Lecture 4 | Chronoamperometry and Transient Mass-Transfer Modeling

Al-Farabi Kazakh National University

Department of Analytical, Colloidal Chemistry and Technology of Rare Elements

Discipline: Modeling in Electrochemistry

Educational program: 7M07103 Chemical Engineering

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Purpose and Expected Learning Outcomes

PURPOSE

Build a quantitative understanding of chronoamperometry and transient mass-transfer modeling.

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

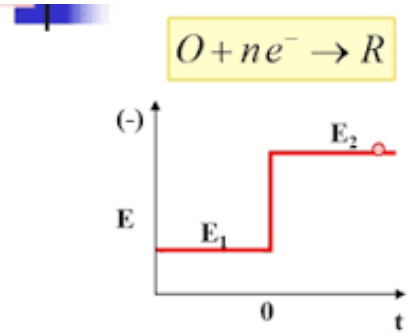
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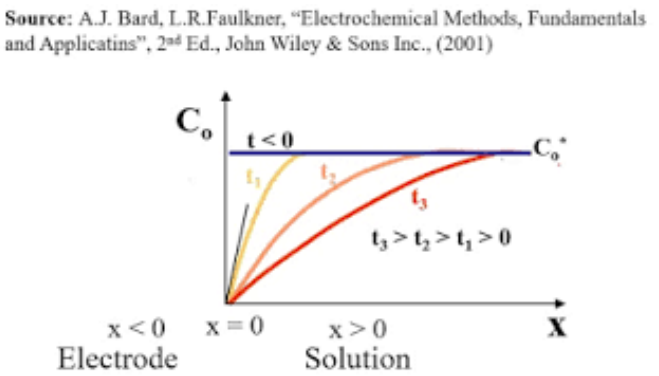
Potential-step experiment

E(t) = E1 for t ≥ 0

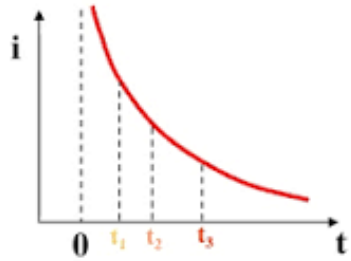
A rapid potential step changes electrode reaction rate.

Record current versus time and separate initial capacitive transients.





$$i \propto \left.\frac{\partial C}{\partial x}\right|_{x=0}$$



MODEL ASSUMPTIONS • EQUATIONS • MEASURABLE RESPONSE

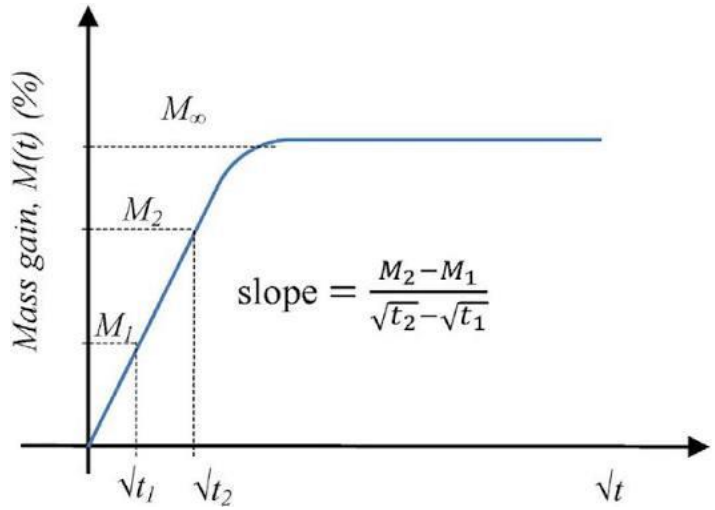
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Fickian diffusion model

$$\partial c/\partial t = D\partial^2 c/\partial x^2$$

Assume quiescent solution and excess supporting electrolyte.

For fast reduction, impose c(0,t)=0 at the electrode.



