

Induction of Polymerization of the Surface Nanostructures of the Electrodes by Electric Field

S.G. Emelyanov¹, A.E. Kuz'ko¹, A.V. Kuz'ko¹, A.P. Kuzmenko¹, P.A. Belov²¹ South West State University, 94, 50 let Oktyabrya Str., 305040 Kursk, Russia² Scientific Research Center (Kursk), the Federal State Unitary Enterprise "18 Central Research University" of the Ministry of Defense of the Russian Federation, 23, Blinova Str., 305040 Kursk, Russia

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The results of experimental studies of the interface of "dielectric liquid - nanostructured metal electrode" after electroconvection is presented. It is discovered the patterns of structuring of areas of polymerization showing disruption of the diffusion layer and the processes of charge injection from the tops of structures.

Keywords: Surface nanostructures, Microelectroconvection, Charge injection, Electric double layer, Polymerization.

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1. INTRODUCTION

Studying of dimensional effects and self-organizing of nanostructures on surfaces of interfaces under the influence of force fields is currently the popular direction of scientific and technological progress [1-2]. The studying of conditions of emergence, properties and application of the self-organized ordered structures is very interesting. The nanostructured ensembles with their unusual properties are created by the nature at dissipation of energy of impact on system. The "dielectric liquid-a metal electrode" interface being under the influence of high-voltage electric fields is important for the practical application. Properties of this interface predetermine the charge formation processes. Possibility of control of the charge formation is a basis for progress in using of electrohydrodynamic currents in effective devices of mass- and heat exchange and chemical industries where the electric field is used as the activator of chemical processes.

It is shown in work [3] that numerical calculation which takes as a basis of regularity of the autoelectron emission (AEE) current (Fowler-Nordheim equation) is confirmed by experimental data of electrohydrodynamic currents with the macroscale peak electrodes. Therefore the AEE model can be used adequately for calculations in the "dielectric liquid - electrode" system. Possibility of control by the charge formation in the area of the nanometer sizes according to geometry of the surfaces structures of electrodes is shown in works [4, 5]. The above description is incomplete therefore it is necessary to consider the existence of the nanoscale electric double layers and also the adsorption and the oxidation processes on a surface of electrodes.

2. EXPERIMENTAL RESULTS

A number of processes is observed at course of the developed electrohydrodynamic currents (for $E > 1$ kV/cm) in system of the plane-parallel copper electrodes polished with quality of 20 nanometers and polymethylsiloxane liquid with degree of polymerization of 50 (PMS-50). These processes are formation of

microelectroconvective currents on the tops nanostructures, different types of polymerization, electroerosive degradation of a surface of electrodes [6]. The surface of the anode is shown in figure 1. Microelectroconvection on tops of nanostructures leads to emergence of the porous polymerized layers of molecules of the polymethylsiloxan liquid (fig. 1).

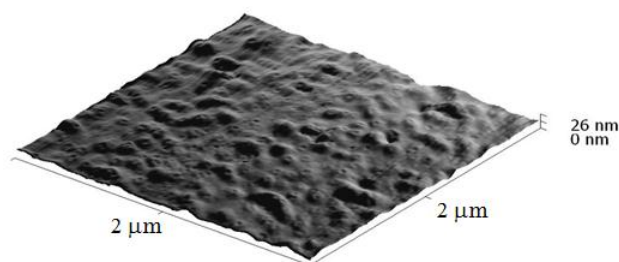


Fig. 1 – Topography of the nanostructured surface of the anode

Charge injection and microconvection in the presence of the double electric layer (DEL) leads to the complex branched porous structure on an electrode surface. The images obtained by the confocal microscope are presented at the focusing to the plane of a surface of an electrode (fig. 2a) and above (fig. 2b). It is visible that structures (callouts of figures 2a, b) for the same area differ at the change of focusing on height. Obviously, the small pores (callout of figures 2a) correspond to movement of charges from tops of protruding nanostructures and the corresponding larger pores (callout of figures 2b) show the areas of the microelectroconvective currents above the tops of nanostructures. It is understood that ion motion takes place through the pores to the highest nanostructures of the copper surface. The polymerized layer between areas of a charge formation creates an obstacle for movement and a discharge of ions to a surface and therefore the mechanism of transport of charges from an electrode occurs in this case only through a time. Calculation of relative surface area that is occupied by the pores in comparison to the whole area respectively gives value 0.033 for callout 2a and 0.117 for callout 2b. Thus the

