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Study of Porous Carbon Materials for Supercapacitors

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Abstract

The work is devoted to the synthesis and study of porous carbon materials: thermally expanded graphite (TEG), carbon nanofibres, and activated carbon. The possibility of using them in electrochemical current sources, in particular, in supercapacitors, was investigated. The physicochemical properties of the obtained samples were studied by low-temperature nitrogen adsorption, cyclic voltammetry, and electron microscopy. The modification of carbon materials was carried out in three ways, and the effect of the modification on the values of specific capacitance and surface area was studied. It is revealed that the samples are characterized by the well developed porous structure: for initial materials, the maximum surface area was 759 m^2/g, while for the composites obtained as a result of the modification, it was 187 m^2/g. It was shown that the highest specific capacitance was typical for the materials possessing micro- and mesoporous structure, with an average pore size of 3–5 nm. Modification of the surface of carbon materials with nickel led to a decrease in the specific surface area, an increase in the average pore diameter, and also, in some cases, to an increase in the specific capacitance. Among the materials with deposited nickel particles, the maximum specific capacitance (116 F/g) was exhibited by a composite of 20 mass % NiO/80 mass % TEG. Treatment with nitric acid and mechanical activation led to an increase in the fraction of micropores in the samples and to an increase in the specific capacitance. The data obtained prove that the studied carbon materials are highly promising for electrochemical applications.

Keywords: carbon materials, thermally expanded graphite, carbon nanofibres, activated carbon, supercapacitors

INTRODUCTION

While the global demand for energy increases, it is necessary to provide a broad introduction of renewable energy sources, such as wind-, waves-based and solar. In view of the inherent instability of the renewable source of energy, their efficient application requires the technologies of energy storage and transformation, in particular for further mobile use. Among various technologies of electricity storage, when high power transmission or absorption is necessary, the most efficient devices for energy accumulation are electrochemical capacitors, also known as supercapacitors (SC) [1]. Therefore, one of the directions in high demand in the area of the development of accumulating sources of electric energy is the elaboration of highly efficient ecologically safe electrochemical capacitors or SC.

A supercapacitor is an electrochemical capacitor in which the natural phenomenon of the formation of a double electric layer (DEL) at the

boundary of the materials with different types of conductivity (electronic and ionic) is involved to establish thermodynamic equilibrium in the formed system [2]. Supercapacitors are principally different from batteries and hence they belong to different classes of chemical current sources. They use the processes of DEL charging/discharging on polarized electrodes with a high specific surface area. The mechanism of DEL charge/discharge is reversible and reproducible up to a hundred thousand cycles; each of them may proceed within a fraction of a second [3].

The electrodes of an SC are made of porous materials with the well-developed specific surface. At present, carbon nanomaterials are widely used as electrode structures for SC [4]. This is due to a number of their unique properties (high corrosion resistance, comparatively high electrical conductivity, thermal stability, high specific surface) and the parameters of the porous structure, which may be changed during the synthesis of the carbon material. An essential role is played by the size of pores in the material involved. For large pore size, the active surface area decreases, while for small pore size, relatively large charge carriers (electrolyte ions) surrounded by solvent molecules cannot get into the pores. According to the results of previous studies [5], an optimal pore size is 1–5 nm. The most widespread material for SC is cheap and available, *e.g.* activated carbon obtained from wood [6] or activated carbon obtained from rice husks [7]. Activated carbon fibres, carbide-derived carbons [8, 9], templates obtained from different forms of carbon [10, 11], carbon nanotubes, carbon nanohorns [12, 13], onion-like carbon [14, 15], carbon foams [16–19] and others are under extensive investigation. These materials demonstrated excellent capacitance characteristics, up to several hundred F/g, with the achievement of a specific surface area exceeding 1000 m^2/g. However, these materials are distinguished by high cost [20].

Currently, active studies are carried out into the possibility of applying new porous carbon materials for electrode structures that would possess high capacitance characteristics, optimal texture characteristics, which are cheap. In this connection, the goal of the present work was to develop porous carbon materials for application as electrodes in SC and to study the dependence of specific capacitance on texture characteristics and the type of carbon material involved.

EXPERIMENTAL

Experimental procedure

Synthesis of carbon materials. Three main types of carbon materials were synthesized and investigated: thermally expanded graphite (TEG), carbon nanofibres (CNFs), and activated carbon (AC).

