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Structural Properties of Porous Carbon Material Formation Activated with Potassium Hydroxide

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The paper is devoted to the study of the influence of chemical and thermal activation on the structure of carbon materials. The main parameters of the specific surface area, namely the overall area of the surface, the total volume and the mean radius of pores are determined by the methods of low-temperature porosimetry and small-angle X-ray spectroscopy. It is established that the carbon material carbonized at 300 ºC and treated with potassium hydroxide at the mass ratio of 1:4 demonstrates the largest surface area of 1608 m^2/g and is characterized by a highly developed microporous surface. The increase of the carbonization temperature up to 400 °C causes a slight reduction of the surface area which is associated with an increase in pore volume compared with a change in their surface area at the fourfold content of KOH. The reason is a rise in the number of micropores with radii of 8-10 Å and an insignificant number of mesopores with a radius of ~25 Å. The greatest value of the specific area (1255 m^2/g) is achieved at KOH/carbon ratio of 1:3.

Keywords: Porous carbon material, Chemical activation, Small-angle X-ray spectroscopy, Specific surface area.

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1. INTRODUCTION

One of the main ways of improving the existing and creating new electrochemical technologies is the development of new electrode materials, which have relatively high electrical conductivity, large specific surface area (SSA) and low chemical activity of the surface [1]. Recent world achievements show that nowadays the greatest attention is paid to high-porous conductive ceramics, metal oxides and polymer materials [2]. However, traditional raw materials for the production of high-quality porous carbon material (PCM) are solid wood, industrial wastes (fruit pits, nutshells) which are characterized by high carbon content and natural micro- and mesoporosity. Due to this, these materials are widely used as electrodes for chemical current sources, supercapacitors and carbon sorbents [3-6].

High-temperature treatment (up to 2000 °C) of carbon precursors in an inert atmosphere (so-called carbonization) and the subsequent oxidation of carbonates at high temperatures by various chemical activators is one of the main methods of obtaining PCM. Because of the part burnout of carbon, there is an increase of the existing pores and development of new ones, the bonding of several small pores into one, the change of surface and volume [7]. Chemical activation involves two stages: impregnation with chemical activators (H_3PO_4, KOH, NaOH) and subsequent heating in the temperature range of 450-900 °C [8-9]. Carbonization and activation proceed simultaneously and this method allows obtaining materials with large specific volume and wide pore size distribution. Transformation and modification of raw materials are carried out by:

1) Acid-basic catalysts such as $ZnCl_2$, $AlCl_3$, K_2S, H_3PO_4;

2) Oxidation-reduction catalysts (carbonates and alkali metal oxides) that can be recovered by carbon and oxidized by oxygen.

3) Both groups of catalysts activate the conversion of aliphatic compounds, lead to the selective removal of oxygen, hydrogen, and other heteroatoms.

The temperature and technological peculiarities of carbonization and activation processes are important factors that influence the formation of a porous carbon structure, and at the almost identical chemical composition of carbonaceous raw materials, the results can differ significantly in structural and texture parameters. In particular, low heating rates contribute to the formation of a microporous structure, and at high heating rates, the pressure of volatiles within the particles of the material increases, which leads to an increase in the number of macro- and mesopores.

The authors of the paper [10] note that the microstructure depends essentially on the raw material texture of vegetable origin, that is, on the lignin and cellulose content. After investigating the hydrolysis of lignin, they put forward the hypothesis that such carbon has higher specific pore volume than carbon derived from crystalline cellulose. In the study on the pyrolysis of lignocellulose waste at high temperatures, it has been proved that high content of lignin affects the final yield of the obtained carbon. Similar results were observed in the work [11] devoted to the carbonization of plum and apricot pits, from which it can be concluded that lignin is the main source of PCM, while hemicellulose and cellulose are volatile fractions. Researchers [12] have suggested that, since the activation rate is

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higher, carbon with a high content of cellulose is lighter than a material with a large amount of lignin. In addition, such material possessed high values of SSA and porosity in comparison with other samples of the investigated materials in which the main contribution was made by cellulose.

