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Manufacturing technology and emission properties of modified metal-porous cathodes of M-type

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The improved manufacturing technology and the results of the study of the emissive properties of metal-porous M-type cathodes modified with polyhedral fulleroid-type nanoparticles of toroidal shape — astralenes, in the refractory matrix and sulfoadduct of carbon nanoclusters — ugleron, in the active substance are presented. It is established that the cathode-grid knots and devices with ugleron-modified cathodes are characterized by increased durability due to the decrease in the evaporation rate of the active substance at the operating temperature of the cathode of 1050 °C. The mechanism of increasing the durability of the cathode is revealed by molecular-dynamic modeling using the density functional method. It is found that the layered carbon nanostructures effectively retain the components of the cathode active substance — Ba and BaO, with the adsorption energy of $\sim 2-3$ eV. Experimental studies have shown that the cathode material containing astralenes has a higher thermionic capacity in the space charge-limited mode compared to similar cathodes whose emitting material does not contain astralenes. Experimental studies of the operation of cathodes whose emitting materials are modified with ugleron and astralenes in various combinations have shown that their service life is 2–6 times longer than that of commercially used M-type cathodes.

Keywords: metal-porous cathode, emission properties, nanocarbon, astralen, ugleron, density functional theory, molecular dynamics modeling.

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Introduction

Currently, electro-vacuum devices (VED) of microwave band (MW) are widely used in radio equipment for theon-ground and aerial applications [1–4]. An urgent problem in development of VED remains increasing the efficiency of the element base, in particular for traveling wave tubes (TWT) it is necessary to simultaneously increase the output power in a given frequency range and the service life. The solution to this problem is to improve the electron source, which shall provide the required current density during the specified service life. The relevant parameter for a TWT used in aerospace devices is the durability of cathodes which shall be no less than 15 years (140 ths. h) at the density of current 1–2 A/cm^2 in continuous operation mode [2,3], and for the powerful pulsed TWT used in the circuits of the airborne radars — the durability of the cathode-grid knot (CGK) of no less than 5000 h at the density of current 5–7 A/cm^2 in the quasi-continuous operation mode [4]. Moreover, for both types of TWT, at least 1.3–1.5-fold margin of cathode durability relative to the specified parameters of the device's service life should be provided. In recent decades in Russia the major commercially used source of electrons in TWT is a metal-porous cathode (MPC) with coatings made of platinum group metals (Os, Ru and etc.) — MPC of M-type. To ensure the above values of current density, it is possible to use scandium cathodes (the cathode material includes scandium and/ or its oxide), however, such cathodes demonstrate a lack of reproducibility of the physical-technical parameters characterizing durability, and at the same time show high sensitivity to vacuum levels, which significantly limits their industrial implementation [5].

To date, certain proposals concerning structure have been elaborated to increase the durability of MPC by increasing the active substance margin in the cathode tungsten matrix. In paper [6] a double-layer structure of the cathode matrix was proposed, in which the porosity of the emissive surface layer makes 20–22 % to reach lower evaporation rate of the active substance from this zone, and for the bottom layer 40–45 % to provide the operating layer replenishment with the active substance. It is such an emitter that is called an M-type cathode with a feeding chamber, and it is currently being mass-produced in TWT of aerospace systems. However, the drawback of such cathodes is the complexity of their manufacture, high consumption of tungsten powder and the need to manufacture special precision tooling. Therefore, to increase the durability of MPCs, there is also another constructive approach to reduce the evaporation rate of the active substance for the construction of MPCs with a single-layer matrix while maintaining the required emission level. Within this approach the papers [7–9] outlined the emission properties of cathodes where metals of platinum group were added (Os, Ru, Ir, Re) into metallic matrix of MPC — cathodes of MM-type. Paper [7] states that cathodes made of osmium and tungsten mixtures are featuring 6–8 times less barium evaporation rate compared to conventional M-type cathodes, and the lowest electron work function is reached with osmium content in the cathodic sponge of 70–75 wt.%. At the same time, the cathodes are comparable in durability: at a current density of 2 A/cm^2, the service life of the MM cathode is 140 thousand h [3], and the M-type cathode with a feeding chamber is — 190 thousand h at a current density of 1.5 A/cm^2 [6]. For comparison — a conventional M-type cathode (Os-Ru coating) without a feeding chamber has a predicted durability of 160 thousand h at a density of 0.6 A/cm^2 [10].

