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The Effect of Thermal Treatment on Porous Structure of Carbon Materials

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Abstract The article investigates the effect of thermal modification of porous carbon material (PCM), obtained by method of hydrothermal carbonization of plant products at a temperature of 750°C, on its porous structure. The implication of the low-temperature porosimetry method has shown that increase of modification temperature (from 300 to 600°C) and time (from 0.25 to 3 h) leads to substantial development of the porous structure of the initial material, accompanied by the doubling of the specific surface area, total volume growth of pores, micro- and mesopores – 2.5, 1.8 and 4.6 times respectively and doubling of the relative proportion of mesopores by the total volume of pores. The pore size distribution (PSD) analysis by means of DFT (Density Functional Theory) allowed to determine that thermal modification most efficiently promotes the development of pores 1.4 and 4 nm in diameter.

Keywords: *porous carbon material, thermal modification, porous structure, pore size distribution*

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1. Introduction

Porous carbon materials (PCM) due to their properties (well-developed specific surface area, great electrical conductivity, high chemical and electrochemical stability, availability to be obtained in dispersion and compact forms and relatively low cost of carbon materials and products made therefrom) play a key role in many branches of modern science and technology, in particular as liquid and gas purifiers [1], mix classifiers [2,3], chemical reaction catalysts [4,5] and materials for accumulation and conversion of electric energy [6-12]. In recent decades special attention is given to the investigation of powder carbon materials of micro- and nanometric dimensions, obtained from the organic feedstock, in order to use them as an electrode material in primary and secondary lithium power sources [8,9,11,12,13]. Their advantage compared to the synthetic precursors due to cheapness, chemical purity, low emissions, sufficient resource base and its reversible, low cost, ease of processing. The main way of obtaining these materials is the carbonization of carbon-containing substances at a high temperature (up to 2000°C) [14]. We have found out that when PCM, obtained by means of hydrothermal carbonization of apricot seeds at different temperatures, is used as a cathode of electrochemical current source, the specific capacity of the electrochemical cell depends mainly on the specific surface area of the material and electrical conductivity [15,16]. The maximum value of the specific capacity (1140 mA·h/g) has the electrochemical cell with PCM, obtained at the carbonization temperature of 750°C. It is evident that to improve the specific energy characteristics it is reasonable to use such PCM modification methods that would allow to increase the mentioned parameters. They may include thermal and chemical treatment [17,18], laser exposure [19], etc.

Thus, the purpose of the article is to perform the thermal modification of the carbon material with maximum energy content at different temperatures and times and to study its influence on the PCM structure.

2. Experiment

The experiment was performed on the basis of the initial PCM, carbonized at the temperature of 750°C, and PCM, obtained by means of modifying the initial material at the temperatures T_{mod} 300, 400, 500°C (modification time t_{mod} was 0.5; 1; 1.5; 2; 2.5; 3 h) and 600°C (t_{mod} was 0.25; 0.5; 0.75 and 1 h). At the temperature 600°C there are less PCM modification times, because at the given temperature longer thermal treatment causes almost complete material burn-off. Thermal modification at the given modes was performed in air in muffle furnace SNOL-40 / 1300.

Structural and adsorption characteristics of the investigated materials (specific surface area, micropore surface, total pore volume, micropore volume, average pore diameter and pore size distribution) were measured by means of nitrogen isothermal adsorption / desorption at the nitrogen boiling temperature (T = 77 K) with the automated sorptometer Quantachrome Autosorb (Nova 2200e). Before study the samples were degasified in vacuum at the temperature 180°C for 20 h.

To characterize the porous structure of the carbon material the following parameters were used: S_{BET} – the value of specific surface area, determined by BET method [20]; S_{micro}, S_{ext} – micropore surface and external surface respectively, calculated by t-method [21]; V – total pore volume, calculated by volume of adsorpted nitrogen under relative pressure $p / p_0 > 0.995$; V_{micro} – micropore volume, obtained by t-method; V_{meso} – mesopore volume, determined by formula $V_{meso} = V - V_{micro}$; d – average pore diameter.

To determine the pore size distribution the DFT method was used, based on the quantum-mechanical approach that requires fundamental molecular parameters, characterizing the interaction gas-gas, gas-liquid and gas-solid [22].

3. Results and Their Discussion

The qualitative analysis of sorption isotherms of initial and thermally modified PCM shows substantial differences (Figure 1). In PCM, modified at 300°C at all modification times, the sorption isotherm doesn't change in sight: it belongs to type I isotherms, characteristic of the microporous materials (Figure 1, Curve 2).

