

# ID Isothermal Lithium-Air Battery

# Introduction

Rechargeable metal-air batteries have recently attracted great interest mainly due to their high specific energy density. Lithium–air batteries have a theoretical energy density value of about 11400 Wh/kg, which is nearly 10 times greater than the lithium-ion batteries.

A unit cell of a lithium–air battery typically consists of a thin lithium sheet as the negative electrode, a porous carbon electrode filled with oxygen/air as the positive electrode, and a separator material between the electrodes. The organic electrolyte used consists of a dissolved lithium salt in an aprotic solvent. The oxidation of lithium at the anode and reduction of oxygen at the cathode induces a current flow.

In this model example, discharge of a lithium–air battery (Ref. 1) is simulated using the Lithium-Ion Battery interface. The transport of oxygen (from external air) in the porous carbon electrode is modeled using the Transport of Diluted Species in Porous Media interface. The electrochemical reaction of oxygen reduction in the carbon electrode leads to changes in concentration of the reaction product and electrode porosity. In this example, model analysis is done for a range of discharge current densities. A comparison of the oxygen concentration, porosity, and film thickness in the positive electrode at low and high discharge current densities is done to understand their effect on the cell voltage profiles. This model can be used for studying the performance of lithium–air batteries and for providing insights toward cell design.

# Model Definition

A 1D isothermal cell model for lithium–air battery is presented. Figure 1 shows the 1D model geometry. It consists of two domains, the separator, and the positive porous carbon electrode filled with oxygen. The lithium metal negative electrode is modeled as a boundary. The unit cell is filled with an organic electrolyte solution.



Figure 1: 1D model geometry of a lithium-air unit cell.

# ELECTROCHEMICAL REACTIONS

The porous carbon electrode provides a site for the electrochemical reduction of oxygen. During operation, oxygen from the external air dissolves in the electrolyte, moves through the pores of the positive electrode and reacts with lithium ions at the active site. The reaction considered at the positive electrode is

$$2\mathrm{Li}^{+} + \mathrm{O}_{2} + 2\mathrm{e}^{-} \rightarrow \mathrm{Li}_{2}\mathrm{O}_{2} \qquad E_{\mathrm{eq}} = 2.96\,\mathrm{V} \tag{1}$$

The reaction product  $(Li_2O_2)$  in the positive electrode is insoluble in the organic electrolyte (beyond its solubility limit in the electrolyte) and deposits as a film on the active surface area in the porous electrode. The kinetic expression for the above electrode reaction is

$$i_{\rm loc} = nF \left\{ k_{\rm a} c_{\rm Li_2O_2} \exp\left(\frac{0.5nF\eta}{RT}\right) - k_{\rm c} (c_{\rm Li^+})^2 c_{\rm O_2} \exp\left(\frac{-0.5nF\eta}{RT}\right) \right\}$$
(2)

where  $i_{loc}$  is the local current density, n is the number of electrons transferred,  $\eta$  is the overpotential,  $k_a$  is the anodic transfer coefficient,  $k_c$  is the cathodic transfer coefficient, and  $c_i$  is the concentration of species i at the active site.

The overpotential  $\eta$  for the reaction is calculated from the electric potential ( $\phi_s$ ), the electrolyte potential ( $\phi_l$ ), the potential drop due to the particle film resistance ( $\Delta \phi_{\rm film}$ ), and the equilibrium potential of the reaction ( $E_{\rm eq}$ ), as follows.

$$\eta = \phi_{\rm s} - \phi_{\rm l} - \Delta \phi_{\rm film} - E_{\rm eq} \tag{3}$$

The potential drop due to the particle film resistance is given as

$$\Delta \phi_{\text{film}} = i_{\text{loc}} R_{\text{film}} \varepsilon_{\text{Li}_2 \text{O}_2} \tag{4}$$

where  $R_{\text{film}}$  is the electrical resistivity across the Li<sub>2</sub>O<sub>2</sub> film and  $\varepsilon_{\text{Li2O2}}$  is the volume fraction of solid Li<sub>2</sub>O<sub>2</sub>.

