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Hybrid capacitor based on carbon matrix for intelligent electric energy storage and transportation system

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Abstract. This paper describes the developed complex of vacuum thin-film technologies for creating electrode materials of energy storage devices for an intelligent source of accumulation, storage and transportation of electricity. Thin-film technologies, in contrast to thick-film technologies, allow more efficient use of surface properties, using nanostructured materials and structures. The developed complex allows us to implement a promising technology for creating a new generation of electrode materials based on a flexible carbon matrix with a highly developed surface. On the basis of the developed electrode material, hybrid capacitors were manufactured and studied, the specific energy of which is currently ~ 20 W·h/kg, which is a higher indicator than the currently available indicators in the literature. The article also discusses ways to increase the energy intensity to ~ 50 W·h/kg.

1. Introduction

The perspectives for the development of global energy are based on the widespread use of renewable energy and increasing efficiency and environmental friendliness in the use and generation of energy. the creation of intelligent sources of accumulation, storage and transportation of electric energy, which allow you to fully control the processes of generation, consumption and transportation of energy due to built-in systems of operational information processing and which will provide a comprehensive solution to these problems, is relevant and timely [1-2]. In modern aviation technology, much attention is paid to capacitor structures and electrochemical energy accumulators in both emergency and standby mode, and in some cases as the main sources of energy. This is due to the trend towards electrification of modern aircraft up to the creation of fully electric aircraft. Such energy storage devices are used both separately and jointly in hybrid power sources, which are widely used in emergency door systems and evacuation platforms in airliners, including in the Airbus 380 jumbo jet, as well as in military aviation as sources of switching power, emergency power sources, in network parameter stabilization systems, when deploying solar satellite panels, as well as on-board electronics.

Intelligent sources of storage and storage of electrical energy provide almost all requirements. The exception is the position on the growth of specific energy intensity. This is because if the circuitry of the control systems and monitoring developed and widely represented in mass production, the circuitry for the storage, stockpiling, and transport of electrical energy is under active development and mostly represented by the chemical current sources, and recently begins to show interest in ultra-high-volume capacitor structures, in which the accumulation of electrical energy occurs in an electric double layer

(EDL). Capacitors, unlike hit, have a lower specific energy consumption, but a higher specific power, more than an order of magnitude the number of cycles, and significantly less charging time. As a result, the connection of chemical current sources and ultra-high-volume capacitor structures in a hybrid intelligent current source expands the range of its functionality [3]. The use of electrode materials with a highly developed surface, on the basis of which energy-intensive capacitors are created, provides the creation of hybrid electrolytic capacitors in which energy is accumulated both through chemical processes and in a double electric layer [4]. This allows the integration of two mechanisms for the accumulation of electrical energy in the cell. Overall, these hybrid capacitors integrate various advantages of conventional supercapacitors and ion batteries, exhibiting superior rate performance, high power density, high energy density and long cycle life. These merits give metal ion hybrid capacitors a promising future in electric vehicles and wearable/portable electronics. Therefore, metal ion hybrid capacitors with good deformability based on reasonable electrode/device structure designs have a wide possible range of applications for flexible/wearable energy storage. These flexible hybrid capacitors can also be combined with flexible solar cells, flexible sensors and other electronics for multifunctional smart applications in future society [5]. In the analytical review of BMPOWER (USA) and in the periodical literature, the results are presented that allow increasing the energy intensity of ultra-high-volume capacitor structures by 2-5 times [6-9]. If we take into account that the capacity of capacitor structures (SCS) reaches 10-15 W·h/kg, then taking into account hybrid capacitors that integrate two energy storage mechanisms, there is a prospect of obtaining energy intensity at the level of 50-60 W·h/kg [10].

Therefore, the aim of the work was to develop a hybrid capacitor with energy characteristics of ~25-50 W·h/kg for an intelligent system for storing and transporting electrical energy.

2. Experimental part

Structurally, hybrid capacitors are an electrolytic cell in which the electrode materials consist of a plastic matrix containing a chemically active material. As a matrix, a carbon fabric type "Busofit" Khimvolokno, Belarus), which has a specific surface area of 1000-1200 m^2/g. The structural element that has a significant difference from chemical current sources and double electric layer (EDL) capacitors in a hybrid electrolytic capacitor cell is electrode materials. The development of the design and manufacturing technology of electrode materials for capacitor structures was based on the use of vacuum thin-film technologies [11].

