A BENCH ARC-FURNACE FACILITY FOR FULLERENE AND SINGLE-WALL NANOTUBES SYNTHESIS

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Recebido em 9/6/00; aceito em 21/3/01

A metallic-sample arc-furnace was modified to synthesize fullerenes and nanotubes. The (reversible) changes and the process for producing single-wall nanotubes (SWNTs) are described.

Keywords: nanotubes; fullerenes; forarco.

INTRODUCTION

Not long after fullerenes were first produced in the laser ablation of a graphite target[1], it was found that they could be synthesized in an arc discharge between two graphite electrodes[2]. With its interest in carbonaceous materials, the Grupo Combustíveis Alternativos (GCA) at Unicamp decided to produce fullerenes. Rather than construct a dedicated fullerene generator, the two existing arc-furnaces - Forarco I and Forarco II, originally designed for melting constituent elements into metallic compounds and alloys[3] - were simply (and easily reversibly) modified to generate fullerene-bearing soot from solid graphite rods. In response to the discoveries of endohedral fullerenes[4] and then single-wall nanotubes (SWNTs)[5], the GCA began generating soots containing these carbon nanostructures as well. Only the variation of production techniques proved necessary, the central one being the introduction of powders into holes in our graphite rods. In this paper we report: (1) the present modifications to Forarco II, and (2) the production technique for SWNTs.

MODIFICATIONS TO FORARCO II

An arc-furnace for melting metallic samples is essentially a controlled-atmosphere chamber containing water-cooled electrodes connected to a d.c. welding power supply. At GCA, both Forarco I and Forarco II are bench-top chambers with vertical axes of symmetry; a 24 cm segment of 20 cm diameter (0.7 cm wall) Pyrex tubing separates a stainless steel base-plate and an aluminum top-plate, sealed by O-rings and secured by non-conducting tie-rods. The positive electrode is a flat copper disk (or hearth) with indentations for sample confinement, while the negative electrode is a probe that holds a tip from which to strike an arc to the hearth. A bellows assembly and a sliding seal allow the arc to be translated about the hearth in order to melt individual samples. (The probe is grounded because it is manipulated manually). A vacuum/gas-handling system (consisting of a pump, valves and gas bottles) permits control of the atmosphere within the furnace chamber.

By 1994, Forarco I and Forarco II had each been modified for fullerene production. Only Forarco II, however, was later fitted with automated probe advance. A diagram of the present configuration of Forarco II is shown in Figure 1; it reflects the following modifications indicated by the numbers on the figure:

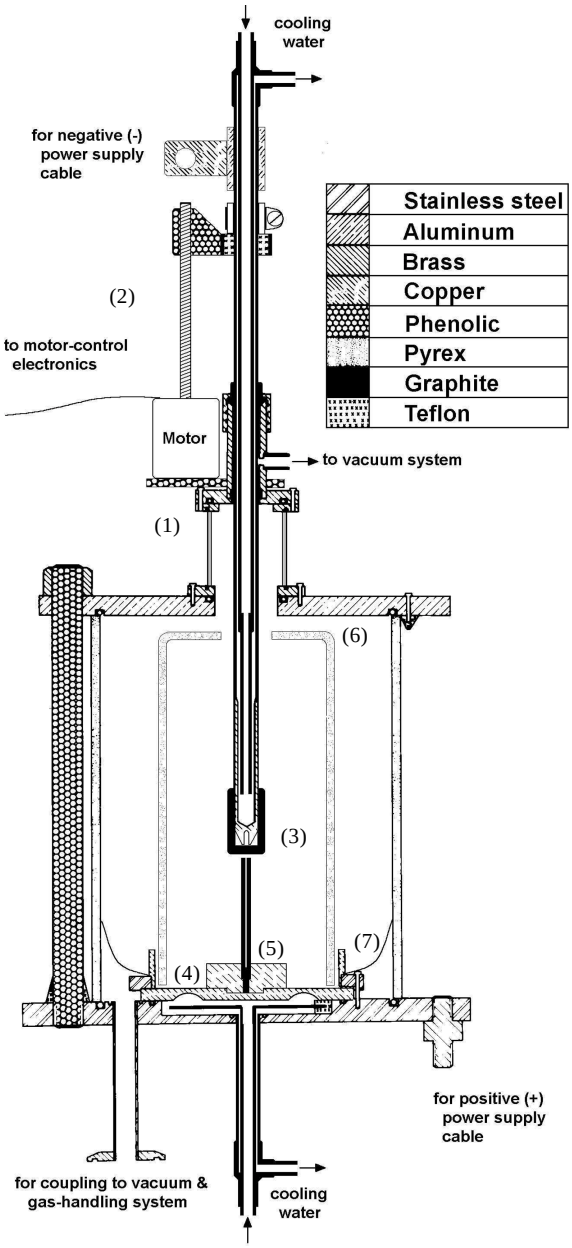

Figure 1. *Diagram of the arc-furnace Forarco II as modified for the synthesis of SWNTs. The numbered modifications are described in the text.*

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(1) The beryllium-copper bellows assembly was replaced by a rigid brass support, and a small phenolic platform was added extending to one side.

