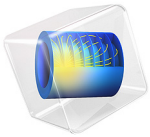

# 1D Isothermal Zinc-Silver Oxide Battery

## *Introduction*

Zinc-Silver oxide (Zn-AgO) batteries are used in different industries due to their high capacity per unit weight. Additionally, they have superior performance characteristics that include long operating life and low self-discharge (long shelf life). Larger size Zn-AgO batteries are used in applications where these performance characteristics are critical, such as in submarine, missile, and aerospace applications. Smaller size button cells are well suited for miniature power sources such as hearing aids, electronic watches and other low power devices. Mathematical models can be very useful for studying the performance of Zn-AgO batteries and for providing insights toward cell design.

In this example, discharge of a Zn-AgO battery (Ref. 1) is simulated using the Battery with Binary Electrolyte interface. The electrochemical reactions in the positive and negative electrodes lead to changes in porosity and species concentration in the electrodes. In this example, model analysis is done to relate the drop in cell voltage at the end of discharge to the concentration of species in the electrode, thereby indicating the limiting electrode in the cell.

## *Model Definition*

A 1D isothermal cell model for Zn-AgO battery is used. The positive electrode is composed of a mixture of AgO and $Ag_2O$, supported by a silver substrate. The negative electrode consists of Zn powder paste on a copper or silver substrate. The substrates act as current collectors. A separator material is used between the electrodes and the unit cell is filled with a solution of concentrated potassium hydroxide (KOH).

Figure 1 shows the 1D model geometry. It consists of three domains, the positive porous electrode, the separator, and the negative porous electrode.

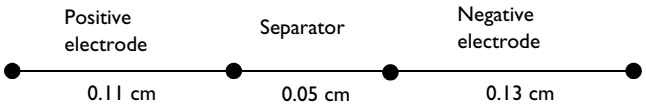


*Figure 1: 1D model geometry of a Zn-AgO unit cell.*

### ELECTROCHEMICAL REACTIONS

During charge and discharge, several electrochemical reactions occur in the porous electrodes. In the positive electrode, the following reactions are considered.

$$Ag_2O + H_2O + 2e^- \rightarrow 2Ag + 2OH^- \qquad E_{eq,1} = 0.342\,V \tag{1}$$

$$2AgO + H_2O + 2e^- \rightarrow Ag_2O + 2OH^- \qquad E_{eq,2} = 0.604\,V \tag{2}$$

The reaction considered in the negative electrode is as follows.

$$Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^- \qquad E_{eq,3} = -1.305\,V \tag{3}$$

The kinetic expressions for the electrode reactions are as follows (the subscripts 1, 2, and 3 refer to the above three reactions respectively),

$$i_{loc1} = i_{01}\left\{\left(\frac{c_{OH^-}}{c_{OH^-,ref}}\right)^2\left(\frac{c_{Ag}}{c_{Ag_2O}}\right)^2 \exp\left(\frac{n\alpha_{a1}F\eta_1}{RT}\right) - \left(\frac{c_{Ag_2O}}{c_{Ag_2O,ref}}\right)\exp\left(\frac{-n\alpha_{c1}F\eta_1}{RT}\right)\right\} \tag{4}$$

$$i_{loc2} = i_{02}\left\{\left(\frac{c_{OH^-}}{c_{OH^-,ref}}\right)^2\left(\frac{c_{Ag_2O}}{c_{AgO,ref}}\right) \exp\left(\frac{n\alpha_{a2}F\eta_2}{RT}\right) - \left(\frac{c_{AgO}}{c_{AgO,ref}}\right)^2\exp\left(\frac{-n\alpha_{c2}F\eta_2}{RT}\right)\right\} \tag{5}$$

$$i_{loc3} = i_{03}\left\{\left(\frac{c_{OH^-}}{c_{OH^-,ref}}\right)^2\left(\frac{c_{Zn}}{c_{Zn,ref}}\right) \exp\left(\frac{n\alpha_{a3}F\eta_3}{RT}\right) - \left(\frac{c_{ZnO}}{c_{Zn,ref}}\right)\exp\left(\frac{-n\alpha_{c3}F\eta_3}{RT}\right)\right\} \tag{6}$$

where $i_{loc}$ is the local current density, $i_0$ is the exchange current density, $\eta$ is the overpotential, $\alpha_a$ is the anodic transfer coefficient, and $\alpha_c$ is the cathodic transfer coefficient, respectively, of the three electrochemical reactions. $c_i$ is the concentration of species $i$ and $n$ is the number of electrons transferred.

The overpotential $\eta$ for each reaction is calculated from the electric potential ($\phi_s$), the electrolyte potential ($\phi_l$), and the equilibrium potential of the respective reaction ($E_{eq}$), as follows.

$$\eta = \phi_s - \phi_l - E_{eq} \tag{7}$$

## PHYSICS SETUP

The Battery with Binary Electrolyte interface describes the following processes:

- Electronic current conduction in the porous electrodes
- Ionic charge transport in the electrolyte present in the porous electrodes and separator
- Material transport in the electrolyte present in the porous electrodes and separator
- Electrochemical reaction kinetics in the porous electrodes

Nonintercalating particles, equilibrium potentials calculated using the Nernst equation, and concentration-dependent exchange current densities in the Butler–Volmer electrode kinetics, are used in the Battery with Binary Electrolyte interface. In the porous electrodes and the separator, the Bruggeman correction is used for the effective electrolyte salt diffusivity. The effective electrolyte conductivity is calculated from the following expression,

$$\sigma_{\mathrm{l,eff}} = \frac{\varepsilon_e F^2}{RT}(D_{\mathrm{K}^+} + D_{\mathrm{OH}^-})c_{\mathrm{l}} \tag{8}$$

where $\varepsilon_{\mathrm{e}}$ is the porosity (of either the porous electrodes or the separator), $c_{\mathrm{l}}$ is the electrolyte salt concentration ($c_{\mathrm{OH\text{-}}}$), and $D_i$ is the diffusion coefficient of species $i$.

