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Potassium loading effects for nano-porous ACF pre-treated with phosphoric acid

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Abstract The objective of this paper is to compare the surface features of two kinds of nano-porous activated carbon fiber (NPACF) treated with potassium and the variation of their properties by phosphoric acid pre-treatment. X-ray diffraction (XRD) patterns indicate that NPACF containing potassium species show better performance for potassium and potassium salts by pre-treatment with phosphoric acid. In order to present the causes of the differences in surface properties and specific surface area after the samples were treated with phosphoric acid, pore structure and surface morphology are investigated by adsorption analysis and SEM. For the chemical composition microanalysis for potassium loading of the NPACF pre-treated with phosphoric acid, samples were analyzed by EDX. Finally, the type and quality of oxygen groups are determined from the method proposed by Boehm.

Key words K-ACF, SEM, XRD, EDX, Boehm titratiom

1. Introduction

In recent years activated carbon fiber, manufactured from polymeric materials such as pitch, cellulose, phenol resin and polyacrylonitrile, has become a widely used adsorbent with numerous applications [1]. Its attractive features and physical properties include extremely high surface area, desirable mechanical properties that offer ability to be shaped, as well as fast adsorption kinetics. Although the fibrous adsorbents have extraordinarily high surface area, its adsorption capacity is not proportional to surface area, but primarily dependent upon the structure of the pores as well as of the pore size. Applications of activated carbon fiber are governed by surface chemical heterogeneity with the presence of heteroatoms such as oxygen, nitrogen, hydrogen, phosphorus and sulfur. The amount of these atoms present in the activated carbon fibers depends on the original polymeric raw materials and method of activation [2]. The most important heteroatoms in the activated carbon are oxygen, which is usually bonded to peripheral carbon atoms at the edges of the crystallites. The most common functional groups are carboxylic, carbonyls, phenols and lactones. The oxidation of carbon surfaces is a frequently used method in the preparation of applicable carbon-based materials. Some various chemicals have been used as oxidizers such as nitric, hydrochloric and sulfuric acid, hydrogen peroxide, perchlorate, permanganate and noble metals [3, 4]. Activated carbons and their fibers treated with metals have been known as excellent materials for the removal of organic and toxic species [5, 6], and anti-bacterial properties [7]. All of the above-mentioned modifications make the cost of materials higher and, in some cases, special precautions must be exercised during the operation process. The objective of this paper is to compare the surface features of two kinds of activated carbon fibers treated with potassium and the variation of their properties by acid pre-treatments. The difference in the method of acid treatment results in dramatically different structural and chemical properties of sorbents.

In this paper, this is the first part of a study on the potassium loading effect for NPACFs system transformed by pre-treatments with phosphoric acid. For characterizations of pre-treatment effects for K-NPACFs, the changes in physicochemical properties of these samples were presented by surface properties obtained from adsorption isotherms. Structural and surface morphologies were investigated XRD results, SEM-EDX analysis and properties of surface functional groups by Boehm titration.

2. Experimental

2.1. Preparation procedures

Self-made activated carbon fiber used as a non-treated carbon fiber material was prepared from PAN based carbon fiber. The carbonized PAN fiber was heated first at

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823 K for burn off, and the carbon fibers were activated by steam diluted with nitrogen in a cylinder quartz grass tube at the temperature range of 953~1073 K for 30 min. These activated carbon fibers were washed with deionized water and dried for 24 h at ambient temperature [5]. The molar concentration of from 0.05 to 0.1 M diluted phosphoric acid at boiling temperature was used in the oxidation treatment to increase the formation of functional groups without the damage of the activated carbon fiber surface. For the fiber impregnation, we prepared solution series of 0.1 mole concentrations with KOH and KCl. For the potassium treatment, 2 g of chop typed ACFs were dipped in to 50 ml of each potassium ion dissolved aqueous solutions and stirred for 12 hours at room temperature. Then, we removed air and bubbles in the solutions under the pressure of about 10^{-2} torr for 30 minutes, and then discarded the solution. Finally, these samples were dried at 268 K for 72 hours in vacuum atmosphere. In order to reduce the experimental error, sample dryness was conformed through the whole experiments prior to use. The preparation procedure and nomenclature of the samples were listed in Table 1.

