

THERMAL EXPANSION OF CARBON MATERIAL FOR SUPERCAPACITOR ELECTRODES

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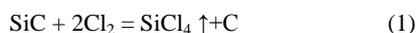
Abstract: Measurements of linear thermal expansion coefficient (TEC) of a nanoporous metal carbide based carbon material were carried out. The values of linear thermal expansion coefficient in the range from 20°C to 300°C were obtained. The measured value of TEC are presented for this material for the first time.

KEYWORDS: TEMPERATURE, THERMAL EXPANSION COEFFICIENT, NANOPOROUS CARBON, DILATOMETER

1. Introduction

Nanotechnological initiatives of the last two decades have emphasized global trends in science and technology that had been formulated long before their recognition as a single field. Nanotechnology is by definition a deliberate employment of devices and materials with dimensions of less than 0.1 μm (100 nm). Examples of these materials are nanostructured carbon materials with considerable surface unit area. Some of them such as activated coal have been known for hundreds of years, and others have only emerged recently.

In the present paper properties of metal carbide based nanoporous carbon (CDC – carbide derived carbon) were studied. Nanoporous carbon belongs to a group of carbon materials with complex structure, which depends on parameters of the fabrication process as well as the type of original carbide. Apart from “CDC” term “skeleton carbon” is often referred to regarding the material above in the English-language literature [1]. This type of nanoporous carbon is usually obtained in process, when original carbide powder is exposed to gaseous chlorine at high temperatures. For instance, the following reaction can be used



As a result of the reaction a volatile metal chloride is formed (Si in particular case). A metal atom in the chloride composition leaves the carbide crystal lattice, while carbon stays in the solid state. Since balance of forces inside the lattice is disturbed due to metal removal, carbon forms a new type of material.

The process kinetics is limited by diffusion of chlorine gas from the surface into the inside of carbide crystal grains, hence the carbon material is formed at the surface of the grains, i.e., predominantly in the form of quasi-two-dimensional crystallites (flakes). A question regarding the number of graphite layers in such flake is not addressed in the literature. Irregularity of the original carbide grain shape as well as stochastic nature of flake formation lead to a situation that exfoliated carbon flakes form an irregular conglomerate. This conglomerate structure is often described using the term “turbostratic” [2]. Cavities between flakes act as pores that determine the further functional use of the material. It is notable that shapes of macroscopic grains (granules) of nanoporous carbon remain almost the same as for the original carbide.

However, the process of graphitization of the obtained mass takes place simultaneously with formation of nanoporous carbon. If the temperature is excessively high and process time is too long, the material undergoes an internal rearrangement. Carbon layers mostly take parallel orientation, similar to that of carbon layers in graphite. Upon that the density of the material is increased and so does its some other properties as stability. However specific surface area decreases. Therefore, a tradeoff between different processes has to be taken into account when fabricating nanoporous carbon.

The technology described above allows for fabrication of different types of nanoporous carbon with parameters presented in the Table 1 [1].

Table 1. Pore system properties for different types of nanoporous carbon

Original carbide	Average density, g/cm ³	Specific pore volume, cm ³ /cm ³	Specific surface, m ² /g	Pore diameter at the maximum of the distribution curve, nm
SiC	0,91	0,67	879	0,6
TiC	0,99	0,72	663	0,6
B ₄ C	0,55	1,08	2200	2,0
Mo ₂ C	0,52	1,31	2110	2,0

It has to be noted that unit surface values in the two bottom rows of the Table 1 are approaching the theoretical limit for a unit surface value in a single-layer graphite sheet (graphen), i.e., 2600 m²/g. This explains high efficiency of using these materials as absorbents, porous electrodes, or catalyst carriers, alongside favoring the above noted material formation and structure model.

It has to be kept in mind that the properties of the pore system, given in the Table 1, were obtained using the BET method [1] of nitrogen absorption, where a regular spherical pore shape is assumed. It bears mentioning that a significant degree of material structure disordering makes it impossible to study the structure in details by X-ray structural methods. The use of other methods for studying the material are considerably limited for different reasons. As a result, a little study has been carried out on the properties of materials falling into that group, and developers who used the material had to rely largely on empirical approach.

In the present paper thermal expansion was studied in-compact samples of pressed nanoporous carbon. Besides new information on the material, features of the material structures were deduced from the measurements.

2. Experiment

The choice of method and sample operating conditions were important aspects of the study. There are high precision dilatometry methods that provide the accuracy within (0.5–1)·10⁻⁹ K⁻¹ [3], however the required equipment set is quite complex, and thus implementation of such method for in production material control is encumbered. For that reason, a fairly simple mechanical dilatometer was employed in the present paper. [4]. Measuring unit of the dilatometer is shown in the Fig. 1. TEC measurement technique is shown in the diagram in the Fig. 2. The dilatometer exerts reasonably small pressure on the sample during measurements. Accuracy of the dilatometer will be shown to be adequate for the materials of choice.

