Lecture 8 | Electrochemical Metal Deposition: Kinetics, Nucleation, and Growth

Al-Farabi Kazakh National University

Department of Analytical, Colloidal Chemistry and Technology of Rare Elements

Discipline: Modeling in Electrochemistry

Educational program: 7M07103 Chemical Engineering

Lecturer: Khaisa Avchukir, PhD, Associate Professor

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Purpose and Expected Learning Outcomes

PURPOSE

Build a quantitative understanding of electrochemical metal deposition: kinetics, nucleation, and growth.

01 Explain the physical assumptions and governing electrochemical equations.

02 Calculate relevant kinetic, transport, and interfacial parameters.

03 Interpret simulated responses and compare them with measurements.

04 Evaluate model limitations and propose a reproducible validation plan.

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Lecture Trajectory and Practical Relevance



Scientific value: link measurable current, potential, concentration, or impedance to mechanistic parameters.

Applications: electroanalysis • energy conversion • electrodeposition • corrosion • process engineering

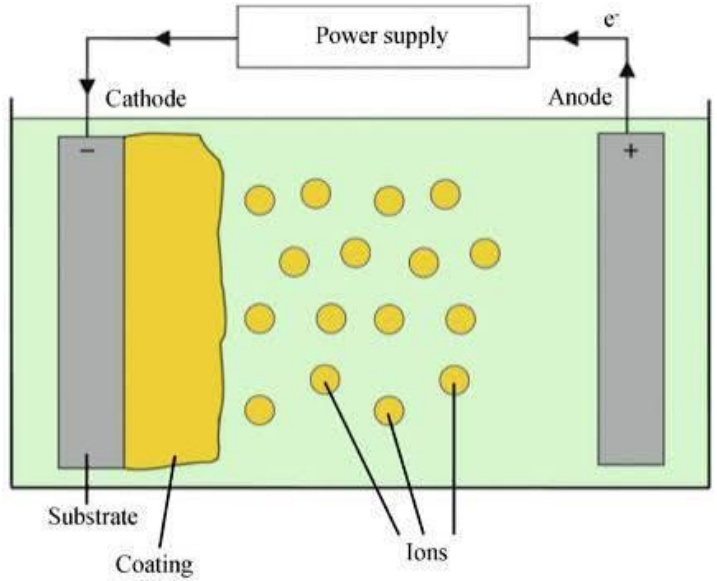
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Electrodeposition stages

$Me^{n+} + ne- \rightarrow Me(s)$

Transport supplies ions; electron transfer produces adsorbed atoms.

Surface diffusion, nucleation, and growth form the coating.



MODEL ASSUMPTIONS • EQUATIONS • MEASURABLE RESPONSE

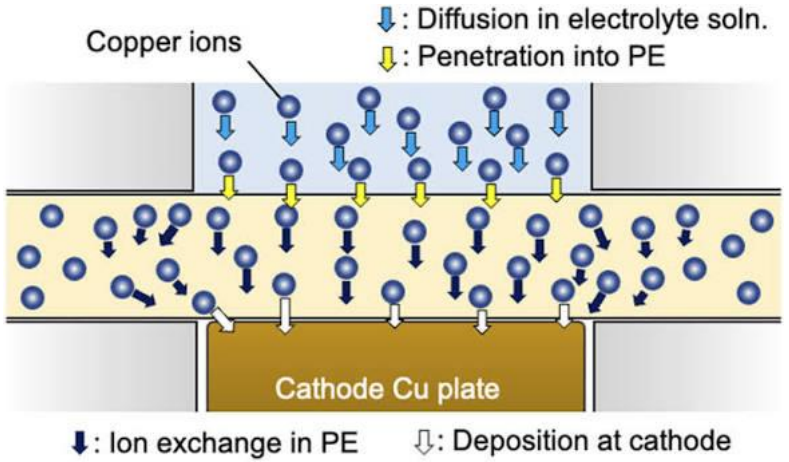
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Transport of depositing ions

$$N_i = -D_i \nabla c_i - (z_i F D_i / RT) c_i \nabla \phi + c_i v$$

Diffusion, migration, and convection may all contribute.

Supporting electrolyte suppresses migration only under suitable conditions.



MODEL ASSUMPTIONS • EQUATIONS • MEASURABLE RESPONSE

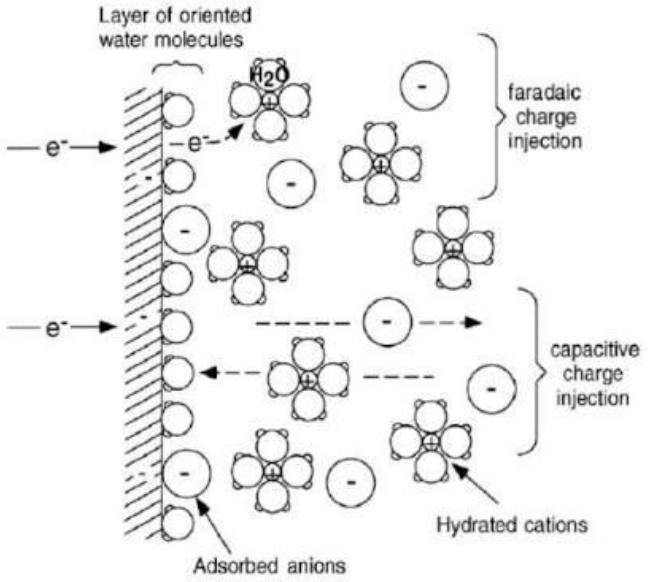
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Interfacial charge transfer

