



Model created in COMSOL Multiphysics 6.4

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 Ag₂O, 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.

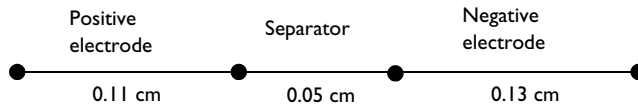
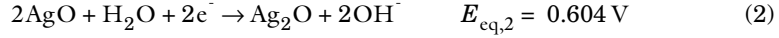


Figure 1: 1D model geometry of a Zn–AgO unit cell.

ELECTROCHEMICAL REACTIONS

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





The reaction considered in the negative electrode is as follows:



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

$$i_{\text{loc}1} = i_{01} \left\{ \left(\frac{c_{\text{OH}^-}}{c_{\text{OH}^-, \text{ref}}} \right)^2 \left(\frac{c_{\text{Ag}}}{c_{\text{Ag}_2\text{O}}} \right)^2 \exp\left(\frac{n\alpha_a 1 F \eta_1}{RT}\right) - \left(\frac{c_{\text{Ag}_2\text{O}}}{c_{\text{Ag}_2\text{O}, \text{ref}}} \right) \exp\left(\frac{-n\alpha_c 1 F \eta_1}{RT}\right) \right\} \quad (4)$$

$$i_{\text{loc}2} = i_{02} \left\{ \left(\frac{c_{\text{OH}^-}}{c_{\text{OH}^-, \text{ref}}} \right)^2 \left(\frac{c_{\text{Ag}_2\text{O}}}{c_{\text{AgO}, \text{ref}}} \right) \exp\left(\frac{n\alpha_a 2 F \eta_2}{RT}\right) - \left(\frac{c_{\text{AgO}}}{c_{\text{AgO}, \text{ref}}} \right)^2 \exp\left(\frac{-n\alpha_c 2 F \eta_2}{RT}\right) \right\} \quad (5)$$

$$i_{\text{loc}3} = i_{03} \left\{ \left(\frac{c_{\text{OH}^-}}{c_{\text{OH}^-, \text{ref}}} \right)^2 \left(\frac{c_{\text{Zn}}}{c_{\text{Zn}, \text{ref}}} \right) \exp\left(\frac{n\alpha_a 3 F \eta_3}{RT}\right) - \left(\frac{c_{\text{ZnO}}}{c_{\text{Zn}, \text{ref}}} \right) \exp\left(\frac{-n\alpha_c 3 F \eta_3}{RT}\right) \right\} \quad (6)$$

where i_{loc} is the local current density, i_0 is the exchange current density, η is the overpotential, α_a is the anodic transfer coefficient, and α_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 η for each reaction is calculated from the electric potential (ϕ_s), the electrolyte potential (ϕ_l), and the equilibrium potential of the respective reaction (E_{eq}), as follows:

$$\eta = \phi_s - \phi_l - E_{\text{eq}} \quad (7)$$

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:

$$\sigma_{l,\text{eff}} = \frac{\varepsilon_e F^2}{RT} (D_{K^+} + D_{\text{OH}^-}) c_1 \quad (8)$$

where ε_e is the porosity (of either the porous electrodes or the separator), c_1 is the electrolyte salt concentration (c_{OH^-}), and D_i is the diffusion coefficient of species i .

The effective electrical conductivity in the porous electrodes is given as

$$\sigma_{s,\text{eff}} = \sum_k m_k^{1.5} \sigma_{s,k} \quad (9)$$

where $\sigma_{s,k}$ 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

$$\frac{\partial c_{\text{Ag}_2\text{O}}}{\partial t} = \frac{1}{2F} a (i_{\text{loc}1} - i_{\text{loc}2}) \quad (10)$$

$$\frac{\partial c_{\text{AgO}}}{\partial t} = \frac{1}{2F} a (2i_{\text{loc}2}) \quad (11)$$

$$\frac{\partial c_{\text{Ag}}}{\partial t} = -\frac{1}{2F} a (2i_{\text{loc}1}) \quad (12)$$

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

$$\frac{\partial c_{\text{Zn}}}{\partial t} = -\frac{1}{2F} a i_{\text{loc}3} \quad (13)$$

$$\frac{\partial c_{\text{ZnO}}}{\partial t} = \frac{1}{2F} a i_{\text{loc}3} \quad (14)$$

