Plasma-chemical synthesis of carbon nanotubes and graphene with mesoporous architecture for energy applications

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Abstract. We develop the universal technique of producing the mesoporous carbon nanomaterials. We manage to synthesize, in one and the same reactor, in the different regimes, carbon nanotubes and graphene. The technique consists in conversion of the carbon containing substances in the helium plasma flow generated by the plasma torch at low pressure. We investigate the samples using the scanning electron microscope and the synchronous thermal analysis. The studies, by the limited evaporation method, of the porous structure show that the graphene flakes and the balled nanotubes are mesoporous and thus provide the specific capacity value rather high for the electrochemical electrodes of the supercapacitor (125–133 F/g) at the charging/discharging resistance of 121/100 Ω.

1. Introduction
Supercapacitors (SC) are the promising energy storage means: they provide both high voltage and excellent capacity, that is, high specific energy values. In the industrial-manufactured SC, the high-disperse carbon materials with developed specific surface, such as the activated coals, serve as the active elements. Graphene might substitute the activated coal – it has both high (maximal for the pure carbon materials) specific surface and high electrical conductivity. Yet, the graphene sheets tendency to aggregation is the main obstacle in its application as the SC electrodes. This tendency results in a decrease of the specific surface accessible for the charged particles and thus in the SC capacity decrease [1]. To overcome the problem, the 3D-materials should be created [2]: application of the thermal plasma jet systems might provide this opportunity [3]. For example, graphene synthesized via the CVD-method [4] or obtained via the mechanical [5] or the liquid-phase [6] graphite exfoliation represents the flat sheet whereas in the plasma jet, it becomes cupola-shaped [3]. For example, graphene synthesized via the CVD-method [4] or obtained via the mechanical [5] or the liquid-phase [6] graphite exfoliation represents the flat sheet whereas in the plasma jet, it becomes cupola-shaped [3]. Then, the material porosity also influences on the specific capacity value [7]. Presence of the mesopores, 20–100 Å in radii, makes it possible to increase essentially the capacitance and the kinetic parameters of the capacitors with the double electric layer as against those with the microporous carbon material [8].

The present work is aimed at determination of possibility to apply, as the supercapacitor electrode component, the carbon nanostructures with the mesoporous architecture, synthesized in the volume of the
helium plasma jet generated by the Plasma torch.

2. Experimental section

To synthesize graphene and carbon nanotubes (CNT), we used the high-power direct current plasma torch with the expanding anode channel [3]. Figure 1 shows the reactor layout. The precursor is introduced into the plasma torch simultaneously with the plasma-forming gas. We managed to decompose the hydrocarbons both in the arc discharge domain and to the plasma jet itself to form a vapor-gas mixture; when cools, it condenses to form the flakes in the collector. The pressure in the reactor was equal to 77–710 Torr; we maintained the dynamic pumping by means of the water pump. We kept the arc current constant and equal to 300–350 A. The plasma torch power reached 35 kW. We took methane, propane-butane mixture, and acetylene as the hydrocarbons and helium as the plasma-forming gas. The mass flow rate of the hydrocarbons and nitrogen varied independently.

For each experiment, we added the hydrocarbons after the temperatures in the collector reached 350–400°C. We monitored the collector temperature by means of the chromel-alumel and chromel-copel thermocouples.

We examined the synthesis products by the traditional methods of studying the doped graphene [8]. To directly register the dimension parameters and the images of the plasma torch pyrolysis products, we engaged the Hitachi S5500 scanning electron microscope (SEM) and applied the in-lens technology to obtain both ultra-high resolution and high sensitivity of the EDS (Energy Dispersive X-ray Spectrometry) analysis.

To evaluate the efficiency of the synthesis, the phase composition and the thermal stability of the carbon products, we used the DSC (Differential Scanning Calorimetry) and the TG (Thermogravimetry) thermal analysis methods (STA 449 F3 Jupiter platform from Netzsch) applying the linear heating in air at 10 K/min within the temperature range of 20–1000°C.

To determine the characteristics of the porous structure (the pore volume, the pore radius, and the surface area), we used a relatively new method of adsorption: “the limited evaporation” (LE) based on the analysis of kinetics of the adsorbate evaporation from the test material [9]. To evaluate the specific surface area of the materials, we applied the classic BET (Brunauer, Emmett, and Teller) method using the Quadrasorb SI low-temperature nitrogen adsorption analyzer.

As the electrode material, we applied the composition of graphene or CNT, commercial activated coal and fluoroplastic. We introduced the carbon nanomaterials in the form of suspension (solid carbon/
alcohol = 0.004/1 and 0.05/1). At the first stage of the electrode preparation, we performed the water-coal mixture homogenization with addition of the necessary quantity of the fluoroplastic suspension. Then, we flattened the paste on the jeweler rolls with the subsequent drying at 200°C. At the second stage, we milled the dried electrode blank until the grit state and pressed it into the necessary thick plate. We obtained the end product by flattening the plate on the roll, under the gradual clearance decrease, up to the necessary thickness (90 to 300 μm). The final electrode area was within 9 cm². We established the treated electrodes mirror-like on the foil with the adhesive and soldered the construction from both sides. Then, we filled up the obtained pocket with the electrolyte: 1-mol Et₄NBF₄ solution in the acetonitrile – and vacuumed and pressurized the construction.