(2) A stepper-motor with a vertical helical driveshaft was attached to the platform. The shaft rotation, controlled electronically by a variable pulse-rate generator, moves a threaded phenolic translator which holds a teflon yoke that slides along the probe. A friction-fit nylon collar, secured around the probe with a hose clamp, rests on the teflon yoke.

(3) The thoriated-tungsten tip of the cathode probe was removed, and a graphite cap with a flat under-surface was slip-fit over the copper end-piece (thin tantalum or zirconium foil is used for spacing if the fit loosens).

(4) The copper hearth was inverted, and a centering indentation was machined into the flat side.

(5) A thicker, narrower, mating copper disk with a central hole was added as a holder for a graphite anode rod.

(6) A central hole was cut in the bottom of a large (11.8 cm diameter x 22.5 cm height), straight-wall, Pyrex beaker (Pyrex No. 6920); and the beaker was placed, inverted, on the hearth as a condenser (or collector).

(7) An aluminum foil shield (actually, a cake mold with the center cut out), held in place by a short segment of 12.6 cm diameter copper tubing, was added to protect the chamber access ports.

PRODUCTION TECHNIQUE FOR SWNTS

Once Forarco II had been modified as described above - originally to fabricate endohedral fullerenes - the production of SWNTs required only the preparation of a catalyst to be packed within a graphite anode rod. We have been using UF-4S (Ultra F Purity) electrode rods from Carbone of America. The rods (one foot length x 6.2 mm diameter) are cut into thirds. Each resulting segment is about 100 mm long, and a 2.0 mm hole of approximate 84 mm depth is drilled into one end. The other end is turned down to slip-fit into the 4.8 mm central hole of the copper holder. A catalyst is prepared by weighing out powders of selected elements, either individually to obtain desired ratios (e. g., Fe:Co:Ni in the ratio 1:1:1), or already combined in a compound with fixed ratios (e. g., $Zr(Fe_{0.5}Ni_{0.5})_2$). Metallic compounds can be made at GCA by arc-melting the constituent elements together in Forarco I; such compounds can be pulverized (immediately if formed congruently, or after being appropriately annealed) and ground into a powder. The use of compounds as catalysts permits experimentation with different combinations of elements than are possible by just mixing those which are available in powders. It also ensures uniform release ratios of the catalytic elements into a plasma from particles that can be ground as finely as desired. This is important if graphitic and catalytic materials are to be delivered into, say, a plasma torch for the possible continuous synthesis of SWNTs (There is an on-going effort at GCA to develop such a delivery and synthesis system.). In any case, whatever the catalyst powder to be used with a graphite rod, it can be diluted to an approximate percentage of the total amount of carbon to be processed by mixing in some of the graphite powder obtained when the rod was drilled out. The catalyst/graphite mixture is then packed into the hole in the rod, the rod is inserted into the copper holder, and the anode is ready.