2.2. Measurement

For the physical parameter measurements, nitrogen isotherms were measured using an ASAP 2010 instruments (Micromeritics, U.S.A.) at 77 K. Scanning electron microscopy (SEM, JSM-5200 JOEL, Japan) was used to observe the surface state and pore structure of K-NPACFs transformed through the pre-treatment with phosphoric acid and the transformed potassium salts state. For the elemental analysis in K-NPACFs transformed through the pre-treatment with phosphoric acid, energy dispersive X-ray analysis (EDX) was also used. X-ray diffraction patterns were taken using an X-ray generator (Shimatz XD-D1, Japan) with Cu Ká radiation.

2.3. Boehm titration

A Boehm titration method [8] was used for the identification of oxygenated surface groups on the carbon surfaces. One gram of K-NPACF sample was placed in 50 ml of the following 0.05 M solutions: sodium hydroxide, sodium carbonate, sodium bicarbonate, and hydrochloric acid. The elenmeyer flasks were sealed and shaken for 24 h and then 5 ml of each filtrate was pipetted and excess of base and acid was titrated with HCl and NaOH, respectively. The numbers of acidic sites of various types were calculated under the assumption that NaOH neutralizes carboxylic, phenolic, and lactonic groups; Na_2CO_3, carboxylic and lactonic groups; and $NaHCO_3$, only carboxylic groups. The number of surface basic sites was calculated from the amount of hydrochloric acid, which reacted with the carbon fiber.

3. Results and Discussion

Table 2 shows the values of BET specific surface area

Table 1
Nomenclatures for potassium loading on NPACFs transformed through pre-treatment with phosphoric acid

Sample	Nomenclature
0.05 M H_3PO_4 + Nano-Porous Activated Carbon Fiber	$PA_{0.05}$-NPACF
0.1 M H_3PO_4 + Nano-Porous Activated Carbon Fiber	$PA_{0.1}$-NPACF
0.05 M H_3PO_4 + Nano-Porous Activated Carbon Fiber + 0.1 KOH	KOH-$PA_{0.05}$-NPACF
0.1 M H_3PO_4 + Nano-Porous Activated Carbon Fiber + 0.1 KOH	KOH-$PA_{0.1}$-NPACF
0.05 M H_3PO_4 + Nano-Porous Activated Carbon Fiber + 0.1 KCl	KCl-$PA_{0.05}$-NPACF
0.1 M H_3PO_4 + Nano-Porous Activated Carbon Fiber + 0.1 KCl	KCl-$PA_{0.1}$-NPACF

Table 2
Comparison of physical parameters of K-NPACFs pre-treated with phosphoric acid

Sample	Parameter			
	S_{BET} (m^2/g)	Micropore volume (ml/g)	Internal surface area (m^2/g)	Average pore diameter (nm)
$PA_{0.05}$-NPACF	1650	0.645	854.2	164.5
$PA_{0.1}$-NPACF	1532	0.642	756.3	163.4
KOH-$PA_{0.05}$-NPACF	1245	0.632	634.8	158.6
KOH-$PA_{0.1}$-NPACF	1265	0.631	624.6	156.5
KCl-$PA_{0.05}$-NPACF	1364	0.626	734.5	157.3
KCl-$PA_{0.1}$-NPACF	1245	0.625	654.7	152.1

(S_{BET}), internal surface area, volume of micropores, and total pore volume for the K-NPACFs. As shown in Table, S_{BET}s were observed to 2234 m^2/g before treatment of phosphoric acid and distributed between 1650 and 1532 m^2/g after the treatment, respectively. Increasing of phosphoric acid concentration leads to a decrease in the values of physical parameters such as micropore volume, internal surface area and average pore diameter. It should be noted that average pore diameters for the K-NPACFs are distributed to the nano-pore range of 152.1~164.5 nm. It is consider that the number of micropores in the K-NPACFs surface decreases with increasing of phosphoric acid concentration and the transformation of pore structure is more significant as acid pre-treatment effect with decreasing of S_{BET}s. According to the further study [9], it was proved that S_{BET}s for the Ag-ACFs obviously decrease with increasing of phosphoric acid concentration.

