Study of the specific energy of universal electrode materials for hybrid ultra-high-volume capacitor systems

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Abstract. The article discusses specific energy of universal electrode materials based on Busofit for ultra-high-volume capacitor systems and hybrid ultra-high-volume capacitor systems based on LiCoO2 and MnO2, which can be used in as sources of pulsed power in satellite solar panel deployment systems and emergency door opening systems and emergency platforms in airliners, including the Airbus 380 jumbo jet. The electroimpulse metallization of electrode materials and dependence of specific energy on weight of LiCoO2 and MnO2 was described. It was shown that hybrid ultra-high-volume capacitor systems increase its energy intensity up to 5.5 times compared with UCS.

1. Introduction

In modern aviation technology, much attention is paid to capacitor structures and electrochemical energy accumulators both in emergency and standby, and in some cases, as the main sources of energy. This is due to the tendency to electrify modern aircraft until the creation of a fully electric aircraft.

Such energy storage are used both separately and jointly in the hybrid power supplies, which are widely used in emergency door and evacuation platform systems in airliners, including the Airbus 380 jumbo jet, and in military aviation as sources of pulsed power, emergency energy supplies, in the stabilization systems of network parameters, in the deployment of solar satellite panels, as well as onboard electronics.

According to the “Bloomberg new energy finance”, in 2040 the electricity generated by burning coal will be reduced from 30% to 13 %, gas – from 24 % to 14 %, fuel oil – from 6% to practically 0%. And also the electricity generated by the hydroelectric and nuclear power station will be reduced slightly. At the same time, the demand for renewable energy sources (RES) will be increased in the market [1].

However, while developing and operating of RES some problems remain to resolve. One of these is the storage of electricity during the period from maximum production to maximum return to consumers.

Today, the traditional solution to solve the problem of accumulation and storage of electricity is the use of lithium-ion accumulators (LIA), providing a maximum energy capacity of 250 Wh/kg, which have some disadvantages [2].

Synthesis of electrode materials of ultra-high-volume capacitor systems (UCS) by using the technology of thin-film metallization on carbon matrix like Busofit or based on ferroelectrics with high dielectric permittivity, allowed to obtain supercapacitor with specific energy of 40-50 Wh/kg, which makes it possible to use them effectively as part of hybrid energy storage, including LIA and UCS. While LIA provides power supply in stationary, UCS will be in transient modes of operation of high-current
equipment. Nowadays UCS reached only 10-15 Wh/kg with the help of standard kick-film technology of forming electrode materials [3-5].

Electrode materials are a key element of ultra-high-capacity capacitor structures, determining their energy and performance characteristics. The main requirements to the electrode material: developed specific surface area, high electrical conductivity, availability of porous structure wetting, chemical inertness to the electrolyte, mechanical strength, the possibility of integration with the current collector determines the knowledge-intensive technological process of its creation.

One of the directions of creating supercapacitors is the construction of an electrolytic capacitor structure using carbon materials as electrodes with a developed surface that provides an area of electrodes hundreds or thousands of times larger than that of a conventional capacitor of the same size. Such material is carbon fiber Busofit.

The main drawback of many carbon electrode capacitors is that their performance is often limited due to the high resistance of most carbon electrodes. This high resistance causes large ohmic losses in the capacitor at the discharge stage. The reduction of the mentioned resistance in double-layer capacitors is achieved mainly by reducing the internal resistance in the electrode.

Recently, various manufacturing techniques have been proposed to reduce the internal resistance of carbon composite electrodes. In [6], a method for manufacturing a carbon-aluminum composite electrode by depositing coal powder and other conductivity-enhancing additives on an aluminum substrate is disclosed.

Another similar solution is disclosed in the patent [7], in which it is proposed to introduce metals, in particular aluminum, into carbon fiber electrodes by weaving metal fibers into carbon fiber billets.

Another method is described in [8-10]. In these solutions, it is demonstrated that metal fibers can be intertwined with a coal billet and sintered to produce an electrically conductive matrix with a stable design that can be used as a composite electrode.

In work [11] describes another solution in which the carbon fiber is immersed in an aqueous solution, so that a layer of electrically conductive metal oxide, preferably transition metal oxide, is formed in the pores of the carbon fibers. Nishino et al. the formation of metallic oxides, such as tin oxide or indium oxide, by vapor deposition is also described. In this work plasma spraying of molten metals, in particular, aluminum, on one side of the polarized electrode to form the corresponding layer performing the function of a current collector is offered.

Thus, modern studies show that the deposition of different metals on carbon electrode materials can reduce resistance and increase specific energy, as well as combine the properties of the electrode and the current collector in one material. So it helps us to reduce weight of power supply and increase its capacity.

The purpose of this work was to study the specific energy of the electrode material of UCS and hybrid UCS like Busofit, which is a porous carbon material with a highly developed surface (1000 m²/g), depending on the addition of chemically active materials as lithium cobalt (LiCoO₂) and manganese oxide (MnO₂).

2. Materials and methods

Developed UCS with simple design has ~ 4 Wh/kg of specific energy density of the material [12]. Porous carbon fiber Busofit was used as an electrode material in these cells. The authors developed the following method to increase the energy density of UCS samples, without changing the assembly conditions, measurements, materials and their sizes. The modification of the electrode material is using porous carbon fiber with a high specific surface area (1000 m²/g) with low surface resistance.

