



Short communication

Carbon materials modified by plasma treatment as electrodes for supercapacitors

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ABSTRACT

The carbon material was modified by RF plasma with various reactive gases: O₂, Ar and CO₂. Physico-chemical properties of the final carbon products were characterized using different techniques such as gas adsorption method and XPS. Plasma modified materials enriched in oxygen functionalities were investigated as electrodes for supercapacitors in acidic medium. The electrochemical measurements have been carried out using cyclic voltammetry, galvanostatic charge/discharge and impedance spectroscopy. The electrochemical measurements have confirmed that capacity characteristics are closely connected with a type of plasma exposition. Modification processes have an influence on the kind and amount of surface functional groups in the carbon matrix. The moderate increase of capacity of carbon materials modified by plasma has been observed using symmetric two-electrode systems. Whereas investigations made in three-electrode system proved that the suitable selection of plasma modification parameters allows to obtain promising negative and positive electrode materials for supercapacitor application.

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1. Introduction

Electric double layer capacitors (EDLCs) have been extensively developed due to the increasing demand for a new kind of electrical energy sources with a high specific power of more than 10 kW kg⁻¹ and a long durability (over 10⁶ cycles). The main advantage of this storage device is the ability of a high dynamic of charge propagation (short-term pulse) that can be useful in the hybrid power sources for electrical vehicles, digital telecommunication systems, uninterruptible power supply (UPS) for computers and pulse laser technique.

EDLCs utilize the electric double layer formed at the electrode/electrolyte interface where charges are accumulated on the electrode surfaces and ions of opposite charge compensate them electrostatically [1–3]. Apart of electrostatic attraction pseudocapacitance effects due to quick faradaic reactions can take place. A great enhancement of capacitance might be realized by using composites with conducting polymers, metal oxides as well as carbons enriched in heteroatoms, e.g. oxygen, nitrogen [4–11]. Plasma treatment is an interesting way to introduce various surface oxygen functional groups. Some research has been already performed for modification of capacitor materials but authors used different plasma conditions and investigation was limited only to two-electrode cell [12–14]. In this work three different plasma O₂,

Ar and CO₂ treatments have been performed on carbon materials used as capacitor electrodes with a special attention on electrode polarity.

2. Experimental

2.1. Carbon material

A commercial activated carbon, Norit[®] SX2 POCH-Poland, was used as raw material. Before plasma treatment the carbon was formed into pressed pellets (9–12 mg) with a geometric surface area of 0.8 cm² per electrode. The electrode was composed of 85 wt.% of carbon, 10 wt.% of polyvinylidene fluoride (PVDF Kynar Flex 2801) and 5 wt.% of acetylene black.

2.2. Plasma treatment

The process of plasma treatment was performed in a parallel plate reactor (Fig. 1) with a radio frequency (RF, 13.56 MHz) glow discharge. A scheme of this reactor is presented in Fig. 1. Samples were exposed to the plasma generated in three gases: O₂, CO₂ and Ar. The flow rate of reactive gases and their initial pressure in the reactor chamber were 8 sccm (standard cubic centimeters per minute) and 10 Pa, respectively. The power of the glow discharge was equal to 10 or 80 W. The time of plasma for all the samples lasted 15 s. After treatment the pellets were turned on the other side and the process was repeated again 15 s.

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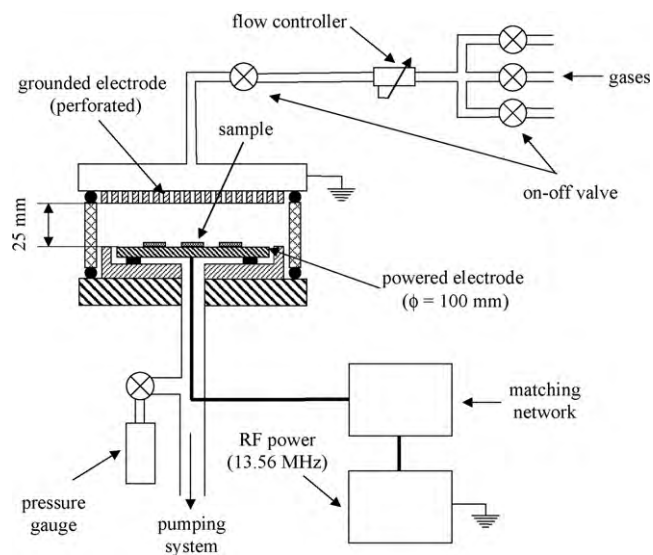


Fig. 1. Scheme of the RF plasma reactor.

