Lecture 10 | Electrochemistry of Microdisk Electrodes

Limiting stages of electrochemical reactions

Modern research methods in electrochemistry

7M05301 Chemistry

Lecturer: Khaisa Avchukir, PhD, Acting Associate Professor

Al-Farabi Kazakh National University

Department of Analytical, Colloidal Chemistry and Technology of Rare Elements

Avchukir Khaisa © 2025

Purpose and expected learning outcomes

Purpose

Understand how microdisk electrode size controls diffusion, charging dynamics, measured current and accessible experimental time scales.

By the end, students can…

- Contrast planar and radial diffusion
- Calculate steady-state microdisk current
- Estimate the RC time constant
- Diagnose kinetic versus transport control
- Select a suitable electrode for challenging media

Avchukir Khaisa © 2025

Lecture trajectory | From geometry to research decisions

01 | Physical basis

Miniaturization → small area, low current, small capacitance

02 | Measurement

Radial diffusion → sigmoidal CV; fast response → transient access

03 | Application

Low-conductivity media, microvolumes, fast kinetics and local sensing

Avchukir Khaisa © 2025

What makes a microdisk electrode different?

Macroelectrode

- Characteristic dimension ≫ diffusion length
- Predominantly planar diffusion
- Peak-shaped CV under unstirred scans
- Larger absolute current and capacitance

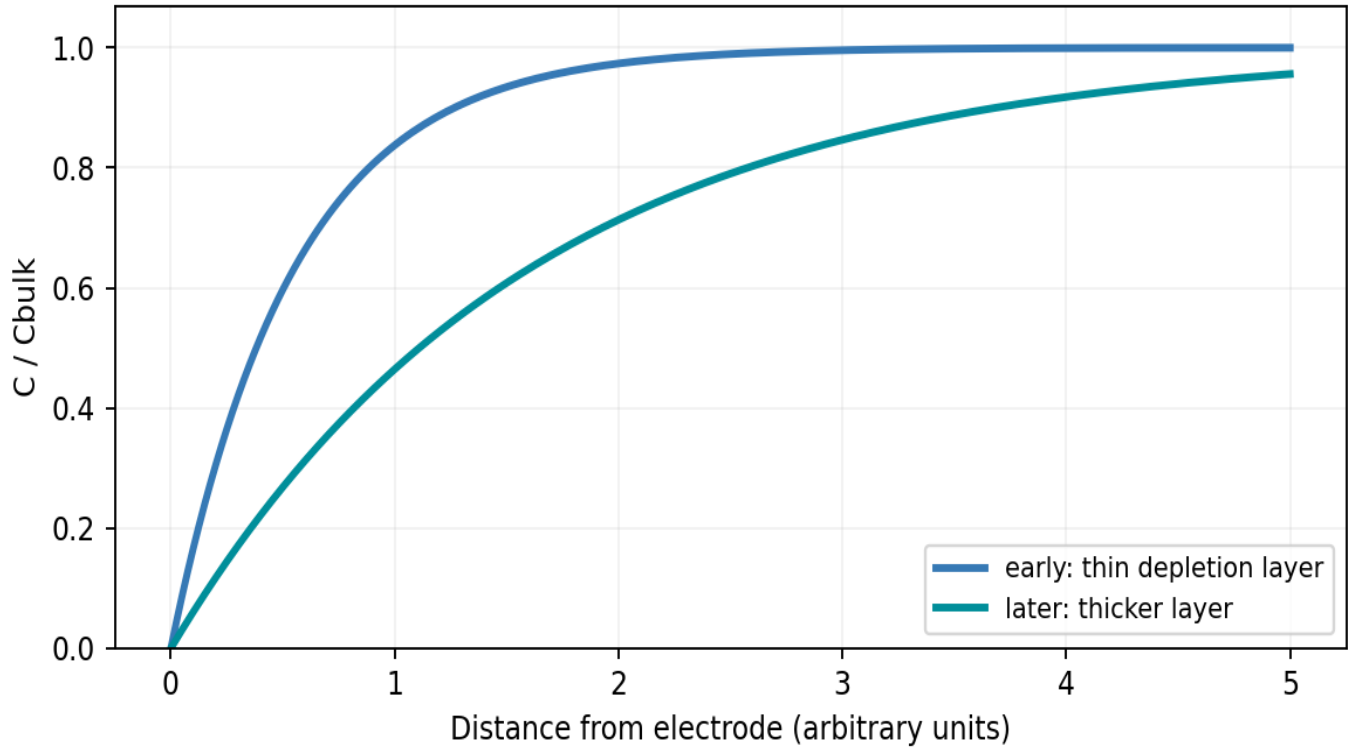
Microdisk / UME

- Micrometer-scale disk radius
- Radial diffusion becomes important
- Quasi-steady-state sigmoidal CV
- Small current reduces iRu distortion

Avchukir Khaisa © 2025

Diffusion geometry evolves with time

Illustrative concentration profiles; radial diffusion is prominent when √(Dt) is comparable to radius.



