Two questions about Kramers-Kronig transformations

Introduction

Using the Kramers-Kronig (KK) transforms, the real part of a transfer function can be calculated, for a causal, stable, linear, time invariant and finite system when $f \rightarrow 0$ and $f \rightarrow \infty$, when the change in its imaginary part, as a function of the frequency, is known. At the opposite, the imaginary part of a transfer function can be calculated when the evolution of its real part is known [Tia72, Mei76, Dia94, Sad04].

When the impedance of an electrode reaction is measured, it is thus possible, to calculate the imaginary part using experimental values for the real part, and to calculate the real part using experimental values for the imaginary part. Comparing calculated impedance Z_{KK} with the experimental impedance Z is a useful tool to check the validity of the impedance measurement with respect to the conditions of applicability of KK transforms.

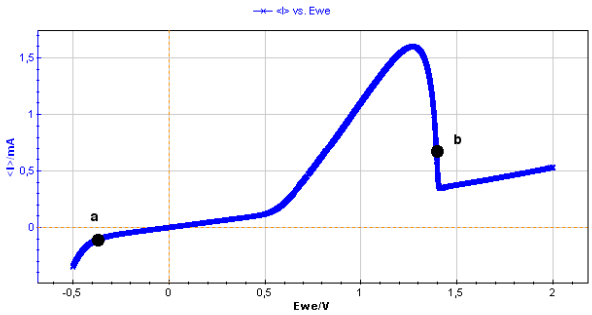


Fig. 1 : Test-box 3, test circuit #3. I vs. E_{we} steady-state curve.

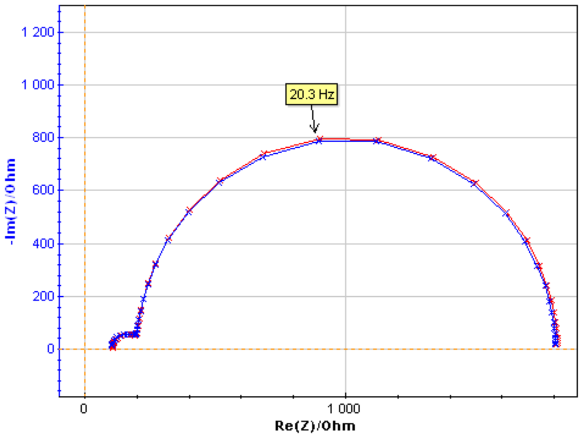


Fig. 2 : Test circuit #3. Nyquist impedance diagram measured at point **a** (Fig. 1) using PEIS technique. $E_{\mathrm{we}} = -0.35\ \mathrm{V}$, $V_{\mathrm{pp}} = 20\ \mathrm{mV}$, $f_{\mathrm{min}} = 0.2\ \mathrm{Hz}$, $f_{\mathrm{max}} = 50\ \mathrm{kHz}$ (blue curve) and Nyquist diagram obtained using KK transforms (red curve).

As an example, the Nyquist impedance diagram shown in Fig. 2 has been measured for circuit #3 of the Bio-Logic test-box 3 using the PEIS technique. Test circuit #3 mainly consists of two transistors. It is a model for metal passivation (cf. Application notes #9 and #14). Nyquist impedance diagram shown in Fig. 2 is made of two capacitive arcs, well separated in frequency. Calculated impedance Z_{KK} using KK transforms is shown in the Fig. 2. Z and Z_{KK} diagrams are similar for all frequencies, therefore impedance measurement has been carried out for a causal, stable, linear and time invariant system.

The Nyquist impedance diagram shown in Fig. 3 has been measured using a large value of the peak to peak potential ($V_{\mathrm{pp}} = 750\ \mathrm{mV}$) of the sinusoidal modulation of potential E_{we}, i. e. for non-linear conditions. This diagram is still made of two capacitive arcs, the low frequency arc being smaller than the corresponding arc in the case of Fig. 2.

