Application Area: Fundamental

Electrochemical Impedance Spectroscopy (EIS)
Part 1 – Basic Principles

Keywords

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

Summary

Electrochemical Impedance Spectroscopy (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 to the system under investigation and measure the response, which can be current, voltage or another signal of interest[1]. A non-linear i-V curve for a theoretical electrochemical system is shown in Figure 1.

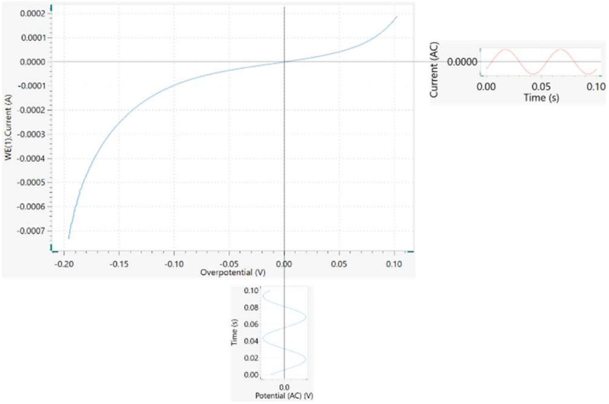

Figure 1 - Potential and current modulation recorded during an impedance measurement

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).

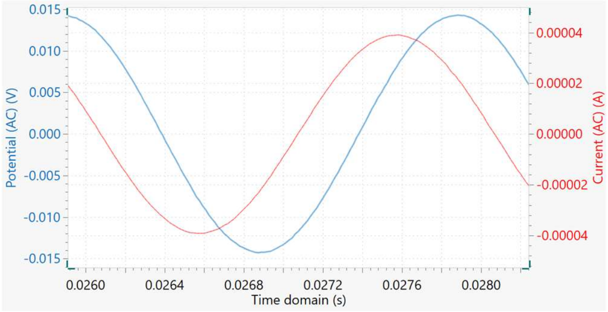

Figure 2 – Time domain plots of the low amplitude AC potential modulation (blue curve) and AC current response (red curve)

The Taylor series expansion for the current is given by:

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

If the magnitude of the perturbing signal ΔE is small, then the response can be considered linear in first approximation.

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[1] For example, in the case of Electrohydrodynamic (EHD) impedance spectroscopy, the signal is the rotation speed.

The higher order terms in the Taylor series can be assumed to be negligible.

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

$$Z_\omega(\Omega) = \frac{E_\omega(V)}{i_\omega(A)} \qquad 2$$

The impedance Z_ω, of the system 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.

As mentioned above, the impedance 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:

$$Z = |Z|e^{\varphi\omega} \qquad 3$$

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

In Cartesian coordinates the impedance is given by:

$$Z = Z' - j \cdot Z'' \qquad 4$$

Where Z' is the real part of the impedance, Z'' is the imaginary part, and $j = \sqrt{-1}$.

Data representation

The plot of the real part of impedance against the imaginary part gives a so-called Nyquist Plot, shown in Figure 3.

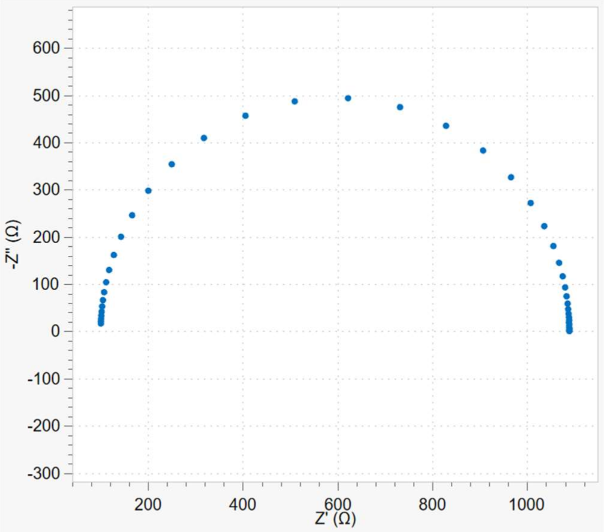

Figure 3 – A typical Nyquist plot.

The advantage of the Nyquist plot is that it gives a quick overview of the data and it is possible to make some qualitative interpretations. In a Nyquist plot, 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 plot is that the frequency information is not present. One way of overcoming this problem is by labeling the frequencies on the curve.

The impedance modulus and the phase shift are plotted as a function of frequency in two different plots, the Bode plot, shown in Figure 4. This is a more complete way of presenting the data.

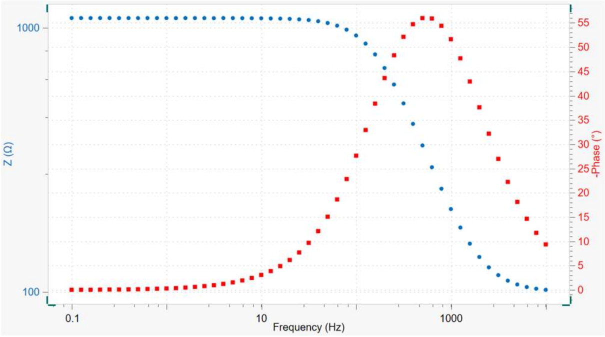

Figure 4 – A typical Bode plot. In blue the modulus vs. frequency. In red, the phase vs. frequency.

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

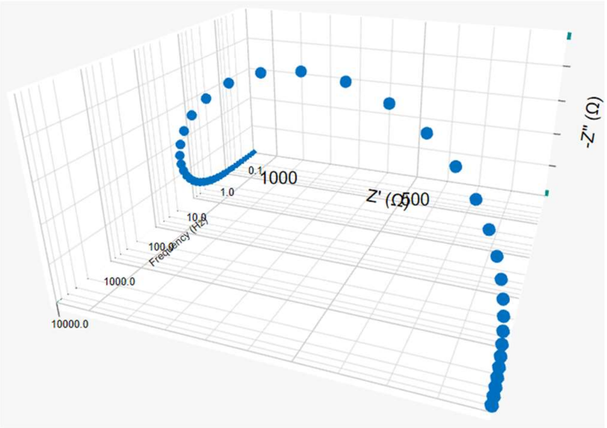

Figure 5 – 3D projection plot

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

$$|Z|^2 = (Z')^2 + (-Z")^2$$
$$\tan(\varphi) = \frac{-Z"}{Z'} \qquad 5$$

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

$$Z' = |Z| \cos\varphi$$
$$-Z" = -|Z| \sin\varphi \qquad 6$$

Conclusions

In this application note, an introduction of electrochemical impedance spectroscopy is given. The basic principles of how the impedance is calculated from the oscillating signals are exposed.

Besides, the Cartesian and polar coordinates to write a complex number, together with the Nyquist plot, Bode plot and 3D representation of the data are given.

Date

September 2019 AN-EIS-001

For more information

Additional information about this application note and the associated NOVA software procedure is available from your local **Metrohm distributor**. Additional instrument specification information can be found at **http://www.metrohm.com/electrochemistry**.