Influence of drift on the impedance measured with the lock-in amplifier technique

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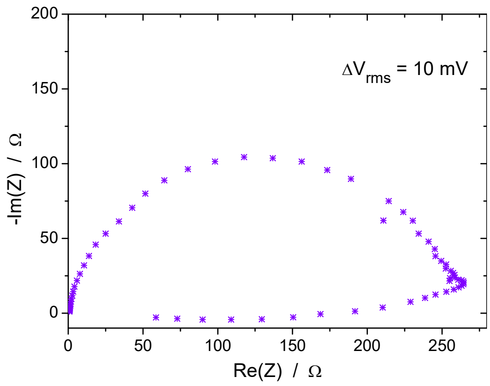
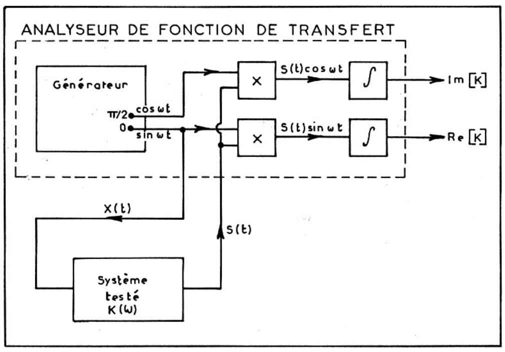
INTRODUCTION



- … inductive loop above the X-axis or capacitive loop below the X-axis
- could not be validated by Kramers-Kronig relationships
- calculate the influence of a linear drift
- define the lock-in amplifier technique
- important to detect and decrease the influence of drift

$$Z_j(\omega) = -\frac{2\omega}{\pi}\int_0^{+\infty} \frac{Z_r(x)}{x^2-\omega^2}\,dx$$

Lock-in amplifier technique



$$K(\omega)=|K(\omega)|\exp(j\phi(\omega))$$

$$x(t)=X_0\sin(\omega t) \qquad \omega = 2\pi f$$

$$S(t)=X_0|K(\omega)|\sin(\omega t+\phi(\omega))+\sum_n A_n\sin(n\omega t+\phi_n)+b(t)$$

harmonics noise

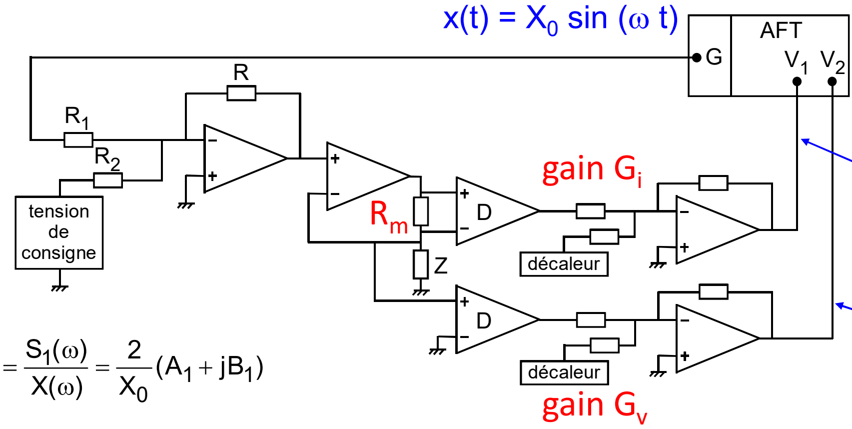
$$A=\frac{1}{NT}\int_{t_0}^{t_0+NT}S(t)\sin\omega t\,dt \Rightarrow A=\frac{1}{2NT}\int_0^{NT}X_0|K(\omega)|\cos(\phi(\omega))\,dt=\frac{X_0}{2}|K(\omega)|\cos(\phi(\omega))=\frac{X_0}{2}\mathrm{Re}[K(\omega)]$$

$$B=\frac{1}{NT}\int_{t_0}^{t_0+NT}S(t)\cos\omega t\,dt \Rightarrow B=\frac{1}{2NT}\int_0^{NT}X_0|K(\omega)|\sin(\phi(\omega))\,dt=\frac{X_0}{2}|K(\omega)|\sin(\phi(\omega))=\frac{X_0}{2}\mathrm{Im}[K(\omega)]$$

$$A+jB=\frac{X_0}{2}K(\omega) \Rightarrow K(\omega)=\frac{2}{X_0}(A+jB)$$

Lock-in amplifier technique

$x(t) = X_0 \sin(\omega t)$



$S_1(t)=R_m G_i I(t)$

$S_2(t)=G_v V(t)$

$$K_1(\omega)=\frac{S_1(\omega)}{X(\omega)}=\frac{2}{X_0}(A_1+jB_1)$$

$$K_2(\omega)=\frac{S_2(\omega)}{X(\omega)}=\frac{2}{X_0}(A_2+jB_2)$$

$$\Rightarrow \frac{S_2(\omega)}{S_1(\omega)}=\frac{A_2+jB_2}{A_1+jB_1}=\frac{G_v}{R_mG_i}\frac{V(\omega)}{I(\omega)} \Rightarrow Z(\omega)=\frac{V(\omega)}{I(\omega)}=\frac{R_m G_i}{G_v}\frac{A_2+jB_2}{A_1+jB_1}$$

