Measurement of Electrical Resistance of Liquid Electrolytes and Materials Containing Them

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Abstract

Measurement of the electrical conductivity of electrolytes and heterogeneous materials containing them is accompanied by numerous physical and electrochemical processes, complicating measuring and interpretation of data. As a result, the measurement of the electrical conductivity of such a system is a difficult and not finally resolved problem. The new method of resistance measurement of the electrolytic systems is substantiated and tested on example of heterogeneous electrolytic system "lignin-calcium chloride water solution" in this article. The method is based on measurement of resistance of the electrolytic system at different voltages (DC) on the cell and the consequent approximation of the acquired data taking into consideration volume charges and potential barriers arising on the boarders of electrodes and electrolytic materials. Extrapolation of the resistance to the limiting small current lets one obtain a characteristic value of the active resistance of the electrolytic system. The method is technically simple, inexpensive and has several advantages compared to the methods based on AC measurements.

Keywords

Electrolyte, Conductivity, Conductometry, Resistance

1. Introduction

Currently, high-frequency contact and non-contact conductometry with the introduction of an equivalent substitution circuit based on the use of lumped parameters R, L, C [1] [2] [3] [4] [5] are mainly used to determine the electrical conductivity of electrolytes. The resistance is the result of the interaction of ions

with each other, preventing the directed movement of ions between the electrodes. Inductance occurs as a manifestation of the energy of an ion as a charged particle as it moves under the action of an external electromagnetic field applied to the electrodes. The appearance of capacitance is caused by both polarization effects and capacities arising between positively and negatively charged ions, like the plates of mini-capacitors.

The complex resistance, according to [1], is defined by the following way:

$$Z = \frac{(R + j\omega L)\left(-j\dfrac{1}{\omega C}\right)}{R + j\left(\omega L - \dfrac{1}{\omega C}\right)};$$

$$Z = \frac{R\dfrac{L}{C} - \dfrac{R}{\omega C}\left(\omega L - \dfrac{1}{\omega C}\right)}{R^2 + \left(\omega L - \dfrac{1}{\omega C}\right)^2} - j\frac{\dfrac{L}{C} - \left(\omega L - \dfrac{1}{\omega C}\right) + \dfrac{R^2}{\omega C}}{R^2 + \left(\omega L - \dfrac{1}{\omega C}\right)^2}.$$

At resonance $I_m Z = 0$:

$$Z = \frac{\dfrac{L}{C} - \left(\omega L - \dfrac{1}{\omega C}\right) + \dfrac{R^2}{\omega C}}{R^2 + \left(\omega L - \dfrac{1}{\omega C}\right)^2} = 0.$$

As a result:

$$R = \sqrt{\omega L - \left(\dfrac{1}{\omega C} - \omega L\right)};$$

$$R = \sqrt{\dfrac{L}{C} - \omega^2 L^2}.$$

To determine the resonant frequency, a known program-set frequency is supplied to the measuring cell from the frequency generator.

We have found that during the measurements of the electrical conductivity of electrolytes and materials containing them with use of methods [1] [2] [3] [4] [5] and their analogues volume charges and potential barriers arise on the surface and near the measuring electrodes due to the establishment of thermodynamic equilibrium between ions and electrodes material. This feature isn't taken into account in these methods.

In accordance with the foregoing, we can conclude, that the main disadvantages of the methods [1] [2] [3] [4] [5] are low accuracy and low efficiency associated with tuning the circuit at resonance, the dependence of capacity between anode, cathode and electrolyte on the magnitude of the normal component of the electric field [6].

We propose a new advanced contact method for determination of electrical conductivity of electrolytes and materials containing them with use of measuring cell. The proposed method takes into account the defined feature. It based on electrical conductivity dependence on the applied constant voltage for a discrete

number of points with further extrapolation of the applied voltage to the polarization threshold voltage region to eliminate the influence of the polarization resistance of the electrodes and non-linear effects of ion dynamics.

During the measurements of the electrical conductivity of electrolytes and materials containing them bulk charges and corresponding potential barriers appear on the surface and near the electrode due to the establishment of thermodynamic equilibrium between the ions and the substance of the electrode [7]. When a current occurs, the concentration of ions in the space charge layer dynamically changes, and over time, in the volume of the electrolyte. The transfer of charged particles is accompanied by diffusion and reduction-oxidation of ions on the surfaces of the electrodes.

