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Energy state of the electronic subsystem of porous carbon material caused by laser irradiation

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The changes in the electronic subsystem of a porous carbon material caused by its doping with Mn, Cr, and Fe and laser irradiation were studied by the method of electron paramagnetic resonance. It has been found that Mn doping leads to the appearance of several paramagnetic centers, and laser irradiation facilitates the redistribution of electrons between different states so that their mobility increases due to the transition from the g = 3.9 to the g = 6.0 state. The Mössbauer spectroscopy of porous Fe-doped carbon material indicates the presence of oxygen ligands for iron ions, in particular the formation of octa- and tetra-complexes with redistribution of electron density between iron and oxygen nuclei, and, accordingly, changes in the degree of covalence of the chemical bond from Fe^{3+} to Fe^{2+}.

Keywords: electron paramagnetic resonance, porous carbon material, porometry, Mössbauer spectroscopy.

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Introduction

Carbonization and activation of the material of plant source in the presence of a pore-forming agent (water vapor) leads to structural transformations of the initial matrix, resulting in the formation of a porous material with a specific surface area of 800-1000 m^2 and a porosity of 50-70%. [1]. Depending on the structural characteristics of the plant material, fractals in the form of chains, grids, and three-dimensional structures containing C-C σ- and π-type bonds are formed in the porous material.

The presence of capillaries in plant material, temperature and pressure in the reactor during its carbonization and activation lead to the formation of acidic groups capable of binding metals into complexes. The existence of acidic groups is confirmed by the result of alkaline titration of the matrix of porous carbon material (PCM), which indicates that the process occurs in steps and indicates differentiation in the detection of acidic properties of carboxyl groups conjugated with the electronic structure and spatial organization of matrix fragments in places of their immobilization (localization).

As a result of technological factors, redox processes can be activated, structural defects can form, and homoletic bond breaks can occur, which together cause the formation of unpaired electron localization zones. To detect these effects, the electron paramagnetic resonance (EPR) spectra were obtained. Changes in the electronic subsystem of PCM doped with Mn, Cr, and Fe were determined using an ELEXSYS E-500 spectrometer from BRUKER with simultaneous control of the frequency in the region of 9800 MHz and the magnetic field intensity at room temperature.

I. Experimental, discussion of the results

Depending on the carbonization temperature (300÷900ºC), a series of C3÷C9 samples were obtained (Table 1). The numbering indicates the carbonization temperature. For example, C4 is a material carbonized at 400 °C, C8 at 800 °C.

Changes in the porous structure of carbon materials at

different temperatures were studied by low-temperature porometry using a Quantachrome Autosorb Nova 2200e instrument. Before the measurements, the carbon samples were degassed at 180 °C for 18 hours. The isotherms of nitrogen adsorption/desorption for the studied samples are shown in Fig.1. The volume of adsorbed nitrogen increases for samples carbonized at temperatures less than 700 °C (Fig. 1) and gradually decreases with further increase in temperature.

The isotherms of nitrogen adsorption/desorption for all carbon samples obtained by hydrothermal carbonization have a similar shape, and the data obtained are consistent with the results presented in [2,3]. According to the IUPAC classification, isotherms can be classified as type I, which are characteristic of microporous solids. Characteristic of all isotherms is the presence of low pressure hysteresis, which is reflected in the difference between the adsorption and desorption branches in the region of low relative pressures p/p_0 (Fig. 1). There are several possible reasons for its occurrence: swelling of the high-molecular framework of the adsorbent; irreversible retention of adsorbate molecules in pores whose size is close to the size of adsorbate molecules; irreversible chemical interaction of adsorbate with adsorbent. From the analysis of adsorption/desorption isotherms, it is possible to determine the characteristics of the porous structure of carbon materials (Table 2), namely: the total surface area, BET (S_{BET}), the values of the area and volume of micro- and mesopores (S_{micro}, S_{mezo}, V_{micro}, V_{mezo}), as well as the average pore size (d).

As can be seen from Table 2, the PCM obtained by hydrothermal carbonization are characterized by a microporous structure with an average pore diameter of 2 nm and a specific surface area of $\approx$ 400 m^2/g. With an increase in the carbonization temperature, the carbon framework burns out, accompanied by a decrease in the number of micropores and their merging into mesopores, as evidenced by an increase in the average pore diameter from 1.89 to 2.67 nm (Table 2).

The DFT method was used to analyze the porous structure of the obtained PCM (Fig. 2). When calculating the pore size distribution, a physical model of carbon particles with slit-like pores was chosen.

According to the results of the DFT method (Fig. 2), it was found that in carbon materials obtained in the temperature range of 500 ÷ 800 °C, the main fraction of pores is micropores with a size of 0.6-1.3 nm. Further increase in the temperature of hydrothermal carbonization leads to a decrease in the specific area of the material (Fig. 2, b) and redistribution of pores, which forms pores with a size of 1.05-1.35 nm. To increase the pore area and obtain a controlled pore size distribution, the obtained carbon materials were additionally thermally and chemically activated [4]. The porous structure and surface morphology will determine the physical and electrochemical properties of the obtained materials.

