Interpretation problems of impedance measurements made on time variant systems

I – INTRODUCTION

Application note #9 [1] deals with impedance measurements performed on linear (and non-linear) time-invariant sys-tems. Electrochemical systems like a battery in operation or a corroding electrode are rarely time-invariant. Impedance graphs obtained on time-variant systems can often mislead to incorrect interpretation and analysis when using equivalent electrical circuit. This application note describes two examples of such misleading interpretations using a commonly used electrical equivalent circuit with a variable resistor.

II – IMPEDANCE DIAGRAM FOR TIME-VARIANT SYSTEM

II - 1 R1+R2(*t*)/C2 CIRCUIT WITH INCREASING R2

The time evolution of systems, such as operating batteries or corroding electrodes, is not known *a priori* and hence cannot be predicted.

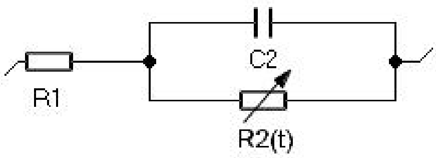

Figure 1: R1+R2(*t*)/C2 circuit.

Let us consider the R1+R2(t)/C2 circuit [2] (ZFit was used to graphically code the circuit) shown in Fig. 1 and assume that the resistance *R*2 increases with time according to the following relationship

$$R2(t) = R2_0 + kt^2 \quad (1)$$

The impedance was calculated for a measurement carried out with one period of sinusoidal signal. The impedance is calculated at the frequency f_n using the *R*2 resistance value at time *t* given by

$$t(f_n) = \sum_{i=1}^{n} t(f_i) = \sum_{i=1}^{n} \frac{1}{f_i} \quad (2)$$

where $t(f_i)$ is the duration of the measurement of one point on the diagram, i.e. the inverse of the measurement frequency [3].

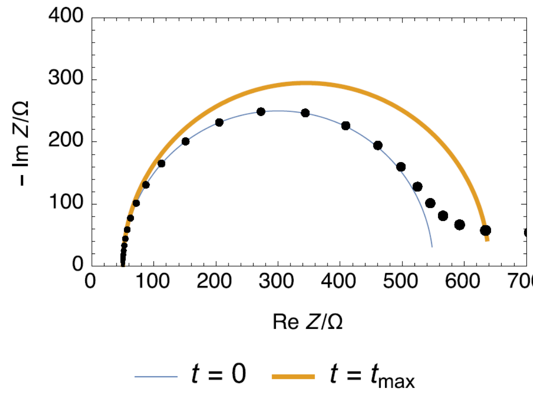

Figure 2: Instantaneous Nyquist impedance diagrams (*t* = 0 and *t* = *t*max) of the circuit R1+R2(t)/C2 (*R*1 = 50 Ω, *R*2$_0$ = 500 Ω, *k* = 10^{-5} Ω s^{-2}, *C*2 = 2.10^{-2} F) and simulation of the measured diagram (•). The dot size increases with increasing time.

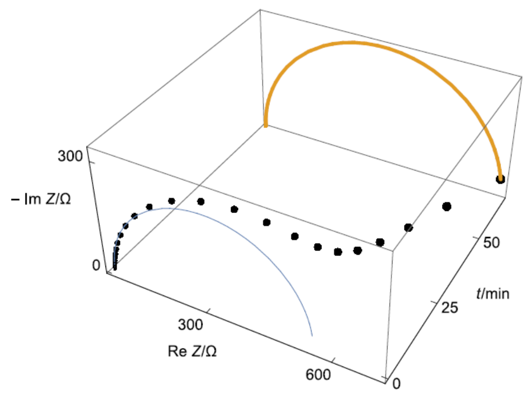

Figure 3: 3D representation of Fig. 2.

The frequency sweep is performed from f_{max} ! f_{min} with f_{max} = 10 Hz and f_{min} = 10^{-3} Hz. All frequencies are logarithmically distributed over 8 points per decade. The parameters used for *R*1, *R*2 and *C*2 are described in the caption of Fig. 2.

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The simulated impedance diagram in Figs. 2 and 3 show the beginning of a low frequency arc. The impedance of the circuit described in Fig. 4 can show a time-invariant Nyquist graph similar to the time-variant Nyquist graph of the circuit shown in Fig. 1.

