Estimation of Parameters Obtained by Electrochemical Impedance Spectroscopy on Systems Containing High Capacities

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Abstract: Electrochemical systems with high capacities demand devices for electrochemical impedance spectroscopy (EIS) with ultra-low frequencies (in order of mHz), that are almost impossible to accomplish with analogue techniques, but this becomes possible by using a computer technique and accompanying digital equipment. Recently, an original software and hardware for electrochemical measurements, intended for electrochemical systems exhibiting high capacities, such as supercapacitors, has been developed. One of the included methods is EIS. In this paper, the method of calculation of circuit parameters from an EIS curve is described. The results of testing on a physical model of an electrochemical system, constructed of known elements (including a 1.6 F capacitor) in a defined arrangement, proved the validity of the system and the method.

Keywords: electrochemical measurements; measurement system; electrochemical impedance spectroscopy; supercapacitors

1. Introduction

Every system may be regarded in a frequency domain displaying frequency logarithm on the X–axis and logarithm of module and/or phase angle of transfer function on the Y–axis (Bode plot) [1–3]. For
the electrochemical system, the transfer function is, in fact, the impedance of an equivalent electrical circuit i.e., its complex form. That is why this method is named electrochemical impedance method (EIS) and it is widely used for characterization of electrochemical systems [4–14]. Applying alternate voltage, \( U(S) \), of different frequencies and constant amplitude to an electrical circuit, responding current, \( I(S) \), will appear [2,3]. Amplitude and phase angle of this current will depend on voltage and impedance, \( Z(S) \), of the circuit at that frequency:

\[
I(S) = \frac{U(S)}{Z(S)}
\]

where \( S = \sigma + j\omega \) is Laplace complex variable. For sinusoidal excitation the real part \( \sigma \) is equal to zero, so the \( S \) becomes \( S = j\omega \), where frequency, \( \omega \), is given in \( s^{-1} \).

Conventional impedance spectra are actually snapshots of transfer functions taken at certain well-defined states of the system (usually stationary, constant potential states). However, for a fuller description of electrochemical systems the evolution of impedance spectra should be investigated during the evolution of the system in both potential and time. With the progress of digital techniques this is becoming increasingly possible [15–17].

The system used for electrochemical measurements consisted of hardware (PC, AD-DA converter NI–621 produced by National Instruments and an analog interface developed at the Technical Faculty in Bor) and software for excitation and measurement (LABVIEW platform and originally developed application software) [18,19]. With the goal of achieving a full mathematical analysis of the measured data directly in the LabVIEW application, it was necessary to develop our own mathematical model which is implemented in the measurement software and described in this work. This was not possible with some commercially available fitting software packages (EqCwin, Z-view) [20].

The possibilities of the software described here are compared with the Thales software of the Zahner EIS firm [21,22]. Our model and software are more adequate to the real system because the model better describes real electrochemical systems taking into account the complexity of the processes. The mathematical model developed herein is adapted to the investigated class of electrochemical systems and it is strongly connected with the physical parameters of the system. That approach enabled us to obtain analytical values of mutual relationships between the physical parameters from the system response and, in that way, to make system optimization following some given criteria. This is a significant advantage in compare to the commercial software, where the model is not “visible”.

2. Theoretical Part

By recording amplitude and phase angle of the response current for every frequency value (excitation voltage known), one can obtain the module and the phase angle of impedance for that frequency; this is presented as one point on the Bode plot which gives the dependence of impedance module, \( Z \), on frequency, \( f \), in logarithmic scale. Logarithm is used in a goal to obtain linear dependences instead of exponential ones. At frequencies obtained by extrapolation of straight segments, some deviation from straight line appears, and the line slope changes gradually. From the heights of the horizontal regions and corner frequencies, one can calculate all the parameters of the circuit of which the Bode plot is recorded, i.e. to estimate the equivalent circuit parameters [23–25].
After years of investigating of electrochemical behavior of different electrode materials, different equivalent electrical circuits that exhibit the same response on excitations as considered electrochemical systems have been found [23–26]. One of the most common was the circuit presented in Figure 1.