The effective electrical conductivity in the porous electrodes is given as

$$\sigma_{\mathrm{s,eff}} = \sum_k m_k^{1.5}\sigma_{s,k} \tag{9}$$

where $\sigma_{\mathrm{s},k}$ and $m_k$ are the electrical conductivity and the mass fraction, respectively, of species $k$ in the solid phase of the porous electrodes.

The expressions for change in concentration of species ($Ag_2O$, AgO, and Ag) in the positive electrode are

$$\frac{\partial c_{\mathrm{Ag_2O}}}{\partial t} = \frac{1}{2F}a(i_{\mathrm{loc1}} - i_{\mathrm{loc2}}) \tag{10}$$

$$\frac{\partial c_{\mathrm{AgO}}}{\partial t} = \frac{1}{2F}a(2i_{\mathrm{loc2}}) \tag{11}$$

$$\frac{\partial c_{\mathrm{Ag}}}{\partial t} = -\frac{1}{2F}a(2i_{\mathrm{loc1}}) \tag{12}$$

where $a$ is the active specific surface area of the electrode.

Similarly, the expressions for change in concentration of species (Zn and ZnO) in the negative electrode are,

$$\frac{\partial c_{\mathrm{Zn}}}{\partial t} = -\frac{1}{2F}a i_{\mathrm{loc3}} \tag{13}$$

$$\frac{\partial c_{\mathrm{ZnO}}}{\partial t} = \frac{1}{2F}a i_{\mathrm{loc3}} \tag{14}$$

The reactants and products of the electrochemical reactions in the porous electrodes have different densities, thereby leading to porosity changes in the electrodes. The porosity change in the positive electrode is given by

$$\Delta\varepsilon_e = (c_{\mathrm{Ag_2O}} - c_{0,\,\mathrm{Ag_2O}}) \times \frac{MW_{\mathrm{Ag_2O}}}{\rho_{\mathrm{Ag_2O}}} + (c_{\mathrm{AgO}} - c_{0,\,\mathrm{AgO}}) \times \frac{MW_{\mathrm{AgO}}}{\rho_{\mathrm{AgO}}} + (c_{\mathrm{Ag}} - c_{0,\,\mathrm{Ag}}) \times \frac{MW_{\mathrm{Ag}}}{\rho_{\mathrm{Ag}}} \tag{15}$$

where $c_{0,i}$, $MW_i$, and $\rho_i$ are the initial concentration, molecular weight, and density of species $i$, respectively.

Similarly, the porosity change in the negative electrode is given as follows.

$$\Delta\varepsilon_e = (c_{\mathrm{Zn}} - c_{0,\,\mathrm{Zn}}) \times \frac{MW_{\mathrm{Zn}}}{\rho_{\mathrm{Zn}}} + (c_{\mathrm{ZnO}} - c_{0,\,\mathrm{ZnO}}) \times \frac{MW_{\mathrm{ZnO}}}{\rho_{\mathrm{ZnO}}} \tag{16}$$

The Dissolving-Depositing Species section of the Porous Electrode node is used for modeling the changes in concentration of species and porosity of the porous electrodes.

### BOUNDARY CONDITIONS

The negative electrode current collector boundary is set to a potential of 0 V (electric ground condition). At the positive electrode current collector boundary, a discharge current density pulse, as shown in Figure 2, is applied.

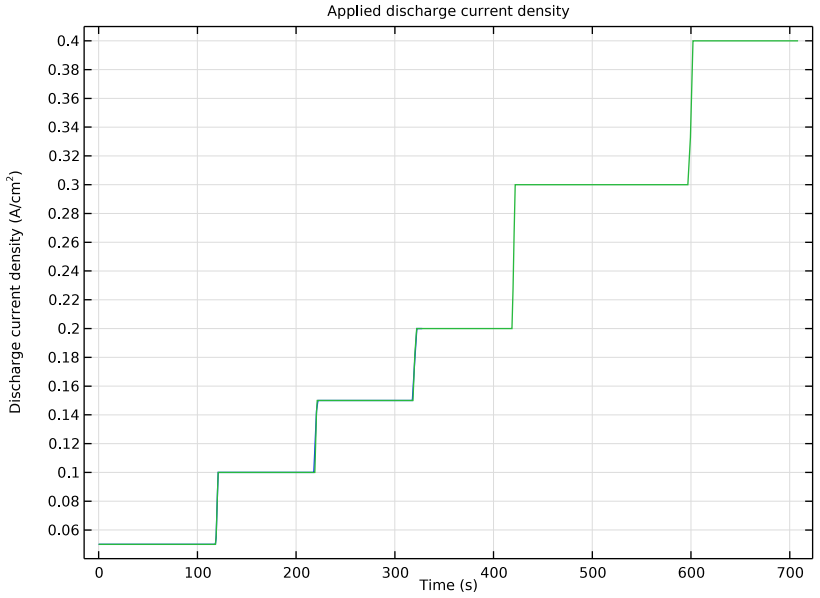


*Figure 2: The applied discharge current density as a function of time.*

A parametric study is done with two initial concentrations of Zn in the negative electrode, to demonstrate the limiting electrode in the cell for each case. The study includes a stop condition with a minimum voltage of 1.25 V.

## *Results and Discussion*

Figure 3 shows the cell voltage profiles for the two initial concentration values of Zn, for the applied discharge current density pulse. The voltage profiles indicate that for the high

value of the initial Zn concentration, the cell lasts for a longer time before reaching the minimum cell voltage.

