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Formation of carbon fibers in corona discharges

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We examine carbon fibers grown at the ends of corona wires during negative point-to-plane corona discharges in hydrocarbon atmospheres. Under certain growth conditions, these fibers are hollow tubes with smooth walls; under other growth conditions, the fibers are also hollow tubes, but have rough surfaces. Scanning electron micrographs of these fibers are discussed and possible applications for these fibers are noted.

There is a large literature on the formation of carbon filaments by catalytic processes.[1-10] Also some work has been done on fiber formation associated with electric discharges. For example, Bacon reported[11-13] formation of graphite whiskers in an arc struck between graphite electrodes under a pressure of 92 atm of argon at 3900 °C. More recently, Kwong *et al.*[14] showed that hydrocarbon polymer whiskers, believed to be of polyethylene type, were formed by hydrocarbon polymerization on drift chamber wires.

We report here observations of carbon fibers grown at the ends of corona wires during negative point-to-plane corona discharges in hydrocarbon atmospheres. Under certain growth conditions, these fibers are hollow tubes with smooth walls; under other conditions, the fibers are also hollow tubes, but have rough and apparently self-similar surfaces. First, the experimental system is described. Then some scanning electron microscope (SEM) photographs of these fibers are presented and discussed.

During studies of hydrocarbon reactions in negative discharges at atmospheric pressure we observed that, during negative corona discharge, fibers grew from the tips of the corona wires in a point-to-plane discharge. Figure 1 is a schematic diagram of the experimental arrangement. Fibers grew from tips of corona wires of tungsten, nickel, and platinum. Initially, the end of the negative corona wire was approximately 1.5 cm from the plane anode and a visible corona developed at the wire tips at around -3000 V, when fibers commenced to grow at the rate of a few mm/s; the corona discharge was maintained thereafter from the growing fiber tip. In an alkane atmosphere, we noted that electrically conductive fibers always grew from the tip of any corona wire sustaining a corona discharge. During many of the experiments, various alkane (n-C_7-n-C_{10}) vapors in nitrogen carrier gas flowed with an average axial velocity of $\sim$2.4 cm/s through the reaction tube past the corona wires toward a plane aluminum anode. In other experiments, pure methane (99.9%) flowed through the reaction tube. In all cases, regardless of the alkane, either with or without flow, fibers always grew from the corona wire tips so long as a corona discharge existed. If flow ceased, the corona current and fiber growth rate tended to decrease after around 1 min, apparently because of the development of space charge. In all cases the pressure in the reaction tube was 1 atm.

At corona currents less than the order of 1. mA per wire, the growing fibers were found to have smooth, uniform surfaces and to be stiff with noticeable elasticity. Figures 2–3 show a few examples of fibers grown under these conditions from n-heptane vapor. Figure 2 shows a branched fiber with a rough surface, grown at 2 mA in n-heptane vapor, lying on a long smooth fiber which was grown at a current of around 1 mA in n-hetpane vapor. Close examination of the surface of the smooth fiber shows a seam toward the left of the figure. Figure 3 examines a break in one of the smooth fibers; Fig. 3 shows that these fibers are hollow tubes, the one shown having a wall thickness somewhat greater than 5 μm. Apparently, the interior surface is also smooth. Associated with the ends of these smooth tubes, we have seen many small tubes truncated at both ends at angles of from 12° to 30° with lengths of around 10 μm and diameters of a few μm. The mechanism of their formation remains to be determined.

At currents in excess of the order of 2 mA per fiber, the fiber morphology changes, and branching of the fiber can occur. The surface becomes rough with a pebble texture. At corona currents in excess of 1 mA in methane, the fibers have the characteristic pebble texture surface shown in Fig. 4. At the end of the fiber shown, branching has taken place, with three distinct tubes projecting from the end. Figure 5 shows in detail the surface of such fibers. It can be seen that the surface is not continuous, but that there are apparent voids present. Further magnification of these surfaces reveals that they may be self-similar and fractal. Fig-

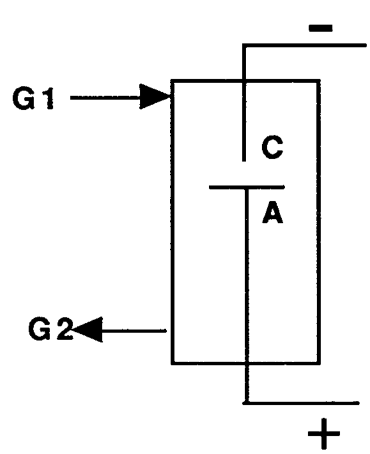

FIG. 1. Simplified schematic diagram of experimental arrangement for production of carbon fibers. C is the cathode wire, A the plane anode, $G1$ is a flow tube for admitting alkane vapor, $G2$ the outlet for flowing alkane vapor.

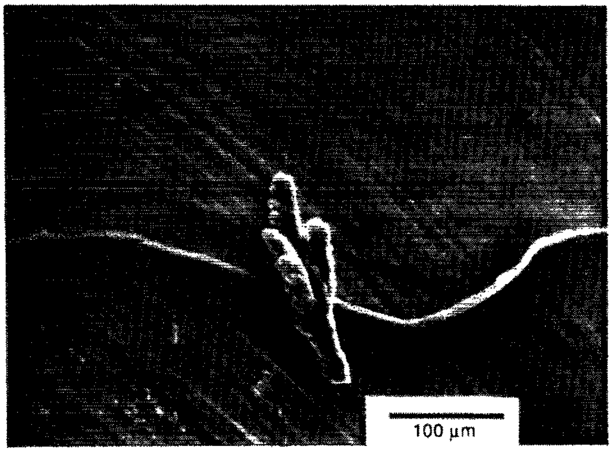

FIG. 2. Branched fiber with a rough surface grown at a corona current of ~2 mA lying on a long smooth fiber grown at ~1 mA, both in *n*-heptane vapor.

