Lecture 5 | Microdisk Electrode Voltammetry and Radial Diffusion

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 microdisk electrode voltammetry and radial diffusion.

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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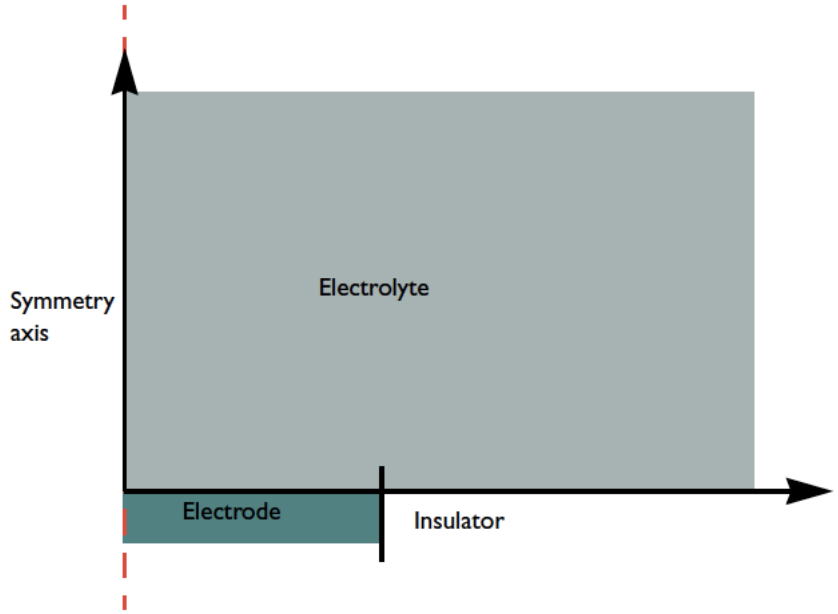
Microdisk geometry and advantages

a = 10 µm

A flush disk in an insulating plane supports radial diffusion.

Small electrodes reduce iR drop and enable fast mass transport.



MODEL ASSUMPTIONS • EQUATIONS • MEASURABLE RESPONSE

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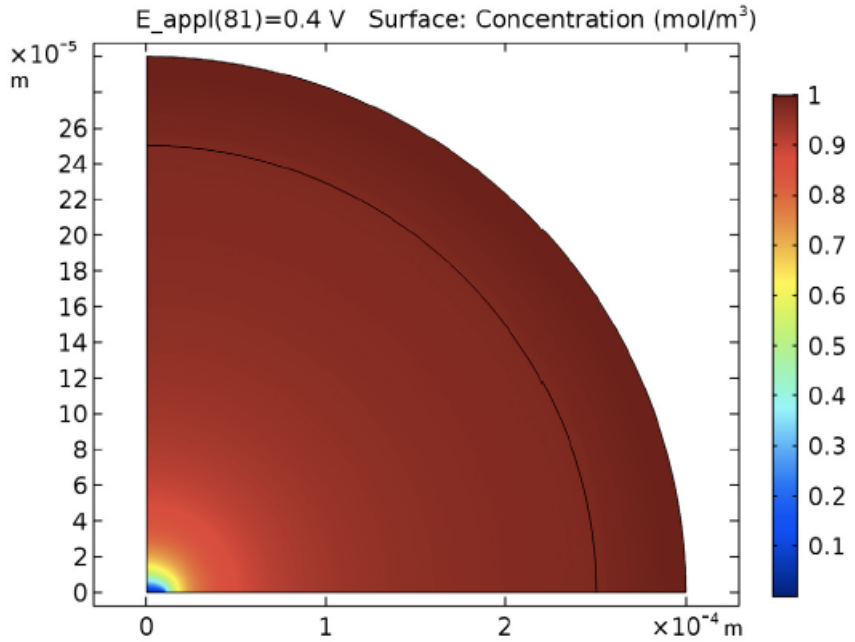
Axisymmetric diffusion model

$$\nabla\cdot(D\nabla c) = 0$$

Steady-state transport can be solved in (r,z) coordinates.

Set no-flux at the insulating plane and bulk concentration far away.



