Lecture 7

Techniques based on concepts of impedance

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:

$$A - e^- \leftrightarrows B$$

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 $\mathbf{k_0}$ is the ***heterogeneous rate constant*** of the reaction, and $\boldsymbol{\eta}$ 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 μF/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 Δφ 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 cm/s.

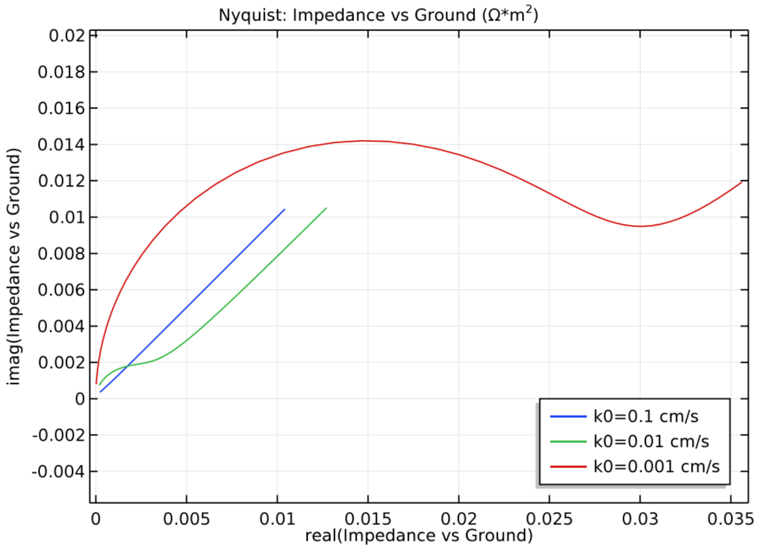

Figure 1. Nyquist plot showing the relation of real to imaginary impedance for a range of frequencies and a range of electrode kinetic heterogeneous rate constants [2].

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