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ELECTROCHEMICAL BEHAVIOR OF HAIRY CARBONS

X. SHUI,[a] C. A. FRYSZ[b] and D. D. L. CHUNG[a,*]
[a]Composite Materials Research Laboratory, Furnas Hall, State University of New York at Buffalo, Buffalo, NY 14260-4400, U.S.A.
[b]Wilson Greatbatch Ltd., 10 000 Wehrle Drive, Clarence, NY 14031, U.S.A.

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Abstract—Hairy carbons were prepared by catalytic growth of carbon hairs (diameter 0.05–0.2 μm, at least partly crystalline) on carbon black, graphite particle and carbon fiber substrates. Of the substrates used, the most abundant hair growth was achieved using carbon black, due to the confinement of the catalyst size by the pores in the carbon black. The cyclic voltammetric response of all hairy carbons was superior to that of the corresponding substrate materials. In the case of hairy carbon black, reversibility was achieved and capacitance, electrochemical area and specific surface area were greatly decreased. In the case of hairy graphite particles and hairy carbon fibers, the electron transfer rate k_s (as studied via the Fe^{2+}/Fe^{3+} redox couple) was increased, but, in contrast to the hairy carbon black, capacitance and electrochemical area were increased. Hair growth, followed by an oxidation heat-treatment, resulted in oxidized hairy carbon black which exhibited higher k_s and better electrochemical reversibility than as-received carbon black, oxidized carbon black, hairy (but not oxidized) carbon black, carbon filaments (i.e. hair by itself) and hairy carbon fibers. This is partly due to the enhancement of the packing density by both hair growth and oxidation. The oxidized hairy carbon black exhibited much lower capacitance and much lower electrochemical area compared to as-received carbon black. The combination of high k_s and low capacitance makes oxidized hairy carbon black technologically attractive for battery and analytical electrodes. The particulate nature of oxidized hairy carbon black is in contrast to the fibrous nature of carbon fibers or carbon filaments, which require secondary operations for dispersion. Additionally, hairy carbon black allows good compaction and electrochemical reversibility without the need for a binder. © 1997 Elsevier Science Ltd

Key Words—A. Catalytically grown carbon, D. electrochemical properties.

1. INTRODUCTION

Hairy carbons refer to carbons which comprise tiny carbon filaments grown on conventional carbon substrates such as carbon blacks, graphite particles and carbon fibers. The hairs are submicron filaments with diameters ranging between 0.05 and 0.2 μm. Filament growth is initiated on the conventional carbon materials using a catalyst and a carbonaceous gas as the carbon source. Hairy carbons differ from conventional carbon fibers, vapor-grown carbon fibers as developed by Tibbetts and coworkers at General Motors [1–3], and carbon filaments as presently produced by Applied Sciences Inc., Cedarville, Ohio. Whereas hairy carbon is catalytically grown from carbonaceous gases, conventional carbon fibers are typically prepared either from a pitch material or from a polymer precursor such as polyacrylonitrile. In contrast to hairy carbon, carbon fibers have diameters of the order of 10 μm. Vapor-grown fibers begin as carbon filaments, but the conditions of the process are such that, in addition to the catalytic filament formation, non-catalytic carbon deposition occurs. This non-catalytic carbon deposition takes place on the outside of the carbon filament causing it to grow radially so that the final product has dimensions characteristic of the conventional carbon fiber. Temperature is the primary variable which determines whether a catalytic filament or a vapor-grown fiber is produced. Carbon filaments are submicron in nature (typical diameters of ~0.1 μm) and are also catalytically grown from carbonaceous source gases such as carbon monoxide, hydrocarbons, methane and other aliphatics, olefins, and aromatics [4–10]. For example, the carbon filaments from Applied Sciences Inc. (Cedarville, Ohio), which were used for comparison with the hairy carbon in this study, were grown from a methane (together with ammonia) gas feedstock, using an iron containing catalyst. Hydrogen sulfide was added to the feedstock in small amounts to increase filament yield [11]. The sulfur addition caused the iron to melt, encouraging filament growth by the vapor–liquid–solid process. (The hydrocarbons adhere better to molten particles and carbon atoms may diffuse more rapidly through molten particles [12].) Current studies center on practical applications for carbon filaments, and most recently, toward use for electrochemical applications such as electrodes [13–18].

There are some shortcomings with respect to the current carbon filament technology, however. They are long and tend to cling to each other (as does cotton wool), making dispersion and mixing difficult. The structural character of the filaments also affect compactability. As noted in a previous study [17], the as-received filaments have high fractional spring-

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*Corresponding author.

back after pressure release when attempting to compact. The high fractional spring-back causes low electrode packing densities, and subsequently, poor electrochemical performance. The compactability of the filaments was found to be important for the electrochemical performance of the filament compact, since a higher compactability meant that a greater number of filaments were exposed per unit area of the electrode's outer surface. A low packing density was observed to result in a high residual current density. In addition to packing density issues, the vapor–liquid–solid process used to produce the filaments (the catalyst is sprayed in the growing chamber and carbon filament growth initiates at the suspended catalyst) allows condensation of polyaromatic hydrocarbons on their surface [19], which was also found to inhibit good electrochemical performance [17]. Carbon filaments therefore require secondary processing (solvent cleansing [17]) to be an effective electrode material. The compactability of the filaments after pressure release was found to be improved by cleansing the filaments. Chopping the filaments in the cleansing medium (acetone or methylene chloride) in a rotary blender also helps decrease the fractional spring-back of the compact after pressure release, due to the decrease in filament length (particularly necessary if the filaments are relatively straight and large in diameter). In contrast to carbon filaments, the hairy carbons can be produced on particulate carbon substrates. The particulate nature of the finished hairy carbon product is preserved without sacrificing their clinginess. In this way, mixing remains easy, making dispersing operations such as chopping in a blender [17] unnecessary, while maintaining good packing characteristics without requiring binders or oils. An added advantage is that the length of the "hair" can be controlled, gearing the finished product toward the intended application. In fact, the hairs can be so short that they resemble nodules. Because the hairy carbon growth process minimizes condensation of polyaromatic hydrocarbons onto the hairy carbon (hairy carbons are grown directly in the harvesting boat, so that they do not need to move through a temperature gradient), cleansing is not needed to generate good electrochemical performance. Hairy carbons, therefore, may better serve specific electrochemical applications requiring ease of dispersion without the need for additives for bindability or the addition of secondary processing steps such as cleansing and chopping.

The electrochemical capability of the carbon material is critical to its performance as an electrode, and the kinetics and reversibility of electrochemical processes strongly depend on the surface character of the electrode. Therefore, surface treatments are commonly applied to electrode materials. These treatments include changes in the surface functional groups, surface crystallographic structure and surface roughness. They may involve chemical treatment, electrochemical treatment, heat treatment, laser treatment, plasma treatment, polishing or other surface activation. In particular, in the case of carbon materials, acid treatment [20–25], electrochemical treatment [26], heat treatment [27,28], laser treatment [29,30], plasma treatment [31] and polishing procedures [32] have been employed. 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).

In contrast to the surface modifications mentioned above, this paper involves a new and different surface modification, i.e. hair (or filament) growth on carbon substrates. Hair growth on substrates is a form of surface treatment which has not previously been applied to carbons. In this work, hairy carbons were found to be superior in their electrochemical behavior compared to that of the plain substrate material. Hair growth consistently increases the electron transfer rate constant. In the case of carbon black, the growth of hairs changed the plain carbon black electrochemical response from irreversible to a measurable k_s of 0.004 cm s^{-1}. In the case of carbon fibers, hair growth increased k_s by 730%.

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 [27]. Slow capacitive charging has been shown to occur when the electrode displays limited conductivity or exhibits an inhomogeneous surface [27]. Carbon black displays a high capacitance but a low electron transfer rate. The electron transfer rate is higher for graphite particles and carbon fibers compared to carbon black, but is still lower than desired for electrode applications. The capacitance of the graphite particles and carbon fibers, on the other hand, is much lower than for carbon black. It is the primary objective of this paper, then, to achieve a high electron transfer rate while maintaining low capacitance by modifying the surfaces of these carbon materials via hair growth. A secondary objective is to develop a functional particulate carbon material that will maintain flexibility and simplicity in electrode fabrication, i.e.

electrodes that pack easily and without the need for secondary materials such as oils or waxes for binding.

