

CAPACITANCE OF CARBON NANOFIBERS ACTIVATED BY KOH

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1. INTRODUCTION:

EDLC is a kind of energy device with high power due to fast charge propagation between the negatively or positively charged plates and ions from electrolytic solution^[1]. CNFs have many advantages such as low resistivity and high stability, especially a marked mesoporous character allowed them to be proposed as attractive electrode materials for EDLC. The interconnected network of CNFs forms open mesopores, which facilitate the transportation of ions especially in organic electrolyte. However, the low surface area of CNF restricts its applications. So, CNF with high surface area is expected.

Chemical activation with alkali compounds such as KOH is a well-known method to prepare activated carbon materials with high surface area^[2-5]. Recently, carbon nanotube (CNT) was activated by KOH and NaOH to develop the porosity in CNT for its new applications^[6,7].

In this paper, CNF was activated by KOH to develop surface area and porosity. The EDLC capacitance of the resultant CNFs were investigated in 1M (C₂H₅)₄NBF₄/PC electrolyte using the two-electrode methods. The effect of surface area, pore size distribution of CNFs on EDLC was analyzed.

2. EXPERIMENTAL:

2.1 Preparation of high surface area CNF

Two kinds of CNFs were used in this paper. The pore structure of as-received CNFs was listed in Table1. The process of KOH activation of CNF was following: firstly KOH was dissolved in ethanol, secondly CNF was added in the solution, and then the solution was stirred for 50min, next the mixture was put into the oven to vaporize the ethanol, and finally the homogeneous mixture of CNF and KOH was got. Put the mixture into a Ni-pan, which was placed in a stainless steel tube reactor and then heated by a standing furnace. Activation conditions were 700-1000°C for 1h with a heating rate of 5°C /min in argon flow of 60ml/min. The activated product was washed with distilled water, filtered and dried at 105°C.

2.2 Characterization of CNFs

BET surface area and total pore volume were calculated by Nitrogen adsorption at 77K using a Sorptomatic 1990 instrument. Before adsorption the samples were outgassed at 200°C for 12hr until constant weight.

The EDLC performance was analyzed with a two-electrode configuration. The capacitor electrodes were pellets formed by pressing a mixture of CNF(80wt%)+carbon black(10wt%)+ Polytetrafluoroethylene (PTFE, 10wt%). The positive and negative electrodes of comparable mass, ranging from 15 to 25mg, are electrically isolated by a glassy fibrous separator. 1M (C₂H₅)₄NBF₄/PC solution was used as electrolyte. The test cell was charged at 2.7V at a constant current of 2.4mA and discharged at the same current until the voltage decreased to 0V. The specific capacitance was then calculated from the following equation:

$$C_w = 2.4 \times (t_2 - t_1) / [(V_1 - V_2) \times W]$$

Where W is the total amount of the carbon nanofiber of two carbon electrodes, V_1 and V_2 are discharge voltage at t_1 and t_2 time respectively.

3. RESULTS and discussion:

3.1 Pore structure of CNFs

Table 1 revealed the pore structure of different CNFs using as EDLC electrode. Nitrogen adsorption-desorption isotherms of CNFs were showed in Fig.1. Both of the adsorption isotherms of cnf1 and its activated forms were Type I, which belong to microporous carbons. While the adsorption isotherms of cnf2 and its activated forms were Type IV, having a marked hysteresis, which belong to mesoporous carbons. With the improvement of activation degree, the hysteresis loop enlarged. That is to say, the content of mesopore increased as the enhancement of surface area. Fig 2 gave the BJH pore distribution of these CNFs. It can be seen that cnf2 and its activated forms have strong pore distribution at about 2nm and 4nm, while cnf1 and its activated forms mainly contain pore less than 2nm.

3.2 Capacitance of CNFs

3.2.1 Charge-discharge properties of CNFs

The typical cycling curves of the EDLC were shown in the Fig.3. The voltage increased and decreased with the change of charge-discharge time in linearity. Compared with other cycles, the first charge time is longer. The reason is as follows: Carried by electrolyte, electric charge moved to the electrodes, penetrated into different pores of carbon electrodes, and formed electric double layer^[8]. It will take longer time to pervasion fully into the pore of CNF for electrolyte in the first charging time. In this course, more impedance should be overcome. Thus, the first charging time will be longer. With the enhancement of cycle numbers, the charge time gradually became stable. There was no obvious different between these ten cycles. Fig4 listed ten cycles charge-discharge capacity of EDLC. Discharge capacitance appeared stable from the first cycle, which showed that CNF has stable electrochemistry properties.

