

Secondary Current Distribution in a Zinc Electrowinning Cell

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Introduction

In a zinc electrowinning cell, zinc deposition is the desired main reaction at the cathode, whereas oxygen is evolved at the anode. A good alignment of the electrodes is required to achieve a uniform current distribution. Even small spatial deviations of the electrode placement in the cell may increase the tendency for short circuits and loss of current efficiency.

This model, which reproduces the results of Bouzek and others (Ref. 1), investigates the effect of the cathode alignment in a zinc electrowinning cell.

Model Definition

The model geometry is shown in Figure 1.



Figure 1: Modeled geometry.

The geometry is a unit cell containing a single electrolyte domain where the anodes and cathodes are modeled as electrode surfaces on the boundaries. The end of the electrodes are isolated using edge strips of isolating material. The stationary problem is solved using a parametric study, investigating the impact of displacing the cathode in the horizontal direction for a range of different values between -60 mm to +40 mm.

Concentration gradients in the electrolyte are neglected. This implies that a secondary current distribution is assumed. The model is set up using the Secondary Current Distribution interface using a constant conductivity of 36.2 S/m in the electrolyte.

At the cathode, zinc ions are reduced according to

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

Hydrogen evolution may also occur at the cathode according to

$$\mathrm{H}^{+} + e^{-} \Leftrightarrow \frac{1}{2}\mathrm{H}_{2}$$

On the anode, oxygen is evolved:

$$\mathbf{H}_{2}\mathbf{O} \Leftrightarrow \frac{1}{2}\mathbf{O}_{2} + 2\mathbf{H}^{+} + 2e$$

Butler-Volmer expressions are used to describe the electrode reaction kinetics for all electrode reactions:

$$i = i_0 \left(\exp\left(\frac{\alpha_a F \eta}{RT}\right) - \exp\left(\frac{-\alpha_c F \eta}{RT}\right) \right)$$

where the overpotentials for the electrode reactions, η are defined by:

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

Using the Nernst equation, the equilibrium potentials, E_{eq} are calculated according to:

$$E_{eq}(Zn^{2+}/Zn) = E^{0}(Zn^{2+}/Zn) - \frac{RT}{2F}\ln\frac{a_{Zn}}{a_{Zn^{2+}}} = -0.797 V$$

$$E_{eq}\left(H^{+}/\frac{1}{2}H_{2}\right) = 0 - \frac{RT}{F}\ln\frac{a_{H_{2}}^{0.5}}{a_{H^{+}}} = 0.016 V$$

$$E_{eq}(O_{2}/H_{2}O) = E^{0}(O_{2}/H_{2}O) - \frac{RT}{2F}\ln\frac{a_{H_{2}O}}{a_{O_{2}}^{0.5}a_{H^{+}}^{2}} = 1.247 V$$

where E^0 is the standard electrode potential for the respective reactions, and a_i denotes the species activity.

The anode and cathode surfaces are modeled using two Electrode Surface nodes, where the electrode reactions above are defined. The electric potential is set to 0 V at the anode and to 3.597 V at the cathode. The voltage of the cathode is thus the cell voltage. All other boundaries are isolated.

Results and Discussion

Figure 2 and Figure 3 show the electrolyte potential distribution for a cathode dislocation of -60 mm and +40 mm, respectively. The difference in electrolyte potential between the

two plots is due to the change of available electrode surface areas, which causes a difference in the average overpotentials at the electrodes.



Figure 2: Electrolyte potential distribution for a cathode displacement of -60 mm.



Figure 3: Electrolyte potential distribution for a cathode displacement of +40 mm.

Figure 4 and Figure 5 show the electrolyte current density and streamlines of the electrolyte current for the same cathodes as in Figure 2 and Figure 3. The location of the maximum in electrolyte current is located toward the end of the shorter electrode.



Figure 4: Electrolyte current density distribution for a cathode displacement of -60 mm.



Figure 5: Electrolyte current density distribution for a cathode displacement of +40 mm.

Figure 6 shows a line graph of the total current density at the cathode for different cathode displacements. The most uniform current density is found for a cathode displacement of -20 mm.



