Electrochemically prepared colloidal, oxidised graphite

Michael J. Hudson,*[a] Frances R. Hunter-Fujita,[b] John W. Peckett[a] and Patricia M. Smith[b]

[a]Department of Chemistry and [b]School of Animal and Microbial Sciences, University of Reading, Box 224, Whiteknights, Reading, Berkshire, UK RG6 2AD

A convenient electrochemical method has been developed for the preparation of a functionalised, colloidal graphite (oxide). The method involves the anodic erosion of graphite electrodes by the generated oxygen when using current densities less than 3 mA cm^{-2}. The suggested mechanism of formation involves the loss of an electron to form the radical cation followed by hydration to form the enol which is in tautomeric equilibrium with a keto group. The surface areas of the colloid were typically 50–80 m^2 g^{-1}. The particle size distributions were trimodal for ethanoic acid and water but trimodal for sulfuric acid. However, the particle size ranges were significantly wider (40–870 nm) when ethanoic acid was used as the electrolyte than when sulfuric was used (40–630 nm). The colloid had an ion exchange capacity of 7 mmol g^{-1} for a monovalent cation. FTIR spectroscopy confirmed the presence of hydroxy (3442 cm^{-1}) and keto groups (1727 cm^{-1}). Electrochemical reduction led to the formation of alcohol and aliphatic hydrocarbon groups.

Interest in colloidal carbon stems, at least in part, from the potential uses of colloidal particles for the extraction of pollutants from industrial steams. A colloidal carbon with functional groups such as carboxyl, hydroxyl and keto groups could prove to be useful when used in conjunction with micro- and ultra-filtration processes in order to carry out separations which are not achievable by microporous activated carbons.[1] The commercial activated carbons are heterogeneous in nature and hence new carbons with well defined chemical groups are required. Another source of interest comes from the use of colloidal oxidised graphites in order to prepare thin protective films.[2] The oxidised graphite is coated onto the surface and then reduced. Although interest in colloids has, of course, been extensive for many years, and Svedberg and Tiselius, for example, spent much effort in preparing sols of elements such as gold and cadmium, the properties of colloidal oxidised graphite prepared by anodic oxidation warrant detailed study.[3]

Although it is not possible to form colloids of unoxidised carbon, colloids of oxidised graphite or graphite oxide have been known for some time. Vinke *et al.* have reported studies on the surface modification of carbon using nitric acid, hypochlorite and ammonia.[4] Reviews of chemical modifications of the surfaces of carbon have been carried out.[5,6] The electrochemical properties of elements including carbon have been reviewed.[7] Discussions of models for graphitic carbon–oxygen surfaces have been attempted by several authors.[8,9] Thus, it has been proposed, for example, that carboxyl groups are left when a carbon ring is destroyed. Typical models of functional groups on the surfaces of oxidised carbons suggest that keto, hydroxyl and carboxylic acid groups may all coexist on the surfaces. However, the mechanisms of fixation, the locations of the sites, the nature of the bonds and the structures of the functional groups all need further elucidation and a comprehensive study of the anodic oxidation of graphitised carbon still needs to be carried out. As a contribution to these continuing studies, some of the properties of electrochemically prepared colloidal oxidised graphite have been studied.

Experimental

Materials and equipment

The electrodes used were graphite rods, 0.5 cm in diameter and 5 cm in length, which may be taken, for example, from zinc–carbon batteries. They were washed with doubly deionised water prior to use and were immersed to a depth of *ca.* 3 cm in the electrolyte, *i.e.* the surface area in contact with the electrolyte was *ca.* 5 cm^2. The electrolytes used in this study were ethanoic acid (0.17 mol dm^{-3}) and sulfuric acid (0.03 mol dm^{-3}). Doubly deionised water was also used. The equipment typically consisted of a dc power-pack (0–33 V) with a voltage reversal unit.