$$j = j_0[\exp(\alpha_a F\eta/RT) - \exp(-\alpha_c F\eta/RT)]$$

Cathodic overpotential drives reduction.

Surface concentration depletion can limit deposition current.



MODEL ASSUMPTIONS • EQUATIONS • MEASURABLE RESPONSE

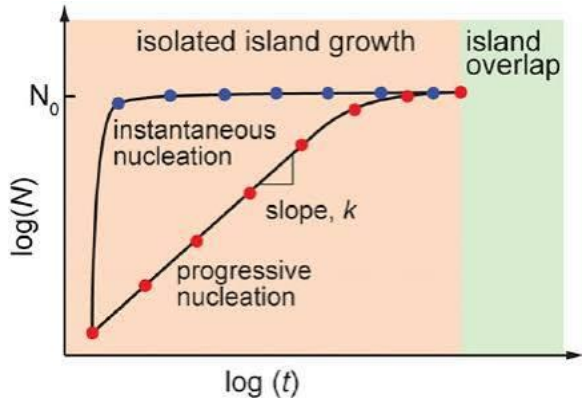
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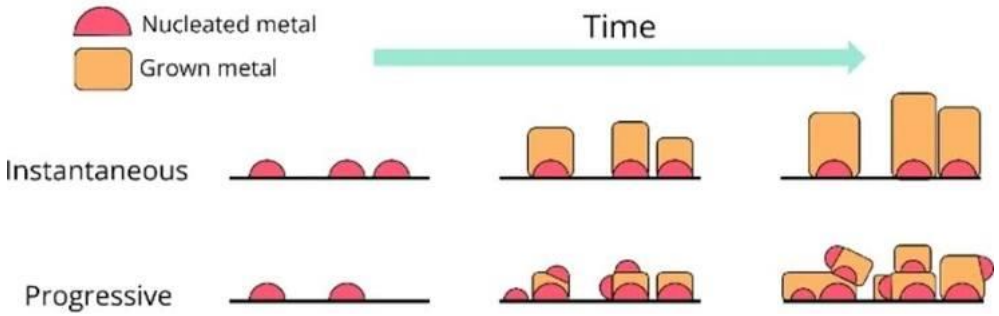
Nucleation: instantaneous versus progressive

$$(i/im)^2 = f(t/tm)$$

Scharifker–Hills transients distinguish idealized nucleation regimes.

A clear smooth maximum is required for meaningful normalized comparison.





MODEL ASSUMPTIONS • EQUATIONS • MEASURABLE RESPONSE

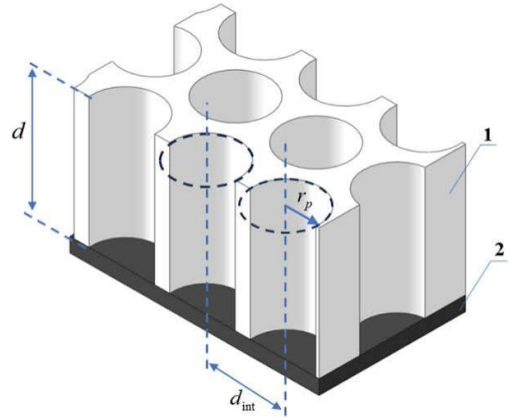
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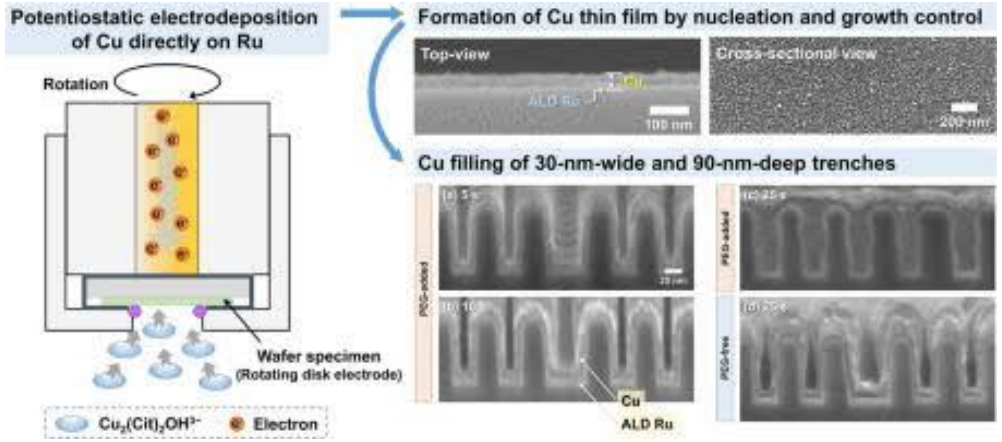
Film growth and Faraday's law

$$h = M\int|j|dt/(nF\rho)$$

Thickness follows charge only if current efficiency is known.

