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ELECTROPHYSICAL PROPERTIES OF CARBON MATERIAL BASED ON COAL OF "SARYADYR" DEPOSIT

Abstract. The article presents the results of heat treatment (carbonization) of grade G coal of the «Saryadyr» deposit («Pyatimetrovyy» layer) in the temperature range 250–550 °C at a heating rate of 10–15 °C/min and holding at 550 °C for 1, 2 and 3 hours. As a result of carbonization, carbon materials (CM) were obtained. Using the methods of thermogravimetric, energy dispersive X-ray spectroscopy, electron microscopy, we studied the technical, elemental composition, and surface morphology of the obtained products. The electrophysical characteristics of the CM were determined by measuring the electrical resistance (R), electric intensity (C), and dielectric constant (ε) of the samples in the temperature range 293–483 K. Based on the data obtained, the band gap (ΔE) of the samples was calculated. The carbon material obtained at 550 ° C for 3 hours has a dielectric constant of 740 thousand at 293 K and will increase to 1.1 billion at 453 K, i.e. up to 109 degrees to colossal values and is a very attractive material for microelectronics, i.e. at 453 K, ε CM is higher than the reference $BaTiO_3$ by about 540 thousand times.
Key words: carbon material (CM), chemical composition, electrophysical properties, electrical resistance, electrical intensity, dielectric constant.

Introduction. Recent decades have been marked by a surge of scientific activity in the development and study of carbon materials (CM). This is reflected in the targeted synthesis of allotropic forms of carbon (carbohydrates, fullerenes, nanotubes, compasses, etc.), as well as in the creation of a wide range of porous materials in a series of mixed (transitional) forms of carbon, which are of practical interest as adsorbents, catalysts, and carriers for catalysts, substrates in new generation current sources (lithium-ion batteries, supercapacitors, ionistors and fuel cells) etc. [1-7].

Promising devices for the accumulation and storage of electrical energy, combining both high energy intensity and relatively high output power, are supercapacitors (SC) and capacitive deionization systems capable of reversibly accumulating charge on the surface of electrode material [8-11]. In [12-14], based on the porous - carbon material of carbon nanotubes, the production of materials with pore sizes up to angstroms for flexible and printing devices with a short response time, as well as nanoparticles of transition metal oxides and nitrides for pseudo-capacitors, which are the latest achievements, was developed and organized in the field of supercapacitors. Natural materials, such as coconut shells, wood, resins, coals, or synthetic materials, such as polymers, are commonly used as precursors. Carbon materials used in capacitors are usually pretreated to remove moisture and most of the functional groups present on the carbon surface to increase stability during cycling, since they can cause wilting of the capacitance and aging of the capacitor [15].

Electrophysical properties is as the main indicator of the carbon material used in electrothermal processes [16], as well as for the manufacture of superconducting materials, capacitors and fuel cells from them. The aim of this work is to study the electrophysical properties of a carbon material based on coal from the Saryadyr deposit (Pyatimetrovyy layer) (Kazakhstan). Coal belongs to high-ash, gas grade "G".

Research methodology. Samples of carbon material were obtained at the "Institute of Coal Chemistry and Technology" LLP (Nur-Sultan) by heat treatment in a tube furnace in the temperature range of 250-550 °C at a heating rate of 10-15 °C/min and holding at 550 °C for 1, 2 and 3 hours.

The elemental composition, structure, and dimensionality of the samples were studied by energy dispersive X-ray spectroscopy on an SEM instrument *(Quanta 3D 200i)* with an attachment for energy dispersive analysis from EDAX. The energy of the exciting electron beam in the analysis was 15 keV.

The heat of combustion of coal and the resulting products was determined by the calorimetric method on the device "Calorimeter V08MA K"

Results and its discussion. The results of the elemental analysis, presented in table 1, show that after heat treatment of coal, most of the heteroatoms (oxygen, hydrogen, sulfur, nitrogen) are removed in the form of gaseous products. Accordingly, the carbon concentration decreases from 82.98 to 67.80 wt. % and the structure of flat aromatic rings developing, uniting into basic structural units or elementary graphite crystallites, develops.

Table 1 – The chemical composition of the carbon material from coal of the «Saryadyr» deposit («Pyatimetrovyy» layer)

Indicators	Content			
	Initial coal	CM, 1 hour exposure	CM, 2 hours exposure	CM, 3 hours exposure
Humidity, W^a, %	1.68	1.36	1.64	2.24
Ash content, A^d, %	37.33	23.72	26.13	27.92
Volatility, V^{daf}, %	26.35	14.11	10.57	8.48
Sulfur per working mass, S^{daf}, %	0.59	0.32	0.27	0.28
Carbon content, C^{daf}, %	82.98	67.97	68.17	67.80
Hydrogen content, H^{daf}, %	5.59	3.07	1.78	0.68
Oxygen content, O^{daf}, %	7.88	3.58	2.45	2.09
Nitrogen content, N^d, %	1.38	1.34	1.20	1.23
Aluminum content, Al, %	2.30	1.90	2.12	2.36
Silicon content, Si, %	5.48	4.50	4.12	4.03
Calorific value, Q^r_i, kcal/kg	5215	6271	5987	5689

The data from table 1 show that a noticeable effect of the exposure time of coal during heat treatment affects the calorific value of the obtained product [17]. At the shortest time (t = 1 hour), the calorific value is the highest and amounts to 6271 kcal/kg, which significantly exceeds the same parameter of the initial coal (5215 kcal/kg). With a further increase in the exposure time, this parameter decreases.

