

EDLC CAPACITANCE ON THE SPECIFIC EDGE AND BASAL PLANES OF CARBON NANOFIBERS

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1. Introduction

Recently, electric double layer capacitor (EDLC) has attracted extensive interest because of its advantages such as fast charge-discharge rate, high power-density in discharging and recharging, excellent cycle lives on the order of 10^5 to 10^6 , many times those of batteries, and environmental friendliness [1-6]. Surface active carbon materials are recognized as an essential component for EDLC. EDLC properties have recognized to depend strongly upon physico-chemical properties such as surface area and pore size of carbon materials [7,8], precursor of carbon materials for carbon electrode [9,10]. In our laboratory, The present authors have developed a high performance carbon material from calcined anisotropic carbon materials through activation with NaOH and KOH for high weight as well as large volume capacitances, 50F/g and 42F/ml in organic capacitor (1M TEA/PC)].

The anisotropic carbon of high density was moderately activated with the particular alkali hydroxide. Performances of edge and basal planes on the surface of the carbon materials have been concerned on their electrochemical properties. The natures of the pore wall must be carefully controlled for the higher capacitance. The surfaces of the ordinary and stress-annealed pyrolytic graphites [11-14] have been examined to measure their capacitances. there is some shortcoming on the effect because of structural defects in the graphite. Significant preference of edge plane was recognized.

Now, the selective synthesis of carbon nanofibers (CNFs) of particular hexagon alignment has been developed. Their surfaces have been fully analyzed and their structural modification has been proposed. Such a series of materials are most suitable to clarify the effects of edge and basal planes of graphite on the EDLC properties, more accurately. CNFs have been recognized to be unique forms of carbon materials [15-18]. The diversity of CNFs has been recognized in various alignments of laminated c-lane layers along the fiber axis, which provides typically three kinds of CNFs such as platelet (alignment perpendicularly to the fiber axis), tubular (alignment parallel to it) and herringbone (alignment angled to it) CNFs. Our previous study demonstrated that the particular surfaces of platelet CNFs (PCNFs) became covered with end-loop caps by post graphitization, which carry small hexagonal planes caged in semi-spherical shape. Such caps were removed by oxidation with HNO_3 , the edge of the hexagon being exposed again [19,20].

In the study, high graphitic platelet carbon nanofibers (PCNF) with edge planes on the surfaces were prepared through the catalytic CVD. The PCNFs were modified to carry particular surfaces by graphitization and nitric acid treatment, respectively. The specific edge contents in a series of carbon nanofibers were carried out by BET surface area measurement, TEM, XRD and Raman spectroscopy. EDLC capacity of such a series of specific carbon nanofibers was examined to elucidate electrochemical behaviors of the specific graphitic edge and basal planes in organic and inorganic capacitors, respectively.

2. Experimental

2.1. Preparation and post-treatment of PCNF

PCNF was prepared from CO and H_2 mixed gases over Fe catalyst at 600°C in a conventional horizontal tube furnace. PCNF was graphitized (GPCNF) at 2800°C for 10min in Ar. GPCNF was mechanically ball-milled in ethanol for 72h (GCNF-M) or chemically

treated in 10% HNO₃ at room temperature for 24h (GCNF-NA).

2.2. Characterization of as-prepared and treated PCNFs

PCNFs were measured by an X-ray diffractometer to calculate the crystallographic parameters according to JSJP standard method [21]. The surface area was analyzed by nitrogen adsorption isotherm using BET method through Soptomatic 1990. The surface of PCNFs was observed under TEM and evaluated by Raman spectroscopy.

2.3. Measurement of specific EDLC capacitance

The specific EDLC capacitance of PCNFs was measured according to conventional three-electrode cell in 30% H₂SO₄ solution (0~0.9V) and 1M Et₄NBF₄/PC (-1.7V~1.2V), while the working electrode was composed of 95% PCNF and 5% PTFE (wt/wt). A potential sweep rate was varied from 5 to 20mV/s Ag/Ag⁺ standard electrode was used as a reference electrode. Stability of the system was confirmed by the blank test without carbon electrode. A commercial activated carbon electrode (twice in weight over working electrode) was used as a counter electrode.

