

Nitrogen-Containing Nanoporous Coal for Electrodes of Supercapacitors

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Chemical activation of nanoporous carbon material with nitric acid, followed by activation in a stream of argon at different temperatures, initiates formation on the surface of the material of amide, pyrrole and pyridine nitrogen compounds that improves the hydrophilic properties and increases its electrical conductivity. Value of the specific capacity of N-enriched carbon material in KOH aqueous solution increases by 30% and an additional heat treatment in the temperature range of 440-460°C increases it by 10%.

Keywords: Nanoporous carbon material, Electric double layer, Pseudocapacitance, Surface functional groups, Supercapacitor.

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1. INTRODUCTION

Activated carbon which is characterized by porous structure, highly-developed surface, good polarization, accessibility and cheapness of production remains the most studied electrode material of supercapacitors (SC). However, there is a number of factors which restrain its wide application in devices of generation and accumulation of electrical energy. Among them one can single out the internal resistance of SC which depends on the ionic conduction of electrolyte and conduction of carbon material. Electrical conduction of nanoporous carbon material (NCM) decreases with the increase in porous structure due to the discontinuity of conduction paths and increase in the contact resistance between particles. Contact resistance depends on the surface state and resistance at the electrode/electrolyte interface [1, 2]. Large specific area of the surface also limits spatial capacity which negatively influences the power properties of SC. Moreover, NCM is characterized by high activity of the surface connected with the presence of different functional groups. Functional groups adsorbed on the carbon surface can interact with electrolyte especially organic one that leads to its decomposition and reduction of the number of working cycles of SC [2].

Carbon materials with functional groups on the surface along with capacity of double electrical layer (DEL), which appears because of the electrostatic adsorption of electrolyte ions at the electrode/electrolyte interface, possess pseudocapacitance connected with charge or mass transfer between electrode material and electrolyte ions [3]. It is shown in the works [3, 4] that presence of O, N, B and P atoms on the NCM surface leads to the increase in the specific energy characteristics of SC due to the initiation of pseudocapacitance. This effect is especially exhibited in the presence of oxygen and nitrogen at the surface [4].

Nitrogen-enriched activated carbon is the promising electrode material. Nitrogen impurity atoms change the electron structure of the surface carbon layer, which influences the charge/discharge processes of DEL, and par-

ticipate in the Faraday reactions responsible for pseudocapacitance. Contribution of pseudocapacitance to the storage process of electrical energy of SC, whose electrodes are produced of N-enriched carbon materials, is shown in [5, 6]. Pseudocapacitance is connected with the reverse redox reactions and depends on the amount of nitrogen in the surface functional compounds and the change in the surface carbon layer that is conditioned by inclusion of nitrogen atoms into its structure. Nitrogen compounds formed on the hexagonal carbon lattices realize the maximum effect. Moreover, this influence can be amplified or attenuated by the surface oxide groups, phenol and carboxyl mainly [7]. Moreover, heteroatoms of activated carbon which are inertial at the working potentials of SC can improve hydrophilicity of the carbon surface by electrolyte. They locally change electrostatic field of pores which amplifies the interaction with polar water molecules [3, 5] and thereby increase the specific capacity of electrodes through better access of electrolyte ions to pores and, correspondingly, involvement of additional surface to the charge/discharge processes.

Contribution of pseudocapacitance for N-enriched carbon material depends significantly on the method of its obtaining. If nitrogen-containing precursor, for example, melamine or polyacrylonitrile is used, then one can obtain a carbon material enriched, first of all, by inactive compounds of nitrogen which change its electron structure. If introduction of nitrogen is performed by chemical modification of NCM by nitrogen-containing reactive substances, for example, ammonium, nitric acid, urea, then reactive compounds of nitrogen, which can participate in Faraday redox reactions [8], are formed on the boundaries of graphene structure. Arrangement of nitrogen functional groups in the structure of carbon material is schematically represented in Fig. 1 [2].

The aim of the present work was to obtain N-enriched NCM, in which chemical modification of precursor by concentrated nitric acid is performed before thermal activation, and to establish the role of surface functional carbon groups on its porous structure and electrochemical properties of SC.