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

$$\Delta \epsilon_e = (c_{\text{Ag}_2\text{O}} - c_{0, \text{Ag}_2\text{O}}) \times \frac{MW_{\text{Ag}_2\text{O}}}{\rho_{\text{Ag}_2\text{O}}} + (c_{\text{AgO}} - c_{0, \text{AgO}}) \times \frac{MW_{\text{AgO}}}{\rho_{\text{AgO}}} + (c_{\text{Ag}} - c_{0, \text{Ag}}) \times \frac{MW_{\text{Ag}}}{\rho_{\text{Ag}}} \quad (15)$$

where $c_{0,i}$, MW_i , and ρ_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:

$$\Delta \epsilon_e = (c_{\text{Zn}} - c_{0, \text{Zn}}) \times \frac{MW_{\text{Zn}}}{\rho_{\text{Zn}}} + (c_{\text{ZnO}} - c_{0, \text{ZnO}}) \times \frac{MW_{\text{ZnO}}}{\rho_{\text{ZnO}}} \quad (16)$$

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.

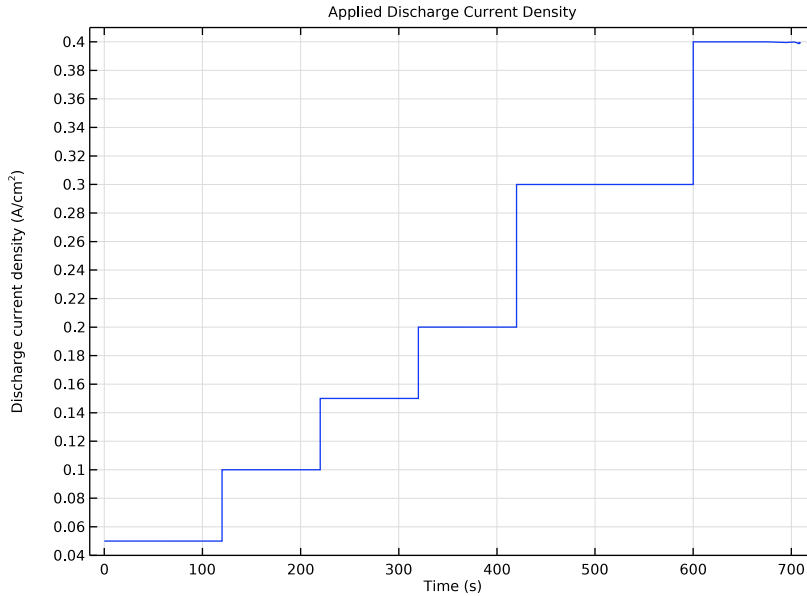


Figure 2: The applied discharge current density as a function of time.

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.

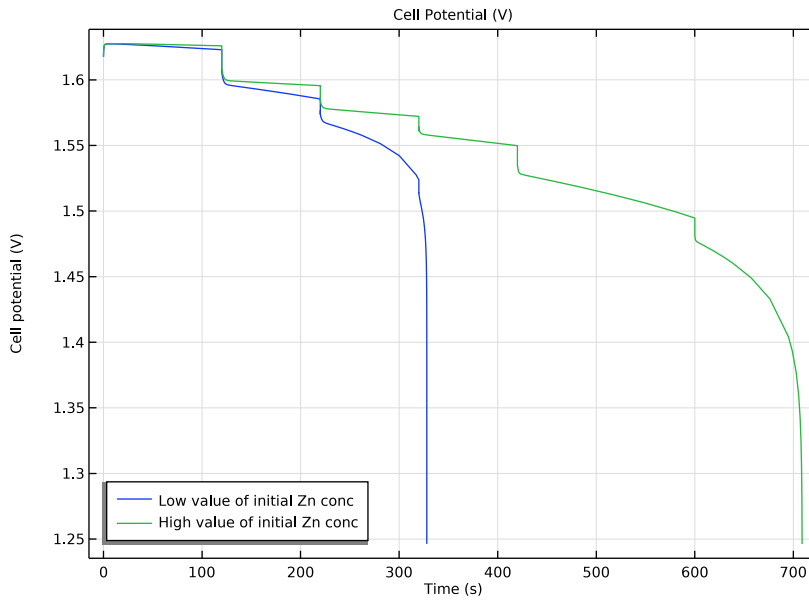


Figure 3: Cell voltage profiles for the applied discharge current density pulse, for the two initial concentration of Zn.

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.