The tendency of variation of physical parameter is one mechanism which could lead to increasing potassium ion adsorption and formation of potassium salts on the fiber surface. Reductive adsorption with ACF removes potassium ion from solution by deposition of K onto the surface. Meanwhile, it is well known that XRD technique for knowing the detailed and precise microstructure, such as the metal salts formation and their crystalline on the fiber surface (Fig. 1). X-ray diffraction patterns of fibers treated with potassium display diffraction peaks for potassium salts on the fiber surface [10]. When the activated carbon fibers were treated with potassium, major peaks were observed; 2T = 28.021, 2T = 40.031 and 2T = 50.031. And also, other peaks were observed as kinds of potassium chloride complexes on the fiber surfaces. One possible explanation is that the formation of surface complexes through the impregnation in the solution including chloride ions exhibit potassium chloride complex for the carbon active sites. It is believe that chloride complexes are formed due to capturing of oxygen function groups as well as adsorption by physicochemical attraction forces.

Figure 2 shows the SEM micrograph for the formation of potassium salts on the NPACF surfaces after impregnation. SEM observation of numerous surfaces and cross-section of potassium complexes containing NPACFs show that the agglomerates are evenly distributed and irregular in shape and size. Comparison of these micrographs shows that the transformation of the carbon fiber surface by pre-treatment of phosphoric acid does signifi-

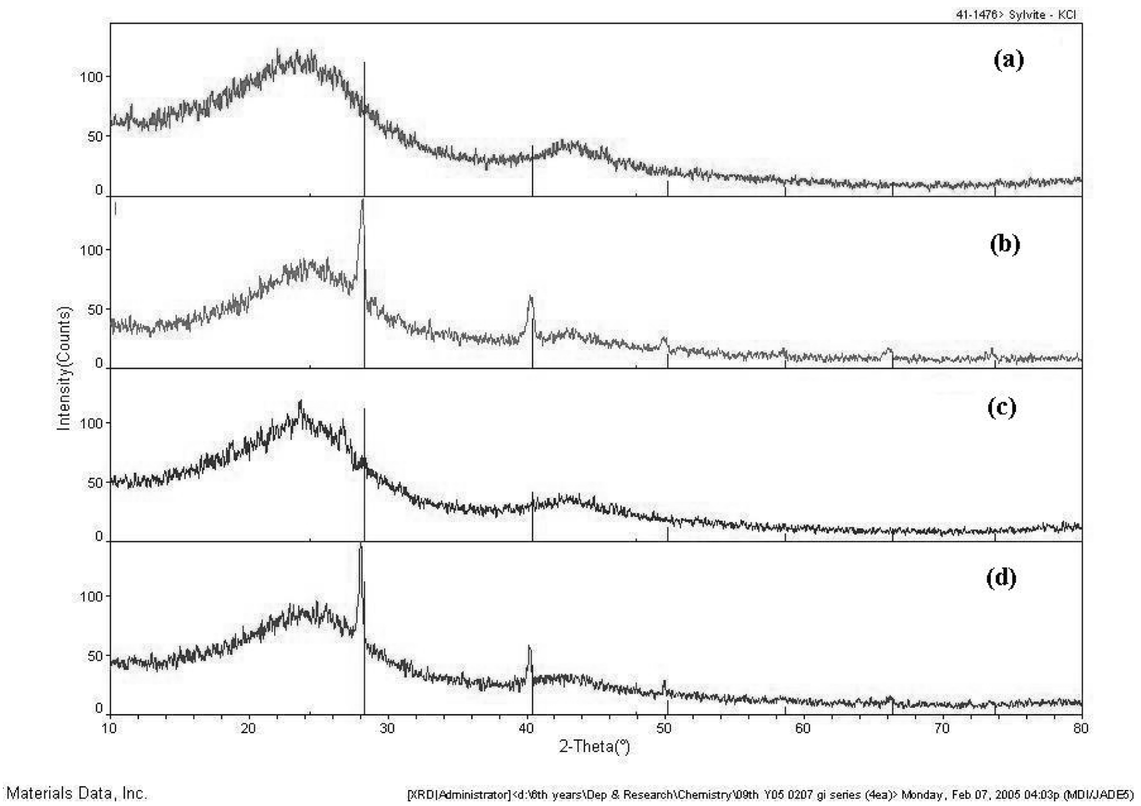


Fig. 1. XRD patterns for PA-NPACF series; (a) KOH-$PA_{0.05}$-NPACF, (b) KOH-$PA_{0.1}$-NPACF, (c) KCl-$PA_{0.05}$-NPACF and (d) KCl-$PA_{0.1}$-NPACF.

