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Virtual Electrolyte Conductivity Analyzer for Microplasma Oxidation Process Control

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***Abstract*-**This paper presents both hardware and software of virtual system for conductivity measurement of electrolyte solution. The distinctive feature of the system is its application for the concentration control of an electrolyte solution component during microplasma oxidation process which is characterized by the conductivity in the range from 0.1 S/m to 30 S/m. The analyzer has virtual control panel and based on module measurement system of National Instrument PXI standard. Structure and main principles of constructing the system components are described. Its technical and metrological parameters are given.

I. Introduction

Microplasma oxidation technique in electrolyte finds wide applications for surface modification of metals providing their necessary functional properties. The electrolyte composition is the most important factor both for microplasma oxidation process and for coating. Electrolyte quality and reaction products contamination result in undesirable change of the microplasma processes, up to their termination. It results in reducing of covering thickness, increasing of porosity and roughness, decreasing of adhesion of oxide layers formed [1]. Hence, at technological processes of the microplasma oxidation coverings it is necessary to control parameters of electrolyte and replace or correct it.

Electrolyte conductivity was chosen as controlled parameter. Investigations of conductivity of the electrolytes used show that the given parameter changes from 0.1 S/m to 30 S/m.

Since virtual devices have been widely distributed [2], the electrolyte conductivity analyzer based on virtual devices technology with application of modular devices of PXI standard has been designed. PXI system is the modular measuring system based on open industrial standard “PCI eXtention for Instrumentation” that provides high efficiency and low price. Use of a modular design makes it possible to configure measuring system for the decision of different tasks at microplasma electrolyte oxidation. The combination of PXI modules may be of any kind that enables to create a control system for all technological process parameters of microplasma oxidation. Virtual electrolyte conductivity analyser is first step to design virtual microplasma oxidation control system [3].

II. Choice and modeling of the electrolyte conductivity sensor

Electrolyte conductivity sensor is an impotent element of the measuring device. There are both electrochemical and electric phenomena [4]. Hence, the sensor design should meet the electrochemical and electric requirements.

The conductivity χ [S/m] can be defined as

$$\chi = \frac{L}{S}\;\frac{1}{R}, \qquad (1)$$

where L [m] is distance between electrodes, S [m^2] is the electrodes area, R [Ω] is electrolyte resistance.

$K=L/S$ is the most simply determined if the sensor is of strictly geometrical form by which force lines of electric field are limited. K is system parameter called the cell-constant which cannot be determined by direct measurement of cell vessel length and the area of its cross section due to:

- dispersion of the force lines of electric field which are not limited to electrolyte column directly between electrodes;
- impossibility to make strictly parallel electrodes and their strictly certain form;
- the complex form of the cell vessel limiting distribution of the force lines of electric field.

The two-electrode conductivity cell is presented in Figure 1.

Such design of the conductivity cell is simple in manufacturing and using. Unfortunately, dispersion of force lines of electric field is not limited by electrolyte column between electrodes. Isolating of external sides and butt ends of electrodes makes it possible to restrict of dispersion of force lines of electric field.

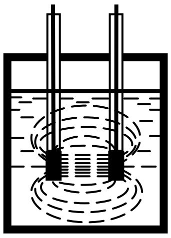
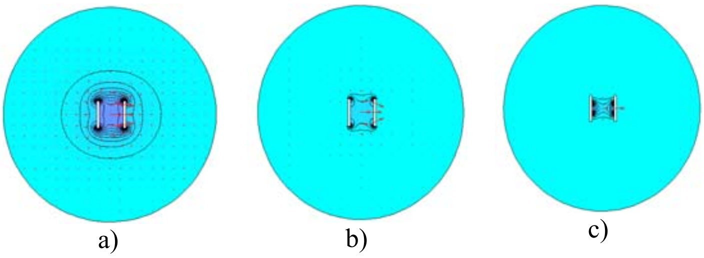


Figure 1. Two-electrode conductivity cell

In Figure 2a the model of dispersion of the force lines of electric field in volume of electrolyte with not isolated electrodes is given, in Figure 2b model of dispersion of force lines of electric field with the isolated external sides and butt ends of electrodes is given, and in Figure 2c the model of dispersion of force lines of electric field in volume of electrolyte about completely isolated electrodes is given, excluding the small areas on internal electrode surfaces lying one opposite to the other.

Modelling was carried out in MatLab.



a) b) c)

Figure 2. Modelling of conductivity cell design

There was a redistribution of the force lines of electric field after isolation of the electrode sides. The force lines of electric field in Figure 2c are distributed in regular intervals and limited to the electrolyte column between electrodes at this electrode isolation. Hence, such isolating of electrodes is the most effective for measurements with the conductivity cell presented on Figure 1.

