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Deposition of Carbon Electrodes for Supercapacitors Using Atmospheric Plasma Torch

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The power and energy-storage capabilities of supercapacitors are closely linked to the physical and chemical characteristics of the carbon electrodes. In the present work, the surfaces of activated carbon electrodes were treated in low pressure oxygen and argon plasma for selected times of 15, 30, 60, 120, 180 and 300 s. The plasma source was a DC glow discharge in argon and oxygen gases generated by magnetron sputter deposition technique with Ni cathode. The working gas pressure was 1.3 Pa – 1.8 Pa and the distance between anode of magnetron and substrate – 30 mm. The dissipated power in plasma was equal to 250 W. The negative – 100 V bias voltage was supplied to the carbon electrode. The conducted studies of carbon surface topography showed that plasma treatment initiated microscopic roughening of the surface of activated carbon which was pronounced for short time (less than 30 s) plasma interaction. This was attributed to an increased of carbon surface area caused by argon-oxygen plasma etching. For discharge times greater than 10 min, combined effects of plasma chemical etching of carbon by oxygen atoms, physical sputtering by argon ions and deposition of nickel oxide deposit appeared to have a smoothing effect and led to a reduction of the measured surface area. Capacitance of electric double layer capacitors (EDLCs) with activated carbon electrodes after 1 min plasma surface treatment was increased by 70 % compared to EDLCs cells with the original activated carbon electrodes without plasma treatment and nickel oxide deposition. The results have shown that the modification by plasma treatment of activated carbon electrodes is a suitable technique for EDLCs used in high current applications.
Keywords: supercapacitors, carbon electrodes, surface modification, plasma treatment.

1. INTRODUCTION

Supercapacitors (also known as 'ultracapacitors') 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, 2]. Supercapacitors are able to store and deliver energy at relatively high rates (beyond those accessible with batteries) because the mechanism of energy storage is a simple charge-separation (as in conventional capacitors). The vast increases in capacitance achieved by supercapacitors are due to the combination of: (i) an extremely small distance that separates the opposite charges, as defined by the electric double-layer; and (ii) highly porous electrodes that embody very high surface-area [3].

The power and energy-storage capabilities of these devices are closely linked to the physical and chemical characteristics of the carbon electrodes. 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 [4]. For example, increases in specific surface-area, obtained through activation of the carbon, generally lead to increased capacitance [4 – 7]. Since only the electrolyte-wetted surface-area contributes to capacitance, the carbon processing is required to generate predominantly 'open' pores that are connected to the bulk pore network. While the supercapacitors available today perform well, it is generally agreed that there is considerable scope for improvement (e. g., improved performance at higher frequencies) [3 – 6]. Thus it is likely that carbon will continue to play a principal role in supercapacitor technology, mainly through further optimization of porosity, surface treatments to promote wettability, and reduced inter-particle contact resistance. In this work, activated carbon electrodes were modified to improve capacitance and energy density of electric double layer capacitors (EDLCs). The work consists of two parts: (i) the fabrication of thick activated carbon electrodes on the stainless steel substrates employing plasma torch carbon deposition technology, and (ii) the modification of surface properties of the activated carbon by simultaneous deposition of NiO_2 on the top of it and plasma treatment in Ar and O_2 plasma to achieve the highest specific capacitance and voltage stability of supercapacitors. The primary deposition variables which define the kinetics of surface topography development and microstructural evolution and, hence, physical and chemical properties of surfaces and deposits formed by techniques with simultaneous deposition of sputtered or evaporated particles and clusters and treatment of surfaces by reactive plasma are: the chemical state of precursors, the incident precursor fluxes, kinetic energies of incident particles, the substrate temperature, the flux and chemical state of incident contaminants, the substrate material, surface cleanliness, crystallinity, and orientation. It is necessary to divide the surface changes on the microscopic (atomic) and

