Lecture 5

Techniques based on microelectrodes.
Voltammetry of a microdisk electrode.

Goal of the Lecture

The goal of this lecture is to introduce students to the fundamental principles and advantages of microelectrode-based electrochemical techniques, with a specific focus on voltammetry at microdisk electrodes. Students will learn the theoretical basis for steady-state behavior, mass transport characteristics unique to microelectrodes, and how to simulate microdisk voltammetry using COMSOL Multiphysics under the quasi-static diffusion approximation.

Lecture Objectives

By the end of this lecture, students will be able to:

1. ***Explain** the physical and operational advantages of microelectrodes in voltammetric analysis.*
2. ***Describe** steady-state diffusion and mass transport phenomena unique to microdisk electrodes.*
3. ***Apply** the Butler–Volmer equation to model electrochemical kinetics at microelectrode surfaces.*
4. ***Simulate** stationary concentration fields and voltammograms using 2D axisymmetric COMSOL models with infinite elements.*
5. ***Interpret** microdisk voltammograms, including the origins of limiting currents and diffusion-controlled behavior.*

Cyclic voltammetry is a common electroanalytical technique. Since the 1980s, it has been common in voltammetry to use a microdisk electrode as the working electrode [1]. This is a disk electrode with a radius of the order of microns, embedded in an insulator whose surface is flush with the electrode (**Figure 1**).

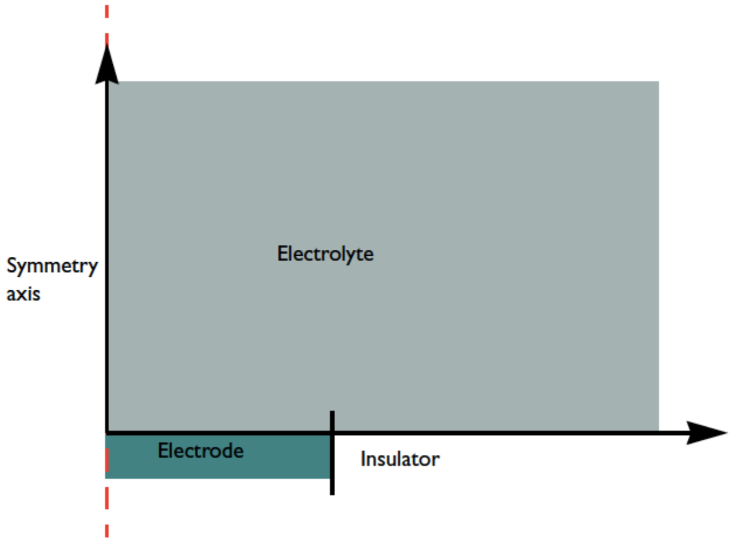

Figure 1. Schematic of the simulation geometry for a microdisk electrode.

These very small electrodes have advantageous mass transport properties that can maximize the measured current density, and so enable the study of electrochemical behavior that would not be observable by conventional voltammetry as performed on a large macroelectrode.

This example demonstrates the use of a common approximation in which an electrode with microscale dimensions is assumed to have stationary (equilibrium) diffusion properties on the timescale of a voltammetry study. This simplifies the analysis because a time-dependent model is not required. Instead, a Parametric Sweep is used to assemble a voltammogram under a quasi-static approximation.

Model definition

The model contains a 2D axisymmetric domain surrounded by a concentric region in which Infinite Elements are used to extend the bulk solution in the model to ‘infinity’. The approximation that the bulk solution is infinitely distant is suitable if the electrochemical cell is several orders of magnitude larger than the electrode.

The z = 0 axis is divided by a point at the electrode radius, r_e, which equals 10 µm. At $r < r_e$, this axis represents the working electrode (microdisk) where the electrochemical reaction takes place. At $r > r_e$, this axis represents the surrounding insulator in-plane with the disk electrode.

Domain equations

We assume the presence of a large quantity of supporting electrolyte. This is inert salt that is added in electroanalytical experiments to increase the conductivity of the electrolyte without otherwise interfering with the reaction chemistry. Under these conditions, the resistance of the solution is sufficiently low that the electric field is negligible, and we can assume that the electrolyte potential ϕ_l = 0 [2].