The aim of this paper is to investigate the influence of the conditions of obtaining and modifying PCM on the porous structure characteristics of carbon materials using the small-angle X-ray spectroscopy and on the basis of nitrogen adsorption/desorption isotherms analysis.

2. MATERIALS AND METHODS

The PCM obtained from raw materials of vegetable origin by its carbonization and activation with potassium hydroxide was used as an electrode material. The raw materials were dry apricot pits, crushed to a fraction of 0.25-1 mm, which were carbonized at 300 ºC; the heating rate was 10 ºC/min. The resulting carbon was mechanically shredded to a fraction of 200-250 µm and was mixed with potassium hydroxide and water in a weight ratio: $X_K = 1, 2, 3, 4$, where $X_K = \text{m(KOH)/m(C)}$.

The obtained mixture was thoroughly stirred for 1-2 h; afterwards, it was dried in a thermostat to a constant mass at 90 °C. The dry material was placed in an oven, heated in an argon atmosphere to 850-920 °C at a heating rate of 10 °C/min, and maintained at this temperature for about 20 min. Solid thermolysis products were washed from alkaline in a 5 % aqueous solution of HCl and distilled water to a neutral pH. The obtained coal was dried at a temperature of 105 ± 10 °C to a constant mass. The samples were numbered according to the temperature of carbonization and the ratio of C and KOH. For example, C43 is a material carbonized at 400 °C and mixed with potassium hydroxide at the ratio of 1:3, and C31 is the carbon obtained by carbonizing the fruit pits at 300 °C and activated with potassium hydroxide at C:KOH ratio of 1:1.

Characteristics of the porous structure (surface area and total pore volume) were determined based on isotherms of nitrogen adsorption/desorption at its boiling point (77 K) with the Quantachrome Autosorb (Nova 2200e). The samples had been degassed at 180 °C for 18 h before measurements. The specific surface area (S_{BET} m^2/g) was determined by the multipoint BET method in the isotherm region limited by the range of relative pressure $P/P_0 = 0.050\text{-}0.035$. The total pore volume (V_{total}, cm^3/g) was calculated from the amount of adsorbed nitrogen at $P/P_0 \sim 1.0$. The volume of micropores (V_{micro}, cm^3/g), the values of SSA of micro- (S_{micro}, m^2/g) and mesopores (S_{mezo}, m^2/g) were found using t-method, BJH method and DFT theory.

Spectra measurements of small-angle scattering were carried out on an X-ray diffractometer DRON-3 in Cu-Kα radiation, ($\lambda = 1.5418$ Å) monochromatized by reflection from LiF single crystal plane (200), in the mode of X-ray beam passing through a sample. To limit the parasitic scattering from monocrystal and entrance slits, as well as to decrease the intensity of background scattering, primary and scattered collimators were used. The applying of the collimation system allows measuring the spectra of small-angle scattering, starting with $s = 0.015$ Å^{-1} ($s = 4\pi\sin\theta/\lambda$ is the wave vector, θ is a half of the scattering angle). A detector was fitted with a gap of 0.1 mm, which corresponds to the spatial separation of the detector $(\Delta 2\theta)_d = 0.02^\circ$. In order to exclude the influence of the primary beam and background scattering on the scattering intensity, the following relation was used:

$$I(2\theta) = 1/K\left\{K \cdot I\exp(2\theta) - I_0(2\theta)\right\},$$

where $I^*(2\theta)$ is the true scattering intensity, $Iexp(2\theta)$ is the experimental scattering intensity, $I_0(2\theta)$ is the intensity distribution of the primary beam, $K = I_0(0)/I_{exp}(0)$ is the absorption coefficient of the sample measured at the zero position of the detector $2\theta = 0°$. The collimation correction for height and width of the detector receiving slit was made to the scattering intensity curves.