2. EXPERIMENTAL

The growth of the hairs on the substrate (carbon black, graphite particles or carbon fibers) was initiated using an iron nitrate $\{Fe(NO_3)_3 \cdot 9H_2O\}$ or a nickel nitrate $\{Ni(NO_3)_2 \cdot 6H_2O\}$ catalyst. The catalyst was applied to the carbon black substrate material by dissolving 5 parts by weight catalyst in methanol, immersing one part by weight substrate in the solution, and then mixing. In the case of graphite particles and carbon fibers, the ratios were 2 parts by weight catalyst and 1 part by weight substrate. The methanol was allowed to evaporate at room temperature. Then the coated substrate was vacuum dried overnight at 60–70°C. The dried substrate coated with catalyst was placed in an alumina boat and inserted into a programmable, three-zone Lindberg tube furnace (the tube was quartz and 2 in. diameter). The ends of the tube in the furnace were sealed with a specially formed glass joint having gas line connectors at the ends. A schematic of the apparatus is shown in Fig. 1. The closed tube in the furnace was purged of air with nitrogen (industrial standard purity) for 1 hour before heating to 500°C. At 500°C, hydrogen was introduced into the atmosphere to reduce the catalyst. The reduction process was conducted over a time period of 2 hours. After 2 hours, the hydrogen gas flow was ceased and the temperature raised to 670°C (~1 hour duration). Although a wide range of temperatures can be used to grow hairy carbons, for the sake of comparison all growth experiments in this work were conducted at the 670°C temperature. The process is represented in Fig. 2. When the growth temperature was reached, the acetylene source gas (also industrial standard purity) was introduced into the tube holding the alumina boat filled with the catalyst treated substrate (a volume ratio of 2:10 acetylene to nitrogen). The filamentous hairs were grown at 670°C over a period of 5 hours and the nodules on the carbon black over 30 minutes. Morphological studies of the catalyst particles on the substrates were conducted after the reduction step, in which case, the furnace was turned off and allowed to cool before extracting a sample. The substrate materials investigated were carbon black (420 μm mean particle size, Shawinigan acetylene black from Chevron, Houston, Texas), short carbon fibers (100 μm length, isotropic pitch based, unsized, P-100, Carboflex from Ashland Petroleum Company, Ashland, Kentucky) and graphite particles (2–18 μm size, Ultra Carbon from Carbone of America, Bay City, Michigan).

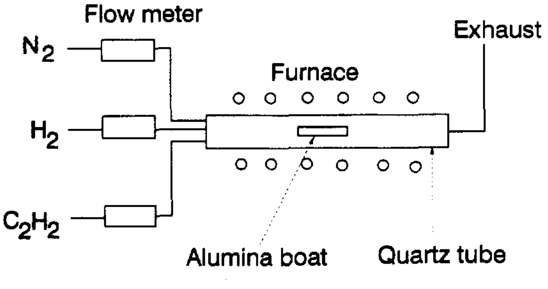

Fig. 1. System used for growing carbon filaments.

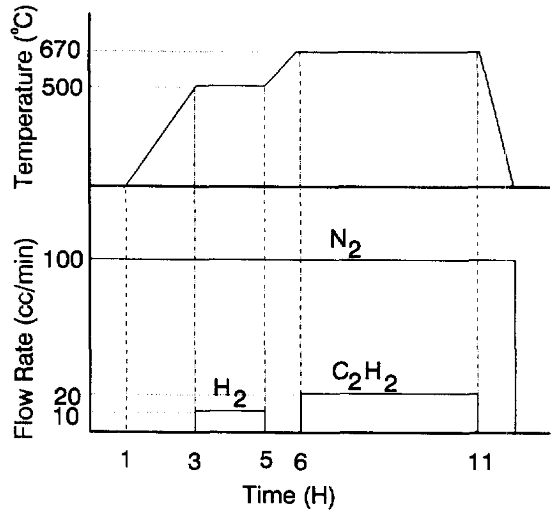

Fig. 2. Schematic representation of the vapor deposition process for carbon filament growth.

X-ray diffraction was conducted using a Nicolet powder diffractometer system and Cu Kα radiation to examine the crystallographic nature of plain carbon black, plain carbon fibers and their hairy counterparts. The 2θ scan rate was $0.2° s^{-1}$.

Oxidation of the hairy carbon black and hairy graphite particle samples were conducted by heating in air at 450°C. Burn-off times to achieve desired weight loss varied between 20 minutes and 1 hour. The heating might cause some degree of oxidation of the residual catalyst, but the amount of catalyst present after growing the hairs is so minute that the impact of oxidation is most likely overshadowed by the impact of the carbon oxidation. Oxidation of plain carbon black was conducted in air at 450 and 600°C for 30 minutes. In this case, burn-off temperature was varied to achieve desired weight loss. The electrochemical performance of the hairy carbons was compared to their as-received versions and to treated and untreated commercially available carbon filaments [17]. No attempt was made to remove the residual catalyst, which might be a metal carbide or other phases.

Cyclic voltammetry (CV) was conducted using the same method and set-up as in ref. [17]. The carbon was packed into the holder cavity at a pressure of 10 MPa without the use of any binder. The circular carbon electrode had an outer planar area of $0.0792 \pm 0.0005\ cm^2$. For the sake of comparison, cyclic voltammetry was also conducted on carbon filaments grown from methane without a substrate by Applied Sciences Inc. (Cedarville, Ohio). The grade was ADNH, which had a diameter of 0.1 μm and a length $>100\ \mu$m. It was also conducted on carbon paste from BAS (CP 1010). The carbon paste consists of the Ultra Carbon graphite particles described earlier and a paraffin oil binder.

The rate constant for electron transfer (k_s), the capacitance and the electrochemical area were obtained from the CV data using the method described in ref. [17] in order to compare the different hairy carbons. In particular, the capacitance (C) was calculated from the cyclic voltammetry data and was expressed in terms of the geometric surface area of the electrode rather than the BET surface area [27].

The specific surface area of the carbon black before and after hair growth was determined by the Brunauer–Emmett–Teller (BET) gas-phase adsorption method. The BET method, based on the Langmuir adsorption isotherm, measures the amount of gas molecules, in this case nitrogen, that adsorb to form a monolayer on the carbon black samples [27].

The packing densities of carbon black and its modified versions after pressing at 10 MPa were assessed using the method and set-up of ref. [17].

3. RESULTS

The substrate materials used to grow hairs yielded different carbon filament morphologies under the same growth conditions (i.e. gas flow rates, time and temperature) due to the manner in which the individual catalyst particles formed on the surface of the substrates. SEM was used to characterize the shape and size of the catalyst particles formed on the substrate surface prior to hair growth. The size of the catalyst particle (located at the tip of the filament) after filament growth is less than the diameter ($\sim 0.1\ \mu$m) of the filament. In the case of carbon black, the iron catalyst developed irregular shapes in sizes ranging from 1 to 2 μm. Figure 3(a) shows the morphology of the iron catalyst on the surface of carbon black. A back scattered electron image of Fig. 3(a) is shown in Fig. 3(b) (the catalyst particles are the bright regions). The fineness in the formation of the catalyst is due to the porosity of the carbon black. Because of its porous nature, the carbon black particles absorbed the catalyst solution, which filled the interconnected pores within the body of the particle via capillary action. During the drying step, the catalyst solution on the outer surface of the carbon black particle evaporated first, allowing that internal to the particle to diffuse outward to the surface, confining the catalyst particle to the size and shape of the pore it filled (10 to several hundred Å). This size of catalyst particle is conducive to filament growth [33–35], facilitating an abundant yield of hairs onto the surface of the carbon black particle, as shown in Fig. 3(c) (which shows curved lines corresponding to hairs and bright clusters corresponding to clumps of hairs). By decreasing the growth time from 5 hours to 30 minutes, the hairs were shortened to the dimension of nodules (0.1–1.0 μm in size). The X-ray diffraction pattern of plain carbon black (Fig. 4) exhibits weak peaks in the vicinity of the 2θ position for the graphite 002 peak and in the vicinity of the 2θ positions (close

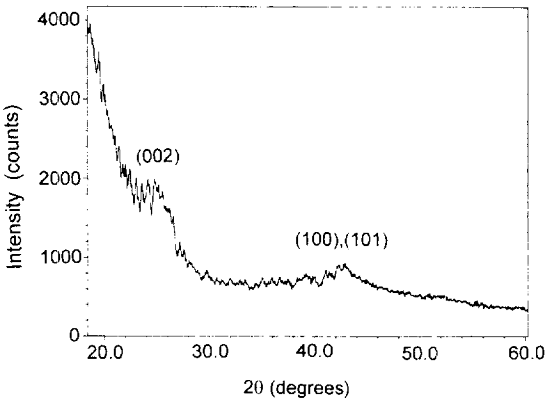

Fig. 4. X-ray diffraction pattern for plain carbon black.

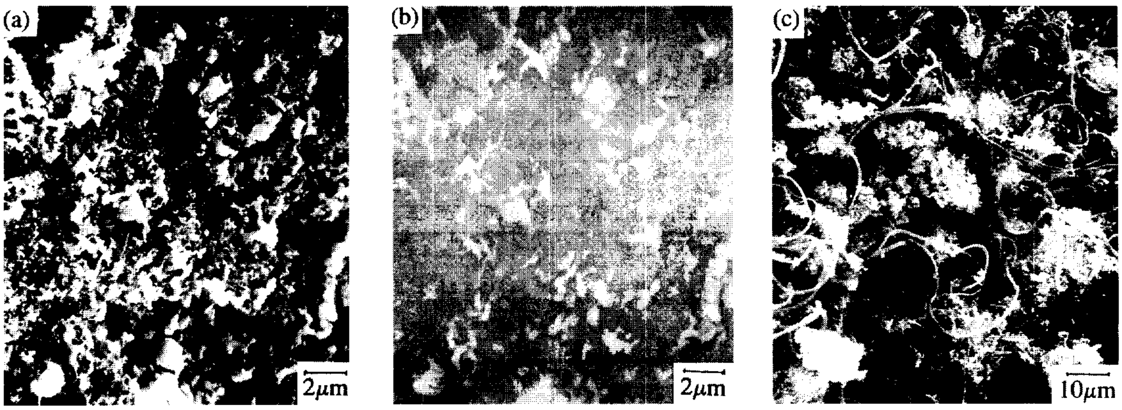

Fig. 3. (a) Morphology of the iron catalyst on the surface of carbon black. (b) Back scattered image corresponding to (a). (c) Carbon filaments grown on carbon black.

together) of the graphite 100 or 101 peaks. The X-ray diffraction pattern of the hairy carbon black displays stronger peaks – a higher intensity diffraction peak at the 2θ position for the graphite 002 peak, and one of lower intensity for the graphite 100/101 peak (Fig. 5), indicating that the hairs were much more crystalline than the carbon black itself.