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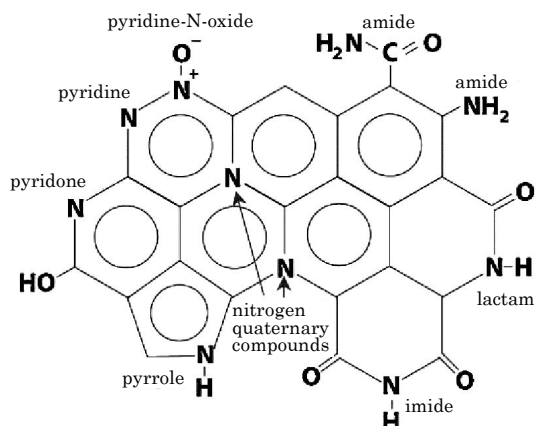


Fig. 1 – Nitrogen functional groups on the surface of carbon material

2. DESCRIPTION OF THE OBJECT AND INVESTIGATION METHODS

The initial material was obtained from phytogetic raw material by the method of hydrothermal carbonization at the water vapor pressure of $12\text{-}15 \cdot 10^5$ Pa [9]. Obtained carbon was mechanically grinded and mixed with potassium hydroxide and water in the ratio of 1:1:1. Obtained mixture was agitated during an hour at the temperature of $50\text{-}80$ °C; then it was held at the temperature of 105 ± 10 °C for 24 hours to constant mass. Thermal activation of the prepared mixture was carried out in vertical tubular oven in dry argon atmosphere. At first, mixture was heated with the rate of 10 °C/min to 900 °C and held at the given temperature during an hour, and then it was rapidly cooled in the argon stream to room temperature. Solid thermolysis products were washed from alkali sequentially by distilled water, 0.1 M HCl solution and water again to the negative response to Cl^- ions (by AgNO_3). Obtained carbon was dried at 105 ± 10 °C to constant mass [10]. Nitric acid was used for the formation of nitrogen heteroatoms on the material surface. To this end, 160 ml of 65% HNO_3 solution were added to 12 g of carbon material. Obtained suspension was thoroughly agitated by using magnetic mixer at room temperature during 3 hours, after then it was washed by distilled water till neutral pH and dried in air at the temperature of 65 ± 5 °C during a day. Activation of the N-enriched NCM was carried out in vertical tubular oven at different temperatures ($150\text{-}750 \pm 10$ °C) in the argon stream during an hour.

Surface area and total volume of NCM pores were defined based on the adsorption/desorption isotherms at the temperature of -196 °C on the device of Quantachrome Autosorb. Before measurements samples were degased at 180 °C during 18 hours. The value of specific surface S_{BET} (m^2/g) was determined by multipoint BET method in the region of isotherm limited by the range of relative pressure $P/P_0 = 0.050\text{-}0.035$. Total volume of pores V_{total} (cm^3/g) is calculated by using the amount of adsorbed nitrogen at $P/P_0 \sim 1.0$. Volume of micropores V_{micro} (cm^3/g), specific surface of micro- S_{micro} (m^2/g) and mesopores S_{meso} (m^2/g) were obtained by t -method [11].

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

Electrochemical investigations were performed in two-electrode cell using spectrometer Autolab PGSTAT/FRA-12. Electrodes of the studied SC were produced in the form of lamels from the mixture of the following composition:

$$\langle \text{NCM} \rangle : \langle \text{CCA} \rangle : \langle \text{PB} \rangle = \langle 75 \rangle : \langle 20 \rangle : \langle 5 \rangle,$$

where CCA is the current-conducting additive (graphite KS-15 of Lonza), PB is the plastic binder F-4D (public Corp. Halogen) [12]. Formed electrodes were percolated by electrolyte, separated by separator and placed to two-electrode cell of the dimension-type of “2525” which was hermetically closed. 30% KOH water solution was used as the electrolyte.