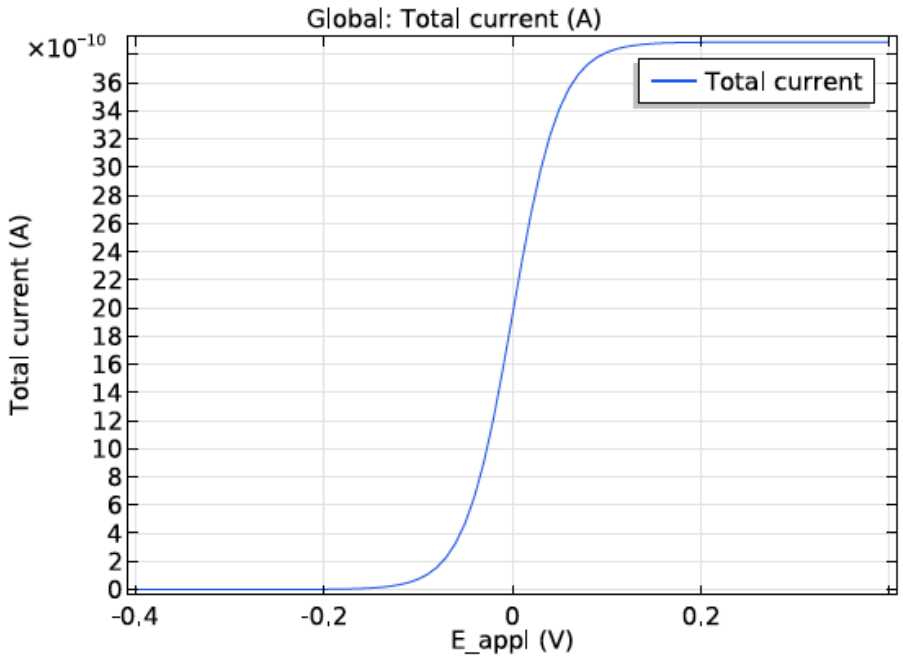
MODEL ASSUMPTIONS • EQUATIONS • MEASURABLE RESPONSE

Steady-state limiting current

$$i_{lim} = 4nFDc_a$$

The limiting current scales with radius, not disk area.

This expression assumes an isolated inlaid disk and diffusion control.



MODEL ASSUMPTIONS • EQUATIONS • MEASURABLE RESPONSE

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

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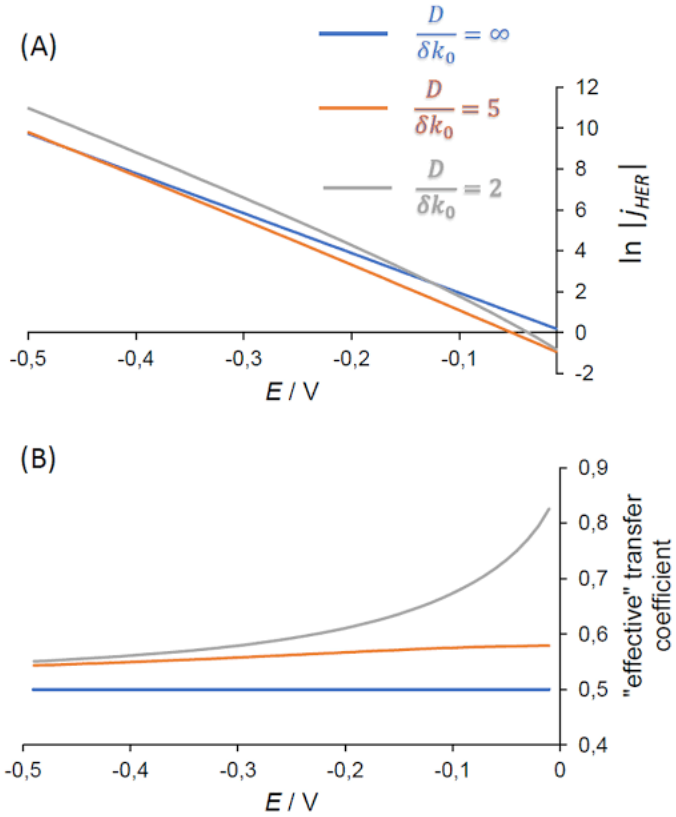
Electron-transfer kinetics

$$j = nFk_0[c_{Red}\exp(\alpha_a F\eta/RT) - c_{Ox}\exp(-\alpha_c F\eta/RT)]$$

Finite heterogeneous kinetics change voltammogram shape.

Surface concentrations must be solved consistently with fluxes.