To study the pore structure of the graphene and the CNT structure, we analyze the cumulative and the differential distributions of the pores over the sizes. When measuring by the LE method, we performed the vaporization using benzol with the critical diameter of 0.6 nm as the adsorbate. We calculated the pore radii from the obtained isotherms using the Kelvin equation (1):

\[ \ln \left( \frac{p}{p_o} \right) = -\frac{k V \sigma}{r R T} \cos \varphi, \]

where, \( \sigma \) is the surface tension, \( V \) – the molar volume of the liquid, \( \varphi \)– the limiting wetting angle, \( k \) – the pore form-factor, \( r \) – the pore radius, Å.

For the electrochemical measurements, we fixed the ready plane-parallel cell between the clamping plates of the Analyzer of the chemical current sources (Russia). Before the measurements, we established the potentio-dynamic mode of the potential scanning (5 mV/s). The process finished when we reached the data reiteration regime per cycle. Then, to obtain the capacitance characteristic, in the galvanic-static mode, we charged the cell up to the voltage of 2.5 V and discharged with the preset currents; and then cycled the cell in the charging-discharging mode by the current of 5.5 mA/cm² within the voltage range of 0–2.5 V and 1.25–2.5 V. We determined the specific (per unit SC volume) SC capacitance at the discharge, according to the formula (2):

\[ C = \frac{(I \ast t)}{((U_{init} - U_{end})^2 \ast 1 \ast S)}, \]

where, I is the discharge current, t – the discharge duration, \( U_{init} \) – the initial discharge voltage, \( U_{end} \) – the final discharge voltage, l – the electrode thickness, S – its area.

3. Results and discussion

The experiments on the propane-butane mixture decomposition show that the maximal yield of the graphene materials is obtained when helium, at the pressure of 350–710 Torr, is engaged as the plasma forming gas and at the hydrocarbon mass flow rate of 0.3 g/s. Depending on the medium pressure, the plasma producing gas flow rate, and the composition, the graphene morphology varies from the crumpled structure up to the large-scale flakes with the transverse size from 50 nm up to 1000 nm. We synthesized the 1000 nm flakes at the helium pressure of 350 Torr and the mass flow rate of 0.75 g/s. Figure 2 shows an example of the SEM image of the synthesized products. In those conditions, the quantity of the graphityzed particles is within 4 mass %. That conclusion is based on the thermo-gravimetric analysis of the synthesized carbon structures.

The carbon nanotubes, 20 nm in diameter (figure 3), occur at 710 Torr of helium and the propane-butane mass flow rate of 0.4 g/s. According to the thermogravimetry, at the specimen heating, the maximal mass loss takes place at 400–600°C; the graphitized particle content is above 20 mass %.
Figure 2. SEM image of crumpled graphene morphology at 500 Torr in helium / propane-butane atmosphere.

Figure 3. SEM-image of the carbon nanotube morphology at 710 Torr, helium propane-butane atmosphere.

Figure 4 shows the data indicating that the pore distribution domains in graphene and in the CNT differ. For the CNT (1), the main peak is located within the range of $r_p = 70–1100$ Å and is divided into two peaks – this is possibly caused by the sub-layer presence. The peak respecting to the sub-layer is within the range of $r_p = 200–1020$ Å. The pores with the $r_p = 200–300$ Å respect to the main layer. Also present is the peak within the lower micropore domain of $r_p = 6.8$ Å. For graphene (2), the main peak is within the range of $r_p = 200–1020$ Å and consists of three peaks. The peak of $r_p = 200–400$ Å respects to the sub-layer domain. The pores within the range of $r_p = 1050$ Å are those of the substrate. We calculated the pore radii from the desorption isotherms with account for the thickness of the adsorption film on the surface of the pores, as well as according to the Broekhoff-de Boer equations [9].

From the cumulative distribution of the pores over the radii (Figure 5), we see that the pore volume curve exhibits the typical rise in the mesopore domain. This effect is caused by the desorption process from the initial mesopores. The measured pore volume for graphene is higher than the same for the CNT.

![Differential pore distribution over the Kelvin radii.](image)

![Cumulative pore distribution over the Kelvin radii (the adsorbate – benzol).](image)

The plot of the specific surface distribution over the pore radii (Figure 6) shows that the predominant surface of the graphene specimen is located in the lower mesopore domain (8–20 Å) and equals to
450 cm$^3$/g. For the CNT, within the same domain, the specific surface equals to 350 cm$^3$/g.