Figures 1–2 show micrographs of samples of the initial coal and carbon materials (with an increase of 5,000 and 50,000 times).

When analyzing the surface morphology of the samples, it was found that the cleaved surface is represented by heterogeneity of the structure and has dense formations with strong agglomerates. Despite the presence of an increased content of the mineral component, the structure is characterized by flocculent inclusions in the carbon matrix; it is also seen that there are elevations and depressions on the surface. This is due to the heterogeneity of the composition and the natural origin of coal.

The results of the analysis of micrographs show that after heat treatment the surface structure changes with smaller particle sizes (up to ~ 170 nm). In CM products, crystallites are arranged irregularly, the gaps between them are filled (or blocked) with amorphous carbon, which is formed upon decomposition of resinous substances. As a result of carbonization, volatile (moisture and partially resin) substances are released from raw materials. At the same time, primary macroporous structures with a diameter of 2 to 30 microns are formed in it.

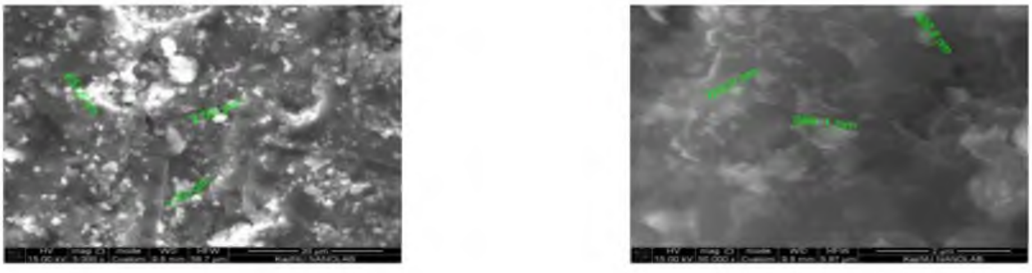
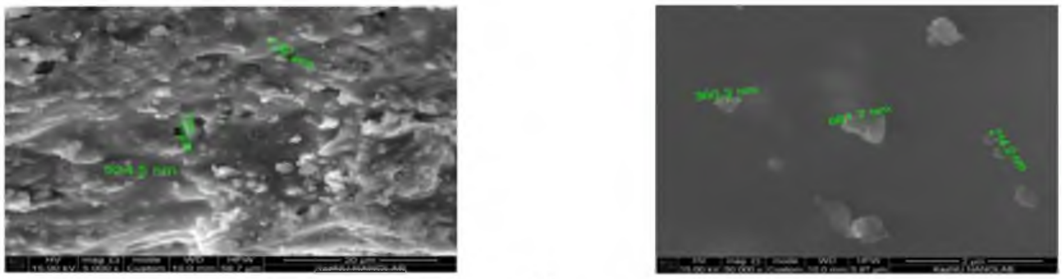


Figure 1 – Electron microscopic images of the Initial coal of the "Saryadyr deposit"



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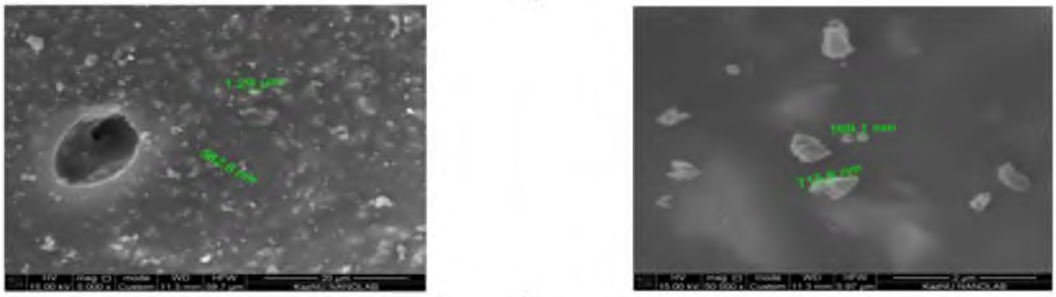

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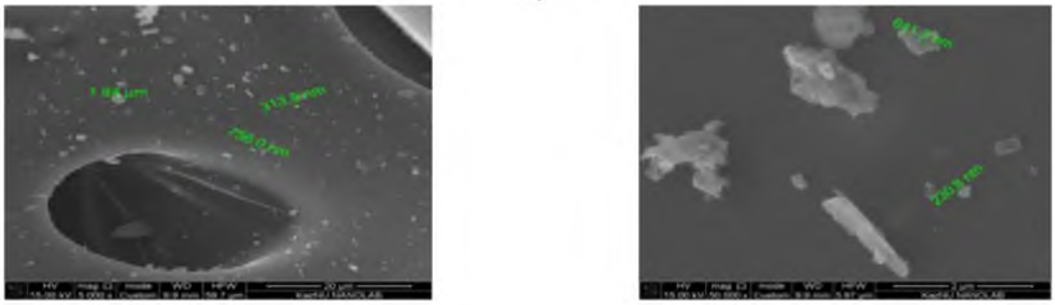

