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Stimulation of the metal doping process of nanoporous carbon material by laser irradiation

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It has been established that the doping of activated carbon material with chromium and manganese increases the specific capacitance of storage devices based on the charge-discharge mechanism of a double electric layer (DEL) by ~70 % and leads to a decrease in their internal resistance by 30-35 %. The main reason for this rise is the transformation of the electron energy spectrum due to an increase in the density of electronic states, as a result of which a much larger number of electrolyte ions (primarily positive ones) participate in the formation of DEL and cause an increase in the specific capacitance of these devices. It has been shown that laser irradiation stimulates the metal penetration into the bulk of carbon material.

Keywords: nanoporous carbon material, doping, chromium, manganese, laser irradiation.

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Introduction

Traditional electrochemical energy storage devices (supercapacitors), whose specific capacitance can reach ~200 F/g when using aqueous electrolytes, operate on the principle of charge/discharge of the DEL, which is formed at the electrode/electrolyte interface.

The main factors influencing the increase in the specific characteristics of DEL are the higher density of electronic states due to changes in the Fermi level of the surface layers of activated carbon and the involvement of as much of the developed surface as possible in charge/discharge processes. One of the possibilities to influence the properties of porous carbon material (PCM) for these purposes is to incorporate metals with a high density of electronic states into its matrix [1, 2].

The use of porous carbon material is due to the fact that, in addition to being low-cost and accessible, PCM is relatively easy to modify, which can be used to control not only the amount of the developed surface, but also its state, pore size distribution, conductivity, etc., which are important for its application.

However, the specific capacitance of the DEL formed by the PCM and electrolyte does not always satisfy the

requirements for the appropriate charge storage devices, due to the fact that PCM, being a semiconductor, contains a low concentration of free charge carriers (electrons) compared to metals.

One of the solutions to this problem is to increase the density of electronic states in the PCM matrix. This idea can be realized by modifying the PCM by doping it with metals with a high density of electronic states, which makes it possible to significantly increase the capacitance of DEL, and, accordingly, of capacitors formed on the basis of PCM modified in this way.

I. Experimental, discussion of the results

An important characteristic of an electronic system is the density of states, i.e., the number of states in a unit energy interval. Since electrons are governed by the Pauli principle, the density of states determines the maximum number of electrons that can be accommodated in a certain energy range.

Considering the fact that the choice of electrolyte concentration is determined by its maximum conductivity,

it is possible to increase the amount of accumulated charge of DEL by increasing the density of electronic states near the Fermi level in the electrode material. Thus, the aim was to purposefully increase the electron density of the valence band of activated carbon by doping. The study [3] shows that 3d transition metals and rare earth elements have the highest density of electronic states near the Fermi level. We focused on 3d transition elements Mn and Cr.

Fig. 1 (a) shows the valence band spectrum of the non-doped activated carbon material, which demonstrates that it has a double-hump structure with a significant decrease in intensity when the binding energy approaches the Fermi level.

When doped with manganese, the appearance of the valence band changes significantly (Fig. 1(b)). It becomes almost single-humped with a significant increase in intensity at the Fermi level.

The results obtained indicate that the doping of PCM with manganese most significantly affects the intensity of its valence band spectra at the Fermi level, and, accordingly, the electronic density, which is displayed in the value of the specific capacitance. In particular, the specific capacitance of ECs based on manganese-doped PCM is ~ 65 % higher than the similar capacitance of ECs formed from non-doped PCM.

The change in the intensity of the valence band spectra of non-doped HFM is also significantly affected by various technological treatments (thermal, chemical, etc.). However, in this case, the spectral pattern of the band remains practically the same (Fig. 2). Obviously, in order to improve the performance parameters of ECs, it is necessary to apply the established procedures in a complex manner.