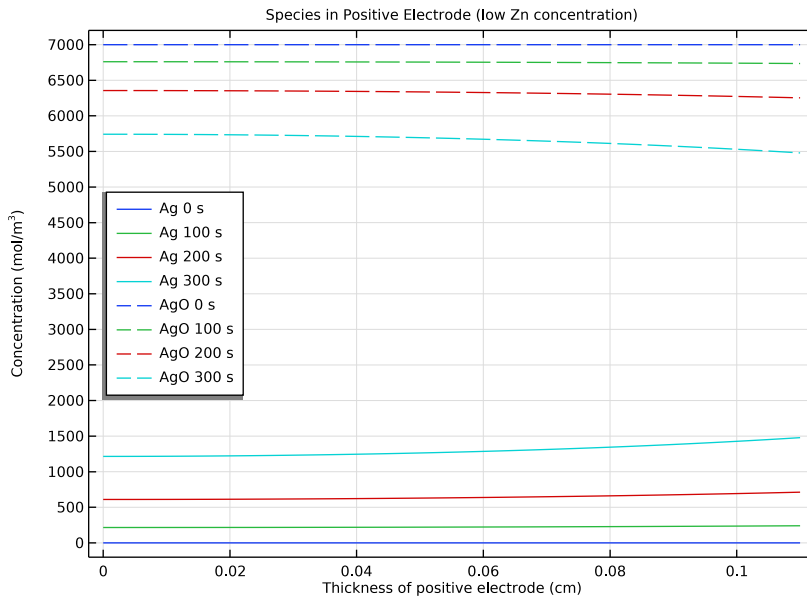


Figure 4: Variation of species concentration in the positive electrode, for the low value of initial concentration of Zn.

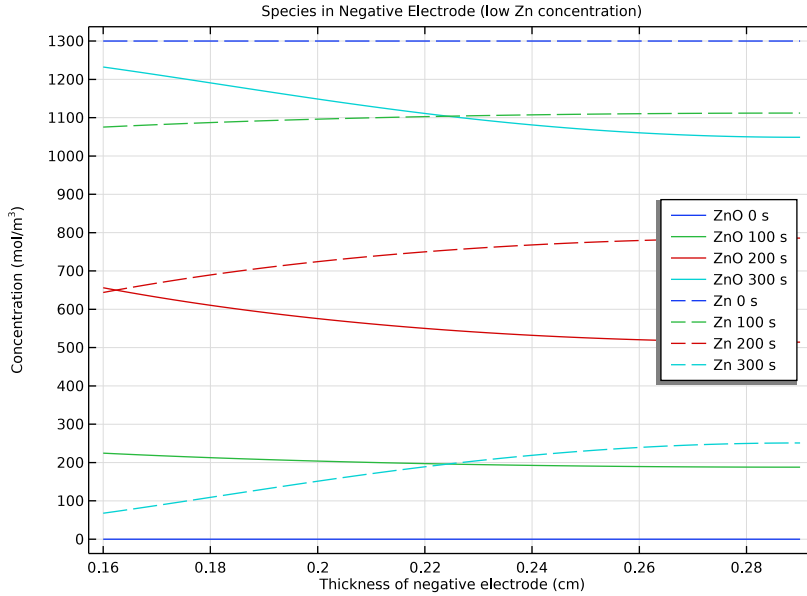


Figure 5: Variation of species concentration in the negative electrode, for the low value of initial concentration of Zn.

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.