Along with these developments, an urgent direction for improving the emission parameters of MPC is its modification with nanocarbon materials, due to their unique electronic and mechanical properties [11–18]. Papers [15–18] describe positive results of integrating the carbon nanostructures directly into MPC, in particular, when modifying the cathodic matrix with astralenes [19] and active substance of cathodes with ugleron [20]: the resource emissive durability of such cathodes as a part of aerospace TWT in continuous operation mode may be no less than 10^6 h with the density of the cathode emission current of up to 0.645 A/cm^2 and $2.5 \cdot 10^5$ h at density of 2 A/cm^2 [18].

The purpose of this work is to identify the mechanism and degree of influence of modification of the emitting material of the metal-porous M-cathode and CMM-cathode (coated MM-type MPC) with such layered carbon nanostructures as „astralenes“ and „ugleron“ to achieve the following: 1) maximal current density when limited by the spatial charge; 2) higher durability. The study of the regularity of carbon structures interaction with barium oxide and barium is carried out using numerical modeling.

1. Metal-porous cathodes modified with nanocarbon and iridium

The following structures — cathode versions were selected for the study:

1) single-layer MPC with Os-Ir-Al coating (M-type) made of tungsten powder A (W-A) with addition of 0.5 % astralenes and impregnated with barium-calcium aluminate 3:0.5:1 ($3BaO{\cdot}0.5CaO{\cdot}Al_2O_3$). Here and further in the text the tungsten grade pure powder for cathodes of A fraction and finer B fraction is described, TU 48–19–70–84, nanocarbon particles are added by weight;

2) single-layer MPC of M-type made of tungsten powder of B fraction (W-B) with addition of 0.5 % of astralenes and impregnated with barium-calcium aluminate 3:0.5:1;

3) single-layer MPC of M-type made of W-A with the addition of 0.5 % astralenes and impregnated with barium-calcium aluminate 3:0.5:1 with addition of 0.2 % ugleron;

4) single-layer MPC of M-type made of W-B with the addition of 0.5 % astralenes and impregnated with barium-calcium aluminate 3:0.5:1 with addition of 0.2 % ugleron [21];

5) single-layer MPC of M-type made of W-A with the addition of 10 % iridium (Ir) and impregnated with barium-calcium aluminate 3:0.5:1;

6) single-layer MPC of M-type made of W-A with the addition of 10 % Ir and impregnated with barium-calcium aluminate 3:0.5:1 with addition of 0.2 % ugleron;

7) single-layer MPC of M-type made of W-A and impregnated with barium-calcium aluminate ($3BaO{\cdot}0.5CaO{\cdot}Al_2O_3{\cdot}0.5SiO_2$) with addition of 0.2 % ugleron.

Previously, single-layer MPC structures were studied in [17,18]: W-B + 0.5 % astralenes impregnated with barium-calcium aluminate and W-B + 0.5 % astralenes impregnated with barium-calcium aluminate with addition of 0.2 % ugleron (structure versions 2 and 4) that demonstrated improved emissive properties of MPC, however their fabrication technology was experimental and required further workout for the purpose of commercial use. Design versions 1 and 3 could not be manufactured due to the unsatisfactory mechanical strength of the cathode tablets. One of the tasks was to achieve an even distribution of astralenes in the tungsten sponge and improve the quality of the tungsten disk structure. The second task was to improve the quality and identity of carbon-modified active compounds from batch to batch.

To solve the first problem, two changes were proposed in the technological process of preparing a powder mixture for the manufacture of a cathode sponge: first, to mix non-annealed tungsten powder (fractions A or B) with astralenes in a drum mill with jasper balls for 3 h to improve the homogenization of nanoparticles and tungsten powder mixture; secondly, to carry out hydrogen annealing of a mixture of powders to form conglomerates of nanocarbon and tungsten particles (Fig. 1) [22].

Cathode tablets with a diameter of 3.5 mm were made from the resulting mixture, while the specific pressing pressure decreased by about 1.5 times relative to the initial experimental technology in order to obtain satisfactory mechanical strength of the workpiece. The resulting tablets were sintered once in hydrogen using commercial method, which provided the necessary parameters of the workpiece. The advantages of the improved technology compared to the previously studied [21] are the elimination of manual mixing of the powder mixture with a pestle, as well as reduced sintering time of discs from 8 to 3 h. According to the standard technology, cathode tablets of proper quality with a diameter of 3.5 mm were also produced from a