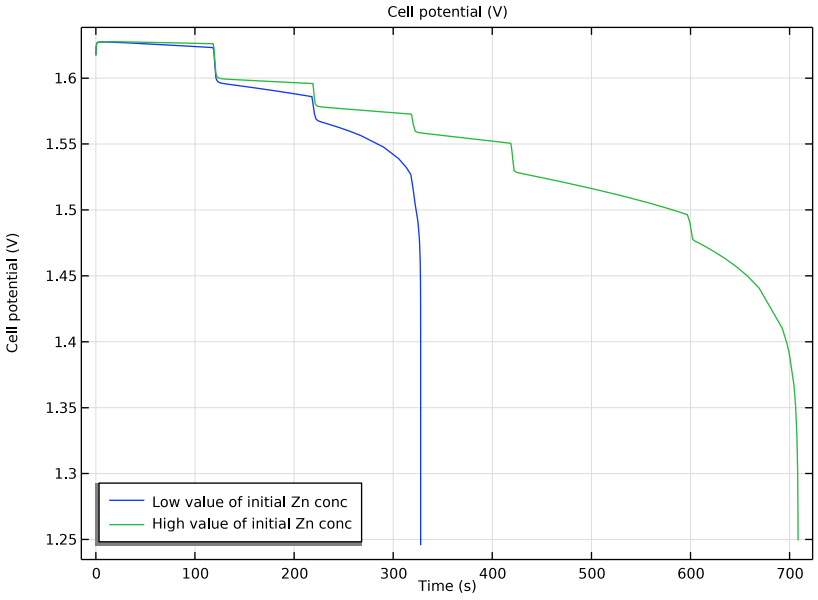


*Figure 3: Cell voltage profiles for the applied discharge current density pulse, for the two initial concentration of Zn.*

Figure 4 and Figure 5 show the variation of the species concentration in the electrodes during the applied discharge current density pulse, for the low value of the initial Zn concentration. Figure 4 shows the variation of concentration of Ag and AgO with time, across the thickness of the positive electrode. Similarly, Figure 5 shows the variation of concentration of Zn and ZnO with time, across the thickness of the negative electrode. For the low value of the initial Zn concentration in the negative electrode, it can be seen that the concentration of Zn drops close to 0 at the separator/negative electrode edge, at

the end of discharge. So, the sharp drop in the cell voltage toward the end of discharge is due to limitation of the negative electrode.

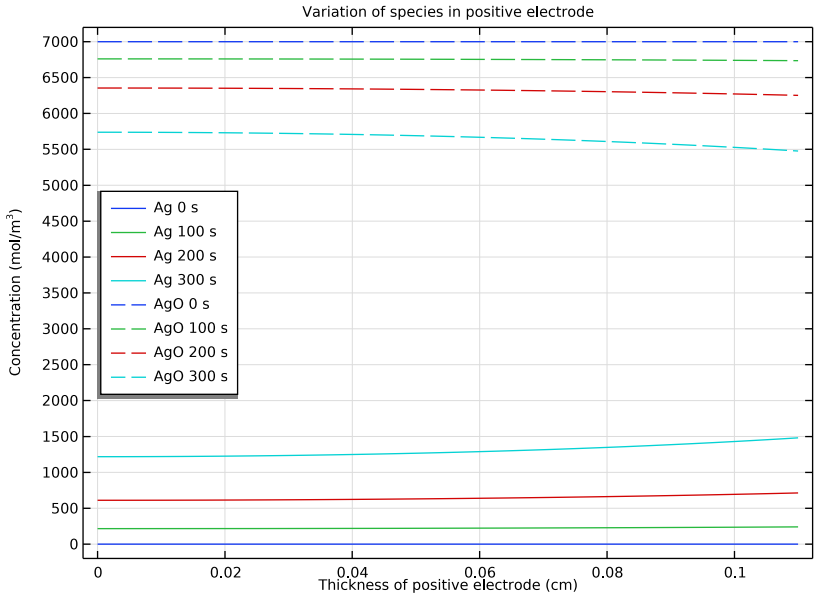


*Figure 4: Variation of species concentration in the positive electrode, for the low value of initial concentration of Zn.*

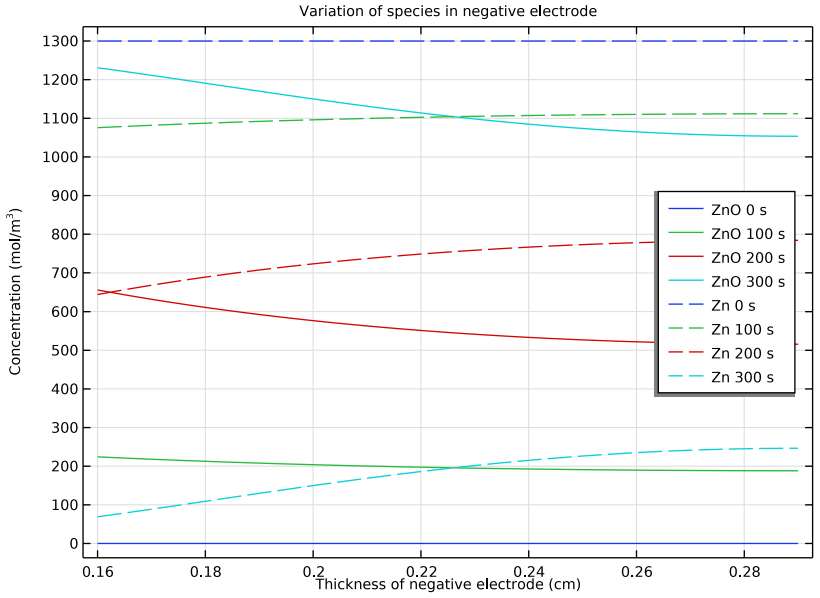


*Figure 5: Variation of species concentration in the negative electrode, for the low value of initial concentration of Zn.*

Figure 6 and Figure 7 similarly show the variation of the species concentration in the electrodes, for the high value of the initial Zn concentration. Figure 6 shows the variation of concentration of Ag and AgO with time, and Figure 7 shows the variation of concentration of Zn and ZnO with time, across the thickness of the positive and negative electrodes, respectively. For the high value of the initial Zn concentration in the negative electrode, it can be seen that the concentration of AgO drops close to 0 at the positive

electrode/separator edge, at the end of discharge. In this case, the sharp drop in the cell voltage toward the end of discharge is due to limitation of the positive electrode.

