

# MESOPOROUS ACTIVATED CARBON FIBERS WITH HIGH SURFACE AREA FOR SUPERCAPACITORS

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## Abstract

In this paper, highly mesoporous activated carbon fibers with high surface area were prepared from polyacrylonitrile (PAN) fibers by NaOH activation, and their electrochemical performances in EDLCs with 7 mol.L<sup>-1</sup> KOH as electrolyte were evaluated. The BET surface area of the as-prepared ACF can reach as high as 3291 m<sup>2</sup>.g<sup>-1</sup> with highly mesoporous structure (mesopore volume percentage 66.7%). Their specific capacitance in aqueous electrolyte can reach as high as 371 F.g<sup>-1</sup>, and it remains 213 F.g<sup>-1</sup> as the current density increases to 10 000 mA.g<sup>-1</sup>. The high capacitance and good rate performances can be attributed to their outstanding high surface area and highly accessible pore size.

## Introduction

Electric double layer capacitors (EDLCs) are promising rechargeable power sources, which have attracted great attentions in recent years because its wide potential applications in electric vehicles and other high-power apparatuses due to their high power density and long cycle life. Porous carbons, such as activated carbon, carbon aerogels and carbon nanotubes, have been used as electrode materials for EDLCs. In general, the capacitance of the carbon electrodes is proportional to their specific surface area. However, only the surface of the pores large enough that the ions can access can contribute to the double layer capacitance. In addition, the larger the pore, the better the mobility of ions in the pores, and hence the higher power density can be delivered. That is to say, the carbon electrode for high performance EDLCs should possess not only high surface area but also large pore size, which poses a challenge for carbon preparation. In this paper, highly mesoporous activated carbons with high surface area were prepared from polyacrylonitrile (PAN) fibers by NaOH activation, and their electrochemical capacitive performances in 7 mol.L<sup>-1</sup> KOH aqueous electrolyte were evaluated.

## Experimental

Polyacrylonitrile (PAN) fibers and NaOH were used as the starting materials and activating agent, respectively. After preoxidized and carbonized, the fibers were soaked in concentrated solution of NaOH under vacuum for several hours. After dried at 150 °C for 5 h, the fibers containing NaOH were put into the tubular furnace and activated at 600 °C for 1 h. The activated samples were washed with 0.5 mol.L<sup>-1</sup> HCl, hot water and distilled water in sequence to remove the residual alkali completely. After dried at 120 °C for 12 h, the final ACFs were obtained. The weight ratio of NaOH to precursor (R value) varies in 1~6:1. The specific surface area and pore structure of the samples were determined by nitrogen adsorption/desorption isotherms at 77 K (Quantachrome Co., NOVA 1200).

For evaluating the electrochemical properties of the ACFs, button-type capacitor was assembled with two carbon electrodes which prepared as pellets by pressing a mixture of ACF with acetylene black and PTFE binder, using 7 mol.L<sup>-1</sup> KOH as electrolyte. The galvanostatic charge/discharge was carried out on a Land cell tester. The capacitors were cycled between 0 and 1.0 V. The specific capacitance ( $C$ ) of a single carbon electrode was determined with the formula  $C = 2It/\Delta Vm$ , where  $I$  is the discharge current,  $t$  the discharge time,  $\Delta V$  the potential change in discharge and  $m$  the mass of the active electrode material.

## Results and discussion

### Characterization of porous structure

Figure 1 shows  $N_2$  adsorption isotherms of the ACFs measured using an automatic adsorption system (Quantachrome Co., NOVA 1200). The shape of the isotherms varies remarkably with R value. ACF1 and ACF2 are type I isotherms according to the IUPAC classification, in which the knee of the isotherms occurs at very low relative pressure ( $p/p_0 < 0.05$ ) and the plateau is fairly flat, indicating typical microporous materials. The isotherm of ACF3 is different from that of ACF1 and ACF2, in which the knee is glasis, and the slope of the plateau increases due to multi-layer adsorption, suggesting the presence of larger micropores and mesopores. When the R value increases to over 4, dramatic changes can be observed. The isotherms of ACF4, ACF5 and ACF6 exhibit a linear increase until  $p/p_0 = 0.5-0.6$ . The widely opened knees and the slowly increasing slopes of the “plateau” during high relative pressure ( $p/p_0 > 0.6$ ) indicate that a considerable amount of mesopores are present in these samples.

