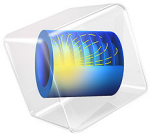


Soluble Lead–Acid Redox Flow Battery

Introduction

In a redox flow battery electrochemical energy is stored as redox couples in the electrolyte, which is stored in tanks outside the electrochemical cell. During operation, electrolyte is pumped through the cell and, due to the electrochemical reactions, the individual concentrations of the active species in the electrolyte are changed.

The state of charge of the flow battery is determined by the electrolyte species concentrations, the total flowing electrolyte volume in the system (tank + pump + hoses + cell), and possibly also by the concentration of solid species on the electrodes. Depending on the cell chemistry the cell can have separated or combined anode and cathode compartments and electrolyte tanks.

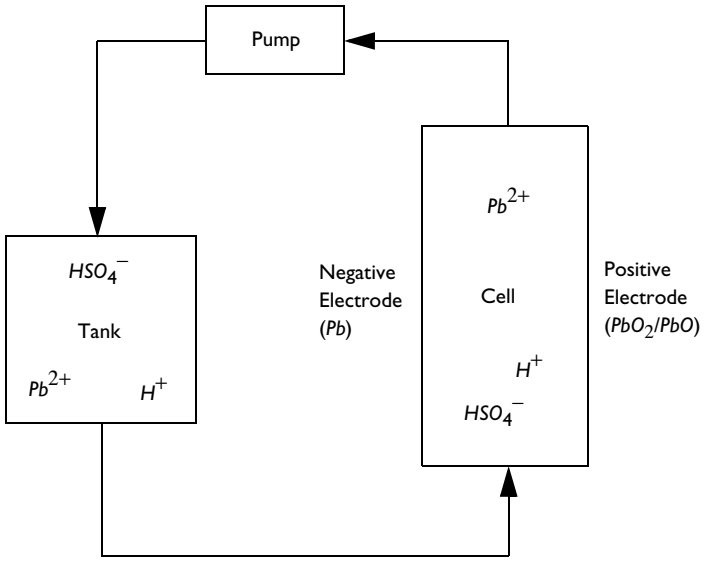


Figure 1: Working principle of the soluble lead–acid flow battery.

In the soluble lead–acid flow battery one electrolyte solution is used. The active component in the electrolyte is the lead ion that reacts on the electrodes to form solid lead (negative electrode) or lead oxide (positive electrode). The electrode chemistry is similar to a traditional lead–acid battery, with the difference that solid lead sulfonate is not formed in the electrodes.

This example simulates a soluble lead–acid flow battery during an applied charge-discharge load cycle. The surface chemistry of the positive electrode is modeled by using two different lead oxides and two different positive electrode reactions in the model.

Model Definition

CELL GEOMETRY AND MESH

The electrochemical cell consist of two flat 10 cm square electrodes, placed in parallel with a 12 mm gap in between. The aspect ratio of the cell motivates modeling the cell in 2D. The cell geometry and mesh is shown in Figure 2.

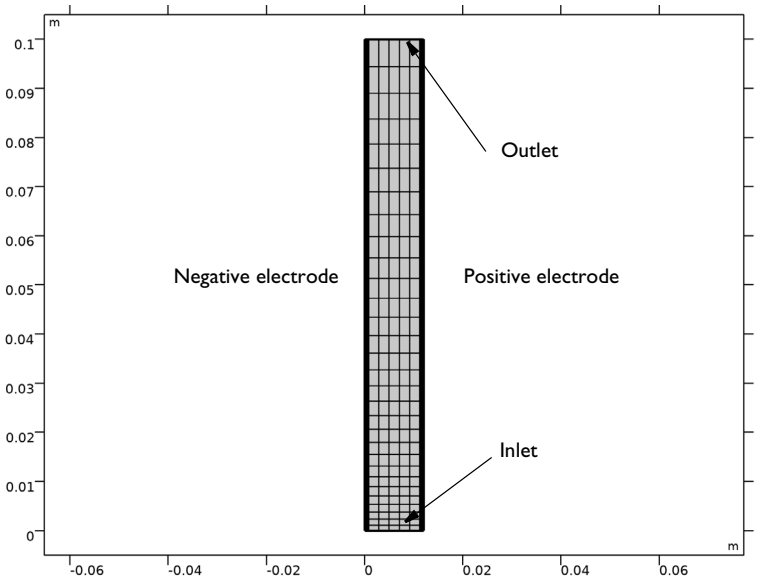


Figure 2: Geometry and mesh of the electrochemical cell.

Due to the very high electrical conductivity of the electrodes, the potential gradients in the electrodes are neglected, and the electrodes are not included in the geometry.

To handle possible edge effects in the electrolyte, 1 mm regions are added at the inlet and outlet, outside the active electrode region.

A mapped rectangular mesh is used, and boundary meshing is used to resolve the steep gradients in the electrolyte close to the electrode surfaces.

ELECTROLYTE MASS AND CURRENT TRANSPORT EQUATIONS

The electrolyte is based on a mixture of lead methane sulfonate, methane sulfonic acid and water, which in this model is assumed to dissociate into an electrolyte consisting of Pb^{2+}, H^+, HSO_4^--ions dissolved in a bulk solution of zero-charged species (mainly water). Electroneutrality is assumed locally in the electrolyte. The combination of these assumptions allow for the use of Tertiary Current Distribution, Nernst-Planck interface for modeling the electrolyte transport.

The electric potential in the electrodes is assumed to be space independent. The negative electrode is grounded. On the positive electrode, an electrode potential is calculated in order to fulfill a current density condition defined by the load cycle (using the Electrode Surface boundary node).

A load cycle of 1 h charge, 20 s rest, 1 h discharge, 20 s is applied twice to the cell. During charge or discharge a constant current density corresponding to a mean current density in the cell 200 A/m^2 is applied.

The species fluxes are defined on the electrode surfaces according to the electrode reactions below. An Inflow condition is used at the inlet with the inlet concentrations ($c_{\text{in, Pb}^{2+}}$ and $c_{\text{in, H}^+}$) taken from the tank model described below. An Outflow condition is set at the outlet. All other boundaries are isolated.

Negative Electrode Reaction

On the negative electrode the following electrode reaction occurs:

$$Pb^{2+} + 2e^- \Leftrightarrow Pb(s)$$

with the kinetics being described by a Butler-Volmer expression:

$$i_{\text{Pb}} = Fk_0^{\text{Pb}} c_{\text{Pb}^{2+}} \left(\exp\left(\frac{F\eta}{RT}\right) - \exp\left(-\frac{F\eta}{RT}\right)\right)$$

Where $k_0^{\text{Pb}+}$ is a rate constant and $c_{\text{Pb}^{2+}}$ is the concentration of lead ions in the electrolyte.

As reference electrode we use the negative electrode at reference conditions. The equilibrium potential for the negative electrode is assumed to follow the Nernst equation according to:

$$E_{0,\text{ neg}} = 0V + \frac{RT}{nF}\ln(c_{\text{Pb}^{2+}})$$

Positive Electrode Main Reaction

The positive electrode main reaction is:

$$PbO_2(s) + 4H^+ + 2e^- \Leftrightarrow Pb^{2+} + 2H_2O$$

with the kinetics being described by a Butler-Volmer expression:

$$i_{PbO_2} = Fk_0^{PbO_2} c_{Pb^{2+}} \frac{c_{H^+}}{c_{H^+}^0} \left(\exp\left(\frac{F\eta}{RT}\right) - \exp\left(-\frac{F\eta}{RT}\right) \right)$$

where $k_0^{PbO_2}$ is a rate constant, c_{H^+} is the electrolyte proton concentration and $c_{H^+}^0$ is the proton reference concentration in the electrolyte at equilibrium.

