Lecture #14 Modeling of Electrodeposition onto Massive Surfaces and Types of Current Distribution

Goal

This lecture introduces the modeling principles of electrodeposition onto massive (macroscopic) surfaces, with a special focus on current distribution. Understanding current distribution is crucial for predicting deposit uniformity, controlling morphology, and ensuring efficient industrial electroplating. Students will learn the fundamental mathematical expressions governing primary, secondary, and tertiary current distributions, and how they influence copper electrodeposition.

Introduction

Electrodeposition involves the deposition of a material onto a surface via electrochemical reduction. This process is widely used in industries such as electroplating, material synthesis, and corrosion protection. Modeling electrodeposition on massive surfaces is essential for understanding layer uniformity, morphology, and efficiency.

One critical aspect of electrodeposition modeling is analyzing the current distribution across the electrode surface. This lecture focuses on the types of current distributions—primary, secondary, and tertiary—and their impact on electrodeposition.

Types of Current Distribution

Primary Current Distribution

The primary current distribution assumes no influence from electrode kinetics or concentration gradients. The current distribution is determined purely by ohmic potential drop in the electrolyte and is governed by Laplace's equation:

$$\nabla^2 \phi = 0$$

Where ϕ is the potential in the electrolyte. This distribution often leads to a non-uniform current due to geometric factors.

Secondary Current Distribution

The secondary current distribution accounts for the influence of electrode kinetics, such as activation overpotential. The distribution is determined by the balance of ohmic drop and electrode reaction kinetics, modeled by the Butler-Volmer equation:

$$i = i_0 [\exp(\alpha F\eta/RT) - \exp(-\beta F\eta/RT)]$$

Where η is the overpotential. This distribution tends to be more uniform than the primary distribution but is still influenced by geometry.

Tertiary Current Distribution

The tertiary current distribution includes the effects of concentration gradients in the electrolyte due to mass transport. This is the most complex and realistic current distribution for modeling electrodeposition, involving coupled equations for potential, concentration, and current density:

$$\partial C/\partial t = D \nabla^2 C - (v \cdot \nabla C) + R(C)$$

Where C is the concentration of electroactive species, D is the diffusion coefficient, v is the velocity field, and R(C) is the reaction rate.

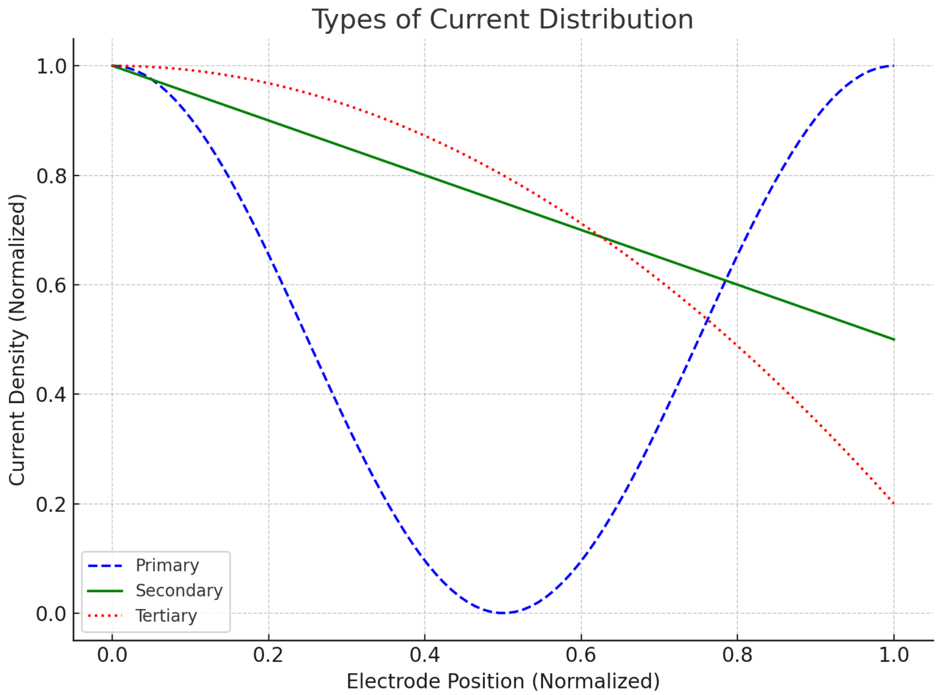
Example: Electrodeposition of Copper

Consider the electrodeposition of copper onto a flat massive electrode from an acidic $CuSO_4$ solution. The key reactions are:

- Cathode reaction: $Cu^{2+} + 2e^- \rightarrow Cu(s)$
- Anode reaction: $H_2O \rightarrow ½O_2 + 2H^+ + 2e^-$

Modeling involves solving the primary, secondary, or tertiary current distribution equations, depending on the desired accuracy. For tertiary distribution, concentration gradients near the electrode are critical and are described by Fick's second law.

Illustration: Current Distributions



The illustration above compares the primary, secondary, and tertiary current distributions. Primary distribution shows strong geometric influence, secondary considers electrode kinetics, and tertiary includes mass transport effects.

Summary

Modeling electrodeposition onto massive surfaces requires an understanding of current distributions. Primary distribution focuses on geometry, secondary adds electrode kinetics, and tertiary includes mass transport effects. These models are essential for predicting deposit uniformity and optimizing industrial processes.

Learning Outcomes

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

1. Define primary, secondary, and tertiary current distributions and distinguish their physical assumptions (related to LO 4, ID 4.3–4.6).

2. Use the Butler–Volmer equation to model secondary current distribution (related to LO 4, ID 4.4–4.5).

3. Formulate tertiary distribution models including mass transport via diffusion, convection, and reaction (related to LO 4, ID 4.5–4.6).
4. Analyze how current distribution affects deposit thickness, uniformity, and industrial plating efficiency (related to LO 4, ID 4.7).
5. Simulate electrodeposition scenarios (basic level) using governing equations for potential, concentration, and reaction kinetics.

Questions and Self-Study Assignments

1. Define primary, secondary, and tertiary current distributions in electrodeposition.
2. Solve Laplace's equation for a simple parallel-plate cell (primary distribution).
3. Write the Butler–Volmer equation and explain its role in secondary distribution.
4. Why does tertiary current distribution require modeling concentration gradients?
5. Describe how mass transport limitations lead to limiting current.
6. Provide an example where tertiary distribution is essential in industry (e.g., copper electroplating).

References

1. Newman, J., & Thomas-Alyea, K. Electrochemical Systems. 3rd ed. Wiley, 2004. Fundamental theory of current distribution (primary, secondary, tertiary), potential fields, Butler–Volmer kinetics.
2. Pletcher, D., & Walsh, F. C. Industrial Electrochemistry. Springer, 1993. Comprehensive treatment of electroplating, electrode kinetics, mass transport, and current distribution.
3. Bockris, J. O'M., & Reddy, A. K. N. Modern Electrochemistry, Volume 2A–2B. Springer, 2002. Detailed theoretical basis for electrodeposition and transport processes.