Metallization of the surface of the carbon matrix based on the "Busofit" type fabric was carried out in order to increase its electrical conductivity [8,12-13], reduce the contact resistance between the elements of the electrolytic cell (current sink-electrode material) and increase electrochemical stability. A layer of titanium or titanium with titanium nitride was applied to the surface of the carbon fabric using a MAGNA TM R vacuum roll unit (Scientific research institute of precision engineering, Russia).

In order to obtain the most uniform coating with the highest growth rate and stable plasma magnetron were selected the following parameters of the Ti coating: the pressure of working Ar gas from 0.3 to 4.4 Pa; operating voltage from 420 to 280 V, and current from 20 to 20.6 A, and metallization time was from 5 to 120 min.

To create a hybrid capacitor cathode, the initial carbon matrix was filled with a chemically active material based on lithium cobalt oxide ($LiCoO_2$) previously crushed in a Netzsch (Bayern, Munich) bead mill, labstar type, at a main shaft rotation speed of 3000 rpm for 8 h, to a particle size of 100 to 350 nm [14,15]. The filling of the carbon matrix was carried out by vacuum impregnation at a pressure in the chamber – 10^3 Pa; the heating temperature of the mixture 70°C; the time of impregnation and degassing was30 and 15 min, respectivly. To impregnate the cathode material of chemical current sources, $LiCoO_2$ was mixed with polycarbonate, which was an integral part of the electrolyte used in the manufacture of the electrolytic cell. Scanning electron microscopy (SEM) photo of a carbon material filament impregnated with $LiCoO_2$ + propylene carbonate dispersion and an X-ray spectral analysis of the material composition performed on a Zeiss EVO 40 (Germany) scanning electron microscope. An aluminum substrate and a voltage of 20 kV were used.

The obtained electrode materials were used in ultra-high-volume capacitor structures with des and hybrid ultra-high-volume capacitor structures based on $LiCoO_2$. Only titanium-metallized carbon material was used as the anode and cathode in the capacitor. A titanium-metallized carbon material was used as the anode in the hybrid capacitor, and a carbon material impregnated with a chemically active material based on $LiCoO_2$ + NMP dispersion was used as the cathode. Due to the fact that the carbon material is flexible, the capacitor cells of both types are also flexible, which is very relevant. The manufacturing and measurement conditions for both types of samples were the same. The measurements of the capacitor cells (specific energy consumption, internal resistance ESR) were carried out on the measuring stand of the experimental stand for studies of the process of multicyclic loading of experimental samples of supercapacitors (RUST-95, Russia).

During the work, a hybrid intelligent source of electric energy storage was developed, which includes a battery, a battery of supercapacitors, converter-switching equipment, battery balancing devices, a mode stabilization system, a microcontroller system, a Wi-Fi receiver-transmitter. The subject of development is an inverter-a frequency converter with the possibility of power supply from a low-voltage constant current source.

Control system and control provides:

- the operation of the drive load of valves with mains voltage, and in its absence, the increased load on the drive;
- energy flows between the rectifier, lithium battery and supercapacitor-based battery within the modes;
- current monitoring of the system operation parameters during charging, discharging and storage, as well as broadcasting the current results to the control system via radio channel;
- protection of components from short circuit, over-discharge and overcharge;
- current diagnostics of the state of the main elements and devices and the output of results to the control system via radio channel.

The expansion of the possibility of practical application of such a system is provided by a frequency-controlled inverter. the device is designed to power a standard three-phase asynchronous motor 220/380 V from a dc source 24 V (±15%) with the ability to adjust the speed in the range from - 90 to + 400% of the rated speed (for the most common motor with a rated speed of 2800 rpm. the speed varies from 280 to 11200 rpm). The device can be used to power equipment containing three-phase asynchronous motors that require rotation speed control by adjusting the frequency of the supply voltage in the following cases: for power supply of three-phase asynchronous motors in places where there is no three-phase 220/380 V network; to ensure uninterrupted operation of the equipment in case of disconnection of the main supply network.

The main characteristics of the inverter:

- Power supply voltage 24 V DC (±15%);
- Output voltage 220/380 V pure sine wave;
- Rated power 1.5 kW, maximum 2.5 kW;
- Efficiency at rated power of 94%;
- Frequency adjustment range 5-200 Hz;
- Operating mode at power not exceeding the nominal-long at maximum power of 15 min;
- When the motor is running at a reduced speed, it provides automatic voltage-frequency dependence;
- Provides the ability to recover braking energy.

