Lecture 6

Analytical techniques for investigating electrochemical reactions. Cyclic voltammetry

Goal of the Lecture

The goal of this lecture is to introduce students to cyclic voltammetry (CV) as a powerful analytical technique for studying electrochemical reaction mechanisms, electron-transfer kinetics, and mass transport behavior. Students will learn the theoretical foundations of CV, its diagnostic features, and how to simulate cyclic voltammograms using diffusion-controlled models in COMSOL Multiphysics.

Lecture Objectives

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

1. ***Describe** the principle, waveform, and operation of cyclic voltammetry.*
2. ***Explain** how electron-transfer kinetics and mass transport influence the shape of a cyclic voltammogram.*
3. ***Apply** Fick's law and the Butler–Volmer equation to model reversible and diffusion-limited processes.*
4. ***Interpret** key diagnostic voltammetric features (peak currents, peak separation, scan rate dependence).*
5. ***Construct and simulate** a 1D time-dependent COMSOL model for cyclic voltammetry at a macroelectrode.*

Cyclic voltammetry is a common analytical technique for investigating electrochemical systems. In this method, the potential difference between a working electrode and a reference electrode is swept linearly in time from a start potential to a vertex potential, and back again (**Figure 1**). The resulting current at the working electrode is recorded and is plotted against the applied electrode potential in a voltammogram.

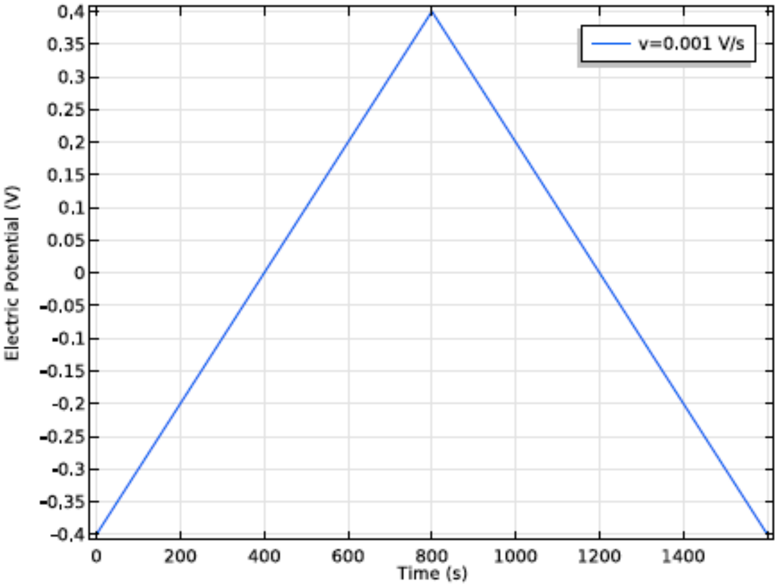

Figure 1. Potential of the working electrode during one voltammetric cycle. The potential is cycled between the vertex potentials 0.4 V and –0.4 V. The scan rate is 1 mV/s [1].

Voltammetry is a valuable technique because information about both the electrochemical reactivity and the transport properties of a system can be extracted simultaneously. For quantitative interpretation of voltammetry, however, we must use numerical methods to solve the physical equations that describe voltammetry. Then, unknown physical quantities in the system can be inferred by ‘fitting’ to experimental data.

This example demonstrates the use of a common approximation in which a large electrode is assumed to have uniform transport behavior across its surface, so only physics occurring normal to the surface need to be considered. By simplifying the model

to 1D, an efficient time-dependent analysis is possible.

In this model, a Parametric Sweep is used to compare voltammetry recorded at different voltammetric scan rates.

The model contains a single 1D domain of length *L*, which is the maximum extent of the diffusion layer over the duration of the voltammetry experiment. A conservative setting for *L* is set to greatly exceed the mean diffusion layer thickness:

$$L = 6\sqrt{Dt_{max}}$$

Here, *D* is the diffusion coefficient of the reactant and t_{max} is the duration of the cyclic voltammogram.

