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The effect of reduced pressure acetylene plasma treatment on physical characteristics of carbon electrodes

Zydrunas Kavaliauskas[1, 2], Vitas Valincius[1], Mindaugas Milieska[1], Liutauras Marcinauskas, [1, 3]

[1]*Lithuanian Energy Institute, Breslaujos str. 3, LT-44403 Kaunas, Lithuania*
[2]*Kauno Kolegija/University of Applied Sciences, Pramones str. 20, LT-50468, Kaunas, Lithuania*
[3]*Kaunas University of Technology, Studentu str. 50,LT-44249, Kaunas, Lithuania*

Abstract: *The capacitors are increasingly being used as energy storage devicesin various power systems. The scientists of the world are tryingto maximize the electrical capacity of the supercapacitors. To achieve this purpose, numerous method sare used: the surface activation of electrodes, the surface etching using the electronbeam, the electrode etching with variousgasplasma, etc. The purpose of this work is toresearch how the properties of carbon electrodes depend on the plasma parameters at whichtheywere formed. The largest surface area ofcarbonelectrodeof47.25*m^2*/gis obtainedat 15 ofAr/*C_2H_2*gasratio. Meanwhile, theSEMimages show that the disruption of structures with low bond energies and the formation of new onesare taking place when the carbon electrodes are etched at acetylene plasma and placed on carbon electrode. The measurements of capacitance showthat capacitors with affectedelectrodes have about10-15% highercapacity than those not treated with acetyleneplasma.*

Keywords: *plasma; voltage; temperature.*

I. INTRODUCTION

Nowadays due to the decrease of fossil fuel sources and increasing environmental pollution the increasing attention is paid to alternatives that would not only produce energy, but also store its excess for a long time. Batteries and accumulators reliably and sufficiently protect and store electricity, but they have very limited operating time and their capacity heavily depends on the number of charge cycles [1, 2]. The high capacity (up to 15 F/g or more) supercapacitors which are characterized by high charging efficiency (up 95 percent) and are not dependent on the number of charge cycles do not have the above-mentioned drawbacks [3, 4]. Capacitors have lower production costs than batteries and accumulators as their electrodes are usually made of carbon with high specific surface area. Capacitors are already widely used for electrical energy storage in various devices and equipment: cars, computers, railway industry, etc. Also, thecapacitors are widely used at electric systems that require very fast (e.g. within 0.5 s) formation of very high density electric current pulses [5, 6]. The operating principle of capacitors is based on the electric double-layer formation when during charging the electrode surface ions interact with the electrolyte ions in accordance with the principles of Coulomb's law [7–9]. The electric capacity of capacitors directly depends on the specific surface area of the electrodes. Various techniques are used to increase the specific surface area: carbon activation in chemically aggressive environments, carbon corrosion using the electronic beam and others [10–12]. The secondary layers which are formed on the electrode material surface are also used to increase the capacitance of capacitors. The secondary layers usually are about 10–100 nm in thickness and are formed from various metal oxides such as nickel oxide and titanium oxide. These secondary layers deposited on the surface of the electrode act as catalysts forcing larger quantity of charged particles to take part in the formation of the electric double layer. However,capacitors also have disadvantages: the operating voltage of a singlecapacitor cell is only about 2 V, so in order to achieve the required electrical voltage and current individual cells have to be connected using parallel and series connection methods. Such connection method greatly increases the size and weight of capacitors. Currently scientists are focused on maximizing the surface area of electrodes and producing cells with higher operating voltage.

The purpose of this study is to determine the influence of etching with reduced pressure (up to 1.5 Pa) acetylene plasma and deposition of secondary carbon layer by magnetron sputtering method on the physical properties and operational degradation of capacitors carbon electrodes.

II. EXPERIMENTAL SETUP

The carbon electrodes of capacitors were produced using the plasma spray technology. The carbon electrodes were sprayed on stainless steel substrates. The surface of carbon electrodes was modified using the magnetron sputtering system. The carbon electrodes were treated in two cases. In the first case the carbon electrodes were placed only into acetylene gas environment, while in the second case carbon electrodes were treated in acetylene gas environment with carbon cathode.