Thermally expanded graphite is a carbon material characterized by low density and the presence of macro- and mesopores. It is distinguished by the developed surface, which predefines its application in SC [21]. Thermally expanded graphite was obtained by heat treatment of intercalated graphite (graphite bisulphate) in the dynamic heating mode (programmable heating). Intercalated graphite was heated in a furnace at a given heating rate (20 °C/min) from room temperature (25 °C) to 400 °C. Heating caused sample expansion with the formation of worm-like particles. After heating, the sample was left to cool in the muffle furnace.

Carbon nanofibres are composed of granules formed by the nanofibres of carbon with nested cone structure. This material was synthesized by the catalytic decomposition of C_1–C_4 hydrocarbons [22–24]. In the present work, we used propane for the synthesis of CNFs. Propane decomposition was carried out in a catalytic flow set-up BTRS Jn (Autoclave Engineers, USA) at a temperature of 600 °C over the catalyst with the composition 50 mass % Ni – 40 mass % Cu – 10 mass % SiO_2. The size of the obtained CNF granules varied within the range from 10 μm to 5 mm, and nanofibre diameter was 15–120 nm.

The third material used in the work was activated carbon material (AC), which is carbon obtained from rice husks through their controlled combustion. Initial rice husks were subjected to acid etching, washed with water, dried, burnt preliminarily in a closed reactor with smoke evacuation and trapping of amorphous carbon. The oxidative combustion of rice husks was carried out in the optimal mode (600 °C, fluidized bed) with controlled oxygen admission. The obtained coal was dried and subjected to chemical activation by the aqueous solution of sodium carbonate (desilication) with a concentration of 10–13 mass %. The resulting material was very soft and was easily ground to particle size less than 45 μm. The synthesis procedure and apparatus arrangement of the experiment were described in [25, 26].

Methods of modification of carbon materials

For the purpose of improving the capacitance characteristics of carbon materials, their modification was carried out using three methods: 1) deposition of nickel oxide and the particles of metallic nickel; 2) treatment with nitric acid; 3) mechanical activation. The main approach involved in the proposed methods to modify the surface of carbon materials is the enhancement of the contribution from pseudocapacitance. Designations of the samples of composite materials are listed in Table 1.

The first method of modification involved the deposition of nickel oxide on TEG. The treatment was carried out in the amount of 20 % with respect to the mass, calculated for pure metal nickel. The deposition was performed by impregnating the carbon material with the solution of nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$), followed by drying at 100 °C and annealing in the furnace at a temperature of 400 °C for about 8 h (sample 1). Samples 2–5 were prepared as follows: nickel was deposited on TEG, CNFs and AC by impregnating the carbon material with the solution of nickel salt, followed by drying at a temperature of 100 °C, annealing for 2 h in the furnace at 350 °C, and reduction in hydrogen flow for about 3 h at 350 °C.

The second method of modification is chemical treatment. The chemical treatment of TEG, CNFs and AC was carried out in the solution of 15 % HNO_3 for the purpose of increasing the content of surface functional groups. The samples were boiled in 15 % HNO_3 for 2 h at 150 °C. Then the vacuum filtration of the resulting mixture was carried out, and the carbon material isolated by filtering was dried for 8 h at 100 °C.

On the basis of chemically treated TEG, CNFs and AC, two composite materials were prepared by mechanical mixing. The compositions of these two materials were: 15 mass % TEG/85 mass % CNFs and 15 mass % TEG/85 mass % AC. The powders were mixed in the listed ratios, and then the mixtures were mechanically activated in an AGO-2C planetary mill. Mechanical activation was carried out for 2 min with the centrifugal acceleration of 15*g*. The cylinder volume was 150 mL. Activation was carried out using the balls made of zirconium dioxide. The ground powders were dried for 8 h at 100 °C. The ratio of material to the ball mass was 1 : 125.

TABLE 1

Designations of composite materials

Sample no.	Composite, mass %
1	20NiO/80TEG
2	20Ni/80CNF
3	85Ni/15TEG
4	20Ni/80AC
5	80Ni/20CNF

Note. Numbers in the designation of composite materials mean the component content (mass %).

Methods of material investigation

The microstructure of the materials was studied by means of scanning electron microscopy (SEM) with field emission using a SU-8000 electron microscope (Hitachi, Japan) in conjugation with the attachment for energy-dispersive spectroscopy (EDS) Oxford Instruments.

Texture characteristics of the obtained carbon materials were studied with the help of low-temperature nitrogen adsorption at 77 K using a NOVA 1000e adsorption set-up (Quantachrome Instruments, USA). Specific surface (A) was calculated according to Brunauer-Emmett-Teller procedure (BET). The specific surface of pores remaining after micropores were filled with the adsorbate (A_t) was calculated using the comparative *t*-method proposed by de Boor and Lippens; the statistic thickness of adsorption film was calculated according to de Boor equation. The method is based on comparing the increments of adsorption on the adsorption isotherm under study and on the standard adsorption isotherm obtained with well characterized non-porous materials [27].

