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Nanoporous Nitrogen-containing Coal for Electrodes of Supercapacitors

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Abstract Chemical activation of nanoporous carbon material with nitric acid followed by activation in a stream of argon at different temperatures initiates formation of amide, pyrrole and pyridine nitrogen compounds on the surface of the material. These activations will improve hydrophilic properties and increase electrical conductivity of the given material. Value of the specific capacitance of the N-enriched carbon material in an aqueous KOH solution can be increased by 30%, and additional heat treatment in the temperature range 440...460 °C will heighten this value by another 10%.

Keywords: *nanoporous carbon material, electric double layer, pseudocapacitance, surface functional groups, supercapacitor*

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1. Introduction

The most studied supercapacitor (SC) electrode material remains activated carbon, which is characterized by a porous structure, highly developed surface, good polarization rate, availability and low cost of production. However, there are several factors that hinder activated carbon's widespread use in energy generating and accumulation devices. The most noticeable factors are: internal resistance of SC, which depends on the ionic conductivity of the electrolyte, and carbon material's conductivity. Electrical conductivity of the nanoporous carbon (NC) will be decreased with increasing porous structure due to the gaps on pathways and higher contact resistance between the particles. Contact resistance depends on the surface condition and on the resistance at the interface between the electrode || electrolyte [1,2]. Large specific surface area limits the spatial capacitance, which affects the power properties of SC. In addition, the NCM is characterized by high surface activity, which is associated with presence of the various functional groups. Being adsorbed on the carbon surface, functional groups can interact with the electrolyte, especially organic, leading to its degradation and reduce the number of cycles of SC [2].

Carbon materials with functional groups on the surface along with the capacitance of the electrical double layer have pseudocapacitance associated with mass or charge transfer between the electrode material and ions of the electrolyte [3]. Capacitance of the electrical double layer is caused by electrostatic adsorption of electrolyte ions at the interface between the electrode || electrolyte. It is shown on [3,4] that the existence of atoms O, N, B and P on the surface NC increases the specific energy characteristics of the SC due to the onset of pseudocapacitance. Especially such effect will appear with presence of oxygen and nitrogen on surface [4].

Activated carbon enriched with nitrogen could be promising electrode material. Nitrogen atoms change the electronic structure of the surface layer of carbon, affecting the processes of charge/discharge of the electrical double layer (DEL) and participating also in Faraday reactions that are responsible of pseudocapacitance. On the [5,6] one can see contribution of the pseudocapacitance to the accumulation of electrical energy of supercapacitors with electrodes made of N-enriched carbon materials. Pseudocapacitance is associated with reversible redox reactions and depends simultaneously on the amount of nitrogen in the surface functional compounds and on the changes within the carbon surface layer due to the inclusion of nitrogen atoms in its structure. Nitrogen compounds formed on the hexagonal lattice of carbon exercise the largest effect. In addition, this effect may be strengthened or weakened by the surface oxide groups, mainly phenolic and carboxylic [7]. In addition, the heteroatoms of activated carbon that are inert at operating potentials of SC can improve the hydrophilicity of the surface carbon by electrolyte. They are locally alter the electrostatic field of pores, enhancing the interaction with polar water molecules [3,5], and there by increasing the specific capacitance of electrodes due to better access of electrolyte ions to the pore and thus attract additional surface in the process of charge/discharge.

Contribution of pseudocapacitance for N-enriched carbon material depends largely on the method of its receipt. In case of using the nitrogen-containing precursor,

such as melamine or poliakrylnitryl, you can get enriched carbon material primarily with inactive nitrogen compounds that alter its electronic structure. If the introduction of nitrogen is realized by chemical modification of NCM with nitrogen-containing reactive substances, such as ammonia, urea, nitric acid, then nitrogen compounds can be formed at the edges of graphene structures and can participate in Faraday redox reactions [8]. Placement of nitrogen functional groups in the structure of the carbon material is shown schematically in Figure 1 [2].

