Lecture 8

Electrochemical deposition of metals. Reaction mechanism and the basic stages.

Goal of the Lecture

The goal of this lecture is to develop students' understanding of the fundamental physicochemical processes underlying electrochemical metal deposition (ECD). This includes the transport of metal ions, interfacial electron transfer, nucleation and growth of metallic phases, and the mathematical models used to represent these processes. Students will gain the theoretical basis needed to simulate and analyze metal deposition in COMSOL Multiphysics.

Lecture Objectives

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

1. **Describe** the sequence of stages involved in electrochemical metal deposition, from mass transport to nucleation and growth.
2. **Explain** the roles of diffusion, migration, and convection in metal ion transport using the Nernst–Planck framework.
3. **Apply** the Butler–Volmer equation to model interfacial charge-transfer kinetics during metal deposition.
4. **Differentiate** between instantaneous and progressive nucleation, and interpret Scharifker–Hills current–time transients.
5. **Analyze** key factors influencing coating morphology, deposition rate, and uniformity in electrochemical systems.

Electrochemical deposition (**ECD**) is the process by which metal ions in an electrolyte are reduced to metallic atoms at an electrode surface, forming a coherent, adherent metal layer. It is a fundamental technique in materials engineering, widely used for: **Surface finishing** (chrome, nickel, gold plating); **Microelectronics** (copper interconnects, thin films); **Energy applications** (electrocatalyst formation, metal batteries).

From a **modelling standpoint**, ECD is an **interdisciplinary process** involving:

1. **Mass transport** in the electrolyte (diffusion, migration, convection),

2. **Interfacial charge transfer** governed by electrochemical kinetics,
3. **Nucleation and growth** processes at the electrode surface,
4. **Morphological evolution** of the deposit.

Each of these stages can be described using mathematical models, allowing prediction and control of the deposition rate, uniformity, and microstructure.

For a generic metal ion Me^{n+} in solution:

$$Me^{n+} + ne^- \leftrightarrows Me_s$$

This is a heterogeneous redox reaction occurring at the electrode–electrolyte interface.

Electrochemical metal deposition consists of a sequence of interdependent **physical and chemical steps**.

Before reduction, metal ions must reach the electrode surface through the electrolyte. Three processes contribute [1]:

Diffusion - movement due to concentration gradient:

$$J_{diff} = -D_i \frac{\partial c_i}{\partial x}$$

Migration - movement due to electric field:

$$J_{mig} = -z_i u_i c_i \frac{\partial \phi}{\partial x}$$

Convection - movement due to fluid flow:

$$J_{conv} = v c_i$$

Combining them gives the Nernst–Planck equation:

$$J_i = -D_i \nabla c_i - z_i u_i c_i \nabla \phi + v c_i$$

Once the ion reaches the electrode surface, it undergoes electron transfer. This is the rate-determining step in many systems.

The kinetics are described by the Butler–Volmer equation:

$$j = j_0 \left(exp\left(\frac{\alpha_a F\eta}{RT}\right) - exp\left(\frac{-\alpha_c F\eta}{2RT}\right)\right)$$

j_0 - exchange current density, measures intrinsic reaction rate at equilibrium.

α_a, α_c - anodic/cathodic transfer coefficients.

After ions are reduced to metal atoms on the surface, these atoms may: adsorb and diffuse on the surface; form stable nuclei (clusters of atoms); grow into grains forming the deposit layer.

Two major nucleation regimes are recognized:

Instantaneous nucleation: all nuclei form at the same time, then grow.

Progressive nucleation: nuclei form continuously over time.

Scharifker–Hills models describe current–time transients under diffusion control [2]:

Instantaneous:

$$\frac{j^2}{j_{max}^2} = \frac{1.9542}{\frac{t}{t_{max}}} \left\{1 - exp\left[-1.2564(\frac{t}{t_{max}})\right]\right\}^2$$

Progressive:

$$\frac{j^2}{j_{max}^2} = \frac{1.2254}{\frac{t}{t_{max}}} \left\{1 - exp\left[-2.3367(\frac{t}{t_{max}})^2\right]\right\}^2$$

By comparing these theoretical transients to experimental chronoamperometry curves, one can identify the nucleation mechanism and growth kinetics.