Electrolytic experiments

The preparation was left running for three weeks (8 h per day) after which time the colloidal carbon had been produced together with some solid particles of carbon, the properties of which will be reported in a separate publication. The colloid was filtered through a Whatman 541 filter paper in order to remove particulate carbon. After switching on the current using an acid electrolyte, it was observed that the oxygen, which was generated at the anode, was evolved as large bubbles partially coming from the interior of the carbon electrode. The preparative details are presented in Table 1 together with observations relating to the behaviour of the electrode during electrolysis. In experiments where the current density was less than 3 mA cm^{-2} the anode slowly eroded to form colloidal carbon plus carbon slurry. Attempts to increase the rate of colloid production by increasing the current density to greater than 4 mA cm^{-2} were unsuccessful owing to the rapid break-up of the electrode. At current densities greater than 3 mA cm^{-2}, the rate of oxygen evolution was greater than the rate of its diffusion through the electrode, hence there was a pressure build-up within the electrode causing the electrode to disintegrate. Similarly, at current densities less than 3 mA cm^{-2} the rate of oxygen evolution was such that, although some pressure built up in the electrode, the gas was able to diffuse out of the electrode before disintegration occurred, small pieces of carbon broke off in the process to form colloidal carbon plus some carbon slurry.

The rate of diffusion of hydrogen at the cathode was such that little or no pressure built up within the electrode and therefore no colloid was produced at this electrode. When doubly deionised water was used as the 'electrolyte', at a current density of 0.2 mA cm^{-2}, the product consisted almost wholly of colloidal carbon with a very small amount of slurry. In all experiments, the colloidal carbon was produced only at the anode and remained within the vicinity of that electrode, indicating that the carbon was negatively charged. Reversal of

Table 1 Some experimental details and observations for the preparation of colloidal carbon

	electrolyte			
	CH_3COOH (0.17 mol dm^{-3})	H_2SO_4 (0.03 mol dm^{-3})	H_2SO_4 (0.03 mol dm^{-3})	doubly deionised water
potential/V of electrode	33	25	25	33
current/mA	3	15	15	1
surface area/cm^2	4.9	4.9	4.9	4.9
current density/mA cm^{-2}	0.61	3.06	3.06	0.2
observations	colloid present plus carbon granules *ca.* 1 mm diameter	colloid present plus carbon granules *ca.* 1 mm diameter	colloid present plus carbon granules *ca.* 1 mm diameter	colloid present plus carbon granules *ca.* 0.1 mm diameter
charge on colloid	negative	negative	negative	negative
time/days	21	21	21	21
polarity reversal	no	no	yes	no
C—H stretch	no	no	yes	no
>C=O	present	present	present	present

the electrode polarity resulted in the surrounding carbon migrating slowly to the new anode. The colloid prepared in sulfuric acid (0.03 mol dm^{-3}) was stable for at least three years, whereas that prepared in doubly deionised water was stable for 3–6 months after which period it precipitated.

Preparation of dried carbon

Methanol precipitated the carbon after two to three days contact. Alternatively, the colloid prepared in either ethanoic or sulfuric acid, was centrifuged and washed twice with methanol and dried overnight at 110 °C. An additional method was to slurry the colloid prepared in doubly deionised water, with ammonium carbonate and evaporate off the water under vacuum. This left a solid dispersion of the colloid in ammonium carbonate which was then sublimed off under vacuum at 35–40 °C to produce a fine carbon powder. For preliminary carbon analysis using the colloid prepared using doubly deionised water, the material was dried at 90 °C in silica crucibles and, when dry, the temperature was raised to 120 °C and held at this temperature overnight. The crucibles were cooled in a desiccator, reweighed and the carbon content calculated.

Surface area measurements

Surface areas of the dried materials were measured for nitrogen adsorption–desorption at 77 K,[8] using a Gemini 2375 surface area analyser, taking the surface area of the nitrogen molecule to be 0.162 nm^2.

Particle size distributions

These were measured by photon correlation spectroscopy using a Malvern 4700C submicron particle analyser.

Decontamination factors (Df)

These were measured at the Atomic Energy Research Establishment, Harwell by shaking 5 cm^3 of the colloidal carbon (prepared in doubly deionised water and containing *ca.* 10 mg carbon) with 50 cm^3 of an aqueous solution of trace β–γ active cations (*ca.* 100 Bq cm^3 or 10^{-6} mol dm^{-3}). The pH was adjusted to 9.6 with NaOH (0.1 mol dm^{-3}). After equilibration, the suspension was passed through a syringe filter with a pore size of 0.02 µm and the β–γ activity counted. Knowing the original count in the feed and that in the sample after equilibration, the Df values were calculated from the expression: Df = Bq cm^{-3} in sample/Bq cm^{-3} in feed.