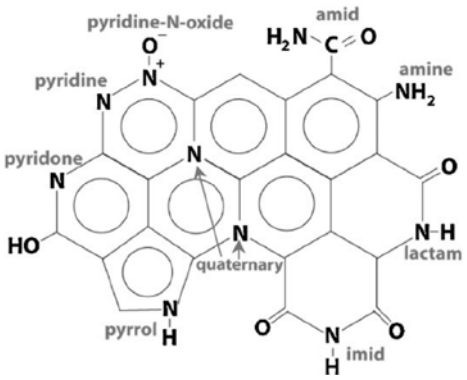

Figure 1. Nitrogen functional groups on the surface of *NC*

This paper describes the method to obtain N-enriched nanoporous carbon material where chemical modification of precursor by concentrated nitric acid is carried out before thermal activation. It is found that there is influence of the surface functional groups of coal on its porous structure and accordingly on the electrochemical properties of the SC with electrodes formed on this coal basis.

2. Experimental Part

The starting material is prepared using raw plant-origin materials by their hydrothermal carbonization at a pressure of water vapor $(12 \div 15)\cdot 10^5$ Pa [9]. The resulting coal mechanically crushed and mixed with potassium hydroxide and water in relation 1:1:1. The resulting mixture was stirred for an one hour at the temperature of 50...80 ºC and then kept at the temperature of 105 ± 10 °C for 24 h to constant weight. Thermal activation of the prepared mixture was carried out in a vertical tubular furnace in an atmosphere of dry argon. Initially, the mixture was heated at a rate 10 ºC/min to 900 ºC and kept at this temperature for an hour, and then quickly cooled in a stream of argon to the room temperature. Solid products of thermolysis were washed off with the alkaline and distilled water, 0.1 M HCl solution and then with water until ions Cl^- negative reaction (by $AgNO_3$). The resulting carbon was dried at 105 ± 10 ºC to constant weight. Nitric acid is used to form nitrogen heteroatoms on the material's surface (addition of 160 ml of 65% HNO_3 solution to 12 g of carbon material). The resulting suspension was thoroughly stirred by magnetic stirrer at room temperature for 3 hours, then washed with distilled water until neutral pH and dried with air at a temperature of 65 ± 5 °C overnight. Thus, activation of N-enriched CM carried out in a vertical tubular furnace at different temperatures (150...750 ± 10 °C) in a stream of argon for one hour. Surface area and total pore volume were determined from NCM isotherm adsorption/desorption of nitrogen at the temperature of -196 °C on the Quantachrome Autosorb device. Before measurements samples were degassed at 180 °C for 18 h. The value of the specific surface area S_{BET} (m^2/g) was determined by multipoint BET method in isotherm range, with a limited range of relative pressure P/P_0 = 0,050 ÷ 0,035. The total pore volume V_{total} (cm^3/g) is calculated by the number of adsorbed nitrogen at P/P_0 ~ 1.0. Volume of micropores V_{micro} (cm^3/g), specific microsurface S_{micro} (m^2/g) and mesopore S_{mezo} (m^2/g) were found by t-plot method.

IR spectra of samples NCM were obtained on device FT-IR Thermo Nicolet in reflection mode. To do so, samples were mixed with KBr in the ratio 1:100.

Electrochemical studies were conducted in double electrode cell using spectrometer Autolab PGSTAT/FRA-12. Electrodes of studied SC were prepared in the form of blades of a mixture: <NC>:<CA>:<PB>=<75>:<20>:<5>, where CA – conductive additive (graphite KS-15 (Lonza Group Ltd.)), PB – polymeric binder Ф-4D. Formed electrodes soaked in electrolyte, separated with separator and placed in double electrode cell size "2525", which was sealed. 30% aqueous KOH was used as the electrolyte.

Potential dynamic and galvanostatic cycling and electrochemical impedance spectroscopy (EIS) in the frequency range 10^{-2}...10^5 Hz were used to investigate the electrochemical properties. Taking into account the discharge current, varied in the range from 1 to 100 mA and using galvanostatic measurements data, specific capacitance of carbon material was calculated. Specific capacitance (C_{sp}) was calculated by the formulae $C_{sp} = \frac{I_d \cdot t_d}{(U - \Delta U)\cdot m}$, where: I_d – discharge current, t_d – discharge time, U – maximum charge voltage, ΔU – voltage drop after closing the discharge circle, m – mass of NC. Data EIS was modeled on the typical equivalent electrical circuits using a computer program ZView2.

