# Equivalent model of an electrochemical cell including the reference electrode impedance and the potentiostat parasitics

## I – EIS BASICS

### I - 1 INTRODUCTION

As a non-intrusive and highly sensitive technique, the Electrochemical Impedance Spectroscopy (EIS) requires basic precautions, often overlooked, or ignored, to obtain reliable results. High impedance cells are more sensitive to capacitive artifacts while the low impedance cells are more sensitive to inductive and resistive artifacts. Artifacts are even more important as the frequency of analysis now tends to cross the megahertz boundary. Ignoring these artifacts can lead to misinterpretation of the results. In this note we focus on the influence of stray capacitances introduced by the instrumentation. We also show that the strange results data obtained with a poor reference electrode can be perfectly explained by a complete model of the cell that includes the instrument artifacts.

### I - 2 AN ANALYSIS DILEMMA

The impedance measurement results are analyzed and compared to the simulated data generated from mathematical or electrical models. Model parameters are obtained from a data fitting process. Important differences between the measured and the simulated data can have two causes: either a wrong or incomplete model or an experimental artifact (Fig. 1).

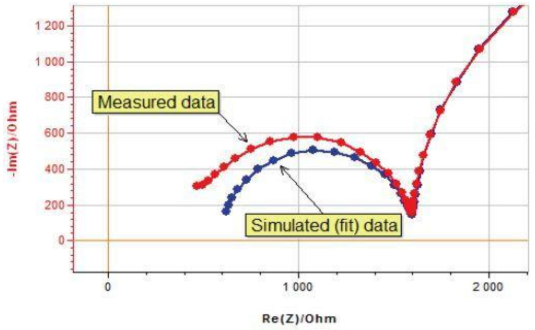
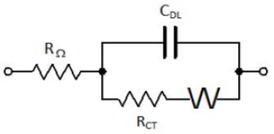
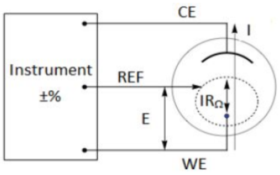


**Figure 1 : Analysis dilemma, measured and simulated data do not match.**

How to identify the origin of this difference. Is this a modeling problem or a measurement problem? Solving this analysis dilemma requires you to be aware of the possible measurement artifacts.

Important differences exist between the true, effective, and measured value of an electrochemical impedance. In Tab. I, the true value is the impedance of a basic redox reaction with a semi-infinite diffusion condition. The equivalent electrical model consists of a charge transfer resistance ($R_{CT}$) in series with a Warburg diffusional element (W). Generally, the true value is the value of interest but it does not take into account the parasitics.

**Table I: True, effective and measured values.**

| | |
|---|---|
| True value:<br>$Z_F = R_{CT} + \dfrac{\sigma}{\sqrt{j\,\omega}}$ |  |
| Effective value:<br>$Z_E = R_\Omega + \dfrac{Z_F}{1 + j\,\omega Z_F C_{DL}}$ |  |
| Measured value:<br>$Z_M = \dfrac{E}{I}$ |  |

The effective value adds to the true value the elements that cannot be avoided in a measurement. In our example these elements are the double layer capacitance ($C_{DL}$) and the ohmic drop due to the solution resistance ($R_\Omega$) related to the electrochemical cell.

The measured or indicated value is the value the instrument displays, hence it reflects its inherent imprecision. A different instrument will show different values. A second

measurement will not give the exact same values.
If the quality of the instrument needs to be checked, a dummy cell with a known impedance should be used. Nonetheless, checking the measurement quality of the instrument with a dummy cell is not good enough.

In typical DC or slow electrochemical measurements with a potentiostat the reference electrode provides a stable voltage reference for the working electrode. However, a reference electrode with a non-zero impedance in combination with the potentiostat finite input impedance may play an important role on fast potential scan experiments or high frequencies impedance measurements.
One can either include the reference electrode and potentiostat input impedance in the effective value or, better, keep them insignificant.