The size, shape and surface character of the graphite particles resulted in the development of coarse catalyst particles ($\sim 1\ \mu$m), as shown in Fig. 6(a) and (b). The predominantly basal plane surface of the graphite particles (patches in Fig. 6(a) and (b)) provided few defect positions for catalyst particles to nucleate. Only the edge sites of the graphite flakes resulted in fine, irregularly shaped catalyst particles. Typical catalyst particle size on the basal plane surfaces measured 1 μm while the edges, being much lower in surface area than the planar surfaces, displayed a small amount of submicron size catalyst particles. Figure 6(c) displays the morphology of the filament growth on graphite particles. A mixture of carbon filaments (of diameter 0.1–0.3 μm) and carbon nodules (of size 0.05–0.5 μm) were grown. Since the catalyst particles were so large, filament growth could only be initiated by the catalyst particles of size $<0.15\ \mu$m [33–35]. The large catalyst particles initiated deposition of nodular carbon black from the vapor phase.

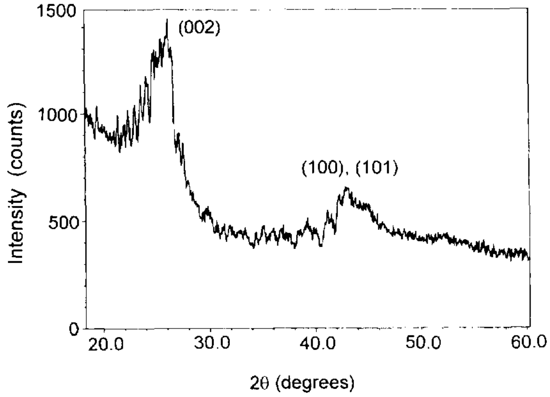

Fig. 5. X-ray diffraction pattern for hairy carbon black.

The carbon fibers were essentially amorphous. X-ray diffraction peaks were absent, though the diffraction pattern had increased noise (i.e. not quite a well-defined peak) 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 and 101 peaks. The catalyst particles formed on the carbon fibers were evenly distributed over the smooth fiber surface, as shown in Fig. 7(a). Catalyst particle size ranged between 0.1 and 1.0 μm, some of which displayed a shape with six-fold symmetry in spite of the essentially amorphous nature of the fiber. The development of the symmetrically shaped catalyst particles, in conjunction with the noise observed in the X-ray diffraction pattern, suggests that the carbon fiber surface contains some crystalline regions. The crystallographic heterogeneity makes coalescence of the catalyst particles more difficult, thus resulting in an abundance of fine filament growth (diameters less than 1 μm), which completely covered the fiber, Fig. 7(b) and (c). The X-ray diffraction pattern of hairy carbon fibers exhibits graphite 002 and 100/101 peaks, indicating that the hairs were at least partly crystalline.

Table 1 compares the substrate materials and the catalyst used to grow hairs. The weights and thicknesses of the catalysts were computed under the assumption that the metal is completely reduced by the hydrogen treatment. In actuality, there may be various oxide levels within the catalyst layer. From the data in Table 1, it is apparent that a small amount of catalyst, regardless of the type used, is sufficient to provide a good hair yield (as low as 9.0×10^{-7} g cm^{-2} in the case of the iron containing catalyst on the carbon black substrate). Also apparent is that the size (i.e. the lateral growth) of the catalyst particles is more important than the thickness (i.e. the vertical growth) of the catalyst layer in generating good yield. The carbon black and carbon fiber substrates capture the extremes in catalyst thick-

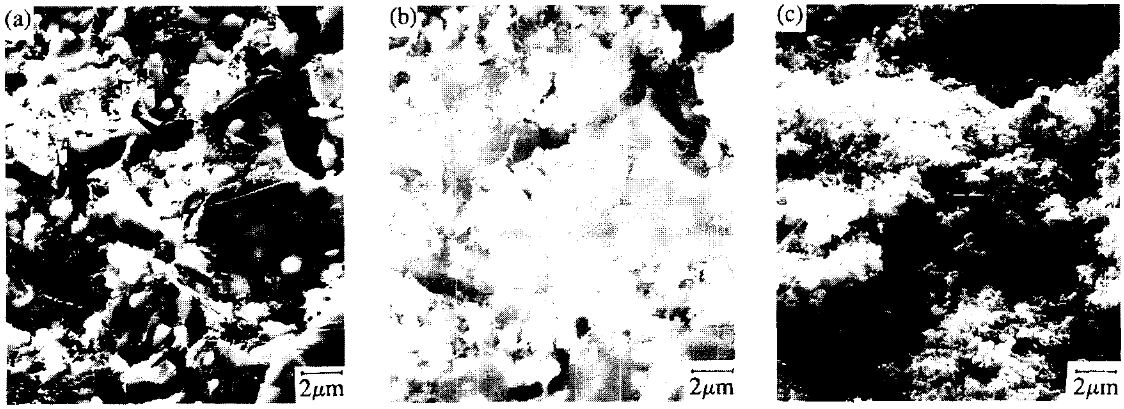

Fig. 6. (a) Morphology of the iron catalyst on the surface of graphite flakes. (b) Back scattered image corresponding to (a). (c) Mixture of carbon filaments and carbon black nodules grown on the graphite flakes.

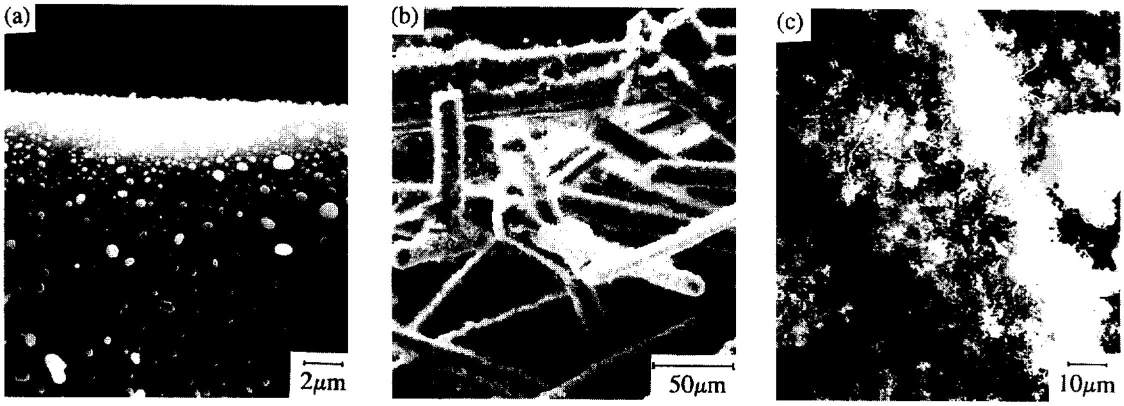

Fig. 7. (a) Morphology of the iron catalyst on the surface of short carbon fibers. (b) Carbon filaments grown on short carbon fibers. (c) Carbon filaments grown on short carbon fibers at a high magnification.

Table 1. Comparison of catalysts used

Carbon substrate type	Catalyst	Weight[a] of catalyst ($g\ cm^{-2}$)	Thickness of catalyst (nm)
Carbon black	$Fe(NO_3)_3 \cdot 9H_2O$	9.0×10^{-7}	1.1
	$Ni(NO_3)_2 \cdot 6H_2O$	1.3×10^{-6}	1.5
Graphite particles	$Fe(NO_3)_3 \cdot 9H_2O$	6.8×10^{-6}	8.6
	$Ni(NO_3)_2 \cdot 6H_2O$	9.9×10^{-6}	11.1
Carbon fibers	$Fe(NO_3)_3 \cdot 9H_2O$	2.7×10^{-4}	345
	$Ni(NO_3)_2 \cdot 6H_2O$	4.0×10^{-4}	445

[a] Calculated assuming complete reduction of the metal.

ness, yet both substrates resulted in more abundant hair growth than the graphite particles with a catalyst thickness approximately eight times larger than carbon black but forty times lower than carbon fibers. As discussed earlier, both the carbon black and carbon fiber substrates used in this study inhibited catalyst particle coalescence, in contrast to the graphite particles. The smaller catalyst particle sizes of the hairy carbon black and carbon fibers resulted in good yield, while the larger catalyst particles observed on the graphite particles negatively impacted yield. Note that both catalyst types resulted in similar catalyst thicknesses for their respective substrate materials.