The reaction considered in the negative electrode is

$$\text{Li} \rightarrow \text{Li}^+ + \text{e}^- \qquad E_{\text{eq}} = 0 \text{V}$$
 (5)

Lithium metal kinetics is used for this reaction at the negative electrode.

## PHYSICS SETUP

The Lithium-Ion Battery interface describes the following processes:

- · Electronic current conduction in the 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

In the positive electrode, spherical nonintercalating particles with concentration dependent electrode kinetics are used in the Lithium-Ion Battery interface. The thin lithium sheet (negative electrode) is represented using the Electrode Surface node with lithium metal electrode kinetics. Bruggeman correction is used for the all the effective transport properties in the positive porous electrode and the separator.

The Transport of Diluted Species in Porous Media interface describes the mass transport of oxygen in the porous carbon positive electrode by diffusion, along with the consumption of oxygen due to the electrochemical reaction (Equation 1).

The change in the concentration of the reaction product  $(Li_2O_2)$  in the solution phase of the positive electrode is given as

$$\frac{\partial (\varepsilon_{\rm l} c_{\rm Li_2O_2})}{\partial t} = \frac{-1}{2F} a i_{\rm loc} \times (c_{\rm Li_2O_2} < c_{\rm max, Li_2O_2})$$
(6)

where  $\varepsilon_{l}$  is the porosity and *a* is the active specific surface area, respectively, of the positive electrode, and  $c_{\max,Li2O2}$  is the solubility limit of Li<sub>2</sub>O<sub>2</sub> dissolved in the electrolyte. Note that  $\varepsilon_{l}$  remains at the initial porosity value until the solubility limit of Li<sub>2</sub>O<sub>2</sub> in the electrolyte is reached. The Domain ODEs and DAEs interface is used for modeling the changes in concentration of the reaction product in the solution phase of the positive electrode.

Beyond its solubility limit in the electrolyte, the reaction product  $(Li_2O_2)$  in the positive electrode deposits as a film on the active surface area. The change in the concentration of solid Li<sub>2</sub>O<sub>2</sub>,  $c_{s,Li2O2}$ , in the positive electrode is given as

$$\frac{\partial c_{s,\text{Li}_2\text{O}_2}}{\partial t} = \frac{1}{2F} a i_{\text{loc}} \times (c_{\text{Li}_2\text{O}_2} \ge c_{\max,\text{Li}_2\text{O}_2})$$
(7)

The porosity change due to solid Li2O2 deposition in the positive electrode is given as

$$\varepsilon_{\text{Li}_{2}\text{O}_{2}} = (c_{s, \text{Li}_{2}\text{O}_{2}} - c_{s0, \text{Li}_{2}\text{O}_{2}}) \times \frac{MW_{\text{Li}_{2}\text{O}_{2}}}{\rho_{\text{Li}_{2}\text{O}_{2}}}$$
(8)

where  $c_{s0,Li2O2}$ ,  $MW_{Li2O2}$  and  $\rho_{Li2O2}$  are the initial concentration, molecular weight and density of solid Li<sub>2</sub>O<sub>2</sub> in the film, respectively. The Dissolving-Depositing Species section of the Porous Electrode node is used to solve for the changes in concentration of the solid reaction product and electrode porosity in the positive porous electrode.

The active specific surface area of the positive porous electrode is decreased by the morphology and dynamic change of porosity due to solid  $\text{Li}_2\text{O}_2$  film formation. The effective local surface area per unit volume of the electrode is given by,

$$a = a_0 \left( 1 - \left( \frac{\varepsilon_{\text{Li}_2 \text{O}_2}}{\varepsilon_{l,0}} \right)^{0.5} \right)$$
(9)

where  $\varepsilon_{l,0}$  is the initial porosity and  $a_0$  is the initial active specific surface area, respectively, of the positive electrode. The value of 0.5 is related to the morphology shape of the solid Li<sub>2</sub>O<sub>2</sub> reaction product.

