Lecture 10

Electrodeposition of metals at forced convection condition.

Goal of the Lecture

The goal of this lecture is to introduce students to the modelling of metal electrodeposition under forced convection, with a focus on the rotating cylinder Hull (RCH) cell. Students will learn how hydrodynamic conditions influence current distribution, potential distribution, concentration fields, and ultimately deposition uniformity. The lecture also develops the modelling hierarchy from primary to secondary and tertiary current distributions, showing how complexity is gradually incorporated in computational electrochemical models.

Lecture Objectives

By the end of this lecture, students will be able to:

1. ***Explain** how forced convection affects mass transport and electrodeposition kinetics.*
2. ***Differentiate** between primary, secondary, and tertiary current distributions and discuss when each is applicable.*
3. ***Apply** hydrodynamic boundary layer concepts to model rotating-cylinder systems.*
4. ***Set up** coupled transport and kinetic models of electrodeposition in COMSOL Multiphysics under convective flow.*
5. ***Interpret** simulation outputs for current density, potential, and concentration distributions in rotating electrode systems.*

The rotating cylinder Hull (RCH) cell provides an effective experimental tool to investigate electrodeposition since a wide range of current densities and controllable hydrodynamic conditions can be achieved in a single experiment. This model example simulates non-uniform current, potential and concentration distributions along the working electrode of the RCH cell. Primary, secondary and tertiary current distributions are compared, demonstrating how complexity can be gradually incorporated in the model. The example is based on a paper by C. T. J. Low and others [1].

Because of the symmetry of the RCH cell geometry, a 2D axisymmetric space dimension is used. Figure 1 shows the model geometry, where the rotating cylinder working electrode, the stationary concentric counter electrode and the electrolyte are highlighted.

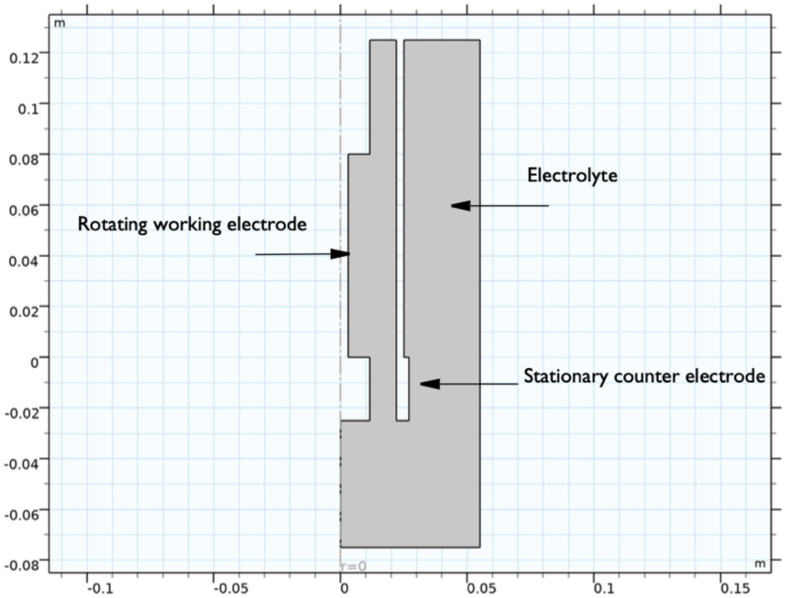

Figure 1. 2D axisymmetric geometry of the RCH cell. The Electrolyte, the rotating working electrode and the stationary counter electrode are highlighted.

On the working electrode surface, couple the cupric ions flux over the boundary to the local current density by using an Electrode-Electrolyte Interface Coupling boundary condition. This sets the flux to be proportional to the electrode current density according to Faraday’s law:

$$nN = \frac{v j_{loc,Cu}}{nF}$$

where **F** is Faraday’s constant (96485 C/mol), **v** the stoichiometric coefficient for cupric ions in the reduction reaction and **n** the number of electrons in the reaction.

The sign convention for **v** is that it should be negative for reactants and positive for products in a reduction reaction. A reduction reaction is one where the electrons participate as reactants. **n** is always positive.

The electrode kinetics to be concentration dependent according to following expression:

$$j_{loc,Cu} = -\left(\frac{c}{c_b}\right) j_0 10^{\frac{\eta}{A_c}}$$

Figure 2 shows the normalized primary current density distribution along the working electrode surface obtained from the numerical model as well as from an analytical expression reported in [1]. The normalized current density is found to decrease with the distance away from the counter electrode surface indicating its dependence on the geometry of RCH cell.