2.3. Analysis of the carbons

The BET specific surface area was determined from N_2 physisorption at 77 K (Micromeritics ASAP 2010 volumetric adsorption system). The XPS technique was applied to estimate surface functional groups using Microlab 350 (Thermo VG).

2.4. Electrochemical characterization

Two- and three-electrode capacitors were assembled in a Swagelok® system with pellets of comparable mass. Electrochemical investigations were performed in 1 M H_2SO_4 . A glassy fibrous material played the role of separator. The capacitance properties of the composite materials (expressed per active mass of a single electrode) were studied by galvanostatic ($50\text{--}20000\text{ mA g}^{-1}$), potentiodynamic cycling at voltage scan rates from 1 to 100 mV s^{-1} , and by impedance spectroscopy (100 kHz to 1 MHz) using VMP2/Z Biologic, France and AUTOLAB 30 FRA2-Netherlands potentiostat–galvanostats.

3. Results and discussion

Plasma treatment has been realized on the carbon pellet of the small mass ca. 10 mg, as a consequence, the moderate power, time and flow conditions seem to be optimal in our case. For example the longer plasma exposition time (5 min) definitively aggravates elec-

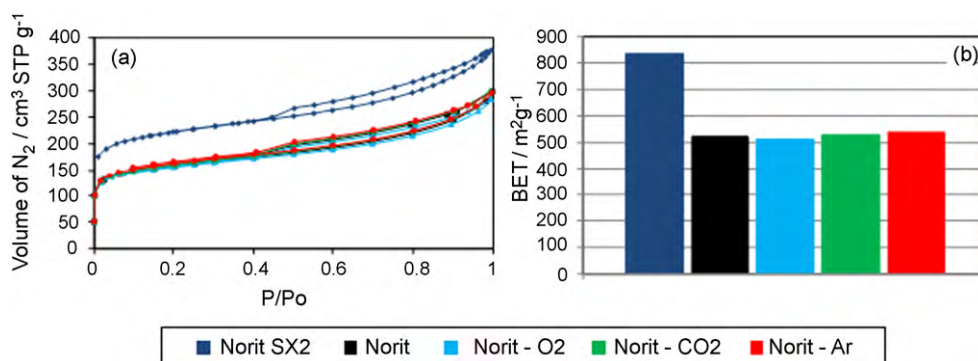


Fig. 2. Nitrogen adsorption/desorption isotherms at 77 K for carbon Norit SX2, pellet from this Norit and pellets treated by plasma (a) and BET specific surface area (b).

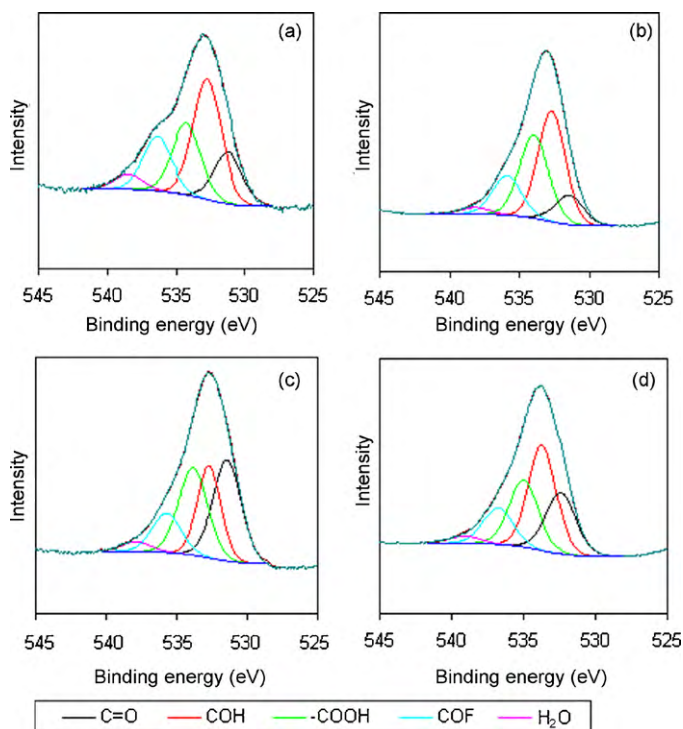


Fig. 3. XPS data for the oxygenated carbon groups: (a) Norit, (b) Norit-Ar, (c) Norit- CO_2 , and (d) Norit- O_2 .

