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Application of the short time Fourier transformation to the continuous frequency method of measurement of electrode impedance

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Summary: A new method of electrode impedance measurement has been presented. It employs a non-stationary potential perturbation signal, which frequency is a linear function of time. Application of the STFT transformation to the analysis of potential perturbation signal and current response allows determination of impedance spectrum. Accuracy of obtained impedance values depends on the size of the window and on the kind of utilized analyzing function.
Key words: *impedance measurements, STFT, digital analysis*

INTRODUCTION

Electrochemical impedance spectroscopy (EIS) is a measuring technique widely applied in many electrochemical investigations. Most frequently it is based on perturbation of examined system with a sine signal of a given frequency and simultaneous analysis of response signal, directly as a function of frequency. This manner of measurement is widely known under the name of frequency response analysis (FRA) [1, 2]. It is characterized by high accuracy and is applied in almost all commercial measuring devices. The time of impedance measurement by this method depends on the specified integration time and the number of analyzed frequencies. It means that in order to increase resolution and accuracy of generated impedance spectrum one must also increase the time of measurement.

Perturbation of electrochemical system with an alternating potential or current signal causes a change in its energy. In order to limit these inconveniences during impedance measurements applied perturbation should be of small enough amplitude, have the shortest possible time of duration and should be continuous over entire time range [2, 3]. The first conditions does not constitute a serious problem at the realization stage. Most of the impedance measuring devices enables application of the perturbation of any amplitude. The way of perturbation signal generation in the FRA method, that is frequency by frequency, results in temporary discontinuities between signals even in commercial devices. Moreover, limitation of the time of measurement is connected with a simultaneous deterioration of the resolution of obtained spectrum or with a decrease in accuracy of the results.

Recently Darowicki and co-workers elaborated new, digital method of electrode impedance measurement. It utilizes one continuous perturbation signal of constant amplitude. The frequency of this signal is a function of time. Short Time Fourier Transformation (STFT) was employed in the analysis of the signal.

THEORETICAL DESCRIPTION OF THE METHOD

Presented method employs constant amplitude, sine potential signal, which frequency is a linear function of time:

$$u(t) = U_0 \cos\left\{\left[w_S + \left(\frac{dw}{dt}\right)t\right]t\right\} \qquad (1)$$

where:
$u(\tau)$ - potential perturbation signal
U_0 - signal amplitude
ω_s - initial frequency

$\frac{dw}{dt}$ - rate of frequency change

τ - time

As a result of this perturbation current response is obtained that, similarly to the perturbation, is a non-stationary signal. In order to determin e impedance spectrum of considered system one needs information about the energy simultaneously as function of time and frequency. Application of classical Fourier transformation allows to obtain only frequency decomposition. As a result of this operation the information about time-varying properties of the analyzed signal becomes hidden [4].

Joined time-frequency characteristic can be obtained with the use of Short Time Fourier Transformation (STFT) [5]:

$$STFT(t,w) = \int s(t)g(t-t)\exp(-jwt)dt \tag{2}$$

where:

STFT (t,ω) - STFT transform

s(τ) - analyzed signal

γ(τ) - window function

It is based on cutting out a fragment of the signal from analyzed characteristic with the use of a window function. Selected fragment is then subjected to Fourier transformation. This process is conducted in the entire time range of analyzed signal. As a result the characteristic in join time-frequency domain is obtained.

Application of modern measuring techniques employing analog-digital converters is in practice connected with utilization of discrete transformation form [5]:

$$STFT[k,n] = \sum_{i-0}^{L-1} s[i]g[i-k]\exp\left(\frac{-j2pni}{L}\right) \tag{3}$$

Performation of the above transformation on discrete time register enables acquisition of certain time-frequency grid, which knots contain information about the energy of analyzed signal (fig. 1).