3. Results

3.1. Properties of as-prepared and treated PCNFs

Table 1 summarizes the preparation conditions and some physical properties of PCNFs. PCNF prepared at a low temperature of 600°C showed very high degree of graphitization, the values of interlayer distance (d₀₀₂) and the height of stacking (L_{c002}) being 0.3363nm and 28nm, respectively. The elemental analysis of PCNF provided 0.035 of H/C atomic ratio, indicating the definite existence of C-H edges on the surface of CNF. Graphitization of PCNF resulted in little improvement of the graphitic properties by XRD, whereas no hydrogen found in the elemental analysis suggests the disappearance of the free edges. The surface area decreased markedly from 91 to 32m²/g by the graphitization. The ball-mill treatment of the GPCNF increased a little the graphitic extent and restored a quarter lost surface area. HNO₃ acid treatment of the GPCNF recovered the surface area of 66m²/g and improved significantly the graphitization extent in terms of both L_c(002) and d₀₀₂.

Figures 1 and 2 display TEM photographs of PCNFs, indicating very notable change of surface structure by three treatments. The edges of the PCNF were closed to loop-ends through the graphitization at 2800°C. The ball-milling treatment distorted and disordered the alignments of the loop-ended graphitic units. The acid treatment cut off the end-loops, consequently exposed the free edges again.

Figure 3 shows Raman spectroscopy of PCNFs. The scattering peaks at 1355 and 1580⁻¹ have been identified to reflect the basal and edge planes, respectively. According to such assignation, as-prepared PCNF and GPCNF-NA exposed the edges on their whole and major surface, respectively. The surfaces of GPCNF and GPCNF-M were covered dominantly by loop ends. The order in the ratio of I₁₃₅₅ to I₁₅₈₀ PCNF>GPCN-NA>GPCNF= GPCNF-M reflected the extent of free edges observed in their TEM images. The intense 1620cm⁻¹ bands of PCNF and GPCNF-NA were emphasized more edge-rich planes on the surfaces than those of the other PCNFs.

3.2. EDLC capacitance of as-prepared and treated PCNFs

Figure 4 shows the cyclic voltammograms of PCNFs in different electrolytic solutions (30% H₂SO₄ and 1M TEA/PC) at a scanning rate of 20mV/s. Table 2 summarized the EDLC capacitance of as-prepared and modified PCNFs with different scanning rates varied from 5mV/s to 20mV/s. All PCNFs display typical rectangular CV curves of the three-electrode cell. As-prepared PCNF showed the maximum weight capacitances of 12F/g in 30% H₂SO₄ and 8F/g 1M TEA/PC, respectively. Graphitization of PCNF (GPCNF) always provided the minimum weight capacitances around 1 to 2F/g depending on the scanning rate from 5 to 20mV/s in both electrolytic solutions. Ball-mill of GPCNF (GPCNF-M) showed a similar capacitance values as those of GPCNF. 10% HNO₃ treatment of GPCNF (GPCNF-NA)

recovered markedly both capacitances to 7-7.4F/g in H₂SO₄ and 3-3.5F/g in organic electrolytes, respectively, slightly depending on the scanning rate. The present series of PCNFs showed larger capacitance in H₂SO₄ electrolyte than in organic electrolyte.

4. Discussion

As-prepared PCNF showed a surface area of 91m²/g and free edges exposed on its surface. The graphitization of PCNF (GPCNF) led to the growth of basal planes through the connection of edges of laminated hexagonal planes to form loop-end structures, inducing the disappearance of free edges on the surface of PCNF and decreasing largely its surface area. So, the amount (surface area) basal planes can be quantified and the contribution of basal planes of graphite to the capacitance can be evaluated accurately. On the other hand, because the change of surface area of basal planes of PCNF is very little, we may assume that amount of basal planes should not change among PCNF and its modified forms. Thus, free edges of PCNF can be quantitatively determined by the difference of surface areas between total surface area and basal planes in PCNF.

According to the above consideration, the amounts of edge and basal planes in PCNFs were calculated and summarized in Table 1. As-prepared PCNF showed the maximum surface area of edge planes, about 60m²/g. Mechanical ball-milling of GPCNF induced the distortion of the closed loop ends to increase its surface area, which did not result in an increase of edge plane. The acidic oxidation treatment recovered largely the alignment of hexagonal planes to be more graphitic to increase the amount of free edge planes.

As summarized in Table 2, basal plane of graphite structure provides capacitances of 2-6uF/cm² in 30% H₂SO₄ electrolyte and 3-7uF/cm² in 1M TEA/PC electrolytic solution, respectively. However, edge plane gives larger capacitances of 18uF/cm² in 30% H₂SO₄ electrolyte and 10uF/cm² in 1M TEA/PC electrolyte, respectively. The calculated total EDLC capacitances of GPCNF-NA in different electrolytes are well coincides with the measured one.

