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Effect of potassium sulfate in mineral precursor on capacitance behavior of as-prepared activated carbon

Huai-Hao Zhang [a,*], Chi Ma [a], Jie Tong [a], Yong-Feng Hu [b], Jing Zhao [a], Bin Hu [a], Chen-Yin Wang [a]

[a] *College of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou 225002, PR China*
[b] *Canadian Light Source, 44 Innovation Boulevard, Saskatoon, SK S7N 2V3, Canada*

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ABSTRACT

Activated carbon (AC) used as supercapacitor electrode materials was successfully synthesized from analog sulfur-containing precursors (ASCPs). The materials were characterized by means of X-ray adsorption near-edge structure spectroscopy (XANES), elemental analysis, X-ray diffraction (XRD), scanning electron microscopy (SEM), ion chromatography and N_2 physical adsorption/desorption. The capacitance behavior was performed by electrochemical measurements. The results indicate that as the mass ratio of KOH to petroleum coke (PC) is 3:1 and 4:1, the synergistic activation effect from K_2SO_4 and KOH can increase pore volume and capacitance performance of AC. However, as for KOH/PC mass ratio is 5:1, the pore structure generated during activation process is destroyed due to K_2SO_4 over-activation, namely, the specific surface area, porosity and capacitance performance of AC decreased. Comparatively, the role of K_2SO_4 is quite different from those of other sulfur species, such as organic dibenzothiophene (DBT) and inorganic FeS_2 during AC activation process.

1. Introduction

The supercapacitors have attracted increasing interest and attention with its potential in large specific capacitance, high power density and long cycle life [1–3]. As the key parts of a supercapacitor, electrode materials have a significant effect on its electrochemical properties. Therefore, it is especially important to develop a high-performance electrode material for supercapacitors. In general, the electrode materials for the supercapacitor can mainly be divided into three categories: carbon-based materials, metal oxides and conducting polymers [4]. As a representative carbon-based material, AC has a large specific surface area, high chemical stability, good conductivity and low price, which has made it the preferred material to prepare the electrode of the supercapacitor [5,6].

There are extensive sources of precursors for AC preparation, mainly classified as mineral and plant precursors. Among them, mineral precursors primarily include petroleum coke (PC) [7], asphalt [8] and various kinds of coal [9–11]. Plant precursors usually contain peanut shell [12], crop straw [13], coconut shell [14], walnut shell [15], oil palm shell [16] and waste pulp solution [17]. At present, the use of mineral as an AC precursor has become more and more important for its rich reserves, low price and high carbon content. However, many types of sulfur-containing material are ubiquitous in mineral precursors. Judged by sulfur content, the market price of mineral precursors is much different. Currently, high sulfur minerals are often utilized as cheap fuel for its high sulfur content, high output and low price. However, due to the deepening strict of environmental requirements and the non-ideal desulphurization technology, the use of high sulfur materials for heating fuel also meet the strict restriction. Therefore, utilization of high sulfur minerals for AC production will be an effective way for the reuse of minerals with high sulfur content. Up to now, some literatures have reported that AC prepared by high sulfur minerals exhibit excellent performance, such as high adsorption capacity [18], developed pore structure [19], effective removal of tetracycline [20] and better catalyst support [21]. Consequently, using high sulfur minerals as precursors for AC production is practical and feasible.

The sulfur forms in mineral are mainly divided into inorganic sulfur and organic sulfur. Moreover, organic sulfur usually includes mercaptan, thioether, disulfide, thiophene, etc. Inorganic sulfur chiefly consists of sulfate and pyrite [22,23]. Obviously, it is important to understand the chemical speciation and content of sulfur in minerals, as this knowledge could influence significantly the structure and capacitance performance of AC. Till now, a small amount of relevant literatures have been reported. Lee and Choi [24] used alkali metal compounds to activate high-sulfur PC. The results show that sulfur contents in the precursor have an obvious impact on specific surface area, pore structure and surface functional groups of AC. Zhang et al. [25] employed high-sulfur PC to prepare AC for gas adsorbent. The results show that sulfur contents in precursor dramatically decrease after KOH activation. However, the above reports are limited to studies on the relationship of total sulfur content and the pore structure of AC. In our previous work, the effect of representative organic sulfur DBT and inorganic sulfur FeS_2 in ASCPs on the structure and capacitance behavior of AC was studied,

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* Corresponding author.
E-mail address: huaihaozhang@163.com (H.-H. Zhang).

