ENHANCED APPROACH TO SYNTHESIZE CARBON ALLOTROPES BY ARC PLASMA

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Abstract. This work allows production of carbon vapor in plasma from graphite electrodes under influence of a buffer gas flow supplied into plasma zone. Carbon vapor is evacuated from hot plasma zone by efficiently organized radial exhaust gas stream. Study of influence of inert gas flow dynamics supplied to hot plasma zone during fullerenes synthesis was performed and relationship between different applied power, diameters of used electrodes, fullerenes productivity and yield were established. It was defined that critical temperature plays important role in production of good carbon vapor suitable for fullerenes synthesis. Proposed method allows significantly increase fullerenes productivity.

1. BACKGROUND

In 1990 W. Kratschmer and D. Huffman developed a simple method to synthesize fullerenes by striking electric arc between two graphite electrodes and producing soot from vaporized carbon [1] now known as Kratschmer's or arc discharge method. This method allows evaporation of 6-10 mm graphite electrodes in 80-150A DC arc discharge having average fullerene yields of 7-10% mass. Fullerene productivity by this method depends on carbon soot production rate and fullerene yield in this soot.

Attempts to increase fullerene productivity by applying higher electric power were not successful because UV radiation produced in arc discharge caused photochemical destruction of fullerenes and fullerene precursors. Experiments of fullerene exposure to different sources of UV radiation demonstrated that complete decomposition of fullerenes occurs under radiation of ultraviolet lamp [2] or solar light [3]. UV photochemical destruction is considered as a serious limitation for scaling up productivity of Kratschmer's method [4].

This paper describes modification of arc discharge method, which significantly reduces destructive effect of UV radiation and improves fullerene productivity using high electric currents and big electrode diameters.

2. EXPERIMENTAL

Reaction vessel used in our experiments comprised graphite anode and graphite cathode with longitudinal central gas channel as shown in Fig.1. Buffer gas was injected through cathode channel into between-electrode gap to create radial gas outflow rapidly evacuating produced carbon vapor from hot plasma zone and preventing UV photochemical decomposition of fullerenes and fullerene precursors. Condensed carbon vapor forms soot, containing fullerenes. Collected carbon soot is subjected to known fullerene recovering and analytical procedures.

Helium gas was used as a buffer gas in all experiments. Buffer gas flow was controlled in the range of 1-300 L/min within precision ± 1%. Electric cur-
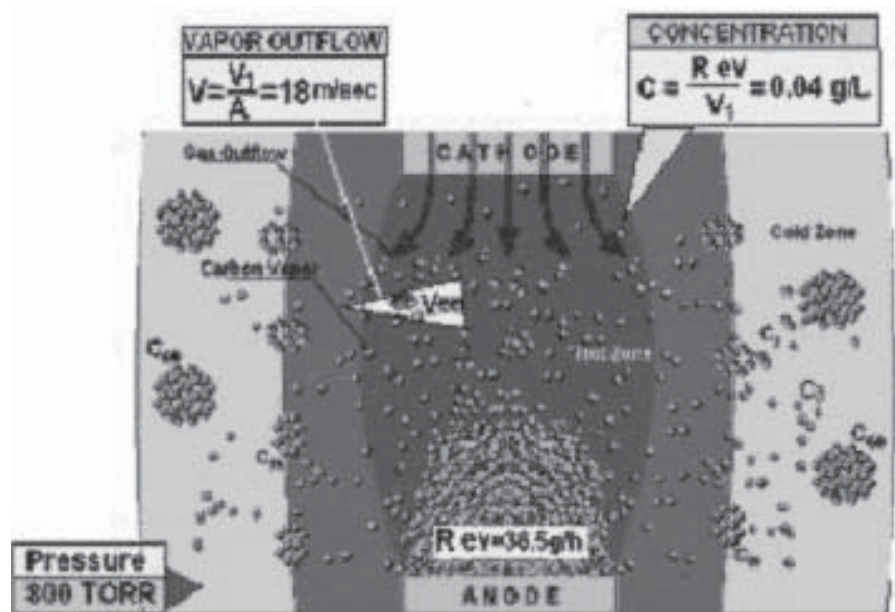

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Fig. 1. Schematic diagram of buffer gas injection into between-electrode gap.

rent and voltage were controlled within ± 3% precision range with brief overshoots up to 20%. Graphite electrodes of industrial grade (typical density 1.70-1.74 g/cc, ash < 0.1%, with diameters 6.4mm (1/4"), 12.7mm (1/2") and 19.1mm (3/4") were used. All input parameters were computer-controlled by data acquisition system.