3.2.2 Correlation between double layer capacitance and surface area

Relationship between capacitance and surface area of CNFs was shown in Fig.5. To comparison, the capacitances of two other kinds of activated carbons were also listed in Fig.5. From this picture, it can be seen clearly that CNF has superiority when it is used as electrode of EDLC for its nano-structure. Enhanced values of capacitance were observed after KOH activation. The capacitance increased with the increasing of surface area, and the highest capacitance could reach to 32.5F/g when the surface area of CNF was 1258m²/g. CNF with higher surface area could provide more space to form double electric layer, which will enhance the ability of electric charge deposition.

Fig.5 shows that a general trend between capacitance and BET surface area exists for all the samples, although it is not a perfect linear relationship. This trend was also observed in previous studies using other carbon materials^[9,10]. These results indicate that although the BET surface area is a very important parameter, the EDLC also seems to depend on other characteristics of the CNF, probably on the pore size distribution.

3.2.3 Correlation between double layer capacitance and pore distribution

From Fig.5 it can be found that though cnf1-H2 and cnf2 have the same surface area, their capacitances were different. The capacitance of cnf1-H2 and cnf2 were 20.3F/g and 13.4F/g

respectively. This different performance of these samples can be explained considering their pore size distribution. The pore distributions of these two kind CNFs were shown in Fig.6. From BJH method pore distribution picture, it can be seen that cnf1-H2 and cnf2 have a strong pore distribution around 2nm and 3.4nm, respectively. From HK method pore distribution, cnf1-H2 and cnf2 have a strong pore distribution around 0.96nm and 1.4nm, respectively. At the same time, the average pore diameter of cnf1-H1 is smaller than that of cnf2 (see Table1). That is to say, cnf1-H2 has abundant micropore and narrow pore size compared with cnf2. So, on the condition of the entry of electrolyte, the existence of a narrow micropore pore size distribution is necessary. At the same time, OG-5A (a kind of carbon molecular sieving) has a very low capacitance compared with CNF with same surface area. This is due to its very small mean pore size, which makes the entry of the organic electrolyte difficult. The non-accessible pores do not contribute to the total double layer capacitance of the material for the ion-sieving effect^[1]. Fig.7 and Fig.8 gave the mesoporous carbons (AC-Fe-5% and AC-Fe-7%) nitrogen adsorption-desorption and BJH pore distribution curves, respectively. It can be found that these two kinds of mesoporous carbons have strong pore distribution at about 4nm, which are larger than that of CNFs. The capacitances of these mesoporous carbons only are 21F/g(S=840m²/g) and 14.8F/g (S=532m²/g) respectively, which are lower than that of CNFs with the same surface area. The results showed that abundant mesoporosity with larger size in carbon materials are not effective for double layer capacitance. So, pore distribution is another key factor on the EDLC properties.

4. Conclusions:

Carbon nanofibers with high capacitance have been prepared by KOH activation process. The results showed that capacitance increased with the surface area, reaching a maximum of 32.5F/g for the surface area of 1258m²/g. At the same time, the capacitance not only depends on surface area, but also on pore size distribution. On the condition of the entry of electrolyte, CNF with abundant micropore and narrow pore size distribution has larger capacitance.

Acknowledgements

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Table1. Pore structure of different CNFs

Sample	$S_{BET}(m^2/g)$	$V_{HK}(cm^3/g)$	$V_{BJH}(cm^3/g)$	Average diameter (nm)
cnf1	143	0.108	0.179	5
cnf1-H1	198	0.150	0.177	3.58
cnf1-H2	301	0.216	0.205	2.72
cnf1-H3	491	0.357	0.326	2.65
cnf2	300	0.447	0.560	7.47
cnf2-H1	548	0.556	0.470	3.43
cnf2-H2	866	0.773	0.646	2.98
cnf2-H3	1258	1.141	1.034	3.29

S_{BET} : BET surface area measured between 0.05-0.35 P/P_0 ;

V_{HK} : total pore volume calculated by HK method;

V_{BJH} : total pore volume calculated by BJH method;

Average diameter: calculated by $4 * V_{BJH}/S_{BET}$.

