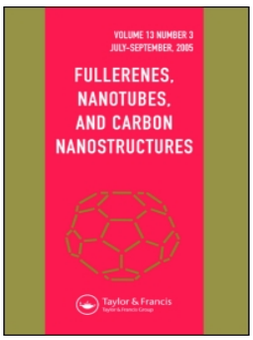

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Controlled synthesis of fullerenes and endohedral metallofullerenes in high frequency arc discharge

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ABSTRACT

The article presents the high-frequency arc discharge setup operating in helium atmosphere and applicable for the syntheses of carbon condensate with different dispersion and structure, along with fullerenes and endohedral metallofullerenes. It also highlights how the change of helium pressure in chamber can control the amount and composition of products in carbon condensate. The setup can be applied for the purposes of analysis, for instance in order to obtain information about the process of fullerenes and endohedral metallofullerenes formation. Also, the fact that the yield of higher fullerenes is increasing with the pressure rise, whereas the yield of endohedral metallofullerenes is decreasing suggests different formation mechanisms.

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KEYWORDS
Fullerene; Endohedral metallofullerenes; High frequency arc discharge; Pressure; Mass spectrum

Introduction

Carbon has three allotropic modification: graphite, diamond and fullerite. If the first two are presented as completed structural atomic formations, the third one, under regular conditions, is presented in the form of a molecular crystal with a face-centered cubic lattice. Fullerite—is the only soluble form of carbon (1). The main method of fullerite production is diffusion of graphite-rod electrodes in DC arc in a helium atmosphere at a pressure of 10–26 kPa (2, 3). Most frequently, the same conditions are also favourable for the synthesis of endohedral metallofullerenes (EMF), i.e., the state with fullerenes encapsulating atoms of metals (in particular rare-earth), is also possible (4, 5). Since the EMF molecule has a positively charged core, an ionized atom-guest, and a negatively charged shell of carbon atoms with a common π electron system, the EMF molecule can be considered as the atom of a big size. Owing to their unique electronic and magnetic molecule characteristics, the EMFs are not only in high demand in modern electronics and medicine, but also make foundation for the research knowledge creation in the field of quantum mechanics (6–9).

Low efficiency of the EMF production setups hinders both the process of research and their practical application (10–12). This results into the need of more advanced setup development suitable for experimental studies of the processes that make foundation of the carbon condensate formation in the arc-discharge possible and will contribute to the development of methods of controlled synthesis and find optimal parameters for various carbon-based materials.

Description of the experiment

Setup description

In this paper we describe the setup (Figure 1), designed and assembled for the purpose of production of nanodispersed carbon materials along with the mechanic studies of their formation.

Our setup, as well as other setups of this type, is based on the process of cooling the carbonaceous plasma in a helium atmosphere. The plasma is obtained as a result of arc-discharge evaporation of graphite rods, or graphite rods are filled with additional substances—dopants (13, 14), i.e. the operation of the setup is based on the W. Kraetchmer's modified method. The distinguished feature of the proposed setup compared to most of the fullerene generators used nowadays, is application of medium frequency alternate-current arc. Symmetrical arrangement of the electrodes allows to reach up to a 100% conversion of the electrode material into the fullerenes and EMF containing carbon condensate (CC) (14,15). As a consequence, this allows to avoid the main disadvantage typical for the setups operating on a direct current. The parameters of synthesis can be varied within the wide range of limits: arc current from 50 to 400 A, current frequency from 20 to 160 kHz, the helium pressure in the chamber from 30 to 400 kPa. This broad variability of parameters allows finding optimal values not only for the regular fullerene (14), but also for the EMFs. The chamber, in which the synthesis is performed, is equipped with quartz windows for visual and spectral studies when the setup is combined with the spectrograph.

The profound increase of the setup capacity combined with the enlarged variety of combination options results into a visibly increased productivity of carbon condensate along with the high amount of fullerenes and EMF as well to obtain renewed experimental results revealing the degree of influence of various synthesis parameters upon the process of various type EMF generation.

