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Study of Capacitive and Electrical Conductivity Characteristics of the System «Nanostructured Electrodes - Dielectric Liquid»

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The results of research of capacitive and conductive characteristics of the system "the nanostructured metal electrodes – dielectric liquid" are given. It is shown the difference of states near the electrodes of electric double layers on the surfaces of copper and tungsten electrodes.

Keywords: Surface nanostructures, Charge injection, Surface topography, Electric double layer.

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1. INTRODUCTION

Electric double layers with nanometer dimensions [1, 2] have the greatest influences on the processes of charge formation at the interface. The joint accounting of features of structuring surfaces of electrodes and properties of the of layers near the electrodes [3] is necessary for the solution of a problem of control of charges injection at the interface "metal electrode - dielectric liquid" in electric field. This interphase boundary is the most promising system for practical applications in devices of heat and mass exchange. In electrohydrodynamics according to the theory of injection and dissociation – recombination of conductivity [4] it is accepted that the surface layers are usually has three-layer structure (in the form of the diffusion layer, nonequilibrium and equilibrium zones of reaction of dissociation - recombination) which distribution depends on intensity of electric field. The studies of the influence of geometry known structures of the surface of electrode systems on the local electric fields and electrical characteristics of the interface are necessary for more exact solution of problems of charges formation on the surface of the electrodes. Possibility of the using of AFM for description of charge formation on the nanostructured surfaces of electrodes at electroconvection is shown in works [5-7].

2. INSTALLATION DESCRIPTION

From these positions the question about joint influence of nanostructures and double electric layers on electric capacitance and conductivity of system "the nanostructured electrodes - dielectric liquid" is very interesting. The study of electric capacity and conductive characteristics of the system "nanostructured metal electrodes - dielectric liquid" was made on the installation which scheme is submitted in figure 1. The right part of the installation (fig. 1) consisting of a universal bridge E7-10 and a source of dc stabilized voltage GPS-2303 is used for measurement of the electrical capacitance of the studied system (being in a measuring cell 1) in a mode of alternate current and polarizing constant voltage. The bridge E7-10 allows measuring the capacitance to 0.01 pF and the conductivity measuring cell to 0.1 nS at alternating voltage 4.3 V at 1 kHz. The bridge has opportunity to give constant polarizing voltage on a measuring cell to 20 V what the source GPS-2303 sets. At capacity measurements the simultaneously balancing of the bridge both on electric capacity and on conductivity is made. The combined picoammeter - source Keithley 6487of a dc voltage is used at measurements of low-voltage conductivity of system at U < 500 V (left part of installation (fig. 1)), it is connected to a cell separately. Oligodimethylsiloxane PMS-50 V was used as dielectric liquid. It is certified by the presence of impurities (manufactured according to GOST, without mechanical impurities, water content is not more than 0.003 %). Oligodimethylsiloxane have sufficiently low viscosity which is a little changing with change of temperature (Tab. 1), resistance to thermal decomposition, high boiling point therefore these liquids are the most suitable for use in electroconvective devices.



Fig. 1 – Electric scheme of installation on research of electrophysical properties of system "the nanostructured electrodes - liquid dielectric": 1 – measuring cell, 2 – the voltameter, 3 – a constant-voltage source, 4 – the universal bridge, 5 – a picoammeter - constant-voltage source, 6 - PC

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Water can greatly influence electroconvection even in small quantities. Therefore before the research PMS-50 are dried in a desiccator with calcium chloride (CaCl₂). Calcium chloride before refueling in the desiccator was calcinated during 1,5 hours at a temperature \sim 300-400 °C.

Table 1 - Property of PMS-50

Dielectric heat carrier	t _{mel} , ⁰C	t₀boil, °C	$v, \rm{mm^{2}/c}$ (t = 20 °C)	<i>v</i> , mm ² /c (<i>t</i> = 50 °C)
Polydimethyl- siloxanes	- 64	> 250	18-105	14-55

The scheme of a measuring cell is shown in fig. 2. The electrodes with the nanostructured surfaces 1, 3 (ASM-images 9, 10) and the dielectric interleaf 2 made from ftoroplastic (the polythenephthalate film) with the calibrated hole in the form of a circle was inserted into a seat for the anode 3 and a press insulating plate 8 of insulating cases 4 previously filled with studied liquid. The screw 6 connects parts of the cell together, excess liquid is removed through the opening of a micrometer screw 7.Contact of cleats 5 with electrodes and the sealing of the measuring system are made by tightening of the screw 7 with the moment 2 N·cm.

All bearing parts of installation are made of plexiglas with specific conductivity ~ 10^{-15} of Sm·m⁻¹ and precisely adjusted (distortions are absent). Before measurements devices got warm within 15-20 minutes according to the maintenance instruction. Picoammeter Keithley 6487 and the stabilized power source have factory calibration and the universal bridge was tested previously according to the operation instruction. On

this installation the research of the nanostructured samples with sizes of $16.3 \times 16.3 \text{ mm}^2$ was made. Characteristics of nanostructures were determined by the technique [5, 6] and are presented in Table 2. Fluoroplastic inserts (thickness of 155 microns) were used for the separation of the electrodes at the certain distance. The calibrated holes (diameter 12.6 mm) were made in the films. The coaxiality of holes was controlled at insertion in space between electrodes. Internal parts of installation and the separating films were cleared previously in alcohol, the distilled water and were dried within day. Search of dependences of dielectric permeability and conductivity of a material of films from thickness was made previously on system of the polished copper electrodes with continuous dividing inserts without holes for definition of characteristics of system.