3. RESULTS AND DUSCUSSION

The process of chemical activation is significant when obtaining PCM with a highly developed micro- and mesoporous surface structure. The choice of the activating agent is of crucial importance since the yield of the final product and its structure depend on the concentration and the ratio of the initial components, temperature and activation time [13]. Potassium hydroxide plays an essential role in chemical activation, as it allows controlling the size distribution of micropores. In general, the activation process consists of two different phenomena: the micropore formation proceeds in the pore expansion. When alkali metal hydroxide is added to coal, it acts as a dehydrating agent at a lower temperature and uniformly impregnates the carbon structure. Further removal of hydroxide during carbonization (with heating) leads to the formation of pores. A small amount of ionic salt leads to the formation of significant porosity.

Fig. 1 shows nitrogen adsorption/desorption isotherms for PCM.

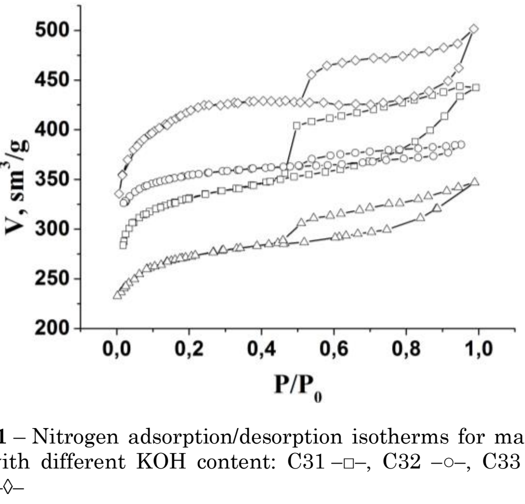


Fig. 1 – Nitrogen adsorption/desorption isotherms for materials with different KOH content: C31 –□–, C32 –○–, C33 –Δ–, C34 –◇–

With increasing percentage of KOH there is a decrease in the number of sorbed N$_2$, and with a fourfold increase of alkali for sample C34 there is an increase in the sorbent volume because of pore unlocking with potassium atoms. Isotherms belong to those that are characteristic of multilayered adsorption in organic mesopores. All samples are characterized by a hysteresis loop type H4 according to the classification of IUPAC with a relative pressure of ~ 0.5 [21]. The growth of the adsorption branch of the isotherm near $P/P_0 = 1$ is caused by multiple condensation processes and evaporation in the meso- and macropores at the nitrogen access.

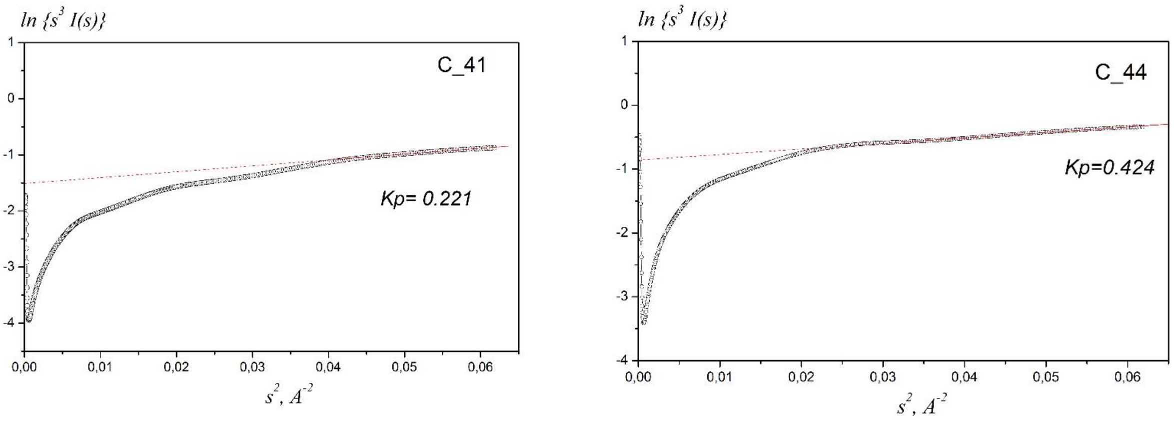
Analysis of adsorption isotherms allowed determining SSA, the total pore volume and the pore size distribution for PCM. The obtained data analysis demonstrates that an increase of KOH amount at chemical activation process leads to an improvement in the structural and adsorption characteristics of PCM, which significantly affects the capacitive properties of the samples under study. Thus, SSA for carbon material C34 is 1608 m^2/g and the total volume reaches almost 0.78 cm^3/g. The material activated with KOH at the ratio of 1:1 has a highly developed mesoporous surface and pores with a mean diameter of 2.2 nm make a major contribution to the total surface area.

