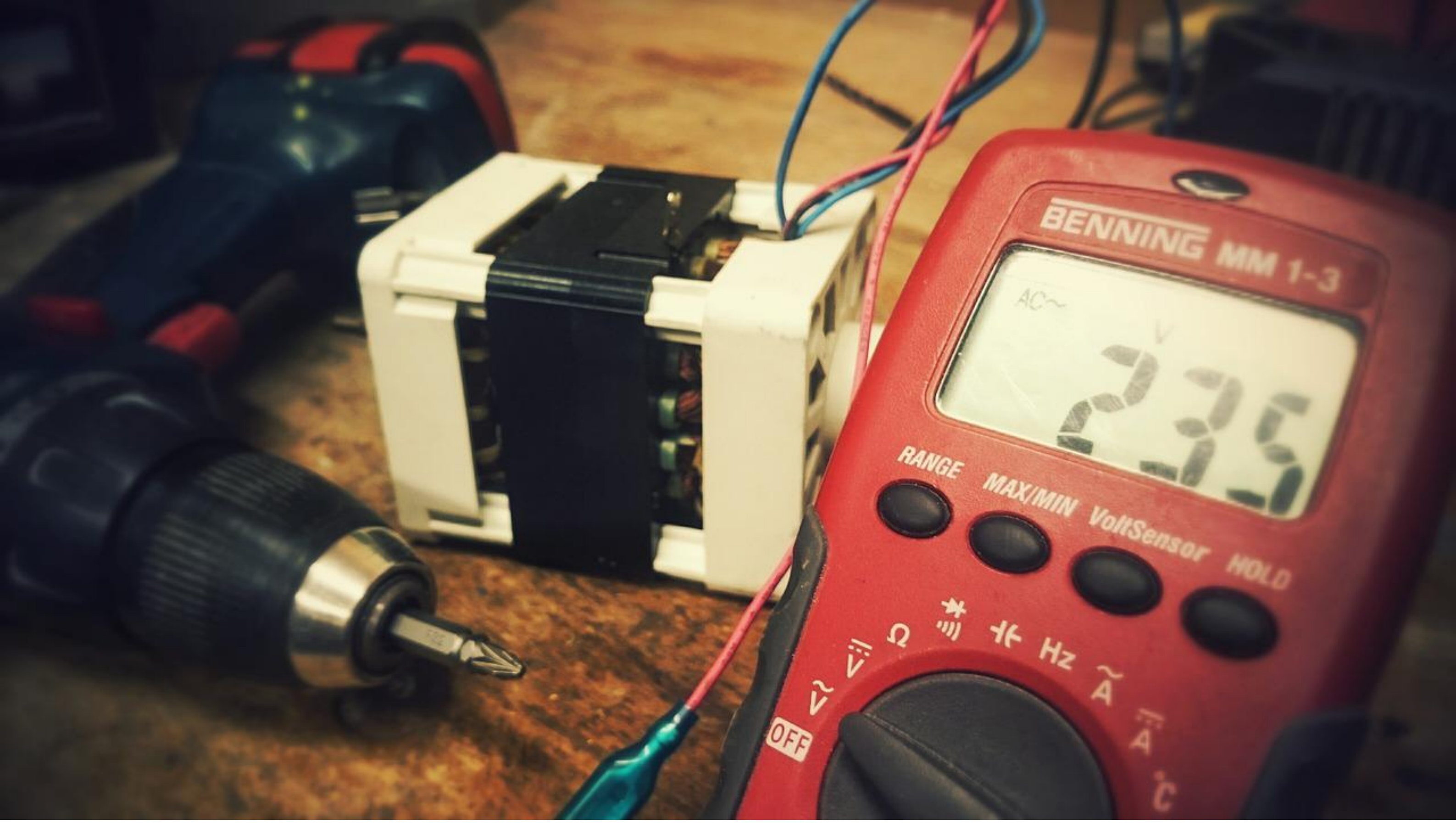


Application Note AN-EIS-001

Electrochemical Impedance Spectroscopy

Part 1 – Basic Principles

Electrochemical impedance spectroscopy (EIS) is a widely used multidisciplinary technique for characterizing the behavior of complex electrochemical systems. What sets EIS apart is its ability to isolate and distinguish the influence of various physical and chemical phenomena at a given applied potential—something which is not possible with «traditional» electrochemical techniques. EIS is employed in the study of a range of complex systems including batteries, catalysis, and corrosion processes.