Key interpretation

Early times: diffusion layer is thin relative to disk radius.

Longer times: edge transport enhances supply of reactant.

The transition depends on D, time and radius.

Avchukir Khaisa © 2025

Macroelectrode peaks vs microdisk waves

Schematic voltammograms, not experimental datasets.

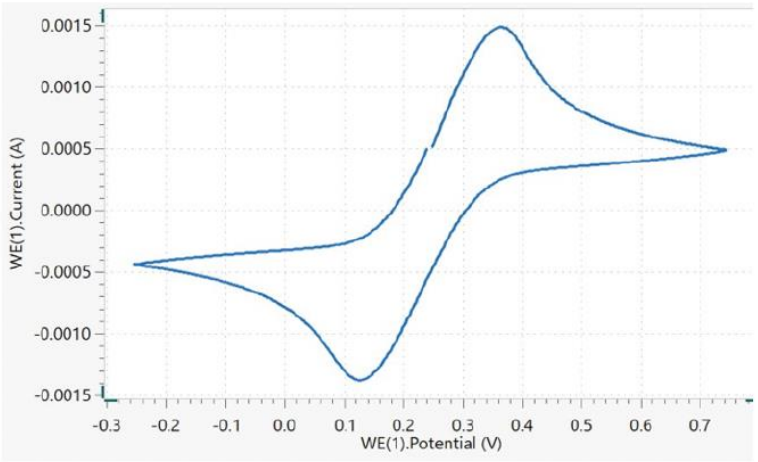


Figure 3. The cyclic voltammogram of a ferri/ferro solution at 100 mV/s with a 3 mm diameter gold electrode.

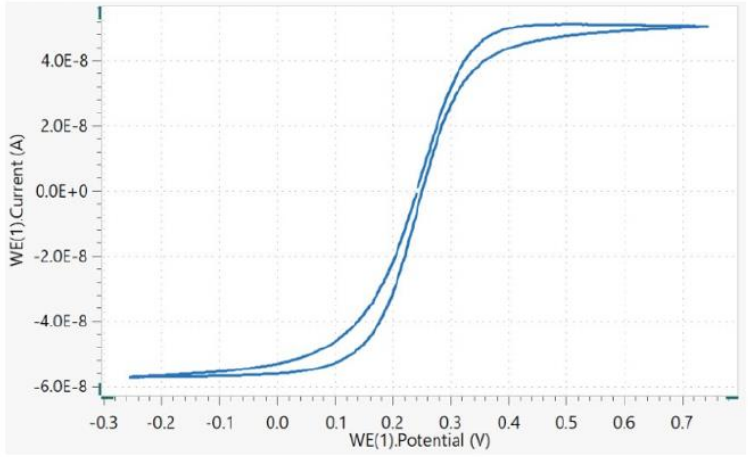


Figure 4. The cyclic voltammogram of a ferri/ferro solution at 100 mV/s with a 10 µm diameter gold electrode.

Diagnostic

Macro: depletion creates transient peaks.

Microdisk: radial replenishment supports near steady-state limiting current.

Scan rate can change the observed regime.

https://www.metrohm.com/en/applications/application-notes/autolabapplikationen-anautolab/an-ec-030.html

Avchukir Khaisa © 2025

Steady-state microdisk limiting current

$$|i_{lim}| = 4\,n\,F\,D\,C^*\,r$$

Variables

n = electrons transferred; F = 96485 C mol^{-1}

D = diffusion coefficient ($cm^2\ s^{-1}$)

C* = bulk concentration ($mol\ cm^{-3}$)

r = disk radius (cm)

