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The Effect of Electrolyte on Surface Composite and Microstructure of Carbon Fiber by Electrochemical Treatment

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The new method of electrochemical alternating anode and cathode was used to treat carbon fibers (CFs) in this article. Scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) were used to study the surface composition and surface microstructure on the PAN-based carbon fibers with electrochemical alternating cathode and anode treatment in different electrolytes. Results show that the method can make the surface of the carbon fiber grooves deepen; when the electrolyte is sulfuric acid, phosphoric acid, sodium sulfate and sodium phosphate, the C content on the surface of the carbon fiber is reduced while the O content increased, and the little influence of ammonium bicarbonate on the surface element of the carbon fiber was discovered; However, each electrolyte chosen can significantly increase the oxygen functional groups COOH content on the carbon fiber surface. Treating carbon fibers in different electrolytes, the anodic oxidation mechanism of the process is different. Treated carbon fibers with electrochemical alternating anode and cathode, the crystal lattice spacing d(002) and the diameter of the carbon fiber increase at the same time.

Keywords: carbon fiber; electrochemical treating; electrolyte; surface composite; XPS

1. INTRODUCTION

The characteristics of CFs' very smooth and inert surface with less reactive functional groups make poor adhesion with a matrix and interface of the composite exists more defects, which hinder the advantages of the carbon fiber and its composites, therefore, it's a hot issue to study the surface modification and increase surface activity of CFs used in composite materials. Currently, the method on carbon fiber surface treatment included the oxidation treatment (vapor phase oxidation, liquid phase

oxidation, electrochemical oxidation) [1-5], the coating process (vapor deposition, surface electrical polymerization, electro-deposition, coating coupling agent, coating polymer and growth whiskers on the surface) [6-9], the plasma processing method [10], etc. In the liquid phase oxidation, electrochemical treatment method involves the type of electrolyte, including different types of acids, bases, salts, such as H_3PO_4 [11], KOH [12], NH_4HCO_3, $(NH_4)_2CO_3$ and $(NH_4)_3PO_4$ [13]. Liu [4] et al. found tensile strength of the fibers and inter laminar shear strength of the composite were higher after electrochemical oxidation 94s in NH_4HCO_3 electrolyte than those untreated, although the diameter of the carbon fibers have a certain degree of reduction. The physical and chemical double effectiveness mechanism was put forward that the physical and chemical state of the carbon fiber surface can be improved simultaneously by the electrochemical oxidation. Liu [14] et al. modified carbon fibers with $(NH_4HCO_3)/(NH_4)_2C_2O_4 \cdot H_2O$ composite electrolyte, with the AFM analysis of carbon fibers before and after electrochemical treatment, the results indicated that the surface roughness Ra of carbon fibers from 2.581 nm to 6.888 nm after the electrochemical modification.

In 2000, Burstein treated the steel with the DC positive and negative alternating pulse, and found that after treatment the surface martensite reduce or disappear, and transform into austenite γ-phase, this phenomenon was known as electrochemically induced annealing (EIA). Burstein thought that water was reduced to hydrogen by electrolysis in the cathode process. Hydrogen atoms entered into the metal and produced obvious lattice strain, leading to microscopic structure and phase change. In 2003, Burstein [15] also found that the metal surface density is increased with positive-negative alternate electrical pulses in the electrochemically process. Li et al. [16] electrochemically dealt with 304L stainless steel with DC pulse generator, found hydrogen from cathodic process diffuse into the steel, while hydrogen cannot be completely oxidized in the anodic process, adversely diffuse into the steel and accumulate inside the steel. Heat dehydrogenation had little effect on martensite transformation after EIA treated, and did not decrease the hardness of steel. In this paper, drawing lessons from EIA, we treat the carbon fibers with electrochemical alternating anode and cathode, on the one hand, study the effect of the processing method and the type of electrolyte on the surface roughness and surface activity of the carbon fiber, on the other hand, study the effect of the hydrogen penetration on the surface structure of the carbon fiber.

2. EXPERIMENTS

2.1. Raw materials and equipment

PAN-based carbon fiber (T300, 3K, China Petroleum Jilin Petrochemical Company); concentrated sulfuric acid (98% H_2SO_4); phosphate acid (H_3PO_4); sodium sulfate (Na_2SO_4); sodium phosphate (Na_3PO_4); ammonium bicarbonate (NH_4HCO_3); electrochemical workstation (CS300).