The carbon electrodes were formed on the stainless steel pallets in the atmospheric pressure argon/acetylene plasma. The Ar/C_2H_2 gas ratio varied in the range from 15 to 55; the plasma generator power was 1000 W, carbon electrode formation time – 150 s, and the distance between the plasma generator and carbon steel substrates – 0.005 m.

When processing the surface of carbon electrode, theacetylene gas pressure in a vacuum chamber of magnetron system reached 1.5 Pa, while the process duration varied in 1 to 5 minute range.The carbon electrode surface micro-relief changes were examined using a scanning electronic microscope (SEM) JSM-5600. Energy-dispersive X-ray spectroscopy (EDS) was used to determine the amount of oxygen contained in the surface of carbon electrode. The specific surface area and pore distribution of carbon were determined using the BET method. During the process of determining the specific surface area, the degassing time was 60 minuteswhile the temperature reached 150^0C. Capacitors were produced from one cell consisting of two carbon electrodes, the separator and charging terminals. The 40 % KOH was used as an electrolyte. The capacity ofsupercapacitors was measured using the classic capacitor charging scheme.

III. RESULTS AND DISCUSSION

After the formation of carbon electrodes with the plasma spray method their specific surface area and pore size distribution dependence on diameter was tested (Fig. 1). The diameter of pores on the surface of carbon electrodes varies from 2 to 25 nm. Meanwhile, the maximum volume is occupied by pores with a diameter of about 2 nm.

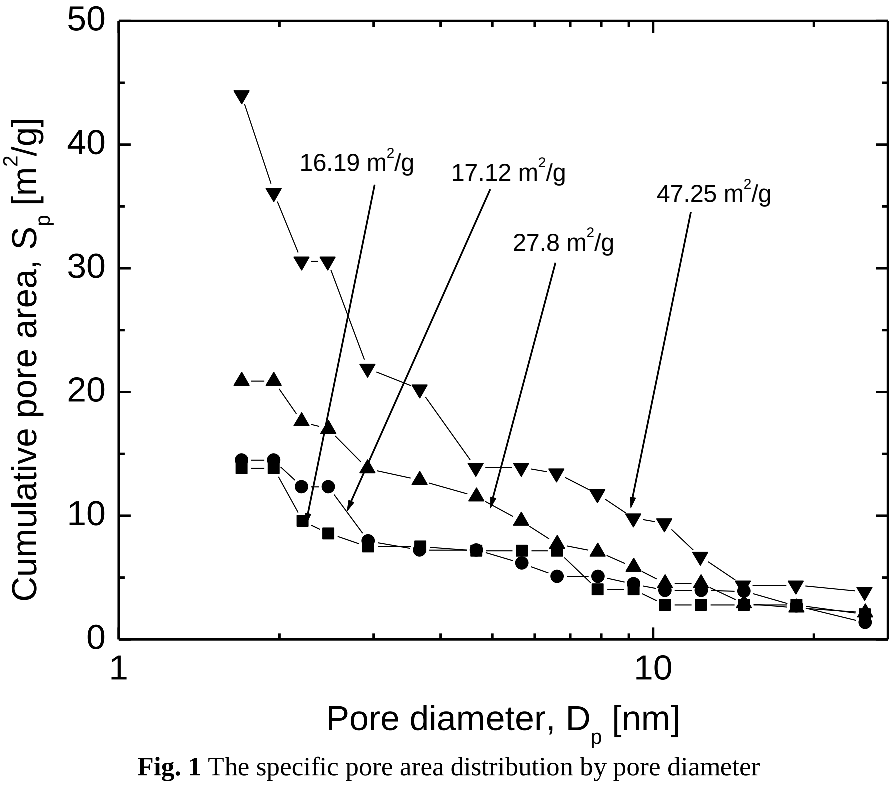

Fig. 1 The specific pore area distribution by pore diameter

The electrode having mainly the smallest diameter (2 nm) pores is characterized with the highest specific surface area (47.25 m^2/g). That is so because smaller diameter pores have higher specific surface area. Meanwhile, for electrodes with the specific surface area of16.19 m^2/g and 17.12 m^2/g, the curves indicating the distribution of pore volume along their diameter is nearly the same.