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respectively [26,27]. As a result, DBT in ASCPs can react with KOH and lead to the deficiency of KOH, bringing the detrimental influence to the pore structure and capacitance performance of AC. However, the negative influence from DBT can be eliminated by increasing KOH amounts. On the other hand, FeS_2 in ASCPs also reacts with KOH to form the hardly dissolved Fe_3O_4, so as to impose a negative effect on capacitance behavior of AC, and the influence was difficult to eliminate by simply increasing the KOH amount. These results indicate that the influence of distinct speciation and contents of sulfur in the mineral precursor on the structure and capacitance behavior of AC is greatly different. Therefore, it is necessary to extend the studies to other sulfur species in mineral precursors.

K_2SO_4, a common inorganic sulfate, exists widely in natural mineral precursors due to its good chemical inertness and environmental stability. In addition, the high melting point characteristics of K_2SO_4 (1074 °C) make it difficult to be removed from minerals by using common thermal desulfurization method. Therefore, it is meaningful to obtain the influence law of relationship among K_2SO_4, pore structure and capacitance behavior of AC. In this work, K_2SO_4 was chosen as the representative sulfate. ASCPs were obtained from PC mixed with different amount of K_2SO_4, and the role of ASCPs had been described in detail in our previous work [26,27]. Furthermore, the activation mechanism of K_2SO_4 in ASCPs on AC structure was analyzed systematically through a series of methods such as elemental analysis, XRD, ion chromatography, XANES, SEM and N_2 physical adsorption/desorption. The capacitance behaviors of AC were tested through cyclic voltammetry (CV), galvanostatic charge–discharge (GCD) and electrochemical impedance spectroscopy (EIS). Accordingly, the influence law of K_2SO_4 in ASCPs on AC capacitance performance was also investigated.

2. Experimental

2.1. Preparation of AC

ASCPs can be obtained from the uniform mixing of a certain amount of K_2SO_4 and 1.0 g PC with a particle size of 0.25–0.3 mm by controlling K_2SO_4/PC mass percentage ratio of 0%, 10%, 40% and 60%, separately. The mass fractions of sulfur element in ASCPs are 0.66% (6.60 mg), 2.27% (25.00 mg), 5.73% (80.20 mg) and 7.31% (117.00 mg), respectively. Then, ASCPs and KOH (at a KOH/PC mass ratio of 3:1, 4:1 and 5:1) were well mixed in the nickel crucible. The obtained mixtures were activated from 20 to 800 °C at a heating rate of 5 $°C \cdot min^{-1}$ and kept for 1 h at 800 °C in a muffle furnace under N_2 atmosphere, and cooled naturally to room temperature. The pH of activated products was adjusted to 7 by washing repeatedly with distilled water. Finally, the samples were obtained by air pump filtration and drying completely. The samples were denoted as AC-X-Y, where X and Y represent the KOH/PC mass ratio and K_2SO_4/PC mass percentage ratio, respectively. Thus, the samples can be named as AC-X-0, AC-X-10, AC-X-40 and AC-X-60 correspondingly. For comparison with FeS_2 in precursor, 0.4 g FeS_2 was added into 1.0 g PC. Then, the sample was prepared by using the same experimental procedure as above, which is named as AC-4-40-FeS_2.

2.2. Structural characterizations and sulfur analyses

S K-edge XANES was measured using the soft X-ray micro characterization Beamline (SXRMB) at the Canadian Light Source. The pore structure and specific surface area of AC samples were measured by N_2 adsorption/desorption at 77 K with ASAP 2020 instrument (Micromeritics, USA). The sulfur content of samples was tested by a Vario EL Cube element analyzer (Elementar, German). Powder X-ray diffraction (XRD) was conducted using a D8 ADVANCE diffractometer (Bruker, Germany) within the 2θ range from 10° to 80° with Cu Kα radiation ($\lambda = 1.5406$ Å), and with the generator current and voltage set at 200 mA and 40 kV, respectively. Quantitative and qualitative analyses of anion in a washing solution were analyzed by an ion chromatography system (ICS2100, Dionex Company, USA). The microstructure and morphology of samples were recorded by the S-4800 II field emission SEM.