# **BOUNDARY CONDITIONS**

The negative electrode (lithium metal) is set to a potential of 0 V (electric ground condition). At the positive electrode current collector boundary, a discharge current density is applied. A parametric study is done for discharge current densities ranging from  $0.05 \text{ mA/cm}^2$  to  $0.5 \text{ mA/cm}^2$ . The study includes a stop condition with a minimum voltage of 2.5 V.

# Results and Discussion

Figure 2 shows the cell voltage profiles plotted as a function of capacity for different values of the discharge current density. At higher current densities, the discharge voltage and cell capacity are lower, as expected.



Figure 2: Cell voltage profiles as a function of specific capacity of the cell for different values of the applied discharge current density.

Figure 3 and Figure 4 show the oxygen concentration in the positive porous electrode at different times (discharge states of the battery), for a low and high value of the discharge current density, respectively. The decreased transport of oxygen in the positive electrode at high discharge currents, as seen in Figure 4, leads to the loss in capacity at high



discharge rates. The electrochemical reaction of oxygen reduction is limited to regions close to the positive electrode/current collector edge, as the discharge rate increases.

Figure 3: Variation of oxygen concentration in the positive electrode at different times (discharge states of the battery), for a low value of the discharge current density.



Figure 4: Variation of oxygen concentration in the positive electrode at different times (discharge states of the battery), for a high value of the discharge current density.

Figure 5 and Figure 6 similarly show the variation of the volume fraction of  $Li_2O_2$  in the positive electrode at different times, for a low and high value of the discharge current density, respectively. At high discharge rates, the  $Li_2O_2$  deposition on the active surface

area of the porous carbon electrode is predominantly limited to regions close to the positive electrode/current collector edge, as seen in Figure 6.



Figure 5: Variation of volume fraction of  $Li_2O_2$  in the positive electrode at different times (discharge states of the battery), for a low value of the discharge current density.



Figure 6: Variation of volume fraction of  $Li_2O_2$  in the positive electrode at different times (discharge states of the battery), for a high value of the discharge current density.

Figure 7 and Figure 8 similarly show the variation of porosity in the positive electrode at different times, for a low and high value of the discharge current density, respectively. The porosity of the porous carbon electrode decreases predominantly at regions close to the positive electrode/current collector edge at high discharge current densities, as seen in





Figure 7: Variation of porosity in the positive electrode at different times (discharge states of the battery), for a low value of the discharge current density.



Figure 8: Variation of porosity in the positive electrode at different times (discharge states of the battery), for a high value of the discharge current density.

# Reference

1. U. Sahapatsombut, H. Cheng, and K. Scott, "Modeling the micro-macro homogeneous cycling behavior of a lithium-air battery," *Journal of Power Sources*, vol. 227, pp. 243–253, 2013.

Application Library path: Battery\_Design\_Module/Batteries,\_Lithium-Ion/ li\_air\_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.

Add a Lithium-Ion Battery interface, a Transport of Diluted Species in Porous Media interface, and Domain ODEs and DAEs interface. The Transport of Diluted Species in Porous Media interface is used for modeling the transport of oxygen (from external air) in the porous carbon electrode. The Domain ODEs and DAEs interface is used for modeling the changes in concentration of the reaction product in the solution phase of the positive electrode.

- 2 In the Select Physics tree, select Electrochemistry>Batteries>Lithium-Ion Battery (liion).
- 3 Click Add.
- 4 In the Electrolyte salt concentration text field, type cLi.
- 5 In the Select Physics tree, select Chemical Species Transport> Transport of Diluted Species in Porous Media (tds).
- 6 Click Add.
- 7 In the Concentrations table, enter the following settings:

c02

- 8 In the Select Physics tree, select Mathematics>ODE and DAE Interfaces> Domain ODEs and DAEs (dode).
- 9 Click Add.
- **10** In the **Dependent variables** table, enter the following settings:

#### ecLi202

- II Click Select Dependent Variable Quantity.
- 12 In the Physical Quantity dialog box, type concentration in the text field.
- I3 Click 🕂 Filter.
- 14 In the tree, select General>Concentration (mol/m^3).
- I5 Click OK.
- 16 In the Model Wizard window, click of Select Source Term Quantity.
- 17 In the Physical Quantity dialog box, type reactionrate in the text field.
- 18 Click 🕂 Filter.
- 19 In the tree, select Transport>Reaction rate (mol/(m^3\*s)).
- 20 Click OK.

