Electrochemical Impedance Spectroscopy (EIS): 3. Data Analysis

The characterization of electrochemical systems with impedance spectroscopy requires the interpretation of the data with the help of suitable models. These models can be divided into two broad categories: equivalent circuit models and process models. The models are regressed to experimental data to estimate parameters that can describe the experimental data adequately and can be used to predict the behavior of the system under various conditions.

Equivalent circuit models

The equivalent circuit models are most commonly used to interpret impedance data. These models are built with the help of well-known passive elements such as, resistors, capacitors, and inductors and distributed elements such as, constant phase element and Warburg impedance. These elements can be combined in series and parallel to give complex equivalent circuits. A certain physical meaning is then assigned to the various elements of the equivalent circuit.

Resistance, R

The circuit element Resistance, R, has an impedance of

$$Z = R$$

The impedance is independent of frequency and has no imaginary part. The current through a resistor is always in phase with the voltage.

Some examples of the use of Resistance, R, to describe electrochemical phenomena are:

1. *Ohmic resistance, R_Ω*

The potential drop between the reference electrode and the working electrode, is the ohmic resistance and can be modelled using R. The ohmic resistance depends on the conductivity of the electrolyte and the geometry of the electrode. For a rotating disc electrode, the ohmic resistance is given by

$$R_\Omega = \frac{1}{4\kappa r}$$

where, κ is the specific conductivity of the bulk electrolyte, r is the radius of the disc.

For more complex geometries the ohmic resistance is determined experimentally and can be estimated by impedance spectroscopy. In a Nyquist plot, the intersection of the impedance data with the real part of the axis at the high frequency end gives the ohmic resistance.

2. *Polarization Resistance, R_P:*

An electrode is polarized when its potential is forced away from its value at open circuit. Polarization of an electrode causes current to flow due to electrochemical reactions it induces at the electrode surface. The magnitude of the current is controlled by reaction kinetics and diffusion of reactants both towards and away from the electrode.

When an electrode undergoes uniform corrosion at open circuit, the open circuit potential is controlled by the equilibrium between anodic and cathodic reactions resulting in anodic and cathodic currents. The open circuit potential is the potential where the two currents are equal. The value of the current for either of the reactions is known as the corrosion current. When the two reactions are under kinetic control, the potential of the cell can be related to the current by the Butler-Volmer equation.

$$I = I_{corr}\left(e^{\frac{\eta}{\beta_a}} - e^{-\frac{\eta}{\beta_c}}\right)$$

where,

I is the measured cell current,
I_{corr} is the corrosion current,
η is the overpotential,
β_a is the anodic Tafel coefficient,
β_c is the cathodic Tafel coefficient.

For small η the above equation can be transformed to:

$$I_{corr} = \frac{\beta_a \beta_c}{(\beta_a + \beta_c)}\left(\frac{1}{R_P}\right)$$

The parameter, R_P, the polarization resistance behaves like a resistor. If the Tafel constants are known, one can calculate the I_{corr} from R_P. I_{corr} can be used to calculate the corrosion rate.

Capacitance, C

The circuit element Capacitance, C, has an impedance of

$$Z = \frac{1}{j\,\omega\,C}$$

The impedance of capacitors is a function of frequency and has only an imaginary part. A capacitor's impedance decreases as the frequency is raised. The current through a capacitor is phase shifted -90° with respect to voltage.

Some examples of the use of Capacitance to describe electrochemical phenomena are:

1. *Double Layer Capacitance, C_{dl}*

An electrical double layer exists at the electrode/electrolyte interface. This double layer is formed as ions from the solution approach the electrode surface. Charges in the electrode are separated from the charges of these ions. The separation is of the order of angstroms. The value of the double layer capacitance depends on many variables including electrode potential, temperature, ionic concentrations, types of ions, oxide layers, electrode roughness, impurity adsorption, etc.

2. *Coating Capacitance, C_C*

For polymer coated substrates, the coating capacitance C_C is given by:

$$C_C = \frac{\varepsilon \varepsilon_0 A}{d}$$

where

ε is the dielectric constant of the coating

ε_0 is the permittivity of vacuum

A is the area of the coating

d is the thickness of the coating

Typical dielectric constants of coatings are in the range 3-4 and of water around 80. When water penetrates the coating, its dielectric constant increases resulting in the increase in the coating capacitance. Hence, C_C can be used to measure the water absorbed by the coating.

Constant Phase Element, CPE

Modelling an electrochemical phenomenon with an ideal capacitor assumes that the surface under investigation is homogeneous which is normally not the case. This lack of homogeneity is modelled with a CPE

$$Z = \frac{1}{(j\omega C)^{\alpha}}$$

where, C is the ideal capacitance and α is an empirical constant, 0 ≤ α ≤ 1. When α = 1, CPE acts as an ideal capacitor. Double layer capacitance and coating capacitance, described in the previous section, are usually modelled with a CPE.

Warburg Impedance, Z_{war}

In electrochemical systems, diffusion of ionic species at the interface is common. Warburg impedance was developed to model this phenomenon. Several expressions, based on different assumptions, are used to describe diffusion impedance. Under the assumption of infinite diffusion layer, the impedance is:

$$Z = \frac{R}{\sqrt{j\omega}}$$

where

R is the diffusion resistance

Under the assumption of a finite diffusion layer thickness (Nernst hypothesis), the impedance is:

$$Z = R\,\frac{\tanh\sqrt{j\omega\tau}}{\sqrt{\tau}}$$

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

where

R is the diffusion resistance

τ is the diffusion time constant

δ is the diffusion layer thickness

D is the diffusion coefficient

Inductance, L

The impedance of element Inductance, L, is

$$Z = j\omega L$$

The impedance of an inductor increases with frequency. Like capacitors, inductors have only an imaginary impedance component. But current through an inductor is phase shifted +90 degrees with respect to the voltage.

The impedance of an electrochemical cell can sometimes appear to be inductive due to adsorption of reactants on the surface and can be modelled using Inductance.

Inductive behaviour can also result from non-uniform current distribution, inductance of cell cables, slow response of reference electrodes and potentiostat non-idealities. In these cases, the appearance of inductance indicates an error in the EIS measurement.

Summary of equivalent circuit elements

Circuit Element	Impedance
R, Resistance	R
C, Capacitance	$\frac{1}{j\omega C}$
L, Inductance	$j\omega L$
CPE, Constant Phase Element,	$\frac{1}{(j\omega C)^{\alpha}}$
W, Warburg Impedance Infinite diffusion length	$\frac{R}{\sqrt{j\omega}}$
W, Warburg Impedance Finite diffusion length	$R\frac{\tanh\sqrt{j\omega\tau}}{\sqrt{\tau}}$