TAILORING OF SURFACE TOPOGRAPHY OF CARBON ELECTRODES FOR SUPERCAPACITORS USING PLASMA TECHNOLOGIES

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ABSTRACT

In this work, we address the issue of controlled modification of the surface topography of carbon materials when subjected to oxygen-based plasma treatment, and we investigate the resulting enhanced surface area as a mean of controlling the capacitance of supercapacitors. It is shown that carbon layers with porous of controllable nanoscale size can be tuned from nanoporous to mesh-like employing atmospheric plasma torch deposition technology and following appropriate plasma processing. The nanoscale carbon processing is optimized to form surface topographies that promote carbon wettability with electrolyte. Three dimensional structures fabricated on carbon are chosen as appropriate surfaces for the enhancement of the capacitance of supercapacitors. This fact underlines the potential application of the proposed technique for fabricating electrolyte-wetted carbon electrodes for supercapacitors.

Key words: supercapacitors, carbon electrodes, surface topography, and plasma technologies

INTRODUCTION

There is a need for a rechargeable energy source that can provide high power, can be recharged quickly, has a high cycle life and is environmentally benign for a myriad of applications including defence, consumer goods, and electric vehicles. Double layer capacitors known as supercapacitors are rechargeable charge storage devices that fulfil this need. A single-cell double layer capacitor consists of two electrodes which store charge (these are called the "active" materials), separated by a permeable membrane which permits ionic but not electronic conductivity. Each electrode is also in contact with a current collector which provides an electrical path to the external environment. The electrodes and the membrane are infused with an electrolyte, and the entire assembly is contained in inert packaging. Multiple cells may be connected in series or in parallel in the final packaged unit [1-3].

The capacitance, or amount of charge that a capacitor can store, is directly related to the surface area of the electrodes. Therefore, electrodes made from conductive materials that possess high surface area (>100 m^2/g) are desirable. By employing various materials and fabrication means,

capacitors have been developed which are capable of delivering very high specific power and energy densities. Because carbon is chemically inert, has a high electronic conductivity, is environmentally benign and is relatively inexpensive, it is a desirable material for fabricating electrodes for supercapacitors. A variety of porous forms of carbon are currently preferred as the supercapacitor electrode materials because they have exceptionally high surface areas, relatively high electronic conductivity, and acceptable cost. Since only the electrolyte-wetted surface-area contributes to capacitance, the nanoscale carbon processing is required to form surface topographies that promote carbon wettability with electrolyte [4,5].

This article concerns the energy storage devices and specifically to a method of making active materials or electrodes. The purpose of this research paper is focused on the surface modification of carbon electrodes using plasma techniques, so as to control the increase in surface roughness in order to improve the capacitance of supercapacitors. In this study, the surfaces of the carbon electrodes were chemically and physically modified by their exposure in low-pressure oxygen plasma. The treated and untreated (as-received) surfaces of the carbon electrodes were subjected to detailed characterization.

EXPERIMENTAL

The experimental includes two parts: (i) the fabrication of thick porous carbon electrodes on stainless steel substrates employing atmospheric plasma torch carbon deposition technology, and (ii) the modification of surface properties of carbon electrodes by their exposure in low pressure oxygen plasma to achieve the highest performance parameters of supercapacitors.

The porous 50 μm thick carbon coatings were deposited on 2 mm thick 1X18H9T stainless steel substrate employing atmospheric plasma torch technology. Details of this technique are disclosed in [6]. The plasma torch parameters were as follows: the arc voltage – 36 V, the arc current – 24 A, the working gas – the mixture of Ar and C_2H_2, and the deposition time – 150 s. The gas flow and gas composition was continuously controlled by mass flow controllers. The thickness of the deposited layer was evaluated by weight method using microbalances.

The modification of surface properties of deposited carbon layers was performed by high-flux, low-energy ion irradiation. The ions were extracted from DC magnetron plasma generated at 5 Pa pressure in the mixture of Ar and O_2 (10 at.%) and accelerated by 350 V negative bias voltage. The magnetron discharge current was variable in the range 10-20 mA. The power density dissipated in plasma was variable in the range 100 - 300 Wcm^{-2}. The plasma parameters were evaluated experimentally using a Langmuir probe. For plasma source, the electron temperature, plasma potential, floating potential and plasma density were 2-4 eV, +5.0 V, +3.5 V and $4 \cdot 10^{10}$ cm^{-3}, respectively. The steady state

substrate temperature of 480 K reached after two minutes of plasma treatment. The characterization of surface topography of as-deposited and plasma treated carbon electrodes were carried out using the atomic force microscope (Micro-mashines NT-206) and the nanoprofilometer (Ambios XP-200). The surface views were analyzed before and after plasma treatment by a scanning electron microscopy (SEM, JEOL JSM – 5600). The elemental composition of plasma treated carbon coatings was analyzed by energy dispersive X–ray spectroscopy (EDX, Bruker Quad 5040).

RESULTS

The surface topography of carbon layers fabricated employing atmospheric plasma torch technology has been studied in previous publications [6, 7]. In this work, the attempts to explain why the capacitance of supercapacitors with C electrodes increases after their additional treatment in $Ar+O_2$ plasma.

