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IMPROVING THE ELECTROCHEMICAL BEHAVIOR OF CARBON BLACK AND CARBON FILAMENTS BY OXIDATION

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Abstract—Oxidation changed the electrochemical behavior of carbon black, catalytically grown carbon filaments and pitch-based carbon fibers from irreversible to reversible, as shown by cyclic voltammetry using the $Fe(CN)_6^{-3/-4}$ redox couple. Thermal oxidation of carbon black (16%) yielded a higher electron transfer rate constant k_s than did chemical (HCl or HNO_3) oxidation. For carbon filaments, chemical oxidation using 50% HCl gave the most beneficial effect of the acids tested, increasing k_s to a higher value than can be achieved by either thermal oxidation or solvent cleansing. Thermal oxidation of carbon fibers to a 17% burn-off was more effective (higher k_s) than thermal oxidation to burn-offs of 7 or 22%. The capacitance C and electrochemical area A of carbon black were decreased by thermal or chemical oxidation, whereas thermal oxidation of carbon filaments increased C and A, and chemical oxidation of carbon filaments decreased C and A. Thermal oxidation of carbon fibers decreased C and A. Carbon filaments exhibited the lowest thermal oxidation resistance, followed by carbon black, then carbon fibers. Thermal oxidation to a similar burn-off gave the highest k_s for carbon filaments, also followed by carbon black, then carbon fibers. Both thermal and chemical oxidation increased the packing densities of carbon black and carbon filaments, thereby increasing k_s. Thermal oxidation removed the tarry coating (2% by weight) on the carbon filaments, and changed the particle size, increased the macropore density and decreased the pH of the carbon black. The use of binders such as oil and wax in electrodes was unnecessary for carbon filaments (oxidized or not) and for thermally oxidized carbon black, but was required for untreated and chemically oxidized carbon black. © 1997 Elsevier Science Ltd

Key Words—A. Carbon black, A. carbon filaments, A. carbon fibers, D. electrochemical properties, D. surface area.

1. INTRODUCTION

Electrochemical systems commonly use carbon black, graphite, glassy carbon, carbon fibers, and, most recently, carbon filaments for electrochemical applications. For such applications, the electrochemical capability of the carbon material is critical to its performance, and the kinetics and reversibility of electrochemical processes strongly depend on the surface character of the carbon material. Surface treatments are, therefore, commonly applied to carbon materials in order to enhance their electrochemical behavior. These treatments include changes in the surface functional groups, surface crystallographic structure and surface roughness, which may involve chemical treatment, electrochemical treatment, heat treatment, laser treatment, plasma treatment, polishing or other surface activation. In the case of carbon materials to be used in electrochemical applications, acid treatment [1–6], electrochemical treatment [7], heat treatment [8,9], laser treatment [10,11], plasma treatment [12], polishing procedures [13], solvent cleansing [14,15] and hair growth [16,17] have been employed. Most of these treatments tend to increase the oxygen-containing functional groups on the surface of the carbon. In the case of high temperature heat treatment in an inert or reducing atmosphere or in vacuum, graphitization of the carbon can take place, thus changing the crystallographic structure both in the surface and in the bulk. In the case of heat treatment in the presence of oxygen, oxidation of the carbon occurs, thus increasing the amount of oxygen-containing functional groups on the surface and even converting the carbon to CO or CO_2 gases (thereby roughening the surface, thus increasing the carbon surface area). In the case of solvent cleansing, contaminants that develop on the surface of certain carbons during their manufacturing process, such as on carbon filaments and porous carbons (specifically reticulated vitreous carbon), are removed, resulting in either a change in the surface functional groups (as is the case when acetone is the solvent used to cleanse) or adsorption of a different species on the carbon surface after cleansing [14,15]. In the case of hair (or filament) growth on carbon substrate materials, modification of the crystallinity, surface area and surface texture of the substrate carbon is achieved [16].

The physical and chemical properties of carbon materials significantly influence their electrochemical nature, however, studies relating the electrochemical

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behavior of carbons to their material properties (such as morphology, particle size, compactability or surface character) are lacking. For example, carbon blacks are a primary choice for current collectors, conductive additives or electrocatalysts in batteries and fuel cells. Much is written relative to the manufacture of carbon blacks [18–21], the mechanism of their nucleation and growth [20], and various aspects of their physical and chemical properties [8,18,19,23,24], but little research has been conducted relative to the electrochemical behavior of carbon materials [8,25–27], and, except for studies conducted to ascertain parameters important for the electrochemical oxidation of carbon black [8], essentially no work was conducted relative to the electrochemical behavior of oxidized carbon black [28,29]. In fact, the only work relative to the electrochemical behavior of carbon blacks as a function of oxidation was conducted on a few furnace blacks [29] and on Vulcan XC-72 from the Cabot Corporation [28]. It is the objective of this paper, therefore, to study the electrochemical behavior of carbon black. A related objective is to improve its electrochemical performance as measured by changes in the electron transfer rate k_s via thermal and chemical oxidation.

Kinoshita summarizes various oxidation processes (e.g. electrochemical, thermal and chemical) conducted either to study the reactivity of the carbon materials or to alter the surface character of various carbon materials [8]. It is generally accepted that the reactivity of carbons is dependent on their morphology, and that carbons with basal-plane sites predominating on their surface have a considerably lower chemical reactivity than do those with edge sites predominating on their surface. Much research has been conducted specifically on the reactivity of carbon with oxygen [8,30–32]. However, studies relative to the influence of oxygen containing surface groups (and the process used to create these surface groups) on the electrochemical behavior of carbons is lacking, particularly studies relative to the effects on the electrochemical behavior of carbon blacks. The double layer capacitance of various carbons (e.g. pyrolytic graphite, glassy carbon, graphite powder, graphite cloth, active carbons and carbon black) has been determined [8,28,33,34], and the impact of oxygen containing surface functional groups on the potentiometric response of carbon to ionic species in solution (for determining the viability of carbon for ion-selective electrodes) has been studied [35]. In the case of carbon blacks, cyclic voltammetry (CV) studies demonstrated that chemical oxidation of graphitized Vulcan XC-72 resulted in clearly defined redox peaks compared to that obtained for the untreated graphitized Vulcan XC-72 [28], and studies on furnace blacks have identified active surface functional groups produced by electrochemical oxidation, but not the impact of the surface functional groups on electrochemical behavior. It is an objective of this paper, therefore, to supplement the work cited by characterizing the electrochemical behavior of Shawinigan acetylene black after various levels of thermal oxidation, and after chemical oxidation in two acids. Another objective is to compare the electrochemical response of thermally and chemically oxidized carbon black with that of thermally and chemically oxidized carbon filaments, a newly emerging carbon material for electrochemical applications [36–39]. A related objective is to compare chemical oxidation of carbon filaments with solvent cleansing of carbon filaments [14] as a surface treatment for electrochemical performance improvement.

Thermal oxidation of radially structured carbon fibers demonstrated that the domination of edge sites produced by thermally removing the basal plane surface skin resulted in the formation of oxygen-containing surface functional groups, a reduction in the fiber surface tension (increasing wettability), and an improvement in electrochemical reversibility [9]. Ref. [9], however, did not report on the effects of oxidation on the electron transfer rate, k_s, double layer capacitance, C, and electrochemical area, A, important parameters for electrochemical applications. It is an objective of this paper, then, to elucidate k_s, C and A for radially structured carbon fibers as-received and after thermal oxidation. Another objective is to compare the electrochemical performance of thermally oxidized carbon filaments and carbon black to that observed for thermally oxidized carbon fibers.

Chemical oxidation of amorphous and graphitic acrylic based carbon fibers in HNO_3 demonstrated that the chemical reactivity of the carbon fibers and the concentration of surface oxygen groups were greater for the amorphous version than it was for the graphitic version [8]. The effects of chemical oxidation in Hummer's reagent (a mixture of H_2SO_4, $NaNO_3$ and $KMnO_4$) were reversed from that observed in HNO_3, i.e. the graphitic carbon fiber resulted in a higher concentration of surface oxygen groups compared to the amorphous version, due to the formation by intercalation of graphite oxide (graphite oxide was not formed in the amorphous version) [8]. It is an objective of this paper to compare the reactivity of carbon black and carbon filaments in various acids.

For electrochemical applications such as i) battery and analytical electrodes and ii) capacitors, electrode capacitance is as important a parameter to performance as electrode kinetics. In the former, it is desirable to have a low capacitance in conjunction with a high electron transfer rate. In the latter, a high capacitance and a high electron transfer rate are sought. High capacitance is often associated with high surface roughness or high concentration of oxygen containing surface functional groups, whereas low capacitance is usually due to poor wetting by the electrolyte [8]. Slow capacitive charging has been shown to occur when the electrode displays limited conductivity or exhibits an inhomogeneous surface

[8]. Carbon black displays a high capacitance but a low electron transfer rate. It is an objective of this paper, then, to achieve a high electron transfer rate while maintaining low capacitance by thermal or chemical oxidation of carbon black.

