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Nanoporous carbons from oxidized green needle coke for use in high performance supercapacitors

Jiu-zhou Wang, Li-qun Wang, Ming-ming Chen*, Cheng-yang Wang, Cui Zhang, Fei He

Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

Abstract: Green needle coke was oxidized by a mixture of HNO_3 and H_2SO_4 (3:7 vol/vol) acids. The resultant oxidized coke was separated into water dispersible and non-dispersible fractions, which were then activated by KOH using the same KOH/coke weight ratio to obtain two kinds of nanoporous carbons with different pore structures. The oxidized coke and the nanoporous carbons were characterized by XPS, XRD, TEM, N_2 adsorption and electrochemical tests. Results indicate that, at the same KOH/coke ratios, the nanoporous carbons derived from the water-dispersible oxidized coke have higher mass specific capacitances and capacitance retention ratios, and lower resistances than those from the non-dispersible ones when used as an electric double layer capacitor electrode in 6 mol/L KOH, but the former have a lower volumetric specific capacitance than the latter.

Key Words: Supercapacitor; Water dispersible intermediate; Surface property; Porous structure; Rate performance

1 Introduction

Electric double-layer capacitors (EDLCs) or supercapacitors, are electrochemical energy storage devices that provide high power density for electric vehicles, backup power systems, and electronic components. Much effort[1-5] has been made to develop appropriate electrode materials, which were key materials to the electrochemical performance of supercapacitors.

Porous carbon materials are widely used material for EDLC electrodes due to their highly developed porous structure and stable electrochemical properties. And pore structure is crucial to the formation of electric double-layers. Some researches resorted to template methods for tuning pores in porous carbon, especially mesopores[6-8]. As for micropores, afterwards activation[9,10] provides some possibility.

Activation of carbonaceous materials is another widely used method for the preparation of porous carbons. Compared with templated carbons, activated carbons have a wide pore size distribution, which includes both micropores and mesopores. Usually, the ratio of micropores to mesopores not only depends on the structure of the precursor but also the activation conditions. A variety of activated carbons were prepared from different precursors including isotropic pitches[11], mesophase pitches[12,13], carbon aerogels[14], biomass carbon[15,16], and green coke[17-19]. Although some of the samples have high surface areas, more and more researchers have convinced that not all the micropores detected by BET surface analysis method are available for

electrolyte ions due to the transport resistance. Reasonable porous structure seems to be more crucial for the EDLC performance.

In previous work[20], we reported an amphiphilic oxidized carbon material having great potential to be an ideal precursor for porous carbon material. No doubt, pre-oxidation of the precursor is indispensable for activation to get a well-developed porous structure which is appropriate as the electrode material for EDLCs. But how and why does the oxidation affect the ultimate porous structure as well as their electrochemical properties are still ambiguous, therefore different kinds of oxidized carbonaceous materials are firstly prepared from green needle coke (GNC) and a comparative study was conducted. Herein, all these oxidized carbonaceous materials are called intermediates, considering that the total synthesis route are from GNC precursor to oxidized carbonaceous materials and finally to porous carbons. We try to figure out the relationship between the final EDLC performance and both surface properties and structure character of intermediates. Also activation conditions, especially the KOH dosage was optimized. The electrochemical performance of EDLCs are compared with those reported in recent literatures.

2 Experimental

2.1 Preparation

GNC derived from residual oil was provided by Jinzhou Petrochemical Co. in China. The coke was prepared around 450-520 °C in a delayed coker, it was pulverized to particles
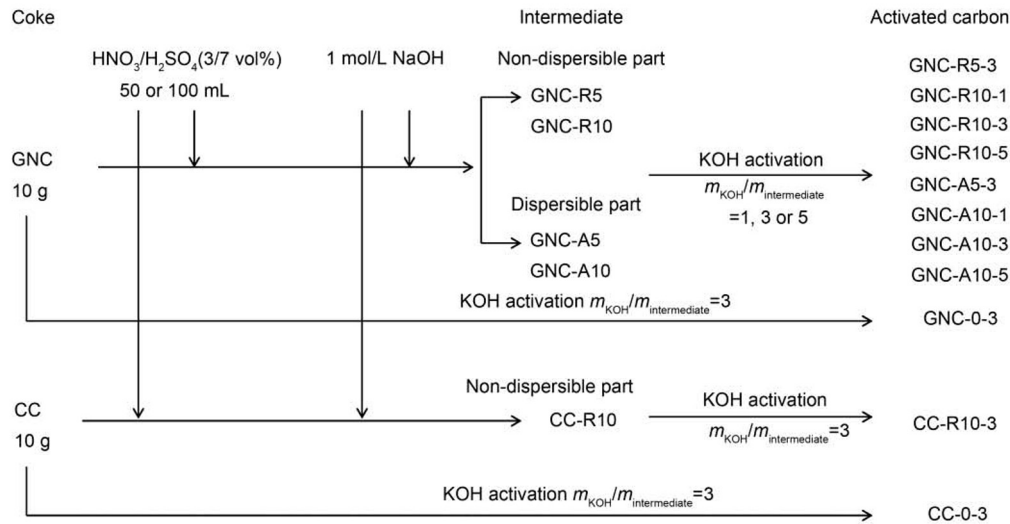
Fig. 1   Flow chart for the preparation of the intermediates and activated carbons.

