

Electrochemical Impedance Spectroscopy

Part 2 – Experimental Setup

A typical electrochemical impedance spectroscopy (EIS) experimental setup consists of an electrochemical cell (the system under investigation), a potentiostat/galvanostat, and a frequency response analyzer (FRA). The FRA applies the sine wave and analyzes the response of the system to determine the

impedance of the system.

This Application Note is the second in a seven-part series introducing EIS, covering the basic theory, experimental setups, and more. Part two introduces common experimental setups as well as details of the main experimental parameters.

THE ELECTROCHEMICAL CELL

The electrochemical cell in an EIS experiment can consist of two, three, or four electrodes. The most basic form of the cell has two electrodes. Usually, the electrode under investigation is called the working electrode, and the electrode necessary to close the electrical circuit is called the counter electrode. The electrodes are usually immersed in a liquid electrolyte. For solid-state systems, there may be a solid electrolyte or no electrolyte. Regardless of the cell configuration:

- The potential is controlled or measured between the reference electrode lead RE and the sense lead S.

TWO-ELECTRODE CELL

A two-electrode configuration for the cell is used when precise control of the potential across the electrochemical interface is not critical (**Figure 1**).

This arrangement is used to investigate electrolyte properties, such as conductivity, or to characterize solid-state systems. Thus, the main application area where this type of setup is most commonly used is during energy and materials research (i.e., batteries). With this configuration, the measured impedance provides information on the complete cell (WE, electrolyte, CE).

THREE-ELECTRODE CELL

A three-electrode configuration for an electrochemical cell is the most common for fundamental electrochemical applications. A third electrode, the reference electrode, is used to accurately determine the potential across the electrochemical interface (**Figure 2**).

Since the absolute potential of a single electrode cannot be measured, all potential measurements in electrochemical systems are performed with respect to a reference electrode. The three-electrode configuration enables researchers to isolate and measure the impedance of phenomena occurring only at the working electrode.

- The current flowing between the counter electrode CE and the working electrode lead WE is measured or controlled, respectively.
- The impedance is then calculated as the ratio between the potential and current (see [AN-EIS-001](#)).



Figure 1. Schematic overview of a two-electrode setup.



Figure 2. Schematic overview of a three-electrode setup.

FOUR-ELECTRODE CELL

A four-electrode cell is used to analyze processes occurring within the electrolyte, e.g., between two electrodes separated by a membrane. In this configuration, the current flows between the working and the counter electrode (Figure 3). Here, the impedance is measured between electrodes connected to RE and S.

This kind of cell is usually used to study ion transport through a membrane or to perform electron or ion conductivity measurements. Therefore, it is most often found in electrocatalysis (i.e., electrolyzers) and in sensing applications. A four-electrode configuration is also necessary for measurements on low impedance solids where the influence of contact and wire resistance should be minimal.



Figure 3. Schematic overview of a four-electrode setup.

EXPERIMENTAL PARAMETERS

The main experimental parameters can be divided into two major categories: the parameters or settings

of the **potentiostat** and the parameters or settings of the **frequency response analyzer**.

INSTRUMENT SETTINGS: POTENTIOSTATIC OR GALVANOSTATIC MODE?

EIS measurements can be done in the potentiostatic or galvanostatic mode. In the potentiostatic mode, experiments are done at a fixed DC potential. A sinusoidal potential perturbation is superimposed on the DC potential and applied to the cell. The resulting current is measured and the impedance of the system is calculated.

In the galvanostatic mode, experiments are done at a fixed DC current. A sinusoidal current perturbation is superimposed on the DC current and is applied to the cell. The resulting potential is measured and the impedance of the system is calculated.

The prevailing mode of choice is usually dependent on both the nature of the sample under test and the research question that needs to be addressed. For example, it is preferred to conduct EIS under galvanostatic rather than potentiostatic control with low impedance devices or in situations where precise control of the working electrode potential is not needed (i.e., batteries). The opposite is true for studying corrosion processes where the prevailing method is potentiostatic, as the potential of the corroding sample needs to be controlled accurately.

DC potential or current

Impedance measurements allow the investigation of the various phenomena occurring at a certain DC potential (or current) of interest. This DC value is also referred to as the bias potential (or current).

Figure 4 shows a typical current-potential curve for the corrosion of iron in a passivating solution. Different regions in this curve can be attributed to various electrochemical phenomena. In theory it is possible to perform EIS measurements at any of the following bias potentials or currents:

- Open circuit potential (OCP), also known as corrosion potential

- Potential or current in the active region
- Potential or current in the passive region
- Potential or current in the limiting current plateau region

Performing EIS in any of these potential regions will produce a different result which relates to the underpinning electrochemical reaction taking place at that point on the polarization curve.



Figure 4. Different regions in the polarization curve.

Note: care must be taken when doing the experiments at OCP. A typical impedance scan takes approximately 10 minutes. For certain systems, the OCP can drift during the impedance experiment. If the OCP is measured at start of the impedance scan and the potential bias is fixed at that value at the beginning of the scan, then as the experiment progresses, the OCP can shift due to changes in the electrode surface. As the bias potential is fixed at the

beginning of the experiment, this can result in a difference between the actual OCP and the potential applied to the working electrode which can create uncertain measurement conditions. To avoid this, it is possible to carry out the EIS measurements in galvanostatic control at zero current (DC), thus eliminating the problem of the OCP shift during the frequency scan.

Perturbation (sine wave) amplitude

It is important that the impedance response of a system is linear. The linearity condition implies that the impedance response is independent of the perturbation amplitude. This can be achieved by using small amplitude perturbations. A very small value can give rise to a poor signal-to-noise ratio and hence noisy data. A large value can result in the violation of the linearity condition. Typically, a value of 10 mV is used for most electrochemical systems.

Experimentally, one can verify the linearity condition by performing the same experiment at different perturbation AC amplitudes. The largest value in this range can be used to give the highest signal-to-noise ratio.

Integration time

As the AC amplitude of the perturbation is decreased, the signal-to-noise ratio becomes poor. To improve this, an average of measurements over several sine waves or cycles can be taken. This process of averaging is also referred to as integration, and the time needed to measure is called the integration time. Increasing integration time improves the signal-to-noise ratio.

AC stabilization time

During a frequency scan, when a new frequency is applied, some time must pass first for the system to

stabilize before measurements can start. This can be achieved by skipping the first few cycles before the actual measurement is taken.

DC stabilization time

It is usually recommended to apply the DC setpoint (E or i) initially without AC perturbation for some time (known as the DC stabilization time) so that the system is able to reach a (pseudo-) steady state prior to the start of the impedance measurement.

Frequency range

In theory, the widest possible frequency range must be chosen to capture all the time constants of the system. In practice, the frequency range is constrained by the instrument limitations and system considerations.

The highest frequency of an impedance scan is often limited by the high frequency limit of the potentiostat and the response of the reference electrode.

The measurement time is the inverse of the frequency. Hence, a very low frequency limit can result in a very long time for the collection of a complete scan. For example, the measurement of one data point at a frequency of 1 mHz will take at least 1000 s. For systems that change with time (e.g., corrosion processes or film growth), this implies that the system has changed during the data collection. Therefore, the low frequency limit should be chosen to ensure that

CONCLUSIONS

In this Application Note, the most common cell setups are shown together with an explanation of the main

experimental parameters.

CONTACT

Metrohm India
Annai Indira Nagar,
Thoraipakkam
600097 Chennai

info@metrohm.in