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Plasma Enrichment of Electrochemical Properties of Conductive Polymers

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Abstract: *The polyaniline and polyaniline with carbon were treated in low temperature plasma process. Two steps treatment was applied, i.e. first with Ar and then with CO_2 reactive gas in a new plasma device with rotary chamber. Textural properties of the polymers were characterized using low temperature isotherms of N_2. Electrochemical properties of the polymers were carried out using galvanostatic studies, cycling voltammetry and electrochemical impedance spectroscopy. The physicochemical and electrochemical measurements have confirmed that capacitance properties are connected with a plasma exposition. Plasma modification process has visible influence on the changes in polymers porosity. The moderate increase of capacitance of the modified polymers has been also observed.*

Keywords: Conductive polymers, Low temperature plasma, Electrochemical properties

1. INTRODUCTION

Within the recent decades intrinsically conductive polymers like polyaniline, polypyrrole and polythiophene have been the area of intense research studies undertaken worldwide both by academic centers and industry. Chemical and physical properties of the polymers have attracted meaningful attention and therefore their potential applications in various areas include: electrochemistry, chemical and physical sensing, development of the memory devices, antistatic and heating materials as well as plastic solar cells and supporting material for catalysis [1-6]. However, it should be noted that, among the others conductive polymers, polyaniline is the most extensively studied because of its thermal and environmental stability as well as its susceptibility to chemical and/or physical modification.

The energy industry is one of the most rapidly growing in the world. The modern devices demand the special kind of power sources, one of them is the electric double layer capacitor (EDLC). It is able to generate the high power pick in a very short time and it can work as a supporting equipment for batteries. The EDLC can be build of various types of carbon materials, but very often is modified by addition of polymers i.e.: polyaniline, polypyrrole or metal oxides. This generation of electrochemical capacitors is often named pseudocapacitors. The additional capacitance arisen from redox reactions of these materials is described as pseudocapacitance [7]. The functional groups of heteroatoms as oxygen located on the surface of carbon material also can generate the pseudocapacitance. They are produced within the activation process. It must be underlined that such treatment also increases porosity of materials, which has significant impact on the electric capacity. The activation processes can be divided into chemical and physical. The most common type of the chemical modification of the surface is the use of KOH activation. Other well-known chemical procedures utilize for example: H_3PO_4 or $ZnCl_2$. These kinds of treatment are more destructive for a basic material than physical treatment [8, 9]. The activation in steam and CO_2 are the most common among various physical methods.

On the other hand, there is another interesting method of surface treatment – a low temperature plasma. The use of the low temperature plasma treatment process offers a potentially valuable method for chemical and/or physical surface modification of various types of materials including metals, polymers, carbons, glass as well as

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other materials. In case of physical treatment, the porosity of the material is being changed while for the chemical treatment, the chemically active species are being produced on the surface under the treatment. In this technique the changes on the surface generally depend on the type of working (carrier) gas. The modifications using oxygen, argon, nitrogen and CO_2 are the most frequently used for carbon materials applied as electrodes in the capacitors [10-16]. The attachment of functional groups to carbon atoms array may be obtained by the oxygen plasma technique, but this type of treatment has not significant influence on increasing the surface area. However, the argon plasma is often supported for the other plasma technique because it changes the surface physically and generates the higher surface area without additional functional groups. The one of the most important parameters during plasma treatment is a power discharge. The lower power creates a more numerous functional groups [8, 11, 14].

The potential applications of materials activated by plasma is very wide and include not only electrochemistry [17, 18] but also textile industry [19], adsorption technologies for purification of water and air [20-23], medicine - improvement of biocompability and controlled drug release [24], electronics [25-27] and the others.

In this paper we have demonstrated the results of polyaniline and composite of polyaniline with carbon black modified within two steps low temperature plasma treatment in a newly designed plasma reactor with rotating chamber. The physical and electrochemical properties of samples before and after the plasma treatment with argon and carbon dioxide were compared. The results presented that plasma treatment can be applied for the improvement of materials used as electrode materials for electrochemical capacitors since noticeably growth of capacitances were observed.