2.2. Treating carbon fiber by electrochemical impulse

In our study, a carbon fiber as the working electrode, a platinum electrode as the auxiliary electrode, a saturated calomel electrode as the reference electrode were used to treat CFs with

electrochemical impulse, and sulfuric acid, phosphoric acid, sodium sulfate, sodium phosphate, ammonium bicarbonate are selected as the electrolyte solution. The cathode charging time was 20min and the anode carbon fiber charging time was 5min, the processing time is 5h on carbon fibers. The anode and cathode charging potential judgments based on cyclic voltammetry (CV).

2.3 Testing

S-3600N type SEM was used to observe the surface morphology and the change in the diameter of the carbon fiber before and after treatment, the accelerating voltage was 20 kV.

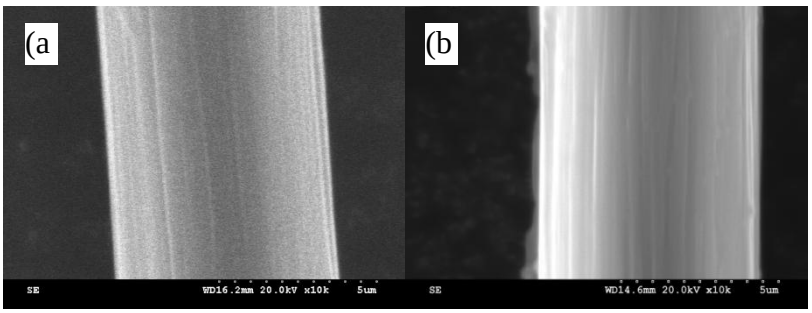
ESCALAB 250 XPS was used to analyze the surface elements and the surface functional groups of the untreated and treated carbon fibers, X-ray source is AlK, Monochromator, power 150W; scans passing energy 30eV.

MSAL type XRD was used to analyze the crystal structure of carbon fibers before and after treatment, measurement conditions: copper target; RS 0.30mm; voltage 40KV; current 100mA.

3. RESULTS AND DISCUSSION

3.1. Surface morphology

Figure 1 (a) is a SEM photograph of the untreated carbon fiber, fine groove-like surface is visible, which is formed in the carbon fibers production. Figure 1(b)-1(f) are SEM photographs of the treated carbon fibers with 1M H_2SO_4、1M H_3PO_4、1M Na_2SO_4、0.5M Na_3PO_4、1M NH_4HCO_3 respectively, and the carbon fiber surface grooves formed in different electrolytes treatment have more or less increased, and the surface roughness increases. 10 untreated and 10 treated carbon fibers in each electrolyte were randomly selected to measure diameters under SEM photographs, get the average diameters are 6.73μm、7.17μm、7.28μm、7.19μm、7.18μm、7.26μm. The result shows that electrochemical impulse treating can increase carbon fiber diameter. This may be caused by hydrogen molecules or hydrogen atoms produced by the electrochemical cathode process entering into the structure of the carbon fibers. However, when using different types of electrolyte, the increase of diameter is different. Currently, the most commonly used electrochemical anodic oxidation treatment (without cathodic process) lead to reduction of carbon fiber's diameter. In paper reported by Liu[4], the diameter was reduced by 3.3%. In our study, the diameter was increased by 6.5%-8.2%.