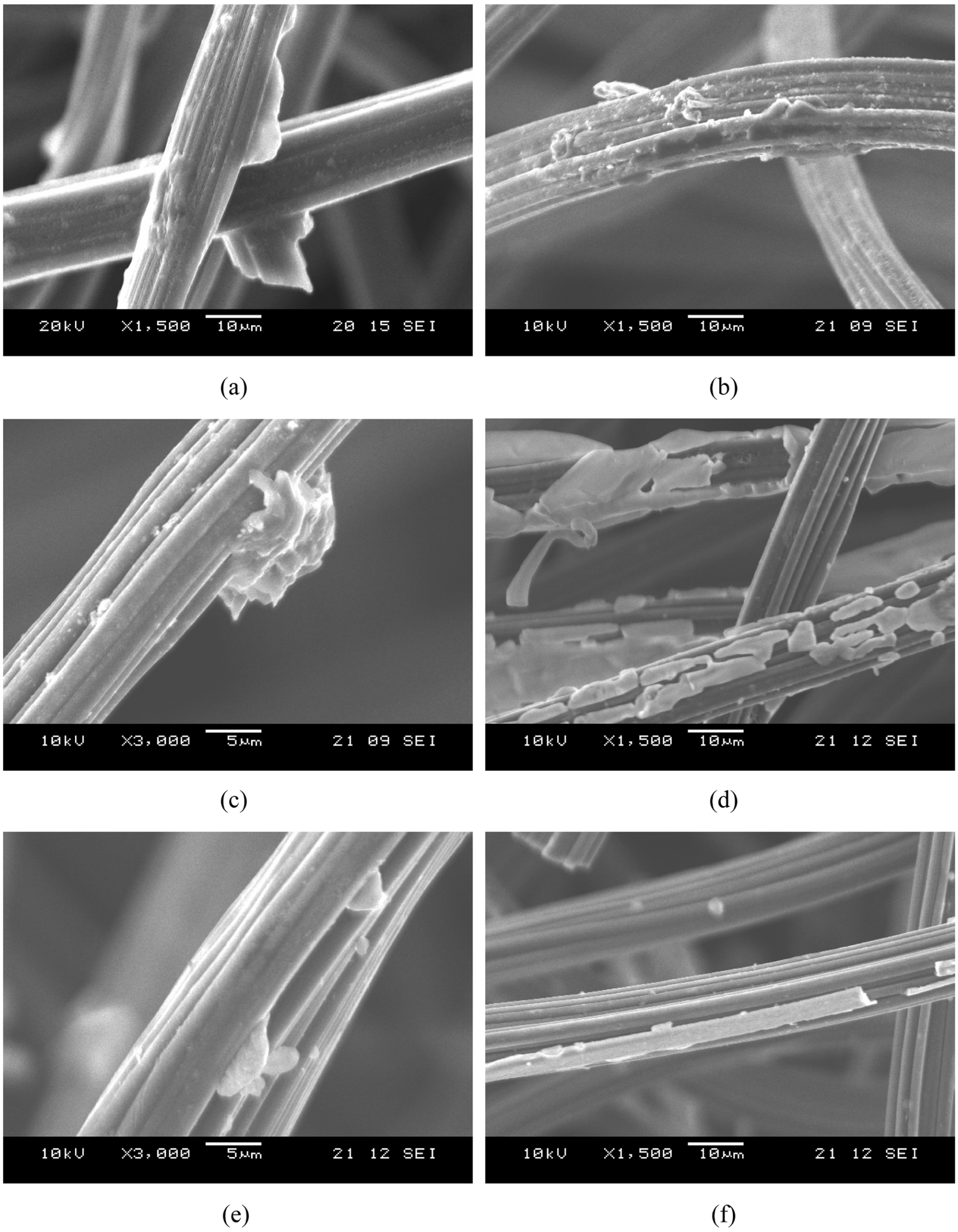
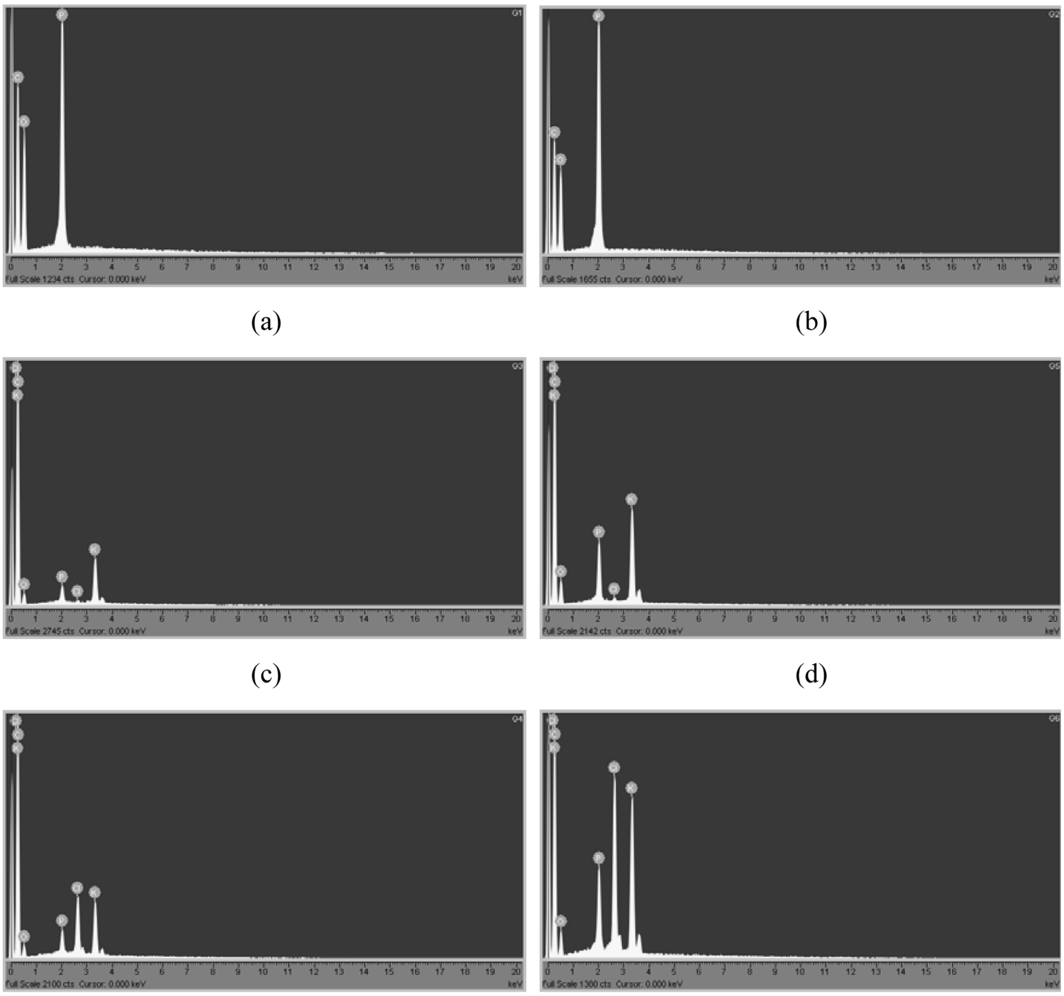