The positive main reaction has the following equilibrium potential, described by the Nernst Equation:

$$E_{0,\,pos} = 1.8V - \frac{RT}{nF} \ln\left(\frac{c_{Pb^{2+}}}{c_{H^+}}\right) \tag{1}$$

Positive Electrode Side Reaction

Multiple types of lead oxides may form on the positive electrode. In this model the following side reaction is investigated:

$$PbO_2(s) + 2H^+ + 2e^- \Leftrightarrow PbO(s) + H_2O$$

where the electrode is kinetics is described by

$$i_{PbO} = F\left(K_0^f c_{PbO}^2 \exp\left(\frac{F\eta}{RT}\right) - K_0^b c_{H^+} c_{PbO_2} \exp\left(-\frac{F\eta}{RT}\right)\right) \tag{2}$$

where the overpotential, η, is the same as for the positive electrode main reaction (Equation 1). (The deviation of the equilibrium potential of the side reaction versus the positive main reaction equilibrium potential is controlled by the rate parameters.)

In Equation 2 K_0^f and K_0^b are rate constants, and c_{PbO} and c_{PbO_2} are the surface concentration of the lead oxides (mol/m^2).

TANK MODEL

The electrolyte flowing out from the cell flows into the tank, undergoes mixing, and is then led into the cell again on the inlet side.

Assuming good mixing in the tank the inlet concentrations, $c_{in,\,Pb^{2+}}$ and $c_{in,\,H^+}$, are governed by the following ODEs:

$$\frac{V}{L}\frac{d}{dt}(c_{\text{in, Pb}^{2+}}) = \int_{\text{outlet}} (\mathbf{N}_{\text{Pb}^{2+}} \cdot \mathbf{n})dS - \int_{\text{inlet}} (\mathbf{N}_{\text{Pb}^{2+}} \cdot \mathbf{n})dS$$

$$\frac{V}{L}\frac{d}{dt}(c_{\text{in, H}^{+}}) = \int_{\text{outlet}} (\mathbf{N}_{\text{H}^{+}} \cdot \mathbf{n})dS - \int_{\text{inlet}} (\mathbf{N}_{\text{H}^{+}} \cdot \mathbf{n})dS$$

Where V is the total volume of flowing electrolyte in the tank, and L is the height of the electrodes. ($\mathbf{N}_{\text{Pb}^{2+}} \cdot \mathbf{n}$ and $\mathbf{N}_{\text{H}^{+}} \cdot \mathbf{n}$ denote the molar fluxes of the respective electrolyte species in the normal direction to the boundary).

The two ODEs are modeled using an ODEs and DAEs interface.

FLUID FLOW EQUATIONS

The fluid is led into the cell at a velocity V_{in} of 2.3 cm/s. The relevant Reynolds number for the flow between the plates is:

$$\text{Re} = \frac{\rho V_{\text{in}} h}{\mu} \approx 300$$

where the parameter values for water are used for the density ρ, 1000 kg/m^3, and viscosity μ, 10^{-3} Pa·s. We can assume that the flow is in the laminar regime ($\text{Re} < 2000$), and hence the Laminar Flow interface is used to model the fluid flow.

V_{in} is applied at the inlet, a pressure condition is applied to the outlet, and no slip conditions are applied to the electrode surfaces and channel walls. The induced convection at the electrode surfaces due to the electrochemical reactions is assumed to be negligible. In this way the flow model is stationary and only solved for once. The convective flow is used as a model input to the Tertiary Current Distribution, Nernst-Planck interface.

SURFACE CONCENTRATIONS ON THE POSITIVE ELECTRODE

Two different lead oxides, PbO and PbO_2, may be formed on the positive electrodes due to the electrochemical reactions. The surface concentrations of these two species, c_{PbO} and c_{PbO_2} (SI unit: mol/m^2), are modeled using the Dissolving-Depositing Species section of the Tertiary Current Distribution, Nernst-Planck interface.

Figure 3 shows the flow field and pressure drop for the cell. The parabolic velocity profile is expected for this rectangular geometry (Poiseuille flow).

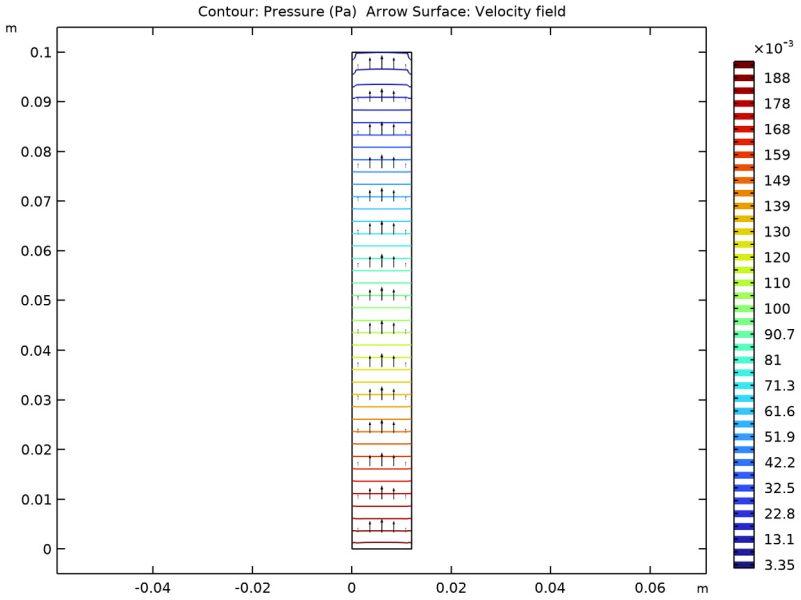


Figure 3: Velocity field and pressure.

Figure 4 shows the cell voltage during the load cycling. The first charge cycle voltages differs from the second.

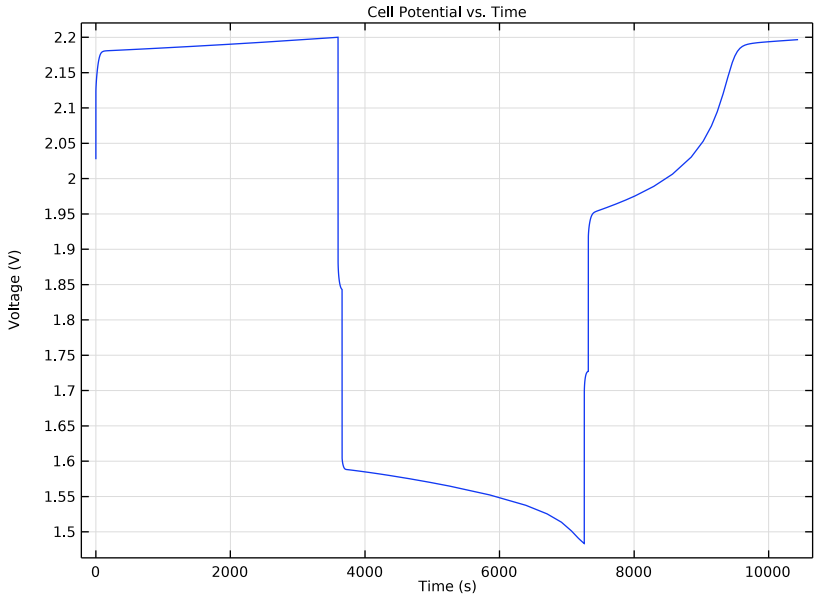


Figure 4: Cell potential versus time.