3. Results and discussion

The appearance of the carbon fabric “Busofit” with a layer of titanium applied show on the figure 1a. Figure 1b demonstrates the threads of the fabric “Busofit” and a single thread (figure 1c, d), where it is seen that titanium is applied in a layer on the entire surface of the thread (figure 1d). Figures 2 show the chemical composition of the surface by electron microscope.

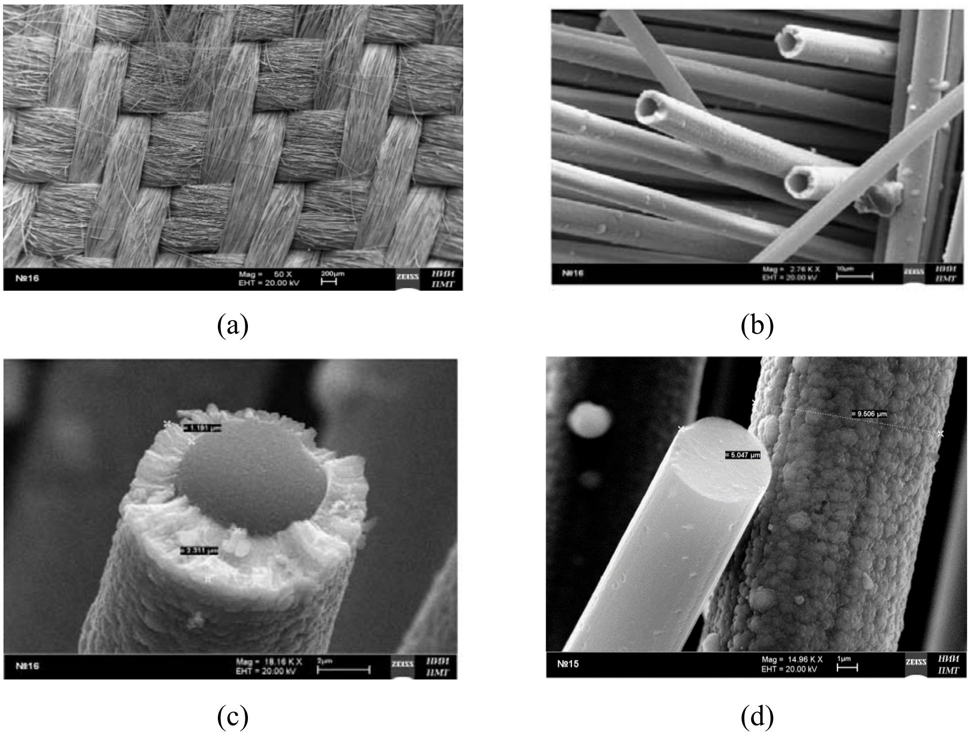


Figure 1. SEM image of the fabric after applying Ti layer (a), a thread of fabric of the "Busofit" inside the Ti layer (b), a single thread of fabric (c, d). A layer of carbon material was coated with Ti with a layer thickness of 8 µm.

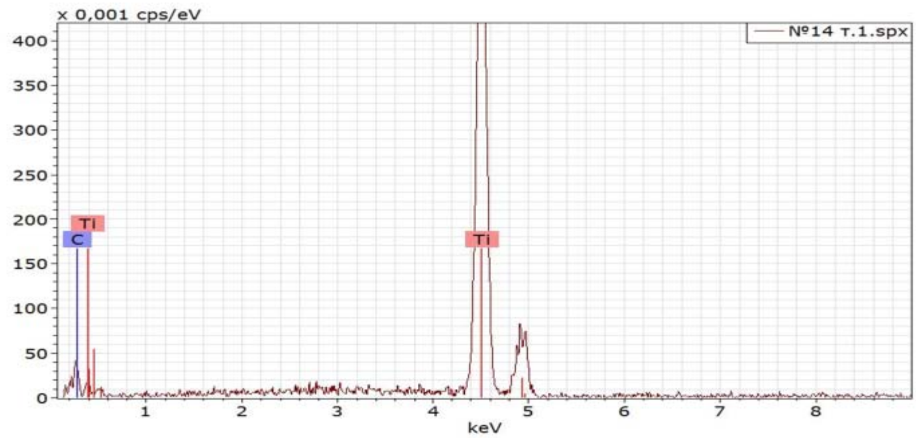
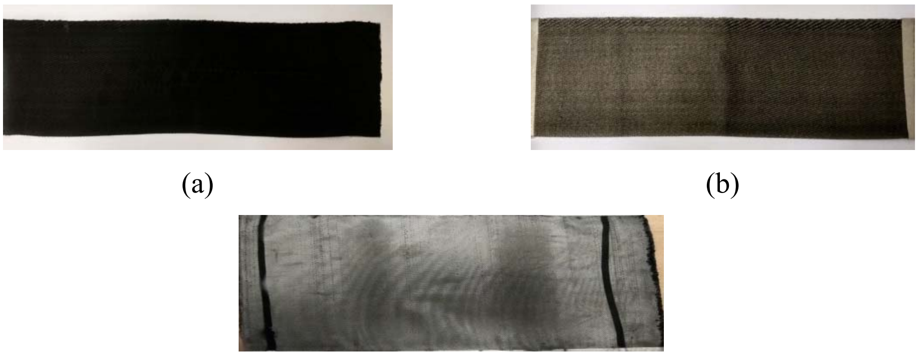


