Effect of Arc and Gas Conditions in Synthesis of C\textsubscript{60} by an Arc Discharge

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Abstract

In order to determine the optimum conditions for the production of C\textsubscript{60}, production properties of C\textsubscript{60} as a function of He gas pressure and DC arc current in an arc discharge with carbon material are studied and useful production characteristics are obtained. Effects of impurity gases (H\textsubscript{2}, O\textsubscript{2}, N\textsubscript{2}), metal vapor impurities and solid obstacles in the production of C\textsubscript{60} in an arc discharge are also examined to investigate the possibility of natural synthesis of fullerenes in space, which shows the strong effect of hydrogen impurity. Further, even in vacuum, C\textsubscript{60} synthesis is found to be possible in a pulsed arc discharge.

Keywords:
mass production of C\textsubscript{60} by arc discharge, fullerene synthesis, effects of arc and gas conditions, accumulation of fullerenes in space, fullerene production in a pulsed discharge, self-organization of carbon clusters

1. Introduction

Fullerenes [1] are produced in large quantities in a DC arc discharge [2,3]. These new kinds of clusters have new characteristic properties and their applications have been investigated [4]. However, C\textsubscript{60} content in the produced carbon soot is limited to a value of about 10–20 W% and the reason for this limit has not been clarified. The mechanism of self-organization of fullerenes in a hot He gas atmosphere is also not clear and several hypotheses have been suggested [5,6]. By combining the ion drift method and the mass spectrometric method, cluster size distribution and structures of many fullerene precursors are measured [7], which suggests the stability of each cluster and that the annealing effect by collisions is an important factor for the production of fullerenes. Fullerenes which satisfy the isolated pentagon rule (C\textsubscript{60}, C\textsubscript{70} and C\textsubscript{2n}, n: integer number larger than 35) [8] are only stable in air.

In order to determine the effect of He gas pressure and discharge current in the production of C\textsubscript{60} by a DC arc discharge, a series of experiments using a closed-type arc reactor [9] are carried out. Production properties as a function of gas pressure or discharge current in the experiment are related with the molecular process in the arc discharge.

Recently, accumulation of C\textsubscript{60} in space is reported from the observations of absorption spectra near the interstellar clouds [10], which indicates that a large amount of C\textsubscript{60} exists in space and that 0.3–0.9 % of interstellar carbon is estimated to be in the form of C\textsubscript{60}. In order to verify this report, the effect of impurity gases on the generation of fullerenes is investigated experimentally under the assumption that fullerenes can be produced around carbon-rich giant stars, because these stars produce many kinds of carbon molecules [11]. Each carbon star has variety of He and C contents compared with that of H near its surface [12,13]. Synthesis properties at low He gas pressure and in a He atmosphere in the presence of impurity gases, metal vapors and solid obstacles, which would...
reduce the probability of generation of fullerenes, are examined in the arc fullerene producer.

Finally, synthesis of fullerenes in vacuum is attempted and C_{60} has been successfully synthesized in a pulsed discharge, which supports the possibility of fullerene synthesis by a pulse heating or compression phenomenon in carbon rich stars and during the explosion of carbon stars.

Brief results of this investigation have already been presented at conferences [14,15].

2. Experimental Setup and Method

The experimental setup (RPX-2 machine) [3,9] is shown in Fig. 1. A stainless vessel 184 mm in diameter and 200 mm high, equipped with an anode (6.5 mm $\phi \times$ 305 mm carbon rod, graphite with weight density of 1.87 g/cm$^3$ by Toyo Tanso Co. (Type A) or graphite with weight density of 1.61 g/cm$^3$ by Sankyo Carbon Co. (type B)), a cathode (15 mm $\phi \times$ 50 mm), a viewing port, a gas feed, a Pirani gauge and a digital pressure sensor (Copal Co. PG-100 Manometer) to measure absolute pressure, is first evacuated by a rotary pump to pressure less than 10^{-2} Torr. After helium gas is filled and the chamber is closed, discharge is started by contact ignition. DC current is supplied by a regulated DC power supply (Daihen Co. ARGO-300P) with constant-current controlling. The voltage between electrodes, $V_{rod} = 25$–35 V, (discharge voltage $V_d = 15$–25 V), discharge current $I_d = 50$–100 A and helium pressure $p = 0$–760 Torr. Gap distance is controlled by inserting the anode rod into the chamber by a motor drive as the rod is consumed in time, and the discharge condition is automatically controlled with an electric comparator which monitors $V_{rod}$ and controls the motor drive. After 1–2 h of discharge, the produced soot is collected at three locations (top, side and bottom parts of the chamber) and weighed. 1–2 mg of each sample is mixed in 7 ml of hexane for 15 min by a supersonic mixer, the C_{60} solution is then filtered and its absorbance spectrum is measured with a UV/visible spectrometer (Shimadzu UV-1200). The C_{60} content in the soot is obtained from the intensity of the C_{60} peak at $\lambda = 329$ nm [3]. Production rate of C_{60} can be obtained from the production rate of soot and the C_{60} content in the soot.