2. EXPERIMENTAL

2.1. Conductive polymers

Two conductive polymers based on polyaniline were used i.e. Polyaniline – Emeraldine Base (PANIEB) – the undoped form of conductive polymer and Polyaniline – Carbon Composite (PANICC) – 20% of polyaniline on carbon black. Both polymers were delivered by Sigma-Aldrich.

2.2. Plasma treatment

To treat the polymers by plasma, samples of PANIEB and PANICC were placed in a rotary chamber of a plasma device schematically presented in Fig. 1. The chamber was evacuated by means of a vacuum pump to the base pressure 1 x 10^{-3} mbar, and back filled at a small flow rate with a selected carrier gases. Two steps of the plasma treatment process was applied i.e. first the samples were treated with argon and then with carbon dioxide. The radio frequency (RF, 13.56 MHz) glow discharge was used. The gas pressure (3 x 10^{-2} mbar) and power of glow discharge (80W) were kept during the treatment. The weight of each sample was about 10 mg and the polymers were on the steel surface inside the rotating plasma chamber of the plasma device. The chamber made one full rotation within 1 minute. Duration of plasma treatment was 30 minutes including 20 minutes with argon and then 10 minutes with carbon dioxide.

2.3. Textural characterization of polymers

Characterization of the porosity of the polymers was carried out by measuring low-temperature nitrogen adsorption-desorption isotherms (77K) with use of automatic Autosorb iQ surface analyzer (Quantachrome Instruments, USA). The porosity of the polymers was evaluated by DFT, DR and BJH model, respectively. Based on the obtained isotherms the following parameters were calculated: the total pore volume (V_{tot}) - for nitrogen adsorbed at a relative pressure p/p_o=0,95, MBET surface area (S_{MBET}), micropore volume ($V_{DFTmicro}$), mezopore volume ($V_{DFTmezo}$, V_{BJH}) and micropore surface area (S_{DR}).

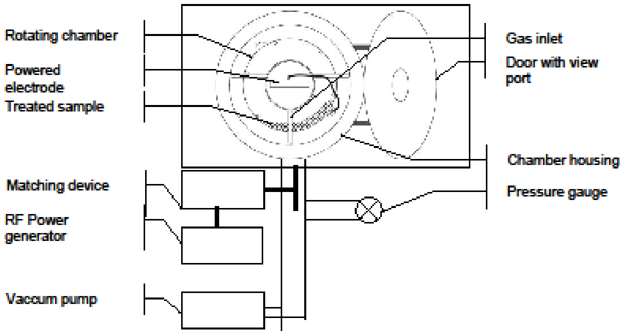

Figure 1. Scheme of the plasma reactor with rotating plasma chamber for polymer treatment.

2.4. Electrochemical characterization

The pellets for electrochemical measurements were prepared by mixing the PANIEB or PANICC material (respectively) with the binder and carbon black. Two- and three – electrode measurements were made in a Swagelok® systems with pellets of comparable masses. Electrochemical measurements were studied in 1 M H_2SO_4 electrolyte. The glassy fibrous material was chosen as separator. The galvanostatic studies, cycling voltammetry (CV) with scan rate from 1 mV s^{-1} to 100 mV s^{-1} and electrochemical impedance spectroscopy (EIS from 100 kHz to 1 mHz) were performed to evaluate the capacitance properties of the electrode materials using VSP Biologic, France.

3. RESULTS AND DISCUSSION

3.1. Textural properties

In previous studies related to the evaluation of the effects of various gases used in plasma process it was observed that the changes in materials structure were strictly dependent on the type of working gas used during the plasma treatment [23, 28]. The increasing of porosity was generally obtained by Ar plasma treatment since this gas is mainly responsible for physical modification. The use of CO_2 as working gas allows to create functional groups on the surface of the material. The power discharge of plasma device is one of the most important parameter. Too high discharges leads to creation of relatively low number of the functional groups, which are responsible for pseudocapacitance and can also destroy the samples physically.