The Electroanalysis interface implements chemical species transport equations for the reactant and product species of the redox couple subject to this assumption. The domain equation is the diffusion equation (also known as Fick's 2nd law), which describes the chemical transport of the electroactive species Ox and Red. At steady-state, this reduces to:

$$\nabla \cdot (D_i \nabla c_i) = 0$$

Boundary equation

At the bulk boundary ($r \to \infty$), we assume a uniform concentration equal to the bulk concentration for the reactant. The product has zero concentration here, as in bulk.

At the insulating surface, the normal flux of both species Ox and Red equals zero, since this surface is impermeable and neither species reacts there.

At the electrode boundary, the reactant species Red oxidizes (loses one electron) to form the product Ox. By convention, electrochemical reactions are written in the reductive direction:

$$Ox + \bar{e} = Red$$

The stoichiometric coefficient is –1 for Ox, the "reactant" in the reductive direction, and + 1 for Red, the "product" in the reductive direction. This formulation is consistent even in examples such as this model where at certain applied potentials, the reaction proceeds
favorably to convert Ox to Red. The number of electrons transferred, n, equals one.

The current density for this reaction is given by the electroanalytical Butler-Volmer equation for an oxidation:

$$i_{loc} = nFk_0\left(c_{Red}exp\left(\frac{(n-\alpha_c)F\eta}{RT}\right) - c_{Ox}exp\left(\frac{-\alpha_a F\eta}{RT}\right)\right)$$

in which k_0 is the *heterogeneous rate constant* of the reaction, α_c is the cathodic *transfer coefficient*, and η is the overpotential at the working electrode.

According to Faraday's laws of electrolysis, the flux of the reactant and product species are proportional to the current density drawn:

$$-\boldsymbol{n} \cdot \boldsymbol{N_i} = \frac{\nu_i i_{loc}}{nF}$$

This is expressed in the Electrode Surface boundary condition.

The total current recorded at the disk electrode can be extracted by integrating the local current density across the electrode surface. It is not sufficient to simply multiply by the area of the electrode, because the current density may be non-uniform. An Integral Component Coupling is used to define an electrode current variable according to:

$$I_{el} = \int_S i_{loc} dA$$

Stationary study

In contrast to macroelectrode voltammetry, a voltammogram recorded at a microdisk does not exhibit hysteresis. Diffusion is so fast on the timescale of the experiment that a stationary approximation is suitable. A quasi-static approximation applies when:

$$\frac{r_e^2}{D} \ll \frac{RT}{Fv}$$

where v is the voltammetric scan rate (V/s). The two terms in this inequality are respectively the diffusive and voltammetric timescales of the system.

Within the Stationary study, a parametric sweep is used to study the range of applied potentials achieved in the voltammogram.

Results and discussion

The stationary concentration profile around a microdisk electrode (**Figure 2**) has a distinct shape. At large distances from the electrode, the concentration profile is roughly hemispherical, but close to the disk edge the flux is elevated. For fast kinetics the concentrations on the electrode surface are roughly equilibrated and so are uniform. This leads to unequal flux over the surface of the electrode — it is nonuniformly accessible.

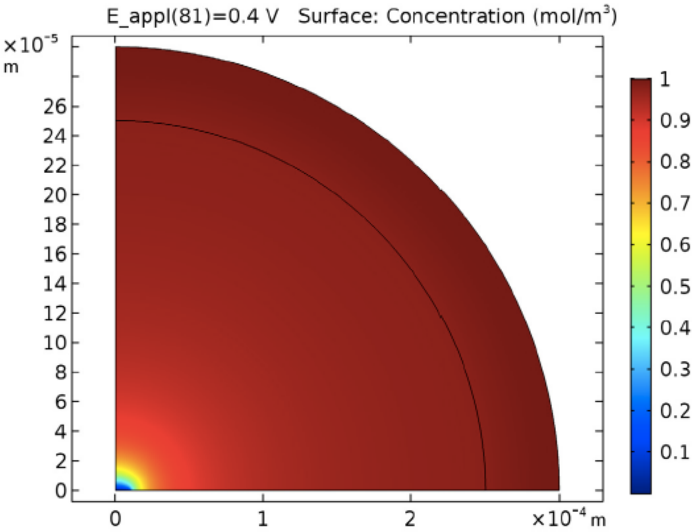

Figure 2. Characteristic concentration profile for transport-controlled oxidation of species Red at a microdisk electrode (2D cross section)

The shape of the cyclic voltammogram (**Figure 3**) illustrates the relation between electrode kinetics and chemical species transport. We can here see the limiting current density as explained below.