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Figure 2 – Electron-microscopic images of CM from coal of the Saryadyr deposit:
a) 1 hour exposure, b) 2 hours exposure, c) 3 hours exposure

An analysis of micrographs (figure 2) at various magnifications indicates that the surface of the CM is represented by an inhomogeneous structure with local clusters of cluster-like (dendritic) and isometric shapes, overlays (secondary textures) are interspersed and streaked. The figures show that finely dispersed carbon nanoparticles with diameters from ~100 to 700 nm were formed on the surface of the sample, this may be due to the fact that, as a result of carbonization, the reactive radicals forming interact with each other with the formation of new substances. The most likely cause of the appearance of nanoparticles on the surface layer is synthesis from the gas phase. The nucleation and growth of ordered carbon during the heat treatment of coal can occur through self-organization of carbon nanoparticles without the participation of the mesophase. Measurements of the electrophysical properties were carried out according to the procedures [18,19].

The study of electrophysical properties (dielectric constant and electrical resistance) was carried out by measuring the electric capacity of the samples on a LCR-800 serial device (Taiwan) at an operating frequency of 1 kHz continuously in dry air in thermostatic mode with a holding time at each fixed temperature.

Plane-parallel samples were preliminarily made in the form of disks with a diameter of 10 mm and a thickness of 5–6 mm with a binder additive (~1.5%). Pressing was carried out under a pressure of 20 kg / cm^2. The resulting disks were fired in a silica furnace at 200 °C for 6 hours. Next, they were thoroughly double-sided grinding.

The dielectric constant was determined from the electric capacity of the sample at known values of the thickness of the sample and the surface area of the electrodes. To obtain the relationship between the electric induction *D* and the electric field *E* was used a Sawyer-Tower circuit. Visual observation of the *D* (*E*-hysteresis loop) was carried out on a *C1-83* oscilloscope with a voltage divider consisting of a resistance of 6 mOhm and 700 kOhm, and a reference capacitor of 0.15 μF. The frequency of the generator is 300 Hz. In all temperature studies, the samples were placed in a furnace, the temperature was measured with a chromel-alumel thermocouple connected to a *B2-34* voltmeter with an error of ±0.1 mV. The rate of temperature change is ~5 K / min. The value of the dielectric constant at each temperature was determined by the formula: $\varepsilon = C/C_0$, where C_0 is the capacitance of the capacitor without the test substance (air).

Below are the results of measurements of the electrophysical characteristics of carbon materials from coal of the Saryadyr deposit.

Table 2 – Electrical properties of CM based on Saryadyr coal (Pyatimetrovyy layer) (τ = 1 hour) (*C* - capacity, *R* - electrical resistance, *ε* - dielectric constant)

T, K	C, nF	R, Ohm	ε	lgε	lgR
293	0.24402	2220000	1335	3.13	6.35
303	0.26692	2101000	1460	3.16	6.32
313	0.33632	1860000	1840	3.26	6.27
323	0.43216	1622000	2364	3.37	6.21
333	0.48451	1535000	2650	3.42	6.19
343	0.50585	1508000	2767	3.44	6.18
353	0.51147	1483000	2798	3.45	6.17
363	0.50135	1489000	2742	3.44	6.17
373	0.53663	1458000	2935	3.47	6.16
383	0.61584	1315000	3369	3.53	6.12
393	1.0248	1025000	5605	3.75	6.01
403	1.8592	716400	10169	4.01	5.86
413	3.3245	504000	18184	4.26	5.70
423	4.7521	387200	25993	4.41	5.59
433	6.5738	317000	35957	4.56	5.50
443	8.5247	276200	46628	4.67	5.44
453	11.202	245900	61273	4.79	5.39
463	13.877	230500	75904	4.88	5.36
473	17.703	219700	96837	4.99	5.34
483	21.427	211300	117201	5.07	5.32

CM obtained at 550 °C for 1 hour, in the entire studied temperature range exhibits semiconductor conductivity. The dielectric constant at the indicated ΔT is also low.

The calculation of the band gap was determined by the formula 1:

$$\Delta E = \frac{2kT_1T_2}{0.43(T_2 - T_1)} \lg \frac{R_1}{R_2}, \quad (1)$$

where *k* - is the Boltzmann constant; for calculating ΔE, it is $8.6173303 \cdot 10^{-5}$ eV·K^{-1}.

The calculation of ΔE was performed in the range 293–483 K. At a temperature of 293 K, the electrical resistance is 6.35, and at 483 K, *log* R = 3.32.

$$\Delta E = \frac{2 \times 0{,}000086173 \times 293 \times 483}{0.43(483 - 293)} \lg \frac{6.35}{5.32} = \frac{24.3902}{81.7} \times 1.1936 = 0.36 eV$$

This carbon material can be attributed to narrow-gap semiconductors.

Table 3 presents the dependence of electrical resistance (*R*), electric capacity (*C*) and dielectric constant (*ε*) on temperature (CM based on Saryadyr coal (Pyatimetrovyy layer) (τ = 2 hours).