MODEL ASSUMPTIONS • EQUATIONS • MEASURABLE RESPONSE

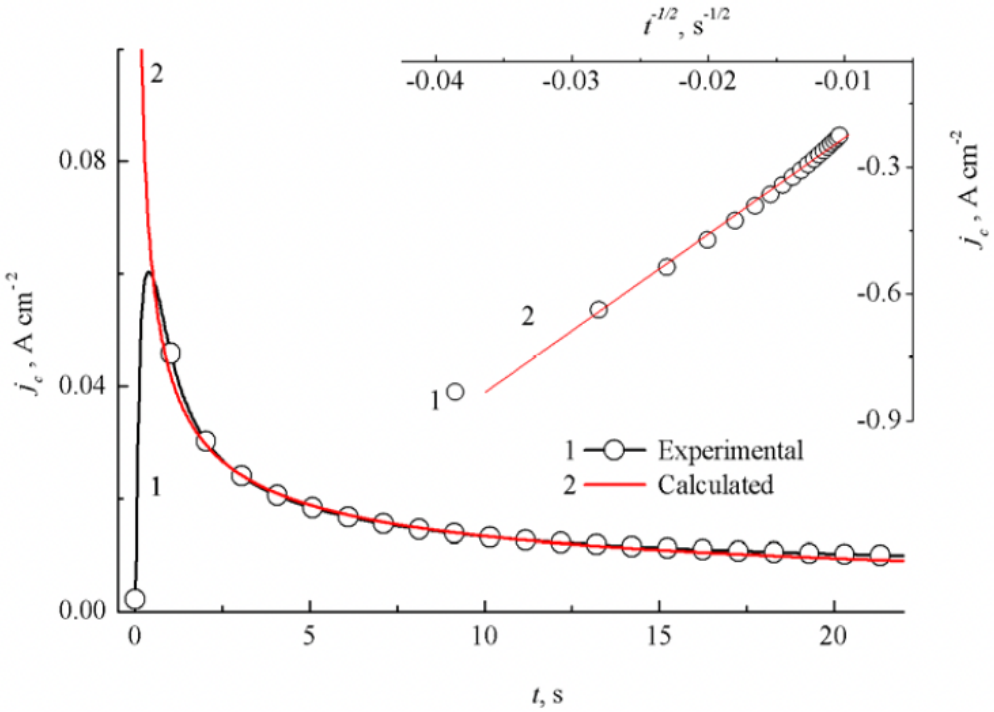
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Cottrell equation

$$|j(t)| = nFc^*\sqrt{(D/(\pi t))}$$

Semi-infinite planar diffusion predicts $t^{-1/2}$ decay.

Valid after charging transients and before finite-cell effects.



MODEL ASSUMPTIONS • EQUATIONS • MEASURABLE RESPONSE

Avchukir, K., N. N. Yessaly, and B. D. Burkitbayeva. "Electrodeposition of indium on glassy carbon from tetrabutylammonium chloride containing solutions." *Eurasian Chemico-Technological Journal* 21.2 (2019): 157-163.

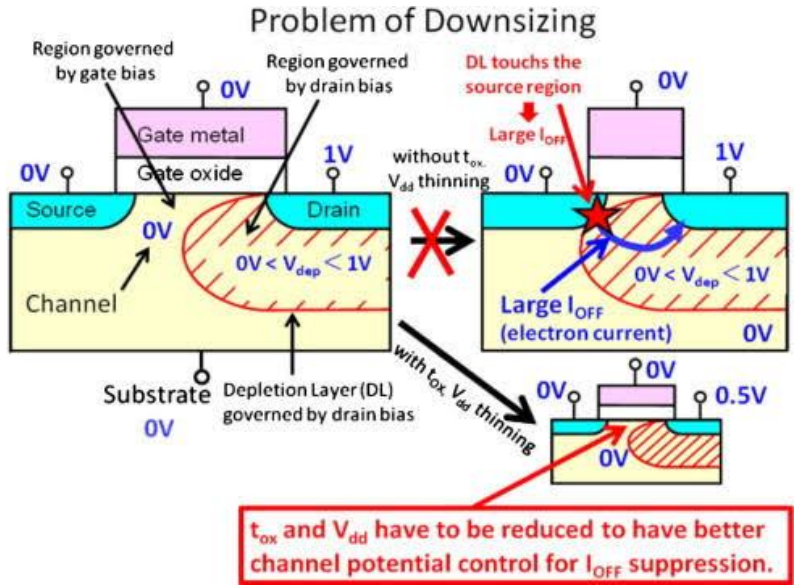
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Finite thin-layer depletion

$$\tau_D \approx L^2/D$$

An impermeable back wall limits the available analyte.

At long times current falls faster than Cottrell behavior.



