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Development of supercapacitors for hybrid energy safety systems

Abstract. *The purpose of this research is focused on the surface modification of carbon electrodes using plasma technologies to optimize the surface topography in order to increase the capacitance of supercapacitors.*

Streszczenie. *Celem przeprowadzonych badań było skupienie się na modyfikacjach powierzchni elektrod węglowych wykorzystując technologie plazmowe w celu optymalizacji topografii powierzchni pod kątem zwiększenia pojemności superkondensatorów. (**Usprawnienia superkondensatorów dla hybrydowych systemów bezpieczeństwa**).*

Keywords: supercapacitors, carbon electrodes, capacitance and plasma technologies.
Słowa kluczowe: superkondensatory, elektrody węglowe, pojemność i technologie plazmowe.

Introduction

Supercapacitors, or electrochemical double-layer capacitors (EDLCs), are devices utilized to store and release energy that are gaining increasing interest not only in their traditional field of application (electronics) but also in other sectors such as power generation, transportation and hybrid energy systems. Specific capacitance values up to 300 F/g have been reported for the investigated experimental supercapacitors by using available activated carbon with a specific surface area reaching 3000 m^2/g [1, 2].

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 tailoring of surface topography is required to form surfaces that promote carbon wettability with electrolyte [3, 4]. By addition of metallic oxides or conductive polymers in the activated carbon used for EDLC electrodes, specific capacitance enhancement takes place [2].

It has been shown [5, 6] that the properties of carbon electrodes are chemically and physically modified by the deposition of small quantities of Ni atoms in oxygen atmosphere on the top of porous carbon layers in order to increase the capacitance of supercapacitors. In the presented work the comparative analysis of electrical parameters of supercapacitors with plasma treated/untreated carbon electrodes is performed, and possible explanations of the registered effects are discussed.

Experimental

The experiment included two stages: (i) the fabrication of thick layers of activated carbon with high effective surface area on the surface of stainless steel substrates employing an atmospheric plasma torch carbon deposition technology, and (ii) the modification of surface properties of as-deposited carbon coatings by deposition of small quantities (5-200 μg/cm^2) of Ni atoms on the top of activated carbon to achieve the highest performance parameters of supercapacitors.

As the first stage, 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 [5]. 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 were continuously controlled by mass flow controllers. The thickness of carbon layer was evaluated by weight method using microbalances.

As the second stage, the modification of surface properties of as-deposited carbon layers was performed in two ways: (i) by the immersion of supercapacitor electrodes covered by C coatings into low-pressure oxygen plasma (10 Pa, 1 min), and (ii) by the deposition of Ni atoms in oxygen atmosphere on the top of as-fabricated carbon layers in vacuum chamber using magnetron sputter-deposition technique. Details are presented in [5].

Results

The C electrodes were fabricated using atmospheric pressure plasma torch and different values of the flux ratio Ar/C_2H_2, and, afterwards, treated in low-pressure O_2+Ar plasma (10 Pa, 1 min). The electrical parameters of plasma untreated and treated supercapacitors were measured. Fig. 1 shows the dependence of the capacitance ratio of supercapacitors with as-deposited and plasma treated carbon electrodes in dependence on the flux ratio Ar/C_2H_2. It is seen that the capacitance of supercapacitor increases after exposition of as-deposited C electrodes in O_2+Ar plasma. This effect depends on the flux ratio of Ar/C_2H_2. The capacitance ratio increases from 1.2 for Ar/C_2H_2=16 up to 8.3 for Ar/C_2H_2=55.

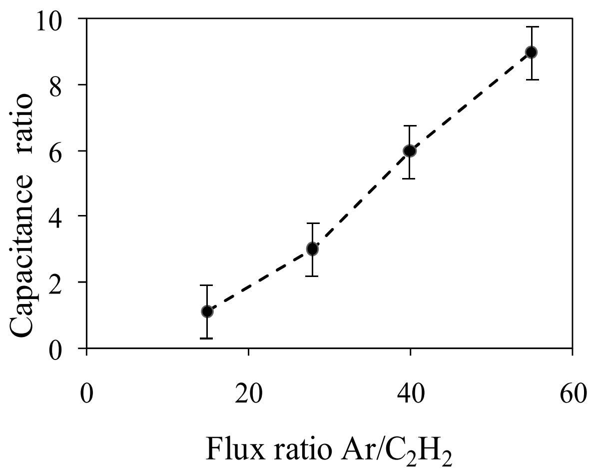

Fig.1. Dependence of the capacitance ratio of supercapacitors (treated/untreated) on the flux ratio Ar/C_2H_2

Fig. 2 includes the dependence of the capacitance ratio of supercapacitors (treated/untreated) on the quantity of deposited Ni.