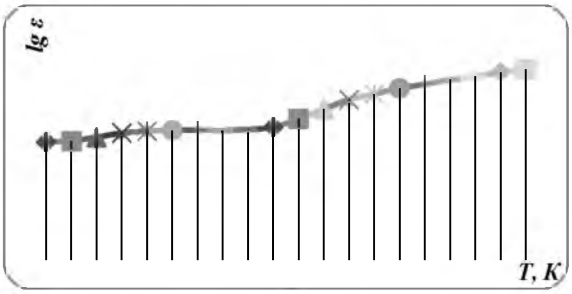
As can be seen from the data in the table, a CM with up to 383 K exhibits a low dielectric constant, then at 463 K it exhibits a relatively high dielectric constant (1.89 million). In the temperature range under study, the CM exhibits semiconductor conductivity; there are small temperature jumps at 333–373 K, which can be neglected. Calculation of the band gap, at T = 293 K, *log R* = 6.62; *T* = 483 K, *log R* = 4.85.

$$\Delta E = \frac{2 \times 0.000086173 \times 293 \times 483}{0.43(483 - 293)} \lg \frac{6.62}{4.85} = \frac{24.3902}{81.7} \times 1.3649 = 0.41 eV$$

Table 3 – Electrical properties of CM based on Saryadyr coal (Pyatimetrovyy layer) (τ= 2 hours)
(*C* - capacity, *R* - electrical resistance, ε - dielectric constant)

T, K	*C*, nF	*R*, Ohm	*ε*	lg*ε*	lg*R*
293	0.05706	4160000	452	2.65	6.62
303	0.03489	4512000	276	2.44	6.65
313	0.03116	4173000	247	2.39	6.62
323	0.0299	4417000	237	2.37	6.65
333	0.02452	4645000	194	2.29	6.67
343	0.02557	4403000	202	2.31	6.64
353	0.05134	3217000	406	2.61	6.51
363	0.07499	3481000	594	2.77	6.54
373	0.04192	4031000	332	2.52	6.61
383	1.0483	730600	8299	3.92	5.86
393	6.2496	342500	49477	4.69	5.53
403	11.135	255300	88154	4.95	5.41
413	19.302	195500	152810	5.18	5.29
423	32.592	162100	258024	5.41	5.21
433	69.704	111500	551833	5.74	5.05
443	113.14	86600	895707	5.95	4.94
453	194.56	70440	1540293	6.19	4.85
463	239.31	65340	1894570	6.28	4.82
473	60.347	104200	477755	5.68	5.02
483	133.0	71250	1052935	6.02	4.85

This CM can also be attributed to narrow-gap semiconductors. Figures 3 and 4 below show the temperature dependence of the samples in the range 293–483 K.



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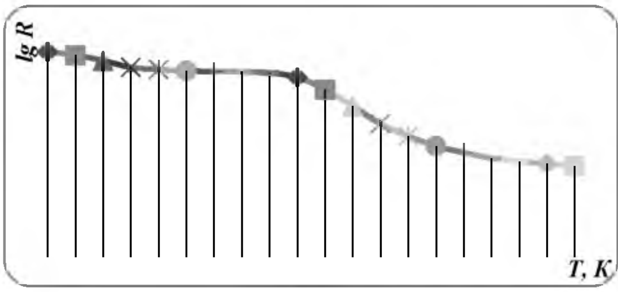
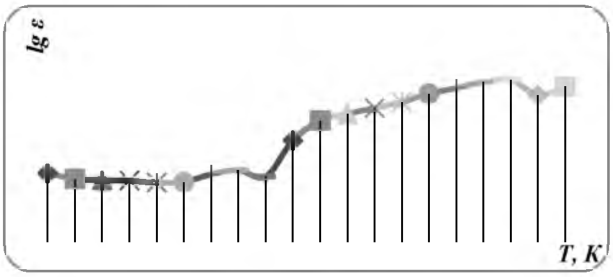


b)

Figure 3 – Temperature dependence of CM based on coal from the Saryadyr deposit
(τ = 1 hour) in the range 293–483 K: a) dielectric constant; b) electrical resistance



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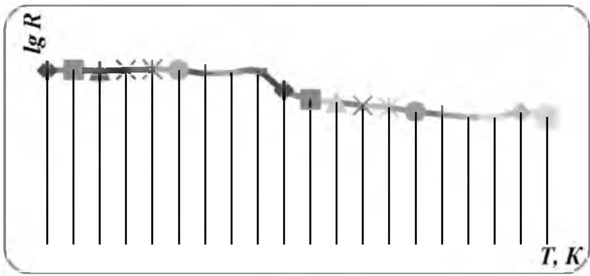


b)

Figure 4 – Temperature dependence of CM based on coal from the Saryadyr deposit
(τ = 2 hours) in the range 293–483 K: a) dielectric constant; b) electrical resistance

Table 4 below shows the results of measuring the electrophysical characteristics of CM based on coal from the Saryadyr deposit, at a holding temperature of 3 hours.

