Electrochemical Impedance Spectroscopy

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Electrochemistry Xpertise Corrosion

Contents

Introduction

There are 2 categories of electrochemical techniques: time domain and frequency domain [1].

Time domain :

- Voltammetry: $I = f(U)$.
- Chronoamperometry: ΔU, $I(t)$.
- Zero Resistance Ammeter: $\int j_{gal} \cdot dt$.
- ...

Frequency domain:

- Electrochemical Impedance Spectroscopy: EIS.
- PhotoElectrochemical Impedance Spectroscopy: PEIS.

Advantages of EIS:

- Measurement in small perturbations (approximately linear).
- Different processes have different time constants.
- Large frequency range from μHz to GHz.

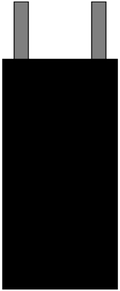
Black Box Approach

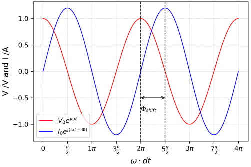
Assume a black box with terminals.

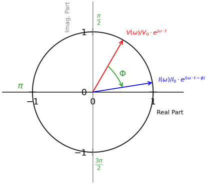
One applies a voltage and measures the current response (or vice versa).

Periodic signal with an angular frequency $\omega = 2\pi f$ with $0 \leq \omega < \infty$:

- Voltage $V(\omega) = V_0 e^{j\omega t}$
- Voltage $I(\omega) = I_0 e^{j\omega t - \Phi}$







What is EIS?

The complex impedance is determined from the imposed voltage/current and the measured current/voltage through the Ohm's law:

$$Z(\omega) = \frac{V(\omega)}{I(\omega)} = \frac{V_0}{I_0} e^{j\Phi} = Z_0 e^{j\Phi}$$

Therefore:

- resistive behavior: $ReZ = Z_0 \cdot \cos \Phi$
- capacitive/Inductive behavior $ImZ = Z_0 \cdot \sin \Phi$

Sometimes, the complex admittance $Y(\omega)$ can also be used which is defined as the inverse of the complex impedance $Z(\omega)$

$$Y(\omega) = \frac{1}{Z(\omega)}$$

Representations I

The impedance $Z(\omega)$ can be represented in two different ways:

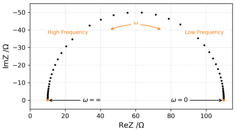
- Nyquist plot: represents the real and imaginary parts of $Z(\omega)$ using cartesian coordinates.
- Bode plot: shows the phase shift and magnitude changes in the rang of applied frequencies.

The Bode plot has great advantages for observing phase changes. Therefore, it is useful for the study of sensors, filters, and transistors in electronic devices.

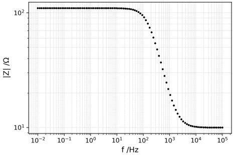
The Nyquist plot provides a better insight into the possible mechanisms.

Representations II

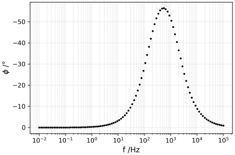
Among these two types of representations, the Nyquist plot is more often used to analyze the characteristics of electrochemical processes occurring during corrosion.



Nyquist Plot



Bode Plot - Modulus



Bode Plot - Phase

Series and parallel connections

Series connections: Z_1 — Z_2 — ...— Z_n

$$Z_{eq} = \sum_{i=1}^{n} Z_i$$

Parallel connections: Z_1 / Z_2 / .../ Z_n

$$\frac{1}{Z_{eq}} = \sum_{i+1}^{n} \frac{1}{Z_i}$$

$$Z_{eq} = \left(\sum_{i=1}^{n} \frac{1}{Z_i} \right)^{-1}$$

Equivalent Circuit Models

The circuit model for EIS consists of a combination of electrical circuit elements[2]:

- ideal elements:
  - resistors (R)
  - capacitors (C)
  - inductors (L)
- nonideal capacitor-like element: Constant Phase Element (CPE or Q)
- diffusion elements:
  - semi-infinite Warburg (W)
  - Finite Length Warburg (W_δ or O)
  - Finite Space Warburg (W_m or T)

The circuit model represents the entire system of the electrochemical cell.

The aim is to build an optimal circuit model that is physically meaningful and minimizes the number of variables [3].

