Fullerene Formation in Carbon Arc: Electrode Gap Dependence and Plasma Spectroscopy

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Carbon plasma was studied using emission spectroscopy during fullerene formation. Temperatures within 3500−5500 K and C_2 volume densities up to 4.5×10^{15} cm^{-2} were determined depending upon the arc gap and input power.

Introduction

The arc discharge technique is presently considered the most efficient method for the production of fullerene.[1−3] In order to understand the phenomena related to fullerene formation and to increase the process yield, it is essential to study the role of many operational parameters of carbon plasma. However, the influences of these parameters are difficult to separate. Further, the yield depends on the high-temperature thermal and photochemical stability of C_{60}, neither of which are yet well defined. While Sundar et al.[4] experimentally determined the decomposition temperature of C_{60} in a vacuum to be relatively low (1000 K), the results of molecular dynamic calculations show[5] that the fullerene cage should sustain a temperature of up to 1800 K. There is a general consensus that C_{60} is a relatively stable molecule. However, Taylor[6] reported degradation of fullerenes under a variety of conditions. In particular, it is believed that the intense light energy emitted from arcs[7−9] may contribute to the decomposition of fullerenes and thus the final process yield. The harmful effect of intense UV radiation on fullerenes has been discussed in other literature.[3,10,11] The degradation results from the long lifetime (microseconds) of the labile triplet state of fullerenes, produced with nearly unit quantum efficiency, due to the large absorption cross section of these molecules.[3,12] Fullerenes, in solid form, are also known to be sensitive to UV and visible light.[13] The arc gap, which bears heavily on the total radiation level, undoubtedly influences fullerene yields. However, the experimental results have been conflicting. Parker et al.,[14] Haufler et al.,[15] and Scrivens and Tour[16] reported maximum-yield conditions using relatively large electrode gaps (2−4 mm). By contrast, in other studies[17] the electrode gap was smaller. Some other results[18,19] are inconclusive, mostly due to the flaws in experimental techniques applied and large experimental errors.

A possible breakdown of fullerenes by UV radiation prompted Chibante et al.[3] to develop an alternative route for producing fullerenes with solar energy. However, this method is still far from optimum.

In this article we report experimental findings, related to the influence of the arc gap on fullerene formation yield, since this factor has not been systematically studied. However, clear evaluation of plasma radiation influence on formation of fullerenes may be possible only after investigation of the differences in characteristics of plasma zones with variation of the gap between the electrodes. For this reason carbon arc was characterized by emission spectroscopy.

TABLE 1: Operating Parameters of Fullerene Synthesis

expt no.	electrode gap (mm)	current (A)	voltage (V)	input power (W)	carbon transport (wt %)	erosion rate (mg/s)
1	0.5	61.5	17.5	1085	53.7	3.1
2	1.0	65.0	18.0	1170	57.6	3.1
3	2.0	67.0	20.5	1375	51.6	3.1
4	3.0	73.0	21.5	1570	46.1	3.1
5	4.0	86.0	24.0	2065	39.3	3.1
6	0.5	65.5	19.0	1245	50.8	5.7
7	1.0	67.0	20.0	1340	52.6	5.7
8	2.0	76.0	21.0	1595	46.6	5.7
9	3.0	96.0	23.0	2210	42.9	5.7
10	4.0	131.0	26.5	3470	32.4	5.7

Experimental Details

The experiments were carried out in a fullerene arc reactor operating in a semi-continuous fashion, described previously in detail by Huczko et al.[20] On the basis of earlier work,[20−22] the parameters, ac or dc feeding mode, input power, buffer gas, and pressure, were optimized and electrode gaps between 0.5 and 4 mm were used for dc arcing. The required gap was controlled using the optoelectronic system (0.2 mm accuracy).[23] The electrodes (6 mm in diameter) were initially positioned close together, and the arc discharge was initiated by a high-voltage glow discharge rather than the conventional method of striking anode against cathode. The tests were performed at a helium pressure of 13.3 kPa. The basic operating parameters are presented in Table 1. The fullerene content in soot resulting from electrode arcing was determined by conventional spectrophotometric techniques.[20]

The astronomical CCD ST6 camera, coupled with a monochromator, was used for plasma diagnostics. Gas temperature was estimated on the basis of the C_2 (d $^3\Pi_g \rightarrow$ a $^3\Pi_u$, 0-0) emission band. The global C_2 radical contents (volume density), i.e. the product of the concentration and absorbing column length, were estimated using the self-absorption effect according to the procedure described earlier.[24]

Results and Discussion

The interelectrode gap strongly influences the electric properties of the arc and characteristics of generated carbon plasma

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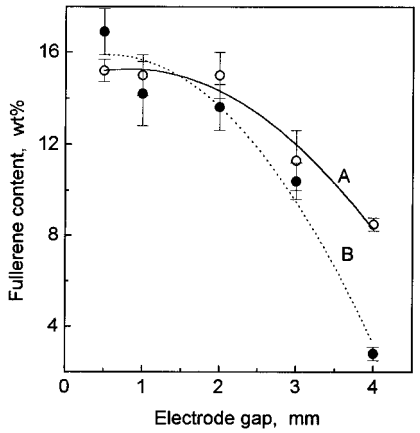

Figure 1. Fullerene content in collected soot vs electrode gap: (A, B) anode erosion rate 3.1 and 5.7 mg/s, respectively.