3. Experimental Results and Discussions

3.1 Effects of He gas pressure and discharge current

![Fig. 2](image-url)  
(a) Maximum produced soot weight, $W_{soot-max}$ and discharge current for maximizing the soot weight, $I_{d-soot-max}$ versus pressure, $p$. (b) Maximum C_{60} content, $X_{max}(C_{60})$, and discharge current for maximizing C_{60} content, $I_{d-C_{60}}$, versus $p$. (c) Maximum production rate of C_{60}, $P_{max}(C_{60})$, and discharge current for maximizing C_{60} production rate, $I_{d-pmax}$, versus $p$. Discharge time $T_d = 2$ h.

![Fig. 1](image-url)  
Fig. 1 Schematic of experimental setup (RPX-2 machine).
production rate of C_{60} as a function of discharge current, I_d, are measured at helium pressures, p = 100, 200, 300, 400, 500 and 600 Torr, and for a discharge time, T_d = 2 h. From these data, the maximum soot weight produced, W_{soot-max}, and discharge current for maximizing the soot weight, I_d_{max}, for each helium pressure are obtained and shown in Fig. 2(a) where I_d is varied between 50 and 80 A. W_{soot-max} has a peak at p = 400 Torr and I_d_{max} is seen to be constant. Maximum C_{60} content, X_{max}(C_{60}), and the current for maximizing the C_{60} content, I_d_{c_{max}} for each helium pressure are shown in Fig. 2(b). X_{max}(C_{60}) increases and I_d_{c_{max}} gradually decreases with an increase of p. The C_{60} content and the produced soot weight show a strong dependence on the helium pressure. Maximum production rate of C_{60}, \Pi_{max}(C_{60}), and discharge current for maximizing the production rate, I_d_{\Pi_{max}}, are shown in Fig. 2(c). \Pi_{max}(C_{60}) has a peak at p = 300 Torr and I_d_{\Pi_{max}} gradually decreases with an increase of p.

From the same measurement, maximum produced soot weight W_{soot-max} and pressure for maximizing the soot weight p_{soot-max} at each discharge current are obtained and shown in Fig. 3(a) for 100–600 Torr. W_{soot-max} linearly increases and p_{soot-max} is almost constant with an increase in I_d. The maximum C_{60} content, X_{max}(C_{60}), and pressure for maximizing the C_{60} content, p_{c_{max}}, at each discharge current are shown in Fig. 3(b). The C_{60} content starts to decrease at I_d = 70 A while p_{c_{max}} starts to decrease at I_d = 60 A with an increase of I_d. The maximum production rate of C_{60}, \Pi_{max}(C_{60}), and pressure for maximizing the production rate p_{\Pi_{max}} as a function of I_d are shown in Fig. 3(c). The production rate attains a maximum at I_d = 70 A and p_{\Pi_{max}} tends to decrease with an increase in I_d.
The production rate of \( \text{C}_{60} \) as a function of gap distance \( d_0 \) at \( p = 300 \text{ Torr}, I_d = 70 \text{ A} \) and \( T_d = 2 \text{ h} \) has been already reported [9] and for \( d_0 = 5-20 \text{ mm}, \) an almost constant production rate of \( \text{C}_{60} \) is obtained. Except at this condition, the production rate considerably decreases.

The production rate of \( \text{C}_{60} \) in an AC discharge has also been already reported [14] and it becomes markedly small (1 order smaller than that in the DC discharge), because alternative heating of two electrodes reduces the heating efficiency and the surface cannot be kept at a sufficiently high temperature.