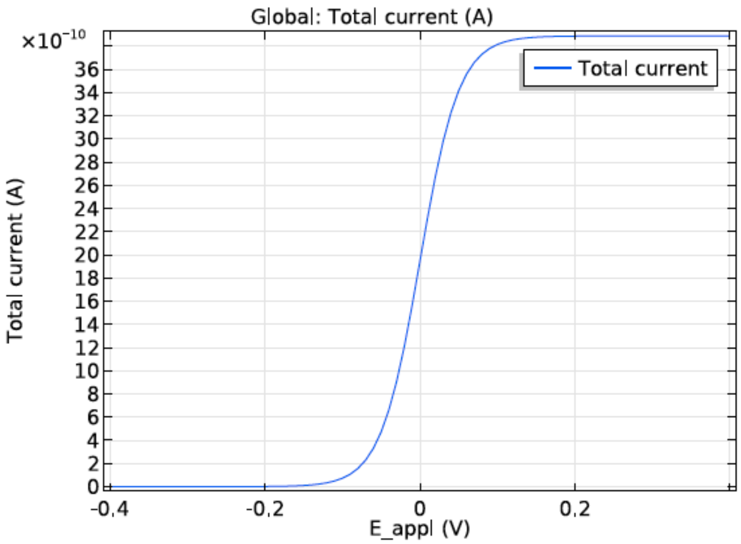

Figure 3. Quasi-static (steady-state) cyclic voltammetry recorded at a microdisk electrode

Initially, at reducing potentials, the oxidation reaction is not driven, and negligible current is drawn. As the potential moves towards the reduction potential of the redox couple (0 V), the oxidation reaction is accelerated and the current increases.

Once the oxidation reaction is fast enough that it consumes significant reactant at the electrode surface, the current becomes limited by the rate of transport of Red towards the working electrode. Because the diffusion layer is equilibrated, this transport-limited
current is constant in time, and independent of applied potential. The analytical Saito equation gives this limiting current as [3]:

$$I_{lim} = 4nFcDr_e$$

where ***c*** is the bulk concentration of reactant.

Negative current is never observed for the “steady-state” voltammetry at a microdisk electrode, since the product species is effectively dispersed to bulk solution. Rapid diffusion on the voltammetric timescale ensures equilibration between the bulk and the electrode surface. Because of the absence of product in bulk, this equilibrium means that the reaction is always oxidative.

A refined mesh is required close to the electrode surface in order to accurately resolve the concentration profile, and hence the current. The mesh is refined further close to the singularity where the electrode and insulator boundaries meet. In the Infinite Element Domain, a Swept mesh is used (**Figure 4**).

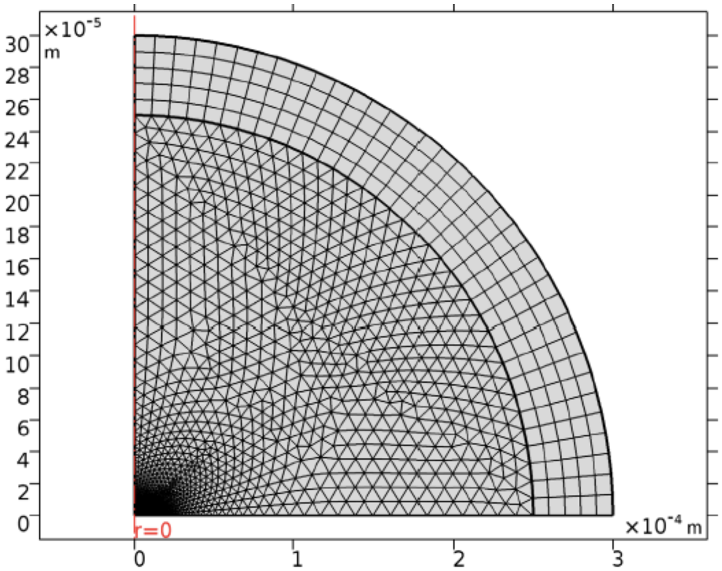

Figure 4. Customized mesh used for the microdisk analysis [4]

