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Fullerene production by carbon arc method in various gases

H. Matsuo, I. Nakagawa, H. Takikawa, T. Sakakibara

Department of Electrical and Electronic Engineering, Toyohashi University of Technology, Toyohashi, Aichi 441, Japan

Fullerene is synthesized by a carbon arc discharge ignited in various ambient gases (He, Ne, Ar, Kr, H_2, CH_4, N_2, O_2, CO_2). Fullerene yields are 16% for He, 7% for Ne, O_2 and CO_2, and lower than 1% for other gases. Fullerene production rates are about 30 mg/min for He, about 25 mg/min for CO_2, about 15 mg/min for O_2, and lower than 1 mg/min for other gases. On the other hand, the arc plasma is spectroscopically diagnosed. As a result, it is found that the fullerene is efficiently produced when the intensity of C_2 molecule radiated from the plasma is strong.

1. INTRODUCTION

Fullerene is mainly produced by a dc carbon arc method. He gas is mostly used as ambient gas. It is reported that fullerene yields in Ar and N_2 ambient gases are lower than that in He gas [1][2]. It is also reported that in the case of CH_4 gas, only tar is synthesized [3]. To reveal the mechanism of fullerene formation process and to improve the fullerene productivity, it is important to clarify the influence of ambient gases on the productivity and to know the relation between plasma conditions and the productivity.

In this paper, fullerene is synthesized in various rare gases (He, Ne, Ar, Kr) and polyatomic gases (H_2, CH_4, N_2, O_2, CO_2). Then raw soot production rate, fullerene yield, and fullerene production rate are obtained as a function of molecular weight of gas. Meanwhile, the arc plasma is spectroscopically diagnosed. From the relation between the fullerene productivity and the intensities of radiation spectra, the plasma condition for efficient fullerene synthesis is discussed.

2. CARBON ARC APPARATUS AND EXPERIMENTAL CONDITIONS

Figure 1 shows a carbon arc apparatus for synthesizing fullerene [4] and a system for measuring intensities of spectra radiated from the arc plasma. Carbon arc was ignited in a vacuum chamber (SUS304, 200ϕ × 300) with a water cooled inner jacket (SUS304, 135ϕ × 200). Observing an image of the arc magnified on a screen, electrode gap length was kept constant during the arc burning.

For the ambient gas being He, it was found that the fullerene productivity had a maximum

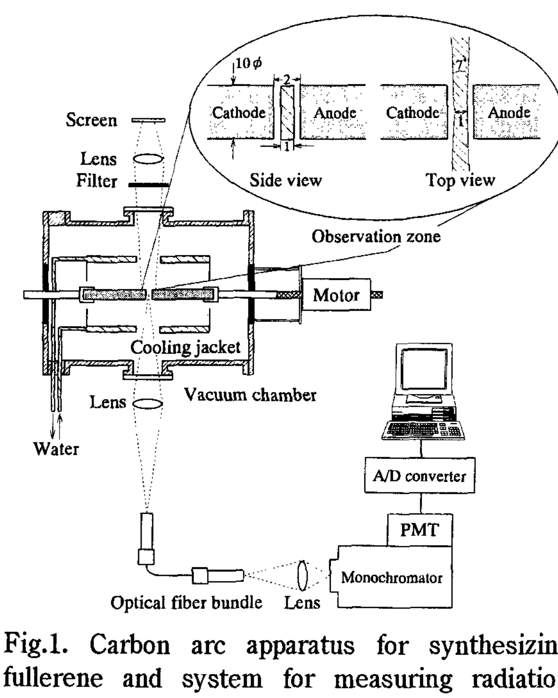

Fig.1. Carbon arc apparatus for synthesizing fullerene and system for measuring radiation spectra from the arc plasma.

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(yield: 16 %, production rate: 30 mg/min) at the following experimental parameters; arc current: 150 A, pressure: 10 kPa, electrode diameter: 10 mm, electrode gap length: 2 mm [4]. These parameters were used during this experiment.

