

# PREPARATION OF ACTIVATED GRAPHITIZED CARBONS

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## Introduction

Porous carbon fibers are used in environmental pollution control due to its 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 is low. On the other hand, a carbon which has not been graphitized becomes less ordered after activation, though its specific surface area is high [6]. Having 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 than 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  $d_{002}$  (a low value reflecting a high degree of graphitization) and  $L_c$  (crystallite domain size) were used to indicate the degree of structural order, which is expected to enhance the electrical conductivity.

## Experimental Methods

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 catalytically grown 0.1  $\mu\text{m}$ -diameter carbon filaments (Sample 3) (provided by Applied Sciences Inc., Cedarville, Ohio) were used in this paper. All samples were cleaned by acetone before any heat treatment. Sample 3 has much higher specific surface area, pore volume and pore size than Samples 1 and 2. Sample 1 has lower  $L_c$  than Samples 2 and 3. Sample 3 has much lower  $d_{002}$  than Samples 1 and 2.

Graphitization was conducted at 2800°C in Ar for 20 min; the heating rate was 25°C/min. Ozone treatment was conducted by exposure to O<sub>3</sub> gas (0.3 vol.% in air) at 175°C for 7 min. Activation was achieved by heating in N<sub>2</sub> to 970°C at 3°C/min, then heating in CO<sub>2</sub> + N<sub>2</sub> in 1:1 volume ratio (could have been pure CO<sub>2</sub>) 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 and x-ray diffraction (XRD) were used to observe the surface functional groups and the structure respectively.

## Results and Discussion

The specific surface area was reduced after graphitization. Moreover,  $d_{002}$  was decreased. For Samples 2 and 3,  $d_{002}$  values were close to 3.335Å (the ideal graphite lattice parameter). Sample 2 was more graphitizable than Sample 1. In addition,  $L_c$  was increased after graphitization;  $L_c$  was larger for Sample 2 than Samples 1 and 3. Subsequent activation increased the specific surface area, but not very much. It also decreased the crystallinity, as shown by increased  $d_{002}$  and  $L_c$ . Table 1 gives the effects of O<sub>3</sub> treatment after graphitization, but before activation. The O<sub>3</sub> treatment increased the specific surface area, pore volume and  $d_{002}$  and decreased  $L_c$ .

Activation of carbons which had not been graphitized yielded quite high specific surface area, although the surface area and  $L_c$  were lower and  $d_{002}$  was higher than those in Table 1. Subsequent to the activation, graphitization was performed. Graphitization greatly decreased the specific surface area, decreased  $d_{002}$  and increased  $L_c$ . Hence, activation followed by graphitization was not able to yield a high specific surface area. Upon subsequent second activation (Table 2), the specific surface area was much increased, while  $d_{002}$  was increased and  $L_c$  was decreased. Hence, the second activation was needed in order to attain a high specific surface area; the surface area and pore volume were lower,  $d_{002}$  was lower and  $L_c$  was higher than those in Table 1. This means that the method involving activation, graphitization and second activation gave lower specific surface area, but more structural order, than the method involving graphitization, ozone treatment and activation.

Table 1 Properties of samples after graphitization, O<sub>3</sub> treatment and then activation (970°C, 45 min)

Sample No.	Specific surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Pore size (Å)	d <sub>002</sub> (Å)	L <sub>c</sub> (002) (Å)
1	412.6	0.199	19.3	3.469	19.2
2	400.2	0.201	20.1	3.442	112.1
3	423.1	0.621	58.7	3.421	80.6

Table 2 Properties of samples after activation (970°C, 30 min), graphitization and then second activation (970°C, 45 min)

Sample No.	Specific surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Pore size (Å)	d <sub>002</sub> (Å)	L <sub>c</sub> (002) (Å)
1	294.3	0.155	21.1	3.427	23.1
2	246.6	0.139	22.6	3.431	180.2
3	227.7	0.335	59.1	3.401	109.8

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<sub>002</sub> than the other two types of carbons (PAN-based and pitch-based carbon fibers). Catalytically grown carbon filaments responded particularly well to the method involving graphitization, ozone treatment and activation, yielding 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. Nevertheless, for all three types of carbons, the method involving graphitization, ozone treatment and activation gave higher specific surface area, higher pore volume, higher d<sub>002</sub> and lower L<sub>c</sub> than the method involving activation, graphitization and second activation.

Ozone treatment increased the surface oxygen-containing functional groups in the form of C-O. These functional groups are believed to facilitate activation.

### Conclusion

The preparation of activated graphitized carbons was studied. The carbons included PAN-based carbon fibers, mesophase pitch-based carbon fibers and catalytically grown 0.1 μm-diameter carbon filaments. All three types of carbons responded similarly to the various treatments. The method involving activation, graphitization and then second activation gave lower specific surface area, but

more structural order, than that involving graphitization, ozone treatment and then activation. The second activation in the former method was essential, as the preceding graphitization step greatly diminished the specific surface area, which was quite high after the first activation. The ozone treatment in the latter method was essential; skipping this step resulted in a low specific surface area, though more structural order. The ozone treatment resulted in an increase in the surface oxygen content, specifically oxygen in the form of functional groups involving C-O. The surface oxygen facilitated activation. At any stage of the treatments, catalytically grown carbon filaments exhibited much larger pore size and pore volume and lower d<sub>002</sub> than PAN-based or pitch-based carbon fibers.

### References

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