Worked example

n = 1; D = 1×10^{-5} $cm^2\ s^{-1}$

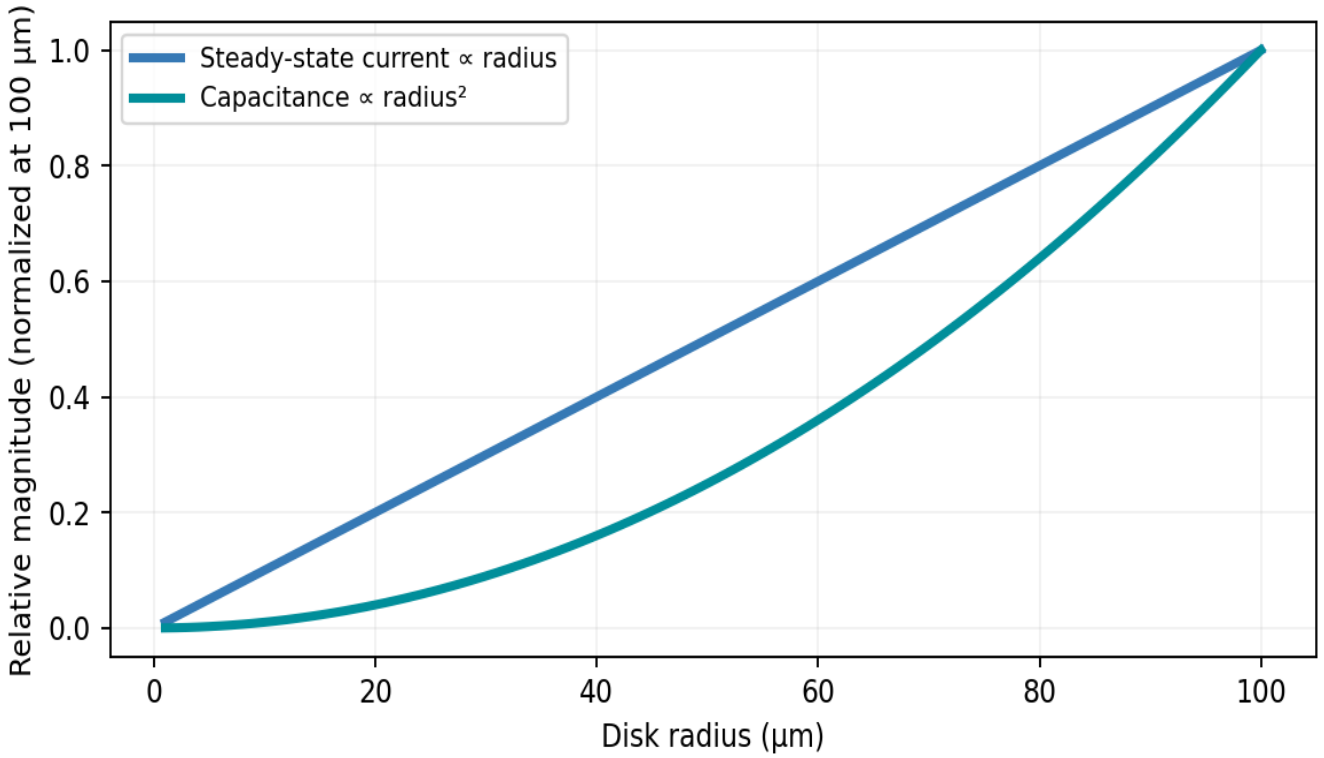
C* = 1 mM = 10^{-6} $mol\ cm^{-3}$

r = 5 µm = 5×10^{-4} cm

$|i_{lim}| \approx 1.93$ nA

Avchukir Khaisa © 2025

Why miniaturization improves time resolution



Electrical consequences

$Ru \approx 1 / (4\kappa r)$

$Cdl = \pi r^2 cdl$

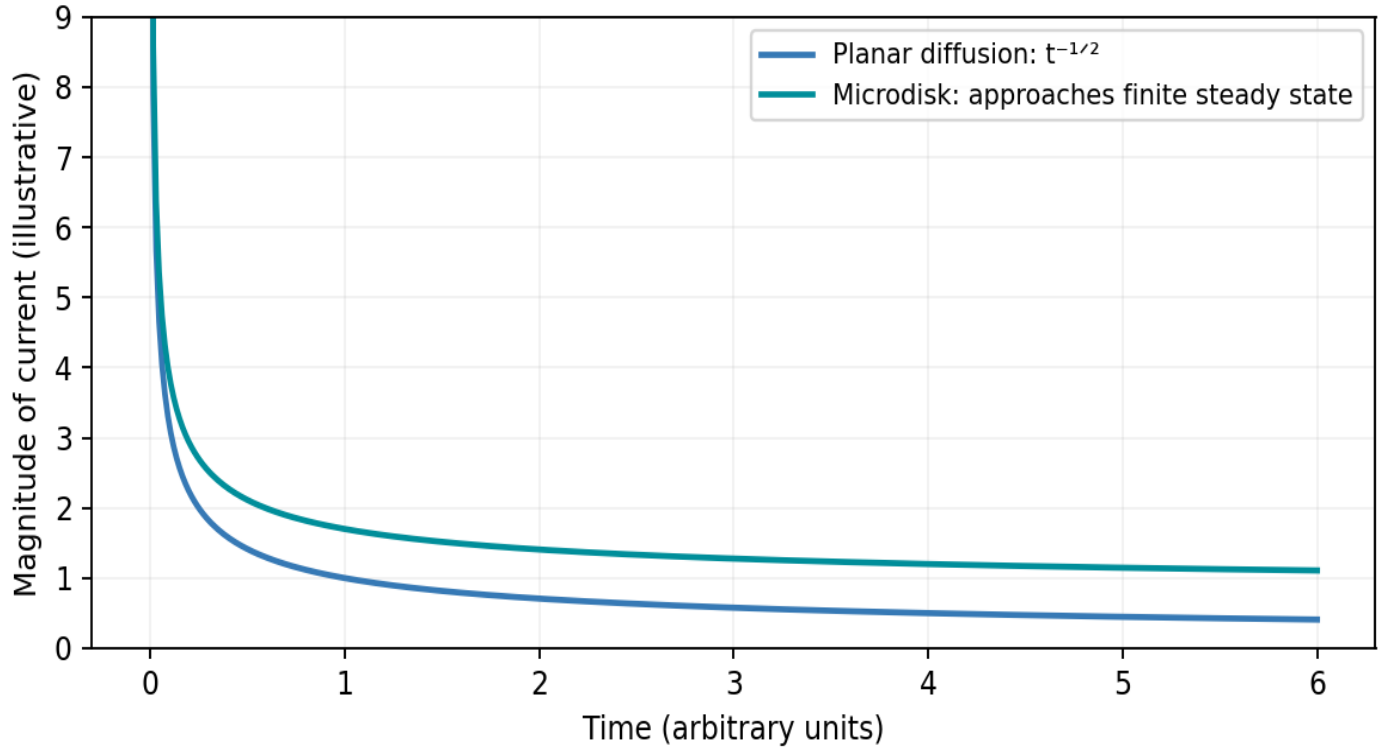
$\tau = RuCdl \approx \pi r\, cdl / (4\kappa)$

For fixed conductivity κ and specific capacitance cdl, τ scales with radius r.

Real systems may include additional stray capacitance.

Avchukir Khaisa © 2025

Limiting stage: kinetics or mass transfer?



Interpretation checklist

- Is a limiting plateau established?
- Is the response scan-rate dependent?
- Are charging and iRu artifacts negligible?
- Does current scale with r as predicted?
- Is electron transfer sufficiently fast?

A plateau alone does not prove fast kinetics.

Avchukir Khaisa © 2025

Conclusions | Selecting the right electrode

Core principles

- Microdisks access radial diffusion and quasi-steady state.
- Current scales with r, capacitance with r^2.
- Smaller RC constants permit faster experiments.

Research relevance

- Localized electroanalysis and microvolumes
- Low-conductivity and nonaqueous electrolytes
- Fast redox kinetics and mechanistic studies

References: Bard, Faulkner & White (2022); Pletcher (1991).

Avchukir Khaisa © 2025

Homework | Quantitative problems and interpretation

1. Calculate $|i_{lim}|$ for n = 2, D = 7×10^{-6} cm^2 s^{-1}, C* = 2 mM and r = 10 µm.

2. A microdisk radius decreases from 50 to 5 µm. By what factors do limiting current, capacitance and ideal RC time constant change?

3. For κ = 0.013 S cm^{-1}, Cdl = 20 µF cm^{-2} and r = 5 µm, estimate Ru, Cdl and τ. State assumptions.

4. Explain why a microdisk CV may be peak-shaped at high scan rate yet sigmoidal at lower scan rate.

5. Design a microdisk experiment to distinguish slow charge transfer from diffusion control.

Avchukir Khaisa © 2025