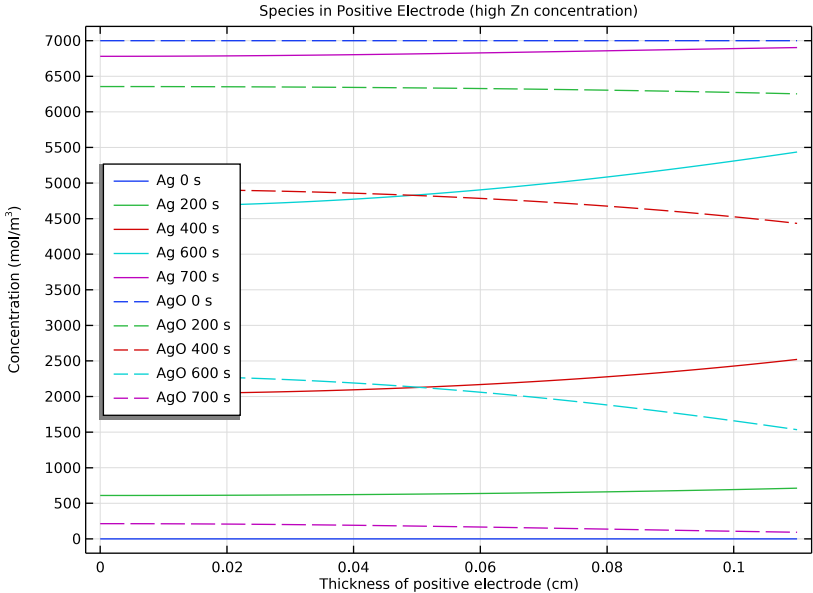


Figure 6: Variation of species concentration in the positive electrode, for the high value of initial concentration of Zn.

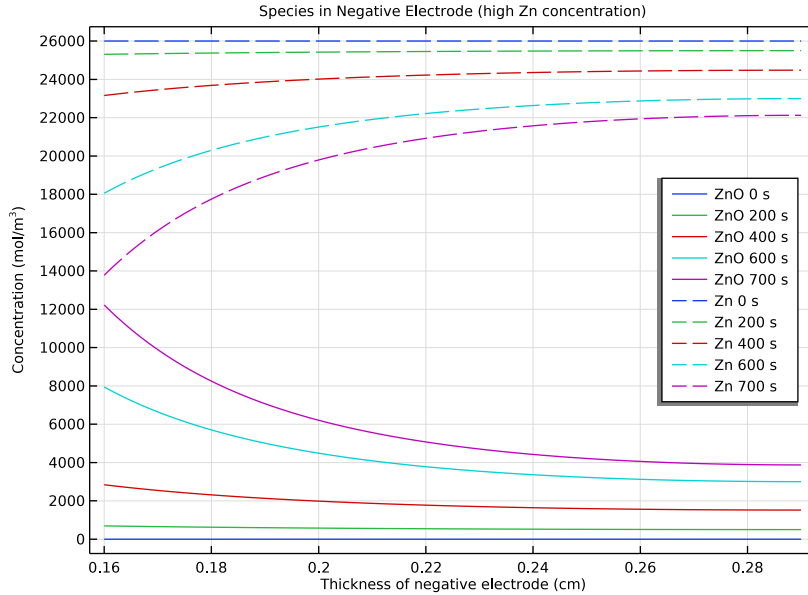


Figure 7: Variation of species concentration in the negative electrode, for the high value of initial concentration of Zn.

Reference


1. F. Torabi, and A. Aliakbar, "A Single-Domain Formulation for Modeling and Simulation of Zinc Silver Oxide Batteries" *J. Electrochem. Soc.*, 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  **ID**.
- 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`.

DEFINITIONS

Variables 1

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

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 **Cross-Sectional Area** section.
- 3 In the A_c text field, type A_{cell} .
- 4 Locate the **Species** section. In the M_{An-} text field, type M_{OH} .
- 5 In the M_{Cat+} text field, type M_K .
- 6 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 σ_1 list, choose **User defined**. In the associated text field, type σ_{1eff} .
- 4 From the D_1 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 $dlnf/dlnc_1$ list, choose **User defined**.
- 7 From the ρ list, choose **User defined**. In the associated text field, type ρ .
- 8 Locate the **Porous Matrix Properties** section. In the ϵ_1 text field, type ϵ_{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 In the **Settings** window for **Porous Electrode**, type Porous Electrode: AgO (positive electrode) in the **Label** text field.
- 3 Select Domain 1 only.
- 4 Locate the **Electrolyte Properties** section. From the σ_1 list, choose **User defined**. In the associated text field, type `sigma1eff`.
- 5 From the D_1 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 $d\ln f/d\ln c_1$ 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 σ_s text field, type `sigma1eff_pos`.
- 10 Locate the **Particle Properties** section. From the list, choose **Nonintercalating particles**.
- 11 Locate the **Porous Matrix Properties** section. In the ϵ_s text field, type `1-batbe.eps1`.
- 12 In the ϵ_1 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 **Electric 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)
AgO	rho_AgO	MW_AgO