Determination of the temperature range for the measure-

ments was one part of the study. In the first series of measurement the TEC was measured up to 500°C. It was found however, that heating above 300°C leads to irreversible changes and destruction of the material. This became evident as the material experienced significant shrinkage when heated above 300°C, as well as in the fact of the material changing its dimensions during thermal cycling.

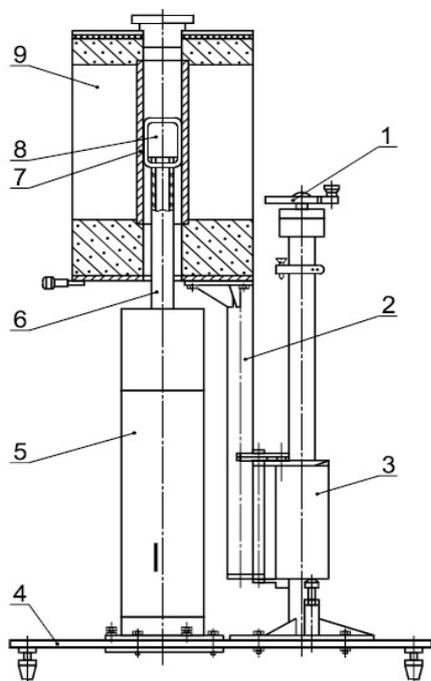


Fig. 1 Measurement unit: 1) carriage; 2) lead screw; 3) lifting mechanism; 4) base; 5) body; 6) tube; 7) pusher; 8) specimen; 9) furnace.

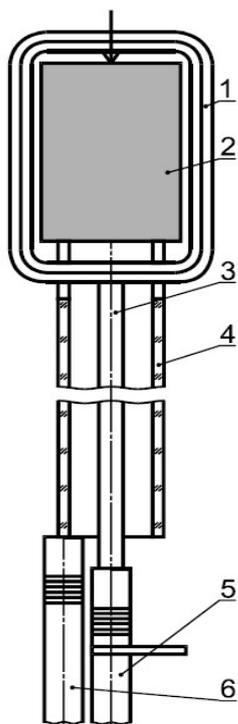


Fig. 2. TEC measurement scheme: 1) frame; 2) specimen; 3) pusher; 4) tube; 5, 6 "Micron 02" instrument displacement inductive transducers.

Examples of such dependences are demonstrated in the Fig. 3.

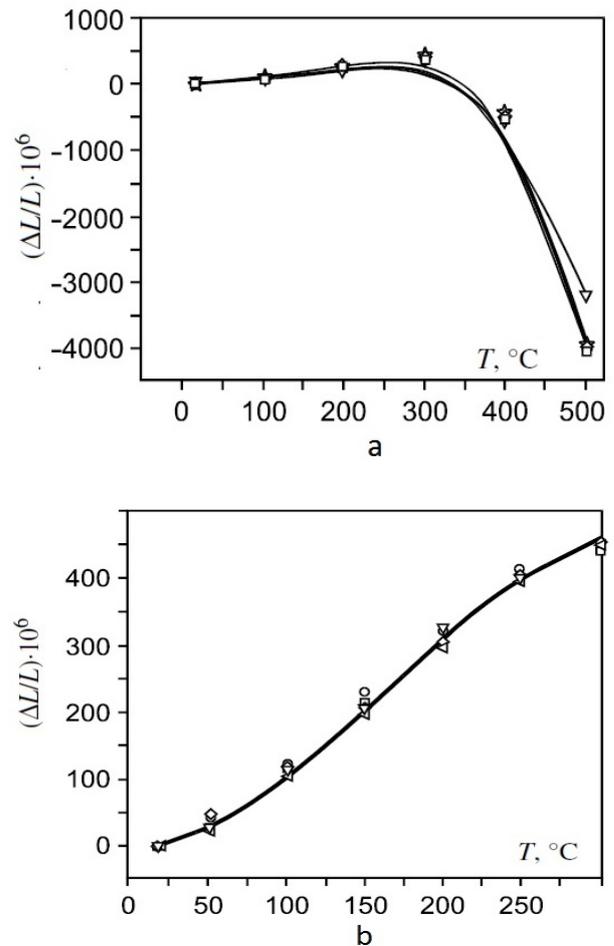


Fig. 3 Dependence of relative nanoporous carbon elongation on temperature of 20-500°C (a) and 20-300°C (b)

The dimensions were carefully checked to be stable for temperatures up to 300°C, and the results of the TEC measurements were found to be reproducible. It can be seen from the dependences given in the Fig. 4.

