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Research Article

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Discharge with a Hollow Electrode is a New Type of ARC Discharge for Fullerene Receipt and Qualities of the Synthesis Process

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Abstract In order to increase a size of fullerene output was made a set on basis of unusual physical principle function. Arc discharge was ignited in a hollow electrode with a pointed work gas and plasma stream. Under these conditions was reaccepted the product without amorphous component and the heavy fullerene yield was increased. An explanation of the result was based on the growth duration of fullerene formation in space with high temperature and plasma density and increased the way forming. An analysis showed that a fullerene trajectory forming was about more then one rotate ring or helix. However the model displayed that came in existence centrifugal force, which at the same time gave any restriction for the limit fullerene mass also.

Keywords hollow electrode, gas-plasma stream, turbulence, formation duration, amorphous component

Introduction

In recent decades, up-to-date nanotechnologies have been created by using the unique properties of fullerenes [1-3] as the main element of functional compositions. To commercialize them on a large scale, economic and environmentally appropriate methods and devices for fullerene synthesis are being developed. In new developments, more attention may be given to heavy fullerenes C_n, where $n \geq 84$, which have an advantage in cross-section and electron affinity energy (EA_i) over the known C_{60} and C_{70} used.

So it was taken into estimation that fullerene-fullerite was a functional structure-material and could able to be a base for an origin plenty of new lines study and to use in industry. Analysis of fullerene synthesis methods showed the advantage of the arc method concerning accepted laser and conditional chemical methods. But the cost of arc discharge fullerene was remained high therefore it was restraining the development a lot of important industry branches and national economy in general.

The aim of the work is to show the peculiarities of the fullerene formation process into arc discharge with a hollow electrode and the pointed work gas stream (He), to show the nature of effectiveness the method fullerene synthesis.

Materials and Methods

Fullerene arc synthesis is a multievent process, the theory of which is not complete. According to more general concepts, C_j fullerene is formed in a discharge space at 2000-5000 K by collisions and sticking together two-tree particles (C, C_2, C_3...) and due to diffusive motion. Fullerene synthesis is represented conventionally as a sequence of attachment events C_k and C_i clusters and with allowance (for relaxation of kinetic energy particles) of inverse processes: annealed $n_f \cdot C_f$ clusters. So synthesis process conditionally to present as the developing according to the equality [4, 5]:

$$C_j = C_к + \sum|_i n_i \cdot C_i - \sum|_f n_f \cdot C_f, \quad (1)$$

where C_k is the initial fullerene cluster formed in the space between electrodes; the coefficients n_i and n_f are integers; in the equality (1) clusters are summed with respect to the subscripts I and f. The parameters of fullerene C_j formation from the sum of intervals: $T_j = \sum|_i t_{Ci}$ - total duration of the process and $L_j = \sum|_i l_{Ci}$ - formation path length develop according to a scheme analogous to (1) in a conventional path.

In usual arc discharge, the diffusive nature of motion in space with temperature decrease along the radius gives a spread in the path parameters of clusters, in the mass and quality of the product; in ordinary arc discharge, the amorphous component makes up a larger proportion (> 50%) of the product.

An analysis of the above-mentioned general concepts led us to the assumption that a carbon product of another quality can be obtained in a space with high temperature, in which more long conventional duration and fullerene formation path length are ensured.

In [4-7] fullerenes were synthesized using a discharger, Fig. 1: Graphite Electrode 1: Ø6 mm for emission spectrum analysis, Graphite Electrode 2: hollow space Ø15 mm, h15 mm with slot-shaped holes, through which the working gas (*He*) is supplied into the hollow space. Part 3 is an important component. It's a graphite cover, which punctually driven to cylindrical part of Graphite Electrode 2. Part 4, which is used for electrical insulation of Electrode 2, is made of high-temperature ceramic. Part 5 and part 6, made of common steel, supply potential to the electrode 2 and hold together the whole structure. The experimental results were obtained with part 4 being a high-temperature crucible installed on top of Part 2 to perform the operation (Priority Date: ~ 4-6 March 2006). Electrodes 1 and 2 have a temperature of T > 3000 K during the discharge. Ceramic part 4 and the work gas coming from the upper part of cylinder via the tube system are heated by the radiation and thermal contact with Electrode 2. Then gas is fed to the hollow part through the slots and goes to the discharge space between Electrode 1 and Electrode 2.