Three series of experiments were performed using mentioned above 6.4, 12.7 and 19.1mm electrodes with central channel in cathode for buffer gas injection. Electric current and radial gas outflow were variable in a wide range. Reactor pressure was at all times maintained at a level of approximately 800 Torr.

HPLC method was used to perform quantitative analysis of fullerene content in carbon soot.

3. RESULTS AND DISCUSSION

Experimental data for fullerene yields in soot and fullerene productivity are presented in Fig. 2. Fig. 2b for 6.4 mm electrodes demonstrates that introduction of buffer gas flow of V_0=3 L/min into between-electrode gap allows to increase fullerene yield from 7.4 to 17.3% using 80 A arc discharge typical for Kratschmer's process. We explain these results by substantial reduction of UV photochemical decomposition of fullerene precursor. Linear velocity v_{lin} of radial gas outflow evacuating produced carbon vapor from hot plasma destructive zone can be expressed by next equation

$$V_{lin} = \frac{V_0 \frac{P_0 T_1}{P_1 T_0}}{\pi dh}, \tag{1}$$

where V_0 is buffer gas flow injected into electrode gap at normal conditions (T_0 = 298K, P_0=765 Torr); T_1 and P_1 are temperature and pressure in arc zone; d is graphite electrode diameter; h is between-electrode gap.

Assuming that pressure in between-electrode gap is equal to reactor pressure $P=P_1$ or 800 Torr, buffer gas is heated up to the temperature of T_1= 4000K typical for arc discharge zone, between-electrode gap h=1.5 mm and optimal buffer gas flow V_0= 3 L/min = 50 cm³/s, linear gas velocity v_{lin} will be equal to 21.3 m/s. Linear gas velocities calculated for other conditions are presented in Table 1. In comparison, evacuation of carbon vapor out of arc zone in Kratschmer's method is controlled by diffusion and thermal convection processes with typical linear gas velocities of 100-1000 times less then in our case. It means that the radial gas outflow is able to reduce UV photochemical decomposition by several orders of magnitude due to fast evacuation of carbon vapor out of arc zone. Therefore, our approach overcomes limitation imposed on fullerene yield by UV-radiation and allows to scale up Kratschmer's method productivity by increasing arc discharge current. Fig. 2a shows that fullerene productivity of 0.3 g/h at 80 A arc discharge under buffer gas flow rate of 3 L/min can be increased up to 3 g/h using

Table 1. Data corresponding to maximum fullerene productivities.