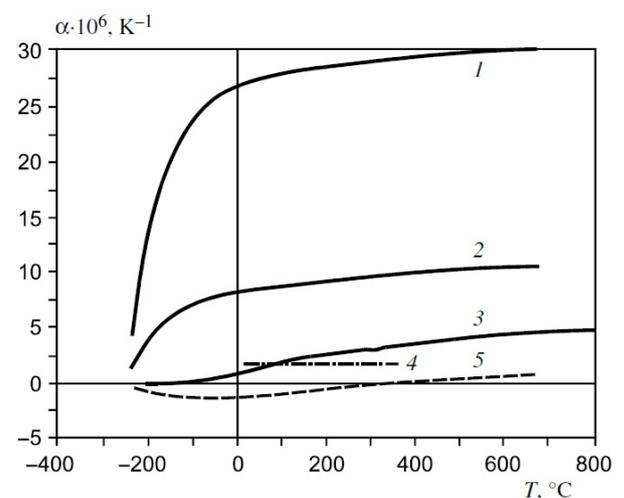


Fig. 4. Shows the differential TEC values as a function of temperature. Also for comparing there are shown the data for expansion of carbon material with sp^3 -bonds (diamond) between atoms of carbon and sp^2 -bonds (graphite) in directions along and perpendicular to the preferred direction [5].

Accuracy of TEC determination was evaluated based on

the curves such as one shown above or similar. The mean square deviation (MSD) for the measurements was found to be $8.6 \cdot 10^{-6}$.

3. TEC determination results and discussion

Resulting thermal expansion (elongation) values are presented in the table 2.

Table 2. Relative elongation as a function of temperature

Measur. number	Relative elongation ($\Delta L/L$) 10^6 at temperature °C				
	100	150	200	250	300
1	144,6	228,9	330,4	-	-
2	124,6	229,6	325,4	415,4	501,0
3	121,0	207,5	326,8	-	-
4	-	205,3	306,1	405,3	458,1
5	106,0	198,2	297,6	398,2	460,2
6	112,5	200,3	-	400,4	444,5
7	115,3	215,3	-	404,7	445,9

Figure 4 shows the differential TCLE values as a function of temperature. Also for comparing there are shown the data for expansion of carbon material with sp³-bonds (diamond) between atoms of carbon and sp²-bonds (graphite) in directions along and perpendicular to the preferred direction [5].

A conglomerate of graphite-like flakes appears to be the most probable structure of nanocarbon material, hence coefficient of thermal expansion of such material can be imagined. Material with a layerwise arrangement of sp² bonded carbon atoms has drastically anisotropic coefficient of thermal expansion. The TEC in the layer plane can be small or even negative at temperatures from –200°C to +300°C. By contrast, the TEC across layers can have large positive value. Since in-plane bonds are much stronger compared to those between layers, thermal expansion of an individual layer (graphene) might be expected to be close to the graphite expansion along its layers.

Thermal expansion, perpendicular to an individual layer of carbon atoms (graphene) is devoid of meaning. Therefore there is neither theoretical evaluations nor experimental data for flakes comprising a small number of layers. General considerations suggest that outer layers of the flake do not have “neighbours” (and bonds) on the outside, and consequently they do not affect expansion. At the qualitative level, it may be suggested that the TCLE of a flake perpendicular to the plane of that object α would be related to the number of carbon layers N is a flake and the TCLE of the layer α_{\perp} by the relationship

$$\alpha_{*} = \alpha_{\perp}(N - 1)/N.$$

Macroscopic material samples are composed of a non-oriented conglomerate of flakes. The thermal expansion coefficient of such samples should be determined in the same way as it is done for polycrystalline samples, which is in terms of α_{\perp} and α_{\parallel} expansion coefficients (expansion coefficients perpendicular to and parallel to the plane of graphite flakes respectively) using the following equation

$$\alpha = \alpha_{*}/3 + 2\alpha_{\parallel}/3 = \alpha_{\perp}(N - 1)/(3N) + 2\alpha_{\parallel}/3.$$

Calculation of the number of the graphene layers N in a carbon flake yields a value of $N = 1.75$ at a temperature of 300 K. That value confirms the current concept of the nanocarbon material structure. It can be inferred from the Fig. 4 that the resulting TEC values obtained in the paper are slightly larger than TEC of graphite along its carbon layers. This validates the nanocarbon material model as described above.

4. Conclusions

The measurements of TEC of nanoporous carbon, conducted for the first time, are described in the present paper. Temperature stability range was determined for the material. Obtained TCLE values are situated between the TCLE values of anisotropic graphite and those of graphite in the carbon atom plane.

4. References

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