# Potentiostatic and Galvanostatic Electrochemical Impedance Spectroscopy

What is GEIS? When to use GEIS or PEIS?

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Compact Electrochemical Interfaces

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# 1 Electrochemical Impedance Spectroscopy

In the last years the popularity of Electrochemical Impedance Spectroscopy (EIS) has experienced a steep increase. One reason for that is that devices capable of EIS became more affordable and more available on the market. Another reason is that many researchers have discovered the versatile opportunities EIS offers for their research projects.
EIS is a non-destructive technique with high sensitivity for interface changes. It is useful for corrosion research, label free detection methods, battery research and many other applications.
In this application note the differences between EIS in potentiostatic (PEIS) and galvanostatic (GEIS) mode will be elaborated.

## 1.1 Basics of EIS

Resistance is in an electronics context a well-known concept. While the term resistance is used during direct current (dc), i.e. constant applied potentials and currents, impedance is used for the same phenomenon during alternating current (ac), i.e. sine wave shaped potentials and currents.
Studying the impedance of an electrochemical system delivers information about the interface in a non-destructive way, because the average of a sine wave is zero.
The measurement setup is a regular electrochemical cell and a potentiostat capable of EIS. A sine wave shaped potential or current is applied to the working electrode and the response, a current or potential, is measured. A requirement is that the response needs to be a sine wave as well. This means the current and potential must have a linear relationship. Additionally the system needs to be in a steady state compared to the time scale of the measurement.
With the sine waves of potential and current the total impedance Z and the phase shift $\phi$ is calculated. Impedance is complex number and in polar coordinates Z is the radius and $\phi$ the angle. To express a complex number in cartesian coordinates it needs to be split in its real and imaginary part. This is the same basic concept used for any other complex number. Thus from Z and $\phi$ the real part Z' and the imaginary part Z'' of the impedance can be calculated.
This procedure is repeated for multiple sine waves with different frequencies. This way a whole spectrum for the impedance values is recorded.
The impedance spectrum is plotted in different ways, but the most common are the Bode plot (lg Z and $\phi$ vs lg f) and the Nyquist plot (-Z'' vs Z').
If the interface or the interaction between a redox probe and the interface change, the spectrum changes its shape and the values. This makes it easy to identify changes, but it is complex to analyze these changes. Usually Equivalent circuit fitting is applied to do so.

### 1.1.1 Equivalent Circuit Fitting

Even simple electrochemical cells have multiple contributions to the Impedance of a system, for example the double layer capacitance, solution resistance or charge-transfer resistance. Calculating the Impedance for these seems like a very difficult task.
To simplify that task each contribution to the impedance is translated into an electronics component with well-known impedance. All these components are then arranged into a circuit. This circuit should be equivalent to the electrochemical cell considering the impedance spectrum. Even the impedance spectrum of complex equivalent circuits can be simulated by the appropriate software nowadays. Usually, the software performs a fit to find the parameters of the equivalent circuit which will bring the simulation as close to the measured data as possible. Once the simulation is close enough to the measured data, the contribution of each component to the total impedance is known. This way the change of a single property can be monitored by using EIS and a lot of information can be acquired. A more detailed description is available on our corrosion website.

# 2 Potentiostatic Electrochemical Impedance Spectroscopy (PEIS)

Most techniques in electrochemistry are potentiostatic, which means the potential is controlled and the current is measured. For most applications potentiostatic EIS is used. Due to this often EIS is used synonymous with PEIS.

From the previous paragraph it is clear that a sine wave needs to be applied for the EIS measurement. Usually the potential amplitudes applied are between 2 and 25 mV. This means the changes induced to the surface during the measurement are negligible.
During PEIS the potential, which the sine wave is oscillating around, is fixed by the potentiostat. This means also a dc potential is applied.
This potential is usually chosen in a way that the system has an approximately linear response and a very sensitive one. This means the dc potential is close to the redox or formal potential of a redox species. This can be a redox probe in solution or a corroding surface.
In some cases it is useful to work with the open circuit potential (OCP) of the system as the dc potential, for example during corrosion studies.
PEIS is the more common technique, but if a conscious choice between PEIS and GEIS is made, PEIS is preferable for high impedance systems, where a small potential change leads to a small current change.
Low impedance systems will respond to low potential excitations with high currents. If you are performing PEIS with a PalmSens4, the current cannot exceed 30 mA and when a Sensit Smart is used the limit is 3 mA. Additional to the instruments limitations it should be considered that high currents could lead to a permanent change of your system. That means PEIS is under these conditions an invasive method.

