Interpretation problems of impedance measurements made on time variant systems

I Introduction

The application note #9 [1] deals with impedance measurements performed on linear (and non-linear) time-invariant systems. 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 a wrong interpretation and analysis when using equivalent electrical circuit. This application note describes two examples of such a mislead interpretation 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.
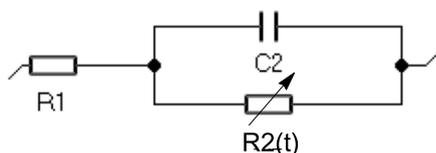

Fig. 1: R1+R2(t)/C2 circuit.

Let us consider the R1+R2(t)/C2 circuit [2] ([1]) shown in Fig. 1 and assume that the resistance

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[1] Z Fit was used to graphically code the circuits.

$R2$ increases with time according to the following relationship

$$R2(t) = R2_0 + k\, t^2 \qquad (1)$$

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 $R2$ resistance value at time t given by

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

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].
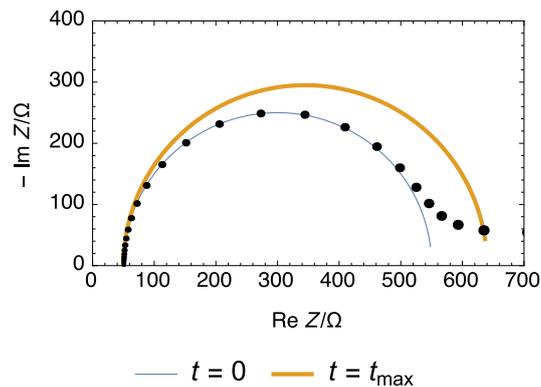

Fig. 2: Instantaneous Nyquist impedance diagrams ($t = 0$ and $t = t_{\mathrm{max}}$) of the circuit R1+R2(t)/C2 ($R1 = 50\ \Omega$, $R2_0 = 500\ \Omega$, $k = 10^{-5}\ \Omega\,\mathrm{s}^{-2}$, $C2 = 2 \times 10^{-2}$ F) and simulation of the measured diagram (•). The dot size increases with increasing time.
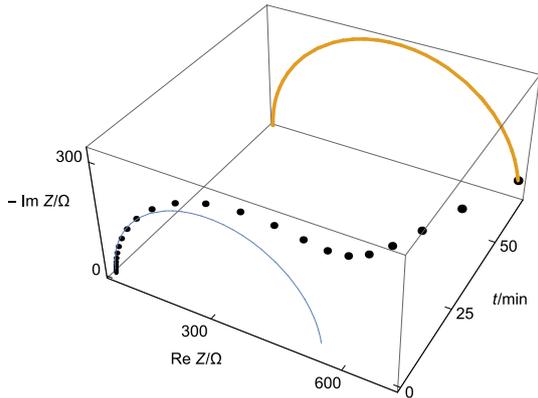
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Fig. 3: 3D representation of Fig. 2.

Fig. 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 $R1 = 50\ \Omega$, $R2 = 500\ \Omega$, $C2 = 10^{-2}$ F, $R3 = 100\ \Omega$, $C3 = 1$ F.

The frequency sweep is performed from $f_{max} \rightarrow f_{min}$ with $f_{max} = 10$ Hz and $f_{min} = 10^{-3}$ Hz. All frequency are logarithmically distributed over 8 points per decade. The parameters used for $R1$, $R2$ and $C2$ are described in the caption of Fig. 2.

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.
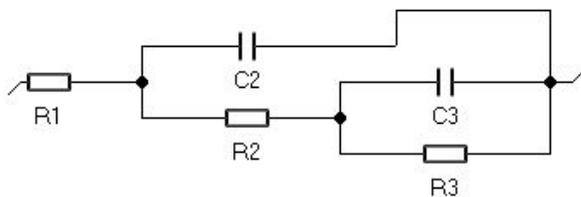

Fig. 4: R1+C2/(R2 +C3/R3) circuit.

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.
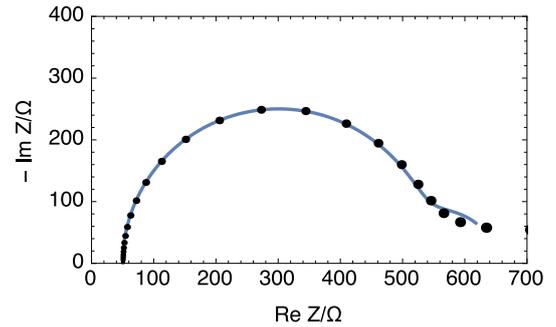
II.2   R1+R2(t)/C2 circuit with decreasing R2

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
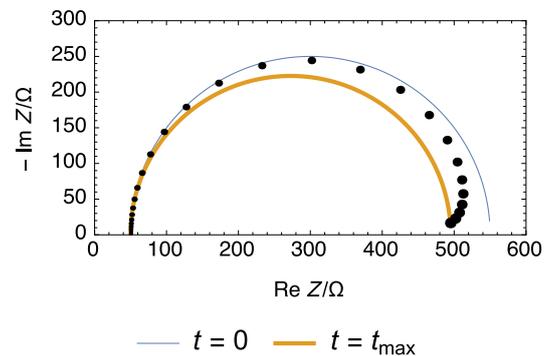
$$R2(t) = R2_0 - k' \sqrt{t} \qquad (3)$$

$\underline{\hspace{1cm}}\ t = 0$ $\rule[0.3ex]{1cm}{2pt}\ t = t_{max}$

Fig. 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 (•).