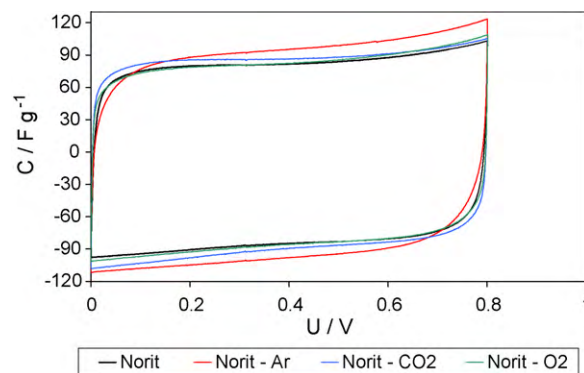


Fig. 4. Cyclic voltammograms of plasma modified pellets at 10 mV s^{-1} scan rate (two-electrode cell).

trochemical behavior of samples. Hence, all samples were plasma treated for 15 s on each side and 80 W power was selected for oxygen and argon plasma whereas 10 W for CO_2 plasma.

Table 1
Contribution of oxygenated groups in plasma treated samples.

Sample	C=O (At.%)	COH (At.%)	-COOH (At.%)	COF (At.%)	H ₂ O (At.%)	O/C
Norit	0.71	1.64	0.98	0.74	0.20	0.048
Norit-Ar	1.58	5.61	4.46	2.11	0.36	0.176
Norit-CO ₂	3.42	2.59	3.03	1.36	0.34	0.131
Norit-O ₂	3.46	5.61	3.79	2.05	0.40	0.194

Fig. 2 illustrates that plasma treatments do not modify microporous texture of pellets, the total specific surface area, calculated from Brunauer–Emmett–Teller (BET) equation in the region of relative pressure P/P_0 from 0 to 0.25, is quite comparable varying only from 512 to 539 m² g⁻¹. Micropore volume for pellets estimated from t -plot is ca. 0.2 cm³ g⁻¹. A small slope of isotherms is a proof of mesopores presence. It is noteworthy that pure carbon material Norit® SX32 has definitely higher specific surface area 835 m² g⁻¹ than pellets made from this material, it suggests that binding sub-

stance (PVDF) used for electrode preparation blocks some pores and/or entrance to pores. On the other hand, presence of acetylene black has also moderate impact on decrease of specific surface area of the final electrode.

Apart of nitrogen sorption data, XPS analysis (Fig. 3) was done for physicochemical characterization of plasma treated samples. XPS spectra show different participation of C=O, COH, and -COOH oxygenated groups in the plasma modified samples. Table 1 presents the contribution of all the carbon–oxygen functionalities and the

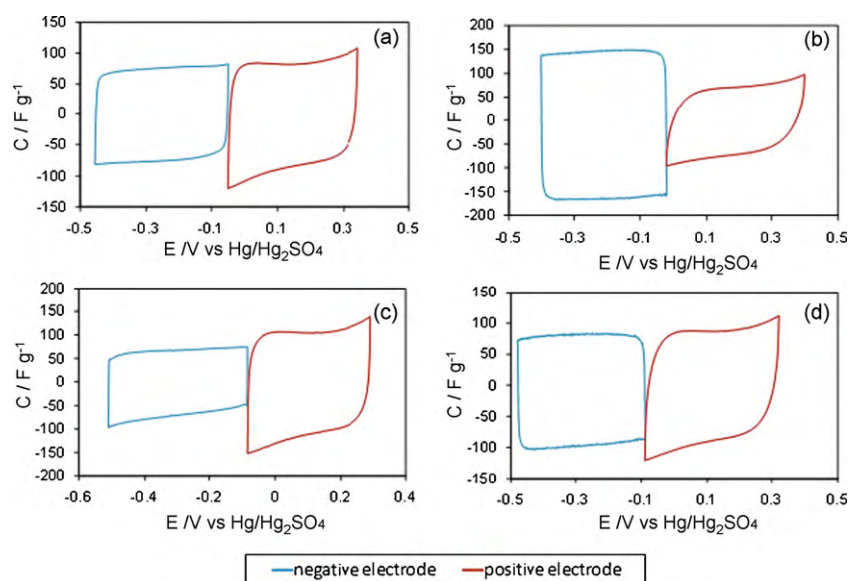


Fig. 5. Cyclic voltammograms at 5 mV s⁻¹ scan rate for three-electrode cell with different samples: (a) Norit, (b) Norit-Ar, (c) Norit-CO₂, and (d) Norit-O₂.