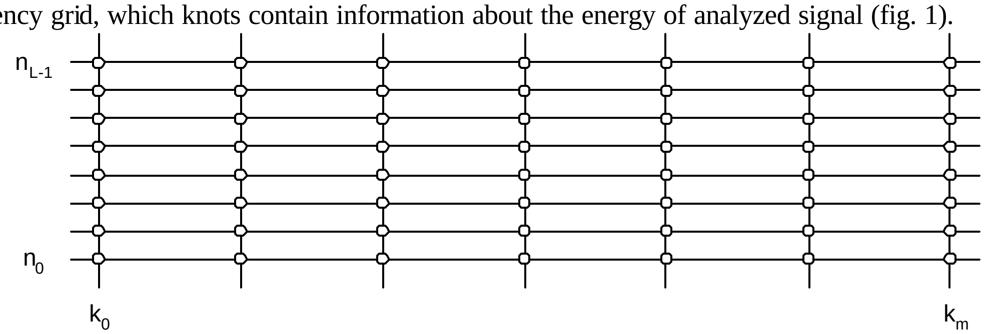

Fig. 1. Time-frequency grid obtained as a result of the STFT operation on discrete time register

Length of the window, that is the number of poin ts of analyzed time register subjected to single Fourier transformation, is equal to the number of frequency lines n. In case of constant sampling frequency this parameter decides about obtained frequency resolution:

$$\Delta f = \frac{f_S}{L-1} \tag{4}$$

where:

Δf - frequency resolution,

f_s - sampling frequency,

L - length of the window

The number of time lines k depends on the number of fragments cut out from the analyzed register with the use of the window function. Their number decides about obtained time resolution.

Not all knots of the time-frequency grid contain useful information allowing to determine values of impedance. Linear change of frequency in time causes that the maximum number of useful knots is given by the following relation:

$$m = \left| \left\lfloor \frac{f_K (L-1)}{f_S} \right\rfloor - \left\lceil \frac{f_P (L-1)}{f_S} \right\rceil \right| + 1 \tag{5}$$

where:
m - maximum number of useful knots
f_k - final frequency of the signal
f_p - initial frequency of the signal

Resolution of generated impedance spectrum (m) obtained at constant sampling frequency (f_S=const) depends on the range of analyzed frequencies (f_K, f_P) and length of the analyzing window.

In practice determination of impedance spectrum with the use of presented technique is a multi-step process. The first step is perturbation of the system with a non-stationary potential signal and simultaneous acquisition of the perturbation signal and response. Next m appropriate fragments of the signal are cut out from the recorded registers. These fragments are multiplied by suitable window function and in the next step they are subjected to Fourier transformation. As a result of this process complex values characterizing perturbation and response signals in frequency domain are obtained. Their quotient gives the value of system's impedance:

$$Z(w) = \frac{STFT(u\{t,w\})}{STFT(i\{t,w\})} \tag{6}$$

where:
$Z(\omega)$ - value of impedance,
$STFT(u\{t,w\})$ - STFT transform of potential perturbation signal,
$STFT(i\{t,w\})$ - STFT transform of current response signal

An important issue in selection of impedance technique is accuracy of obtained results. In classical impedance measuring methods, just as FRA, an increase in precision is attained by the elongation of time of measurement (integration time). It is known however, that it imposes a negative impact on the stability of analyzed system. In presented technique time of measurement depends on the rate of frequency change of the perturbation signal. Moreover, as equation (6) implies, accuracy of the results will be also dependent on the process of the STFT transformation, that is kind of applied window function and its length.

EXPERIMENTAL

Measurement system consisted of Agilent 33120A generator, Elpan EP-20 potentiostat and measuring card National Instruments PCI-MIO-16XE-50. Frequency of the perturbation signal having 10 mV amplitude was changed linearly from the initial value of f_s=100Hz to the final value of f_F=1000Hz. Constant sampling frequency f_s of 10000Hz was applied. For control of the measuring devices and analysis of the results computer programmes created with Lab View 5.1 National Instruments software were used.