Thermal activation of carbonized carbon material in air promotes the development of micropores with a diameter of ~1.25 nm and mesopores of ~4 nm [4]. Thermal activation of carbon samples under conditions of holding at 400°C for different time intervals results in the transformation of the carbon matrix structure, coupled with the generation of paramagnetic centers [5]. The dependence of the EPR signal intensity on the exposure time gives reason to assert that in this case there is a sequence of structural transformations: amorphization with defect formation and reduction of surface energy due to the interaction between defects, which allow us to consistently record the formation of a developed surface caused by the action at this stage. According to the EPR method, in the structure of the carbon matrix at different stages of its formation, the action of external factors causes the generation of both localized on broken bonds and collectivized electrons that are delocalized in different fragments of a carbon material of heterogeneous origin [5]. Depending on the process conditions, nanoporous material has a different morphology and a maximum surface area of up to 900 m^2/g [6].

In the EPR spectra, a superposition of signals is observed, the parameters of which are given in Table 3. The unpaired electron content is approximately 10^{17} spins

Table 1.

Designation of carbon materials obtained at different carbonization temperatures

t, °C	300	400	500	600	700	800	900
PCM	C3	C4	C5	C6	C7	C8	C9
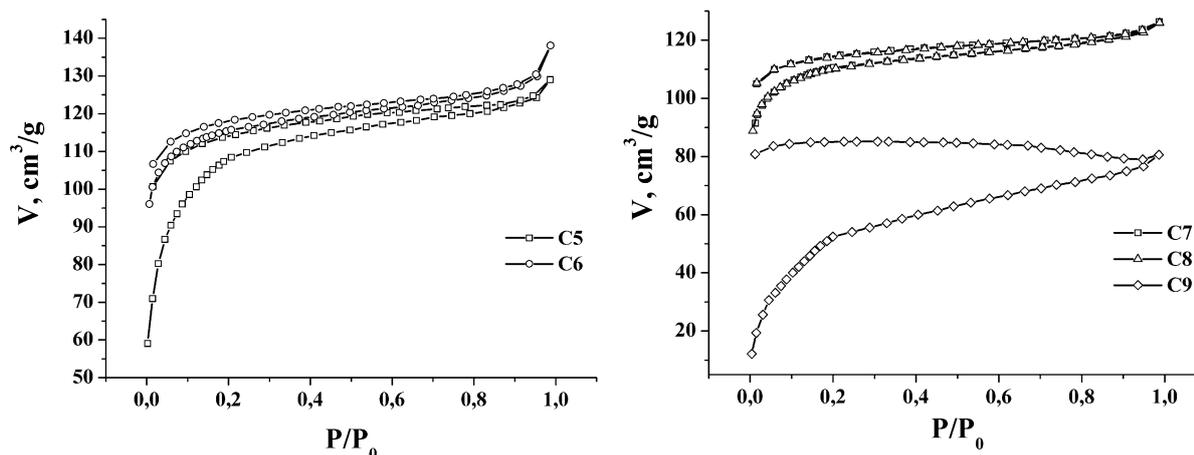
Fig. 1. Isotherms of nitrogen adsorption/desorption of the PCM.

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per 1 g of PVM.

As can be seen from Table 3, three types of paramagnetic centers can be identified in the EPR spectrum. Based on the results of elemental analysis, which show that there is no significant content of elements other than carbon, oxygen, and hydrogen, we can expect the spin density to be distributed among centers formed mainly by carbon atoms. The main characteristics of the EPR spectra are the g-factor and the peak width ΔH. The EPR parameters (g, ΔH) indicate the existence of collectivized electron states with a high rate of inter-electron exchange, i.e., a short lifetime of electrons in certain defined states (migration along chains, fragments, including those involving the massive matrix).

In the process of obtaining PCMs, it is not always possible to achieve predefined parameters, in particular, the resistivity and specific capacitance of the double electric layer (DEL) formed at the PCM/electrolyte interface, so to achieve optimal performance of electrochemical capacitors (ECs), PCMs are modified

Table 2.