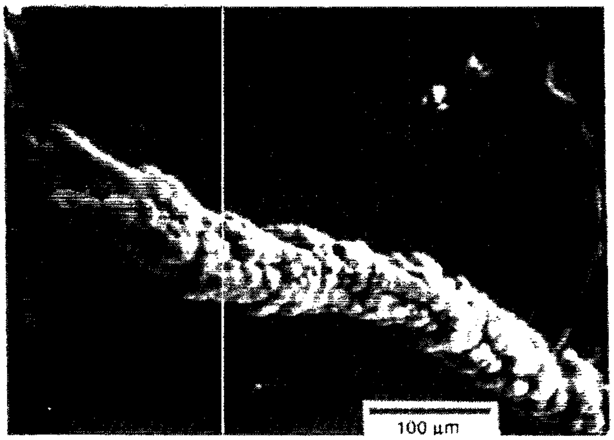

FIG. 4. Rough-surfaced fiber grown at 2 mA in pure methane with characteristic pebble texture and branching.

ure 6 shows a break in one of these rough surfaced fibers. Apparently, these fibers are also hollow tubes with interior surfaces matching the exterior surfaces.

Several previous studies suggest chemical mechanisms in the fiber growth process. Ion formation was investigated in a glow discharge in methane.[15] In this study, highest ion intensities were measured in the region close to the cathode. Some of the reactions with high cross section were:

$$CH^+ + CH_4 \rightarrow C_2H_2^+ + H_2 + H$$

$$CH_2^+ + CH_4 \rightarrow C_2H_3^+ + H_2 + H.$$

It seems likely that these species contribute to the formation of the graphite fibers, although close to the growing fiber tip, we suggest that hydrogen would be removed. This is consistent with conclusions from a recent study[16] of carbon cluster growth kinetics indicating that a rapid mechanism exists of eliminating hydrogen from carbon clusters formed by polymer ablation.

The surface morphology of the fibers suggests the growth mechanism. The morphologies displayed in Figs. 2,4–6 are similar to those found with ballistic growth models and in thin films formed by sputtering.[17] This is consistent with the occurrence of rough surfaces when corona currents are high, implying large electric fields and ballistic trajectories for charged species depositing on the growing fiber tip; at lower electric fields, diffusive motion is more important and permits deposition of hydrocarbon species to take place at perferred sites on the growing fiber tip, thereby leading to smooth, closed surfaces. It is significant that with either ballistic or diffusive deposition, hollow tubes are formed.

The fibers formed during the corona discharge have some interesting properties, which could be exploited for a number of purposes. It has been noted[1] that for present liquid double-layer capacitors to be more effective, major improvements are necessary. For one, while the active carbon now used has high surface area, its electrical conductivity is very low. Fibers grown by corona discharge obvi-

FIG. 3. Details of a break in a smooth-surfaced fiber showing that these fibers are hollow tubes.

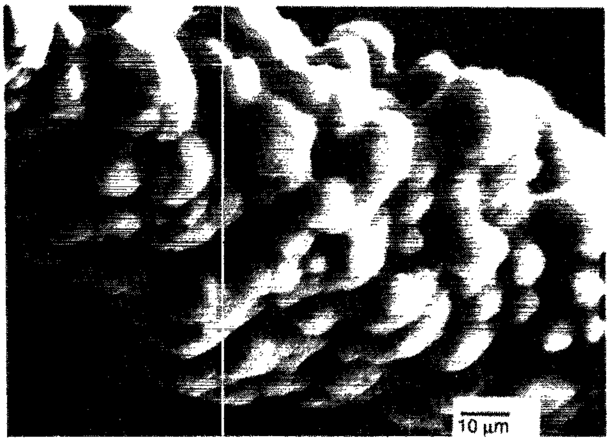

FIG. 5. Detail of a rough-surfaced fiber grown in pure methane showing presence of voids. Additional magnification suggests that these surfaces may be self similar.

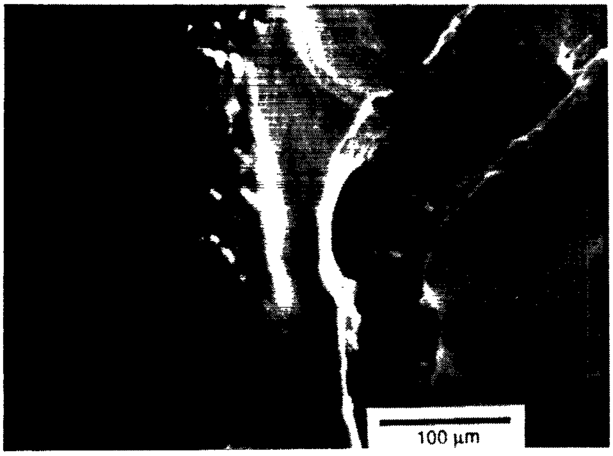

FIG. 6. Detail of a break in a rough-surfaced fiber showing that these fibers are also hollow tubes. Interior walls resemble the exterior surfaces.

ously have high electrical conductivity since the fibers sustain a corona discharge. The fibers grown at high currents have a complex surface, as Figs. 4–6 show. Also, these fibers might be easily produced in the presence of other chemical species, leading to fibers with interesting properties. A subject of current investigation is the growth of diamond-like fibers in these discharges. Such fibers will be reported in another letter.

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