Carbon filaments are a recent technological development (within the last 15 years). They are submicron in diameter (typically ~0.1 μm), exhibit a high aspect ratio and high electrical conductivity, and are grown catalytically from carbonaceous gases, typically carbon monoxide or a hydrocarbon [8,40–49]. Carbon filaments differ from conventional carbon fibers in their fabrication process and in their size. In contrast to carbon filaments, conventional carbon fibers are typically 10 μm in diameter, and are prepared either from a pitch material or from a polymer precursor such as polyacrylonitrile, in the absence of a catalyst. Carbon filaments also differ from vapor-grown carbon fibers, which begin as carbon filaments, but grow in diameter (dimensions characteristic of the conventional carbon fiber), due to non-catalytic carbon deposition on the outside of the carbon filament [40–42]. The carbon filaments used in this study (ADNH of Applied Sciences Inc., Cedarville, Ohio) were made using methane as the primary source gas and an iron containing catalyst. Hydrogen sulfide was added to the feedstock in small amounts to increase filament yield [50]. Flowing air was used to harvest the filaments from the growing chamber. ESCA determined the atomic sulfur percentage of the as-received filaments to be 0.5 before and 0.4 after removal of the top 20 Å from the carbon filament surface [14]. Solvent (acetone) cleansing was effective in removing the sulfur. In addition, solvent cleansing removed the contaminant in the form of a tarry residue (primarily polyaromatic hydrocarbons) and improved the compactability of the carbon filaments, making the use of a binder (such as oil or wax) unnecessary [14]. This paper compares the effectiveness of various acids in improving the electrochemical performance of the filaments. Further, it is an objective of this paper to assess the impact of chemical treatment on the compactability of the carbon filaments, as compactability affects the electrochemical performance.

Carbon blacks are highly structured carbons (described by their clustering capability). Their performance is governed by their particle size, surface area and surface chemistry. Various surface groups containing oxygen, hydrogen, nitrogen, sulfur, halogens and other elements have been identified on carbon blacks [8]. These elements are introduced into the carbon black during their manufacturing process. The carbon black studied in this work is Shawinigan acetylene black from Chevron, Houston, Texas (425 Å mean particle size). Chevron's petrochemical operation produces its Shawinigan carbon black from a high purity feedstock (99.9% pure acetylene gas). The process involves continuous thermal pyrolysis of acetylene at temperatures above 1500°C, in the absence of air [51].

In general, carbon black electrodes require the use of binding agents for compaction and shapeability. The use of binders is particularly evident in analytical electrodes (oil or wax) and battery current collectors (polymeric powder such as Teflon). In the case of analytical electrodes, the binders available for use tend to dissolve in nonaqueous electrolytes, resulting in disintegration of the carbon electrode. In the case of battery current collectors, the binder, although beneficial in the sense that compaction and shapeability are facilitated, is a passive material which occupies volume that could otherwise be filled with active material, potentially extending battery life. The compactability and shapeability of carbon black were achieved by modifying the surface via hair growth [16,17], but this treatment is labor intensive, inefficient and of low yield. Additionally, residual catalyst remains on the hairy carbon particle, which may be undesirable for certain electrochemical applications. It is an objective of this paper, therefore, to develop a simpler, more efficient surface treatment that enhances bindability of carbon black, specifically, to investigate the impact of thermal and chemical oxidation on the bindability of carbon black.

2. EXPERIMENTAL METHODS

The carbon materials investigated were carbon black (425 Å mean particle size, Shawinigan acetylene black from Chevron, Houston, Texas), carbon filaments (grade ADNH, 1500 Å in diameter, greater than 100 μm in length from Applied Sciences Inc., Cedarville, Ohio), and carbon fibers (same as in ref. [9], i.e. Thornel P100, radially structured, unsized, high-modulus, mesophase-pitch-based graphite fibers, 10 μm diameter, with a graphite basal plane skin, from Amoco Performance Products, Atlanta, Georgia).

Thermal oxidation was conducted by heating in air for the times and at the temperatures shown in Table 1. Chemical oxidation was achieved by immersing the carbon in an acid medium in a beaker on a Fisher Scientific Model 210T stirring plate. The mixture was stirred for 10 minutes, and then was filtered. That cleansing was occurring was evident by a yellow

Table 1. Effect of thermal oxidation on weight

Sample	Heating time (hours)	Heating temperature (°C)	Burn-off (%)
Carbon black	0.5	250	1
Carbon black	0.5	350	3
Carbon black	0.5	450	5
Carbon black	0.5	600	16
Carbon filaments	2	450	15
Carbon fibers	0.5	600	7
Carbon fibers	3	600	17
Carbon fibers	5	600	22

to brown discoloration of the acid medium. The carbon was returned to the beaker containing deionized water before stirring an additional 5 minutes, then filtering again. This process was repeated until the filtrate tested neutral with litmus paper. The carbon was allowed to air dry in a low humidity environment ($<1\%$ *RH*) overnight before testing. The acids used to chemically oxidize carbon filaments (in order of decreasing relative strength) were HCl, HNO_3, H_2SO_4, H_3PO_4 and CH_3COOH. (HCl is not classified as an oxidizing acid, so the effects of the HCl may not be oxidation, even though the HCl treatment is grouped with the other acids under chemical oxidation.) The relative strength of the acid was determined from its dissociation constant. (The dissociation constants are given along with the dissociation reactions in Table 2. The larger the dissociation constant, the stronger the acid.)

To assess thermal oxidation resistance of carbon black and carbon filaments, thermogravimetric analysis (TGA) was conducted using a Perkin–Elmer 7 Series Thermal Analysis System. The air flow during analysis was $40\ cm^3\ min^{-1}$. The temperature was increased at a rate of $20^\circ C\ min^{-1}$ to 750°C, and then cooled to room temperature at $50^\circ C\ min^{-1}$. TGA was conducted during heating. TGA was also used to determine the carbon filament contaminant level. In this case, TGA was conducted in nitrogen ($flow = 40\ cm^3\ min^{-1}$, though a small amount of air probably remained) using the same heating and cooling rates.

The effects of oxidation on the morphology (particle size, macropore size and macropore density) of carbon black prior to compaction were ascertained by SEM inspection. In this work, the carbon black particle is defined as that part of the carbon black agglomerate comprising a single individual sphere of carbon. The macropores are those within a carbon black agglomerate. The macropore density was determined in two dimensions by multiplying the macropore area by the number of macropores per unit area.

To assess the acid character of carbon black after oxidation, the pH of a carbon black slurry was determined in accordance with ASTM D 1512-90, "Standard Method of Testing Carbon Black – pH Value". The carbon slurry was prepared by placing 1.5 g of the carbon black into 20 ml of deionized water contained in a 30 ml beaker. Two drops of acetone and a magnetic stir bar were added to the mixture to facilitate dispersion of the carbon black sample. The beaker was covered with a watch glass and inserted into an ultrasonic bath containing water to a depth of 40 mm and at a temperature of $\sim 10^\circ C$ below ambient. While stirring the mixture vigorously with the stir bar, sonication was conducted for 3 minutes. All agitation was ceased and the pH measurement was taken after a 2 minute equilibration period. Three readings per sample were taken.

Cyclic voltammetry (CV) was conducted using the method and set-up described in ref. [14]. A saturated calomel electrode served as the reference and a platinum wire as the auxiliary electrode. The working electrode for carbon black or carbon filaments was a purchased BAS holder normally used for carbon paste. The carbon filaments were packed into the holder cavity at a pressure of 10 MPa without the use of any binder, whereas the carbon black samples were packed with and without a mineral oil binder (a liquid petroleum derivative from Witco Corporation, Greenwich, Connecticut) so as to assess the effect of treatment on carbon black bindability. The circular carbon electrode had an outer planar area of $0.0792 \pm 0.0005\ cm^2$. The working electrode comprising Thornel P100 carbon fibers was fabricated by cutting a bundle of 3000 fibers, 25.4 mm long, wrapping the end of the bundle with a copper wire and inserting the assembly into a glass tube. The unbound end of the fiber bundle was fixed at 3.175 mm from the edge of the glass tube. The glass tube was filled with polyester and the polyester cured, leaving the extending carbon fibers exposed and uncontaminated for CV testing. The CV current densities were calculated by dividing the measured current by the area of the electrode outer surface. Voltammograms began sufficiently negative of the ferricyanide potential to allow reduction of the electroactive species in solution to ferrocyanide. Cycling then began with the oxidation half cycle at scan rates of 20, 50, 75, 100, 125, 150, 175 and $200\ mV\ s^{-1}$.

The rate constant for electron transfer (k_s), the capacitance (C) and the electrochemical area (A) were calculated from the CV data, using the method of ref. [14].

