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Short communication

SHORT COMMUNICATION

Experimental study of physical parameters significant in fullerene synthesis

B. TODOROVIĆ-MARKOVIĆ*, Z. MARKOVIĆ, M. MARINKOVIĆ and T. NENADOVIĆ

Vinča Institute of Nuclear Sciences, P. O. Box 522, Belgrade, Serbia and Montenegro

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Abstract: In this work, the effect of physical parameters on the yield of fullerene, synthesized in a hollow cathode plasma reactor is investigated. The experimental investigations done previously have shown that the fullerene yield depended on tehcnical parameters - the current intensity, inert gas pressure, type of gas and interelectrode gap. The aim of this work was to show that the fullerene yield depends on physical parameters - carbon concentration, carbon flow rate from the interelectrode gap, axial temperature and temperature gradient between the arc channel and the chamber walls as well. It was found that fullerene synthesis occurs in an inert heat bath with dimensions determined by the temperature gradient. The lower temperature limit is around 2000 K and the value of the upper limit is the value of the axis temperature which depends on the discharge conditions. The synthesis of fullerenes is more effective if the carbon concentration in the heat bath is large and the carbon flow rate from that zone to colder parts of chamber is small.

Keywords: fullerene, carbon arc, carbon concentration, temperature.

INTRODUCTION

Experimental investigations of fullerene synthesis by the arc method have showed that the fullerene yield depended on the technical parameters (current intensity, inert gas pressure, *etc.*). The fullerenes are obtained as a result of plasma chemical reactions among carbon atoms and clusters in an inert heat bath. These reactions are described by the equations of Smoluchovski[1,2] as follows:

$$\frac{\mathrm{d}c_{\mathrm{k}}}{\mathrm{d}X} = \sum_{j=1}^{k_m} \sqrt{1-\frac{X}{C}}\,\widetilde{K}_{k-j,j}\,c_{k-j}\,c_j \; - \sum_{j=1}^{99} \sqrt{1-\frac{X}{C}}\,\widetilde{K}_{kj}\,c_k\,c_j \qquad (1)$$

The quantity c_k is the normalized concentration of cluster C_k, $k \in [1.99]$. The dimensionless variable $X = Ar$ (r-radial coordinate), parameter $C = AB$, the temperature parameter B and the normalized reaction constant are defined as follows:

* Corresponding author. E-mail: biljatod@rt270.vin.bg.ac.yu

$$\widetilde{K}_{ij} = \sqrt{\frac{i+j}{i \cdot j}} \frac{\sigma_{ij}}{\sigma_{11}}, \quad A = \frac{N_c \sigma_{11}}{\upsilon} \sqrt{\frac{8k}{\pi M_c} T_0} \left\langle P_{ij} \right\rangle, \quad B = RT_0/(T_0 - T_w)$$

The fullerene yield ($Y_{c60} = 60c_{60}$) depends on four physical parameters simultanoeusly: the carbon concentration (N_c), the velocity of the helium/carbon jet from the interelectrode space (υ), the axial temperature (T_0) and the temperature gradient between the arc channel and the chamber walls.[2]

In this work, the effect of these physical parameters on the fullerene yield were investigated with the goal to verify the theoretical predictions. Based on the obtained results, it is possible to design a model of the reactor for the synthesis of large quantities of fullerenes.

EXPERIMENTAL

The synthesis of fullerenes takes place in a vacuum stainless steel chamber pumped by an oil rotary pump to a base pressure of 4×10^{-2} mbar and then filled with helium to a pressure of 700 mbar. The experimental setup of a hollow cathode arc reactor is presented in Fig. 1. The arc is supplied from a welding generator with DC current of 100 A. The arc is stabilized magnetically by a DC current, which flows through the water cooled copper coils. The gap between electrodes is kept constant (d = 6 mm).