Structural and adsorption characteristics of PCM

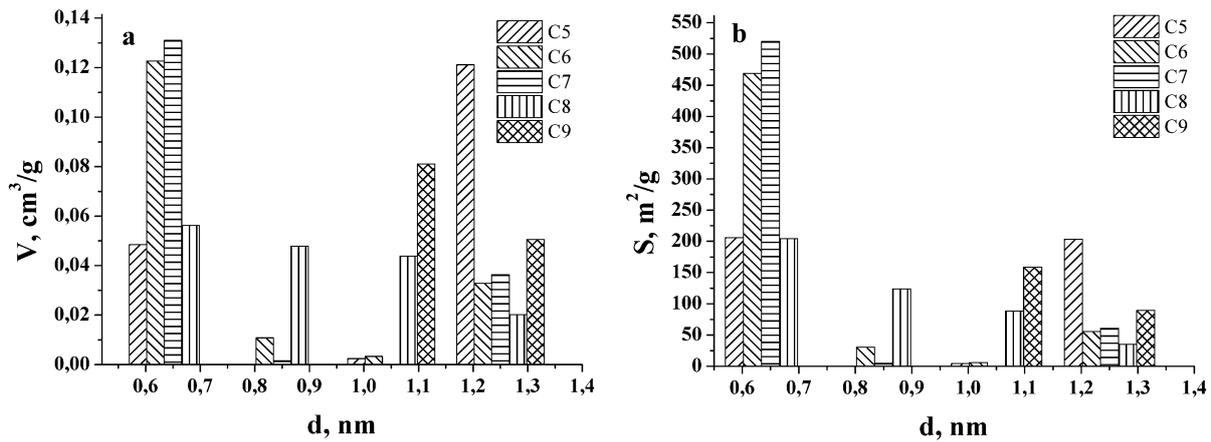| Sample	S_{BET}, m²/g	S_{micro}, m²/g	V_{micro}, cm³/g	S_{meso}, m²/g	V_{total}, cm³/g	d, nm
C5	400	383	0.15	17	0.20	1.98
C6	434	408	0.16	26	0.21	1.95
C7	412	388	0.16	24	0.19	1.89
C8	410	385	0.16	25	0.19	1.91
C9	186	146	0.07	40	0.12	2.67

Fig. 2. Distribution of pores by size of PCM according to the DFT method: a – pore volume, b – pore area.

Table 3.

Characteristics of EPR spectra of PVM

Sample	g	ΔH	I/I_{total}
PCM	2.696	680.5989	0.58
	2.119	569.7772	0.4
	1.996	20.12962	0.02
PCM + 0.6 % Mn	8.328	770	0.13
	3.942	1070	0.79
	2.319	270	0.02
	1.999	480	0.06
PCM + 0.6 % Mn+ laser	6.015	1260	0.49
	3.563	1650	0.38
	2.303	390	0.04
	1.996	450	0.09
PCM +20% Fe + laser	5.155	1330	0.27
	3.627	760	0.03
	2.285	2040	0.62
	2.093	605	0.08
PCM +20% Fe + laser+ aging	4.331	1250	0.12
	2.142	1430	0.88
PCM + 0.4 % Cr	4.139	1800	0.62
	2.626	2240	0.379
	1.987	116	0.001
PCM + 0.4 % Cr + laser	2.093	675	0.999
	1.999	100	0.001

under the influence of various factors. These include chemical treatment of PCMs, additional heat treatment, and doping with metals with high electron density.

Based on the general physical principles and topology of the developed surface, one of the ways to solve this problem is to increase the density of electronic states in the PVM matrix and involve as much of the developed surface as possible in the formation of DEL, since up to 50% of the pore surface is not wetted by aqueous electrolyte due to the presence of graphite incorporations. Therefore, the PCM was modified by doping it with metals with a high density of electronic states, which opened up the possibility of significantly increasing the capacitance of DEL, and, accordingly, of capacitors formed on the basis of the modified PCM. However, the doping technique does not ensure metal localization on the surface of the PCM. As a result, during repeated cycling of electrochemical capacitors (ECs), metal atoms are leached by the electrolyte and the EC parameters degrade. In order to prevent this effect, we carried out additional treatment of the doped PCM by irradiation with a neodymium laser operating in a pulsed mode (τ = 15 ns, f = 56 Hz), irradiation time 100-150 s.

The EPR spectra obtained from the manganese-doped PCM indicate the presence of several types of paramagnetic centers that cause the superposition of the corresponding signals (Fig. 3, Table 3).

By comparing the EPR parameters of different valence forms of manganese, taking into account the conditions of measurement and the parameters of the EPR signals of the modified matrix, it was found that only the signal with the parameter g = 1.999 corresponds to Mn^{2+}. The other forms are electrons delocalized between matrix fragments of different nature. Since the integral intensity of the line is proportional to the number of unpaired electrons of the corresponding type, the fraction of unpaired electrons of the Mn^{2+} electron shell is insignificant and amounts to less than 10% (Table 3).

Pulsed laser irradiation of manganese-doped PCM results in the redistribution of electrons between their different states. Some of the electrons move from the g = 3.9 to the g = 6.0 state, i.e., their mobility increases. Thus, laser irradiation reduces the potential barriers that prevent the transition of electrons from one state to another. These data correlate with the results of studies of manganese-doped PCM by the method of small-angle X-ray scattering, which indicate structural transformations that occur under laser irradiation.