The packing densities of carbon black and its modified versions were assessed by pressing the carbon sample into a stainless steel sample cup (8.05 mm internal diameter and 6.35 mm deep) using a pressure controlled arbor press fitted with a flat tip pressing fixture (8.00 mm diameter). The pressing

Table 2. Relative strengths of the acids used in the chemical oxidation of carbon; the acids are listed in order of decreasing dissociation constant

Acid	Dissociation reaction	Dissociation constant, K_A
HCl	$HCl + H_2O \leftrightarrow H_3O^+ + Cl^-$	1.3×10^6
HNO_3	$HNO_3 + H_2O \leftrightarrow H_3O^+ + NO_3^-$	2.4×10^1
H_2SO_4	$H_2SO_4 + H_2O \leftrightarrow H_3O^+ + HSO_4^-$	1.2×10^{-2}
H_3PO_4	$H_3PO_4 + H_2O \leftrightarrow H_3O^+ + H_2PO_4^-$	7.1×10^{-3}
CH_3COOH	$CH_3COOH + H_2O \leftrightarrow H_3O^+ + CH_3COO^-$	1.8×10^{-5}

pressure was fixed at 10 MPa (the same pressure used to pack the CV working electrode) and the carbon sample weight was fixed at 0.05 g. A Mitutoyo Digimatic displacement transducer was used to measure the carbon sample compact thickness after pressure release, as shown in Fig. 1. To the transducer arm was attached a flat, circular disk (8.00 mm in diameter) for measuring the carbon sample compact thickness after pressure release. The empty sample cup was placed, first, under the transducer with the circular disk attached to the arm to zero. The sample cup was loaded with the carbon material, placed on the pressing support stage, upon which the pressing arm was lowered to apply pressure. The pressing arm was raised and the sample cup with the compacted carbon sample (now free of pressure) was placed under the transducer arm attached with the circular disk. The arm was lowered to the carbon compact surface (no pressure was applied by the transducer arm) and the indicated thickness of the compact was recorded. Results were compared to those obtained in a previous study for carbon filaments [14].

3. RESULTS

Table 1 displays the percentage burn-off (percentage weight loss) achieved for carbon black, carbon filaments and carbon fibers after thermal oxidation. The data at 600°C directly compare the thermal oxidation characteristics of carbon black with carbon fibers. Indicated is that carbon black more readily oxidizes (or is less resistant to thermal oxidation) than the carbon fibers. TGA results (in air) for the same three samples (Fig. 2) show that the carbon fibers are most oxidation resistant, followed by carbon black and then carbon filaments. For the carbon filaments, extensive burn-off in air starts at ~540°C upon heating, although minor burn-off occurs even at 100°C. The carbon fibers reported in this work are more graphitic than either the carbon black or the carbon filaments, so their having the highest oxidation resistance is expected.

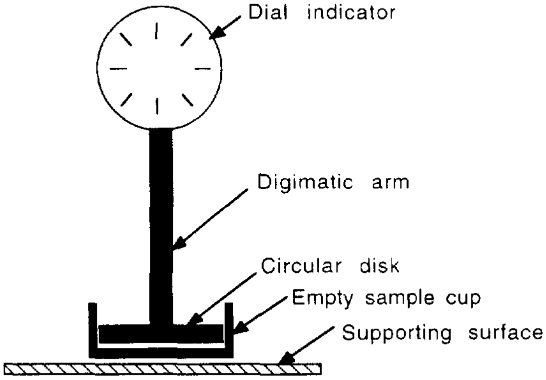

Fig. 1. Set-up for packing density measurements of carbon compacts after pressure release.

X-ray diffraction compares the graphitic nature of the carbon filaments and the carbon black. For carbon black, the X-ray diffraction pattern [16] exhibits weak peaks in the vicinity of the 2θ position for the graphite 002 peak and in the vicinity of the 2θ positions (close together) of the graphite 100 or 101 peaks. The X-ray diffraction pattern of the carbon filaments [14] displays a stronger, higher intensity diffraction peak at the 2θ position for the graphite 002 peak. Since X-ray diffraction suggests that the carbon filaments are more crystalline than the carbon black, the TGA results were unexpected, and are attributed to the morphology of the carbon filaments compared to carbon black. The carbon filaments (as determined by electron diffraction [14]) display a basal plane orientation dubbed a fishbone structure, in which the basal plane is at an angle from the filament axis so that the edge sites are exposed at the filament surface. Carbon black, on the other hand, has an essentially crystalline skin with the basal plane of the crystallites preferentially oriented at the surface of the carbon black particle [8]. Since the edge sites are more active than the basal sites, the carbon black, having the basal sites exposed to the surface, resists thermal oxidation more than the carbon filaments.

Tables 3 and 4 summarize the electrochemical behavior of the carbon materials, as-received and after treatment by air oxidation or acid. The CV plots comparing as-received carbon black with thermally oxidized (16% burn-off) carbon black are shown in Figs 3 and 4, respectively. The curve with the lowest positive peak current density is associated with the $20\,\mathrm{mV\,s^{-1}}$ scan, whereas that with the highest positive peak current density is associated with the $200\,\mathrm{mV\,s^{-1}}$ scan. No evidence of redox peaks is present in the as-received carbon black (Fig. 3, sample 1 in Table 3). However, the redox peaks are clearly observed after thermal oxidation to a burn-off of 16% (Fig. 4, sample 5 in Table 3). In general, the peaks begin to become more visible, even at the lowest burn-off of 1%, improving in shape as burn-off increases (samples 1–5 in Table 3). The reaction reversibility, however, remains irreversible or quasi-reversible until the 16% burn-off is reached (samples 1–5, Table 4). The 16% burn-off gives the best electrochemical reversibility of the redox reaction, as indicated by the smallest value of the peak separation, ΔE, in Table 3. Burn-off of carbon filaments in air to a 15% weight loss also demonstrates enhanced electrochemical behavior (Fig. 5, as-received, sample 8 in Table 3; Fig. 6, after 15% burn-off, sample 12 in Table 3). The peak separation ΔE decreases from 530 to 110 mV (Table 3), and the redox reaction is rendered reversible with a k_s value of $0.0110\,\mathrm{cm\,s^{-1}}$ (Table 4). The high residual current associated with this sample (increasing with increasing scan rate, Fig. 6) is attributed to the increased oxygen on the treated carbon filament surface, since

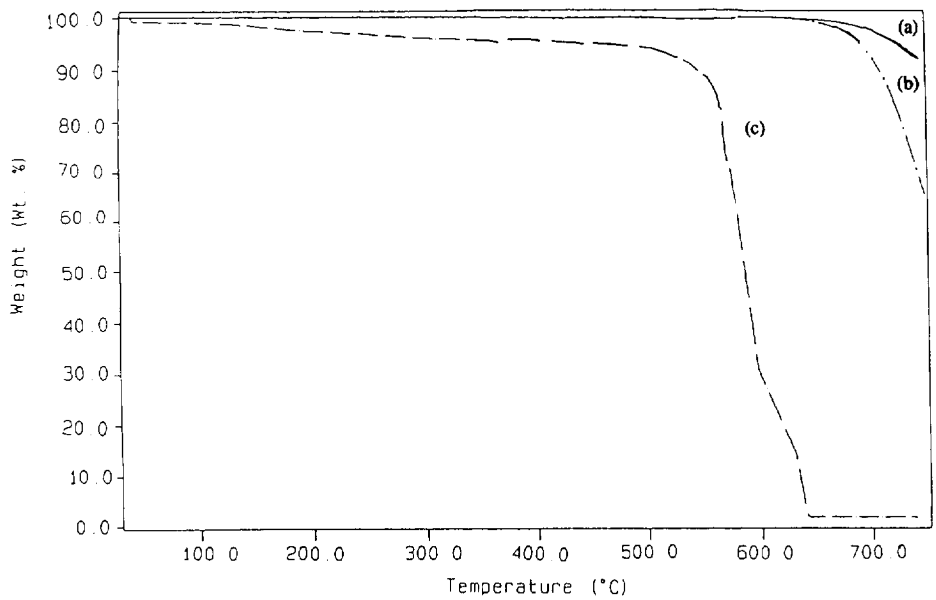

Fig. 2. TGA results (in air) for (a) carbon fibers, (b) carbon black and (c) carbon filaments.

Table 3. Cyclic voltammetry results obtained at a potential scan rate of 200 mV s^{-1}

Sample	Anodic peak current density, I_a (mA cm^{-2}) (±25)	Cathodic peak current density, I_c (mA cm^{-2}) (±25)	I_a/I_c (±0.2)	Peak separation, ΔE (mV) (±10)
Carbon black				
1: As-received	9000	8297	NA	NA
2: Oxidized 1%	1303	231	5.6	352
3: Oxidized 3%	887	177	5.0	468
4: Oxidized 5%	1780	761	2.3	278
5: Oxidized 16%	976	894	1.1	136
6: 10% HCl	2181	1051	2.1	210
7: 10% HNO_3	2220	1058	2.1	236
Carbon filaments				
8: As-received[a]	7800	1650	4.7	530
9: Acetone cleansed[a]	13575	8467	1.6	196
10: Acetone cleansed and chopped[a]	1680	1450	1.2	130
11: Methylene chloride cleansed and chopped[a]	2000	1750	1.1	90
12: Oxidized 15%	845	759	1.1	110
13: 100% HCl	8125	6351	1.3	116
14: 50% HCl	1975	1745	1.1	80
15: 10% HCl	1892	1681	1.1	104
16: 10% HNO_3	1604	1415	1.1	112
17: 10% H_2SO_4	1145	942	1.2	138
18: 10% H_3PO_4	1603	1363	1.2	120
19: 10% CH_3COOH	1705	1527	1.1	96
20: Treated in nitrogen	971	1306	0.8	124
Carbon fibers[b]				
21: As-received	82	451	5.5	364
22: Oxidized 7%	445	866	1.9	354
23: Oxidized 17%	517	614	1.2	188
24: Oxidized 22%	575	724	1.3	216

[a] From ref. [14].
[b] From ref. [9].

its high capacitance (Table 4) indicates good wetting of the electrode by the electrolyte [8].