**Figure 1.** Considered equivalent electrical circuit.

![Equivalent electrical circuit](image)

R₀ corresponds to the resistance of electrolyte and electrode material, and its value is on an order of magnitude of milliohms (mΩ) or Ohms (Ω). Capacity C₀ corresponds to double layer formed on the electrolyte side. Resistances R₁ and R₂ (order of magnitude ohm to tens Ohms) are related to slow processes of adsorption and diffusion, as well as the capacitances C₁ and C₂. As a matter of fact, the branch R₁C₁ exhibits and describes the inconstancy of parameters in R₂C₂ branch. R₃ is resistance of self-discharging, meaning that it is reciprocal to leakage current. Its value is on the order of hundreds of Ohms to tens of kiloohms.

For the adopted equivalent circuit (Figure 1) in a general case the impedance equation is complex and not clear enough. So, here a step by step method is applied, one frequency domain after other, knowing the nature of the process, i.e. orders of magnitude of the circuit parameters. For very low frequencies (on the order of μHz) all capacitors do not conduct electricity, so the impedance of the circuit remains the serial connection of R₀ and R₃:

\[ Z₁ = R₀ + R₃ \]

where Z₁ is correlated to the first (the highest) horizontal plateau in Figure 5. At frequencies on the order of mHz capacitor C₂ conducts, while C₁ and C₀ still are infinite resistances; so, the equivalent circuit has the shape presented in Figure 2.

**Figure 2.** Equivalent circuit for the second frequency domain (on the order of mHz).

![Equivalent circuit for the second frequency domain](image)
The impedance of the circuit presented in Figure 2 is:

\[ Z = \frac{S\left(\left( R_1 + R_2\right) \cdot R_0 \cdot C_2 + R_2 \cdot R_1 \cdot C_2 \right) + R_0 + R_3}{SC_2\left( R_2 + R_3\right) + 1} \]

From the conditions for the impedance zero and pole, the corner frequencies may be obtained as:

\[ f_1 = \frac{1}{2\pi \left( R_2 + R_3\right) \cdot C_2} \]

\[ f_2 = \frac{R_0 + R_3}{2\pi \left( \left( R_2 + R_3\right) \cdot R_0 \cdot C_2 + R_2 \cdot R_1 \cdot C_2 \right)} \]

At some higher frequencies (in order of dozens mHz) \( C_2 \) becomes short circuit, while \( C_0 \) and \( C_1 \) are still in break, so the height of this horizontal region is:

\[ Z_2 = R_0 + R_{23} \quad \text{where} \quad R_{23} = \frac{R_2 \cdot R_3}{R_2 + R_3} \]

At frequencies on the order of hundreds of mHz, \( C_1 \) starts conducting, \( C_0 \) is still in break, and \( C_2 \) is a short circuit; the equivalent circuit then has the shape given in Figure 3.

**Figure 3.** Equivalent circuit for fourth frequency domain (on the order of hundreds of mHz).

The impedance of the circuit is then:

\[ Z = \frac{S\left(\left( R_1 + R_{23}\right) \cdot R_0 \cdot C_1 + R_{23} \cdot R_1 \cdot C_1 \right) + R_0 + R_{23}}{SC_1\left( R_1 + R_{23}\right) + 1} \]

From the previous equation, corner frequencies may be obtained as:

\[ f_3 = \frac{1}{2\pi \left( R_1 + R_{23}\right) \cdot C_1} \]

and

\[ f_4 = \frac{R_0 + R_{23}}{2\pi \left( \left( R_1 + R_{23}\right) \cdot R_0 \cdot C_1 + R_{23} \cdot R_1 \cdot C_1 \right)} \]

Next horizontal region is obtained at frequencies higher then 1 Hz, when capacitor \( C_1 \) becomes a short circuit, as well as \( C_2 \), while \( C_0 \) still does not conduct; so it can be written:
\[ Z_3 = R_0 + R_{123} \]

where \( R_{123} \) is a parallel connection of \( R_1, R_2 \) and \( R_3 \).