Circuit Elements

R (Resistor): $Z(\omega) = R$

C (Capacitor): $Z(\omega) = \frac{1}{jC\omega}$

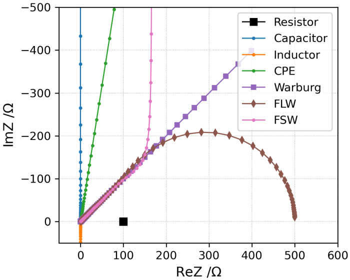
L (Inductor): $Z(\omega) = jL\omega$

Q (CPE[4]): $Z(\omega) = \frac{1}{Q(j\omega)^{\alpha}}$

W (SIW[1]): $Z(\omega) = \frac{\sigma}{\sqrt{\omega}} \cdot (1 - j)$

W_δ (FLW[2]): $Z(\omega) = \frac{R_\delta \cdot \tanh \sqrt{j\omega\tau}}{\sqrt{j\omega\tau}}$

W_m (FSW[3]): $Z(\omega) = \frac{R_m \cdot \coth \sqrt{j\omega\tau}}{\sqrt{j\omega\tau}}$



[1]SIW = Semi-Infinite Warburg
[2]FLW = Finite Length Warburg
[3]FSW = Finite Space Warburg
[4]CPE = Constant Phase Element

Circuit Elements and Physical Parameters

Resistors can be linked to resistivity or kinetics [4]

$R = \rho \cdot \frac{\delta}{A}$

$R = \frac{RT}{FAj_0(\alpha_a+\alpha_c)} = \frac{RT}{AF^2k^0K_c(\alpha_a+\alpha_c)}$

Capacitors can be linked to layer thickness:

$C = \frac{\epsilon\epsilon_0 A}{\delta}$

Warburg elements can be linked to diffusion

$\sigma = \frac{RT}{Az^2F^2\sqrt{2}} \cdot \left(\frac{1}{\sqrt{D}C_O^*} + \frac{1}{\sqrt{D}C_R^*}\right)$

$R = \frac{RT}{Az^2F^2\sqrt{2}} \cdot \frac{\delta}{DC^*}$

$\tau = \frac{\delta^2}{D}$

Coupling with other electrochemical techniques helps for determining all necessary parameters.

R: resistance [Ω]
ρ: resistivity [$\Omega \cdot m$]
δ: thickness [m]
A: Area [m^2]
j_0: exchange current density [$A \cdot m^{-2}$]
k^0: kinetics constant [$m \cdot s^{-1}$]
α_a: anodic transfer coefficient
α_c: cathodic transfer coefficient
ϵ: relative permittivity
ϵ_0: vaccum permittivity [$F \cdot m^{-1}$]
C^*: bulk concentration [$mol \cdot m^{-3}$]

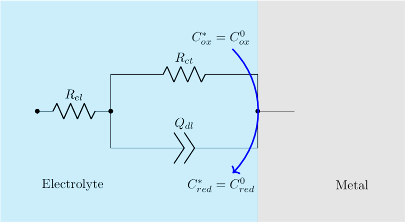
Simplified Randles Circuit

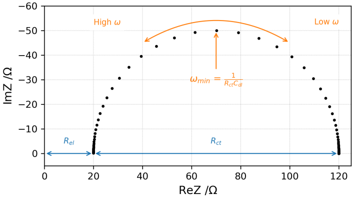
Reflects an electrochemical reaction controlled only by kinetics [5].

R_{el}: electrolyte resistance

$R_c t$: charge transfer resistance

C_{dl}: double layer capacitance





Randles Circuit

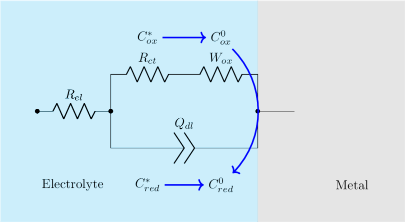
Reflects electrochemical reaction controlled by kinetics and diffusion [5].

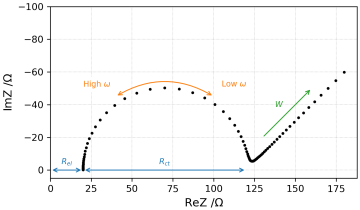
R_{el}: electrolyte resistance

R_ct: charge transfer resistance

C_{dl}: double layer capacitance

W: semi-infinite diffusion





References I

[1] A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2nd ed. New York: John Wiley & Sons, Inc., 2001.

[2] M. E. Orazem and B. Tribollet, *Electrochemical Impedance Spectroscopy*. Wiley, Feb. 2008.

[3] B. Boukamp, "A Nonlinear Least Squares Fit Procedure for Analysis of Immittance Data of Electrochemical Systems," *Solid State Ionics*, pp. 31–44, 1986.

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[5] A. C. Lazanas and M. I. Prodromidis, "Electrochemical Impedance Spectroscopy – A Tutorial," *ACS Meas. Sci. Au*, vol. 3, no. 3, pp. 162–193, Jun. 2023.