Fig. 2. SEM images obtained from PA-NPACF series; (a) $PA_{0.05}$-NPACF, (b) $PA_{0.1}$-NPACF, (c) KOH-$PA_{0.05}$-NPACF, (d) KOH-$PA_{0.1}$-NPACF, (e) KCl-$PA_{0.05}$-NPACF and (f) KCl-$PA_{0.1}$-NPACF.

cantly change the amount of potassium contents on the surfaces of the matrix of the NPACF. These figures can be observed the surface morphology and potassium complexes attached on the NPACF surfaces. Analyzing texture, the modification by potassium pre-treated on the NPACFs, which are clogged by the adsorbed potassium molecule and complexes. Various levels of brightness indicate differences in the surface chemistry, as a function of the phosphoric acid concentration. This also explains the reasons for the reduction in the surface area of potassium-NPACFs as compared with non-treated NPACFs [11]. From the SEM results, it was shown that the number of potassium compounds on the fiber surface increase with increasing of the phosphoric acid concentration. In addition to, external surface polluted with dendrite formation could be observed.

The EDX spectra for the K-NPACFs system, which are shown in Fig. 3. It is clearly seen that the modification of NPACFs by phosphoric acid improves the treatment effect for the potassium. These spectra were shown the presence of C, O and P with strong K peak. Most of these samples are richer in carbon and major



(a) (b)

(c) (d)

(e) (f)

Fig. 3. EDX elemental micro-analysis spectra obtained from PA-NPACF series; (a) $PA_{0.05}$-NPACF, (b) $PA_{0.1}$-NPACF, (c) KOH-$PA_{0.05}$-NPACF, (d) KOH-$PA_{0.1}$-NPACF, (e) KCl-$PA_{0.05}$-NPACF and (f) KCl-$PA_{0.1}$-NPACF.