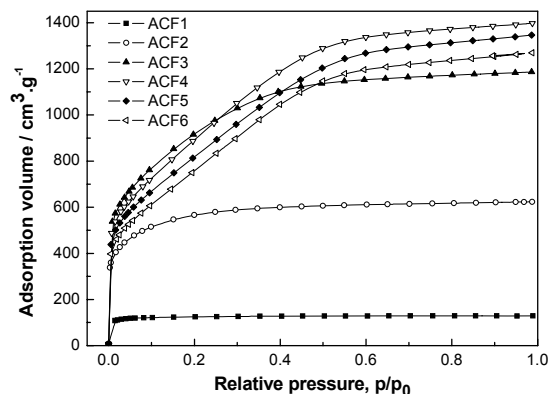


Figure 1.  $N_2$  Adsorption Isotherms of the ACF Samples.

Figure 2 shows the pore size distribution of the ACF samples calculated by density function theory (DFT) method, which are in good accordance with the results of the adsorption isotherms in Figure 1. Sample ACF1 and ACF2 are microporous with a unimodal distribution around 1 nm. For the R value over 3, the ACFs have a more dispersed pore size distribution over the wide range from 0.5-5 nm, with bimodal at  $\sim 1.5$  and  $\sim 3$  nm, indicating highly microporous and mesoporous materials.

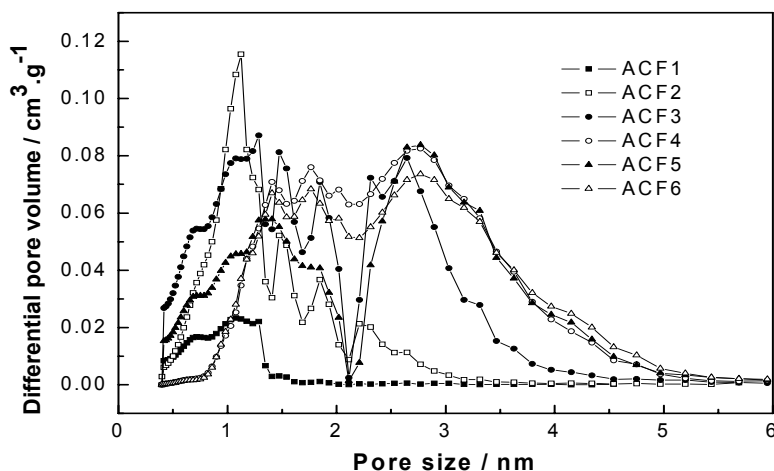


Figure 2. Pore Size Distribution of the ACF Samples.

The yield and pore characteristics of ACFs prepared with different R value are summarized in Table 1. It can be seen that the higher the R value the lower the yields. The BET surface area increases with R value and reaches its maximum value  $3291 \text{ m}^2 \cdot \text{g}^{-1}$  at the R value 4, then decrease slightly with the further increase of R value. The total pore volume shows same tendency as BET surface area with a maximum value of  $2.162 \text{ cm}^3 \cdot \text{g}^{-1}$ . The mesopore percentage and average diameter all

increase with R value. It is well-known that there are two mechanisms involved in chemical activation process, pore formation mechanism and pore widening mechanism. Pore widening usually begins when a number of opened pores already exist and the chemical activation agent is abundant inside the pores. In this work, when the R value increases to 3, pore widening becomes to be significant, so the mesopore volume increased while the micropore volume decreased. As the R value is further increased, the abundant alkali etched off some of the pore walls entirely, resulting in the decreasing of specific surface area and total pore volume. As far as the specific surface area and mesopore volume are concerned, the optimum R value should be 4. At this condition, highly mesoporous (the percentage of mesopore volume to total pore volume 66.7%) ACFs with high surface area ( $3291 \text{ m}^2 \cdot \text{g}^{-1}$ ) have been obtained, and the yield of 27.1 % is also acceptable.