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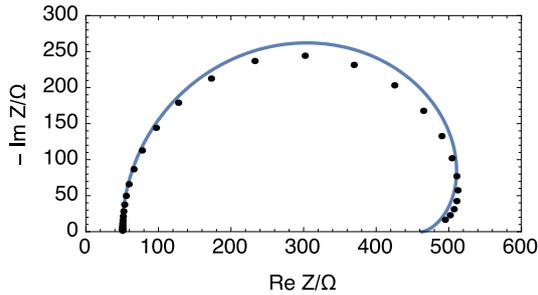Tel: +33 476 98 68 31 - Fax: +33 476 98 69 09 www.bio-logic.info

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Fig. 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 $R1 = 50\ \Omega$, $R2 = 534.375\ \Omega$, $C2 = 1.1 \times 10^{-2}$ F, $R3 = -123.75\ \Omega$, $C3 = -0.125$ 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]
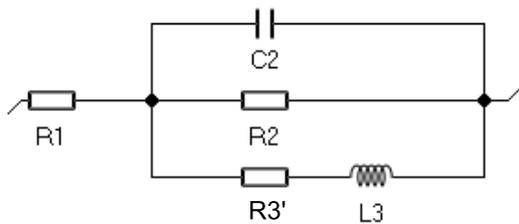
$$R3' = -\frac{R2(R2 + R3)}{R3}, \; L3 = -R2^2 C3 \quad (4)$$

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

III   Check of system stationarity

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

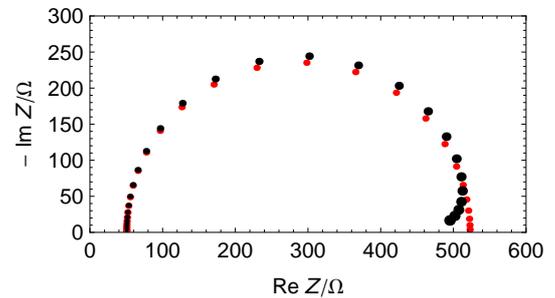has not been carried out for a time invariant system [5].

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

III.2   Successive measurements

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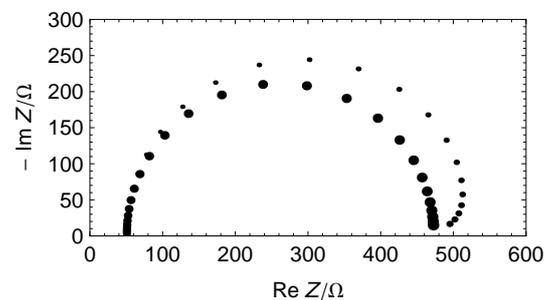

Fig. 10:   Simulated Nyquist impedance diagram of the circuit R1+R2(t)/C2 for two successive impedance measurements with scan $f_{max} \rightarrow f_{min}$.

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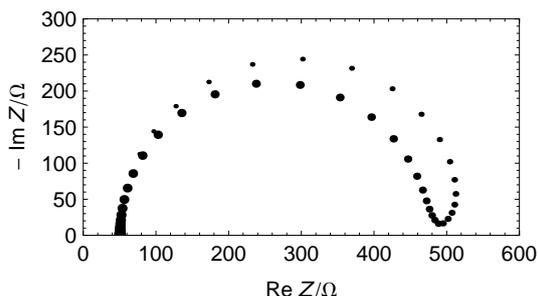**Tel: +33 476 98 68 31 - Fax: +33 476 98 69 09** www.bio-logic.info

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Fig. 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 varying.

IV 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. www.bio-logic.info/potentiostat/notesan.html.

[2] Z. STOYNOV and B. SAVOVA-STOYNOV, *J. Electroanal. Chem.* **183**, 133 (1985).

[3] F. BERTHIER, J.-P. DIARD, A. JUSSIAUME, and J.-J. RAMEAU, *Corrosion Science* **30**, 239 (1990).

[4] J.-P. DIARD, B. LE GORREC, and C. MONTELLA, *Cinétique électrochimique*, Hermann, Paris, 1996.

[5] Application note #15. Two questions about Kramers-Kronig transformations. www.bio-logic.info/potentiostat/notesan.html.

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