Model equivalent circuit consisted of 31.2 Ω resistor connected in parallel with a capacitor of capacitance equal to 94.7 µF. Generated impedance spectra were analyzed using Boukamp software [6].

RESULTS AND DISCUSSION

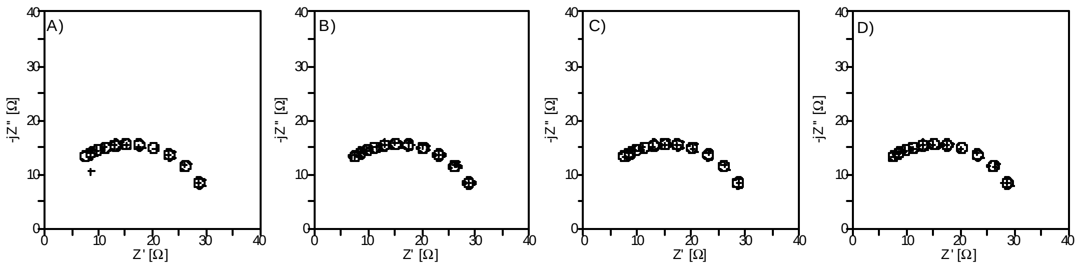

Fig. 2. Impedance spectra generated for different rates of frequency change. Rectangular window, window length L=127, A) df/dτ=9000Hz/s, B) df/dτ=900Hz/s, C) df/dτ=90Hz/s, D) df/dτ=9 Hz/s, + measured value, ○ theoretical value.

On fig. 2 there are presented impedance spectra of the investigated system generated by application of different rates of perturbation signal frequency change. Introduction of a window of the length 127 allowed, according to the equation (5), to obtain 11 complex values of impedance. Visible concentration of the spectrum in the range of higher frequencies is caused by linear frequency resolution. Relative errors committed during determination of values of system's components (tab. 1) are small. There is no visible decreasing trend in their magnitude with diminishing rate of scanning. It suggests that the rate of frequency change, so the time required for measurements, is not a factor having influence on the accuracy of the method.

Rate of frequency change [Hz/s]	ΔR/R 100%	ΔC/C 100%
9000	0,51	0,56
900	0,34	0,36
90	0,39	0,41
9	0,43	0,45

Table 1. Relative errors committed during determination of values of investigated system's elements for different rates of perturbation signal frequency change, rectangular window, length 127

For the highest rate of scanning 9000 [Hz/s] extreme value of impedance differs significantly from the other ones constituting the spectrum (fig. 2). The reason is an increase in the rate of perturbation signal frequency change that causes decrease in the length of obtained registers. If the size of registers is not appropriate then boundary fragments of the signal subjected to Fourier transformation are of not sufficient length - they are shorter than the analyzing window. These shortages can be substituted with zero values or with appropriate fragments of the signal; however, values of impedance obtained on their basis will be burdened with bigger error.

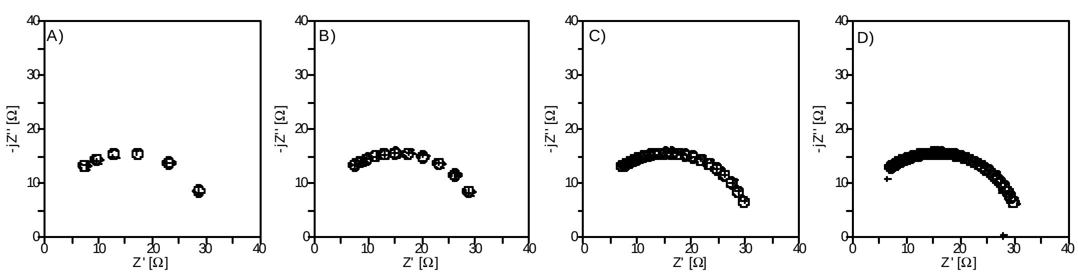

Fig. 3. Impedance spectra generated for constant rate of frequency change df/dτ=900Hz/s and rectangular window of the length: A) L=63, B) L=127, C) L=255, D) L=511, + measured value, ○ theoretical value.