Bauer investigated the electrochemical property of basal planes from ordinary pyrolytic graphite and gave capacitances of 12 and 60uF/cm² for cleaving and polishing, respectively [11]. Randin gave a different capacitance of 16uF/cm² for the polished basal plane of ordinary pyrolytic graphite [12]. The discrepancy was attributed to the different origin and preparation of the sample. The latter authors further studied EDLC properties of stress-annealed pyrolytic graphite and gave capacitances of 3 and 50-70 uF/cm² for basal plane (peeled off) and edge orientation (polished), respectively [11,14].

Our present study also indicates edge plane of graphite is certainly higher than basal plane, 3 and 1.4 times large for edge and basal planes for 30% H₂SO₄ and organic electrolytic solutions, respectively. The present measurement using PCNF as working electrode may reflect better the real capacitance of edge and basal planes of graphite based on the structural controllability of PCNF and quantitative analysis of amount of edge and basal planes. The capacitance of basal planes is considered as a space charge on the inside of the graphite basal plane interface and behaves like the ionic diffuse-layer capacitance in metal-electrolyte property at metals [22]. Free edges of graphite behave like that of a normal metal/solution interface where the capacitance is determined by the combination of an ionic/electronic Helmholtz compact-layer capacitance with ionic diffuse-layer capacitance, displaying a larger capacitance [22]. So, the contribution from ionic/electronic Helmholtz compact-layer to the total capacitance is certainly larger than from ionic diffuse-layer capacitance. Edge plane provides more adsorption sites to adsorb cation and anion and larger surface charge, which are responsible for large capacitances from as-prepared PCNF and GPCNF-NA. In contrast, basal plane gives less adsorption sites and smaller surface charge, providing small capacitances from GPCNF and GPCNF-M.

5. Conclusions

In summary, the present study compared the structural change of as-prepared and modified PCNFs from a view of design and control of microstructure or nanostructure of graphite. Quantitative analysis of amount of edge and basal planes of PCNF was carried out to their real capacitances, 10-18 μ F/cm² and 2-7 μ F/cm² in different electrolytes, respectively. It is very useful to understand further the electrochemical property of carbon materials, especially, to develop a high capacitance through effective modification such as activation using CNFs as starting materials.

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Table 1. Preparation conditions and some physical properties of PCNFs.

Samples	Preparation conditions	H/C	XRD properties		Surface area (m ² /g)		
			d002 (nm)	Lc(002) (nm)	Total	Edge plane	Basal plane
PCNF	As-prepared	0.035	0.3363	28	91	59	32
GPCNF	Graphitized at 2800°C	0.000	0.3363	32	32	0	32
GPCNF-M	Ball-milling for 72 h	-	0.3360	40	45	0	45
GPCNF-NA	10% HNO ₃ for 24 h	-	0.3356	137	66	34	32

Table 2 Raman characteristic values of as-prepared and modified PCNFs

	PCNF	GPCNF	GPCNF-M	GPCNF-NA
$I_{1355}/I_{1580}^{\dagger}$	1.35	0.24	0.25	0.65
$\Delta v(1580)^{\ddagger}$	30	28	27	27

[†] The intensity ratio of the 1355 cm⁻¹ (G band) to the 1580 cm⁻¹ (D band).

[‡] The full width at half maximum of the 1580 cm⁻¹ band.

Table 3 EDLC capacitance of as-prepared and modified PCNFs

Sample	Scanning rate	Electrolytic solution							
		30% H ₂ SO ₄				1M Et ₄ NBF ₄			
		EDLC capacitance*							
	mV/s	F/g		uF/cm ²		F/g		uF/cm ²	
		Measured	Calculated	Edge	Basal	Measured	Calculated	Edge	Basal
PCNF	5	12.0	12.0	18.3	3.7	7.5	7.5	10.0	5.0
	10	12.5	12.5	18.4	5.0	8.1	8.1	10.5	5.9
	20	12.0	12.0	16.9	6.2	8.4	8.4	10.3	7.2
GPCNF	5	1.2	1.2		3.7	1.6	1.6		5.0
	10	1.6	1.6		5.0	1.9	1.9		5.9
	20	2.0	2.0		6.2	2.3	2.3		7.2
GPCNF-M	5	1.0	1.0		2.2	1.4	1.4		3.1
	10	1.1	1.1		2.4	1.8	1.8		4.0
	20	1.3	1.3		2.9	2.0	2.0		4.4
GPCNF-NA	5	7.0	7.4	18.3	3.7	3.0	5.0	10.0	5.0
	10	7.4	7.8	18.4	5.0	3.5	5.5	10.5	5.9
	20	7.4	7.7	16.9	6.2	3.5	5.8	10.3	7.2

*Base: CNF. EDLC capacitances in 30% H₂SO₄ and 1M Et₄NBF₄ were calculated according to 0.3V and 0V, respectively.