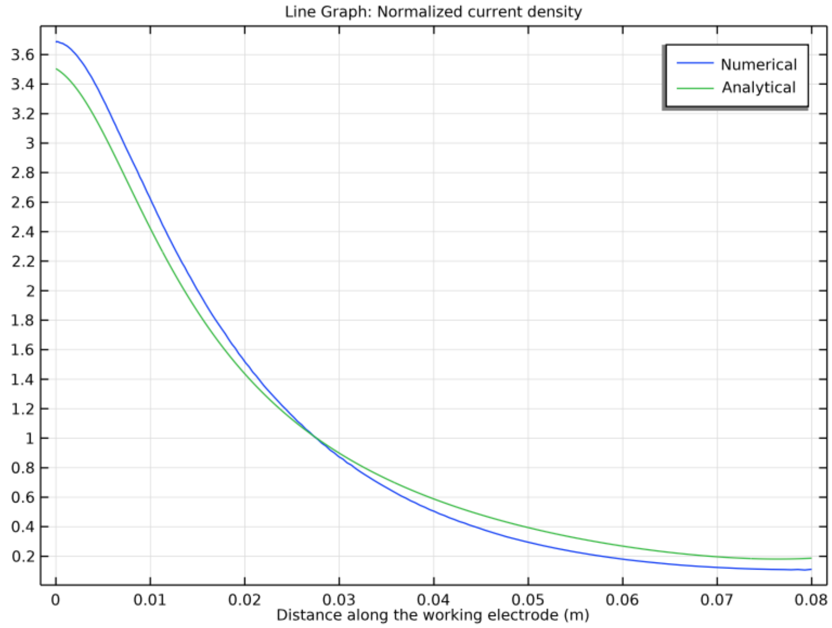

Figure 2. Normalized primary current density distribution obtained from the numerical model and the analytical expression.

Figure 3 shows the normalized current density variation along the working electrode surface obtained from the model for primary, secondary and tertiary current distributions at the representative applied current density of 100 A/m^2. The primary current distribution is the most non-uniform, followed by the secondary and then the tertiary current distribution. The primary current distribution model is not adequate for capturing the electrodeposition process under non-equilibrium conditions. The secondary current distribution is applicable for the lower applied current densities, where the electrodeposition reaction is kinetic limited. The tertiary current distribution is valid when concentration gradients cannot be neglected, which is the case for the higher applied current densities.

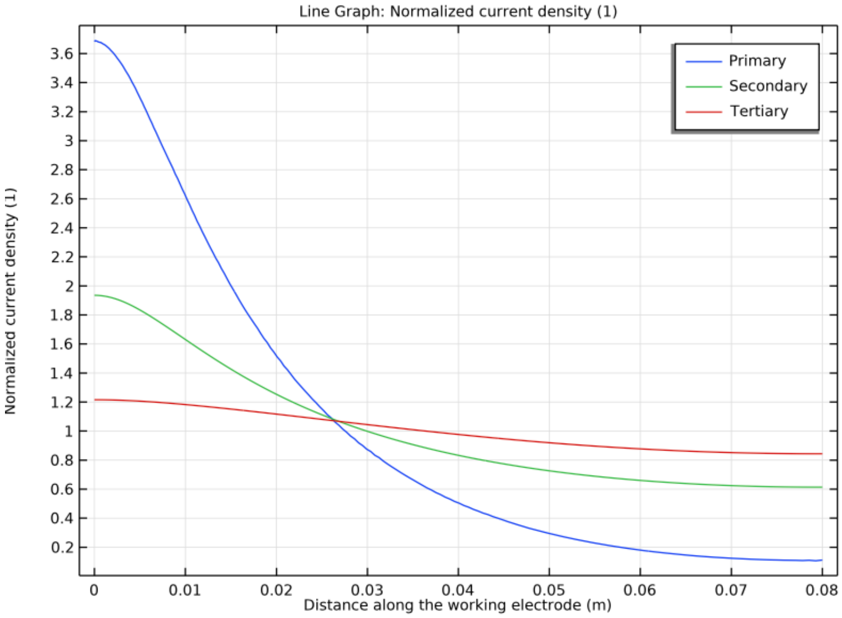

Figure 3. Normalized current density variation for primary, secondary and tertiary current distributions at the representative applied current density of 100 A/m^2 [2].