In recent years, EIS has also become more popular for investigating semiconductor interfaces and the diffusion of ions across membranes.

This seven-part series introduces EIS and covers basic theory, experimental setups, common equivalent circuits used for fitting data, and tips for improving the quality of the measured data and fitting. This Application Note (Part 1) focuses on the basic principles of EIS measurements.

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 typical i-V curve for a theoretical electrochemical system is shown in Figure 1.

1 *For example, in the case of Electrohydrodynamic (EHD) impedance spectroscopy, the signal is the rotation speed of the working electrode.*

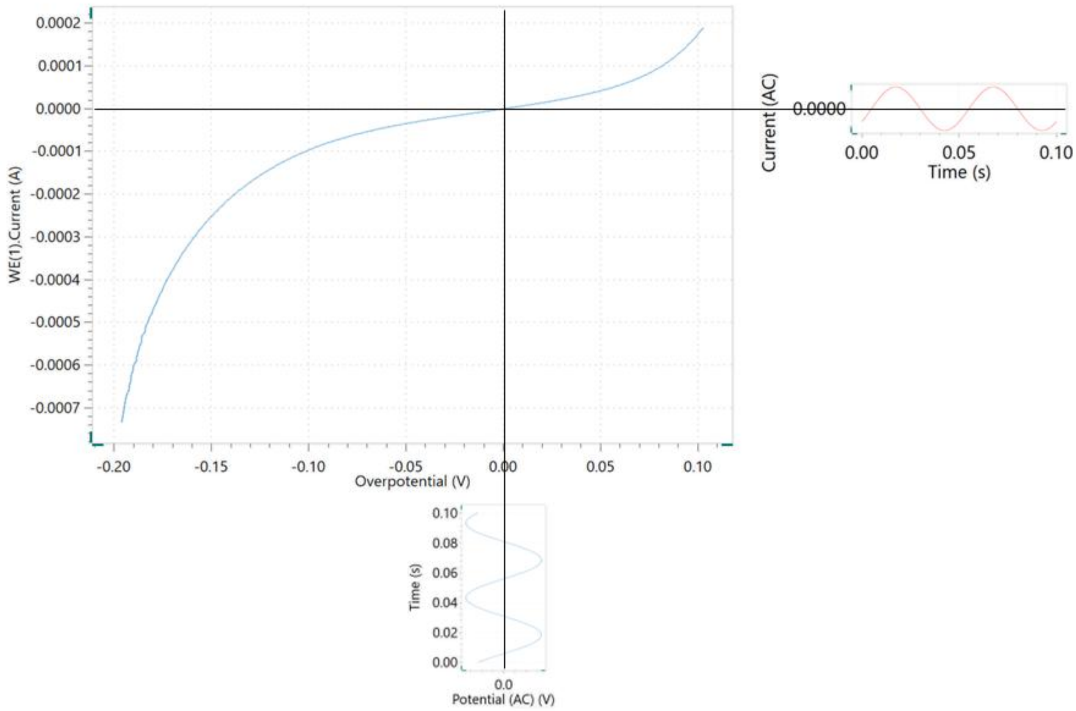


Figure 1. Curve showing the modulated potential signal applied and the resulting modulated current signal recorded during a potentiostatic impedance measurement.

In potentiostatic EIS, a low amplitude sine wave $\Delta E \sin(\omega t)$ 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 $\Delta i \sin(\omega t + \phi)$. The current response is shifted with respect to the applied potential (Figure 2).

