Electrophoretic deposition and capacitive characteristics of composite electrode materials based on CNTs and ruthenium oxide for planar supercapacitors

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Abstract. In this work, a method for the formation of planar supercapacitors, which combines electrophoretic deposition of composite electrode materials based on CNTs and ruthenium oxide, and laser engraving, is proposed. The features of electrophoretic deposition are considered and the influence of the main technological modes on the morphology and composition of the formed layers of electrode materials is determined. The conducted studies of the electrophysical characteristics of the formed samples confirmed the possibility of producing planar capacitors with a high capacity and their potential applicability for a number of applications in microelectronics.

1. Introduction
The advance of miniaturized electronics and Internet of Things has a great impact on the development of miniaturized energy storage devices [1]. Planar supercapacitors are considered a promising device in this area due to their significant energy and power density, and long life cycle [2, 3]. It is known that electrochemical capacitors accumulate charge not only due to the electric double layer formation, but also due to the Faraday pseudocapacitance of reversible redox reactions. The combination of these two mechanisms of charge storage at once can significantly increase the capacitive characteristics of the device.

For practical implementation, it is necessary to develop a method for the formation of composite electrode materials in which heterogeneous components will be responsible for different mechanisms of energy storage [4, 5]. Great efforts have been made to maximize their performance with new carbon nanomaterials and to increase their specific capacity and energy density by utilization of transition metal oxides such as RuO₂, MnO₂, NiO, Co₃O₄, SnO₂, ZnO, TiO₂, CuO, Fe₂O₃, WO₃ [6]. One of the approaches to creating multicomponent electrode materials for supercapacitors is electrophoretic deposition (EPD) - a simple method that allows the formation of layers on conductive substrates with a given composition, morphology, and porosity [7-9].

Therefore, within the framework of this work, the features of the electrophoretic deposition of composite electrode materials based on CNTs and ruthenium oxide will be investigated, their capacitive characteristics are determined, and a method for the formation of planar supercapacitors is proposed.
2. Experiment
In this work, the objects of study were “sandwich-like” and planar supercapacitors, a schematic representation of the route of their production is shown in figure 1. Nickel foil was used as substrates for bulk samples, and sitall plates with a 300 nm thick layer of nickel deposited by magnetron sputtering were used for planar samples. The formation of composite electrode materials on their surface was carried out by the method of electrophoretic deposition on a setup consisting of two electrodes (a substrate and a counter electrode) connected to a power source and a container with a suspension. Preparation of suspensions was carried out by ultrasonic dispersion of components in a solvent. The main components of the suspension in this work were few walls carbon nanotubes (FWCNTs) synthesized by CVD method [10] and ruthenium oxide hydrate produced by Alfa Aesar. Acetone, isopropyl alcohol, ethanol and their combinations were used as solvents. The concentrations of carbon nanotubes and ruthenium oxide were 0.2 mg/ml.

Figure 1. Schematic representation of supercapacitor formation processes.

EPD of composite materials was produced in potentiostatic mode - the electric field strength varied from 50 to 150 V/cm. To determine the mass of the sediment, the samples were weighed before and after the deposition process, and the deposition area was limited using overhead masks-templates. The morphology and composition of the materials were controlled using SEM and energy dispersive X-ray analysis. After the deposition of composite materials, electrodes were formed - for “sandwich-like” samples, they were cut with scissors, and planar supercapacitors were manufactured using laser engraving on a CNC 3018 Pro machine. “Sandwich-like” supercapacitors consisted of two electrodes separated by a separator and placed in a sealed bag filled with electrolyte. For measuring the capacitance characteristics planar supercapacitors were placed in a container with an electrolyte. In both cases, a 1 M aqueous solution of KOH was used as the electrolyte. The capacitance characteristics were measured by the method of cyclic voltammetry in the voltage range from 0 to 1 V with a sweep rate of 10 and 100 mV/s.

3. Results
At the first stage of the study, the dependence of the stability of the suspension on the selected solvent was experimentally determined. Acetone, isopropyl and ethyl alcohols, and their mixtures were used as solvents. The stability assessment was carried out on the basis of photographs of the suspensions taken at 0.5, 1, 2, 24 and 48 hours after preparation. The change in transparency and the formation of sediment at the bottom of the tube were visually assessed. Within the framework of this work, a suspension was considered stable if the time of its visual stability was many times greater than the duration of the electrophoretic deposition process. Figure 2 shows an example of a set of photographs
for an acetone solvent. The carried out experimental work showed that the most stable suspensions were obtained with ethyl alcohol - acetone (E-Ac) and isopropyl alcohol - acetone (IPA - Ac) solvents mixed in equal volume fractions.

