Thin film vacuum technologies for a production of highly-capacitive electrolytic capacitors

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Abstract. The article describes the study of vacuum thin-film technology for producing electrode materials for highly-capacitive electrolytic capacitors (EC) based on a roll carbon fabric called Busofit, with a highly developed surface (more than 1000 m²/g). Laboratory technology has been developed for a metal film coating of carbon fabric used as electrode material for a production of EC cells. The electrical properties of the manufactured cell prototypes, such as specific energy and capacitance and internal resistance, were investigated. The prospects of using thin-film technologies for creating highly-capacitive ECs is shown.

The main tendencies in the power industry, which unequivocally indicate a crucial changes, include an increase in the generation of electrical energy from renewable energy sources (RES) and a reduction in its cost, which will lead to a reduction in the cost of generation for other types of energy sources. Due to the instability of the electricity generation from RES, systems for accumulation and redistribution of energy – for smoothing out the peaks of generation and consumption – will obtain extensive development. Therefore, accumulation and optimal redistribution of electricity will become a separate phenomenon in the energy industry.

Speaking about automotive industry, electric transportation systems and vehicles are already emerging and rapidly developing, as well as its basic technologies: fast-charge and regenerative braking technologies [1]. In this regard, there is a need for new sources of electric energy with improved specific characteristics, long service life, increased reliability and safety during operation. Such power supplies should be cheap and easy in manufacturing and also affordable. Along with secondary batteries, in terms of service life, number of charge-discharge cycles, as well as maximum specific power and operating temperature range, highly-capacitive electrochemical supercapacitors and hybrid power sources based on them are promising technologies [2].

The purpose of this work is a development of vacuum thin-film technology for a coating of the electrode materials on a basis of a roll carbon fabric for high-capacitance ECs. The main scientific and technical challenge of this work is to develop technological and constructional solutions for the deposition of metal coatings on the surface of a porous electrode material without reducing the value of its initial specific surface.
The schematic diagram of the EC cell is shown in figure 1 and consists of two current collectors (1) and two charge storage electrodes: the anode (4) and the cathode (2), saturated with an electrolyte, and a separator (3) between them. The EC cell is wrapped in a casing of laminated aluminum foil (5).

![Figure 1](image1.png)

Figure 1. The schematic diagram of the EC cell. 1 – current collector; 2 – cathode; 3 – separator; 4 – anode; 5 – laminated aluminum foil.

The material used for the storage electrodes (1) and (2) in a cell prototypes was a carbon fabric "Busofit-UL-50". Due to various chemical reactions, carbon materials can be prepared with a high degree of microporosity, and thus, with a highly developed surface area, which can exceed the geometric surface by a factor of 105; for Busofit-UL-50 the value of the surface area equals of 1000 to 1100 m²/g. In addition to a highly developed surface area, electrode materials must exhibit low electrical resistance, both along and across the sheet, since high resistance impacts such a properties of the EC cell as the internal resistance, limiting its current output.

In this respect, to obtain a highly conductive electrode from a roll carbon fabric, it is required to reduce its electrical resistance [3]. This problem was solved by the vacuum thin-film metal coating technology by the method of ion-plasma sputtering. Ion-plasma modification of the carbon fabric “Busofit-UL-50” was produced on the Elna-2 magnetron sputtering system. The experiment consisted of magnetron sputtering of a piece of titatium and condensation of its vapors on the carbon fabric roll, rewinding in the vacuum chamber of the module. Argon was used as a plasma-forming gas at an operating pressure of 0.8 to 2 Pa.

The figure 2(a) shows the electron microscope photograph of the original carbon fabric sheet Busofit, the figure 2(b) shows the photograph of its single thread before metal coating and the figure 2(c) shows the photograph of the thread with a deposited Ti layer on its surface. The metal layer performs the function of the current collector, increasing the conductivity across the fabric, and the thin-film deposition ensures the formation of a minimum resistance at the interface between the carbon thread and the current collector [3, 4].

![Figure 2](image2.png)

Figure 2. The electron microscope photographs: (a) the original carbon fabric sheet; (b) the single thread before coating; (c) the single thread with a coated Ti later. The latter picture shows the thickness of the metal layer of about 3.344 μm.

To protect electrode materials from undesirable exposure to a moisture of an atmospheric air, electrolyte saturation of the coated Busofit samples was accomplished in a vacuum, while EC cell prototypes were assembled in a VPB-1 glove box with an argon atmosphere. The cells were wrapped in a laminated aluminum foil and sealed in a Boss Vacuum MAX 36 vacuum sealer. Electrophysical properties of the cell prototypes were measured by a standard technique on a specially developed measuring complex [3, 5].

The capacitance of an EC depends mostly on the size of the surface of the electrodes (figure 3). The deposition of a metal coating on a Busofit fabric leads to a decrease in the internal resistance.
(ESR) and an increase in the capacitance of the EC cell. The EC, shown in figure 3, speaking of its equivalent circuit, consists of two capacitors connected in series. In this case, full capacitance of the EC cell is determined by the following equation (1):

\[ C = \frac{C_1 \cdot C_2}{C_1 + C_2} \]  

(1)

From the equation (1) it follows that the capacitances of the capacitors C1 and C2 will be maximum if they are equal. In this case, the capacity of a single capacitor will be twice the capacity of the EC cell (C1 = C2 = 2C). Therefore, with a total maximum capacitance of a capacitor structure of 10 F/g, the maximum capacitance of a single capacitor reaches 20 F/g. If we consider that the weight of the electrodes in the cell is about 20%, we can assume that a gram of the electrode material has a capacity of 100 F.

Figure 3. The dependence of specific capacitance on the contact area of electrodes in the cells.

Figure 4. The dependence of the ESR of the EC cells on the electrodes contact area.

Figure 4 shows the dependence of the ESR of the EC cell on the contact area of electrodes. Comparing figures 3 and 4, it can be concluded that the specific energy of the EC grows in direct proportion to the contact area of the electrode in the cell and inversely proportional to its ESR.

The ESR of a EC cell is determined by the sum of independent properties (resistance of electrode material, resistances on a contacts at the interface of the electrode material-current collector, electrolyte, and a number of minor, negligible factors). The contact area of the current collector on the electrode is one of the determining property. Therefore, it can be assumed that a decrease in ESR in a EC cell leads to an increase in specific energy consumption, and thin-film technologies, unlike conventional thick-film methods, are able control this property over a wide range of metal materials and thicknesses [6].

Figure 5. A pair of the assembled cell prototypes.

After the assembly, the cell prototypes were marked and cycled on a measuring equipment to remove the possible traces of air moisture for increasing the operating voltage (figure 5). As a result, this was made possible to increase the operating voltage to a ranges of 4.5 to 5 Volts. This corresponds to a
maximum specific energy of 25 to 30 W*h/kg. With the same materials, it is possible to increase the operating voltage above 5 Volts when assembled in a dry room with no moisture at all. In this case, the specific energy of the EC cell may exceed the specific energy of a lead-acid batteries.

Conclusions:
1. The conducted research and the obtained results allow us to conclude that the use of thin-film vacuum technology for the creation of electrode materials and its implementing in an EC cells, resulting in a higher specific energy, is a highly perspective.
2. The development and improvement of technology and design allows us to create ECs with higher performance. An increase in the electrical conductivity of electrolytes and the transition to solid electrolytes with a reduced thickness of the electrical double layer, makes it possible to produce even more energy-capacious EC cells.

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