3. Results and Discussions

Information about the status of NC surface with surface functional groups present before and after treatment with nitric acid can be obtained after IR-spectroscopy data analysis. IR spectroscopy is mainly used as a qualitative method to assess the chemical structure of carbon materials [7]. These spectra served in inverse form because of absorption of most of the visible spectrum emission by carbon material, and the absorption peaks are usually the result of overlapping spectra of different types of groups [10].

All spectra (Figure 2) are characterized by absorption bands in the vicinity 256 cm^{-1}, that is associated with deformation vibrations δ (-C-C-) of paraffinic compounds (their frequency decreases with extension chain). Absorption bands that are placed below 800 cm^{-1}, attributed lateral deformation vibrations of C-H groups located at the edges of aromatic planes [11]. After chemical activation with nitric acid, these bands disappear. For the initial carbon material AC (Table 1) bands observed in the vicinity of 1453 and 1950 cm^{-1}, that are indicating respectively the stretching vibrations ν (-C-C- or -C=C-) and planar deformation vibrations δ (-C-C- or -

C=C-). Besides the band 1400...1460 cm^{-1} are indicated fluctuation modes of C-OH, C-C aromatic compounds and benzene CH_2/CH_3 relations (1454 cm^{-1}). Reduced intensity and the absorption peak shift (1450 cm^{-1}) in the IR spectrum of the sample CN-0, caused probably by the chemical composition change of the surface material due to acid treatment. This supposition is confirmed by the superposition oscillation modes of C-N-H (1400...1460 cm^{-1}), N-H and C=N (1560...1570 cm^{-1}) in that band, indicating the formation of amide, pyrrole and pyridine nitrogen compounds [7,11].

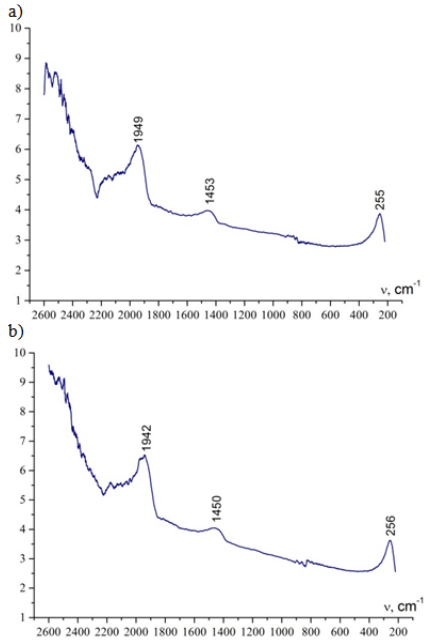

Figure 2. IR spectra of the surface of the NC before (a) and after (b) treatment with nitric acid

Isotherms of adsorption/desorption of N_2 at the temperature of -196 °C for various NCs are shown in Figure 3. The forms of isotherm models do not change for chemically modified samples. There is a slight decrease in the volume of sorbed nitrogen for samples CN-0 and CN-1 relatively to isotherms for AC, indicating the blocking of pores nitrogen by heteroatoms. With increasing temperature of heat treatment of carbon materials from 150 °C to 450 °C, there is an increase of sorbed nitrogen, and then above 450 °C is its decline. All isotherms are type I according to the IUPAC classification, having a category H4 hysteresis loop at relative pressure of ~ 0.5. In other words, sorption processes occur mainly in the narrow micropores [12].

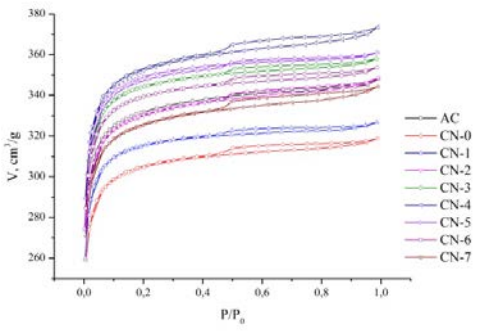

Figure 3. Isotherms of adsorption/desorption of nitrogen

In Table 1 the characteristics of the surface and porous structure of carbon materials before and after chemical activation, obtained from isotherm adsorption/desorption are shown (Figure 3).