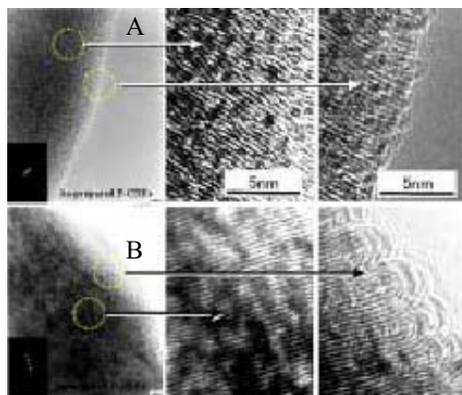


Figure 1 HR-TEM images of as-prepared and graphitized PCNFs.
A. As-prepared PCNF; B. Graphitized PCNF

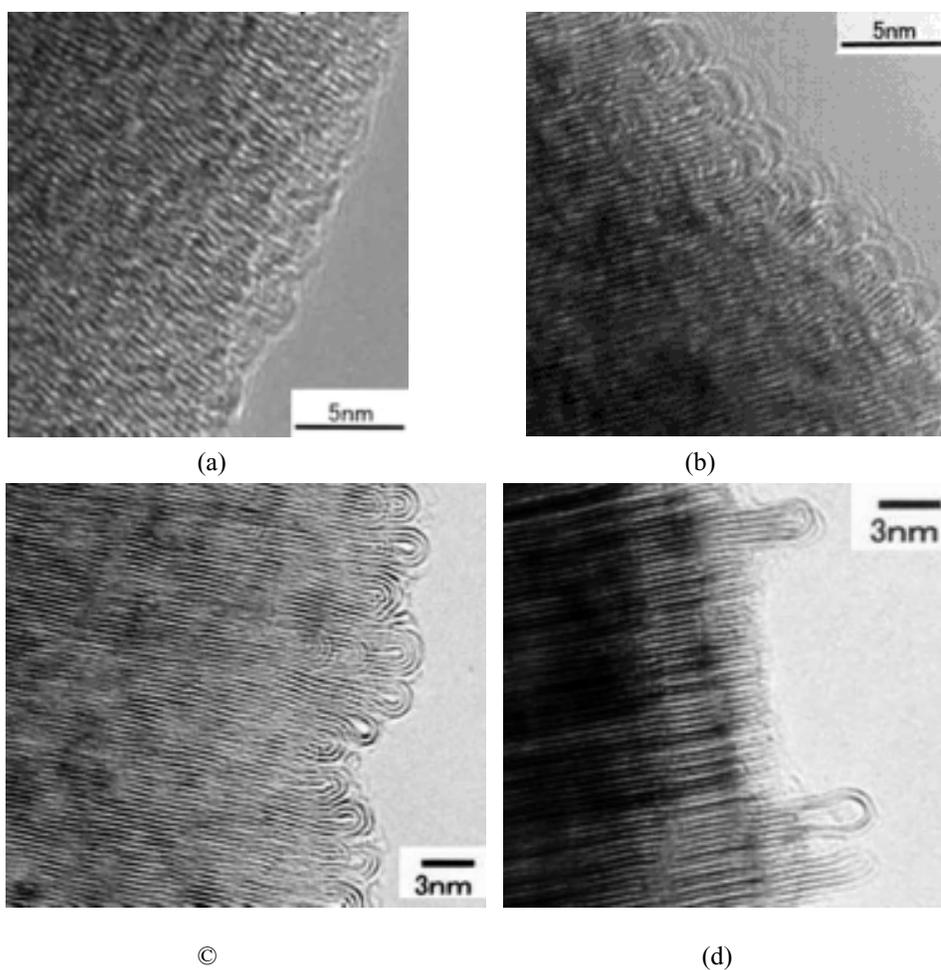


Figure 2 HR-TEM photographs of as-prepared (a), graphitized (b), graphitized and ball-milled(c) and graphitized and acid treated (d) PCNFs.