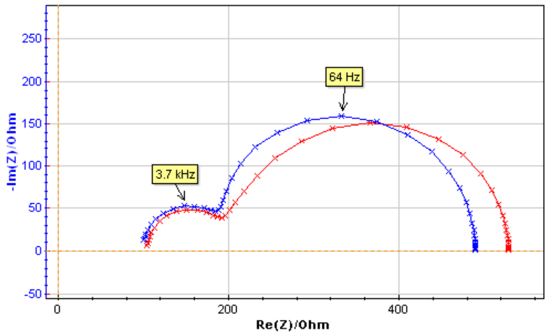


Fig. 3 : Test circuit #3. Nyquist impedance diagram measured using PEIS technique. $E_{\mathrm{we}} = -0.35\ \mathrm{V}$, $V_{\mathrm{pp}} = 750\ \mathrm{mV}$, $f_{\min} = 0.2\ \mathrm{Hz}$, $f_{\max} = 50\ \mathrm{kHz}$ (blue curve) and Nyquist impedance diagram obtained using KK transforms (red curve).

Calculated impedance Z_{KK} using KK transforms is shown on the Fig. 3. This two impedance diagrams are different showing that impedance measurement has been carried out for non-linear conditions.

What can we do with a truncated impedance ?

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

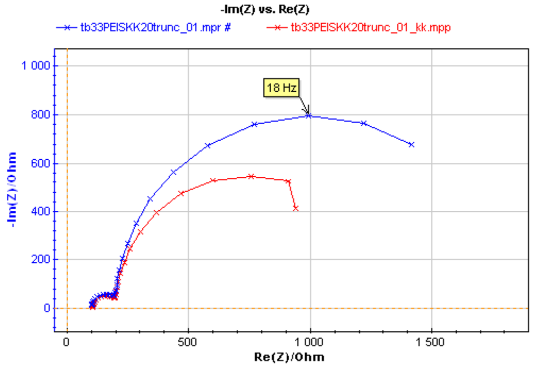
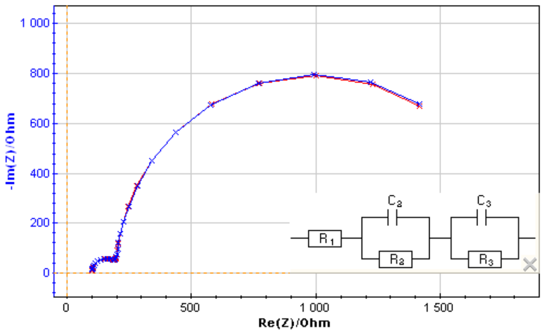
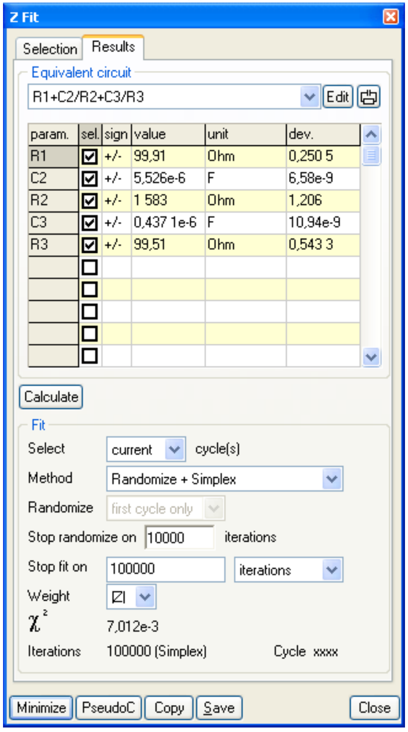


Fig. 4 : Truncated impedance diagram obtained for limited-range frequency values. $E_{\mathrm{we}} = -0.35\ \mathrm{V}$, $V_{\mathrm{pp}} = 20\ \mathrm{mV}$, $f_{\min} = 10\ \mathrm{Hz}$, $f_{\max} = 50\ \mathrm{kHz}$ (blue curve) and Nyquist diagram obtained using KK transforms (red curve).

