A Microporous Carbon produced by Arc-evaporation

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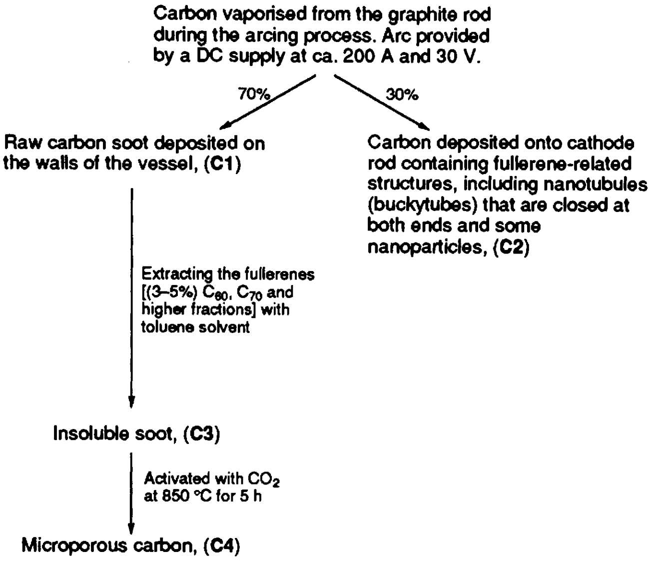
A carbon soot formed by arc evaporation and activated by heating under carbon dioxide is found to have a surprisingly high internal micropore volume (>0.25 ml g^{-1}) and an apparent BET surface area of *ca.* 700 m^2 g^{-1}, a large proportion of the pores are *ca.* ≤5 Å; transmission electron microscopy shows a highly disordered microstructure, which electron irradiation readily transforms into quasi spherical concentric nanoparticles of diameter of *ca.* 60 Å, the carbon material, which is highly absorbent to methane, shows molecular sieving properties and is more inert to oxidation than other forms of high surface area carbon.

In 1990 Krätschmer and coworkers showed that buckminsterfullerene, C_{60}, could be prepared in macroscopic amounts by arc-vaporisation of graphite rods in an atmosphere of inert gas.[1] Much of the vapour emitted from the carbon rods deposits as a black soot on the cooled walls of the reaction vessel. This soot contains C_{60}, C_{70} and higher fullerenes which may be extracted from the soot using organic solvents. In this work this carbon soot was prepared from an arc struck between two electrolytic grade graphite rods (8 mm o.d., 15 cm in length, purity >99%) in 100 Torr (1 Torr ≃ 133 Pa) of helium using a voltage of 30 V and a DC current of 180–200 A. Under these conditions the anode graphite rod is steadily vaporised (10 g h^{-1}) and *ca.* 70% of the carbon from the anode is deposited on the reaction vessel walls as **C1** soot whilst the remaining *ca.* 30% is transferred onto the end of the cathode carbon rod, which grows in length accordingly. This cathode carbon deposit **C2** is rich in carbon nanotubules and related structures, as we have described elsewhere.[2] Refluxing **C1** with toluene extracts the soluble fullerenes. The residual insoluble soot **C3** was dried and then activated for pore development by treatment with a stream of carbon dioxide at a flow rate of 20 ml min^{-1} and at 850 °C for typically, 5 h. Under these conditions the reaction $C + CO_2 \rightarrow 2CO$ occurs and after the 5 h period the **C3** lost 14.6% mass. The resulting activated carbon is denoted as **C4**. The preparation of the various forms of carbon discussed here is summarised in Scheme 1.

Here, we report the unusual properties of the activated carbon **C4**.