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macroscopic level [8]. The macroscopic irregularities on the surface of electrodes modify the surface topography. A variety of porous forms of carbon are currently preferred as the electrode materials because they have exceptionally high surface areas. The microscopic state of surface plays a dominant role in the kinetics of heterogeneous processes. Thus, optimization of porosity of carbon electrodes together with their surface treatments on the atomistic level to promote wettability, and reduced inter-particle contact resistance may result in the vast increases in capacitance achieved by supercapacitors. Plasma interaction with materials modifies surface properties. The ejection of atoms from the top monolayers of materials is accompanied by microscopic changes of the surface geometry. After prolonged irradiation generated surface vacancies and adatoms form macroscopic clusters and craters [9, 10]. Contrary to physical sputtering, chemical sputtering (etching) is very selective and highly isotropic. Carbon atoms confining electrode immersed in plasmas containing oxygen forms volatile compounds as heterogeneous reaction $C + 2O = CO_2$ proceeds. The presence of the chemical compounds on the surface, which do not react with oxygen, hinders etching process. If the surface is covered by the islands of deposited NiO_2 which do not react with oxygen the surface will be etched inhomogeneously resulting to the variety of geometrical formations. Keeping in the mind that chemical etching is highly isotropic, the geometry of these formations may be very sharp.

2. EXPERIMENTAL

A two-step technology was used for the formation of supercapacitor electrodes. As the first step, the atmospheric plasma torch technology was used for the fabrication of thick coatings of activated carbon with a high effective surface area on the surface of stainless steel 1X18H9T substrates. The coating growth rate was determined from the slope of the sample's weight change obtained using a microbalance with a weight uncertainty of 2 μg. The 50 μm thick carbon coatings with high effective surface area were fabricated using plasma torch with the following parameters: the arc voltage – 36 V, the arc current – 24 A, the ratio of working gases Ar/C_2H_2 was 55, the distance between plasma gun outlet and sample – 10 mm, and the deposition time – 150 s.

As the second stage, the deposition of NiO_2 on the top of activated carbon layer was performed using magnetron sputter-deposition technique with a water-cooled substrate holder and a shutter located in front of magnetron. The target-to-substrate distance was 30 mm. The chamber was evacuated to a typical background pressure of 10^{-5} Pa to 10^{-4} Pa by a pumping unit. This unit includes a turbomolecular pump at pumping speed about 150 $\ell \cdot s^{-1}$ for Ar which was controlled by a throttle valve. The magnetron discharge current was variable in the range 0.1 mA – 10 mA corresponding to a dissipated power density of 5 W cm^{-2} – 500 W cm^{-2}. The quantity of the deposited material was estimated by a weight method. The quantity of nickel oxide corresponding to homogeneous 100 nm thick film was deposited in about 120 s. The sample temperature was controlled with the accuracy ±5 °C. The steady state sample holder temperature 400 K was reached after two minutes of deposition. The surface topography analysis was carried out using a scanning electronic microscope (JSM-5600). The electrical characteristics of fabricated supercapacitors were measured using typical electrical circuit.

3. RESULTS

Fig. 1 includes the dependences of supercapacitor capacitance and stabilization voltage on the quantity of deposited NiO_2 expressed in effective film thickness units. It is seen that small quantities of deposited NiO_2 (up to 72 nm) increase the specific capacitance and stability voltage. The following increase of the deposited amount of NiO_2 decreases the capacitance, meanwhile stability voltage remain constant.

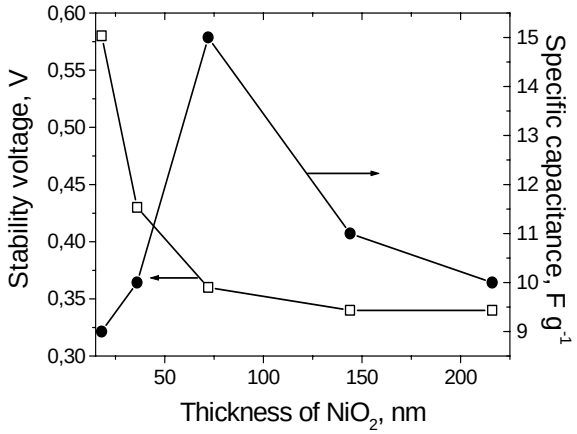
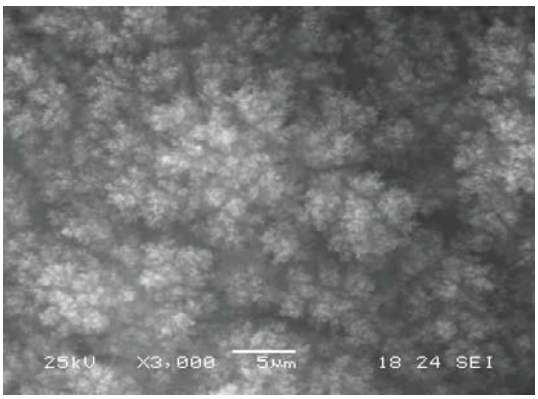


