Universal electrode materials for CCS and SC based on carbon textile «Busofit»

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Abstract. The article discusses the ion-plasma modification of carbon textile "Busofit" for supercondensators systems (SC) and chemical current sources (CCS). The technique of vacuum metallization is described; the images obtained by scanning electron microscopy (SEM) and X-ray spectral microanalysis are presented. Measurements of resistance of multilayer structures with electrode materials with different treatment are presented. It significantly determines the internal resistance (ESR) of SC and CCS.

1. Introduction
Currently, the demand for electric energy storage in electronic devices, transport, communication systems and other areas is so high that their production becomes an independent industry. The main power sources are chemical current sources and supercapacitor structures [1].

To improve the specific capacitance characteristics of supercapacitors, various methods of modifying the surface of electrode structures are used, in particular, the deposition of thin films of transition metals and their oxides on high-porous carbon materials, in particular Busofit, which allow to reduce the internal resistance and increase the output power [2]. The purpose of this work is to reduce the equivalent series resistance of the electrode material, which will increase the capacitance characteristics, as well as protection of the electrodes from the chemical effects of the electrolyte.

2. Metallization of electrode material
Ion-plasma modification of the electrode material from carbon fabric based on Busofit-UL-50 was carried out on the ELNA-2 vacuum magnetron sputtering unit. The equipment operation is based on the method of vacuum sputtering of titanium cathode on magnetron sources and condensation of its vapors on carbon fabric tape, rewound in the vacuum chamber. Argon was used as a plasma-forming gas at operating pressure from 0.8 to 2 Pa. A thin layer of titanium nitride was applied to the metallized electrode material to protect it from the chemical effects of the electrolyte at an argon pressure of 0.3 Pa and a partial nitrogen pressure of up to 0.8 Pa [3–4]. The samples were studied by scanning electron microscopy (SEM) and X-ray spectral microanalysis. Typical SEM images of carbon fiber before and after ion-plasma treatment are shown in figure 1.

3. Analysis of Ti and TiN coating
The study revealed the presence of a globular structure of the titanium film and the peeling of the titanium coating from the carbon filament, thereby reducing the equivalent series resistance (ESR) and...
increasing the surface area of the samples. Samples with a thickness of more than 3 microns have areas that completely cover the relief of carbon fabric. As the thickness of the titanium layer on the carbon filament increases, the coating asymmetry increases. The side that is closer to the magnetron has a layer of titanium of greater thickness. There is the effect of shading, however, revealed that the titanium covers the surface of filaments Busofit from all sides to a depth of 3–5 layers.

![SEM pictures of the carbon fiber "Busofit".](image1)

X-ray microanalysis showed that carbon and titanium are present in the coating (figure 2(a)), and in the case of titanium nitride – carbon, titanium and nitrogen, with other elements on the spectra (figure 2(b)) is not observed. This allows us to conclude that the electrode materials obtained by vacuum technology are sufficiently clean.

4. Analysis of electrical characteristics of electrode material with Ti and TiN coatings

In order to protect the titanium electrodes from the electrolyte, as well as to reduce ESR, leakage currents, a film of titanium nitride with a thickness of up to 1 µm was deposited.

To measure end-to-end electrical resistance of electrode materials an experimental stand on the basis of the multimeter Fluke 107 600V cat III was used.

![X-ray microanalysis: (a) – Busofit coated with Ti; (b) – Busofit with Ti and TiN.](image2)

Resistance of the four combinations of electrode materials and titanium foil was measured: 1, a titanium foil (50 µm) 50x60 mm and 60x60 mm Busofit with deposited titanium coating on two sides; 2 – titanium foil (50 µm) 50x60 mm with a deposited titanium nitride from both sides, h ≈ 1 µm and Busofit 60x60 mm with deposited titanium with two sides, h ≈ 5 microns and titanium nitride of two
sides, h ≈ 1 µm; 3 – titanium foil (50 µm) 50x60 mm and 60x60 mm Busofit with deposited titanium with two sides, h ≈ 5 microns and titanium nitride of two sides; 4 – titanium foil (50 µm) 50x60 mm with titanium nitride coated on both sides, h ≈ 1 µm and Busofit 60x60 mm with titanium coated on both sides, h ≈ 5 µm.

Carbon fiber was placed between the two titanium foil contacts. The construction was pressed with different pressure: from 0 to 7.84 N/m² and to the opposite sides of the upper and lower contact the multimeter probes were applied. The data obtained from the end-to-end resistance measurement are shown in figure 3 and table 1.

![Figure 3](image_url)

**Figure 3.** The general graph of the dependence of the resistance on compression.

| Pressure, N/m² | (Ti foil) + (Busofit+Ti) | (Ti foil) + (Busofit+Ti+TIN) | (Ti foil + TiN) + (Busofit+Ti) | (Ti foil + TiN) + (Busofit+Ti) |
|---------------|--------------------------|-----------------------------|-------------------------------|-------------------------------|
| 0             | 75,9                     | 176,0                       | 91,4                          | 16,6                          |
| 1,96          | 22,7                     | 38,6                        | 9,7                           | 3,3                           |
| 3,92          | 11,6                     | 30,7                        | 7,3                           | 1,9                           |
| 5,88          | 10,9                     | 18,7                        | 5,8                           | 1,8                           |
| 7,84          | 6,1                      | 15,6                        | 5,1                           | 1,5                           |

Also the contact resistance between the titanium foil without Busofit was measured, the results of measurement of the resistance showed that the best resistance is in combination of (Ti foil+TiN) + (Ti foil+TiN) (less than 0.01 Ω). The results are shown in figure 4 and table 2.

5. Conclusions

The obtained results allow drawing the following conclusions:

1) The coating obtained by vacuum technology does not contain any third-party impurities, which indicates a high purity of electrode materials.

2) With coating thicknesses of 2 µm, the formation of a globular structure begins, which leads to the formation of a high specific surface area.

3) The best result of the through resistance measurements was obtained in the experiment with two contacts of titanium foil with titanium nitride and carbon fiber with metallized coating. What determines the prospect of using a TiN+Ti Busofit with in further studies.
Figure 4. The general graph of the dependence of the resistance on compression of titanium electrodes.

Table 2. The dependence of the resistance on compression of titanium electrodes.

| Pressure, N/m² | Resistance, Ω |
|---------------|--------------|
| (Ti foil) + (Ti foil) | (Ti foil) + (Ti foil + TiN) | (Ti foil + TiN) + (Ti foil + TiN) |
| 0 | 15,0 | 1,3 | 0,9 |
| 1,96 | 1,4 | 0,9 | 0,01 |
| 3,92 | 1,3 | 0,9 | 0,01 |
| 5,88 | 0,9 | 0,9 | 0,01 |
| 7,84 | 0,9 | 0,9 | 0,01 |

4) The smallest resistance of titanium electrodes was obtained in the experiment with two contacts of titanium foil both with titanium nitride.

5) The application of titanium nitride on a current collector of a titanium foil has led to a decrease in the resistance between the foil and Busofit.

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