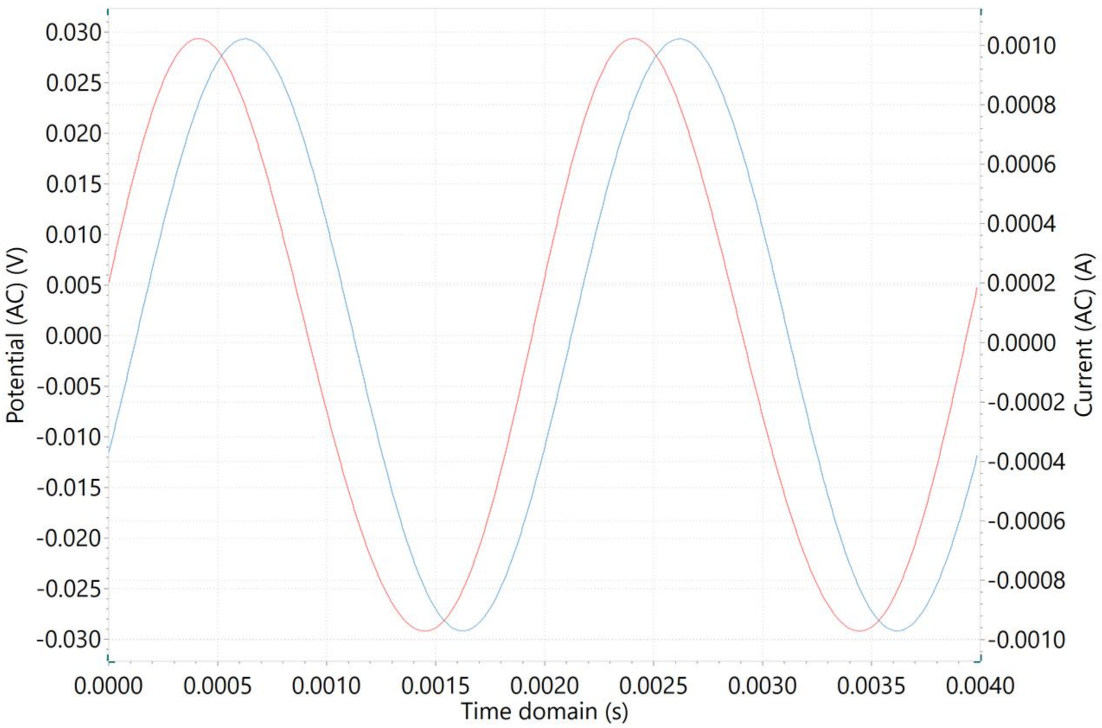


Figure 2. Time domain plots of the low amplitude AC potential modulation (blue curve) and AC current response (red curve).

The Taylor series expansion for the current is given by:

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

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

$$z_\omega = \frac{E_\omega\ (V)}{i_\omega\ (A)}$$

The impedance of the system is a complex quantity with a magnitude and a phase shift which depend on the frequency of the signal. Therefore, by varying the frequency of the applied signal, one can calculate the impedance of the system as a function of frequency. Typically, a frequency range of 100 kHz to 0.1 Hz is used in electrochemistry.

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:

$$z = |Z| \, e^{\varphi\omega}$$

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

In Cartesian coordinates, the impedance is given by:

$$z = z' - j \, . z''$$

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, as shown in Figure 3.

