Linear *vs*. non-linear systems in impedance measurements

I – INTRODUCTION

Electrochemical Impedance Spectroscopy (EIS) is an interesting tool devoted to the study of linear systems. However, electrochemical systems are often non-linear. Before explaining the different ways of dealing with this issue, we will point out the main differences between linear and non-linear systems. These differences of behavior are shown in Table I. The impedance measurement was performed using the potentiostatic mode. The potential is defined by:

$$E(t) = E_{WE} + V_a \sin(2\pi ft) \qquad (1)$$

where E_{WE} is the stationary potential for the impedance measurement, V_a is the potential amplitude of the sine signal, f is the frequency, and t is the time.

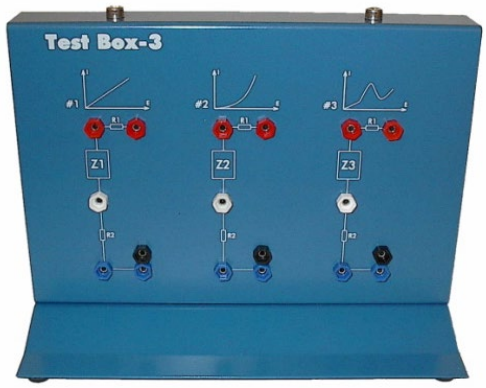
Table I: Differences between linear and non-linear systems.

	Linear system	**Non-linear system**
Steady-state *I vs.* E_{WE} curve	Straight line $I = f(E_{WE})$	$I = f(E_{WE})$
Impedance *vs.* E_{WE}	Invariant with E_{WE}	Variant with E_{WE}: $Z(E_{WE})$
Impedance *vs.* V_a	Invariant with V_a for all V_a values	Invariant with V_a only for low V_a values

Three test circuits have been designed in order to highlight the differences in behavior between linear and non-linear systems.

II – TEST BOX-3

The experiments described on this paper were performed with a test box specifically designed to teach users how to achieve impedance measurements on linear and non-linear electrochemical systems.



There are three different electrical circuits inside the test box simulating real electrochemical systems. With Test Box-3, it is possible to study general electrochemistry protocols like Cyclic Voltammetry or corrosion protocols such as Linear Polarization and Generalized Corrosion.

III – TEST CIRCUIT #1

Figure 1 shows the electrical circuit of the test circuit #1, the corresponding steady-state curve (I *vs.* E_{WE}), and the Nyquist diagram of the impedance measured at points **a** and **b** of the steady-state curve. The impedance diagrams do not depend on the steady-state potential E_{WE} or on the amplitude V_a. The Nyquist impedance diagram displays two semi-circles. Only one impedance measurement is needed to characterize the equivalent test circuit #1. It is a worthwhile exercise to determine the different frequencies characterizing circuit test #1 and compare them with the experimental values shown on the impedance diagram of Fig. 3.

Impedance is measured at steady-state points a and b (Fig. 2, Fig. 3). The arrow indicates increasing frequencies. R_0 = 501 Ω, R_1 = 1 kΩ, R_2 = 3.56 kΩ, C_1 = 10 nF, C_2 = 2.3 µF.

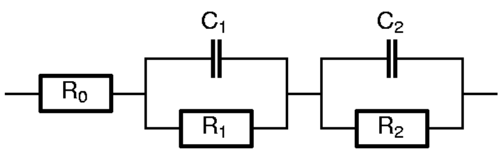


Figure 1: Test circuit #1.

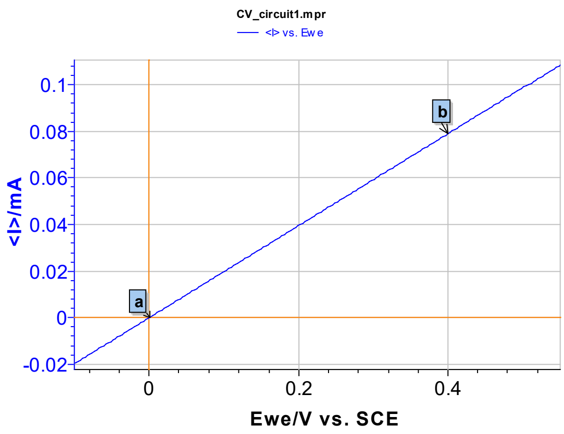


Figure 2: *I vs. E*$_{WE}$ steady-state curve.