Domain equation

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 ϕ_l = 0.

The Electroanalysis interface implements chemical 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) to describe the chemical transport of the electroactive species Red and Ox:

$$\frac{\partial c_i}{\partial t} = \nabla \cdot (D_i \nabla c_i)$$

Boundary equation

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

At the electrode boundary ($x = 0$), the reactant species Red oxidizes 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 Red to Ox. 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:

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

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. This overpotential is the difference between the applied potential and the equilibrium potential (formal reduction potential) of the redox couple of species Red and Ox.

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 applied triangular waveform for the cyclic voltammetry study is specified in the Electrode Surface boundary condition according to two vertex potentials—forming a potential window between –0.4 V and +0.4 V, either side of the equilibrium reduction potential and a voltammetric scan rate, v (V/s), which is the rate at which the applied potential is changed.

In the 1D approximation, the total current is related to the current density simply by multiplying by the electrode area Red:

$$I_{el} = i_{loc} A$$

In the cyclic voltammetry experiment, the potential applied to the working electrode surface is varied linearly as a function of time. A Parametric Sweep is used to compare the voltammetry recorded at different scan rates.

The shape of the cyclic voltammogram (**Figure 2**) shows the relation between electrode kinetics and chemical species transport - diffusion.

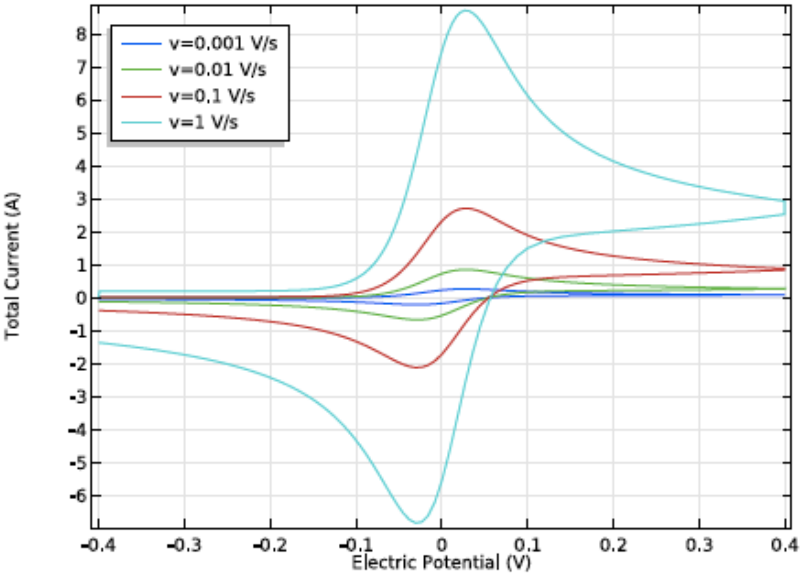

Figure 2. Cyclic voltammetry recorded at a macroelectrode.

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, the oxidation reaction is accelerated and the current increases. Once the oxidation reaction has consumed the reactant at the electrode surface, the current becomes limited by the rate of transport of Red towards the working electrode. Therefore, a peak current is observed, and at higher potentials, the voltammetric current falls off at a potential-independent rate; this region is termed "diffusion-controlled" or "transport-controlled".

On sweeping back towards more reducing potentials, the reconversion of the product Ox into the original reactant Red gives a negative (cathodic, reductive) current. Depletion of the reacting species Ox causes a negative peak current and reconversion thereafter proceeds at a diffusion-controlled rate.

The magnitude of the current on the forward peak, I_{pf}, is a common diagnostic variable in voltammetry. For fast electrode kinetics and at a macroelectrode under the 1D approximation, its value is given theoretically by the Randles–Ševcík equation [2, 3]:

$$I_{pf} = 0.446nFAc\sqrt{\frac{nF}{RT}Dv}$$

where *A* is the electrode area, *c* is the bulk concentration of the reactant, and *D* is the diffusion coefficient of the reactant.