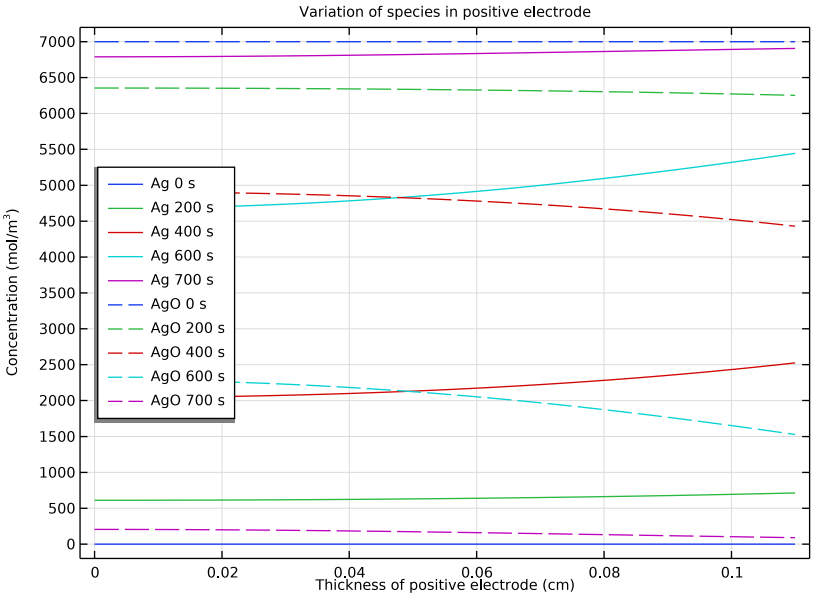


*Figure 6: Variation of species concentration in the positive electrode, for the high value of initial concentration of Zn.*

.

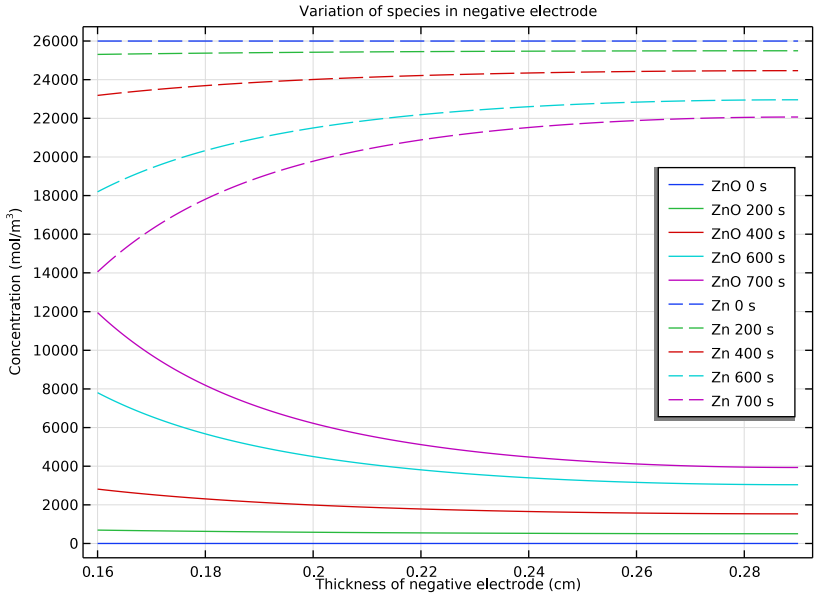


*Figure 7: Variation of species concentration in the negative electrode, for the high value of initial concentration of Zn.*

## *Reference*

1. F. Torabi, and A. Aliakbar, "A Single-Domain Formulation for Modeling and Simulation of Zinc Silver Oxide Batteries" *Journal of The Electrochemical Society*, vol. 159, no. 12, pp. A1986–A1992, 2012.

**Application Library path:** `Battery_Design_Module/Batteries,_General/zn_ago_battery_1d`

## *Modeling Instructions*

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

**NEW**

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

### MODEL WIZARD

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

2 In the **Select Physics** tree, select **Electrochemistry>Batteries>Battery with Binary Electrolyte (batbe)**.

3 Click **Add**.

4 Click **Study**.

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

6 Click **Done**.

### GLOBAL DEFINITIONS

Add model parameters, load cycle and model variables from text files.

*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 `zn_ago_battery_1d_parameters.txt`.

*Piecewise 1 (pw1)*

1 In the **Home** toolbar, click **Functions** and choose **Global>Piecewise**.

2 In the **Settings** window for **Piecewise**, type `I` in the **Function name** text field.

3 Locate the **Definition** section. From the **Smoothing** list, choose **Continuous function**.

4 In the **Size of transition zone** text field, type `0.01`.

5 Find the **Intervals** subsection. Click **Load from File**.

6 Browse to the model's Application Libraries folder and double-click the file `zn_ago_battery_1d_pulse.txt`.

7 Locate the **Units** section. In the **Arguments** text field, type `s`.

8 In the **Function** text field, type `A/cm^2`.

### DEFINITIONS

*Variables 1*

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 `zn_ago_battery_1d_variables.txt`.

### GEOMETRY 1

The geometry contains three domains, the positive porous electrode, the separator and the negative porous electrode. Create the geometry by specifying the coordinates of the boundaries.

*Interval 1 (i1)*

1 In the **Model Builder** window, under **Component 1 (comp1)** right-click **Geometry 1** and choose **Interval**.

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

3 From the **Specify** list, choose **Interval lengths**.

4 In the table, enter the following settings:

| Lengths (m) |
|---|
| L_AgO |
| L_sep |
| L_Zn |

5 In the **Home** toolbar, click **Build All**.

### DEFINITIONS

A boundary integration variable can be used to access the cell voltage at the end terminal during the computation.