Figure 2 demonstrates the block scheme of the setup. The chamber, in which the synthesis is performed, is cooled by water. Two pairs of graphite electrodes placed on water-cooled

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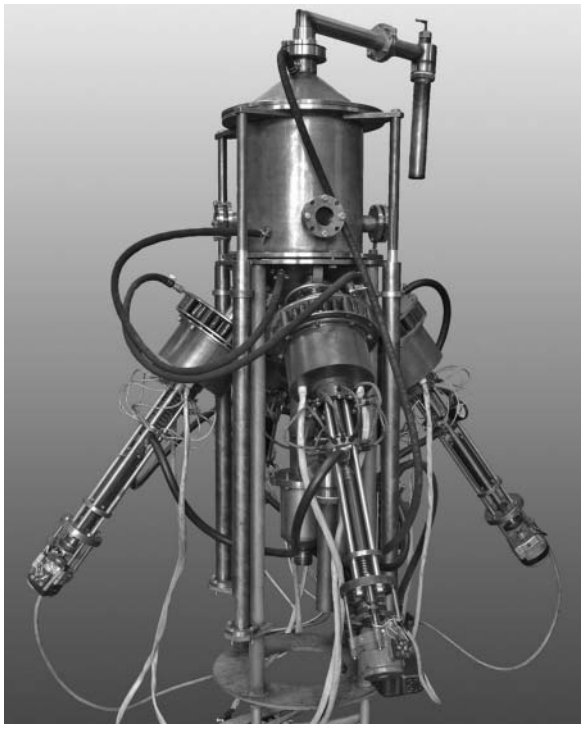

Figure 1. Setup for carbon condensate synthesis containing fullerenes and EMF.

rods on the ends are evenly placed into the chamber. The feeding of each rod is made by a special mechanical drive, activated by the stepping motor connected to the control unit. The control unit adjusts the flow rate of the rods so that the arc current remains constant corresponding to a predetermined initial current in the range of 2–3%.

The pressure of the helium, which is fed directly from the cylinder through a pressure regulator and a nitrogen trap into the chamber, also kept constant, with a special device, made on the basis of a controlled non-return valve and matching to given number, in the range of 2–3%. Power of each pair of electrodes is carried out by a separate generator G1 and G2, 25 kW, via the matching blocks. Figure 3 shows a circuit diagram of the installation, in which we can see that a matching unit consists of two reducing transformers T1 and T2 with a

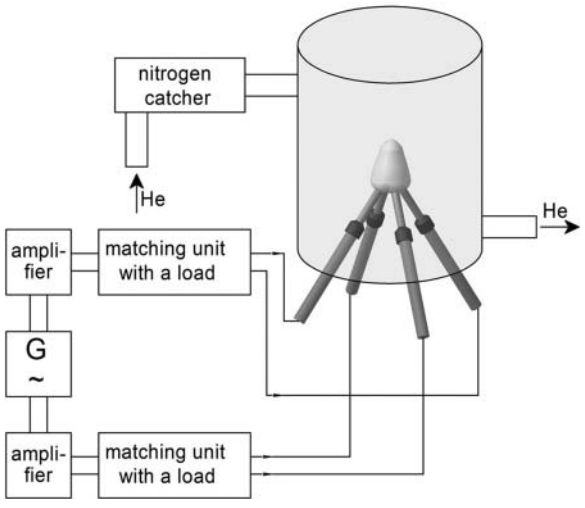

Figure 2. Block scheme of the setup for the synthesis of carbon condensate.