Galvanostatic and potentiodynamic cycling and electrochemical impedance spectroscopy (EIS) in the frequency range of $10^{-2}\text{-}10^5$ Hz were used for the investigation of the electrochemical properties. By using the data of galvanostatic measurements, specific capacity of carbon material depending on the discharge current which was varied in the range from 1 to 100 mA was calculated. Specific capacity (C_{num}) and internal resistance (R) were calculated by the formulas $C_{\text{num}} = 2I_d t_d / [(U - \Delta U)m]$ and $R = 0.5 \Delta U / I_d$, where I_d is the discharging current; t_d is the discharge time; U is the maximum charge voltage; ΔU is the voltage drop after closing of the discharging chain; m is the NCM mass.

The EIS data was simulated to typical equivalent electrical schemes by using computer program ZView2.

3. DESCRIPTION AND ANALYSIS OF THE RESULTS

Information about the NCM surface state before and after treatment by nitric acid concerning the presence of surface functional groups can be obtained based on the analysis of the IR-spectroscopy data which is used, mainly, as a qualitative method for the estimation of the chemical structure of carbon materials [7]. The obtained spectra are presented in the inverse form in connection with absorption of almost the whole radiation of visible spectrum by carbon material, and absorption peaks, as a rule, are the result of an overlapping of the spectra of different group types [13].

All spectra (Fig. 2) are characterized by absorption bands in the vicinity of 256 cm^{-1} which is connected with deformation vibrations $\delta(-\text{C}-\text{C}-)$ of paraffin compounds whose frequency decreases with chain elongation. Absorption bands which lie below 800 cm^{-1} are assigned to side deformation vibrations of $\text{C}-\text{H}$ groups located on the edges of aromatic planes [14]. After chemical activation by nitric acid these bands disappear. Bands in the vicinity of 1453 and 1950 cm^{-1} which correspondingly denote the equivalent vibrations $\nu(-\text{C}-\text{C}-$ or $-\text{C}=\text{C}-)$ and plane deformation vibrations $\delta(-\text{C}-\text{C}-$ or $-\text{C}=\text{C}-)$ are observed for the initial carbon material AC (Table 1). Moreover, band $1400\text{-}1460$ cm^{-1} indicates oscillation modes of $\text{C}-\text{OH}$, aromatic $\text{C}-\text{C}$ compounds and benzol CH_2/CH_3 bonds (1454 cm^{-1}). Decrease in the intensity and shift of the absorption peak (1450 cm^{-1}) in the IR-spectrum of CN-0 sample is probably conditioned by the change in the chemical composition of material surface because of the acid treatment. The given assum-

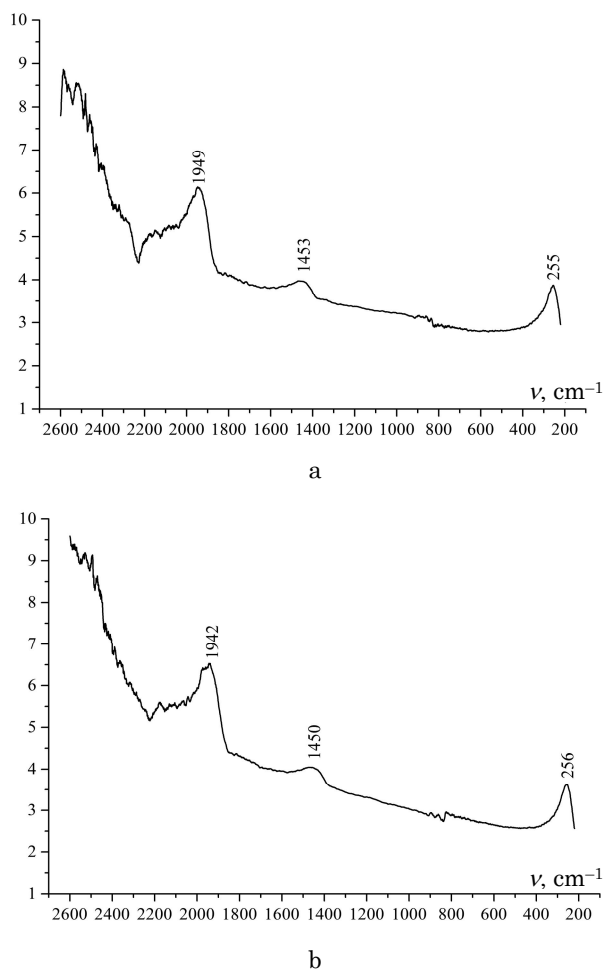


Fig. 2 – IR-spectra of the NCM surface before (a) and after (b) treatment by nitric acid