UV–VIS spectra

UV–VIS spectra were recorded using a Kontron Uvicon spectrophotometer with silica cells.

Titres with the colloidal carbon

Doubly deionised water (3 cm^3) was pipetted into a silica cell and colloidal carbon (200 µl) of known concentration was pipetted into the sample cell. Water (200 µl) was pipetted into the reference cell. The spectrum was then recorded and the absorption noted at λ_{max} (189–228 nm). To each cell was then added known, equal volumes of standard acid and the spectrum was again recorded.

FTIR spectra

These were recorded using a Perkin Elmer 1720-X FTIR spectrophotometer. The pellet was prepared by adding the colloid to solid KBr, evaporating to dryness at 110 °C, grinding and pressing into a 13 mm diameter pellet. A pellet of the original material was prepared by scraping the electrode to remove some carbon, grinding with KBr and pressing the pellet as before.

Scanning electron microscopy

The physical appearance of the dried solid was determined using a JEOL 840 scanning electron microscope.

Results and Discussion

The concentrations of these negatively charged colloids were typically of the order of 0.1 mol dm^{-3}. The surface areas of the colloidal oxidised carbons varied from 50 to 80 m^2 g^{-1} according to the electrolyte used. The overall results are given in Table 2 together with the estimated surface areas. The expected particle size distribution for a polydispersed system corresponds to a simple Gaussian distribution curve.[9] However, the colloids prepared here had a broad bi- or trimodal particle size distribution curve (Fig. 1). The colloid prepared in ethanoic acid had a significantly wider particle size range (40–870 nm) than those prepared in sulfuric acid (30–630 nm) and doubly deionised water (40–630 nm), values of which were compatible with the surface areas given earlier. The trimodal distributions suggest that the colloids comprised three major types of particles, the surface areas of which are all rather low, indicating that there is little overall porosity (Table 2). The desorption pore volume plot also showed that the pore volumes were low with a broad, rather ill-defined maximum at 20 nm (not shown). These particles, therefore, showed some mesoporosity but little microporosity.

UV–VIS spectroscopy

A typical UV–VIS spectrum of colloidal oxidised carbon prepared in ethanoic acid (0.17 mol dm^{-3}) is given in Fig. 2,

Table 2 Some physical properties of the colloidal carbons

	electrolyte		
	CH_3COOH (0.17 mol dm^{-3})	H_2SO_4 (0.03 mol dm^{-3})	doubly deionised water
surface area/m^2 g^{-1}	50	75	79
calc. surface area/m^2 g^{-1}	14	39	17
particle size/nm	40–870	30–630	40–630
av. particle size/nm	202	133	182

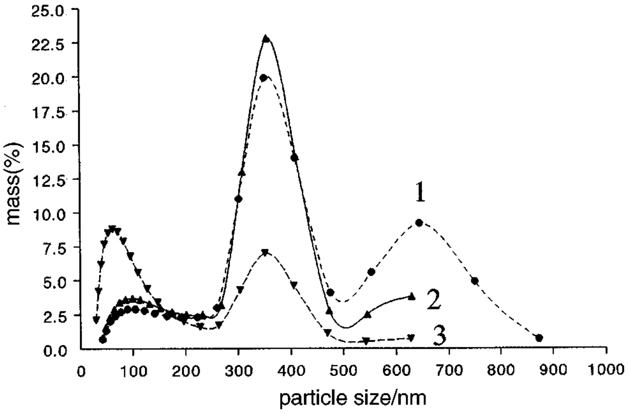

Fig. 1 Particle size distributions of the colloidal carbons. Carbon prepared in (1) ethanoic acid (0.017 mol dm^{-3}), (2) doubly deionised water and (3) sulfuric acid (0.03 mol dm^{-3}).