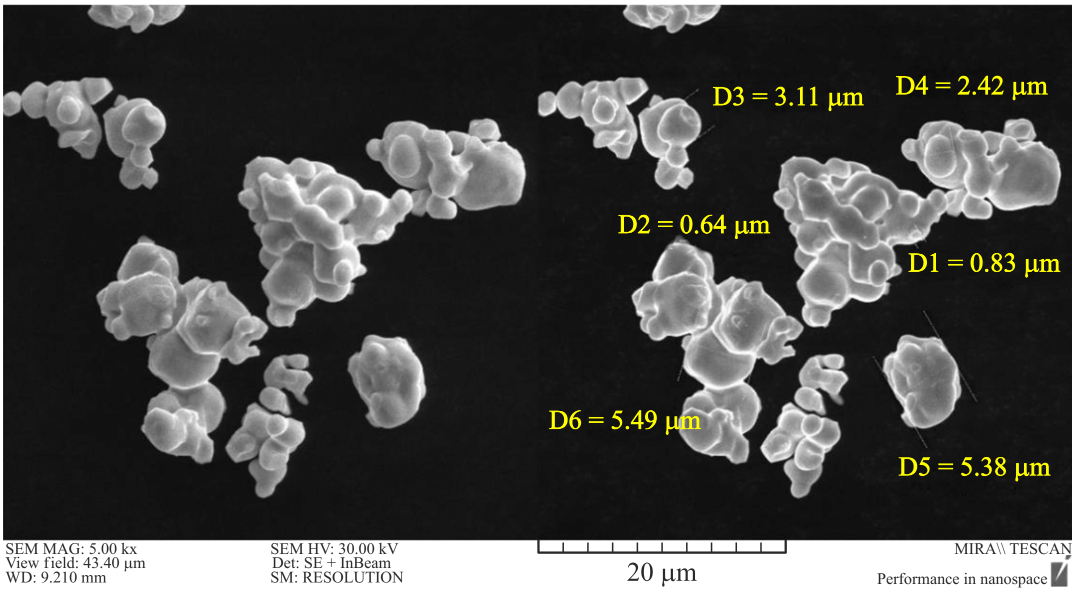

Figure 1. Mixture of W-A powders with astralenes.

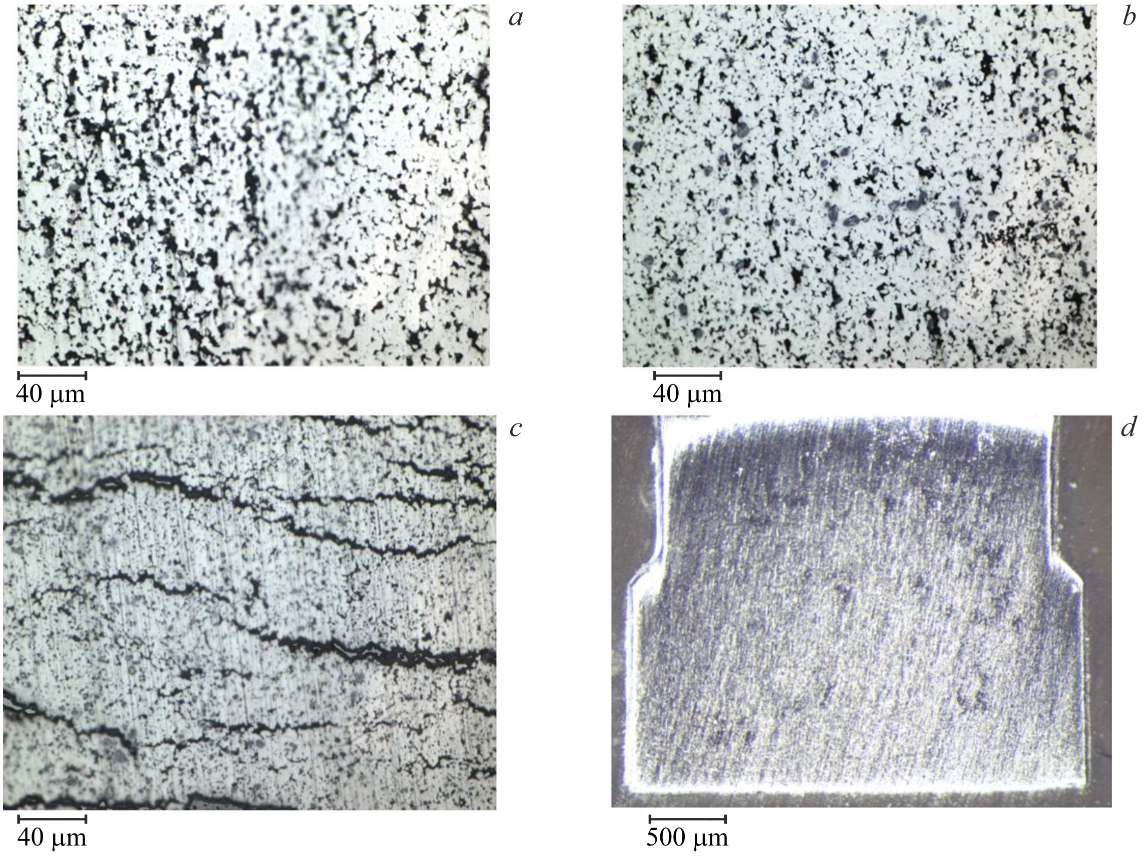

Figure 2. Images from the optical microscope MBS, thin sections 1/3 of cathode tablets: *a* — W-A with astralenes; *b* — W-B with astralenes; *c* — W-B with astralenes: *d* — W-A with Ir.