d, mm	A, cm²	h, mm	R, g/hour	Q_{max}, g/hour	C_f,% mass	V_0, L/min	v_{lin}, m/s
6.4	0.32	1.5	39.0	3.1	8.5	8.5	60.3
12.7	1.27	2	153	10.6	7.3	38	102
19.1	2.86	3	355	25.0	7.3	175	208
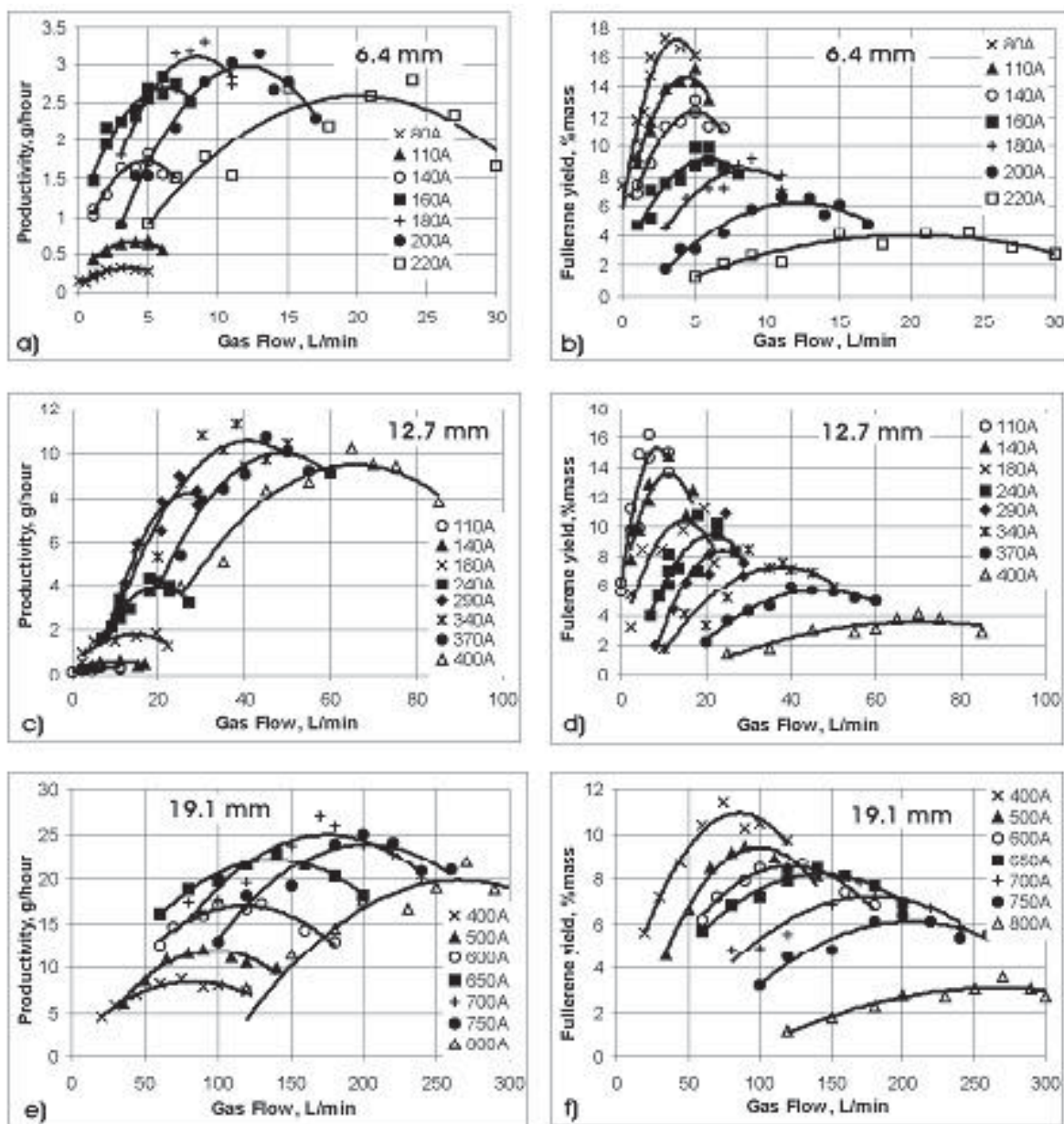
Fig. 2. Experimental results for fullerene yields and fullerene productivities.

Table 2. Enthalpies of formation for carbon clusters C_1-C_7.

Carbon cluster	C_1	C_2	C_3	C_4	C_5	C_6	C_7
$\Delta_f H$, kJ/mol	711	817	831	1052	1081	1312	1325

180 A electrical current under buffer gas flow rate of 8.5 L/min.

At the same time, performed analysis of fullerene yield showed that fullerene yield dropped from 17.3% down to 8.5%. We suppose that this surprising effect is connected with presence of carbon clusters of different size in graphite vapor. It was reported earlier [5] that carbon clusters from C_1 to C_{20} were detected by mass-spectrometry during graphite evaporation process. Enthalpies of formation for carbon clusters $C_1...C_7$ at average temperatures 2450-2750K measured by high-temperature Knudsen effusion mass spectrometric method are shown in Table 2 [6].

Enthalpy of formation $\Delta_f H$ of carbon clusters C_n in our case equals to their enthalpy of vaporization $\Delta_v H$, which can be expressed by Clausius-Clapeyron equation

$$\Delta_v H = -R \frac{d(\ln(P))}{d(1/T)}, \quad (2)$$

where R – molar gas constant; P – saturated vapor pressure; T – temperature. Eq. (2) applied to gas mixtures describes partial pressures of gas components. Therefore, data from Table 2 demonstrate that partial vapor pressure of bigger carbon clusters grows faster with temperature then partial vapor pressure of smaller clusters. It means that percentage of small clusters in graphite vapor reduces with temperature increase.