In the two-dimensional (2D) structure, which is

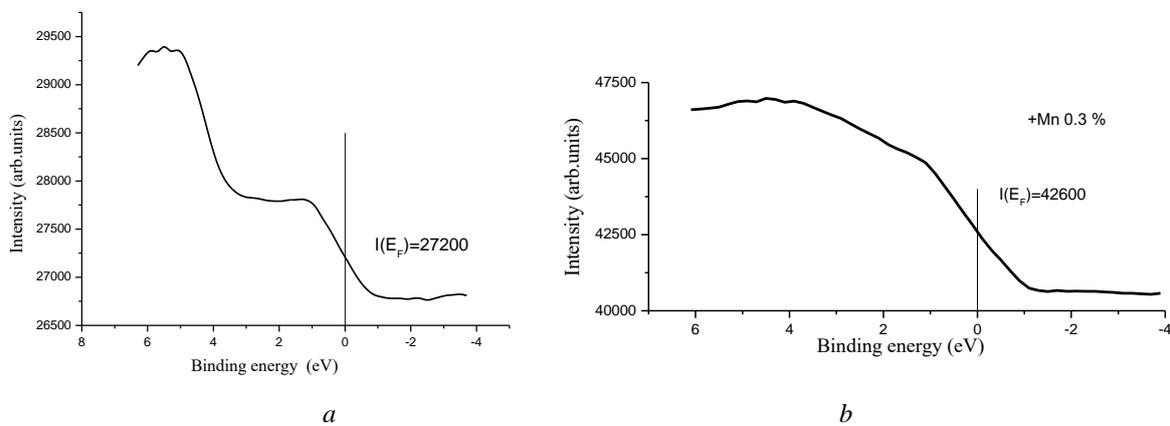


Fig.1. Valence band spectrum of PCM: *a* - non-doped PCM; *b* - PCM doped with manganese.

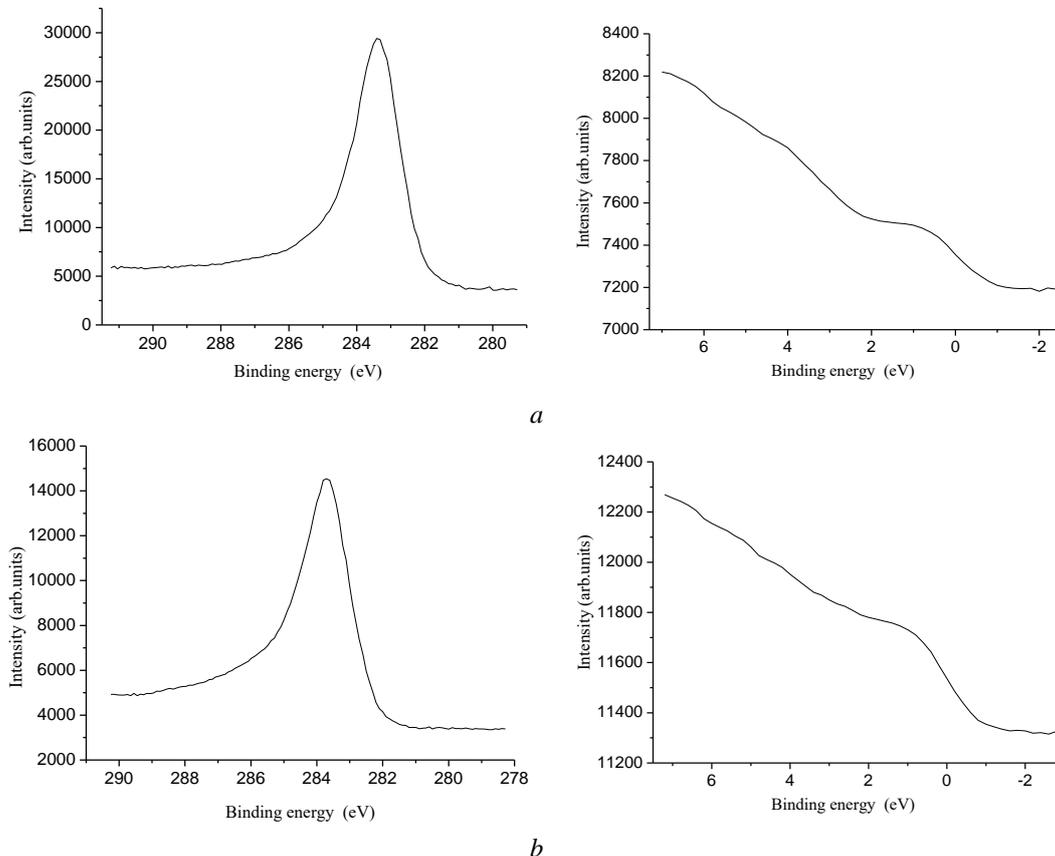


Fig.2. Intensity of the valence band spectra: *a* - carbonized PCM; *b* - carbonized and heat-treated PCM.