- 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 $cAg20/cAg20_init$.
- 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 i01.
- 10 In the α_a text field, type $\alpha1 * n$.
- 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 (I)
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_{eq} list, choose **Nernst equation**.
- 4 In the $E_{eq,ref}(T)$ text field, type Eeq2.
- 5 In the C_R text field, type $(c1/Coh_ref)^2 * (cAg20/cAg0_init)$.
- 6 In the C_O text field, type $\max(cAg0/cAg0_init, 1e-6)^2$.
- 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 $i_{0,ref}(T)$ text field, type i02.
- 10 In the α_a text field, type α_a2*n .
- 11 Locate the **Active Specific Surface Area** section. From the **Active specific surface area** list, choose **User defined**. In the α_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 (I)
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–Depositng Species 1



- 1 In the **Physics** toolbar, click  **Attributes** and choose **Initial Values for Dissolving–Depositng Species**.
- 2 In the **Settings** window for **Initial Values for Dissolving–Depositng Species**, locate the **Initial Values for Dissolving–Depositng Species** section.

3 In the table, enter the following settings:

Species	Concentration (mol/m ³)
Ag ₂ O	cAg ₂ O_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 σ_1 list, choose **User defined**. In the associated text field, type sigma₁eff.
- 5 From the D_1 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 $d\ln f/d\ln c_1$ 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 σ_s text field, type sigma_seff_neg.
- 10 Locate the **Particle Properties** section. From the list, choose **Nonintercalating particles**.
- 11 Locate the **Porous Matrix Properties** section. In the ϵ_s text field, type 1-batbe.eps1.
- 12 In the ϵ_1 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 **Electric 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 $(c1/Coh_ref)^2 * (cZn/cZn_init)$.
- 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 α_a text field, type $\alpha3*n$.
- 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 (I)
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 I

- 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 I



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.

Load Cycle I

- 1 In the **Physics** toolbar, click  **Boundaries** and choose **Load Cycle**.
- 2 Select Boundary 1 only.
- 3 In the **Settings** window for **Load Cycle**, locate the **Load Type** section.
- 4 From the list, choose **Galvanostatic**.
- 5 Locate the **Continuation Conditions** section. Select the **Use elapsed time only** checkbox.
- 6 Locate the **Cycling Stop Condition** section. From the list, choose **Minimum voltage**.
- 7 In the E_{\min} text field, type 1.25[V].

Current I


- 1 In the **Physics** toolbar, click  **Attributes** and choose **Current**.
- 2 In the **Settings** window for **Current**, locate the **Current** section.
- 3 From the **Input type** list, choose **Step sequence**.
- 4 In the I_0 text field, type -0.05[A].
- 5 From the **Input type** list, choose **Step sequence**.
- 6 Click  **Load from File**.
- 7 Browse to the model's Application Libraries folder and double-click the file zn_ago_battery_1d_pulse.txt.

Initial Values 1

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

- 1 In the **Model Builder** window, under **Component 1 (comp1) > Battery with Binary Electrolyte (batbe)** click **Initial Values 1**.
- 2 In the **Settings** window for **Initial Values**, locate the **Initial Values** section.
- 3 In the *phil* text field, type $-E_{eq3}$.
- 4 In the *cl* text field, type *cl_init*.
- 5 In the *phis* text field, type $(E_{eq1}+E_{eq2})/2-E_{eq3}$.

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 $-E_{eq3}$.
- 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.

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 In the **Model Builder** window, click **Study 1**.
- 15 In the **Settings** window for **Study**, locate the **Study Settings** section.
- 16 Clear the **Generate default plots** checkbox.

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

RESULTS

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

Applied Discharge Current Density

- 1 In the **Results** toolbar, click  **ID Plot Group**.
- 2 In the **Settings** window for **ID Plot Group**, type Applied Discharge Current Density in the **Label** text field.