The surface area of the carbon samples have been measured by Brunauer–Emmett–Teller (BET)[3] method using nitrogen at −196 °C. Table 1 shows the measured BET surface areas of pure C_{60}, and the carbons **C1**, **C2**, **C3** and **C4**. The surface areas of powdered graphite and commercial microporous carbons are also included for comparison. **C2** has a low BET surface area of 21.0 m^2 g^{-1}, but, as we have reported, heating



Scheme 1

$C2$ under CO_2 for 5 h at 850 °C increases the surface area to 31.7 $m^2\ g^{-1}$ and forms uncapped nanotubes.[4] The raw soot **C1** has a high apparent BET surface area of about 300 $m^2\ g^{-1}$. The surface area remains virtually unchanged for the carbon **C3** from which the fullerenes have been extracted. However, the surface area of the activated carbon **C4** is about 700 $m^2\ g^{-1}$ and has increased substantially over **C3**. Further treatment of **C4** with CO_2 at 850 °C did not produce a significant further increase in surface area. The higher surface area of **C4** compared to **C3** may be due to the removal of reactive carbonaceous contaminants trapped in the pores of **C3**.

The activated carbon **C4** can absorb substantial volumes of methane at room temp. and ambient pressure, for example, **C4** absorbs more methane than the commercial porous carbon (GS60) although the latter is found to have a much higher BET surface area (see Table 1).

The absorption by **C4** of various hydrocarbons at 20 °C and various pressures has been measured and the Dubinin–Astakhov equation[5] has been used to calculate the limiting volumes, as shown in Table 2. The limiting volume for **C4** is about 0.25 ml g^{-1} for methane, ethane and propane. However, the limiting volume drops to about 0.1 ml g^{-1} when larger molecules, *n*-butane and isobutane were used. This molecular sieve behaviour coupled with the apparent high surface area measured by the BET method, suggests that the activated soot is highly microporous with a large proportion of the pore sizes lying in the ultramicroporous region of $\leqslant 5$ Å.

We have made a comparative study of the reactivity of **C4** with that of the carbon GS60 and a comparable surface area activated charcoal (Phase Separation Ltd) using the method of temperature-programmed heating of the carbon samples (16 mg) under CO_2 from 740–950 °C with a ramping rate of 3 °C min^{-1}, at ambient pressure and with a flow rate of 20 ml min^{-1}. The volatile products were monitored by a quadrupole mass selective detector (HP 5971A). The temperature-programmed reactions of these three carbons are shown in Fig. 1. No carbon monoxide was detected in the case of the **C4** sample. However, under the same conditions, the other two carbons gave large amounts of carbon monoxide. Indeed most of the GS60 and activated charcoal were burnt off while no apparent mass loss occurred for **C4**. The activated charcoal was also heated under CO_2 at 850 °C for 5 h, however, virtually no charcoal (only traces of dust) was left. Thus, C4 is surprisingly inert.

Table 1

Adsorbent	BET surface area/$m^2\ g^{-1}$
Powdered graphite rod	28.4
Purified C_{60}	34.4
Raw soot (**C1**)	296.8
Carbon deposited on cathode (**C2**)	21.0
Extracted soot (**C3**)	301.2
Extracted soot treated at 850 °C for 5 h under CO_2 (**C4**)	692.0
Carbon deposited on cathode treated at 850 °C for 5 h under CO_2	31.7
GS60	1429.5
Activated charcoal	730.1

Table 2 Limiting adsorption volumes of **C4** carbon calculated using Dubinin–Astakhov equation (ref. 4)

Molecule (size/Å)	W_o/ml g^{-1}
CH_4 (3.8)	0.21
C_2H_6	0.23
C_3H_6	0.26
Bu^n (4.3)	0.12
Bu^i (5.0)	0.11

The activated carbon **C4** and other carbon samples were also examined by transmission electron microscopy (TEM). Specimens were prepared by grinding the material gently in a pestle and mortar and dusting the powder directly onto holey carbon films. High-resolution imaging of the samples was carried out on a JEOL 4000FX instrument with an approximate point resolution of 1.6 Å, operated at Scherzer defocus with an accelerating voltage of 400 kV. Only thin regions that protruded over holes in the support film were examined.

A typical high resolution electron micrograph of **C4** is shown in Fig. 2(*a*). The image shows the material to be highly disordered, with very little obvious graphitisation, although a thread-like microstructure of curved graphitic layers is evident, particularly near the edge of the particle. The micrographs are consistent with a highly porous, disordered structure with a narrow pore size distribution. In some areas, graphitic nanoparticles similar to those found at the centre of the cathodic rod[2,6] were observed. Selected area diffraction patterns were similar to those obtained from amorphous carbon films, although the ring at 3.4 Å was somewhat sharper owing to the presence of graphitic particles.

