Comparative analysis of two methods for synthesis of fullerenes at different helium pressures

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The results of the effect of helium pressure in the chamber on the amount and composition of the produced fullerenes (C_{60}, C_{70}, etc.) synthesized in the arc plasma with graphite electrodes are presented. The findings obtained when the arc is powered by a direct (DC) and alternating (AC) currents of low frequency were compared in the same chamber with the electrodes located at the same angle to each other. These two methods are drastically different. The complete conversion of graphite into fullerene soot in AC occurs, but a part of the graphite is converted into a cathode deposit that does not contain fullerenes in DC, the relative amount of which increases when decreasing the helium pressure in the chamber. The highest fullerene content in fullerene soot of 10.2 wt.% is produced at a pressure of 127.5 kPa in AC arc, but in DC arc, the highest content of fullerenes in fullerene soot of 8.3 wt.% is produced at a pressure of 33.3 kPa.

Keywords: fullerene synthesis, alternating current, direct current

1. Introduction

A method of fullerene soot (FS) production process described by W. Krätschmer et al. in a plasma of the direct current (DC) arc in a helium atmosphere at pressure of 13.3 kPa [1] and its various modifications remains one of the most effective until recently [2–6]. At the beginning of the 90s of the last century, there appeared many scientific publications on new methods for producing fullerenes and on the influence of various parameters on their formation [7–11]. Interest was to find out the most commercially viable synthesis method on the one hand, and to understand the formation mechanisms of closed spheroidal carbon structures, i.e. fullerenes, on the other hand. At present, the fundamental interest in fullerene formation processes is much higher than the commercial one.

The efficiency of fullerene formation depends on many parameters: pressure and purity of helium, current magnitude, chemical composition of electrodes, and their size and location geometry. Even small changes in the parameters do affect the efficiency of fullerene formation both for synthesis

in plasma of the DC arc and for alternating current (AC). As mentioned above, it is inadmissible to compare the results obtained using different set-ups.

An analysis of the literature showed that a comparison of two methods for the fullerene synthesis in DC and AC using the same set-up and under the same conditions has not been carried out yet. Comparison of these two methods is of current interest, both from a fundamental and an applied point of view. The general patterns of plasma-chemical synthesis of fullerenes will also correspond to the plasma-chemical synthesis of any nanodispersed substances such as nanotubes, particles with core-carbon shell structure, metal carbides, etc. Currently, helium pressure is well known to be the main parameter which the amount and composition of the produced fullerenes is depended on [12–15]. Accordingly, the results and parameters of the fullerene synthesis in arc discharge plasma of DC and AC (frequency 66 kHz) carried out at different chamber helium pressures in the range of 13.3–353 kPa are presented in the given work.

2. Experimental procedures

The synthesis of fullerenes was performed on the set-up we developed, Figure 1 [16]. The chamber diameter is 24 cm, the height of the chamber body is 30 cm. To maintain the given arc current, the set up provides an automatic electrode feed, with the current magnitude matching the certain electrode gap. The syntheses were performed on two electrodes located at an angle of 74° to each other. Graphite rods for spectral analysis with a diameter of 6 mm were used as electrodes. The rods were preannealed at a pressure of 7 mPa under the temperature of 1500 °C for 30 min. Helium (grade – A, purity – 99.995%) was fed through a nitrogen trap (3) at a rate of 6 l/min. The studied pressures ranged from 13.3 to 353 kPa. The DC circuit consisted of a three-phase autotransformer, step-down transformer, diode rectifier and choke, Figure 1. The current form in the load circuit was detected with an oscilloscope connected to an ammeter shunt. A power amplifier working in the frequency range 40–120 kHz was used for synthesis of fullerenes in low frequency AC. Synthesis was conducted at a frequency of 66 kHz. The current form in the power amplifier circuit was also detected using an oscilloscope on a current transformer. The current forms of DC and AC arc are shown in the oscillogram of Figure 2. The arc current for all syntheses was 130±10 A.

