

Precautions for good impedance measurements

Available instruments

| Instrument | MPG | VMP | VMP2 | BiStat |
|-------------|-----|-----|------|--------|
| Used | | | | |
| Alternative | | | | |

INTRODUCTION

From biological cells analysis to fuel cells tests, from coatings to cement paste quality control, the electrochemical impedance spectroscopy (EIS) has become a powerful tool in the vast environment of electrochemistry. As a non-intrusive and highly sensitive technique, EIS requires basic precautions, often overlooked, to achieve error free data. This document aims to highlight the nature of the error sources placed outside the electrochemical cell and their effects in the study of the electrochemical systems with the EIS technique with an accent on high and low impedance cells. General conditions for accurate measurements related to the sample linearity, causality, time independence and stability are beyond the scope of this note.

During the EIS monitoring, a small amplitude AC voltage or current signal is applied to the cell, over a wide range of frequencies. For each frequency in the range, the measured impedance of the cell is a complex ratio between the cell potential, usually collected between the reference electrode (RE) and the working electrode (WE), and the cell current, measured as a potential drop over a precision resistor in series with the cell. Obviously, any cell property, experimental parameter, electronic device characteristics, external factor or design limitation, which may influence the potential and current measurements, will affect the accuracy of the EIS experiment.

SOURCES OF ERROR

There are three basic sources of error around an electrochemical cell: connecting cables, environmental noise and instrumentation limitations. The major part of problems comes from cable connections often done with long unguarded wires, weak contacts and corroded crocodile clips. Noise is also a common problem in

electrochemistry whenever high impedances samples are involved. Pick-up noise at 50/60Hz is very usual and can be greatly reduced by placing the cell in a Faraday cage. Instrumentation limitations are particularly related to the electrometer input. Voltage measurements, for instance, are susceptible to voltage divider if the reference electrode approaches the electrometer input impedance. While good reference electrodes will not induce any errors at all, a highly resistive reference electrode may lead to a considerable loss of accuracy.

Generally, troubles comes-up with the frequency increase as well for very high as for very low impedance cells. The following sections will focus on specific problems encountered when using these types of cells.

High impedance cells

High impedance cells are prone to errors mainly because of the presence of stray capacitances. A stray capacitance designates the capacitance incidental to the wiring. Do not attempt to associate a stray capacitance to the common electrical device made of a nice dielectric in the middle of a pair of conductors. No, a stray capacitance of a wire for example has one conductor, which is the wire while the other conductor is the rest of the universe and the dielectric holds for very diverse materials.

Through a stray capacitance not only that the cell current can find a different path to the ground but also external noise sources can find a way to perturb the cell.

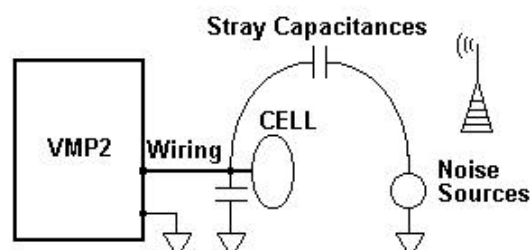


Figure 1 – Stray capacitances are related to wiring

A straightforward method to reduce the influence of the external noise sources is to use an earthed Faraday cage. Since the electrical capacitance of an object depends on the objects in the

neighbourhood, the Faraday cage will increase the stray capacitance to the ground, which may become an important consideration as the frequency increases.

A capacitive reactance decrease as the frequency increase (Equation 1), which leads to an increased current flow outside the cell, thus, it may affect the accuracy of fast signal transitions and high frequency impedance measurements:

$$Z_c = \frac{1}{j\omega C} \quad (1)$$

In slow variation signals or low frequencies conditions, the influence of the stray capacitance is insignificant and can be ignored. Note that a stray capacitance cannot be detected with a simple digital voltmeter.