Analysis of the intensity curves constructed in Porod coordinates has shown that these objects are characterized by a smooth surface of the separation between the pores and the carbon base (Fig. 2a, b).

Table 1 – Porous structure parameters of the investigated materials

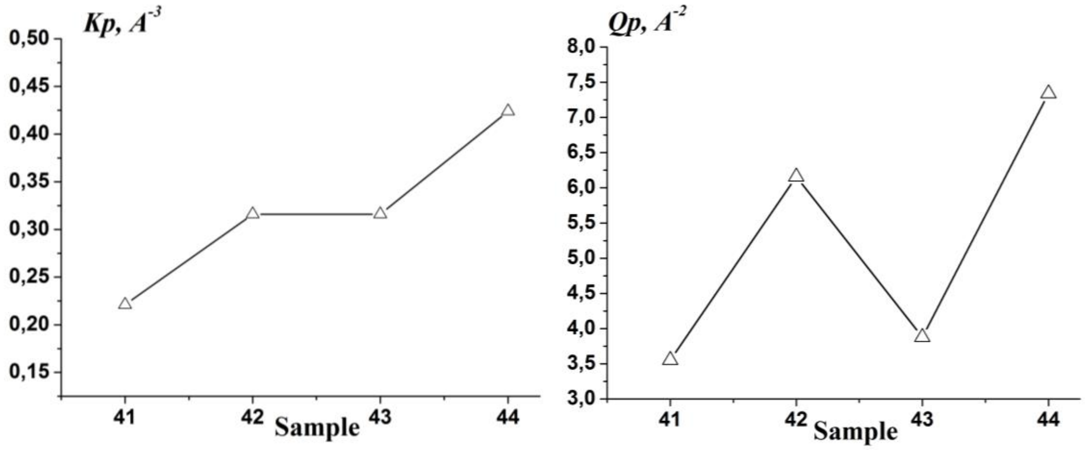
Sample	SBET, m^2/g	SDFT, m^2/g	S_{micro}, m^2/g	V_{micro}, cm^3/g	S_{meso}, m^2/g	V_{total}, cm^3/g	d_{mean}, nm
C31	1313	1196	1067	0.438	246	0.6844	2.213
C32	1334	1292	1266	0.508	68	0.5837	1.744
C33	1027	1100	913	0.3693	105	0.5368	2.09
C34	1608	1579	1426	0.5457	182	0.7743	1994

Increase in the KOH content leads to an increase in the Porod constant (Fig. 3a), and hence the total surface area of the pores. The dependence of the Porod invariant (Fig. 3b) depicts a nonmonotonic character. A value of Q_p that is proportional to the total pore volume correlates with the change in material density.



a b

Fig. 2 – Intensity curves in Porod coordinates



a b

Fig. 3 – Dependence of the Porod constant (a) and invariant (b)on the KOH content

The specific surface area of the pores also reveals similar character (Fig. 4). The highest value of SSA is achieved at KOH/carbon ratio of 1:3 (1255 m^2/g). Some reduction of the area under the fourfold content of KOH is due to an increase in the pore volume compared with the change in their surface area. The reason for this is an increase of the pore mean radius.

To calculate the functions of the pore radii distribution, the correction for height and width of the detector receiving slit was made to the scattering intensity curves. In addition, the indirect Fourier transform method was used, implemented in the GNOM program package in the approximation of the polydisperse spherical particles system. Fig. 5 shows the volume distribution functions, which express the dependence of the relative pore volume on their radii.