The primary current distribution is first implemented using the Primary Current Distribution interface and the Electrode Surface node for the working electrode surface.

The secondary current distribution is then implemented by introducing the electrode kinetics for the working electrode surface using the Electrode Surface node.

Finally, the tertiary current distribution is implemented by coupling the Transport of Diluted Species interface with the Secondary Current Distribution interface.

A parametric sweep study type is used to vary the current density applied at the working electrode surface for the secondary and tertiary current distributions.

Questions for Self-Examination

1. What advantages does a rotating cylinder Hull (RCH) cell provide for electrodeposition studies?
2. How does forced convection enhance mass transport compared to natural diffusion?

3. Explain the conceptual differences between primary, secondary, and tertiary current distributions.
4. Under what conditions is each current distribution model appropriate?
5. Why does current density decrease along the cylinder electrode as the distance from the counter electrode increases?
6. What role does electrode kinetics play in secondary current distribution modeling?
7. Why must concentration gradients be included for tertiary current distributions?
8. In which situations would tertiary current distribution become the dominant modelling approach?

Self-Study Assignment

Assignment Title:

Simulation of Electrodeposition in a Rotating Cylinder Hull (RCH) Cell: Primary, Secondary, and Tertiary Current Distribution Models

Objective:

To simulate electrodeposition under forced convection in an RCH cell geometry using COMSOL Multiphysics, compare the three levels of current distribution (primary, secondary, tertiary), and examine how hydrodynamics and mass transport influence deposition uniformity.

Tasks

1. Geometry Setup

- Construct the **2D axisymmetric** geometry of a rotating cylinder Hull cell:
    - Rotating cylindrical cathode
    - Stationary concentric anode
    - Electrolyte region
- Use dimensions similar to those in the COMSOL example.

2. Physics Interfaces

Model successively increasing complexity:

1. **Primary Current Distribution**
    - Electric Currents interface
    - Assume uniform conductivity and neglect kinetics
    - Only solve for potential and current distribution
2. **Secondary Current Distribution**
    - Add Butler–Volmer kinetics on the electrode surface
    - Include concentration-dependent overpotential if needed
3. **Tertiary Current Distribution**
    - Couple **Transport of Diluted Species (tds)** with Secondary Current Distribution
    - Include convective mass transport (forced convection velocity profile)

3. Boundary Conditions

- On working electrode (cathode):
    - Electrode–electrolyte boundary with kinetics
    - Ion flux:

$$N_{\mathrm{Cu}^{2+}} = -\frac{i}{nF}$$

- On anode (counter electrode):
    - Metal dissolution with opposite sign of v
- Fluid flow (if included): rotating cylinder velocity boundary condition

4. Simulations

Run simulations for applied current densities (example: 50, 100, 150 A/m²) under:

- Primary
- Secondary
- Tertiary
  current distribution.

For tertiary, include:

- Concentration boundary layers
- Depletion effects at high current

5. Output and Analysis

Produce plots of:

1. **Current density distribution** along the rotating electrode
2. **Potential distribution** in the electrolyte
3. **Concentration profiles** (tertiary distribution only)

Analyze:

- Why the primary current distribution is the most non-uniform
- How kinetics smooth the secondary current distribution
- How mass transport further modifies tertiary current distribution

6. Optimization Discussion

Suggest strategies for improving deposition uniformity, such as:

- Changing electrode spacing
- Adjusting rotation speed
- Modifying electrolyte conductivity or viscosity
- Redesigning electrode geometry

Learning Outcomes

Learning Outcome (LO)	Indicator of Achievement (ID)	Description
LO 3: Explain the principles of key computational and numerical modeling techniques used in electrochemical science.	ID 3.4: Modelling of electrodeposition at forced convection conditions.	Students will model electrodeposition with hydrodynamics and evaluate how convection influences current distribution and deposition behavior.

Reference

1. C.T.J. Low, E.P.L. Roberts, and F.C. Walsh, “Numerical simulation of the current, potential and concentration distributions along the cathode of a rotating cylinder Hull cell,” Electrochimica Acta, vol. 52, pp 3831–3840, 2007.
2. COMSOL Multiphysics. Application Library path: Electrodeposition_Module/ Verification_Examples/rotating_cylinder_hull_cell