3. DEPENDENCE OF AMBIENT GASES ON FULLERENE PRODUCTIVITY

After about 10 min arc burning, raw soot stuck on inner walls of the cooling jacket and the chamber was collected. More than 90 % of raw soot was stuck on the inner wall of the cooling jacket. Soot production rate was obtained from weight of the raw soot divided by discharge time. The result is shown in Fig.2. For convenience, the axis of abscissas is represented by molecular weight of ambient gas. It is found that in the case of rare gas the soot production rate for He is the highest (190 mg/min). Others are less than 20 mg/min. The rates for CO_2, N_2 and O_2 are much higher (300 to 370 mg/min) than that for He. The rates for CH_4 and H_2 are less than 80 mg/min.

Fullerene was extracted from the raw soot by Soxhlet extraction with toluene solvent and then dried. Fullerene yield, defined as the ratio of the extracted fullerene weight to the collected soot weight is shown in Fig.3. In the case of rare gas, the yield for He gas has a maximum (16 %) and exponentially decreases with molecular weight; Ne: 7 %, Ar: 4 %, Kr: 2 %. The yields for CO_2 and O_2 gases are as high as that for Ne gas. The yield for N_2 is only 0.7 %. The value for N_2 is very similar to Haufler's value (0.8 %) [2]. For H_2 and CH_4 gas, fullerene was not obtained at all, but tar of 6 % was extracted.

From Fig.2 and Fig.3, fullerene production rate, which is the weight of fullerene produced per one minute, is calculated. The result is shown in Fig.4. The highest fullerene production rate is for He gas (30 mg/min), the second is for CO_2 gas (25 mg/min), the third is for O_2 gas (15 mg/min). For He gas, the rate is contributed by the highest fullerene yield while for CO_2 and O_2, it is contributed by higher soot production rate. For other gases, the fullerene production rates are less than 1 mg/min.

Composition of the extracted fullerene was analyzed by high precision liquid chromatography (HPLC). The result showed that the composition ratio was the same in any ambient gas (C_{60}: 80 %, C_{70}: 15 %, higher fullerenes (include $C_{60}O$ and $C_{70}O$): 5%).

4. SPECTRA RADIATED FROM ARC PLASMA

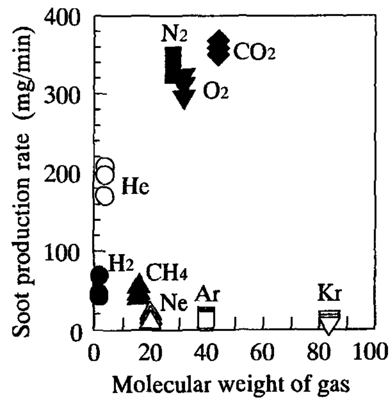


Fig.2. Raw soot production rates in various gases.

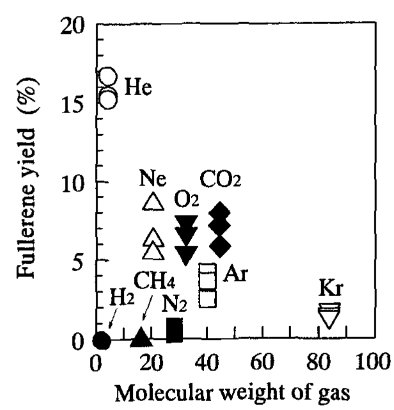


Fig.3. Fullerene yields in various gases.

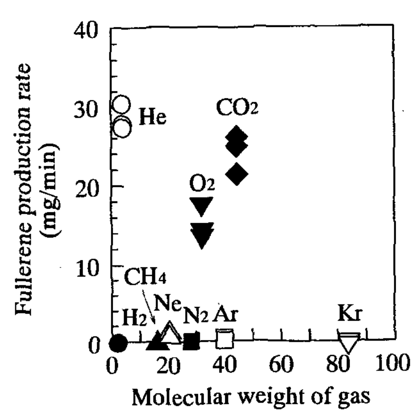


Fig.4. Fullerene production rates in various.

Spectra radiated from the arc plasma were measured with a monochormator. Observation zone is shown in upper part of Fig.1. The side view shows the area (1× 10 mm^2) of the focal plane in the center region of the electrode gap. The top view shows the detectable area along the optical axis. The result is shown in Fig.5. The intensity is not corrected for the sensitivity of the optical devices on a function of wavelength. The result shows as follows;

(a) He gas: The spectral intensities of C_2 Swan and C_2 Deslandres-d'Azambuja bands (C_2 DA) are very strong, while the intensity of C^+ is very weak (not appear in Fig.(a)).