The square-root relationship between peak current and scan rate is characteristic of macroelectrode cyclic voltammetry under the above conditions.

Questions for Self-Examination (QS)

1. What is the purpose of scanning the electrode potential forward and backward during cyclic voltammetry?
2. How does the magnitude of the scan rate affect the thickness of the diffusion layer?
3. Write Fick's second law and describe the physical meaning of each term in the context of CV.

4. What assumptions justify the 1D diffusion approximation at a macroelectrode?
5. Explain the distinction between **kinetically controlled**, **diffusion-controlled**, and **mixed-control** regions in a voltammogram.
6. Why does a reversible system show a characteristic peak-shaped voltammogram?
7. What does the Randles–Ševčík equation tell us about the dependence of peak current on scan rate?
8. What causes the difference between anodic and cathodic peak currents in reversible CV?
9. Why is migration neglected when modeling CV in the presence of supporting electrolyte?
10. How can cyclic voltammetry be used to estimate diffusion coefficients?

Self-Study Assignment

Assignment Title:

Time-Dependent Simulation of Cyclic Voltammetry at a Macroelectrode Using Fick's Law and Butler–Volmer Kinetics

Objective:
To simulate cyclic voltammetry at a planar macroelectrode using a 1D diffusion model in COMSOL Multiphysics and analyze how scan rate influences peak currents and mass transport.

Tasks

1. Geometry and Domain Setup

- Create a **1D domain** of length **L**, chosen to be much larger than the diffusion layer thickness:

$$L \geq 6\sqrt{Dt_{\mathrm{CV}}}$$

- Example: use **L = 500 μm**.

2. Physics Interfaces

Use **Electroanalysis** or **Transport of Diluted Species (tds)** with:

- Diffusion-only transport (migration omitted due to supporting electrolyte).
- Two species: reactant R and product O.
- Butler–Volmer kinetics at electrode.

3. Boundary Conditions

- **Electrode boundary (x = 0):**
  - Apply a triangular potential waveform between –0.4 V and +0.4 V.
  - Use Butler–Volmer equation with given parameters (k_0, α, E^o).
- **Bulk boundary (x = L):**
  - R concentration fixed at bulk value.
  - O concentration fixed at zero.

4. Time-Dependent Study

- Implement the triangular potential sweep via the Boundary Electrode condition.
- Run CV simulations at multiple scan rates:
  - v = 5 mV/s
  - v = 20 mV/s
  - v = 100 mV/s
- Use appropriate time stepping to resolve the transient diffusion.

5. Output and Analysis

- Extract current density and compute total current (i = jA).
- Plot **full voltammograms** (i vs. E).
- Identify:
  - Anodic peak current (i_p,a)
  - Cathodic peak current (i_p,c)
  - Peak separation (ΔEp)
- Examine how peak currents vary with $\sqrt{\nu}$ and test the Randles–Ševčík relationship.

6. Compare with Theory

- The Randles–Ševčík equation:

$$i_p = 0.4463nFAc\sqrt{\frac{nFvD}{RT}}$$

- Plot i_p vs. $\sqrt{v}$ to verify linearity.

7. Write a Report (2–3 pages)

Include:

- Modeling assumptions
- Explanation of potential waveform
- Comparison of simulated peaks to theoretical predictions
- Discussion of deviations at high scan rates
- Interpretation of mass transport and kinetics effects

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 2.3: Investigation of electrochemical behaviour of electrode/electrolyte interface using cyclic voltammetry.	Students will simulate cyclic voltammetry and analyze electrochemical behavior through time-dependent diffusion modeling.

References

1. https://www.comsol.com/model/cyclic-voltammetry-at-a-macroelectrode-in-1d-12849
2. R.G. Compton and C.E. Banks, Understanding Voltammetry, 2nd ed., London, 2011.

3. 2. A.J. Bard and L.R. Faulkner, Electrochemical Methods, Fundamentals and Applications, 2nd ed., Wiley, New York, 2001.