**2I** In the **Model Wizard** window, click  $\rightarrow$  **Study**.

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

**23** Click **M** Done.

#### GLOBAL DEFINITIONS

Load model parameters from a text file.

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 **b** Load from File.
- 4 Browse to the model's Application Libraries folder and double-click the file li\_air\_battery\_1d\_parameters.txt

#### GEOMETRY I

The geometry contains two domains, the separator and the positive 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)

Lsep

Lpos

5 In the Home toolbar, click 📗 Build All.

## DEFINITIONS

Load the model variables from a text file.

Variables I

- I In the Home toolbar, click  $\partial =$  Variables and choose Local Variables.
- 2 In the Settings window for Variables, locate the Geometric Entity Selection section.
- 3 From the Geometric entity level list, choose Domain.

- **4** Select Domain 2 only.
- **5** Locate the **Variables** section. Click *b* Load from File.
- 6 Browse to the model's Application Libraries folder and double-click the file li\_air\_battery\_1d\_variables.txt.

# Integration 1 (intop1)

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

- 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 **3** only.

## LITHIUM-ION BATTERY (LIION)

Set up the physics in the battery interface starting with the separator and the positive porous electrode. The lithium metal negative electrode is modeled using the Electrode Surface condition with lithium metal electrode kinetics.

## Separator I

- I In the Model Builder window, under Component I (comp1) right-click Lithium-Ion Battery (liion) and choose Separator.
- **2** Select Domain 1 only.
- 3 In the Settings window for Separator, locate the Electrolyte Properties section.
- **4** From the  $\sigma_l$  list, choose **User defined**. In the associated text field, type kappaLi.
- **5** From the  $D_1$  list, choose **User defined**. In the associated text field, type DLi.
- **6** From the  $t_{\pm}$  list, choose **User defined**. In the associated text field, type tplus.
- 7 From the dlnf/dlnc<sub>1</sub> list, choose User defined. In the associated text field, type dlnfdlnc.
- 8 Locate the Porous Matrix Properties section. In the  $\varepsilon_1$  text field, type epsilonsep.

## Porous Electrode 1

Set up the positive electrode parameters. Use Dissolving-Depositing Species formulation for modeling the change in porosity of the positive electrode.

I In the Physics toolbar, click — Domains and choose Porous Electrode.

- **2** Select Domain 2 only.
- 3 In the Settings window for Porous Electrode, locate the Electrolyte Properties section.
- **4** From the  $\sigma_l$  list, choose **User defined**. In the associated text field, type kappaLi.
- **5** From the  $D_1$  list, choose **User defined**. In the associated text field, type DLi.
- **6** From the  $t_+$  list, choose **User defined**. In the associated text field, type tplus.
- 7 From the dlnf/dlnc1 list, choose User defined. In the associated text field, type dlnfdlnc.
- 8 Locate the **Electrode Properties** section. From the  $\sigma_s$  list, choose **User defined**. In the associated text field, type Kpos.
- 9 Locate the Particle Properties section. From the list, choose Nonintercalating particles.
- IO Locate the Porous Matrix Properties section. In the  $\varepsilon_s$  text field, type epsilons0.
- II In the  $\varepsilon_1$  text field, type epsilon10.
- 12 Click to expand the Dissolving-Depositing Species section. Click + Add.
- **I3** In the table, enter the following settings:

Species	Density (kg/m^3)	Molar mass (kg/mol)
s1	rhoLi2O2	MLi202

14 Clear the Add volume change to electrode volume fraction check box.

- I5 Click to expand the Film Resistance section. From the Film resistance list, choose Surface resistance.
- **I6** In the  $R_{\text{film}}$  text field, type Rfilm\*epsilonLi202.