Results & Discussion

The set of measurements was made with the working gas consumption rate of q = 5 cm^3/sec and the discharge current sequence of 60, 80, 70, 70 A. The first two conditions demonstrated the lower (electrodes made red-hot for about an hour but product in cavity was absent) and the upper (see further) limits of carbon vapor pressure. The optimum fullerene samples were obtained with the discharge current of 70 A. This being the case, the product does not contain amorphous component, which can be separated in benzene. In the said discharge, the reference path length and formation time of fullerenes were increased by growing and forming fullerenes according to Scheme (1) in a hollow electrode under the turbulent flow of gas plasma (T > 2000 K) created by the work gas. The synthesized product, as usual, deposited on the cooled wall of the discharge chamber, while the synthesized product gathered from the wall had no amorphous deposit in benzene. This means that the vaporized graphite was almost completely converted into the target product-fullerenes.

In the preliminary part investigated several crucibles, which functioned as Part 4, in which a part of the sidewall was removed *with* a diamond tool to pass *the work gas* through. The part was shaped as a flower bud with 6 or 8 petals on top covered Part 2 with weak or even without contacting it. The project determined the dimension limits of the area to be cut out. That was the way for regulation of an initial temperature work gas.

The synthesized product was analyzed in a solid fullerite phase on the AUTOFLEX ^{R}IILRF 20 time-of-flight mass spectrometer with pulsed N_2 laser (Germany). The mass spectrum at the optimal discharge current *I* = 70 A was presented in articles [4 -7]. The values of the peaks of the fullerenes C_{60}, C_{70}, C_{84}, …, C_{150} in the mass spectrum are as follow: 100, 57, 78, …, 6. The descent of the envelope curve spectrum peaks with increasing number of atoms in the cluster is common.

The presented peculiarity is waited taking into account the equality (1): probably ought to be watching slump intensity in a row of fullerenes with mass growth, because fullerene of more mass are formed from sticking of more particles number. In discharge with hollow electrode, however, the decrease in the values of peaks is smaller and the value of the C_{84} peak is larger than that of the C_{70} peak. The last peculiarity shows that the structure of the C_{84} cluster apparently was formed by the optimal number of covalent electron bonds, which have a three-dimensional

structure. As a result, the C_{84} cluster has been obtained, which is stronger than other fullerenes. Fullerene C_{84} has a difference from other fullerenes on collection of symmetry classes [8].

A little conditional presentation on the special feature synthesis of the discharge with a hollow electrode would be got from a simple computation of fullerene trajectory forming (FTF). For the FTF calculation were used a set data, an experimental data and temperature data of the arc discharge.

The feature would be clear from fig. 1. At need size of flow work gas goes in discharge cavity through $4X90^0$ openings. As can see from fig.1 the flow way is passing over the canal with length to 7 mm. At the motion during discharge helium flow lowers particles temperature (do harden product), preserves cavity wall from fullerene acumulating and carry out from cavity formed fullerenes.

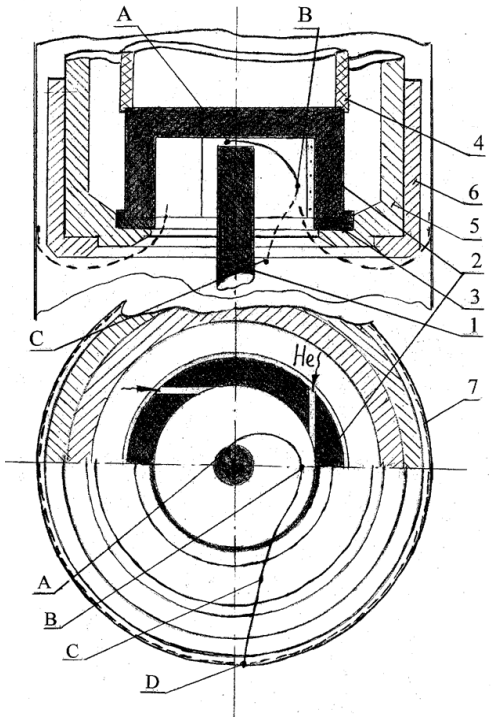

Figure 1: Projections of the parts of an arc discharge device with a hollow electrode and the conventional path A→B→C→D of fullerene formation.