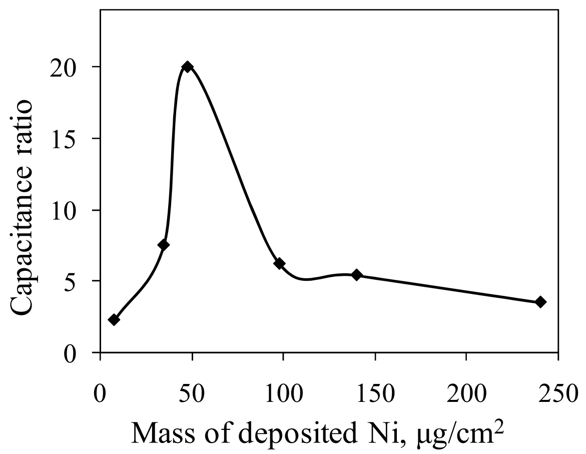

Fig.2. Dependence of the capacitance ratio on the mass of deposited Ni

Fig. 3 shows that the capacitance of supercapacitor decreases as the flux ratio Ar/C_2H_2 increases for fixed amount of deposited Ni equal to about 50 μg/cm^2. Surface topography analysis shows that it is related to the decrease of as-deposited carbon layer porosity. As C coating density increases the accessibility of reactive O atoms into the bulk of C coating decreases. In this way, the three dimensional surface topography is formed [6].

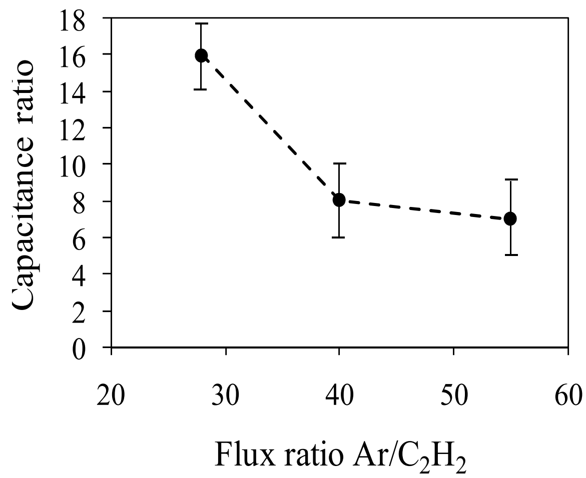

Fig.3. Dependence of the capacitance ratio on the flux ratio of Ar/C_2H_2

Discussions and conclusions

Plasmochemical etching tailors topography of an as-deposited C electrode. Common etching methods can be used. Topography can be controlled by varying parameters that produce the C electrode or the etching parameters or both.

The surface topography of carbon materials has been optimized to increase the capacitance of supercapacitors. It is supposed that the high capacity of supercapacitor is obtained due to fabrication of porous electrodes with surface topography accessible for electrolyte to form double charge layer. The carbon etching in oxygen plasma is accompanied by nanoscale changes of the surface geometry. The oxygen plasma treatments cause 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 min significantly (up to 8 times) increase the capacitance of supercapacitor. This effect depends on the microstructure of plasma untreated carbon layers.

Carbon layer after deposition of small quantity of Ni atoms on the top of it has a surface comprising at least two elements one of which is metal and another one is chemically reactive with oxygen atoms. Etching removes a portion of the carbon preferentially, to achieve the specified topography. Control is possible regarding: roughness, distribution and number density of pits and channels, as well as their depth, width, size. Processing parameters that have been correlated to topography features in the C-Ni system include the deposition and etching phases on a surface. The relative influence of the processing parameters can be correlated to establish a relationship between values for processing parameters and degree of topography feature.

It is concluded that the modification of surface topography of carbon layers by plasma deposition/etching technologies is a suitable technique for the improvements of the electrical properties of supercapacitors.

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