Influence of the Microchannel Height on the Impedance of a Flow Electrochemical Cell with Planar Interdigitated Electrodes

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Abstract: The article considers an analytical approach for determining the impedance of an electrochemical cell with planar interdigitated microelectrodes located in a microchannel and for estimation of the effect on the impedance characteristics of the microchannel height. The proposed approach is based on the use of an electric equivalent circuit of the electrochemical cell for determining its impedance and a mathematical simulation of the distribution of the electrical potential in the structure of interdigital microelectrodes located in a microchannel to determine the constant electrochemical cell. Using this approach, the analysis of impedance dependencies is performed and the frequency dependences of the real and imaginary parts, the modulus and the argument of the impedance of the electrochemical cell with the specific geometry of the interdigital microelectrodes for different microchannel heights are determined.

Keywords – electrochemical cell, interdigitated microelectrodes, impedance, cell constant, impedance dependence

1. Introduction
Presently, non-destructive methods for investigating substances and materials become more and more urgent. One of these methods is the method of impedance spectroscopy. Sensors that implement impedance measurements are used in a wide variety of fields, such as medical and microbiological researches, measurement and control of substance concentrations, study of corrosion inhibitors of metals and nanostructures, monitoring of energy carriers (batteries, solar cells, fuel cells) [1–4].

The method of impedance spectroscopy is based on the study of the response of the system to the external electric effect and the measurement of its impedance at various frequencies. For measuring the impedance, special electrochemical cells with two or three electrodes are used, whose design, depending on the object of control and the purposes of the investigation, can be different. A large number of electrodes for the impedance measurement are known, such as coaxial electrodes, disk and ring-shaped, planar and volume, symmetric and asymmetric ones [5]. Among the microelectrodes the planar interdigitated ones were most widely used [6–10].
Presently, impedance methods are widely used in microsystem technology to develop microanalytical systems. In these systems, flow electrochemical cells are used for the analysis of liquid substances, in which the microelectrode system is located in the microchannel and contacts with the flow of the liquid being analyzed. For this structure of the electrochemical cell, the results of the analysis are affected by a number of additional factors that require detailed consideration and must be taken into account in the development of microsystems for measuring impedance and interpretation and using analysis results.

2. Formulation of the Problem
Measurement of the impedance in a flow electrochemical cell has a number of features, among which the main ones are the following:
1) the test substance (liquid) is constantly shifted relative to the electrode system, and this can affect the magnitude of the impedance;
2) the channel of the electrochemical cell in the electrodes region has limited dimensions, which affect the magnitude of the impedance.

At a low flow velocity, the first feature can be ignored, due to the small effect on the magnitude of the impedance. The second feature relates with small channel sizes and leads to an increase in the measured value of the impedance.

Currently, flow electrochemical cells with interdigital electrodes obtained by the methods of microsystem technology are beginning to be widely used in measuring impedance. In these cells, the microelectrode system is located in a microchannel, the height of which is limited and slightly different from the size of the microelectrode dimensions. For these systems, the estimation of the influence of the microchannel dimensions on the measured impedance is an actual problem.

In this regard, the aim of this paper is to develop the analytical approach that allows one to estimate the influence of the microchannel height on the impedance of a flow electrochemical cell with planar interdigitated electrodes.

3. Theory
Figure 1(a) shows the design of the flow electrochemical cell with planar interdigitated microelectrodes (IME). To analyze the impedance of the electrochemical cell, one should consider its equivalent circuit, which is shown in figure 1(b). The elements of this circuit characterize the various physical processes occurring in the cell. The resistances \( R_e \) represent the resistances of the interdigitated microelectrodes themselves. The active resistance of the electrolyte solution between the microelectrodes is characterized by the resistance \( R_{se} \). The capacitances of the double electrical layers at the boundary of the microelectrodes with the electrolyte and the capacity of the electrochemical cell are represented by capacitances \( C_{dl} \) and \( C_c \), respectively.

Based on the equivalent electrical circuit of the electrochemical cell, its impedance can be represented as follows

\[
Z_c = \frac{C_{dl}(2C_c + C_{dl})R_{se} - j\omega C_c C_{dl}^2 R_{se}^2}{\omega^2 C_c^2 C_{dl}^2 R_{se}^2 + (2C_c + C_{dl})^2} + 2R_e,
\]

where \( Z_c \) is the impedance of the electrochemical cell; \( \omega \) is the frequency.
The parameters included in the expression for the impedance of the electrochemical cell, depending on the influence of the microchannel height on them, can be divided into two groups:

1) parameters that do not depend on the microchannel height;
2) parameters that depend on the microchannel height.