Table 1. Physical properties of carbon materials

Sample	T^b, °C	S_{total}, m^2/g	S_{micro}, m^2/g	S_{meso}, m^2/g	V_{total}, cm^3/g	V_{micro}, cm^3/g
AC[a]	-	1257	1230	27	0,539	0,495
CN-0	-	1158	1130	27	0,493	0,453
CN-1	150	1197	1170	26	0,506	0,469
CN-2	250	1251	1219	31	0,539	0,491
CN-3	350	1308	1278	30	0,554	0,512
CN-4	450	1339	1303	36	0,577	0,523
CN-5	550	1329	1299	30	0,558	0,517
CN-6	650	1292	1261	31	0,547	0,504
CN-7	750	1237	1203	33	0,533	0,483

[a]AC – initial carbon material;
[b]T – activation temperature in a stream of argon.

Results are showing a decrease in the specific surface area and pore volume NC after the chemical action of concentrated nitric acid. Firstly, this is because carbon materials can adsorb ions and molecules of reactive substances, causing reduced active area and pore volume, and, secondly, surface heteroatoms may reduce pore size and even cover some micropores [6]. After heat treatment at temperatures ≤450 °C in a stream of argon, an increase of surface area is observed, due to the release of a number of surface functional groups on the material's surface. Burning of carbon material with heteroatoms of oxygen and nitrogen may occur with temperature increase, resulting in reduced microporous surface [9].

Figure 4 shows pore size distribution of carbon material obtained by DFT. It can be seen that almost the entire surface is formed by micropores with size 0.65...1.25 nm. Chemical treatment increases the amount of pore with size 0.65...0.85 nm, and an additional heat treatment at 450 °C causes an increase in pore size from 0.65...1.05 nm to 1.25 nm, as a result of the evaporation of individual adsorbed compounds during the synthesis of the material and some surface compounds burning.

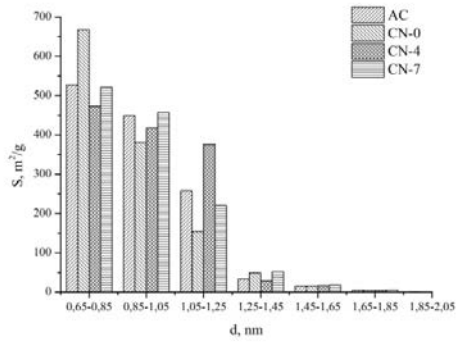

Figure 4. Histogram with pore size distribution of NC comparison

In Figure 5a was filed the dependence of specific capacitance on discharge current. As it shown in Figure 5a, introduction of nitrogen in the NCM increases specific capacitance of SC by 30%, even while reducing the

specific surface area of carbon material, CN-0 sample. Thus, contribution to the total capacitance makes not only DEL capacitance, which is proportional to the surface area, but also the capacitance due to the presence of functional groups that initiate Faradaic processes. Analysis of IR spectra NC indicates that as a result of treatment with acid nitrogen compounds are formed on the surface of nanoporous carbon. It is known that they are active in alkaline electrolytes. It is result of the additional charge accumulation at the expense of pseudocapacitance [2,3]. It is noticeable that the nitrogen and oxygen heteroatoms are increasing the polarity, improving the hydrophilic properties – thus increasing the adsorption of electrolyte ions and the active surface area, which is involved in the formation of DEL. Besides increasing the specific capacitance of SC is possible owning to thermal activation of N-enriched NCM in a stream of argon. SC capacitance is increased by 10% with heightening activation temperature up to the 450 °C. It caused by opening of the pores by surface heteroatoms. However, further increasing of activation temperature above 450 °C will reduce the capacitance value because of burnout of porous structure. These results are related well with the porometry data that are showing a decrease in specific surface for thermally activated samples at the temperatures over 550 °C. Obviously, the properties of the carbon electrode material depends not only on the quantity but also on the type of the surface groups. It is typical for porous electrodes to decrease specific capacitance with increasing discharge current (Figure 5a) due to the diffusion of ions in the pores of the electrolyte. Increasing the diffusion resistance of the transfer of ions to the surface of the material is particularly evident in the micropores [3].

