

Lecture 7

Techniques based on concepts of impedance

Goal of the Lecture

The goal of this lecture is to introduce students to electrochemical impedance spectroscopy (EIS), focusing on its theoretical foundations, diagnostic value, and computational implementation. Students will learn how impedance measurements reveal kinetic, capacitive, and mass transport properties of electrochemical systems and how EIS simulations can be performed in COMSOL Multiphysics using linear perturbation analysis.

Lecture Objectives

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

1. **Explain** the physical meaning of electrochemical impedance and its relationship to electrode processes.
2. **Differentiate** impedance contributions arising from kinetics, double-layer capacitance, and mass transport.
3. **Interpret** Nyquist and Bode plots and identify characteristic regimes (kinetic vs. diffusion control).
4. **Apply** the Butler–Volmer equation and double-layer capacitance to formulate a harmonic perturbation model.
5. **Construct and simulate** basic EIS models in COMSOL Multiphysics to study frequency-dependent behavior.

Electrochemical impedance spectroscopy (**EIS**) is a common technique in electroanalysis. It is used to study the harmonic response of an electrochemical system. A small, **sinusoidal variation** is applied to the potential at the working electrode, and the resulting current is analyzed in the frequency domain.

The real and imaginary components of the impedance give information about the kinetic and mass transport properties of the cell, as well as its capacitive properties. By measuring impedance at a range of frequencies, the relative influence of the various constituent physics of the system can be interpreted as a function of time scale

The purpose of the application is to understand EIS, Nyquist, and Bode plots. The app lets you vary the following parameters:

- Bulk concentration.
- Diffusion coefficient.
- Double layer interfacial capacitance.
- Heterogeneous rate constant.
- Maximum and minimum frequency.

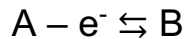
The diffusion coefficient and the bulk concentration are assumed to be equal for both species. In the application, the impedance of an electrode surface, as depicted by Nyquist and Bode plots, is simulated for a cell consisting of a redox couple in an aqueous electrolyte. A Nyquist plot is an Argand diagram of the complex value of the impedance as a function of frequency. In a Bode plot, either the magnitude or the phase of the complex impedance is plotted against frequency.

EIS modelling in COMSOL Multiphysics

The model contains a single 1D domain, where one of the boundaries is defined as the working electrode. The domain equation is the diffusion equation to describe the chemical transport of the electroactive species A and B:

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

At the working electrode surface, the reactant species A oxidizes to form the product B. By convention, electrochemical reactions are written in the reductive direction:



The **current density** (i_{loc}) for this reaction is given by the electroanalytical Butler-Volmer equation for an oxidation:

$$i_{loc} = Fk_0 \left(c_A \exp\left(\frac{F\eta}{2RT}\right) - c_B \exp\left(\frac{-F\eta}{2RT}\right) \right)$$

in which k_0 is the **heterogeneous rate constant** of the reaction, and η is the **overpotential** at the working electrode. This overpotential is the difference between the applied potential and the equilibrium potential of the redox couple of species A and B, E_{eq} :

$$\eta = \phi_{s,ext} - E_{eq}$$

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

$$-nN_i = \frac{v_i i_{loc}}{F}$$

An additional capacitance is applied at the working electrode. The default value of 20 $\mu\text{F}/\text{cm}^2$ is a typical value for a water-metal interface. The real value of this capacitance can be established by impedance spectroscopy of the blank solution containing only the supporting electrolyte, or by an alternative voltammetric method. A harmonic perturbation of frequency f is applied to the electrode potential, which in this case is fixed to the equilibrium potential of the redox couple:

$$\phi_{s,ext} = E_{eq} + \Delta\phi e^{j\omega t}$$

where

$$\omega = 2\pi f$$

The app solves for a small perturbation $\Delta\phi$ around the equilibrium potential for the provided bulk concentration, for a range of applied frequencies.

A Nyquist plot (Figure 1) is the most common means of plotting the results of an impedance experiment. It is an Argand diagram of the complex value of the impedance as a function of frequency; the real component of impedance (resistance) is plotted on the x-axis, and the imaginary component (reactance) is plotted on the y-axis.

For a fast electrochemical reaction with respect to the frequency of the electrochemical impedance study, the impedance always results from the limitation to the current due to the finite diffusivity of the redox species in the solution. It is known from theory that the real and imaginary impedances are linearly correlated in this “transport-controlled” regime [1].

For a slow electrochemical reaction with respect to the frequency, the mass transport is unimportant as the rate of electron transfer is limited by the rate of reaction at the surface is the “kinetically controlled” regime. This regime is characterized by a semi-circular Nyquist plot.

It is common to observe both regimes in a single plot, since the relevant timescale of the experiment changes with the frequency of the harmonic perturbation. At low frequency, mass transport dominates, but at high frequency (towards the bottom-left of the plot), there is a transition to kinetic control. This transition is most marked for the slowest electrochemical reaction studied, where $k_0 = 0.001 \text{ cm/s}$.