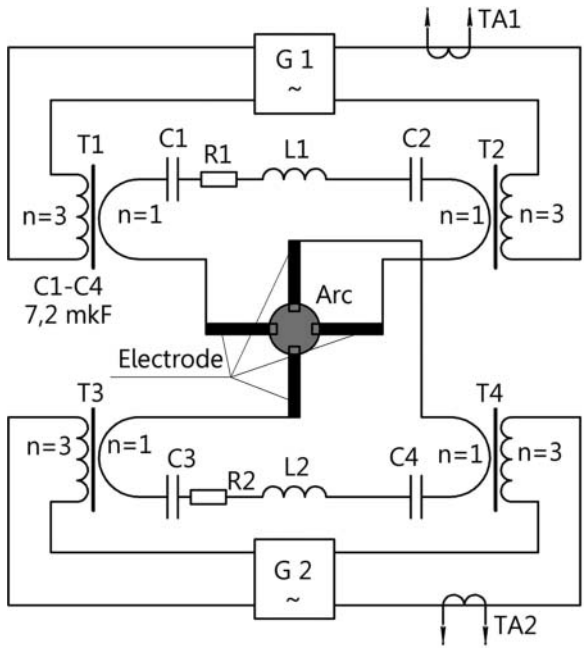

Figure 3. Electrical scheme of the setup.

transformation ratio of 3:1. The secondary windings of transformers are connected sequentially to two capacitors C1 and C2, an inductance coil L1, a ballast resistor R1, and two graphite electrodes with the arc in a gap between them. Another matching unit also consists of two reducing transformers T3 and T4 with a transformer ratio 3:1 and an analogous set of capacitors (C3 and C4), resistor (R2), inductive coil (L2), and another pair of graphite electrodes. The voltage of current transformer TA1 and TA2 is supplied to the unit controlling the feed rate.

Synthesis of nano-dispersed substances based on carbon, performed on setup developed in this work, is possible using graphite rods with a diameter of 4–20 mm. Rods of 6 mm in diameter and 100 mm long were evaporated. The rods were annealed preliminarily in a water-cooled chamber at 10 Pa, at a temperature of 1800–2000 K for 30 minutes. The same rods, only pre-drilled along the central axis, were used for the EMF synthesis.

A hole with a diameter of 3 mm and a length of 85 mm was filled with a mixture of graphite powder and metal oxide in mass ratio of 1:1. Annealing was performed under the same conditions as those used in the preparation of the rods to obtain conventional fullerenes.

Prior to the synthesis, the chamber is warmed up with the water heated to a temperature of 60–70 °C during 15 minutes. Then through the top entrance nitrogen trap the chamber is purged with helium for 1–2 minutes at the speed of 4–6 L/min. During the synthesis process, for chamber is cooled by the cold water with a temperature of 10–30 °C, and helium is supplied at a rate of 9 L/min through the flowmeter and pressure regulator, directly from the cylinder container. Cooling of the trap is carried out by liquid nitrogen.

Analytical procedures

Fullerene yields were measured by applying atomic-emission analysis which was performed on the setup, consisting of

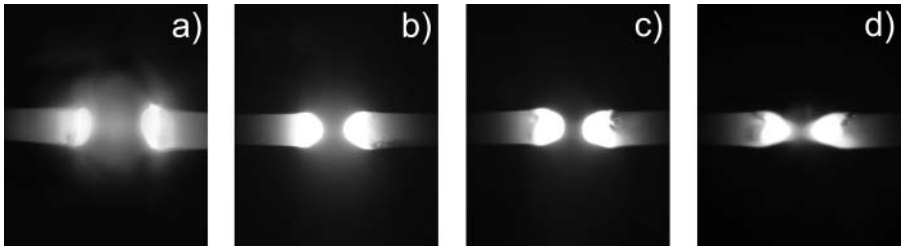

Figure 4. Plasma discharge between graphite electrodes at different chamber pressure: 30 kPa (a), 60 kPa (b), 120 kPa (c), 360 kPa (d).

