity Selection** section.

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

4 From the **Selection** list, choose **Membrane**.

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

Name	Expression	Description
phil	phil_m	Electrolyte potential (for postprocessing)

6 Right-click **Model 1>Definitions>Variables 2** and choose **Rename**.

7 Go to the **Rename Variables** dialog box and type `Membrane Variables` in the **New name** edit field.

8 Click **OK**.

Variables 3

1 Right-click **Definitions** and choose **Variables**.

2 In the **Variables** settings window, locate the **Geometric Entity Selection** section.

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

4 From the **Selection** list, choose **Positive Electrode**.

5 Locate the **Variables** section. Click **Load from File**.

6 Browse to the model's Model Library folder and double-click the file `v_flow_battery_positive_variables.txt`.

7 Right-click **Model 1>Definitions>Variables 3** and choose **Rename**.

8 Go to the **Rename Variables** dialog box and type `Positive Electrode Variables` in the **New name** edit field.

9 Click **OK**.

TERTIARY CURRENT DISTRIBUTION, NERNST-PLANCK

Now start defining the current distribution models. Start with the negative porous electrode.

1 In the **Tertiary Current Distribution, Nernst-Planck** settings window, locate the **Domain Selection** section.

2 From the **Selection** list, choose **Negative Electrode**.

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Porous Electrode 1

1 Right-click **Model 1>Tertiary Current Distribution, Nernst-Planck** and choose **Porous Electrode**.

2 In the **Porous Electrode** settings window, locate the **Model Inputs** section.

3 In the **u** table, enter the following settings:

0	x
v	y

4 Locate the **Domain Selection** section. From the **Selection** list, choose **Negative Electrode**.

5 Locate the **Model Inputs** section. In the T edit field, type `T`.

6 Locate the **Electrode Current Conduction** section. From the σ_s list, choose **User defined**. In the associated edit field, type `sigma_e`.

7 Locate the **Diffusion** section. In the $D_{\mathrm{cSO4}neg}$ edit field, type `DSO4`.

8 In the $D_{\mathrm{cHSO4}neg}$ edit field, type `DHSO4`.

9 In the D_{cHneg} edit field, type `DH`.

10 In the D_{cV2} edit field, type `DV2`.

11 In the D_{cV3} edit field, type `DV3`.

12 Locate the **Migration in Electric Field** section. In the $z_{\mathrm{cSO4}neg}$ edit field, type `-2`.

13 In the $z_{\mathrm{cHSO4}neg}$ edit field, type `-1`.

14 In the z_{cHneg} edit field, type `1`.

15 In the z_{cV2} edit field, type `2`.

16 In the z_{cV3} edit field, type `3`.

17 Locate the **Volume Fractions** section. In the ε_l edit field, type `epsilon`.

18 Locate the **Effective Transport Parameter Correction** section. From the **Diffusion** list, choose **Bruggeman**.

Porous Electrode Reaction 1

1 In the **Model Builder** window, expand the **Porous Electrode 1** node, then click **Porous Electrode Reaction 1**.

2 In the **Porous Electrode Reaction** settings window, locate the **Model Inputs** section.

3 In the T edit field, type `T`.

4 Locate the **Equilibrium Potential** section. In the $E_{\mathrm{eq},ref}$ edit field, type `Eeq_neg`.

5 Locate the **Electrode Kinetics** section. From the **Kinetics expression type** list, choose **Butler-Volmer**.

6 In the i_0 edit field, type `i0_neg`.

7 In the α_a edit field, type `1-alpha_neg`.

8 In the α_c edit field, type `alpha_neg`.

9 Locate the **Active Specific Surface Area** section. In the a_v edit field, type `a`.

10 Locate the **Stoichiometric Coefficients** section. In the ν_{cV2} edit field, type `1`.

11 In the ν_{cV3} edit field, type `-1`.

Reactions 1

1 In the **Model Builder** window, right-click **Tertiary Current Distribution, Nernst-Planck** and choose **Additional Sources>Reactions**.