Figures 2 and 3 compare the N_2 adsorption-desorption isotherms and the pore size distributions for the untreated polymers and the polymers treated with plasma. As it can be seen, samples of untreated polymers present a type 2 isotherm where the intermediate

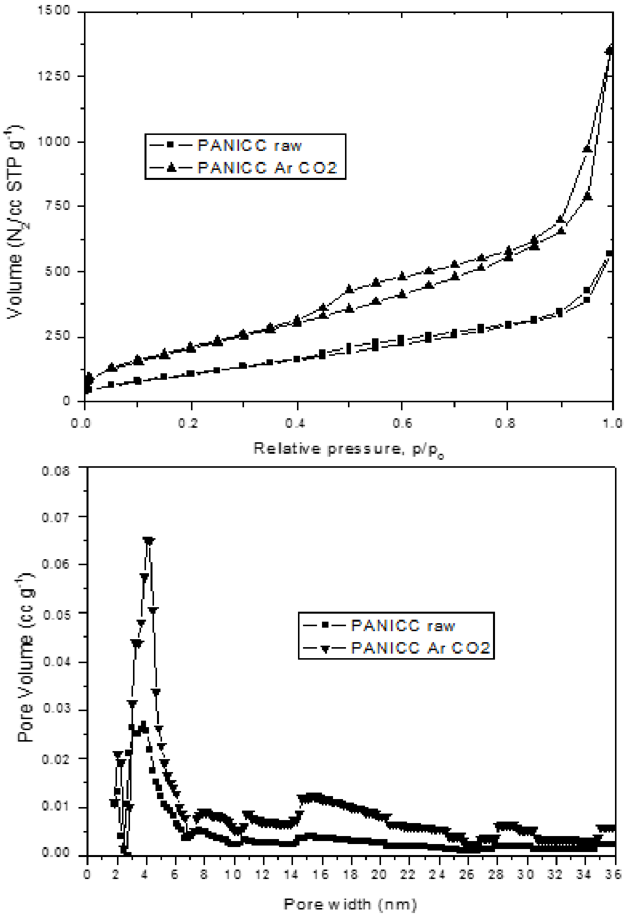

Figure 2. Nitrogen isotherms at 77K and pore size distribution for plasma treated and untreated PANICC.

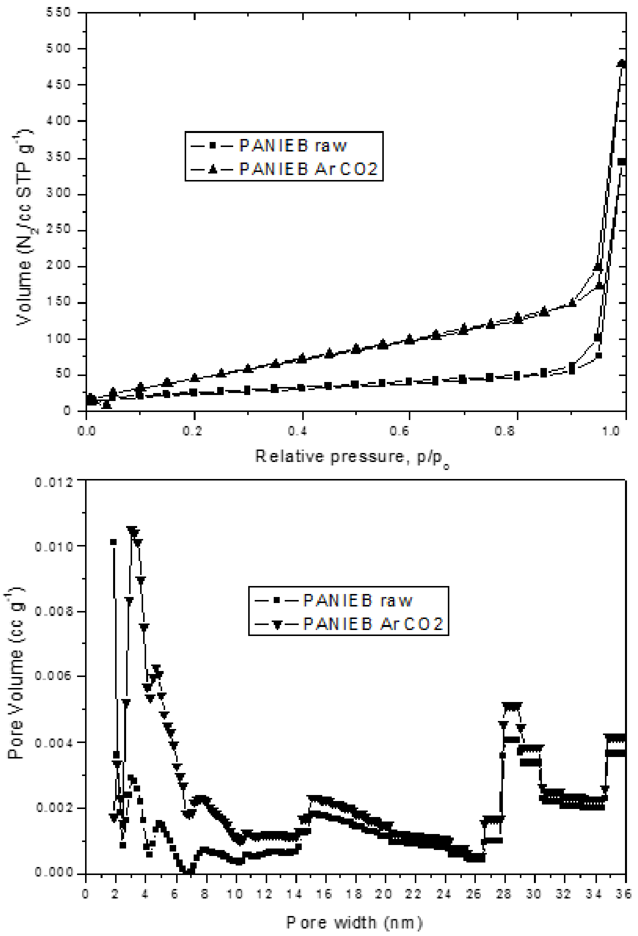

Figure 3. Nitrogen isotherms at 77K and pore size distribution for plasma treated and untreated PANIEB.