In common practice, to define the cell constant the standard conductivity sample is applied. The relative error of the certificated standard sample is 0.25 %. After measurement of the cell resistance filled with standard conductivity sample with known value χ, the cell constant K is easily calculated from formula (2):

$$K = \chi R \,, \tag{2}$$

where K [m^{-1}] is cell constant, χ [S/m] is conductivity, R [Ω] is the electrolyte resistance.

The equivalent circuit of two-electrode conductivity sensor is presented in Figure 3 [5].

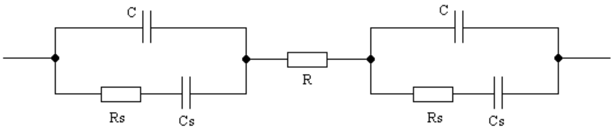


Figure 3. Equivalent circuit of the conductivity cell

In the equivalent circuit C is double layer capacitance, R_S and C_S are resistance and capacitance produced by polarization, R is resistance of electrolyte investigated. It is possible to obtain the full two-electrode conductivity sensor impedance as:

$$Z = R + \Delta R_S - 2j\frac{\omega^2 R_S^2 C_S^2 C + C_S + C}{\omega^2 R_S^2 C_S^2 C^2 + (C_S + C)^2} \,, \tag{3}$$

where Z is full resistance of cell, R is resistance of electrolyte, R_S is polarization resistance, C_S is polarization capacitance, ω is frequency of current, C is double layer capacitance.

In this expression R is the real solution resistance, ΔR_S is the error caused by the polarization phenomenon and the third imaginary part defines the phase difference between current and voltage of the cell. Error ΔR_S can be calculated by (4):

$$\Delta R_S = \frac{2 R_S C_S^2}{\omega^2 R_S^2 C_S^2 C^2 + (C_S + C)^2} \,. \tag{4}$$

It is possible to remove ΔR_S by increasing the frequency.

Dependence of R_S on frequency is expressed by (5):

$$R_S = \frac{\eta}{\sqrt{\omega}}\,, \tag{5}$$

where η is constant representing dependence of electrolyte on concentration, factor of diffusion and potential in a double layer.

Dependence of C_S on frequency is expressed by (6):

$$C_S = \frac{1}{\eta\sqrt{\omega}}\,. \tag{6}$$

It was experimentally proven that at frequencies higher then 5000 Hz for the stainless steel electrodes the polarization do not influence the measurement result.

III. Analyzer structure

The computer measuring system consists of three parts: personal computer (PC), modular measuring system on PXI platform and two-electrode conductivity sensor. The structure of analyzer is presented in Figure 4.

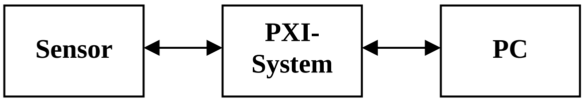


Figure 4. Analyzer structure

Analyzer is based on the technology of virtual instrumentation. The faceplate of the real device is simulated on the computer screen and software is used for measurement and control.

The block diagram of computer measuring system is presented in Figure 5. Conductivity analyzer is given in Figure 6.

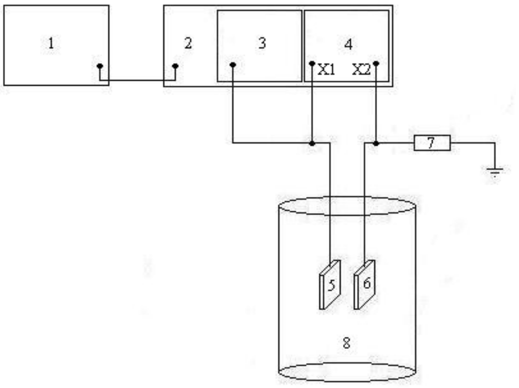


Figure 5. Block diagram of measurement system

Figure 6. Conductivity analyzer

The personal computer (1) is used for information processing and control of system PXI (2). Modules of the signal generator (3) and two-channel oscilloscope (4) are installed in PXI system (2). The signal from generator (4) enters the sensor electrode (5,6) of electrochemical cell with liquid (8). Measurement of voltage on electrodes (5) and (6) is carried out with oscilloscope (4). Measurement results are processed by the personal computer and the conductivity value is displayed on PC. Conductivity is:

$$\chi = K\frac{U_{X2}}{(U_{X1} - U_{X2})R}\,, \tag{7}$$

where χ is conductivity, R is resistance 7 (Figure 5), *Ux1* is amplitude of signal *x1*, *Ux2* is amplitude of signal *x2*, *K* is the constant of the electrolyte cell.