2 In the **Reactions** settings window, locate the **Domain Selection** section.

3 From the **Selection** list, choose **Negative Electrode**.

4 Locate the **Reactions** section. In the $R_{cSO4neg}$ edit field, type `-rd`.

5 In the $R_{cHSO4neg}$ edit field, type `rd`.

6 In the R_{cHneg} edit field, type `-rd`.

Electric Ground 1

1 Right-click **Tertiary Current Distribution, Nernst-Planck** and choose **Electrode>Electric Ground**.

2 Select Boundary 1 only.

Concentration 1

1 Right-click **Tertiary Current Distribution, Nernst-Planck** and choose **Electrolyte>Concentration**.

2 Select Boundary 2 only.

3 In the **Concentration** settings window, locate the **Concentration** section.

4 Select the **Species cHSO4_neg** check box.

5 In the $c_{0,cHSO4neg}$ edit field, type `cHSO4_0_neg`.

6 Select the **Species cH_neg** check box.

7 In the $c_{0,cHneg}$ edit field, type `cH_0_neg`.

8 Select the **Species cV2** check box.

9 In the $c_{0,cV2}$ edit field, type `cV2_0`.

10 Select the **Species cV3** check box.

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11 In the $c_{0,cV3}$ edit field, type `cV3_0`.

Outflow 1

1 Right-click **Tertiary Current Distribution, Nernst-Planck** and choose **Electrolyte>Outflow**.

2 Select Boundary 3 only.

Electrolyte Current Density 1

Couple the current and the proton flux on the porous electrode-membrane boundary to the electrolyte current density in the Secondary Current Distribution interface.

1 Right-click **Tertiary Current Distribution, Nernst-Planck** and choose **Electrolyte>Electrolyte Current Density**.

2 Select Boundary 4 only.

3 In the **Electrolyte Current Density** settings window, locate the **Electrolyte Current Density** section.

4 In the i_0 edit field, type `-siec.Ilx`.

Flux 1

1 Right-click **Tertiary Current Distribution, Nernst-Planck** and choose **Electrolyte>Flux**.

2 Select Boundary 4 only.

3 In the **Flux** settings window, locate the **Inward Flux** section.

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

5 In the $N_{0,cHneg}$ edit field, type `-siec.Ilx/F_const`.

Initial Values 1

1 In the **Model Builder** window, under **Model 1>Tertiary Current Distribution, Nernst-Planck** click **Initial Values 1**.

2 In the **Initial Values** settings window, locate the **Initial Values** section.

3 In the $cHSO4_{neg}$ edit field, type `cHSO4_0_neg`.

4 In the cH_{neg} edit field, type `cH_0_neg`.

5 In the $cV2$ edit field, type `cV2_0`.

6 In the $cV3$ edit field, type `cV3_0`.

7 In the $phil_{neg}$ edit field, type `-E0_neg`.

SECONDARY CURRENT DISTRIBUTION

Now set up the Secondary Current Distribution model for the membrane.

1 In the **Model Builder** window, under **Model 1** click **Secondary Current Distribution**.
2 In the **Secondary Current Distribution** settings window, locate the **Domain Selection** section.
3 From the **Selection** list, choose **Membrane**.

Electrolyte 1

1 In the **Model Builder** window, under **Model 1>Secondary Current Distribution** click **Electrolyte 1**.
2 In the **Electrolyte** settings window, locate the **Electrolyte** section.
3 From the σ_l list, choose **User defined**. In the associated edit field, type `sigma_m`.

Electrolyte Potential 1

Now couple the electrolyte potential in the membrane to the electrolyte potentials and hydrogen concentrations in the Tertiary Current Distribution interfaces by the use of Donnan potential expressions on the boundaries between the membrane and the porous electrodes.

1 In the **Model Builder** window, right-click **Secondary Current Distribution** and choose **Electrolyte>Electrolyte Potential**.
2 Select Boundary 4 only.
3 In the **Electrolyte Potential** settings window, locate the **Electrolyte Potential** section.
4 In the $\phi_{l,bnd}$ edit field, type `phil_neg-Nernst(0,T,aH/aHm)`.

