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Investigation of Electrical Characteristics of the Carbon Electrodes

Abstract. *In the present work, the atmospheric pressure plasma jet and magnetron sputtering deposition technology was used for the fabrication of supercapacitor electrodes. It was shown that the parameters of supercapacitors strongly depend on the secondary carbon layer thickness. The increase of the carbon layer thickness from 1 to 2 μm, the relative oxygen quantity decreases from 8 dawn to 1.5 at.%, meanwhile the supercapacitor capacity increases from 7 up to 16 mF.*

Streszczenie*. W niniejszej pracy opisano zastosowanie technologii strumieni plazmowych pod ciśnieniem atmosferycznym i rozpylania magnetronowego do wytwarzania elektrod superkondensatorów. Wykazano, że parametry superkondensatorów w dużym stopniu zależą od grubości wtórnej warstwy węgla. W wyniku zwiększenia grubości warstwy węgla od 1 do 2 μm względna zawartość tlenu spada od 8% do 1,5%, powodując jednocześnie wzrost pojemności superkondensatora od 7 mF do 16 mF. (****Badania elektrycznych charakterystyk elektrod węglowych****).*

Keywords: plasma, supercapacitor, electrodes, carbon layer.
Słowa kluczowe: plazma, superkondensator, elektrody, warstwa węgla.

Introduction

Recently developed low inertial high-power uninterruptable power supply systems start using new kinds of power sources: hybrid of battery-capacitor and supercapacitor (also known as 'ultracapacitor'). Supercapacitors offer a promising alternative approach to meeting the increasing power demands of energy storage systems in general and of portable (digital) electronic devices in particular [1]. The power and energy-storage capabilities of these devices are closely linked to the physical and chemical properties of the carbon electrodes. The vast increases in capacitance achieved by supercapacitors are due to the combination of an extremely small distance that separates the opposite charges, as defined by the electric double-layer; and highly porous electrodes that embody very high surface area. A variety of porous forms of carbon are currently preferred as the electrode materials because they have exceptionally high surface areas, relatively high electronic conductivity, and acceptable cost. To improve the supercapacitors electrical characteristics (the capacity and charging-discharging cycles) the secondary layer is used. This layer can be composed of metal oxides (NiO, TiO, MgO, CuO) or of conductive polymers and of carbon [2]. The secondary layer increases the effective surface area, reduces the thickness of electrical double layer, stabilizes electrical charge carriers, and also reduces thermal oscillations. The secondary layer of supercapacitor electrode can not exceed 100 nm of thickness, however should not be less than 5 nm [3, 4]. It was demonstrated that the addition of the NiO on the carbon layer increases capacity 10 or more times [4]. Our previous investigations demonstrated that the highest capacity values were obtained at Ar/C_2H_2 = 55 ratio. Also it was found that deposition of NiO layer increases the capacity values up to 10 times [5, 6].

The material for the electrode production must be chemically resistance to the impact of electrolyte [7-10]. The electrolyte concentration must be sufficient to avoid depletion of the electrode material. The scientific literature states that the sufficient concentration of KOH is 20% and working temperature should not exceed 30°C [11, 12].

The main objective of this work was to evaluate the influence of the secondary carbon layer thickness on the supercapacitors electrical characteristics (the capacity, and charge-discharge time).

Experimental technique

In this study, the two-stage electrode formation method is used, encompassing the methods of plasma spray and magnetron sputtering deposition. The plasma spray is used for the deposition of the activated carbon [13]. While, the magnetron sputtering technique is used to deposit secondary carbon layer on the top of the carbon layer.

The carbon electrodes were produced using plasma torch at atmospheric pressure: the torch power was 840 W, Ar/C_2H_2 gas ratio - 55, the distance between the anode nozzle exit and the substrate - 5 mm, the carbon layer deposition time - 150 s. The stainless steel 1X18H9T was used as substrate [5, 6]. The secondary layer of carbon was deposited by magnetron sputtering method. The deposition time was 40, 60 and 80 min, which leads to the carbon thickness of 1 μm, 1.5 μm, and 2 μm, respectively. Argon pressure in the vacuum chamber varied in the rage of 1.4-1.8 Pa.

The surface morphology was characterized by scanning electron microscopy (SEM) model JEOL JSM–5600. The energy-dispersive spectrometry (EDS, Bruker AXS Microanalysis GmbH) analysis was used to determine the elemental composition of carbon electrodes. Bonding structure of carbon coatings were characterized using X-ray diffraction (XRD) measurements and Raman scattering (RS) spectroscopy. The structure was characterized by Raman scattering spectroscopy (Ivon Jobin spectrometer using Spectra – Physics Nd:YAG laser (532.3 nm, 50 mW, spot size 0.32 mm). The microstructure of coatings was analyzed using X-ray diffraction (XRD) in the Bragg-Brentano configuration with the 2Θ angle in the range 20-70° using CuK_α radiation in steps of 0.05°.

Aqueous solution (dilute KOH electrolyte (40%) was used as the electrolyte. A separator was used to keep the electrodes from contacting each other. The stainless steel was used as the current collector. The charge-discharge curves measurements at constant current (4.0 mA) were carried out on unit cell capacitor.