Fig. 1. The dependences of specific capacitance and stability voltage of supercapacitors on thickness of NiO_2 film

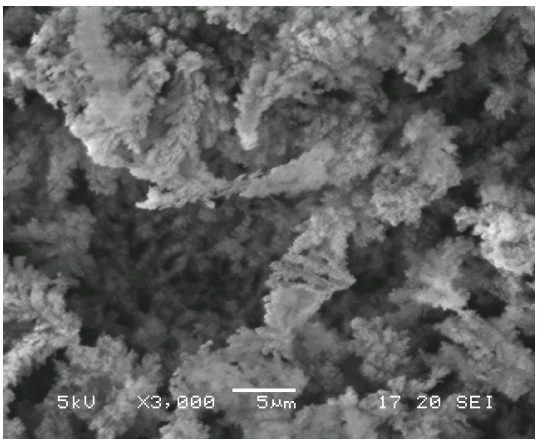
The SEM surface views of carbon coatings after deposition of different amounts of NiO_2 for the fixed ratio Ar/C_2H_2 – 55 are presented in Fig. 2. The as-deposited carbon layer demonstrates self-developed microformations and includes many loosely adhered particles (Fig. 2, a). It is seen that surface topography of carbon significantly changes after short time (less than 30 s) interaction with plasma (Fig. 2, b). It can be seen that the structure of net form is highlighted, when the nickel oxide layer of 72 nm thickness was deposited (Fig. 2, c). The surface microstructure of the electrode with the 216 nm NiO_2 consists from granules and branches (Fig. 2, d).

4. DISCUSSIONS

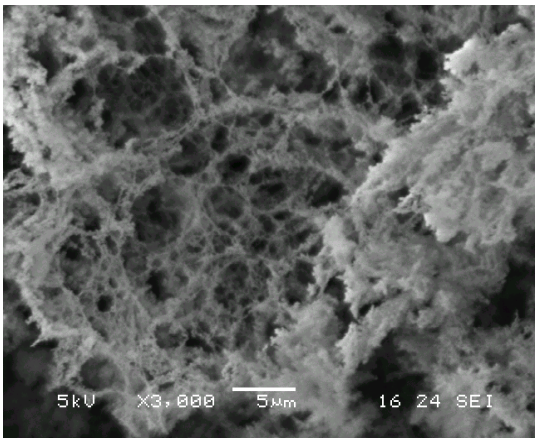
Fig. 3 reproduced from the publication [12] illustrates sputtering effects on the microscopic surface topography. It is seen how the surface topography of Al(111) changes after 300 eV Xe^+ ion irradiation by different fluences in scanning tunneling microscope. The main characteristic features of sputtering effects are low elemental selectivity and high erosion anisotropy [11, 12]. We came to conclusion that the sharp increase in capacitance (Fig. 1) after short time (less than 30 s) of interaction with plasma is the result of the increase of the specific surface area of carbon electrode initiated by sputtering effects.



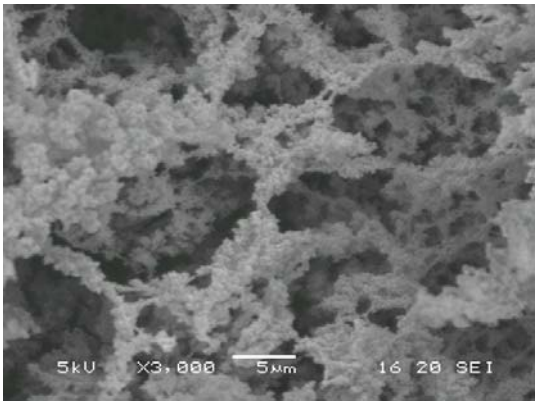
a



b



c



d

Fig. 2. SEM surface views of as-deposited carbon layer (a), and after deposition of nickel oxide films of different thickness (b) 36 nm, (c) 72 nm, and (d) 216 nm