It's known [8], that in the field of application of the Debye-Hückel theory of electrical conductivity of electrolytes, conduction ions undergo ion inhibition by the ionic atmosphere, which is localized around the central ion and moves in the opposite direction due to the electric field, and when the ions interact with current increase, the ionic atmosphere deforms and its shift to the "tail" region of the main ion. To describe concentrated solutions, it is necessary to take into account the non-Coulomb part of the inter-ion interaction, in particular, the size of ions.

Qualitatively, the picture is presented in such a way that the ions, moving under the action of an electric field, make forced movements across the field, "flowing around" electron clouds with a coincident charge. In addition, the ions that fall into the region of attraction of an ion of the opposite sign (making up the "cloud"), slow down their main movement due to the action of the external field.

It's possible to build the analogy between the charge transfer in the electrolyte and the hydrodynamics of deformable particles. Since the frictional force in the flow around an elongated ellipsoid and a uniform ball is slightly different at low flow velocities [9], the forced transverse motion of ions caused by interaction with other ions and ionic clouds can be considered a more significant factor affecting resistance. In the first approximation, the degree of "stretching" of a cloud is proportional to the strength of the current, and at the same time the "resistance" to charge transfer decreases due to a decrease in the cross section of the cloud and, accordingly, the amplitude of the transverse "flow" of the cloud with ions.

The combination of electrostatic and dynamic processes in the cell leads to complex current-voltage characteristics of electrolytes at a constant current and, especially, at an alternating and pulsed current.

Taking as the "unperturbed" resistance of the electrolyte electrical resistance in the conditions of the minimal influence of the above-mentioned dynamic effects of ion transport and polarization effects, as well as the effects of accumulation of electrochemical products reactions, we come to the need for a minimum measurement time and extrapolation of measurement results to zero current and threshold cell voltage. Positioning the approximant of the function $R = R(U)$, we define the desired unperturbed resistance

$$R_0 = \left.\frac{\mathrm{d}U}{\mathrm{d}I}\right|_{U \to U_0}, \tag{1}$$

where U_0 is the effective threshold voltage on the cell.

Then

$$\mathrm{d}I = \mathrm{d}\left(\frac{U}{R(U)}\right) = \frac{R(U)\mathrm{d}U - U\left(\mathrm{d}R/\mathrm{d}U\right)\mathrm{d}U}{R(U)^2}; \tag{2}$$

$$R_0 = \left.\frac{R(U)^2}{R(U) - U\left(\mathrm{d}R/\mathrm{d}U\right)}\right|_{U \to U_0}. \tag{3}$$

For approximants of the form $R = aU/(1 + bU)$, the effective threshold voltage on the cell is $U_0 = -1/b$. Corresponding expressions for approximants of other types can be easily obtained.

2. Description of the Proposed Method

The proposed new method is based on the using of device developed by the authors and described in paper [10]. The method includes the following steps.

1) Filling the measuring cell with the studied material.

2) Performing a series of measurements at a constant current. Measurements should be started with the minimum currents and the measurement time should be minimized. Each measurement should be accompanied by a mirror inverted current pulse to minimize the effects of a change in space charge and the accumulation of products of electrochemical reactions. To minimize random errors, for each measurement, 10 readings of the analog-to-digital converter should be performed. The time diagram of voltage changing is given in **Figure 1**.

3) Approximation of measurement results by an adequate function, and determination the threshold polarization voltage U_0. As approximating functions, Pade approximants of low order should be used [11]:
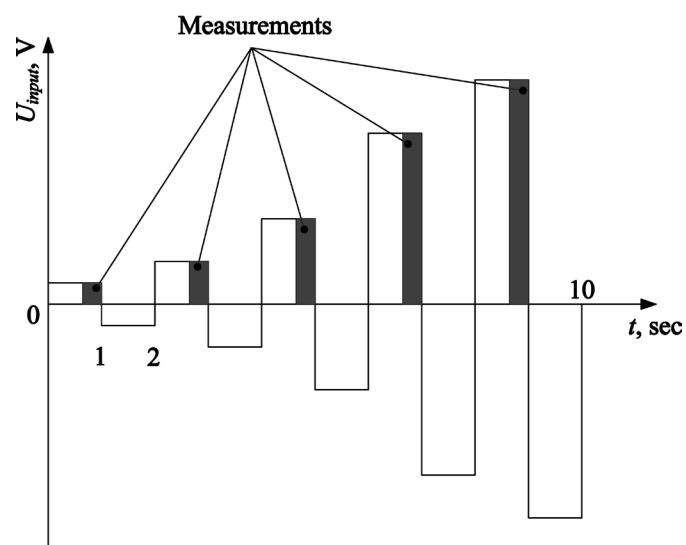
Figure 1. Time diagram of voltage on a measuring cell.