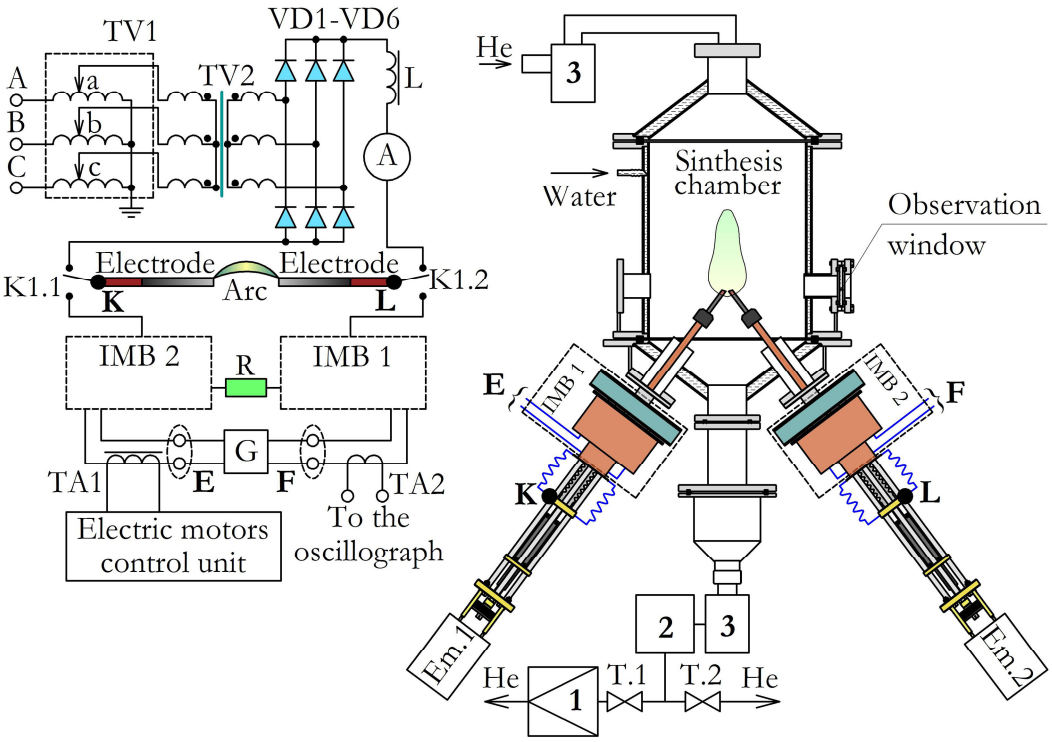


Figure 1. Functional diagram of the set-up for the synthesis of fullerenes.

Em.1 and Em.2 – electrode feed motors; IMB1 and IMB2 – impedance match block of the generator and the load; TA1, TA2 – current transformers; G – power amplifier; K, L – points of the power supply to the load; E, F – points of the power amplifier; T.1 and T.2 – ball valves; 1 – forepump; 2 – device for maintaining a given chamber pressure; 3 – nitrogen trap.