As the amount of the deposited NiO_2 increases, the surface restructuring and relaxation processes change geometry of microformations on the surface. The process of coalescence of neighboring carbon formations has been observed, which leads to formation of new energetically favorable microstructures. It was observed that these new formations are well adhered and resistant in electrolytic solution. It is seen that as the amount of deposited NiO_2 exceeds about 200 nm, the surface becomes covered by the granules consisting of many fragments (Fig. 2, d). The stability voltage correlates with changes of the capacitor capacitance. The changes of surface topography during ion sputtering, plasma etching and deposition of atoms and clusters have been widely studied [11]. However, the simultaneous action of these processes can not be considered as the sum of the above mentioned processes and requires deeper understanding. High capacitances of supercapacitors are achieved due to fabrication of highly porous electrodes with very high surface-area. A porous structure of carbon coating is obtained by plasma torch deposition technology. Carbon deposition rate is very high (about 500 nm/s) and gas carrier (Ar and C_2H_2) is incorporated in the growing coating. Porous forms are formed by the action of stress and internal gas pressure in the layer. Cracks or channels can be formed by which gas from deeper layers is released to the surface. Surfaces generally demonstrate many features which are determined by parameters related to the plasma jet characteristics (e. g., the composition of working gas, arc current, construction of deposition technique) and to the substrate material (e. g., composition, structure, pretreatment, temperature) [13, 14].

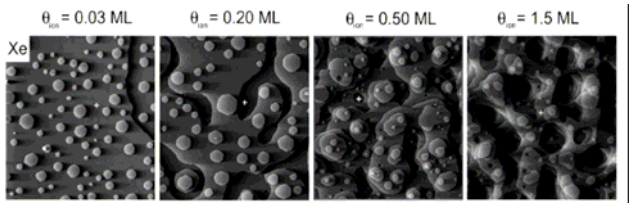


Fig. 3. The changes of surface geometry after 300 eV Xe^+ irradiation of Al(111) substrate by different fluences observed in scanning tunneling microscope [12]

Many authors indicated that the capacity is related to the effective surface area. Usually the capacitors with higher surface roughness have higher surface areas and due to it higher capacitance values [2 – 4]. However, it was reported that the capacity depends on the heat treatment and non-stoichiometric nature (or defective nature) of the nickel oxide. This phenomenon was explained due to changes in the surface area of the prepared nickel oxide with varying temperatures [15]. Yuan et al. [5] reported that the BET surface area of the activated-carbon decreased upon nickel oxide loading compared to that of the starting material. However, the specific capacitance of the capacitor increased 10.84 %. This result indicated that the capacity exchanges with addition of the nickel oxide. The optimal ratio of surface area and loaded nickel oxide amount in the experiments was when capacity is 15 Fg^{-1}. The significant reduction of the capacitor capacity is observed since with the increase of nickel oxide layer thickness the effective surface area of electrodes

diminishes. The increases in capacitance are achieved due to the modification of surface microstructure by deposition of Ni in the argon and oxygen plasma on the top of activated carbon coatings under negative bias voltage. Usually, if the surface is initially rough (effective surface is high), plasma etching phenomena leads to the smoothening of surface geometry and the decrease of the effective surface as plasma etching of bums and tips dominates the plasma etching of dips and caves. Reactive deposition of Ni leads to the formation of nanometric islands of NiO_2 on the top of carbon protrusions and bottoms of dips and caves. Oxygen atoms arriving from plasma intensively react with available carbon atoms and initiate chemical plasma etching, which results in different surface geometries. As islands of NiO_2 are deposited, the chemical plasma etching of surface becomes highly inhomogeneous. The areas covered by NiO_2 are protected from etching and the effective surface increases. The high quantities of deposited NiO_2 have opposite effect: the NiO_2 formations block heterogeneous reaction between carbon and oxygen atoms and the increasing amount of deposited NiO_2 smoothes surface geometry. Additionally to it, a distance that separates the opposite charges of supercapacitor increases.

5. CONCLUSIONS

Plasma treatment technologies have been used to achieve the highest specific capacitance and voltage stability of supercapacitors. The capacitance was increased by the optimization of properties of activated carbon electrodes in the following way: (i) the formation of carbon layers with high effective surface area by plasma torch technology, and (ii) the modification of microscopic structure of fabricated electrodes by deposition of small amount of NiO_2 and simultaneous plasma treatment. The results have shown that the modification by plasma treatment of activated carbon electrodes is a suitable technique for the improvements of the electrical properties of supercapacitors.

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