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Preparation of conductive carbons with high surface area

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Abstract

The preparation of graphitized carbons with high specific surface area was achieved by graphitization, followed by ozone treatment and then activation. This method gave a higher specific surface area, but less structural order, than that involving activation, followed by graphitization and then a second activation (needed because the preceding graphitization step greatly diminished the specific surface area). Excluding the ozone treatment step resulted in low specific surface areas, though it yielded carbons with more structural order. The ozone treatment increased the surface oxygen content of all carbons. At any stage of the treatments, catalytically grown submicron carbon filaments exhibited much larger pore size and pore volume and lower d_{002} than PAN-based or pitch-based carbon fibers. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: A. Carbon fibers; Carbon filaments; B. Activation; Graphitization; C. Surface areas

1. Introduction

Porous carbon fibers are used in environmental pollution control due to their high adsorption volume and fast adsorption and desorption rates [1–3]. In many applications, a high specific surface area and good electrical conductivity (associated with structural order [4]) are required.

A graphitized carbon maintains its structure (conductivity) after activation, though the specific surface area remains low. On the other hand, a carbon which has not been graphitized becomes less ordered after activation, though its specific surface area is high after activation [6]. Producing carbons with both structural order (high conductivity) and a porous surface structure is a challenge.

In this study, two methods were used to prepare graphitized carbon with high specific surface area: (1) Activating graphitized carbon after ozone treatment; (2) activating carbon which has not been graphitized, followed by graphitization and second activation. The second method is more conventional that the first, as it is well known that carbon which has not been graphitized can be activated more easily than carbon which has been graphitized. We found that the first method yields higher specific surface area than the second. Moreover, the first method is less expensive than the second. The crystallographic parameters d_{002} (graphite interlayer spacing, with a low value reflecting a high degree of graphitization) and L_c (crystallite domain size), as well as the electrical resistivity, were used to monitor the degree of structural order.

2. Experimental

PAN-based carbon fibers (Sample 1), mesophase pitch-based carbon fibers (Sample 2) (both Samples 1 and 2 provided by Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, P.R. China) and 0.1 μm diameter carbon filaments grown from methane gas using an iron-based catalyst (Sample 3) (provided by Applied Sciences Inc., Cedarville, Ohio) were used in this study.

All the samples were cleaned by washing them with acetone at room temperature before any treatment. The carbon filaments as received were covered by some tar oil produced during the process of filament fabrication. To cleanse them, the filaments were immersed in acetone and stirred for 10 min. The filaments were separated from the acetone by pouring the mixture through filter paper. This was repeated four times. Then the filaments were heated in an oven at 120°C for 6 h. Only 0.2% by weight was lost by each sample as a result of the acetone washing step.

The basic properties of the three samples are shown in

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Table 1
Properties of samples without treatment

Sample No.	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (Å)	d_{002} (Å)	L_c[a] (002) (Å)	Electrical resistivity (10^{-3} Ωcm)
1	6.8	0.0031	18.2	3.441	21.9	2.6
2	5.03	0.0024	19.1	3.432	125.2	2.1
3	53.9	0.1101	81.7	3.367	89.2	/

[a] Height of parallel stacking domain, calculated from halfwidth of the 002 diffraction peak using Scherrer's formula.

Table 1. The BET surface area, pore volume and BJH pore diameter were determined by N_2 adsorption at 77 K using the ASAP 2010 analyzer produced by Micromeritics (Norcross, GA). Before adsorption analyses, samples were degassed at 150°C in vacuum for 3 h.

Graphitization was conducted in a tube furnace at 2800°C by flowing argon gas for 20 min; the heating rate was 25°C/min. Ozone treatment was conducted by exposure to flowing ozone gas (0.3 vol. % in air) at 175°C for 7 min. Activation was achieved by heating in flowing nitrogen gas to 970°C at 3°C/min, and then heating in CO_2+N_2 in 1:1 volume ratio at 970°C for either 30 or 45 min [5]. The 30 min time was used for activation before graphitization; the 45 min time was used for activation after graphitization.

ESCA (Electron Spectroscopy for Chemical Analysis, spot size 1000 μm, monochromatized Al Kα X-ray) was used to observe the surface functional groups. The crystallographic parameters d_{002} and L_c were measured by using a Siemens X-ray Diffractometer, with Cu Kα radiation. The 2θ scan rate was 0.02° per s.