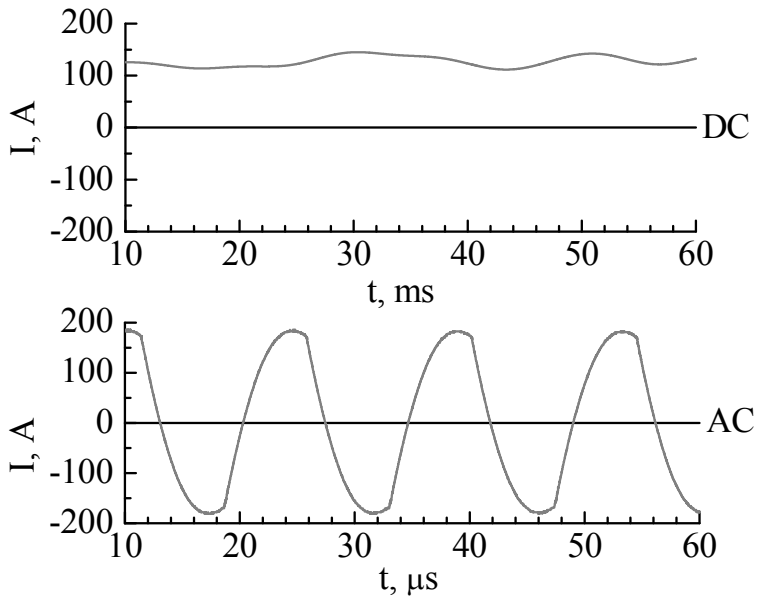


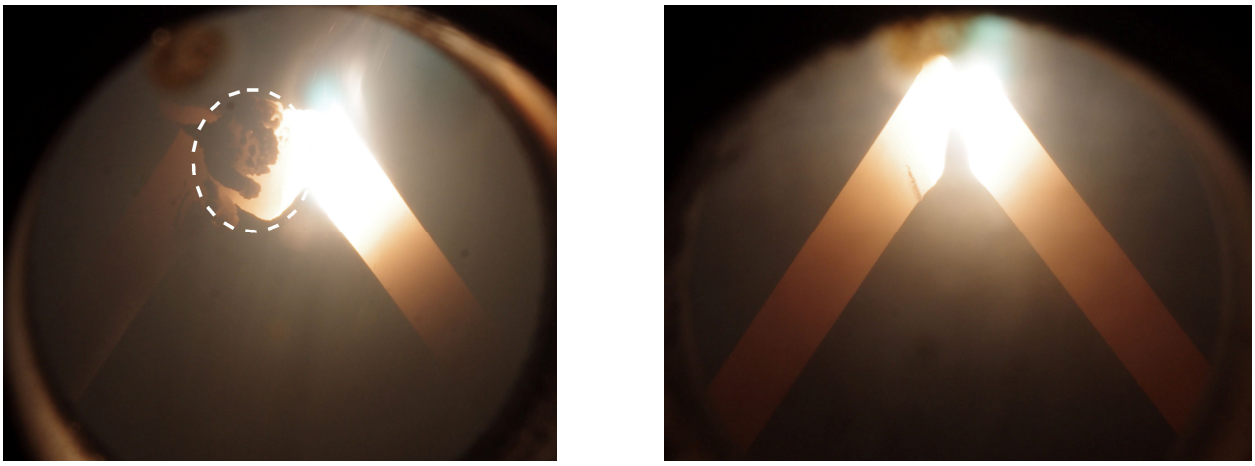
Figure 2. Oscillograms of the arc current at a pressure of 33.3 kPa

The fraction of cathode deposit (CD) produced during DC synthesis was determined as the CD/(CD+FS) ratio, with the erosion rate of the electrodes given as the ratio of the mass of evaporated

part of the graphite rod to the synthesis time. Fullerenes were separated from FS with benzene in a Soxhlet apparatus. The fullerene content was measured by the weight method, as the ratio of the weight of fullerene extract (FE) to the weight of the used FS. The error was determined by three syntheses for each pressure being no more than 0.8 wt.%. The isolated fullerenes were redissolved in toluene and analyzed by high performance liquid chromatography (HPLC) using an Agilent Technologies 1200 Series chromatograph equipped with a Cosmosil Buckyprep-M (10 mm × 250 mm) column. The chromatograms were detected at 324 nm. The nature of fullerene solubility is cluster type, the solubility and absorption coefficients of the individual fullerenes in toluene haven`t currently been identified. Accordingly, solutions of the same concentration were prepared using the same weighed quantity of FE for both synthesis methods and analyzed by HPLC. The relative content of individual fullerenes C_n (n = 60, 70, 76, 78, 80, 84, etc.) was determined as the ratio $S_{Cn}/S_{Fullerenes}$, where S_{Cn} is the peak area of individual fullerene in the FE chromatogram, and $S_{Fullerenes}$ is the total area of all detected peaks. A comparison of individual fullerene formation efficiency in the plasma of AC arc with respect to that in the plasma of DC arc was presented as the $C_n(AC)/C_n(DC)$ ratio. Where, $C_n(AC)$ is the relative content of individual fullerene in FS obtained in the plasma of AC arc, and $C_n(DC)$ is similar for DC.