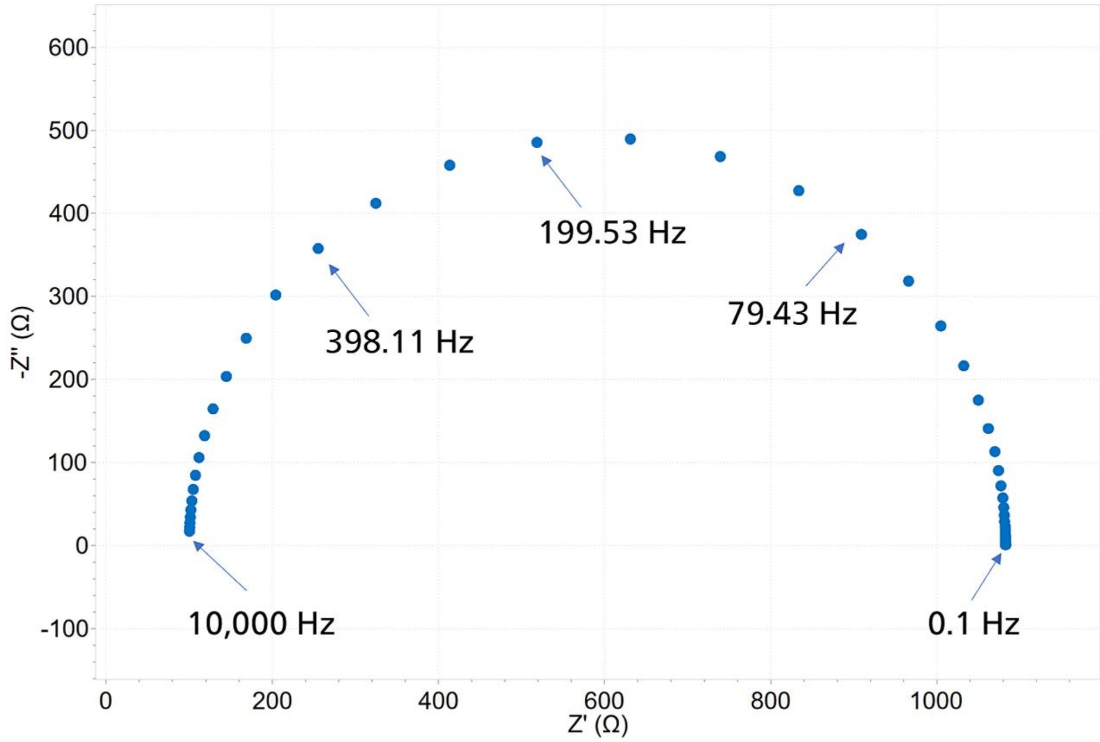


Figure 3. A typical Nyquist plot. For clarity purposes, the corresponding frequencies which produced some of the data points have been labeled.

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 (i.e., isometric axes) so as not to distort the shape of the curve. The shape of the curve is important in order to make qualitative interpretations of the data. The disadvantage of the Nyquist plot is that the frequency information is not present. One way of overcoming this issue is by labeling some frequencies on the curve, as was done in Figure 3.