Carbon materials were tested as electrodes for SC with the help of voltammetry. Experiments were carried out using an Elins P-30SM potentiostat (Elins, Russia). A three-electrode scheme was used: the working, auxiliary, and reference electrodes. The working electrode was a graphite rod with the material under investigation deposited onto it; the auxiliary electrode was a platinum plate with an area of 10 cm^2, the reference electrode was a saturated silver chloride electrode. The solution of sulphuric acid (H_2SO_4) with the concentration 3.5 mol/L was used as the electrolyte. The investigation procedure was described in more detail in [28]. The parameter under investigation is specific capacitance (C_{sp}). Measurements were carried out at room temperature and three sweep rate values: 2, 5, 10 mV/s. Specific capacitance was calculated according to the equation:

$C_{sp} = J/vm$

where C_{sp} is the specific capacitance of the material under investigation, F/g; J is the total current at the cathode and anode ($J = J_c + J_a$), which was determined from stripping voltammetric measurements at 500 mV; m is the mass of the material, g; v is the potential sweep rate, mV/s.

RESULTS AND DISCUSSION

According to the data of SEM of TEG, CNFs and AC samples, the morphology of the material, the presence of pores and defects may be evaluated. The SEM micrographs of carbon materials are shown in Fig 1. TEG sample is represented by comparatively large graphite particles with a size of several ten micrometers. The particles are very curved, which is connected with the method of obtaining the material when the gas formed during bisulphate decomposition causes sample swelling while evolving. Graphite plates formed through thermal exfoliation may also be seen on the surface of the material.

CNFs sample is represented by dense granules composed of interlaced carbon nanofibres (see Fig. 1, *g*, *h*). One can see that the structures of different diameters are formed as a result of synthesis. Microphotographs taken by means of transmission electron microscopy (TEM) show that the sample is represented by a mixture of different types of nanofibres, which are strongly curved. Nanofibres with both the nested cones and card pack structures are in the sample (see Fig. 1, *g*).

The AC sample consists of porous particles with pore sizes varying from 4 to 10 μm. Most pores are asymmetric and elongated along one of the coordinates.

According to the data of EDS, TEG sample contains elements: C (92.09 at. %), O (6.98 at. %), Si (0.21 at. %), S (0.72 at. %). Indeed, according to the data of X-ray diffraction, interlayer spacing d_{002} for TEG is equal to 3.354 Å. Calculation according to Meier–Mering equation shows graphitization degree almost equal to 100 %. Relying on this result, one cannot speak of the presence of surface functional groups in TEG because of the high degree of graphitization. So, the presence of oxygen in TEG in the amount of approximately 7 at. % is due to the presence of the fragments of its precursor, graphite bisulphate.

CNFs contain the following elements: C (90.11 at. %), O (8.60 at. %), Si (1.29 at. %). In addition to oxygen and carbon, the sample also contains silicon as an admixture. Activated carbon contains substantially higher amount of oxygen, which is formed during activation (C – 67.55 at. %, O – 26.44 at. %), silicon (4.86 at. %) and a large amount of other admixtures (Na, Mg, Al, K, Ca, Cu – the total content is 1.15 at. %).

Texture characteristics

Carbon materials under investigation are characterized by the presence of various hysteresis loops (Fig. 2), which is an indirect indication that they may be related to different kinds of carbon materials and hence to different texture characteristics.

According to the type of adsorption and desorption isotherms, it may be concluded that all samples possess a non-uniform porous structure. For the TEG sample (see Fig. 2, *a*), a sharp rise of the isotherm in the region of relative pressure $P/P_0 < 0.4$ is evidence of the presence of micropores in the structure, which may have a positive effect on the sorption properties of the materials. With an increase in relative pressure within the range $P/P_0 = 0.4–1.0$, an insignificant loop of capillary condensation hysteresis of H4 type is observed, which is due to the presence of slit-shaped mesopores [29]. Mesopores dominate over micropores in AC and CNFs samples, while TEG, quite contrary, is characterized by the high content of the latter.

The type of hysteresis loop H3 observed for the CNFs sample (see Fig. 2, *b*) points to the presence of mainly isolated pores with bottle-like shapes with very large radii of the broad parts and narrow necks.