There is still no common theory describing mechanism of fullerene formation. Many alternative hypotheses can be found in literature [7-9]. Nevertheless, majority of them agree that first stages of fullerene formation require presence of small carbon clusters as precursor. Clear evidence of this statement was obtained through $^{12}C/^{13}C$ isotopes scrambling experiments [10], what demonstrated that carbon vapor consists of the smallest clusters before the process of fullerene formation starts. According to our previous conclusion temperature increase reduces the percentage of building blocks in graphite vapor available for fullerene formation. This is the reason why fullerene yield drops when electric current increases above certain level. As shown in Fig. 2, high currents providing too high anode temperature do not improve fullerene productivity because more abundant at these conditions large carbon clusters can't be used in formation of fullerene molecules. That is why fullerene productivity in our experiments is lower above 180 A of applied current.

Figs. 2c-2f shows that the same tendency is found for 12.7 and 19.1 mm electrodes evaporated at higher currents. In all cases both fullerene yield and fullerene productivity significantly increase with introduction of radial gas outflow. Maximum fullerene productivities Q_{max} for each electrode diameter d used in our experiments, corresponding fullerene yields C_f, anode evaporation rates R and buffer gas injection flow rates V_0 are presented in Table 1. Electrode cross-sectional areas A, typical between-electrode gaps h and linear gas velocities v_{lin} for maximum fullerene productivities calculated by formula (1) are also cited in Table 1.

Our analysis shows that anode evaporation rate R at the point of maximum fullerene productivity attributed to electrode cross-sectional area A remains constant

$$R_s = \frac{R}{A}, \quad (3)$$

where R_s is specific anode evaporation rate. Values of R_s calculated for different diameter electrodes used in our experiments are presented in Fig. 3.

According to Knudsen formula [11] specific evaporation rate [mol/(m²·s)] of solids can be calculated by

$$R_s = \alpha \frac{P_s - P}{\sqrt{(2\pi mkT)}}, \quad (4)$$

where α is evaporation coefficient; T is surface temperature; P_s is saturated pressure of vapor at temperature T; P is actual pressure; m is molar mass; k is Boltzmann's constant.
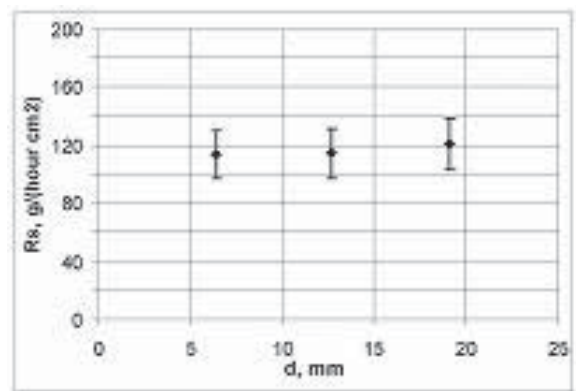

Fig. 3. Dependence of specific anode evaporation rate from electrode diameter.

Helium pressure of *P*=800 Torr was maintained in reaction vessel during all the experiments and graphite electrodes of the same quality were used. Uniformity of these factors determines the univocal dependence of evaporation coefficient a [12] and average molar mass *m* of graphite vapor from anode surface temperature *T*. At the same time, saturated pressure of graphite vapor P_s is also the function of temperature *T*. Therefore, specific evaporation rates R_s presented in Fig. 3 can have the same values only if anode surface temperature *T* remains constant at all points of maximum fullerene productivity. What means that some critical anode temperature exists above which regardless of high evaporation rate vapor quality is not suitable for fullerene formation. Critical temperature provides maximum potential fullerene productivity and defines method's scalability. According to experimental data this potential is about 8.5-9.0 g/hour of fullerene mixture obtained from 1 cm^2 of anode cross-sectional area.

4. CONCLUSION

Present work has demonstrated that injection of inert buffer gas directly into electrode gap reduces UV photochemical destruction and, simultaneously, increases carbon vapor quenching rate. It was defined that maximum graphite evaporation rate is determined by critical anode surface temperature above which quality of carbon vapor suitable to fullerene synthesis drops. It was also shown that the use of large electrodes and higher electric currents in the presence of buffer gas outflow can make this fullerene production process scaleable.

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