(b) Ne gas: The spectral intensities of C_2 become weak while that of C^+ becomes strong, compared with those for He gas. Many Ne spectra appear.

(c) Ar gas: The intensities of C_2 become still weaker and that of C^+ becomes stronger. Many strong lines of Ar spectra and some of Ar^+ spectra appear.

(d) Kr gas: The intensities of C_2 become much weaker and that of C^+ become still stronger. Many Kr spectra and strong Kr^+ spectra appear.

(e) H_2 gas: The intensities of C_2 are quite strong and that of C^+ is very strong. H spectra and CH spectrum appear.

(f) CH_4 gas: Almost same as for H_2.

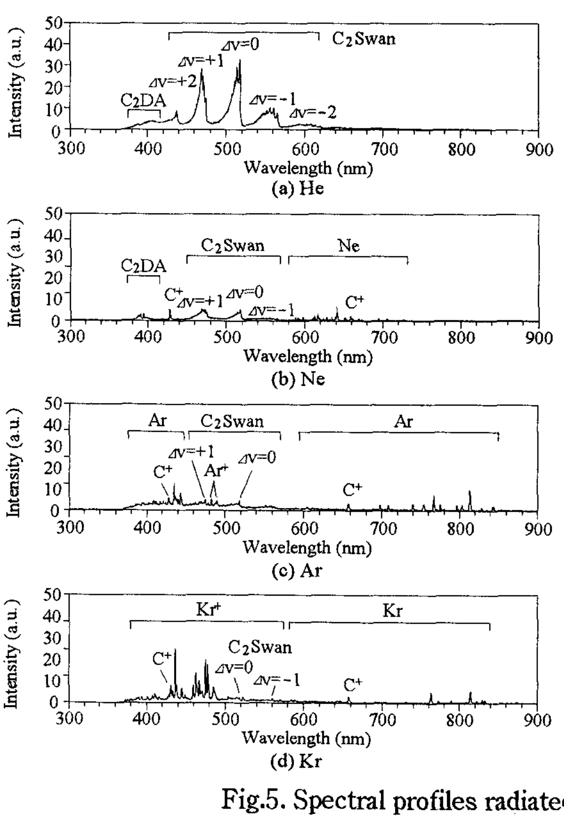
(g) N_2 gas: The intensities of C_2 and CN are very strong, while those of C^+ are very weak.

(h) O_2 gas: The intensities of C_2 are as strong as that for He gas, and those of C^+ and O are very weak.

(i) CO_2 gas: The intensities of C_2 are the strongest among all cases. The intensities of C^+ and O are very weak.

5. DISCUSSION AND REMARKS

The spectral intensity roughly indicates the density of the particle. The correlations between the fullerene yield or the fullerene production rate