   Change the Constraint settings so that only the dependent electrolyte potential variable in the Secondary Current Distribution is constrained by this Dirichlet condition. (Otherwise this condition will contribute to the reaction terms also for the hydrogen concentration and electrolyte potential dependent variables in the Tertiary Current Distribution interface).
5 In the **Model Builder** window's toolbar, click the **Show** button and select **Advanced Physics Options** in the menu.
6 In the **Electrolyte Potential** settings window, click to expand the **Constraint Settings** section.
7 From the **Apply reaction terms on** list, choose **Individual dependent variables**.

Electrolyte Potential 2

1 Right-click **Secondary Current Distribution** and choose **Electrolyte>Electrolyte Potential**.
2 Select Boundary 7 only.

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3 In the **Electrolyte Potential** settings window, locate the **Electrolyte Potential** section.

4 In the $\phi_{l,bnd}$ edit field, type `phil_pos-Nernst(0,T,aH/aHm)`.

5 Locate the **Constraint Settings** section. From the **Apply reaction terms on** list, choose **Individual dependent variables**.

Initial Values 1

1 In the **Model Builder** window, under **Model 1>Secondary Current Distribution** click **Initial Values 1**.

2 In the **Initial Values** settings window, locate the **Initial Values** section.

3 In the $phil_{\mathrm{m}}$ edit field, type `-E0_neg`.

TERTIARY CURRENT DISTRIBUTION, NERNST-PLANCK 2

Finish the physics settings by setting up the tertiary current distribution model for the positive porous electrode.

1 In the **Model Builder** window, under **Model 1** click **Tertiary Current Distribution, Nernst-Planck 2**.

2 In the **Tertiary Current Distribution, Nernst-Planck** settings window, locate the **Domain Selection** section.

3 From the **Selection** list, choose **Positive Electrode**.

Porous Electrode 1

1 Right-click **Model 1>Tertiary Current Distribution, Nernst-Planck 2** and choose **Porous Electrode**.

2 In the **Porous Electrode** settings window, locate the **Domain Selection** section.

3 From the **Selection** list, choose **Positive Electrode**.

4 Locate the **Model Inputs** section. In the $\mathbf{u}$ table, enter the following settings:

0	x
v	y

5 In the T edit field, type `T`.

6 Locate the **Electrode Current Conduction** section. From the σ_{s} list, choose **User defined**. In the associated edit field, type `sigma_e`.

7 Locate the **Diffusion** section. In the $D_{\mathrm{cSO4}pos}$ edit field, type `DSO4`.

8 In the $D_{\mathrm{cHSO4}pos}$ edit field, type `DHSO4`.

9 In the D_{cHpos} edit field, type `DH`.

10 In the D_{cV4} edit field, type `DV4`.

11 In the D_{cV5} edit field, type `DV5`.

12 Locate the **Migration in Electric Field** section. In the $z_{cSO4pos}$ edit field, type `-2`.

13 In the $z_{cHSO4pos}$ edit field, type `-1`.

14 In the z_{cHpos} edit field, type `1`.

15 In the z_{cV4} edit field, type `2`.

16 In the z_{cV5} edit field, type `1`.

17 Locate the **Volume Fractions** section. In the ε_l edit field, type `epsilon`.

18 Locate the **Effective Transport Parameter Correction** section. From the **Diffusion** list, choose **Bruggeman**.

Porous Electrode Reaction 1

1 In the **Model Builder** window, expand the **Porous Electrode 1** node, then click **Porous Electrode Reaction 1**.

2 In the **Porous Electrode Reaction** settings window, locate the **Model Inputs** section.

3 In the T edit field, type `T`.

4 Locate the **Equilibrium Potential** section. In the $E_{eq,ref}$ edit field, type `E0_pos`.

5 Locate the **Electrode Kinetics** section. From the **Kinetics expression type** list, choose **Butler-Volmer**.

6 In the i_0 edit field, type `i0_pos`.

7 In the α_a edit field, type `1-alpha_pos`.

8 In the α_c edit field, type `alpha_pos`.

9 Locate the **Active Specific Surface Area** section. In the a_v edit field, type `a`.

10 Locate the **Stoichiometric Coefficients** section. In the ν_{cHpos} edit field, type `-2`.

11 In the ν_{cV4} edit field, type `1`.

12 In the ν_{cV5} edit field, type `-1`.

Reactions 1

1 In the **Model Builder** window, right-click **Tertiary Current Distribution, Nernst-Planck 2** and choose **Additional Sources>Reactions**.