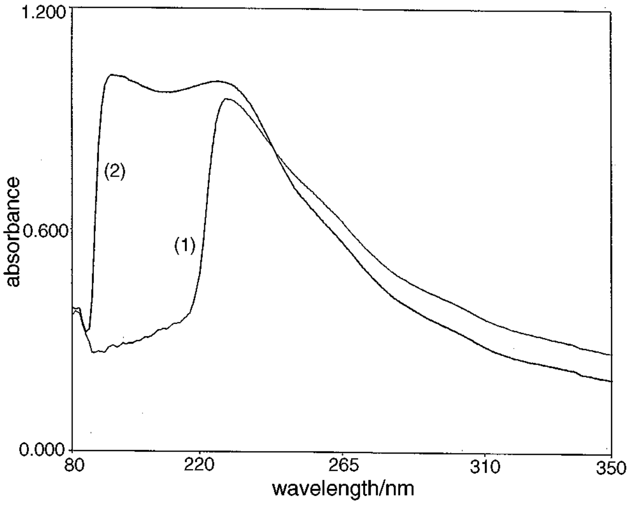

Fig. 2 UV–VIS spectra of some of the colloidal carbons. (1) Carbon prepared in ethanoic acid and (2) carbon prepared in doubly deionised water.

spectrum (1), showing λ_{max} to be at 228 nm. The spectrum of colloidal carbon, prepared from doubly deionised water is also shown [spectrum (2)] and shows λ_{max} now at 189 nm. The difference between these two spectra suggested that the ethanoic acid had possibly protonated the functional groups on the carbon or had catalysed a keto–enol tautomerism. Accordingly, a sample of carbon prepared by electrolysis in doubly deionised water was acidified with ethanoic acid (0.17 mol dm^{-3}) and its spectrum recorded. This also resulted in the appearance of a peak at 189 nm with the spectrum being identical to that obtained from colloidal carbon prepared in ethanoic acid [spectrum (1)]. The experiment was repeated using both HCl and H_2SO_4 with similar peaks appearing at *ca.* 190 cm^{-1}.

Titration with acids. Sub-micro titration with acids was carried out on the colloidal carbon prepared using doubly deionised water as the electrolyte. Thus, there were no added species present other than colloidal carbon and water plus the electrochemically produced species. Three spectrophotometric titrations were carried out using standard ethanoic, hydrochloric and sulfuric acids. The absorptions at λ_{max} were plotted as a function of the volumes of acid added. Fig. 3, for example, shows the effect of titrating the carbon with hydrochloric acid but similar curves were obtained with both ethanoic and sulfuric acids (Table 3). The UV–VIS spectrum of the colloid prepared in doubly deionised water contained two peaks [Fig. 2, spectrum (2)]. However, the peak at the higher energy end of the spectrum was suppressed by the addition of standard acid, the amount of which required was the same as that obtained from carbon prepared in 0.17 mol dm^{-3} ethanoic acid [Fig. 2, spectrum (1)]. This amount corresponded to the concentration of acid required to titrate the carbon to the first point of discontinuity (point B, Fig. 3) and was comparable to that obtained for titrations with standard ethanoic, hydrochloric and sulfuric acids (Table 3). Consequently, it appeared that a quantitative protonation had taken place between the acid and the oxidised carbon the surface of which consisted of carbon and oxygen-containing groups which may be formulated as $C_n{\cdot}C{=}O$. The proton uptake was calculated from knowing the mass of carbon present and the concentrations and volumes of acid required to take the system up to point B (Fig. 3), then n can be calculated. Averaging the results (Table 3) gave a molar carbon : oxygen ratio of 12 : 1, *i.e.* $n = 11$. The proton exchange capacity was *ca.* 7 mmol g^{-1}. The regions BC, CD and DE (Fig. 3) are related to the formation of acid-containing solvation shells surrounding the carbon particles.

FTIR spectroscopy

The FTIR spectrum of the original graphite electrode prior to modification, Fig. 4, spectrum (1), showed no significant features (the small bands present were from the potassium bro-

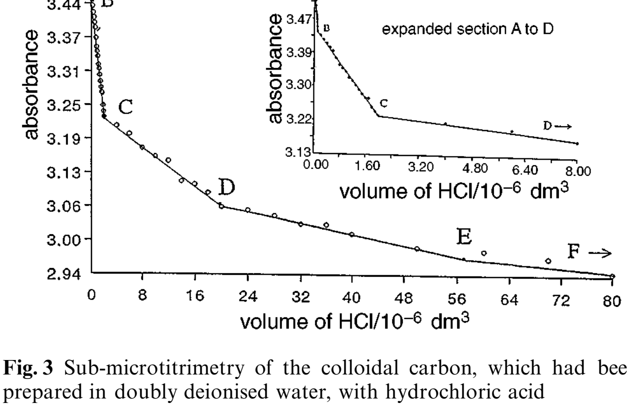

Fig. 3 Sub-microtitrimetry of the colloidal carbon, which had been prepared in doubly deionised water, with hydrochloric acid