Table 1 – Physical characteristics of NCM

Sample	T^2 , °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 ¹	-	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

¹ AC is the initial carbon material;

² T is the activation temperature in the argon stream.

ption is confirmed by an overlapping in the mentioned band of oscillation modes C – N – H (1400-1460 cm⁻¹), N – H and C = N (1560-1570 cm⁻¹) that indicates the formation of amide, pyrrole, and pyrodine nitrogen compounds [7, 13].

Adsorption/desorption isotherms of N₂ at the temperature of – 196 °C for different NCM are illustrated in Fig. 3. Shapes of the isotherms are not changed for the chemically modified samples. One can observe a slight decrease in the volume of sorb nitrogen for CN-0 and CN-1 samples relative to the isotherm for AC that implies blocking of pores by nitrogen heteroatoms. With the increase in the temperature of thermal treatment of

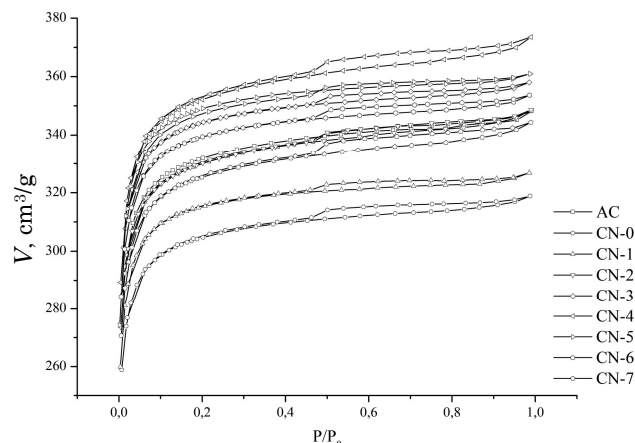


Fig. 3 – Adsorption/desorption isotherms of nitrogen at the temperature of – 196 °C

carbon materials from 150 °C to 450 °C one can observe the increase in the amount of sorb nitrogen, and after 450 °C its decay takes place. All isotherms belong to the I-st type in accordance with the IUPAC classification, for which hysteresis loop of the H4 category at the relative pressure of ~ 0.5 is typical. In other words, sorption processes occur in narrow micropores mainly [15].

Characteristics of the surface and porous structure of carbon materials before and after chemical activation obtained from the adsorption/desorption isotherms (see Fig. 3) are given in Table 1. The results have shown the decrease in the surface specific area and volume of NCM pores after chemical action of concentrated nitric acid. Firstly, this is conditioned by the fact that carbon materials adsorb ions and molecules of reactive substances, whereby active area and pore volume are decreased, and, secondly, surface heteroatoms decrease the pore size and even can shut a part of micropores [6]. Increase in the specific area conditioned by extraction of some amount of surface functional groups from the material surface is observed in the argon stream after thermal treatment at the temperatures of ≤ 450 °C. Burning of carbon material with participation of oxygen and nitrogen heteroatoms occurs with the temperature increase, and, as a result, microporous surface decreases [9].

In Fig. 4 we illustrate the distribution of pores by sizes for carbon materials obtained by the DFT method. As it follows from the figure, almost the whole surface is formed due to micropores of the sizes of 0.65-1.25 nm. Chemical treatment increases amount of pores of the sizes of 0.65-0.85 nm, and additional thermal treatment at 450 °C induces the increase in the size of pores from 0.65-1.05 nm to 1.05-1.25 nm because of evaporation of separate adsorbed substances in the process of material synthesis and burning of some surface compounds.