The size of analyzing window is a factor deciding about the resolution of generated impedance spectrum. Its length is directly proportional to the number of obtained impedance values (fig. 3). The size of the window has a significant influence on the accuracy of obtained results. Increase in the length results in considerable improvement of the accuracy. However, application of too long window may lead to the appearance of erroneous results at the end of generated spectrum what has been already suggested (fig. 3D).

Size of analyzing window	ΔR/R 100%	ΔC/C 100%
63	0,95	1
127	0,34	0,36
255	0,19	0,20
511	0,11	0,12

Table 2. Relative errors committed during determination of values of investigated system's elements for different sizes of the analyzing window, rectangular window, the rate of frequency change 900 Hz/s

A phenomenon of the spectrum leakage to the side leaves is frequently encountered during transformation of signals from time domain into frequency domain [7]. It is caused by existence of the frequencies in the analyzed signal that are located between the n lines determined during the process of discrete Fourier transformation. In order to diminish this inconvenient effect a window technique is widely used. It is based on multiplication of the input signal by a suitable even function. A side effect of application of the window function is almost double degradation of frequency resolution.

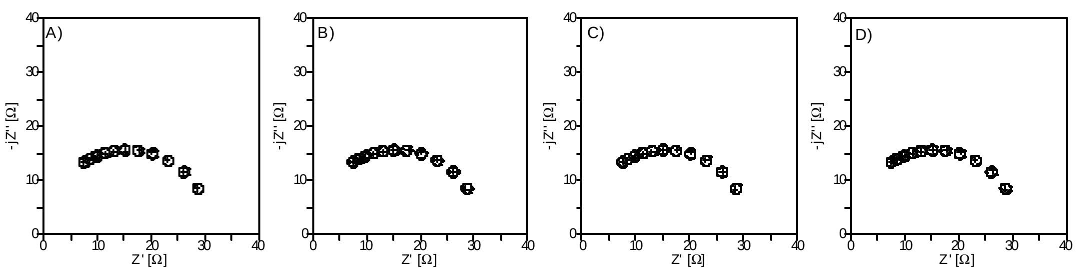

Fig. 4. Impedance spectra generated with the use of the window of length L=127, constant rate of frequency change $df/d\tau$=900Hz/s and window functions: A) Gauss' λ=1, B) Hamming's, C) Hanning's D) Rectangle, + measured value, ○ theoretical value.

The STFT transformation applied in the presented technique employs window function for the same purpose. Fig. 4 presents impedance spectra generated with the use of typical analyzing windows: Gauss', Hamming's, Hanning's and rectangular. The characteristics look similar, no significant deflections from the theoretical spectrum are visible. Errors, which burden determined values of the system's elements, show that the best accuracy of the results is attained with the use of rectangular window (tab. 3).

Analyzing window	ΔR/R 100%	ΔC/C 100%
Gauss λ=1	0,36	0,38
Gauss λ=10	0,46	0,49
Gauss λ=50	1,57	1,63
Hamming	0,41	0,43
Hanning	0,42	0,45
Prostok¹t	0,34	0,36

Table 3. Relative errors committed during determination of values of investigated system's elements for different functions of analyzing window, the rate of frequency change 900Hz/s, window length L=127

SUMMARY

Presented impedance measuring technique differs from presented so far by the type of perturbation and the method of analysis. Frequency of a constant amplitude perturbation signal changes in continuous way. Due to that fact investigated system is less likely to loose stability. Potential perturbation and current response are non-stationary signals that can be analyzed using the STFT transformation.

The investigations conducted on model equivalent circuit indicate that the rate of frequency change (time of measurement) does not influence the accuracy of obtained results in visible way. This feature enables application of presented technique to fairly stable systems where short time of measurement is required. It has been found that the magnitude of error depends on the length and type of applied window. Accuracy of the results increases with the increase in length of the register subjected to Fourier transformation; the best analyzing window is rectangular one.

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