Activated carbon has slit-shaped pores with narrowing, which is evidenced by the hysteresis loop of H4 type over the whole region of relative pressure from 0.2 to 1.0 (see Fig. 2, *c*).

Results of the studies of texture characteristics of initial carbon materials are presented in Table 2: total specific surface (A, m^2/g), specific surface of micropores (A_m, m^2/g), average pore diameter (d_{pore}, nm), and total pore volume (V, cm^3/g). The TEG sample possessed the largest specific surface area, and the micropore surface area was 455 m^2/g. Activated carbon may be considered as mainly microporous material with the specific surface of micropores $A_m = 114$ m^2/g.

It follows from the data shown in Table 2 that the minimal pore size is inherent for AC with the minimal pore volume, and the maximal specific surface was shown by TEG.

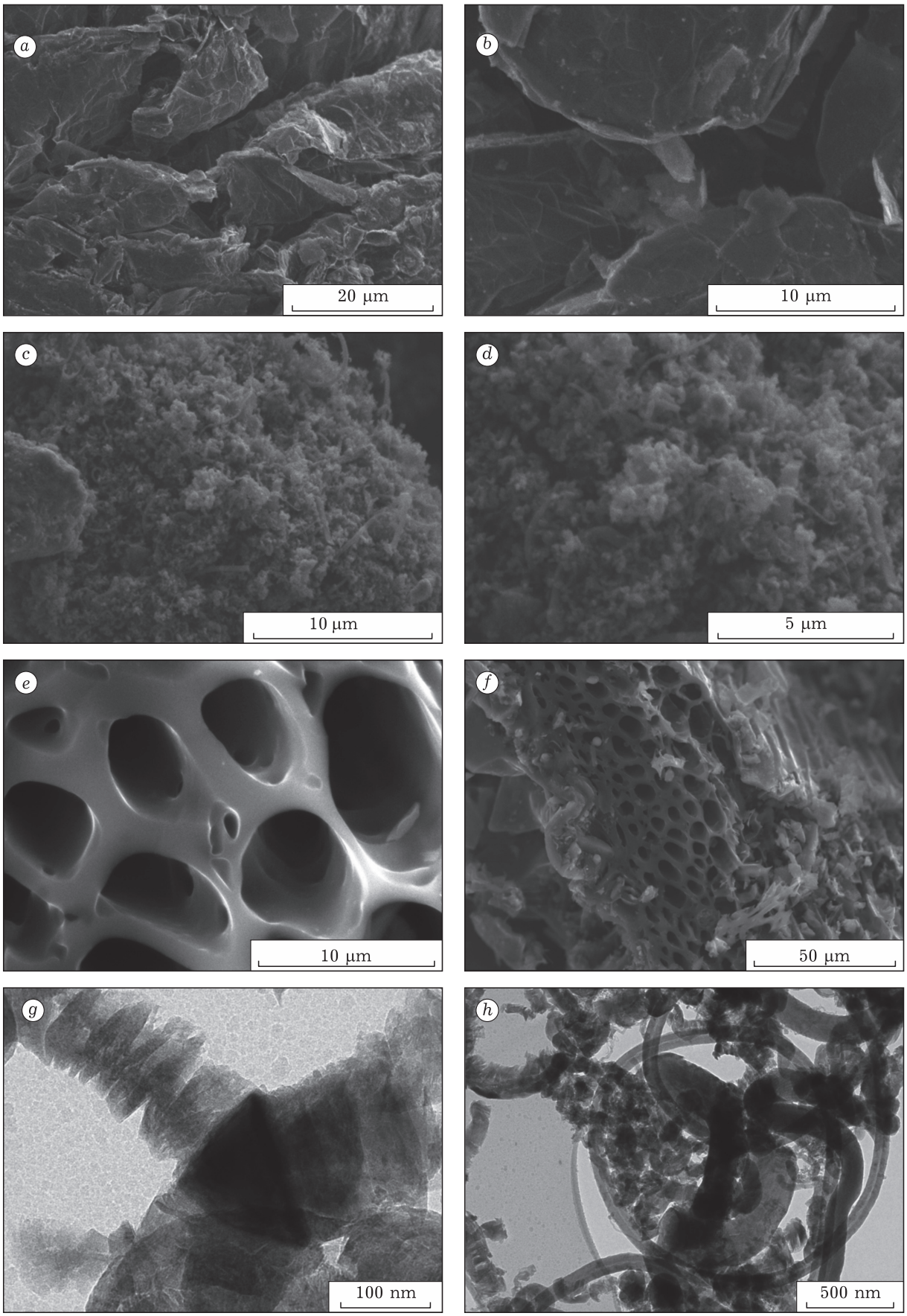

Fig. 1. SEM microphotographs of samples (*a*, *b* – TEG; *c*, *d* – CNFs; *e*, *f* – AC) and TEM microphotographs of CNFs (*g*, *h*).