The cathode is made of spectroscopic grade graphite, 12.5 mm in diameter with a hole of 6 mm. The spectroscopic grade graphite anode is inserted into a water cooled stainless steel holder. The holder is inserted into the vacuum chamber through a Wilson seal, which allows axial motion of this electrode in the vacuum. The flow of the gas through the cathode is realized by a ventilator placed in a small vacuum chamber. By ignition of the ventilator, circular flow of inert gas He is established. The gas flow is measured by a floating ball flowmeter placed above the ventilator. The run time of each experiment was in the range of 2–5 min. The plasma emission is monitored through chamber window using a medium resolution spectroscope (ISP-51). The mean plasma temperature was measured by analyzing the emission spectra of the vibrational band $\Delta\upsilon = -1$ of the C_2 carbon clusters. The fullerene yield was determined by comparing the absorption of soot solution and absorption of the referent solution of pure C_{60} in the visible region of the spectra.

RESULTS AND DISCUSSION

In a hollow cathode reactor, the reactions among the carbon clusters occur in the funnel shaped jet parallel to the anode. In Fig. 1, V_a is the velocity of the jet caused by thermal expansion of the gas from the interelectrode space. Due to the blowing of inert gas through cathode, the carbon jet also has a velocity component V_b parallel to the anode.[3]

In order to obtain velocity V_a as low as possible, all experiments were performed at the high pressure of 700 mbar with a small current of 100 A. The gas flow rate was 100 l/h. The anode erosion rate was varied by the application of electrodes (anodes) with different diameters.

In our experiments, the fullerene yield was measured as a function of the anode erosion rate, gas flow rate and mean plasma temperature. The anode erosion rate (ER) is proportional to the product of the carbon concentration and the jet velocity ($ER \approx N_c V_c$), while the gas flow rate is proportional to the velocity of the carbon vapor ($F \approx V_c$).

In order to compare the theoretical results with the experimental ones, the fullerene yield given by $X' = ER^* T_{av}^{1/2}/F^2$ was measured. The quantity T_{av} is the mean plasma temperature which is proportional to the axis temperature.[4] The influence of the temperature gradient B on the fullerene yield was not investigated because it was assumed that $B = R$

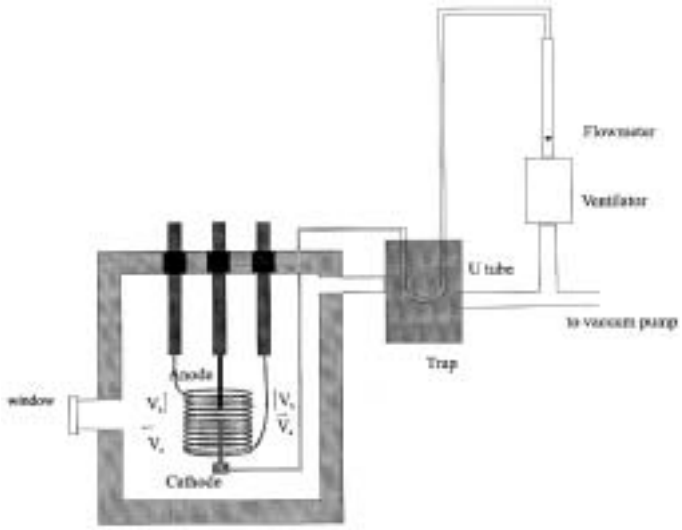

Fig. 1. Experimental set-up of a hollow cathode plasma arc reactor.

($T_w << T_0$). The experimental dependence of the fullerene yield given by X' is presented in Fig. 2. The variable X' is proportional to the theoretical variable X which combines the values of the carbon concentration, the velocity of the carbon jet and the temperature gradient.

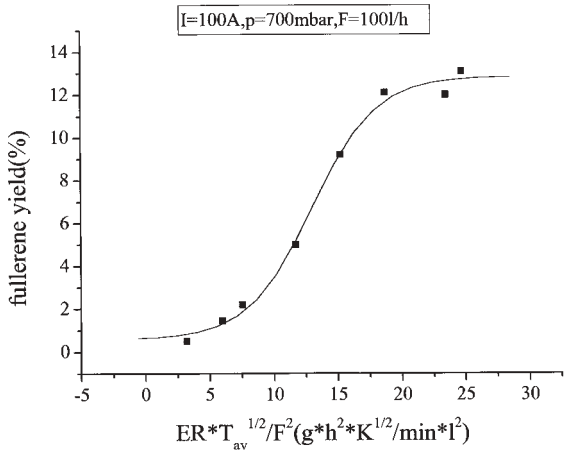

Fig. 2. Experimental dependence of the fullerene yield on the ratio of the anode erosion rate and the square of the gas flow rate.