On fig.1 presented a conditional FTF as the half coil. The FTF have the beginning at point A, which is in the very middle of space between electrodes. The temperature at this point T* = 5000± 1000 K. The temperature taking was made with using code Specair 2.2 [7].

The later following points are in space with less temperature. Accordingly at these points at collisions of evaporized from electrodes carbon atoms, ions and clusters at helium environment begins successive fullerene forming. The next point B of trajectory is about formed work gas flow, so particle is not accumulated at cavity wall. The lowest part of trajectory marked as point C. After this part under the action of the convention flow formed fullerenes are carried out from cavity and during walking up upward are accumulated on the wall discharge chamber 7 at temperature, which is defined with cooling system. For point D fig.1 there is temperature T ≈ 300 K.

The FTF has the next parameters: duration of process forming τ, a length of forming trajectory *L*, the velocity (middle) on the trajectory *v* and form of trajectory.

At estimate was taken into account that flow rate work gas (mass) is many times more then outlay of fullerenes and from this is following that speed of fullerenes at process forming become approximately equal to that of work gas flow [5]. The synthesis passed at the consumption of gas $q_0 = 5$ cm^3/s. The flow at motion at in cavity was warmed from 300 K to ≈ 3000 K. So the duration of process forming τ is formed from the equality: $\tau = V / q = 0{,}038$ c, where $V \approx 1{,}9$ cm^3 – is a free space at hollow electrode at work position of electrode 1 as shown at fig.1.

The length of FTF was defined from a ratio: $L \approx V/S = 7.4$ cm, where $S = 0.256$ cm^2 – is an area of orifices, over which work gas was come at the cavity. For a given electrodes geometry a middle of one coil at a hollow electrode is $l = 3.8$ cm, so at forming in the hollow electrode fullerene as a middle doing $N = L / l \approx 2$ coils with a middle speed motion of formed fullerenes $v = L / \tau \approx 195$ cm/c.

From analysis of the picture presented here process synthesis was founded an unexpected effect. This has a tie with a form of the FTF. At a rotation of the circular trajectory, if it has about ring form with any thickness, in it arise a centrifugal force (F). The force F which is operated on every fullerene has a difference size. As follows from formula for this force $F = M \bullet v^2/R$, where $M = m_c \bullet n$; m_c is carbon mass, n is the fullerene number carbon atoms, v is speed motion of ring and R is the radius of ring. For fullerene with more number the centrifugal force more and radius is more. Therefore the centrifugal force may be used for the separation fullerenes on number of carbon atoms.

At the beginning of the paper was marked an advantage in cross-section and electron affinity energy EA_i of heavy fullerenes C_n, where $n \geq 84$, over the known C_{60} and C_{70} used. These materials and design of a discharge device with the hollow electrode were presented in Ref [4-7]. The papers presented the results of calculation of electron affinity energy EA_i and ionization energy IE_i values and there was done the explanation of the observed differences between the mass spectra of fullerenes with positive and negative charge also. Calculations of EA_i and IE_i were done with use the C_{60} data from [8].

Conclusion

- The existence of such arc discharge type as hollow-electrode arc discharge with work gas flow (HEAD-WGF) was demonstrated.
- The HEAD-WGF was used to synthesize fullerenes. Carbon vapors were converted into fullerenes in the discharge with the specific geometry of the discharge electrodes, at optimal value of discharge current, and the work gas flow.
- For the first time for the explanation of large amount fullerene yield was used a conception fullerene trajectory forming under the pointed flow work gas action and the trajectory has form of spiral, helix.
- From analysis of the synthesis process in the discharge cavity the existence of centrifugal force was found; after the following study the effect, apparently may be used on the set with ring orbits for separation fullerenes on mass.

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