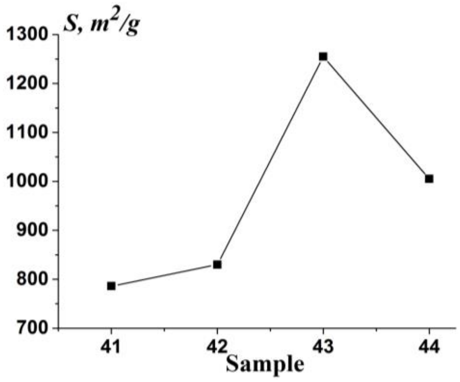


Fig. 4 – Change of the specific surface area of pores

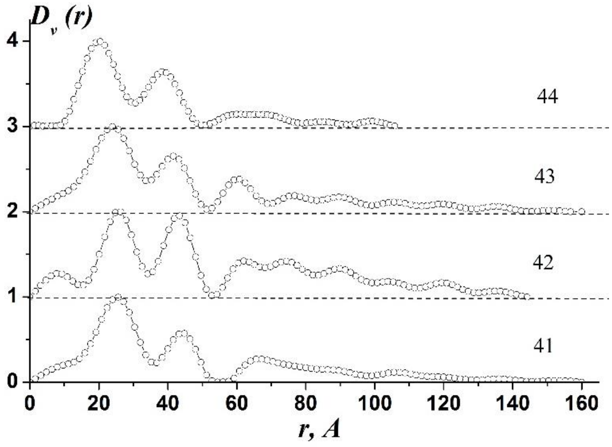


Fig. 5 – Volume distribution functions of pores

As can be seen, the main contribution to the porous volume formation is made by pores with a radius of 50 Å (Table 2). The samples for which KOH/precursor ratio is 1:1-1:3 display a significant number of micropores with radii of 8-10 Å, while they are practically absent in C44 sample. Fig. 6 demonstrates the pore distribution function that expresses the dependence of the pore relative number on radius.

Calculations have exposed that the materials are characterized by a microporous structure and the main contribution is pores with a radius of 8-10 Å. Furthermore, the presence of mesoscopic pores with a radius of ~ 25 Å should be noted, which is especially manifested in samples C41-C43. More significant changes in the pore distribution are observed in the sample treated with KOH ratio of 1:4. The porous structure of this sample is formed by pores with a radius of ~ 20 Å.

Fig. 7 presents the dependences of the most probable and mean pore radii.

The uniform pore distribution is observed for sample C44, and the mean value of the pore radius reaches 24 Å. The received result allows us to explain the decrease in SSA of this sample. The main structural parameters of the surface of C4 sample series are given in Table 2.

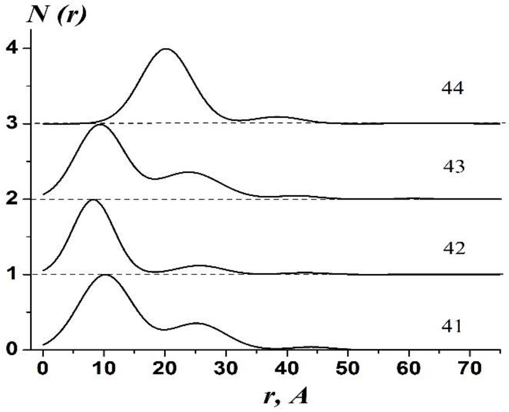
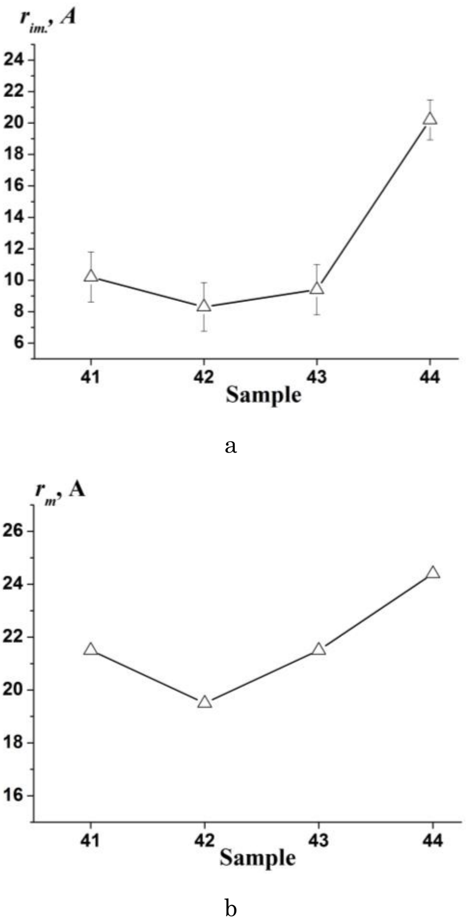