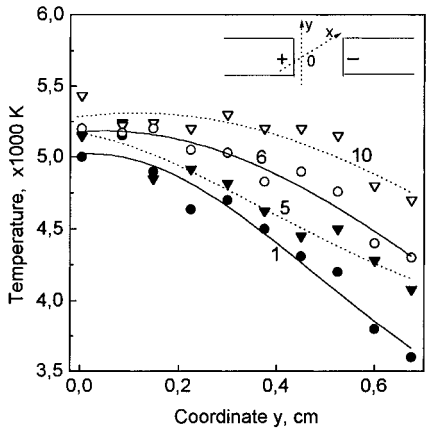

Figure 2. Average temperature distributions at the anode surface for experiments 1, 5, 6, and 10.

as well as the radiation level and heat exchange between the plasma and the surrounding high-temperature zone. Since those factors strongly effect fullerene formation, the process yield was studied while the distance between electrodes was varied. The ablation rate of the anode was held constant at two levels for different electrode gaps (Table 1). Maintaining the anode ablation constant required the adjustment of arc power input, causing the power at lower and higher erosion rates to vary between 1085 and 3470 W, respectively. With the increase of electrode gap distance, the fraction of total ablated carbon involved in an interelectrode transport (related to the formation of the cathode deposit by carbon gas) decreased steadily (Table 1). This was caused not only by the possibly more pronounced expansion of carbon species into surrounding space but also by the strong spallation of the anode material at high currents.[20] Since initial carbon gas concentration and its expansion phenomena inevitably bear on the final efficiency of fullerene formation, the remaining operating variables were fixed in order to make the results comparable.

The results presented in Figure 1 suggest that the increase in an electrode gap results in the decrease of fullerene content. This dependence appears to be significantly outside the experimental error. While there are no distinct differences at small distances (<2 mm) between electrodes, this effect is more pronounced with increasing gap distance. An especially profound decrease of fullerene yield was observed with a relatively large gap (4 mm) and the highest input power (Table 1), despite equal graphite vaporization rates. By increasing the electrode gap and arc power, the UV and visible radiation flux increases, thereby increasing the formation of labile triplet state fullerenes in the gas phase.

Spectroscopic measurements of temperatures at the anode zone for the smallest and largest electrode gaps are presented in Figure 2. These are average values since the temperatures were determined directly from integrated radiation along the *x*-axis as shown in Figure 2. The average accuracy was estimated to be ±200 K. Despite the wide range of input powers (Table 1), the temperatures in the arc zone differ only slightly with a tendency to increase with a rise in power and electrode gap (curves 1, 5 and 6, 10). At a given arc gap, a more pronounced gas temperature increase is observed when anode erosion is augmented (curves 1, 6 and 5, 10).

The spatial distributions of volume densities of C_2 (a $^3\prod_u$, $v = 0$) for the same experiments are shown in Figure 3. When the electrode gap is small (curves 1, 6), even a moderate increase of input power results in higher volume densities of the radicals as well as their concentration in the arc zone. Since for both experiments the final fullerene contents were similar, this result

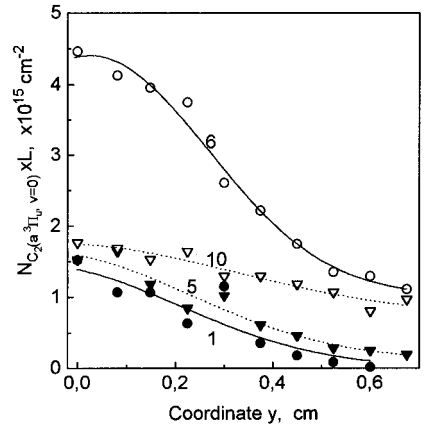

Figure 3. Volume density distributions of C_2(a $^3\Pi_u$, $v = 0$) at the anode surface for experiments 1, 5, 6, and 10.

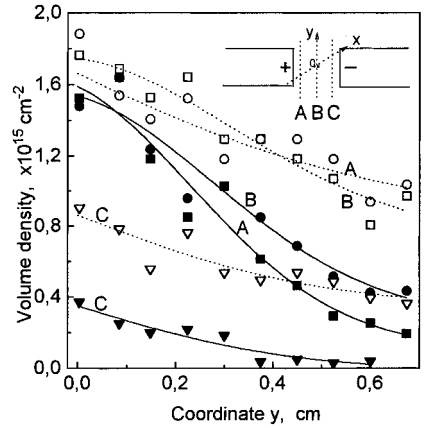

Figure 4. Volume density distribution of C_2(a $^3\Pi_u$, $v = 0$) at anode (A) and cathode (C) surface and in arc center (B). Electrode gap 4 mm. Solid and dotted lines: experiments 5 and 10, respectively.

would imply the involvement of species also other than C_2 in fullerene formation. At large electrode gaps (curves 5 and 10), the volume densities were similar and remained on a low level, despite the much higher input power (Table 1). In such a case not only anode sublimation but also spallation, leading to effective generation of graphite microcrystallites,[20,25] heavily bears on total anode erosion rate. This result would explain the lower fullerene content at high electrode gap distances.

Figure 4 shows a similar C_2 content within a 2 mm distance from the anode (curves A and B). The sublimation process is always characterized by strong spatial gradients at a surface. Therefore one can conclude from Figure 4 that some finely divided graphite crystallites remaining in an arc zone are also

a source of carbon vapors.[25] At the cathode surface, the C_2 gradient was higher because of carbon surface deposition (curves C and A, B), material volume expansion and the relatively large distance from the anode. It explains much lower carbon mass transfer (Table 1).

The form of the presented curves was arbitrarily chosen to simply show the trend in spatial distributions of the respective experimental results. It is obvious that the distributions of temperature and volume density in an arc discharge plasma have a nearly axial symmetry,[26] which is reflected by our data.

From the presented results, it follows that not only plasma radiation but also complex vaporization and mass transport phenomena must be taken into account when discussing the fullerene yield in the context of the electrode gap influence.

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