Figure 6: Electrode density at the cathode for different cathode displacements normalized to the electrode density at x = 0.

Reference

1. K. Bouzek, K. Korve, O.A. Lorentsen, K. Osmundsen, I. Rousar, and J. Thonstad, "Current Distribution at the Electrodes in Zinc Electrowinning Cells," *J. Electrochemical Society*, vol. 142, no. 1, 1995.

Application Library path: Electrodeposition_Module/Verification_Examples/ zn_electrowinning

Modeling Instructions

From the File menu, choose New.

NEW

In the New window, click <u>Model Wizard</u>.

MODEL WIZARD

- I In the Model Wizard window, click 🧐 2D.
- 2 In the Select Physics tree, select Electrochemistry>

Primary and Secondary Current Distribution>Secondary Current Distribution (cd).

- 3 Click Add.
- 4 Click \bigcirc Study.
- 5 In the Select Study tree, select General Studies>Stationary.
- 6 Click **M** Done.

GLOBAL DEFINITIONS

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 electrowinning parameters.txt.

GEOMETRY I

Rectangle 1 (r1)

- I In the Geometry toolbar, click Rectangle.
- 2 In the Settings window for Rectangle, locate the Size and Shape section.
- 3 In the Width text field, type 16+12+13.
- 4 In the **Height** text field, type 2*d4+d1+d5+d2.
- 5 Click 📄 Build Selected.

Rectangle 2 (r2)

- I In the **Geometry** toolbar, click **Rectangle**.
- 2 In the Settings window for Rectangle, locate the Size and Shape section.
- 3 In the Width text field, type 16+disp.
- 4 In the **Height** text field, type d4.
- 5 Click 틤 Build Selected.

Rectangle 3 (r3)

- I In the Geometry toolbar, click Rectangle.
- 2 In the Settings window for Rectangle, locate the Size and Shape section.
- **3** In the **Width** text field, type 15.
- 4 In the **Height** text field, type d5.
- 5 Locate the **Position** section. In the **y** text field, type d2+d4.
- 6 Click 틤 Build Selected.

Rectangle 4 (r4)

- I In the Geometry toolbar, click Rectangle.
- 2 In the Settings window for Rectangle, locate the Size and Shape section.
- **3** In the **Width** text field, type 16+disp.
- **4** In the **Height** text field, type d4.
- **5** Locate the **Position** section. In the **y** text field, type d4+d1+d5+d2.



Rectangle 5 (r5)

- I In the Geometry toolbar, click Rectangle.
- 2 In the Settings window for Rectangle, locate the Size and Shape section.
- 3 In the Width text field, type 12.

- 4 In the **Height** text field, type d3+d4.
- **5** Locate the **Position** section. In the **x** text field, type 16+disp.
- 6 Click 📄 Build Selected.

Rectangle 6 (r6)

- I In the Geometry toolbar, click Rectangle.
- 2 In the Settings window for Rectangle, locate the Size and Shape section.
- **3** In the **Width** text field, type 14.
- 4 In the **Height** text field, type d5+2*d6.
- **5** Locate the **Position** section. In the **x** text field, type **15**.
- 6 In the y text field, type d2+d4-d6.
- 7 Click 📄 Build Selected.

Rectangle 7 (r7)

- I In the **Geometry** toolbar, click **Rectangle**.
- 2 In the Settings window for Rectangle, locate the Size and Shape section.
- **3** In the **Width** text field, type 12.
- 4 In the **Height** text field, type d3+d4.
- **5** Locate the **Position** section. In the **x** text field, type 16+disp.
- **6** In the **y** text field, type d4+d1+d5+d2-d3.



Difference I (dif1)

I In the Geometry toolbar, click 📃 Booleans and Partitions and choose Difference.

- 2 Select the object rl only.
- 3 In the Settings window for Difference, locate the Difference section.
- **4** Find the **Objects to subtract** subsection. Select the **Delivate Selection** toggle button.
- 5 Select the objects r2, r3, r4, r5, r6, and r7 only (I.e. the other six rectangles).