Table 3
EDX elemental microanalysis of K-NPACFs pre-treated with phosphoric acid

Sample	O	P	Cl	K
$PA_{0.05}$-NPACF	62.46	37.54		
$PA_{0.1}$-NPACF	57.52	42.48		
KOH-$PA_{0.05}$-NPACF	49.77	14.77	1.25	34.93
KOH-$PA_{0.1}$-NPACF	44.06	15.60	1.42	38.21
KCl-$PA_{0.05}$-NPACF	37.02	8.43	25.01	29.54
KCl-$PA_{0.1}$-NPACF	30.62	10.53	27.07	31.77

potassium treated than any other elements. The results of EDX elemental microanalysis of K-NPACFs were listed in Table 3. In the case of most of the samples, carbon and potassium were presented as major elements in the K-NPACFs. These results were observed for each sample show the spectra corresponding to almost all samples rich in major elements like a K, P and Cl with an increase with increasing of the phosphoric acid concentration. It should be noted that the increase of the potassium content with a decreasing of the C content are observed for the almost all sample series, which become more heterogeneously transformed on the NPACF surface through the pre-treatment of phosphoric acid.

The EDX spectra transformation described above are due to a modification of the carbon fiber surface though the introduction of oxygen groups from matrix by acid treatment. The type and quality of oxygen groups were traditionally determined with titration method proposed by Boehm [8]. The results obtained from Boehm titration method are listed in Table 4. It can be observed that the total acidity and the distributions of groups of various strengths have very different values. The effect of surface acidity and basity was also evaluated from correlations as a function of NaOH, $NaHCO_3$ and Na_2CO_3

Table 4
Number of surface species (meq/g) obtained from boehm titration

Sample	Functional Group (meg/g)				
	Carboxylic	Lactonic	Phenolic	Acidic	Basic
PA$_{0.05}$-NPACF	0.24	0.26	0.23	0.73	0.36
PA$_{0.1}$-NPACF	0.49	0.37	0.37	1.23	0.31
KOH-PA$_{0.05}$-NPACF	0.82	6.1	5.3	12.2	0.28
KOH-PA$_{0.1}$-NPACF	0.50	6.5	4.8	11.8	0.36
KCl-PA$_{0.05}$-NPACF	1.22	5.4	4.4	11.02	0.20
KCl-PA$_{0.1}$-NPACF	0.86	5.3	4.0	10.16	0.21

uptake. It is obviously seen that the values of surface acidity increase with increasing of the amount of phosphoric acid treated, but the values decrease with treatment of the potassium salts. It should be noted that KOH-PA$_{0.05}$-NPACF has the highest number of oxidation groups such as carboxylic, lactonic and phenolic groups. This can be attributed to the lowest local pH of carbon fiber surface due to phosphoric acid treatment. It is consider that the affinity of NPACF for potassium depends on the amount of surface functional groups. A positive influence of the acidic groups on the carbon fiber surface by phosphoric acid treatment is also demonstrated by an increase in the amounts of potassium complexes with variation of acidic groups calculated from Boehm titration. When distribution of acidic groups is properly introduced, active sites on the carbon fiber surface should be play important role in the deposition of metallic ions [5]. As expected, acid oxidation introduces a significant number of oxygen containing groups in almost each category classified by Boehm.

4. Conclusion

In this paper, it is the first part of a study on the potassium loading effect for NPACFs system transformed by pre-treatments with phosphoric acid. From the surface analysis, average pore diameters for the K-NPACFs system transformed through pre-treatments with phosphoric acid are distributed to the nano-pore range of 152.1~164.5 nm. XRD patterns indicate that NPACF containing potassium species show better performance for potassium and potassium salts by pre-treatment with phosphoric acid. SEM shows that the transformation of the carbon fiber surface by pre-treatment of phosphoric acid does significantly change the amount of potassium contents on the surfaces of the matrix of the K-NPACF. EDX spectra were shown that the modification of NPACFs by phosphoric acid improves the treatment effect for the potassium with the presence of C, O and P with strong K peak. Finally, a positive influence of the acidic groups on the carbon fiber surface by phosphoric acid treatment is also demonstrated by an increase in the amounts of potassium complexes with variation of acidic groups calculated from Boehm titration.

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