## Porous Electrode Reaction I

Set up the porous electrode reaction parameters. Beyond its solubility limit in the electrolyte, the reaction product (Li2O2) in the positive electrode deposits as a film on the active surface area.

- 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  $E_{\rm eq}$  list, choose User defined. In the associated text field, type Eeq.
- 4 Locate the Electrode Kinetics section. From the Kinetics expression type list, choose Concentration dependent kinetics.
- **5** In the  $i_0$  text field, type 1.
- 6 In the  $\alpha_a$  text field, type 0.5\*n.

- 7 In the  $\alpha_c$  text field, type 0.5\*n.
- 8 In the  $C_{\rm R}$  text field, type CRpos.
- **9** In the  $C_{\rm O}$  text field, type COpos.
- 10 Locate the Active Specific Surface Area section. From the Active specific surface area list, choose User defined. In the  $a_v$  text field, type apos.
- II Locate the **Stoichiometric Coefficients** section. In the *n* text field, type n.
- **12** In the  $v_{Li+}$  text field, type -2.
- **13** In the **Stoichiometric coefficients for dissolving-depositing species:** table, enter the following settings:

Species	Stoichiometric coefficient (I)
sl	1*(cLi202>=cmaxLi202)

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

### Electrode Surface 1

- I In the Physics toolbar, click Boundaries and choose Electrode Surface.
- **2** Select Boundary 1 only.

# Electrode Reaction 1

- I In the Model Builder window, click Electrode Reaction I.
- 2 In the Settings window for Electrode Reaction, locate the Equilibrium Potential section.
- 3 From the  $E_{eq}$  list, choose User defined. Locate the Electrode Kinetics section. In the  $i_{0,ref}(T)$  text field, type iOrefLi.
- 4 Click to expand the Heat of Reaction section. From the list, choose User defined.

#### Electrode Current Density I

Set up a current density at the positive electrode.

- I In the Physics toolbar, click Boundaries and choose Electrode Current Density.
- **2** Select Boundary **3** 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\_app.

#### Initial Values 1

It is important 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 *cLi* text field, type cLi0.
- 4 In the *phis* text field, type Eeq.

## Initial Values 2

- I In the Physics toolbar, click Domains and choose Initial Values.
- **2** Select Domain 1 only.
- 3 In the Settings window for Initial Values, locate the Initial Values section.
- **4** In the *cLi* text field, type cLi0.

#### TRANSPORT OF DILUTED SPECIES IN POROUS MEDIA (TDS)

Set up the physics in the porous media transport interface. Mass transport of oxygen in the positive porous electrode is by diffusion only. Quadratic elements are used for oxygen concentration. Also, provide a concentration boundary condition at the positive electrode.

- I In the Model Builder window, under Component I (comp1) click Transport of Diluted Species in Porous Media (tds).
- **2** Select Domain 2 only.
- **3** In the Settings window for Transport of Diluted Species in Porous Media, locate the Transport Mechanisms section.
- 4 Clear the Convection check box.
- 5 Click to expand the Discretization section. From the Concentration list, choose Quadratic.

#### Fluid I

- I In the Model Builder window, expand the Porous Medium I node, then click Fluid I.
- 2 In the Settings window for Fluid, locate the Diffusion section.
- **3** In the  $D_{\text{F,cO2}}$  text field, type D02.
- 4 From the Effective diffusivity model list, choose Bruggeman model.

## Porous Matrix I

- I In the Model Builder window, click Porous Matrix I.
- 2 In the Settings window for Porous Matrix, locate the Matrix Properties section.
- 3 From the  $\varepsilon_p$  list, choose User defined. In the associated text field, type liion.epsl.

#### Concentration 1

- I In the Physics toolbar, click Boundaries and choose Concentration.
- 2 Select Boundary 3 only.

- 3 In the Settings window for Concentration, locate the Concentration section.
- 4 Select the Species c02 check box.
- **5** In the  $c_{0,cO2}$  text field, type c020.

# Initial Values 1

Specify an initial value for oxygen concentration.

- 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 cO2 text field, type c020.