In Fig. 5 we present the dependence of the specific capacity on the discharge current. As seen from Fig. 5, introduction of nitrogen to NCM increases the specific capacity of the corresponding SC by 30% even at the decrease in the specific surface of carbon material (CN0 sample). Thus, contribution to the total capacity is performed not only by the DEL capacity which is proportional to the surface area, but also by the capacity conditioned by the presence of functional groups which initiate the Faraday processes. Analysis of the IR-spectra of NCM implies that nitrogen compounds are formed on

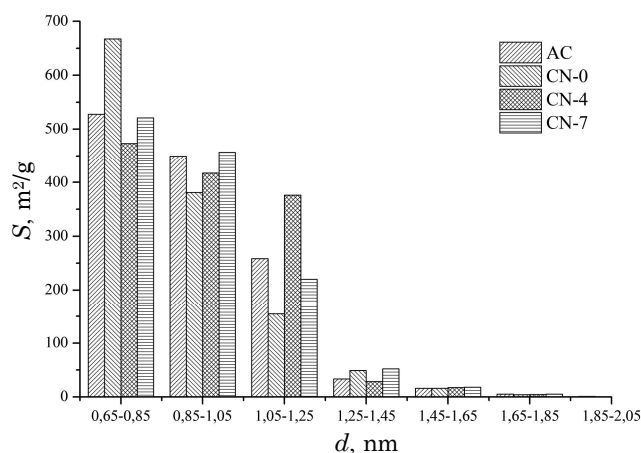


Fig. 4 – Histogram of comparison of the distribution of pores over NCM size

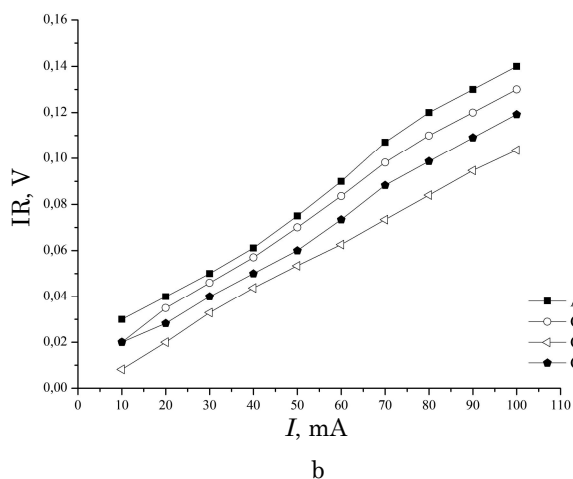
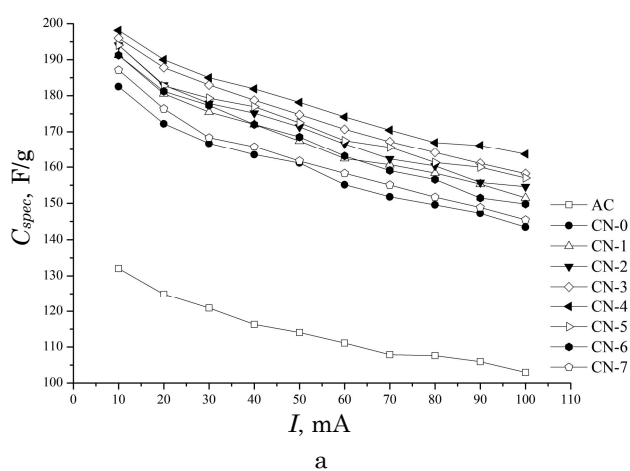


Fig. 5 – Dependences of the SC specific capacity (a) and voltage jump (b) on the discharge current

the surface of nanoporous carbon as a result of an acid treatment. It is known that they are active in alkaline electrolytes, and, as a consequence, additional charge storage due to pseudocapacitance takes place [2, 3]. We should note that nitrogen and oxygen heteroatoms increase the polarity and improve the hydrophilic properties of NCM increasing the adsorption of electrolyte ions and active surface area which participates in the formation of DEL. Moreover, increase in the SC specific capacity

is possible because of thermal activation of N-enriched NCM in the argon stream. SC capacity increases by 10% with the increase in the activation temperature to 450 °C that is conditioned by the opening of pores by surface heteroatoms. However, further increase in the activation temperature more than 450 °C decreases the capacity value because of the burning of porous structure. These results agree well with the data of porosimetry which has shown the decrease in the specific surface for thermally activated samples at temperatures larger than 550 °C. It is obvious that properties of the electrode carbon material depend not only on the amount but also on the type of surface groups.