Chemical treatment, in general, improves the reversibility of the redox reaction of both carbon black (samples 6 and 7 in Table 3) and carbon filaments (samples 13–19 in Table 3). The improved electrochemical performance is attributed to either an increase in the adsorbed oxygen from the acid

Table 4. Electrochemical behavior of as-received and treated carbons

Sample	k_s (cm s^{-1}) ± 0.0002	Capacitance[a] (μF cm^{-2}) ± 0.05	Electrochemical area (cm^2) ± 5
Carbon black			
1: As-received	Irreversible	27.50	431
2: Oxidized 1%	Irreversible	2.12	23
3: Oxidized 3%	Irreversible	1.50	16
4: Oxidized 5%	Irreversible	2.21	24
5: Oxidized 16%	0.0073	2.01	22
6: 10% HCl	0.0029	4.41	48
7: 10% HNO_3	0.0013	2.69	29
Carbon filaments			
8: As-received[b]	Irreversible	5.93	65
9: Acetone cleansed[b]	0.0037	27.27	299
10: Acetone cleansed and choppped[a]	0.0082	1.92	30
11: Methylene chloride cleansed and chopped[a]	0.0209	2.62	29
12: Oxidized 15%	0.0110	17.46	275
13: 100% HCl	0.0125	2.34	26
14: 50% HCl	0.0371	2.28	25
15: 10% HCl	0.0139	2.17	24
16: 10% HNO_3	0.0120	1.93	21
17: 10% H_2SO_4	0.0071	2.20	24
18: 10% H_3PO_4	0.0097	2.05	23
19: 10% CH_3COOH	0.0133	2.42	27
20: Treated nitrogen	0.0092	5.11	560
Carbon fibers[c]			
21: As-received	Irreversible	0.50	394
22: Oxidized 7%	Irreversible	0.45	359
23: Oxidized 17%	0.0042	0.27	152
24: Oxidized 22%	0.0025	0.28	166

[a] Calculated using outer planar area of 0.0792 ± 0.0005 cm^2 for carbon black and carbon filaments and 6 ± 1 cm^2 for carbon fibers.

[b] From ref. [14].

[c] From ref. [9].

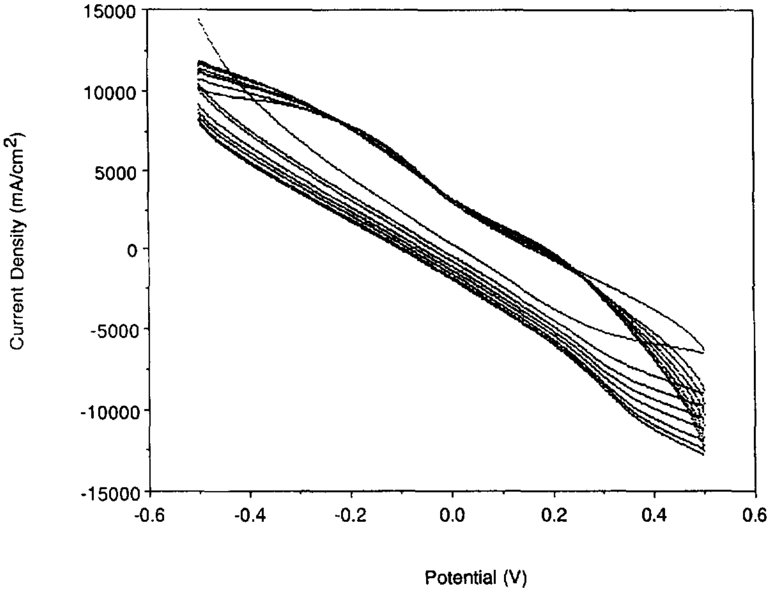

Fig. 3. Cyclic voltammetry results for plain carbon black.

solution on the surface of the carbon, the formation of carbon complexes favorable to electrochemical performance, or, specifically in the case of carbon filaments, the removal of the tarry coating present on their surface exposing oxygen containing surface functional groups. Oxygen adsorption is known to improve the electrochemical performance of carbons [8–10], and the reactivity of halogens toward carbon, forming stable carbon–halogen complexes, are well-known [8]. Further, the removal of the tarry coating

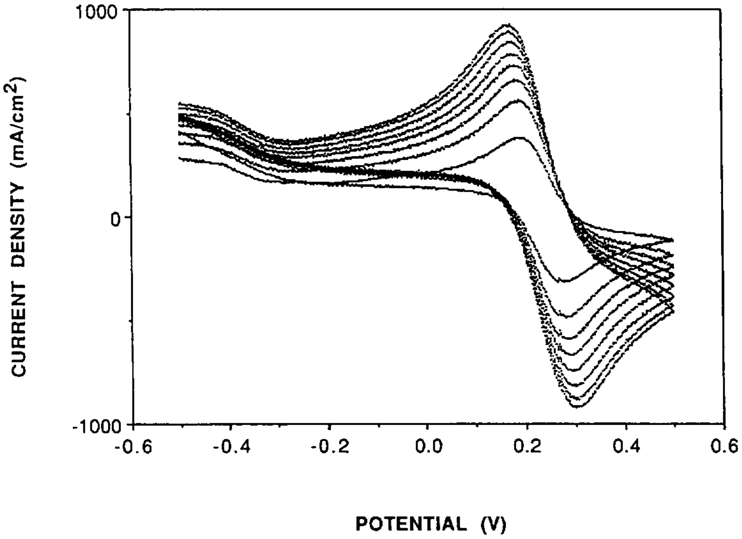

Fig. 4. Cyclic voltammetry results for thermally oxidized carbon black (burn-off of 16% by weight).

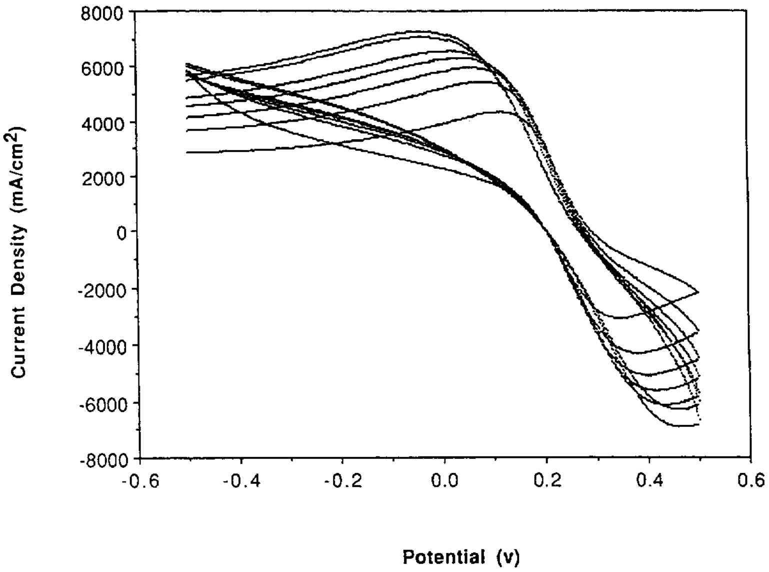

Fig. 5. Cyclic voltammetry results for as-received carbon filaments.

from the filament surface by solvent cleansing was shown to expose oxygen containing surface functional groups which subsequently improved their electrochemical performance [14]. Of the acids having a 10% concentration, the highest k_s was achieved with HCl, whether used to treat carbon black (sample 6 in Table 4) or carbon filaments (sample 15 in Table 4). This was expected since HCl is the strongest (considered so because of its large dissociation constant) of the acids evaluated. Further, carbon readily reacts with halogen containing aqueous solutions [8]. Of the acids having a 10% concentration used to treat carbon filaments, CH_3COOH resulted in the next highest k_s. This was unexpected, since CH_3COOH is the weakest of the acids evaluated. This result is attributed to the nature of the surface functional group formed. The dissociation of CH_3COOH into H_3O^+ and CH_3COO^- (Table 2) allows the formation of carboxylic surface functional groups on the carbon surface, which, in turn, results in improved electrochemical behavior [9]. The most dramatic improvement was observed for carbon filaments treated with 50% HCl (Fig. 7 and sample 14 in Table 3 and Table 4), where the chemical treatment changes the electrochemical response from irreversible to reversible, and the k_s achieved (0.0371 cm s^{-1}) is the highest of all the treatments applied. The 100% HCl solution (sample 13 in Tables 3 and 4) has insufficient water present to enhance the carbon–halogen reaction. The 10% HCl solution (sample 15 in Tables 3 and 4), on the other hand, contains too low a concentration of the acid,