typical for our case, when the large area of the developed surface is of major importance, for each quantum level with energy E_i the total number of states

$$Z(E) = \frac{m_e(E-E_i)S}{(2\pi k)^2},$$

where S – is the sample area.

The state density, which in this case is calculated per unit area, is determined by the sum of the numbers of all levels whose energies E_i are lower than E [4]:

$$D_{2D}(E) = \frac{2}{S} \sum_i \frac{dZ(E_i)}{dE}.$$

The PCM was chemically doped with chromium by reducing it from an aqueous solution of $\text{Cr}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$. For this purpose, a weight of salt dissolved in distilled water was mixed with PCM to a homogeneous mixture, hydrochloric acid was added to create an acidic environment in which to carry out the reduction, and finely dispersed zinc was added. The resulting precipitate was dissolved in water in appropriate ratios, mixed with PCM, and dried at 140°C to a constant weight. KMnO_4 was used as a manganese doping agent, where Mn has the highest oxidation degree, which is 7^+ . For this, ethanol was added to a 5% solution of KMnO_4 and, after the reaction was completed, HNO_3 was added and heated to a temperature of 80°C . The resulting precipitate was washed with water deionization until NO_3^- ions were removed, and dried to a constant weight at room temperature. After that, the precipitate was dissolved in water in appropriate ratios, mixed with PVM and dried at 140°C to a constant weight.

The influence of injected metals on the behavior of electrochemical capacitor systems formed on the basis of PCM + metal was studied by impedance spectroscopy. The dependence of the specific capacitance of the doped PCM on the content of chromium and manganese is shown in Fig. 3.

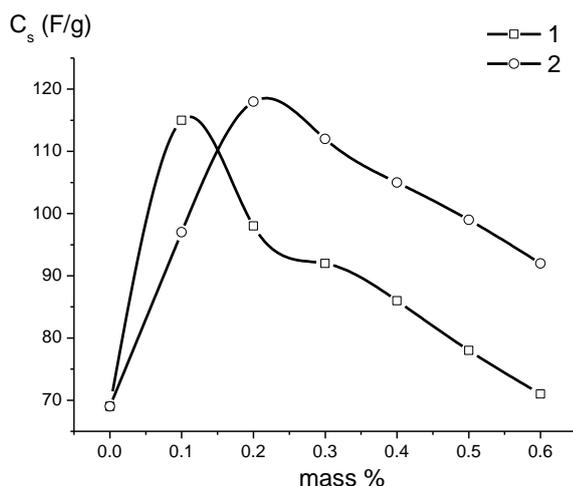


Fig.3. Dependence of the specific capacitance of PCM on the content of chromium (1) and manganese (2).

To obtain the Nyquist diagrams, a three-electrode electrochemical cell was used (Fig. 4), in which PCM with the appropriate content of chromium or manganese was used as the working electrode. The impedance

measurements were performed using an Autolab PGSTAT / FRA-2 spectrometer (Netherlands) in the frequency range $10^{-2} - 10^5$ Hz.

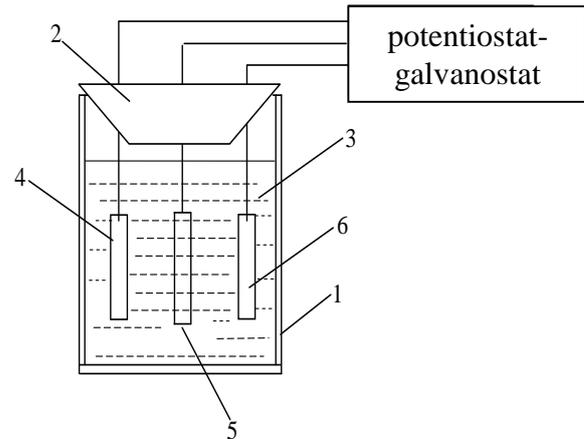


Fig.4. Electrochemical cell: 1 - glass cell; 2 - sealing lid; 3 - electrolyte; 4 - working electrode; 5 - reference electrode; 6 auxiliary electrode.

