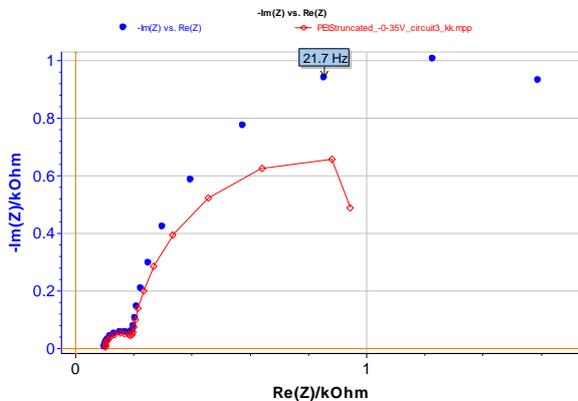


**Figure 3: Test circuit #3. Nyquist impedance diagram measured using PEIS technique.  $E_{WE} = -0.35$  V,  $V_a = 375$  mV,  $f_{min} = 0.2$  Hz,  $f_{max} = 50$  kHz (blue markers) and Nyquist impedance diagram obtained using KK transforms (red curve).**

## II – WHAT CAN WE DO WITH TRUNCATED IMPEDANCE?

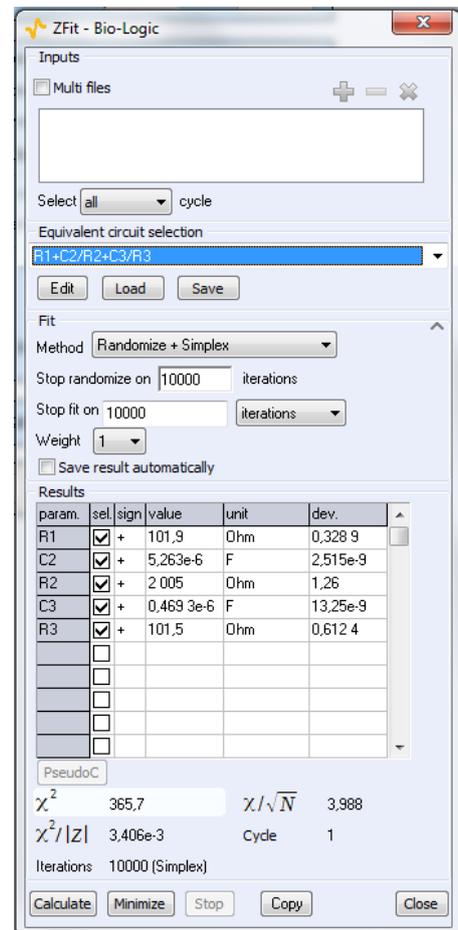
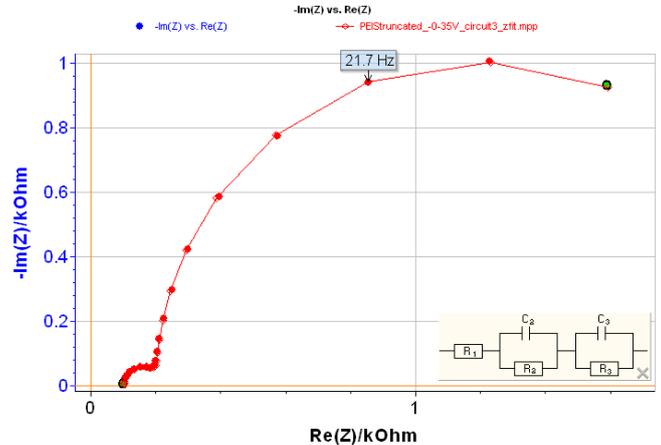
Let us suppose that, for some reason, the Nyquist diagram has been measured for a limited-range frequency values (Figure 4).



**Figure 4: Truncated impedance diagram obtained for limited-range frequency values.  $E_{WE} = -0.35$  V,  $V_a = 10$  mV,  $f_{min} = 10$  Hz,  $f_{max} = 50$  kHz (blue curve) and Nyquist diagram obtained using KK transforms (red curve).**

Obviously Z and  $Z_{KK}$  impedance diagrams show a large discrepancy. What can we do to check the validity of the experimental impedance diagram shown in Figure 4? It is always possible to check this validity using ZFit [6] with a measurement model, *i.e.* a Voigt circuit  $R1+C2/R2+C3/R3$ . As the measurement model is consistent with the KK relations, it allows

the user to check the consistency of experimental data without using the KK relationships [7]. The theoretical impedance shown in Figure 5 shows the validity of the truncated experimental impedance diagram.