Electrical measurements of the SC parameters with the electrode made of the active carbon material (the F-4D fluoroplast suspension) and the metal current feeder (the А 99 foil, 20 μm thick) confirm these suppositions. We added the CNT and graphene, with the different concentration, under the normal conditions, at the room temperature and the atmospheric pressure, into the active carbon material (the activated coal). Figure 7 shows the histograms reflecting the influence of the carbon nanotubes and graphene presence in the electrode mass composition on the SC characteristics (the volumetric specific capacity). Note that graphene exhibits the maximal effect of the specimens taken.

![Figure 6. Distribution of the specific surface over the pore radii.](image)

![Figure 7. Histograms reflecting the effect of the presence of carbon nanotubes and graphene in the composition of the electrode mass on the characteristics of the SC (a volumetric specific capacity).](image)

The results of SC cell parameter measurements show that with the CNT adding, the values of the specific SC capacitance equal to 125 F/g whereas with the graphene adding – to 133–132 F/g. Note that if we varied the graphene content in the electrode from 0.004 to 0.05 mass %, then the values of the resistance during charging decreased strictly from 165 to 100 $\Omega$. We suppose that the graphene morphology facilitates the molecule orientation under the electric field application.

In general, the results of this work are consistent with the data in [10] that graphene is a more efficient material for chemical current sources than carbon nanotubes.

**4. Conclusion**

We investigate the electrochemical properties of the double-layered supercapacitor: its combined cell includes graphene and carbon nanotubes. We show that the high-disperse carbon nanomaterials synthesized in the plasma jet are mesoporous, with the specific surface up to 500 m$^2$/g. We develop the technique of preparation of the electrode mass with those materials. We added graphene and the carbon nanotubes into the electrodes as the ultrasound treated solutions. We investigate the electrical parameters of the prototype of the double-layered supercapacitor with the non-water electrolyte on the acetonitrile base. We show the possibility of increase of the supercapacitor power via adding the carbon nanomaterials. We state that by varying the graphene adding concentration in the electrode, we might reduce the supercapacitor resistance.
Acknowledgments
The work is supported by the Russian Foundation for Basic Research, project #18-08-00165 and #19-08-00145.

References
[1] Eletsy AV, Zycerman V Yu and Kobzev G A 2015 Nanocarbon materials: Physicochemical and exploitation properties, synthesis methods, and energetic applications. High Temperature. 53 130 doi.org/10.7868/S0040364415010032
[2] El-Kady M F, Ihns M, Li M, Hwang J, Mousavi M, Chaney L, Lech A and Kaner R 2015 Engineering three-dimensional hybrid supercapacitors and microsupercapacitors for high-performance integrated energy storage Proceedings of the National Academy of Sciences. 112 4233 doi.org/10.1073/pnas.1420398112
[3] Shavelkina M B, Filimonova E A, Amirov R Kh and Isakaev E Kh 2018 Methane/nitrogen plasma-assisted synthesis of graphene and carbon nanotubes. J. Phys. D: Appl. Phys. 51 294005 doi: 10.1088/1361-6463/aacc3d
[4] Pan Y, Zhang H G, Shi D X, Sun J T, Du S X, Liu F, and Gao H-J 2009 Highly Ordered, Millimeter-scale, continuous, single-crystalline graphene monolayer formed on Ru (0001) Adv Mater. 21 2777 doi.org/10.1002/adma.200800761
[5] Novoselov KS, Geim AK, Morozov SV, Jiang D, Zhang Y, Dubonos SV, Grigorieva I V, and Firsov A A 2004 Electric field effect in atomically thin carbon films. Science 306 666 doi: 10.1126/science.1102896
[6] Cooper A J, Wilson N R, Kinloch I A and Dryfe R A W 2014 Single stage electrochemical exfoliation method for the production of few-layer Graphene via intercalation of tetraalkylammonium cations Carbon 66 173 doi.org/10.1016/j.carbon.2013.09.009
[7] Kötz R and Carlen M 2000 Principles and applications of electrochemical capacitors. Electrochimica Acta 45 2483 doi.org/10.1016/S0013-4686(00)00354-6
[8] Wang H, Varghese J and Pilon L 2011 Simulation of electric double layer capacitors with mesoporous electrodes: Effects of morphology and electrolyte permittivity Electrochimica Acta 56 6189 doi: 10.1016/j.electacta.2011.03.140
[9] Shkolnikov E I, Sidorova E V, Malakhov A O, Volkov V V, Julbe A and Ayral A 2011 Estimation of pore size distribution in MCM-41-type silica using a simple desorption technique. Adsorption 17 911 doi: 10.1007/s10450-011-9368-9
[10] Karimov KS, Fatima N, Siddiqui K J and Khan M I 2019 Flexible thermoelectric cells fabricated by rubbing-in technology with rubber-carbon nanotubes/graphene composites Mater. Sci. Energy Technol. 2 551 doi.org/10.1016/j.mset.2019.06.001