## II – INSTRUMENTATION PARASITICS

### II - 1 MEASUREMENT METHOD

The measurement principle diagram of the BioLogic SP-200 potentiostat and impedance analyser is shown in Fig. 2. A sinusoidal signal is generated and applied to the cell over a wide range of frequencies. The working electrode voltage versus the reference is measured by the voltmeter $V_2$. The current is calculated using the voltage $V_1$ measured across the precision resistor $R_m$.

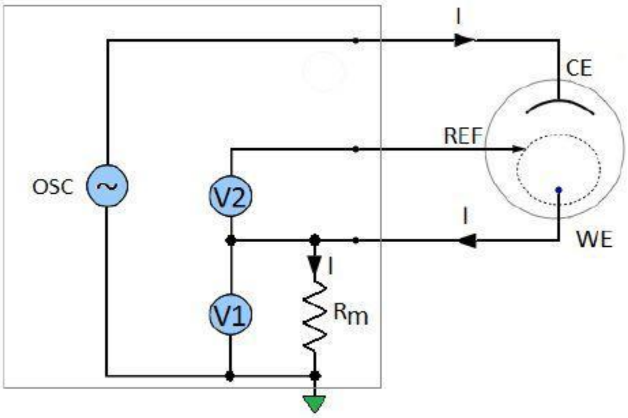


**Figure 2: Measurement principle diagram of the Biologic SP-200 potentiostat and impedance analyser.**

The unknown impedance of the working electrode is calculated from the measured voltage and current values (Fig. 2):

$$Z_{\mathrm{M}} = \frac{V_2}{I} = \frac{V_2}{V_1} R_m \qquad (1)$$

### II - 2 POTENTIOSTAT STRAY CAPACITANCES

An instrument is made of real, hence imperfect components. At high frequencies, most of the artifacts comes from the input stray capacitances. A model of the instrument is shown in Fig. 3 which includes the four stray capacitances between the counter and the reference electrodes, the reference electrode and the ground, the reference and the working electrodes, and the working electrode and the ground.

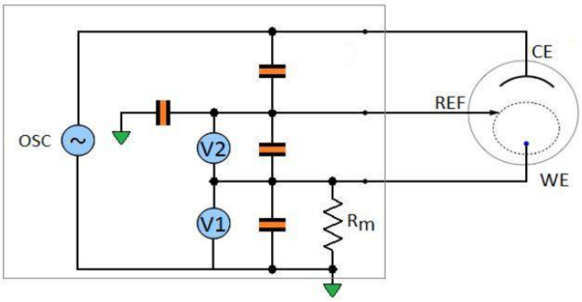


**Figure 3: Model of the potentiostat including the four main stray capacitances.**

The influence of the stray capacitances of the reference to the working and of the working to the ground are cancelled by the calibration of the instrument at the factory. To calibrate the instrument, standard devices are connected at the terminals of the standard cable and the instrument is adjusted (through computation/data storage) so that it measures within the specified accuracy.

### II - 3 EIS ACCURACY PLOT

In Fig. 4 the shaded areas shows different ranges of impedances that can be measured within a specified error in magnitude and in phase. Residual stray capacitances and stray inductances limit the high frequency accuracy on high impedance cells and the low impedance cells respectively. However, this accuracy plot shows the best accuracy one can have with standard devices. The electrochemical cell and its environment make the real accuracy not as good as the one in this plot. It is important then to understand the origin of the artifacts and to try to minimize them.

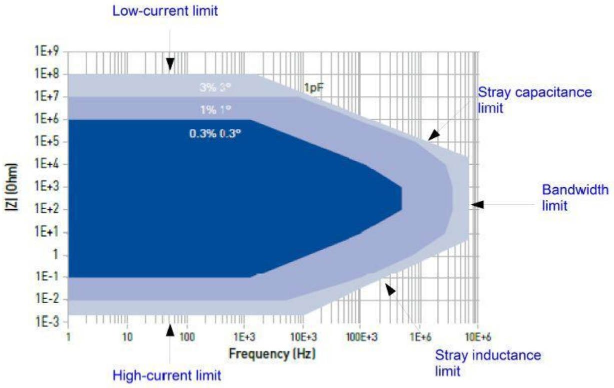


**Figure 4: SP-200 contour plot.**

## II - 4 EIS ON AN ELECTRICAL CIRCUIT

For the sake of simplicity an electrical circuit in the middle range of the potentiostat impedance accuracy plot (dark blue area) has been chosen.