mixture of tungsten powder of fraction A with Ir, the only difference being that the mixture of pre-annealed tungsten powder and the initial Ir was mixed similarly to the mixture with astralenes in the drum mill with jasper balls for 3 hours. According to the results of metallographic analysis, all cathode tablets with astralenes (Fig. 2, *a, b*) have a uniform qualitative structure, where there are no seals and cracks, which were observed with the initial technology (Fig. 2, *c*). Tablets with Ir have no cracks, small seals are present, however, they also have a generally satisfactory appearance (Fig. 2, *d*). The results obtained open up the possibility of manufacturing cathodes with a 10 mm diameter astralenes for high-power pulsed TWT, which was impossible during manufacture using the original technology because of unsatisfactory parameters of the cathode tablet and its low mechanical strength.

To solve the second problem — to improve the quality and identity of carbon-modified active compounds — it was proposed to improve the process of dissolving nanocarbon particles in a polar solvent (deionized water). Thus, relative to the initial manufacturing cycle of the modified active substance, the ranges of ultrasound treatment time and power, the number of ultrasound treatment cycles, as well as the settling time of the solution until the nanocarbon particles were completely dissolved were expanded [23]. Using an improved technology for modifying the active substance, aluminate and barium-calcium aluminosilicate were manufactured to impregnate previously manufactured cathode tablets with which the cathodes were made. The quality of the obtained compositions was controlled via X-ray phase analysis using X-ray diffractometer DRON-8T. From the analysis it follows that both substances have similar main phase of barium-calcium aluminate $Ba_5CaAl_4O_{12}$.

2. Study of emissive properties of modified cathodes

The emission characteristics of the modified cathodes and standard design cathodes with a diameter of 2.8 mm were studied; additionally, their parameters were compared with parameters of the modified cathodes fabricated using the original technology. Initially the emissive capacity of cathodes was assessed at the current density of 1 A/cm^2 based on characteristic temperature Tx (normal value Tx for M-type MPC according to JSC „RPE „Almaz“ makes $\leq 900\,^\circ$C), at which the cathode starts operating from the charge limited operation to the temperature limitation mode (Table 1).

It follows from the table that the average value of Tx for all cathodes with astralenes is lower relative to typical and iridium cathodes, which indicates their higher emission capacity, in addition, for W-B cathodes with astralenes manufactured using a new technology with standard impregnation, the values of Tx is lower than for MPCs manufactured using the original technology.

At the next stage, a study of the maximum emission capacity of the cathodes was carried out. To determine the operating mode of the cathode, the current-voltage curves (CVC) were first plotted in the pulse mode in the cathode temperature range 1150–800 °C (Tc). Next, the non-local characteristics for different current densities were removed (J), the measurement results are shown in Table 2.

It follows from the table that M-type cathodes modified with astralenes or iridium have the best emission capacity, while modified cathodes made using a new technology from W-B with astralenes show the maximum. The data obtained for cathodes fabricated using standard technology and with Ir (10 %) is consistent with data given in papers [24,25].

At the last stage, the cathodes were tested for durability as part of diodes, CGK and devices in a temperature-accelerated mode. The diodes were tested with a current draw of 1 A/cm^2 and with the maximum allowable acceleration coefficient at which the test temperature of the cathode was $1180\,^\circ C_{br}$. Accordingly, the maximum acceleration coefficient was obtained on more emission-active cathodes due to their low characteristic temperature. The typical and carbon-modified cathodes in CGK and in the device were tested in continuous burning mode with a coefficient 7 without current draw, the typical cathode (diameter 10 mm) was tested in TWT with a current draw of 5 A/cm^2 at rated temperature. Criteria of the cathode operability monitored during the tests: 1) difference between the operating and characteristic temperature of the cathode (ΔTx) not lower than 50 °C; 2) drop of the cathode current (Ic) in the operating point below 10 %. The characteristic temperature Tx of cathodes was defined based on a 20 % decline of the current relative to the operating current. In diodes and CGK with typical cathode also pressure was detected in the mockup (P). The test results are provided in the table 3 below.