2.3. Electrode preparation and electrochemical measurement

A mixture was prepared using AC, conducting agent graphite and binder (60 wt.% PTFE) at a mass ratio of 85:10:5. By dropping an appropriate amount of ethanol into the mixture, a paste was obtained and smeared uniformly on a nickel mesh with an area of 1 cm^2. Then, the residual ethanol was removed by desiccation at 90 °C for 4 h. Subsequently, the mesh was pressed into thin slice under the pressure of 10 MP with the oil press. Electrochemical measurements were carried out in 6 M KOH aqueous electrolyte with a three-electrode system that the as-prepared electrode, platinum sheet and Ag/AgCl electrode were used as working electrode, counter electrode, and reference electrode, respectively. CV and GCD measurements were conducted on a CHI 660E electrochemical workstation (Chenhua, Shanghai China). CV was measured from -1 to 0 V at a scan rate from 5 to 100 $mV \cdot s^{-1}$. GCD was tested within a potential range of -1 to 0 V at a current density from 300 to 5000 $mA \cdot g^{-1}$. EIS was analyzed by the potential amplitude of 5 mV using a frequency range from 0.01 to 10^5 Hz with the AutoLab-PGSTAT30.

3. Results and discussion

3.1. Sulfur analyses in activation process

As listed in Table 1, the sulfur mass and mass fraction in AC all slightly increased with the increment of K_2SO_4 amounts in ASCPs, suggesting that K_2SO_4 in ASCPs was possibly involved in KOH activation reaction and there was a trace of sulfur transformed into a part of AC itself, which is much different from the elemental analysis results of organic DBT and inorganic FeS_2 in ASCPs [26,27].

As displayed in Fig. 1(a), it can be seen that the peak shape of these unwashed samples (UWAC-X-Y, the activated products without washing process) is very similar, indicating that activation products are the same with the increasing of K_2SO_4 amounts. According to the PDF standard card, the characteristic peaks at $2\theta = 20.9°$, 24.1°, 34.0°, 49.0° and 61.5° represent K_2S (77-2152); the characteristic peaks at $2\theta = 30.0°$, 31.7°, 32.0°, 32.1° and 34.1° represent K_2CO_3 (71-1466); the characteristic peaks at $2\theta = 22.8°$, 30.0°, 30.4°, 35.2° and 41.5° represent K_2SO_4 (85-0939). It indicates that K_2S, K_2CO_3 and other possible products are generated after KOH activation reaction. As Fig. 1(b) shows, the peak shape is almost the same for all washed samples. To be specific, the characteristic peaks of K_2SO_4, K_2S and K_2CO_3 completely disappear, and the diffraction peak of graphitic carbon appears at $2\theta = 43.5°$ according to the PDF standard card (75-2078). This shows that K_2SO_4 and K_2CO_3 are almost removed by washing, and the disappearance of K_2S is attributed to hydrolysis reaction with the generation of H_2S.

The chromatogram data of AC-4-0 and AC-4-60 are from the washing solution undergoing 10 times and 50 times dilution treatment, respectively. As demonstrated in Fig. 2 and Table 2, two samples have the same peak positions, corresponding to Cl^{-1}, NO_3^{-1}, CO_3^{2-} and SO_4^{2-}, respectively, approximately the same with the chromatographic results of organic DBT in ASCPs [26]. In particularly, Cl^{-1} originated from distilled washing water, and NO_3^{-1}, CO_3^{2-} should be from the N,

Table 1
Elemental analysis of AC samples.

Sample	Mass fraction (wt.%)					AC/ASCP (wt.%)	*S* in AC (mg)
	C	H	O	N	S		
PC	90.23	3.86	3.32	1.80	0.66		
AC-4-0	87.37	3.42	8.17	0.21	0.07	46.28	0.32
AC-4-10	86.64	3.47	9.02	0.20	0.11	41.23	0.50
AC-4-40	82.82	3.77	12.13	0.28	0.23	30.31	0.98