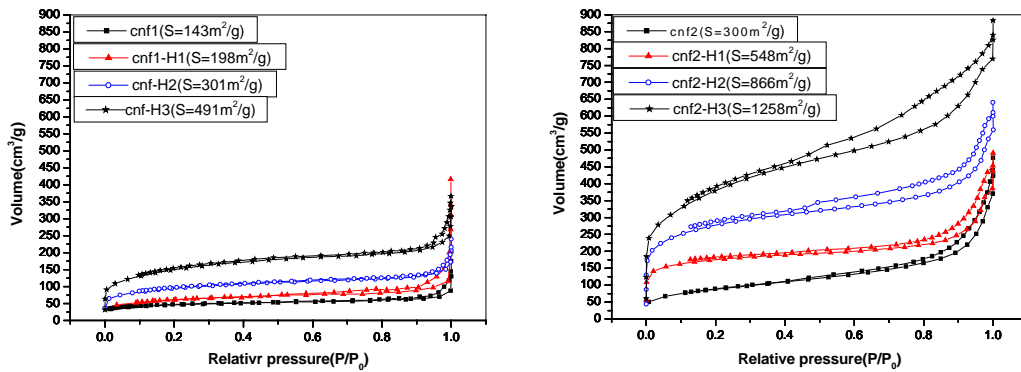


Fig.1 Nitrogen adsorption isotherms of CNFs

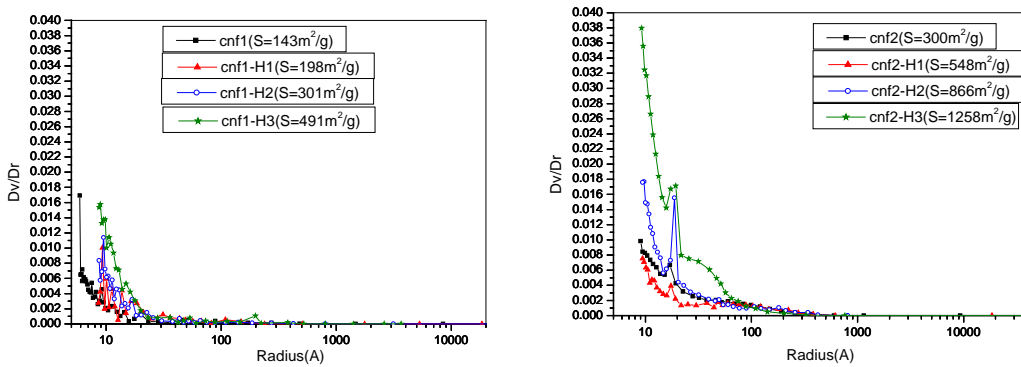


Fig.2 BJH pore distribution of different CNFs

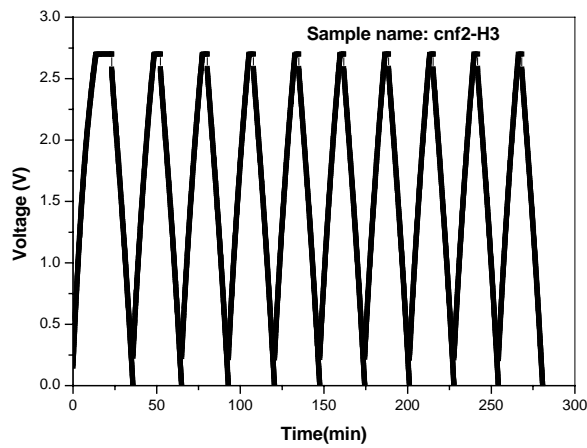


Fig.3 Cycling curves of the EDLC with CC/CV method

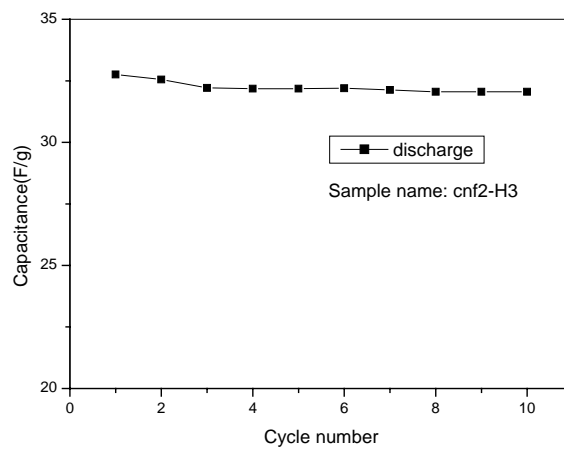


Fig.4 Influence of cycle number on the EDLC capacitance