Table 2 summarizes CV results. The hair growth, in all cases, improved the reversibility of the redox reaction (as indicated by the shape of the CV curves and the reduction of the peak separation, ΔE) from the as-received substrate material. The most dramatic improvement was observed for carbon black (labeled 1 in Table 2), where hairy carbon black changed the electrochemical response from irreversible to quasi-reversible, whether the hairs were filaments (labeled 5 in Table 2) or nodules (labeled 4 in Table 2). Typical hair diameter was 0.05–0.2 μm; typical nodule size was 0.5 μm. Hair growth decreased the specific surface area of the carbon black, as shown by BET nitrogen gas adsorption (Table 3). This effect is attributed to the blockage of some of the pores of the original carbon black by the catalyst and to the high surface area of the original carbon black. Since hair growth resulted in an overall decrease in the specific surface area, the improved electrochemical performance due to hair growth is attributed to the connectivity imparted by the hairs (since a binder is no longer necessary for good CV results), and/or the electrochemical activity of the hairs (shown by X-ray diffraction to be graphitic). The hairy carbon with filaments (labeled 5 in Table 2, $\Delta E = 190$ mV) was more reversible than the hairy carbon with nodules (labeled 4 in Table 2, $\Delta E = 214$ mV). Figure 8 displays the CV data for plain carbon black (labeled 1 in Table 2). The data include 8 curves, which were obtained at potential scan rates of 20, 50, 75, 100, 125, 150, 175 and 200 mV s^{-1}. The curve with the lowest positive peak current density is associated with the lowest potential scan of 20 mV s^{-1}, whereas that with the highest positive peak current density is associated with the highest scan rate of 200 mV s^{-1}. None of the curves display redox peaks, and the slope of the curves indicates high impedance, most likely due to the slow electron transfer across the electrode surface (as opposed to incomplete wetting of the electrode, since the electrode was held immersed in solution for 15 minutes prior to CV, and since the electrode displays high capacitance normally indicative of good electrode wetting). The CV plots for hairy carbon with filaments (labeled 5 in Table 2) and with nodules (labeled 4 in Table 2) are displayed in Figs 9 and 10, respectively. Under the same CV testing parameters, the redox peaks are clearly observed in both cases. The hairy carbon

Table 2. Hairy carbon 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 5%	1780	761	2.3	278
3: Oxidized 16%	976	894	1.1	136
4: Hairy, with nodules[a]	2175	1383	1.6	214
5: Hairy, with filaments[a]	1313	789	1.7	190
6: Hairy, oxidized 6%[a]	1523	1345	1.1	114
7: Hairy, oxidized 13%[a]	1731	1899	0.9	76
8: Hairy, oxidized 20%[a]	1628	1299	1.3	154
9: Hairy, as-grown[b]	978	849	1.2	118
10: Hairy, acetone cleansed[b]	323	241	1.3	174
11: Hairy, methylene chloride cleansed[b]	590	484	1.2	120
Graphite particles				
12: As-received	1158	611	1.9	224
13: Hairy[a]	2769	1602	1.7	198
14: Hairy, oxidized 2.6%[a]	1159	604	1.9	254
15: Carbon paste	975	704	1.4	222
Carbon fibers				
16: As-received	1499	923	1.6	174
17: Hairy[a]	4811	2850	1.7	78
Carbon filaments[c]				
18: As-received	7800	1650	4.7	530
19: Acetone cleansed	13575	8467	1.6	196
20: Acetone cleansed and chopped	1680	1450	1.2	130
21: Methylene chloride cleansed and chopped	2000	1750	1.1	90

[a] $Fe(NO_3)_3 \cdot 9H_2O$ catalyst.
[b] $Ni(NO_3)_2 \cdot 6H_2O$ catalyst.
[c] From ref. [17].

Table 3. BET nitrogen gas adsorption results for carbon black

Carbon type	Specific surface area (m^2 g^{-1} @ STP)
Carbon black	70.5
Hairy carbon black ($NiNO_3$ catalyst)	23.5
Hairy carbon black ($FeNO_3$ catalyst)	27.6

samples display lower current densities than plain carbon black, due to the lower particle surface area. Nevertheless, a higher current density was displayed by the hairy carbon with nodules than for the hairy carbon with filaments. In this case, the higher current density for the hairy carbon with nodules reflects the shortness of the hairs and the influence on current density capability of the carbon black substrate material. With longer hairs on carbon black, i.e. with the filaments, the influence of the filaments is observed over that of the carbon black substrate. Other than the peaks associated with the Fe^{2+}/Fe^{3+} redox couples, no peak was observed in the CV results of hairy carbons, suggesting that the residual catalyst did not undergo any redox reaction that would affect the CV results of hairy carbons.

Figures 9 and 11 compare the effects of the type of catalyst used to produce hairy carbon black on the CV response. The use of the nickel based catalyst (Fig. 11) resulted in a higher degree of reversibility (labeled 9 in Table 2, $\Delta E = 118$ mV) than did the use of an iron based catalyst (Fig. 9, labeled 5 in Table 2, $\Delta E = 190$ mV). The k_s of the hairy carbon grown using the nickel catalyst was also higher and the capacitance and electrochemical area slightly lower compared to that produced using the iron based catalyst (Note: No attempt was made to remove residual catalyst from any hairy sample prior to electrochemical testing, Table 4.) This was expected since it was observed that handleability of the nickel containing catalyst was easier than the iron containing catalyst. In contrast to the nickel containing catalyst, the iron containing catalyst tended to clump and stick to anything with which it contacted. The CV results, in conjunction with the handling observations, suggest that the nickel containing catalyst encourages a more even and homogeneous distribution of the catalyst particles, even though the BET surface area was somewhat lower than for the iron containing catalyzed sample (Table 3).

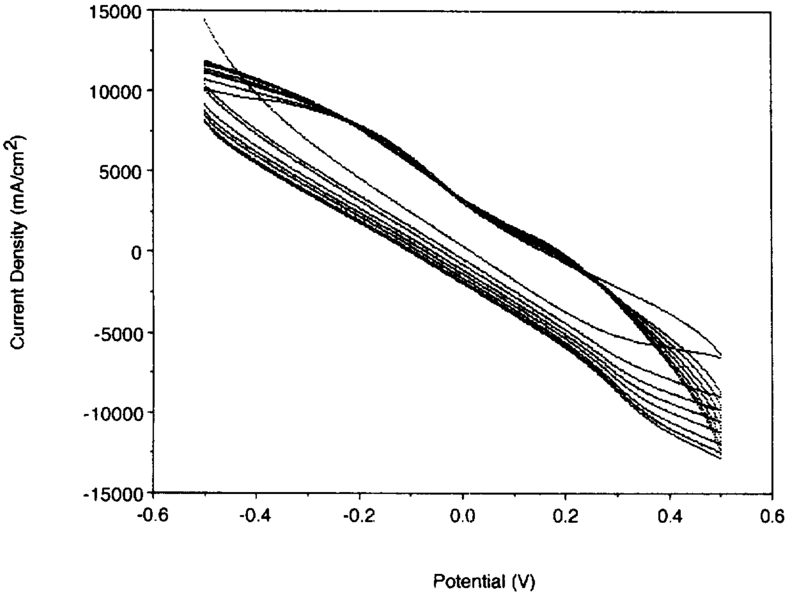

Fig. 8. Cyclic voltammetry results for plain carbon black.

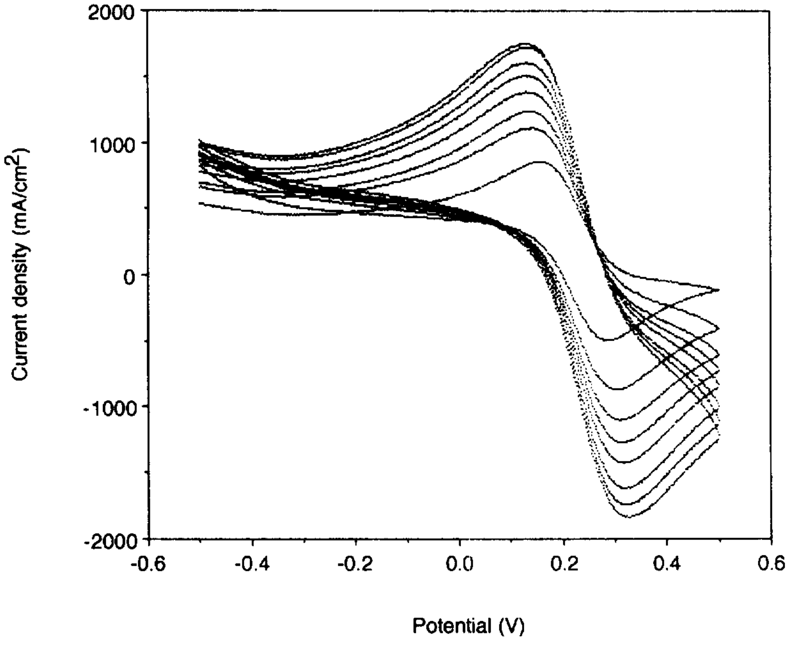

Fig. 9. Cyclic voltammetry results for hairy carbon black with filaments grown with an iron based catalyst.

