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# Experimental evidence for high-yield $C_{74}$ production in an arc periphery plasma

R. Hatakeyama,[a] T. Hirata, H. Ishida, and N. Sato
*Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan*

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Spatial profiles and buffer-gas pressure dependences of fullerenes contained in primary carbon soots are measured in order to investigate production ratios of higher fullerenes to $C_{60}$ in an arc-discharge fullerene generator. It is found that $C_{74}$ is efficiently produced in the arc periphery-plasma region while $C_{60}$ is mainly produced in the core-plasma region, being the most dominant higher fullerene under the condition of a higher helium-gas pressure (>100 Torr). © *1998 American Institute of Physics.* [S0003-6951(98)03633-X]

The arc production method discovered by Krätschmer *et al.*[1] led to large-quantity production of fullerenes. Thereafter much effort has been devoted to isolating and characterizing higher fullerenes[2–5] and $C_{70}$, $C_{76}$, $C_{78}$, $C_{82}$, $C_{84}$, $C_{90}$, $C_{94}$, etc. have successfully been isolated. Then it has been considered that the production yields of the fullerenes become smaller in the order, $C_{60}$, $C_{70}$, $C_{84}$, etc. as a general tendency[6–8] in graphite resistive-heating,[1] arc-discharge,[9] and laser-vaporization[10] methods. On the other hand, $C_{74}$ has attracted much attention because it is theoretically predicted to be suitable for the synthesis of endohedral metallofullerenes.[11] To our knowledge, however, no experimental result on producing macroscopic quantities of $C_{74}$ has been reported. This may mainly be due to a fact that the mass analysis and isolation are exclusively performed after the primary soots produced are dissolved in the solvents such as xylene, etc., where $C_{74}$ is not soluble. Since there is a possibility that the solubility of $C_{74}$ is enhanced in other solvents such as pyridine,[12] the question then arises as to the classification of the fullerene-production ratio mentioned above. Here we report direct analyses of the soots produced under various conditions of an arc-discharge plasma in order to demonstrate the high-yield production of $C_{74}$.

The experiment is carried out with an arc-discharge fullerene generator of 20.8 cm in diameter and of 106 cm in total length in a helium atmosphere of the pressure $P_{\mathrm{He}}$, where a carbon anode of 0.6 cm and a carbon cathode of 3.0 cm in diameter are installed at a distance 43.5 cm from the bottom lid, as shown in Fig. 1. Dc voltages $V_k$ are externally applied to the cathode with respect to the grounded anode. A pair of water-cooled electrode arrays with a distance of 7 cm in the *z* direction is set between the discharge electrodes and the generator upper lid at $y=33$ cm ($y=0$: position of the discharge-electrode axis) in order to investigate spatial profiles of fullerenes produced by the arc discharge, which consists of 1.4-cm-diam disc plates at convenient intervals along the y direction (see Fig. 1). The disc plates are electrically connected together and kept at a floating potential. The bottom of the disc support is located at $y=3$ cm. The gap distance between the anode and cathode is kept at 0.2–0.3 cm during the discharge. Movable Langmuir probes of 0.8 cm in diameter are inserted around the arc point ($x=y=z=0$) in order to obtain a relation between some parameters of the arc-discharge plasma and the fullerene production. Primary soots accumulated on the disc plates and their support are directly analyzed by a reflectron time-of-flight (TOF) mass spectrometer[6] with a maximum resolution of $m/\Delta m \sim 2000$ (Shimadzu/Cratos MALDI III). The laser-desorption time-of-flight (LD-TOF) mass spectra are averaged over typically 100 laser shots mainly in the positive ion mode.

