

Lecture #14

Modeling of Electrodeposition onto Massive Surfaces and Types of Current Distribution

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:

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

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

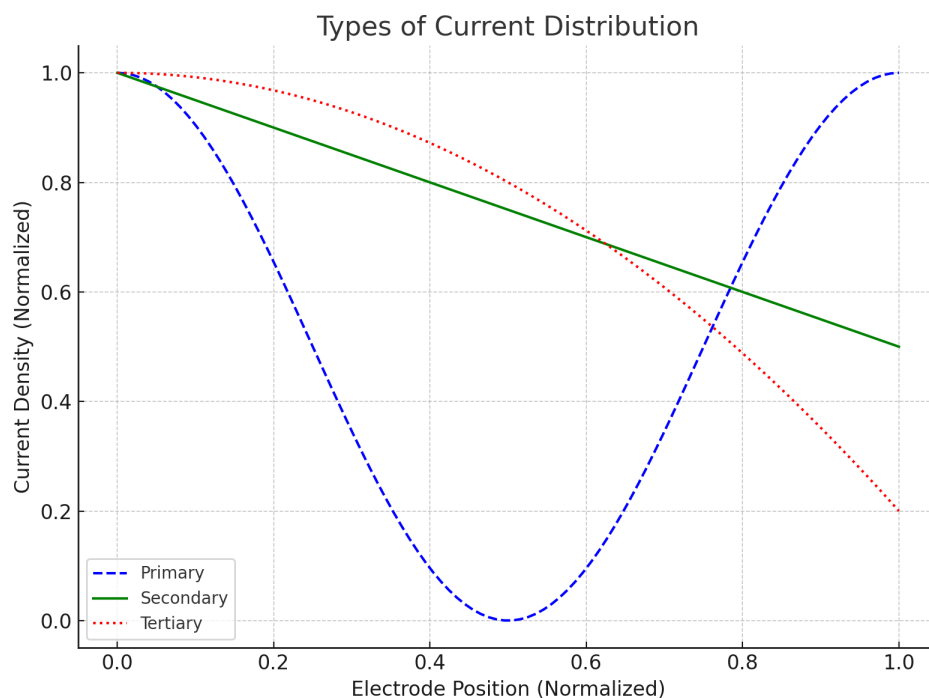
Example: Electrodeposition of Copper

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

- Cathode reaction: $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu(s)}$
- Anode reaction: $\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^-$

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.