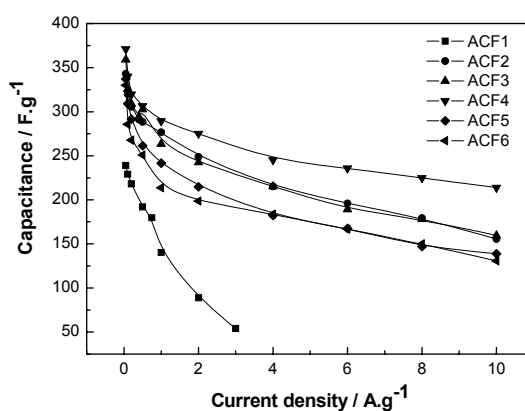
**Table.1** Pore Characteristics and Capacitance of the Activated Carbon Fibers.

Sample	Ratio	Yield (%)	SBET ( $\text{m}^2 \cdot \text{g}^{-1}$ )	Pore volume ( $\text{cm}^3 \cdot \text{g}^{-1}$ )			Mesopore percentage (%)	Average diameter (nm)	Capacitance ( $\text{F} \cdot \text{g}^{-1}$ )
				Total	Micro	Meso			
ACF1	1	87.0	498	0.199	0.193	0.006	3.0	1.599	239
ACF2	2	45.5	2085	0.964	0.834	0.130	13.5	1.850	344
ACF3	3	34.0	3211	1.835	1.060	0.775	42.2	2.285	356
ACF4	4	27.1	3291	2.162	0.721	1.441	66.7	2.627	371
ACF5	5	19.2	3001	2.083	0.583	1.500	72.0	2.776	337
ACF6	6	15.6	2839	1.964	0.505	1.459	74.3	2.767	330

### Electrochemical performances

Galvanostatic charge/discharge was performed to determine the capacitance of the activated carbon fibers. The voltage range of charge/discharge is limited between 1.0 and 0 V. The capacitance of the ACFs is also presented in Table 1. It can be seen that all the ACFs can provide high capacitance above  $239 \text{ F} \cdot \text{g}^{-1}$  in  $7 \text{ mol} \cdot \text{L}^{-1}$  KOH electrolyte. The specific capacitance increases with the increasing of the R ratio and reaches the maximum value of  $371 \text{ F} \cdot \text{g}^{-1}$  with R value 4, then decreases with the further increase of R ratio. To the best of our known, the highest capacitance of activated carbon in aqueous electrolyte reported before is  $320 \text{ F} \cdot \text{g}^{-1}$ . That is to say, the ACF is an attractive high capacitance electrode material for EDLCs.

Rate capability is an important feature of the EDLCs. The capacitance of the ACFs as a function of current density is shown in Figure 3. The specific capacitance of all of the ACFs but ACF1 decreases slightly with the current density increasing, indicating that these ACFs allow rapid ion diffusion. The ACF4 has a better rate capability because of its higher surface area and more developed mesoporous structure as shown in Table 1. As the current density increases from  $50 \text{ mA g}^{-1}$  to  $10\,000 \text{ mA g}^{-1}$ , its specific capacitance can remain  $213 \text{ F g}^{-1}$ , which is an attractive value for EDLCs.



**Figure 3.** Rate Performance of ACFs in  $7 \text{ mol} \cdot \text{L}^{-1}$  KOH Aqueous.

### Conclusion

Highly mesoporous activated carbon fibers with high surface area were prepared from polyacrylonitrile (PAN) fibers by NaOH activation. The BET surface area of the as-prepared ACF can reach as high as  $3291 \text{ m}^2 \cdot \text{g}^{-1}$  with highly mesoporous structure (mesopore volume percentage 66.7%). The ACFs shows a very high specific capacitance ( $371 \text{ F} \cdot \text{g}^{-1}$ ) and good rate capability in aqueous electrolyte, which can be attributed to the outstanding high surface area and the highly accessible pore size. The primary results indicate that the as-prepared ACFs are promising electrode materials for EDLCs.

## References

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