Investigation of the deposition of metal nanoclusters on the hidden surface of porous electrode materials by electrophoresis

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Abstract. The formation of a coating on the entire surface of a highly porous electrode material based on magnetron sputtering and subsequent deposition of a colloidal solution of metals is considered. The experimental results show the possibility of metallization of the hidden surfaces of porous carbon materials by metal nanoclusters of 2-10 nm size by electrophoresis without reducing their initial porosity.

1. Introduction
Miniaturization of electronics has led to the fact that the main volume and weight of many devices is a power source, which are increasingly demanding in terms of battery life, the amount of stored energy, the number of recharge cycles and service life, which should be at least the service life of the electronic device itself. Thus, today there is a need for a sharp increase in the energy characteristics of current sources, which can be achieved by using microelectronic technologies and nanotechnologies in their production [1, 2].

Priority directions of improvement of the miniature sources of electrical energy become chemical current sources, primarily, lithium batteries and supercapacitors. Being inferior to chemical current sources in nominal energy, supercapacitors significantly exceed them in specific power and stability of charge-discharge characteristics in a wide temperature range.

Microelectronic technologies and nanotechnologies will be in demand to improve the characteristics of electrode materials as the main elements of chemical current sources and supercapacitor structures [3, 4].

Prospective electrode materials must meet several criteria: developed surface area, high electrical conductivity, availability of porous structure to wetting, chemical inertness to structural materials and so on. The most fully listed requirements are met by carbon materials of varying degrees of porosity [5-10]. One of the promising materials in this group are carbon cloths from activated carbon fibers – “busofit” (figure 1) [11]. The capacitance of the capacitor depends primarily on the surface area, which in carbon materials can increase in comparison with the geometric surface by 10³–10⁵ times. In addition to a highly developed surface, electrode materials must have a low electrical resistance, both along the layer and across, as this determines the internal resistance of the current source, limiting its output current. To reduce the electrical resistance of busofit and the creation of electrode material on its basis it is necessary to solve two problems.

First, apply a continuous layer of metal to the surface of the busophyte, which will be a current
collector and reduce the internal resistance. This operation can be successfully realized with the help of magnetron sputtering. Since, this is a well-known and studied process, within the framework of this article, we will not dwell on its consideration.

Secondly, it is necessary to deposit a layer of metal on each filament of the busophyte, which, on the one hand, will lower their electrical resistance, and on the other hand will increase the specific surface. To solve this problem, it is proposed to use the technology of depositing nanoclusters of metals on the surface of porous materials by electrophoresis. As is known, nanometer-sized particles have a number of unique properties. They carry a positive charge, and their electrophysical and physicochemical properties are determined by the size of the nanoclusters. Therefore, the main task is to obtain metal particles with the desired size range and then position them in the pore space by electrophoresis. In this case, the nanoparticles should have a uniform distribution over the surface.

2. Experimental
In the studies, the serial carbon cloth Busofit T-40 and similar carbon materials Busofit T-1, Busofit-T, Busofit-TM-4 were used. On the busofit threads, nanoclusters of nickel and silver were applied from the hydrocol. The preparation of metal nanoclusters was carried out by the method of electropulse dispersion due to an electric discharge between electrodes made of the metal immersed in distilled water [12]. The interelectrode distance was 100 μm, air gap of 1 mm, capacitor voltage up to 3 kV, capacitance of 1000 pF. Produced nanoclusters of metals are shown in figure 2.

Under such a synthesis process, colloidal solutions of silver and nickel were obtained in which the initial sizes of the nanoclusters were 25–40 nm and 2–10 nm, respectively.
To metallize busofit with metal nanoclusters, an experimental laboratory reactor were developed using electrophoresis, its 3D model and a photograph of which is shown in figure 3.

Figure 3. 3D model (a) and photo of the reactor for the application of metal nanoclusters (b): 1 - upper clamping cover, 2 - upper electrode, 3 - carbon cloth "busofit", 4 - base, 5 - lower electrode. Busofit (3) was placed between the electrodes (2 and 5), after which the reactor was filled with a colloidal solution with silver or nickel nanoclusters and connected to an AC power source with a voltage of 40 V. Colloid particles have a charge, so they can move in an electric field. Reaching the destination electrode, the particles lose their charge and stick together - the colloidal solution coagulates on the surface of the material.

Figure 4. The busofit fibers metallized with silver (a), nickel (b), silver over nickel (c), (d).
Figure 4 shows shots of metallized busofit fibers obtained with an electron beam microscope. As can be seen, nickel is deposited on the busofit in a thin layer, and silver on the surface of the busofit fibers is formed in the form of large nanoparticles and crystallites, developing the surface of the fiber. The experiment of silver deposition on pre-nickel-plated busofit fibers also did not allow a single layer of silver to be deposited on the nickel sublayer as well as the initial busofit fibers. Apparently, this metallization result is associated with the initial size of metal nanoclusters, thin-film coatings are obtained from nanoclusters with sizes of 2–10 nm, and large nanoparticles and crystallites are formed from nanoclusters of a larger fraction.

3. Conclusions
The possibility of metallization of hidden surfaces of porous materials with metal nanoclusters is shown by electrophoresis without reducing their initial porosity. Such processing, combined with magnetron sputtering on the outer surfaces, allows the formation of a metal coating on the entire surface of a highly porous material, which reduces the electrical resistance and stabilizes the parameters of the electrode material.

To further study the metallization of highly porous materials, it is planned to use graduated colloidal solutions with a smaller spread of nanoclusters from different metals and alloys.

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