

UNIFORM ACTIVATION OF LARGE CARBON FIBER COMPOSITES

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Introduction

High surface area activated carbon fiber composites have been produced with high permeabilities for applications in gas separation and water treatment. The project involves a collaboration between the Oak Ridge National Laboratory (ORNL) and the Center for Applied Energy Research (CAER), University of Kentucky.

One of the main objectives in this work has been to find a satisfactory means to uniformly activate large samples of formed composite. Attempts have been made using activation in steam and CO₂, and a less conventional method that was first described by Nandi et al¹ and has been researched more recently by Quinn et al². The procedure involves the chemisorption of oxygen at low temperatures (e.g.<250°C) followed by heat treatment in nitrogen or other inert gas at temperatures up to about 900°C. It appears that slow oxygen chemisorption produces a uniform distribution of surface oxygen groups that are then thermally decomposed to remove carbon as CO and CO₂. Because of the limited oxygen uptake at low temperatures it is necessary to complete several cycles before there is appreciable surface area development.

In this paper, we describe the effect of the different activation methods on the development of surface area in activated carbon fiber composites, and its variation through the body of the composite.

Experimental

Samples of carbon fiber composite were produced at ORNL using milled carbon fiber produced from petroleum pitch (P-200; ~ 17.5 micron diameter; average length 380micron; supplied by courtesy of Ashland Carbon Fibers Division, Ashland Inc.). The composites were formed by methods described elsewhere^{3,4} and were heat treated to 650°C. Smaller specimens were cut from the parent sample(15x20x5cm), each measuring approximately 6cm x 10cm x 5cm and weighing up to 150 g. In attempting to uniformly activate the composites in steam or CO₂ different reactor configurations have been investigated. In a more successful arrangement, steam is

introduced at several points along the length of the composite. The activation temperature was varied from 800-900°C for reaction times from 0.5-3 hrs. Activation in CO₂ was carried out at temperatures from 850-950°C, for reaction times of 1-3 hours. The flow rate of pure CO₂ was varied from 2-3 l/min with the same multiple point gas introduction configuration.

For activation by oxygen chemisorption/heat treatment, the samples were exposed to an atmosphere of 50% O₂ in N₂ at temperatures ranging from 170-240°C for periods of 1-6 hours. The samples were subsequently heat treated in inert atmosphere at temperatures from 800-900°C for 1-3 hours to develop porosity. Surface area and pore size distributions were measured by adsorption of nitrogen at 77K. Surface areas were determined from the isotherms by the BET method, and pore volumes by the D-R method (micropores) and the BJH method (mesopores)⁵.

Results and Discussion

The uniformity of surface area development in steam activated samples is shown by the data in Table 1. The surface area was measured at three different points A, B and C, and only the two extreme results are reported. The standard deviation of all three measurements is also reported in Table 1. In some cases the deviation was within experimental error ($\pm 2\%$), but in most cases it exceeded this value. The variation in surface area was lower for CO₂ activation, which may relate to the slower rate of reaction.

Based upon these results, it was considered that the oxygen chemisorption-heat treatment technique could help to improve the uniformity of activation. Since chemisorption is performed at temperatures where there is no carbon burn-off, the amount of oxygen uptake will reach a limiting value. As long as sufficient time is allowed for the oxygen to diffuse to all of the available surface, the extent of chemisorption will be uniform throughout the sample. Similarly, upon heat treatment, the removal of carbon as CO_x will also be uniform. The surface area development over positions A-C in two different samples is shown in Table 2 for one heat treatment cycle. The standard deviation in

surface area in both cases is very small and close to the experimental reproducibility.

By repeating the cycles of oxygen chemisorption and heat treatment, the surface area increases slightly with each step, Figure 2. It is evident that for each cycle of activation, new micropores are opened, and the porosity development is found to be very uniform. It also seems possible that this treatment could lead to a narrow pore size distribution which implies that higher surface areas would be obtained at lower burn-off than with steam or CO₂ activation. A disadvantage is the extended processing time.

Table 1: Uniformity of surface area in steam activated carbon fiber composites (44% H₂O/ 56% N₂; 100% CO₂)

Burn off (%)	Act. temp (°C)	BETs.a. range (m ² /g)	st.dev in BET s.a (%)
<i>Steam</i>			
19	877	465-568	10
19	877	734-1101	18
25	900	812-867	5
27	800	762-865	9
41	877	1089-1109	1
<i>CO₂</i>			
11	900	443-426	5
20	900	632-578	6

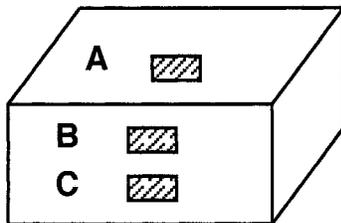


Figure 1: Schematic of composite sample indicating position of sample for surface area measurement.

Table 2: Surface area development in activated carbon fiber composites produced by chemisorption.

HTT(°C)	B.off (wt%)	BET (m ² /g)	micporev. (cc/g)	st.dev (%)	
250/900	6	A	408	0.21	6
		B	391	0.2	
		C	362	0.18	
250/925	6	A	225	0.13	3
		B	227	0.12	
		C	238	0.14	

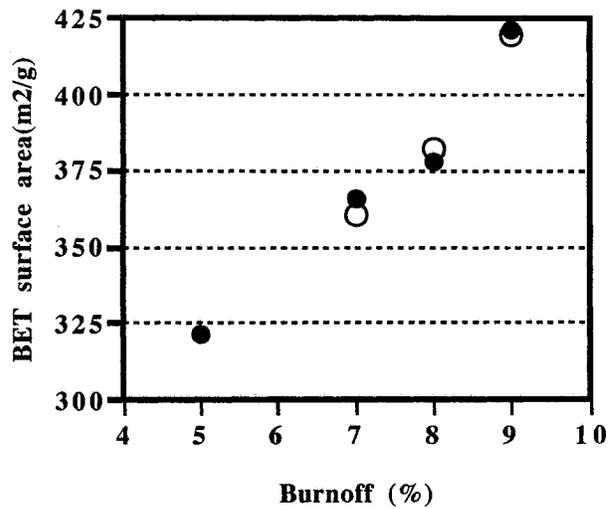


Figure 2: Surface area development during activation by oxygen chemisorption at 250°C followed by carbonization at 900°C. [Open and filled circles indicate two different sub-samples from one composite]

References

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