3. Results and discussion

In course of fullerene synthesis in DC, the conversion of graphite to FS is significantly reduced due to the CD formation, Figure 3a. The synthesis of fullerenes in an arc discharge of AC allows one to avoid the CD formation, with the transformation of graphite into FS occurring with complete conversion without loss, Figure 3b. The dependence of the produced CD amount on the helium pressure is shown in Figure 4. When increasing pressure during DC synthesis, the CD fraction is seen to decrease. The maximum CD content (47 wt.%) corresponds to the maximum amount of fullerenes in FS (8.3 wt.%) at a pressure of 33.3 kPa. In addition, high cathode erosion occurs at a pressure of 225.5 kPa and above. For instance, the cathode loses as much as 32 wt.% at a pressure of 353 kPa.



(a) (b)

Figure 3. Photographs of graphite electrodes at a pressure of 33.3 kPa: (a) DC (the circled area is CD formation), (b) AC.

The erosion patterns of the rods during DC and AC discharge power supply are also different. Anode erosion occurs in DC, both electrodes erode in AC. The electrode area with the most severe erosion has the highest luminosity (Figure 3), with the luminescence intensity of the areas closest to the discharge in DC being higher than in AC. Observing two discharge rates between graphite electrodes, AC discharge is seen to have the diffuse nature, while it is more constricted in DC. The difference of plasma formation process in AC and DC is due to the difference of the nature of current flow. In the former case, the current is equal to zero twice over the period, and in the latter case it remains constant throughout the discharge burns, Figure 2. In AC, there is a frequent transient, which ensures the diffuse nature of the discharge even at high pressure, up to 353 kPa.

The study results of the fullerene content in FS, the electrode erosion rate, and also the rate of CD formation as a function of the helium pressure in the chamber for DC and AC are shown in Figure 4. For DC, the significant increase in electrode erosion rate is observed with increasing pressure, which reaches 47 mg/s at a pressure of 353 kPa. For AC, the erosion rate also increases with increasing pressure and reaches 18 mg/s at a pressure of 353 kPa. The fullerene content in FS substantially depends on the chamber pressure and, in DC, reaches 8.3 wt.% at a pressure of 33.3 kPa, Figure 4a. The second maximum of 6.5 wt.% corresponds to a pressure of 82.6 kPa. Thus, for the efficient synthesis of fullerenes in DC, a decreased helium pressure in the chamber, according to the published data [14], has to be used.

In AC, the fullerene content in FS is characterized by two distinct maxima, at pressures below and above atmospheric pressure, Figure 4b. The maxima of fullerene content in FS are 10.0 wt.% and 10.2 wt.% observed at helium pressures in the chamber of 50 and 127.5 kPa, respectively.