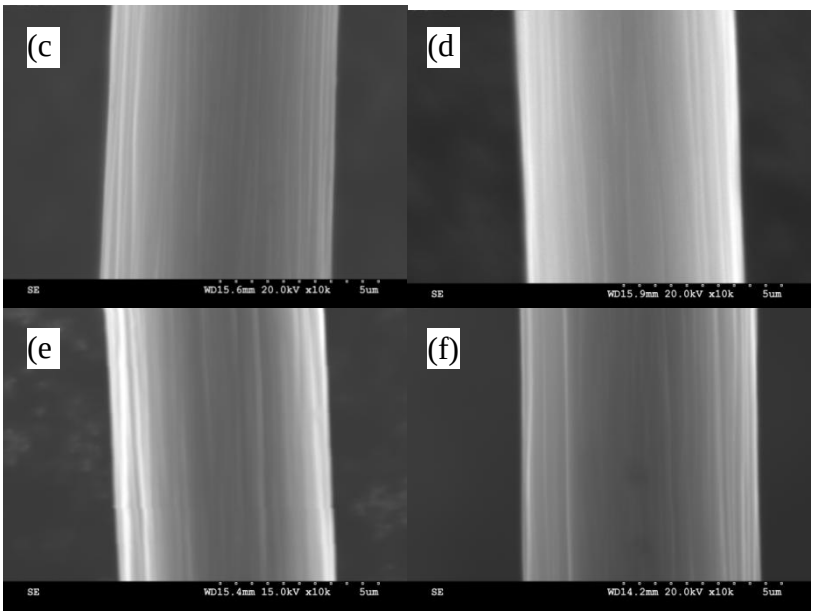


Figure 1. SEM photographs of carbon fibers untreated and treated (a)untreated (b) in 1M H_2SO_4 (c) in 1M H_3PO_4 (d) in 1M Na_2SO_4 (e) in 0.5M Na_3PO_4 (f) in1M NH_4HCO_3

Table 1. Diameters of CFs untreated and treated in different electrolytes

Samples	Diameter/μm
untreated	6.73
1M H_2SO_4	7.17
1M H_3PO_4	7.28
1M Na_2SO_4	7.19
0.5M Na_3PO_4	7.18
1M NH_4HCO_3	7.26

3.2. Surface elements and functional groups

Surface elements and functional groups have a significant effect on the interfacial bounding strength between CFs and resin matrix, especially oxygen-containing functional groups. Oxygen-containing functional groups can increase the surface polarity, which benefit to interfacial adhesion between CFs and resin matrix. Figure 2 is a full spectrum of XPS of the untreated and treated CFs in 1M H_2SO_4 for 5h, XPS scan was also carried out to the CFs treated in other electrolytes, and the content of the surface elements of the CFs before and after treatment are shown in Table 2. According to the electron binding energy of functional groups, C-C(285eV), C-OH (286.5eV), CO (288eV), COOH (289eV), C1s peak can be fitted with XPS peak4.1 software, and functional group contents of the carbon fiber surface are shown in Table 3.

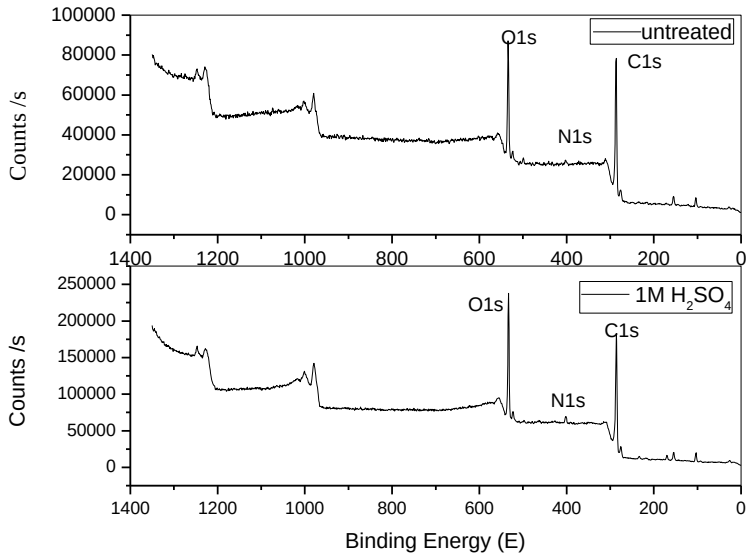


Figure 2. Full XPS spectrum of the untreated CFs and CFs treated in 1M H_2SO_4 for 5h

Table 2. Contents of the surface elements of the CFs before and after treatment

Samples	C/At%	O /At%	N/ At%	O/C
untreated	82.07	17.02	0.9	0.207
1M H_2SO_4	72.23	24.71	3.06	0.342
1M H_3PO_4	79.9	18.73	1.38	0.234
1M Na_2SO_4	79.81	18.6	1.58	0.233
0.5M Na_3PO_4	71.85	26.91	1.24	0.375
1M NH_4HCO_3	82.55	15.68	1.77	0.190