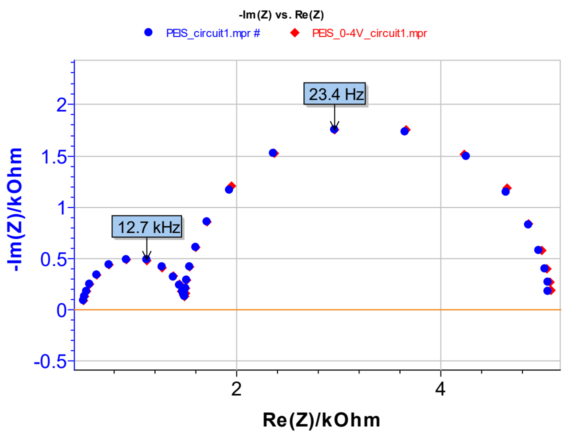


Figure 3: Nyquist diagram for the impedance.

Values of the various parameters of circuit #1 are obtained using ZFit, available in EC-Lab® and EC-Lab Express software. The result of the fit is given in Figure 4 .

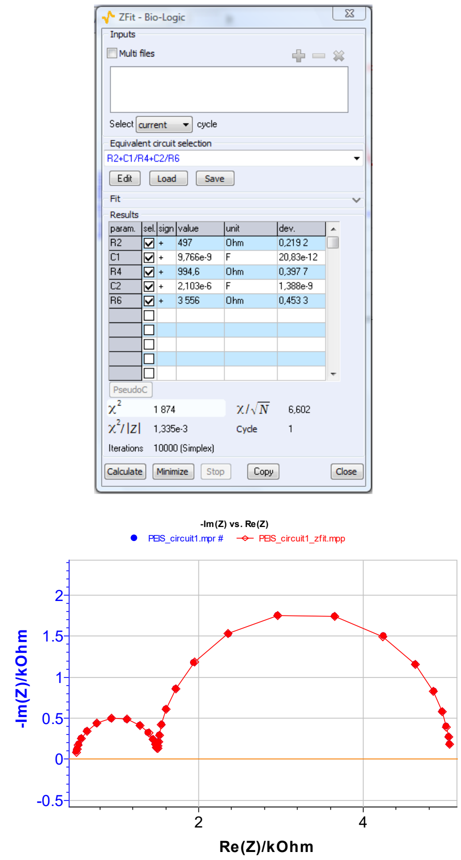


Figure 4: ZFit result on circuit #1 of Test Box-3.

To verify these results with test circuit #1, you can perform the following experiments:

1) Plot the steady-state *I vs. E*$_{WE}$ curve using cyclic voltammetry technique (in EC-Lab® software, load the CV_circuit1.mps file, accept, and run the experiment).

2) Select the PEIS technique. Apply a constant potential E_{WE} = 0 V and perform an impedance measurement from f_i = 200 kHz to f_f = 1 Hz frequency with a low amplitude V_a = 10 mV (it is also possible to load the PEIS_circuit1.mps file).

3) In the PEIS technique, apply a constant potential E_{WE} = 0.4 V and perform an impedance measurement from f_i = 200 kHz to f_f = 1 Hz frequency with a low amplitude V_a = **10** mV (it is also possible to load the PEIS_0-4V_circuit1.mps file).

4) In the PEIS technique, apply a constant potential E_{WE} = 0.4 V and perform an impedance measurement from f_i = 200 kHz to f_f = 1 Hz frequency with a high amplitude V_a = **100** mV (it is

also possible to load the PEIS_ampl100mV_circuit1.mps file).

5) Overlay the three impedance measurement curves in the Nyquist plot mode.

As test circuit #1 is a linear system, the three impedance diagrams should be identical.

IV – TEST CIRCUIT #2

Test circuit #2 is made mainly of two semi-conductor diodes. This is a model for exponential non-linearity. Test circuit #2 results from a circuit studied in [1].

