Lecture 8

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

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.

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.