Application Area: Fundamental

Electrochemical Impedance Spectroscopy (EIS) Part 6 – Measuring raw signals in EIS

Keywords

Electrochemical impedance spectroscopy; frequency response analysis; Nyquist and Bode representations; raw data; Resolution plot, Lissajous plot

Summary

Electrochemical Impedance Spectroscopy (EIS) involves the study of the variation of the impedance of an electrochemical system with the frequency of a small-amplitude AC perturbation. In practice, the time-domain of the input and output signals are converted into a complex quantity that is a function of a frequency. The input and the resulting output signals are hardware and software processed to yield a frequency-dependent transfer function. More details about the instrumentation and the data conversion process are described in the available literature.

The Nyquist, Bode phase and Bode modulus plots are the most often used data plots in impedance spectroscopy. These plots are representations of calculated (processed) data. Because of this, it is difficult for the user to evaluate in real time or after the measurement if the measured data fulfils all the above conditions. Moreover, if the Nyquist and Bode plots do not show the expected behavior of the system, it is difficult for the user to pinpoint the cause of the problem (e.g., noise in the system, or lack of sensitivity).

In this application note, the advantage of recording the raw time domain data for each individual frequency during an electrochemical impedance measurement is described.

Experimental conditions for a valid EIS measurement

From the experimental point of view, in order for the electrochemical impedance measurement data to be valid, three conditions have to be fulfilled:

- **Linearity:** the applied AC amplitude must be small enough so that the response of the cell can be assumed to be linear, in first approximation, but still large enough to measure a response, Figure 1.
- **Stability:** the overall state of the system must not change significantly during the acquisition of the data. The choice of the frequency range and measurement conditions have an influence on this condition.
- **Causality**: The measured AC response of the system must be directly correlated to the applied AC stimulus. The shielding of the cell from outside perturbations is important in this case.

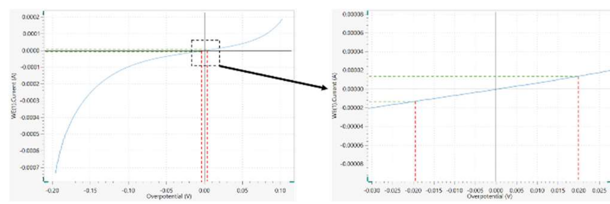

Figure 1 – Example of a linear i-V response which fulfils the linearity condition

Possible tests for the validity of EIS data

Kronig-Kramers test

The Kronig-Kramers (KK) relations are mathematical properties which connect the real and imaginary parts of any complex function. These relations are often used to relate the real and imaginary parts of a complex transfer function, like the electrochemical impedance Z. During the KK test, the experimental data points are fitted using a special model circuit which always satisfies the KK relations. If the measured data set can be represented with this circuit, then the data set should also satisfy Kronig-Kramers assumptions.

Satisfaction of the Kramers-Kronig test is a necessary but not sufficient condition for meeting the above mentioned requirements.

Monitoring the raw signal (time domain)

In impedance spectroscopy, the raw signal is the actual applied sinewave and the resulting response (AC and DC). These can be recorded individually for each frequency during a frequency scan. Even though there are other experimental methods which can be used for the assessment of consistency of the electrochemical impedance measurements, monitoring the raw signals and recording the specific plots for each individual applied frequency in the dataset is one of the most convenient ways to get a fast and reliable image over the validity of the measurement.

Advantages of recording the raw data in EIS

In the Autolab Nova software, during a frequency scan, the values of the following six signals are *derived* from a synchronized measurement of the potential and current sine waves in the time domain:

- **Frequency** (Hz)**:** the frequency of the applied sinewave.
- **Time** (s)**:** the time coordinate, corresponding to the measured data point in the spectrum.
- $\boldsymbol{Z}$ $(\boldsymbol{\Omega})$**:** the modulus of the impedance.
- $\boldsymbol{Z'}$ $(\boldsymbol{\Omega})$**:** the real part of the impedance.
- $-\boldsymbol{Z''}$ $(\boldsymbol{\Omega})$**:** the imaginary part of the impedance.
- $-\boldsymbol{Phase}$ $(°)$**:** the phase shift.

Other additional signals can be recorded in Nova, using the dedicated FRA sampler (see Figure 2):

- **Sample time domain:** contains the relative time coordinates of the measured sinewaves.
- **Sample frequency domain:** the frequency component of potential and current.
- **Sample DC:** the DC component of potential and current.
- **Calculate Admittance:** the software will calculate the admittance values from the impedance.