### Porous Electrode Coupling I

Add porous electrode coupling feature to model the consumption of oxygen due to the electrochemical reaction.

- I In the Physics toolbar, click Domains and choose Porous Electrode Coupling.
- **2** Select Domain 2 only.

Reaction Coefficients 1

- I In the Model Builder window, expand the Porous Electrode Coupling I node, then click Reaction Coefficients I.
- 2 In the Settings window for Reaction Coefficients, locate the Model Inputs section.
- 3 From the  $i_v$  list, choose Local current source, Porous Electrode Reaction I (liion/pcel/ perl).
- **4** Locate the **Stoichiometric Coefficients** section. In the *n* text field, type n.
- **5** In the  $v_{cO2}$  text field, type -1.

# DOMAIN ODES AND DAES: CONCENTRATION OF LI202

Set up the physics to model the change in concentration of the reaction product (Li2O2) in the solution phase of the positive electrode, by specifying the appropriate source term. Lagrange (Quadratic) elements are used for concentration of the reaction product.

- I In the Model Builder window, under Component I (comp1) click Domain ODEs and DAEs (dode).
- 2 In the Settings window for Domain ODEs and DAEs, type Domain ODEs and DAEs: Concentration of Li202 in the Label text field.
- **3** Select Domain 2 only.
- 4 Click to expand the **Discretization** section. From the **Shape function type** list, choose **Lagrange**.

### Distributed ODE I

I In the Model Builder window, under Component I (compl)>

Domain ODEs and DAEs: Concentration of Li2O2 (dode) click Distributed ODE I.

- 2 In the Settings window for Distributed ODE, locate the Source Term section.
- **3** In the *f* text field, type ((-liion.ivtot\*1)/(2\*F\_const))\*(cLi202<cmaxLi202).

## 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.

# MESH I

Select a finer mesh for this model.

- I In the Model Builder window, under Component I (compl) click Mesh I.
- 2 In the Settings window for Mesh, locate the Physics-Controlled Mesh section.
- 3 From the Element size list, choose Finer.
- 4 Click 📗 Build All.

#### STUDY I

Set up a parametric study for a range of discharge current densities.

#### 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
a (Used in parametric sweep)	1 2 4 10	

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 1e7.
- 4 From the Tolerance list, choose User controlled.
- 5 In the Relative tolerance text field, type 1e-4.

#### Solution 1 (soll)

I In the Study toolbar, click **The Show Default Solver**.

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

- 2 In the Model Builder window, expand the Solution I (soll) node, then click Time-Dependent Solver I.
- 3 In the Settings window for Time-Dependent Solver, locate the General section.
- 4 From the Times to store list, choose Steps taken by solver.

Store only every 3rd time step. This reduces the size of the stored solution and the size of model file.

- 5 In the Store every Nth step text field, type 3.
- 6 Right-click Study I>Solver Configurations>Solution I (soll)>Time-Dependent Solver I and choose Stop Condition.
- 7 In the Settings window for Stop Condition, locate the Stop Expressions section.
- 8 Click + Add.
- 9 In the table, enter the following settings:

Stop expression	Stop if	Active	Description
<pre>comp1.EndTerminal(comp1.phis)&lt; 2.5</pre>	True (>=1)	$\checkmark$	Stop expression 1

**IO** Locate the **Output at Stop** section. Clear the **Add warning** check box.

II In the Model Builder window, click Study I.

12 In the Settings window for Study, locate the Study Settings section.

**I3** Clear the **Generate default plots** check box.

**I4** In the **Study** toolbar, click **= Compute**.

# RESULTS

Cell Voltages for different iapp

First plot the cell voltage for the different discharge current densities (see Figure 2).