As expected, the impedance measurement performed with the SP-200 in the high frequency range from 7 MHz to 1 kHz corresponds to the effective impedance of the cell (Fig. 6).

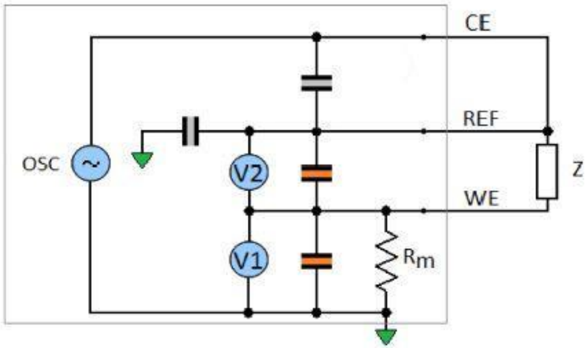


**Figure 5: Equivalent model of the potentiostat with simplified artifacts.**

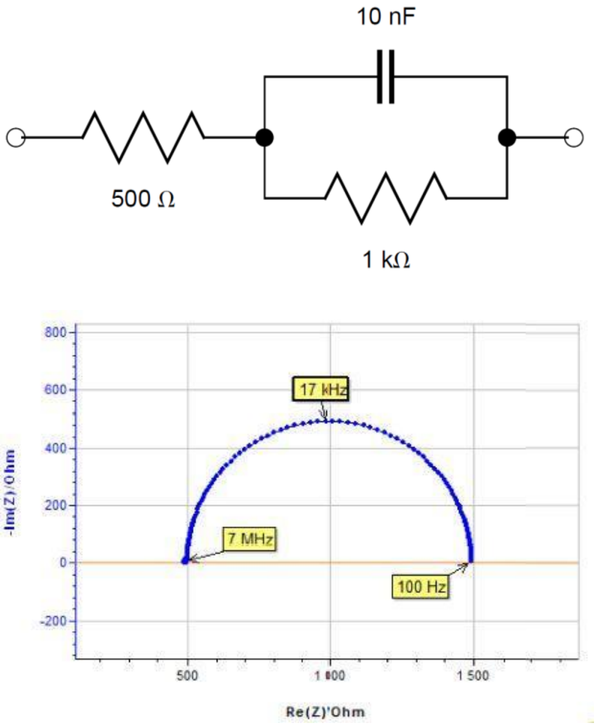


**Figure 6: Top) Electrical circuit in the middle range of the potentiostat impedance accuracy plot; Bottom) corresponding Nyquist impedance diagram.**

The same experiment is now performed with a 10 kΩ resistor mimicking a poor reference electrode (Fig. 7).

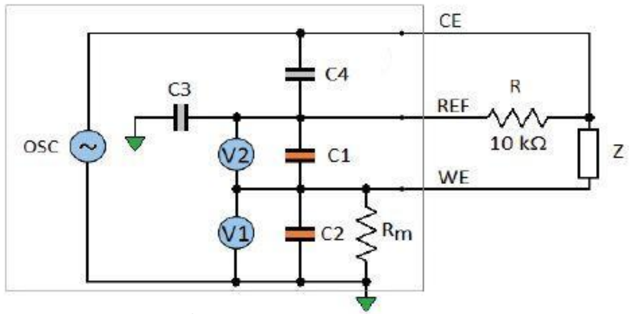


**Figure 7: Model of the potentiostat with an additional resistor mimicking a poor reference electrode.**

The measured impedance (Figs. 6 bottom and 8), represented in red in the Nyquist diagram is far from the previous measurement in blue. The equivalent measured impedance can be obtained from the Kirchhoff's laws:

$$Z_{\mathrm{M}} = \frac{Z(1 + j\omega R_m C_2)(1 + j\omega R C_4) - j\omega R R_m C_3}{1 + j\omega R(C_1 + C_3 + C_4) + j\omega R_m\big(C_2 + j\omega R C_1 C_3 + j\omega R C_2(C_1 + C_3 + C_4)\big)} \quad (2)$$

It can be noted that if *R* is zero, the measured impedance $Z_{\mathrm{M}}$ equals the effective impedance *Z* given by (Fig. 6):

$$Z = r_1 + \frac{r_2}{1 + j\omega r_2 c_2} \quad (3)$$

With $r_1$=500 Ω, $r_2$=1 kΩ and $c_2$=10 nF.