2 In the **Reactions** settings window, locate the **Domain Selection** section.

3 From the **Selection** list, choose **Positive Electrode**.

4 Locate the **Reactions** section. In the $R_{cSO4pos}$ edit field, type `-rd`.

5 In the $R_{cHSO4pos}$ edit field, type `rd`.

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6 In the R_{cHpos} edit field, type `-rd`.

Electrode Current 1

1 Right-click **Tertiary Current Distribution, Nernst-Planck 2** and choose **Electrode>Electrode Current**.

2 In the **Electrode Current** settings window, locate the **Electrode Current** section.

3 From the list, choose **Average current density**.

4 Select Boundary 10 only.

5 In the $i_{\mathrm{s},average}$ edit field, type `i_avg`.

Concentration 1

1 Right-click **Tertiary Current Distribution, Nernst-Planck 2** and choose **Electrolyte>Concentration**.

2 Select Boundary 8 only.

3 In the **Concentration** settings window, locate the **Concentration** section.

4 Select the **Species cHSO4_pos** check box.

5 In the $c_{0,\mathrm{cHSO4}pos}$ edit field, type `cHSO4_0_pos`.

6 Select the **Species cH_pos** check box.

7 In the $c_{0,\mathrm{cHpos}}$ edit field, type `cH_0_pos`.

8 Select the **Species cV4** check box.

9 In the $c_{0,\mathrm{cV4}}$ edit field, type `cV4_0`.

10 Select the **Species cV5** check box.

11 In the $c_{0,\mathrm{cV5}}$ edit field, type `cV5_0`.

Outflow 1

1 Right-click **Tertiary Current Distribution, Nernst-Planck 2** and choose **Electrolyte>Outflow**.

2 Select Boundary 9 only.

Electrolyte Current Density 1

1 Right-click **Tertiary Current Distribution, Nernst-Planck 2** and choose **Electrolyte>Electrolyte Current Density**.

2 Select Boundary 7 only.

3 In the **Electrolyte Current Density** settings window, locate the **Electrolyte Current Density** section.

4 In the i_0 edit field, type `siec.Ilx`.

Flux 1

1 Right-click **Tertiary Current Distribution, Nernst-Planck 2** and choose **Electrolyte>Flux**.

2 Select Boundary 7 only.

3 In the **Flux** settings window, locate the **Inward Flux** section.

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

5 In the $N_{0,\mathrm{cHpos}}$ edit field, type `siec.Ilx/F_const`.

Initial Values 1

1 In the **Model Builder** window, under **Model 1>Tertiary Current Distribution, Nernst-Planck 2** click **Initial Values 1**.

2 In the **Initial Values** settings window, locate the **Initial Values** section.

3 In the $cHSO4_{\mathrm{pos}}$ edit field, type `cHSO4_0_pos`.

4 In the cH_{pos} edit field, type `cH_0_pos`.

5 In the $cV4$ edit field, type `cV4_0`.

6 In the $cV5$ edit field, type `cV5_0`.

7 In the $phil_{\mathrm{pos}}$ edit field, type `-E0_neg`.

8 In the $phis_{\mathrm{pos}}$ edit field, type `E0_pos-E0_neg`.

MESH 1

Create a mapped mesh with higher resolution in the porous electrodes towards the membrane.

Mapped 1

In the **Model Builder** window, under **Model 1** right-click **Mesh 1** and choose **Mapped**.

Distribution 1

1 In the **Model Builder** window, under **Model 1>Mesh 1** right-click **Mapped 1** and choose **Distribution**.

2 Select Boundaries 5 and 6 only.

3 In the **Distribution** settings window, locate the **Distribution** section.

4 In the **Number of elements** edit field, type 3.

Distribution 2

1 Right-click **Mapped 1** and choose **Distribution**.

2 Select Boundaries 2 and 3 only.

3 In the **Distribution** settings window, locate the **Distribution** section.

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4 From the **Distribution properties** list, choose **Predefined distribution type**.