Cyclic voltammograms of carbon material electrodes were obtained in the potential range of $-1 \div 0.2$ V using the above three-electrode cell with a chlorine-silver reference electrode; the scan rate was 5, 8, 10, 20, 30, 40, and 50 mV/s, respectively.

The impedance curves obtained at potentials of $-1 \div 0.2$ V (in this case, the potential difference between the working electrode and the reference electrode) and the automatic calculation of the parameters of the equivalent circuit (primarily, the capacitance) made it possible to plot the volt-faradic dependencies for the studied activated carbon material with different dopant concentrations (Fig. 5, a, b). The criterion for selecting the interval of applied potentials is to change the parameters of the equivalent circuit by no more than 10%. In addition, in the negative potential region, the maximum of the curve $C = f(E)$ is also one of the factors in choosing the applied potential.

As follows from these dependencies, an increase in the percentage of manganese leads to both an increase in the specific capacitance of the active material and a certain symmetry of the $C-U$ dependencies, i.e., the penetration of manganese into the nanoporous carbon material allows for the grafting of OH-groups of the solvent in the positive potential region, resulting in an increase in the capacitance in the positive potential region. When chromium is incorporated, on the $C = f(U)$ dependence, chromium doping does not align both branches of the $C-U$ dependence, resulting in a capacitance of such materials in the positive potential region that is even lower than that of pure PCM.

Fig. 5 shows the DEL capacitance at the electrode-electrolyte interface, so the mismatch of both curves in the positive potential region indicates an additional contribution to the total capacitance, pseudocapacitance due to Faraday processes involving functional groups (e.g., $\text{COOH} > \text{C} = \text{H}, \text{OH}$). It is known [5-7] that the existence of functional groups can affect the capacitance of ECs, both due to the possible occurrence of redox Faraday reactions involving these groups and due to changes in the specific capacitance by the specific value

Table 1.

Specific capacitance of PCM (F/g) in aqueous electrolyte (30% KOH solution in water)

Material	Method of research		
	impedance spectroscopy	voltammetry	chronoamperometry
PCM	156	164	169
PCM + 0,2 % Cr	204	206	215
PCM + 0,3 % Cr	185	188	194
PCM + 0,4 % Cr	180	185	190
PCM + 0,2 % Mn	188	191	197
PCM + 0,3 % Mn	205	210	218
PCM + 0,4 % Mn	200	205	212

of the interfacial surface.

A characteristic feature of the process of chemical modification of PCM with the above metals is that chromium and manganese significantly reduce the value of the Warburg diffusion impedance W (Fig. 6) compared to the unmodified material. Due to the fact that for all samples there is a general tendency to decrease W when the potential changes to the negative region, this parameter can be associated with diffusion processes involving K^+ ions in the carbon matrix [8, 9].

From the results obtained, it follows that an increase in the percentage of chromium increases the specific capacitance of PCM compared to pure PCM. The material with 0.2% Cr content by weight has the highest capacitance; further increase in Cr content leads to a decrease in capacitance. Most probably, this fact is associated with a decrease in the specific surface area of the carbon material due to the blocking of pores by chromium ions, as a result of which less potassium ions are involved in the formation of DEL.