Figure 5 shows the average surface concentrations of PbO and PbO_2 at the positive electrode during the load cycle. The build-up of PbO_2 starts during the first charge cycle, whereas there is only small amounts of PbO formed until the beginning of the discharge cycle. The presence of PbO alters the kinetics of the positive electrode during the second charge cycle. Figure 7 shows the difference in local current densities between the different parts of the load cycle. The modified kinetics on the positive electrode impacts the overpotentials, which in turn explains the difference in cell voltages during the first and second charge cycles in Figure 4.

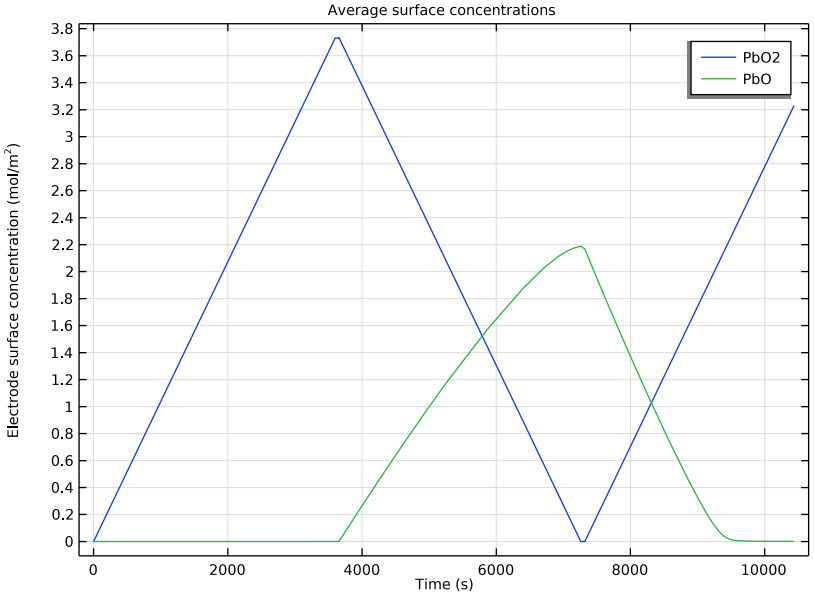


Figure 5: Average surface concentrations of the two different lead oxides on the positive electrode.

Figure 6 shows the inlet concentrations of lead ions and protons from the tank model during the load cycling. The lead ion concentrations is lower and the proton concentration is higher at the beginning of the second charge cycle, compared to the initial values. The reasons for these variations are due to the lead ion consumption to form the lead oxide layer, and the proton release from water molecules in the same process.

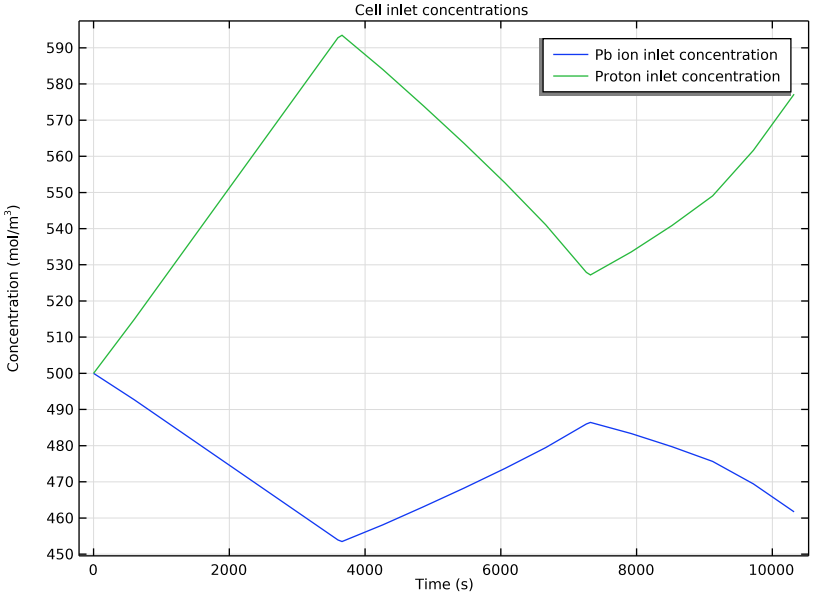


Figure 6: Inlet lead ion and proton concentrations versus time.

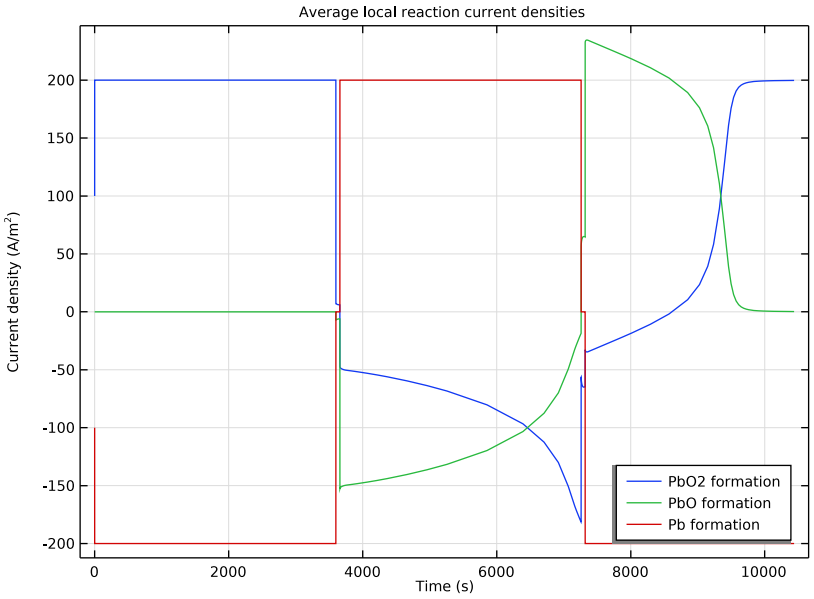


Figure 7: Local current densities of the electrode reactions. The PbO_2 and PbO reactions occurring on the positive electrode, Pb on the negative.

Figure 8 and Figure 9 depict the Pb^{2+} concentration distribution in the electrolyte at the end of the first charge and discharge step, respectively. Large gradients are present in the boundary layer close to the electrode surfaces.