The problem of reducing the internal resistance of the electrode material was resolved by obtaining a metal current collector for flexible electrode with minimal transfer resistance, i.e., applying a continuous layer of metal on the surface of Busofit, which will be the current collector and reduce the internal resistance of the cell, as well as by electro-plating a separate carbon fiber material using such metals as silver (figure 1). Metallization allowed not only to reduce the internal resistance of the UCS cell (ESR), but also contributed to an increase in the specific surface area of the carbon material, and
consequently an increase in the specific energy of the material by 63%, which amounted to a specific energy intensity of the UCS material of 6.5 Wh/kg.

![Image](https://via.placeholder.com/150)

**Figure 1.** Metallization of electrode material filament of UCS: (a) a single filament of electrode material with a deposited layer of metal; (b) modified with silver nanoclusters of filament Busofit.

Measurement of electrical characteristics of the samples was carried out under the same conditions on the stand for experimental studies of multicyclic loading of UCS samples. The samples under study are subjected to multicyclic loading in the experimental stand by a set number of charge/discharge cycles and a given current. Charge/discharge cycles are recorded in the stand and automated measurements of parameters of experimental samples of UCS (capacitance, operating voltage, charge and discharge currents, leakage currents) are carried out.

In addition to UCS, hybrid UCS were developed and manufactured based on LiCoO2 and MnO2. The energy density of chemical current sources made by standard thick-film technology based on LiCoO2 and MnO2 reaches 160 mAh/g and 150 mAh/g, respectively [13, 14].

A highly porous carbon fabric Busofit with the specific surface of 1000 m²/g was selected as a matrix for LiCoO2 and MnO2. The chemically active material filled in the pores of the carbon matrix and covered the filaments of the Busofit with a thin layer [15].

Measurement of electrical characteristics of the samples was carried out under the same conditions on the stand for experimental studies of multicyclic loading of UCS samples. The samples under study are subjected to multicyclic loading in the experimental stand by a set number of charge/discharge cycles and a given current. Charge/discharge cycles are recorded in the stand and automated measurements of parameters of experimental samples of UCS (capacitance, operating voltage, charge and discharge currents, leakage currents) are carried out.

3. Results and discussion

Figure 2 shows that the value of the specific energy density of the cathode is related to the weight percentage of chemically active material (lithium cobalt) of the carbon matrix. The maximum specific energy of the hybrid UCS cathode is achieved when the weight percentage of the chemically active substance of the electrode material is ~100% of Busofit matrix. As a result, the specific energy of the electrode materials is achieved 29 Wh/kg.

And the relation between the specific energy of the cathode material based on LiCoO2 and surface area of the electrode material was studied. It was found that the specific energy density of the electrode material is related to the surface area of the electrode material while hybrid UCS was made based on lithium cobalt (LiCoO2) with the same materials, assembly conditions and measurement. According to the results of measurements, increasing the surface area of the electrode material by 3 times allows to
increase the energy density of the material by 21%, as well as to reduce the internal resistance (ESR) of hybrid UCS cell by 2.5 times.

![Figure 2](image2.png)

*Figure 2.* The relation between the specific energy of the cathode and the weight percentage of LiCoO₂ in the carbon matrix.

As part of this research, hybrid UCS based on manganese oxide (MnO₂) was constructed and studied. The specific energy of the hybrid UCS primarily depends on the weight percentage of MnO₂ in the cell. Increasing the specific weight of MnO₂ by 2 times allow to increase the specific energy density of the material by 7 times, as well as to increase the working voltage by 1.8 times. The specific energy density of the material of hybrid UCS reaches 21.2 Wh/kg when MnO₂ is used (figure 3).

![Figure 3](image3.png)

*Figure 3.* The relation between the specific energy of cathode material and the specific weight of MnO₂.

Figure 4 shows a diagram of specific energy density values of materials of produced samples UCS and hybrid UCS:
• ultra-high-capacity capacitor structures (UCS) - 4.1 Wh/kg;
• ultra-high-capacity capacitor structures with metallization - 6.5 Wh/kg;
• hybrid UCS based on manganese oxide (MnO2) - 21.2 Wh/kg;
• hybrid UCS based on lithium cobalt (LiCoO2) - 22.6 Wh/kg.

Figure 4. The specific energy of the material of the produced samples UCS and hybrid UCS.

Analysis of the results of the specific energy density of materials of ultra-high-volume capacitor systems, ultra-high-volume capacitor systems (UCS) with metallization, hybrid UCS based on lithium cobalt and hybrid UCS based on manganese dioxide, which are constructed and tested under the same conditions, design and materials, shows that the specific energy density of hybrid UCS based on manganese oxide and hybrid UCS based on lithium cobalt is contributing respectively 5.2 and 5.5 times more than UCS.

4. Conclusions
The obtained results allow drawing the following conclusions:

1. Electro-impulse metallization of electrode materials for ultra-high-capacity capacitor structures allows increasing energy density by 63% compared with the non-metallized electrode material.
2. Increasing the specific weight of manganese dioxide by 2 times is allowed to increase the specific energy density of the material by 7 times, as well as to increase the working voltage by 1.8 times.
3. Increasing the surface area of the electrode material by 3 times allows to increase the energy density of the material by 21%, as well as to reduce the internal resistance (ESR) of the cell by 2.5 times.
4. The developing of hybrid UCS based on LiCoO2 and MnO2 allows increasing energy density up to 5.5 times compared to UCS and UCS with metallization of Busofit using electro-impulse technology and to reduce the weight of the final power supply, which will be used in aircraft as an emergency power supply, by combining the properties of the electrode and the current collector in one material and increasing the energy intensity due to metallization.
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