

Application Area: Fundamental

Electrochemical Impedance Spectroscopy (EIS) Part 2 – Experimental Setup

Keywords

Electrochemical impedance spectroscopy; frequency response analysis; Electrochemical cell.

Summary

A typical electrochemical impedance 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 analyses the response of the system to determine the impedance of the system.

The Electrochemical Cell

The electrochemical cell in an impedance 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 measured between the reference electrode lead RE and the sense lead S, and the current is measured at the working electrode lead WE. The impedance is then calculated as the ratio between the potential and current (see AN-EIS-001 application note).

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 (see Figure 1).



Figure 1 – Schematic overview of the two electrode setup

This arrangement is used to investigate electrolyte properties, such as conductivity, or to characterize solid-state systems.

Three electrode cell

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



Figure 2 – Schematic overview of the three electrode setup

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. A reference electrode, therefore, should be reversible, and its potential should remain constant during the course of the measurement.

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 working electrode and the counter enable current flow, Figure 3.

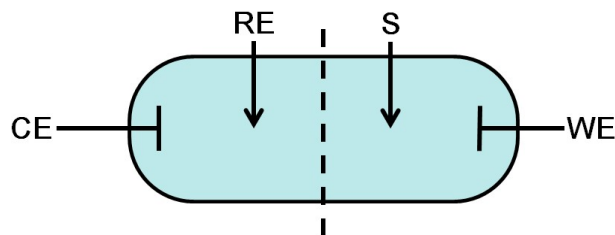


Figure 3 – Schematic overview of the four electrode setup

This kind of a cell is usually used to study ion transport through a membrane or to perform electron or ion conductivity measurements. A four-electrode configuration is also necessary for measurements on low impedance solids where the influence of contact and wire resistance should be minimal.

Main experimental parameters

The main experiment parameters can be divided in the parameters or settings of the potentiostat and the parameters or settings of the FRA.

Instrumental settings

Potentiostatic or Galvanostatic Mode

EIS measurements can be done in the potentiostatic or galvanostatic mode. In 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 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.

Typically impedance experiments are done under potentiostatic control. In some cases, like electrodeposition at constant current and battery research, impedance experiments are performed under galvanostatic control.

DC potential or current

Impedance measurements allow the investigation, in detail, 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). In

Figure 4, a typical current-potential curve for corrosion of iron in passivating solution is shown.

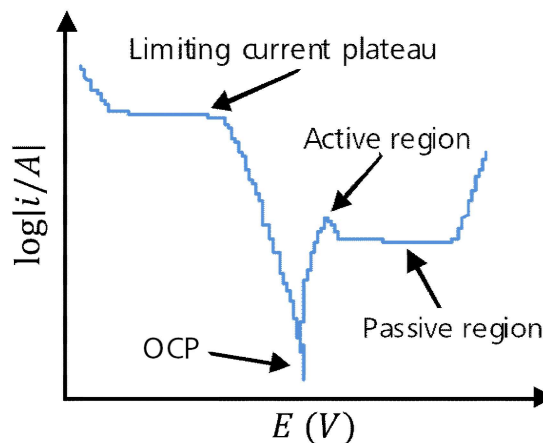


Figure 4 – Different regions in the polarization curve

In this case, EIS measurements can be performed at 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

Note: care must be taken when doing the experiments at OCP. A typical impedance scan takes around 10 minutes. For certain systems, the OCP can drift during the course of the impedance experiment. If the OCP is measured at start of the impedance scan and the potential bias fixed at that value at the beginning of the scan, then as the experiment progresses, the OCP can change 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 OCP and the potential applied to the working electrode causing in errors. It is desirable that the measurements are done under galvanostatic control at zero current, thus eliminating the problem.

FRA Parameters or Settings

AC Mode - Single sine or Multi sine

Typically measurements are done in the single sine mode. Multi sine (5 or 15) can be used to save time when measuring very low frequencies.

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 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 amplitude. The range for which the impedance is independent of the perturbation amplitude provides the acceptable range of perturbation amplitudes. The largest value in this range can be used to give the highest signal to noise ratio.

Integration time

As the amplitude of the perturbation is decreased the signal to noise ratio becomes poor. To improve the signal to noise ratio 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 increases the signal to noise ratio.

Wait for steady state

During a scan when a new frequency is applied, one needs to wait for some time for the system to stabilize before measurements can start. This can be achieved by skipping the first few cycles.

Frequency range

In theory, one must choose the widest possible frequency range 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 slow response of the reference electrode. Typically, potentiostats can go up to 1 MHz, or higher.

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 are changing with time (e.g., due to corrosion or growth of a film), this implies that the system has changed during the course of the data

collection. Therefore, the low frequency limit should be chosen to ensure minimal change in the system during data collection.

A frequency range of 100 kHz – 0.1 Hz is typically used for most electrochemical systems. The total measurement time for this frequency range is around 10 minutes.

Frequency distribution

The frequency can be distributed over the frequency range linearly, logarithmically, with a square root distribution or with a defined number of points per decade. The most common distribution is 10 points per decade.

Conclusions

In this application note, the most common cell setups are shown, together with an explanation of the main experimental parameters.

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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>.