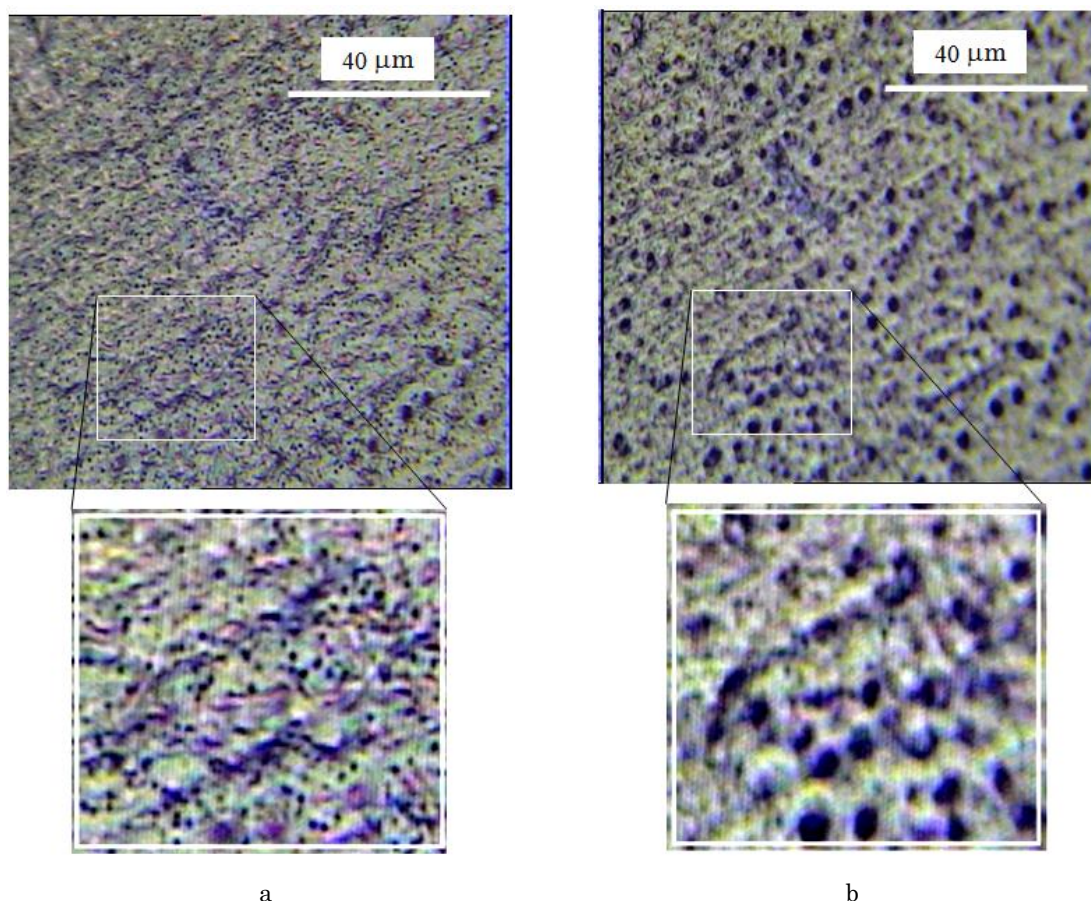


Fig. 2 – Formation of a film with the centers of charge formation at EC in PMS-50 on the anode

filling of area of callouts by the pores in figure 2b is 3.5 times greater than 2a. We can assume that the counted pore area will determine the surface areas of tops of nanostructures from which charge injection at AEE occurs. Moreover, the let-through current without returnable streams is possibly formed in the pores of figure 2a and the microvortices with processes of polymerization are occurred in a figure 2b.