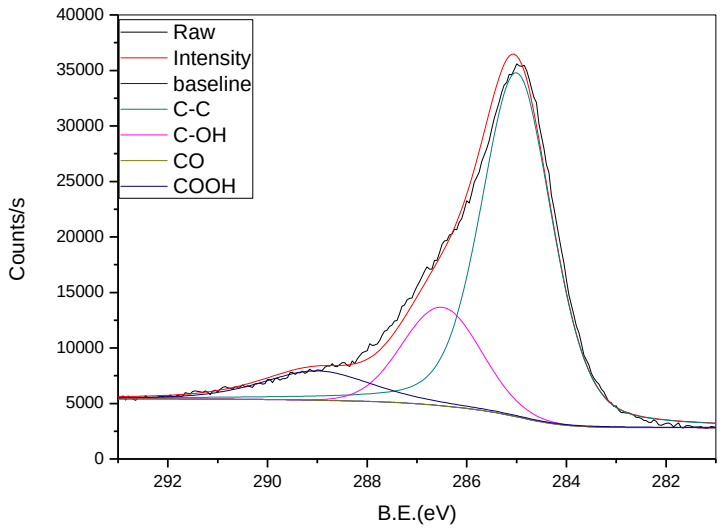


Figure 3. C1s peak separation of CFs treated in 1M H_2SO_4 for 5h

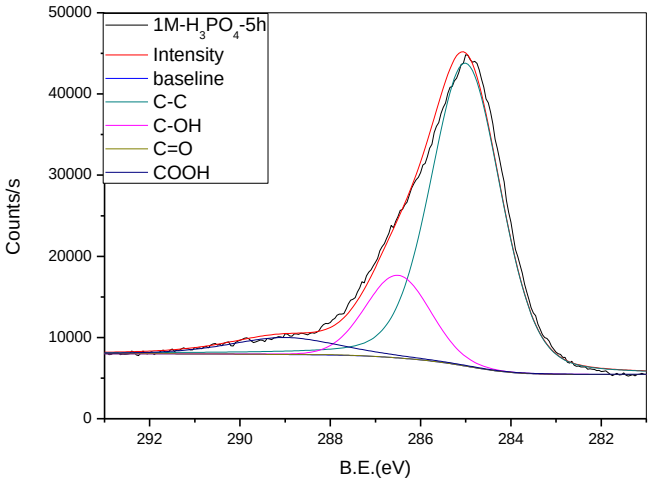


Figure 4. C1s peak separation of CFs treated in 1M H_3PO_4 for 5h

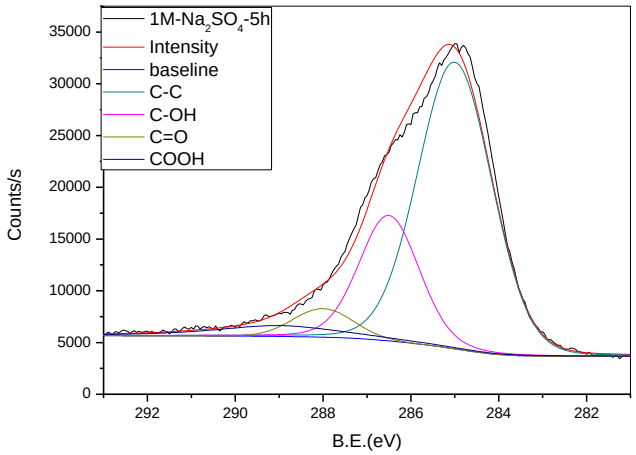


Figure 5. C1s peak separation of CFs treated in 1M Na_2SO_4 for 5h

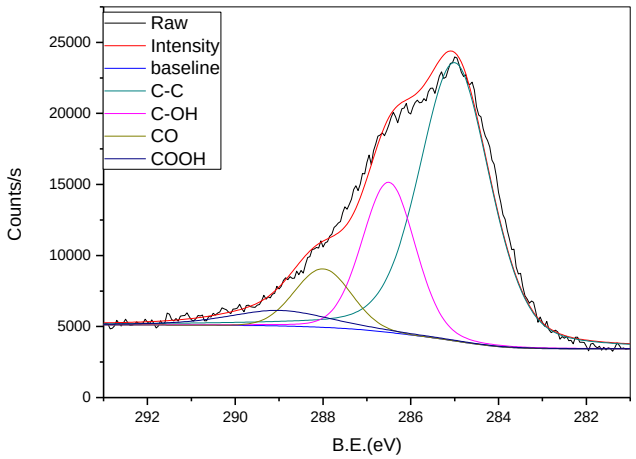


Figure 6. C1s peak separation of CFs treated in 0.5M Na_3PO_4 for 5h

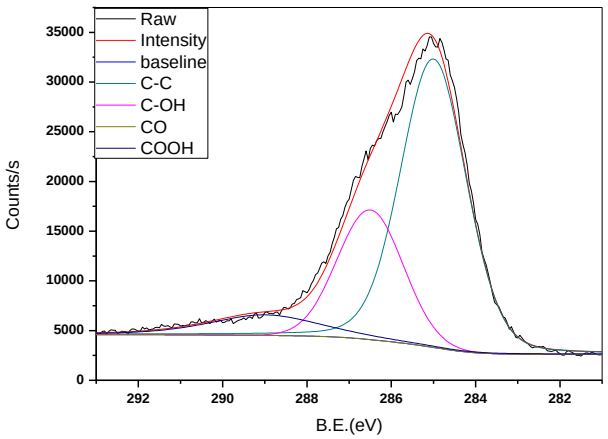


Figure 7. C1s peak separation of CFs treated in 1M NH_4HCO_3 for 5h

Table 3. Contents of surface functional groups of the CFs untreated or treated in different electrolytes

Samples	C-C	C-OH	CO	COOH
untreated	69.1	26.1	0	4.8
1M-H_2SO_4	70.68	19.60	0	9.72
1M-H_3PO_4	75.53	17.54	0.05	6.88
1M-Na_2SO_4	65.45	24.00	5.09	5.46
0.5M-Na_3PO_4	62.46	23.25	9.08	5.21
1M-NH_4HCO_3	64.40	26.91	0	8.69

From Table 2, we can see the contents of C on carbon fiber surface reduced and the contents of O on carbon fiber surface increased after electrochemical impulse treating in H_2SO_4, H_3PO_4, Na_2SO_4, Na_3PO_4, and achieving the purpose of the surface treatment. The elevated degree of oxygen content on the carbon fiber surface can be obtained by the O/C value, and the oxygen content is obviously elevated treated in sulfuric acid and sodium phosphate, and is slightly lower in NH_4HCO_3.

From Table 3, the change of the functional group content show, when acids (H_2SO_4, H_3PO_4) for the electrolytes, the surface of the C-OH contents reduce, COOH contents increase, the CO contents are almost constant, the reaction mechanism may be that strong oxidizing ability of acid oxidize the C-OH on the CFs surface to COOH directly, and portion C atoms on the CFs surface