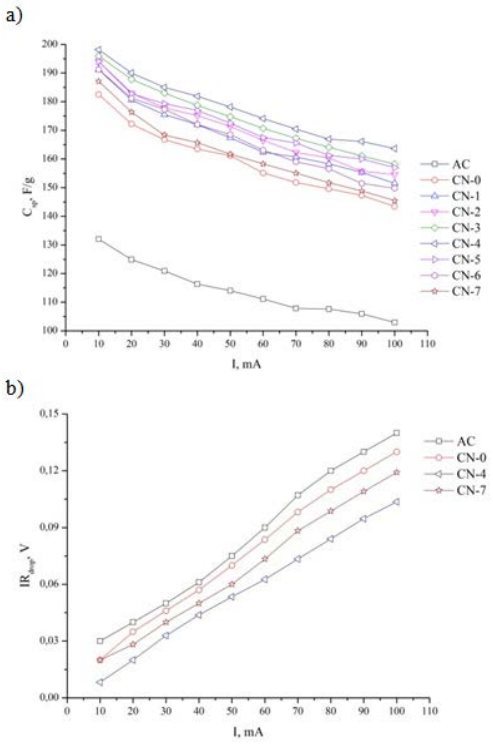

Figure 5. Dependency of specific capacitance (a) and surges (b) of SC on current

Chemical activation NCM does not change the dependency of the capacitance on the discharge current. The largest values of capacitance 200 F/g at 10 mA were obtained for sample CN-4. Increasing the discharge current up to the 100 mA leads to the reduction of capacitance by 17%. In Figure 5b is shown voltage drop in the SC on the discharge current, which indicates the presence of internal resistance and depends on the resistance shunts, the conductivity of the electrolyte and electrode material, also on the ion transfer resistance. As it had been mentioned, chemical treatment with HNO_3 causes formation of surface nitrogen heteroatoms that enhance hydrophilicity of the surface of carbon materials, reducing the internal resistance by 40% (Figure 5b). Further heat treatment of N-enriched material at temperatures up to 450 °C also reduces the potential jump by 20% as a result of unlocking mesopores and allocation oxide groups. By increasing the activation temperature above 450 °C there is electrical resistance raising in that is caused by a decrease in the hydrophilic ability of surface of active material resulting from the allocation of nitrogen compounds.

Figure 6 shows the cyclic voltammogramms for carbon materials in 30% aqueous KOH at linear scanning electrode potential of 1 mV/s. These curves have almost symmetrical rectangular shape with no obvious redox peaks, indicating the dominance of electrostatic processes of electric charge accumulation at the interface between the electrode || electrolyte [3]. Small peak at potentials 0.85...1 V caused by releasing of oxygen that was dissolved in the electrolyte and adsorbed by surface of active material [1]. N-enriched samples of CN-0...CN-7 can accumulate large energy amounts through electrochemically active compounds of nitrogen. The experimental data confirm the theoretical calculations performed in [13].

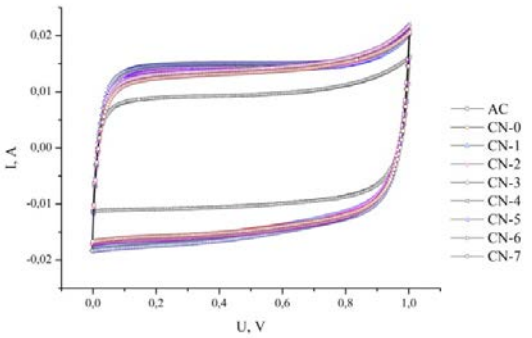

Figure 6. Potential dynamic characteristics of SC based on nanoporous carbon materials, s = 1 mV/s

Quantum-chemical calculations [13] showed that the pyrrole nitrogen compounds stimulate the charge transfer in the carbon matrix, providing it with semiconducting properties and increasing catalysis susceptibility of coal in electron transfer reactions. Energy amount accumulated in the SC with thermally modified carbon electrodes increases and reaches its maximum at the temperature of 450 °C, and then decreases with increasing temperature activation. These results confirm previous findings that heat treatment affects only the surface area involved in the formation of DEL.