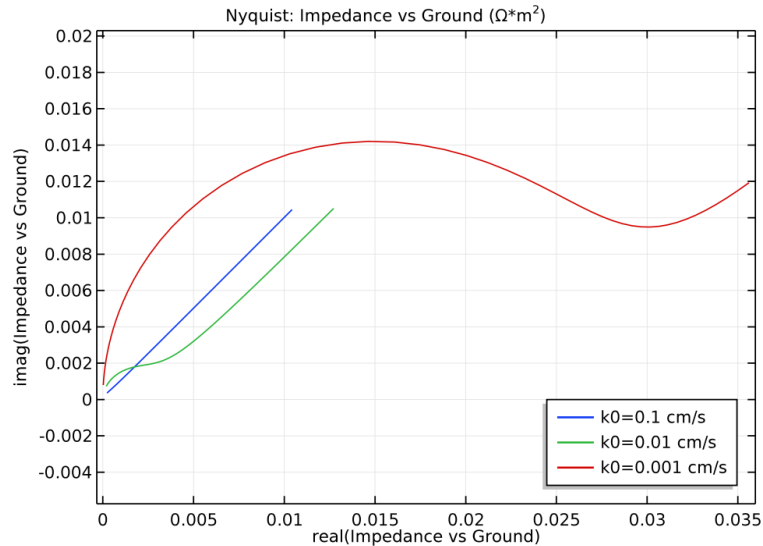


Figure 1. Nyquist plot showing the relation of real to imaginary impedance for a range of frequencies and a range of electrode kinetic heterogeneous rate constants [2].

Questions for Self-Examination

1. What is electrochemical impedance and how is it measured experimentally?
2. Why must the potential perturbation in EIS be “small amplitude”?
3. Explain the difference between **kinetic control** and **diffusion control** in an EIS experiment.
4. What physical information can be obtained from Nyquist plots?
5. What does the semicircle in a Nyquist plot correspond to?
6. Why does the low-frequency region often show a 45° Warburg diffusion line?
7. What role does double-layer capacitance play in the total impedance?
8. How does the heterogeneous rate constant (k_0) affect the shape of the EIS response?
9. What assumptions justify the harmonic perturbation approach used in COMSOL Multiphysics?
10. How would decreasing the diffusion coefficient influence the Nyquist plot?

Self-Study Assignment (IWS 7 – COMSOL-Related Task)

Assignment Title:

Simulation of Electrochemical Impedance Spectroscopy (EIS) Using Harmonic Perturbation Analysis in COMSOL Multiphysics

Objective:

To simulate the impedance response of a simple redox system over a range of frequencies and to analyze transitions between kinetic and diffusion-controlled regimes.

Tasks

1. Geometry and Model Setup

- Create a **1D domain** (length sufficient for diffusion layer at lowest frequency, e.g., 500 μm).
- Use **Transport of Diluted Species (tds)** for diffusion.
- Couple to **Electrode Surface Reaction** conditions on the working electrode boundary.

2. Governing Equations

- Implement Fick's diffusion equation for A and B:

$$\frac{\partial c_i}{\partial t} = D \frac{\partial^2 c_i}{\partial x^2}$$

- Use a linearized Butler–Volmer expression at equilibrium potential:

$$i_{\text{loc}} = k_0 F (c_A - c_B) + C_{\text{dl}} \frac{d\phi}{dt}$$

3. Boundary Conditions

- **Working electrode ($x = 0$):**
 - Electrode kinetics using Butler–Volmer.
 - Add double-layer capacitance (typical value: 20 $\mu\text{F}/\text{cm}^2$).

- Apply harmonic perturbation:

$$\phi(t) = E_{eq} + \Delta\phi \sin(2\pi ft)$$

- **Bulk boundary (x = L):**
 - Fixed concentrations for A and B.

4. Frequency Sweep

- Use Frequency Domain perturbation study.
- Sweep logarithmically over **0.01 Hz to 100 kHz**.
- Run the model for three heterogeneous rate constants:
 - $k_0 = 10^{-3}$ cm/s
 - $k_0 = 10^{-2}$ cm/s
 - $k_0 = 10^{-1}$ cm/s

5. Output Analysis

- Generate Nyquist plots ($-\text{Im}(Z)$ vs. $\text{Re}(Z)$).
- Generate Bode magnitude and phase plots.
- Identify:
 - High-frequency kinetic semicircle
 - Low-frequency diffusion (Warburg) region
 - Transition frequency between regimes

6. Interpretation & Theoretical Comparison

- Compare simulated Nyquist behavior with analytical expectations:
 - Semicircle radius ~ charge transfer resistance
 - 45° Warburg line for diffusion control
- Discuss how changing k_0 and D modifies the plot shape.

Learning Outcomes

Learning Outcome (LO)	Indicator of Achievement (ID)	Description
LO 3: Explain the principles of key computational and numerical modeling techniques used in electrochemical science.	ID 3.1: Modelling of electrochemical impedance spectroscopy measurements of simple electrochemical systems.	Students will simulate and interpret impedance spectra, differentiating kinetic and diffusion-controlled regimes.

Reference

1. A.J. Bard and L.R. Faulkner, Electrochemical Methods, Fundamentals and Applications, 2nd ed., Wiley, New York, 2001.
2. COMSOL Multiphysics, Application Library path: Electrochemistry_Module/Applications/electrochemical_impedance_spectroscopy