is oxidized simultaneously. With salts (Na_2SO_4, Na_3PO_4), the contents of the C-OH reduce, while the contents of COOH and CO increase, the mechanism may be the C-OH oxidized to CO and COOH in turn in the anode process, and portion C atoms on the CFs surface are oxidized simultaneously.

And for the weak acid-weak base salt (NH_4HCO_3), C-C on the CFs surface reduce after treatment, COOH increase, while the C-OH and CO are almost constant, which may be a small amount of active C atoms on the CFs surface are directly oxidized to COOH.

In our study, we can find out that each of the chosen electrolytes can make the oxygen functional groups COOH content increased significantly on the CFs surface, and COOH functional group plays an important role in enhancing the interlaminar shear strength, which has proved in Liu

[14]'s paper. Qian [13] chose three different kinds of ammonium-salt solutions such as NH_4HCO_3, $(NH_4)_2CO_3$ and $(NH_4)_3PO_4$ as the electrolytes respectively, COOH was reduced.

3.3. Crystal structure

CFs structure is composed by six-membered aromatic rings, carbon atoms between layers have no fixed position, which belong to the turbostratic structure. Figure 8 is XRD curves of the CFs treated in different electrolytes, we can see the XRD diffraction patterns of the carbon fiber has no significant difference, all characteristic peaks of the graphite structure appears in the vicinity of 2θ=25° (002 diffraction peak), the diffraction angles and the lattice spacing d(002) are obtained by Jade 5 software, the microcrystalline stacking thickness Lc shown in Table 4 can be obtained by the Scherrer formula [17] : $L = \frac{K\lambda}{\beta \cos\theta}$, K is 1 when Lc is calculated by the (002) crystal plane.