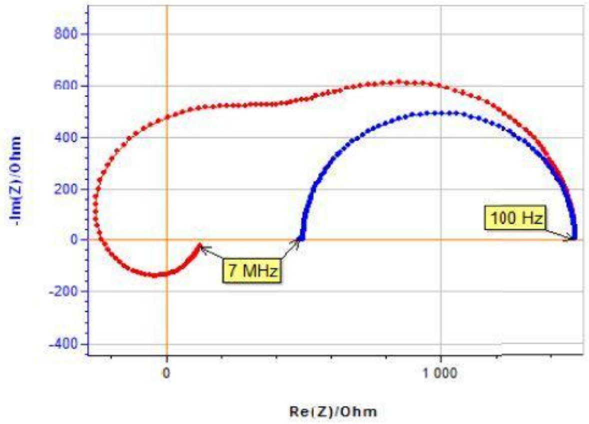


**Figure 8: Measured impedance with poor reference electrode (red dots) and expected impedance diagram shown in Fig. 6 (blue dots).**

## II - 5 FOCUS ON REFERENCE ELECTRODE

### *a. Model Fit*

The Mathematica software was used to fit the measured data with the equation of $Z_{\mathrm{M}}$ (Eq. 2). The plot obtained using the fit parameters (r1 = 500 Ω, r2 = 1.00 kΩ, c2 = 9.99 nF, R = 10.0 kΩ, C4 = 17.8 pF, Rm = 1.00 kΩ, C1 = 8.56 pF, C2 = 0.344 nF, C3 = 52.0 pF), match well the experimental data (Fig. 9). Also, the fit values of stray capacitances of the instrument are in good agreement with the expected values. Thus, we can say that the potentiostat model with artifacts we have proposed is most likely to be the correct one.

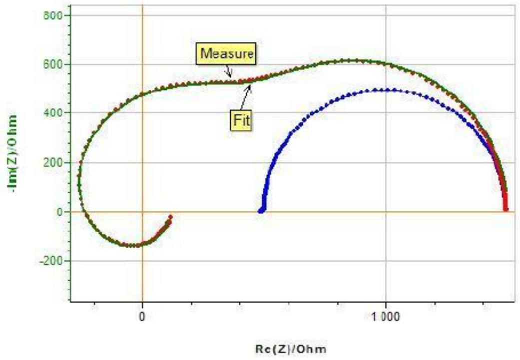


**Figure 9: Measured impedance with poor reference electrode (red dots), impedance diagram shown in Fig. 6 (blue dots) and fitted curve (green curve).**

Generally, a platinum wire and a parallel bypass capacitor should be added to the reference electrode to overcome the EIS high frequency artifacts. BioLogic provides a special EIS R-XR820 reference electrode model which includes a bypass 10 nF capacitor. This capacitor makes the reference electrode continue to provide a constant voltage reference while its impedance (reactance) decreases as the frequency increases. Why 10 nF ? The value of this capacitor could be higher but it would not change very much as 1 MHz impedance of a 10 nF capacitor is only 16 Ω. Figure 10 shows the change of $Z_{\mathrm{M}}$ with the C4 value. For the sake of simplicity we considered C4 as a reference bypass capacitor. Note that $Z_{\mathrm{M}}$ for C4 = 10 nF.

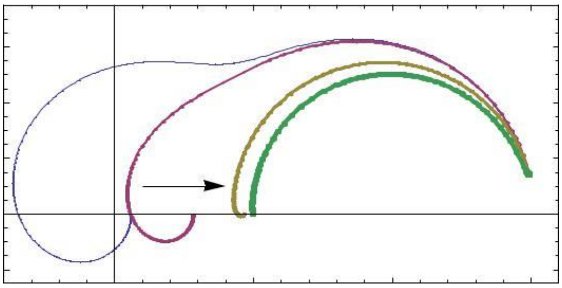


**Figure 10: Change of Nyquist diagram of Zm with C4 value. C4/nF = 0:01; 0:1; 1; 10, from left to right.**

### b. *Complex electrochemist's life*

The impedance spectrum (Fig. 11) of a glassy carbon electrode in a ferrocene solution was measured with a R-XR300 Ag/AgCl reference electrode fitted with a bridge tube. An unadvised user could even find a good fit with a non-realistic equivalent electric circuit.