The surface microstructure was observed by scanning electron microscopy (SEM) for Samples 1 and 2 only. This was conducted by using a Hitachi S-4000 field emission SEM, operated at 30 KeV. Samples had not been coated prior to SEM observation.

Electrical resistivity measurement was conducted on single fibers (Samples 1 and 2 only) by using the four-probe method and silver paint for electrical contacts; the distance between the inner probes was 1 cm. Due to the small diameter, single filament electrical resistivity measurement and SEM microstructural examination were not conducted for Sample 3. Four specimens were tested in terms of the electrical resistivity for each of Samples 1 and 2.

3. Results and discussion

For Sample 3 (carbon filaments) after any heat treatment, including activation and graphitization, no inorganic contaminant (e.g., iron) was observed by ESCA. This

Table 2
Properties of samples after graphitization at 2800°C

Sample No.	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (Å)	d_{002} (Å)	L_c (002) (Å)	Electrical resistivity (10^{-3} Ωcm)
1	0.5	#[a]	/	3.411	61.2	1.7
2	0.2	/	/	3.381	321.2	0.9
3	26.4	0.0341	51.7	3.360	182.4	/

[a] Too small to be measured.

Table 3
Properties of samples after graphitization and activation (970°C, 45 min)

Sample No.	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (Å)	d_{002} (Å)	L_c (002) (Å)	Electrical resistivity (10^{-3} Ωcm)
1	51.1	0.0245	19.2	3.421	29.1	2.2
2	53.2	0.0275	20.8	3.398	223.4	2.0
3	80.1	0.1145	57.2	3.392	126.2	/

Table 4
Properties of samples after graphitization, O_3 treatment and then activation (970°C, 45 min)

Sample No.	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (Å)	d_{002} (Å)	L_c (002) (Å)	Electrical resistivity (10^{-3} Ωcm)
1	412.6	0.1992	19.3	3.469	19.2	3.6
2	400.2	0.2011	20.1	3.442	112.1	2.7
3	423.1	0.6212	58.7	3.421	80.6	/

indicates that the residual iron catalyst at the tip of each filament was not exposed.

Table 2 shows that the specific surface area of all samples tested was reduced after graphitization. Moreover, d_{002} values also decreased. For Samples 2 and 3, d_{002} values were close to 3.335 Å (the ideal graphite lattice parameter). Sample 2 was more graphitizable than Sample 1. In addition, L_c values increased upon graphitization; L_c was larger for Sample 2 than for Samples 1 and 3. Moreover, the electrical resistivity was decreased by graphitization for both Samples 1 and 2.

Table 3 lists the results obtained after graphitization and activation. Activation at the condition chosen increased the specific surface area of all samples, but not by much. Activation after graphitization also increased the electrical resistivity, but only to a level below that attained prior to graphitization (Table 1). Moreover, this treatment protocol decreased the crystallinity, as shown by a decrease in d_{002} and an increase in L_c. This means that the activation was made more difficult by pre-graphitization.

A comparison of Tables 3 and 4 shows the effects of O_3 treatment after graphitization, but before activation. The intermediate O_3 treatment led to higher specific surface area, pore volume and d_{002} and lower L_c. Moreover, it increased the electrical resistivity of Samples 1 and 2.

Table 5 shows that activation of as-received carbons which had not been previously graphitized yielded quite high electrical resistivity and specific surface area, although the surface area and L_c were lower and d_{002} was higher than those listed in Table 4. Subsequent to the activation of the samples described in Table 5, graphitization was performed. As shown in Table 6, graphitization following activation greatly decreased the electrical resistivity and the specific surface area, decreased d_{002} and increased L_c for all three samples. Hence, the protocol involving activation followed by graphitization failed to yield a high specific surface area. Upon a subsequent or second activation step (Table 7), the specific surface area was significantly increased, while d_{002} was increased and L_c was decreased. Hence, the second activation step was needed in order to attain a high specific surface area. However, the surface area and pore volume were lower, d_{002} was lower, L_c was higher, and the electrical resistivity was lower than those listed in Tables 4 and 5. This means that the method involving activation, graphitization and a second activation gave a lower specific surface area, but

Table 5
Properties of samples after activation (970°C, 30 min)

Sample No.	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (Å)	d_{002} (Å)	L_c (002) (Å)	Electrical resistivity (10^{-3} Ωcm)
1	387.3	0.177	18.3	3.510	6.9	6.1
2	326.1	0.1565	19.2	3.489	73.4	4.2
3	298.5	0.4274	57.3	3.481	47.8	/