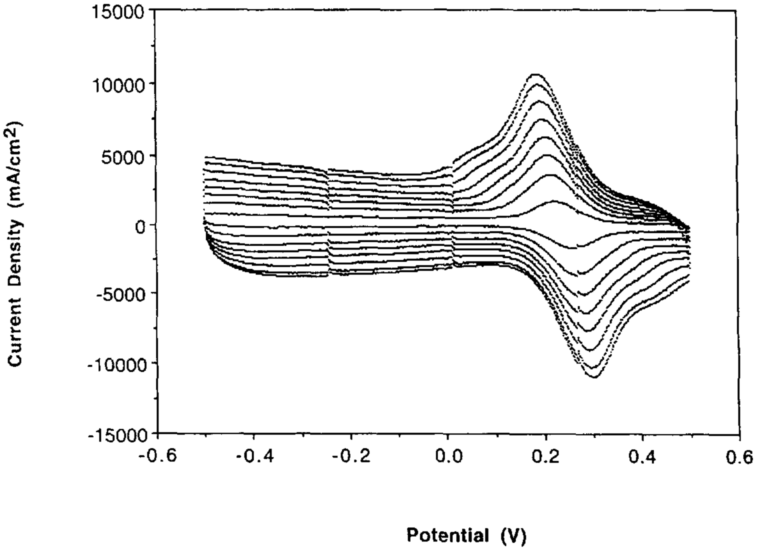

Fig. 6. Cyclic voltammetry results for oxidized carbon filaments (burn-off of 15% by weight).

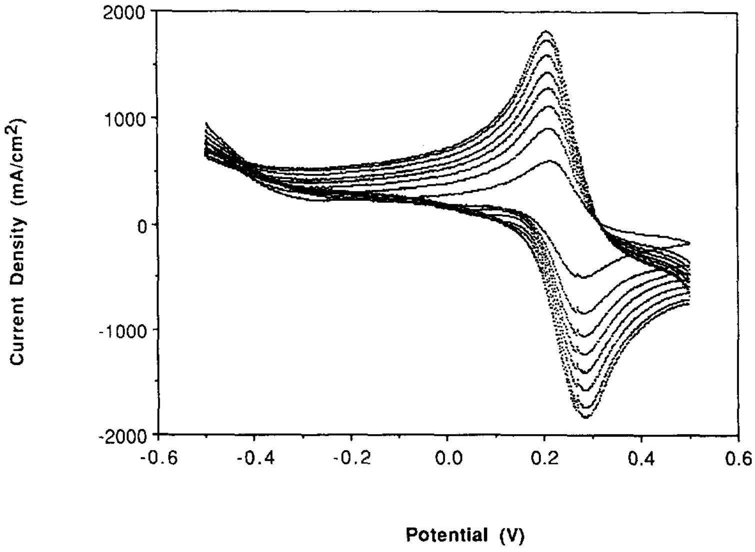

Fig. 7. Cyclic voltammetry results for 50% HCl treated carbon filaments.

and therefore, an insufficient number of dissociated ions (H_3O^+ and Cl^-) to promote adequate halide complexing.

Thermal and chemical oxidation treatments significantly decrease the capacitance of the carbon black (Table 4). The effect on capacitance is believed to be due to the changes in the carbon black compactability and morphology effected by the oxidation process. The oxidation of the carbon black, both thermally and chemically, results in better compactability of the carbon black (Table 5). The improved compactability is, in turn, attributed to the changes in morphology. The morphological changes are shown in the SEM photographs of Fig. 8, and the data in Table 6, in which thermal oxidation of carbon black was found to increase the macropore density, decrease the macropore size and decrease the size of the carbon black particle. The carbon black particle size was determined by measurement from the SEM photograph. In this work, the carbon black particle is defined as that part of the carbon black agglomerate comprising a single individual sphere of carbon. Pore size was also determined by measurement from the SEM photograph. In this case, the pores are defined as the macropores within a carbon black agglomerate. Macropore density was determined by counting the number of macropores present in a given area, and then dividing by that area. The macropore size, macropore density and carbon particle size were all determined prior to compaction. In the case of thermal oxidation (Fig. 8(b)), the macropore density is the highest and

Table 5. Packing density k_s, and electrochemical area A of as-received and treated carbon black and carbon filaments, all after pressing at 10 MPa; sample numbers correspond to those in Table 3 and Table 4

Sample	Condition	Packing density (g cm^{-3}) ±0.002	k_s (cm s^{-1}) ±0.0002	A (cm^2) ±5
1: Carbon black	As-received	0.637	Irreversible	431
4: Carbon black	Oxidized 5%	0.656	Irreversible	24
5: Carbon black	Oxidized 16%	0.702	0.0073	22
6: Carbon black	10% HCl	0.682	0.0029	48
7: Carbon black	10% HNO_3	0.676	0.0013	29
[a]8: Carbon filaments	As-received	0.465	Irreversible	65
[a]9: Carbon filaments	Acetone cleansed	0.680	0.0037	299
[a]10: Carbon filaments	Acetone cleansed and chopped	0.737	0.0082	30
[a]11: Carbon filaments	Methylene chloride cleansed and chopped	0.820	0.0209	29
12: Carbon filaments	Oxidized 15%	0.751	0.0110	275
13: Carbon filaments	100% HCl	0.782	0.0125	26
14: Carbon filaments	50% HCl	0.847	0.0371	25
15: Carbon filaments	10% HCl	0.793	0.0139	24
16: Carbon filaments	10% HNO_3	0.777	0.0120	21
17: Carbon filaments	10% H_2SO_4	0.722	0.0071	24
18: Carbon filaments	10% H_3PO_4	0.743	0.0097	23
19: Carbon filaments	10% CH_3COOH	0.789	0.0133	27

[a]From ref. [14].

the size of the particle is the smallest, compared to Fig. 8(a) (as-received) and Fig. 8(c) (chemically oxidized). Additionally, the thermally oxidized carbon black particles are less spherical, with the presence of "dimples" in the surface evident, suggesting that some hollowing of the particle occurs. In the case of chemical oxidation (Fig. 8(c)), an increase in particle size compared to the as-received condition was observed, along with some increase in macropore density, with a larger decrease in macropore size compared to thermal oxidation. The increase in macropore density is less than that observed by thermal oxidation. The increase in particle size from the as-received carbon black is believed to be due to the fact that chemical oxidation was conducted under what is considered mild oxidizing conditions, i.e. room temperature exposure in a fairly dilute acid for a relatively short duration. Under these circumstances, oxidation of carbon to acidic surface groups can be achieved without substantial damage to the fundamental carbon structure [8], and may, in fact, cause the carbon black particle to swell as a result of the formation of surface oxide groups. The fact that the sphericity of the particles is maintained without evidence of surface dimpling supports this notion. Contributing to the decrease in capacitance after thermal or chemical oxidation may be a decrease in the roughness of the outer surface of the electrode, which develops as a result of the improved packing density. The surface roughness may be less for the thermally oxidized carbon black compared to the chemically oxidized carbon black due to the fact that the former can smooth out on collapse of the partially hollowed particles more easily, and because of its smaller particle size.

Thermal and chemical oxidation of carbon black by HNO_3 produce similar capacitances, whereas, chemical treatment by HCl yields a capacitance twice that achieved by HNO_3. The higher capacitance achieved with HCl is probably due to different surface functional groups. This is suggested by the lower pH value (demonstrating a higher degree of acidification of the carbon black, Table 6). The electrochemical area correspondingly decreases with decreasing capacitance, as expected.