Table 4 – Electrical properties of CM based on Saryadyr (Pyatimetrovyy layer) (τ) = 3 hours) (*C* - capacity, *R* - electrical resistance, ε - dielectric constant)

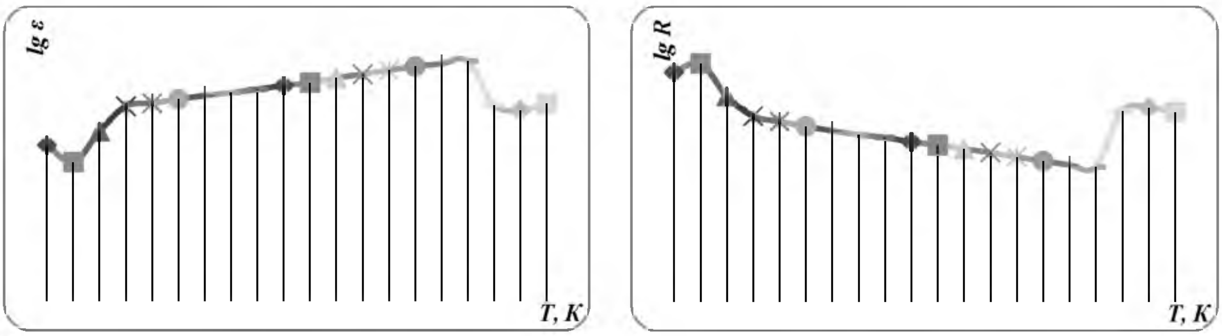
T, K	*C*, nF	*R*, Ohm	*ε*	lg*ε*	lg*R*
293	65.899	148600	739879	5.87	5.17
303	15.198	234800	170635	5.23	5.37
313	217.17	42510	2438268	6.39	4.63
323	1927.1	15120	21636446	7.34	4.18
333	2529.8	11450	28403239	7.45	4.06
343	3630.1	8885	40756817	7.61	3.95
353	4884.2	7061	54837180	7.74	3.85
363	6286.9	5780	70585944	7.85	3.76
373	8504.2	4963	95480600	7.98	3.70
383	11653	3991	130833639	8.12	3.60
393	15050	3385	168973335	8.23	3.53
403	22778	2764	255739177	8.41	3.44
413	31371	2290	352216776	8.55	3.36
423	44725	1833	502148332	8.70	3.26
433	61763	1469	693441866	8.84	3.17
443	77146	1212	866153946	8.94	3.08
453	97302	1103	1092454712	9.04	3.04
463	2156.9	20030	24216517	7.38	4.30
473	1383.4	23290	15532074	7.19	4.37
483	2454.3	18670	27555565	7.44	4.27

As can be seen from the data obtained, the CM in the interval 293–453 K exhibits semiconductor properties, at ΔT = 453–473 K - metal and at ΔT = 473–483 K - the semiconductor nature of conductivity.

Figure 5 below shows the temperature dependence of the CM Saryadyr (Pyatimetrovyy layer) (τ = 3 hours) in the range 293–453 K.

The calculation of ΔE was performed in the range of 293–453 K. At a temperature of 293 K, the electrical resistance is 5.17, and at 453 K, *log R* = 3.04.

$$\Delta E = \frac{2\times 0{,}000086173\times 293\times 453}{0.43(453-293)}\lg\frac{5.17}{3.04} = \frac{22.8753}{68.8}\times 1.7007 = 0.57eV$$



a) b)

Figure 5 – Temperature dependence of UM based on coal from the Saryadyr deposit (τ = 3 hours) in the range 293–483 K: a) dielectric constant; b) electrical resistance

The obtained carbon material in the range 293–453 K exhibits semiconductor conductivity characteristic of narrow-gap semiconductors. This CM have large values of dielectric constant, which from 740 thousand at 293 K reaches up to 1.1 billion at 453 K, i.e. up to 10^9 degrees to a colossal value and is very attractive as a promising material for microelectronics, i.e. at 453 K, ε of CM exceeds the reference $BaTiO_3$ by about 540 thousand times.

This is explained by a phase transition and the formation of carbon nanoparticles ranging in size from 100–700 nm on the surface of the sample, which is evidenced by electron microscopic images (3 hours exposure) (figure 2).

Conclusion. Thus, a chemical analysis of carbon materials from coal from the Saryadyr deposit (Pyatimetrovy layer) was carried out in the work. In the temperature range 293–483 K, their electrophysical characteristics C, R, ε were determined. The analysis showed that the obtained carbon material from Saryadyr coal is promising as a capacitive material, fuel cell and semiconductor, as well as for the manufacture of electrodes.

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«САРЫАДЫР» КЕН ОРНЫНЫҢ КӨМІРІ АРҚЫЛЫ АЛЫНҒАН КӨМІРТЕКТІ МАТЕРИАЛДЫҢ ЭЛЕКТРОФИЗИКАЛЫҚ ҚАСИЕТТЕРІ

