CAPACITANCE OF SUPERCAPACITORS WITH ELECTRODES BASED ON CARBON NANOCOMPOSITE MATERIAL

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Résumé

Cet article présente les résultats de notre recherche de la structure et des caractéristiques pratiquement importantes d'un matériau nanocomposite sur la base de carbone nanoporeux et graphite exfolié thermiquement. Ce travail montre que l'utilisation de la composition ci-dessus dans les électrodes de supercondensateurs permet d'atteindre le niveau de leur capacité électrique spécifique au (155 ... 160) F / g.

Mots clés : carbone, nanocomposite, supercondensateurs

Abstract

This work presents the results of our research of the structure and practically important characteristics of a nanocomposite material on the basis of nanoporous carbon and thermally exfoliated graphite. This work shows that the use of the above-mentioned composition in electrodes for supercapacitors allows to attain the level of their specific electrical capacitance at (155...160) F/g.

Keywords: carbon, nanocomposite, supercapacitors

ملخص.

ويعرض هذا العمل عن نتائج أبحاثنا من هيكل وخصائص هامة عمليا من مادة بمركب متناهي في الصغر على أساس الكربون والجرافيت تقشر نانوية مسامية حراريا. ويبين هذا العمل أن استخدام تركيبة المذكورة أعلاه في أقطاب لالمكثفات الفائقة يسمح لبلوغ مستوى من السعة الكهربائية الخاصة بهم محددة في (155 ... 160) F / G.

الكلمات المفتاحية: الكربون، بمركب متناهي في الصغر، والمكثفات الفائقة

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Introduction :

The concept of a «supercapacitor» (SC) appeared in the scientific world about 20-25 years ago. Today there are already SCs, the capacitance of which is greater than 1 farad, which is approximately 1,500 times greater than the electrical capacitance of the globe and is very close to the capacitance of Jupiter. The capacitance of SCs is determined by the characteristics of their electrodes, the type of electrolyte, collectors, separators and other constituent components. Energetics and kinetics of electrode processes which occur in the area between the electrodes in devices that operate by the charge-discharge of the double electrical layer (DEL), are key in making electrochemical SCs.

Nomenclature

DEL	double electrical layer
d	cross-section of TEG particles
NPC	nanoporous carbon
C_{NCM}	specific capacitance of NCM
C_V	volume concentration (vol. %)
C_{V_C}	percolation threshold
I	discharge current
NCM	nanocomposite material
S	specific area
SC	supercapacitor
TEG	thermally exfoliated graphite

The advantages of SCs over other portable electronic devices and power sources include improved specific characteristics, longer life and a greater number of charge-discharge cycles. Moreover, and this is the main advantage, they are capable to put out a great electric power in a short time and get charged quickly.

At the same time, certain limitations need to be taken into account when making SCs. As such, its characteristics are largely dependent on the type of electrolyte used: it is responsible for the internal resistance of the capacitor, while the operating voltage cannot exceed the potential of solvent decomposition. That is why water electrolyte solution systems have relatively low internal electrical resistance, while voltage cannot exceed 1.2 V (decomposition potential of water). Specific capacitance of SCs depends on the electrodes area and increases with its bigger size. In addition, an active electrode material for making SCs with optimal performance characteristics should have high conductivity of the electronic component. It should also be indifferent to electrolyte solution and be "perfectly polarized" in the range of potentials limited by the potential of the solvent decomposition. As the previous studies have shown - for example, the ones presented in work [1] - nanoporous carbon (NPC) is the most promising material for the use in electrodes of SCs at present. Such carbon can be obtained by method of hydrocarbonization of fruit stones. This carbon has a highly developed surface with a specific area of $S > 1,000$ m^2/g, but its specific conductivity is low. In order to overcome this drawback, we have developed a nanocomposite material (NCM) made of a mixture of NPC powders and thermally-exfoliated graphite (TEG). The resistance of TEG with $S \sim 50$ m^2/g is significantly lower than the resistance of NPC and its value at the density of 0.5 g/cm^3 is approximately $2 \cdot 10^{-3}$ ohm$\cdot$ m [2].

TEG used as a conductive component of NCMs, which are used in manufacturing of SC electrodes, provides an increased concentration of free charge carriers. However, the optimal size of TEG particles needs to be determined so that on one hand it would not greatly reduce the specific surface area of the electrodes, and on the other hand it needs to raise its conductivity to optimize capacitance of capacitors.

