Lecture 10

Electrodeposition of metals at forced convection condition.

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.

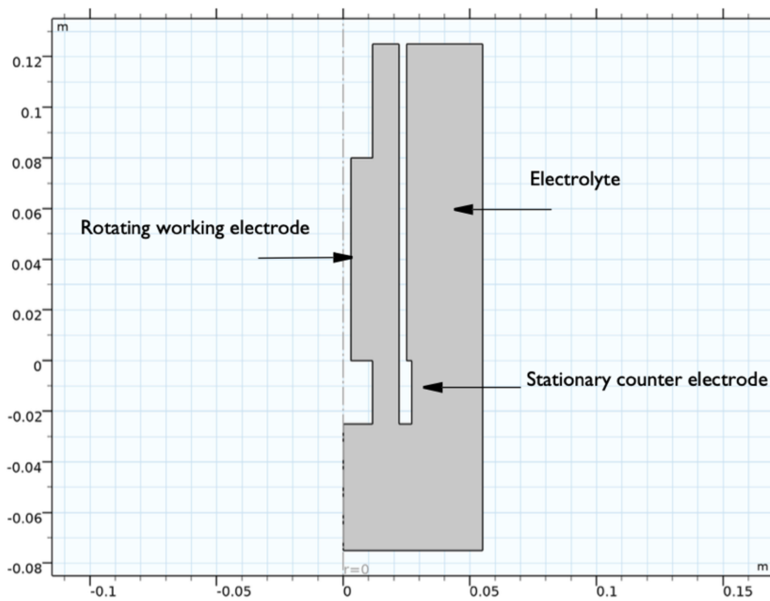

Figure 1. 2D axisymmetric geometry of the RCH cell. The Electrolyte, the rotating working electrode and the stationary counter electrode are highlighted.

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:

$$nN = \frac{vj_{loc,Cu}}{nF}$$

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.

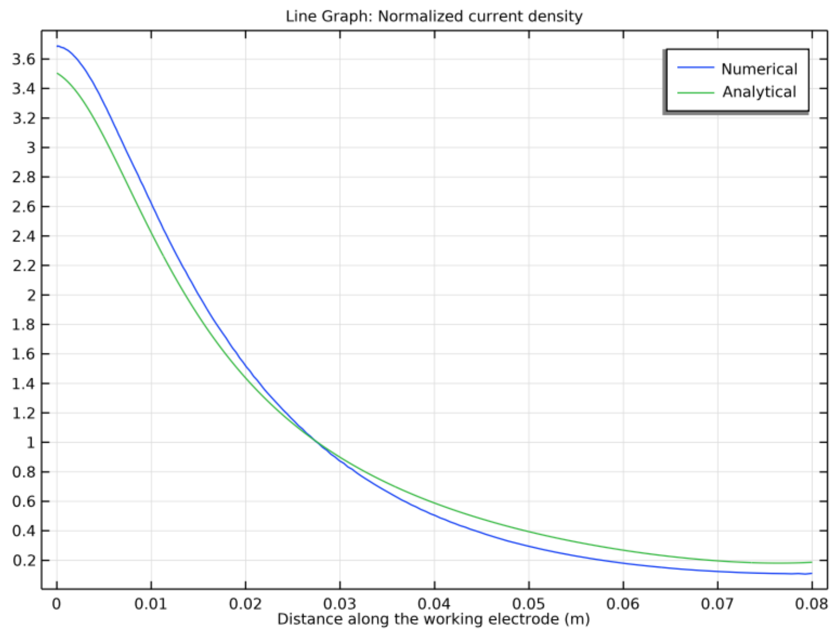

Figure 2. Normalized primary current density distribution obtained from the numerical model and the analytical expression.

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.

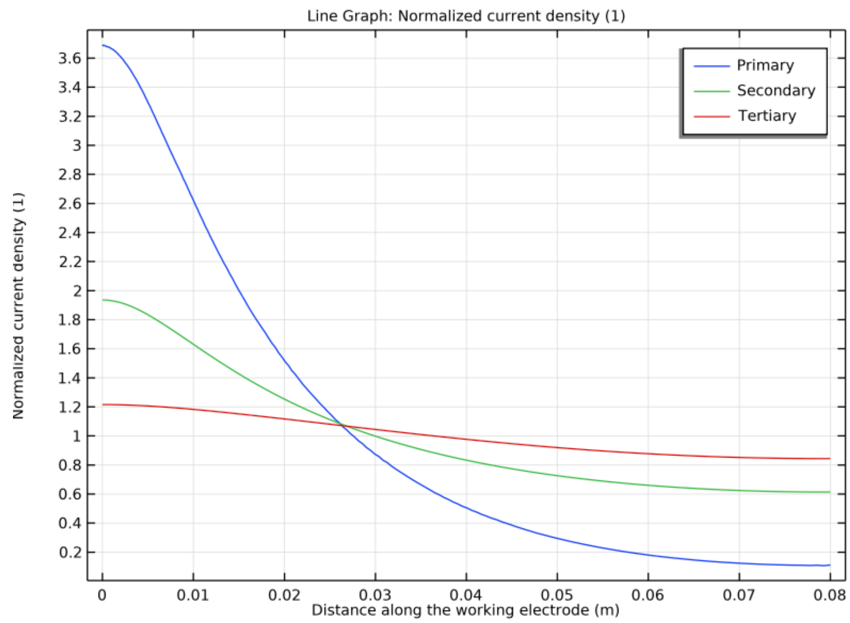

Figure 3. Normalized current density variation for primary, secondary and tertiary current distributions at the representative applied current density of 100 A/m^2 [2].

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.

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