Table 3 Some chemical properties of collidal carbon

	titrant		
	CH_3COOH ($17.6\ mol\ dm^{-3}$)	HCl ($10.56\ mol\ dm^{-3}$)	H_2SO_4 ($18.95\ mol\ dm^{-3}$)
proton/m mol g^{-1} dry carbon	7.9	4.8	7.5
molecules of acid/carbon atom (shell 1)[a]	1.7	0.9	1.8
molecules of acid/carbon atom (shell 2)[a]	16.0	8.9	20.3
molecules of acid/carbon atom (shell 3)[a]	20.1	18.3	17.4

[a] Estimated values from microtitrimetry.

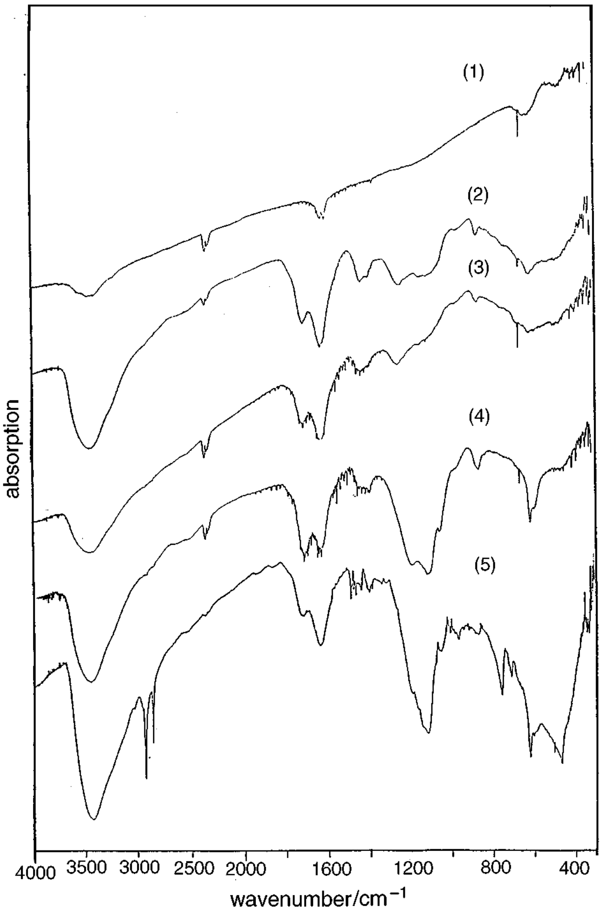

Fig. 4 FTIR spectra of colloidal carbons. (1) The original material, (2) carbon prepared in doubly deionised water, (3) carbon prepared in ethanoic acid ($0.17\ mol\ dm^{-3}$), (4) carbon prepared in sulfuric acid ($0.03\ mol\ dm^{-3}$) and (5) carbon prepared in sulfuric acid ($0.03\ mol\ dm^{-3}$) in which the polarity of the electrode had been reversed; note the appearance of peaks which may be assigned to (aliphatic) C—H stretches.

mide). The FTIR spectra of the carbons, which had been dried previously at 110 °C, and had been prepared in doubly deionised water, spectrum (2), and ethanoic acid, spectrum (3), were identical, both showing absorption bands at 3442 (OH), 1727 (>C=O) and 1645 cm^{-1} (C=C). Spectrum (4) is that of the colloid prepared in H_2SO_4 ($0.03\ mol\ dm^{-3}$) and was also similar. However, the bands below 1300 cm^{-1} were due to the presence of sulfate groups either bound or as the free acid; the samples had been washed free of sulfate in the eluent. Spectrum (5) is that of colloidal carbon prepared in H_2SO_4 ($0.03\ mol\ dm^{-3}$) where the electrode polarity was reversed every 10 min, *i.e.* the colloidal carbon came into contact with (nascent) hydrogen. There are additional peaks, for example, spectra (2)–(4) all show a trace of the doublet at 2907 and 2835 cm^{-1} owing to the presence of aliphatic C—H bonds. Spectrum (5), however, shows the doublet to be enhanced considerably. This is attributed to the reduction of double bonds present in the carbon, by the (nascent) hydrogen produced at the cathode. The bands below 1300 cm^{-1} were due to free or bound sulfate groups. Since the surface areas of the colloidal carbons were low, most of the bound functional groups were probably on the exterior surface of the particle.