Obviously Z and Z_{KK} impedance diagrams show a large discrepancy. What can we do to check the validity of experimental impedance diagram shown in Fig. 4 ? It is always possible to check this validity using ZFit (cf. Application notes #14) 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 [Shu04].





Equivalent circuit

R1+C2/R2+C3/R3

param.	sel.	sign	value	unit	dev.
R1	☑	+/-	99,91	Ohm	0,250 5
C2	☑	+/-	5,526e-6	F	6,58e-9
R2	☑	+/-	1 583	Ohm	1,206
C3	☑	+/-	0,437 1e-6	F	10,94e-9
R3	☑	+/-	99,51	Ohm	0,543 3
	☐				
	☐				
	☐				
	☐				
	☐				

Fit

Select current cycle(s)
Method Randomize + Simplex
Randomize first cycle only
Stop randomize on 10000 iterations
Stop fit on 100000 iterations
Weight |Z|
χ^2 7,012e-3
Iterations 100000 (Simplex) Cycle xxxx

Fig. 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).

The theoretical impedance shown in Fig. 5 shows the validity of the truncated experimental impedance diagram.

What can we do with an unstable system under galvanostatic control (GC) ?

Test Box-3 #3

The Nyquist impedance diagram shown in Fig. 6 has been measured at point **b** of the steady-state curve (Fig. 1) of circuit #3 of the Bio-Logic test-box 3 using the PEIS techniq i. e. under potential control (PC). Nyquist impedance diagram shown in Fig. 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..

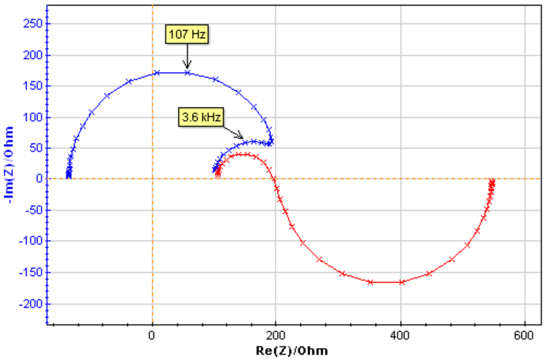


Fig. 6: Test circuit #3. Nyquist impedance diagram measured at point **b** (Fig. 1) using PEIS technique. $E_{\mathrm{we}} = 1.35\ \mathrm{V}$, $V_{\mathrm{pp}} = 20\ \mathrm{mV}$, $f_{\min} = 1\ \mathrm{Hz}$, $f_{\max} = 100\ \mathrm{kHz}$ (blue curve) and Nyquist impedance diagram obtained using KK transforms (red curve).

The result of KK transform (Fig. 6) shows a large discrepancy in the low frequency domain. It has been shown [Mac90, Gab91] that it is not possible to verify directly 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 Fig. 1 cannot be entirely drawn under galvanostatic control (GC), whereas it could be under PC. Gabrielli et al. [Gab91] have demonstrated that, in this case, it was possible to calculate the admittance and then verify the validity of the admittance using KK transforms.

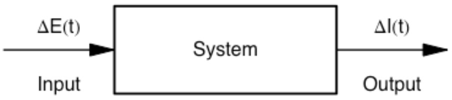


Fig. 7: Sketch of the study of a scalar linear system under PC.

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

$$H(s) = \frac{\mathrm{L}[\mathrm{output}(t)]}{\mathrm{L}[\mathrm{input}(t)]}$$

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

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

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

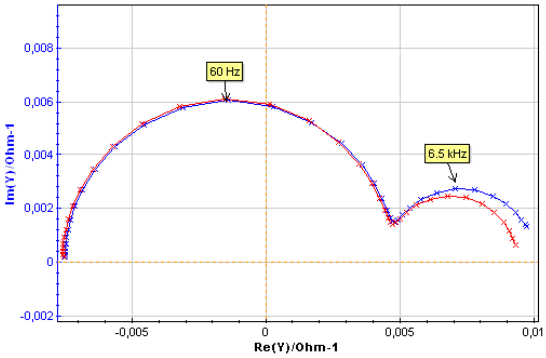


Fig. 8: Test circuit #3. Nyquist admittance diagram measured using PEIS technique. $E_{\mathrm{we}} = 1\ \mathrm{V}$, $V_{\mathrm{pp}} = 20\ \mathrm{mV}$, $f_{\min} = 1\ \mathrm{Hz}$, $f_{\max} = 100\ \mathrm{kHz}$ (blue curve) and Nyquist admittance diagram obtained using KK transforms (red curve).