MODEL ASSUMPTIONS • EQUATIONS • MEASURABLE RESPONSE

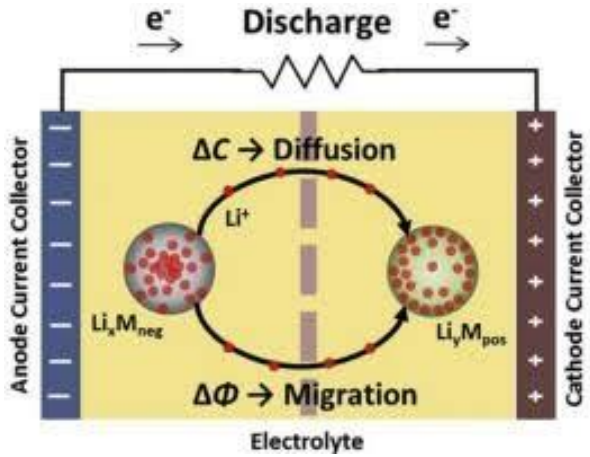
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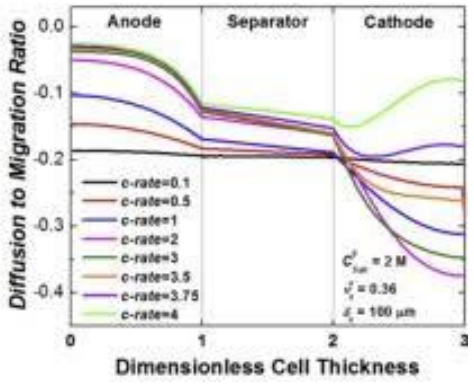
Integrated charge and concentration

$$Q_\infty = nFALc_0$$

Complete conversion of a thin-layer inventory yields total charge.

Subtract background and consider side reactions when estimating c0.





MODEL ASSUMPTIONS • EQUATIONS • MEASURABLE RESPONSE

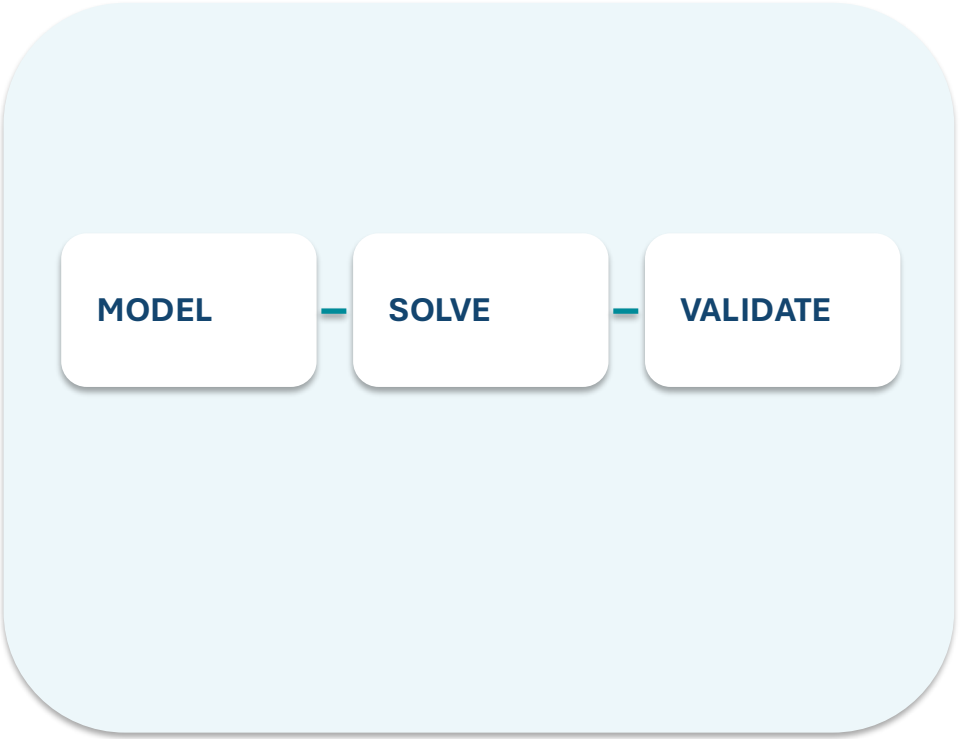
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Simulation and interpretation

$$j = nFD(\partial c/\partial x)|x=0$$

Resolve the near-electrode gradient with fine spatial mesh.

Compare transient current, charge integral, and mass balance.



MODEL ASSUMPTIONS • EQUATIONS • MEASURABLE RESPONSE

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Conclusions: From Physical Mechanisms to Predictive Models

1. Potential-step experiment

$E(t) = E1$ for $t \geq 0$

2. Fickian diffusion model

$\partial c/\partial t = D\partial^2 c/\partial x^2$

3. Cottrell equation

$|j(t)| = nFc^*\sqrt{(D/(\pi t))}$

4. Finite thin-layer depletion

$\tau D \approx L^2/D$

5. Integrated charge and concentration

$Q\infty = nFALc0$

6. Simulation and interpretation

$j = nFD(\partial c/\partial x)|x=0$

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Homework: Quantitative and Research-Oriented Problems

CONCEPTUAL Compare the assumptions underlying “Potential-step experiment” and “Cottrell equation”.

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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