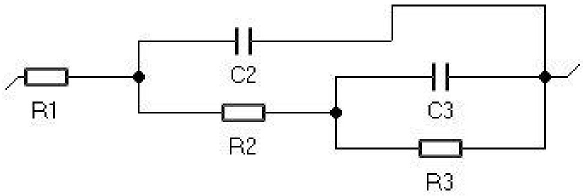

Figure 4: R1+C2/(R2+C3/R3) circuit.

Both graphs are compared in Fig. 5. This shows that a user unaware of the time-variance of the system can mistakenly try to fit the data with a more complicated equivalent circuit than the one required.

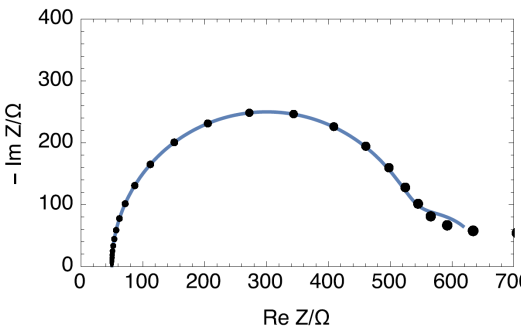

Figure 5: Nyquist impedance diagram of the time-variant circuit R1+R2(t)/C2 (•) and Nyquist impedance diagram of the time-invariant circuit R1+C2/(R2+C3/R3), with *R1* = 50 Ω, *R2* = 500 Ω, *C2* = 10^{2} F, *R3* = 100 Ω, *C3* = 1 F.

II - 2 R1+R2(*t*)/C2 CIRCUIT WITH DECREASING R2

A second case of variation of the resistance R2 is shown in Fig. 6. The value of resistor R2 is henceforth supposed to decrease with time according to

$$R2(t) = R20 - k'\sqrt{t} \quad (3)$$

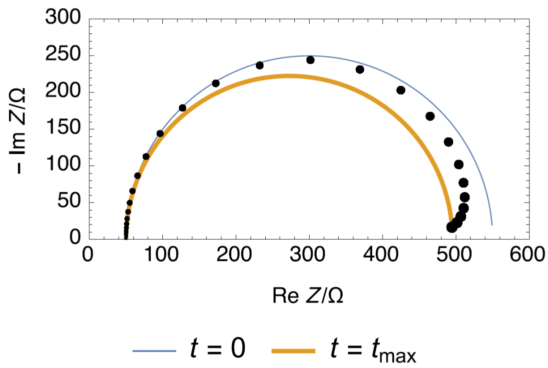

Figure 6: Instantaneous Nyquist impedance diagrams (*t* = 0 and *t* = t_{max}) of the circuit time-variant R1+R2(t)/C2 and simulation of the measured diagram (•).

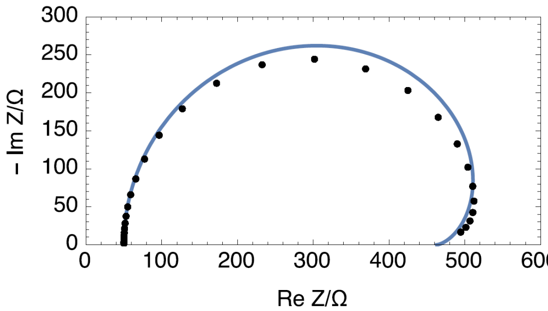

Figure 7: Nyquist impedance diagram of the time-variant circuit R1+R2(t)/C2 (•) and Nyquist impedance diagram of the time-invariant circuit R1+C2/(R2+C3/R3), with *R1* = 50 Ω, *R2* = 534.375 Ω, *C2* = $1.1.10^{2}$ F, *R3* = 123.75 Ω, *C3* = 0.125 F.

Remember that it is possible to convert the circuit shown in Fig. 4 with *R3* < 0 and *C3* < 0 to the circuit R1+C2/R2/(R3'+L3) shown in Fig. 8 with *R3* > 0 and *L3* > 0 where [4]

$$R3' = -\frac{R2(R2+R3)}{R3}, L3 = -R2^2 C3 \quad (4)$$

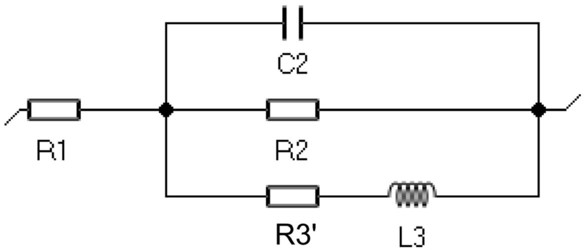

Figure 8: Circuit R1+C2/R2(R3'+L3).