Lock-in amplifier technique

- potentiostatic mode (similar calculation for galvanostatic mode) $V(t) = X_0 \sin\omega t$

$$S_2(t) = G_v\, V(t) = G_v\, X_0 \sin\omega t \;\Rightarrow\; S_1(t) = R_m G_i\, I(t) = R_m G_i \frac{X_0}{|Z(\omega)|}\sin(\omega t - \Psi(\omega))$$

$$Z(\omega) = \frac{V(\omega)}{I(\omega)} = \frac{R_m\, G_i}{G_v}\frac{A_2 + jB_2}{A_1 + jB_1} \qquad \text{with} \quad Z(\omega) = |Z(\omega)|\, e^{j\Psi(\omega)}$$

$$A_1 = \frac{1}{NT}\int_{t_o}^{t_o+NT} S_1(t)\sin\omega t\, dt = \ldots = \frac{R_m G_i\, X_0^2}{2|Z(\omega)|}\cos\Psi(\omega)$$

$$B_1 = \frac{1}{NT}\int_{t_o}^{t_o+NT} S_1(t)\cos\omega t\, dt = \ldots = -\frac{R_m G_i\, X_0^2}{2|Z(\omega)|}\sin\Psi(\omega)$$

$$A_1 + jB_1 = \frac{R_m G_i\, X_0^2}{2|Z(\omega)|}(\cos\Psi(\omega) - j\sin\Psi(\omega))$$

$$A_2 = \frac{1}{NT}\int_{t_o}^{t_o+NT} S_2(t)\sin\omega t\, dt = \ldots = \frac{G_v\, X_0^2}{2}$$

$$B_2 = \frac{1}{NT}\int_{t_o}^{t_o+NT} S_2(t)\cos\omega t\, dt = \ldots = 0$$

$$\Rightarrow \frac{R_m\, G_i}{G_v}\frac{A_2 + jB_2}{A_1 + jB_1} = |Z(\omega)|\, e^{j\Psi(\omega)} = Z(\omega)$$

Influence of a linear drift

- potentiostatic mode (similar calculation for galvanostatic mode) $V(t) = X_0 \sin\omega t$

$$S_2(t) = G_v\, V(t) = G_v\, X_0 \sin\omega t \;\Rightarrow\; S_1(t) = R_m G_i \left[\frac{X_0}{|Z(\omega)|}\sin(\omega t - \Psi(\omega)) + a_i\, t + b\right]$$

$$Z(\omega) = \frac{V(\omega)}{I(\omega)} = \frac{R_m\, G_i}{G_v}\frac{A_2 + jB_2}{A_1 + jB_1} \qquad \text{with} \quad Z(\omega) = |Z(\omega)|\, e^{j\Psi(\omega)}$$

$$A_1 = \frac{1}{NT}\int_{t_o}^{t_o+NT} S_1(t)\sin\omega t\, dt = \ldots = \frac{R_m G_i\, X_0^2}{2|Z(\omega)|}\cos\Psi(\omega) - R_m G_i\, X_0 \frac{a_i}{\omega}\cos\omega t_o$$

$$B_1 = \frac{1}{NT}\int_{t_o}^{t_o+NT} S_1(t)\cos\omega t\, dt = \ldots = -\frac{R_m G_i\, X_0^2}{2|Z(\omega)|}\sin\Psi(\omega) + R_m G_i\, X_0 \frac{a_i}{\omega}\sin\omega t_o$$

$$A_2 = \frac{1}{NT}\int_{t_o}^{t_o+NT} S_2(t)\sin\omega t\, dt = \ldots = \frac{G_v\, X_0^2}{2}$$

$$B_2 = \frac{1}{NT}\int_{t_o}^{t_o+NT} S_2(t)\cos\omega t\, dt = \ldots = 0$$

$$Z_{meas}(\omega) = \frac{R_m\, G_i}{G_v}\frac{A_2 + jB_2}{A_1 + jB_1} = \frac{1}{\dfrac{1}{Z(\omega)} - \dfrac{2a_i}{\omega X_0}e^{-j\omega t_o}}$$

