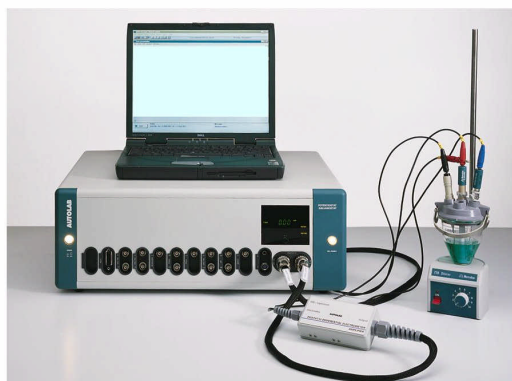


Electrochemical Impedance Spectroscopy (EIS): 2. Experimental Set-up

A typical electrochemical impedance experimental set-up consists of an electrochemical cell (the system under investigation), a potentiostat/galvanostat, and a frequency response analyser (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.

1. 2 electrode cell

A two-electrode configuration for the cell is used when precise control of the potential is not critical. This arrangement is used to investigate electrolyte properties, such as conductivity, or to characterize solid-state systems.

2. 3 electrode cell

A three-electrode configuration for an electrochemical cell is most common for typical electrochemical applications. A third electrode (the reference electrode) is used to determine the potential of the working electrode precisely. 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.

3. 4 electrode cell

A four-electrode cell is used to analyse processes occurring within the electrolyte, between two measuring electrodes separated by a membrane. In this configuration, the working electrode and the counter enable current flow. 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 Experiment Parameters

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

Potentiostat Parameters or Settings

1. Potentiostatic or Galvanostatic Mode

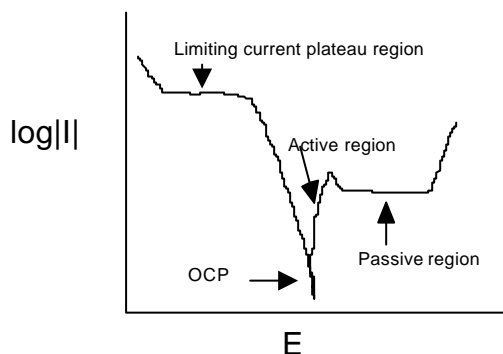
EIS measurements can be done in the potentiostatic or galvanostatic mode. In the potentiostatic mode, experiments are done at a fixed DC potential. A sinusoidal potential perturbation is superimposed on the DC potential and applied to the cell. The resulting current is measured to determine the impedance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

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 to determine the impedance of the system. Typically impedance experiments are done under potentiostatic control. In some cases, e.g. electrodeposition at constant current and battery research, impedance experiments can be performed under galvanostatic control.

2. 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 the following figure a typical current potential curve for a corrosion of iron in passivating solution is shown. EIS measurements, in this case, can be performed at the following bias potentials or currents:

- Open circuit potential (OCP), corrosion potential or zero current
- 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 OCP is measured dynamically at each frequency or the measurements are done under galvanostatic control at zero current, thus eliminating the problem.

FRA Parameters or Settings

1. 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.

2. 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 10mV 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. The largest value in this range can be used to give the highest signal to noise ratio.

3. 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.

4. 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.

5. 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 1MHz.

The measurement time at each frequency 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 1mHz will take 1000s. For systems that are changing with time (e.g. due to corrosion, growth of a film etc.) 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 100kHz – 0.1Hz is typically used for most electrochemical systems. The total measurement time for this frequency range is around 10 mins.

6. Frequency Distribution

The frequency can be distributed over the frequency range linearly, logarithmically or with a square root distribution. The most common distribution is logarithmic distribution.