To evaluate the reliability of this assumption, acid titration of manganese-modified PCM before and after
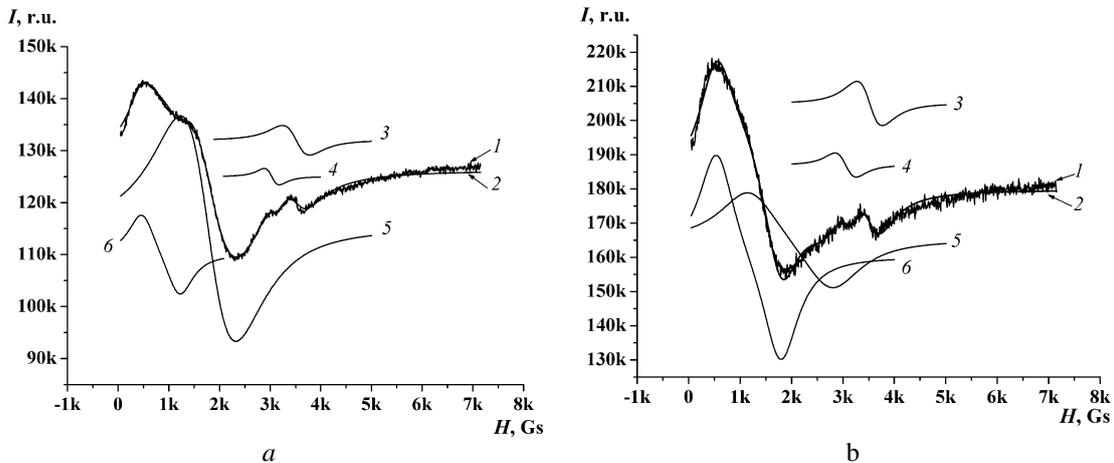

Fig. 3. EPR spectra for Mn-modified PCM before (a) and after (b) irradiation with laser pulses:
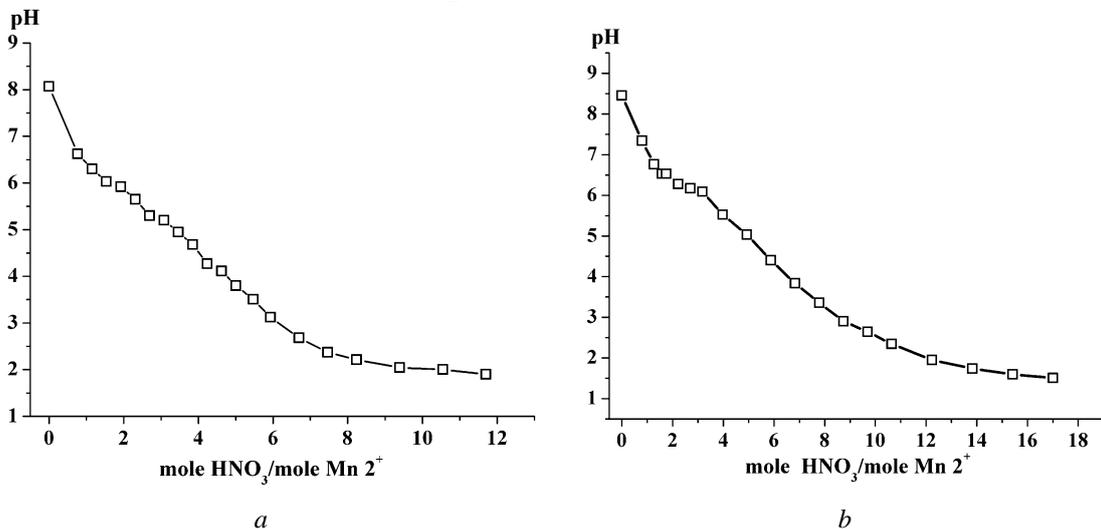1 - experimental, 2 - modeling result, 3 - Mn^{2+}, 4,5,6 - collectivized electrons.

Fig. 4. Titration of PCM modified with Mn before (a) and after (b) laser irradiation
with 0.1 molar solution of HNO_3.

laser irradiation was performed. The titration, as in the case of the initial PVM (Fig. 4), is of a stepwise nature. For manganese-doped PVM, titration occurs in three stages, which indicates the existence of three types of functional groups that can be titrated (Fig. 4, a). However, after laser irradiation, the number of stages and, accordingly, the types of functional groups decrease (Fig. 4, b).

At the same time, the state of manganese practically does not change. Therefore, it can be assumed that the role of manganese is reduced to the participation of its localization centers in the processes of generating collectivized electrons and changing their state.

A similar situation is observed when PCM is doped with chromium ions. The fraction of the integrated intensity of the Cr^{3+} signal in the total intensity of the spectrum of all unpaired electrons in the EPR system is less than 1 % (Fig. 5,a). Laser irradiation transfers all collectivized electrons to one state, which is characterized by a signal in the EPR spectrum with parameters g = 2.09, ΔH = 675 A/m (Table 3).

However, in comparison to the manganese-doped sample, these parameters of the EPR spectra indicate a

decrease in electron mobility.

The analysis of the EPR line shape of laser-irradiated chromium-doped PCM shows that the actually observed signal is a superposition of signals dominating in the system of delocalized electrons and unpaired Cr^{3+} electrons, whose content is 0.1 % (Fig. 5, b).