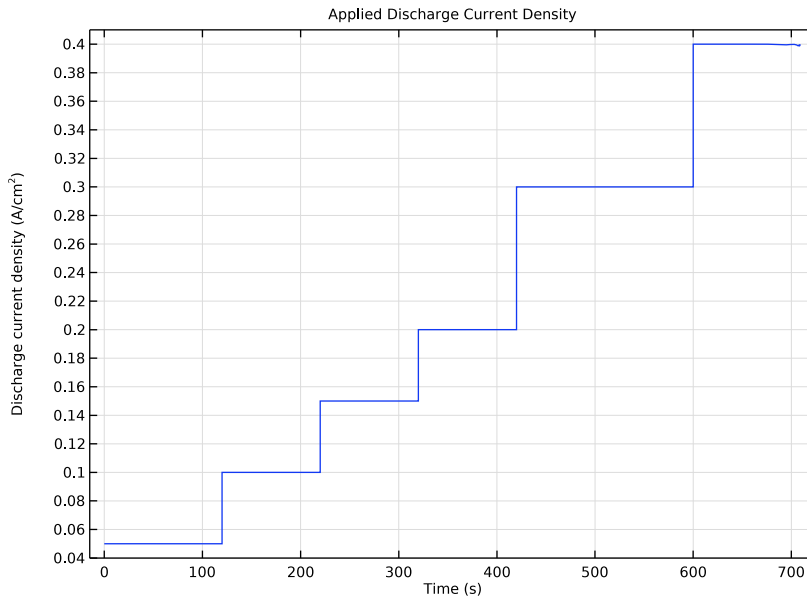
Point Graph 1

- 1 Right-click **Applied Discharge Current Density** and choose **Point Graph**.
- 2 Select Boundary 1 only.
- 3 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 > batbe.nls - Normal electrode current density - A/m²**.
- 4 Locate the **y-Axis Data** section. In the **Unit** field, type A/cm².

Applied Discharge Current Density

- 1 In the **Model Builder** window, click **Applied Discharge Current Density**.
- 2 In the **Settings** window for **ID Plot Group**, click to expand the **Title** section.
- 3 From the **Title type** list, choose **Label**.
- 4 Locate the **Plot Settings** section.
- 5 Select the **y-axis label** checkbox. In the associated text field, type Discharge current density (A/cm²).

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



Cell Potential (V)

- 1 Right-click **Applied Discharge Current Density** and choose **Duplicate**.
- 2 In the **Settings** window for **ID Plot Group**, type **Cell Potential (V)** 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 In the **Model Builder** window, expand the **Applied Discharge Current Density 1** node, then click **Results > Cell Potential (V) > 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 > phi_s - Electric potential - V**.
- 3 Click to expand the **Legends** section. Select the **Show legends** checkbox.
- 4 From the **Legends** list, choose **Manual**.


5 In the table, enter the following settings:

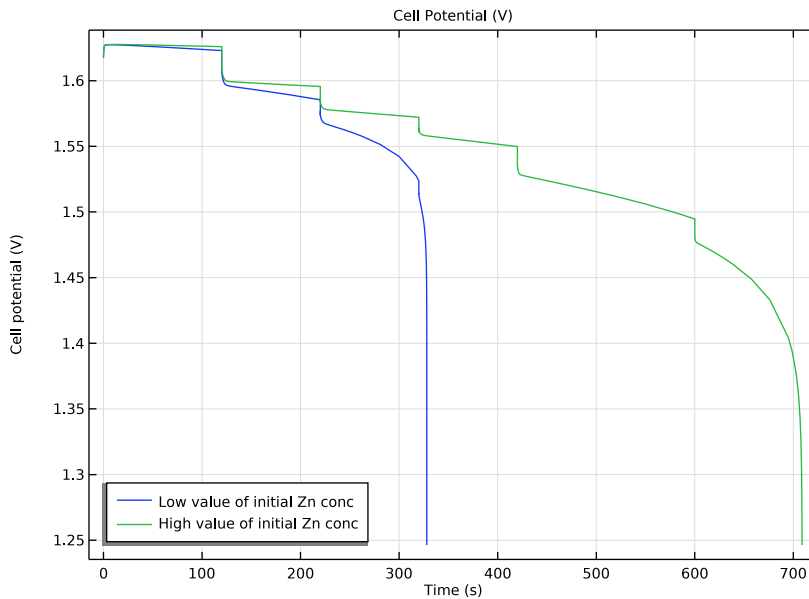
Legends

Low value of initial Zn conc

High value of initial Zn conc


Cell Potential (V)

- 1 In the **Model Builder** window, click **Cell Potential (V)**.
- 2 In the **Settings** window for **ID Plot Group**, locate the **Plot Settings** section.
- 3 In the **y-axis label** text field, type Cell potential (V).
- 4 Locate the **Legend** section. From the **Position** list, choose **Lower left**.
- 5 In the **Cell Potential (V)** toolbar, click  **Plot**.



Species in Positive Electrode (low Zn concentration)

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 **Results** toolbar, click  **ID Plot Group**.
- 2 In the **Settings** window for **ID Plot Group**, type Species in Positive Electrode (low Zn concentration) 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 in Positive Electrode (low Zn concentration)** 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** checkbox.
- 8 From the **Legends** list, choose **Evaluated**.
- 9 In the **Legend** text field, type $Ag_{eval}(t, s) \text{ s}$.