Ugarte has shown that exposure of amorphous carbon, carbon nanotubes and nanoparticles, to a highly intense and focused electron beam induces structural transformations to quasi-spherical concentric fullerene particles (buckyonions).[7,8] He found these buckyonions varied widely in size depending on the sizes of the initial nanotubes and nanoparticles. We have irradiated the carbon **C4** using a JEOL 2000FX microscope operated at 200 kV with the condenser aperture removed and the beam focused on a small region of the sample. Under these conditions a transformation to the quasi-spherical carbon particles (buckyonions) was observed after 20–30 min; a typical micrograph of the irradiated material is shown in Fig. 2(*b*). This micrograph clearly shows that the activated carbon **C4** has been essentially converted quantitatively and that the resulting buckyonions formed are very homogeneous in size with an averge diameter of approx. 60 Å. Fig. 2(*c*) is a higher magnification image of an irradiated

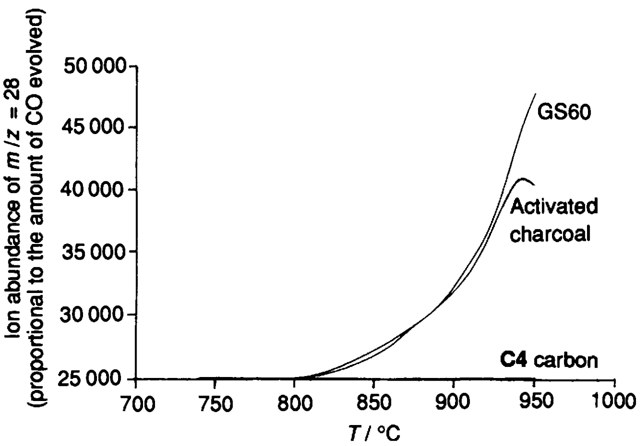


Fig. 1 Comparison of the oxidative reactivity of **C4** porous carbon soot with GS60 carbon and activated charcoal in the presence of carbon dioxide.