*Integration 1 (intop1)*

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

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

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

4 Select Boundary 1 only.

### BATTERY WITH BINARY ELECTROLYTE (BATBE)

Start with setting up the physics in the battery interface. Set up the physics to model the porosity change in the porous electrodes, by specifying appropriate source terms and initial values. Note that the porosity of the separator remains constant.

1 In the **Model Builder** window, under **Component 1 (comp1)** click **Battery with Binary Electrolyte (batbe)**.

2 In the **Settings** window for **Battery with Binary Electrolyte**, locate the **Species** section.

3 In the $M_{An-}$ text field, type `M_OH`.

4 In the $M_{Cat+}$ text field, type `M_K`.

5 In the $M_0$ text field, type `M_H2O`.

*Separator 1*

1 In the **Model Builder** window, under **Component 1 (comp1)>** **Battery with Binary Electrolyte (batbe)** click **Separator 1**.

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

3 From the $\sigma_l$ list, choose **User defined**. In the associated text field, type `sigmaleff`.

4 From the $D_l$ list, choose **User defined**. In the associated text field, type `D_OH`.

5 From the $t_+$ list, choose **User defined**. In the associated text field, type `t_plus`.

6 From the $\mathrm{d}\ln f/\mathrm{d}\ln c_l$ list, choose **User defined**.

7 From the $\rho$ list, choose **User defined**. In the associated text field, type `rho`.

8 Locate the **Porous Matrix Properties** section. In the $\varepsilon_l$ text field, type `eps_e_sep`.

9 Locate the **Effective Transport Parameter Correction** section. From the **Electrolyte conductivity** list, choose **No correction**.

*Porous Electrode: AgO (positive electrode)*

Set up the positive electrode parameters. Use Dissolving-Depositing Species formulation for modeling the changes in porosity and species concentration in the positive electrode.

1 In the **Physics** toolbar, click **Domains** and choose **Porous Electrode**.

2 Select Domain 1 only.

3 In the **Settings** window for **Porous Electrode**, type `Porous Electrode: AgO (positive electrode)` in the **Label** text field.

4 Locate the **Electrolyte Properties** section. From the $\sigma_l$ list, choose **User defined**. In the associated text field, type `sigmaleff`.

5 From the $D_l$ list, choose **User defined**. In the associated text field, type `D_OH`.

6 From the $t_+$ list, choose **User defined**. In the associated text field, type `t_plus`.

7 From the $\mathrm{d}\ln f/\mathrm{d}\ln c_l$ list, choose **User defined**.

8 From the $\rho$ list, choose **User defined**. In the associated text field, type `rho`.

9 Locate the **Electrode Properties** section. In the $\sigma_s$ text field, type `sigmaseff_pos`.

10 Locate the **Particle Properties** section. From the list, choose **Nonintercalating particles**.

11 Locate the **Porous Matrix Properties** section. In the $\varepsilon_s$ text field, type `1-batbe.epsl`.

12 In the $\varepsilon_l$ text field, type `eps_e_pos`.

13 Locate the **Effective Transport Parameter Correction** section. From the **Electrolyte conductivity** list, choose **No correction**.

14 From the **Electrical conductivity** list, choose **No correction**.

15 Click to expand the **Dissolving-Depositing Species** section. Click + **Add**.

16 In the table, enter the following settings:

| Species | Density (kg/m^3) | Molar mass (kg/mol) |
|---|---|---|
| Ag2O | rho_Ag2O | MW_Ag2O |

17 Click + **Add**.

18 In the table, enter the following settings:

| Species | Density (kg/m^3) | Molar mass (kg/mol) |
|---|---|---|
| Ag0 | rho_Ag0 | MW_Ag0 |

19 Click + **Add**.

20 In the table, enter the following settings:

| Species | Density (kg/m^3) | Molar mass (kg/mol) |
|---|---|---|
| Ag | rho_Ag | MW_Ag |

### *Porous Electrode Reaction 1*

Set up the two electrode reactions for the positive electrode.

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

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

3 From the $E_{eq}$ list, choose **Nernst equation**.

4 In the $E_{eq,ref}(T)$ text field, type `Eeq1`.

5 In the $C_R$ text field, type `(c1/Coh_ref)^2*(cAg/cAg2O)^2`.

6 In the $C_O$ text field, type `cAg2O/cAg2O_init`.

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

8 From the **Exchange current density type** list, choose **From Nernst Equation**.

9 In the $i_{0,\mathrm{ref}}(T)$ text field, type `i01`.

10 In the $\alpha_a$ text field, type `alphaa1*n`.

11 Locate the **Active Specific Surface Area** section. From the **Active specific surface area** list, choose **User defined**. In the $a_v$ text field, type `a`.

12 Locate the **Stoichiometric Coefficients** section. In the $n$ text field, type `n`.

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

| Species | Stoichiometric coefficient (1) |
|---|---|
| Ag2O | -1 |
| AgO | 0 |
| Ag | 2 |

14 Click to expand the **Heat of Reaction** section. From the  list, choose **User defined**.

*Porous Electrode: AgO (positive electrode)*

In the **Model Builder** window, click **Porous Electrode: AgO (positive electrode)**.

*Porous Electrode Reaction 2*

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

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

3 From the $E_{\mathrm{eq}}$ list, choose **Nernst equation**.

4 In the $E_{\mathrm{eq,ref}}(T)$ text field, type `Eeq2`.

5 In the $C_{\mathrm{R}}$ text field, type `(cl/Coh_ref)^2*(cAg2O/cAgO_init)`.

6 In the $C_{\mathrm{O}}$ text field, type `max(cAgO/cAgO_init,1e-6)^2`.

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

8 From the **Exchange current density type** list, choose **From Nernst Equation**.

9 In the $i_{0,\mathrm{ref}}(T)$ text field, type `i02`.

10 In the $\alpha_a$ text field, type `alphaa2*n`.

11 Locate the **Active Specific Surface Area** section. From the **Active specific surface area** list, choose **User defined**. In the $a_v$ text field, type `a`.