5 In the **Number of elements** edit field, type 40.

6 In the **Element ratio** edit field, type 20.

Distribution 3

1 Right-click **Model 1>Mesh 1>Mapped 1>Distribution 2** and choose **Duplicate**.

2 In the **Distribution** settings window, locate the **Boundary Selection** section.

3 Click **Clear Selection**.

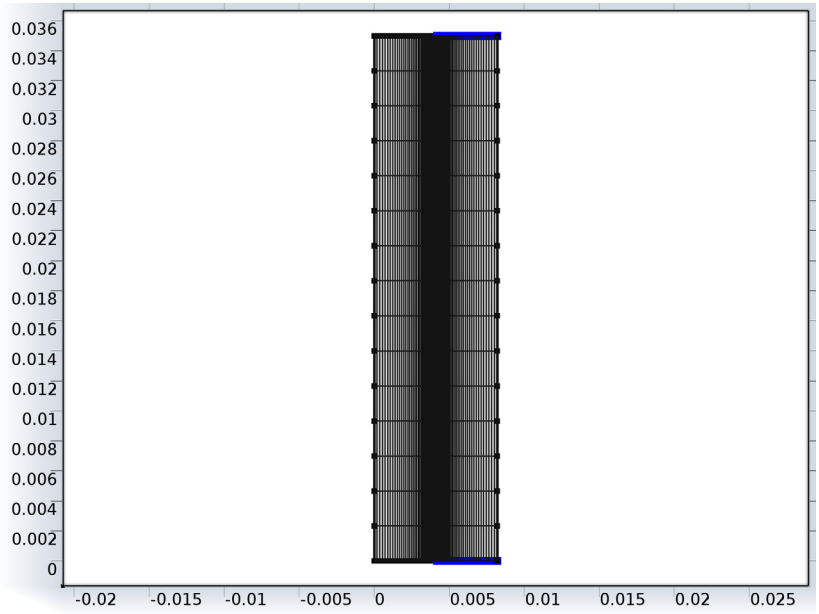
4 Select Boundaries 8 and 9 only.

5 In the **Distribution** settings window, locate the **Distribution** section.

6 Select the **Reverse direction** check box.

7 Click the **Build All** button.

Your mesh should now look like this:



STUDY 1

The problem is now ready for solving.

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

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

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

4 Click the **Compute** button.

RESULTS

Reproduce the plots from the Results and Discussion section in the following way:

2D Plot Group 1

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

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

3 In the **Surface** settings window, locate the **Expression** section.

4 In the **Expression** edit field, type `cV3`.

5 Right-click **Results>2D Plot Group 1>Surface 1** and choose **Height Expression**.

6 Right-click **Results>2D Plot Group 1>Surface 1** and choose **Duplicate**.

7 In the **Surface** settings window, locate the **Expression** section.

8 In the **Expression** edit field, type `cV4`.

9 Click to expand the **Inherit Style** section. From the **Plot** list, choose **Surface 1**.

10 Click the **Plot** button.

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

12 Go to the **Rename 2D Plot Group** dialog box and type `V3/V4 Species Concentration` in the **New name** edit field.

13 Click **OK**.

V3/V4 Species Concentration 1

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

Now modify the plot group that was created by the duplicate operation.

2 In the **Model Builder** window, expand the **V3/V4 Species Concentration 1** node, then click **Surface 1**.

3 In the **Surface** settings window, locate the **Expression** section.

4 In the **Expression** edit field, type `cV2`.

5 In the **Model Builder** window, under **Results>V3/V4 Species Concentration 1** click **Surface 2**.

6 In the **Surface** settings window, locate the **Expression** section.

7 In the **Expression** edit field, type `cV5`.

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8 In the **Model Builder** window, right-click **V3/V4 Species Concentration 1** and choose **Plot**.