It follows from the test results that nanocarbon-modified cathodes have high service durability: MPCs with carbon only show greater durability relative to cathodes with typical impregnation, and cathodes with astralenes only show more stable emission characteristics with running time, and their tests continue. CMM-type cathodes with Ir (10 %) within the indicated running hours demonstrated no any durability benefits compared to the typical M-type MPCs, so the durability tests are continued.

3. Theoretical study of the interaction of carbon structures with barium and barium oxide at the cathode operating temperature

The following mechanisms were proposed in papers [18,26] as mechanisms explaining the increased durability of nano-carbon MPCs — with astralenes and ugleron: increasing the safety of the emission film Os-Ir-Al on the cathode surface by slowing down the mutual diffusion between the film and tungsten in the presence of astralenes; resistance of the cathode emissive material with astralenes to vacuum and the reduced evaporation rate of the active substance with carbon. These mechanisms have been experimentally confirmed. Preliminary results of numerical computer modeling, presented in [26] and obtained with the participation of the authors of this work, showed that barium atoms and barium oxide molecules are retained between

Table 1. Characteristic temperatures of cathodes

№p.	Technology type	Composition of cathode tablet	Tx, °C$_{br}$	Tx(av), °C
Impregnation with typical aluminate				
1	New technology	W-A with astralenes	850	850
2			850	
3		W-B with astralenes	815	828
4			840	
5	Standard technology	W-A with Ir	895	877
6			860	
7	Technology [22]	W-B with astralenes	877	849
8			840	
9			830	
10	Standard technology	W-A	885	867
12			850	
12			865	
Impregnation with aluminate with ugleron				
13	New technology	W-A with astralenes	847	851
14			868	
15			840	
16		W-B with astralenes	840	850
17			845	
18			865	
19	Typical technology	W-A with Ir	853	858
20			860	
21			860	

Table 2. Maximal current density when limited by the spatial charge

Typical technology				Technology [22]		New technology			
W-A		W-A with Ir		W-B with astralenes		W-B with astralenes		W-A with astralenes	
J, A/cm^2	Tc, °C$_{br}$	J, A/cm^2	Tc, °C$_{br}$	J, A/cm^2	Tc, °C$_{br}$	J, A/cm^2	Tc, °C$_{br}$	J, A/cm^2	Tc, °C$_{br}$
5	980	4	965	2.6	915	4	960	4	950
$\tilde{8}$	1010	8	970	5.6	955	8	970	8	960
12	1035	12	985	10.1	990	12	980	12	1020
20	1070	20	1040	20	1040	20	1030	20	1040
–	–	–	–	33	1070	33	1040	–	–

the sheets of bilayer graphene. This effect explained the decrease in the rate of evaporation of barium from the cathode surface. The research in paper jcite26 was carried out through the density functional test (DFT), which uses, like other quantum mechanical approaches, the Born-Oppenheimer approximation. The latter involves changing only the electron temperature, the nuclei remain stationary, and the interaction of electrons is considered

Table 3. Results of cathodes durability tests

Type of mockup	Type of technology	Composition of cathode tablet/ impregnation	ΔTx, °C in operating point, %	Decline of Ic	P, Torr	Real running hours, h	Resource durability, h
Diode	Standard	W-A/ typical aluminate	48	6.7	$2.2 \cdot 10^{-6}$	4010	64160
		W-A/ aluminate with ugleron	49	5.16	$2.9 \cdot 10^{-6}$	8824	141184
	[22]	W-B with astralenes/ aluminate with ugleron	90	1.13	$5.6 \cdot 10^{-6}$	6665	106640
	New technology	W-A with astralenes/	45	6.69	$8.6 \cdot 10^{-7}$	164	167936
		W-B with astralenes/ typical aluminate	60	3.65	$9.5 \cdot 10^{-7}$	164	221564
	Standard	W-A with Ir/ typical aluminate	65	5.26	$9.8 \cdot 10^{-7}$	164	48216
CGK		W-A/ alumosilicate with ugleron	77	2.8	–	900	6300
		W-A/ typical alumosilicate	50	3.55	$1.8 \cdot 10^{-5}$	450	3240
TWT		W-A/ alumosilicate with ugleron	80	0.1	–	539	3773
		W-A/ typical alumosilicate	60	0.5	–	1235	1445

in the potential field of stationary nuclei. The electron temperature determines the Fermi-Dirac quantum statistics and, accordingly, the distribution of electrons by states. In paper [26], the electron temperature was 300 K, and the temperature in the classical sense, determined by the speed of movement of atoms, was 0 K.