Thermal oxidation of carbon filaments, on the other hand, results in large increases in capacitance and electrochemical area (samples 8 and 12 in Table 4). In this case, the domination of edge sites on the filament surface promotes the development of oxygen containing surface functional groups. The additional oxygen on the filament surface after thermal oxidation results in increased capacitance and electrochemical area. Chemical oxidation of carbon filaments, however, results in lower capacitances and electrochemical areas compared to the as-received version (sample 8 compared to samples 13–19 in Table 4), and much lower compared to thermal oxidation. This effect is probably due to two factors: i) thermal oxidation is more effective in removing the tarry coating from the filament surface, making more readily available the basal plane edge sites for oxygen chemisorption, and ii) the types of oxygen-containing functional groups on the filament surface differ as a result of the oxidation method used. Heating during thermal oxidation completely removes the tarry coating, since the tarry coating is a hydrocarbon [14], which is volatilized at the temperature (450°C) used in this work. TGA of the carbon filaments in nitrogen (Fig. 9) showed that the tarry coating present on the surface amounts to 2% of the filament weight (volatilized at up to 300°C). The large weight loss which starts at ~580°C (Fig. 9) is attributed to thermal oxidation resulting from the small amount of oxygen

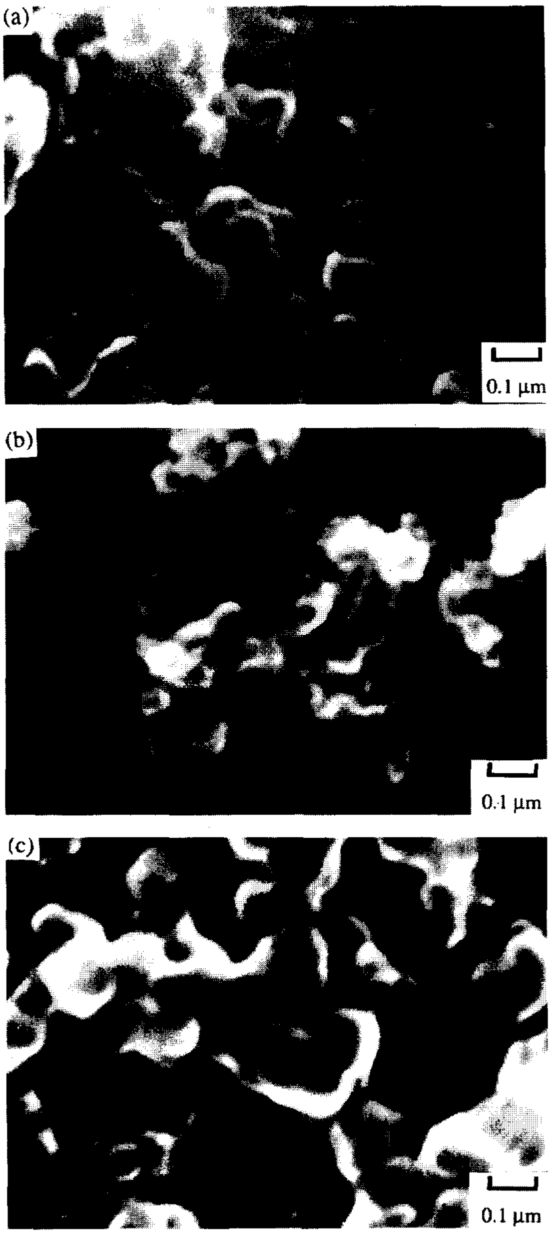

Fig. 8. SEM photographs of (a) as-received carbon black, (b) thermally oxidized (16%) carbon black and (c) chemically oxidized carbon black (HNO_3).

remaining in the ambient. CV conducted on the sample treated in nitrogen confirms the impact of the removal of the tarry coating on the electrochemical performance of the carbon filaments (Fig. 10). Further, the effect on residual current is minimal due to the exposing rather than addition of the oxygen surface functional groups (sample 20 in Table 3). This is also reflected in the capacitance of the sample in that capacitance for the carbon filaments heat treated in nitrogen (sample 20 in Table 4) is lower than that heat treated in air (sample 12 in Table 4).

Since, in the case of chemical treatment, oxidation occurs as a result of chemical reaction with the carbon, the tarry coating is the first reactant, and only when the tarry coating is completely removed can oxidation of the basal plane edge sites on the surface of the filaments take place. The fact that the tarry coating was at least partly removed by chemical oxidation was evident by a yellowing of the acid during cleansing, and a lesser degree of stickiness of the wet filaments after cleansing. (The association of these effects to cleansing and the exposure of the oxygen surface groups after cleansing had been demonstrated in the case of solvent cleansing using acetone and methylene chloride [14].) Since the carbon filament immersion time in the acids was short, the reactivity of the acids with the tarry coating may be different from that of the solvents, thus the chemical oxidation treatment may have been insufficient in all cases for the complete removal of the tarry coating. Moreover, the oxidizing capabilities of the various acids most likely differ, so the degrees of oxidation, and therefore, all electrochemical responses (k_s, C and A) also differ.

As cited in ref. [9], thermal oxidation of the carbon fibers to a 7% burn-off roughens the surface, whereby thinning of the basal plane "skin" occurs and randomly dispersed "holes" (or areas of total depletion in the basal plane "skin") develop over the fiber surface. The "holes" were proposed to be fully exposed basal plane edge and defect sites, at which development of oxygen surface functional groups is known to occur [8,9]. As shown in Table 4 (sample 22), k_s remains irreversible at the 7% burn-off level compared to the as-received carbon fiber, and changes in capacitance and electrochemical area are small, suggesting that thermal oxidation to a 7% burn-off results in an insufficient concentration of surface oxygen groups. Complete removal of the "skin", with minor penetration of the holes into the fiber interior, occurs at 17% burn-off [9]. Electrochemical activity then is predominantly associated with the newly exposed basal plane edge and defect sites, which results in the highest k_s of all the

Table 6. Microstructure and pH values for treated and untreated carbon black prior to compaction

Condition	Particle size (Å) ±25	Macropore size (Å) ±25	Macropore density (mm^{-2}) ±0.005	pH ±0.2
As-received	900	3500	0.032	8.3
Thermally oxidized (16%)	600	2500	0.084	5.0
Chemically oxidized, HCl	1400	2100	0.042	4.3
Chemically oxidized, HNO_3	1400	2000	0.053	5.0

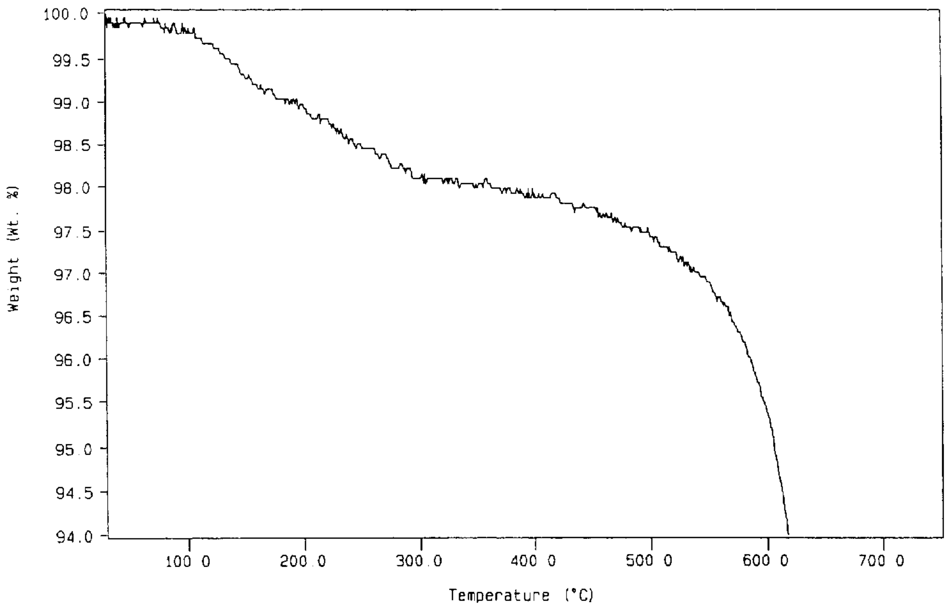

Fig. 9. TGA results (in nitrogen) for carbon filaments.

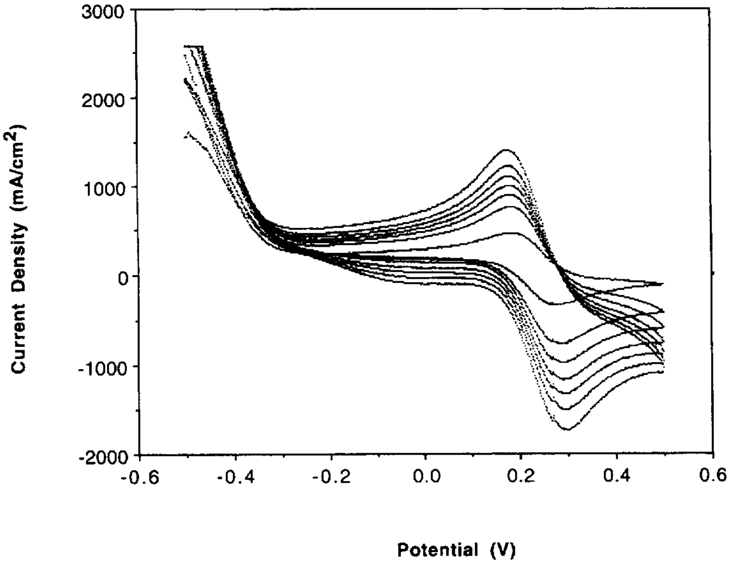

Fig. 10. Cyclic voltammetry results for carbon filaments treated in nitrogen.