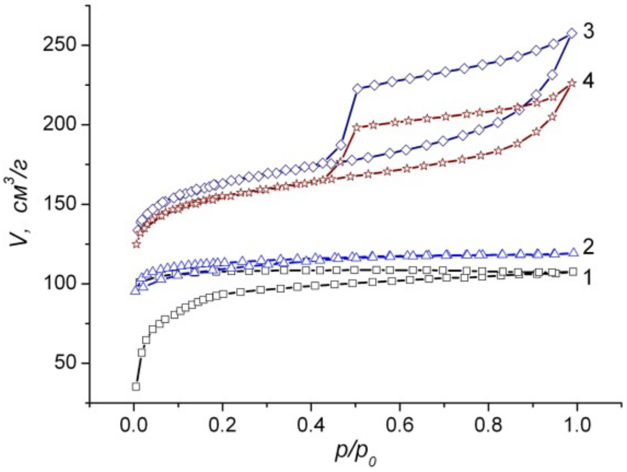

Figure 1. The sorption isotherms of initial PCM (1) and modified ones at temperatures of 300 (2), 400 (3), and 500°C (4)

In contrast with the initial material, the low-pressure hysteresis in the given samples is less that is perhaps caused by the permanent latching of nitrogen molecules in pores, the sizes of which are proximal to the nitrogen molecule sizes due to the emergence of carbon particles belonging to oxygen-bearing functional groups. The volume of the adsorbed gas for the given materials is a little bigger than for the initial sample. The same isotherm is characteristic of the PCM, modified at 400°C for 30 min. However, with as time (t_{mod} = 1 ÷3 h) and modification temperature increase up to 500°C the situation changes drastically. The sorption isotherms of the given materials show the hysteresis in the range of relative pressures $p / p_0 >$ 0.42 ÷ 1, which is related to the type H4 according to the IUPAC classification [23] and, as a rule, is connected with capillary condensation in mesopores (Figure 1, Curves 3 and 4).

The value of hysteresis rises with the increased modification duration and is within the limits of ΔV = 3 ÷ 43 cm^3/g (T_{mod} = 400°C) and ΔV = 8 ÷ 31 cm^3/g (T_{mod} = 500°C). The low-pressure hysteresis is not available in the given samples. In case of PCM, modified at 600°C, the sorption isotherm is similar to Curves 3 and 4 in Figure 1, but because of shorter modification times the high-pressure hysteresis is less (its value under the pressure $p / p_0 > 0.7$ is 3 cm^3/g) and at t_{mod} = 1 h it disappears, which indicates the formation of microporous material.

Quantitative analysis of sorption isotherms allowed to determine the parameters of porous structure of modified PCM (Table 1). As it follows from the obtained data, thermal modification of PCM at all used temperatures increase the specific surface area and micropore surface. The effect is most evident at modification temperatures 400 and 500°C, when the given values increase almost twofold. The situation is connected mainly with partial burn-off of the near-surface layers of carbon particles, resulting in the opening of the closed material porosity. The development of mesoporous PCM structure is somewhat different. If in case of carbon material, modified at the temperatures 400 and 500°C, the number and volume of mesopores increase several times in relation to the initial material, modification at the temperatures 300 and 600°C, on the contrary, causes reduction of the values. We believe that the temperature 300°C is not enough for the efficient burn-off of carbon atoms, loosely bound at the surface, and, as a consequence, fusion of micropores into mesopores.

In case of modification at the temperature of 600°C there appear strong temperature gradients in PCM grain volume, as a result of which their structure transforms – most likely graphene layers solidify and particles converge, reducing the pore diameter and causing transition of mesopores into micropores. The benefit of the latter may be proved by the data on determining the average pore diameter (Table 1), according to which its value reduces from 1.937 nm (initial sample) to 1.650 nm (t_{mod} = 3 h). We would like to note that the proportion of micropores in all PCM regardless of modification temperature and time exceeds 80 %, and at the temperatures of 300 and 600°C it reaches 96 %.

We would like to analyze the changes in pore volume following the modification. The micropore volume and their surface increase for all materials; there is the clear correlation between relations $V_{micro} = f(T_{mod}, t_{mod})$ and $S_{micro} = f(T_{mod}, t_{mod})$. The total pore volume increases too, however, in case of PCM, modified at 300°C, value increase is not substantial in comparison with other temperatures and makes up only 0.022 cm^3/g for t_{mod} = 3 h (by contrast for the same modification times in regard to the initial sample the pore volume increases by 0.247 and 0.128 cm^3/g for T_{mod} = 400°C and T_{mod} = 500°C respectively). The change mesopore volume is similar to the change of their surface, caused by the above mentioned reasons. The biggest number of mesopores is formed in samples, modified at the temperatures of 400 and 500°C – their proportion in the total pore volume is about 50 %.