12 Locate the **Stoichiometric Coefficients** section. In the $n$ text field, type `n`.

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

| Species | Stoichiometric coefficient (1) |
|---|---|
| Ag2O | 1 |
| AgO | -2 |
| Ag | 0 |

**14** Locate the **Heat of Reaction** section. From the  list, choose **User defined**.

*Porous Electrode: AgO (positive electrode)*

Set up the initial values for the positive electrode species.

In the **Model Builder** window, click **Porous Electrode: AgO (positive electrode)**.

*Initial Values for Dissolving-Depositing Species 1*

**1** In the **Physics** toolbar, click **Attributes** and choose **Initial Values for Dissolving-Depositing Species**.

**2** In the **Settings** window for **Initial Values for Dissolving-Depositing Species**, locate the **Initial Values for Dissolving-Depositing Species** section.

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

| Species | Concentration (mol/m^3) |
|---|---|
| Ag2O | `cAg2O_init` |
| AgO | `cAgO_init` |

*Porous Electrode: Zn (negative electrode)*

Set up the negative electrode parameters. Use Dissolving-Depositing Species formulation for modeling the changes in porosity and species concentration in the negative electrode.

**1** In the **Physics** toolbar, click **Domains** and choose **Porous Electrode**.

**2** In the **Settings** window for **Porous Electrode**, type `Porous Electrode: Zn (negative electrode)` in the **Label** text field.

**3** Select Domain 3 only.

**4** Locate the **Electrolyte Properties** section. From the $\sigma_l$ list, choose **User defined**. In the associated text field, type `sigmaleff`.

**5** From the $D_l$ list, choose **User defined**. In the associated text field, type `D_OH`.

**6** From the $t_+$ list, choose **User defined**. In the associated text field, type `t_plus`.

**7** From the $\mathrm{dln}f/\mathrm{dln}c_l$ list, choose **User defined**.

8 From the ρ list, choose **User defined**. In the associated text field, type `rho`.

9 Locate the **Electrode Properties** section. In the $\sigma_s$ text field, type `sigmaseff_neg`.

10 Locate the **Particle Properties** section. From the list, choose **Nonintercalating particles**.

11 Locate the **Porous Matrix Properties** section. In the $\varepsilon_s$ text field, type `1-batbe.epsl`.

12 In the $\varepsilon_l$ text field, type `eps_e_neg`.

13 Locate the **Effective Transport Parameter Correction** section. From the **Electrolyte conductivity** list, choose **No correction**.

14 From the **Electrical conductivity** list, choose **No correction**.

15 Locate the **Dissolving-Depositing Species** section. Click + **Add**.

16 In the table, enter the following settings:

| Species | Density (kg/m^3) | Molar mass (kg/mol) |
|---|---|---|
| Zn | rho_Zn | MW_Zn |

17 Click + **Add**.

18 In the table, enter the following settings:

| Species | Density (kg/m^3) | Molar mass (kg/mol) |
|---|---|---|
| ZnO | rho_ZnO | MW_ZnO |

*Porous Electrode Reaction 1*

Set up the electrode reaction at the negative electrode.

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

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

3 From the $E_{eq}$ list, choose **Nernst equation**.

4 In the $E_{eq,ref}(T)$ text field, type `Eeq3`.

5 In the $C_R$ text field, type `(cl/Coh_ref)^2*(cZn/cZn_init)`.

6 In the $C_O$ text field, type `cZnO/cZn_init`.

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

8 From the **Exchange current density type** list, choose **From Nernst Equation**.

9 In the $i_{0,ref}(T)$ text field, type `i03`.

10 In the $\alpha_a$ text field, type `alphaa3*n`.

11 Locate the **Active Specific Surface Area** section. From the **Active specific surface area** list, choose **User defined**. In the $a_v$ text field, type `a`.

12 Locate the **Stoichiometric Coefficients** section. In the $n$ text field, type `n`.

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

| Species | Stoichiometric coefficient (1) |
|---|---|
| Zn | 1 |
| ZnO | -1 |

14 Locate the **Heat of Reaction** section. From the  list, choose **User defined**.

*Porous Electrode: Zn (negative electrode)*

Set up the initial values for the negative electrode species.

In the **Model Builder** window, click **Porous Electrode: Zn (negative electrode)**.

*Initial Values for Dissolving-Depositing Species 1*

1 In the **Physics** toolbar, click **Attributes** and choose **Initial Values for Dissolving-Depositing Species**.

2 In the **Settings** window for **Initial Values for Dissolving-Depositing Species**, locate the **Initial Values for Dissolving-Depositing Species** section.

3 In the table, enter the following settings:

| Species | Concentration (mol/m^3) |
|---|---|
| Zn | `cZn_init` |

*Electric Ground 1*

Specify the boundary conditions. Ground the negative electrode and set up a current density at the positive electrode.

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

2 Select Boundary 4 only.

*Electrode Current Density 1*

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

2 Select Boundary 1 only.

3 In the **Settings** window for **Electrode Current Density**, locate the **Electrode Current Density** section.

4 In the $i_{n,s}$ text field, type `-I(t)`.

*Initial Values 1*

It is essential to provide appropriate initial values in the model.

1 In the **Model Builder** window, click **Initial Values 1**.

2 In the **Settings** window for **Initial Values**, locate the **Initial Values** section.

3 In the *phil* text field, type `-Eeq3`.

4 In the *cl* text field, type `cl_init`.

5 In the *phis* text field, type `Eeq2-Eeq3`.

*Initial Values 2*

1 In the **Physics** toolbar, click **Domains** and choose **Initial Values**.

2 Select Domains 2 and 3 only.

3 In the **Settings** window for **Initial Values**, locate the **Initial Values** section.

4 In the *phil* text field, type `-Eeq3`.

5 In the *cl* text field, type `cl_init`.

## 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`.

## STUDY 1

Set up a parametric study with two initial concentrations of Zn. Also include a stop condition with a minimum voltage of 1.25 V.