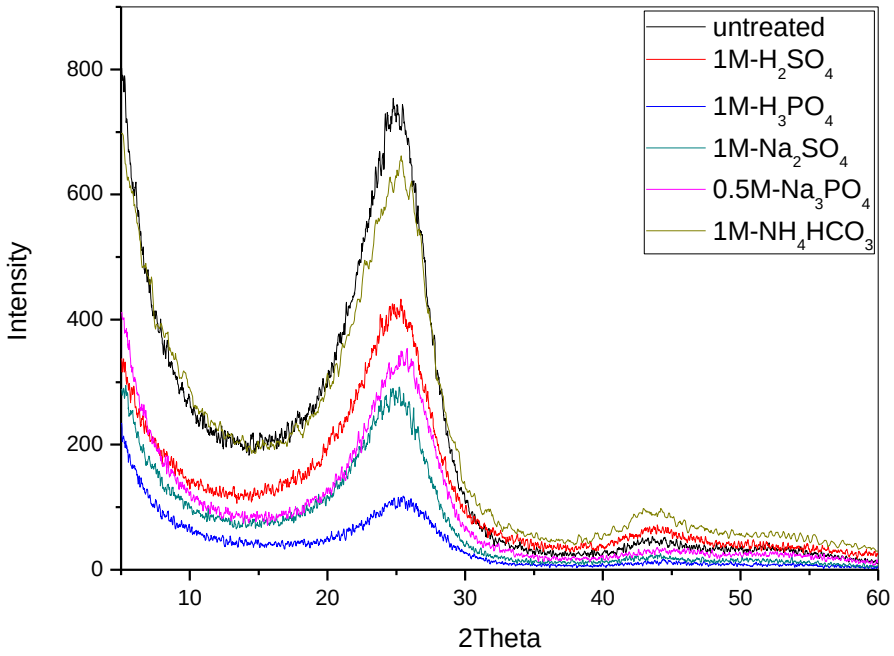


Figure 8. The XRD curves of CFs treated in different electrolytes

Table 4. (002) crystal plane spacing and stacking thickness of CFs treated in different electrolytes

Samples	2θ	d(002)/nm	Lc/nm
untreated	24.816	0.3585	1.67
1M H_2SO_4	24.092	0.3691	1.64
1M H_3PO_4	24.995	0.3560	1.81
1M Na_2SO_4	24.121	0.3687	1.74
0.5M Na_3PO_4	24.603	0.3615	1.80
1M NH_4HCO_3	24.366	0.3650	1.66

Seen from Table 4, the (002) interplanar spaces of the CFs in the different electrolytes (except phosphate) by electrochemical impulse treatment are increased. The stacking thicknesses Lc are increased in different electrolytes, besides Lc keeps basicly constant treated in H_2SO_4, NH_4HCO_3 solution. The characteristics of graphitic structures determined the mechanical properties of CFs [18]. Interplanar spacing increases, the graphite structure becomes loose, which is not conducive to an increase in tensile strength theoretically, while the increase in the thickness of the stacking makes the degree of graphitization of the carbon fiber increased, which is conducive to the improvement of the modulus theoretically [19]. There are both advantages and disadvantages when discussed only from the crystal structure changes.

4. CONCLUSION

1、 The surface grooves of carbon fibers increase by electrochemical alternating anode and cathode treatment in different electrolytes including H_2SO_4, H_3PO_4, Na_2SO_4, Na_3PO_4, NH_4HCO_3, which are beneficial for physical anchor-hold of the carbon fiber and matrix. After the new treatment in different electrolytes, the diameter of the carbon fiber increases, which was concluded from SEM photos.

2、 With electrochemical impulse treatment, acids (H_2SO_4, H_3PO_4) as the electrolytes, on carbon fiber surface, the C-OH contents decrease and COOH contents increase, the CO contents are almost constant; salts (Na_2SO_4, Na_3PO_4) as the electrolytes, the C-OH contents reduce, COOH and CO contents increase; weak acid-weak base salt (NH_4HCO_3) as the electrolyte, the C-C contents reduce, COOH increase, while the C-OH and CO are almost constant.

3、 The (002) interplanar spaces of the carbon fibers treated in the different electrolytes (except phosphate) by electrochemical impulse treatment are increased. The stacking thicknesses Lc are increased in different electrolytes, besides Lc keeps basicly constant treated in H_2SO_4, NH_4HCO_3 solution.

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