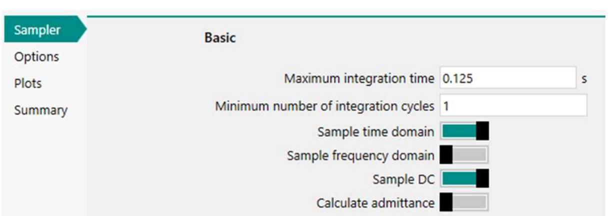

Figure 2 – The FRA sampler in NOVA

The additional signals which represent the raw, measured signals can be used to build additional plots in Nova. To add these signals to the measurement, the FRA Plots window is used, Figure 3.

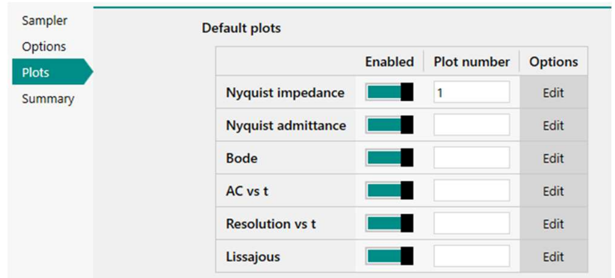

Figure 3 – The FRA plots in NOVA

The plots which can be shown are the

- **Nyquist impedance:** present by default
- **Nyquist admittance:** if toggled, the Calculate Admittance in the FRA Sampler will be automatically toggled as well.
- **Bode** present by default
- **AC vs t:** the raw values of the potential and current.
- **Resolution vs t:** the measured resolution for potential and current, respectively, expressed in %.
- **Lissajous:** the AC current versus the AC potential.

The last three plots can be used very conveniently for a clear and correct evaluation of the fulfillment of the linearity and causality conditions.

AC vs t plot

In Figure 4, an example of the AC potential vs. time, blue line, and AC current vs. time, red line is shown.

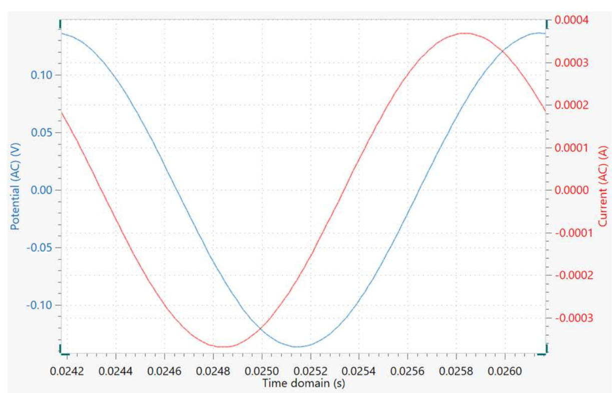

Figure 4 – AC Potential vs. time, blue line, and AC current vs. time, red line.

With the AC vs. time plots, it is possible to notice the eventual phase shift of the two signals. Furthermore, it is possible to see if the measured signal is noisy.

Resolution vs t plot

The resolution plot typically shows the AC Current and/or AC Potential resolution on the Y-axis versus the time domain data on the X-axis. The resolution of a signal is calculated with Equation 1:

$$x_{res} = 100 \cdot \frac{x}{0.5 \cdot (x_{MAX} - x_{min})} \qquad 1$$

Where

- x_{res} (%) is the potential or current signal resolution
- x is the value of the potential or current signal
- x_{MAX} is the maximum value of the potential or current signal
- x_{min} is the maximum value of the potential or current signal

The resolution plots will indicate if the sensitivity of the system is high enough so that the errors in the processed data will be minimal.

Figure 5 shows an example of resolution plot with enough resolution on both signals (AC potential, in blue and AC current, in red).

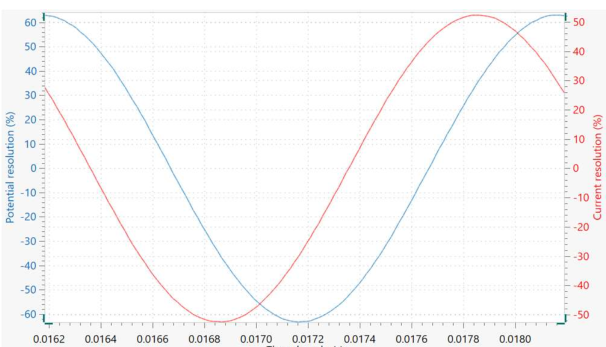

Figure 5 – A resolution plot showing large resolution values for both AC Potential and AC Current.