Decrease in the specific capacity with the increase in the discharge current due to the diffusion in pores of electrolyte ions is typical for porous electrodes (Fig. 5a). Increase in the diffusion resistance of the ion transfer to the material surface is especially exhibited in micropores [3]. Chemical activation of NCM does not change the dependence of the capacity on the discharge current. The maximum capacity value 200 F/g at 10 mA is obtained for CN-4 sample. Increase in the discharge current to 100 mA leads to the decrease in the capacity by 17%.

In Fig. 5 we illustrate the voltage drop on SC on the discharge current which indicates the presence of the internal resistance and depends on the resistance of electrical leads, conduction of electrolyte and electrode material, ion transfer resistance. As it was mentioned, chemical treatment of HNO_3 induces the formation of surface nitrogen heteroatoms which improve the hydrophilicity of the surface of carbon materials that leads to the decrease in the internal resistance by 40% (Fig. 5b). Further thermal treatment of N-enriched material at the temperatures below 450 °C also decreases potential jump by 20% more that is conditioned by deblocking of mesopores and extraction of oxide groups. With the increase in the activation temperature more than 450 °C one can observe the increase in the electrical resistance that is induced by the decrease in the hydrophilic ability of the surface of active material as a result of the extraction of nitrogen compounds.

In Fig. 6 we represent the cyclic voltammograms of carbon materials in 30% KOH aqueous solution at linear sweep of the electrode potential 1 mV/s. Curves have symmetrical almost rectangular shape without obvious redox peaks that implies the dominance of the processes of electrostatical storage of electrical charge on the electrode/electrolyte interfaces [3]. Insignificant peak at the potentials of 0.85-1 V is conditioned by extraction of oxygen which is dissolved in electrolyte and adsorbed by the surface of active material [1]. N-enriched samples CN0-CN7 can accumulate a larger amount of energy that is induced by the electrochemically active nitrogen compounds. Obtained experimental data confirms the theoretical calculations carried out in [16]. Quantum-chemical calculations [16] have shown that pyrrole nitrogen compounds stimulate the charge transfer in carbon matrix endowing it with semiconductor characteristics and increasing the catalytic susceptibility of coal in the electron transfer reaction. Energy accumulated in SC with thermally modified carbon electrodes increases and reaches the maximum value at the temperature of 450 °C and then decays with the increase in the activation temperature. These results confirm the previ-

ous conclusions that thermal treatment influences only the surface area which participates in the DEL formation.

In Fig. 7 we illustrate the hodographs of the impedance of the investigated samples in the frequency range of 10^{-2} - 10^5 Hz. Semicircle in the high-frequencies range is observed for AC sample that indicates the resistance between electrode and electrical lead as well as the low electrical conduction between carbon particles [17]. On the hodographs of the impedance for CN0-CN7 samples in the high-frequency range one can observe flattening of the given region since heteroatoms which are formed as a result of the oxidation of the activated carbon surface by nitric acid improve the electrical conduction of carbon surface. As seen from Fig. 7, resistance decays with temperature increase to 250 °C. Increase in the activation temperature leads to the removal of surface functional groups. At temperatures higher than 550 °C electrical resistance of capacitor system is not almost changed. Presence of a semicircle in the range of high and medium frequencies implies the Faraday resistance induced by pseudocapacitance. Imaginary part of the impedance sharply increases in the low-frequency range on the angle close to 90°, i.e. energy storage occurs due to the DEL formation on the electrode/electrolyte interface [4].

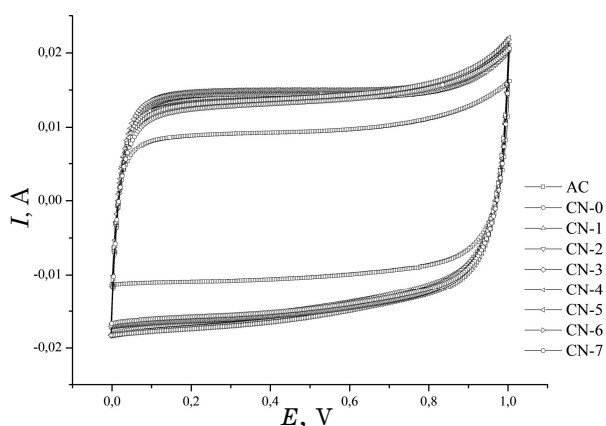


Fig. 6 – Potentiodynamic characteristics of SC formed based on nanoporous carbon materials, $s = 1$ mV/s