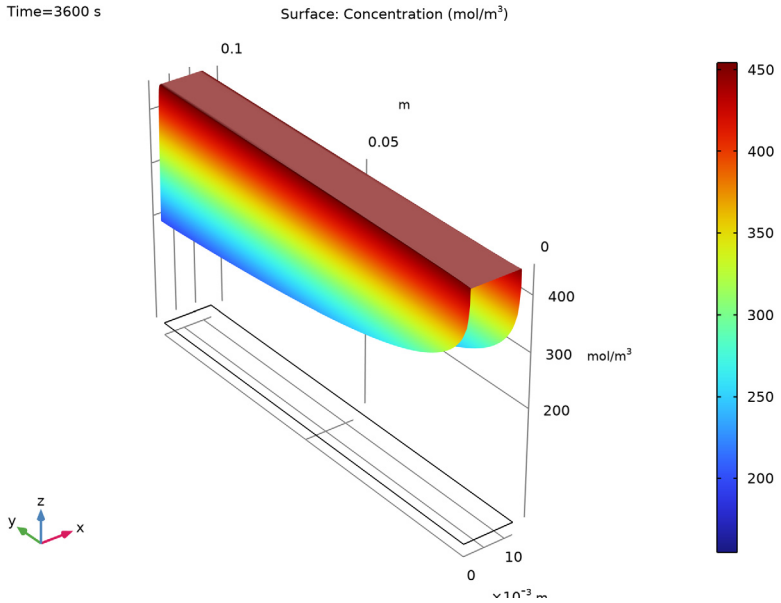


Figure 8: Lead ion concentration in the electrolyte at the end of the first charging cycle.

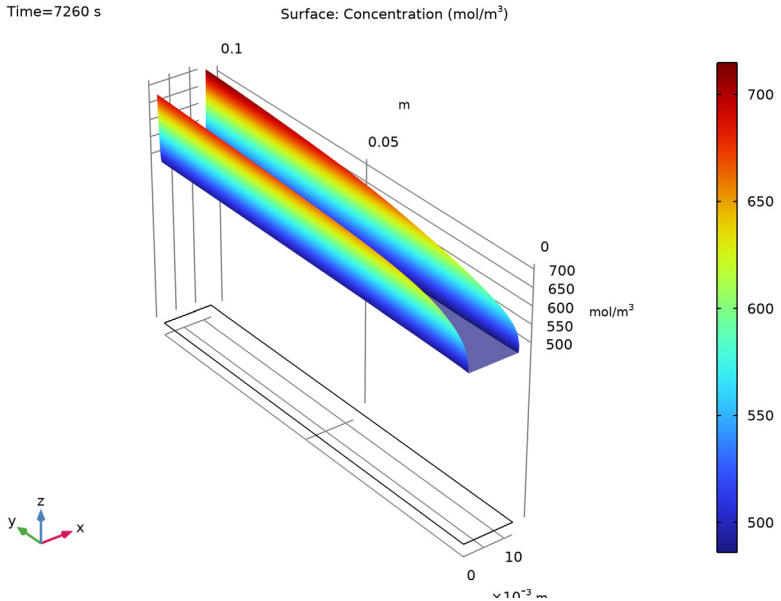


Figure 9: Lead ion concentration in the electrolyte at the end of the discharge cycle.

Figure 10 and Figure 11 plot the proton concentration distributions in the electrolyte at the end of the first charge and discharge step. Also for this species large gradients are present in the boundary layer close to the electrode surfaces.

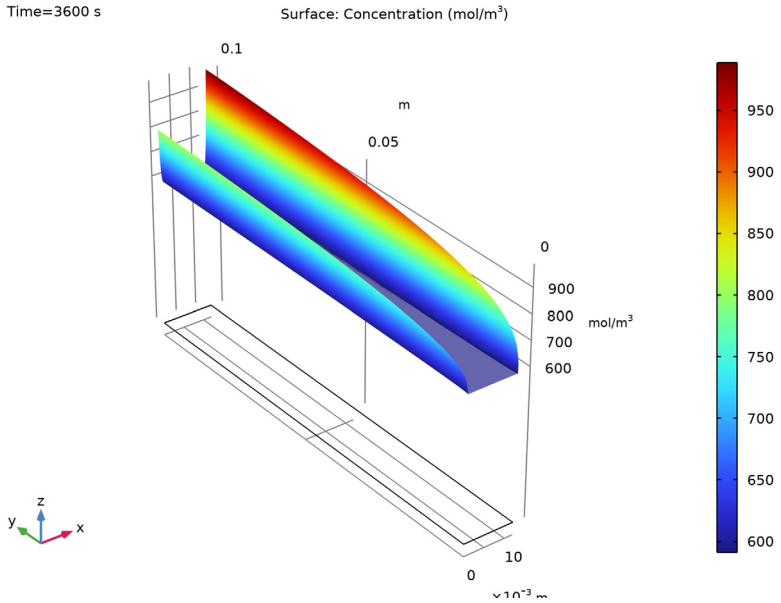


Figure 10: Hydrogen ion concentration in the electrolyte at the end of the first charging cycle.

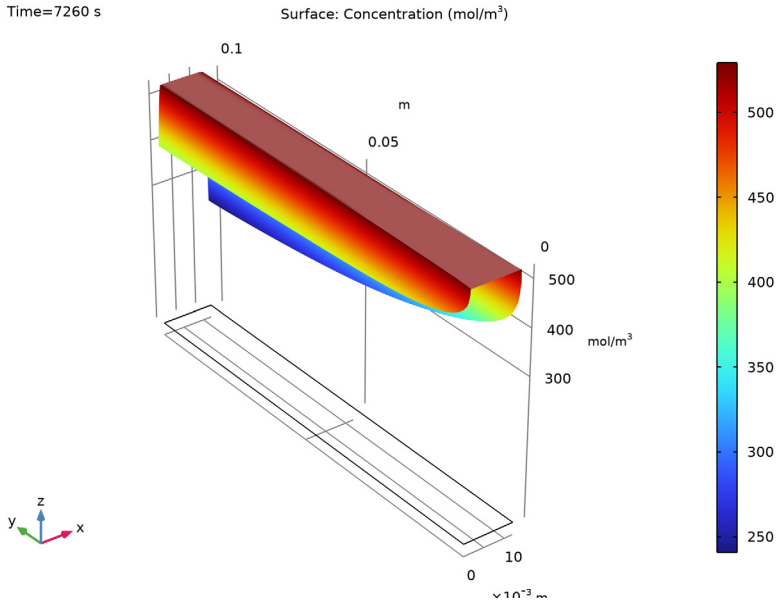


Figure 11: Hydrogen ion concentration at the end of the discharge cycle.

References

1. R. Willis, J. Collins, D. Stratton-Campbell, C. Low, D. Pletcher, and F. Walsh, "Developments in the Soluble Lead–acid Flow Battery," *J. Appl. Electrochem*, vol. 40, pp. 955–965, 2010.

2. A. Shah, R. Wills, and F. Walsh, "A Mathematical Model for the Soluble Lead–Acid Flow Battery," *J. Electrochem. Soc.*, vol. 157, pp. A589–A599, 2010.