In the EPR spectra of iron-containing samples irradiated by laser pulses (Fig. 6, a), lines of collectivized electrons are observed, the concentration of which is of the same order as the Fe^{3+} content, which is identified in three forms with different chromophores Fe_5O', Fe_5O, Fe_6O. It is known [7] that iron ions in the Fe_5O chromophore and in the modified $Fe5O'$ chromophore are chemically active, and therefore the environmental parameters are unstable in time. Indeed, the analysis of the EPR spectrum of this sample a year after irradiation showed that the dominant chromophore of Fe^{+3} ions is Fe_6O, which is most stable in a chemically active environment (H_2O, CO_2, O_2) (Fig. 6,b).

Analyzing the data of chemical titration of PCM doped with 20% Fe irradiated by laser (Fig. 7), the formation of compounds with a strongly pronounced acidic function was revealed, which is explained by the
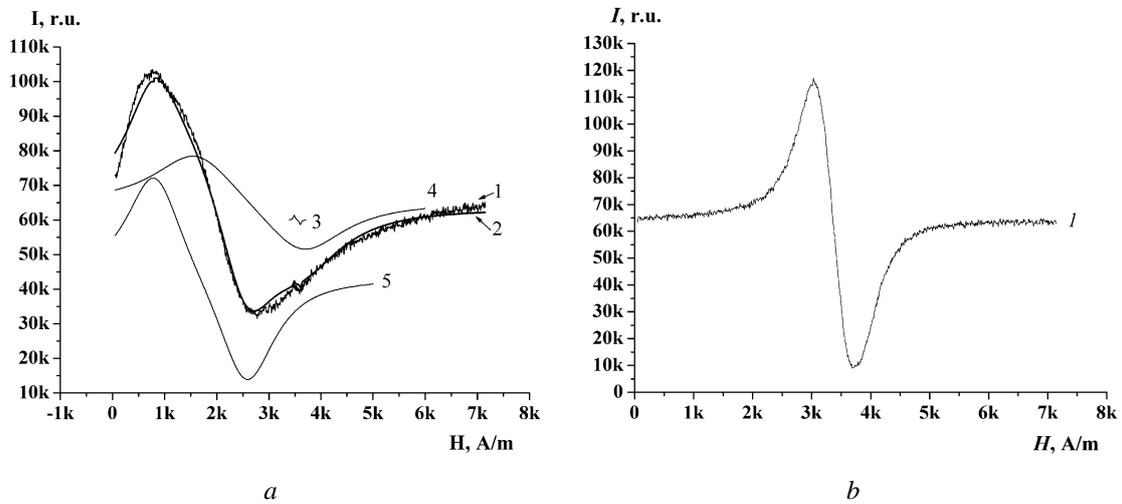

a   *b*

Fig. 5. EPR spectra for Cr-modified PVM before (a) and after (b) irradiation with laser pulses:
1 – experimental, 2 – modeling result, 3 – Cr^{3+}, 4, 5, – collectivized electron.
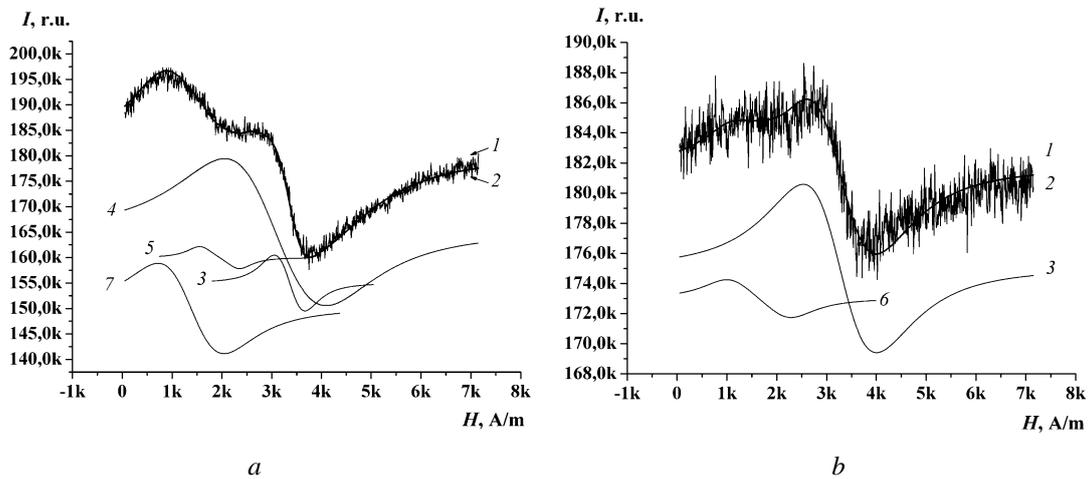

a   *b*

Fig. 6. EPR spectra of PCMs of modified Fe
irradiated by laser pulses (a) and irradiated by laser pulses after aging for 1 year (b):
1 – experimental, 2 – modeling result, 3 – Fe_6O, 4 – Fe_5O, 5 – Fe_5O', 6 – Fe_6O, 7 – collectivized electrons.