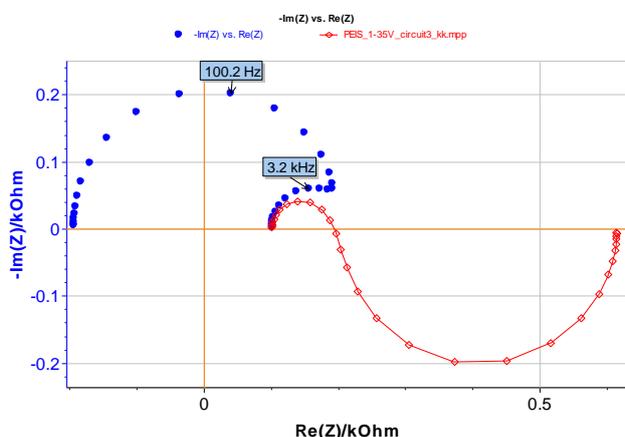


**Figure 5: Truncated impedance diagram obtained for limited-range frequency values (blue curve), ZFit window for Voigt circuit  $R1+C2/R2+C3/R3$  and theoretical impedance diagram (red curve).**

### III – WHAT CAN WE DO WITH AN UNSTABLE SYSTEM UNDER GALVANOSTATIC CONTROL (GC)?

#### III - 1 TEST-BOX 3 CIRCUIT 3

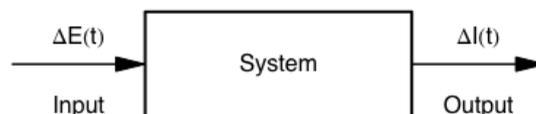
The Nyquist impedance diagram shown in Figure 6 has been measured at point **b** of the steady-state curve (Figure 1) of circuit #3 of the Bio-Logic test-box 3 using the PEIS technique, *i.e.* under potential control (PC). The Nyquist impedance diagram shown in Figure 6 is still made of two capacitive arcs, well separated in frequency with a negative value of the real part of the impedance in low frequency, according to the bell-shaped steady-state curve.



**Figure 6: Test circuit #3. Nyquist impedance diagram measured at point b (Figure 1) using PEIS technique.  $E_{WE} = 1.35$  V,  $V_a = 10$  mV,  $f_{min} = 1$  Hz,  $f_{max} = 100$  kHz (blue markers) and Nyquist impedance diagram obtained using KK transforms (red curve).**

The result of the KK transform (Figure 6) shows a large discrepancy in the low frequency domain. It has been shown [8, 9] that it is not possible to directly verify the validity of an impedance diagram measurement of an « unstable » electrochemical system, such as it would be found, for instance, in the case of a steady-state current density vs. electrode potential curve exhibiting a part with a negative slope. In fact, the KK transforms do not really fail. The bell-shaped curve steady-state current vs. potential curve shown in Figure 1 cannot be entirely drawn under galvanostatic control

(GC), whereas it could under potentiostatic control (PC). Gabrielli et al. [9] have demonstrated that, in this case, it was possible to calculate the admittance and then verify the validity of the admittance using KK transforms.



**Figure 7: Sketch of the study of a scalar linear system under potentiostatic control (PC).**

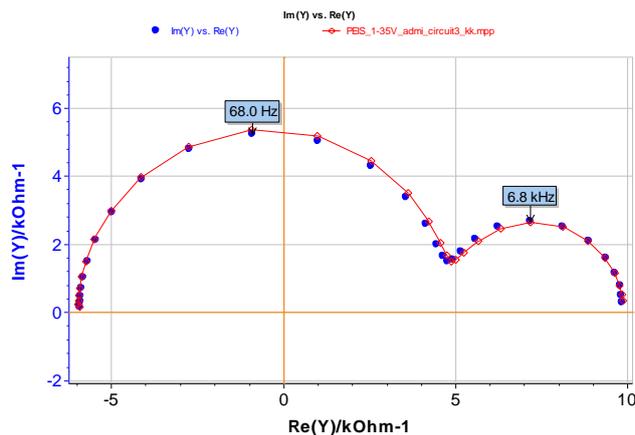
This problem is due to the electrochemist's bad habit consisting of working under PC and plotting the impedance diagram instead of an admittance diagram. Under PC, the transfer function  $H(s)$  of a system is not impedance but admittance. As a matter of fact, a transfer function is given by Figure 7:

$$H(s) = \frac{\mathcal{L}[\text{output}(t)]}{\mathcal{L}[\text{input}(t)]} \quad (1)$$

where  $s$  is the Laplace variable and  $L$  denotes the Laplace transform. Under PC, the transfer function of an electrochemical system is:

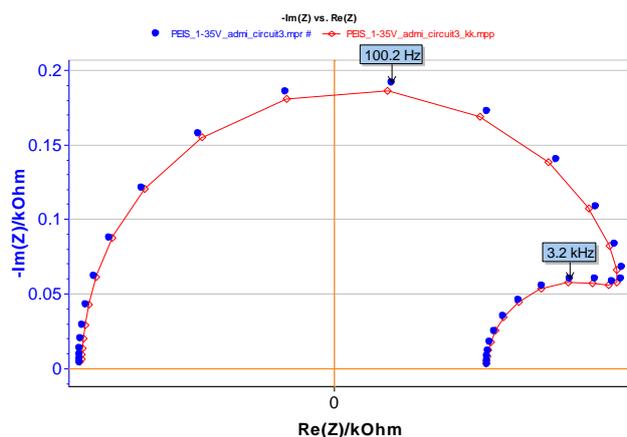
$$H(s) = \frac{\mathcal{L}[\Delta I(t)]}{\mathcal{L}[\Delta E(t)]} = \frac{1}{Z(s)} = Y(s) \quad (2)$$

Therefore, checking the consistency of the experimental impedance diagram shown in Figure 6 should be made with admittance data instead of impedance data. Figure 8 shows the good agreement between  $Y$  and  $Y_{KK}$  admittance diagrams and the consistency of the measured impedance.