3. J. Newman and K. Thomas-Alyea, *Electrochemical Systems*, p. 284, Table 11.1, John Wiley & Sons, 2004.

Application Library path: `Battery_Design_Module/Flow_Batteries/pb_flow_battery`

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

NEW

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

MODEL WIZARD

1 In the **Model Wizard** window, click **2D**.

2 In the **Select Physics** tree, select **Fluid Flow>Single-Phase Flow>Laminar Flow (spf)**.

3 Click **Add**.

4 Click **Study**.

5 In the **Select Study** tree, select **General Studies>Stationary**.

6 Click **Done**.

GEOMETRY 1

Rectangle 1 (r1)

1 In the **Geometry** toolbar, click **Rectangle**.

2 In the **Settings** window for **Rectangle**, locate the **Size and Shape** section.

3 In the **Width** text field, type `12[mm]`.

4 In the **Height** text field, type `10[cm]`.

5 Click **Build All Objects**.

GLOBAL DEFINITIONS

Parameters 1

1 In the **Model Builder** window, under **Global Definitions** click **Parameters 1**.

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

3 Click **Load from File**.

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

DEFINITIONS

Inlet

1 In the **Definitions** toolbar, click **Explicit**.

2 In the **Settings** window for **Explicit**, type `Inlet` in the **Label** text field.

3 Locate the **Input Entities** section. From the **Geometric entity level** list, choose **Boundary**.

4 Select Boundary 2 only.

Outlet

1 In the **Definitions** toolbar, click **Explicit**.

2 In the **Settings** window for **Explicit**, type `Outlet` in the **Label** text field.

3 Locate the **Input Entities** section. From the **Geometric entity level** list, choose **Boundary**.

4 Select Boundary 3 only.

Positive electrode

1 In the **Definitions** toolbar, click **Explicit**.

2 In the **Settings** window for **Explicit**, type `Positive electrode` in the **Label** text field.

3 Locate the **Input Entities** section. From the **Geometric entity level** list, choose **Boundary**.

4 Select Boundary 4 only.

Negative electrode

1 In the **Definitions** toolbar, click **Explicit**.

2 In the **Settings** window for **Explicit**, type `Negative electrode` in the **Label** text field.

3 Locate the **Input Entities** section. From the **Geometric entity level** list, choose **Boundary**.

4 Select Boundary 1 only.

MATERIALS

Use the material parameter values for water from the model library.

ADD MATERIAL

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

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

3 In the tree, select **Built-in>Water, liquid**.

4 Click **Add to Component** in the window toolbar.

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

LAMINAR FLOW (SPF)

Inlet 1

1 In the **Model Builder** window, under **Component 1 (comp1)** right-click **Laminar Flow (spf)** and choose **Inlet**.

2 In the **Settings** window for **Inlet**, locate the **Boundary Selection** section.

3 From the **Selection** list, choose **Inlet**.

4 Locate the **Boundary Condition** section. From the list, choose **Fully developed flow**.

5 Locate the **Fully Developed Flow** section. In the U_{av} text field, type `U_in`.

Outlet 1

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

2 In the **Settings** window for **Outlet**, locate the **Boundary Selection** section.

3 From the **Selection** list, choose **Outlet**.

4 Locate the **Pressure Conditions** section. Select the **Normal flow** check box.

MESH 1

The rectangular geometry makes a mapped mesh suitable for this problem.

Edge 1

1 In the **Mesh** toolbar, click **Edge**.

2 Select Boundaries 1 and 4 only.

Distribution 1

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

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

3 From the **Distribution type** list, choose **Predefined**.

4 In the **Number of elements** text field, type `30`.

5 In the **Element ratio** text field, type `5`.

Edge 2

1 In the **Mesh** toolbar, click **Edge**.

2 Select Boundaries 2 and 3 only.

Distribution 1

Right-click **Edge 2** and choose **Distribution**.

Mapped 1

In the **Mesh** toolbar, click **Mapped**.

Boundary Layers 1

1 In the **Mesh** toolbar, click **Boundary Layers**.

2 In the **Settings** window for **Boundary Layers**, click to expand the **Transition** section.

3 Clear the **Smooth transition to interior mesh** check box.

Boundary Layer Properties

1 In the **Model Builder** window, click **Boundary Layer Properties**.

2 Select Boundaries 1 and 4 only.

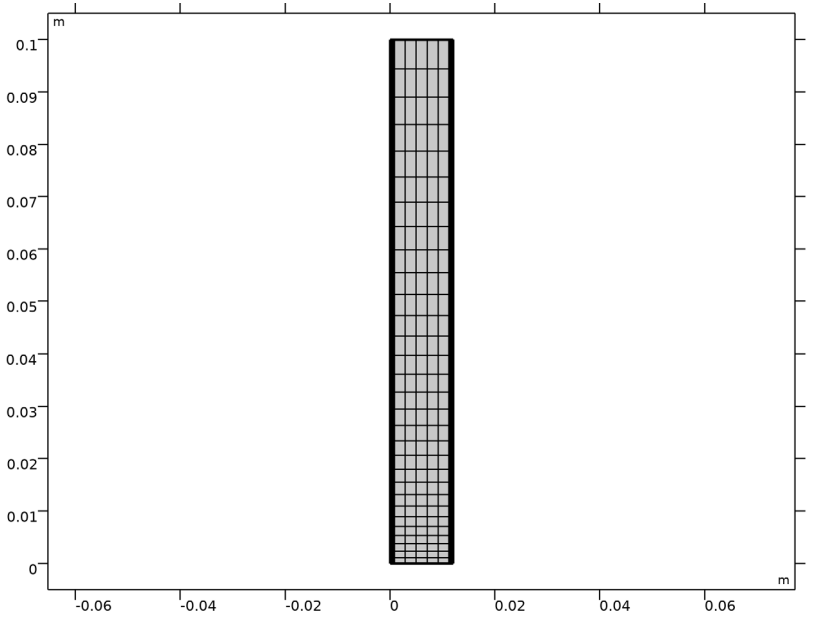
3 In the **Settings** window for **Boundary Layer Properties**, locate the **Layers** section.

4 From the **Thickness specification** list, choose **First layer**.

5 In the **Thickness** text field, type `5e-5`.

6 In the **Model Builder** window, right-click **Mesh 1** and choose **Build All**.

7 In the **Settings** window for **Mesh**, click **Build All**.



STUDY 1

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

RESULTS

Arrow Surface 1

1 In the **Model Builder** window, right-click **Pressure (spf)** and choose **Arrow Surface**.

2 In the **Settings** window for **Arrow Surface**, locate the **Arrow Positioning** section.

3 Find the **x grid points** subsection. In the **Points** text field, type `5`.

4 Locate the **Coloring and Style** section. From the **Color** list, choose **Black**.

5 In the **Pressure (spf)** toolbar, click **Plot**.

Flow

1 In the **Model Builder** window, under **Results** click **Pressure (spf)**.

2 In the **Settings** window for **2D Plot Group**, type `Flow` in the **Label** text field.

COMPONENT 1 (COMP1)

Now add the electrochemistry to the model, start by adding the appropriate physics interface.

ADD PHYSICS

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

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

3 In the tree, select **Electrochemistry>Tertiary Current Distribution, Nernst-Planck>Tertiary, Electroneutrality (tcd)**.

4 Click to expand the **Dependent Variables** section. Click **Add Concentration**.

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

cPbII
cH
cHSO4

6 Find the **Physics interfaces in study** subsection. In the table, clear the **Solve** check box for **Study 1**.

7 Click **Add to Component 1** in the window toolbar.

8 In the tree, select **Mathematics>ODE and DAE Interfaces>Global ODEs and DAEs (ge)**.

9 In the table, clear the **Solve** check box for **Study 1**.

10 Click **Add to Component 1** in the window toolbar.

11 In the **Home** toolbar, click **Add Physics** to close the **Add Physics** window.

ADD STUDY

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

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

3 Find the **Studies** subsection. In the **Select Study** tree, select **General Studies> Time Dependent**.

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

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

DEFINITIONS

Rectangle 1 (rect1)

Use a number of rectangle functions to set up the charge/discharge cycle that will be a function of time.

