Metrohm Autolab B.V.

## Autolab Application Note EIS06

# 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, lack of sensitivity etc.).

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. (see 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.

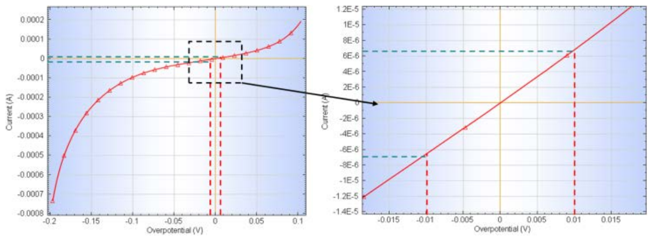

Figure 1 – Example of a linear i-V response which fulfils the linearity condition

**Possible tests for the validity of EIS data**

*Kronig-Kramers (KK) 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 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. More details regarding the KK test can be found in the Impedance spectroscopy tutorial, in Nova and also in the specified reference material.

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 sinwave 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.
- **Z, modulus (Ohm):** the modulus of the measured impedance.
- **Z', real part (Ohm):** the real part of the measured impedance.
- **-Z", imaginary part (Ohm):** the imaginary part of the measurement impedance.
- **-Phase (°):** the phase shift.

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

- **Potential (DC) and Current (DC):** the DC component of the potential and current, respectively.
- **Time domain (s):** contains the relative time coordinates of the measured sinewaves.
- **Potential and Current resolution (%):** the measured resolution for Potential and Current, respectively, expressed in % of ADC range.
- **Potential (AC) and Current (AC):** the raw values of the Potential (in Volt) and the Current (in Ampere).
- **Frequency domain (Hz):** the frequency component of the power spectrum of the Potential and Current.
- **Potential and Current frequency domain (a.u):** the magnitude of the spectral power of the Potential and Current, expressed in arbitrary units.

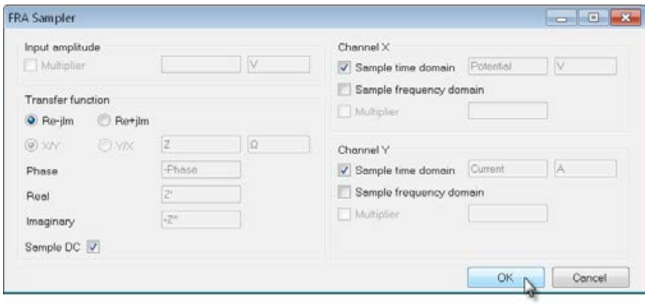


Figure 2 – Sampling the raw data in NOVA

The ten 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 sampler window (shown in Figure 2), is used. Details on how to setup the Nova software to sample the raw signals and build the specific plots, can be found in the *Nova Technical note #15 – Raw FRA data* available on www.metrohm-autolab.com.

These plots can be used very conveniently for a clear and correct evaluation of the fulfillment of the linearity and causality conditions (e.g. Lissajous plot, $E_{ac}$ and $i_{ac}$ vs time, see Figure 3, Figure 4, Figure 5 and Figure 6).

*Lissajous plot*

The Lissajous plot typically shows the AC Potential on 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 3). 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 4.

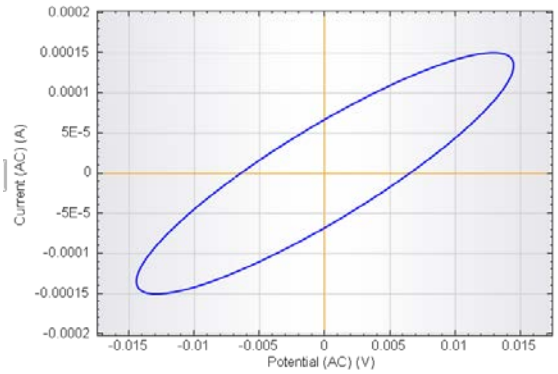


Figure 3 – A typical Lissajous plot for a linear system

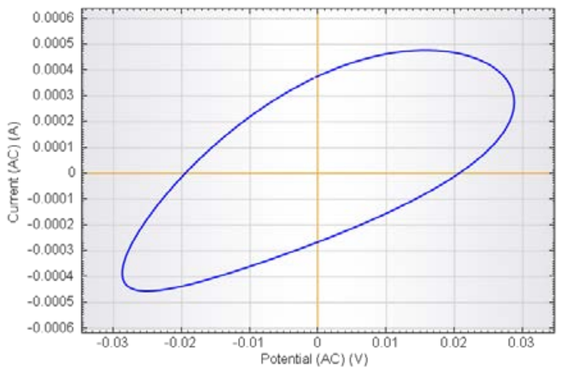


Figure 4 – A Lissajous plot showing a non-linear response

*Resolution 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. Alternatively, the raw AC Current and/or Potential can be used instead. 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 current and AC potential). 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. The impedance data derived from these raw values will be less accurate.

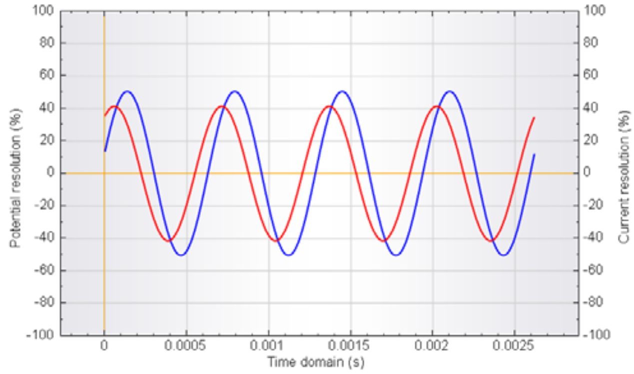


Figure 5 – A resolution plot showing large resolution values for both Potential (AC) and Current (AC)

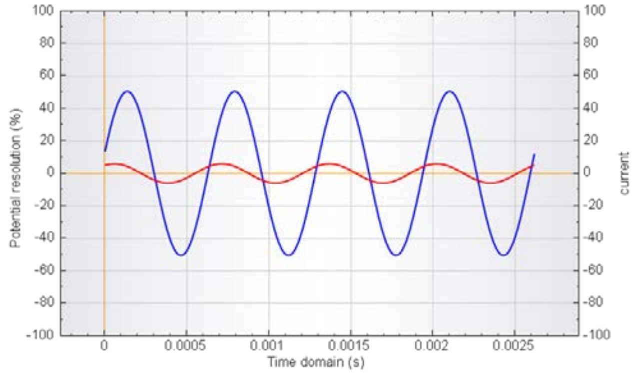


Figure 6 – A resolution plot showing large resolution values for Potential (AC) but low resolution for the Current (AC)

## Conclusions

It is clear that analyzing the raw measured signal, besides the classical Nyquist and Bode plots, 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 and, if necessary, to pinpoint the source or error(s) in an electrochemical impedance measurement

## References


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


## Date

20 December 2011