Both oxidation and hair growth independently improved the packing density of the substrate material. Oxidation of plain carbon black to a 16% burn-off resulted in a 10% increase in packing density. Hair growth on the carbon black resulted in an 8% increase in packing density. By combining the two treatments, i.e. 13% oxidation of the hairy carbon black, a synergistic effect resulted yielding a 30% increase in packing density (the highest packing density achieved, 0.831 g cm^{-3}).

As shown in Table 5, oxidation increased the packing density for both carbon black and hairy carbon black, except when oxidation was excessive, as in the case of 20% oxidation of the hairy carbon black. As reported in ref. [17], solvent cleansing using acetone or methylene chloride, followed by chopping, increased the packing density of carbon filaments. Within each of the three sample categories in Table 5, the highest packing density corresponded to the highest k_s. Of all the samples in Table 5, oxidized (13%) hairy carbon black exhibited the highest packing density as well as the highest k_s. Excessive oxidation (20%) of hairy carbon black decreased the packing density to a value below that without oxida-

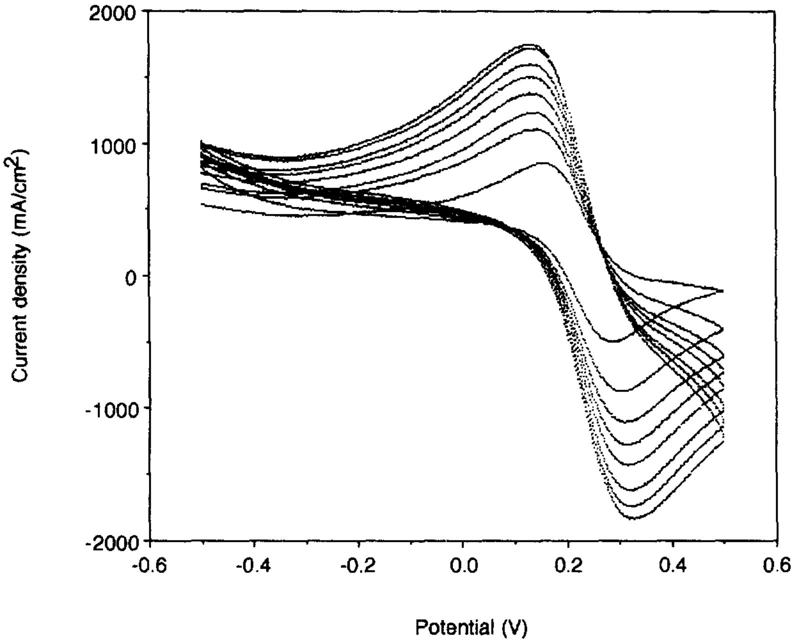

Fig. 10. Cyclic voltammetry results for hairy carbon black with nodules grown with an iron based catalyst.

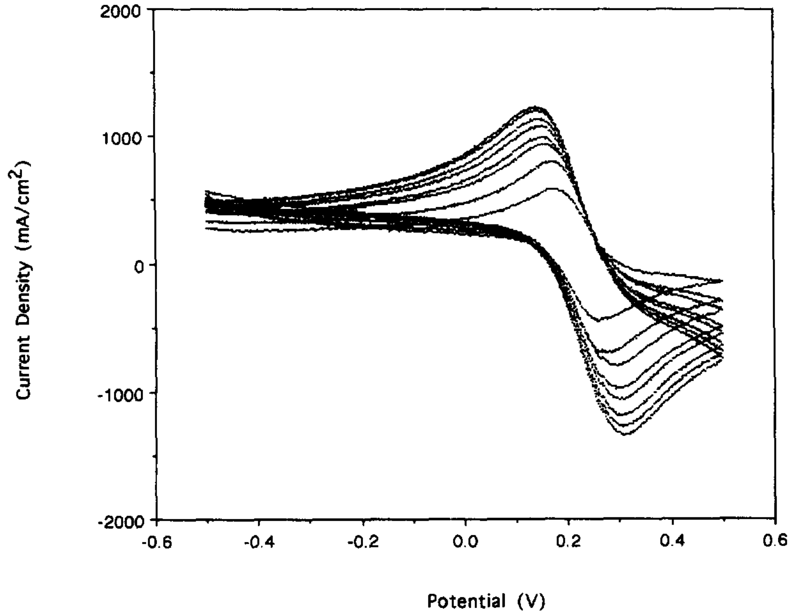

Fig. 11. Cyclic voltammetry results for hairy carbon black with filaments grown with a nickel based catalyst.

tion, probably because of partial volatilization of the hairs, so k_s was also decreased.

Figures 12 and 14 display the CV plots for the as-received graphite particles (labeled 12 in Table 2) and carbon fibers (labeled 16 in Table 2), respectively. Compare these results with their hairy counterparts in Fig. 14 (hairy graphite particles labeled 13 in Table 2) and Fig. 15 (hairy carbon fibers labeled 17 in Table 2). Hair growth resulted in increased current densities and decreased ΔE, for both graphite particles and carbon fibers. The improvements are attributed to both an increased surface area and the particulate connectivity imparted by the hairs. The graphite particles used to grow hairs for this experiment were the same particles used to manufacture the carbon paste commercially available for analytical electrodes. Compare the as-received graphite powder without binder (Fig. 12, sample 12 in Table 2) with the current technology using the graphite particles with an oil binder (Fig. 16, labeled 15 in Table 2). This comparison demonstrates that the oil binder is necessary to achieve a reasonable electrochemical

Table 4. Electrochemical behavior of various 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 5%	Irreversible	2.21	24
3: Oxidized 16%	0.0073	2.01	22
4: Hairy, with nodules[b]	0.0027	3.85	42
5: Hairy, with filaments[b]	0.0041	1.74	19
6: Hairy, oxidized 6%[b]	0.0115	2.03	22
7: Hairy, oxidized 13%[b]	0.0463	3.42	37
8: Hairy, oxidized 20%[b]	0.0063	2.04	22
9: Hairy, as-grown[c]	0.0105	1.41	15
10: Hairy, acetone cleansed[c]	0.0050	0.80	9
11: Hairy, methylene chloride cleansed[c]	0.0100	1.16	13
Graphite particles			
12: As-received	0.0021	2.02	22
13: Hairy[b]	0.0036	5.92	65
14: Hairy, oxidized 2.6%[b]	0.0004	1.88	21
15: Carbon paste	0.0023	2.43	27
Carbon fibers			
16: As-received	0.0050	2.72	30
17: Hairy[b]	0.0417	4.48	49
Carbon filaments[d]			
18: As-received	Irreversible	5.93	65
19: Acetone cleansed	0.0037	27.30	298
20: Acetone cleansed and chopped	0.0082	1.92	30
21: Methylene chloride cleansed and chopped	0.0209	2.62	29

[a] Capacitance per unit outer planar area (0.0792 cm^2).
[b] $Fe(NO_3)_3 \cdot 9H_2O$ catalyst.
[c] $Ni(NO_3)_2 \cdot 6H_2O$ catalyst.
[d] From ref. [17].

Table 5. Packing densities of carbon black as-received and after various modifications, all after pressing at 10 MPa; sample numbers correspond to those in Figs 2 and 3

Sample	Condition	Packing density (g cm^{-3}) (±0.002)	k_s (cm s^{-1}) (±0.0002)
1: Carbon black	As-received	0.637	Irreversible
2: Carbon black	Oxidized 5%	0.656	Irreversible
3: Carbon black	Oxidized 16%	0.702	0.0073
5: Hairy carbon black	As-received	0.688	0.0041
6: Hairy carbon black	Oxidized 6%	0.713	0.0115
7: Hairy carbon black	Oxidized 13%	0.831	0.0463
8: Hairy carbon black	Oxidized 20%	0.669	0.0063
18: Carbon filaments[a]	As-received	0.465	Irreversible
20: Carbon filaments[a]	Acetone cleansed and chopped	0.737	0.0082
21: Carbon filaments[a]	Methylene chloride cleansed and chopped	0.820	0.0209

[a] From ref. [17].

response from the graphite particles. The addition of a binder to the graphite particles results in more consistent CV plots with less of a dependence on the scan rate for good electrochemical performance. The effect is due to the improved bindability of the graphite particles imparted by the oil. The same effect with respect to scan rate independence is achieved by the hairy graphite particles without using a binding oil, as shown by comparing Fig. 16 with Fig. 14. From the data in Table 2, the growth of the hairs (sample 13) improves the electrochemical response of the dry graphite particles (sample 12) so much so that it surpasses that of the current carbon paste technology (sample 15). This is of practical importance in studies whereby the binding oils or waxes are incompatible with the media being studied.