The parameters that are independent of the microchannel height include the resistances of the interdigitated microelectrodes and the capacitances of the double electrical layers at the boundary of the microelectrodes with the electrolyte solution. The resistance of the interdigitated microelectrode can approximately be determined as the sum of the resistance of the connecting film conductor and the resistance of the series of parallel-connected finger electrodes

\[ R_c \approx R_{\text{be}} + \frac{R_f}{N}, \]  

where \( R_{\text{be}} \) and \( R_f \) are the resistance of the connecting film conductor and the resistance of the finger electrode, respectively; \( N \) is the number of fingers in the microelectrode.

The resistances \( R_{\text{be}} \) and \( R_{\text{be}} \) can be determined using the characteristics of the film layer from which the microelectrodes are made and the geometric dimensions of these microelectrodes, as follows

\[ R_{\text{be}} = \rho_s \frac{L_{\text{be}}}{b_{\text{be}}}, \]  

\[ R_f = \rho_s \frac{L_f}{b_f}, \]

where \( \rho_s \) is the specific surface resistance of the film layer; \( L_{\text{be}} \) and \( L_f \) is the length of the connecting film conductor and the finger electrode, respectively; \( b_{\text{be}} \) and \( b_f \) is the width of the connecting film conductor and the finger electrode, respectively.

**Figure 1.** Structure (a) and equivalent electrical device (b) of the electrochemical cell.
The capacity of the double electrical layer at the interface between the electrolyte solution and the electrode is equal to
\[ C_{\text{dl}} = (L_{\text{el}}b_{\text{el}} + NL_{\text{el}}b_{\text{el}})C_0, \]
where \( C_0 \) is the specific capacitance of the double electrical layer at the interface between the electrolyte solution and the electrode.

The parameters whose values depend on the microchannel height are the resistance of the electrolyte solution between the microelectrodes and the capacity of the electrochemical cell. For electrochemical cells, these parameters depend on the properties of the electrolyte, the shape, the geometric dimensions and location of the microelectrodes and the shape and dimensions of the cell itself. The dependencies of above-mentioned parameters on these factors can be represented as follows
\[ R_e = K_e\rho_e, \]
\[ C_e = \frac{\varepsilon_0\varepsilon_r}{K_e}, \]
where \( K_e \) is the cell constant with IME; \( \rho_e \) is the specific resistance of electrolyte; \( \varepsilon_0 \) is the electrical constant; \( \varepsilon_r \) is the relative permittivity of the electrolyte solution.

In expressions (6) and (7), the parameter \( \rho_e \) and the product \( \varepsilon_0\varepsilon_r \) characterize the properties of the electrolyte solution. The cell constant \( K_e \) entering into these expressions is determined by the geometrical characteristics of the cell and the electrodes, that is, their shape, dimensions and location. The microchannel height is a geometric characteristic of the flow electrochemical cell and affects the value of the cell constant and, consequently, the resistance of the electrolyte solution between the electrodes.

The values of the resistance of the electrolyte solution between the electrodes and the capacitance of the electrochemical cell can be determined analytically using expressions (6) and (7). The following algorithm is proposed for this:
1) the potential distribution in the cell with the IME at a constant electric field is determined;
2) based on the potential distribution in the cell with IME, the resistance of the electrolyte solution between the electrodes at a constant current is determined;
3) using the expression (6), the value of the cell constant is found;
4) using the expression (7), the value of the capacitance of the electrochemical cell is determined.
Consider the steps of the proposed algorithm in detail.

3.1. Determination of the potential distribution in the cell with the IME at a constant electric field

To determine the potential distribution in the electrochemical cell at a constant electric field, the analytical method proposed in [11] is used. According to this method, an elementary cell is allocated in the system of the IME, the translational transfer of which can form the entire system of the IME. The allocated unit cell is the modeling domain and is shown in figure 2(a). For this cell, the distribution of the electric potential is determined by replacing the modeling domain with an equivalent structure and dividing this structure into three regions (figure 2(b)).
\[ \varphi_j = \frac{1}{l_j b_j \sigma_e} \left[ \delta_0^{(j,i)} - \delta_0^{(j,a)} + \delta_0^{(j,v)} \right] + \frac{2}{l_j b_j \sigma_e} \sum_{k=1}^{\infty} \left[ (-1)^k \delta_0^{(j,x)} - \delta_0^{(j,a)} + \delta_0^{(j,v)} \right] \]

\[ \cdot \frac{1}{(k \pi / l_j)^2} \cos \left( \frac{k \pi x_j}{l_j} \right) \cos \left( \frac{m \pi y_j}{b_j} \right) + \frac{4}{l_j b_j \sigma_e} \sum_{m=1}^{\infty} \sum_{k=1}^{\infty} \left[ (-1)^k \delta_0^{(j,x)} - (-1)^m \delta_0^{(j,a)} + \delta_0^{(j,v)} \right] \]