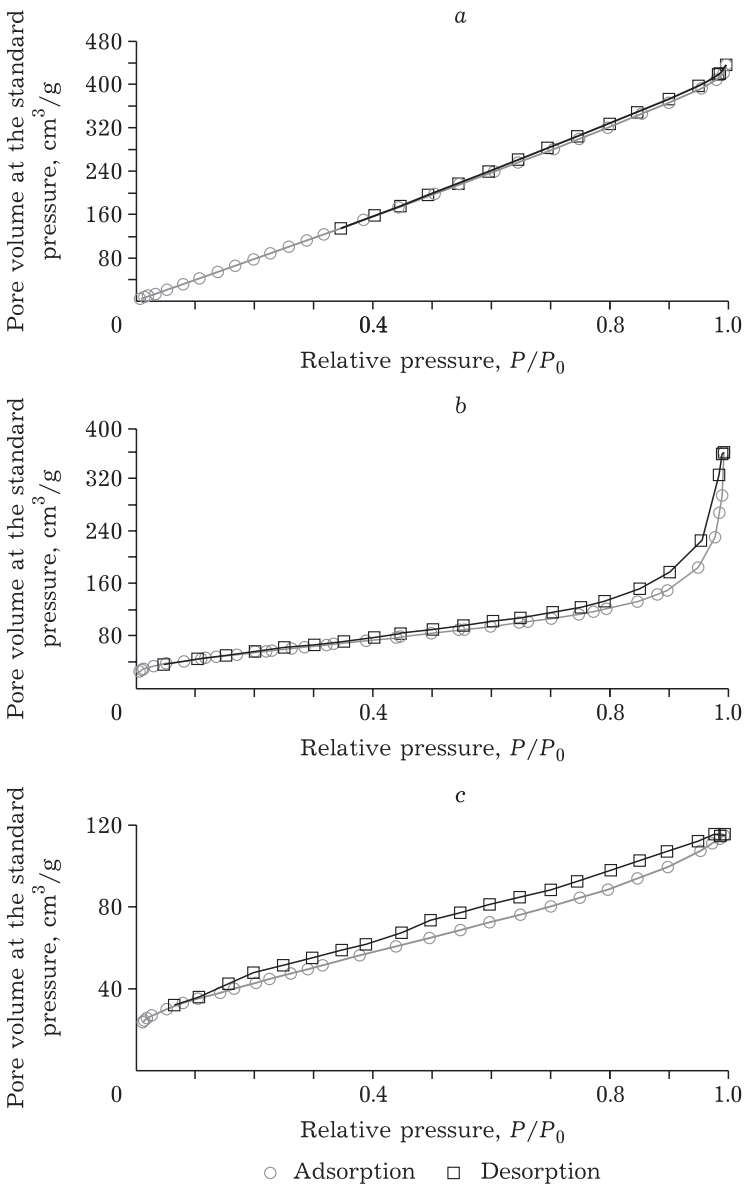

Fig. 2. Isotherms of adsorption and desorption for samples (*a* – TEG; *b* – CNFs; *c* – AC).

Voltammetric investigation

Results of the investigation of initial carbon materials by means of voltammetry are shown in Table 2. One can see that an increase in specific capacitance occurs with a decrease in the sweep rate. The maximal specific capacitance at the sweep rate of 2 mV/s is characteristic of AC with the smallest specific surface and average pore diameter. With an increase in sweep rate, the CNFs sample demonstrated larger specific capacitance (14 F/g). TEG sample, due to the high degree of graphitization and therefore very low content of the surface functional groups, demonstrated the smallest specific capacitance, though its porosity is much higher than that of other samples. Taking into account oxygen content in the samples, determined by means of EDS (TEG – 6.98 at. %; CNFs – 8.60 at. %; AC – 26.44 at. %), we may conclude that specific capacitance increases with an increase in oxygen content in the samples and exhibits not so substantial dependence on the specific surface area.