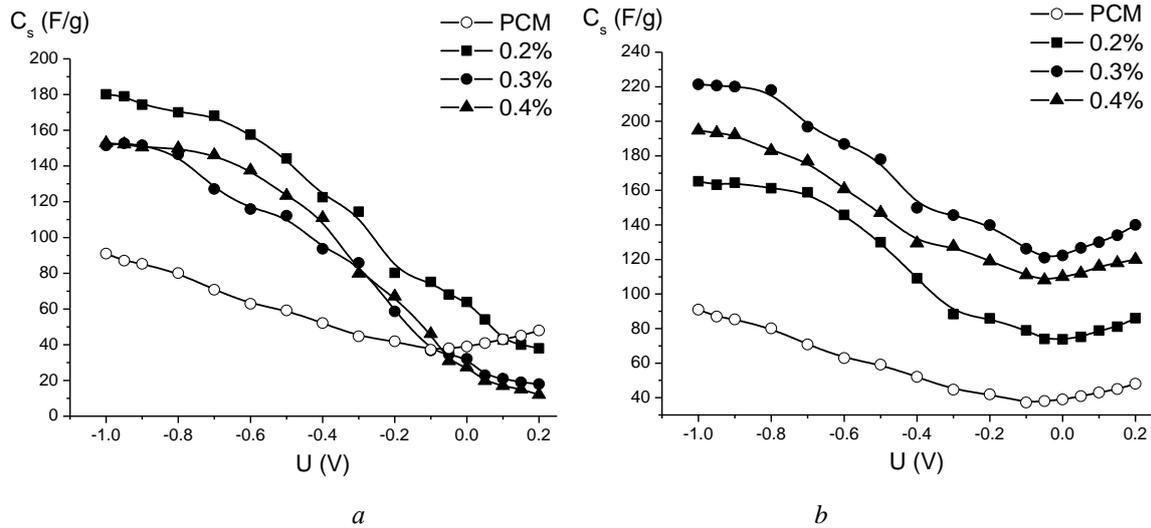


Fig.5. Volt-faradic dependences for PCM with different percentage of: a - chromium; b – manganese.

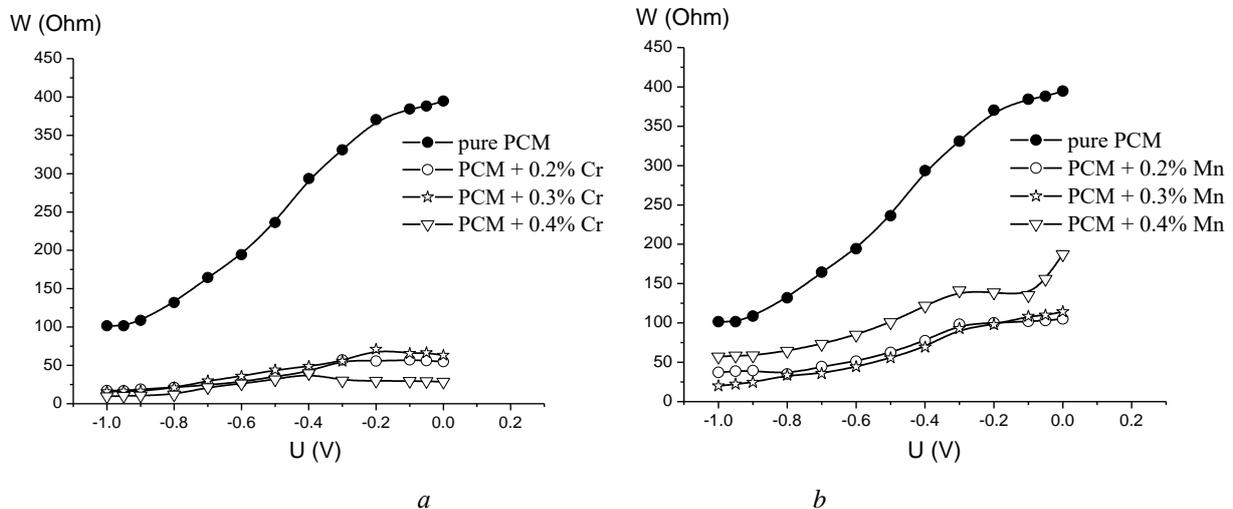


Fig.6. Dependence of Warburg impedance on the applied potential for PCM with different percentage of chromium (a) and manganese (b).

The implementation of manganese also leads to an increase in the specific capacitance. However, the dependence of the last one on the scan rate, in comparison to Cr-doped PCM, is non-monotonic with respect to the percentage of Mn ions (Table 1).