flat region in the isotherm corresponds to monolayer formation. However, after the plasma treatment it can be observed that the amount of N_2 adsorbed increases together with the very moderate improvement of the microporosity which is reflected by a widening of the part of the isotherms at low relative pressures. According to the obtained results (N_2 isothmers and the distribution of the pores) it could be observed physical influence of the plasma on the development of new micropores (diameter <2 nm) and increase the number and the volume of the mesopores (diameters between 2 and 50 nm). Furthermore, plasma treated polymers exhibit a certain amount adsorbed in the relative pressure range 0.1 – 0.99 due to the increase of the microporosity and mesoporosity. Table 1 presents a compilation of the basic porosity parameters obtained after application of various analysis from N_2 adsorption – desorption data. In both cases the BET surface area of the polymers has increased after the plasma treatment from 389 m^2 g^{-1} to 778 m^2 g^{-1} (PANICC) and from 82 m^2 g^{-1} to 185 m^2 g^{-1} (PANIEB). Moreover, the total micropore volume (V_{tot}) calculated from N_2 adsorption isotherms at a relative pressure 0.95 indicates that the plasma modifies the physical structure of the pores. For samples of polymers with carbon (PANICC) the total pore volume increased more than 100%, from 0.599 cc g^{-1} to 1.218 cc g^{-1}, and for samples containing only polymer from 0.116 cc g^{-1} to 0.266 cc g^{-1}.

It is interesting to analyse the influence of the plasma on the number and volume of the micropores and mesopores. In case of samples of the composite PANICC (polianiline with carbon) it can be observed that the microporosity increases more that 100 percent.

Table 1. Textural characterization of the samples (untreated and treated polymers).

Sample	V_{tot} (cc g^{-1})	S_{MBET} (m^2 g^{-1})	$V_{DFTmicro}$ (cc g^{-1})	$V_{DFTmezo}$ (cc g^{-1})	V_{BJH} (cc g^{-1})	S_{DR} (m^2 g^{-1})
PANICC raw	0.599	389	0.0276	0.665	0.560	828.06
PANICC Ar CO2	1.218	778	0.0524	1.600	1.401	1596.32
PANIEB raw	0.116	82	0.0154	0.244	0.112	171.49
PANIEB Ar CO2	0.266	185	0.0072	0.420	0.246	370.33

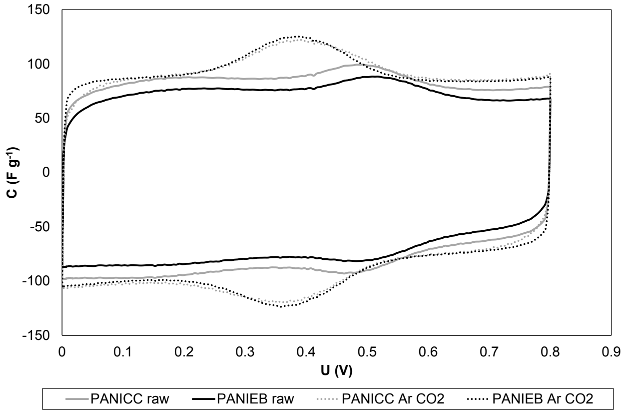

Figure 4. Cyclic voltammograms of PANIEB and PANICC before and after plasma treatment at 10 mV s^{-1}.