1. Preparation of samples

The characteristics of NCM components and the information on the methods for their preparation are given in the work [1]. TEG was dispersed in a mechanical grinder. Separation into fractions was done by sifting TEG powder through appropriate sieves. Six powder samples with different average cross-sectional dimensions of d-particles were selected (Table 1).

Table 1. Composite material samples designation

dTEG, μm	d < 60	60… 100	100… 160	160… 200	200… 315	d > 315
Sample	C1	C2	C3	C4	C5	C6

Samples of compositions were prepared by thoroughly mixing NPC and TEG powders in the ratio of 85 to 15. This ratio of the components provides the maximum value of specific capacitance of SC [1]. Electrodes were made from compressed NCM placed in nickel grids. The made electrodes were separated by a separator and placed into a cell, which was sealed after filling with electrolyte (water solution of KOH).

2. Results and discussion

SEM images of the microstructure of NPC and TEG obtained with JSM-6490LV scanning electron microscope by JEOL (Japan) are presented in Fig. 1. Since electric charge is accumulated by a supercapacitor mainly due to formation of DEL at the electrode‖electrolyte boundary, its capacitance becomes greater the larger is the electrode surface area. In our case the more porous our carbon electrode is, the larger becomes the surface. Particles of NPC have a distinguished frame structure. Their size (Fig. 1) varies in the range of 160 to 240 micrometers, and the size of transport pores is from 4 to 20 nm. The internal surface of NPC has a large number of pores, the sizes of which range between 0.2 and 2 nm (Fig. 1, b).

All in all, the analysis of the microstructure of nanoporous carbon allows to conclude that it includes both macro-(> 50 nm), meso- (from 50 to 2 nm) and micropores (<2 nm), and the specific capacitance of SC will largely depend on their proportion. TEG introduced into NCM raises its electrical conductivity and also affects the capacitor's capacitance.
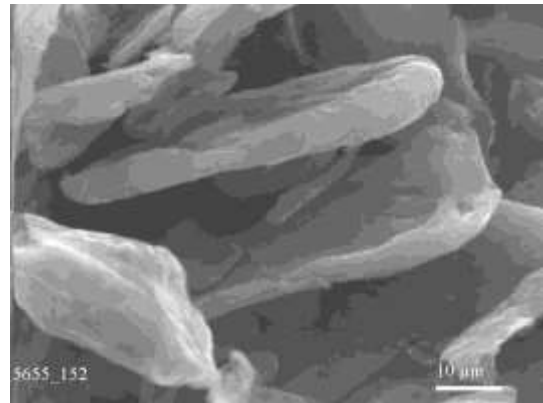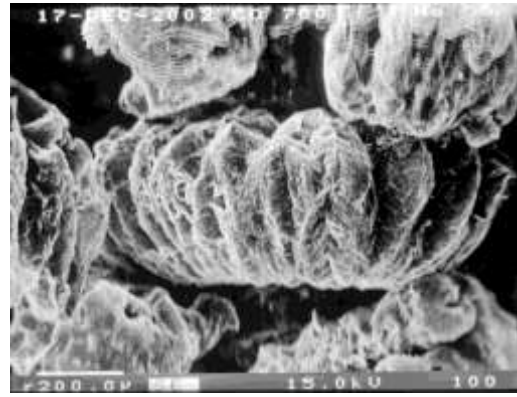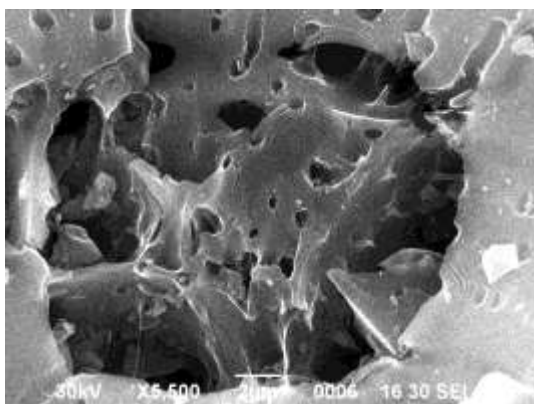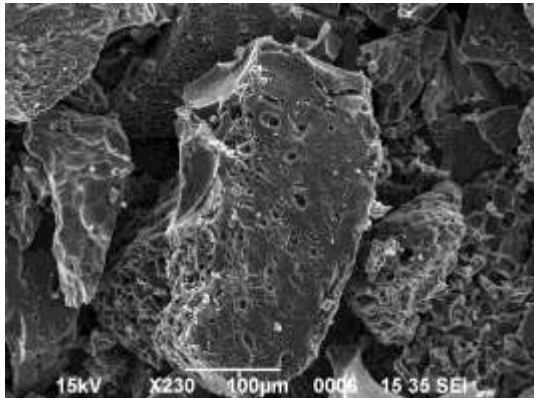