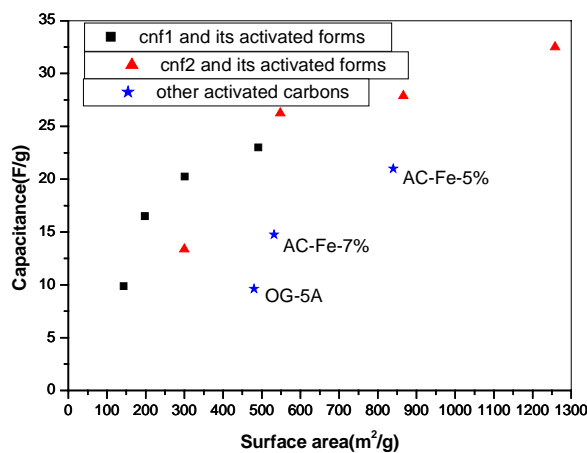


Fig.5 Relationship between capacitance and surface area of different CNFs

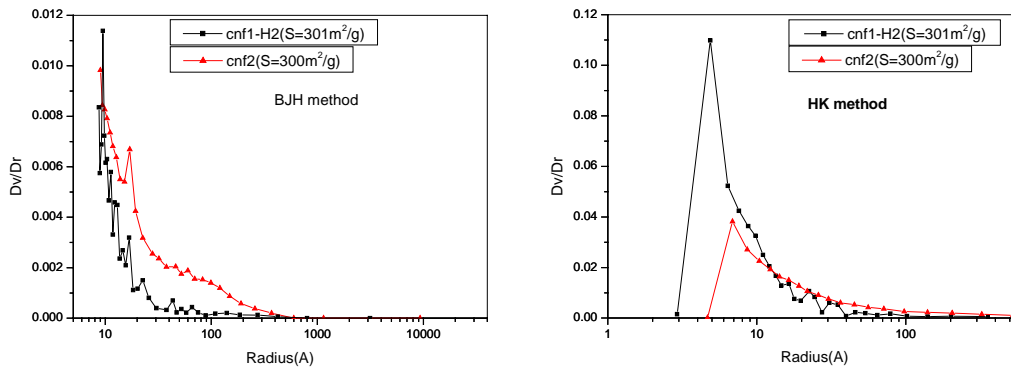


Fig.6 Pore distribution of CNFs with same surface area

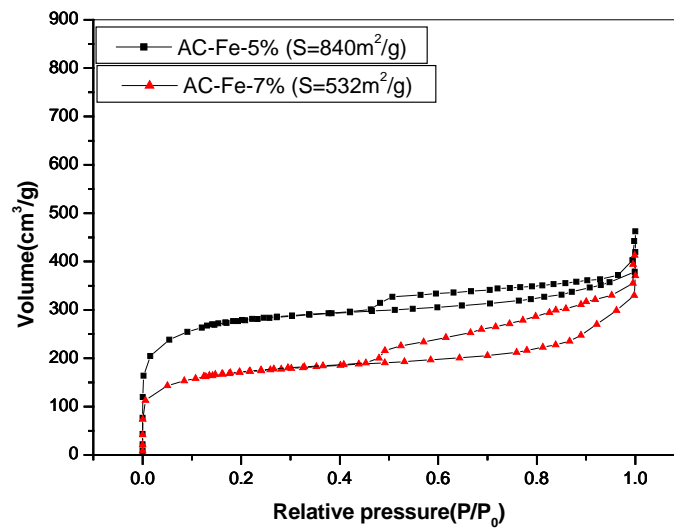


Fig.7 Nitrogen adsorption isotherms of ACs

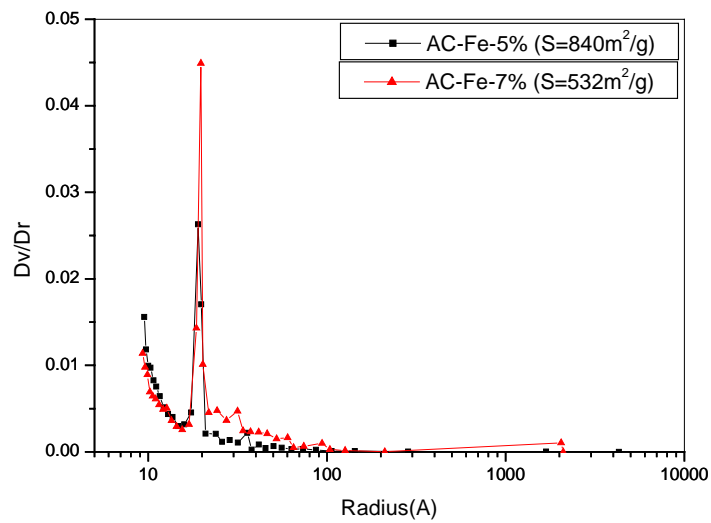


Fig.8 BJH Pore distribution of ACs