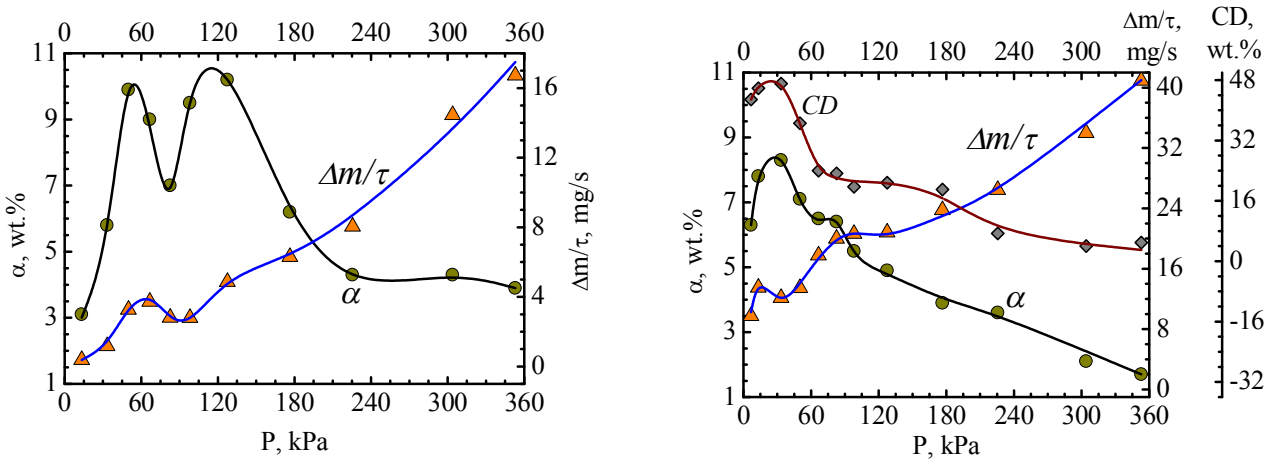


Figure 4. Dependence of fullerene content in FS (α), electrode erosion rate ($\Delta m/\tau$) and CD fraction on helium pressure in the chamber: (a) DC, (b) AC.

The qualitative composition of FE obtained in DC does not differ from the composition of FE obtained in AC, however, some differences in the ratios of higher fullerenes are observed, Figure 5.

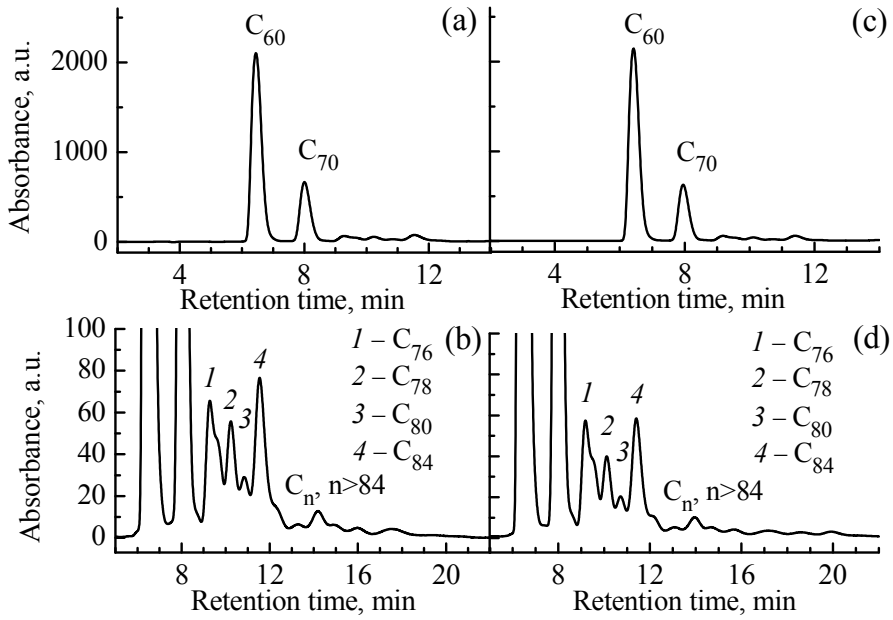


Figure 5. Chromatograms of FE obtained in DC (a, b) and AC (c, d) at a pressure of 127.5 kPa. Sample injection was 0.57 mg, eluent rate (toluene) was 5 mL/min.

In accordance with the method described above, the use of the relative content of individual fullerenes allows one not to take into account the particular value of the absorption coefficients and to evaluate the influence of the current type on the synthesis efficiency. Table 1 shows the data on five pressures: 13.3 kPa is a pressure mostly indicated as the pressure wherein the fullerene content in FS is maximum during the synthesis in DC arc [1,2]; 33.3 kPa is the first maximum of fullerene content in

FS for the DC synthesis; 82.6 kPa is the second maximum of fullerene content in FS for the DC synthesis; 127.5 kPa corresponds to the second maximum of fullerene content in FS for the AC synthesis; 353 kPa is considered as the limiting point in the studied range.