Table 1. The parameters of porous structure of modified PCM

T_{mod}, K	t_{mod}, h	S, m^2/g	S_{micro}, m^2/g	S_{ext}, m^2/g	$\frac{S_{micro}}{S}$, %	V, cm^3/g	V_{micro}, cm^3/g	V_{meso}, cm^3/g	$\frac{V_{micro}}{V}$, %	d, nm
initial	–	343	292	51	86	0.166	0.123	0.043	74	1.937
300	0.5	361	339	51	94	0.158	0.145	0.013	92	1.746
	1	443	425	18	96	0.179	0.174	0.005	97	1.620
	1.5	434	410	24	95	0.179	0.163	0.016	91	1.654
	2	439	418	21	95	0.180	0.166	0.014	92	1.643
	2.5	451	424	27	94	0.184	0.164	0.020	89	1.637
	3	450	423	27	94	0.188	0.168	0.020	89	1.672
400	0.5	433	380	53	88	0.175	0.165	0.010	84	1.752
	1	513	453	60	88	0.232	0.179	0.053	77	1.809
	1.5	542	478	74	88	0.260	0.191	0.069	73	1.917
	2	573	500	73	87	0.285	0.203	0.085	71	1.990
	2.5	614	504	110	82	0.398	0.205	0.193	52	2.595
	3	652	535	117	82	0.413	0.215	0.198	52	2.538
500	0.5	526	463	63	88	0.252	0.186	0.066	74	1.913
	1	623	522	101	84	0.354	0.211	0.143	60	2.274
	1.5	616	519	97	84	0.361	0.211	0.150	58	2.344
	2	653	550	103	84	0.384	0.223	0.161	58	2.350
	2.5	586	492	94	84	0.350	0.200	0.150	57	2.387
	3	479	404	75	84	0.294	0.165	0.129	56	2.459
600	0.25	465	411	54	88	0.217	0.165	0.052	76	1.867
	0.5	497	464	33	93	0.221	0.184	0.037	83	1.778
	0.75	464	441	23	95	0.194	0.172	0.022	87	1.672
	1	457	439	18	96	0.189	0.171	0.018	90	1.650

Thus, we may state that the choice of modification temperature and time and carbonization temperature of the feedstock are the factors, effecting the control of porous structure and texture of PCM, assigning their area of implementation.

Now let's clarify what happens with PSD during modification of the initial PCM. To calculate the distribution data we use the DFT method; the distribution is represented as a range of bar charts. As it follows from the obtained results, in the PCM of the initial sample there prevail the micropores with the maximum near of 1.4 nm in diameter (Figure 2, a). The same distribution is peculiar to PCM, modified at 300°C for 0.5 ÷2 h. With the modification time increased to 2.5 hours in PSD there appears a small number of mesopores, the sizes of which are in the range of 2.5 ÷ 4 nm (Figure 2, b). A small number of mesopores with identical micropore distribution is characteristic of PCM, modified at 400°C for 1 h. However, the increased modification duration causes the appearance of a big proportion of mesopores (27 %) in PSD near of 4 nm, the peak intensity of which falls at t_{mod} = 2.5 h (Figure 2, c).

PSD for the materials, modified at the temperature 500°C (t_{mod} = 0.5 ÷ 3 h) doesn't substantially differ from the PSD in Figure 2, c; there is only the redistribution of intensity between micro- and mesopores (Figure 2, d). In case of PCM, modified at 600°C (t_{mod} = 0.25 h) (Figure 2, e), the PSD is presented, mainly, by micropores and negligible quantity of mesopores. The increased modification time leads to the quantity reduction of mesopores (Figure 2, f), which is supported by the data in Table 1.

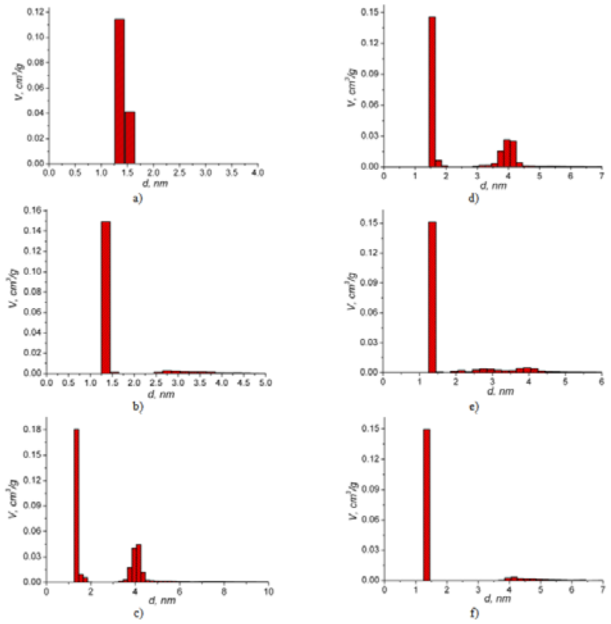

Figure 2. Pore size distribution of PCM at different modes of modification: a) initial sample; b) T_{mod} = 300°C, t_{mod} = 2,5 h; c) T_{mod} = 400°C, t_{mod} = 2,5 h; d) T_{mod} = 500°C, t_{mod} = 3 h; e) T_{mod} = 600°C, t_{mod} = 0,25 h; f) T_{mod} = 600°C, t_{mod} = 1 h

4. Conclusions

Thermal modification of the initial sample results in the PCM, the structure of which contains both micro- and mesopores, the number and maximum sizes of which can be efficiently regulated by means of choosing modification temperature and time. It is shown that the most substantial changes of the porous structure are observed in samples, modified at 400 and 500°C for 2.5 and 3 h. Lower temperatures and less modification times, though causing significant growth of the microporous structure in comparison with initial material, are not enough for the efficient formation of mesopores. There is a clear correlation between the volume and surface of micropores and modification temperature and time of PCM. The change of modification modes of carbon materials is an efficient tool for regulating their porous structure, allowing to obtain samples with the predetermined texture and counted pore size distribution.

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