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

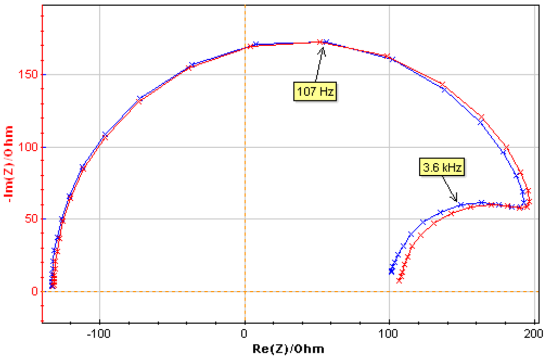


Fig. 9: Z (blue curve) and Z_{KK} (red curve) impedance diagrams obtained by inversing admittance diagrams shown in Fig. 8.

Ni electrode in acidic medium

The well-known impedance diagram obtained for Ni electrode in H_2SO_4 medium using PEIS technique is shown in Fig. 10 [Ked72, Ber04]. 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. 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.

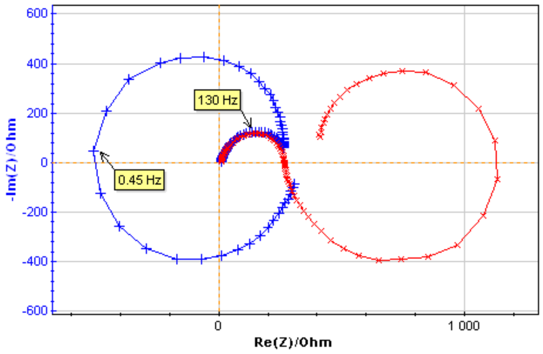


Fig. 10 : Ni electrode in acidic medium (H_2SO_4 1 mol L^{-1}, $\phi = 2\,\mathrm{mm}$). Nyquist impedance diagram measured using PEIS technique. $E_{\mathrm{we}} = 0{,}9\ \mathrm{V/ECS}$, $V_{\mathrm{pp}} = 25\ \mathrm{mV}$, $f_{\mathrm{min}} = 50\ \mathrm{mHz}$, $f_{\mathrm{max}} = 10\ \mathrm{kHz}$ with 25 points per decade (blue curve) and Nyquist diagram obtained using KK transforms (red curve).

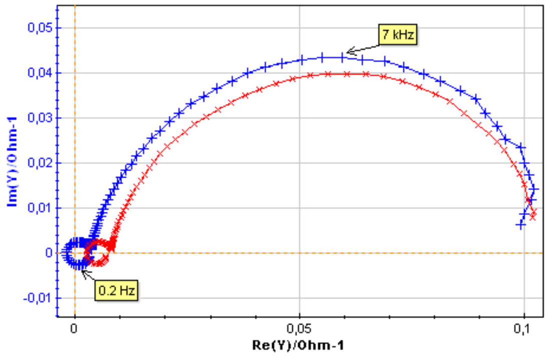


Fig. 11 :. Ni electrode in acidic medium. Nyquist admittance diagram measured using PEIS technique. $E_{\mathrm{we}} = 0{,}9\ \mathrm{V/ECS}$, $V_{\mathrm{pp}} = 25\ \mathrm{mV}$, $f_{\mathrm{min}} = 50\ \mathrm{mHz}$, $f_{\mathrm{max}} = 10\ \mathrm{kHz}$ with 25 points per decade (blue curve) and Nyquist admittance diagram obtained using KK transforms (red curve).

Fig. 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 $f \to \infty$.

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