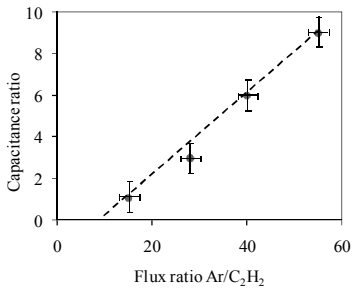

Fig.1 – The dependence of the ratio of capacitances for supercapacitors with C electrodes treated and untreated in oxygen plasma (10 Pa, 1 min) on the flux ratio of Ar/C_2H_2 [7]

Fig.1 includes the dependence of the ratio of capacitances for supercapacitors with C electrodes treated and untreated in oxygen plasma (10 Pa, 1 min) on the flux ratio of Ar/C_2H_2 for plasma torch. It is seen that the capacitance increases up to 10 times for Ar/C_2H_2=55.

Fig.2a and *Fig.2b* include SEM surface views of carbon electrodes: a - as-deposited employing atmospheric pressure plasma torch technology for flux ratio Ar/C2H2=40, and b - after following treatment in low-pressure oxygen plasma (10 Pa, 1 min), respectively. It seen that the granular structure of as-deposited carbon becomes highly porous with channels accessible for electrolyte.

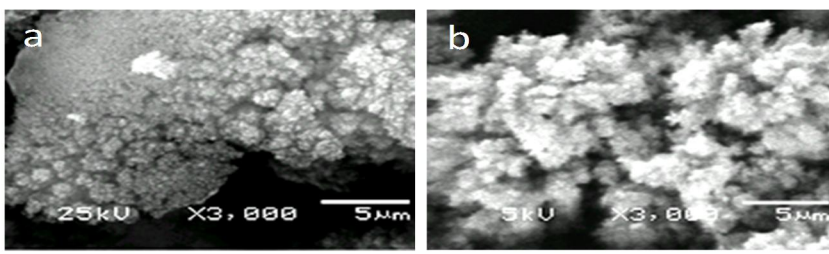

Fig. 2. – The SEM surface views of carbon electrodes: a – as-deposited, b – after treatment in oxygen plasma

MODELLING OF SURFACE STRUCTURE FORMATION

The modelling of surface structure formation has been performed in an attempt to explain the significant increase of the capacitance of supercapacitor which was experimentally registered. The understanding of processes which lead to this effect is not complete.

The simultaneous action of three processes has been considered on the surface of carbon electrode immersed in O2+Ar plasma: (i) the isotropic plasmochemical etching of C ($C+2O \rightarrow CO_2\uparrow$), (ii) the adsorption of C atoms, and (iii) the anisotropic physical sputtering of surface by energetic incident oxygen and argon ions.

Fig.3 includes profiles of single carbon formation calculated on the basis of kinetic equations describing simultaneous action of the processes of carbon deposition, isotropic plasmochemical and anisotropic physical ion sputtering after different durations of plasma treatment (to=0, 1, 2, 3, and 4, curves 1 -5, respectively) in relative units for the case when the carbon deposition rate is equal to the plasmochemical etching rate (Fig.3a) , and when the carbon deposition rate exceeds the carbon plasmochemical etching rate (3X)(Fig.3b). Curve 1 - the initial profile. It is demonstrated that different surface structure formations may be generated in dependence on the deposition and plasma treatment parameters.

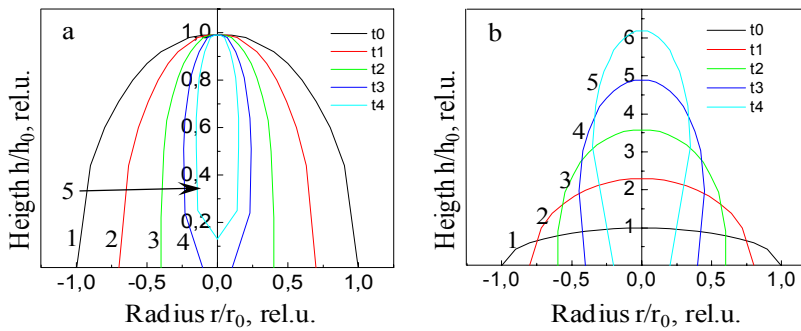

Fig.3. – Calculated profiles of single carbon formation on the surface of plasma treated carbon for different deposition/etching parameters: a – the deposition and plasmochemical etcing rates are equal, and b – the deposition exceeds plasmochemical etching rate (3X) after different treatment durations: t=0 (as deposited), 1, 2, 3 and 4 in relative units, curves 1-5, respectively

DISCUSSIONS AND CONCLUSIONS

The surface topography of carbon materials has been optimized to promote carbon wettability with electrolyte and to increase the capacitance of supercapacitors. High capacity of supercapacitor is obtained due to fabrication of porous electrodes with surface topography accessible for electrolyte to form dou-

ble charge layer. The carbon etching in oxygen plasma is accompanied by nanoscale changes of the surface geometry. The oxygen plasma treatments caused ablation of the carbon electrode surface, removing carbon atoms and molecules such as CO and CO_2. Carbon electrodes treated in oxygen plasma for 1-3 min significantly (up to 10 times) increases the capacitance of supercapacitor. This effect depends on the microstructure of plasma untreated carbon layers. The conclusion is made that the modification of surface topography of carbon electrodes by oxygen plasma is a suitable technique for the improvements of the electrical properties of supercapacitors.

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