Supercapacitor with electrodes based on high-purity single-walled carbon nanotubes

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Abstract. We studied a supercapacitor with high purity carbon paper electrodes \cite{1} with a specific gravity of 20 g/m\textsuperscript{2}. The specific capacitance of the electrode during assembly in a coin cell housing with an aqueous 6M KOH electrolyte, at a scan rate of 1 mV/s, is 52 F/g. The specific power is 195.42 W/kg and the specific energy is 0.19 W\cdot h/kg at a scan rate of 100 mV/s, which is included in the region of supercapacitors in the Ragone plot.

1. Introduction
Modern technologies involve significant waste of electrical energy and place high demands on storage elements. One type of device that allows you to accumulate and save electrical energy are capacitors, including ionitors or supercapacitors \cite{2,3,4}. 

A promising direction for improving supercapacitors is the use of porous carbon materials as electrodes, in which charges accumulate in the form of a double electric layer on a developed porous surface of carbon structures \cite{3}. The issue of increasing the specific capacitance of supercapacitors remains relevant at present. New materials for electrodes and their combinations, alloying, surface modification, selection of the composition of electrolytes - these are the main directions for improving the characteristics of supercapacitors \cite{4,5}.

Therefore, it is important to study any, even already well-known material, if it has distinctive features. In this work, a preliminary study of the electrodes for a supercapacitor of single-walled carbon nanotubes with a high degree of purification was carried out. A review of the literature showed that the electrodes of activated carbon and nanotubes can have a specific capacity of up to 100 and 280 F/g, respectively \cite{2}, while in ordinary electrolytic capacitors this value is several orders of magnitude lower. Important characteristics in the description of supercapacitors are energy density and power density, the value of the potential window. Typical values for supercapacitors with carbon electrodes are: energy densities up to 80 W/kg and power densities 6–30 kWh/kg, potential window values of the order of ±0.8 V when using aqueous electrolytes and symmetric electrode schemes \cite{2}.

2. Methodology
In the manufacture of electrodes used carbon paper from nanotubes or SWN – buckypaper. Carbon paper consists of weaving high-strength nanotubes into agglomerates and agglomerates into sheet material, where the individual elements are firmly held together by mechanical weaving and the intermolecular forces of Van der Waals (Figure 1). For the manufacture of electrodes used paper with different specific weighing 3 and 20 g/m\textsuperscript{2}.
Figure 1. Samples of SWN agglomerates – buckypaper. A – Individual agglomerates of nanotubes with an increase of $\times 16$, B – agglomerates with an increase of $\times 32$, C – a sample of buckypaper (20 g/m²) at magnification $\times 8$.

Pairs of carbon paper electrodes should be of the same mass, if possible, so it is difficult to produce them by mechanical cutting. To increase the manufacturing accuracy, a laser cutting method was used on an installation of the LRS–50M model, with a coordinate table, a radiation wavelength of 1.064 $\mu$m, an average pulse power of 10 W, and a pulse repetition rate of 10 Hz. The carbon paper blank was placed on a metal lining, pressing weights were installed on top to prevent deformation during cutting and holding the blank in the focus of the laser beam (Figure 2A).

Figure 2. Laser cutting of electrodes from buckypaper (A), paper cut from nanotubes at magnification $\times 32$ (B), appearance of electrodes (C).
In the area of the cut, the buckypaper is stratified, however, in this case, the cut-out electrode retains the shape of the regular circle of Figure 1C and Figure 2C. For the convenience of measurements, samples of electrodes from a high degree of purity SWN-buckypaper up to 99.9 % [1] were placed in a standard coin cell CR2025 battery case. A 6 M aqueous KOH solution with a volume of 50 μl per well was used as an electrolyte. In Figure 3 shows blanks for assembling electrodes in a housing. The electrodes 3 of the SWN-buckypaper accumulate charge in a double electric layer, the metal collectors 2 provide reliable electrical contact between the carbon material and the housing 1. The dielectric separator 4 made of polymer non-woven fiber is an insulator between the electrodes and does not interfere with the free movement of ions in the electrolyte.

Figure 3. Elements for assembling a coin cell CR2025: 1 – two parts of the outer case made of stainless steel, 2 – metal electrodes-collectors, 3 – electrodes from high-purity SWN-buckypaper, 4 – separator.

Cyclic voltammograms (CV) of samples were obtained according to a two-electrode circuit using a P-50 PRO potentiostat-galvanostat (LLC Elins, Russia) in the scan rate 1–100 mV/s, with a potential window of ± 500 mV, to determine the specific electric capacitance of the electrode material.

3. Results
Preliminary measurements of the assembled coin cell showed the promise of research on the use of electrodes from high-purity buckypaper as plates of capacitors of increased capacity. In Figure 4 shows cyclic voltammograms (CV) for carbon paper of various specific gravity at a sweep speed of 100 mV/s.

The area of the figure in a limited graph corresponds to the capacitor power for one charge – discharge cycle. For a sample with a specific gravity of the electrode of 3 g/m² and 20 g/m² (Figure 4), the calculated specific capacities were 1.7 F/g and 3.2 F/g, respectively. Graph (Figure 4B) has a shape close to rectangular, which is typical for reversible processes of charge and discharge of a double electric layer [7]. For a sample with a large specific gravity of the electrode (Figure 4B), the calculated specific capacitance is almost twice as large. An increase in the specific capacity with a larger mass of the electrode, ceteris paribus, indicates the influence of factors not related to the material of the electrodes. For example, a low specific capacitance may be due to poor electrical contact between the thinner carbon paper and the metal collector electrode or an improperly selected electrolyte, it is also possible that the separator material does not provide sufficient ion permeability. For the sample, the general laws characteristic of electrodes made of a porous carbon material are observed [6,7]. With a decrease in the potential scan rate from 100 to 1 mV/s (for the sample 20 g/m²), the specific
capacitance of the electrodes increases from 3.2 to 52 F/g, respectively, which is also characteristic of supercapacitors [7]. In Figure 5 shows the CV for the assembled capacitor at voltages U = ± 450 mV, the charge – discharge current reaches 70 μA.

The stored energy in the capacitor under these conditions is of the order of 220 mJ per cycle. Given the mass of carbon fiber electrodes $m_1 = 9.37$ mg, $m_2 = 9.09$ mg, the specific capacity of this material was calculated $S_{sp} = 52$ F/g. Specific power and energy at a sweep speed of 100 mV/s reach 195.42 W/kg and 0.19 Wh/kg, respectively, these values are in the region of supercapacitors in the Ragone plot [2]. However, this is not a high enough indicator for carbon materials and additional experiments with different types of separators and coin cell sizes are needed to ensure better electrical contact and greater mobility of electrolyte ions.

4. Conclusion
As a result of the work done, the laser cutting mode of carbon paper buckypaper is set. Mode parameters: average pulse power of 10 W, pulse repetition rate of 10 Hz. The specific capacitance of the electrode during assembly in a coin cell housing with an aqueous 6M KOH electrolyte, at a potentiostatic sweep speed of 1 mV/s, is 52 F/g. A strong dependence of the electrical characteristics of the cell on the specific gravity of the carbon electrode is observed, which is associated with the peculiarities of the assembly of the coin cell. The specific power is 195.42 W/kg and the specific
energy is 0.19 Wh/kg at a scan rate of 100 mV/s, which is included in the region of supercapacitors in the Ragone plot.

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