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

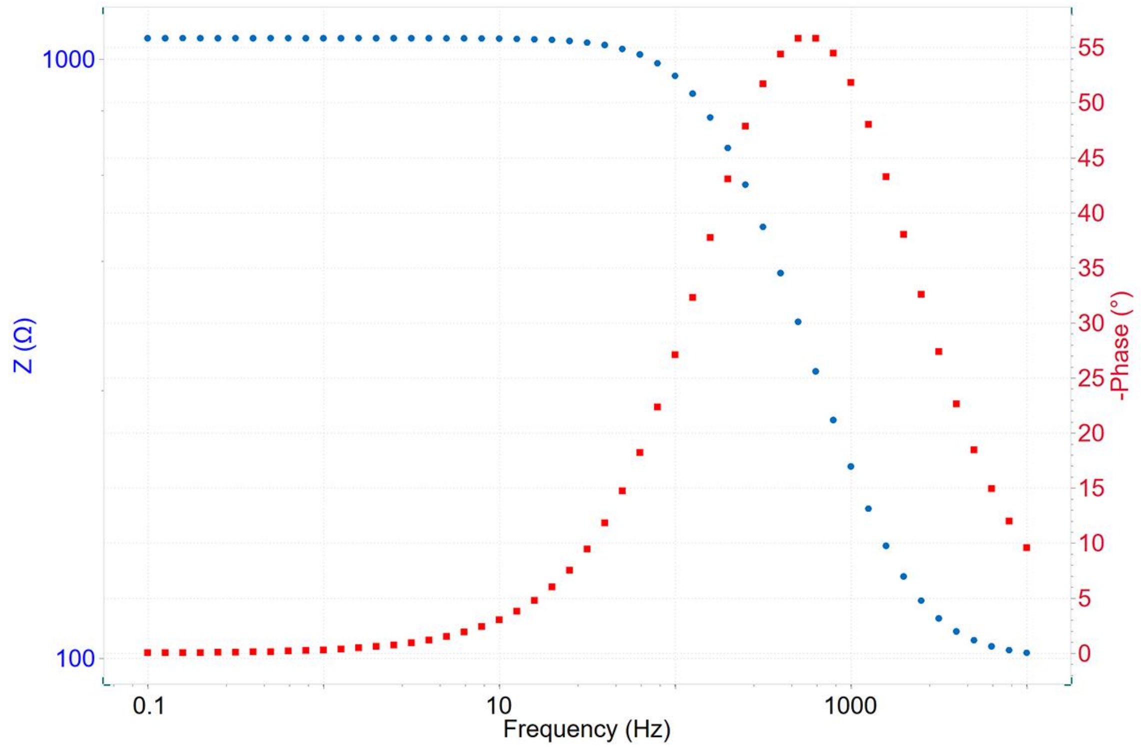


Figure 4. A typical Bode plot.

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

$$|z|^2 = (z')^2 + (z'')^2$$

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

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

$$z' = |z| \cos\varphi$$

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

CONCLUSIONS

An introduction to electrochemical impedance spectroscopy (EIS) is given in this Application Note. The basic principles of how the impedance is calculated from the oscillating signals are discussed. Additionally, 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.

CONTACT

Metrohm Vietnam
Phan Dinh Giot
70000 Herisau
info@metrohm.vn

CONFIGURATION

VIONIC

VIONIC is our new-generation potentiostat/galvanostat that is powered by Autolab's new **INTELLO** software.

VIONIC offers the **most versatile combined specifications of any single instrument** currently on the market.

- Compliance voltage: ± 50 V
- Standard current ± 6 A
- EIS frequency: up to 10 MHz
- Sampling interval: down to 1 µs

Also included in **VIONIC's** price are features that would usually carry an additional cost with most other instruments such as:

- Electrochemical Impedance Spectroscopy (EIS)
- Selectable Floating
- Second Sense (S2)
- Analog Scan

Autolab PGSTAT204

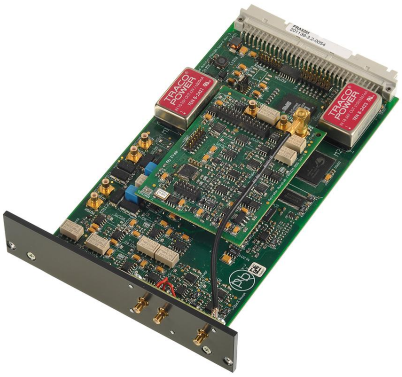
The PGSTAT204 combines the small footprint with a modular design. The instrument includes a base potentiostat/galvanostat with a compliance voltage of 20 V and a maximum current of 400 mA or 10 A in combination with the BOOSTER10A. The potentiostat can be expanded at any time with one additional module, for example the FRA32M electrochemical impedance spectroscopy (EIS) module.

The PGSTAT204 is an affordable instrument which can be located anywhere in the lab. Analog and digital inputs/outputs are available to control Autolab accessories and external devices are available. The PGSTAT204 includes a built-in analog integrator. In combination with the powerful NOVA software it can be used for most of the standard electrochemical techniques.

Autolab PGSTAT302N

This high end, high current potentiostat/galvanostat, with a compliance voltage of 30 V and a bandwidth of 1 MHz, combined with our FRA32M module, is specially designed for electrochemical impedance spectroscopy.

The PGSTAT302N is the successor of the popular PGSTAT30. The maximum current is 2 A, the current range can be extended to 20 A with the BOOSTER20A, the current resolution is 30 fA at a current range of 10 nA.



Electrochemical impedance spectroscopy module

The FRA32M provides the means to perform impedance and electrochemical impedance measurements in combination with the Autolab. This module allows one to perform both potentiostatic and galvanostatic impedance measurements over a wide frequency range of 10 µHz to 32 MHz (limited to 1 MHz in combination with the Autolab PGSTAT). In addition to the classical EIS, the NOVA software also allows the users to modulate other outside signals such as rotation speed of a rotating disk electrode or the frequency of a light source to perform Electro-hydrodynamic or Photo-modulated impedance spectroscopy.

The FRA32M module comes with a powerful fit and simulation software for the analysis of impedance data.