The carbon electrodes were produced using plasma spraying technique at various Ar/C_2H_2 gas ratios (Fig. 2). Argon was used as a plasma-forming gas and acetylene as a carbon electrode forming gas on the steel pallets.The carbon electrodes characterized by highest specific surface area were formed at the 15 Ar/C_2H_2 gas ratio. Increasing the Ar/C_2H_2 gas ratio results in the decrease of the specific surface area, and at the maximum Ar/C_2H_2 ratio of 55 the electrode surface area is only 16.19 m^2/g. The electrodes with the highest specific surface area (47.25 m^2/g) have the highest specific capacity (7.5 F/g).

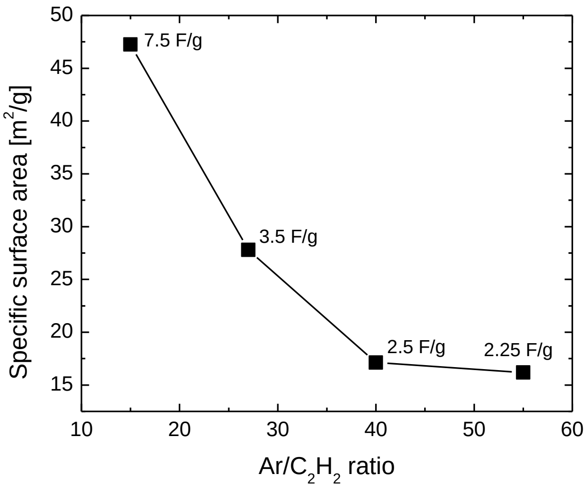

Fig. 2 The electrode surface are a dependence on Ar/C_2H_2ratio

In order to stabilize the carbon super capacitor electrode surface micro formations, the magnetron sputtering system was used. The interaction between the carbon electrode surface and acetylene plasma causes the etching of micro formations with lowest bond energy. Meanwhile, when the electrodes are placed on the carbon cathode the growth contributes to etching. The derivatives with minimum bond energy are removed and the new ones with higher bond energy to the surface are grown instead. This way, the surface micro-relief is stabilized. For this reason, the electric double layer formed during the charging of a capacitor is also more stable. After three minutes of interaction with acetylene plasma the surface of capacitors electrodes are composed of irregularly shaped micro formations, but with clearly visible boundaries (Fig. 3a). When the carbon electrode interacts with acetylene plasma for 5 minutes (Fig. 3b), the derivatives with larger dimensions are visible on the surface compared to those which interacted for 3 minutes. That is explained by the fact that small derivatives interacting for a long time decompose and only large size derivatives remain. When the carbon electrodes are placed on the carbon cathode not only etching but also growth takes place. Figure 3c shows the surface of the electrode which was placed on the carbon cathode for 2 minutes. As shown, the surface structure reminiscent of honeycomb is formed. Meanwhile, the spherical shape structures with diameters around 10 mm appear on the surface of carbon electrode after 4 minutes exposure on the cathode (Fig. 3d).