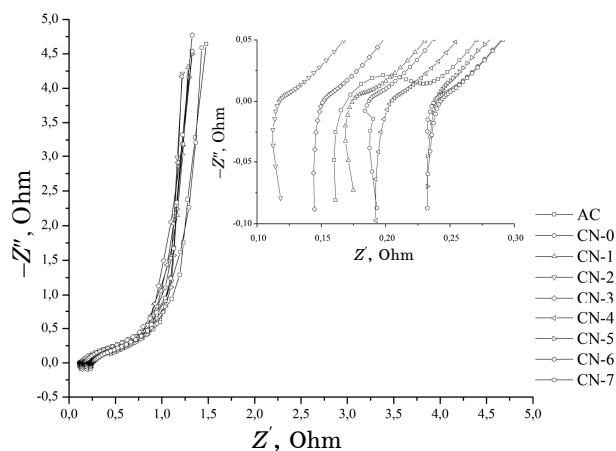


Fig. 7 – Nyquist diagrams for capacitor systems in KOH aqueous electrolyte

Modeling of the results of the impedance spectroscopy allows to analyze the electrochemical behavior of capacitors. In Fig. 8 we represent the equivalent electrical scheme of N-enriched NCM. In the scheme R is the resistance of electrolyte, electrode material and resistance conditioned by the cell design. Conductors and double contacts induce inductance L . Elements $C1$ and $R1$, respectively, model capacity of the grain boundaries and resistance of the charge transfer through the grain boundaries inside the electrode material [1]. Moreover, element $R1$ takes into account changes of the electrical properties of carbon surface induced by nitrogen compounds. Constant phase element CPE is connected with the mechanism of pseudocapacitive energy storage as a result of the redox reactions of nitrogen heteroatoms, it also takes into consideration inhomogeneity of capacity conditioned by NCM porous structure. RC -chains correspond to the DEL capacity and electrolyte resistance inside pores of different size. Comparing the data of the distribution of pores over sizes (see Fig. 4) with RC -elements of the equivalent scheme, one can state that elements $C2$ and $R2$ correspond to pores with the sizes of 1.25-1.85 nm, $C3$ and $R3$ – to pores with the diameter of 1.05-1.25 nm, $C4$ and $R4$ – 0.85-1.05 nm, $C5$ and $R5$ – 0.65-0.85 nm.

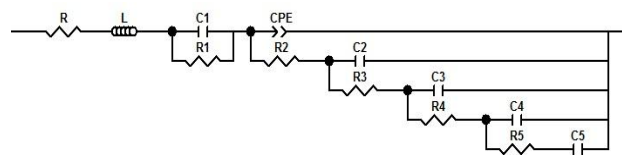


Fig. 8 – Equivalent electrical scheme for supercapacitor based on modified carbon material

4. CONCLUSIONS

1. We have developed the method of nitrogen intrusion into NCM obtained from phytogetic raw material by chemical washing in the concentrated nitric acid and further thermal activation in the argon stream.

2. Additional thermal activation of the nitrogen-containing carbon materials increases the specific surface area from 1160 m²/g to 1340 m²/g at the temperature increase to 450 °C; and, as a result, capacity increases by 10% and two-fold decrease in the internal electrical resistance takes place.

3. Analysis of the IR-spectra of the carbon materials surface indicates the presence of surface functional groups which are responsible for the oscillation modes C – N – H, N – H and C = N that implies the formation of amide, pyrrole, and pyridine nitrogen compounds on the NCM surface.

4. According to the data of the electrochemical investigations it is established that nitrogen heteroatoms improve the hydrophilic characteristics of the surface of NCM and increase its conduction. As a result, specific capacity of NCM increases by 30% (from 114 to 154 F/g at the discharge current of 50 mA).

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