6 In the Geometry toolbar, click 🟢 Build All.

The geometry is now complete.



DEFINITIONS

Anode

- I In the **Definitions** toolbar, click **herefore Explicit**.
- 2 Right-click Explicit I and choose Rename.
- 3 In the Rename Explicit dialog box, type Anode in the New label text field.
- 4 Click OK.
- 5 In the Settings window for Explicit, locate the Input Entities section.
- 6 From the Geometric entity level list, choose Boundary.





Cathode

I In the Definitions toolbar, click 堶 Explicit.

- 2 In the Model Builder window, right-click Explicit 2 and choose Rename.
- 3 In the Rename Explicit dialog box, type Cathode in the New label text field.
- 4 Click OK.
- 5 In the Settings window for Explicit, locate the Input Entities section.
- 6 From the Geometric entity level list, choose Boundary.





Integration 1 (intop1)

I In the Definitions toolbar, click 🖉 Nonlocal Couplings and choose Integration.

- 2 In the Settings window for Integration, locate the Source Selection section.
- 3 From the Geometric entity level list, choose Point.
- 4 Select Point 4 only.

SECONDARY CURRENT DISTRIBUTION (CD)

Electrolyte I

- I In the Model Builder window, under Component I (compl)> Secondary Current Distribution (cd) click Electrolyte I.
- 2 In the Settings window for Electrolyte, locate the Electrolyte section.
- **3** From the σ_l list, choose **User defined**. In the associated text field, type sigma_1.

Electrode Surface 1

- I In the Physics toolbar, click Boundaries and choose Electrode Surface.
- 2 In the Settings window for Electrode Surface, locate the Boundary Selection section.
- 3 From the Selection list, choose Anode.
- 4 Locate the Electrode Phase Potential Condition section. In the $\phi_{s,ext}$ text field, type phisext.

Oxygen evolution

- I In the Model Builder window, expand the Electrode Surface I node.
- 2 Right-click Electrode Reaction I and choose Rename.
- **3** In the **Rename Electrode Reaction** dialog box, type **Oxygen evolution** in the **New label** text field.
- 4 Click OK.
- 5 In the Settings window for Electrode Reaction, locate the Equilibrium Potential section.
- **6** In the E_{eq} text field, type E_02.
- 7 Locate the Electrode Kinetics section. From the Kinetics expression type list, choose Butler-Volmer.
- **8** In the i_0 text field, type i0_02.
- **9** In the α_a text field, type alphaa_02.
- **IO** In the α_c text field, type alphac_02.

Electrode Surface 2

- I In the Physics toolbar, click Boundaries and choose Electrode Surface.
- 2 In the Settings window for Electrode Surface, locate the Boundary Selection section.
- **3** From the **Selection** list, choose **Cathode**.

Zinc reaction

- I In the Model Builder window, expand the Electrode Surface 2 node.
- 2 Right-click Electrode Reaction I and choose Rename.
- **3** In the **Rename Electrode Reaction** dialog box, type **Zinc reaction** in the **New label** text field.
- 4 Click OK.
- 5 In the Settings window for Electrode Reaction, locate the Equilibrium Potential section.
- **6** In the E_{eq} text field, type E_Zn.
- 7 Locate the Electrode Kinetics section. From the Kinetics expression type list, choose Butler-Volmer.
- **8** In the i_0 text field, type i0_Zn.
- 9 In the α_a text field, type alphaa_Zn.
- IO In the α_c text field, type alphac_Zn.

Electrode Surface 2

In the Model Builder window, click Electrode Surface 2.

Hydrogen evolution

- I In the Physics toolbar, click 🔙 Attributes and choose Electrode Reaction.
- 2 Right-click Electrode Reaction 2 and choose Rename.
- 3 In the Rename Electrode Reaction dialog box, type Hydrogen evolution in the New label text field.
- 4 Click OK.
- 5 In the Settings window for Electrode Reaction, locate the Equilibrium Potential section.
- **6** In the E_{eq} text field, type E_H.
- 7 Locate the Electrode Kinetics section. From the Kinetics expression type list, choose Butler-Volmer.
- **8** In the i_0 text field, type i0_H.