Mechanism of formation

The following mechanism is proposed for the oxidative processes occurring at the electrodes. The unsaturated bonds within the graphite were oxidised to form a radical cation, which may be converted to an enol form which is in an acid-catalysed tautomeric equilibrium with the keto form.

Anode reaction.

$$>C{=}C< \xrightarrow{e-} \underset{\text{radical cation}}{[>C^{+}{-}C^{\bullet}<] \xrightarrow{OH^{\bullet -}} [>C(OH){-}C^{\bullet}<]} \xrightarrow{H^{\bullet}}$$

$$\underset{\text{enol form}}{-C(OH){=}C(H)-} \leftrightarrow \underset{\text{keto form}}{-C(O){-}C(H)_2-} \qquad (1)$$

Since the reaction takes place in acid media then we have the acid-catalysed tautomeric equilibrium.

Table 4 Decontamination factors for some radioactive cations (% cation removed with time in brackets)

	contact time/h				
cation	1	2	4	6	24
Cs	1.0 (50)	6.1 (8.6)	12.3 (92.5)	16.3 (94.2)	32.7 (97)
Co	43 (97.7)	28 (96.6)	14 (93.3)	10.2 (91.1)	7.5 (88.2)
Ru	3.6 (78.3)	4.3 (81.1)	4.8 (82.8)	4.3 (81.1)	5.4 (84.4)
Ag	5.4 (84.4)	11.6 (92.1)	23.3 (95.9)	23.3 (95.9)	35.0 (97.2)
Mn	31 (96.9)	8.9 (89.9)	4.8 (82.8)	3.8 (79.2)	3.0 (75.0)
Zn	>1000 (99.9)	228 (99.6)	570 (99.8)	>1000 (99.9)	570 (99.8)
Fe	>500 (99.8)	>500 (99.8)	>500 (99.8)	183.3 (99.5)	183.3 (99.5)
Hg	2.26 (72.2)	>3.6 (78.3)	6.6 (86.8)	6.2 (86.1)	9.5 (90.5)
Cd	>100 (>99)	>100 (>99)	>100 (>99)	>100 (>99)	>100 (>99)
Cr^{III}	354 (99.7)	500 (99.8)	>1000 (99.9)	1200 (99.9)	330 (99.7)

$$-CH_2-C(O)-\underset{\text{slow}}{\overset{H^+\text{fast}}{\leftrightarrow}}[-CH_2-C(O^+H)-]\underset{H^+\text{fast}}{\overset{-H^+\text{slow}}{\leftrightarrow}}-CH=C(OH)- \quad (2)$$

It is quite possible that, in addition to the keto and enol groups, there are carboxyl groups present when the colloid is prepared from doubly deionised water. Sulfate groups are also present when the colloid is prepared using sulfuric acid as the electrolyte.

Cathode reaction. The following cathode reactions took place when the electrode polarity was reversed and the colloidal carbon came into contact with (nascent) hydrogen. The carbonyl groups (3) and unsaturated linkages (4) were reduced:

$$>C=O \overset{-e^-}{\rightarrow} \underset{\text{radical anion}}{>C^{\bullet}-O^-} \overset{[H^+]}{\rightarrow} >C^{\bullet}(OH) \underset{\text{radical}}{\overset{[H]}{\rightarrow}} >CH(OH) \quad (3)$$

Reduction of the double bond is also caused by the nascent hydrogen, *i.e.*

$$-C(OH)=C< \overset{[H]}{\rightarrow} -CH(OH)-CH_2- \quad (4)$$

Thus, electrochemical reduction provides a means of changing the functional groups on the carbons. It is interesting to note that the electrochemical reduction leads to aliphatic C—H bonds. This implies that there had been extensive oxidative ring-opening prior to the reduction of the rings. The combined oxidation and reduction gave a measure of control over the nature of the functional groups.

Scanning electron microscopy

The scanning electron micrographs of the surfaces of the dried colloids show that considerable exfoliation has occurred in the graphite, Fig. 5. There are holes in the material which were formed when the oxygen-containing species passed forcibly through the layers of the graphite. There is evidence for partial retention of the original layered structure.