Thus, the chemical modification of PCM with chromium and manganese leads to an increase in the specific capacitance of PCM [1, 10, 11]. The main reason for this increase, according to previous studies, is the transformation of the valence band of the carbon material due to the introduction of additional electronic states from the incorporated metals, as a result of which a much larger number of ions participate in the formation of the DEL, and thus causes an increase in the specific capacitance.

However, the doping technique does not provide metal localization on the surface of the PCM. As a result, during repeated cycling of electrochemical capacitors, metal atoms are removed by the electrolyte and the EC parameters become worse. In order to prevent this phenomenon, we carried out additional treatment of the doped PCM by irradiation with a neodymium laser operating in a pulsed mode.

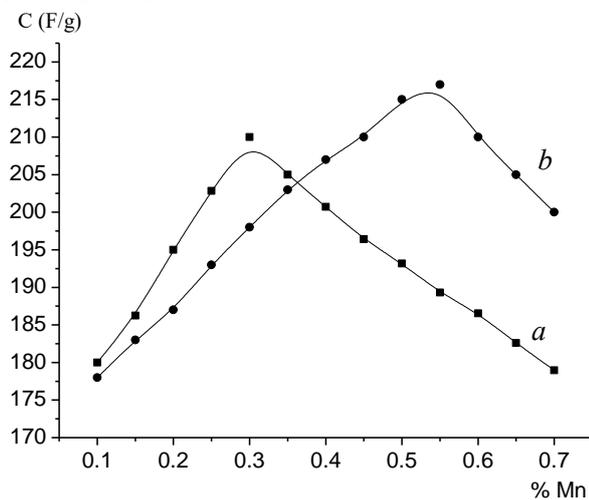


Fig.7. Dependence of the specific capacitance of the electrolyte/Mn-doped PCM system on the amount of manganese introduced before (a) and after (b) laser irradiation.

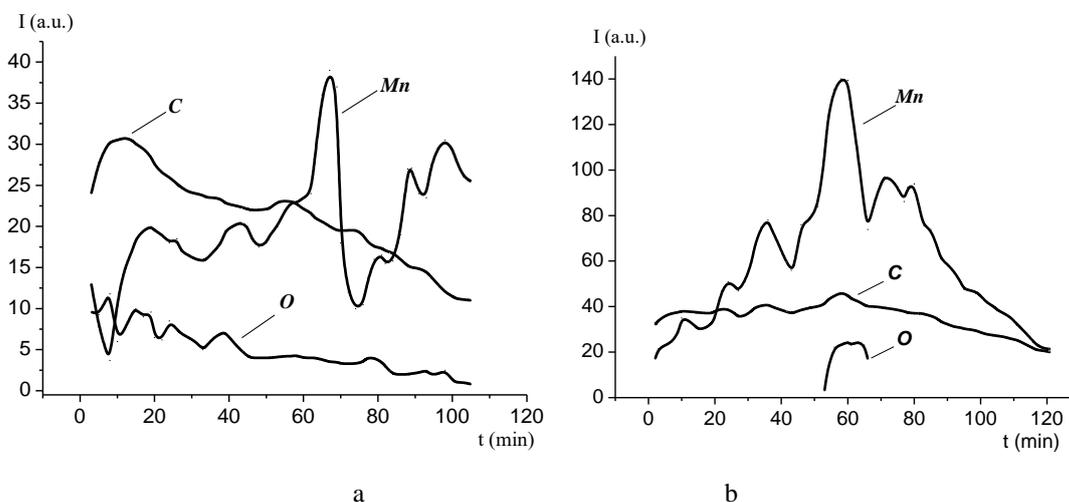


Fig.8. Depth distribution profile of C, O, Mn elements of manganese-doped PCM depending on the etching time t for non-irradiated (a) and irradiated (b) samples.

Laser irradiation leads to a reduction in the size of such fragmentary formations in the PCM matrix, which makes it possible to doping with more metal without blocking the pores of the developed PCM surface. As a result of irradiation with laser pulses, the maximum specific capacitance is shifted toward higher metal fractions (Fig. 7, b).

