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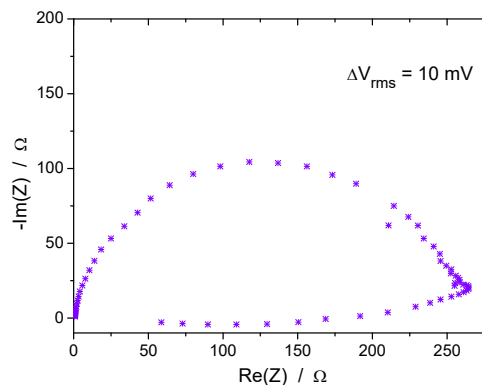
Influence of drift on the impedance measured with the lock-in amplifier technique

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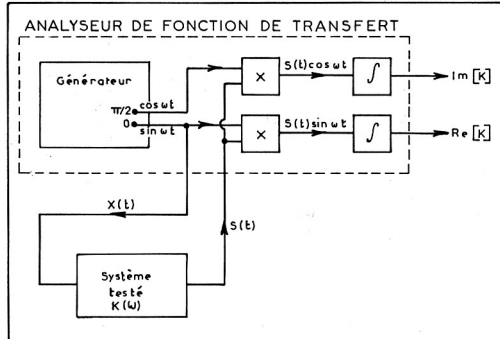
INTRODUCTION



- ... 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



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

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

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

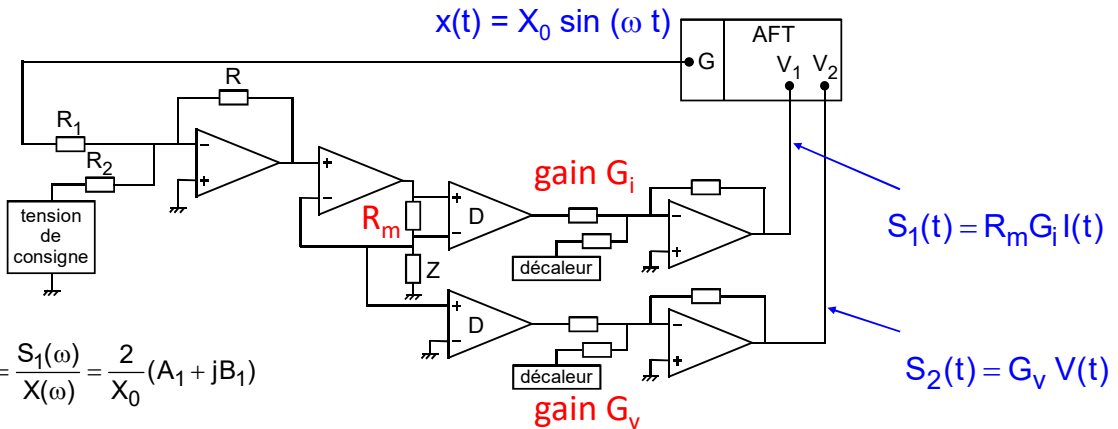
harmonics noise

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

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

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

Lock-in amplifier technique



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

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

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

Lock-in amplifier technique

➤ potentiostatic mode (similar calculation for galvanostatic mode)

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

$$S_2(t) = G_V V(t) = G_V X_0 \sin \omega t \quad \rightarrow \quad S_1(t) = R_m G_i I(t) = R_m G_i \frac{X_0}{|Z(\omega)|} \sin(\omega t - \Psi(\omega))$$

$$Z(\omega) = \frac{V(\omega)}{I(\omega)} = \frac{R_m G_i}{G_V} \frac{A_2 + jB_2}{A_1 + jB_1}$$

$$\text{with } Z(\omega) = |Z(\omega)| e^{j\Psi(\omega)}$$

$$A_1 = \frac{1}{NT} \int_{t_0}^{t_0+NT} S_1(t) \sin \omega t \, dt = \dots = \frac{R_m G_i X_0^2}{2|Z(\omega)|} \cos \Psi(\omega)$$

$$B_1 = \frac{1}{NT} \int_{t_0}^{t_0+NT} S_1(t) \cos \omega t \, dt = \dots = -\frac{R_m G_i X_0^2}{2|Z(\omega)|} \sin \Psi(\omega)$$

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

$$A_2 = \frac{1}{NT} \int_{t_0}^{t_0+NT} S_2(t) \sin \omega t \, dt = \dots = \frac{G_V X_0^2}{2}$$

$$B_2 = \frac{1}{NT} \int_{t_0}^{t_0+NT} S_2(t) \cos \omega t \, dt = \dots = 0$$

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

Influence of a linear drift

➤ potentiostatic mode (similar calculation for galvanostatic mode)