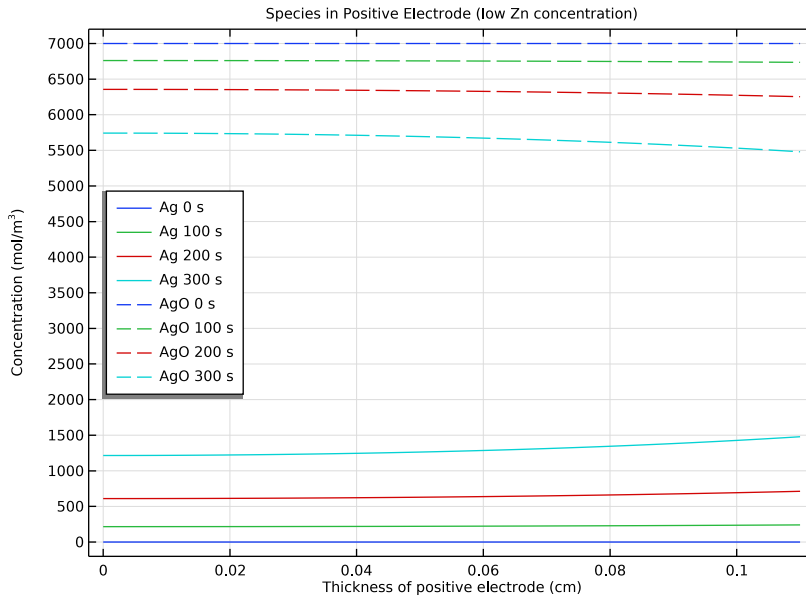
Line Graph 2

- 1 Right-click **Line Graph 1** and choose **Duplicate**.
- 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 From the **Color** list, choose **Cycle (reset)**.
- 6 Locate the **Legends** section. In the **Legend** text field, type $AgO_{eval}(t, s) \text{ s}$.


Species in Positive Electrode (low Zn concentration)

- 1 In the **Model Builder** window, click **Species in Positive Electrode (low Zn concentration)**.
- 2 In the **Settings** window for **ID Plot Group**, locate the **Title** section.
- 3 From the **Title type** list, choose **Label**.
- 4 Locate the **Plot Settings** section.

- 5 Select the **x-axis label** checkbox. In the associated text field, type Thickness of positive electrode (cm).
- 6 Select the **y-axis label** checkbox. In the associated text field, type Concentration (mol/m³).
- 7 Locate the **Legend** section. From the **Position** list, choose **Middle left**.
- 8 In the **Species in Positive Electrode (low Zn concentration)** toolbar, click  **Plot**.



Species in Negative Electrode (low Zn concentration)

- 1 In the **Results** toolbar, click  **ID Plot Group**.
- 2 In the **Settings** window for **ID Plot Group**, type Species in Negative Electrode (low Zn concentration) 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 in Negative Electrode (low Zn concentration)** 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 > cZn0 - Concentration of Zn0 - 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** checkbox.
- 8 From the **Legends** list, choose **Evaluated**.
- 9 In the **Legend** text field, type $Zn0 \text{ eval}(t, s) \text{ s}$.