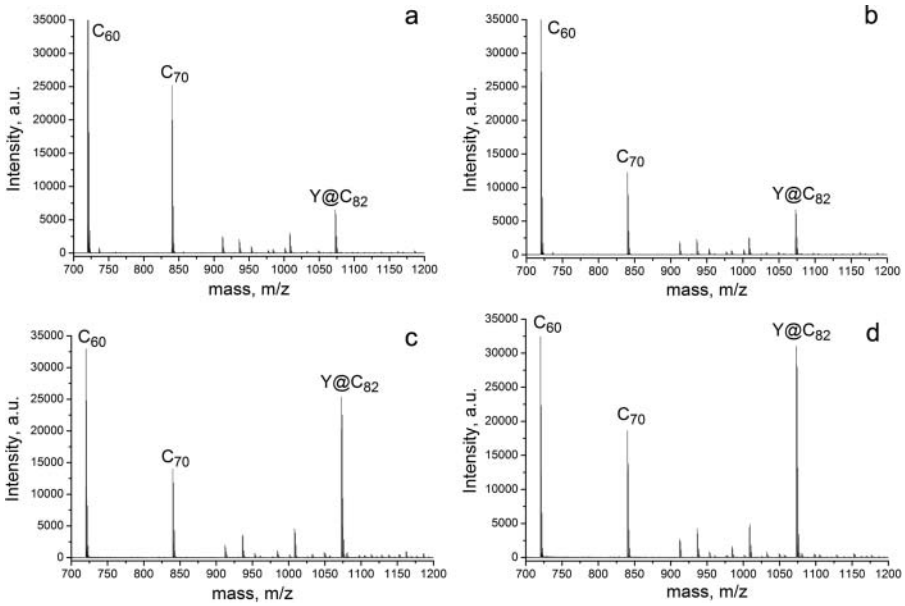

Figure 5. Mass spectral (positive-ion) analysis of fullerenes, detached from CC synthesized under different chamber pressure:30 kPa (a), 60 kPa (b), 120 kPa (c), 360 kPa (d) with the addition of Y_2O_3.

plasma atomizer–HF discharge in a stream of argon with copper and graphite electrodes, the spectrograph PGS-2 and a computerized spectral registrator. The mass spectra of sample were recorded by Bruker Autoflex time of flight mass spectrometer with laser desorption.

Synthesis of fullerenes and EMF

To optimize the synthesis condition, we studied the influence of current range, frequency and helium gas pressure in chamber on the structure of formed CC, content of different type of fullerenes and the EMF. This analysis showed that variations of current parameters and gas pressure lead to a similar result within the limits of parameters available for the given setup. In other words, the structure of the CC, the quantitative content of the fullerenes and EMF in the CC and their composition are largely dependent on the pressure. All changes, which can be obtained by modifying the current and the frequency can be obtained by the changing the pressure in the chamber. For instance, the increase in frequency leads to a change of the luminous discharge area structure similar to the change of the luminous area with decreasing current or pressure, as shown in Figure 4. Mass spectra of fullerene, detached from the CC synthesized with the addition of Y_2O_3 under different chamber pressure are presented in Figure 5.

Previously we examined the influence on the content of fullerene in the CC depending on the pressure, at which the synthesis was performed (16). At a pressure of 120 kPa the content of all fullerenes was 12 wt% of the total weight of CC. With the increase of the pressure, the content was decreasing and reached 7.5 wt% at the pressure of 360 kPa. The contents of C_{70} and higher fullerenes on the contrary increased and amounted to 360 kPa at 30 and 10 wt% for all fullerenes, respectively. Since EMF are the highest fullerenes molecules only with an atom-

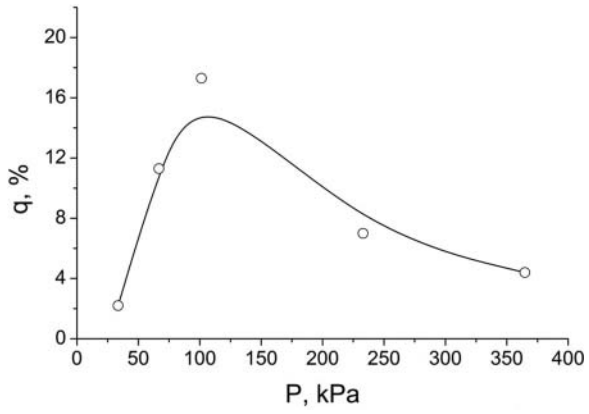

Figure 6. Content ratio dependency of $Y@C_{82}$ in, detached from CC, obtained under different pressure, fullerene mixture.