Figure 2. Photographs of the evolution of acetone-based suspensions over time.

At the next stage, the effect of the solvent on the morphology and capacitive characteristics of the formed electrode materials was studied. For this, suspensions were prepared based on E-Ac and IPA-Ac, and deposition was carried out on substrates made of nickel foil at electric field strength of 100 V/cm. Figure 3 shows SEM images of the obtained composites.

Figure 3. SEM images of FWCNT-RuO$_2$ composite layer deposited from a suspension based on ethanol-acetone (EA-Ac) (left) and isopropyl alcohol – acetone (IPA-Ac) (right).

The layers obtained from the IPA-Ac based slurry have a more porous structure. This feature can make a positive impact on the capacitive characteristics of a supercapacitor, since the effective electrode-electrolyte contact area will be larger, and, hence, the contribution to the total capacity of the electric double layer. This hypothesis was confirmed by studying the capacitive characteristics of “sandwich-like” supercapacitors with electrodes based on the materials mentioned above. Figure 4 shows cyclic voltammograms obtained with sweep rates of 10 and 100 mV/s.

At a sweep rate of 10 mV/s, the specific capacitance of supercapacitors with electrodes formed from suspensions based on E-Ac and IPA-Ac was 8.1 mF and 10.3 mF and at 100 mV/s – 4.1 and 5.3 mF respectively. Further, the influence of the electric field strength on the deposition rate and the morphology of the formed sediments was investigated. An IPA-Ac suspension was used for the experiments. Figure 5 shows SEM images of the morphology of the formed sediments at electric field strengths of 50 and 150 V/cm. Based on the obtained experimental results, the field strength insignificantly affects the morphology.

The uniformity of the distribution of components in the sediment was monitored using elemental analysis. Figure 6 shows the distribution maps of the components over the surface of the layer of the
composite electrode material CNT - ruthenium oxide formed from the IPA-Ac suspension. Obtained results indicate a uniform distribution of elements in the sediment.

![Figure 4](image.png)

**Figure 4.** Cyclic sweeps of the samples at 10 mV/s (left) and 100 mV/s (right).

![Figure 5](image.png)

**Figure 5.** Layer of FWCNT-RuO$_2$ composite applied from the IPA-Ac suspension at field strengths of 50 V/cm (left) and 150 V/cm (right) respectively.

![Figure 6](image.png)

**Figure 6.** Maps of the distribution of elements over the surface of a composite electrode material.

The presence of dark areas on the maps of the distribution of elements may be due to the fact that after the solvent dried out, the layer cracked and had a porous and rough structure. The presence of micro and macro pores can have a positive effect on the capacitive and power characteristics, since the contact area between the electrode material and the electrolyte will increase.

The deposition rate increases linearly with an increase of electric field strength in the range from 50 to 150 V/cm - the obtained experimental dependence is shown in figure 7.

After examining the “sandwich-like” samples, experiments were carried out with the samples based on sitall substrate having a planar structure. The formation of electrode materials by the EPD method was carried out from IPA-Ac suspensions in similar modes.
Figure 7. Graph of the dependence of the deposition rate on the electric field strength.

Figure 8. Cyclic sweep of the planar supercapacitor at 10 mV/s and 100 mV/s.

Figure 8 shows cyclic sweeps for a sample of a planar supercapacitor with composite electrode materials based on CNTs and ruthenium oxide, taken at a sweep rate of 10 and 100 mV/s. The average calculated specific gravimetric capacitance values for 10 measurement cycles for sweep rates of 10 and 100 mV/s were 35.3 and 9.2 F/g, respectively. For planar supercapacitors, the more correct specific unit of measurement is "F/cm²", since their location is implied directly next to the consumer on the chip. The specific capacitance per unit surface area for this sample was 44.5 and 11.6 mF/cm².

4. Conclusions
In this work, an approach to create planar supercapacitors with composite electrodes based on carbon nanotubes and ruthenium oxide was proposed. The electrode materials were formed using electrophoretic deposition, and the structure of the planar power source was formed using laser engraving. To optimize the EPD, the influence of the solvent composition on the suspension stability, porosity and morphology of the resulting precipitates was investigated, and the deposition rate of the material was determined. The dependence of the capacitive characteristics of sandwich-like samples and planar supercapacitors on the measurement modes was also investigated. The measured specific values for planar supercapacitors were 44.5 and 11.6 F/cm² for sweep rates of 10 and 100 mV/s.

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