burn-off levels, suggesting that, at a 17% burn-off, the concentration of oxygen surface groups is highest of the three levels evaluated. At this level of burn-off, however, the smallest *C* and *A* were achieved, which is unexpected since the oxidation process increases surface roughness, surface oxygen concentration and electrolyte wettability [9], all of which are associated with high *C* and *A*. Further, *C* and *A* were observed to increase slightly with a 22% burn-off, which, as reported in ref. [9], results in deeper penetration of the holes into the interior of the fiber, thereby exposing more of the basal plane of the radially structured layers. Since the capacitance of the basal plane is known to be lower than the basal plane edge sites, the *C* and *A* should have decreased instead. The variation of capacitance with potential scan rate was therefore investigated. For the radially structured carbon fibers, the capacitance of the 17% burn-off sample increases as the scan rate decreases from 200 to 20 mV s^{-1} (Table 7). This trend was also observed in the 7 and 22% burn-off samples, but not in the as-received sample. Furthermore, as shown in Table 8, for the similarly oxidized carbon black and carbon filaments, *C* was essentially invariant with respect to the scan rate. The scan rate dependence of *C* observed for carbon fibers is reflective of the space charge layer. The effect is due to the fact that the charging rate at the carbon fiber surface lags

Table 7. Capacitance of radially structured carbon fibers as a function of potential scan rate

	Capacitance, C (μF cm^{-2})			
Scan rate (mV s^{-1})	As-received	7% burn-off	17% burn-off	22% burn-off
20	0.50	0.50	0.39	0.40
50	0.51	0.50	0.35	0.36
75	0.50	0.49	0.33	0.35
100	0.49	0.48	0.31	0.32
125	0.48	0.48	0.30	0.31
150	0.51	0.46	0.29	0.29
175	0.49	0.45	0.28	0.28
200	0.50	0.45	0.27	0.28

Table 8. Capacitance of various carbons as a function of potential scan rate

	Capacitance, C (μF cm^{-2})		
Scan rate (mV s^{-1})	Carbon black 16% burn-off	Carbon filaments 15% burn-off	Carbon fibers 17% burn-off
20	1.98	17.46	0.39
50	1.99	17.44	0.35
75	2.01	17.45	0.33
100	2.01	17.42	0.31
125	2.00	17.47	0.30
150	1.99	17.44	0.29
175	1.98	17.42	0.28
200	2.01	17.46	0.27

behind the potential scanning rate, thereby causing C as well as k_s to be low. This is in contrast to carbon black and carbon filaments, the C values of which do not change with scan rate, thereby reflecting the dominance of the ionic double layer over the space charge layer. Such a scan rate dependence had been previously observed by Oren and Soffer in the case of graphite cloth [54].

Carbon fibers do, however, display the highest A of the materials evaluated. Since A depends on the current carrying capability of the carbon material, and since the carbon fiber electrode consists of continuous carbon fibers of large diameter (compared to the discontinuous carbon black or carbon filaments), the current carrying capability of the carbon fibers is substantially greater than for carbon black or carbon filaments. Only in the case of as-received carbon black and acetone cleansed (but not chopped) and thermally oxidized carbon filaments, does A approach or exceed that obtained by the carbon fibers. In the case of as-received carbon black, the high A is attributed to its low packing density (Table 5), allowing the electrolyte to penetrate more deeply into the electrode compact. The low packing density (consequently higher electrolyte penetrability) also accounts for the high A observed for acetone cleansed but not chopped carbon filaments. In the case of as-received carbon filaments, the low A is attributed not to the packing density, but to the presence of the tarry residue. In the case of the thermally oxidized carbon filaments, the high A is attributed to the concentration of surface oxygen groups, as reflected by the high C.

Thermally oxidized carbon filaments yield the highest C and A compared to similarly oxidized (similar burn-off) carbon black and carbon fibers. The as-received carbon filaments, however, display the lowest A, while C falls between carbon black and carbon fibers (as-received carbon fibers having the lowest C). The increased C and A of carbon filaments after thermal oxidation are attributed to the complete removal of the tarry coating, and subsequent exposure of the basal plane edges and increase in surface oxygen. Of the materials evaluated, the carbon filaments, being of small diameter (1500 Å) and having a fishbone crystalline structure, result in the highest concentration of basal plane edge sites compared to carbon black and the carbon fibers. Carbon black has its surface covered by the basal plane, both before and after thermal oxidation. Carbon fibers have their surface covered by the basal plane before oxidation, but thermal oxidation to 17% burn-off removes the skin, thereby exposing basal plane edges. However, the large diameter of the fibers compared to the filaments makes the concentration of basal plane edge sites not as high as for the filaments that have had their tarry residue removed. Furthermore, the carbon filaments are the least oxidation resistant of the materials evaluated. Therefore, the concentration of oxygen on their surface is most likely the highest. This translates into high C and high A.

Both thermal and chemical oxidation independently improve the packing density of the carbon materials. Thermal oxidation of plain carbon black to a 16% burn-off results in a 10% increase in packing density, while the packing density of carbon filaments increases by 65% after thermal oxidation. Acid treatment of the carbon black results in a 6 to 7% increase in packing density, whereas acid treatment of carbon filaments increases packing density by 55 to 82%, depending on the acid used for treatment. Regardless of the treatment executed, the effect is much greater for carbon filaments than for carbon black. Within each of the sample categories in Table 5, the highest packing density corresponds to the highest k_s. Of all the samples in Table 5, acid treatment of carbon filaments using 50% HCl (labeled 14) gives the highest packing density as well as the highest k_s; these values are even higher than those obtained by solvent cleansing and chopping of the carbon filaments (samples 10 and 11 in Table 5) [14]. The fact that k_s is substantially higher using 50% HCl compared to methylene chloride cleansing and chopping (which give the highest k_s among the solvent cleansed samples) is attributed to the combined functions of cleansing and oxidizing of the 50% HCl solution, in contrast to the sole cleansing function of solvent cleansing.

Akin to solvent cleansing [14], thermal or chemical oxidation results in improved compactability of the carbon filaments. Whether treated or not, the filaments do not need any oil or wax for CV electrode fabrication. In the case of carbon black, a binder is needed when the carbon black has not been treated, but thermal oxidation improves the compaction and eliminates the need for a binder; no distinguishable difference in CV results or in the shape of the CV curves were noted upon addition of a binder to thermally oxidized carbon black. The chemically oxidized carbon black, on the other hand, still requires a binder for good CV results. As shown by comparing Figs 11 with 12, the absence of an oil binder (Fig. 11) results in high residual current density, and the oxidation of some species at lower negative potentials; the addition of an oil binder (Fig. 12) minimizes the residual current density and eliminates the oxidation effect at the lower negative potentials.

4. DISCUSSION

Analysis of the cyclic voltammograms gives the electron transfer rate constant k_s (transfer of electron between electrode and electrolyte), capacitance C (i.e. the electric double layer capacitance, given in units of μF per unit outer planar area) and electrochemical surface area A (in cm^2), as listed in Table 4. When the electrochemical response is irreversible, k_s cannot be determined. The electrochemical surface area A, as expected, is much larger than the outer planar area, which is 0.0792 ± 0.0005 cm^2 for carbon black and carbon filaments, and 6 ± 1 cm^2 for the carbon fibers. Regardless of the material tested, thermal or chemical oxidation increases k_s; the effect is most significant for carbon filaments and least significant for carbon fibers. The fact that thermally oxidized carbon filaments (15%) exhibit a higher k_s than oxidized carbon black (16%) or oxidized carbon fibers (17%) is attributed to the higher compactability and better inherent bindability of the oxidized carbon filaments over both oxidized carbon black and oxidized carbon fibers.

Thermal oxidation of carbon black has a greater effect on k_s than chemical oxidation; thermal oxidation results in bindability of the carbon black without the need for binder (as evidenced by CV), but chemical oxidation does not. The higher macropore

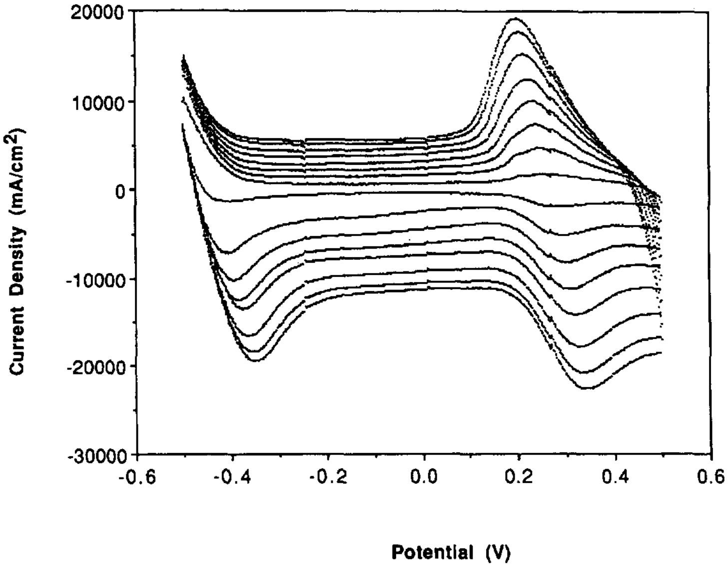

Fig. 11. Cyclic voltammetry results for chemically oxidized carbon black without using a binding oil.