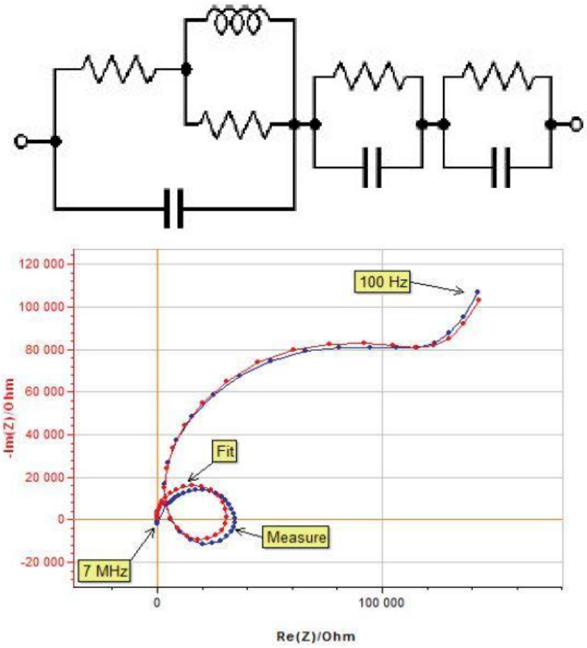


**Figure 11: Impedance spectrum of a glassy carbon electrode in a ferrocene solution with a poor reference electrode and fit of the data using the circuit model.**

The same experiment was carried out with the R-XR820 AC bypass reference electrode. The two plots move away from each other at relatively low frequency (Fig. 12).

## III – CONCLUSION

Reducing the reference electrode impedance can be a straightforward method to minimize instrumentation artifacts coming from the reference electrode. As a general precaution, a special care must be taken with the reference electrode to have accurate impedance measurements at high frequencies.

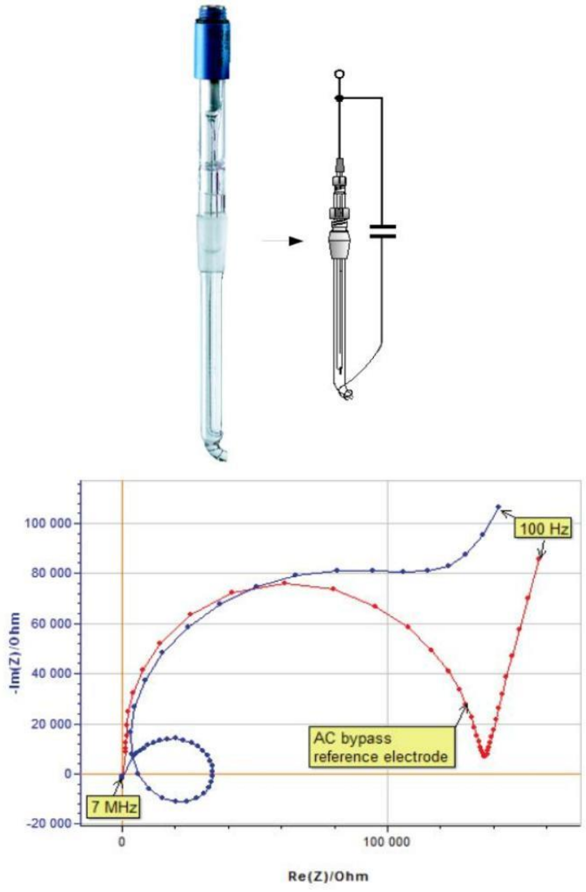


**Figure 12: Impedance spectra of a glassy carbon electrode with and without an AC bypass reference electrode (R-XR820).**

## REFERENCES

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