Table 6
Properties of samples after activation (970°C, 30 min) and graphitization

Sample No.	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (Å)	d_{002} (Å)	L_c (002) (Å)	Electrical resistivity (10^{-3} Ωcm)
1	1.2	/	/	3.426	53.7	2.4
2	0.9	/	/	3.394	286.5	2.1
3	31.2	0.0447	57.3	3.362	148.1	/

Table 7
Properties of samples after activation (970°C, 30 min), graphitization and then a second activation (970°C, 45 min)

Sample No.	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (Å)	d_{002} (Å)	L_c (002) (Å)	Electrical resistivity (10^{-3} Ωcm)
1	294.3	0.155	21.1	3.427	23.1	3.1
2	246.6	0.1394	22.6	3.431	180.2	2.0
3	227.1	0.3354	59.1	3.401	109.8	/

greater structural order, than the method involving graphitization, ozone treatment and activation and the method of simple activation.

Comparison among the three types of carbons (Samples 1, 2 and 3) shows that, at any stage of the treatments, catalytically grown carbon filaments exhibited much larger pore size and pore volume and lower d_{002} than the other two types of carbons (PAN-based and pitch-based carbon fibers). Catalytically grown carbon filaments, with a higher initial surface area (Table 1), responded particularly well to the method involving graphitization, ozone treatment and activation (Table 4), yielding a higher specific surface area than the other two types of carbons. PAN-based carbon fibers responded to the method involving activation, graphitization and second activation better than the other two types of carbons, as shown by the relatively high specific surface area attained by Sample 1 (Table 7). Nevertheless, for all three types of carbon, the method involving graphitization, ozone treatment and activation (Table 4) gave higher specific surface area, higher pore volume, higher d_{002} and lower L_c than the method involving activation, graphitization and a second activation (Table 7).

Table 8 shows that ozone treatment after graphitization increased the surface oxygen-containing functional groups in the form of C–O. This treatment is believed to facilitate activation.

Fig. 1 shows SEM photographs of Sample 1. In the as-received state, the surface was featureless (Fig. 1(a), Table 1). After graphitization at 2800°C, the surface exhibited striations along the fiber axis (Fig. 1(b), Table 2). After graphitization and activation (970°C, 45 min), the surface became a little rougher (Fig. 1(c), Table 3). After graphitization, O_3 treatment and then activation (970°C, 45 min), the surface was even rougher (Fig. 1(d), Table 4) than that produced by excluding the O_3 treatment (Fig. 1(c), Table 3). In contrast, after simple activation (970°C, 30 min) the surface was featureless (Fig. 1(e), Table 5). After activation (970°C, 30 min) and graphitization, the surface exhibited striations along the fiber axis (Fig. 1(f), Table 6). After activation (970°C, 30 min), graphitization and then a second activation (970°C, 45 min), the surface became a little rough and the surface striations were almost absent (Fig. 1(g), Table 7). Similar surface microstructural effects were observed for Sample 2. These effects are as expected for graphitization, which results in striations in the fiber axis [7], and for activation, which roughens the surface [8].

Table 8
Effects of O_3 treatment (after graphitization) on surface composition indicated by ESCA

Sample No.	Before O_3 treatment (at. %)			After O_3 treatment (at. %)		
	$(C–H)_n^a$	C–O	C=O	$(C–H)_n^a$	C–O	C=O
1	99.2	0.8	0	91.7	8.3	0
2	98.7	1.3	0	92.1	7.9	0
3	98.1	1.9	0	91.6	8.4	0

[a] $(C–H)_n$ includes C–H and C–C.

4. Conclusion

Methods for the preparation of highly conductive activated carbons were studied. The carbons studied included PAN-based carbon fibers, mesophase pitch-based carbon fibers and catalytically grown 0.1 μm diameter carbon filaments. All three types of carbon responded similarly to the various treatments employed. The method involving activation, graphitization and a second activation gave carbons with a lower specific surface area, but more structural order, than that involving graphitization, ozone treatment and activation. The second activation in the former method was essential, as the preceding graphitization step greatly diminished the specific surface area, which had been quite high after the first activation step. The ozone treatment in the latter method was essential; excluding this step resulted in carbons with a low specific surface area, though with more structural order. The ozone treatment resulted in an increase in the surface oxygen content, specifically in the form of functional groups involving C–O. This treatment facilitated activation. At any stage of the treatments, catalytically grown carbon filaments exhibited much larger pore size and pore volume and lower d_{002} than PAN-based or pitch-based carbon fibers.