Influence of a linear drift

- potentiostatic mode

$$Z_{meas}(\omega) = \frac{1}{\frac{1}{Z(\omega)} - \frac{2a_i}{\omega X_0} e^{-j\omega t_o}}$$

most often X_0 = 10 mV_{rms}

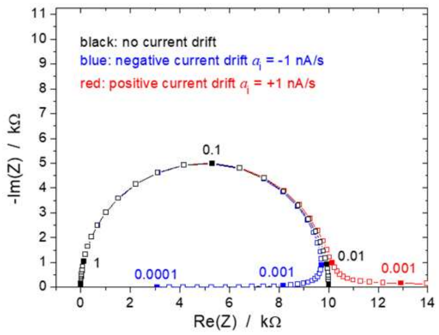
- galvanostatic mode

$$Z_{meas}(\omega) = Z(\omega) - \frac{2a_v}{\omega X_0 K} e^{-j\omega t_o}$$

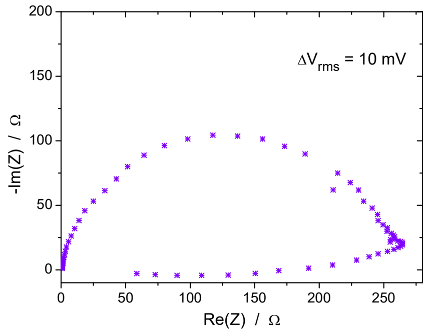
K in A/V
X_0 K = amplitude of the current sine wave

- example   dummy cell r + (R // C)   with r = 10 Ω, R = 10 kΩ, C = 150 µF

X_0= 10 mV_{rms}, t_o = 0, a_i = 1 nA/s ➡ 10 mV for one period at 1 mHz

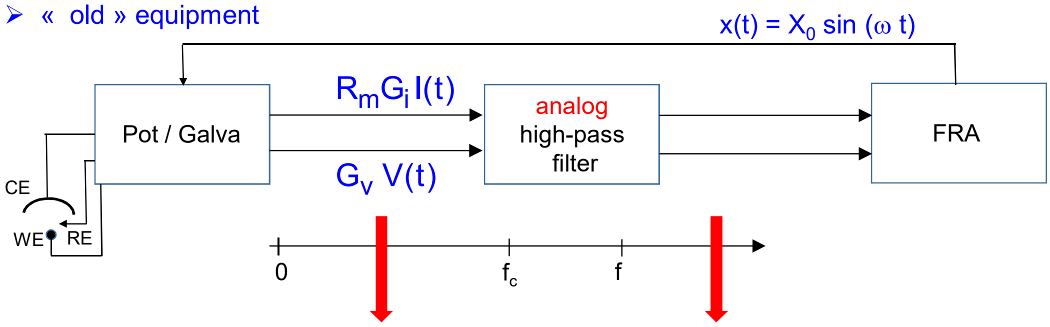


similar effect for the electrochemical system

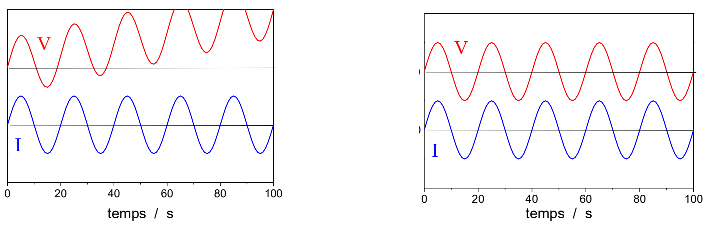


How to detect and decrease the influence of a drift on impedance?

- « old » equipment

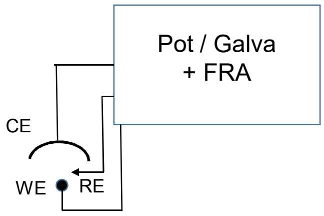


on the oscilloscope
in galvanostatic mode

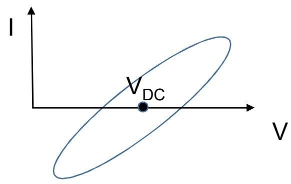


How to detect and decrease the influence of a drift on impedance?

➢ « new » equipment



- no possibility of oscilloscope (except for some equipment with BNC connections giving access to V and I)
- no possibility of adding an analog high-pass filter
- possibility for the manufacturers to implement digital high-pass filtering
- with Lissajous ellipse:



- in galvanostatic mode: check if DC potential drifts with time
- in potentiostatic mode: check if DC current drifts with time

Conclusions

➢ lock-in amplifier technique

➢ influence of a linear drift on the impedance value

➢ how to detect the non-stationarity of V and I signals during the impedance measurement

➢ how to limit the drift influence during the impedance measurement for « old » potentiostats