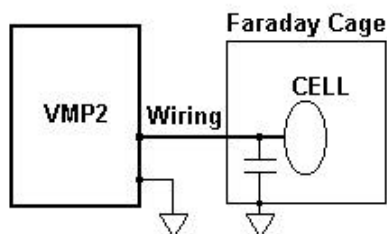


Figure 2 – A Faraday Cage cut-off the noise but increase the stray capacitance to the ground

Is there a way to evaluate the stray capacitance, for a simple interconnecting wire for example? Well, from the electromagnetism laws^[1] we know that a straight cylindrical wire manifest self inductance and capacitance given by the following equations:

$$L = 0.2 \cdot h \cdot \left[\ln \left(\frac{4h}{d} - 0.75 \right) \right] \mu\text{H} \quad (2)$$

$$C = \frac{h}{0.044 \cdot \ln \left(\frac{4h}{d} - 0.75 \right)} \text{ pF} \quad (3)$$

where d and h are the diameter and length of the wire in meters, L the inductance in micro-Henries and C the capacitance in pico-Farads.

A 1mm diameter wire, for example, exhibits about 1.46μH inductance and 3.12pF capacitance per meter. This is what theory says for a single straight wire. In practice, the situation is much more complicated for different reasons: interconnecting wires are placed in the vicinity of other objects grounded or not, leads ends with banana plugs which are not simple straight wires, diameter and length of leads can change to adapt further experimental requirements. For a given interconnection length, we expect the capacitance

to be larger than for a same length straight wire. The best way to estimate the stray capacitance of the experimental set-up is to do an impedance measurement in the air or on a well-known dummy cell which impedance is close to that of the studied electrochemical cell.

An example of the influence of the stray capacitance on impedance measurements is shown in Figure 3. Tests were run on a VMP2 outfitted with a low current option. Counter and reference leads were stick-together (CA1, REF3 and REF2) as well as the working and the sense lead (CA2 with REF1). The VMP2 low current probe was placed in the middle of a 40x20x60cm earthed Faraday cage. Three impedance tests were done in potentiostatic mode from 100kHz to 0.1Hz with 1Vpp amplitude: A – no cell, B – a simple 10cm length 0.5mm diameter wire hanging from the counter and reference, C – same as B but the wire ends with a 4mm banana plug.

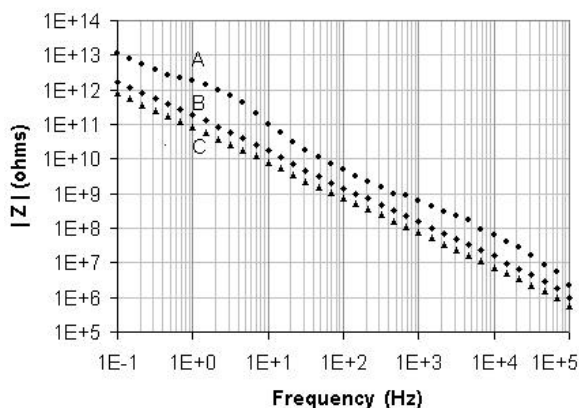


Figure 3 – Impedance data A: no cell, B: 10cm wire, C: 10cm wire + 4mm banana plug

All the plots are consistent with a capacitive behaviour. Analysis software like the ZSimpWin package gives a stray capacitance of 0.12pF for “no cell” data, 0.98pF for the 10cm wire alone and 2.1pF when a banana plug is attached to the wire. If we subtract the “no cell” 0.12pF capacitance, that should corresponds to the electrometer input capacitance, we find 0.86pF for the 10cm wire capacitance that, as expected, is more than the theoretical value because of the grounded metallic objects in the surrounding area. Also by subtraction, we find that the 4mm banana plug adds 1.12pF to the wiring.

What does this mean? These tests simply illustrates that the stray capacitance can affect the accuracy of high impedance samples at high frequencies. For example, for frequencies over 10kHz, the measured impedance of a 10Mohm resistor with 10cm of wiring will correspond to the stray capacitance reactance and not to the value of the resistor.

Low impedance samples

We have seen that the stray capacitance must be considered for high impedance samples at high frequencies. Low impedance samples are not at all concerned by the stray capacitances since the stray capacitance is somehow in parallel to the sample. On the other hand, the stray inductances should be seen in series with the sample and have to be carefully analysed since they are the origin of the most perturbing factors at high frequencies.