**Figure 8: Test circuit #3. Nyquist admittance diagram measured using PEIS technique.  $E_{WE} = 1.35$  V,  $V_a = 10$  mV,  $f_{min} = 1$  Hz,  $f_{max} = 100$  kHz (blue markers) and Nyquist admittance diagram obtained using KK transforms (red curve).**

To conclude, it is therefore possible to transform  $Y_{KK}$  admittance diagrams into  $Z_{KK}$  impedance diagrams as it is shown in Fig. 9.

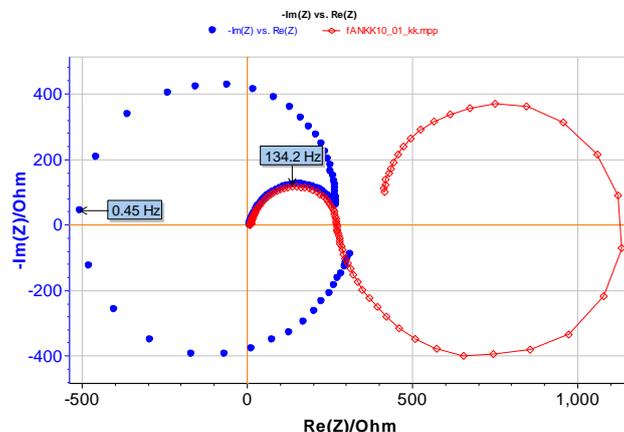


**Figure 9: Z (blue markers) and  $Z_{KK}$  (red curve) impedance diagrams obtained by inverting admittance diagrams shown in Figure 8.**

### III - 2 NI ELECTRODE IN ACIDIC MEDIUM

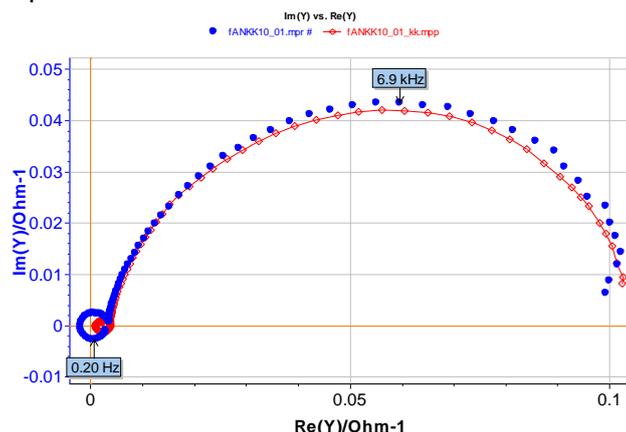
The well-known impedance diagram obtained for Ni electrode in  $H_2SO_4$  medium using the PEIS technique is shown in Fig. 10 [10, 11]. Such diagrams are obtained for anodic dissolution-passivation of Ni under PC in the instability range of the electrode|electrolyte interface with respect to current control. The impedance diagram is made of two parts, a near semi-circle in the high frequency domain and a near circle arc in the low frequency

domain. Obviously, the Z and  $Z_{KK}$  Nyquist diagrams are quite different, and the experimental impedance Z does not obey the KK relationships.



**Figure 10: Ni electrode in acidic medium ( $H_2SO_4$  1 mol.L<sup>-1</sup>,  $\Phi = 2$  mm). Nyquist impedance diagram measured using PEIS technique.  $E_{WE} = 0.9$  V/ECS,  $V_a = 12.5$  mV,  $f_{min} = 50$  mHz,  $f_{max} = 10$  kHz with 25 points per decade (blue markers) and Nyquist diagram obtained using KK transforms (red curve).**

Figure 11 shows the good agreement between  $Y$  and  $Y_{KK}$  admittance diagrams and the consistency of the measured impedance of Ni electrode in acidic medium. The shift between the admittance diagrams is due to the measurement error of the real part of the impedance for  $f \rightarrow \infty$ .



**Figure 11: Ni electrode in acidic medium. Nyquist admittance diagram measured using PEIS technique.  $E_{WE} = 0.9$  V/ECS,  $V_a = 12.5$  mV,  $f_{min} = 50$  mHz,  $f_{max} = 10$  kHz with 25 points per decade (blue markers) and Nyquist admittance diagram obtained using KK transforms (red curve).**

## IV – CONCLUSION

In this note, we have introduced the KK transform, available in EC-Lab® to obtain impedance diagrams. The KK transform is a useful tool, but in some cases, we have to be careful: If we work with truncated impedance and little data, it is better to use ZFit. If we work with an unstable system, we should work with admittance diagrams and convert them to impedance if necessary.

*Data files can be found in :*

*C:\Users\xxx\Documents\EC-Lab\Data\Samples\EIS\AN15\_X*

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*Revised in 07/2018*