1 In the **Home** toolbar, click **Functions** and choose **Local>Rectangle**.
2 In the **Settings** window for **Rectangle**, type `charge1` in the **Function name** text field.
3 Locate the **Parameters** section. In the **Lower limit** text field, type `0`.
4 In the **Upper limit** text field, type `t_charge`.
5 Click to expand the **Smoothing** section. In the **Size of transition zone** text field, type `1`.

Rectangle 2 (rect2)

1 In the **Home** toolbar, click **Functions** and choose **Local>Rectangle**.
2 In the **Settings** window for **Rectangle**, type `discharge1` in the **Function name** text field.
3 Locate the **Parameters** section. In the **Lower limit** text field, type `t_charge+t_rest`.
4 In the **Upper limit** text field, type `t_charge+t_rest+t_discharge`.
5 Locate the **Smoothing** section. In the **Size of transition zone** text field, type `1`.

Rectangle 3 (rect3)

1 In the **Home** toolbar, click **Functions** and choose **Local>Rectangle**.
2 In the **Settings** window for **Rectangle**, type `charge2` in the **Function name** text field.
3 Locate the **Parameters** section. In the **Lower limit** text field, type `t_charge+t_rest+t_discharge+t_rest`.
4 In the **Upper limit** text field, type `2*t_charge+t_rest+t_discharge+t_rest`.
5 Locate the **Smoothing** section. In the **Size of transition zone** text field, type `1`.

Variables 1

Now the defined analytical functions can be used to set up variables on the negative and positive electrodes. Load the variables from a text file.

1 In the **Home** toolbar, click **Variables** and choose **Local Variables**.
2 In the **Settings** window for **Variables**, locate the **Variables** section.
3 Click **Load from File**.

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

(The `tcd.phisext` variable is the electric potential on the boundary.)

TERTIARY CURRENT DISTRIBUTION, NERNST-PLANCK (TCD)

1 In the **Model Builder** window, under **Component 1 (comp1)** click **Tertiary Current Distribution, Nernst-Planck (tcd)**.

2 In the **Settings** window for **Tertiary Current Distribution, Nernst-Planck**, locate the **Electrolyte Charge Conservation** section.

3 From the **From electroneutrality** list, choose **cHSO4**.

Species Charges 1

1 In the **Model Builder** window, under **Component 1 (comp1)>Tertiary Current Distribution, Nernst-Planck (tcd)** click **Species Charges 1**.

2 In the **Settings** window for **Species Charges**, locate the **Charge** section.

3 In the z_{cPbII} text field, type `2`.

4 In the z_{cH} text field, type `1`.

5 In the z_{cHSO4} text field, type `-1`.

Electrolyte 1

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

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

3 From the $\mathbf{u}$ list, choose **Velocity field (spf)**.

4 Locate the **Diffusion** section. In the D_{cPbII} text field, type `D_PbII`.

5 In the D_{cH} text field, type `D_H`.

6 In the D_{cHSO4} text field, type `D_HSO4`.

Inflow 1

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

2 In the **Settings** window for **Inflow**, locate the **Boundary Selection** section.

3 From the **Selection** list, choose **Inlet**.

4 Locate the **Concentration** section. In the $c_{0,\mathrm{cPbII}}$ text field, type `cPbII_in`.

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

6 Locate the **Boundary Condition Type** section. From the list, choose **Flux (Danckwerts)**.

Outflow 1

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

2 In the **Settings** window for **Outflow**, locate the **Boundary Selection** section.

3 From the **Selection** list, choose **Outlet**.

Negative Electrode

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

2 In the **Settings** window for **Electrode Surface**, type `Negative Electrode` in the **Label** text field.

3 Locate the **Boundary Selection** section. From the **Selection** list, choose **Negative electrode**.

Electrode Reaction 1

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

2 In the **Settings** window for **Electrode Reaction**, locate the **Stoichiometric Coefficients** section.

3 In the n text field, type `2`.

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

5 Locate the **Electrode Kinetics** section. From the **Exchange current density type** list, choose **Lumped multistep**.

6 In the $i_{0,ref}(T)$ text field, type `i0ref_neg`.

7 In the table, enter the following settings:

Electrolyte species	γ_i (1)
cPbII	1

8 In the α_a text field, type `1`.

9 In the α_c text field, type `1`.

Positive Electrode

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

2 In the **Settings** window for **Electrode Surface**, type `Positive Electrode` in the **Label** text field.

3 Locate the **Boundary Selection** section. From the **Selection** list, choose **Positive electrode**.

4 Locate the **Electrode Phase Potential Condition** section. From the **Electrode phase potential condition** list, choose **Average current density**.

5 In the $i_{l,average}$ text field, type `i_cycle`.

6 In the $\phi_{s,ext,init}$ text field, type `E0_pos`.

Electrode Reaction 1

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

2 In the **Settings** window for **Electrode Reaction**, locate the **Stoichiometric Coefficients** section.

3 In the n text field, type `2`.

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

5 In the ν_{cH} text field, type `-4`.

6 Locate the **Equilibrium Potential** section. In the $E_{eq,ref}(T)$ text field, type `Eeq_pos`.

7 Click to expand the **Reference Concentrations** section. In the table, enter the following settings:

Electrolyte species	Reference concentrations (mol/m^3)
cH	`0.5[M]`

8 Locate the **Electrode Kinetics** section. From the **Exchange current density type** list, choose **Lumped multistep**.

9 In the $i_{0,ref}(T)$ text field, type `i0ref_pos`.

10 In the table, enter the following settings:

Electrolyte species	γ_i (1)
cPbII	1
cH	1

Positive Electrode

In the **Model Builder** window, click **Positive Electrode**.

Electrode Reaction 2

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

Main Reaction

1 In the **Model Builder** window, under **Component 1 (comp1)>Tertiary Current Distribution, Nernst-Planck (tcd)>Positive Electrode** click **Electrode Reaction 1**.

2 In the **Settings** window for **Electrode Reaction**, type `Main Reaction` in the **Label** text field.

Side Reaction

1 In the **Model Builder** window, under **Component 1 (comp1)>Tertiary Current Distribution, Nernst-Planck (tcd)>Positive Electrode** click **Electrode Reaction 2**.

2 In the **Settings** window for **Electrode Reaction**, type `Side Reaction` in the **Label** text field.

3 Locate the **Stoichiometric Coefficients** section. In the n text field, type `2`.

4 In the ν_{cH} text field, type `-2`.

5 Locate the **Equilibrium Potential** section. From the E_{eq} list, choose **User defined**. Locate the **Electrode Kinetics** section. From the $i_{loc,expr}$ list, choose **User defined**. In the associated text field, type `i_Pb0`.