Table 1   Elemental analysis of carbon precursors.

Cokes	$w/\%$				
	C	O	H	N	S
GNC	94.60	0.26	3.83	0.45	0.86
CC	96.20	0.19	2.96	0.23	0.42

of 50-100 μm. A calcined coke (CC) with the same particle size was prepared by calcination of the GNC at around 1 300 ^{o}C, and used for comparison. Their elemental compositions were listed in Table 1. The GNC contains a larger amount of heteroatoms (O, H, N and S) than the CC.

10 g GNC powder was oxidized at room temperature for 1 h by either 50 or 100 mL (V_{acid}/m_{coke} = 5 or 10) of a concentrated acid mixture consisting of concentrated nitric and sulfuric acid with a ratio of $V_{nitric}/V_{sulfuric}$=3/7. After oxidation, the suspension was poured into cold water and the oxidized coke was separated by centrifugation and washed with water until the oxidized coke reached a pH value of 3. Then the oxidized coke was added into a 1 mol/L NaOH aqueous solution, stirred for 1 h and separated into two components through centrifugation, water dispersable part and precipitated part. The non-dispersible part was obtained through washing the precipitated part with water until the pH value reached 3 and dried at 80 ^{o}C, then pulverized to particles with almost the same size as the starting coke. This non-dispersible part is labeled using R with the amount of acid used (V_{acid}/m_{coke}), e.g. GNC-R10. The dispersible part was recovered from the filtrate by adding 1 mol/L HCl until the pH of the solution was below 2, followed by washing with water until the pH value reached 3 and was dried to obtain a fine powder. This dispersible part is labeled using A with V_{acid}/m_{coke}, e.g. GNC-A10; A is used since it is assumed to be amphiphilic according to the literatures[21, 22]. The CC was oxidized under the same conditions with V_{acid}/m_{coke} = 10 and separated into two components labeled as CC-R10 and CC-A10. The yield of

the intermediates was calculated from the equation (1):

$$Yield = m_{intermediate}/m_{coke} \times 100\% \qquad (1)$$

Where m is the mass of samples.

The resultant oxidized coke powders (intermediates) were activated by mixing with KOH ($m_{KOH}/m_{intermediate}$ = 1, 3 or 5) and heating to 800 °C at a rate of 5 °C/min, then maintained at 800 °C for 1 h and cooled to room temperature. The cooled activated products were then washed several times with HCl aqueous solution and distilled water consecutively. Finally, the products were dried at 110 ^{o}C for 12 h. For CC, only the non-dispersible part, CC-R10, was activated because the yield of the dispersible part CC-A10 was very small. For comparison, GNC and CC were also activated by using 3:1 KOH/coke ratio (labeled as GNC-0-3 and CC-0-3, respectively). In Fig. 1, a flow chart for the preparation procedure of the intermediates and activated carbons is shown. The prepared samples are in bold type. For example, GNC-R10-3 is the non-dispersible part of the GNC after oxidation in 100 mL of mixed acid and activated by KOH with a ratio of 3:1 (KOH/intermediate) at 800 ^{o}C.

2.2   Characterization

The pore structures of the final nanoporous carbon materials were characterized by N_2 adsorption/desorption at 77 K using Micrometrics ASAP 2020. Before measurements, the samples were degassed below 1.33 Pa at 90 °C for 1 h and heated to 300 °C (10 °C/min) and maintained at this temperature for 5 h. The specific surface area S_{BET} was calculated by the Brunauer-Emmett-Teller (BET) method at the relative pressure ranging from 0.1 to 0.3. The mesoporous surface area Smes and mesopore volume Vmes were calculated using the Barrett–Joyner–Halenda (BJH) method from the desorption branch. The total pore volume V_{tot} was calculated from the amount of N_2 adsorbed at a relative