The potential difference between the anode and cathode $V_k$, floating potential $\phi_f$ of the small disc electrodes, and positive saturation current $I_+$ of the Langmuir probe at $x=z=0$, $y=3$ cm are measured as a function of $P_{\mathrm{He}}$ in the case of a typical discharge current ($I_{\mathrm{arc}}=100$ A), as shown in Fig. 2(a). Here the $\phi_f$ and $I_+$ dependences are considered to be proportional to the plasma potential $\phi_s$ and density $n_p$ dependences, respectively. When $P_{\mathrm{He}}$ is increased, as a general feature $V_k$ and $I_+$ become more negative and smaller, respectively, except a region of very low $P_{\mathrm{He}}$. This is because the resistivity of the arc-discharge plasma increases and the arc plasma column is squeezed with an increase in $P_{\mathrm{He}}$. The $\phi_f$ dependence on $P_{\mathrm{He}}$ may basically be determined by the $V_k$ dependence, but a minimum of $\phi_f$ and maximum of $I_+$ are observed in the region of $P_{\mathrm{He}}$

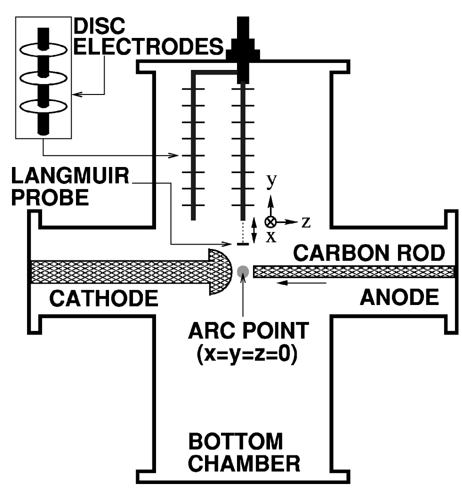


FIG. 1. Schematic of arc-discharge fullerene generator.

[a]Electronic mail: hatake@ecei.tohoku.ac.jp

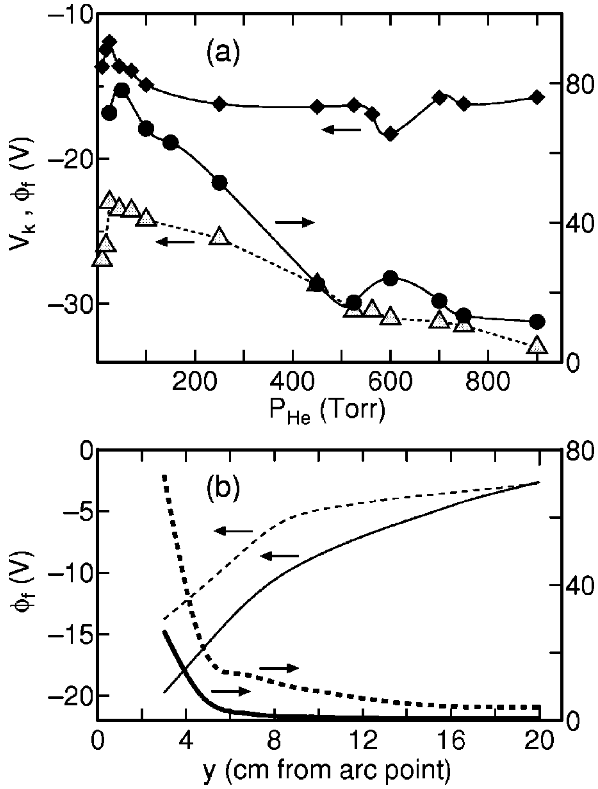


FIG. 2. (a) Cathode potential $V_k$ (open triangles) and floating potential $\phi_f$ of the disc plates (closed diamonds) and positive saturation current $I_+$ of the Langmuir probe (closed circles) vs helium gas pressure $P_{He}$ with $I_{arc}=100$ A. (b) $\phi_f$ and $I_+$ vs distance $y$ from the arc point in the cases of $P_{He}=25$ (dotted curves) and 600 Torr (solid curves) with $I_{arc}=100$ A.

$=600$ Torr. Figure 2(b) shows spatial profiles of $\phi_f$ and $I_+$ for the typical values of $P_{He}=25$ and 600 Torr, where a rapid decrease of $n_p$ and an increase in $\phi_s$ along the $y$ direction are observed to be enhanced when $P_{He}$ is increased. The voltage-current characteristic of the probe clearly indicates a presence of negative ions in the arc core plasma for $y \lesssim 3$ cm, and gives the values of $n_p=10^8-10^9$ cm$^{-3}$, $\phi_s \simeq$ minus a few V, and electron temperature$\simeq$a few eV in the periphery plasma at $y \simeq 7$ cm.