$$R_x(U) = \frac{aU}{1 + bU}; \; R_x(U) = \frac{r - aU}{1 - bU}; \; R_x(U) = \frac{r - aU + bU^2}{1 + cU^2}.$$

When choosing a function approximating measurements, we proceed from the assumption of monotonicity and continuity $R_x = f(U_x)$ at $U_x \to U_0$ (in the region of minimum measurement voltages).

4) Extrapolation of measurement results using model (3) and calculation of the corresponding unperturbed electrical resistance R_0.

5) Calculation of the electrical conductivity (ρ) in accordance with the formula:

$$\rho = A/l \cdot R_0 ,$$

where A is the area of the measuring electrode; l is the distance between the measuring electrodes.

The algorithm corresponding to the measurement process with use of the proposed method and device, presented in paper [10], is given in **Figure 2**.

3. Results of the Proposed Method Testing and Their Analysis

The new method was tested by measuring active resistance of heterogeneous electrolytic system "lignin-calcium chloride water solution". It was lignin, containing
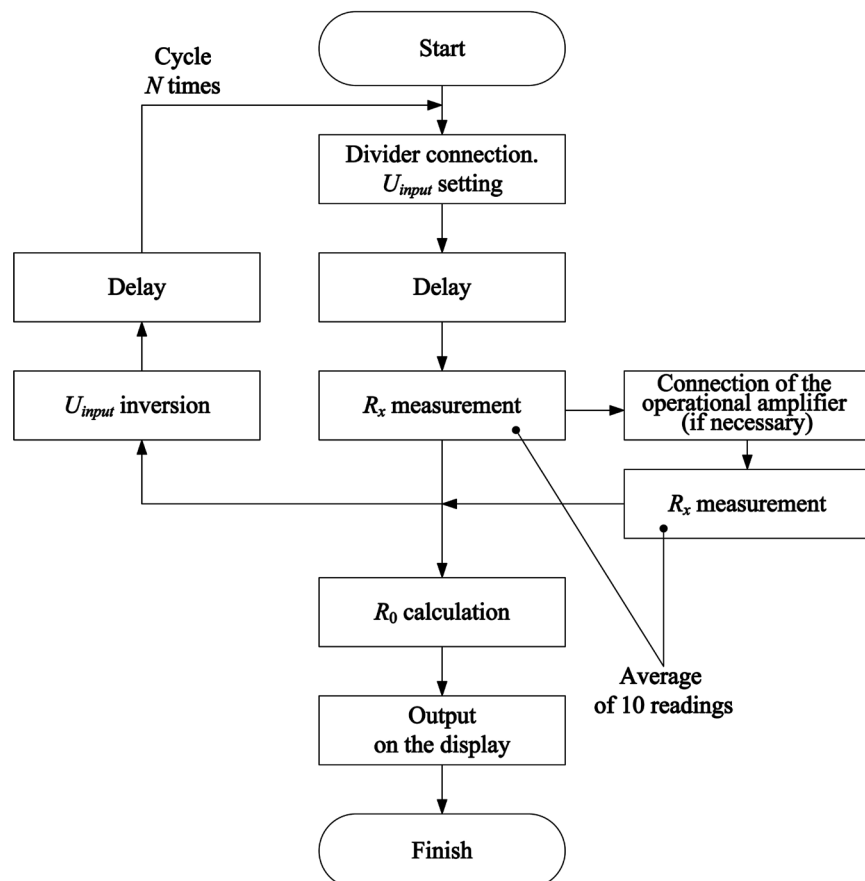
Figure 2. The algorithm of the measurement process with use of the proposed method and device, presented in paper [10].

saturated calcium chloride ($CaCl_2$) water solution. Lignin was in the form of fine crumb with characteristic size 0.1 - 0.5 mm. It actively absorbed $CaCl_2$ water solution in a quantity up to 2:3 mass parts. Four samples were prepared for experiments. They are characterized by mass concentration of $CaCl_2$ water solution of 25%, 33%, 50% and 60%. The last sample concentration is close to the maximum sorption capacity of lignin. The prepared samples were placed in a measurement cell—a hermetic rectangular container with two opposite sides covered with thin stainless steel plates.