Positive Electrode

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

2 In the **Settings** window for **Electrode Surface**, click to expand the **Dissolving-Depositing Species** section.

3 Click + **Add** twice.

4 In the table, enter the following settings:

Species	Density (kg/m^3)	Molar mass (kg/mol)
Pb02	9.38[g/cm^3]	0.2392
Pb0	9.53[g/cm^3]	0.2232

Main Reaction

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

2 In the **Settings** window for **Electrode Reaction**, locate the **Stoichiometric Coefficients** section.

3 In the **Stoichiometric coefficients for dissolving-depositing species:** table, enter the following settings:

Species	Stoichiometric coefficient (1)
PbO2	-1
PbO	0

Side Reaction

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

2 In the **Settings** window for **Electrode Reaction**, locate the **Stoichiometric Coefficients** section.

3 In the **Stoichiometric coefficients for dissolving-depositing species:** table, enter the following settings:

Species	Stoichiometric coefficient (1)
PbO2	-1
PbO	1

Initial Values 1

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 *cPbII* text field, type `c0_PbII`.

4 In the *cH* text field, type `c0_H`.

5 In the *phil* text field, type `-E0_neg`.

GLOBAL DEFINITIONS

Default Model Inputs

Set up the temperature value used in the entire model.

1 In the **Model Builder** window, under **Global Definitions** click **Default Model Inputs**.

2 In the **Settings** window for **Default Model Inputs**, locate the **Browse Model Inputs** section.

3 In the tree, select **General>Temperature (K) - minput.T**.

4 Find the **Expression for remaining selection** subsection. In the **Temperature** text field, type `T`.

DEFINITIONS

The tank model is based on two ODEs and the integrals of the ion fluxes over the electrode boundaries.

Integration 1 (intop1)

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

2 In the **Settings** window for **Integration**, type `int_inlet` in the **Operator name** text field.

3 Locate the **Source Selection** section. From the **Geometric entity level** list, choose **Boundary**.

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

Integration 2 (intop2)

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

2 In the **Settings** window for **Integration**, type `int_outlet` in the **Operator name** text field.

3 Locate the **Source Selection** section. From the **Geometric entity level** list, choose **Boundary**.

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

GLOBAL ODES AND DAES (GE)

Global Equations 1

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

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

3 In the table, enter the following settings:

Name	f(u,ut,utt,t) (1)	Initial value (u_0) (1)	Initial value (u_t0) (1/s)	Description
cPbII_in	cPbII_int-L/V*(comp1.int_outlet(comp1.tcd.tflux_cPbIIy)-comp1.int_inlet(comp1.tcd.tflux_cPbIIy))	c0_PbII	0	Pb ion inlet concentration
cH_in	cH_int-L/V*(comp1.int_outlet(comp1.tcd.tflux_cHy)-comp1.int_inlet(comp1.tcd.tflux_cHy))	c0_H	0	Proton inlet concentration

4 Locate the **Units** section. Click **Select Dependent Variable Quantity**.

5 In the **Physical Quantity** dialog box, type `concentration` in the text field.

6 Click **Filter**.

7 In the tree, select **General>Concentration (mol/m^3)**.

8 Click **OK**.

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

10 Click **Select Source Term Quantity**.

11 In the **Physical Quantity** dialog box, type `reactionrate` in the text field.

12 Click **Filter**.

13 In the tree, select **Transport>Reaction rate (mol/(m^3*s))**.

14 Click **OK**.

DEFINITIONS

Use Boundary Probes to store certain variables for all time steps during the solver sequence, and to be able to plot these results while solving.

Boundary Probe 1 (bnd1)

This creates a probe for the electric potential at the positive electrode.

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

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

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

4 Locate the **Expression** section. In the **Expression** text field, type `tcd.phisext`.

Boundary Probe 2 (bnd2)

This creates a probe for the PbO2-current density at the positive electrode.

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

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

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

4 Locate the **Expression** section. In the **Expression** text field, type `tcd.iloc_er1`.

Boundary Probe 3 (bnd3)

This creates a probe for the PbO-current density at the positive electrode.

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

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

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

4 Locate the **Expression** section. In the **Expression** text field, type `tcd.iloc_er2`.

Boundary Probe 4 (bnd4)

This creates a probe for the local current density at the negative electrode.

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

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

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

4 Locate the **Expression** section. In the **Expression** text field, type `tcd.iloc_er1`.

Boundary Probe 5 (bnd5)

This creates probes for the average surface concentrations at the positive electrode.

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

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

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

4 Locate the **Expression** section. In the **Expression** text field, type `tcd.c_es2_PbO2`.

Boundary Probe 6 (bnd6)

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

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

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

4 Locate the **Expression** section. In the **Expression** text field, type `tcd.c_es2_PbO`.

STUDY 2

Now set up the solver. Do not solve for the velocity field; instead, use the velocity field from the first study.

Step 1: Time Dependent

1 In the **Model Builder** window, under **Study 2** click **Step 1: Time Dependent**.

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

3 In the **Output times** text field, type `range(0,600,3600) range(3660,600,7260) range(7320,600,10900)`.

4 Locate the **Physics and Variables Selection** section. In the table, clear the **Solve for** check box for **Laminar Flow (spf)**.

5 Click to expand the **Values of Dependent Variables** section. Find the **Values of variables not solved for** subsection. From the **Settings** list, choose **User controlled**.

6 From the **Method** list, choose **Solution**.

7 From the **Study** list, choose **Study 1, Stationary**.

8 From the **Selection** list, choose **1**.

Solution 2 (sol2)

Tweak the scales of the dependent variables manually to improve the accuracy of the solver.

1 In the **Study** toolbar, click **Show Default Solver**.

2 In the **Model Builder** window, expand the **Solution 2 (sol2)** node.

3 In the **Model Builder** window, expand the **Study 2>Solver Configurations> Solution 2 (sol2)>Dependent Variables 1** node, then click **Concentration (comp1.cH)**.

4 In the **Settings** window for **Field**, locate the **Scaling** section.

5 From the **Method** list, choose **Initial value based**.

6 In the **Model Builder** window, under **Study 2>Solver Configurations>Solution 2 (sol2)> Dependent Variables 1** click **Concentration (comp1.cPbII)**.

7 In the **Settings** window for **Field**, locate the **Scaling** section.

8 From the **Method** list, choose **Initial value based**.

9 In the **Model Builder** window, under **Study 2>Solver Configurations>Solution 2 (sol2)> Dependent Variables 1** click **Dissolving-depositing species concentration (comp1.tcd.es2.c)**.

10 In the **Settings** window for **Field**, locate the **Scaling** section.

11 From the **Method** list, choose **Manual**.

12 In the **Scale** text field, type `c0_PbII*V/(L*1[m^2])`.

13 In the **Model Builder** window, under **Study 2>Solver Configurations>Solution 2 (sol2)> Dependent Variables 1** click **comp1.ODE1**.

14 In the **Settings** window for **State**, locate the **Scaling** section.

15 From the **Method** list, choose **Initial value based**.

16 In the **Model Builder** window, under **Study 2>Solver Configurations>Solution 2 (sol2)** click **Time-Dependent Solver 1**.

17 In the **Settings** window for **Time-Dependent Solver**, click to expand the **Time Stepping** section.

The automatic initial step of the time-dependent solver is a fraction (0.1%) of the simulated end time. For better accuracy, specify a user-defined initial time step.