Investigation of modified carbon materials

Results of the investigation of TEG modified with nickel, having the composition 85 mass % Ni/15 mass % TEG, show that specific capacitance was 12 F/g, with a specific

TABLE 2

Texture characteristics and specific capacitance of initial carbon materials and their composites

Sample	A, m^2/g	A_m, m^2/g	d_{pore}, nm	V, cm^3/g	C_{sp}, F/g		
					Sweep rate, mV/s		
					10	5	2
Initial carbon materials							
CNF	248	116	9	0.535	14	23	38
TEG	759	455	4	0.817	3	7	12
AC	145	114	3	0.109	6	16	47
Composites							
20NiO/80TEG	42	6.0	8	0.078	–	–	116
20Ni/80CNF	151	5.4	13	0.505	–	–	21
85Ni/15TEG	11	10.5	27	0.071	–	–	14
20Ni/80AC	34	3.4	18	0.153	–	–	11
80Ni/20CNF	17	2.0	11	0.044	–	–	16

Notes. 1. Dash means that measurements were not carried out. 2. For designations, see Table 1. 3. Here and in Table 3: A – specific surface; A_m – specific surface of micropores; d_{pore} – average pore diameter; V – total pore volume; C_{sp} – specific capacitance.

surface area equal to 33 m^2/g. The average pore size is 31 nm. The second composite material under investigation had the composition 20 mass % NiO/80 mass % TEG. It was determined in the studies that its specific capacitance was 32 F/g, the specific surface area reached 79 m^2/g, and the pore size was 14 nm.

The low values of specific capacitance may be due to the large pore size and low specific surface area. At the same time, judging from the obtained values, the following dependence is observed: the specific capacitance increases with an increase in the specific surface area.

Modification of carbon materials with nickel particles resulted in obtaining composite materials with six compositions. Results of the studies of

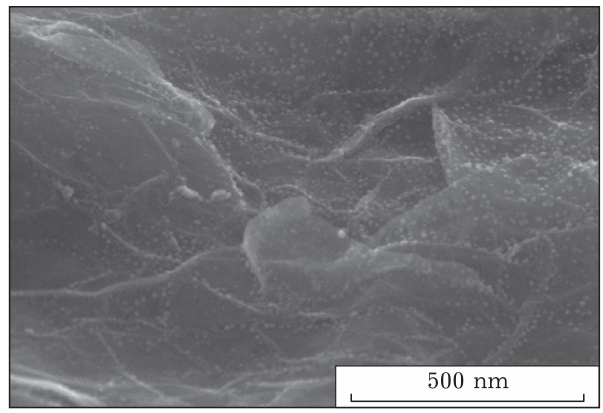

Fig. 3. SEM image of the distribution of nickel particles over the surface of TEG.

TABLE 3

Texture characteristics and specific capacitance of carbon materials after chemical treatment and joint mechanical activation

Sample	A, m^2/g	A_m, m^2/g	d_{pore}, nm	V, cm^3/g	C_{sp}, F/g (sweep rate 2 mV/s)
Carbon materials after chemical treatment					
CNF_{HNO_3}	146	36	9	0.319	33
TEG_{HNO_3}	87	33	5	0.107	27
AC_{HNO_3}	187	161	3	0.143	179
Composites after joint mechanical activation (MA)					
15TEG/85CNF (MA)	133	36	11	0.364	19
15TEG/85AC (MA)	155	115	4	0.164	90

Note. For designations, see Tables 1, 2.