This paper continues the previous studies and is aimed at studying the effect of Ba and BaO retention at the operating temperature of cathode 1050 °C (1323.15 K). To calculate the electron structure of „graphene+Ba/BaO“ complexes and energy of interaction of the carbon structure with Ba/BaO the DFT method is also used implemented in SIESTA 4.1.5 software suite [27,28]. The basis set with a double ξ polarization (DZP) was used. When partitioning the Brillouin zone, a Monkhorst-Pack grid with a size of $32 \times 32 \times 1$ was used. The energy of Van der Waals interaction was calculated using Grimme's dispersion correction method DFT-D2 [29]:

$$E_{total} = E_{DFT} + E_{disp}, \tag{1}$$

where E_{disp} — empirical correction to account for dispersion interactions:

$$E_{disp} = -s_6 \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{C_6^{ij}}{R_{ij}^6} f_{dmp}(R_{ij}), \tag{2}$$

where s_6 — scaling coefficient which depends on the used functional; C_6^{ij} — coefficient of dispersion interaction for a pair of atoms i and j; R_{ij} — distance between the atoms i and j; f_{dmp} (R_{ij}) — a damping function that reduces the contribution of dispersive interactions at short distances.

To implement the simulation at the cathode operating temperature, the molecular dynamics (MD) method was used, where temporal evolution of the atomic system is tracked by integrating Newton's equations of motion. The total force acting on each atom was determined through the potential energy gradient, which is calculated using the above-mentioned DFT method. Thus, modeling the interaction of objects in „graphene+Ba/BaO“ system at a temperature of $T = 1050$ °C (1323.15 K) was carried out using a semiclassical approach: the energy of the system was calculated using one of the *ab initio* methods; the trajectories of atoms were calculated within the framework of classical mechanics, taking into account the initial conditions of the atomic configuration of a crystal cell corresponding to the equilibrium state. The initial values of the atomic velocities are set according to the required temperature. To maintain this temperature during MD modeling, one of the well-known „thermostat“ algorithm was used — Nose-Hoover algorithm. All developed algorithms are based on the molecular kinetic theory of gases, according to which the temperature is a value proportional to the average kinetic energy of atoms. Any „thermostat“ algorithm does not ensure temperature constancy throughout the entire time interval of numerical simulation, therefore, the temperature value throughout the MD simulation fluctuates around the set value within ±15 %. This inevitably leads to fluctuations in kinetic and potential energies, as well as the energy of interaction of the system's individual objects with each other. Molecular dynamic modeling is implemented in the same SIESTA 4.1.5 package. First, (before MD modeling) a