The ratios of the spectrum-peak intensities for the typical higher fullerenes ($C_{70}$, $C_{74}$, $C_{84}$) to $C_{60}$ are measured as a function of $P_{He}$ in the case of $I_{arc}=100$ A as presented in Fig. 3, where the mass spectra obtained from all the disc electrodes for $y>7$ cm are averaged for a fixed value of $P_{He}$. When $P_{He}$ is lower ($P_{He} \lesssim 25$ Torr), both the ratios $C_{74}/C_{60}$ and $C_{84}/C_{60}$ are very small ($\lesssim 0.1$) while the ratio $C_{70}/C_{60}$ is about 0.4. The ratio $C_{74}/C_{60}$ rapidly increases with an increase in $P_{He}$ and attains to 0.35 at $P_{He} \simeq 100$ Torr. The ratios $C_{70}/C_{60}$ and $C_{84}/C_{60}$ are almost unchanged or only slightly increase in this region of $P_{He}$. $C_{74}/C_{60}$ becomes comparable to $C_{70}/C_{60}$ (0.4~0.45) in the region of $100 \lesssim P_{He} < 500$ Torr, where $C_{84}/C_{60}$ is almost constant ($>0.1$). For a further increase in $P_{He}$ ($\gtrsim 500$ Torr), $C_{74}/C_{60}$ rapidly increases again and attains to a maximum value of about 1.0 at $P_{He} \simeq 600$ Torr. It starts to decrease with an increase in $P_{He}$ and attain to about 0.6 at $P_{He} \simeq 900$ Torr. The $C_{60}$ production quantity is observed to apparently decrease only in the region of $P_{He}=600$ Torr. The mechanism of this decrease is not clarified at the moment. Since $C_{70}/C_{60}$ and $C_{84}/C_{60}$ do not change so much in the region of $500 \lesssim P_{He} \lesssim 900$ Torr except a slight increase at $P_{He} \simeq 600$ Torr, $C_{74}$ is superior to $C_{70}$ and highly superior to $C_{84}$ in the production quantity.

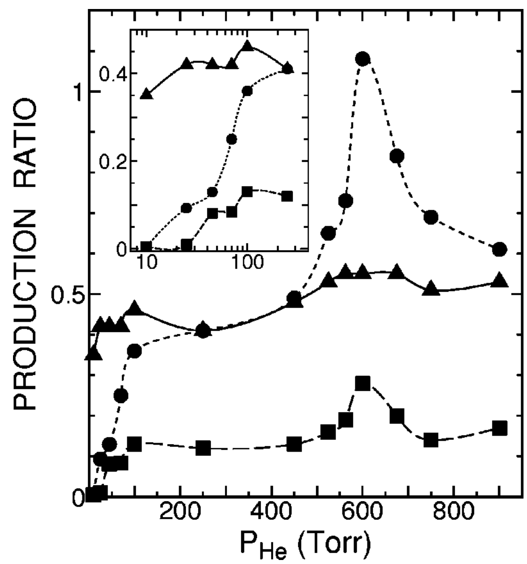


FIG. 3. Production ratios of typical higher fullerenes to $C_{60}$ vs helium gas pressure $P_{He}$ with $I_{arc}=100$ A. The lower pressure region is enlarged in the inset. $C_{70}/C_{60}$: closed triangles, $C_{74}/C_{60}$: closed circles, and $C_{84}/C_{60}$: closed squares.

Figure 4 shows spatial ($y$) profiles of the spectrum-peak intensities for $C_{60}$, $C_{70}$, $C_{74}$, $C_{84}$, and their ratios in the case of $I_{arc}=100$ A and $P_{He}=600$ Torr, which are obtained from the soots on the disc plates and their support at $x=z=0$. A