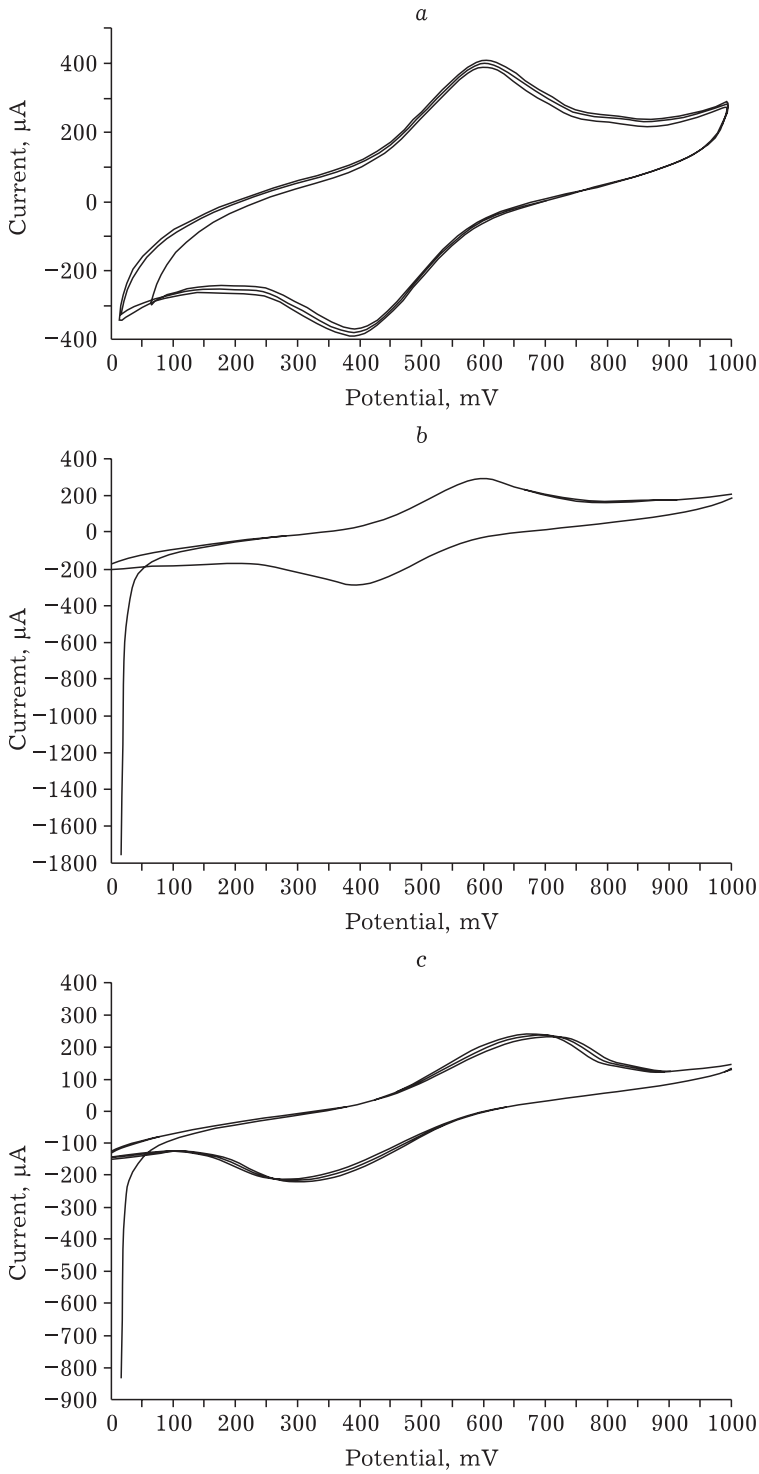

Fig. 4. The curves of cyclic voltammetry of carbon samples after chemical treatment, at the sweep rate of 2 mV/s: *a* – AC, *b* – CNFs, *c* – TEG.

texture and capacitance characteristics in composite materials are presented in Table 2.

One can see that the maximal specific capacitance corresponds to the composite with the composition 20 mass % NiO/80 mass % TEG. At the same time, the average pore size is 8 nm, and the specific surface area is 42 m^2/g. It should be stressed that specific capacity increases with a decrease in pore size. The uniformity of nickel particle deposition in the TEG matrix is confirmed by SEM microphotographs (Fig. 3). According to the data of EDS, the following element content was recorded within this