3. Results and discussion

The SEM study shows that the deposition time has very strong influence on the electrode surface microstructure (Fig.1). The figure1a shows the surface of carbon electrode without the secondary layer. The surface of carbon electrode consists of the microgranular structure. The diameter of irregular-shaped granules changes in range of

5-20 μm. Meanwhile, after the secondary carbon layer deposition, when thickness of layer is 1 μm, the mesh-like structure was formed (Fig. 1b). When, the thickness is 1.5 μm (Fig. 1c) the surface of the electrode is sufficiently uniform. The structure is composed of very small diameter granules if we look at higher magnify. Meanwhile, when the thickness of layer is 2 μm the electrode structure is similar to the structure when thickness was 1 μm, but in this case the filaments of mesh consists of 0.5 μm granules (Fig. 1d).

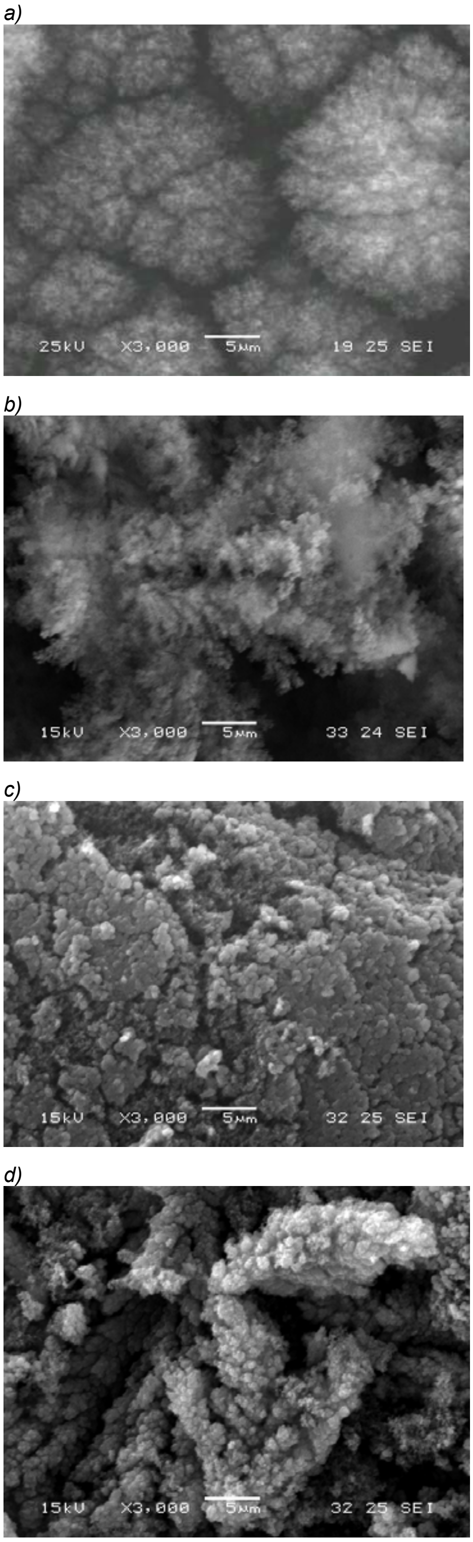

Fig.1. SEM surface views of as-deposited carbon layer *(a)*, and after the secondary carbon layer deposition *(b)* thickness 1 μm *(c)* – 1.5 μm, and *(d)* – 2 μm

Ar/C_2H_2=55 gas ratio is optimal when the plasma torch power is 840 watts, because these conditions are favorable for the formation of electrical double layer. The previous investigations of supercapacitors capacity this statement confirms [5]. Thus, the surface area of carbon electrodes is highest in these formation conditions. However, the surface of single-layer electrode is unstable. The surface is very rough and existing cavities are filled by the oxygen, for this reason, total electrode surface area is not exploited for the formation of the double electrical layer. The concentration of the oxygen in the deposited carbon layer was ~20 at.%.

The secondary carbon layer was deposited hoping that it will reduce the thermal oscillations due to decrease of the oxygen quantity. However, if the thickness of secondary carbon layer would be too thick or too thin, it would not improve the electrical parameters of supercapacitors. The investigations show that with too high secondary layer, the capacity of supercapacitors could be even lower than without the secondary carbon layer [2].

The EDS measurements demonstrated that the concentration of the oxygen in the surface layer decreases with the increase of the secondary carbon layer thickness. The oxygen concentration is only 1.5 at.%, when the secondary carbon layer thickness is 2 μm.

Fig. 2 shows the dependence of supercapacitor capacity on the relative quantity of the oxygen in carbon electrodes. It was found that the oxygen concentration drastically decreases the capacity values. The existence 20 at.% of the oxygen in the film reduces capacity values about 45 % [2]. The deposition of the secondary carbon layer increases the capacity values. The capacity increases from 5 up to 16 mF is due to reduction of the oxygen concentration from 20 dawn to 1.5 at.%.