The *I vs.* E_{WE} steady-state curve is not a straight line for test circuit #2. Therefore the test circuit #2 is a non-linear circuit. The impedance of this circuit depends on the steady-state value of the working electrode potential E_{WE} and on the amplitude V_a.

The Nyquist diagram of the impedance measurement performed on test circuit #2 is a semi-circle whose diameter changes along with the electrode potential E_{WE}. (Fig. 6). The impedance of a non-linear system is potential dependent.

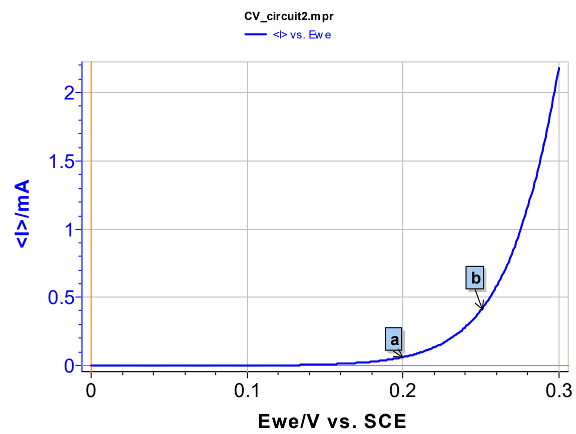


Figure 5: *I vs.* E_{WE} steady-state curve.

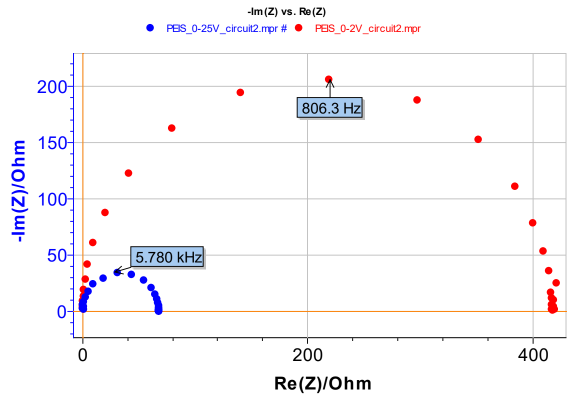


Figure 6: Nyquist diagram for the impedance measured at point a and b. Arrows indicate increasing frequencies.

Figure 8 shows the impedance change versus the amplitude V_a for a given E_{we} value. We can clearly see that the semi-circle diameter decreases when V_a values increase. The impedance does not depend on the amplitude of the excitation signal for low values of amplitude (Fig. 8). In that case, this system's behavior is similar to that of a linear system.
Therefore, one impedance measurement is not sufficient to characterize a non-linear system. It can be a good exercise to try and find an equivalent electrical circuit for test circuit #2. The user can also determine the electrical components' values when its behavior can be compared to one of a linear system.

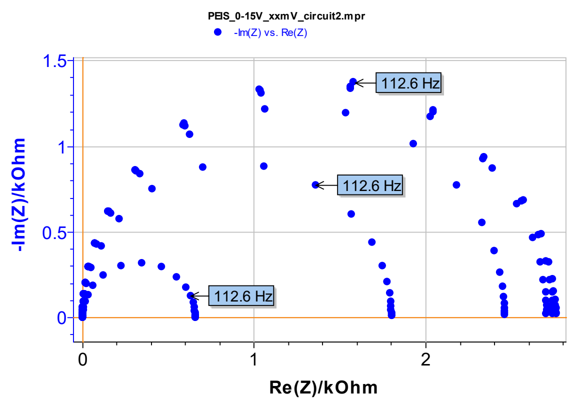


Figure 7: Nyquist impedance diagram measured for different values of potential (E_{WE} = 0.15 V).