Questions for Self-Examination

1. What advantages do microelectrodes offer compared to traditional macroelectrodes in voltammetry?
2. Why can voltammetry at a microdisk electrode typically be treated as a **steady-state** (stationary) process?
3. Explain why infinite elements are used in modeling microdisk electrode systems.
4. Describe the diffusion field around a microdisk electrode. How does it differ from planar diffusion at macroelectrodes?
5. Write the Butler–Volmer equation for oxidation and identify each parameter.
6. Why is the electrolyte potential assumed to be zero when large supporting electrolyte is present?
7. What causes the **limiting current** in microdisk voltammetry?
8. Explain why microdisk voltammograms do **not exhibit hysteresis** during cyclic voltammetry.
9. Why must the mesh be refined near the electrode edge in COMSOL simulations?

Self-Study Assignment (IWS 5 – COMSOL-Related Task)

Assignment Title:

Simulation of Steady-State Voltammetry at a Microdisk Electrode Using 2D Axisymmetric Modelling

Objective:
To simulate species transport and current response during steady-state voltammetry at a microdisk electrode, and to understand how diffusion geometry and reaction kinetics shape the voltammogram.

Tasks

1. Geometry and Physics Setup

- Construct a **2D axisymmetric** model with:
  - Microdisk radius: **r = 10 µm**
  - Surrounding electrolyte domain extended outward and upward several electrode radii
- Surround the domain with an **Infinite Element Domain** to represent bulk electrolyte.

2. Define Species and Parameters

- Include two species: reactant **R** and product **O**.
- Assume:
  - Excess supporting electrolyte → migration neglected
  - No convection
  - Only diffusion governs mass transport

Governing steady-state form:

$$\nabla^2 c = 0$$

3. Boundary Conditions

- **Electrode surface (r < 10 µm):**
  - Apply Butler–Volmer kinetics
  - Use transfer coefficient, heterogeneous rate constant, and one-electron process

- **Insulating surfaces:**
    - Zero flux
- **Bulk boundary (infinite element edge):**
    - R concentration = bulk
    - O concentration = 0

4. Stationary Study Using Parametric Sweep

- Sweep applied potential from **–0.2 V to +0.6 V** relative to formal potential.
- For each potential, compute:
    - Stationary concentration fields of R and O
    - Local current density
    - Total current via boundary integration

5. Extract Results

- Plot stationary concentration fields at an oxidizing potential.
- Generate the cyclic voltammogram (forward → reverse potentials).
- Identify:
    - Onset of oxidation current
    - Limiting current plateau
    - Absence of hysteresis

6. Comparison to Theory

- Compute the **Saito limiting current**:

$$i_{\text{lim}} = 4nFDcr$$

- Compare COMSOL results to analytical prediction.

7. Report

Write a 2–3 page report including:

- Modeling method and boundary conditions
- Discussion of diffusion geometry
- Comparison of simulated vs. analytical limiting current
- Physical interpretation of quasi-static behavior

Learning Outcomes (According to Syllabus)

Learning Outcome (LO)	Indicator of Achievement (ID)	Description
LO 2: Select a computational or numerical technique appropriate for a given electrochemical process.	ID 2.2:Application and theory of voltammetry.	Students will apply voltammetric theory and perform microdisk simulations to generate, interpret, and analyze steady-state cyclic voltammograms.

References

1. R.G. Compton and C.E. Banks, Understanding Voltammetry, 2nd ed., London, 2011.
2. A.J. Bard and L.R. Faulkner, Electrochemical Methods, Fundamentals and Applications, 2nd ed., Hoboken, 2001.
3. Y. Saito, Review of Polarography (Japan), vol. 15, pp. 177-187, 1968.
4. https://www.comsol.com/model/voltammetry-at-a-microdisk-electrode-12877