Аннотация. Мақалада «Сарыадыр» («Пятиметровый» қабаты) кен орнындағы Г маркалы көмірді 250–550 °С температурада 10–15 °С/мин жалдамдықта және 550 °С-та 1, 2 және 3 сағат көлеміде термиялық өңдеудің (карбонизация) нәтижелері келтірілген. Карбонизация нәтижесінде көміртекті материалдар (КМ) алынды. Термогравиметриялық, энергодисперсиялық рентгендік спектроскопия, электронды микроскопия әдістерін қолдана отырып, алынған өнімнің техникалық, элементтік құрамы мен беттік морфологиясы зерттелді. КМ-дың электрофизикалық сипаттамалары 293–483 К температура диапазонындағы үлгілердің электрлік кедергісін (R), электр сыйымдылығы (С) және диэлектриктік өткізгіштігін (ε) өлшеу арқылы анықталды. Алынған мәліметтер негізінде үлгілердің тыйым салынған аймақ ені (ΔЕ) есептелінді. 3 сағат ішінде 550 °С температурада алынған көміртегі материал үлкен диэлектрлік тұрақты мәнге ие, оның мәні 293 К-де 740 мыннан 453 К кезінде 1,1 млрд.-қа дейін жетеді, яғни 10^9 дейінгі үлкен мәнге ие және микроэлектроника үшін перспективті материал болып табылады, яғни 453 К кезінде диэлектрилік өткізгіштігі ε эталон $BaTiO_3$-тен шамамен 540 мың есе асады. Үлгілердің элементтік құрамы, құрылымы және өлшемі SEM (Quanta 3D 200i) құралында энергия дисперсиялық талдау EDAX көмегімен энергиялық дисперсиялық рентгендік спектроскопия көмегімен зерттелді. Талдаудағы электронды сәуленің энергиясы 15 кэВ. Элементтік талдау нәтижелері көмірді термиялық өңдеуден кейін гетероатомдардың көп бөлігі (оттегі, сутегі, күкірт, азот) газ тәрізді өнімдер түрінде бөлінеді. Тиісінше, көміртегі концентрациясы 82,98-ден 67.80 мас. %-ға дейін төмендейді және қарапайым құрылымдық блоктарға немесе қарапайым графит кристаллиттеріне біріктірілген ароматты сақиналардың құрылымы дамиды. Микросуреттерді талдау нәтижелері термоөңдеуден кейін беттік құрылымында кіші бөлшектер (~ 170 нм дейін) пайда болғанын көрсетеді. КМ өнімдерінде кристаллиттер тұрақты емес орналасады, олардың арасындағы саңылаулар шайырлы заттардың ыдырауы кезінде пайда болатын аморфты көміртегімен толтырылған. Карбонизация нәтижесінде ұшқыш заттар шикізаттан бөлініп, диаметрі 2-ден 30 мкм-ге дейінгі бастапқы макропорлы құрылымдар пайда болады. Электрлік қасиеттерді (электр өткізгіштік пен электр кедергісі) зерттеу LCR-800 сериялы қондырғысындағы (Тайвань) үлгілердің электр сыйымдылығын 1 кГц тұрақты жиіліктегі құрғақ ауада термостатикалық режимде әр белгіленген температурада ұстап тұру уақытымен өлшеу арқылы жүргізілді. 550 ^{0}С температурада 1 сағатта алынған КМ, зерттелген температура диапазонында жартылай өткізгіштік қасиет көрсетеді. Көрсетілген ΔТ диэлектрлік константаның мәні де төмен. Бұл көміртекті материалды тар аймақты жартылай өткізгіштерге жатқызуға болады. 550 ^{0}С температурада 2 сағат ішінде 383 К дейін алынған КМ төмен диэлектрлік тұрақты, ал 463 К кезінде салыстырмалы түрде жоғары диэлектрлік тұрақты (1,89 млн) көрсетеді. Зерттеліп жатқан температура диапазонында КМ жартылай өткізгіштік қасетке ие, 333–373 К температурада кішігірім ауытқулар байқалады, оларды ескермеуге болады. T = 293 K, lg R = 6.62 T = 483 K, lgR = 4.85 кезінде тыйым салынған аймақ ені есептелінді (ΔЕ). Бұл КМ-ды жартылай өткізгіштерге де жатқызуға болады. 3 сағат ұстау температурасында алынған 293-453 К диапазонында жартылай өткізгіштік қасиеттері бар, ΔТ = 453–473 К - металлдық және ΔТ = 473–483 К кезінде - жартылай өткізгіштік. ΔЕ есептеу 293–453 К аралығында жүргізілді, 293 К температурада электр кедергісі 5,17, ал 453 К температурада R = 3.04. Алынған көміртегі материалдар 293-453 К диапазонында жартылай өткізгіштікке ие. Бұл КМ диэлектрлік өткізгіштік мәні өте жоғары, олар 293 К-де 740 мыннан 453 К 1,1 миллиардқа жетеді, яғни 10^9 дәрежесіне дейінгі үлкен мәнге ие және микроэлектроника үшін перспективті материал болып табылады. Мұны фазаның ауысуымен және үлгінің бетінде мөлшері 100-700 нм-ге дейін болатын көміртекті нанобөлшектердің түзілуімен түсіндіріледі, электронды микроскопиялық суреттермен дәлелденеді. Сонымен, жұмыс барысында «Сарыадыр» кен орны көмірінен («Пятиметровый» қатпары) алынған көміртекті материалға химиялық талдау жүргізілді. 293–483 К температуралық диапазонда олардың электрофизикалық сипаттамалары C, R, ε анықталды. Талдау нәтижесі Сарыадыр көмірінен алынған көміртекті материал сыйымдылық материал ретінде, отын элементі және жартылай өткізгіш ретінде, сондай-ақ электродтар өндірісі үшін перспективті материал екенін көрсетті.

Түйін сөздер: көміртекті материал (КМ), химиялық құрамы, электрофизикалық қасиеттер, электркедергі, электрсыйымдылық, диэлектриктік өткізгіштік.