- I In the Home toolbar, click 🚛 Add Plot Group and choose ID Plot Group.
- 2 In the Settings window for ID Plot Group, type Cell Voltages for different iapp 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 Cell Voltages for different iapp and choose Point Graph.
- **2** Select Boundary **3** 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 I (compl)> Lithium-lon Battery>phis Electric potential V.
- 4 Locate the x-Axis Data section. From the Parameter list, choose Expression.
- 5 Click Replace Expression in the upper-right corner of the x-Axis Data section. From the menu, choose Component I (compl)>Definitions>Variables>capacity Specific capacity of cell C/kg.
- 6 Click to expand the Legends section. Select the Show legends check box.
- 7 From the Legends list, choose Evaluated.
- 8 In the Legend text field, type eval(-i\_app,mA/cm^2) mA/cm^2.

#### Cell Voltages for different iapp

- I In the Model Builder window, click Cell Voltages for different iapp.
- 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 Specific capacity of cell (mAh/g).
- 4 Select the y-axis label check box. In the associated text field, type Cell Voltage (V).
- 5 Click to expand the Title section. From the Title type list, choose Manual.
- 6 In the **Title** text area, type Cell Voltage.
- 7 Locate the Legend section. From the Position list, choose Lower right.
- 8 In the Cell Voltages for different iapp toolbar, click 💿 Plot.

#### Oxygen conc in positive electrode, iapp = 0.1 mA/cm2

Next, plot the oxygen concentration in the positive electrode for a low and high value of the discharge current density (see Figure 3 and Figure 4).

I In the Home toolbar, click 🚛 Add Plot Group and choose ID Plot Group.

- 2 In the Settings window for ID Plot Group, type Oxygen conc in positive electrode, iapp = 0.1mA/cm2 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 (a) list, choose From list.
- 5 In the Parameter values (a) list, select 2.

#### Line Graph 1

- I Right-click Oxygen conc in positive electrode, iapp = 0.1mA/cm2 and choose Line Graph.
- **2** Select Domain 2 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)> Transport of Diluted Species in Porous Media>Species c02>c02 - Concentration - mol/m<sup>3</sup>.
- 4 Locate the x-Axis Data section. From the Parameter list, choose Expression.
- **5** In the **Expression** text field, type x/(Lsep+Lpos).
- **6** Select the **Description** check box. In the associated text field, type **Dimensionless** thickness of positive electrode.

Oxygen conc in positive electrode, iapp = 0.1 mA/cm2

- I In the Model Builder window, click Oxygen conc in positive electrode, iapp = 0.1mA/cm2.
- 2 In the Settings window for ID Plot Group, locate the Title section.
- **3** From the **Title type** list, choose **Manual**.
- **4** In the **Title** text area, type Oxygen concentration in positive electrode.
- 5 In the Oxygen conc in positive electrode, iapp = 0.1mA/cm2 toolbar, click 💽 Plot.

Oxygen conc in positive electrode, iapp = 0.5mA/cm2

- I Right-click Oxygen conc in positive electrode, iapp = 0.1mA/cm2 and choose Duplicate.
- 2 In the Settings window for ID Plot Group, type Oxygen conc in positive electrode, iapp = 0.5mA/cm2 in the Label text field.
- 3 Locate the Data section. In the Parameter values (a) list, select 10.
- **4** In the **Oxygen conc in positive electrode, iapp = 0.5mA/cm2** toolbar, click **O Plot**.

Volume fraction of Li2O2 in positive electrode, iapp = 0.1 mA/cm2

Plot the volume fraction of Li2O2 in the positive electrode for a low and high value of the discharge current density (see Figure 5 and Figure 6), as follows.

I In the Home toolbar, click 🚛 Add Plot Group and choose ID Plot Group.

- 2 In the Settings window for ID Plot Group, type Volume fraction of Li202 in positive electrode, iapp = 0.1mA/cm2 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 (a) list, choose From list.
- 5 In the Parameter values (a) list, select 2.
- 6 From the Time selection list, choose Interpolated.
- 7 In the Times (s) text field, type 1 2e5 5e5 1e6 1.15e6.

Line Graph 1

- I Right-click Volume fraction of Li2O2 in positive electrode, iapp = 0.1mA/cm2 and choose Line Graph.
- **2** Select Domain 2 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>epsilonLi2O2 Volume fraction of Li2O2.
- 4 Locate the x-Axis Data section. From the Parameter list, choose Expression.
- 5 In the Expression text field, type x/(Lsep+Lpos).
- **6** Select the **Description** check box. In the associated text field, type **Dimensionless** thickness of positive electrode.