# 3 Galvanostatic Electrochemical Impedance Spectroscopy (GEIS)

During GEIS a current sine wave is applied and the resulting potential is measured. Although galvanostatic EIS is not as popular as PEIS it is necessary under certain conditions to record the spectrum with GEIS. One of these conditions is the low-impedance system just mentioned in the previous paragraph.
A low-impedance system will give a strong current response to even small potential changes, which can lead to changes of the system under investigation. During GEIS the current sine wave is controlled. A small amplitude in the range of mA is applied and the potential response is measured. This response will be in the range of mV or µV, which should not be sufficient to induce changes to the electrochemical cell.
Another property of GEIS, which can be an advantage or disadvantage, is that it will always be performed around the OCP.
The current sine wave is oscillating around 0 A, which means the state where no current is flowing. The potential of an electrochemical cell with no current flowing is the OCP. Should the OCP of the system change the GEIS measurement will automatically still take place around the new OCP. To achieve the same for a PEIS the OCP needs to be measured between the measurements.

GEIS should be used for a system with low impedance or drifting OCP.

# 4 PEIS and GEIS are equal

If the right parameters are chosen and the system does not have a low impedance, which makes PEIS difficult due to high currents, or a high impedance, which makes GEIS difficult due to low potentials, PEIS and GEIS should deliver the same results. In Figure 1 you can see two EIS measurements with our PalmSens dummy cell WE C. This circuit is a simplified Randles Circuit with a 560 Ohm serial resistor and a 10 kOhm resistor parallel with a 33 nF capacitor.
Both techniques provide the same results with the chosen parameters.

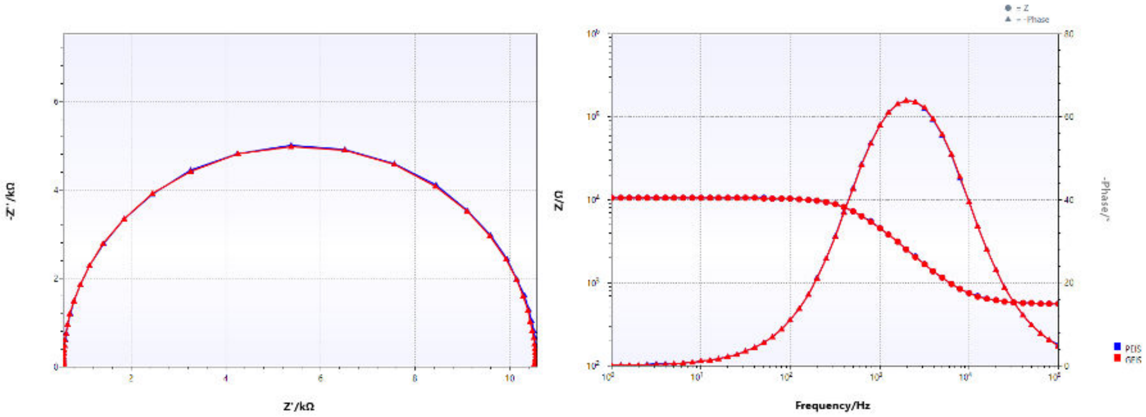


*Figure 1 PEIS (blue) and GEIS (red) of the PalmSens dummy cell WE C as Nyquist plot (left) and Bode plot (right)*

The parameters for these measurements were:

*Table 1 PEIS parameters for Figure 1*

| Parameter | Value |
|---|---|
| **Technique** | Impedance Spectroscopy |
| **t equilibration** | 4 s |
| **Scan type** | Fixed |
| **E dc** | 0 V |
| **E ac** | 0.01 V |
| **Frequency type** | Scan |
| **n frequencies** | 51 = 10 /dec. |
| **Max. frequency** | 100 000 Hz |
| **Min. frequen** | 1 Hz |

*Table 2 GEIS parameters for Figure 1*

| Parameter | Value |
|---|---|
| **Technique** | Galvanostatic Impedance Spectroscopy |
| **t equilibration** | 4 s |
| **Applied current range** | 1 mA |
| **Scan type** | Fixed |
| **i dc** | 0*range |
| **i ac** | 0.01*range |
| **Frequency type** | Scan |
| **n frequencies** | 51 = 10 /dec. |
| **Max. frequency** | 100 000 Hz |
| **Min. frequen** | 1 Hz |

# 5 PEIS and GEIS Equipment

The EmStat Pico, Sensit Smart and Sensit BT are all capable of performing PEIS up to a frequency of 200 kHz.
The PalmSens4 is capable of performing PEIS and GEIS up to a frequency of 1 MHz..
Feel free to browse our website and get a quotation within a work day.