Lecture 9

Modelling of the metal finishing technologies. Electroplating. Reaction kinetics.

Goal of the Lecture

The goal of this lecture is to introduce students to the principles and modelling strategies used in electroplating technologies. Students will understand the coupled physical phenomena that govern metal finishing processes and learn how to model current distribution, reaction kinetics, and deposition thickness evolution using numerical tools such as COMSOL Multiphysics.

Lecture Objectives

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

1. ***Explain*** *the electrochemical principles underlying electroplating and metal finishing.*
2. ***Describe*** *the coupled transport processes (ionic, electronic, hydrodynamic) that influence deposition rate and uniformity.*
3. ***Apply*** *Butler–Volmer kinetics to model metal dissolution at the anode and metal deposition at the cathode.*
4. ***Analyze*** *the roles of primary, secondary, and tertiary current distributions in plating cells.*
5. ***Interpret*** *simulated thickness profiles and propose strategies to optimize plating uniformity.*

Metal finishing refers to a family of technologies used to modify the surface of a metal object by depositing a thin metallic layer. The most common and industrially important process is electroplating, which relies on electrochemical deposition principles. Electroplating is used for: corrosion protection (e.g., Zn, Ni, Cr coatings); decorative finishes (gold, silver); functional coatings (wear resistance, conductivity); electronic and MEMS applications (Cu, Ni–P microstructures).

From Modelling Perspective

Electroplating involves complex coupled phenomena:

- Ionic transport in electrolyte,
- Electron transport in the substrate,

- Charge transfer reactions at the interface,
- Nucleation and growth on the surface,
- Hydrodynamics and flow patterns.

The goal of modelling is to quantitatively predict:

- Current and potential distribution,
- Deposition rate and uniformity,
- Thickness distribution,
- Surface morphology,
- Energy efficiency.

For example, model of decorative electroplating models a secondary current distribution with full Butler–Volmer kinetics for both anode and cathode. The thickness of the deposited layer at the cathode is computed along with the surface thickness change on the anode caused by metal dissolution. Each of these stages can be described using mathematical models, allowing prediction and control of the deposition rate, uniformity, and microstructure.

The model geometry is shown in Figure 1. The anode is a planar dissolving anode. The cathode represents a furniture fitting that is to be decorated by metal plating.

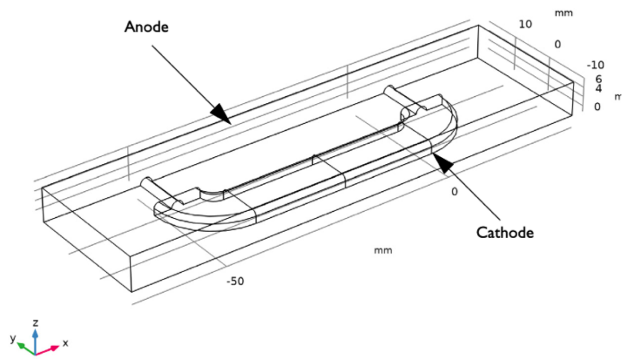

Figure 1: The model geometry.

The main electrode reaction on both the anode and the cathode surfaces is the nickel deposition/dissolution reaction according to

$$Ni^{2+} + 2e^{-} \leftrightarrows Ni_s$$

According to a Butler–Volmer expression the local current density sets as following:

$$j_{loc,Ni} = j_{0,Ni}\left(exp\left(\frac{\alpha_a F\eta_{Ni}}{RT}\right) - exp\left(\frac{-\alpha_c F\eta_{Ni}}{RT}\right)\right)$$

The rate of deposition at the cathode boundary surfaces and the rate of dissolution at the anode boundary surface, with a velocity in the normal direction, v (m/s), is calculated according to

$$v = \frac{j_{loc,Ni}M}{nF\rho}$$

where M is the mean molar mass (59 g/mol) and ρ is the density (8900 kg/m^3) of the nickel atoms and **n** is number of participating electrons. Note that the local current density is positive at the anode surface and negative at the cathode surfaces.

Figure 2 shows the change in the total electrode thickness for the cathode surfaces indicating the deposition thickness after 600 s. It can be seen that the deposition thickness is quite nonuniform. The lowest deposition thickness is found at the bottom end of the cathode geometry, farthest from the anode surface. The deposition thickness could be optimized further by changing design parameters such as plating cell geometry, distance between the anode and cathode surface, conductivity of the electrolyte and operational parameters such as applied current or potential.