The impedance data derived from these signals will be very accurate.

On the other hand, Figure 6 displays low resolution values for the recorded AC current.

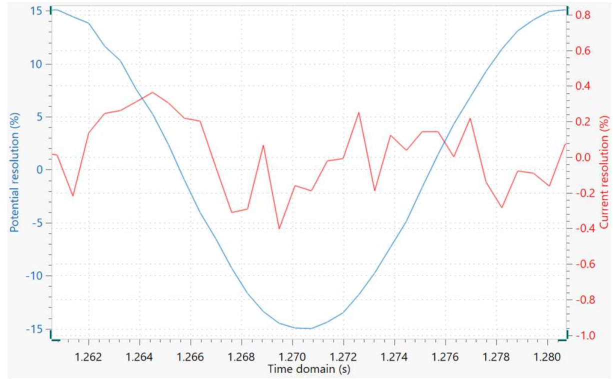

Figure 6 – A resolution plot showing large resolution values for AC potential but low resolution for the AC current.

The impedance data derived from these raw values will be less accurate.

Lissajous plot

The Lissajous plot typically shows the AC potential on the X-axis and the AC current on the Y-axis. When the linearity condition is respected, the plot exhibits a central symmetry with respect to the origin of the plot (see Figure 7).

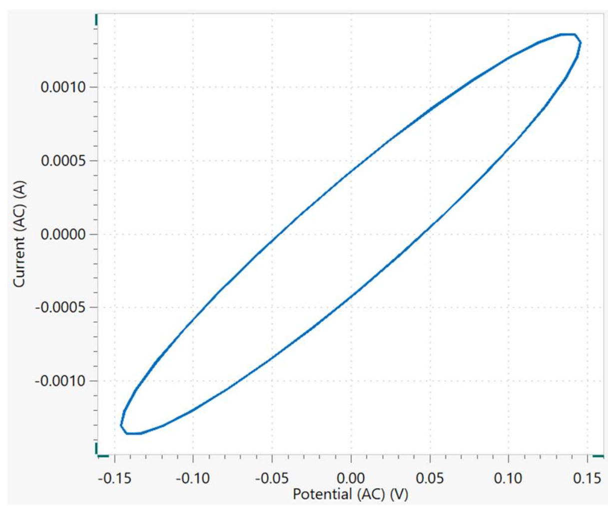

Figure 7 – A typical Lissajous plot for a linear system

The plot shape changes from a straight line to a perfect circle, depending on the phase shift.

A non-linear response can be observed in the Lissajous plot when the central symmetry of the plot is not respected, as illustrated in Figure 8.

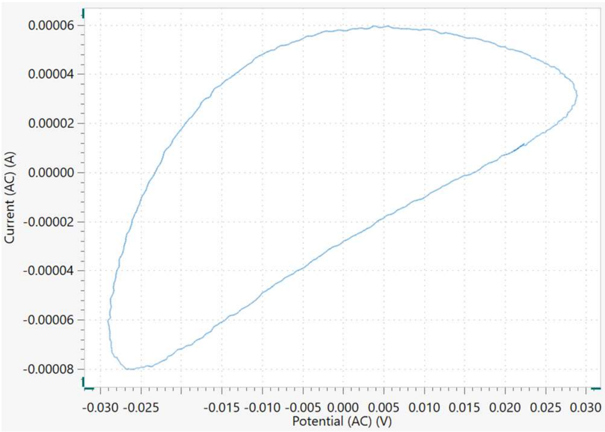

Figure 8 – A Lissajous plot showing a non-linear response

Conclusions

It is clear that analyzing the raw signal is a very straightforward and easy to use tool which can help the user to make sure that the linearity, stability and causality conditions are fulfilled. Furthermore, plotting the raw signals helps to pinpoint the source of errors in an electrochemical impedance spectroscopy measurement.

References

Bernard Tribollet & Mark E. Orazem: Electrochemical Impedance Spectroscopy, Wiley-Interscience, 2008

Date

September 2019 AN-EIS-006

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**.