The production properties at a lower He gas pressure are examined. In this measurement, the type B anode material is used. For \( p = 5-300 \text{ Torr} \), produced soot weight, \( \text{W}_{\text{soot}} \), \( \text{C}_{60} \) content, \( \chi(\text{C}_{60}) \), and production rate of \( \text{C}_{60} \), \( \Pi(\text{C}_{60}) \) as a function of \( p \) are measured and shown in Figs. 4(a) and (b), where \( p = 300 \text{ Torr}, I_d = 70 \text{ A}, T_d = 1 \text{ h} \) and \( d_0 = 5 \text{ mm} \). The \( \text{C}_{60} \) content monotonically decreases with a decrease of \( p \) to almost 0 at \( p = 30 \text{ Torr} \). \( \text{W}_{\text{soot}} \) decreases from 300 to 100 Torr, and then increases from 100 to 5 Torr, where collisions between sublimated carbon molecules and He atoms are insufficient and carbon molecules move straight towards the chamber wall without sufficient reaction. At \( p = 5 \text{ Torr} \), the appearance of the deposited carbon is completely different from that at high pressure with a sponge-like structure and is like a coated graphite film with a high mass density. \( \Pi(\text{C}_{60}) \) decreases monotonically with a decrease in \( p \) and becomes almost 0 at \( p = 30 \text{ Torr} \).

Why does the production rate of \( \text{C}_{60} \) change with changing gas pressure and discharge current? This appears to be due to several factors. First, the evaporation rate of carbon atoms from the anode is important. For a small discharge current, the temperature of the arc spot is not sufficiently high to cause the evaporation of carbon atoms, however, at a high discharge current in this experiment, the temperature is too high to cause the evaporation of the carbon in the atomic state and does not become the source of fullerenes. Next, the discharge has a strong dependence on the gas pressure. At pressures below 100 Torr, the discharge voltage increases and the electrons bombard the rod surface with high energy, which effectively sublimes the carbon electrodes. At pressures above 100 Torr, the thermal plasma tends to heat the anode to a high temperature. Redeposition of carbon particles by frequent collisions would reduce the sublimation rate at the higher gas pressures. These factors determine the evaporation rate of carbon atoms. In order to obtain a higher production rate, a higher evaporation rate of carbon atoms (not carbon clusters) is necessary.

The second important factor is frequent collisions among carbon molecules and helium gas atoms in the high temperature gas phase. At a pressure less than 50 Torr, mean-free-path between carbon atoms and helium atoms is not short enough for sufficient atomic collisions. Thus, the carbon atoms and small carbon clusters move straight and attach to the inner walls of the chamber without forming cage-like clusters. It is also very important that carbon clusters near the arc region are annealed by frequent collisions of thermal helium atoms, which results in the formation of stable carbon bonds. Thus, helium temperature and helium pressure are also important parameters.

These mechanisms change the production rate of \( \text{C}_{60} \). In this experiment, the optimum condition of \( \text{C}_{60} \) production is obtained at \( p = 300 \text{ Torr} \) and \( I_d = 75 \text{ A} \). At this condition, an adequate discharge current effectively sublimes carbon atoms and an adequate gas pressure results in sufficient collision frequency to bond
carbon molecules and to anneal carbon molecules to be self-organized into the stable cage-like structure.

### 3.2 Effects of impurities and solid obstacles

If fullerenes are naturally produced in space, many kinds of impurities and natural factors would obstruct or aid the reaction [16]. In usual fixed stars and interstellar clouds, hydrogen atoms and molecules are the most abundant species. In usual carbon rich giant stars, elements such as helium, carbon, oxygen, nitrogen and so on are condensed in the interior, which are being blown off in the circumstellar environment of the star. However, the amounts of hydrogen in normal carbon stars are generally not smaller than those of another elements [12]. Therefore, the effect of hydrogen in the synthesis of C60 in space is considered to be the most important factor. The impurity effect of hydrogen gas in He for the production of C60 is measured and shown in Figs. 5(a) and (b), where total pressure is maintained at 300 Torr, \( I_d = 70 \) A, \( T_d = 1 \) h and \( d_G = 5 \) mm and type B carbon anode is used. Only in this measurement, the flow rates of He and H2 are kept constant during the experiment using mass flow controllers, in order to reduce the effect of consumption of H2 at low H2 partial pressure. C60 content almost monotonically decreases with an increase of hydrogen partial pressure \( p(\text{H}_2) \) and it becomes 0 at \( p = 20 \) Torr. \( W_{\text{soot}} \) gradually decreases with \( p(\text{H}_2) \) and production rate of C60, \( \Pi(\text{C}_6\text{O}) \) almost monotonically decreases with \( p(\text{H}_2) \) and it becomes 0 at \( p(\text{H}_2) = 20 \) Torr. As a result, hydrogen gas has a very large effect on the production of C60, and it is impossible to expect synthesis of C60 in the arc discharge at high H2 pressures.