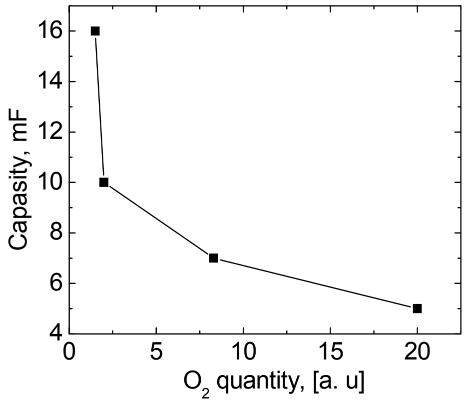

Fig.2. The dependence of supercapacitor capacity on the relative oxygen quantity

The RS spectroscopy analysis was used to evaluate the bonding structure of the fabricated carbon electrodes in dependence of secondary carbon layer thickness. The RS spectrum of the first carbon layer shows two separated and similar intensity D (1374 cm^{-1}) and G (1596 cm^{-1}) peaks. The relative integrated intensity ratio (I_D/I_G) is 1.60. Similar intensity values of both D and G bands associated with existence of the glassy carbon inserts in the layer. The I_D/I_G ratio indicates that the fraction of sp^2 bonded carbon dominates in the film [13]. It was obtained that the D and G peaks positions shift to the lower values from 1374 to 1338 cm^{-1} and from 1596 to 1582 cm^{-1}, respectively with the increase of secondary carbon layer thickness. The full width at half-maxima (FWHM) of D-band becomes narrower (changes from 230 to 209 cm^{-1}), while the FWHM of G-band slightly increases from 95 to 102 cm^{-1}. The I_D/I_G ratio increases up to 1.86. The increase of the I_D/I_G ratio indicates higher fraction of the sp^2 C=C sites. The narrowing of the D band is related to presence of less sp^2 carbon bond angle distortion [5].

The microstructure of as-deposited carbon coatings and after deposition of the secondary layer was analyzed by XRD. For all considered cases electrode material showed an amorphous phase and we did not found any difference between these electrodes structure.

The RS and XRD studies demonstrated only negligible structural changes. The fraction of sp^2 sites slighly increases with the increase of the secondary layer thickness. It is very logical because the secondary layer mainly consists of sp^2 bonded carbon. As the layer thickness increases the fraction of the sp^2 bonded carbon also becomes higher in the electrode.

It is known that oxygen functionalities, which preferentially form at the edges of the graphite like microcrystallites, increase the barrier for electrons to transfer from one microcrystalline element to the next for this reason the presence of surface oxygen increases the resistivity of carbon electrodes [2]. In addition, there is a possibility that a secondary layer of carbon reduces the thickness of electrical double layer, since a part of electrical charge carriers are fixed onto his surface in located free levels of energy. The deposition of the secondary carbon layer also changes the surface roughness and consequently the surface area of the electrodes and pores size. The similar electrodes structure lead to suggestion that the increase of the capacity is mainly connected with the decrease of the oxygen concentration.

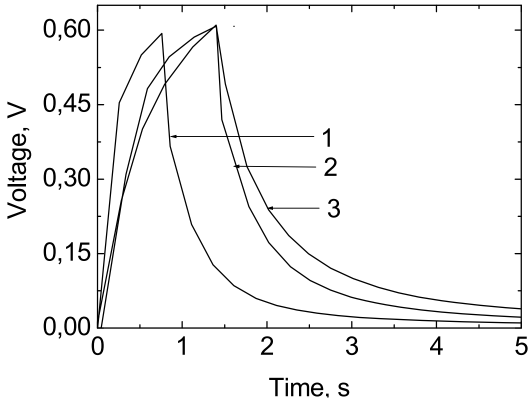

Fig.3. The charge-discharge curves of carbon capacitors, at different thickness of secondary carbon layer: 1 – 1 µm, 2 – 1.5 µm and 3 – 2 µm

The charge-discharge cycles of supercapacitors were measured in potential range between 0 V and 0.6 V at electric current 4 mA (Fig. 3). The investigations shows that the maximum (2.3 s) capacitor charge-discharge time is when the capacity is the largest (the thickness of secondary carbon layer is 2 µm). Meanwhile, the shortest time (1.3 s) of capacitors charge is when the capacity is the lowest (thickness of secondary carbon layer is 1 µm). This can be explained by the fact that a greater capacity needed more time. The similar results were obtained by others authors [2, 9].

It may be noted that the charging-discharging cycle's geometry isn't as well-shaped triangle as an ideal capacitive behavior should be. It indicates the ohmic resistance of the cell, and existence of chemical reaction between the electrode and electrolyte [2]. This reaction is not desirable because destroy porous structure of the carbon electrode surface.

4. Conclusions

The deposition of the secondary carbon layer changes the electrodes surface topography and increases the sp^2 C=C sites fraction. The formation of the secondary carbon layer allows to increase the capacity values. The capacity increases from 5 up to 16 mF due to reduction of the oxygen concentration from 20 dawn to 1.5 at.%. The charge-discharge cycle last longer for the supercapacitor with the highest capacity value.

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