9 Right-click **V3/V4 Species Concentration 1** and choose **Rename**.

10 Go to the **Rename 2D Plot Group** dialog box and type `V2/V5 Species Concentration` in the **New name** edit field.

11 Click **OK**.

2D Plot Group 3

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

2 In the **Model Builder** window, under **Results** right-click **2D Plot Group 3** and choose **Surface**.

3 In the **Surface** settings window, locate the **Expression** section.

4 In the **Expression** edit field, type `phil`.

5 Click the **Plot** button.

6 In the **Model Builder** window, right-click **2D Plot Group 3** and choose **Rename**.

7 Go to the **Rename 2D Plot Group** dialog box and type `Electrolyte potential 2D` in the **New name** edit field.

8 Click **OK**.

Data Sets

1 In the **Model Builder** window, under **Results** right-click **Data Sets** and choose **Cut Line 2D**.

2 In the **Cut Line 2D** settings window, locate the **Line Data** section.

3 In row **Point 2**, set **x** to `L_e*2+L_m`.

4 In row **Point 1**, set **y** to `H_cell/2`.

5 In row **Point 2**, set **y** to `H_cell/2`.

1D Plot Group 4

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

2 In the **1D Plot Group** settings window, locate the **Data** section.

3 From the **Data set** list, choose **Cut Line 2D 1**.

4 Right-click **Results>1D Plot Group 4** and choose **Line Graph**.

5 Right-click **Results>1D Plot Group 4>Line Graph 1** and choose **Plot**.

6 Right-click **1D Plot Group 4** and choose **Rename**.

7 Go to the **Rename 1D Plot Group** dialog box and type `Electrolyte potential` in the **New name** edit field.

8 Click **OK**.

1D Plot Group 5

1 Right-click **Results** and choose **1D Plot Group**.

2 In the **Model Builder** window, under **Results** right-click **1D Plot Group 5** and choose **Line Graph**.

3 In the **Line Graph** settings window, locate the **Data** section.

4 From the **Data set** list, choose **Cut Line 2D 1**.

5 Click **Replace Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Tertiary Current Distribution, Nernst-Planck>Electrode kinetics>Electrode reaction source (tcdee.ivtot)**.

6 Click the **Plot** button.

7 Right-click **Results>1D Plot Group 5>Line Graph 1** and choose **Duplicate**.

8 In the **Line Graph** settings window, locate the **y-Axis Data** section.

9 In the **Expression** edit field, type `tcdee2.ivtot`.

10 Click the **Plot** button.

11 In the **Model Builder** window, right-click **1D Plot Group 5** and choose **Rename**.

12 Go to the **Rename 1D Plot Group** dialog box and type `Electrode reaction current densities` in the **New name** edit field.

13 Click **OK**.

2D Plot Group 6

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

2 In the **Model Builder** window, under **Results** right-click **2D Plot Group 6** and choose **Surface**.

3 In the **Surface** settings window, locate the **Expression** section.

4 In the **Expression** edit field, type `rd`.

5 Click the **Plot** button.

6 In the **Model Builder** window, right-click **2D Plot Group 6** and choose **Rename**.

7 Go to the **Rename 2D Plot Group** dialog box and type `Dissociation rate` in the **New name** edit field.

8 Click **OK**.

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1D Plot Group 7

1 Right-click **Results** and choose **1D Plot Group**.

2 In the **1D Plot Group** settings window, locate the **Data** section.

3 From the **Data set** list, choose **Cut Line 2D 1**.

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

5 In the **Line Graph** settings window, locate the **y-Axis Data** section.

6 In the **Expression** edit field, type `aH`.

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

8 From the **Legends** list, choose **Manual**.

9 In the table, enter the following settings:

Legends
aH

10 Right-click **Results>1D Plot Group 7>Line Graph 1** and choose **Duplicate**.

11 In the **Line Graph** settings window, locate the **y-Axis Data** section.

12 In the **Expression** edit field, type `aHSO4`.

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

Legends
aHSO4

14 Right-click **Results>1D Plot Group 7>Line Graph 2** and choose **Duplicate**.

15 In the **Line Graph** settings window, locate the **y-Axis Data** section.

16 In the **Expression** edit field, type `aSO4`.

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

Legends
aSO4

18 Click the **Plot** button.

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

20 Right-click **1D Plot Group 7** and choose **Rename**.

21 Go to the **Rename 1D Plot Group** dialog box and type `Sulphuric acid species` in the **New name** edit field.

22 Click **OK**.

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