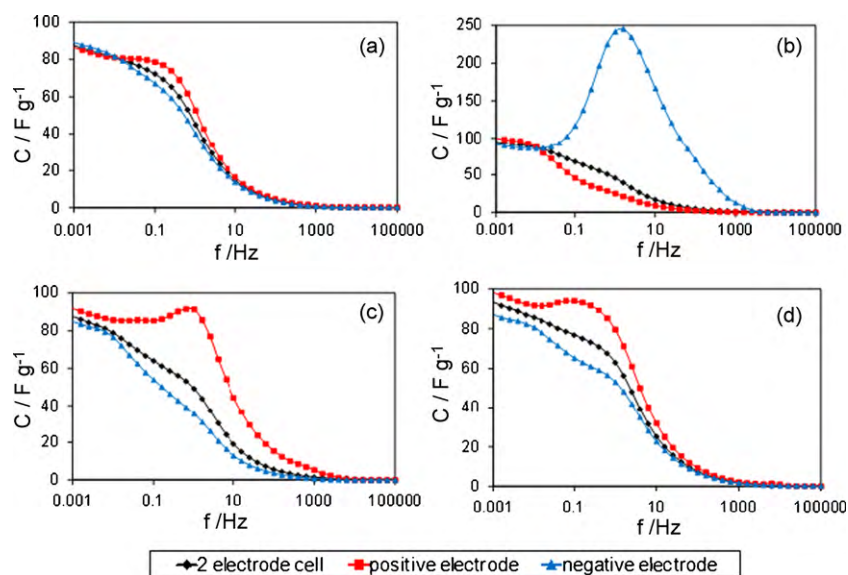


Fig. 6. Capacitance–frequency dependence for the plasma treated carbons: (a) Norit, (b) Norit-Ar, (c) Norit-CO₂, and (d) Norit-O₂.

total O/C ratio which increases from 0.048 to 0.194. The peaks for oxygenated groups (O 1s) are positioned at the following binding energies: C=O at 531.6 eV, COH at 532.9 eV, –COOH at 534.2 eV, COF at 536.1 eV and H₂O ads. at 538.3 eV. A significant increase of COH and –COOH complexes are observed after Ar plasma. For dioxide plasma the carbonyl groups are formed, preferentially. The electrochemical properties of modified electrodes have been investigated in two- and three-electrode cell using aqueous electrolyte. In organic medium, faradaic reactions are not expected because of the lack of protons. Hence, 1 M sulfuric acid as electrolytic solution has been used. For two-electrode cell only moderate effect of plasma treatment on capacitance characteristics was observed whatever the reactant gases. Voltammetry characteristics at 10 mV s⁻¹ scan rate (Fig. 4) for all the samples are almost overlapped, however, ca. 10% increase of capacitance for Ar treated sample is observed. On the other hand, a careful analysis of single electrodes performed in a three-electrode cell shows significant differences depending on the polarity of electrodes (Fig. 5). For example a perfect charge propagation is observed for negative electrode in the case of Ar plasma treated sample (Fig. 5b). It seems that a relatively high amount of carboxylic groups 4.46 At.% with an acidic character and phenolic groups (5.61 At.%) could be responsible for efficient sorption/desorption of protons (H₃O⁺). On the other hand, the best results for positive electrode have been observed in the case of sample modified with CO₂ plasma treatment (Fig. 5c). Capacitance of (+) electrode reached 108 F g⁻¹ with a good charge/discharge response. Reversible redox reactions of quinone/hydroquinone groups could be responsible for such a behavior that has been proved by many authors.

Table 2 illustrates all the capacitance data for plasma modified carbon pellets collected by different electrochemical techniques for two- and three-electrode cells as well as equivalent resistance values and galvanostatic cycling results at 1 A g⁻¹. Analysis of capacitance after 5000 cycles shows that capacitance loss is only 7% for Ar plasma treated and 11% for sample after carbon dioxide plasma, 18% capacitance decay is observed for capacitor built with oxygen plasma treatment.