Figure 2. Chemical composition of the coating.

It was revealed that at a coating thickness of 8 µm, the curve of the dependence of the electrical resistance on the thickness reaches saturation, which indicates the metallization of the porous material to the maximum thickness. Thus, a coating with a thickness of 8 µm (figure 3c) is advisable to use for a current collector. The thickness of the coating on the back of the carbon material is 2 µm (figure 3b).

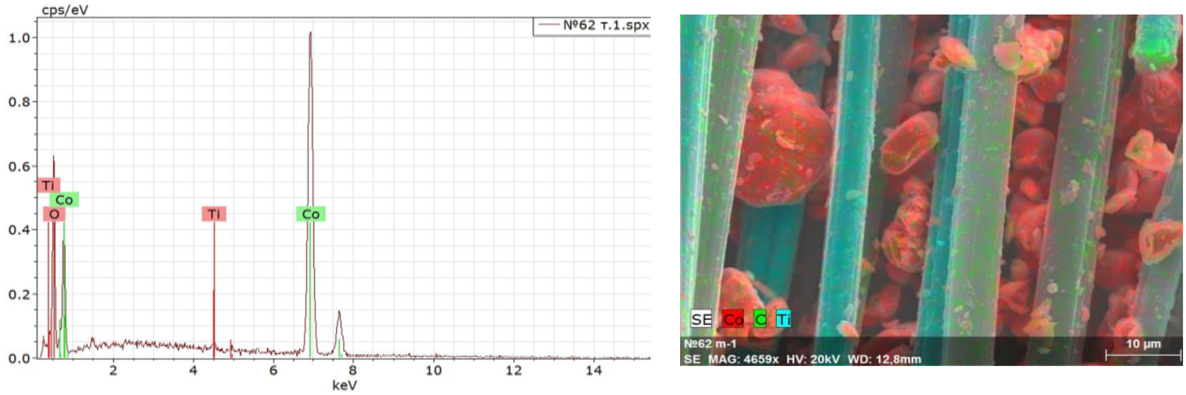
Figure 4 shows a SEM photo of a carbon material filament impregnated with $LiCoO_2$ + propylene carbonate dispersion and an X-ray spectral analysis. X-ray spectral analysis did not reveal any third-party impurities in the formed coating. It can be seen that finely dispersed $LiCoO_2$ is distributed over the surface of the thread, and micron-sized particles fill the space between the threads of the "Busofit" type fabric.



(a) (b)

(c)

Figure 3. The appearance of the workpiece for electrode materials “Busofit”: starting material (a), with Ti coating thickness of 2 µm (b) and 8 µm (c).



(a) (b)

Figure 4. Chemical composition (a) and microscopic image of the distribution of a chemically active material in an flexible carbon matrix (b).

It was found that the maximum specific energy intensity of the hybrid ultra-high-volume capacitor structures cathode is achieved when the cell contains ~ 100% of the chemically active substance from the mass of the electrode material, hybrid ultra-high-volume capacitor structures based on $LiCoO_2$ with the same materials and conditions of assembly and measurement, have a dependence of the energy intensity of the material on the area of the electrode material. According to the results of measurements, an increase in the area of the electrode material by 3 times, allows increasing the energy intensity of the material by 21%, as well as reducing the internal resistance of the hybrid ultra-high-volume capacitor structures cell by 2.5 times.