Fig. 6 – Dependence of the pore relative number on radius



a

b

Fig. 7 – Dependence of the most probable (a) and mean (b) pore radii on the KOH content

Table 2 – Parameters of the porous structure obtained by small-angle X-ray spectroscopy

Sample	ρ, g/cm³	W	S, m²/g	$R_{i\text{м.}}$, Å	R_c, Å
C41	0.76	0.60	786	10.2 ± 1.6	21.5 ± 1.6
C42	0.44	0.77	830	8.3 ± 1.5	19.5 ± 1.5
C43	0.51	0.73	1255	9.4 ± 1.6	21.5 ± 1.6
C44	0.33	0.83	1005	20.2 ± 1.3	24.4 ± 1.3

4. CONCLUSIONS

On the basis of synthesis and analysis of the received results it has been established that one of the most optimal methods for obtaining highly porous carbon material is carbonization of the raw material (fruit pits) in a closed furnace at a temperature of 270-420 °C and the subsequent chemical activation with potassium hydroxide with different ratios of KOH/C in the temperature range 870-900 °C.

The data of the structure and adsorption characteristics of carbon materials showed that an increase in the amount of KOH during the chemical activation contributes to the growth of the specific surface area and micropore area due to degeneration of narrow micropores and an increase in total volume from 0.66844 cm^3/g to 0.77743 cm^3/g. Optimization of modification parameters allows to obtain a material with a developed micro- and mesoporous structure (~ 1300-1600 m^2/g) and wide pore size distribution (2-25 nm).

Using the method of small-angle X-ray scattering it has been found that the chemical activation of carbon material causes changes in the internal structure of the sample. An increase in the percentage content of potassium hydroxide leads to the rise of the Porod constant from 0.22 $Å^{-3}$ to 0.43 $Å^{-3}$, and consequently, to the increase in the total pore area. Dependence of the Porod invariant is proportional to the total pore volume and correlates with the change in the material density.

It has been proved that with increasing concentration of KOH there are intense changes in the carbon matrix and the development of porosity of the investigated material. Carbonization of raw materials of vegetable origin and potassium hydroxide activation with potassium hydroxide determines the activity of surface centers, which can be the basis for obtaining carbon with predetermined adsorption characteristics. These findings have a valuable practical interest as it shows that such carbon materials can be used not only as an electrode material for electrochemical power sources, but also as efficient sorbents.

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Структурні особливості формування пористого вуглецевого матеріалу, активованого гідроксидом калію

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Робота присвячена дослідженню впливу хімічної та термічної активації на структуру вуглецевих матеріалів. Методами низькотемпературної порометрії та малокутової рентгенівської спектроскопії визначені основні параметри питомої поверхні, а саме загальна площа поверхні, сумарний об’єм та середній радіус пор. Встановлено, що вуглецевий матеріал карбонізований при 300 °C та оброблений гідроксидом калію у масовому співвідношенні 1:4 демонструє найбільшу площу поверхні 1608 $м^2/г$ та характеризується високо розвиненою мікропористою поверхнею. Зростання температури карбонізації до 400 °C зумовлює деяке зменшення площі поверхні, пов’язане із збільшенням об’єму пор порівняно зі зміною їх площі поверхні при чотирикратному вмісті KOH. Причиною є збільшення кількості мікропор радіусами 8-10 Å та незначне число мезопор радіусом ~ 25 Å. Найбільше значення питомої площі (1255 $м^2/г$) досягається при співвідношенні KOH/вуглець – 1:3.

Ключові слова: Пористий вуглецевий матеріал, Хімічна активація, Малокутова рентгенівська спектроскопія, Питома площа поверхні.