18 Select the **Initial step** check box. In the associated text field, type `0.01`.

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

RESULTS

Probe Values

1 In the **Model Builder** window, under **Results** click **Probe Plot Group 13**.

2 In the **Settings** window for **1D Plot Group**, type `Probe Values` in the **Label** text field.

1D Plot Group 14

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

2 In the **Settings** window for **1D Plot Group**, click to expand the **Title** section.

3 From the **Title type** list, choose **Manual**.

4 In the **Title** text area, type `Cell Potential vs. Time`.

5 Locate the **Plot Settings** section.

6 Select the **y-axis label** check box. In the associated text field, type `Voltage (V)`.

Table Graph 1

1 Right-click **1D Plot Group 14** and choose **Table Graph**.

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

3 From the **Plot columns** list, choose **Manual**.

4 In the **Columns** list, select **External electric potential (V), Boundary Probe 1**.

Cell Potential

1 In the **Model Builder** window, under **Results** click **1D Plot Group 14**.

2 In the **Settings** window for **1D Plot Group**, type `Cell Potential` in the **Label** text field.

3 In the **Cell Potential** toolbar, click  **Plot**.

4 Click the  **Zoom Extents** button in the **Graphics** toolbar.

1D Plot Group 15

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

2 In the **Settings** window for **1D Plot Group**, locate the **Title** section.

3 From the **Title type** list, choose **Manual**.

4 In the **Title** text area, type `Average local reaction current densities`.

5 Locate the **Plot Settings** section.

6 Select the **y-axis label** check box. In the associated text field, type `Current density (A/m<sup>2</sup>)`.

7 Locate the **Legend** section. From the **Position** list, choose **Lower right**.

Table Graph 1

1 Right-click **1D Plot Group 15** and choose **Table Graph**.

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

3 From the **Plot columns** list, choose **Manual**.

4 In the **Columns** list, choose **Local current density (A/m^2), Boundary Probe 2**, **Local current density (A/m^2), Boundary Probe 3**, and **Local current density (A/m^2), Boundary Probe 4**.

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

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

7 In the table, enter the following settings:

Legends
PbO2 formation
PbO formation
Pb formation

8 In the **1D Plot Group 15** toolbar, click **Plot**.

9 Click the **Zoom Extents** button in the **Graphics** toolbar.

Local Current Densities

1 In the **Model Builder** window, under **Results** click **1D Plot Group 15**.

2 In the **Settings** window for **1D Plot Group**, type `Local Current Densities` in the **Label** text field.

1D Plot Group 16

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

2 In the **Settings** window for **1D Plot Group**, locate the **Title** section.

3 From the **Title type** list, choose **Manual**.

4 In the **Title** text area, type `Average surface concentrations`.

5 Locate the **Plot Settings** section.

6 Select the **x-axis label** check box. In the associated text field, type `Time (s)`.

7 Select the **y-axis label** check box. In the associated text field, type `Electrode surface concentration (mol/m<sup>2</sup>)`.

Table Graph 1

1 Right-click **1D Plot Group 16** and choose **Table Graph**.

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

3 From the **Plot columns** list, choose **Manual**.

4 In the **Columns** list, choose **Dissolving-depositing species concentration , 1-component (mol/m^2), Boundary Probe 5** and **Dissolving-depositing species concentration , 2-component (mol/m^2), Boundary Probe 6**.

5 Locate the **Legends** section. Select the **Show legends** check box.

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

7 In the table, enter the following settings:

Legends
Pb02
Pb0

8 In the **1D Plot Group 16** toolbar, click **Plot**.

9 Click the **Zoom Extents** button in the **Graphics** toolbar.

Surface Concentrations

1 In the **Model Builder** window, under **Results** click **1D Plot Group 16**.

2 In the **Settings** window for **1D Plot Group**, type `Surface Concentrations` in the **Label** text field.

Electrolyte Concentrations

1 In the **Model Builder** window, under **Results** click **1D Plot Group 12**.

2 In the **Settings** window for **1D Plot Group**, type `Electrolyte Concentrations` in the **Label** text field.

3 Locate the **Title** section. From the **Title type** list, choose **Manual**.

4 In the **Title** text area, type `Cell inlet concentrations`.

5 Locate the **Plot Settings** section. Select the **x-axis label** check box.

6 Select the **y-axis label** check box. In the associated text field, type `Concentration (mol/m<sup>3</sup>)`.

2D Plot Group 17

1 In the **Home** toolbar, click **Add Plot Group** and choose **2D Plot Group**.

2 In the **Settings** window for **2D Plot Group**, locate the **Data** section.

3 From the **Dataset** list, choose **Study 2/Solution 2 (sol2)**.

4 From the **Time (s)** list, choose **3600**.

Surface 1

1 Right-click **2D Plot Group 17** and choose **Surface**.

2 In the **Settings** window for **Surface**, click **Replace Expression** in the upper-right corner of the **Expression** section. From the menu, choose **Component 1 (comp1)> Tertiary Current Distribution, Nernst-Planck>Species cH>cH - Concentration - mol/m³**.

Height Expression 1

1 Right-click **Surface 1** and choose **Height Expression**.

2 In the **2D Plot Group 17** toolbar, click **Plot**.

3 Click the **Zoom Extents** button in the **Graphics** toolbar.

H+ Concentration Distribution

1 In the **Model Builder** window, under **Results** click **2D Plot Group 17**.

2 In the **Settings** window for **2D Plot Group**, type `H+ Concentration Distribution` in the **Label** text field.

3 Locate the **Data** section. From the **Time (s)** list, choose **7260**.

4 In the **H+ Concentration Distribution** toolbar, click **Plot**.

5 Click the **Zoom Extents** button in the **Graphics** toolbar.

H+ Concentration Distribution 1

1 Right-click **H+ Concentration Distribution** and choose **Duplicate**.

2 In the **Settings** window for **2D Plot Group**, locate the **Data** section.

3 From the **Time (s)** list, choose **3600**.

Surface 1

1 In the **Model Builder** window, expand the **H+ Concentration Distribution 1** node, then click **Surface 1**.

2 In the **Settings** window for **Surface**, click **Replace Expression** in the upper-right corner of the **Expression** section. From the menu, choose **Component 1 (comp1)> Tertiary Current Distribution, Nernst-Planck>Species cPbII>cPbII - Concentration - mol/m³**.

3 In the **H+ Concentration Distribution 1** toolbar, click **Plot**.

4 Click the **Zoom Extents** button in the **Graphics** toolbar.

PbII Concentration Distribution

1 In the **Model Builder** window, under **Results** click **H+ Concentration Distribution 1**.

2 In the **Settings** window for **2D Plot Group**, type `PbII Concentration Distribution` in the **Label** text field.

3 Locate the **Data** section. From the **Time (s)** list, choose **7260**.

4 In the **PbII Concentration Distribution** toolbar, click **Plot**.

5 Click the **Zoom Extents** button in the **Graphics** toolbar.

PbO Surface Concentration

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

2 In the **Settings** window for **1D Plot Group**, type `PbO Surface Concentration` in the **Label** text field.

Line Graph 1

1. In the **PbO Surface Concentration** toolbar, click **Line Graph**.
2. In the **Settings** window for **Line Graph**, locate the **y-Axis Data** section.
3. In the **Expression** text field, type `tcd.c_es2_PbO`.
4. Locate the **Data** section. From the **Dataset** list, choose **Study 2/Solution 2 (sol2)**.
5. Locate the **Selection** section. From the **Selection** list, choose **Positive electrode**.