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ЭЛЕКТРОФИЗИЧЕСКИЕ СВОЙСТВА УГЛЕРОДНОГО МАТЕРИАЛА НА ОСНОВЕ УГЛЯ МЕСТОРОЖДЕНИЯ «САРЫАДЫР»

Аннотация. В статье приведены результаты термической обработки (карбонизации) угля марки Г месторождения «Сарыадыр» (пласт «Пятиметровый») в интервале температур 250–550 °С при скорости нагрева 10–15 °С/мин и с выдержкой при 550 °С в течение 1, 2 и 3 часов. В результате карбонизации получены углеродные материалы (УМ). Методами термогравиметрического, энергодисперсионной рентгеновской спектроскопии, электронной микроскопии изучены технический, элементный состав, морфология поверхности полученных продуктов. Определены электрофизические характеристики УМ путем измерения электросопротивления (R), электроемкости (C) и диэлектрической проницаемости (ε) образцов в интервале температур 293–483 K. На основании полученных данных рассчитаны ширина запрещенной зоны (ΔE) образцов. Углеродный материал, полученный при 550 °С в течение 3 часов, обладает большими значениями диэлектрической проницаемости, которая от 740 тыс. при 293 К достигает до 1.1 млрд при 453 К до 10^9 степени до колоссального значения и является очень привлекательным в качестве перспективного материала для микроэлектроники, при 453 К *ε* УМ превышает эталонного $BaTiO_3$ примерно в 540 тыс. раз. Исследование элементного состава, структуры и размерности образцов проводили методом энергодисперсионной рентгеновской спектроскопии на приборе *SEM* (*Quanta 3D 200i*) с приставкой для энергодисперсионного анализа от *EDAX*. Энергия возбуждающего пучка электронов при анализе была 15 кэВ. Результаты проведенного элементного анализа показали, что большая часть гетероатомов (кислород, водород, сера, азот) удаляется в виде газообразных продуктов. Соответственно уменьшается концентрация углерода с 82,98 до 67,80 мас. % и развивается структура плоских ароматических колец, объединяющихся в основные структурные единицы или элементарные графитовые кристаллиты. Результаты анализа микроснимков показывают, что после термической обработки поверхностная структура изменяется с меньшими размерами частиц (до ~170 нм). В продуктах УМ кристаллиты расположены нерегулярно, промежутки между ними заполнены (или блокированы) аморфным углеродом, который образуется при разложении смолистых веществ. Как известно, в результате карбонизации из сырья выделяются летучие (влага и частично смолы) вещества. Одновременно в нем образуются первичные макропористые структуры диаметром от 2 до 30 мкм. Исследование электрофизических свойств (диэлектрической проницаемости и электрического сопротивления) проводилось путем измерения электроемкости образцов на серийном приборе LCR-800 при рабочей частоте 1кГц непрерывно в сухом воздухе в термостатном режиме со временем выдержки при каждой фиксированной температуре. УМ, полученный при 550 °С в течение 1 часа, во всем исследуемом интервале температуры проявляет полупроводниковую проводимость. Диэлектрическая проницаемость также при указанном ΔT невысокая. Данный углеродный материал можно отнести к узкозонным полупроводникам. УМ, полученный при 550 °С в течение 2 часов, до 383 К проявляет низкую диэлектрическую проницаемость, далее при 463 К он проявляет относительно высокую диэлектрическую проницаемость (1.89 млн.). УМ проявляет в исследуемом интервале температуры полупроводниковую проводимость, есть небольшие скачки температуры при 333−373 К, которыми можно пренебречь. Рассчитана ширина запрещенной зоны при T = 293 K, lg R=6,62; T = 483 K, lg R=4,85. Данный УМ можно также отнести к узкозонным полупроводникам. УМ, полученный при температуре выдержки 3 часа в интервале 293−453 К, проявляет полупроводниковые свойства, при ΔT = 453−473 К – металлическую и при ΔT = 473−483 К – полупроводниковый характер проводимости. Расчет ΔE произведен в интервале 293−453 К. При температуре 293 К электросопротивление составляет 5.17, а при 453 K lg R = 3.04. Полученный углеродный материал в интервале 293−453 К проявляет полупроводниковую проводимость, характерную узкозонным полупроводникам. Данный УМ обладает большими значениями диэлектрической проницаемости, которая от 740 тыс. при 293 К достигает до 1.1 млрд при 453 К, т.е. до 10^9 степени до колоссального значения и является очень привлекательным в качестве перспективного материала для микроэлектроники. Это объясняется фазовым переходом и образованием углеродных наночастиц размером от 100–700 нм на поверхности образца, о чем свидетельствуют электронно-микроскопические снимки. Таким образом, в работе проведен химический анализ углеродных материалов из угля месторождения «Сарыадыр» (пласт «Пятиметровый»). В интервале температур 293−483 К определены их электрофизические характеристики C, R, ε. Проведенный анализ показал, что полученный углеродный материал из Сарыадырского угля представляется перспективным в качестве емкостного материала, топливного элемента и полупроводника, а также для изготовления электродов.

Ключевые слова: углеродный материал (УМ), химический состав, электрофизические свойства, электросопротивление, электроемкость, диэлектрическая проницаемость.