photocatalytic oxidation of fractal structures of the carbon matrix. The process of titration of these compositions is similar to the alkaline titration of the initial PCM matrix after neutralization of acidic groups.
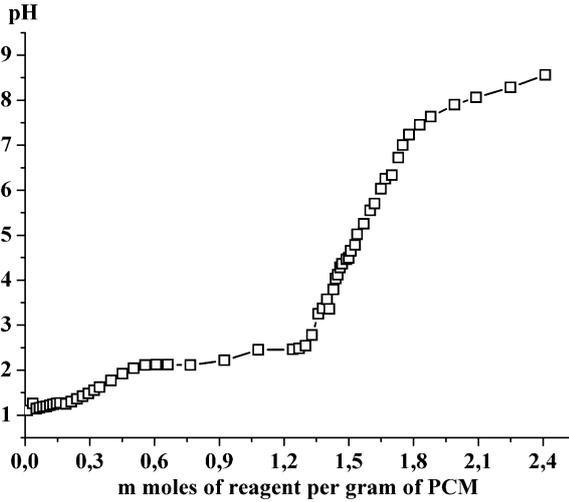

Fig. 7. Titration of PCM matrix modified with 20% Fe after laser irradiation with 0.15 molar NaOH solution.

The changes in the charge state and near-field characteristics of iron ions introduced into the PVM matrix initiated by laser irradiation were studied by Mössbauer spectroscopy (Fig. 8). The Mössbauer spectrum of PVM doped with 20% Fe^{57} (Fig. 8, a) consists of two quadrupole doublets. The values of their isomeric shifts are $I_{S1} = 0.394$ mm/s and $I_{S2} = 0.385$ mm/s, respectively, and the values of quadrupole splitting are $Q_{S1} = 0.98$ mm/s and $Q_{S2} = 0.55$ mm/s, respectively. This indicates the presence of Fe^{57} nuclei in the PCM as part of the chemical compounds $FeO_n \cdot H_2O$ and β-FeOOH or the existence of Fe^{3+} in an unstable ionized state. The presence of Fe^{3+} ions in the free state in this material is improbable since the final stage of synthesis was calcination at a temperature of 300 °C for 1 hour. The doublets with parameters ($I_{S2} = 0.385$ mm/s, $Q_{S2} = 0.55$ mm/s) can be interpreted as the result of resonant absorption of γ quanta by Fe^{57} nuclei in the β-FeOOH compound. The doublet with the parameters ($I_{S1} = 0.394$ mm/s, $Q_{S1} = 0.98$ mm/s) is characterized by relatively higher values of quadrupole splitting, which indicates the presence of oxygen ligands for iron ions - the formation of octa- and tetra-complexes with redistribution of electron density between Fe and O nuclei and, accordingly, changes in the degree of covalence of the chemical bond from Fe^{3+} to Fe^{2+} in the $FeO_n \cdot H_2O$ compound. The existence of numerous free OH^- groups in these materials makes it impossible to accurately separate the contributions of octa- and tetra-complexes due to the distorted electrical quadrupole interactions.

Under pulsed laser irradiation of this PCM, changes occur in the near environment and the nature of
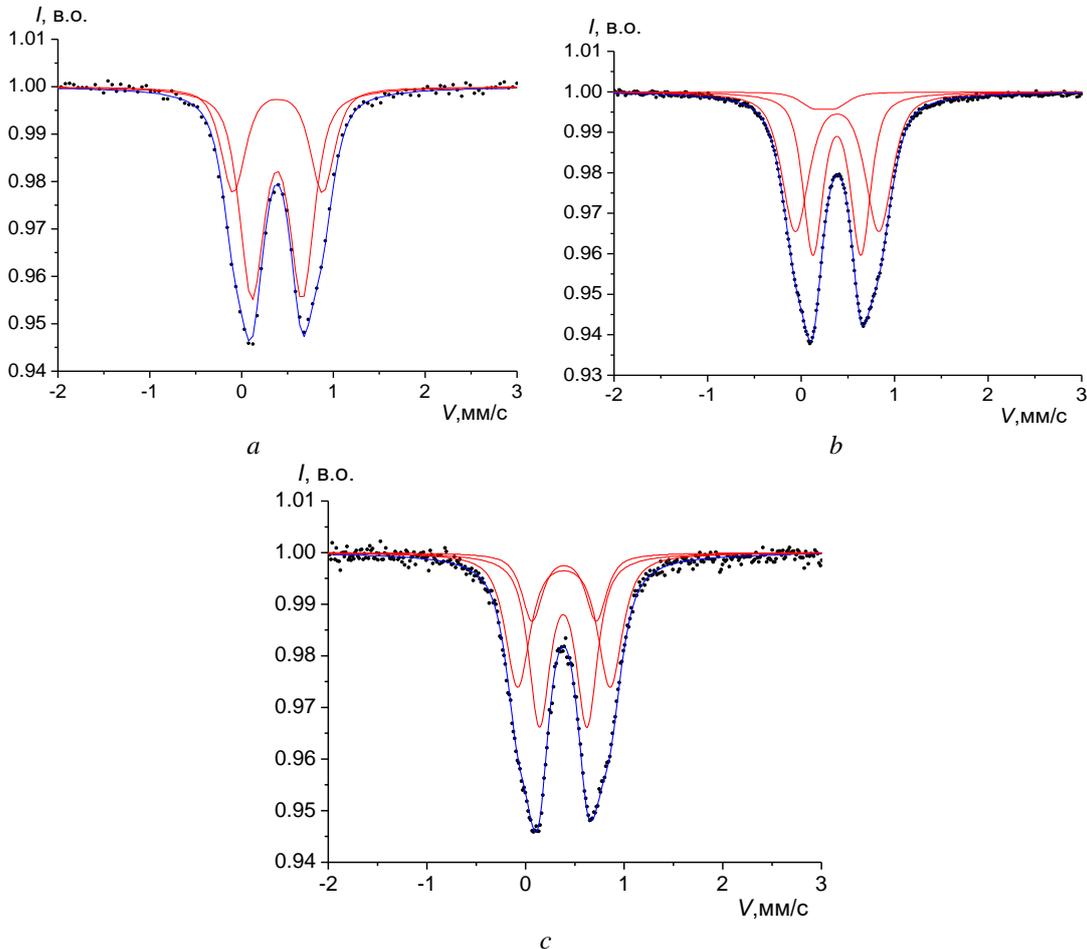