The results of measurements obtained in accordance with the new method are presented in Table 1. Note, that zero threshold voltage was estimated for the system and resistance was evaluated by extrapolation of the $f = R(U)$ function to zero voltage.

For comparative evaluation of the new method, we have performed alternative resistance measurements by means of industrial LCR meter. The device operated in sinusoidal AC regime at different settings of the frequency and amplitude (voltage) of the measuring signal. The amplitude of the measuring signal was varied from 0.05 to 1 V. The results of measurements performed at an industrial frequency of 50 Hz are presented in Table 2.

The data show that resistances measured by the new method are in reasonable correspondence with the data obtained by AC measurements. At the same time measurements, performed with use of LCR meter are characterized by several disadvantages. According to the data presented in Table 2, measured resistances depend on voltage of the measuring signal (in our case resistance grows by ~20% with the growth of the signal). Measured resistance depends even stronger on frequency of the signal. These factors introduce uncertainties to the results of measurement.

4. Conclusion

The proposed method of measuring of the resistance of electrolytes and materials,

Table 1. The resistance and electrical conductivity of lignin containing $CaCl_2$ water solution obtained by the proposed method.

Value of the indicator		
U_0, V	R, kΩ	$\rho \cdot 10^{-2}$, S/cm
Lignin, characterized by $CaCl_2$ water solution content of 25 wt.%		
0	6.97	0.0287
Lignin, characterized by $CaCl_2$ water solution content of 33 wt.%		
0	3.05	0.066
Lignin, characterized by $CaCl_2$ water solution content of 50 wt.%		
0	1.28	0.156
Lignin, characterized by $CaCl_2$ water solution content of 60 wt.%		
0	0.85	0.235

Table 2. The resistance and electrical conductivity of lignin containing CaCl$_2$ water solution obtained with use of LCR meter.

					Value of the indicator						
U, V	0.05	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1
Lignin, characterized by CaCl$_2$ water solution content of 25 wt.%											
R, kΩ	200	197	191	184	197	175	173	171	169	169	167
$\rho \cdot 10^{-2}$, S/cm	1	1.02	1.05	1.09	1.02	1.14	1.16	1.17	1.18	1.18	1.2
Lignin, characterized by CaCl$_2$ water solution content of 33 wt.%											
R, kΩ	40.1	39.8	39.2	38.6	38.2	37.5	37	36.6	36.2	35.8	35.7
$\rho \cdot 10^{-2}$, S/cm	4.99	5.03	5.1	5.18	5.24	5.33	5.41	5.46	5.52	5.59	5.6
Lignin, characterized by CaCl$_2$ water solution content of 50 wt.%											
R, kΩ	4.75	4.7	4.6	4,5	4.44	4.35	4.25	4.1	4.1	4	3.9
$\rho \cdot 10^{-2}$, S/cm	42.1	42.6	43.5	44.4	45	46	47.1	47.8	48.8	50	51.3
Lignin, characterized by CaCl$_2$ water solution content of 60 wt.%											
R, kΩ	1	1.1	1	1	0.98	0.95	0.93	0.91	0.89	0.88	0.87
$\rho \cdot 10^{-2}$, S/cm	200	182	200	200	204	211	215	220	225	227	230

containing them, is characterized by the following properties:

- it takes into account the dependence of the electrical conductivity of the material on the voltage applied during the measurement;
- the time of voltage applying substantially exceeds the time of stationary current establishment, but much less than the time of electrolysis and electrochemical deposition influencing the measurement results.

The advantages of the method are simplicity and low cost. It can be widely used in such areas as electrochemical energy storage, medicine, agriculture, chemical industry, food industry, pharmacology [12].

It worth mention that utilization of the new method demands rather sophisticated algorithms of processing of series of data (or VAC) because of complicated and sometimes unpredictable character of the VAC. It is reasonable to further develop the method, particularly increasing the number of the measurements in a series and improving algorithms of data approximation and extrapolating.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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