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

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

$$Z(\omega) = \frac{V(\omega)}{I(\omega)} = \frac{R_m G_i}{G_V} \frac{A_2 + jB_2}{A_1 + jB_1}$$

$$\text{with } Z(\omega) = |Z(\omega)| e^{j\Psi(\omega)}$$

$$A_1 = \frac{1}{NT} \int_{t_0}^{t_0+NT} S_1(t) \sin \omega t \, dt = \dots = \frac{R_m G_i X_0^2}{2|Z(\omega)|} \cos \Psi(\omega) - R_m G_i X_0 \frac{a_i}{\omega} \cos \omega t_0$$

$$B_1 = \frac{1}{NT} \int_{t_0}^{t_0+NT} S_1(t) \cos \omega t \, dt = \dots = -\frac{R_m G_i X_0^2}{2|Z(\omega)|} \sin \Psi(\omega) + R_m G_i X_0 \frac{a_i}{\omega} \sin \omega t_0$$

$$A_2 = \frac{1}{NT} \int_{t_0}^{t_0+NT} S_2(t) \sin \omega t \, dt = \dots = \frac{G_V X_0^2}{2}$$

$$B_2 = \frac{1}{NT} \int_{t_0}^{t_0+NT} S_2(t) \cos \omega t \, dt = \dots = 0$$

$$Z_{\text{meas}}(\omega) = \frac{R_m G_i}{G_V} \frac{A_2 + jB_2}{A_1 + jB_1} = \frac{1}{\frac{1}{Z(\omega)} - \frac{2a_i}{\omega X_0} e^{-j\omega t_0}}$$

Influence of a linear drift

➤ potentiostatic mode

$$Z_{\text{meas}}(\omega) = \frac{1}{\frac{1}{Z(\omega)} - \frac{2a_i}{\omega X_0} e^{-j\omega t_0}}$$

most often $X_0 = 10 \text{ mV}_{\text{rms}}$

➤ galvanostatic mode

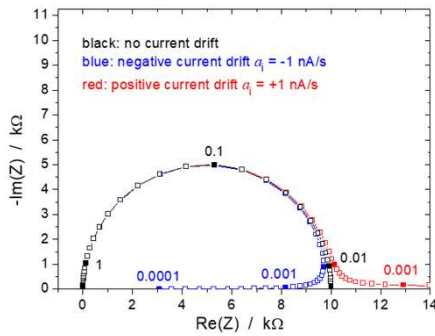
$$Z_{\text{meas}}(\omega) = Z(\omega) - \frac{2a_v}{\omega X_0 K} e^{-j\omega t_0}$$

K in A/V

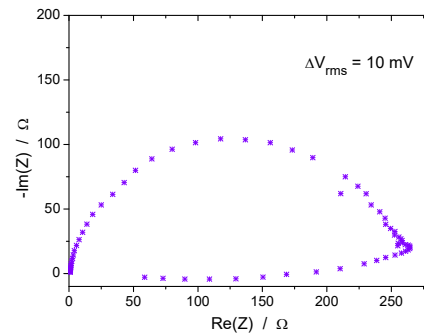
$X_0 K =$ amplitude of the current sine wave

➤ example dummy cell $r + (R // C)$ with $r = 10 \Omega$, $R = 10 \text{ k}\Omega$, $C = 150 \mu\text{F}$

$X_0 = 10 \text{ mV}_{\text{rms}}$, $t_0 = 0$, $a_i = 1 \text{ nA/s}$ ➔ **10 mV for one period at 1 mHz**



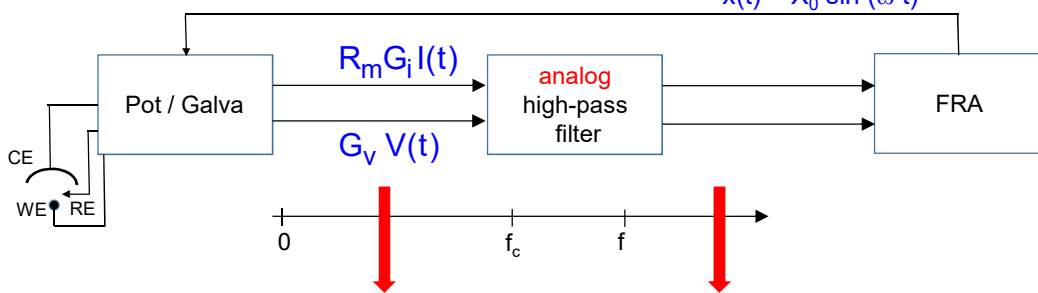
similar effect for the electrochemical system



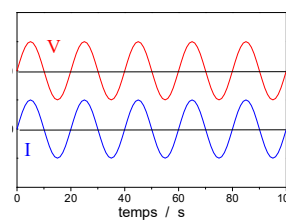
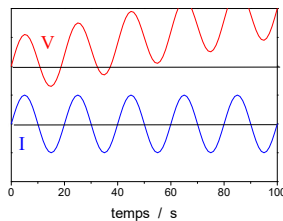
How to detect and decrease the influence of a drift on impedance?

➤ « old » equipment

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

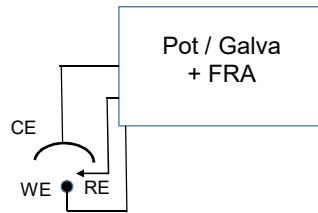


on the oscilloscope in galvanostatic mode

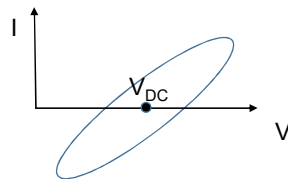


How to detect and decrease the influence of a drift on impedance?

➤ « 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