a

b

c

Fig. 8. Mössbauer spectrum of PCM and its interpretation using the Univem 7.02 program:
a – PCM doped with 20% iron, b – PCM doped with 20% iron and laser irradiated,
c – PCM doped with 20% iron and laser irradiated after aging for a year.

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interactions with it for the resonant Fe^{57} nuclei, which is reflected in the spectrum (Fig. 8, b), which is the superposition of three quadrupole doublet. The doublets with parameters $I_{S1} = 0.385$ mm/s, $Q_{S1} = 0.89$ mm/s and $I_{S2} = 0.383$ mm/s, $Q_{S2} = 0.51$ mm/s are interpreted as the result of the resonance of Fe^{57} nuclei of octa- and tetra-complexes of Fe^{3+} in $FeOn*H_2O$ and b-FeOOH compounds, respectively. The doublet with the parameters $I_{S3} = 0.248$ mm/s, $Q_{S3} = 0.25$ mm/s corresponds to the presence of Fe^{3+} ions in the sample as part of the $Fe(H_2O)_6$ complex. This aqua complex can be localized in pores with a diameter of 3-5 nm. The mechanism of formation of the $Fe(H_2O)_6$ complex under laser irradiation requires further study. The ionizing effect of laser irradiation is demonstrated by a decrease in the parameters of the spectral components, namely the doublet corresponding to Fe^{3+} octa- and tetracomplexes in $FeOn*H_2O$ and b-FeOOH compounds (Fig. 8, a).

This indicates a shift in the valence degree of iron ions to the Fe^{3+} state. Laser irradiation also leads to a redistribution of the relative content of $FeO_n \cdot H_2O$ and b-FeOOH compounds from a ratio of 34%/66% in the initial sample to 51%/44% and 4% Fe^{3+} in the aqua complex after irradiation.

The Mössbauer spectrum of the irradiated PCM aged for a year (Fig. 8, c) also consists of three quadrupole doublets. The doublets with parameters $I_{S1} = 0.389$ mm/s, $Q_{S1} = 0.94$ mm/s and $I_{S2} = 0.392$ mm/s, $Q_{S2} = 0.65$ mm/s can be interpreted similarly to the initial spectrum (Fig. 8, a) as the result of the resonance of the nuclei of Fe^{57} octa- and tetra- complexes of Fe^{3+} in $FeO_n \cdot H_2O$ and b-FeOOH compounds, respectively. The doublet with the parameters $I_{S3} = 0.382$ mm/s, $Q_{S3} = 0.48$ mm/s can also be assigned to the compound b-FeOOH, which is formed as a result of the decomposition of the $Fe(H_2O)_6$ aqua complex.

After aging for 1 year, as a result of adsorption of additional OH⁻ groups from the air by the initial material, additional shared electrons appear, and, as a result, the valence of iron ions in $FeO_n \cdot H_2O$ and b-FeOOH compounds shifts towards Fe^{2+}, as indicated by an increase in the values of isomeric shifts and quadrupole splits of all Mössbauer doublet. The exposure time also leads to a leveling off of the laser processing effect - the parameters of the Mössbauer spectra and phase content are practically restored.