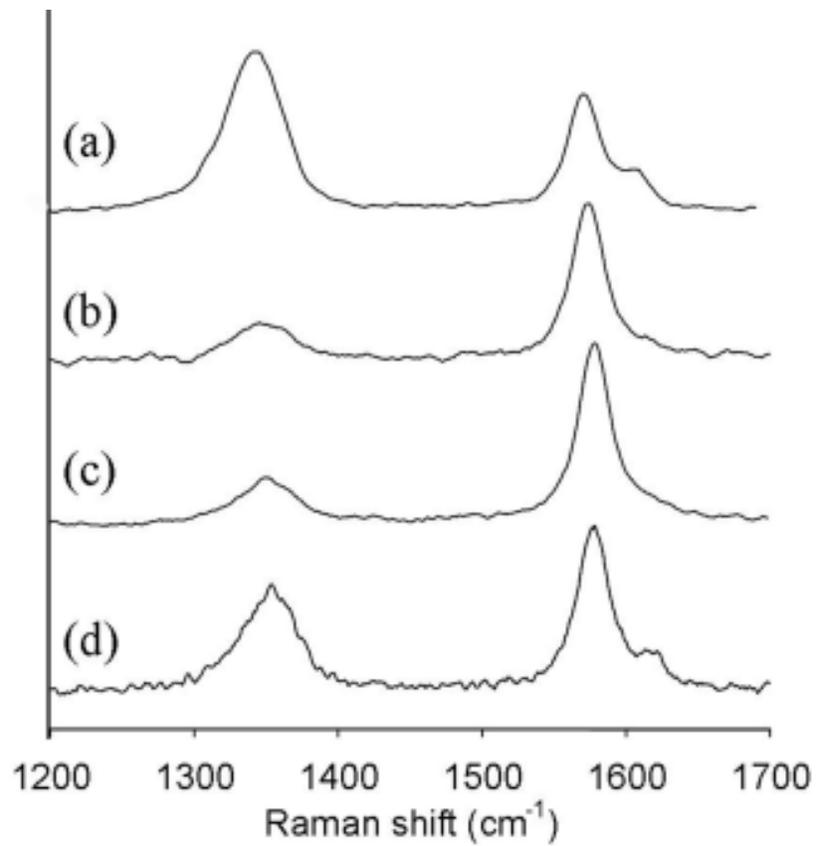


Figure 3 Raman spectra of as-prepared (a), graphitized (b), graphitized and ball-milled(c) and graphitized and acid treated (d) PCNFs.

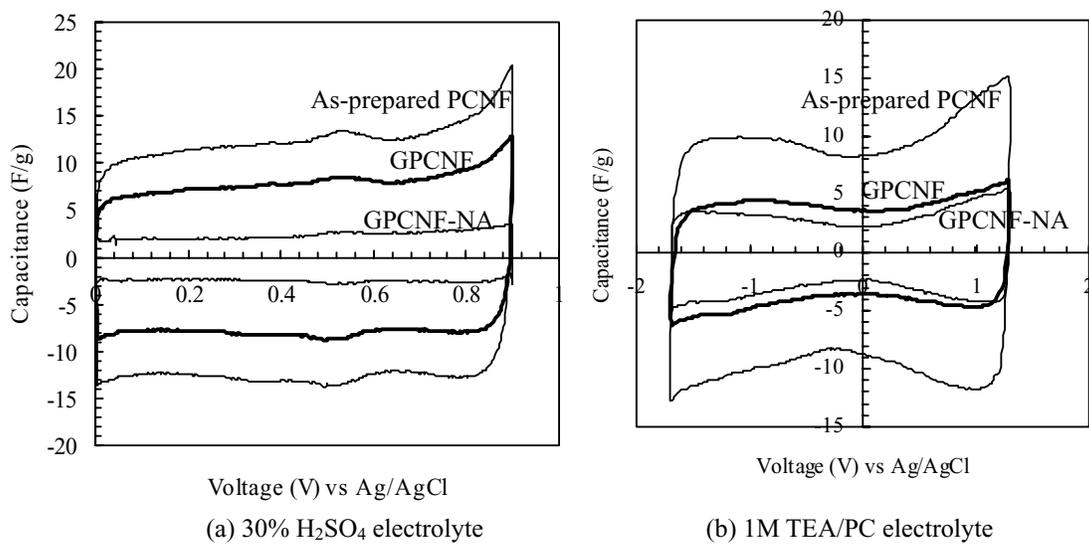


Figure 4 Cyclic voltammogram of PCNFs in different electrolytic solutions (scanning rate: 20mV/s)