Fig. 5 shows cyclic voltammograms (5 mV s⁻¹) for all carbon pellets and Fig. 6 presents capacitance vs. frequency dependence. Good correlation is observed between the rectangular shape of potentiodynamic curve and capacitance vs. frequency response. Charge propagation is perfect in some cases. For example a rapid increase of capacitance until 250 F g⁻¹ exists at relatively high frequency 1–10 Hz in Fig. 6b for Ar plasma treated sample which serves as negative electrode (sorption/desorption of H₃O⁺). Such phenomena is quite rare and can be explained by intrinsic properties of carbon, e.g. electron properties, presence of pseudo-capacitance due to surface groups facilitating proton sorption as well as various redox reactions (quinone/hydroquinone pair, etc.). Obviously always the carbon/electrolyte interface, not only carbon material, plays a crucial role on the final capacitive behavior.

It is also well remarked that positive electrode shows peculiar capacitance properties in the case of CO₂ plasma treated sample used as positive electrode (Fig. 6c).

However, it must be stressed that even if single electrode pointed out definitively better capacitive performance, total capacitance is determined by a smaller value. Finally to take a profit from plasma modified electrodes it would be necessary to built asymmetric system in which both electrodes would be obtained from various plasma reactant gases, e.g. negative electrode obtained from argon plasma treatment and positive one modified by CO₂ plasma.

In our experiments the carbon pellets were used for plasma treatment but not pure carbon powder. In the composition of pellets the binding substance, i.e. PVDF is present. As a consequence some change in COF bonding has been proved by XPS. One can

Table 2
Capacitance values and ESR of different plasma treated carbon samples.

Sample	Cycling voltammetry		Impedance spectroscopy				Cycle number (1000 mA g ⁻¹)										
	2 ele. cell 10 mV s ⁻¹ (F g ⁻¹)	Positive ele. 5 mV s ⁻¹ (F g ⁻¹)	Negative ele. 5 mV s ⁻¹ (F g ⁻¹)	Twoele. cell (F g ⁻¹)		ESR 1 kHz (ohm)	1 (F g ⁻¹)	500 (F g ⁻¹)	1000 (F g ⁻¹)	2000 (F g ⁻¹)	3000 (F g ⁻¹)	4000 (F g ⁻¹)	5000 (F g ⁻¹)				
				Positive ele. 1 Hz	Negative ele. 1 Hz												
Norit	82	82	72	88	45	86	53	89	40	0.895	84	80	77	74	73	72	71
Norit-Ar	92	64	151	95	46	100	25	91	242	0.328	91	89	88	88	86	86	85
Norit-CO ₂	87	108	78	88	49	92	92	85	36	0.331	88	85	82	82	80	78	78
Norit-O ₂	82	84	85	93	63	98	80	87	53	0.359	85	79	77	74	72	71	70

expect that it can affect wettability of electrodes, fluorination of carbon could be at the origin of slightly increasing hydrophobic character whereas oxygenated groups would give hydrophilic properties. In the future carbon fabric, felt or monolith form will be used to eliminate effect of binder with fluorine. In conclusion it can be said that plasma treatment is a profitable way to elucidate the role of various oxygenated surface groups on capacitance behavior of electrodes depending on their polarity. It seems that useful amount of oxygenated groups has some limit (e.g. for oxygen plasma treated sample), it is clear that too big amount of oxygen (over 15%) will dramatically deteriorate conductivity of the carbon electrode, in turn, aggravate capacitance and charge propagation. On the other hand, moderate amount of oxygen looks to diminish ESR from 0.895 ohm for untreated electrode to 0.328 ohm for Ar plasma treated electrode. As a consequence, the lower ESR the better capacitor characteristics. The further investigations are needed to elucidate more precisely the role of surface groups in plasma modified carbon samples on electrochemical properties.

4. Conclusions

Plasma treatment is an interesting way to modify surface properties of carbon materials. Generally, taking into account a very strong oxidative effect of plasma, in turn, aggravation of conducting properties of carbon, quite moderate conditions of RF plasma treatment were selected. It has been shown that depending on the reactant gases Ar, CO₂ and oxygen the different surface functionalities are developed. Ar plasma treatment seems to be profitable for performance of negative electrode operating in acidic medium whereas carbon dioxide plasma gives a good capacitive behavior

of electrode with positive polarity. Good cycling behavior was also confirmed in these two cases. For the further investigation a hybrid configuration is planned with the electrodes of different plasma treatment. More careful selection of the raw carbon materials can give even better results.

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