Initial Values 1

- I In the Settings window for Initial Values, locate the Initial Values section.
- 2 In the *phil* text field, type 1.

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

- 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 Extremely fine.



STUDY I

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
disp (Cathode displacement in	0.04 0.02 0 -0.01 -0.02	m
parametric sweep)	-0.04 -0.06	

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

RESULTS

Electrolyte Potential (cd)

The default plot shows the electrolyte potential for the last displacement value in the sweep, that is -60 mm. Compare the plot in the **Graphics** window with that in Figure 2. Visualize the potential for the displacement +40 mm as follows:

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

- 2 In the Settings window for 2D Plot Group, locate the Data section.
- 3 From the Parameter value (disp (m)) list, choose 0.04.
- **4** In the **Electrolyte Potential (cd)** toolbar, click **O** Plot.

Compare the result with that in Figure 3.

2D Plot Group 5

Next, visualize the electrolyte current density field for the same two displacement values in a combined surface and streamline plot.

- I In the Home toolbar, click 📠 Add Plot Group and choose 2D Plot Group.
- 2 In the Settings window for 2D Plot Group, locate the Data section.
- 3 From the Dataset list, choose Study I/Parametric Solutions I (sol2).

Surface 1

- I Right-click 2D Plot Group 5 and choose Surface.
- In the Settings window for Surface, click Replace Expression in the upper-right corner of the Expression section. From the menu, choose Component I (compl)>
 Secondary Current Distribution>cd.IIMag Electrolyte current density magnitude A/m².

Streamline 1

- I In the Model Builder window, right-click 2D Plot Group 5 and choose Streamline.
- In the Settings window for Streamline, click Replace Expression in the upper-right corner of the Expression section. From the menu, choose Component I (compl)>
 Secondary Current Distribution>cd.llx,cd.lly Electrolyte current density vector.
- **3** Select Boundaries **3** and **5** only.

Electrolyte current density

- I In the Model Builder window, click 2D Plot Group 5.
- 2 In the 2D Plot Group 5 toolbar, click 🗿 Plot.

Compare the resulting plot with that in Figure 4.

- 3 In the Settings window for 2D Plot Group, locate the Data section.
- 4 From the Parameter value (disp (m)) list, choose 0.04.
- 5 In the 2D Plot Group 5 toolbar, click 💽 Plot.

Compare the result with the plot in Figure 5.

- 6 Right-click 2D Plot Group 5 and choose Rename.
- 7 In the Rename 2D Plot Group dialog box, type Electrolyte current density in the New label text field.

8 Click OK.

ID Plot Group 6

Finally, reproduce the plot of the current density distribution at the anode shown in Figure 6.

- I In the Home toolbar, click 📠 Add Plot Group and choose ID Plot Group.
- 2 In the Settings window for ID Plot Group, locate the Data section.
- 3 From the Dataset list, choose Study I/Parametric Solutions I (sol2).
- 4 Click to expand the Title section. From the Title type list, choose Manual.
- **5** In the **Title** text area, type Anode current density distribution for different cathode displacements.
- 6 Locate the Plot Settings section. Select the y-axis label check box.
- 7 In the associated text field, type Electrode current density (Normalized at x=0).

Cathode current distribution

- I Right-click ID Plot Group 6 and choose Line Graph.
- **2** Select Boundary 6 only.
- 3 In the Settings window for Line Graph, locate the y-Axis Data section.
- **4** In the **Expression** text field, type cd.itot/comp1.intop1(cd.itot).
- 5 Locate the x-Axis Data section. From the Parameter list, choose Expression.
- **6** In the **Expression** text field, type **x**.
- 7 Click to expand the Legends section. Select the Show legends check box.
- 8 In the ID Plot Group 6 toolbar, click 🗿 Plot.
- 9 Right-click Line Graph I and choose Rename.
- IO In the Rename Line Graph dialog box, type Cathode current distribution in the New label text field.

II Click OK.

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