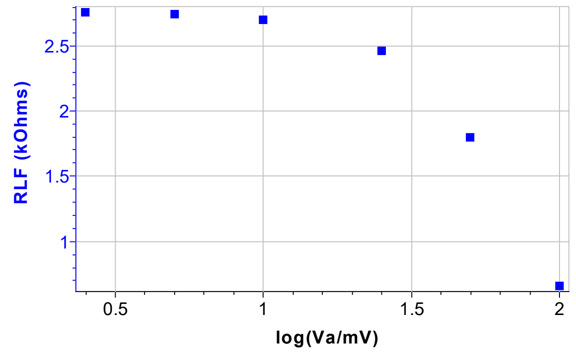


Figure 8: diagram displaying the in-phase impedance (evaluated for a limiting value in low frequencies) versus log(V_a).

It is possible to verify these results with test circuit #2:

1) Plot the steady-state *I vs.* E_{WE} curve using cyclic voltammetry technique (in EC-Lab® software, load the CV_circuit2.mps file, accept, and run the experiment).

2) Select PEIS technique. Apply a constant potential $E_{WE} = 0.2$ V and perform an impedance measurement from frequency $f_i = 200$ kHz to $f_f = 1$ Hz with an amplitude $V_a = 1$ mV (it is also possible to load the PEIS_0-2V_circuit2.mps file).

3) In the PEIS technique, apply a constant potential $E_{WE} = 0.25$ V and perform an impedance measurement from frequency $f_i = 200$ kHz to $f_f = 1$ Hz with an amplitude $V_a = 1$ mV (it is also possible to load the PEIS_0-25V_circuit2.mps file).

4) In the PEIS technique, apply a constant potential $E_{WE} = 0.15$ V and perform several impedance measurements from frequency $f_i = 200$ kHz to $f_f = 1$ Hz with an amplitude V_a/mV= 2.5, 5, 10, 25, 50, 100 (it is also possible to load the PEIS_0-15V_xxmV_circuit2.mps files for the different values of V_{pp}).

V – TEST CIRCUIT #3

Test circuit #3 mainly consists of two transistors. It is a model for metal passivation which has been extracted from [2]. This circuit has also been studied in [1-4].

The shape of the impedance diagram evolves along with the electrode potential E_{WE} as it can be observed in Figs. 9, 10 and 11. Let us consider the steady-state *I vs.* E_{WE} curve showing a peak (as in the case of metal passivation, Fig. 9). For low frequencies, the in-phase impedance is negative. Therefore, a part of the impedance diagram is on the left side of the complex plot, *i.e.* *Re*(Z(w)) < 0.

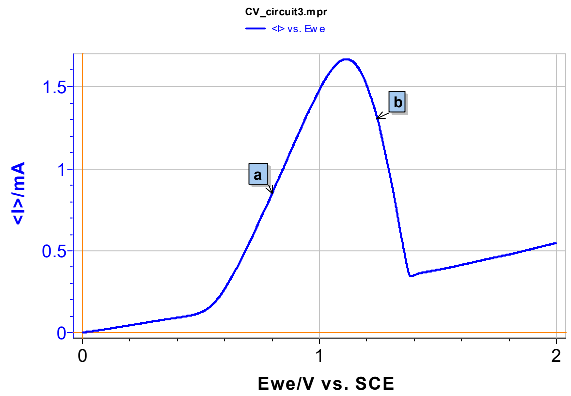


Figure 9: *I vs.* E_{WE} steady-state curve.

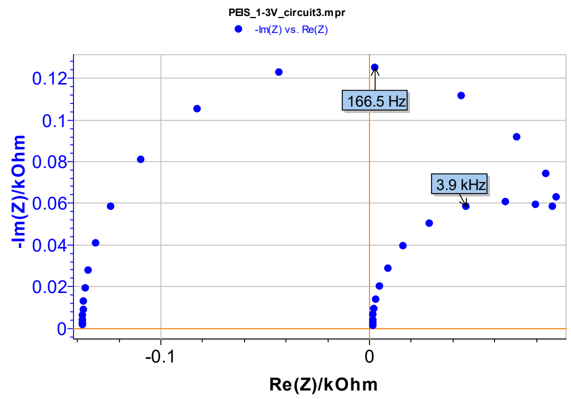


Figure 10: Nyquist diagram for the impedance which has been measured at point b. The arrow indicates increasing frequencies.