Since oxygen containing surface functional groups are known to improve electrochemical behavior of

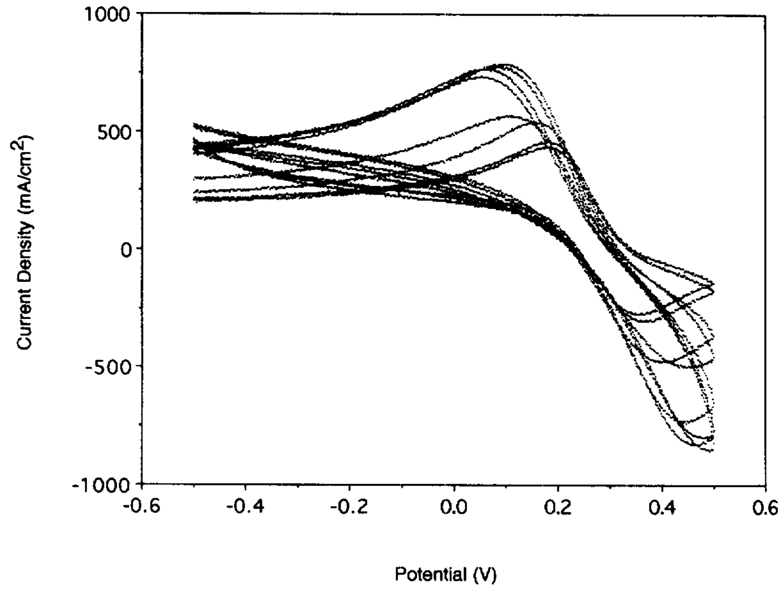

Fig. 12. Cyclic voltammetry results for as-received graphite particles.

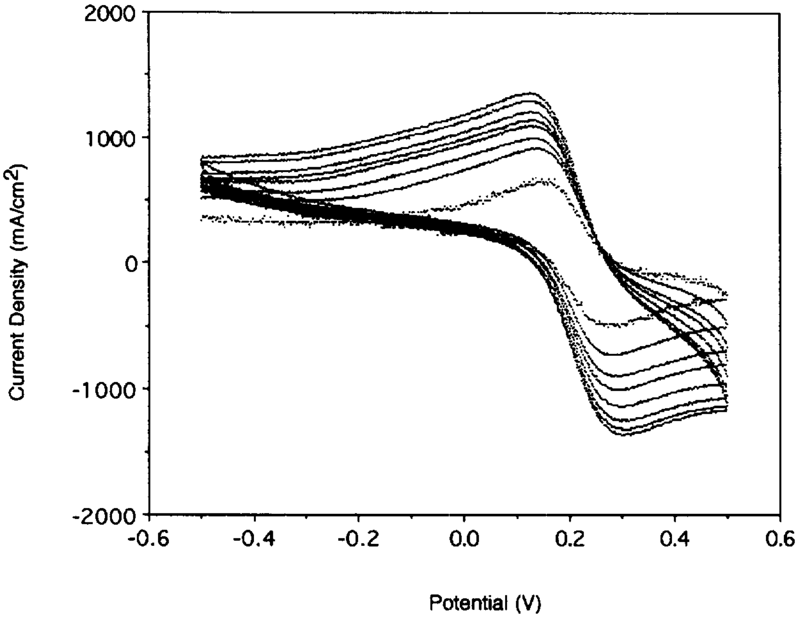

Fig. 13. Cyclic voltammetry results for as-received carbon fibers.

carbon materials [27,28], oxidation of the carbon black samples was conducted. The oxidation of plain carbon black to a 16% burn-off improved the electrochemical reversibility even more than the growing of hairs, as shown by ΔE in Table 2 (labeled 3) and the CV plot of Fig. 17. In contrast to hairy carbon black, however, the current density capability decreased by a factor of ten. Oxidation of the hairy carbon black (labeled 6, 7 and 8 in Table 2), on the other hand, had a larger effect on reversibility, with a lesser effect on current density capability. For the three levels of burn-off tested, 13% achieved the best response (Fig. 18, labeled 7 in Table 2), nearly resulting in complete reversibility ($\Delta E = 76$ mV). It is believed that oxidation of both the carbon black and the hairs occur, and the abundance of hairs present in hairy carbon black allows sufficient remaining hairs to significantly influence electrochemical performance. In the case of hairy graphite particles, oxidation (labeled 14 in Table 2, $\Delta E = 254$ mV) had no benefit compared to as-received graphite particles (labeled 12 in Table 2, $\Delta E = 224$ mV) and reversed any benefits achieved in the electrochemical performance of the as-grown hairy graphite particles ($\Delta E = 198$ mV). Since the abundance of hairs grown on graphite particles is far less than those grown on carbon black,

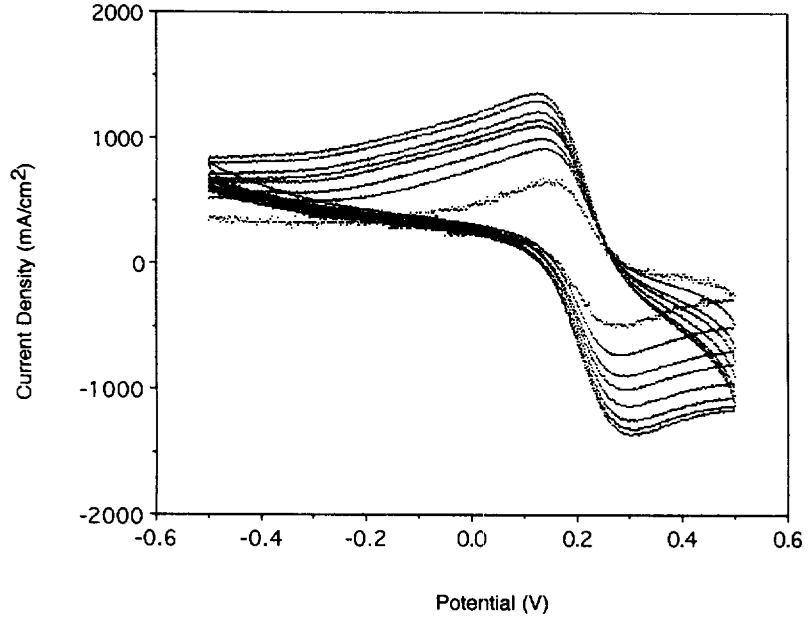

Fig. 14. Cyclic voltammetry results for hairy carbon fibers grown with an iron catalyst.

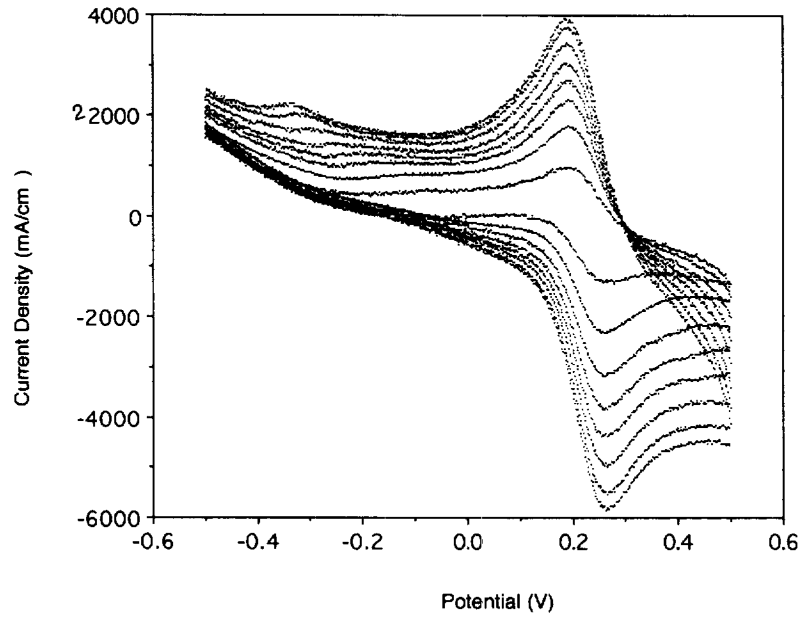

Fig. 15. Cyclic voltammetry results for hairy carbon fibers grown with an iron based catalyst.

it is believed that, in contrast to hairy carbon black, the burn-off completely volatilizes any hairs that were grown. In addition, the predominant basal plane surface of the graphite particles made oxidation very difficult (only 2.6% burn-off was achieved after 1 hour for the hairy graphite particles, in contrast to 20% for hairy carbon black).

Because a tarry residue that can be removed by solvent cleansing is associated with the carbon filament growth process conducted by Applied Sciences Inc. [17], cleansing of the hairy carbon was attempted to demonstrate that the hairy carbon black growth process as conducted at SUNY/Buffalo minimizes condensation of the tarry residue. (Nevertheless, at SUNY/Buffalo, the tarry substance tends to accumulate on the walls of the quartz tube of the furnace.) In contrast to the carbon filaments in which growth is initiated by a catalyst mist sprayed into the cavity of the growing chamber, cleansing of the hairy carbon had no beneficial effect on electrochemical behavior. Rather, the use of acetone resulted in a wider potential peak separation ($\Delta E = 174$ mV after acetone cleansing, labeled 10 in Table 2, vs $\Delta E = 118$ mV for as-grown hairy carbon black, labeled 9 in Table 2),

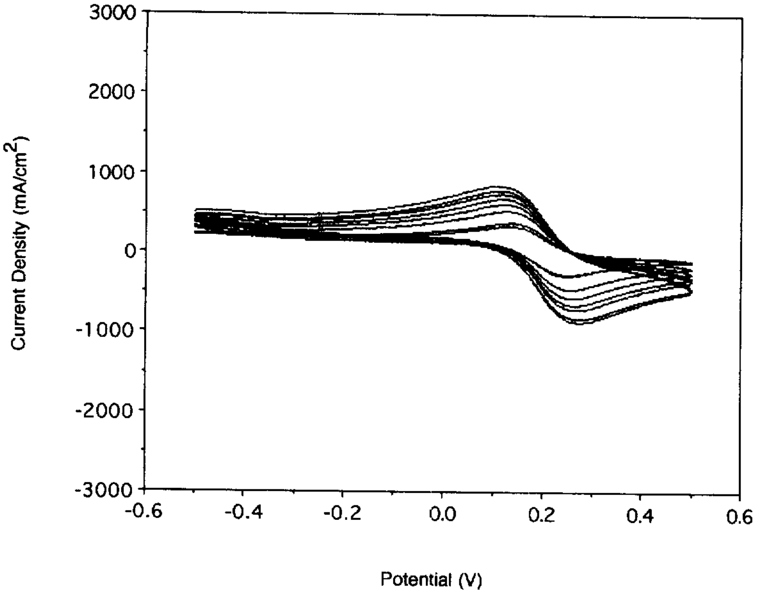

Fig. 16. Cyclic voltammetry results for carbon paste.