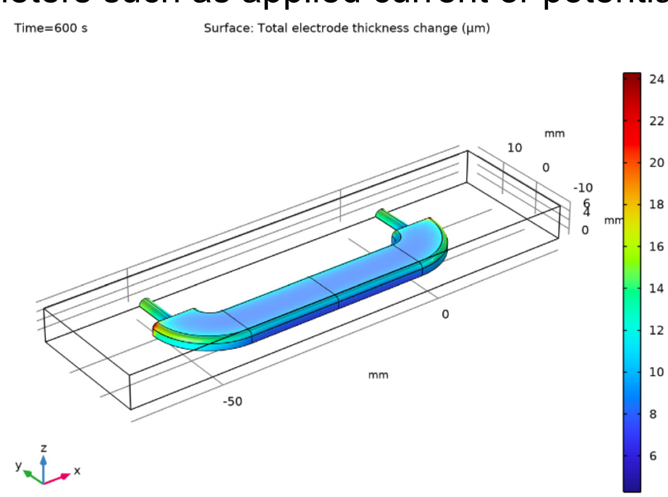

Figure 2: The simulated results of the change in the total electrode thickness [1].

Questions for Self-Examination

1. What are the most common industrial applications of electroplating?

2. Explain the difference between primary, secondary, and tertiary current distributions.
3. Why is Butler–Volmer kinetics necessary for modelling practical plating systems?
4. How does electrolyte conductivity influence plating uniformity?
5. What factors lead to non-uniform deposition thickness in real electroplating geometries?
6. Write the general electroplating reaction for Ni^{2+} and explain the meaning of the stoichiometric coefficients.
7. Describe how local current density affects deposition and dissolution rates.
8. Why is the deposition rate proportional to current density? Relate this to Faraday's laws.
9. What design modifications could improve plating uniformity in the system shown in Figure 1?
10. How does electrode shape influence electric field and thus deposition thickness?

Self-Study Assignment

Assignment Title:

Simulation of Electroplating Thickness Distribution Using Secondary Current Distribution and Butler–Volmer Kinetics

Objective:
To model electrodeposition of nickel on a complex cathode geometry and analyze deposition thickness uniformity using COMSOL Multiphysics.

Tasks

1. Geometry and Physics Setup

- Build a 2D or 3D geometry representing:
    - A dissolving planar anode
    - A complex cathode part (similar to decorative plating example)
- Add the following physics interfaces:
    - **Secondary Current Distribution** (ionic + electronic conduction)
    - **Electrode Surface Reactions** (Butler–Volmer kinetics)

- **Moving Mesh / Deformed Geometry** (optional for thickness evolution)

2. Material and Electrochemical Parameters

- Electrolyte conductivity σ (e.g., 10–15 S/m).
- Ni^{2+} redox reaction:

$$\mathrm{Ni}^{2+} + 2e^{-} \rightarrow \mathrm{Ni(s)}$$

- Use Butler–Volmer kinetics:

$$i = i_0\left[e^{\alpha_a F\eta/RT} - e^{-\alpha_c F\eta/RT}\right]$$

- Set:
  - Exchange current density i_0
  - Transfer coefficients α_a, α_c
  - Applied potential or total cell current

3. Simulation of Current Distribution

- Solve for the stationary electrolyte potential.
- Compute the local current density distribution at the cathode.
- Identify regions of high or low current density.

4. Deposition Thickness Calculation

Use Faraday's law to compute local deposition velocity:

$$v = \frac{M}{nF\rho} i$$

- Simulate deposition for **t = 600 s**.
- Generate a thickness plot along the cathode surface.

5. Parametric Study

Perform a study varying one parameter at a time:

- Electrode spacing
- Electrolyte conductivity
- Cathode geometry (e.g., protrusions, recesses)
- Applied current

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 3.3: Modelling of metal finishing technologies.	Students will model electroplating systems and interpret deposition thickness distributions based on reaction kinetics and current distribution.

Reference

1. COMSOL Multiphysics. Application Library path: Electrodeposition_Module/ Tutorials/decorative_plating
2. Bard, A. J., Faulkner, L. R., *Electrochemical Methods*, 2nd Ed., Wiley, 2001.