Working frequency for measurements was experimentally determined. Dependence of phase shift vs frequency is shown at various concentrations in Table 1. Investigations were carried out in KCl aqueous solution.

Table 1. Dependence of phase shift

Frequency [Hz]	Phase difference [degree]		
	Concentration of KCl 75 g/l	Concentration of KCl 7.5 g/l	Concentration of KCl 0.75 g/l
100	37	36	12
1000	20	15	5
10000	8	5	2
100000	0.3	0.3	0.3
1000000	0.3	0.3	0.3

Dependence of electrolyte resistance vs frequency at various concentration of KCl aqueous solution is shown in Table 2.

Table 2. Dependence of electrolyte resistance

Frequency [Hz]	Resistance [Ω]		
	Concentration of KCl 75 g/l	Concentration of KCl 7.5 g/l	Concentration of KCl 0.75 g/l
100	20.8	35	272.45
1000	8.83	30.6	250.38
10000	3.85	27.52	236.61
100000	3.13	26.27	242.75
1000000	3.13	26.24	242.68

From the experiment it follows that at frequencies above 100 kHz the resistance of electrolyte measured remains constant. The phase difference between input and target signals is equal 0.3°. Hence, it is possible to measure the electrolyte conductivity at frequency 100 kHz.

The constant of cell *K* was determined experimentally. As standard samples the KCl aqueous solution with various concentration were used. After measuring the resistance of the cell filled with standard samples, the constant of cell was calculated from (7). Experimental results are shown in Table 3. Measurements were carried out at temperature 21°C.

Table 3. Constant of cell

Concentration of KCl, [g/l]	Resistance [Ω]	Standard samples of KCl, [S/m]	Constant of cell K, [m^{-1}]
0.75	242.75	0.13	31.55
7.5	26.27	1.2	31.52
75	3.13	10.4	32.55

As constant of cell *K* the average value from constants of cell presented in Table 3 is accepted. Average value for constant of cell equal 32 m^{-1}.

It was experimentally determined that constant of cell does not depend on the cell volume. Experimental results are shown in Table 4.

Table 4. Dependence of cell constant

Volume of cell, [ml]	Concentration of KCl, [g/l]	Resistance, [Ω]
100	0.75	242.79
	7.5	26.28
	75	3.13
200	0.75	242.75
	7.5	26.27
	75	3.13
400	0.75	242.74
	7.5	26.25
	75	3.11

IV. Accuracy calculation

Accuracy of the measuring channel was experimentally determined. It was determined by method of direct conductivity measurement of the KCl aqueous solution reference-standard at various concentrations. By this, the observations were repeatedly carried out. Number of observations was n=50. Measurements were carried out at temperature 21°C. The average of measurement data ($\tilde{A}$), the standard deviation ($\sigma(\tilde{A})$), the precision (ε) at the 95 percent confidence level, the directional bias error (Δ_S) were calculated. Calculations results are given in Table 5.

Table 5. Error components

Concentration of KCl, [g/l]	$\tilde{A}$, [S/m]	$\sigma(\tilde{A})$, [S/m]	Δ_S , [S/m]
0.75	0.1312	0.00116	0.00075
7.5	1.2	0.117	0.0087
75	10.35	0.134	0.0119

As $\Delta_S \; / \sigma(\tilde{A})$ is less than 0.8 for all concentration we guess that bias error is negligible. Final results are shown in Table 10.

Table 6. Accuracy calculation result

Concentration of KCl, [g/l]	ε , [S/m]	Accuracy, [%]
0.75	± 0.0022	- 1.15 -÷ + 2.22
7.5	± 0.23	- 1.17 ÷ + 2.02
75	± 0.26	- 2.98 ÷ + 2.96

The largest of the values received is accepted as accuracy of the measuring channel. Hence, the accuracy of the measuring channel makes 3 %.

V. Conclusion

Electrolyte conductivity analyzer made is based on the technology of virtual instrumentation with application of PXI modular devices. The approach presented makes it possible to design a measurement instrument with changeable functionality. The software developed in LabVIEW allows to adjust analyzer for various types of conductivity sensors and to carry out the statistical control of parameters of electrolyte at microplasma oxidation. In this paper the recommendations as to the choice of electrodes being invariant to a measuring cell were given. The error of the measurement system developed was also estimated.

Electrolyte conductivity analyzer is used in the technological process of protective and decorative coverings. Conductivity investigations are the first stage for multi-parameter control of electrolyte and definition of its component concentration.

VI. Acknowledgments

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