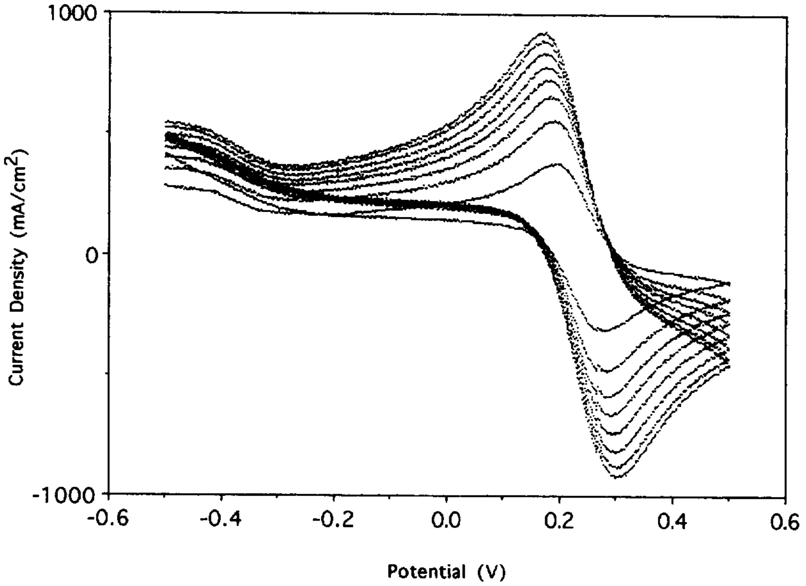

Fig. 17. Cyclic voltammetry results for oxidized carbon black (burn-off of 16% by weight).

and lower current density capability, probably due to unfavorable changes in carbon surface functional groups. The use of methylene chloride had little effect on potential peak separation (labeled 11 in Table 2), but some effect on current density capability compared to as-grown hairy carbon black. The effect on the current density capability, however, was less using methylene chloride than acetone.

For all carbons processed, growth of the hairs improved k_s compared to the as-received substrate material (Table 4). In the case of carbon black, k_s after hair growth was calculable, whereas the as-received sample displayed an irreversible electrochemical response. In the case of the carbon fibers, over a 700% increase in the k_s was obtained by growing the hairs. Whereas cleansing with acetone or methylene chloride improved the k_s of the carbon filaments, the k_s of hairy carbon black was unaffected (using methylene chloride) or degraded (using acetone), compared to the as-grown hairy carbon black. A 13% burn-off of the hairy carbon black improved the k_s by one order of magnitude compared to the as-grown sample, yielding a higher k_s than any of the carbon in Table 4.

A dramatic decrease in capacitance and electrochemical area were achieved by making carbon black hairy (samples 1 and 5 in Table 4). The decrease in electrochemical area is consistent with the decrease

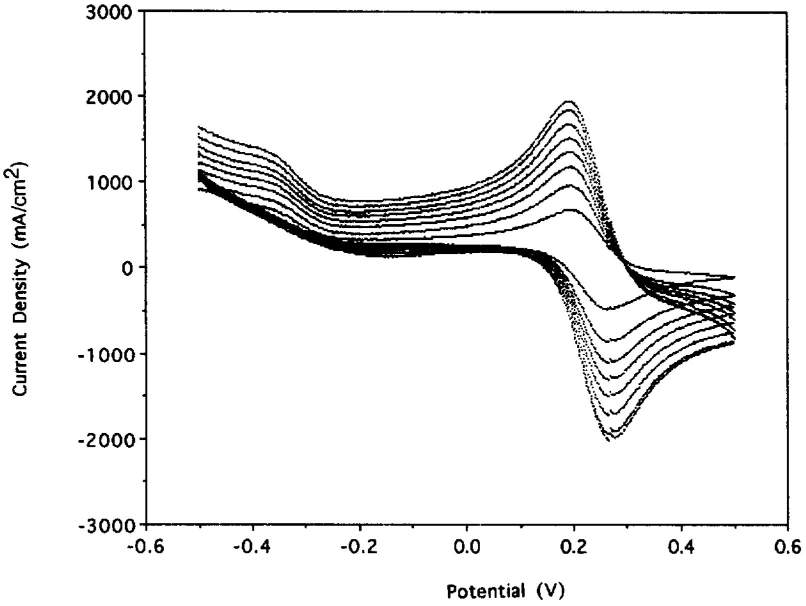

Fig. 18. Cyclic voltammetry results for oxidized hairy carbon black (burn-off of 13% by weight).

in specific surface area (Table 3). The effect on capacitance and electrochemical area by the hairy carbon black with filaments (labeled 5 in Table 4) was greater than that with nodules (labeled 4 in Table 4) due to the proportional difference between the filaments and the carbon black compared to the nodules and the carbon black, i.e. due to the fact that the filaments are longer than the nodules, making the relative amount of filaments with corresponding surface area higher than the relative amount and surface area of nodules. In the former, the filament hairs are longer and form a thicker fluffy covering of the carbon black particle, thereby generating a larger effect on capacitance and electrochemical area, whereas, in the latter, the shorter nodules form a thinner covering of the carbon black particle, allowing more influence on the electrochemical character of the hairy carbon by the carbon black itself. In either case, the hairy growth covers the substrate material completely such that the original particle is not visible from the hairs. This is clearly shown for hairy carbon black (with filaments rather than nodules) in the SEM photo of Fig. 19(a). A higher magnification of the individual hairs is shown in Fig. 19(b).

The capacitance of oxidized hairy carbon black is the highest after 13% burn-off, although oxidation at any of the three levels (6, 13 and 20%) studied increased the capacitance. The effect of oxidation is expected since higher capacitance is associated with higher concentration of oxygen surface functional groups [27]. The electrochemical area is also highest for the 13% burn-off, supporting the notion that a higher compactability translates into a greater number of filaments exposed per unit area of the electrode's outer surface. In the case of graphite particles and carbon fibers, the effect of hairiness on capacitance and electrochemical area is the opposite of that observed for carbon black. The difference in behavior is due to the intrinsically low capacitance and electrochemical area of graphite particles and carbon fibers compared to carbon black.

4. DISCUSSION

Of the three substrate materials used to grow hairs, carbon black was found to have the most abundant yield due to the high porosity of this substrate as well as to the small size of the pores which controlled the shape and size of the catalyst particles initiating filament growth. (As mentioned earlier, previous reports indicate that filament growth could only be initiated by the catalyst particles of size <0.15 μm [33,34].) The relationship between the pore structure of the carbon black and the catalyst size results in a more reproducible degree of hairiness of the carbon black, which translates into a more reproducible electrochemical behavior of the hairy carbon black than it does for the hairy graphite particles and hairy carbon fibers. As seen with studies using carbon pellets [35], the nature of the graphite particle and carbon fiber surfaces may allow initial formation of very fine catalyst particles during the reduction step which then easily coalesce into irregular agglomerates, resulting in very little, if any, filament growth. To yield filament growth on these substrate surfaces, it is vital that the catalyst coalescence process be controlled. Because of the large basal plane area of the graphite particles and its crystallographic homogeneity, controlling the coalescence of catalyst particles proved more difficult, making filament yields inconsistent. In the case of the carbon fibers in this

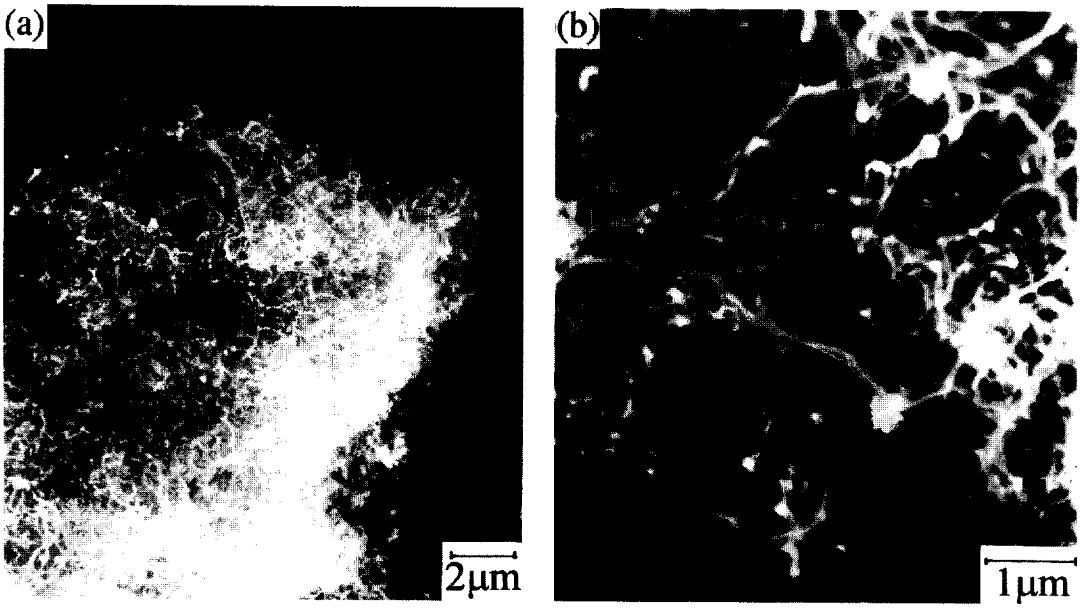

Fig. 19. Scanning electron microscope photograph of (a) hairy carbon black and (b) the individual hairs of hairy carbon black.

study, the crystallographic heterogeneity probably helped restrict the coalescence, making filament yield higher than the graphite particle case.