The decrease in the size of the "metallic" fragments should obviously be accompanied by a certain decrease in the electron density at the Fermi level.

The distribution of individual elements in the depth of the sample was determined for three types of samples in which chromium and manganese were incorporated. Fig. 8 shows a typical profile of element distribution in the samples of PCM doped with manganese to the level of 0.5 wt. %.

In Fig. 8, the etching time is proportional to the etching depth, and the shape of the obtained dependence at the qualitative level reflects the concentration distribution of elements by thickness in the near-surface region.

Due to the etching speed, the surface layers with a thickness of no more than 50-100 nm are available for analysis with an analysis time of about 7200 s.

As can be seen from Fig. 8, a, the distribution of manganese over the depth of the sample is quite irregular. An increase in the amount of manganese introduced above 0.5 wt. % leads to the fact that the signal intensity from manganese becomes greater than the signal intensity of carbon and oxygen. Therefore, we do not present the other profiles, although they, similarly to the profile in Fig. 8, a, there is an uneven distribution of manganese.

Laser irradiation ($E = 0.1 \text{ J/cm}^2$, $\tau = 15 \text{ ns}$, pulse repetition rate $f = 56 \text{ Hz}$, irradiation time 180 s) leads to a significant redistribution of the analyzed elements along the depth of the sample (Fig. 8, b). In particular, the depth h_m , which corresponds to the main maximum of the manganese distribution profile, practically does not change when the sample is irradiated. At the same time, manganese atoms both from the near-surface region $x < h_m$ and from a depth greater than h_m are concentrated in the neighborhood of h_m . In addition, laser irradiation leads to

a slight appearance of oxygen compared to the non-irradiated sample, and then only in the region of the maximum intensity of the manganese peak, which may be due to the formation of Mn_xO_y oxide [12].

As for samples of chromium-doped nanoporous carbon, studies by other methods have shown that the dielectric constant in such samples increases several times, which leads to an increase in the background of the useful mass spectrum signal as a result of electrification of the sample surface. Therefore, it was impossible to obtain high-quality mass spectra of laser-irradiated samples with a chromium content exceeding 0.1 wt. %.

Conclusions

1. The optimal method for producing carbon electrode material for electrochemical capacitors from plant-based raw materials (fruit pits) is hydrothermal treatment at high pressure $(6 \div 8) \cdot 10^5$ Pa. Additional thermal vacuum annealing of the resulting activated carbon at a temperature of 723-743 K in a chamber with a residual pressure of no more than 1.33 Pa for 60-70 minutes increases the specific capacitance of the corresponding capacitors by 10-15 % due to the desorption of uncontrolled impurities from the formed pores.

2. The total capacitance of the non-doped PCM/electrolyte system is a component of two capacitances - the PES capacitance (94 - 97 %) and the pseudocapacitance (6 - 3 %). The increase in the specific

capacitance of electrochemical capacitors based on chemically modified activated carbon is due to an increase in the contribution of these components by 88 - 92 % and 12 - 8 %, respectively. On the basis of doped activated carbon material, laboratory samples of ECs were formed in 2525-size cases, the maximum specific capacitance of which is 150 F/g for aqueous electrolyte (30% solution of KOH in water).

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Стимуляція процесу легування металами нанопористого вуглецевого матеріалу лазерним опроміненням

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Встановлено, що легування активованого вуглецевого матеріалу хромом і марганцем збільшує питому ємність пристроїв накопичення заряду, що працюють за принципом заряду-розряду подвійного електричного шару (ПЕШ), на ~70 % та призводить до зменшення їх внутрішнього опору на 30-35 %. Основною причиною такого зростання є трансформація енергетичного спектру електронів за рахунок збільшення густини електронних станів, в результаті чого значно більша кількість іонів електроліту (насамперед, позитивних) приймає участь у формуванні ПЕШ і зумовлює ріст питомої ємності даних пристроїв. Показано, що лазерне опромінення стимулює проникнення металів у об'єм вуглецевого матеріалу.

Ключові слова: нанопористий вуглецевий матеріал, легування, хром, марганець, лазерне опромінення.