Decontamination factors

The availability of the functional groups for chemical reaction was determined by the removal of contaminants from simulated industrial wastes. The decontamination factors, Table 3, indicate the possible ion-exchange potential of the colloidal carbons. A decontamination factor (Df) of 100 represents $>99\%$ removal of the cation under investigation. A number of cations was studied with decontamination factors ranging from 2.6 for mercury to >1000 for zinc. Overall, the colloidal particles were quite effective for removal of the ions studied and may provide a useful alternative to flocculated metal hydroxides or oxides.

Conclusions

An electrochemical method has been developed for the preparation of functionalised, colloidal graphites. The method involves the anodic erosion of graphite electrodes by the generated oxygen. The suggested mechanism of formation involves the loss of an electron to form the radical cation followed by hydration to form the enol which is in an acid-catalysed tautomeric equilibrium with a keto group. The surface areas of the colloidal particles were typically 50–79 m^2 g^{-1} and most of the functional groups must be on the surface of the material. The colloid prepared using distilled water had an ion exchange capacity of 7 mmol g^{-1} for a monovalent cation and appeared to be effective for the removal of cations from water. FTIR spectroscopy confirmed the presence of hydroxyl (3442 cm^{-1}) and keto groups (1727 cm^{-1}). Electrochemical reduction of the ruptured rings resulted in the formation of aliphatic C—H bonds. The combined electrochemical oxidation and reduction allow for some control of the nature of the functional groups.

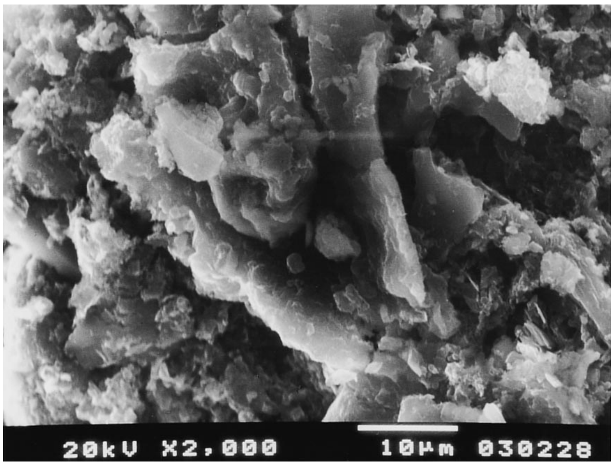

Fig. 5 Scanning electron micrograph of the carbon prepared using distilled water (the exfoliation of the carbon can be seen, plus the holes formed by oxygen-containing gaseous species which passed through the layers of the original graphite anode)

The authors would like to thank J. A. Knowles and C. Bruschini for surface area measurements; D. Gleeson and M. T. J. Keene for the FTIR spectra, C. Malde for particle size analysis, and Professor P. Parsons, F. R. Fujita-Hunter and P. M. Smith are thanked for useful discussions.

References

1 E. W. Hooper, in *Insights into Speciality Inorganic Chemicals*, ed. D. Thompson, Royal Society of Chemistry, Cambridge, 1995.
2 N. A. Kotov, I. Dekany and J. H. Fendler, *Adv. Mater.*, 1996, **8**, 637.
3 T. Svedberg and A. Tiselius, *Colloid Chemistry*, Monograph, American Chemical Society, New York, 1928.
4 P. Vinke, M. van der Euk, M. Verbree, A. F. Voskamp and H. van Bekkum, *Carbon*, 1994, **32**, 675.
5 A. Girir, D. Richard and P. Gallezot, in *Heterogeneous Catalysis and Fine Chemicals*, ed. M. Guisnet, Elsevier Science Publishers, Amsterdam, 1988.
6 M. A. Schegler, P. Vinke and H. van Bekkum, *Appl. Catal. A*, 1992, **80**, 41.
7 *Encyclopaedia of the Electrochemistry of the Elements*, ed. A. J. Bard, Marcel Dekker, New York, 1976, vol. VII.
8 H. P. Boehm, *Adv. Catal.*, 1966, **16**, 179.
9 D. Bauer, *Bull. Soc. Chim. Fr.*, 1967, 944.

Paper 6/03982K; *Received* 6*th June*, 1996