When the Forarco II chamber has been emptied, cleaned, and closed; the top-plate is simply lifted up; the copper holder is centered on the hearth; the Pyrex collector is set in place, and the top-plate put back down. The chamber is then evacuated, and the lock-nuts on the tie-rods secured. After the chamber has pumped down to a few tens of millitorr, the anode and cathode are short-circuited by lowering the sliding probe until its graphite end-piece is in firm contact with the tip of the graphite rod. With the valve to the vacuum pump still open and with cooling water flowing, d.c. current is turned on at its minimum setting (60 A for our power supply). The graphite rod heats up and is observed to glow a dull red, and the chamber pressure increases as the rod and its contents outgas. After the pressure has peaked, the current is increased by 10-20 A. The rod glows brighter red, and the pressure peaks again. This process is repeated as felt necessary. An eventual sustained (about 15 minutes) current of 100-120 A adequately outgasses the system. If an oxide powder, however, has been mixed into the catalyst further current increase may be required before the oxygen reacts out. Once the current has been shut off and the vacuum pumping stopped, a partial atmosphere of high purity helium (usually about 400 torr) is introduced into the chamber. The phenolic translator is raised to its extreme on the helical shaft along with the nylon collar around the probe. The probe is then lifted slightly to open a 1-2 mm gap between the graphite electrodes; and with the cooling water still flowing (and all persons present wearing welder's goggles), the power supply is turned on at its minimum setting. The probe is eased back down until an arc is struck between the pieces of graphite; then the current is increased to a chosen value (80 A to 120 A for the 6.2 mm rods). A gap is seen to open up as the anode begins to be consumed into the arc plasma. When the gap becomes several mm, the stepper-motor feed is initiated. The nylon collar around the probe rests on the teflon yoke, and as the yoke is lowered, so is the probe. Vacuum grease on the probe facilitates the transit through the sliding seal, but gravity sometimes needs assistance with gentle manual force on the probe. Control of the pulse rate to the stepper-motor allows the cathode to be advanced steadily downward at any selected speed. Other than current control within the power supply, there is no feedback in our system. Nonetheless, the consumption rate of the anode seems to self-regulate such that a fairly constant gap voltage (we actually measure between the terminals on the probe and base-plate and see values around 30 V) is maintained for a constant cathode advance. While the arc is still visible before material deposited on the collector obscures the view, the gap appears to remain at several mm even as a cathode deposit is building to extend the cathode surface further downward. For our favored advance rate, it take around eight minutes until the rod is reduced to a stub in the copper holder and the gap voltage drops. It should be noted that the collector becomes very hot during a pyrolysis. The lower portion (in line of sight of the arc) glows red and even softens such that with repeated usage, the beaker shows a bulge in its diameter and can develop a lean, Also, the pressure of the helium atmosphere within the chamber can as much as double. The Pyrex wall of the chamber becomes too hot to touch, but it does not suffer. The cooling water is kept flowing after the current has been shut off. In no more than an hour, the chamber has cooled and may be opened. The helium atmosphere is pumped out, the lock-nuts are removed, and the chamber is vented with air.

The products of the pyrolysis are almost entirely confined within the inverted beaker collector; this makes recovery of those products and clean-up of the chamber quite simple. In opening the chamber, the blackened probe is brought up through the hole in the collector as the top-plate is carefully lifted and placed on a bracket. The collector is removed and set onto a clean tray. The pyrolysis products are then retrieved and contained separately for processing and/or analysis. We describe here the products retrieved when a combination of catalyst and production parameters gives a visibly reasonable yield of SWNTs:

(1) The cathode deposit is a solid, lightweight, cinder-like, irregular cylinder that builds downward from the cathode under-surface; it is known to contain multi-wall nanotubes (MWNTs) but not SWNTs.

(2) The collar is a soft, cottony, multi-tendrilled growth that flowers around the cathode deposit (it falls off when the probe emerges from the hole in the collector and is picked up with tweezers); it has been found to be richest in SWNTs[6].

(3) The material on the interior walls of the collector is a sponge-rubbery, cloth-like coating which is swept off with a long-handled artist's brush; while less dense in SWNTs[6], it comes from a large, easily-cleaned surface and is uncontaminated by debris or possibly vacuum grease.

(4) Everything else that adheres to the probe or collects on the floor (copper hearth and holder) is swept up together.

A yield is felt to be particularly good when what appear to be old, dirty cobwebs are draped on the probe and in the upper region of the collector interior. This has been observed most strikingly with our choice of Fe:Co:Ni (1:1:1) as catalyst. An empty UF4S graphite rod has a mass of around 4.8 gm, and the stub remaining in the copper holder after pyrolysis is about 0.7 gm. Also, 0.1 to 0.2 gm of graphite powder are in the catalyst mix, so at least 4 gm of carbon are fed into the plasma during a pyrolysis. In the case of the aforementioned Fe:Co:Ni (1:1:1) catalyst, approximately 0.6 gm of the transition metals are evaporated into the plasma - some three atomic percent relative to the carbon. The accumulated products of eight pyrolysis with this catalyst are being processed and analyzed[7], and the results will be reported elsewhere.

CONCLUSIONS

We have described above (1) the conversion of the arc-furnace Forarco II at GCA into a generator of fullerenes and nanotubes, and (2) the process by which this device is used to produce SWNTs. The miracle of the transformation of a graphite rod into a rich harvest of SWNTs - via a plasma with the presence of catalytic elements - can be observed on a bench top. Significantly, the combination of the conventional Forarco I and the modified Forarco II (along with our simplified catalyst-in-a-hole technique) uniquely position the GCA to study the role and effects of catalysts in the formation of SWNTs.

ACKNOWLEGMENTS

The authors are grateful to G. Ciampi for his technical support, to F. Felfli and L. Montoro for their help with the figure, to M. Rosolen for useful discussions, and to FAPESP and CNPq for appropriate funding.

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