Understanding the reaction mechanism and stages of electrochemical metal deposition is crucial for:

- Designing efficient and uniform coatings,
- Controlling microstructure and texture,
- Preventing dendritic growth in batteries,
- Developing predictive models for industrial processes.

Mathematical modelling serves as the bridge between fundamental electrochemical theory and practical electrode design, allowing optimization of parameters before experimentation.

Questions for Self-Examination

1. What are the major industrial applications of electrochemical metal deposition?
2. Describe the contributions of diffusion, migration, and convection to ion transport. Under which conditions does each term dominate?
3. Write the Nernst–Planck equation and explain the physical meaning of each term.

4. What is the role of the **exchange current density (i_0)** in electrodeposition kinetics?
5. How do the transfer coefficients (α_a, α_c) influence the Butler–Volmer reaction rate?
6. Compare instantaneous and progressive nucleation. What experimental signatures differentiate them?
7. Describe how the Scharifker–Hills models can be used to identify nucleation mechanisms.
8. Why is modeling ECD important for controlling deposit uniformity and preventing dendritic growth?
9. What steps follow electron transfer in the overall deposition process?
10. How do electrolyte composition, temperature, and overpotential affect nucleation density and grain growth?

Self-Study Assignment

Assignment Title:
Modeling Metal Ion Reduction and Nucleation Behavior Using the Electrodeposition Framework in COMSOL Multiphysics

Objective:
To simulate electrochemical metal deposition at a planar electrode using the Nernst–Planck and Butler–Volmer frameworks, and to examine the influence of kinetic and transport parameters on deposition behavior.

Tasks

1. Model Setup

- Create a **1D model** representing the electrolyte domain (e.g., 0–200 μm).
- Include one metal ion species (e.g., M^{2+}) and optionally the deposited metal (solid phase).
- Use **Transport of Diluted Species (tds)** with migration enabled (Nernst–Planck).

2. Define Ion Transport

Include diffusion, migration, and optional convection (if desired):

$$\mathbf{N}_M = -D\nabla c_M - uzFc_M\nabla\phi$$

3. Electrode Boundary Conditions

At x = 0 (cathode surface):

- Implement charge-transfer kinetics using **Butler–Volmer**:

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

- Apply a potential step or a range of potentials.
- No flux for all spectator ions.

4. Simulation Tasks

1. **Simulate diffusion–migration of metal ions** under steady applied potential.
2. **Compute and plot**:
   - Concentration profiles c_M(x)
   - Interfacial current density i
   - Deposition flux
3. Perform a **parametric sweep** over:
   - Overpotential (η)
   - Diffusion coefficient (D)
   - Exchange current density (i_0)
4. **Optional advanced task:**
   - Implement nucleation kinetics by adding a surface concentration variable for newly formed nuclei.
   - Compare instantaneous vs. progressive nucleation using Scharifker–Hills theory.

5. Analysis

- Identify deposition rates under different overpotentials.
- Discuss how mass transport limitations develop at high current densities.
- Analyze how varying D and i_0 influences current–time behavior.
- Interpret whether nucleation tends toward instantaneous or progressive modes.

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 3.2: Explain fundamentals of electrodeposition.	Students will describe and model the mechanisms of electrochemical metal deposition, including ion transport, electron transfer, and nucleation processes.

Reference

1. A.J. Bard and L.R. Faulkner, Electrochemical Methods, Fundamentals and Applications, 2nd ed., Wiley, New York, 2001.
2. Avchukir, Khaisa, et al. "Influence of tetrabutylammonium chloride on the electrodeposition of indium from chloride solution on a glassy carbon electrode." Journal of Electroanalytical Chemistry 842 (2019): 176-183.