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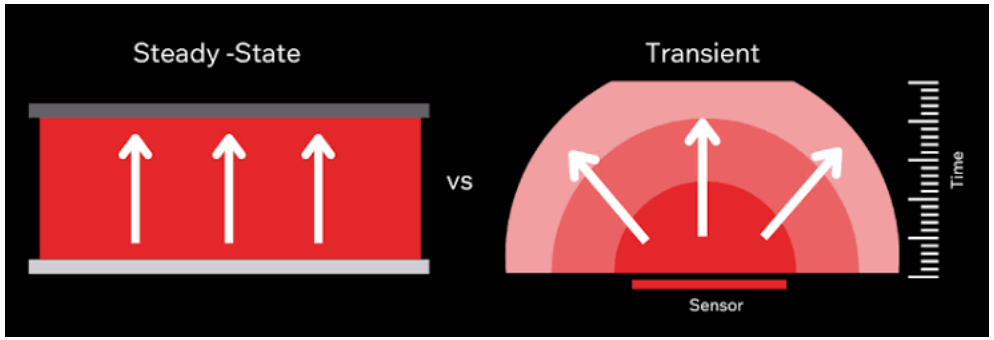
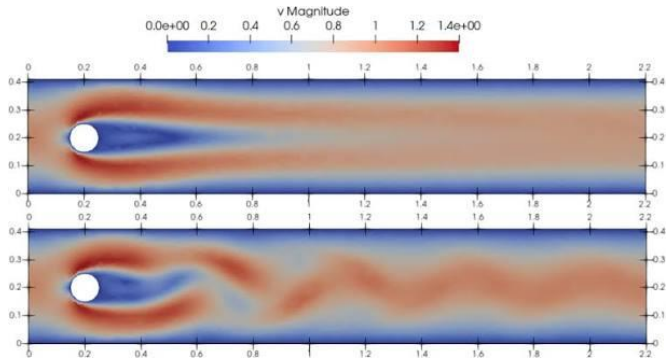
Steady-state versus transient regimes

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

For scan times much longer than a^2/D, a steady-state approximation may hold.

Fast scans require a time-dependent diffusion calculation.





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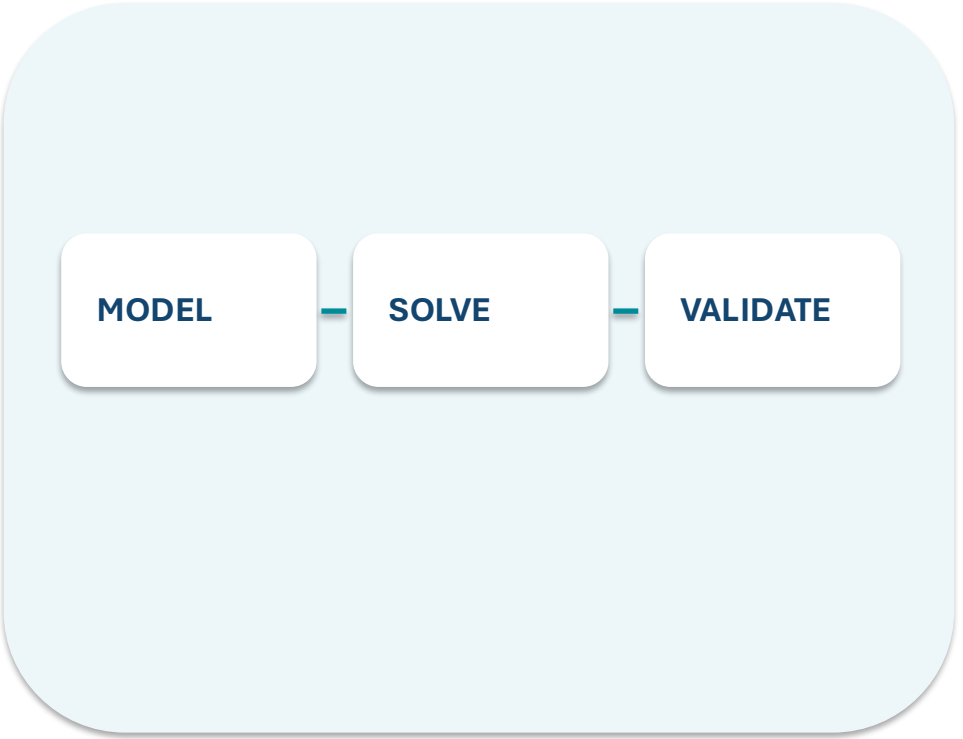
Experimental applications and limits

$$iR \approx iR_u$$

Microdisks enable low-conductivity and fast-kinetics studies.

Beware of surface fouling, nonideal geometry, and background current.



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Conclusions: From Physical Mechanisms to Predictive Models

1. Microdisk geometry and advantages

a = 10 μm (source example)

2. Axisymmetric diffusion model

$\nabla \cdot (D \nabla c) = 0$

3. Steady-state limiting current

$i_{lim} = 4nFDca$

4. Electron-transfer kinetics

$j = nFk_0[c_{Red} \exp(\alpha_a F\eta/RT) - c_{Ox} \exp(-\alpha_c F\eta/RT)]$

5. Steady-state versus transient regimes

$\tau_D \approx a^2/D$

6. Experimental applications and limits

$iR \approx iRu$

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Homework: Quantitative and Research-Oriented Problems

CONCEPTUAL Compare the assumptions underlying “Microdisk geometry and advantages” and “Steady-state limiting current”.

CALCULATION Given $T = 298.15$ K, $F = 96485$ C mol^{-1}, $R = 8.314$ J mol^{-1} K^{-1}, $D = 1.0 \times 10^{-9}$ 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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