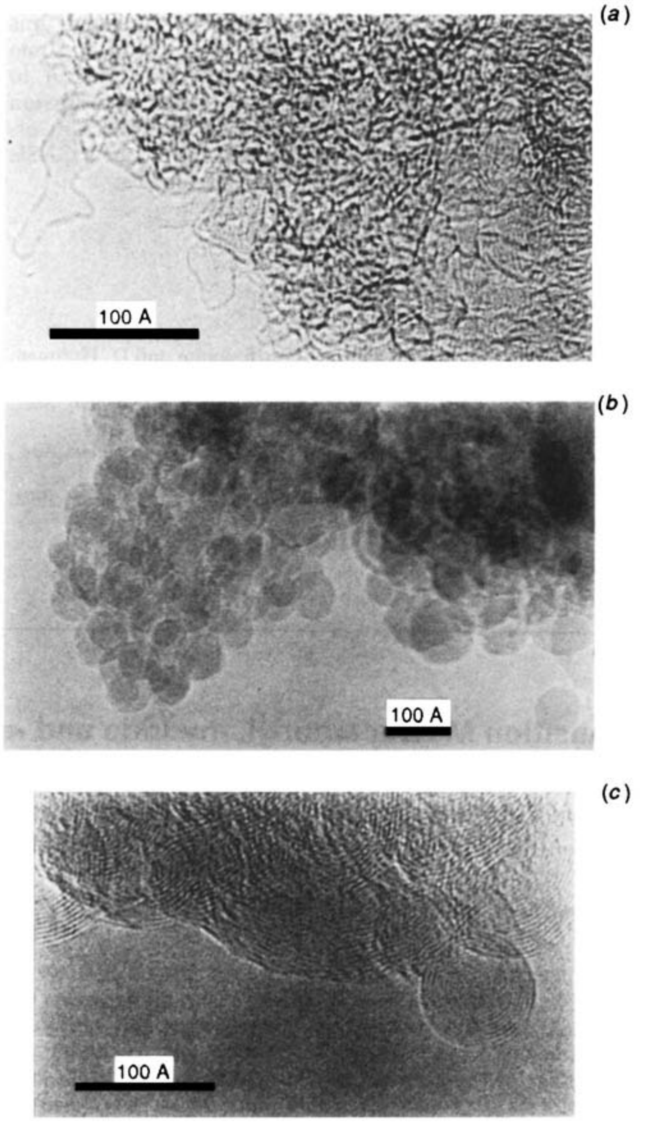


Fig. 2 High-resolution electron micrography of (*a*) **C4** porous carbon soot following removal of fullerenes and activation in carbon dioxide at 850 °C. (*b*) Transformation of **C4** porous carbon soot into spherical concentric fullerene particles following irradiation in an intense electron beam. (*c*) A region partially transformed into concentric fullerene particles.

sample, showing a region in which the transformation to 'buckyonions' is incomplete. It appears that **C4** contains the seeds or the templates for the formation of 'buckyonions'. In a control experiment, a sample of the high surface area commercial microporous carbon GS60, which is derived from coconut shell, was exposed to a similar intense electron beam. No buckyonions were formed, even after 120 min of irradiation, but some graphitisation and rounding of the overall morphology was observed.

We have also found that on heating the carbon **C4** using a positive-hearth electron gun (4 kV, 0.4 A) it converts to a mixture of nanoparticles, onion-like structures and nanotubes, similar to those found in the raw cathodic soot **C2**. The electron gun has been described previously.[9] Since the voltages used are much lower than those employed in the electron microscope irradiation experiments it seems likely that the conversion of **C4** to nanostructures is mainly a thermal effect. Ugarte has also found that amorphous arc-produced carbon can be converted to hollow nanometric carbon onions and nanotubes by resistively heating to about 2400 °C.[10]

We conclude that **C4** has very unusual properties. The surface area measurements coupled with high-resolution electron microscopy show that the structure is highly microporous. Carbon with these characteristics can be formed by pyrolysis of carbonaceous materials (natural or synthetic) which already have a microporous structure, but it is surprising that this microporous material is produced from the exceptionally low surface area graphite rod with no intrinsic porous framework. The growth of carbon may be through a vapour-phase condensation process. The carbon would have been exposed to exceptionally high temperatures during the arcing process. One might expect these extreme conditions to drive the structure to minimise its surface energy. However, if the structure is fullerene-related curved carbon then elimination of dangling bonds might override the need to minimise surface area. Moreover, we have shown that **C4** carbon is much more stable towards oxidation by CO_2 than conventional high surface area carbons, suggesting that it has far fewer dangling bonds. Further, unlike other conventional amorphous carbons it converts readily on heating to fullerene-related structures.

The type of structure that best fits these observations is one in which the presence of non-six-membered rings in graphite-like planes produces continuous curvature, rather than one made up of a mass of discrete curved 'ribbons' of graphite as in other forms of microporous carbon. One possibility is that the structure contains a random distribution of five-membered rings. According to the 'pentagon road' theory of fullerene assembly, the formation of isolated pentagonal rings is energetically favoured during condensation as this leads to a minimisation of the number of dangling bonds.[11] Kroto and McKay considered a similar scenario, but assumed that pentagons would stack epitaxially one above the other, rather than randomly, leading to spiral shell structures;[12] such structures were not seen here.

An alternative possibility is that the structure of **C4** contains seven- or eight-membered rings. Carbons of this type, which have been christened schwartzites, have been discussed theoretically by a number of authors.[13–18] The presence of rings with more than six members produces negative, or saddle-like, curvature and the resulting lattice is highly porous with either periodic[13–16,18] or random[17] structures.

Finally, the new carbon **C4** may have important applications as a catalyst or an absorbent and might also have interesting electronic and optical properties. Moreover, the present work could have astrophysical implications. It has been suggested[19] that fullerenes and related carbons could be the carriers of trapped inert gases in meteorites. The high internal area of the carbon described here would make it readily capable of fulfilling this role.

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