At relatively high frequencies (on the order of kHz) \( C_0 \) starts leading, while \( C_1 \) and \( C_2 \) are short circuits, so the equivalent circuit becomes as in Figure 4.

**Figure 4.** Equivalent circuit for sixth frequency domain (on the order of kHz).

![Equivalent Circuit Diagram](image)

The impedance of such circuit is:

\[
Z = \frac{SRC_0 + R_0 + R_{123}}{SR_{123}C_0 + 1}
\]

and corner frequencies are:

\[
f_5 = \frac{1}{2\pi R_{123} C_0}
\]

\[
f_6 = \frac{R_0 + R_{123}}{2\pi R_0 R_{123} C_0}
\]

At the end, the lowest horizontal part of Bode plot is obtained at highest frequencies (on the order of tens of kHz) when \( C_0 \) is in short circuit, too, so:

\[ Z_4 = R_0 \]

The theoretical Bode plot for the whole equivalent circuit given in Figure 1 is presented in Figure 5.

**Figure 5.** Theoretical Bode plot for adopted equivalent circuit.

![Bode Plot Diagram](image)
3. Experimental

Testing of the system and developed method was done on a physical model of the electrochemical system, constructed of known elements in a defined arrangement as in Figure 1.

The elements that the physical model was made of were: $R_0 = 3 \, \Omega$; $R_1 = 39 \, \Omega$, $R_2 = 90 \, \Omega$; $C_0 = 0,12 \, \mu F$; $C_1 = 30 \, mF$; $C_2 = 1,6 \, F$ and $R_3 = 1 \, k\Omega$ (alternatively $R_3 = 150 \, \Omega$). Experiments were performed using the following parameters: DC level 10 mV, AC amplitude 5 mV, frequency range 30 $\mu$Hz up to 1 Hz. The obtained curves are presented in Figures 6 and 7.

**Figure 6.** Experimentaly obtained Bode plot for the physical model ($R_3 = 1 \, k\Omega$).

$\text{Figure 6.}$

**Figure 7.** Experimentaly obtained Bode plot for the physical model ($R_3 = 150 \, \Omega$).

$\text{Figure 7.}$
From the experimentally obtained Bode curve, all parameters of the system have been determined by following the next steps:

From the plateau 4, $R_0$ is obtained immediately from $R_0 = Z_4$;

Horizontal region 1 is equal to $Z_1$, and then $R_3$ can be calculated from:

$$R_3 = Z_1 - R_0$$

Plateau 2 gives $Z_2$, and then applying:

$$R_{23} = Z_2 - R_0$$

Using the method described above, values of the circuit parameters have been calculated from the plot given in Figure 6. The results are compared with those obtained using the commercial software EqCwin applied to the data from Figure 6 (Table 1).

| Parameter | Actual value | Measured value | EqCwin value |
|-----------|--------------|----------------|--------------|
| $R_1$ [Ω] | 39           | 41             | 45           |
| $C_1$ [F] | 0.03         | 0.03           | 0.028        |
| $R_2$ [Ω] | 90           | 93             | 93.4         |
| $C_2$ [F] | 1.6          | 1.58           | 1.59         |
| $R_3$ [Ω] | 1,000        | 992            | 1,003        |
The plot in Figure 7 gives similar results, except $R_3$, that is, in this case, 150 $\Omega$. Plots in Figures 6 and 7 do not have the fourth plateau for highest frequencies, so $R_0$ could not be determined from such a curve.

4. Conclusions

Table 1 shows a very good agreement between the actual values of the electrical components forming the investigated physical model, the values obtained by the method described in this work and the values obtained using a commercial software product. In that way the method, hardware and software are fully confirmed. It should be emphasized that this method describes the system very well and clearly, but its big disadvantage is that it works with very low frequencies (on the order of $\mu$Hz), that means a need for special equipment (like this described in the present work, or similar) and the experiments have a very long duration. The second problem may be resolved by starting the experiment from a frequency $f_2$ (much higher than previously indicated), but in that case $R_3$ must be determined by some other method (for example potentiostatic).

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