It was found that the use of a chemically active mass ($LiCoO_2$) can increase the specific energy intensity by 5.5 times, the energy consumption of the cell is then 22.6 W·h/kg. The use of a multilayer structure with a total area of the electrode material based on the carbon material Busofit ~ 600 cm^2 gives an increase in the energy intensity by ~ 2 times. Thus, it can be assumed that if a hybrid capacitor with $LiCoO_2$ uses a multi-layer structure, the energy intensity can reach ~ 50 W·h/kg (figure5), which is a higher indicator than the current capacitor structures, in which the energy intensity does not exceed 10-15 W·h/kg

The resulting UCS and hybrid UCS are part of the developed intelligent system for the accumulation, storage and transportation of electricity-a hybrid intelligent power source.

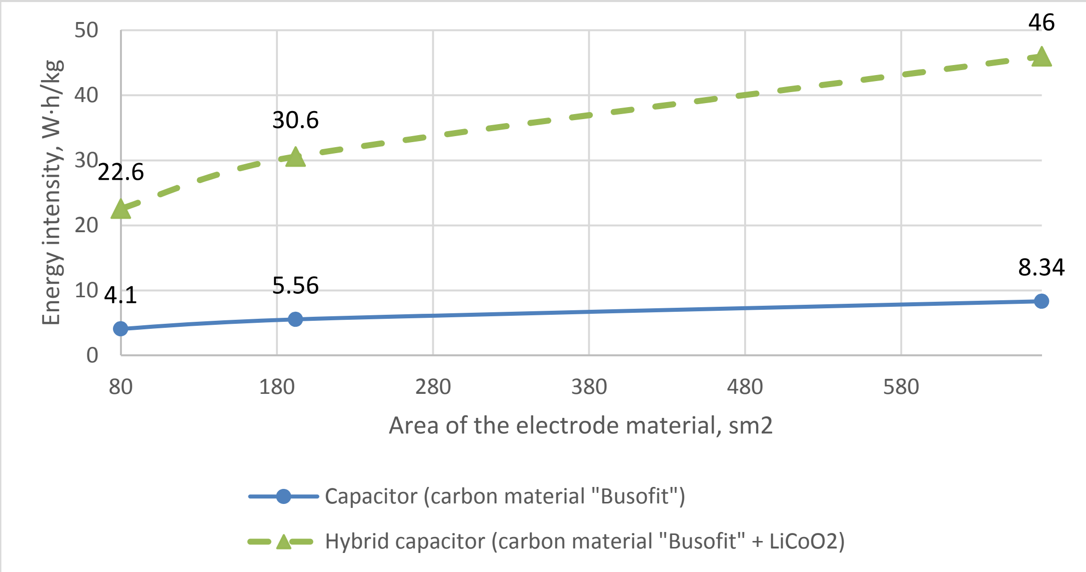


Figure 5. The dependence of the energy intensity of capacitors based on the carbon material "Busofit" and hybrid capacitors (carbon material "Busofit" + $LiCoO_2$) on the area of the electrode material.

As a result, the design and tests of a hybrid intelligent current source (development of the authors) based on chemical current sources, ultra-high-volume capacitor structures and control system, which provides zero switching time from centralized, mains power to an uninterruptible power supply system, were developed and tested (figure 6, 7). Safety during storage and transportation is ensured by the integrated monitoring and control system, which provides a wide range of monitoring of incoming and outgoing power.

Figure 6. Experimental test bench of hybrid intelligent current source.

Figure 7. Intelligent source of accumulation storage and transportation of electrical energy.

4. Conclusion

A complex of vacuum thin-film nanotechnologies for creating electrode materials for current sources has been developed, which allows implementing a promising technology for creating a new generation of electrode materials based on a flexible carbon matrix with a highly developed surface. Analysis of the results of specific ultra-high-volume capacitor structures and hybrid ultra-high-volume capacitor structures based on $LiCoO_2$, manufactured and tested under the same conditions and with the same design shows that the specific energy consumption of hybrid capacitor based on $LiCoO_2$, have values exceeding the specific energy of ultra-high-volume capacitor structures 5.5 times.

Thus, the energy intensity of the developed hybrid capacitors based on a carbon matrix was 22.6 W·h/kg. To further increase the specific energy consumption, it is necessary to use a multi-layer design of the capacitor, which will allow you to get ~ 50 W·h/kg. The resulting samples were used in an intelligent system for storing and transporting electrical energy.

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