Competing hydrogen evolution lowers metal deposition efficiency.





MODEL ASSUMPTIONS • EQUATIONS • MEASURABLE RESPONSE

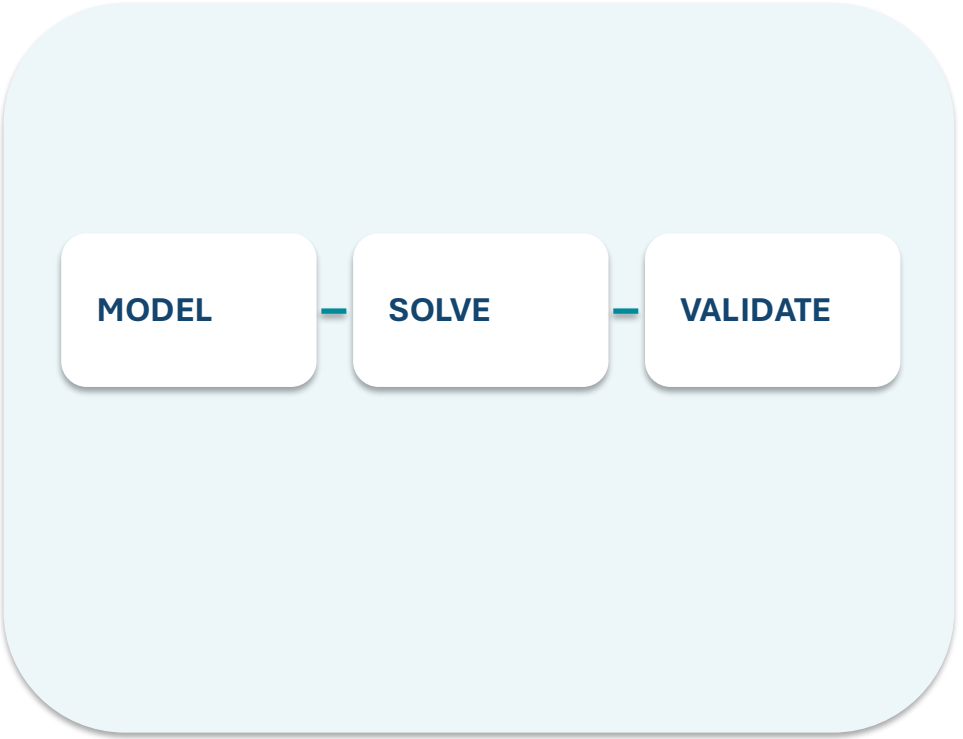
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Morphology and mechanistic limits

Da = kinetic rate / transport rate

Current distribution and additives affect deposit uniformity.

Scharifker–Hills assumptions can fail for overlapping processes.



MODEL ASSUMPTIONS • EQUATIONS • MEASURABLE RESPONSE

Reference: Bard, Faulkner & White, Electrochemical Methods (3rd ed.); source lecture PDF.

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Conclusions: From Physical Mechanisms to Predictive Models

1. Electrodeposition stages

$Me^{n+} + ne- \rightarrow Me(s)$

2. Transport of depositing ions

$Ni = -Di\nabla ci - (ziFDi/RT)ci\nabla\phi + civ$

3. Interfacial charge transfer

$j = j0[\exp(\alpha aF\eta/RT) - \exp(-\alpha cF\eta/RT)]$

4. Nucleation: instantaneous versus progressive

$(i/im)^2 = f(t/tm)$

5. Film growth and Faraday's law

$h = M\int|j|dt/(nF\rho)$

6. Morphology and mechanistic limits

Da = kinetic rate / transport rate

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Homework: Quantitative and Research-Oriented Problems

CONCEPTUAL Compare the assumptions underlying “Electrodeposition stages” and “Interfacial charge transfer”.

CALCULATION Given T = 298.15 K, F = 96485 C mol^{-1}, R = 8.314 J mol^{-1} K^{-1}, D = 1.0×10^{-9} m^2 s^{-1}, c = 1.0 mol m^{-3}, A = 1.0 cm^2, n = 1, compute a relevant transport or kinetic prediction and state assumptions.

DATA INTERPRETATION For simulated normalized signals (t/s, response): (0.2,0.82), (0.5,0.61), (1.0,0.44), (2.0,0.30), identify the trend and test a plausible physical model.

CRITICAL THINKING Predict how a tenfold change in the controlling kinetic or transport parameter changes the response; distinguish hypotheses.

RESEARCH TASK Design a COMSOL or Python model with geometry, boundary conditions, mesh-convergence test, and an experimental validation plan.

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