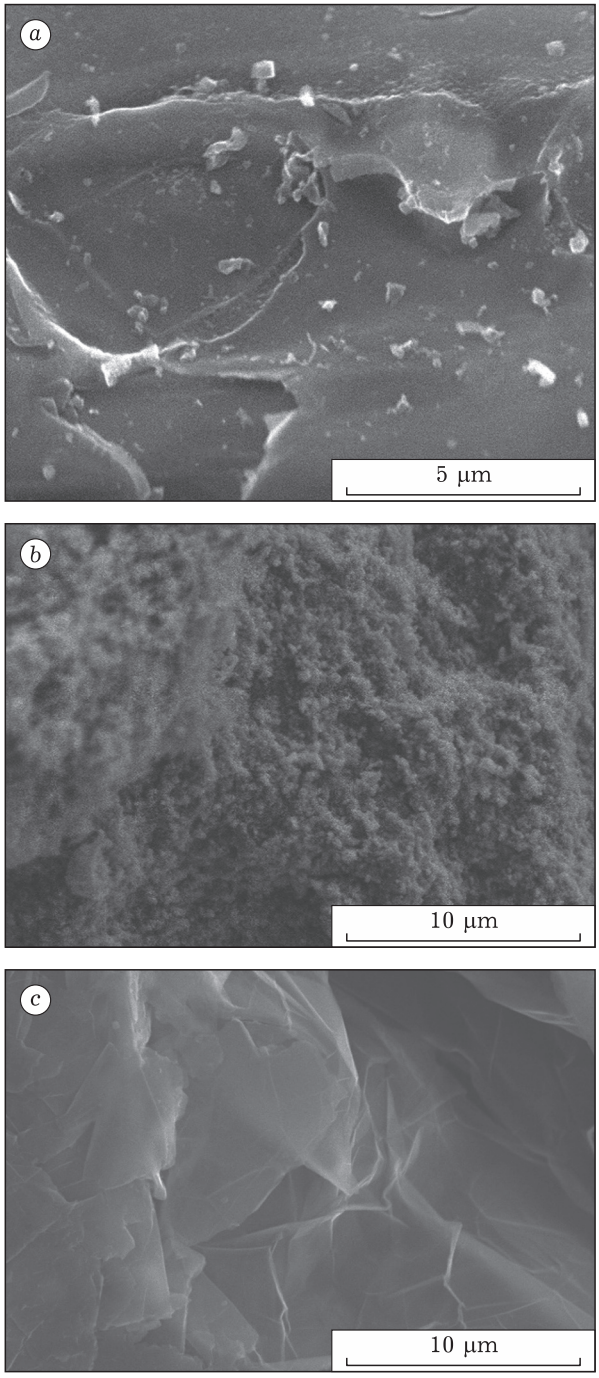

Fig. 5. SEM microphotographs of samples after treatment with HNO_3: a – AC; b – CNFs; c – TEG.

region: Ni – 4.35 at. %; C – 80.45 at. %, O – 14.0 at. %, S – 1.2 at. %.

At the next stage, we studied carbon materials after chemical treatment with nitric acid. Results are shown in Table 3.

Voltammetric curves of carbon samples after chemical treatment are shown in Fig. 4.

As far as texture characteristics are concerned, the specific surface area of CNFs after treatment decreased from 248 to 146 m^2/g. Thermally expanded graphite after treatment demonstrated a record low specific surface area (87 m^2/g), which may be connected with pore closing during filtration and sample washing. At the same time, an increase in the specific surface area from 145 to 187 m^2/g was detected for AC. The fraction of micropores in the sample somewhat increased (79 % before treatment and 86 % after it), while the average pore size did not change. The specific capacitance of TEG increased after treatment, while in the CNFs sample it slightly decreased (TEG – from 12 to 27 F/g; CNFs – from 38 to 33 F/g).

The best results were obtained for the sample of AC from rice husks: its specific capacitance increased from 47 to 179 F/g. It may be assumed that the highest specific capacitance is provided by the large specific surface, a substantial fraction of micropores, and small average pore size.

Investigation of the microstructure of chemically modified carbon materials by means of SEM revealed (Fig. 5) that after treatment, the surface of the materials became less defective, and the amount of admixtures in the material decreased.

At the final stage, we carried out the studies of carbon materials after mechanical activation. The compositions of composite materials and the results of the studies are presented in Table 3.

Results of the studies showed that the composite based on TEG and AC possesses the best capacitance and texture characteristics. We observed the above-mentioned dependence of specific capacitance on the number of micropores and on their average size. It was determined that with a decrease in the size and an increase in the number of micropores approximately by a factor of 3, specific capacitance increases approximately by a factor of 5.

CONCLUSION

Three types of carbon materials, such as thermally expanded graphite (TEG), carbon nanofibres (CNFs), and activated carbon (AC) from rice husks, were studied. Composite materials were synthesized through modification of the initial carbon materials with nickel oxide, with metal nickel particles, through treatment with nitric acid, and by means of mechanical activation.

Investigation of the texture characteristics confirmed the presence of developed specific

surface in the studied materials. The maximal specific surface area of initial materials reached 759 m^2/g, while for the obtained composites, it was 187 m^2/g.

Analysis of the results of specific capacitance determination showed that the maximal value of this parameter was characteristic of the materials possessing micro- and mesoporous structure, with an average pore size of 3–5 nm. The highest specific capacitance was determined for AC from rice husks: 57 F/g. In the case of modified materials, the largest specific capacitance was that of AC from rice husks, treated with nitric acid: 179 F/g. Among the materials with deposited nickel particles, the maximal specific capacitance (116 F/g) was exhibited by the composition 20 mass % NiO/80 mass % TEG.

The modification of the surface of carbon materials with nickel caused a decrease in the specific surface area, an increase in the average pore diameter; and in some cases, it caused an increase in the specific capacitance. The treatment with nitric acid and mechanical activation cause an increase in the fraction of micropores in the samples and the specific capacitance of the material, but in the case of TEG, a decrease in the specific surface area is observed.

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