Figure 7 gives the impedance locus of the samples in the frequency range 10^{-2}...10^{5} Hz. For standard AC semicircle observed in the high frequency range, showing resistance between the electrode and shunts, as well as low conductivity between carbon particles [14]. On the

impedance locus for samples CN-0...CN-7 in the high-frequency range leveling of the site is observed, as heteroatoms formed by oxidation of the activated carbon surface with nitric acid, improving electrical conductivity of carbon surface.

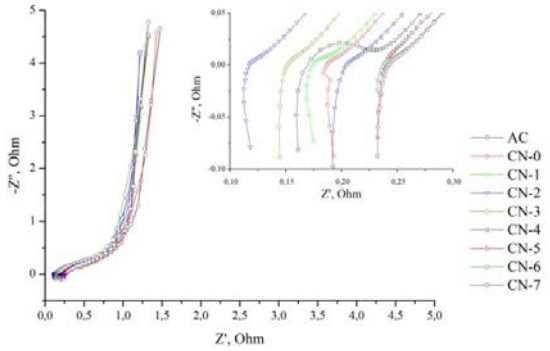

Figure 7. Nyquist diagram for condenser systems in aqueous KOH electrolyte

As shown in Figure 7, resistance decreases with temperature growth to 250 °C. Such increase of activation temperature leads to removal of the surface functional groups. At temperatures above 550 °C electrical resistance of the capacitor does not change. Having a semicircle in the range of high and medium frequencies indicates Faradaic resistance caused by pseudocapacitance. The imaginary part of the impedance is being increased sharply in the low-frequency range of angle close to 90°, i.e. energy storage is possible due to the formation of DEL at the interface electrode || electrolyte [4].

Modeling of impedance spectroscopy results allows us to analyze the electrochemical behavior of capacitors. Figure 8 presents equivalent circuit diagram of N-enriched NC. On the scheme: *R0* – electrolyte and electrode material resistance, inlet contacts and conductors. Leaders and contacts elements of cell causing inductance *L*. Elements *C1* and *R1* are: modeling capacitance of intergrain borders and charge transfer resistance through intergrain borders in the electrode material respectively [1].

In addition, the element *R1* considers carbon surface electrical properties change caused by nitrogen compounds. *CPE1* constant phase element is associated with the mechanism of pseudocapacitance energy storage as a result of redox reactions of nitrogen heteroatoms. It is also related to the heterogeneity of capacitance due to the porous structure of NC. RC-branches correspond to DEL capacitance and resistance of the electrolyte in the pores of different sizes. Comparing the pore sizes distribution (Figure 4) with RC-equivalent circuit elements, it can be argued that the pores with dimensions of 1.25...1.85 nm correspond to the elements of *C3* and *R3*, *C4* and *R4* – pores with a diameter of 1.05...1.25 nm, *C5* and *R5* – 0.65... 1.05 nm.

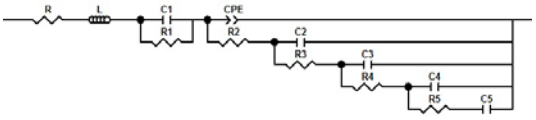

Figure 8. Equivalent circuit diagram for supercapacitor based on modified carbon material

4. Conclusions

Described method of the nitrogen introduction into the NCM produced using raw plant-origin materials by chemical washing in concentrated nitric acid and subsequent thermal activation in a stream of argon.

Additional thermal activation of nitrogen-containing carbon materials can develop specific surface area from 1160 m^2/g to 1340 m^2/g with increasing temperature up to 450 °C, resulting in 10% capacitance growth and halving of an internal electrical resistance.

Analysis of the IR spectra of the surface of carbon materials indicates presence of the surface functional groups – the reason of existence of oscillation modes C-N-H, N-H and C=N, indicating the formation of surface NCM amide, pyrrole and pyridine nitrogen compounds.

According to the electrochemical studies it was found that nitrogen heteroatoms can improve hydrophilic surface characteristics NCM and increase its conductivity. As a result, the specific capacitance NCM can be increased by 30% (from 114 F/g to 154 F/g at discharge current of 50 mA).

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