Like the stray capacitance, the stray inductance is related to the wiring. Obviously from the equation 2 any piece of wire exhibits inductance. This includes also the physical dimensions of your cell. Typically, impedance measurements carried on cylindrical batteries show an inductive effect at high frequencies. Replacing the battery by a wire of the same length will generally give the same imaginary part values at frequencies over 10kHz.

According to the expression of the inductance impedance, an inductance will oppose more and more to the current flow as the frequency increases:

$$Z_L = j\omega L \quad (4)$$

For instance, a 10cm length and 1mm diameter wire has about 146nH of inductance that at 100kHz results in a 92mΩ of reactance.

An impedance test run with a VMP2 in galvanostatic mode with 200mA amplitude on a 10cm wire is shown in Figure 4. The wire was placed between the reference shorted to the counter (CA2, REF3 and REF2) and the working (CA2 with REF1) leads.

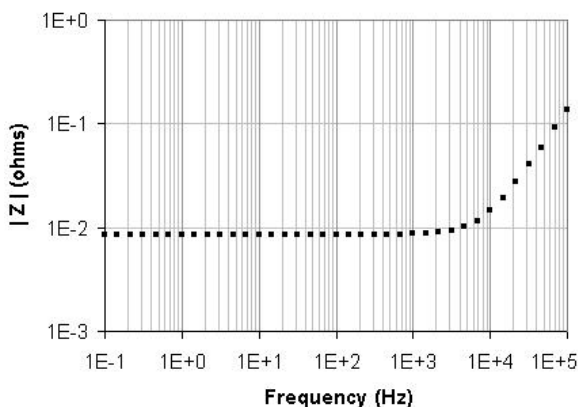


Figure 4 – Impedance data for a straight 10cm wire

The plot confirms an inductive behaviour. The best numerical fit corresponds to a 202nH inductance in series with an 8.5mΩ resistance.

Besides the self-inductance of the wiring, a variable magnetic field can also corrupt EIS measurements taken on low impedance samples.

Basic electromagnetism laws say that every variable current flowing through a wire creates a variable magnetic field around the wire and also that a variable magnetic field induces an electromotive force in a loop (Faraday's law):

$$E_{mf} = - \frac{\Delta B \cdot A}{\Delta t} \quad (5)$$

where ΔB is the magnetic field variation during the Δt time and A is the area of the loop.

The cables connecting the cell to the instrument have two current leads, which drive the cell current and two potential sensing leads through which no (or very small) current flows. The variable cell current flowing through the current leads will create a variable magnetic field that will induce a voltage in the potential sensing leads. This is the magnetic coupling effect that may appear as a fake positive or negative inductance in series with the analysed sample:

$$Z_{meas} = Z_{real} \pm j\omega L \quad (6)$$

The sign depends on the direction of the magnetic field through the loop area (Figure 7).

Several tests have been done to illustrate the magnetic coupling effect. On a VMP2 cable, the current leads (CA1 and CA2) and the voltage sensing leads (REF1 and REF2) have to be shortened together, in pairs, and then brought to a common point, as in Figure 5.

Although the REF3 lead does not have any contribution to the measurement it should be connected either to the ground lead or together with REF1 and REF2 to avoid error messages with the EC-Lab software.

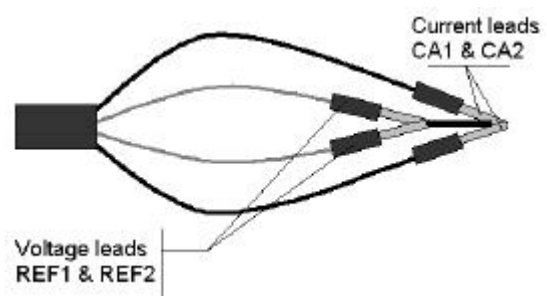


Figure 5 – Magnetic coupling set-up

Measurements have been carried out with a VMP2 in galvanostatic mode with 200mA amplitude from 100kHz to 0.1Hz on the 1A current range. The result of the experiment may look like Figure 6 and 7.

