

ID 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 critical applications such as in submarines, missiles, 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 presented. The positive electrode is composed of a mixture of AgO and Ag₂O, supported by a silver substrate. The negative electrode is made of Zn powder pasted 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.

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

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

The reaction considered in the negative electrode is as follows.

$$Zn + 2OH \rightarrow ZnO + H_2O + 2e^{-1} \qquad E_{eq,3} = -1.305 V$$
 (3)

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

$$i_{\text{loc1}} = i_{01} \left\{ \left(\frac{c_{\text{OH}^-}}{c_{\text{OH}^-}, \text{ref}} \right)^2 \left(\frac{c_{\text{Ag}}}{c_{\text{Ag}_2\text{O}}} \right)^2 \exp\left(\frac{n\alpha_{a1}F\eta_1}{RT} \right) - \left(\frac{c_{\text{Ag}_2\text{O}}}{c_{\text{Ag}_2\text{O}}, \text{ref}} \right) \exp\left(\frac{-n\alpha_{c1}F\eta_1}{RT} \right) \right\}$$
(4)

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

$$i_{\rm loc3} = i_{03} \left\{ \left(\frac{c_{\rm OH^-}}{c_{\rm OH^-}, \rm ref} \right)^2 \left(\frac{c_{\rm Zn}}{c_{\rm Zn, ref}} \right) \exp\left(\frac{n\alpha_{a3}F\eta_3}{RT} \right) - \left(\frac{c_{\rm ZnO}}{c_{\rm Zn, ref}} \right) \exp\left(\frac{-n\alpha_{c3}F\eta_3}{RT} \right) \right\}$$
(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_1), and the equilibrium potential of the respective reaction (E_{eq}), as follows.

$$\eta = \phi_{\rm s} - \phi_{\rm l} - E_{\rm eq} \tag{7}$$

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

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

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

where ε_{e} is the porosity (of either the porous electrodes or the separator), c_{l} 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,

$$\sigma_{\rm s,eff} = \sum_{k} m_k^{1.5} \sigma_{s,k} \tag{9}$$

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 (Ag₂O, AgO and Ag) in the positive electrode are,

$$\frac{\partial c_{\mathrm{Ag}_2\mathrm{O}}}{\partial t} = \frac{1}{2F}a(i_{\mathrm{loc1}} - i_{\mathrm{loc2}}) \tag{10}$$

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

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

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,

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

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

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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

$$\Delta \varepsilon_{e} = (c_{Ag_{2}O} - c_{0, Ag_{2}O}) \times \frac{MW_{Ag_{2}O}}{\rho_{Ag_{2}O}} + (c_{AgO} - c_{0, AgO}) \times \frac{MW_{AgO}}{\rho_{AgO}} + (c_{Ag} - c_{0, AgO}) \times \frac{MW_{AgO}}{\rho_{AgO}}$$
(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.

$$\Delta \varepsilon_{e} = (c_{Zn} - c_{0,Zn}) \times \frac{MW_{Zn}}{\rho_{Zn}} + (c_{ZnO} - c_{0,ZnO}) \times \frac{MW_{ZnO}}{\rho_{ZnO}}$$
(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

- I 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

- I In the Model Builder window, under Global Definitions click Parameters I.
- 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 I (pwI)

- I In the Home toolbar, click f(X) 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/cm².

DEFINITIONS

Variables I

- I In the Home toolbar, click a= 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 I

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 I (i1)

- I In the Model Builder window, under Component I (compl) right-click Geometry I 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_Ag0	
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)

- I 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.

- I In the Model Builder window, under Component I (compl) click Battery with Binary Electrolyte (batbe).
- 2 In the Settings window for Battery with Binary Electrolyte, locate the Species section.
- **3** In the $M_{\rm An-}$ text field, type M_OH.
- **4** In the $M_{\text{Cat+}}$ text field, type M_K.
- **5** In the M_0 text field, type M_H20.

Separator 1

- I In the Physics toolbar, click Domains and choose Separator.
- **2** Select Domain 2 only.
- 3 In the Settings window for Separator, locate the Electrolyte Properties section.
- **4** From the σ_1 list, choose **User defined**. In the associated text field, type sigmaleff.
- **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 dln*f*/dln*c*₁ list, choose **User defined**.
- **8** From the ρ list, choose **User defined**. In the associated text field, type rho.
- **9** Locate the **Porous Matrix Properties** section. In the ε_1 text field, type eps_e_sep.

IO 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.

- I 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 σ_l list, choose **User defined**. In the associated text field, type sigmaleff.
- **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 dln*f*/dln*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. From the σ_s list, choose User defined. In the associated text field, type sigmaseff_pos.
- 10 Locate the Particle Properties section. From the list, choose Nonintercalating particles.
- II Locate the **Porous Matrix Properties** section. In the ε_s text field, type 1-batbe.eps1.
- **12** In the ε_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.
- IS Click to expand the Dissolving-Depositing Species section. Click + Add.

I6 In the table, enter the following settings:

Species	Density (kg/m^3)	Molar mass (kg/mol)
Ag20	rho_Ag20	MW_Ag20

17 Click + Add.

18 In the table, enter the following settings:

Species	Density (kg/m^3)	Molar mass (kg/mol)
Ag0	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 I

Set up the two electrode reactions for the positive electrode.

- I In the Model Builder window, click Porous Electrode Reaction I.
- **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 $C_{\rm R}$ text field, type (cl/Coh_ref)^2*(cAg/cAg20)^2.
- **6** In the $C_{\rm O}$ 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.
- **IO** In the α_a text field, type alphaa1*n.
- II 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.
- **I3** 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

- I 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 $C_{\rm R}$ text field, type (cl/Coh_ref)^2*(cAg20/cAg0_init).
- 6 In the $C_{\rm O}$ 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 $i_{0,\text{ref}}(T)$ text field, type i02.
- **IO** In the α_a text field, type alphaa2*n.
- II 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	-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 I

- I 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	cAg20_init	
AgO	cAg0_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.