Fig. 1. SEM image of NPC surface at (a) ×230; (b) ×5,500 and (a) thermally exfoliated graphite (c) before dispersion and (d) after dispersion

The initial shape of TEG (Fig. 1,c) is vermicular. These vermicular particles each consist of lenticular flakes, the distance between which ranging between 10 nm and 10 micrometers, and the size of nanostructure fragments, which can be separated, ranges within several to hundreds nanometers [3]. Nanoscale of TEG determines its high ability to form infinite clusters in respective compositions. Therefore, the percolation threshold of polymer NCMs, calculated by concentration dependences of the electrical resistivity, does not exceed $C_{V_C} \approx 3.9$ vol.%.

The value of C_{V_C} shifts to higher concentrations with the increase of the dispersion degree of TEG particles, but it does not exceed 15 vol. % as is seen, for example, on Fig. 2. That is why the concentration of TEG in NPC-TEG nanocomposite material was chosen at $C_V \geq 15$ vol.%, which has provided the maximum capacity of SC for the composition with non-dispersed graphite [1]. At the same time, the total specific surface area of the active material is not reduced more than 8%. As micropores of NPC form 90% of its total surface area, it needs to be taken into account that the capacity of SC will ultimately depend on the extent to which the dispersed particles of TEG will block access of electrolyte to the micropores. As with

11

conventional capacitors, the capacitance of SCs decreases monotonously with the increase of the discharge current (I).
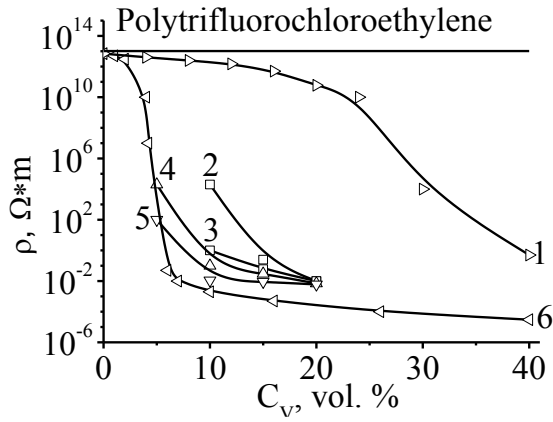

Fig. 2. Concentration behavior of resistivity of (1) composite materials: polytrifluorochloroethylene - spectrally pure graphite and nanocomposite materials: polytrifluorochloroethylene - thermally exfoliated graphite, with TEG dispersion d (μm) = 40 (2); 80 (3); 180 (4); 260 (5); initial TEG (6)

In carbon materials this is caused, as a rule, by an increase of ohmic resistance due to presence of micropores which limit access to the internal surface of the material. The maximum discharge current for them is 100 mA. This is due to the fact that further increase of the current value causes a drop in the discharge voltage of more than 20%, and that is much. The greatest decrease of capacitance was observed for samples C1, C5 and C6. This was 30, 35 and 20%, respectively. In the first case, TEG grains block access to micropores. In this regard, the electrolyte ions do not have enough time to quickly form DEL at high current values, and consequently the resistance increases (Fig. 3b).
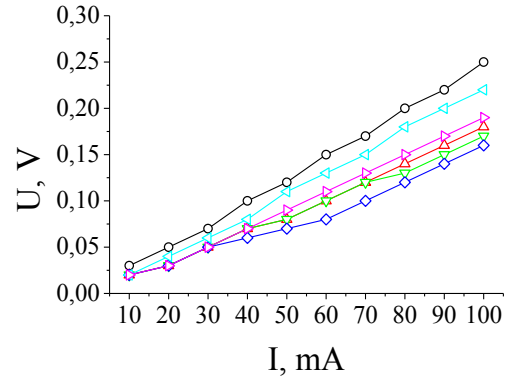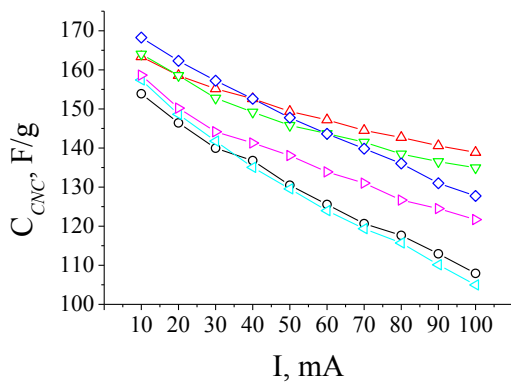