*Parametric Sweep*

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

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

3 Click **Add**.

4 In the table, enter the following settings:

| Parameter name | Parameter value list | Parameter unit |
|---|---|---|
| cZn_param (For parametric sweep) | 1 20 | |

*Step 1: Time Dependent*

1 In the **Model Builder** window, 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 0 1000.

*Solution 1 (sol1)*

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

2 In the **Model Builder** window, expand the **Solution 1 (sol1)** node.

3 In the **Model Builder** window, expand the **Study 1>Solver Configurations> Solution 1 (sol1)>Dependent Variables 1** node, then click **Dissolving-depositing species concentration (comp1.batbe.pce1.c)**.

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

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

6 In the **Scale** text field, type 10000.

7 In the **Model Builder** window, under **Study 1>Solver Configurations>Solution 1 (sol1)> Dependent Variables 1** click **Dissolving-depositing species concentration (comp1.batbe.pce2.c)**.

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

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

10 In the **Scale** text field, type 10000.

Store the actual steps taken by the solver to make sure to capture any sudden steep voltage changes.

11 In the **Model Builder** window, under **Study 1>Solver Configurations>Solution 1 (sol1)** click **Time-Dependent Solver 1**.

12 In the **Settings** window for **Time-Dependent Solver**, locate the **General** section.

13 From the **Times to store** list, choose **Steps taken by solver**.

14 Right-click **Study 1>Solver Configurations>Solution 1 (sol1)>Time-Dependent Solver 1** and choose **Stop Condition**.

15 In the **Settings** window for **Stop Condition**, locate the **Stop Expressions** section.

16 Click + **Add**.

17 In the table, enter the following settings:

| Stop expression | Stop if | Active | Description |
|---|---|---|---|
| `comp1.EndTerminal(comp1.phis)<1.25` | True (>=1) | √ | `Stop expression 1` |

18 Locate the **Output at Stop** section. From the **Add solution** list, choose **Steps before and after stop**.

19 Clear the **Add warning** check box.

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

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

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

23 In the **Study** toolbar, click = **Compute**.

## RESULTS

First plot the applied current density pulse (Figure 2) and the cell voltage (Figure 3).

### *Current Density*

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

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

3 Locate the **Data** section. From the **Dataset** list, choose **Study 1/ Parametric Solutions 1 (sol2)**.

### *Point Graph 1*

1 Right-click **Current Density** and choose **Point Graph**.

2 Select Boundary 1 only.

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

4 In the **Expression** text field, type `I(t)`.

5 In the **Unit** field, type `A/cm^2`.

### *Current Density*

1 In the **Model Builder** window, click **Current Density**.

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

3 Select the **y-axis label** check box. In the associated text field, type `Discharge current density (A/cm<sup>2</sup>)`.

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

5 In the **Title** text area, type `Applied discharge current density`.

6 In the **Current Density** toolbar, click **Plot**.

7 Right-click **Current Density** and choose **Duplicate**.

*Cell Voltage*

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

*Point Graph 1*

1 In the **Model Builder** window, expand the **Current Density 1** node, then click **Results> Cell Voltage>Point Graph 1**.

2 In the **Settings** window for **Point Graph**, click **Replace Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Component 1 (comp1)> Battery with Binary Electrolyte>phis - Electric potential - V**.

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

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

5 In the table, enter the following settings:

| Legends |
| --- |
| `Low value of initial Zn conc` |
| `High value of initial Zn conc` |

*Cell Voltage*

1 In the **Model Builder** window, click **Cell Voltage**.

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

3 In the **y-axis label** text field, type `Cell potential (V)`.

4 Locate the **Title** section. In the **Title** text area, type `Cell potential (V)`.

5 Locate the **Legend** section. From the **Position** list, choose **Lower left**.

6 In the **Cell Voltage** toolbar, click **Plot**.

*Species: Positive electrode (cZn_param = 1)*

Now plot the concentration of species in the positive and negative electrodes for the low value of initial Zn concentration (Figure 4 and Figure 5).

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

2 In the **Settings** window for **1D Plot Group**, type `Species: Positive electrode (cZn_param = 1)` in the **Label** text field.

3 Locate the **Data** section. From the **Dataset** list, choose **Study 1/ Parametric Solutions 1 (sol2)**.

4 From the **Parameter selection (cZn_param)** list, choose **First**.

5 From the **Time selection** list, choose **Interpolated**.

6 In the **Times (s)** text field, type `0 100 200 300`.

*Line Graph 1*

1 Right-click **Species: Positive electrode (cZn_param = 1)** and choose **Line Graph**.

2 Select Domain 1 only.

3 In the **Settings** window for **Line Graph**, click **Replace Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Component 1 (comp1)>Definitions> Variables>cAg - Concentration of Ag - mol/m³**.

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

5 In the **Expression** text field, type `x`.

6 From the **Unit** list, choose **cm**.

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

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

9 In the **Legend** text field, type `Ag eval(t,s) s`.

10 Right-click **Line Graph 1** and choose **Duplicate**.

*Line Graph 2*

1 In the **Model Builder** window, click **Line Graph 2**.

2 In the **Settings** window for **Line Graph**, click **Replace Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Component 1 (comp1)>Definitions> Variables>cAgO - Concentration of AgO - mol/m³**.

3 Click to expand the **Coloring and Style** section. From the **Color** list, choose **Cycle (reset)**.

4 Find the **Line style** subsection. From the **Line** list, choose **Dashed**.

5 Locate the **Legends** section. In the **Legend** text field, type `AgO eval(t,s) s`.

*Species: Positive electrode (cZn_param = 1)*

1 In the **Model Builder** window, click **Species: Positive electrode (cZn_param = 1)**.

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

3 Select the **x-axis label** check box. In the associated text field, type `Thickness of positive electrode (cm)`.

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

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

6 In the **Title** text area, type `Variation of species in positive electrode`.

7 Locate the **Legend** section. From the **Position** list, choose **Middle left**.

*Species: Negative electrode (cZn_param = 1)*

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

2 In the **Settings** window for **1D Plot Group**, type `Species: Negative electrode (cZn_param = 1)` in the **Label** text field.