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REFERENCES

[1] Abramov A.A. (2003) Processing, enrichment and integrated use of solid minerals. M.: MSTU. T. I. 470 p. (in Russ.).

[2] Ermagambet B.T., Kasenov B.K., Nurgaliev N.U., Nabiev M.A., Kasenova Zh.M., Kazankapova M.K., Zikirina A.M. (2018) Electrophysical properties and heat capacity of shale from the Kendyrlyk deposit, Solid Fuel Chemistry, 52 (2): 11-14. DOI 10.3103/S0361521918020039 (in Eng.).

[3] Rybak L.V., Alekseev G.F., Burtsev S.V., Efimov V.I., Korchagina T.V., Shapranko D.S. (2018) [Coal – Russian Coal Journal] 7: 62. DOI: http://dx.doi.org/10.18796/0041-5790-2018-7-62-67 (in Russ.).

[4] Hoang V.C., Hassan M., Gomes V.G. (2018) Coal derived carbon nanomaterials–recent advances in synthesis and applications, Applied Materials Today, 12: 342-358. DOI: https://doi.org/10.1016/j.apmt.2018.06.007 (in Eng.).

[5] Moothi K., Iyuke S.E., Meyyappan M., Falcon R. (2012) Coal as a carbon source for carbon nanotube synthesis, Carbon, 50 (8): 2679-2690. https://doi.org/10.1016/j.carbon.2012.02.048 (in Eng.).

[6] Kalybay A.A., Teltayev B.B., Abzhaliyev A.K. (2019) Nanoenergetic materials and low-carbon nanoenergetics: regularities, technology and raw products // News of the National Academy of Sciences of the Republic of Kazakhstan. Series of Geology and Technical sciences. 2019. Vol. 3, 435. P. 189-202. ISSN 2518-170X (Online), ISSN 2224-5278 (Print). https://doi.org/10.32014/2019.2518-170X.85 (in Eng.).

[7] Shabanova T.A., Glagolev V.A. (2019) Graphen and natural formations, News of the National Academy of Sciences of the Republic of Kazakhstan. Series of Geology and Technical sciences. 2019. Vol. 3, 435. P. 80-84. ISSN 2518-170X (Online), ISSN 2224-5278 (Print). https://doi.org/10.32014/2019.2518-170X.71 (in Eng.).

[8] Uvarov N.F. (2018) Mesoporous carbon materials and their use in capacitive electrochemical devices. Materials of the V International Russian-Kazakhstan Scientific and Practical Conference "Chemical Technologies of Functional Materials". P. 3-6 (in Russ.).

[9] Simon P., Gogotsi Y. (2008) Materials for electrochemical capacitors, Nature materials, 7 (11): 845-854. DOI:10.1038/nmat2297 (in Eng.).

[10] Ignatov V.G., Kokin A.V. (2003) Methods for processing coal, M .: Phoenix. 512 p. (in Russ.).

[11] Dresselhaus M., Dresselhaus G., Elkund P. (1996) Science of Fullerenes and Carbon Nanotubes, New York: Academic Press. 965 p. (in Eng.).

[12] Marsh H., Rodriguez-Reinoso F. (2006) Activated Carbon, Elsevier Science & Technology Books. 536 p. (in Eng.).

[13] Khare R. et al. (2005) Carbon nanotube based composites - a review, Journal of minerals and Materials Characterization and Engineering, 4 (01): 31. ISBN: 0080444636

[14] Rashevsky N.D., Kronik V.S., Moroz V.A., Neelova I.P. (2001) Problems of the collection, processing and disposal of waste, Sat. scientific articles. Odessa: OSTNEI. P. 290-295 (in Russ.).

[15] Qiu J.S., Zhang F., Zhou Y., Han H.M., Hu D.S., Tsang S.C., Harris P.G. (2002) Carbon nanomaterials from eleven caking coals, Fuel, 81 (11-12): 1509-1514 (in Eng.).

[16] Novikova G.V., Zhdankin G.V., Mikhailova O.V., Belova M.V., Semenov V.G., Baimukanov D.A., Iskhan K.Zh., Karynbayev A.K. (2019) Installations for complex influence of electrophysical factors on raw materials // News of the National Academy of Sciences of the Republic of Kazakhstan. Series of Geology and Technical sciences. 2019. Vol. 4, 436. P. 54-61. ISSN 2518-170X (Online), ISSN 2224-5278 (Print). https://doi.org/10.32014/2019.2518-170X.97 (in Eng.).

[17] Yermagambet B.T., Nurgaliyev N.U., Kazankapova M.K., Kasenova Zh.M., Abylgazina L.D. (2019) Smokeless fuel production - semi-coke from coal // News of the National Academy of Sciences of the Republic of Kazakhstan. Series of Geology and Technical sciences, 2: 144-148. DOI: 10.32014/2019.2518-170X.48 (in Eng.).

[18] Okazaki K. (1976) Technology of ceramic dielectrics. M.: Energy. 256 p. (in Russ.).

[19] Zhumadilov E.K., Davrenbekov S.Zh., Mustafin E.S., Kasenov B.K., Edilbaeva S.T. (2004) Investigation of the electrophysical properties of $GdSrCr_2O_{5.5}$ chromite // Bulletin of NAS RK. 5: 114-118.