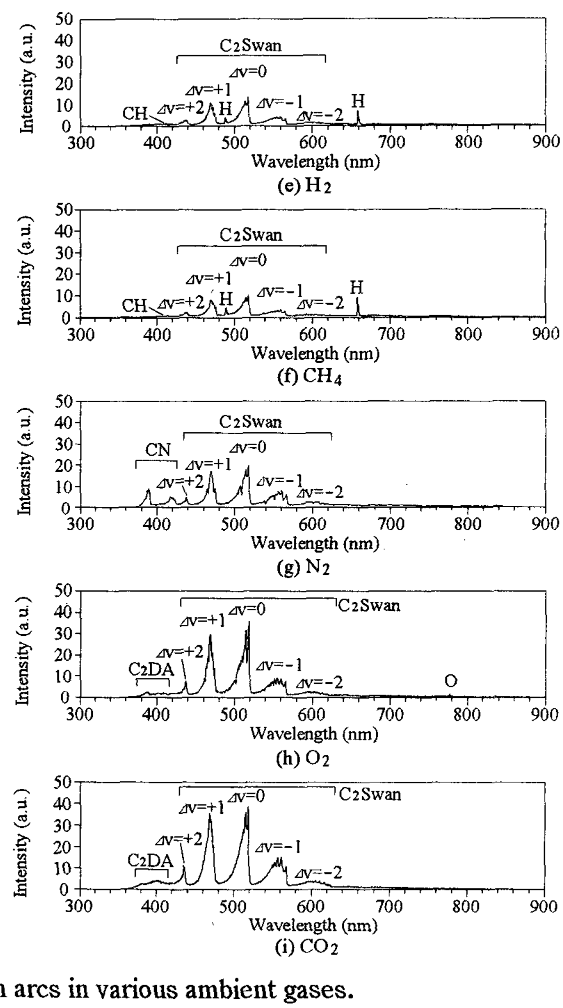
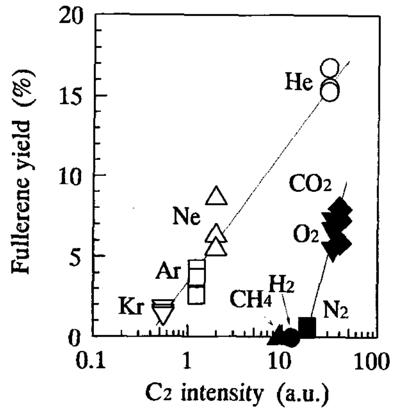
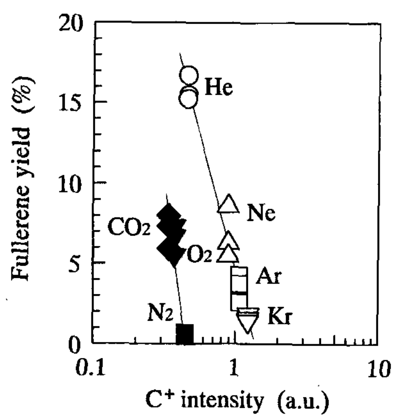


Fig.5. Spectral profiles radiated from arcs in various ambient gases.

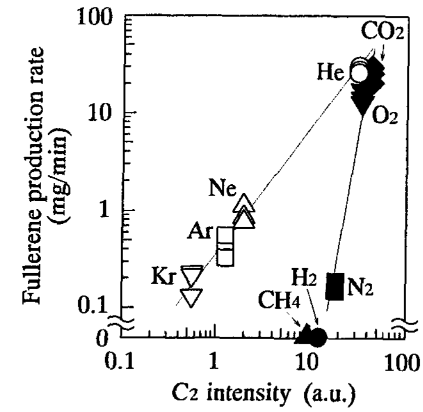


(a) C_2 (516.7nm)

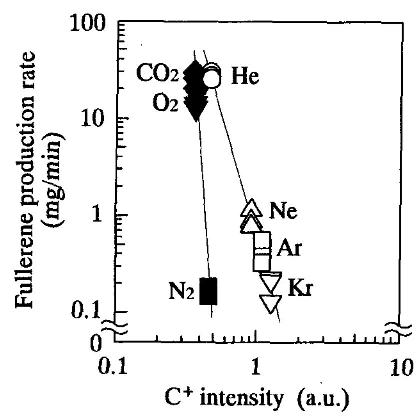


(b) C^+ (657.8nm)

Fig.6. Correlations between fullerene yield and spectral intensities of C_2 and C^+.



(a) C_2 (516.7nm)



(b) C^+ (657.8nm)

Fig.7. Correlations between fullerene production rate and spectral intensities of C_2 and C^+.

and the intensity of C_2 (Swan band (0,0) bandhead: 516.7 nm) or that of C^+ (657.8 nm) are shown in figs.6 and 7. From these figures, it is found that for rare gases, the fullerene yield and the fullerene production rate become higher as the intensity of C_2 becomes stronger and that of C^+ becomes weaker. Similar tendency is found for polyatomic gases. However, the fullerene yield and the production rate of polyatomic gases are lower than those of rare gases.

From these experimental results, we can conclude the conditions under which the fullerene is efficiently synthesized as follows. First, the plasma needs to contain C_2 molecule of high density and C^+ of low density (case; He, O_2, CO_2). This means that the plasma temperature should not be as high as the temperature where the evaporated carbon particles are ionized, and also suggests that key particle in plasma for fullerene formation is not C^+ ion, but C_2 molecule. Secondarily, ambient gas should not include hydrogen or nitrogen. In such case (H_2, CH_4, N_2 gases), carbon particles do not react with each other but with hydrogen or nitrogen so that fullerene is not synthesized.

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