III –STATIONARY SYSTEM CHECK

III - 1 KRAMERS-KRONIG (KK) TRANSFORMS

Calculated impedance ZKK using KK transforms is shown in Fig. 9. Nyquist impedance Z and ZKK diagrams are not similar for all frequencies, therefore impedance measurement has not been carried out for a time invariant system [5].

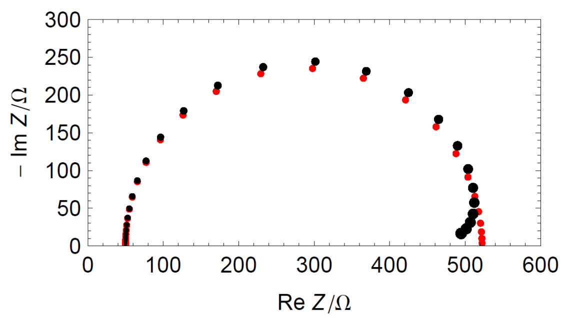

Figure 9: Simulation of the measured Nyquist diagram of the R1+R2(*t*)/C2 circuit (•) and Nyquist impedance diagram obtained using KK transform (•).

III - 2 SUCCESSIVE MEASUREMENTS

A simpler method is to successively perform two identical measurements (Fig. 10). One trick is to successively link two impedance measurements by decreasing frequency $f_{max} \rightarrow f_{min}$ then immediately by increasing frequency $f_{min} \rightarrow f_{max}$ (Fig. 11).

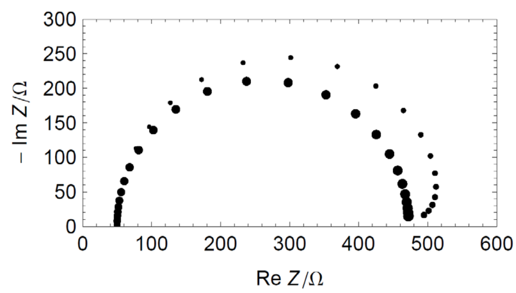

Figure 10: Simulated Nyquist impedance diagram of the circuit R1+R2(t)/C2 for two successive impedance measurements with scan $f_{max} \rightarrow f_{min}$.

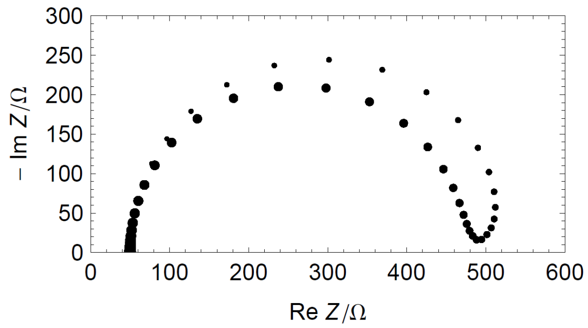

Figure 11: Simulated Nyquist impedance diagram of the circuit R1+R2(t)/C2 and for two successive impedance measurements with scan $f_{max} \rightarrow f_{min} \rightarrow f_{max}$.

The two impedance diagrams shown in Figs. 10 and 11 are different, which proves that the studied system is time variant.

III – CONCLUSION

It is essential to check the stationarity of the system studied by EIS before any interpretation of experimental results. When a electrochemical system changes with time the complexity of the impedance diagram increases and the electrical circuit chosen to interpret the experimental results may be unnecessarily complex.

REFERENCES

1) Application note #9 “Linear *vs.* non linear systems in impedance measurements.”
2) Z. Stoynov and B. Savova-Stoynov, J. Electroanal. Chem. 183 (1985) 133.
3) F. Berthier, J.-P. Diard, A. Jussiaume, and J.-J. Rameau, Corrosion Science 30 (1990) 239.
4) J.-P. Diard, B. Le Gorrec, and C. Montella, *Cinetique électrochimique*, Hermann, Paris, (1996).
5) Application note #15 “Two questions about Kramers-Kronig transformations.”

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