The charge injection at electroconvection begins with the highest peaks of nanostructures polished to 20 nm in our case. A number of mechanisms [7] involved in the electroconvection in charge formation process. Injection of electrons from tops of structures is facilitated by three factors: 1) when the potential barrier is lowered the high-voltage local electric field generated by an external field [8] (as well as on the "vacuum-metal" border), 2) when the molecules of the electric double layer directly adjacent to the top of the structure increase the field, 3) when the electron acceptor impurities are added in dielectric liquid. Therefore, molecules of the liquid or the impurities molecules immediately capture an electron, leading to ionic charge injection. On the flip side the molecule of electric double layer of liquid reduce a potential barrier for an exit of ions of a crystal lattice of metal that at the developed electro convection and the combination of redox reactions leads to emergence of the erosive structures. The erosion of metal proceeds in space under the oxide film of a surface of metal if the oxide film isn't metallized at the current destruction of structure. The double electric layer has the same nanometer sizes [9] as well as the considered

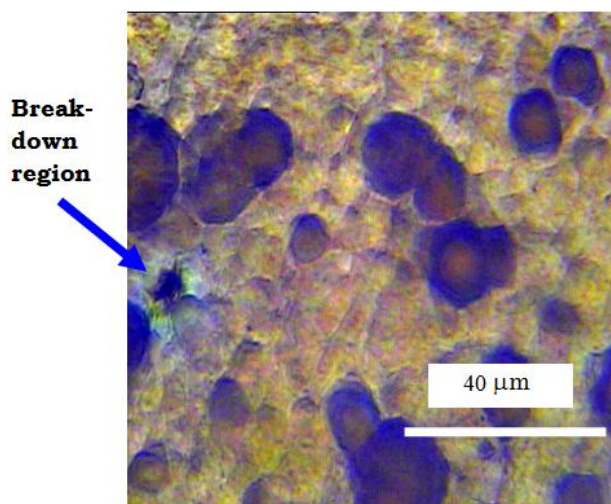


Fig. 3 – the emergence of the organized cluster structures

above nanostructures.

If the sizes of structure exceed the thickness of the diffusion layer the breakaway of a diffusive layer in the field of top of structure and nanostructures is the most probable that is accompanied by resonant neutralization, ionization and an exit of the ions of crystal lattices (erosion). Decrease of thickness of the diffusion layer induces the erosion even below the main surface of the metal (of the horizontal oxide film).

It is shown the clusters formed in the breakdown

region in figure 3 (a other kind of polymerization). The clusters during its growth come in close contact so that their shape is deformed and becomes similar to the pentagon. Clusters are not of the same nature, they differ in color. The light clusters are formed around the

charged core (copper crystallites), and the dark clusters are formed around the adsorbed particles of the iodine ejected at the breakdown moment in the volume of liquid. Next the resulting clusters are concentrated at the exposed surface of the metal.

REFERENCES

1. V.I. Roldughin, *Russ. Chem. Rev.* **73** No 2, 115 (2004).
2. Yu.D. Tretyakov, *Russ. Chem. Rev.* **72** No 8, 651 (2003).
3. Yu.K. Stishkov, V.A. Chirkov, *Tech. Phys.* **58** No 12, 1822 (2013).
4. A.I. Zhakin, A.P. Kuzmenko, A.E. Kuzko, *Proc. South-West State University* **40** No 1, 60 (2012).
5. A.P. Kuz'menko, A.E. Kuz'ko, D.I. Timakov, *Tech. Phys.* **58** No 2, 239 (2013).
6. A.I. Zhakin, A.E. Kuz'ko, A.V. Kuz'ko, P.V. Abakumov, *J. Nano-Electron. Phys.* **5** No 4, 04030 (2013).
7. A.I. Zhakin, *Phys. Usp.* **49** No3, 275 (2006).
8. B.V. Stetsenko, A.I. Shchurenko, *Plasma Physics* No 1, 136 (2009).
9. O.A. Petrii, G.A. Tsirlina, *Russ. Chem. Rev.* **70** No4, 285 (2001).