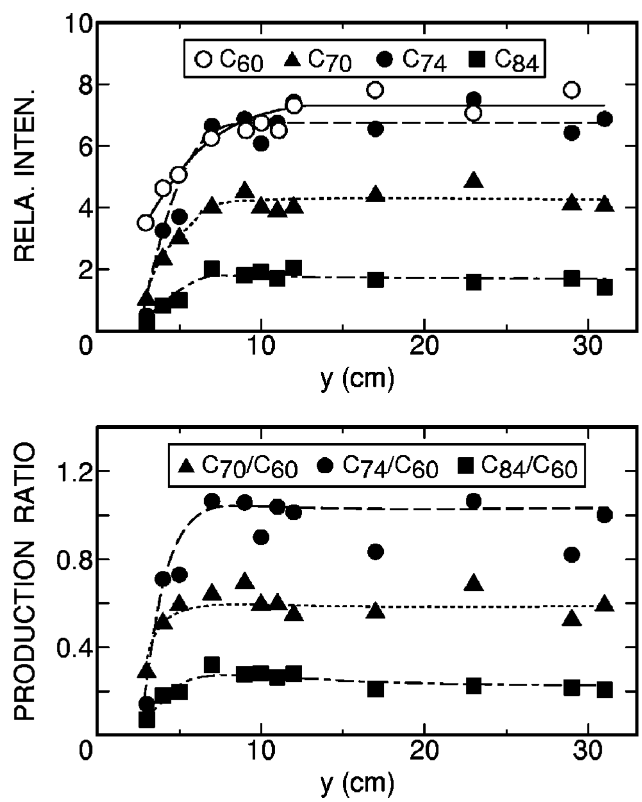


FIG. 4. Spectrum-peak intensities for $C_{60}$ and typical higher fullerenes, and their ratios to $C_{60}$ vs distance $y$ from the arc point ($x=z=0$). $I_{arc}=100$ A and $P_{He}=600$ Torr.

large amount of $C_{60}$ is already produced at $y=3$ cm from the arc point while the higher fullerenes are little produced there. The higher-fullerene quantities increase up to $y\simeq 7$ cm with an increase in $y$, although they saturate for $y\gtrsim 7$ cm. This increase is especially big in the case of $C_{74}$. It is surprising that the production ratio of $C_{74}$ to $C_{60}$ almost attains to a value of about 1.0 for $y>7$ cm. The ratios $C_{70}/C_{60}$ and $C_{84}/C_{60}$ are observed to be approximately 0.55–0.6 and 0.2–0.25 for $y>7$ cm, respectively. Thus, $C_{74}$ rather than $C_{70}$ is considered to be the major higher-fullerene in our arc-discharge generator.

When the arc-discharge current is varied in the case of $P_{\mathrm{He}}=600$ Torr, the ratio $C_{74}/C_{60}$ increases with an increase in $I_{arc}$ ($>50$ A), attaining to the maximum value at $I_{\mathrm{arc}}\simeq 100$ A. For $I_{\mathrm{arc}}>100$ A, $C_{74}/C_{60}$ is almost unchanged but starts to decrease for a further increase in $I_{\mathrm{arc}}$ ($>150$ A). The LD-TOF mass analysis as a function of laser fluence indicates that secondary effects of the laser irradiation such as additional fullerene synthesis and fragmentation do not seriously influence the conclusion described above. It is also clarified that the solubility of $C_{74}$ is highest in pyridine.

In our experiment the pressure and $y$-profile dependences of $\phi_f$, $I_+$, and $C_{74}/C_{60}$ are observed to be well correlated. Here we briefly mention a $C_{74}$-formation process. In general the higher the buffer gas pressure, the more frequently occurs embryo coalescence leading to the fullerene formation.[7,8] The cooling rate in the arc core plasma, where thermal equilibrium between the plasma and gas temperatures can be expected, is considered to be suitable for the $C_{60}$ formation. Since neutral or negatively-charged carbon clusters transported from the core region by the gas convection or potential gradient are cooled too rapidly in the periphery plasma, where the gas temperature is lower in the absence of the high density plasma, it seems to be hard for them to attain the closed structures with high symmetry. Thus, $C_{74}$ with structural strain may predominantly be formed there. In conclusion, $C_{74}$ is a negligibly-small fullerene in the production quantity in the low He pressure region below 100 Torr, but turns out to be the most dominant higher fullerene in the high pressure region above 100 Torr.

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