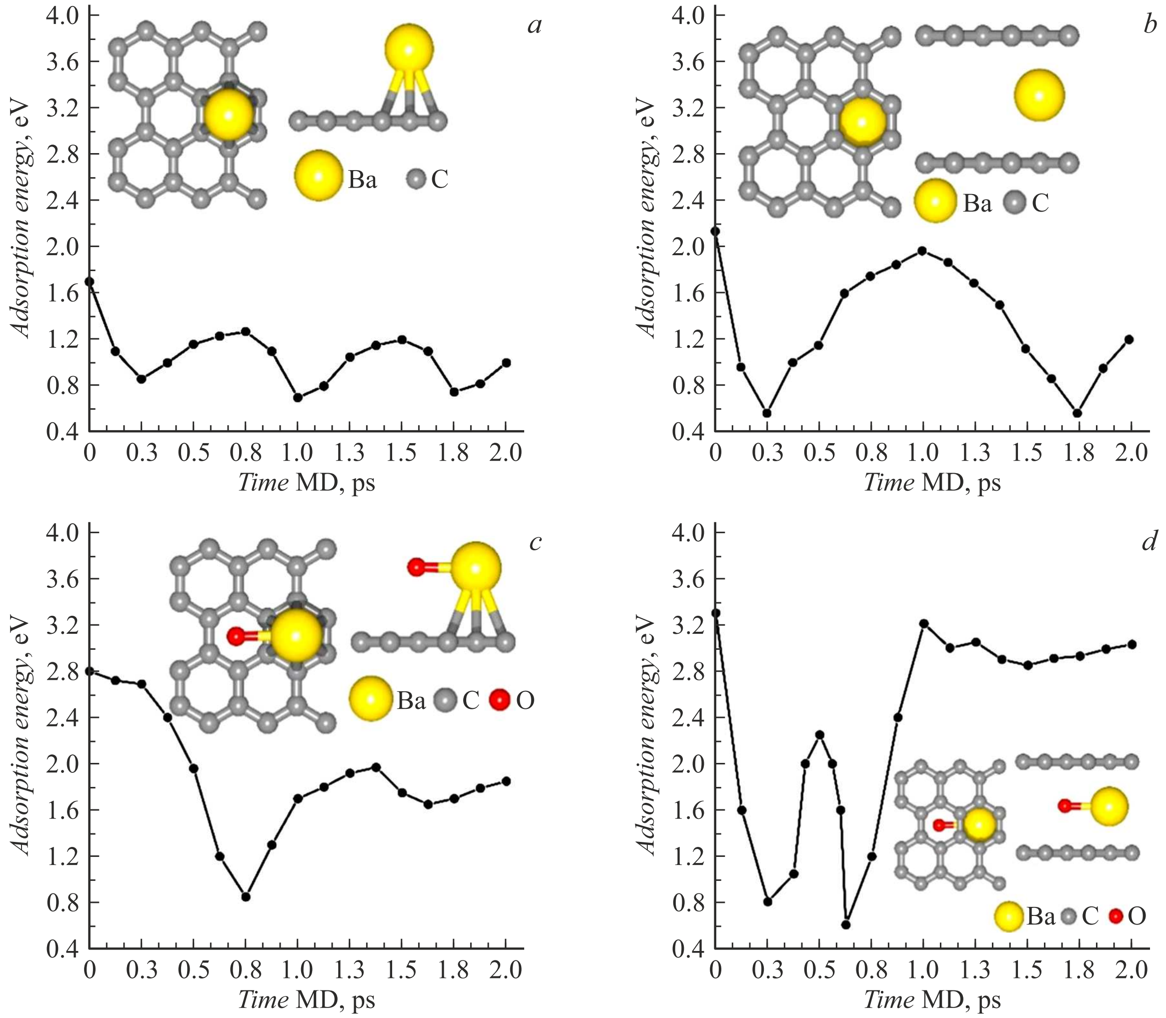

Figure 3. Profile of the change in adsorption energy for structures: *a* — graphene+Barium, *b* — graphene+Barium oxide, *c* — bi-layered graphene+Barium, *d* — bi-layered graphene+Barium oxide.

search was performed to find the equilibrium configuration of the crystalline supercell lattice using modified Broyden algorithm [30] and the Pooley corrections, which take into account the force acting on each atom of at least 0.04 eV/Å. To find an equilibrium configuration corresponding to the global minimum of the system total energy, one of the optimal mathematical algorithms for global optimization was applied — „annealing simulation algorithm".

The interaction of carbon structures with barium atoms/barium oxide molecules is characterized by a certain energy — adsorption energy E_{ads}. It is calculated as the modulus of the potential energy difference of graphene+Ba/BaO" and its individual components before interaction. The value of this energy characterizes the intensity of interaction of Ba/BaO with the graphene surface. Its positive value indicates the stability of „graphene+Ba/BaO" complex, as well as the fact that its formation is energetically beneficial. The higher the temperature, the greater the energy of thermal motion of Ba/BaO, therefore, at $T = 1050\,^{\circ}\mathrm{C}$ Ba/BaO objects will not stay in place, moving along the graphene surface, and therefore, it is expected that the intensity of Ba/BaO interaction — graphene and the adsorption energy E_{ads} will constantly change over time.

A series of numerical MD experiments was carried out to identify how the objects of „graphene+Ba/BaO" interact over time at a temperature of 1050 °C (1323.15 K). The equilibrium configuration of the super cell of 2*D*-complexes of „graphene+Ba/BaO", found in this paper is characterized by the translation vectors $L_x = 8.52\,\text{Å}$ and $L_y = 7.38\,\text{Å}$. Numerical MD experiments were performed for these supercells for two picoseconds to establish the pattern of temporal evolution of the change in adsorption energy. Figure 3 shows the results obtained — graphs of the change in adsorption energy in the time interval (0; 2) ps, the supercells are also shown there. The adsorption energy change is the same in the interval (0.4–4.0) eV. In all cases, there is a change in energy over time, as suggested above. At the initial moment of time the adsorption energy corresponds to the temperature 0 K (for nuclei) and 300 K (for electrons). Energy fluctuations are of periodic nature.