Fig. 3. Variations in (a) specific capacitance and (b) SC's voltage drop with discharge current for samples C1 —○—, C2 —△—, C3 —▽—, C4 —◇—, C5 —◁—, C6 —▷—

It is known that TEG has good elastoplastic characteristics [2]. Consequently, when it is mixed with NPC, pores get blocked and potential barriers between closely situated agglomerations are increased.

In other words, resultant from these processes are a decrease in SC capacitance and an increase of its resistance. The best result was obtained for sample C2: its capacitance variation with an increase of the discharge current did not exceed 15%.

The dependence of SC's voltage drop on the current after closing of the discharge circuit is shown on Fig. 3b. For samples C1 and C5, we have observed a significant increase in resistance caused not only by blocking of some transport pores (samples C1), but also by a reduction of the contact surface of the active material and electrolyte (sample C5). The voltage drop on all other studied samples did not exceed 20% at the maximum discharge current of 100 mA. It should be noted that the voltage drop for all the samples in the range of (10 ... 40 mA) is almost the same, which indicates that there is the same concentration of free charge carriers involved in formation of DEL.

Capacitance-voltage dependencies were obtained on the basis of the voltamperometry data (Fig.4). As is seen from these curves, an insignificant increase of the specific capacitance was observed in the range of potentials (0.1 ... 0.5) V at the sweep rate of 1 mV/s (Fig. 4a). It can be therefore stated that presence of redox reactions on the surface of the active material is the cause of this phenomenon. No increase of capacitance was though observed at the sweep rate of 5 mV/s (Fig. 4b). This is connected with the fact that the speed of chemical reactions is lower than the rate of DEL formation at the electrode||electrolyte interface. A slight peak on the curves shown on Fig. 4a, where the potential approaches 1V, is explainable by a release of non-

molecular oxygen from the electrolyte and from the volume of active material [4].
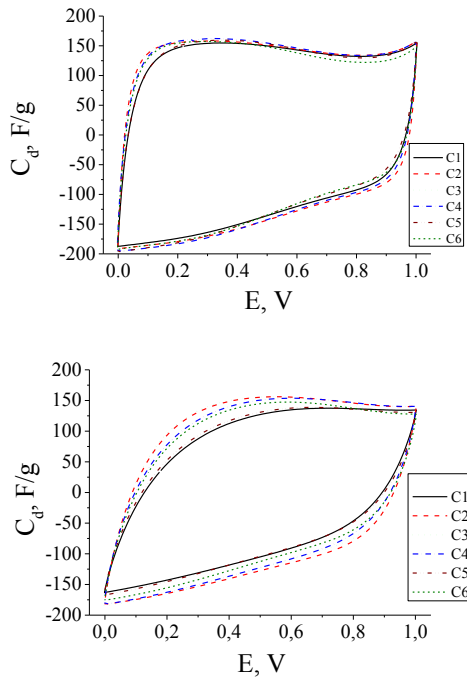

Fig. 4. Volt-faradic dependences based on voltage-dynamic characteristics of the studied samples at different sweep rates: (a) 1 mV/s; (b) 5 mV/s.

Values of specific capacitance of the studied samples at the variation rate of applied potential of 5 mV/s were calculated using cyclic voltamperograms of the composite material (Table 2).

It can be seen that the sample with TEG particles size of 160…200 micrometers has the largest capacitance.

Table 2. Specific capacitance of SCs studied by the method of voltamperomentry.

Sample	C_{NCM}, F/g
C1	155
C2	159
C3	158
C4	162
C5	159
C6	157

Conclusion

All in all, it has been established that the use of the developed nanocomposite materials on the basis of nanoporous carbon and thermally exfoliated graphite for manufacturing of electrodes of supercapacitors allows to obtain SCs with maximum specific capacitance $C_{NCM} = (155…160)$ F/g, with the dispersion degree of TEG particles d = (160...200) micrometers and its concentration in NCM composition $C_V = 15$ vol.%. The above-specified SC parameters are attained owing to a large specific surface area of NPC in NCM and a decrease in its resistance owing to the use of TEG with concentrations exceeding its percolation threshold.

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