Volume fraction of Li2O2 in positive electrode, iapp = 0.1 mA/cm2

- I In the Model Builder window, click Volume fraction of Li2O2 in positive electrode, iapp = 0.1mA/cm2.
- 2 In the Settings window for ID Plot Group, locate the Title section.
- **3** From the **Title type** list, choose **Manual**.
- 4 In the Title text area, type Volume fraction of Li202 in positive electrode.
- **5** Locate the **Axis** section. Select the **Manual axis limits** check box.
- 6 In the **y maximum** text field, type 0.6.
- 7 In the Volume fraction of Li2O2 in positive electrode, iapp = 0.1mA/cm2 toolbar, click
   Plot.

Volume fraction of Li2O2 in positive electrode, iapp = 0.5mA/cm2

I Right-click Volume fraction of Li2O2 in positive electrode, iapp = 0.1mA/cm2 and choose Duplicate.

- 2 In the Settings window for ID Plot Group, type Volume fraction of Li202 in positive electrode, iapp = 0.5mA/cm2 in the Label text field.
- 3 Locate the Data section. In the Parameter values (a) list, select 10.
- 4 In the Times (s) text field, type 1 5e3 2e4 4e4.
- 5 In the Volume fraction of Li2O2 in positive electrode, iapp = 0.5mA/cm2 toolbar, click
   Plot.

Porosity of positive electrode, iapp = 0.1 mA/cm2

Plot the porosity in the positive electrode for a low and high value of the discharge current density (see Figure 7 and Figure 8), as follows.

- I In the Home toolbar, click 🚛 Add Plot Group and choose ID Plot Group.
- 2 In the Settings window for ID Plot Group, type Porosity of positive electrode, iapp = 0.1mA/cm2 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 (a) list, choose From list.
- 5 In the Parameter values (a) list, select 2.
- 6 From the Time selection list, choose Interpolated.
- 7 In the Times (s) text field, type 1 2e5 5e5 1e6 1.15e6.

Line Graph 1

- I Right-click Porosity of positive electrode, iapp = 0.1mA/cm2 and choose Line Graph.
- **2** Select Domain 2 only.
- 3 In the Settings window for Line Graph, locate the y-Axis Data section.
- **4** In the **Expression** text field, type liion.epsl.
- **5** Select the **Description** check box. In the associated text field, type **Porosity**.
- 6 Locate the x-Axis Data section. From the Parameter list, choose Expression.
- 7 In the Expression text field, type x/(Lsep+Lpos).
- 8 Select the **Description** check box. In the associated text field, type **Dimensionless** thickness of positive electrode.

Porosity of positive electrode, iapp = 0.1 mA/cm2

- I In the Model Builder window, click Porosity of positive electrode, iapp = 0.1mA/cm2.
- 2 In the Settings window for ID Plot Group, locate the Title section.
- **3** From the **Title type** list, choose **Manual**.

- 4 In the **Title** text area, type Porosity of positive electrode.
- **5** Locate the **Axis** section. Select the **Manual axis limits** check box.
- 6 In the y minimum text field, type 0.15.
- 7 In the **y maximum** text field, type 0.75.
- 8 In the Porosity of positive electrode, iapp = 0.1mA/cm2 toolbar, click i Plot.

Porosity of positive electrode, iapp = 0.5mA/cm2

- I Right-click Porosity of positive electrode, iapp = 0.1mA/cm2 and choose Duplicate.
- 2 In the Settings window for ID Plot Group, type Porosity of positive electrode, iapp = 0.5mA/cm2 in the Label text field.
- 3 Locate the Data section. In the Parameter values (a) list, select 10.
- 4 In the Times (s) text field, type 1 5e3 2e4 4e4.
- 5 In the Porosity of positive electrode, iapp = 0.5mA/cm2 toolbar, click **O** Plot.