- I 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_l list, choose **User defined**. In the associated text field, type sigmaleff.
- **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 dln//dlnc₁ 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. From the σ_s list, choose User defined. In the associated text field, type sigmaseff_neg.
- 10 Locate the Particle Properties section. From the list, choose Nonintercalating particles.
- II Locate the Porous Matrix Properties section. In the ϵ_s text field, type 1-batbe.epsl.
- **12** In the ε_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.

I5 Locate the **Dissolving-Depositing Species** section. Click + **Add**.

I6 In the table, enter the following settings:

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

I7 Click + Add.

18 In the table, enter the following settings:

Species	Density (kg/m^3)	Molar mass (kg/mol)
Zn0	rho_ZnO	MW_Zn0

Porous Electrode Reaction 1

Set up the electrode reaction at the negative electrode.

- I In the Model Builder window, click Porous Electrode Reaction I.
- **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 $E_{\text{eq.ref}}(T)$ text field, type Eeq3.
- 5 In the C_R text field, type (cl/Coh_ref)^2*(cZn/cZn_init).
- **6** In the C_{Ω} text field, type cZn0/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.

- **IO** In the α_a text field, type alphaa3*n.
- II 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

- I 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.

- I In the Physics toolbar, click Boundaries and choose Electric Ground.
- **2** Select Boundary 4 only.

Electrode Current Density 1

- I 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.

- I In the Model Builder window, click Initial Values I.
- 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

- I 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.

- I 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 I

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

- I 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	1 20	
sweep)		

Step 1: Time Dependent

- I In the Model Builder window, click Step I: 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 (soll)

- I In the Study toolbar, click **The Show Default Solver**.
- 2 In the Model Builder window, expand the Solution I (soll) node.
- 3 In the Model Builder window, expand the Study I>Solver Configurations> Solution I (soll)>Dependent Variables I node, then click Dissolvingdepositing species concentration (compl.batbe.pcel.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 I>Solver Configurations>Solution I (soll)> Dependent Variables I click Dissolvingdepositing species concentration (compl.batbe.pce2.c).
- 8 In the Settings window for Field, locate the Scaling section.
- 9 From the Method list, choose Manual.
- **IO** 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.

- II In the Model Builder window, under Study I>Solver Configurations>Solution I (soll) click Time-Dependent Solver I.
- 12 In the Settings window for Time-Dependent Solver, locate the General section.
- **I3** 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.

I7 In the table, enter the following settings:

Stop expression	Stop if	Active	Description
<pre>comp1.EndTerminal(comp1.phis)<1 .25</pre>	True (>=1)	\checkmark	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 I.
- 21 In the Settings window for Study, locate the Study Settings section.
- **2** 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

- I In the Home toolbar, click 🚛 Add Plot Group and choose ID Plot Group.
- 2 In the Settings window for ID Plot Group, type Current Density in the Label text field.
- 3 Locate the Data section. From the Dataset list, choose Study I/ Parametric Solutions I (sol2).

Point Graph 1

- I 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/cm².

Current Density

- I In the Model Builder window, click Current Density.
- 2 In the Settings window for ID 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/cm²).
- 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.

Cell Voltage

- I Right-click Current Density and choose Duplicate.
- 2 In the Settings window for ID Plot Group, type Cell Voltage in the Label text field.

Point Graph 1

- In the Model Builder window, expand the Current Density I node, then click Results> Cell Voltage>Point Graph I.
- 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 I (compl)> 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

- I In the Model Builder window, click Cell Voltage.
- 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 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).

- I In the Home toolbar, click 🚛 Add Plot Group and choose ID Plot Group.
- 2 In the Settings window for ID 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

- I Right-click Species: Positive electrode (cZn_param = I) 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 I (compl)>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.

Line Graph 2

- I Right-click Line Graph I 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 I (compl)>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 $(cZn_param = 1)$

- I In the Model Builder window, click Species: Positive electrode (cZn_param = I).
- 2 In the Settings window for ID 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/m³).
- 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 $(cZn_param = 1)$

- I In the Home toolbar, click 🚛 Add Plot Group and choose ID Plot Group.
- 2 In the Settings window for ID 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 I/ Parametric Solutions I (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 I

- I 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 I (compl)>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.

Line Graph 2

- I Right-click Line Graph I and choose Duplicate.
- 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 I (compl)>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 $(cZn_param = 1)$

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

- 2 In the Settings window for ID 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/m³).
- 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).

- I In the Home toolbar, click 🚛 Add Plot Group and choose ID Plot Group.
- 2 In the Settings window for ID 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 I/ Parametric Solutions I (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 I

- I 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 I (compl)>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.

Line Graph 2

- I Right-click Line Graph I 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 I (compl)>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 ($cZn_param = 20$)

- I In the Model Builder window, click Species: Positive electrode (cZn_param = 20).
- 2 In the Settings window for ID 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/m³).
- 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 ($cZn_param = 20$)

- I In the Home toolbar, click 🚛 Add Plot Group and choose ID Plot Group.
- 2 In the Settings window for ID 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

- I 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 I (compl)>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.

Line Graph 2

- I Right-click Line Graph I 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 I (compl)>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 ($cZn_param = 20$)

- I In the Model Builder window, click Species: Negative electrode (cZn_param = 20).
- 2 In the Settings window for ID 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/m³).
- 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.