The impurity effect of N2 gas in He is examined. The production rate of C60 as a function of N2 partial pressure, \( p(\text{N}_2) \) is shown in Figs. 6(a) and (b). Total pressure is maintained at 300 Torr, \( I_d = 70 \) A, \( T_d = 1 \) h and \( d_G = 5 \) mm. In this case, the C60 content decreases monotonically with \( p(\text{N}_2) \) but the effect of impurity is smaller than that in H2. At \( p(\text{N}_2) = 200 \) Torr, \( X(\text{C}_6\text{O}) \) becomes almost 0. \( W_{\text{soot}} \) increases with \( p(\text{N}_2) \), the reason for which is attributed to the high temperature reaction of the carbon anode surface with hot nitrogen gas, which hastens the sublimation of the carbon rod

![Fig. 6](image6.png)  
Fig. 6 (a) Produced soot weight and C60 content as a function of nitrogen partial pressure, \( p(\text{N}_2) \). (b) Production rate of C60 versus \( p(\text{N}_2) \). Total pressure is kept at 300 Torr, \( I_d = 70 \) A and \( T_d = 1 \) h.

![Fig. 7](image7.png)  
Fig. 7 (a) Produced soot weight and C60 content as a function of oxygen partial pressure, \( p(\text{O}_2) \). (b) Production rate of C60 versus \( p(\text{O}_2) \). Total pressure is kept at 300 Torr, \( I_d = 70 \) A and \( T_d = 1 \) h.
and produces cyanide molecules. \( \Pi(C_{60}) \) monotonically decreases with \( p(N_2) \).

The effect of \( O_2 \) gas in He in the production of \( C_{60} \) is examined and the results are shown in Figs. 7(a) and (b). Total pressure is kept at 300 Torr, \( I_d = 70 \) A, \( T_d = 1 \) h and \( d_G = 5 \) mm. For high \( p(O_2) \) (at \( p(O_2) = 100 \) Torr), \( \chi(C_{60}) \) decreases to about its half at value, but a strong reduction such as in the case of \( H_2 \) is not observed. Oxygen molecules have a weak effect on the reactions of carbon molecules. \( W_{soot} \) gradually increases with \( p(O_2) \), which is attributed to the high temperature reaction of the carbon anode with hot oxygen gas, and hastens the sublimation of the carbon rod, producing CO and \( CO_2 \) molecules.

The effects of metal vapors in the production of \( C_{60} \) are examined and the results are shown in Figs. 8 (a)-(c). A bore is made in the carbon anode and a 0.3 mm\( \phi \), 300 mm long pure Fe wire or pure Al wire is inserted and vaporized with the carbon rod. A pure Si powder (100 mesh size) is also filled in the carbon rod hole and this rod is also sublimated, where \( p(He) = 300 \) Torr, \( I_d = 70 \) A, \( T_d = 1 \) h. The result for pure carbon anode is also shown for reference in the figure. \( \chi(C_{60}) \) values for Fe or Al mixtures are almost the same as that in the absence of impurities. For the Si mixture, \( \chi(C_{60}) \) is reduced to be one-third of that for the pure carbon rod, which is attributable to the strong reaction of Si with hot carbon material to form SiC molecules and the synthesis of \( C_{60} \) is obstructed. Metal mixtures weakly affect the \( W_{soot} \) values. \( \Pi(C_{60}) \) becomes much smaller for a Si powder mixture. For other mixtures such as Au, Pu and W, the production rates of \( C_{60} \) are examined and these mixtures have almost no influence on the synthesis.