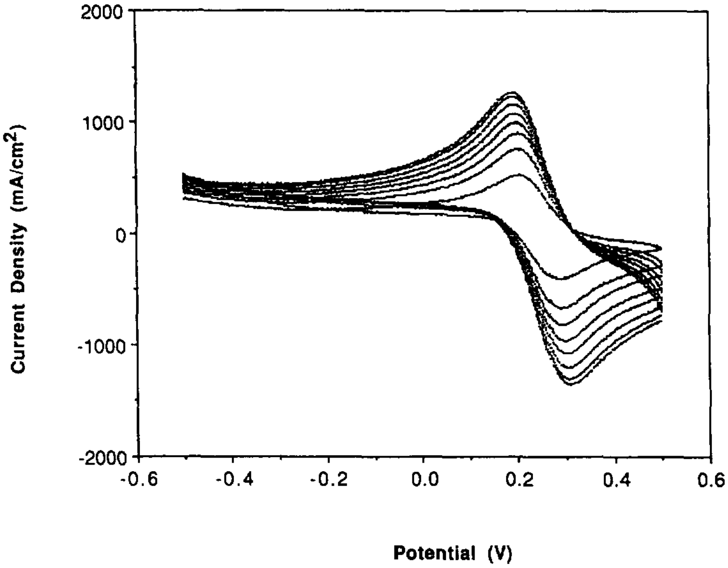

Fig. 12. Cyclic voltammetry results for chemically oxidized carbon black using a binding oil.

density after thermal oxidation compared to chemical oxidation, and the change in carbon particle sphericity (which does not occur when chemically oxidized) are believed to offer better mechanical interlocking of the thermally oxidized carbon particles. Further, the packing density is higher for the thermally oxidized version (16% burn-off) compared to the chemically oxidized versions (Table 5). A high value of A is associated with a high value of C, as expected. Oxidation greatly decreases both C and A for carbon black, whether thermally or chemically, most likely due to the increased compactability and the resultant smoother electrode surface.

Thermal oxidation, however, increases both C and A of carbon filaments, whereas chemical oxidation decreases C and A. The former is probably due to the filament fishbone morphology, whereas the latter is probably due to the insufficient effectiveness of the acid in removing the tarry coating from the filament surface, and in the type of oxygen containing surface functional group created on the filament surface. In the case of thermal oxidation, the exposed edge sites promote the development of oxygen containing surface functional groups, known to improve the electron transfer rate. The chemical oxidation, on the other hand, although generating enough oxygen containing surface functional groups on the filament surface to enhance electron transfer rate, probably insufficiently removes the tarry coating compared to burning the coating off during thermal oxidation, causing a varying degree of oxygen concentration on the filament surface, not only among the acids evaluated, but also compared to that achieved by thermal oxidation. Further, because of the differences in dissociated species, the type of oxygen containing surface functional groups could vary. In either case, C and A are lower after chemical oxidation than after thermal oxidation.

Thermal oxidation decreases C and A for carbon fibers. This was not expected since surface roughness, surface oxygen concentration and wettability by the electrolyte were increased upon oxidation, which characteristically increase capacitance. In the case of capacitance, it is believed that the substantially rougher (or inhomogeneous) surface accounts for the lower capacitance, since slow capacitive charging is associated with this condition. In the case of lower electrochemical area, it is believed that the change in surface roughness may have increased the contact resistance between the fibers, which, in turn, would affect electrochemical area.

For battery and analytical electrodes, a high k_s and a low C are desirable in order to have fast response. For capacitor electrodes, a high k_s and a high C are desirable. Thermal oxidation greatly increases reversibility and decreases C for carbon black, so it is attractive for carbon black that is used for battery or analytical electrodes. The increase in reversibility is due to an increase in macropore density and decrease in particle size (as evidenced by SEM). The latter, together with particle dimpling, enhances electrode compactability, thereby decreasing the roughness of the electrode outer surface and hence decreasing C. The particle dimpling may involve some hollowing out of the carbon black particle (a reaction occurring in the interior of the carbon black particle), leaving a somewhat capsular structure [8]. Researchers [3–5] have shown that the interior of carbon particles is rapidly attacked by oxygen, leaving a hollow shell for the particle.

The oxidation of carbon black using acids also increases k_s (but to a lesser extent than thermal oxidation), while decreasing C and A, although C and A are slightly higher for carbon black treated with HCl compared to HNO_3. The conditions for oxidation result in the development of acidic surface groups [3–5], resulting in an increase in the concentration of surface oxide groups, thus improving electrochemical performance.

A yellow discoloration was observed for both solvent cleansing and chemical oxidation of carbon filaments. The effectiveness in removing the tarry coating present on the surface of carbon filaments probably varies with the type of acid used, as it does with the type of solvent used. This was suggested by the CV results obtained. A higher concentration (but not too high) of a strong acid is more effective in improving the electrochemical behavior of carbon filaments compared to solvent cleansing, most likely due to a synergy between the cleansing of the filaments and the oxidizing of the filament surface.

Finally, the k_s of thermally oxidized carbon filaments, carbon black and carbon fibers follow a trend which is opposite to their thermal oxidation resistance. The highest k_s but lowest thermal oxidation resistance was observed for carbon filaments, the next highest k_s but next lowest thermal oxidation resistance occurred for carbon black, and the lowest k_s but greatest thermal oxidation resistance was demonstrated for carbon fibers. The basal plane orientation of the various carbons accounts for both the oxidation resistance trend and the trend in k_s. The surface of carbon black consists primarily of basal plane layers, which are known to display higher thermal stability and lower electrochemical activity (lower k_s) than the edge of the layers. At the other extreme are the carbon filaments exhibiting a fishbone crystalline structure, such that the basal plane edge sites are exposed on their surface. The carbon fibers used in this study fall in between the carbon black and carbon filaments, since they comprise a basal outer skin surrounding a radially structured center.

5. CONCLUSIONS

Oxidation of carbon black, carbon filaments and carbon fibers changed the electrochemical behavior from being irreversible to being reversible. For carbon black, thermal oxidation (16%) gave higher k_s than chemical (HCl or HNO_3) oxidation or thermal oxidation to $\leq 5\%$. For carbon filaments, chemical (50% HCl) oxidation gave higher k_s than thermal oxidation (15%) or chemical oxidation using 100% HCl, 10% HCl, 10% HNO_3, 10% H_2SO_4, 10% H_3PO_4 or 10% CH_3COOH. For carbon fibers, thermal oxidation (17%) gave higher k_s than thermal oxidation to 7 or 22%. For carbon black, both thermal and chemical oxidation decreased C and A; for carbon filaments, thermal oxidation increased C and A, while chemical oxidation decreased C and A; for carbon fibers, thermal oxidation decreased C and A. After thermal oxidation (15–17%), carbon filaments gave the highest k_s, followed by carbon black, while carbon fibers gave the lowest k_s. Thermal oxidation resistance was least for carbon filaments, followed by carbon black, and greatest for carbon fibers. Without any treatment, the electrochemical area A was largest for carbon black, followed by carbon fibers and least for carbon filaments, whereas the capacitance C was largest for carbon black, followed by carbon filaments and least for carbon fibers. After thermal oxidation (15–17%), A was largest for carbon filaments, followed by carbon fibers and least for carbon black, whereas C was largest for carbon filaments, followed by carbon black and least for carbon fibers. Thermal or chemical oxidation of carbon black increased the macropore density (particularly after thermal oxidation) and decreased the pH. In addition, thermal oxidation decreased the particle size, while chemical oxidation increased the particle size. Thermal and chemical oxidation (particularly thermal oxidation) removed hydrocarbon residue (tarry coating, 2 wt% of filaments) from the surface of the carbon filaments, akin to solvent cleansing. Thermal oxidation (17%) of carbon fibers removed the surface skin, thereby exposing basal plane edges [9]. Further oxidation to 22% caused holes from the surface to penetrate radially, thereby exposing basal plane surfaces [9]. The packing density of carbon black and carbon filaments was increased by thermal or chemical oxidation. A high packing density correlates with a high k_s for both carbon black and carbon filaments. The CV electrodes required a binder for untreated carbon black and for chemically oxidized carbon black, but not for thermally oxidized carbon black. No binder was needed for carbon filaments, whether treated or not. The fact that oxidation increased the macropore density, increased the packing density and decreased the pH (indicating acidification by formation of acidic oxygen containing surface functional groups) of carbon black partly explains its improved electrochemical behavior, decreased C and A, and increased k_s. The fact that oxidation removed the tarry coating and increased the packing density of carbon filaments partly explains their improved electrochemical behavior, increased k_s, C and A. The fact that thermal oxidation of carbon fibers removed the basal plane surface skin (exposing the basal plane edge sites) partly explains its improved electrochemical behavior, decreased C and A and increased k_s. Finally, the fact that the electrochemical effect (i.e. k_s) of thermal oxidation on carbon filaments, carbon black and carbon fibers follow a trend opposite from their thermal oxidation resistance (i.e. highest k_s and lowest thermal oxidation resistance for carbon filaments, next highest k_s and next lowest thermal oxidation resistance for carbon black, and lowest k_s and greatest thermal oxidation resistance for carbon fibers) is due to the microstructural differences among the carbons and the importance of microstructure (basal plane orientation) to both characteristics. [22, 52, 53]

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