The absence of Zeeman sextets in the obtained spectra indicates that chemical doping with iron ions and laser irradiation does not lead to the formation of iron carbides, i.e., iron ions do not penetrate the structure of carbon grains. Instead, the formation of $FeO_n \cdot H_2O$ and b-FeOOH compounds, as evidenced by the quantitative characteristics of quadrupole doublet, indicates that iron

remains bound on the surface of carbon grain pores by unstable hydrogen bonds through OH adsorption centers.

Acknowledgement

Conclusions

1. It was found that the doping of porous carbon material with metals with a high density of electronic states (Mn, Cr, Fe) leads to the appearance of three types of paramagnetic centers, as indicated by the spectra of electronic paramagnetic resonance. At the same time, there are no traces of other elements in these spectra.

2. It has been shown that under pulsed laser irradiation of manganese-doped PCM, electrons are redistributed between their different states. Part of the electrons transfers from the state with g = 3.9 to the state with g = 6.0, i.e., their mobility increases. Thus, laser irradiation reduces the potential barriers that prevent the transition of electrons from one state to another. These data correlate with the results of studies of manganese-doped PCM by the method of small-angle X-ray scattering, which indicate structural transformations occurring under laser irradiation.

3. By the method of Mössbauer spectroscopy, the EPR spectra of iron-containing laser-irradiated samples revealed lines of collectivized electrons, the concentration of which is of the same order of magnitude as the Fe^{3+} content, which is identified in three forms with different chromophores Fe_5O', Fe_5O, Fe_6O. Indeed, from the analysis of the EPR spectra of these samples, it was found that the dominant chromophore of Fe^{+3} ions is Fe_6O, which is the most stable in a chemically active environment (H_2O, CO_2, O_2).

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[1] I.M. Budzulyak, B.I. Rachiy, V.O. Kotsyubynsky, L.S. Yablon, O.V. Morushko, Synthesis, structure and electrochemical properties of nanoporous carbon material and composites based on it. Ivano-Frankivsk, 2021.

[2] V.I. Mandziuk, R.P. Lisovskiy, N.I Nahirna, B.I. Rachiy, *Structure of porous carbon materials according to the nitrogen adsorption/desorption method*, Physical engineering of the surface, 11(1), 112 (2013).

[3] Budzulyak I.M., Berkeschuk M.V., Popovych D.I. and other. VIth International Conference ["Ion Implantation and Other Applications of Ions and Electrons (ION2006)"], (Kazimierz Dolny, Poland, 2006). pp. 112–113.

[4] B.K. Ostafiychuk, I.M. Budzulyak, N.Ya. Ivanichok, R.P. Lisovskiy, B.I. Rachiy, *The Effect of Thermal Modification on Development of Carbon Materials Microporous Structure*, Physics and Chemistry of Solid State 14(4), 891 (2013).

[5] V.O. Kotsyubynsky, V.M. Boychuk, R.I. Zapukhlyak, M.A. Hodlevskyi, I.M. Budzulyak, A.I. Kachmar, , M.A. Hodlevska, L.V. Turovska, *Electrophysical and Morphological Properties of a Hydrothermally Synthesized CuFe2O4 and CuFe2O4 / Reduced Graphene OxideComposite,* Physics and Chemistry of Solid State 22 (2), 372 (2021); https://doi.org/10.15330/pcss.22.2.372-379.

[6] Y. Starchuk, N. Ivanichok, I. Budzulyak, S.V. Sklepova, O. Popovych, P. Kolkovskyi, & B. Rachiy, *Electrochemical properties of nanoporous carbon material subjected to multiple chemical activation*, Fullerenes, Nanotubes and Carbon Nanostructures, 30(9), 936 (2022); https://doi.org/10.1080/1536383X.2022.2043285.

[7] Gulaim A. Seisenbaeva, Suresh Gohil, Evgeniya V. Suslova, The synthesis of iron (III) ethoxide revisited: Characterization of the metathesis products of iron (III) halides and sodium ethoxide, Inorganica Chimica Acta, 358(12), 3506 (2005); https://doi.org/10.1016/j.ica.2005.03.048.

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Енергетичний стан електронної підсистеми пористого вуглецевого матеріалу, ініційований лазерним опроміненням

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Методом електронного парамагнітного резонансу проведено дослідження змін в електронній підсистемі пористого вуглецевого матеріалу, обумовлені його легуванням Mn, Cr та Fe і лазерним опроміненням. Встановлено, що легування Mn призводить до появи де-кількох парамагнітних центрів, а лазерне опромінення сприяє перерозподілу електронів між різними станами так, що зростає їх рухливість внаслідок переходу із стану $g = 3,9$ у стан $g = 6,0$. Мессбауерівська спектроскопія пористого вуглецевого матеріалу, легованого Fe, свідчить про наявність кисневих лігандів для йонів заліза – формування окта-тетра-комплексів з перерозподілом електронної густини між ядрами заліза і кисню, а, відповідно, змінами ступеня ковалентності хімічного зв'язку від Fe^{3+} до Fe^{2+}.

Ключові слова: електронний парамагнітний резонанс, пористий вуглецевий матеріал, порометрія, мессбауерівська спектроскопія.