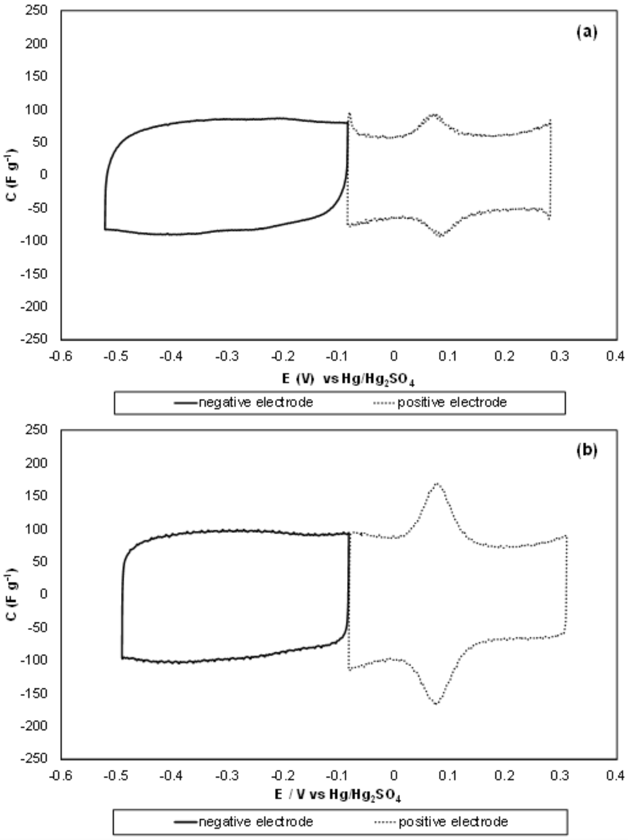

Figure 5. Cyclic voltammograms at 5mVs^{-1} scane rate for the three-electrode cell with different sample: (a) PANIEB raw (b) PANIEB Ar CO_2.

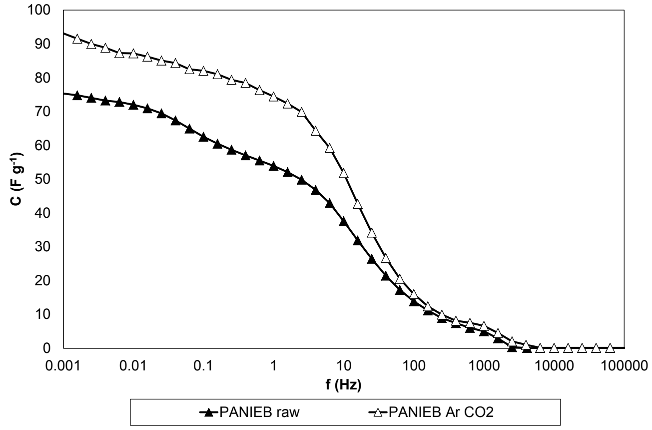

Figure 6. Figure 6. Capacitance – frequence depenence for the plasma treated polyaniline.

Mesoporosity in case of PANICC increased almost three times (from 0.665 cc g^{-1} to 1.600 cc g^{-1}). In case of the samples of the PANIEB (only polymer) the effects of the plasma treatment are not so spectacular and are totally different. The microporosity of the PANIEB was decreased (from 0.0154 cc g^{-1} to 0.0072 cc g^{-1}) and the mesoporosity was increased twice (from 0.244 cc g^{-1} to 0.420 cc g^{-1}). Based on that comparison it could be concluded that in case of polymers the plasma affects improvement of the mesopores. Confirmation of that observation could be done of the basis of the mesoporosity measurements with BJH model. The volume of mesopores of raw PANICC samples was 0.560 cc g^{-1} and for plasma treated was 1.401 cc g^{-1}. In case of mesopores of PANIEB the raw samples had 0.112 cc g^{-1} and the plasma treated had 0.246 cc g^{-1}.

The complete picture of the plasma influence on the polymers tested within this research it could be pointed out that the values of the surface area calculated with Dubinin-Radushkevich model confirmed improvement of the porosity of the polymers. In both cases of polymers i.e. for PANICC and PANIEB the surface area was increased almost twice.

3.2. Electrochemical properties

The electrochemical properties of materials before and after plasma modification have been studied in two- and three- electrode cells using acid (1 M H_2SO_4) electrolyte. Voltammetric characteristics at 10 mV s^{-1} are shown in Fig. 4 and differences in capacitances between the raw materials and materials after plasma treatment are noticeably. For the plasma treated polyaniline was noticed 22% increased of the capacitance and for the composite PANI/carbon black about 10% enhance. It can be result of creating higher amount of micro and mesopores after plasma treatment. The modified material have more available surface for the electrolyte ions which allows for the development of larger double layer.