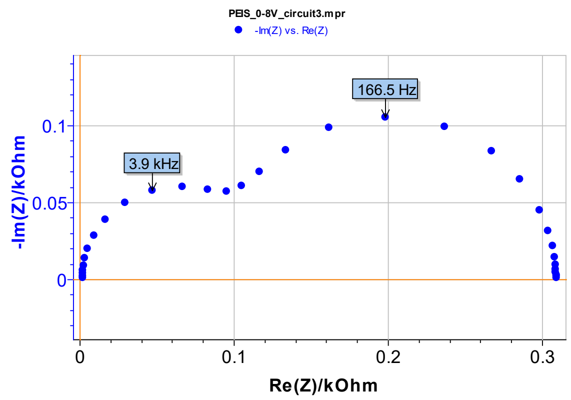


Figure 11: Nyquist diagram for the impedance which has been measured at point a. The arrow indicates increasing frequencies.

It is possible to verify these results with test circuit #3 by performing the following experiments:

1) Plot the steady-state *I vs.* E_{WE} curve using cyclic voltammetry technique (in EC-Lab® software, load the CV_circuit3.mps file, accept, and run the experiment).

2) To plot diagram **a** on Fig. 11: select the PEIS technique and apply a constant potential E_{WE} = 0.8 V and perform an impedance measurement from frequency f_i = 200 kHz to f_f = 1 Hz with an amplitude V_a = 10 mV (it is also possible to load the PEIS_0-8V_circuit3.mps file).

3) To plot the **b** diagram (Fig. 10): in the PEIS technique apply a constant potential E_{WE} = 1.3 V and perform an impedance measurement from frequency f_i = 200 kHz to f_f = 1 Hz with an amplitude V_a = 10 mV (it is also possible to load the PEIS_1-3V_circuit3.mps file).

VI – CONCLUSION

Linear systems are simpler to study. Only one impedance measurement is sufficient to characterize their behavior.

On the other hand, dealing with non-linear systems can become complicated. Several impedance measurements are necessary to characterize their behavior. In order to study a non-linear system with impedance measurement by assimilating its behavior with a linear system behavior, it is necessary to use a low modulation amplitude, V_a.

Data files can be found in :
C:\Users\xxx\Documents\EC-Lab\Data\Samples\Corrosion\Application Note 09

REFERENCES

1) J.-P. Diard, B. Le Gorrec, and C. Montella, J. Electroanal. Chem., 432 (1997) 27.
2) K. Mahadevan, and Y. Gopala, *Electronic Engineering*, (1973) 20.
3) J.-P. Diard, and B. Le Gorrec, J. Electroanal. Chem. 103 (1979) 363.
4) J.-P. Diard, P. Landaud, B. Le Gorrec, and C. Montella, Electroanal. Chem., (2003) 1.

Exercise answers:

- circuit test #1: the characteristic frequency, *i.e.* the frequency at the top of the semi-circle of an RC circuit, is given by

$$f_c = \frac{1}{2\pi RC}$$

The two characteristic frequencies for circuit test #1 are:

$$f_{c1} = \frac{1}{2\pi \times 10^3 \times 10^{-8}} \approx 16 \text{ kHz}$$

$$f_{c2} = \frac{1}{2\pi \times 3.57 \times 10^3 \times 2.2 \times 10^{-6}} \approx 20 \text{ Hz}$$

These values are close to the frequency values given at the top of the semi-circles present on Fig. 3.

- Circuit test #2: the impedance diagram represents a semi-circle. The equivalent electrical circuit can be assimilated to an RC circuit. It is possible to determine the circuit resistance values on the *Im*(Z) *vs. Re*(Z) plot. They correspond to the in-phase impedance for the lowest frequencies (-*Im*(Z) ≈ 0). *R* value varies with E_{we}.

For point **a** of the steady-state curve, we find: R_a = 420 Ω

and for point **b**: R_b = 70 Ω.

With the resistance values determined above, the user can determine the capacitance using the following equation:

$$C = \frac{1}{2\pi f_c R}$$

where f_c is the frequency at the top of the semi-circle. The results should be similar for R_a and R_b. We find *C*~490 nF.

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