The maximum yield of fullerene was obtained using electrodes with diameters of 3, 4 and 5 mm. The minimum yields of fullerene were obtained when electrodes with diameter 9 and 12 mm were applied. In these cases, the erosion rate and mean plasma temperature were the smallest. The maximum yield was 13.1 %. At this buffer gas pressure, other authors obtained much lower yields of fullerene (2.5 %,[5] 4 %,[6] 11 %[7]). In this study, it has been shown that yields over 10 % can be obtained with careful control of the technical parameters.

The experimental dependence of the fullerene yield on the physical parameters (X') is almost identical with the theoretical dependence. This means that the theoretical model

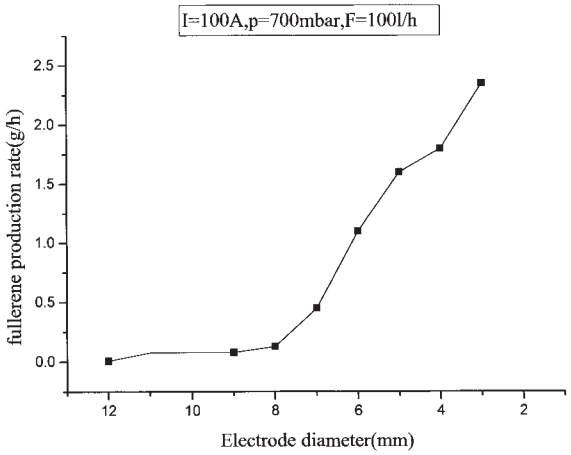

Fig. 3. Fullerene production rate as a function of the electrode diameter.

based on the Smoluchovski equation describes the fullerene formation process correctly. It is obviously evident that fullerenes can be produced effectively, if the physical parameter ratio is chosen well.

Based on the yield of fullerene and the anode erosion rate, the fullerene production rate was calculated. The fullerene production rate as a function of the electrode diameter is presented in Fig. 3. As can be seen from the diagram, the fullerene production rate increases monotonically with decreasing electrode diameters starting at an electrode diameter of 8 mm.

During the evaporation of the electrode of 3 mm diameter, the fullerene synthesis is more efficient (20 %) than during the evaporation of the electrode of 4 mm diameter. At a current intensity of 100 A, the electrodes of 12, 9 and 8 mm diameter are very inefficient carbon vapour sources and the fullerene production rate is almost constant and very small.

CONCLUSION

In this work, the previously developed theoretical model of fullerene formation in an arc plasma reactor was verified.

It was established that the experimental results are in a good agreement with the theoretical ones. This means that industrial production of fullerenes is possible in reactors where independent control of the carbon concentration, velocity of plasma and temperature gradient is ensured.

ИЗВОД

ЕКСПЕРИМЕНТАЛНО ИСПИТИВАЊЕ ФИЗИЧКИХ ПАРАМЕТЕРА ЗНАЧАЈНИХ ЗА СИНТЕЗУ ФУЛЕРЕНА

Б. ТОДОРОВИЋ-МАРКОВИЋ, З. МАРКОВИЋ, Т. НЕНАДОВИЋ

Институт за нуклеарне науке „Винча", п. пр. 522, 11001 Београд

У овом раду је испитиван утицај физичких параметара на принос фулерена образованих у плазма реактору са шупљом катодом. Ранија експериментална истраживања су показала да принос фулерена зависи од техничких параметара-интензитета струје, притиска гаса, врсте

гаса и међуелектродног простора. Циљ овог рада је да покаже да принос фулерена зависи од физичких параметара-концентрације угљеника, брзине протока угљеничног млаза из међуелектродног простора, осне температуре и температурског градијента између лучног канала и зидова коморе. Утврђено је да се синтеза фулерена дешава у инертном топлотном купатилу чије димензије одређује температурски градијент. Вредност доње граничне температуре је око 2000 K, док је горња гранична температура – температура на оси лука која зависи од услова пражњења. Синтеза фулерена је ефикаснија ако је концентрација угљеника у инертном топлотном купатилу велика, а брзина угљеничног млаза из те зоне ка хладнијим деловима коморе мала.

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