The hairs were crystalline, whereas the substrates were crystalline for graphite particles, slightly crystalline for carbon black and essentially amorphous for carbon fibers. This means that the crystallinity of the hairs causes the crystallinity of carbon black and carbon fibers to be increased after hair growth, whereas the crystallinity of graphite particles is not much affected by the hair growth. On the other hand, the surface area of the substrates also differed. Carbon black (without hair) had a much higher surface area than the carbon fibers or graphite particles. Thus, hair growth increased the surface area of carbon fibers and graphite particles, but not for carbon black. In the case of carbon black, hair growth substantially reduced the surface area. Hair growth, then, provides a new means of modifying the crystallinity, surface area, surface texture and even the connectivity of carbons. This method of surface modification results in changes that are different from those resulting from conventional surface modification methods. For example, surface modification by oxidation rather than hair growth can change the surface area and surface texture, but not the crystallinity or connectivity.

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 F per unit geometric area) and electrochemical surface area A, 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 $0.0792 \pm 0.0005\ \text{cm}^2$ for all types of electrodes. Whether for carbon black, graphite particles or carbon fibers, the hair growth increased k_s; the effect is most significant for carbon black and least significant for graphite particles. A high value of A is associated with a high value of C, as expected. Hair growth greatly decreased both C and A for carbon black, but increased both C and A for graphite particles and carbon fibers.

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. Hair growth greatly increased reversibility (in spite of the presence of residual catalyst) and decreased 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 the existence of the hair (rather than the existence of the residual catalyst), while the decrease in C is due to the decrease in electrochemical surface area, which is in turn due to the blocking of some of the pores of the carbon black by the catalyst used in hair growth. The oxidation of hairy carbon black, as achieved by heating in air at 450°C for 30 minutes to a burn-off of 13%, greatly increased k_s, while increasing C and A, though C and A remained much lower than those of as-received carbon black. After similar oxidation of as-received carbon black at 450°C (sample 2 in Table 4), only a 5% burn-off was achieved and the electrochemical response remained irreversible, though C was decreased from the value for as-received carbon black. The large positive effect of oxidation on hairy carbon black is believed to be associated with a surface effect on both the hair and the carbon black, although a surface effect on the residual catalyst may play a role. The oxidation treatment is believed to have increased the surface edge and defect sites of both the hair and the carbon black as similarly seen for carbon fibers [28]. The development of the edge and defect sites allowed increased levels of oxygen chemisorption. The increase in oxygen concentration and the formation of oxygen containing surface functional groups, shown to be a function of the level of burn-off in the carbon fiber study, resulted in increasing improvement in electrochemical activity. The enhancement of the electrochemical activity was evidenced by an increased electron transfer rate and improved reversibility. The best overall performance for carbon black was obtained after hair growth and subsequent oxidation. Almost as good were hairy carbon fibers, which exhibited slightly lower k_s and higher C. Even after hair growth, graphite particles exhibited yet lower k_s and yet higher C. The increases in C and A upon hair growth for graphite particles and carbon fibers are due to the large surface area of the hair compared to the surface area of the as-received graphite particles or as-received carbon fibers. Further advantages of oxidized hairy carbon black over hairy carbon fibers lie in the former's particulate nature, which facilitates electrode preparation, and lower cost. Since the particulate nature of the finished hairy carbon black product is preserved without sacrificing their clinginess, good packing characteristics are maintained without the need for binders or oils which may be incompatible with electrolyte systems selected for study.

Both oxidation and hair growth independently improved the packing densities of the carbon black samples. In the case of oxidation, the carbon black structure densifies probably by virtue of the fact that the surface is partly volatilized, thereby changing the structural characteristics of the carbon black. The weaker, less structured carbon black can then be more easily compressed. In the case of hair growth, the clinginess of the hairs allows connectivity between the carbon black particles, therefore the spring-back tendency of carbon black is hampered, again increasing the packing density. The improvement in CV response is consistent with that found in a previous study in which increased packing density [17] and oxygen containing surface functional groups [28] were shown to improve electrode kinetics for commercially available carbon filaments. Of the oxidation levels evaluated for hairy carbon black, the best electrochemical result was observed for the 13% burn-off; 20% burn-off was excessive. The combination of hair growth and oxidation (not excessive) produced a synergistic effect on reaction kinetics, whereby the reaction kinetics of carbon black subjected to the combined treatments (sample 7, Table 5) are markedly better than the reaction kinetics of the carbon black that has been subjected to only one of these treatments (samples 3 and 5, Table 5). The synergy achieved is probably due to oxidation of both the carbon black and the hairs. In the case of the carbon black, the change in structure as described above helps to reduce its natural spring-back. In the case of the hairs, oxidation probably roughens the hair surfaces, encouraging further the hair-to-hair mechanical locking of the carbon black particles.

Oxidized carbon black to a 16% burn-off (sample 3 in Table 4) exhibited higher k_s than carbon filaments (i.e. hair grown without a substrate), even after cleansing or graphitization treatments of the carbon filaments. On the other hand, the capacitance is comparable except for acetone cleansed carbon filaments. This means that oxidized hairy carbon black is more attractive than carbon filaments. The superiority of oxidized hairy carbon black over both as-received carbon black and the carbon filaments indicates why oxidized hairy carbon black should be considered a distinct complex that is of value technologically.

The hairs grown in this study are crystalline, but their 002 X-ray diffraction peak is not as narrow in 2θ as that of commercially available carbon filaments [17], indicating a smaller grain size. On the other hand, they have the advantage of being relatively free of a tarry residue, which is present on commercially available carbon filaments [17]. The cleanliness makes secondary operations involving cleansing unnecessary. The absence of the tarry residue on hairy carbons is related to their growth process. Whereas commercial carbon filaments fall down from a hotter zone to a colder zone in the growth chamber (condensation of polyaromatic hydrocarbons occurs in the colder zone), hairy carbons are produced in a ceramic boat (no falling down of the hairy carbon takes place) and the cool down is more gradual than would be experienced in the former process, thereby minimizing condensation of the contaminant.

5. CONCLUSIONS

Hairy carbons in the form of hairy carbon black, hairy graphite particles and hairy carbon fibers were prepared by catalytic growth of carbon hairs (at least partly crystalline) of diameters between 0.05 and 0.2 μm on the respective carbons. The hair growth was more abundant on carbon black than on the graphite particles or carbon fibers due to the ability to develop the finest catalyst particles (10 to several hundred Å) of the three substrates evaluated. Hair growth on carbon black rendered the cyclic voltammetry (Fe^{2+}/Fe^{3+} redox couple) response reversible, decreased capacitance by 97%, decreased electrochemical area by 98% and decreased specific surface area by 61%. Hair growth on graphite particles or carbon fibers also increased k_s, but, in contrast to the hairy carbon black, increased capacitance and electrochemical area. Oxidation of hairy carbon black to a burn-off of 13% by heating at 450°C increased k_s by 1060% from the level before oxidation, while increasing capacitance and electrochemical area. Less effects were obtained after burn-offs to 6% and 20%. The increases in k_s after hair growth and after oxidation are partly due to the increases in the packing density. Oxidized (13%) hairy carbon black exhibited higher k_s than oxidized (not hairy) carbon black, hairy graphite particles and hairy carbon fibers. Hairy graphite particles exhibited higher k_s than commercial carbon paste. Commercial carbon filaments exhibited irreversible voltammetric response as-received, but the response became reversible after solvent cleansing, and k_s remained below that of oxidized (13%) hairy carbon black. Similar cleansing of hairy carbon black did not affect k_s much, suggesting that the hair had much less tarry residue than commercial carbon filaments. Oxidation of carbon black rendered the voltammetric response reversible, decreased capacitance by 93% and decreased electrochemical area by 95%. All hairy carbon required no binder, in contrast to conventional carbon black. Hairy carbon black and hairy graphite particles are particulate in nature, in contrast to the fibrous nature of carbon fibers and carbon filaments.

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