\[ \cdot \frac{1}{(k \pi / b_j)^2 + (m \pi / b_j)^2} \cos \left( \frac{k \pi x_j}{l_j} \right) \cos \left( \frac{m \pi y_j}{b_j} \right), \]

where \( \varphi_j \) is the potential in the region \( j \); \( l_j \) and \( b_j \) are the length and width of the region \( j \), respectively; \( \sigma_e \) is the specific electrical conductivity of the electrolyte; \( x_j, y_j \) - coordinates of the region \( j \); \( k \) and \( m \) are summation indices with respect to the coordinates \( x_j \) and \( y_j \), respectively; \( s, t, u, v \) are the indices of regions adjacent to the region \( j \); \( \delta \) are the weight coefficients that characterize the components of the current density on the boundaries between the region.
In order to determine the unknown weight coefficients in the expressions for the potential distribution in the regions of the unit cell, the adjoint boundary conditions are used on the boundaries between adjacent regions. A detailed description of this technique is presented in [11].

3.2. Determination of the resistance of the electrolyte solution between the electrodes at a constant current.

Using the electric potential distribution in the unit cell, the linear resistance between the electrodes located in the cell is determined

\[
\vec{R}_e = \frac{\varphi_{el2} - \varphi_{el1}}{b/2},
\]

where \( \vec{R}_e \) is the linear resistance of the electrolyte between the electrodes in the unit cell at a constant current; \( \varphi_{el1}, \varphi_{el2} \) are the potentials of the electrodes 1 and 2, respectively; \( j_i \) is the current density on the electrode 1, which is determined from the potential distribution in region 1.

Using the found value of the linear resistance between the electrodes in the unit cell, the resistance of the electrolyte solution at a constant current is calculated for the entire electrochemical cell with IME according to the following formula

\[
\vec{R}_e = \frac{\vec{R}_a}{L_i (2N - 1)},
\]

where \( \vec{R}_e \) is the resistance of the electrolyte between the electrodes in the electrochemical cell at a constant current.

3.3. Determining the value of the cell constant

The value of the cell constant is determined on the basis of the relation (6), using the following expression

\[
K_c = \vec{R}_e \sigma_c
\]

3.4. Determination of the capacitance of the electrochemical cell

The capacitance of the electrochemical cell is determined using the relationship (7) and the found value of the cell constant (11).

4. Results of Modeling

The obtained model was used to investigate the effect of microchannel height on the impedance of an electrochemical cell with interdigitated microelectrodes. As the material of microelectrodes, platinum with a specific resistivity equal to \( 1.07 \cdot 10^{-6} \, \Omega \cdot m \) was chosen. The geometric dimensions of the microelectrodes fingers had the following values: thickness – 0.5 \( \mu \)m, length – 1000 \( \mu \)m, width – 150 \( \mu \)m. The distance between the microelectrodes fingers was chosen to be 150 \( \mu \)m. The number of the fingers in one microelectrode was assumed to be 14. The specific capacity of the double electrical layer at the interface of the electrolyte solution-electrode was chosen to be equal to 10 \( \mu F/cm^2 \).
Figure 3 shows the impedance dependencies of the electrochemical cell with IME for the five microchannel height values: 50 μm, 100 μm, 150 μm, 200 μm and 500 μm for the fixed values of the conductivity ($\sigma_e=5\cdot10^{-5}$ S/m) and the relative dielectric permeability ($\varepsilon_r=27$) of the electrolyte solution. Figures 4 and 5 present the frequency dependences of the real and imaginary parts of the impedance of the electrochemical cell with IME for different values of the microchannel height and for the values of the electrolyte solution parameters indicated above. Figures 6 and 7 show the frequency dependences of the modulus and the argument of the impedance of the electrochemical cell with IME for the different values of the microchannel height and for the electrolyte solution parameters indicated above.

**Figure 3.** Impedance dependences of the electrochemical cell for the different values of microchannel height $h$: $\sigma_e=5\cdot10^{-5}$ S/m; $\varepsilon_r=27$.

**Figure 4.** Frequency dependences of the real part of the electrochemical cell impedance for the different values of microchannel height $h$: $\sigma_e=5\cdot10^{-5}$ S/m; $\varepsilon_r=27$.

5. The results

The analysis of the impedance dependences of the electrochemical cell with IME, presented in figure 3, shows that, for small values of the microchannel height, the impedance of the cell strongly depends on the microchannel height. In the range of the microchannel height equal to 50...150 μm, a significant change of the impedance of the electrochemical cell from the microchannel height is observed. Beginning with the microchannel height of 200 μm, the impedance depends little on the height.