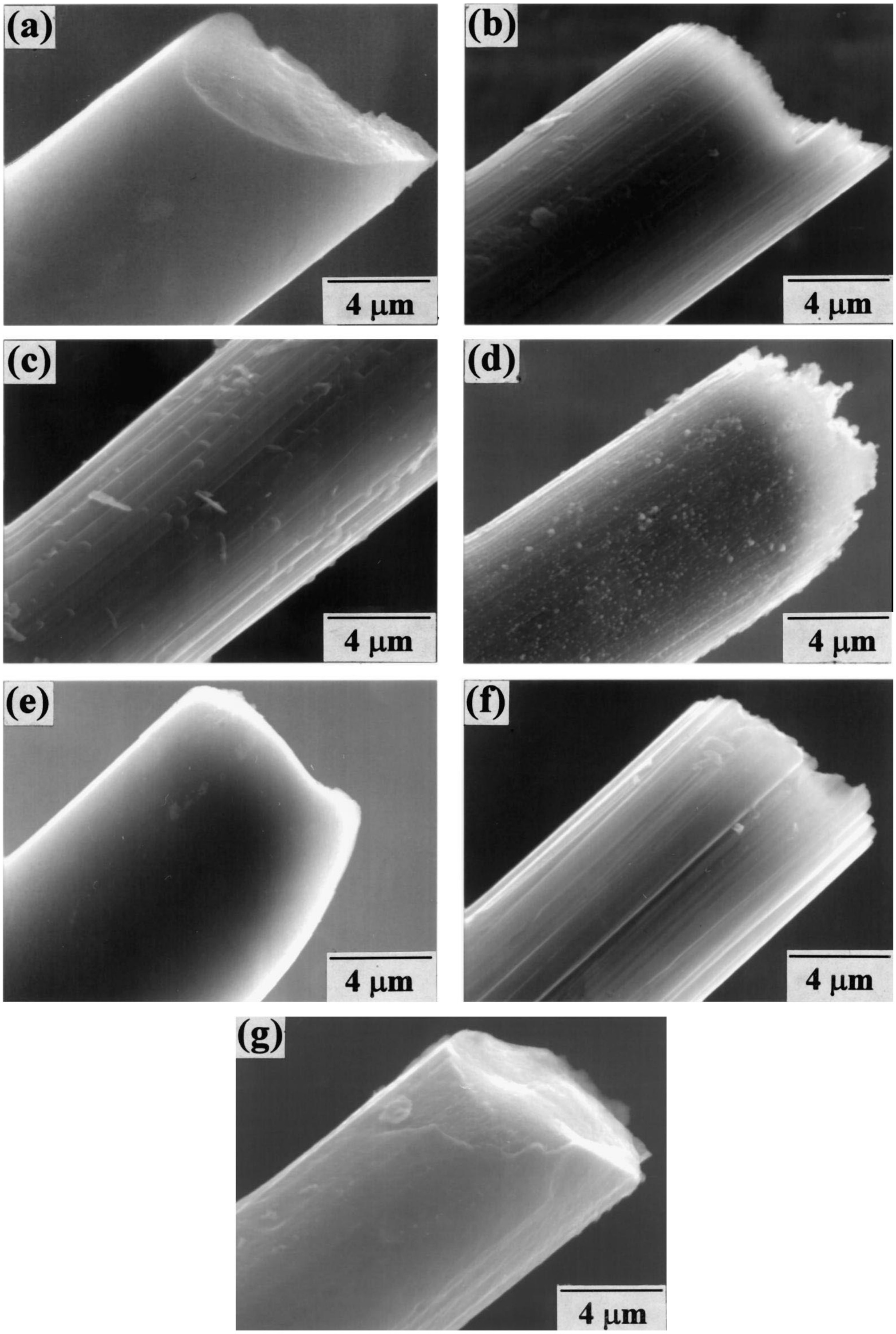

Fig. 1. SEM photographs of Sample 1 at conditions given in (a) Table 1, (b) Table 2, (c) Table 3, (d) Table 4, (e) Table 5, (f) Table 6 and (g) Table 7.

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