Table 4. Energy of Ba/BaO adsorption with layered graphene structures

Structure		Graphene+Ba	Graphene+BaO	Bigraphene+Ba	Bigraphene+BaO
Energy of adsorption, eV	Temperature 0 K	1.70	2.79	2.14	3.30
	Temperature 1323.15 K	0.70	1.62	1.97	3.21

Adsorption of barium atoms on mono-/bilayer graphene is characterized by a periodic change in time (Fig. 3, *a, b*). The minima E_{ads} correspond to the maximum distance of Ba from graphene at a distance of 3.98 Å for a monolayer and the closest approach to one of the graphene layers in case of a bilayer, when the distance to both layers is 2.80 and 2.856 Å with an interlayer distance of 5.656 Å. These minima E_{ads} are caused by the increasing energy of electron repulsion as atoms approach each other. The minimal value of $E_{\text{ads}} \sim (1.27 \pm 0.03)/(1.97 \pm 0.03)$ eV for the mono/bi-layered graphene. Maximum E_{ads} is achieved vice-versa when Ba-atom „sticks“ to the graphene monolayer ($(\sim 1.27 \pm 0.02)$ eV) and when Ba-atom is in the intermedium position between the two layers of graphene ($(\sim 1.97 \pm 0.03)$ eV). With the help of MD modeling, the reason for the periodic nature of adsorption energy change has been established. It is caused by the migration (due to thermal motion) of Barium atom along graphene. In this case, Barium atom appears at one moment above the carbon atom, then it appears in the „potential well“ of hexagon, as shown in Fig. 3, *a, b* (insert window). Since the atomic grid of graphene has a periodic character, such transitions between the localization of barium atoms are accompanied by overcoming some potential barrier, which leads to periodicity of the change E_{ads}. For the monolayer the period makes ~ 0.75 ps, for the bi-layer — ~ 1.5 ps. The increase of period in case of the bilayer is caused by a more complex trajectory of barium atoms relative to the atomic grid of the bilayer.

The adsorption of BaO complexes is fundamentally different from the previous case, because chemically active oxygen is present in this complex (Fig. 3, *c, d*). MD modelling demonstrated that in case of graphene monolayer O-atom as part of BaO is quickly moving trying to tear off BaO from the surface (time interval 0–0.8 ps), when adsorption energy decreases to 0.85 eV. However, in the next moments of time BaO complex is drawn to graphene with the formation of a covalent bond C-O and „bridge C-O-Ba“. The bridge is being formed at the moment of time ~ 1.4 ps, when the adsorption energy reaches its maximal value ~ 2 eV. Further, the adsorption energy changes very little and fluctuates around this value, since the formed covalent bond C-O does not allow the barium atom to be removed and migrate through graphene.

The behavior of BaO complex in the interlayer space of the bilayer is even more complex. This character is due to the influence of two factors: the migration of BaO along graphene; the oscillatory motion between the bilayer layers. As a result, there is a sharp decrease in the adsorption energy when BaO approaches one of the graphene layers, followed by a sharp increase to ~ 3.2 eV. This energy value corresponds to the formation of a covalent bond C-O with one of the graphene layers. As in the previous case the „bridge C-O-Ba“ is formed. Further this energy changes not so drastically.

Table 4 provides the calculated adsorption energy values for the two temperature values: 0 and 1323.15 K (for this temperature the average value E_{ads} is given which corresponds to the maxima). The data shown in the table indicates that the localization of Ba atoms and BaO molecules in the interlayer space of layered graphene is the most beneficial in terms of energy. This conclusion is physically correct and valid, respectively, for other layered carbon nanostructures.

Therefore, evaporation of active substance — Ba/BaO — when ugleron is added to MPC structure is decreased and thus extends the cathode service life.

Conclusion

Experimental studies have proved the high emission properties — the emission level and emission durability of MPCs modified with astralenes and ugleron, and manufactured using advanced technology. MPCs with ugleron only show greater durability relative to cathodes with typical impregnation, and cathodes with astralenes only show more stable emission characteristics with running time. This fact, previously established experimentally, was investigated by *in-silico* using molecular dynamic modeling in order to identify a mechanism for increasing durability at the cathode operating temperature of 1050°C. A high value of the adsorption energy — up to 3 eV, of the active substance with carbon graphene layers has been found, which ensures the retention of the substance and a decrease in its evaporation rate. The new technology of fabricating the nano-carbon based cathodes allows getting both, the 2.8 mm diameter cathodes for the aerospace TWT with the current density of 2 A/cm^2 and service durability of over 15 years, and the 10 mm diameter cathodes for the powerful pulsed TWT with the current density of 5–7 A/cm^2 with predicted durability of over 5000 h; Thus we may state that further development and testing of such cathodes is relevant. M-type MPCs with a 10 % additive of Ir in tungsten matrix have not shown significant emission advantages relative to typical M-type MPCs, durability tests are ongoing. Taking into account the study [25], in the future it is possible to consider increasing the percentage of Ir content in the matrix to 50 % with further investigation of the durability of such cathodes.

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Conflict of interest

The authors declare that they have no conflict of interest.

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