3 Locate the **Data** section. From the **Dataset** list, choose **Study 1/ Parametric Solutions 1 (sol2)**.

4 From the **Parameter selection (cZn_param)** list, choose **First**.

5 From the **Time selection** list, choose **Interpolated**.

6 In the **Times (s)** text field, type `0 100 200 300`.

*Line Graph 1*

1 Right-click **Species: Negative electrode (cZn_param = 1)** and choose **Line Graph**.

2 Select Domain 3 only.

3 In the **Settings** window for **Line Graph**, click **Replace Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Component 1 (comp1)>Definitions> Variables>cZnO - Concentration of ZnO - mol/m³**.

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

5 In the **Expression** text field, type `x`.

6 From the **Unit** list, choose **cm**.

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

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

9 In the **Legend** text field, type `ZnO eval(t,s) s`.

10 Right-click **Line Graph 1** and choose **Duplicate**.

*Line Graph 2*

1 In the **Model Builder** window, click **Line Graph 2**.

2 In the **Settings** window for **Line Graph**, click **Replace Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Component 1 (comp1)>Definitions> Variables>cZn - Concentration of Zn - mol/m³**.

3 Locate the **Coloring and Style** section. From the **Color** list, choose **Cycle (reset)**.

4 Find the **Line style** subsection. From the **Line** list, choose **Dashed**.

5 Locate the **Legends** section. In the **Legend** text field, type `Zn eval(t,s) s`.

*Species: Negative electrode (cZn_param = 1)*

1 In the **Model Builder** window, click **Species: Negative electrode (cZn_param = 1)**.

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

3 Select the **x-axis label** check box. In the associated text field, type `Thickness of negative electrode (cm)`.

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

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

6 In the **Title** text area, type `Variation of species in negative electrode`.

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

*Species: Positive electrode (cZn_param = 20)*

Now plot the concentration of species in the positive and negative electrodes for the high value of initial Zn concentration (Figure 6 and Figure 7).

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

2 In the **Settings** window for **1D Plot Group**, type `Species: Positive electrode (cZn_param = 20)` in the **Label** text field.

3 Locate the **Data** section. From the **Dataset** list, choose **Study 1/ Parametric Solutions 1 (sol2)**.

4 From the **Parameter selection (cZn_param)** list, choose **Last**.

5 From the **Time selection** list, choose **Interpolated**.

6 In the **Times (s)** text field, type `0 200 400 600 700`.

*Line Graph 1*

1 Right-click **Species: Positive electrode (cZn_param = 20)** and choose **Line Graph**.

2 Select Domain 1 only.

3 In the **Settings** window for **Line Graph**, click **Replace Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Component 1 (comp1)>Definitions> Variables>cAg - Concentration of Ag - mol/m³**.

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

5 In the **Expression** text field, type `x`.

6 From the **Unit** list, choose **cm**.

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

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

9 In the **Legend** text field, type `Ag eval(t,s) s`.

10 Right-click **Line Graph 1** and choose **Duplicate**.

*Line Graph 2*

1 In the **Model Builder** window, click **Line Graph 2**.

2 In the **Settings** window for **Line Graph**, click **Replace Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Component 1 (comp1)>Definitions> Variables>cAgO - Concentration of AgO - mol/m³**.

3 Locate the **Coloring and Style** section. From the **Color** list, choose **Cycle (reset)**.

4 Find the **Line style** subsection. From the **Line** list, choose **Dashed**.

5 Locate the **Legends** section. In the **Legend** text field, type `AgO eval(t,s) s`.

*Species: Positive electrode (cZn_param = 20)*

1 In the **Model Builder** window, click **Species: Positive electrode (cZn_param = 20)**.

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

3 Select the **x-axis label** check box. In the associated text field, type `Thickness of positive electrode (cm)`.

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

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

6 In the **Title** text area, type `Variation of species in positive electrode`.

7 Locate the **Legend** section. From the **Position** list, choose **Middle left**.

*Species: Negative electrode (cZn_param = 20)*

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

2 In the **Settings** window for **1D Plot Group**, type `Species: Negative electrode (cZn_param = 20)` in the **Label** text field.

3 Locate the **Data** section. From the **Dataset** list, choose **Study 1/ Parametric Solutions 1 (sol2)**.

4 From the **Parameter selection (cZn_param)** list, choose **Last**.

5 From the **Time selection** list, choose **Interpolated**.

6 In the **Times (s)** text field, type `0 200 400 600 700`.

*Line Graph 1*

1 Right-click **Species: Negative electrode (cZn_param = 20)** and choose **Line Graph**.

2 Select Domain 3 only.

3 In the **Settings** window for **Line Graph**, click **Replace Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Component 1 (comp1)>Definitions> Variables>cZnO - Concentration of ZnO - mol/m³**.

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

5 In the **Expression** text field, type `x`.

6 From the **Unit** list, choose **cm**.

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

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

9 In the **Legend** text field, type `ZnO eval(t,s) s`.

10 Right-click **Line Graph 1** and choose **Duplicate**.

*Line Graph 2*

1 In the **Model Builder** window, click **Line Graph 2**.

2 In the **Settings** window for **Line Graph**, click **Replace Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Component 1 (comp1)>Definitions> Variables>cZn - Concentration of Zn - mol/m³**.

3 Locate the **Coloring and Style** section. From the **Color** list, choose **Cycle (reset)**.

4 Find the **Line style** subsection. From the **Line** list, choose **Dashed**.

5 Locate the **Legends** section. In the **Legend** text field, type `Zn eval(t,s) s`.

*Species: Negative electrode (cZn_param = 20)*

1 In the **Model Builder** window, click **Species: Negative electrode (cZn_param = 20)**.

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

3 Select the **x-axis label** check box. In the associated text field, type `Thickness of negative electrode (cm)`.

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

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

6 In the **Title** text area, type `Variation of species in negative electrode`.

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