The result of definition of characteristics of structures shows that at creation of unipolar injection in the volume of dielectric liquid by means of introduction of the donor additives as the injecting cathode most of all approaches a tungsten surface. Intensity of electric field at tops of tungsten structures is created rather large it is sufficient for existence of autoelectronic emission at the specified geometrical sizes of studied parts of installation. The copper sample was taken as the anode because the copper surface is smoother and therefore having a small injecting ability.

Results of research of dependence of conductivity and dielectric permeability of systems of the nanostructured electrodes (Cu, W) and dielectric liquid (PMS-50)



Fig. 2 – Measuring cell for studying of interphase borders "the nanostructured electrodes - dielectric liquid": 1 - cathode; 2 - insulating inserts with an holes; 3 - anode; 4 - case; 5 - connecting plugs of electrodes; 6 - fastening screws; 7 - micrometric screws; 8 - press insulating plate with a seat for an electrode; 9 and 10 - ASM-topology of a surface of copper and tungsten electrodes polished to quality of 20 nanometers

Table 2 – Characterist	ics of structures
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Material of electrodes	Average height (< <i>h</i> >), nm	Average size (< <i>d</i> >), nm	Aspect relation (<h>/<d>>)</d></h>	Density of structures $(\rho = N/S),$ $\times 10^8 \text{ cm}^{-2}$	Radius of cur- vature of tops of structures <i>r</i> , nm	Local intensity $E, \times 10^7$ V/cm
Cu	26	12.4	2.1	69	289	0.70
W	230	58	3.9	9.4	14.8	8.55



Fig. 3 – Dependences of dielectric permeability on interelectrode distance: 1 -fluoroplastic-4; 2 -PMS-50 in system of electrodes "the cathode – Cu, the anode – Cu"; 3 -PMS-50 in system of electrodes "the cathode – W, the anode – Cu"



Fig. 4 – Dependences of electric conductivity on interelectrode distance: 1 – fluoroplastic -4; 2 – PMS-50 in system of electrodes "the cathode – Cu, the anode – Cu"; 3 – PMS-50 in system of electrodes "the cathode – W, the anode – Cu"

from distance between electrodes are presented in figures 3, 4.

Calculation of dielectric permeability was made on the formula considering polarization of molecules of dielectric liquid on the non-working part of electrodes (C') and dependence of dielectric permeability of the fluoroplastic plates from thickness of a layer ($\mathcal{E}_2(H)$):

$$\varepsilon_1(H) = \frac{(C_{\rm ch} - C')}{\varepsilon_0 S_1} H - \varepsilon_2(H) \frac{S_2}{S_1}$$

where $\varepsilon_1(H)$ and $\varepsilon_2(H)$ – dielectric permeability of liquid and the of fluoroplastic inserts (plates) depending on H(fig. 3, 1), C_{ch} – the capacity of system measured in experiment, C' – the capacity amendment on polarization of molecules of dielectric liquid on the non-working party contacting to liquid, S_1 and S_2 – respectively the area of electrodes in a zone of an hole and the zone closed by fluoroplastic dividing inserts. Calculation of the conductivity of the system is made taking into account parasitic conductivity of the liquid contacting to the non-working parts of electrodes and dependence of conductivity the fluoroplastic of inserts from thickness:

$$G_1(H) = (G_{ch} - G') - G_2(H) \frac{S_2}{S_1},$$

where $G_1(H)$ and $G_2(H)$ – liquid conductivity and conductivity of the fluoroplastic inserts (plates) depending on H (fig. 4, 1), G_{ch} –conductivity of system measured in experiment, G' – the experimental amendment of conductivity on conductivity work liquids through a nonworking zone.

Values of each experimental point was determined by average value of three measurements executed in the direction up-down-up.

3. CONCLUSIONS

Dependences of dielectric permeability in fig. 3 show the need of the accounting of change of dielectric permeability with distance between counter electrodes and of influences on values of local intensity of electric field depending on geometrical characteristics of nanostructures and diffusive layers at calculation of charge formation at tops of micro-and nanostructures. Figure 4 qualitatively is confirmed by the analysis of characteristics of nanostructures presented in Table 2. As it is known [8] main charge formation at electroconvection occurs from the cathode. Taking into account dielectric permeability (fig. 3) the maximum local intensity was ~ $4.3 \cdot 10^6$ V/cm in system of electrodes the "anode (the polished copper) - the cathode (the nanostructured tungsten)" at distance between them 150 microns. Local intensity of system of electrodes with the cathode from tungsten was more than five times higher in comparison with system where the cathode was the copper electrode with more flat nanostructures that proves the existence of the low-emission [9, 10]. Low-field emission for tungsten is facilitated, according to our assumption, the presence of the self-organized ensembles of threefour nanostructures in which there is a charge formation on higher top due to quantum transitions at tunneling of electrons with the lower tops.

On the other hand the increase in conductivity is explained by the fact that the diffusion layer isn't created at highest tops of the tungsten structures (in contrast to the more flat structures of copper) that facilitates the movement of uncompensated charges from tops and increases the zone of non-equilibrium dissociation-recombination reaction on the cathode before disappearance of an equilibrium zone.

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