Electrochemical Impedance Spectroscopy (EIS): 1. Basic Principles

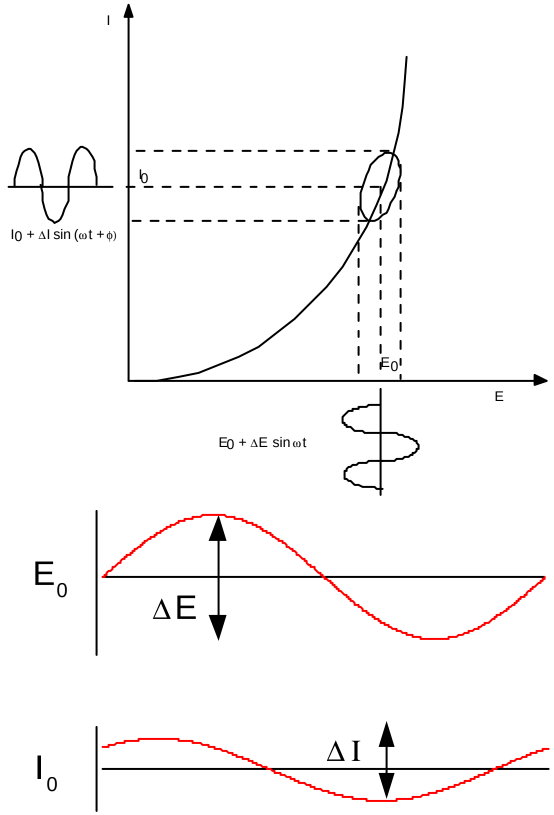
Electrochemical Impedance Spectroscopy or EIS is a powerful technique for the characterization of electrochemical systems. The promise of EIS is that, with a single experimental procedure encompassing a sufficiently broad range of frequencies, the influence of the governing physical and chemical phenomena may be isolated and distinguished at a given applied potential.

In recent years, EIS has found widespread applications in the field of characterization of materials. It is routinely used in the characterization of coatings, batteries, fuel cells, and corrosion phenomena. It has also been used extensively as a tool for investigating mechanisms in electrodeposition, electrodissolution, passivity, and corrosion studies. It is gaining popularity in the investigation of diffusion of ions across membranes and in the study of semiconductor interfaces.

Principles of EIS measurements

The fundamental approach of all impedance methods is to apply a small amplitude sinusoidal excitation signal[1] to the system under investigation and measure the response (current or voltage or another signal of interest). In the following figure, a non-linear I-V curve for a theoretical electrochemical system is shown.

[1] This signal is typically voltage or current but can be any other signal of interest, e.g. in the case of Electro-hydro-dynamic (EHD) impedance spectroscopy, the signal is rotation speed.



A low amplitude sine wave $\Delta E\sin(\omega t)$, of a particular frequency, is superimposed on the dc polarization voltage E_0. This results in a current response of a sine wave $\Delta I\sin(\omega t+\phi)$ superimposed on the dc current I_0. The current response is shifted with respect to the applied potential. The Taylor series expansion for the current is given by

$$\Delta I = \left(\frac{dI}{dE}\right)_{E_0,I_0} \Delta E + \frac{1}{2}\left(\frac{d^2 I}{dE^2}\right)_{E_0,I_0} \Delta E^2 + \ldots.$$

If the magnitude of the perturbing signal ΔE is small, then the higher order terms

$$\frac{1}{2}\left(\frac{d^2 I}{dE^2}\right)_{E_0,I_0} \Delta E^2 + \ldots..$$

in the first equation can be assumed to be negligible. The impedance of the system can then be calculated using Ohm's law as,

$$Z(\omega) = \frac{\Delta E(\omega)}{\Delta I(\omega)}$$

This ratio is called impedance, Z(ω), of the system and is a complex quantity with a magnitude and a phase shift which depends on the frequency of the signal. Therefore by varying the frequency of the applied signal one can get the impedance of the system as a function of frequency. Typically in electrochemistry, a frequency range of 100kHz – 0.1Hz is used.

The impedance, $Z(\omega)$, as mentioned above is a complex quantity and can be represented in Cartesian as well as polar co-ordinates.

In polar co-ordinates the impedance of the data is represented by,

$$Z(\omega) = |Z(\omega)| e^{\phi(\omega)}$$

where $|Z|$ is magnitude of the impedance and ϕ is the phase shift.

In Cartesian co-ordinates the impedance is given by,

$$Z(\omega) = Z_r(\omega) + jZ_j(\omega)$$

where Z_r is the real part of the impedance and Z_j is the imaginary part and $j = \sqrt{-1}$.

The plot of the real part of impedance against the imaginary part gives a Nyquist Plot, as shown in the left part of the following figure. The advantage of Nyquist representation is that it gives a quick overview of the data and one can make some qualitative interpretations. While plotting data in the Nyquist format the real axis must be equal to the imaginary axis so as not to distort the shape of the curve. The shape of the curve is important in making qualitative interpretations of the data. The disadvantage of the Nyquist representation is that one loses the frequency dimension of the data. One way of overcoming this problem is by labelling the frequencies on the curve.

The absolute value of impedance and the phase shifts are plotted as a function of frequency in two different plots giving a Bode plot, as shown in the right part of the following figure. This is the more complete way of presenting the data.

The relationship between the two ways of representing the data is as follows:

$$|Z|^2 = (\mathrm{Re}\,Z)^2 + (\mathrm{Im}\,Z)^2$$

$$f = \tan^{-1}\frac{\mathrm{Im}\,Z}{\mathrm{Re}\,Z}$$

or

$$\mathrm{Re}(Z) = |Z|\cos f$$

$$\mathrm{Im}(Z) = |Z|\sin f$$