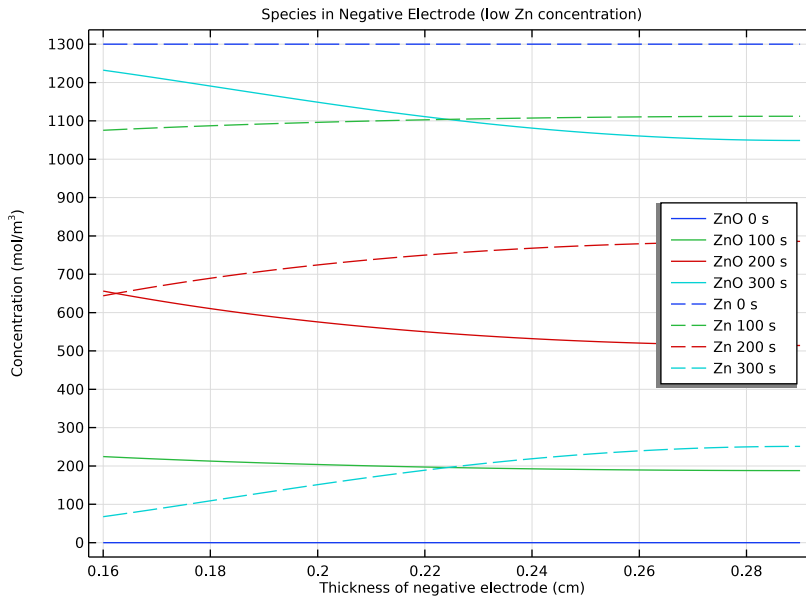
Line Graph 2

- 1 Right-click **Line Graph 1** and choose **Duplicate**.
- 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. Find the **Line style** subsection. From the **Line** list, choose **Dashed**.
- 4 From the **Color** list, choose **Cycle (reset)**.
- 5 Locate the **Legends** section. In the **Legend** text field, type $Zn \text{ eval}(t, s) \text{ s}$.

Species in Negative Electrode (low Zn concentration)

- 1 In the **Model Builder** window, click **Species in Negative Electrode (low Zn concentration)**.
- 2 In the **Settings** window for **ID Plot Group**, locate the **Title** section.
- 3 From the **Title type** list, choose **Label**.
- 4 Locate the **Plot Settings** section.
- 5 Select the **x-axis label** checkbox. In the associated text field, type Thickness of negative electrode (cm).
- 6 Select the **y-axis label** checkbox. In the associated text field, type Concentration (mol/m³).
- 7 Locate the **Legend** section. From the **Position** list, choose **Middle right**.

8 In the **Species in Negative Electrode (low Zn concentration)** toolbar, click  **Plot**.



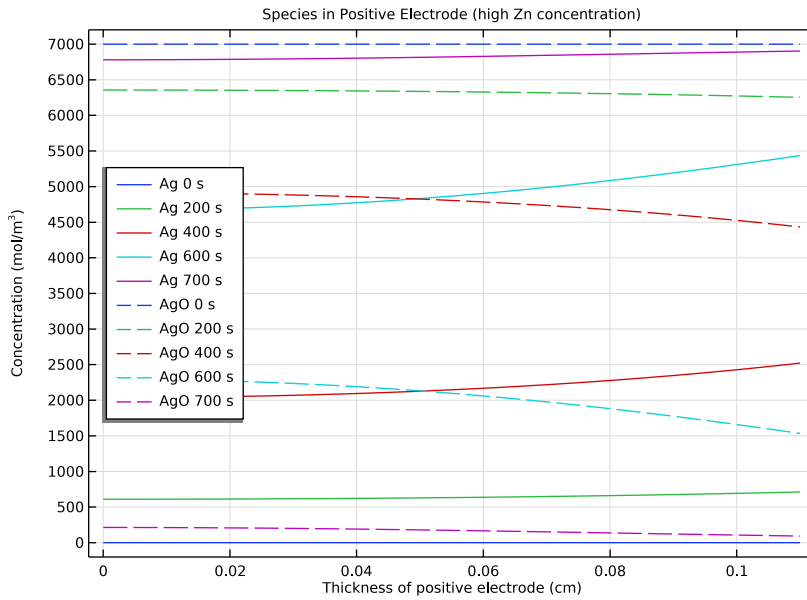
Species in Positive Electrode (low Zn concentration)

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).

Species in Positive Electrode (high Zn concentration)

- 1 In the **Model Builder** window, right-click **Species in Positive Electrode (low Zn concentration)** and choose **Duplicate**.
- 2 In the **Settings** window for **ID Plot Group**, type **Species in Positive Electrode (high Zn concentration)** in the **Label** text field.
- 3 Locate the **Data** section. From the **Parameter selection (cZn_param)** list, choose **Last**.
- 4 In the **Times (s)** text field, type 0 200 400 600 700.

5 In the **Species in Positive Electrode (high Zn concentration)** toolbar, click  **Plot**.



Species in Negative Electrode (high Zn concentration)

- 1 In the **Model Builder** window, right-click **Species in Negative Electrode (low Zn concentration)** and choose **Duplicate**.
- 2 In the **Settings** window for **ID Plot Group**, type **Species in Negative Electrode (high Zn concentration)** in the **Label** text field.
- 3 Locate the **Data** section. From the **Parameter selection (cZn_param)** list, choose **Last**.
- 4 In the **Times (s)** text field, type 0 200 400 600 700.

5 In the **Species in Negative Electrode (high Zn concentration)** toolbar, click  **Plot**.