The frequency dependences of the real part of the impedance of the electrochemical cell with IME (figure 4) have the following features. With increasing the microchannel height, the real part of the impedance of the electrochemical cell with IME decreases. In the frequency range from 1 kHz to 1 MHz, the real part of the impedance does not depend on the frequency for all considered microchannel height values. It is determined by the resistance of the electrolyte solution in the cell with IME. At frequencies above 1 MHz, the real part of the impedance decreases with increasing the frequency.

For the frequency dependences of the imaginary part of the impedance of the electrochemical cell with IME (figure 5), the following features are characteristic. At low frequencies (up to 15 kHz), the imaginary part of the impedance decreases with increasing the frequency. This is due to the effect of the capacitance of the double electrical layers on the boundaries between the electrolyte solution and the electrodes. Further, the imaginary part of the impedance of the electrochemical cell increases with increasing the
frequency and reaches a maximum at 8...10 MHz. After reaching the maximum, the imaginary part of the impedance of the electrochemical cell decreases. The main influence on the change of the imaginary part of the impedance in the high-frequency region is provided by the capacitance of the electrochemical cell. With increasing the channel height, the imaginary part of the cell impedance decreases throughout the frequency range.

The analysis of the frequency dependences of the electrochemical cell impedance module, presented in figure 6, shows that the impedance module at frequencies from 1 kHz to 1 MHz is determined by the real part of the impedance. This follows from a comparison of the frequency dependences of the real part of the impedance (figure 4) and the impedance module (figure 6). In the frequency range from 1 to 10 MHz, the impedance module is determined by the real and imaginary parts of the impedance. Above 10 MHz, the value of the impedance module is mainly due to its imaginary part.

The frequency dependences of the argument of the impedance of the electrochemical cell with IME (figure 7) have the following features. Firstly, the argument of the electrochemical cell impedance at the frequencies above 10 kHz is practically independent of the microchannel height. For the all considered microchannel heights, the frequency dependences of the argument at these frequencies have the same view. The second feature is that the argument of the impedance has in the certain frequency range (approximately 5 to 60 kHz) the maximum value. Below the lower cutoff frequency (5 kHz) the argument decreases due to the influence of the capacitance of the electric double layers on the boundaries of the electrolyte solution - electrodes. In this frequency range, the dependence of the argument on the

Figure 5. Frequency dependences of the imaginary part of the electrochemical cell impedance for the different values of microchannel height $h$: $\sigma_e=5\cdot 10^{-5}$ S/m; $\varepsilon_r = 27$.

Figure 6. Frequency dependences of the module of the electrochemical cell impedance for the different values of microchannel height $h$: $\sigma_e=5\cdot 10^{-5}$ S/m; $\varepsilon_r = 27$. 
microchannel height of the electrochemical cell is observed. Above the upper limit of the indicated frequency range, the decrease in the impedance argument is due to the influence of the capacitance of the electrochemical cell.

Figure 7. Frequency dependences of the argument of the electrochemical cell impedance for the different values of microchannel height $h$: $\sigma_e = 5 \cdot 10^{-5}$ S/m; $\varepsilon_r = 27$.

Using the obtained results, it is possible to indicate the frequency ranges in which the parameters of the electrolyte solutions under investigation should be determined from the results of the impedance measurements. The conductivity of the electrolyte solution should be determined from the frequency dependence of the real part of the impedance in the frequency range where the real part of the impedance is constant. For the electrochemical cell under consideration, this frequency range lies below 1 MHz. In this case it is necessary to take into account that the real part of the impedance depends on the microchannel height. The relative permittivity of the electrolyte solution should be determined from the frequency dependence of the impedance argument with the known conductivity of this solution found from the frequency dependence of the real part of the impedance. The frequency range at which the relative permittivity of the electrolyte solution should be determined must be chosen above 10 MHz.

6. Conclusion
The approach is proposed for determining the impedance dependence of the electrochemical cell with interdigitated microelectrodes and the frequency dependences of the impedance characteristics of the cell. The account of the electrochemical processes taking place in the electrochemical cell is carried out on the basis of its equivalent electric circuit. To find the cell constant, an analytical model is used allowing one to determine the potential distribution in the interdigitated microelectrode system and the current density at the boundary between the electrode and the electrolyte solution.

Using the proposed approach, the impedance dependences of the specific electrochemical cell with interdigitated microelectrodes, as well as the frequency dependences of the real and imaginary parts of the impedance, the module and the argument of the impedance have been determined for the different microchannel heights. The results of modeling these dependences allow one to specify the frequency ranges on which the impedance characteristics of the electrochemical cell can be used to determine the parameters of the electrolyte solution under study.
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