The analysis of single electrodes performed in a three-electrode cell shows significant difference depending on the polarity of electrodes (Fig. 5). The voltammetric characteristic for all negative electrodes showed regular rectangle shape and the perfect charge propagation. However, the significant increasing of capacitance of positive electrode is observed for the electrode consists of the polyaniline after plasma modification. The materials modified by plasma display higher participation of pseudocapacitance in whole capacitance. The picks of oxidation and reduction of polianiline groups in three-electrode system studies are better observable after plasma modification and it can be said that these faradaic reactions

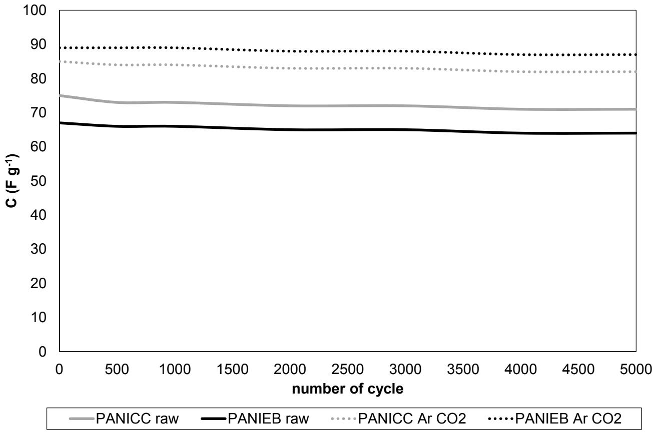

Figure 7. Cycling stability of different samples with current density 2 Ag^{-1}.

are visible when polymers are used as materials of the positive electrode.

At least, the analysis of electrochemical impedance spectroscopy was carried out. The results were not exhibited the change of capacitance after plasma treated composite of polyaniline – carbon black. On the other hand, the Fig. 6. presents capacitance vs. frequency response, we can see the improvement of charge propagation for material after plasma treatment. Table 2 illustrates the capacitance data from CV (two-electrode system studied at 10 mV s^{-1} and three-electrode systems at 5 mV s^{-1}) and EIS for two- and three-electrode systems at 1 mHz.

Moreover, the tested materials display the considerable stability during cycling measurements. After the 5000 cycles of galvanostatic charge/discharge with current density 2 Ag^{-1} the capacitances of all electrode systems were decreased only a few percent. It is very important parameter for future practical application of modified materials. As shown in Fig. 7, PANIEB Ar CO_2 exhibits long-term stability, maintaining 98% of its original capacitance after 5000 cycles.

4. CONCLUSION

The plasma technique is considered as one of the promising ways for surface modification of various materials. The results presented and discussed in this paper has shown that the low temperature plasma treatment of conductive polymer (polyaniline) or the composite of the polymer with carbon could be successfully used for the improvement of electrochemical properties of the materials destined for the electrochemical applications. However, the characteristic feature of electrode system based on the plasma treated polymers showed that the capacitance of this is not spectacular, it is good enough for some electronic devices. Additionally, both the positive and negative electrodes of investigated materials are promising for used them in the asymmetric and hybrid electrochemical capacitors.

The presented study provides considerable attractive information related to the application of novel surface treatment technique for the improvement of electrochemical properties of electrode materials. However, since only two different working gases were used during the plasma treatment, one power discharge and the duration of the process was limited, more detailed investigations concerning influence of these factors are needed.

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Table 2. Capacitance values of different plasma treated polymer samples.

Sample	Cycling voltammetry ($F g^{-1}$)			Impedance spectroscopy ($F g^{-1}$)		
	2-ele. cell 10 mV s^{-1}	positive ele. 5 mV s^{-1}	negative ele. 5 mV s^{-1}	2-ele. cell at 1 mHz	positive ele. at 1 mHz	negative ele. at 1 mHz
PANIEB raw	73	60	84	75	75	79
PANICC raw	84	84	83	80	80	84
PANIEB Ar CO_2	94	91	93	93	97	89
PANICC Ar CO_2	93	84	97	95	96	92

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