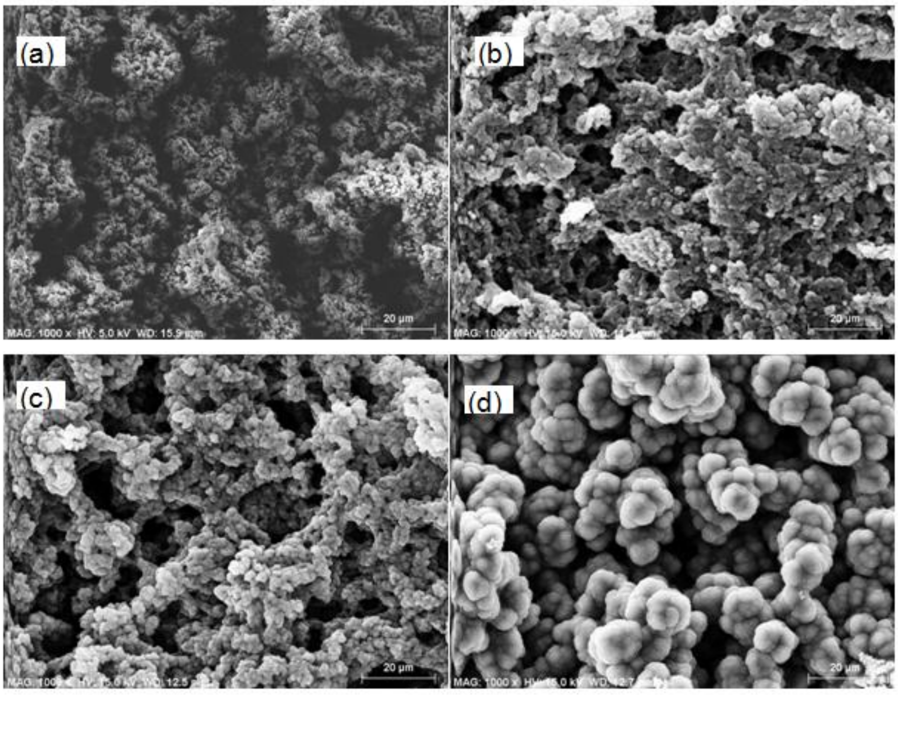

Fig. 3. SEM images of capacitor electrodes: a and b – electrodes were etched in C_2H_2 plasma for 3 and 5 minutes, respectively, c and d – the electrodes were placed on the carbon cathode surface and etched in C_2H_2 plasma for 2 and 4 minutes, respectively.

These spherical structures are the result of ongoing growth caused by the evaporation of carbon cathode. Carbon electrodes with the highest specific surface area and the highest specific capacity were modified using the magnetron sputtering technology**.**

Magnetron power, W	Magnetron voltage, V	Specific capacity, F/g	Process time, min	Oxygen, %	Carbon, %
2	1000	8	5	5	89
2	1000	5.28	2	13	85

Table 1. The samples were etchedin C_2H_2 gas environment only

In the first case, the carbon electrodes were etched with the use of acetylene gas. In the acetylene gas environment, the micro formations having the lowest bond energy with the surface are removed. For this reason, the surface relief becomes more stable, thus the electric double layer formed during charging consists of more electric particles. As the higher quantity of electric particles is involved in the formation of electric layer, the capacity increase of around 10% (Table 1) is observed when the etching time is 5 minutes. However, when the etching time is 2 minutes, the decrease in the specific capacity of about 20% is observed. This can be explained by the fact that when the etching time is too short part of the surface structures become unstable and thus the formation of electric double layer becomes difficult.

Magnetron power, W	Magnetron voltage, V	Specific capacity, F/g	Process time, min	Oxygen, %	Carbon, %
260	460	9	2	4	84
260	460	9.5	4	6	93

Table 2. The specimen was placed on the cathode and etched in C_2H_2 gas environment

In the second case, the carbon electrodes were not only etched with acetylene gas, but also placed on the carbon cathode. In this case, the double process of etching and growth takes place. The research shows that during these processes the increase of specific capacity of about 15% is observed. This can be explained by the fact that during etching and growth the surface of carbon electrodes is covered with a secondary carbon layer which results in higher electric double layer stability and the increase of the amount of electric particles involved in the formation of this layer.

Also, in the first case the oxygen content at the carbon electrode surface is almost twice higher than in the second case. The existence of oxygen hampers the formation of electric double layer and as the result reduces the specific capacity of supercapacitors.

IV. CONCLUSIONS

As the research of porosity and specific surface area of non-affected electrodes shows, the highest surface area (47.25 m^2/g) is found in the electrode with the highest quantity of smallest diameter pores in the surface; it was formed at 15 Ar/C_2H_2 gas ratio. The capacitors formed of these electrodes have the maximum capacity. Meanwhile, the curves of pore distribution by diameter and surface area of electrodes having similar surface area almost coincide. As shown in the SEM images the lowest bond energy structures are removed from the surface after etching with acetylene plasma. The surface consists of strict form micro formations with high bond energy. Meanwhile, after placing electrodes on carbon cathode not only etching but also growth process takes place. The surface is formed of ball-shaped micro formations. After the effect of acetylene plasma on carbon electrodes for 5 minutes the increase in specific capacity of about 10% is observed. When the carbon electrode is not only etched by acetylene plasma but also placed on the carbon cathode, the specific capacity of capacitor is 15% higher compared to untreatedcapacitor electrodes.

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