The effect of a solid surface in the production of \( C_{60} \) is examined by placing a large carbon block (50 mm in diameter and 50 mm long) near the arc plasma region as shown in Fig. 9(a), which obstructs the arc reaction. By reducing the distance between the center of the arc and the bottom surface of the carbon block, \( Z_{CB} \), the \( C_{60} \) content is measured and shown in Fig. 9(b). \( \chi(C_{60}) \) starts to decrease monotonically from \( Z_{CB} = 2 \) cm. The hot He gas is blown upwards by strong heat convection, where it hits the solid surface and cools down. \( Z_{CB} = 2 \) cm is the boundary region where the arc plasma suddenly cools down from about 10,000 K to 1,200 K and the strong emission of carbon molecules (the swan bands of \( C_2 \)) disappears, which can be clearly observed by the naked eye. From this measurement and temperature measurements with K-type thermocouples, it is concluded that fullerenes cannot be

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![Fig. 8](image_url)  
*Fig. 8 [a] Produced soot weight, \( W_{soot} \); [b] \( C_{60} \) content, \( \chi(C_{60}) \); and [c] production rate of \( C_{60} \), \( \Pi(C_{60}) \) for mixed carbon materials (Si, Al and Fe). \( p(He) = 300 \) Torr, \( I_d = 70 \) A and \( T_d = 1 \) h.*

![Fig. 9](image_url)  
*Fig. 9 [b] \( C_{60} \) content versus position of the carbon block, \( Z_{CB} \). The block position is illustrated in the upper figure (a), \( p(He) = 300 \) Torr, \( I_d = 70 \) A and \( T_d = 1 \) h.*
produced at 1,200 K or at lower gas temperatures. Almost all fullerenes are produced only in the hot arc region at a gas temperature of several 1,000 K. As the solid surface cannot be kept at several 1,000 K and cools the gas to less than 1,200 K, the solid surface always obstructs the synthesis of C60.

3.3 C60 synthesis in pulsed discharge in vacuum

As shown in Fig. 4, production rate significantly decreases when the He pressure is very low. If the role of He is only as a buffer gas to reflect carbon atoms, it can be expected that high-density carbon molecules can themselves play the role of the buffer gas. In order to examine this effect, pulsed discharge in vacuum is carried out and the generation of C60 is measured. When helium gas is not introduced and the chamber is in vacuum (p ~ 10^-2 Torr), synthesis of C60 in the DC arc discharge is not observed in fact. However, in the pulsed discharge, the synthesis of C60 is confirmed from the UV/visible spectrum measurement and by the laser desorption time-of-flight mass analyzer (Shimadzu Co., MALDI III) measurement. The discharge current is pulse modulated at 1 Hz, with a duty cycle of 50%, and the modulation depth AId is changed keeping the minimum discharge current at 30 A. After 30 min of discharge, 50 mg of soot sticking to the top part of the chamber is mixed in xylene and absorbance of the solution after filtering is measured by the spectrometer as shown in Fig. 10. Absorbance of C60 at λ = 335 nm, which is proportional to the C60 content as a function of modulation depth AId, is obtained. The C60 content increases monotonically with AId. At AId = 90 A, the C60 content in the produced soot is about 0.01 W% and the production rate is about 0.1 mg/h. The mechanism of this synthesis is considered to be as follows. When the arc current is pulse modulated, carbon molecules are suddenly sublimated for a short time at a high discharge current and they collide with each other near the arc region to become fullerenes even if He buffer gas is not present. Fullerenes synthesis in hydrogen gas (p(H2) = 300 Torr) by the pulsed discharge method was attempted, but no fullerenes were obtained. Near carbon stars or near new star formation regions, carbon molecules can react to form fullerenes even if the atmosphere is not permeated with buffer gas.

In space, the effect of ultraviolet rays or x rays is important, which tend to strip hydrogen atoms from hydride molecules and many kinds of radicals are generated. In fact, long chain carbon molecules such as HC1lN have been observed in space [17]. Regarding the long lifetimes of such radical molecules in the interstellar space, they may have a chance to bond to each other to make fullerenes. The effect of the radiation field is not examined in the present study.

4. Conclusions

1) Production properties of C60 as a function of discharge current and He gas pressure are examined, and they are seen to strongly depend on these two parameters, because the sublimation rate of carbon atoms from the carbon anode and their collision and annealing frequencies near the arc region are important factors in the production of C60.

2) The effect of impurity gas is examined. As a result, H2 gas is found to be the most effective in obstructing fullerene production among the examined impurities. N2 and Si also strongly influence the production. O2, Fe, Al, Au, Pt and W have weak influence on the production. Therefore, in space, hydrogen is the most obstructive particle in generation of fullerenes from carbon molecules. In normal carbon stars, hydrogen atom content is high and the production of fullerenes is difficult, while special carbon stars with little hydrogen content near the surface [12,13] have adequate atmosphere to synthesize fullerenes.

3) Pulse discharge without He gas can generate C60, which supports the production of C60 in space, where the carbon rich material is blown off abruptly at high temperatures during the stellar explosion.

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