Table 1. The ratio of the peak area corresponding to the individual fullerene to the summed area of all peaks of the FE chromatogram.

Current type	AC					DC				
P, kPa	13.3	33.3	82.6	127.5	353	13.3	33.3	82.6	127.5	353
$S_{C60}/S_{Fullerenes}$, %	79.0	77.1	75.4	68.9	59.0	75.4	70.6	66.6	64.4	64.0
$S_{C70}/S_{Fullerenes}$, %	18.9	19.1	19.8	20.9	24.6	17.8	18.6	21.5	21.6	21.9
$S_{Cn}/S_{Fullerenes}$ (n>70), %	2.1	3.8	4.2	10.2	16.4	6.8	10.8	11.9	14.0	14.1
$S_{C76}/S_{Fullerenes}$, %	1.2	1.9	2.0	3.0	4.0	2.4	3.1	3.4	3.6	3.2
$S_{C78}/S_{Fullerenes}$, %	0.1	0.3	0.4	1.5	2.9	0.9	1.5	1.9	2.3	2.1
$S_{C80}/S_{Fullerenes}$, %	0.1	0.2	0.3	0.7	1.4	0.5	0.8	0.9	1.1	1.0
$S_{C84}/S_{Fullerenes}$, %	0.6	1.2	1.2	3.1	5.8	1.9	2.9	3.6	4.4	4.6
$S_{Cn}/S_{Fullerenes}$ (n>84), %	0.1	0.2	0.3	1.9	2.3	1.1	2.5	2.1	2.6	3.2

Since the summed area of all peaks in the chromatogram ($S_{Fullerenes}$) corresponds to the same weight for all FE studied, it is possible to compare the formation efficiency of each individual fullerene in different types of discharge plasma. The relative content of individual fullerenes in FE obtained in the DC discharge and in the AC discharge can be seen in Table 1 to be different. To evaluate the synthesis efficiency in terms of graphite conversion to individual fullerene during DC and AC discharge power supply, the values of C_n(AC)/C_n(DC) were calculated for all studied pressures, Table 2. To synthesize the higher fullerenes C_n (n>70) at a pressure of 225.5 kPa and lower, direct current is used more efficiently, and at pressures above 225.5 kPa is AC as shown in Table 2. Both DC and AC can be used with the same efficiency in the entire studied pressure range 13.3–353 kPa for the synthesis of C_{60} and C_{70} fullerenes.

Table 2. The efficiency of the formation of individual fullerenes in the AC and DC arc plasma.

P, kPa	13.3	33.3	50	66.6	82.6	98.1	127.5	176.5	225.5	304	353
C_{60}(AC)/C_{60}(DC)	1.05	1.09	1.02	1.00	1.13	0.99	1.07	1.00	1.06	0.96	0.92
C_{70}(AC)/C_{70}(DC)	1.06	1.03	0.98	0.88	0.92	0.95	0.97	0.97	0.93	1.09	1.12
C_{76}(AC)/C_{76}(DC)	0.5	0.61	0.96	1.01	0.59	0.54	0.83	0.44	0.46	1.08	1.25
C_{84}(AC)/C_{84}(DC)	0.32	0.41	0.74	1.20	0.33	0.52	0.70	0.44	0.37	1.04	1.26

4. Conclusions

Thus, FE isolated from FS synthesized in DC and AC differ in composition. The presence of graphite losses due to the CD formation in DC syntheses and their absence during AC synthesis prove the advantage of the latter. Indeed, to obtain the same amount of fullerenes during the DC synthesis, it is necessary to use twice as much as graphite than during the AC synthesis. In this work, as in [15], the diffuse nature of the discharge was shown to be in accord with higher content of fullerenes in FS. As shown in the studies this can be achieved even at a pressure above atmospheric pressure (127.5 kPa) in the 66 kHz AC, and in DC only at pressures below atmospheric pressure (33.3 kPa is best used).

Acknowledgments

The reported study was funded by RFBR according to the research project № 18-32-20011.

Conflict of interest

The authors declare that they have no conflict of interest.

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