

Autolab Application Note EIS01

Electrochemical Impedance Spectroscopy (EIS) Part 1 – Basic Principles

Keywords

Electrochemical impedance spectroscopy; frequency response analysis; Nyquist and Bode presentations

Summary

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 electro-deposition, electro-dissolution, 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 to the system under investigation and measure the response (current or voltage or another signal of interest¹). In the following figure, a non-linear *i*-*V* curve for a theoretical electrochemical system is shown in Figure 1.

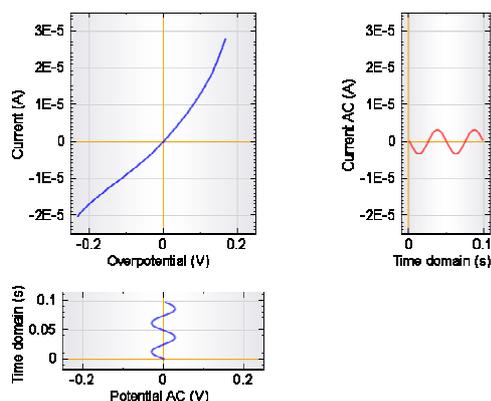


Figure 1 - Potential and current modulation recorded during an impedance measurement

A low amplitude sinewave $\Delta E \cdot \sin(\omega t)$, of a particular frequency ω , is superimposed on the DC polarization voltage E_0 . This results in a current response of a sine wave superimposed on the DC current $\Delta i \cdot \sin(\omega t + \phi)$. The current response is shifted with respect to the applied potential (see Figure 2).

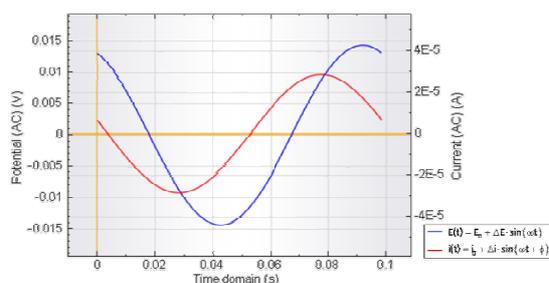


Figure 2 – Time domain plots of the low amplitude AC modulation and response

The Taylor series expansion for the current is given by:

$$\Delta i = \left(\frac{di}{dE} \right)_{E_0, i_0} \Delta E + \frac{1}{2} \left(\frac{d^2i}{dE^2} \right)_{E_0, i_0} \Delta E^2 + \dots$$

If the magnitude of the perturbing signal ΔE is small, then the response can be considered linear in first approximation. The higher order terms in the Taylor series can be assumed to be negligible.

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

The impedance of the system can then be calculated using Ohm's law as:

$$Z(\omega) = \frac{E(\omega)}{i(\omega)}$$

This ratio is called impedance, $Z(\omega)$, 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 100 kHz – 0.1 Hz is used.

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

In polar coordinates the impedance of the data is represented by:

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

Where $|Z(\omega)|$ is the magnitude of the impedance and φ is the phase shift.

In Cartesian coordinates the impedance is given by:

$$Z(\omega) = Z'(\omega) - j \cdot Z''(\omega)$$

where $Z'(\omega)$ is the real part of the impedance and $Z''(\omega)$ is the imaginary part and $j = \sqrt{-1}$.

Data presentation

The plot of the real part of impedance against the imaginary part gives a Nyquist Plot, as shown in Figure 3. 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 labeling 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 Figure 4. This is the more complete way of presenting the data.

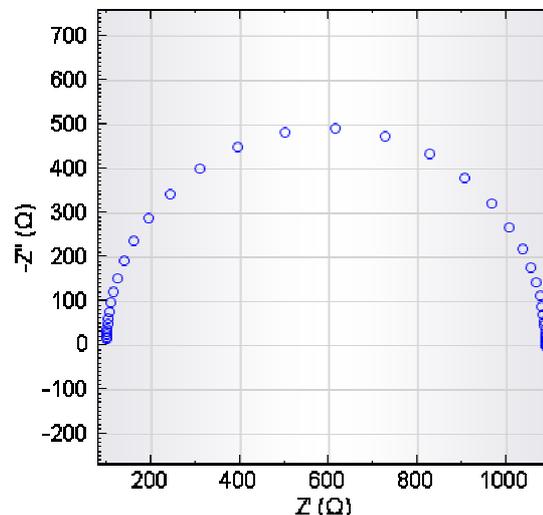


Figure 3 – A typical Nyquist plot

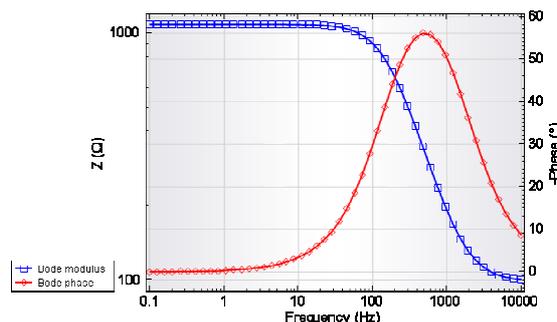


Figure 4 – A typical Bode plot

A third data presentation mode involving a 3D plot, is available. In this presentation mode the real and imaginary components are plotted on the X and Y axis, respectively and the logarithm of the frequency is plotted on the Z axis (see Figure 5).

The relationship between the two ways of representing the data is given by:

$$|Z|^2 = (Z')^2 + (-Z'')^2$$

$$\tan(\varphi) = \frac{-Z''}{Z'}$$

Alternatively, the real and imaginary components can be obtained from:

$$Z' = |Z| \cos \varphi$$

$$-Z'' = -|Z| \sin \varphi$$

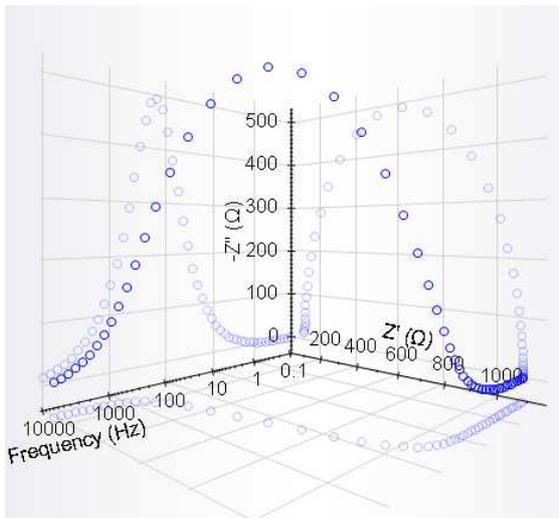


Figure 5 – 3D projection plot

Date

1 July 2011