The shapes of these curves show the inductive effect of the magnetic coupling. When the current leads are far from each other and the voltage sensing leads are spaced out, in other words when the induced loop area is maximised, the coupling effect is amplified (not twisted cables curves in Figure 6). The numerical fit for a LR series model gives: 145nH for the inductance and

50 $\mu\Omega$ for the resistance. The magnetic coupling induces a constant positive or negative 90° phase shift at high frequencies. As stated above the sign of the phase shift depends on the direction of the magnetically induced current.

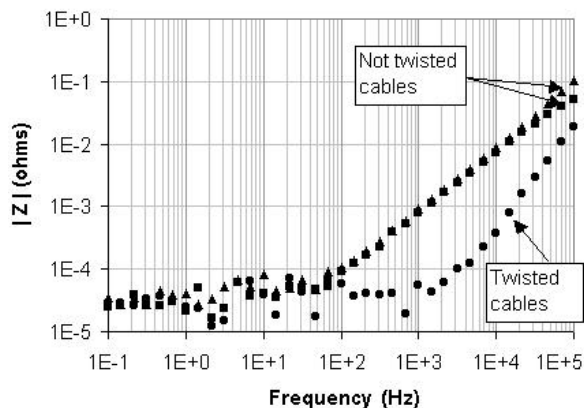


Figure 6 – Magnitude spectra of the magnetic coupling

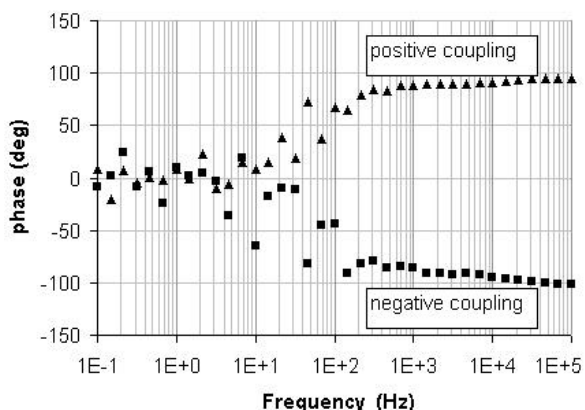


Figure 7 – Phase spectra of the magnetic coupling

Reducing both the magnetic field by twisting together the current leads (CA1 and CA2) and the induced loop area by twisting together the sense leads (REF1, REF2 and REF3) helps to minimise the magnetic coupling (twisted cables curve in Figure 6). The magnetic coupling that can be seen even with twisted cables should be some residual coupling equivalent to a series inductance of about 25nH.

Note as well that external variable magnetic fields can induce voltages in the sense leads. Voltage can also be induced by a static magnetic field if the cell connection vibrates or simply moves.

SUMMARY

Generally, impedance data can easily be misinterpreted for low or high impedance cells at high frequencies. To improve the measurements accuracy special care must be taken as for the cell design, connections and cell environment. High impedance cells are more sensitive to the stray capacitance while low impedance cells are more sensitive to the stray inductance. Placing the cell inside a large and earthed Faraday cage can reduce the stray capacitance. Wiring should be kept as short and small as possible to reduce both the stray capacitance and the stray inductance. The magnetic coupling effect can be reduced by reducing both the magnetic field (by twisting the current leads) and the induced loop (by twisting the sense leads).

For the largest part of applications, these errors are not very important. However, a perfect understanding of the measurement limitations is the key for a correct interpretation of the results. When making precise measurements close to limit conditions one should be aware of sources that contribute to the measurements errors. The remaining source of errors should be added to the measurement uncertainty.

Although this document focuses on common sources of errors in the impedance measurements, there is no reason to not consider them for other electrochemical techniques. Simply EIS is a technique that "exhibits" all the imperfections of the measurement set-up very often accentuated by the desire to go higher and higher in frequency.

REFERENCE:

[1] F. W. Grover, Inductance Calculations. Princeton, NJ: Van Nostrand, 1946