Facile synthesis of hierarchically porous carbon for supercapacitor derived from water-soluble pitch

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Abstract. Hierarchical porosity carbons have been synthesized via carbonization and activation using water-soluble pitch as carbon source. By further introducing potassium acetate as an activation agent, the obtained materials have a high specific BET surface area of 1108 m² g⁻¹ with N, O and S doping. The effects of different activation temperatures on the pore structure and composition of the carbon were investigated. The obtained carbon samples exhibits a maximum gravimetric capacitance of 208 F g⁻¹ when evaluated as an electrode material in 6 mol L⁻¹ KOH aqueous solution and good rate capability of 69.5% retention at 20 A g⁻¹. Furthermore, it demonstrates good cyclic stability, showing a high capacitance retention of 96.3% over 10000 charge-discharge cycles at a current density of 2 A g⁻¹.

Keywords: Hierarchically porous carbon; Water soluble pitch; Potassium acetate; Supercapacitors.

1. Introduction
As one of the most promising energy-storage systems, supercapacitors have already obtained the widespread application in many fields. Compared with secondary batteries, supercapacitors own higher power density, fast charge-discharge rates and excellent cycling lifetime [1]. Hierarchical porous carbon are commonly used for supercapacitors due to their outstanding electrochemical properties due to the synergistic action between each pore level [2]. Hierarchical porous carbon is usually prepared by two methods, activation method and template method. The template method can precisely control the pore size distribution, while the major disadvantage lies in the economics of the process. The activation method has the advantages of adjustable pore structure, simple techniques, reliable property and low costs [3]. Traditional activation agents (NaOH and KOH) are highly corrosive. Therefore, it is still a challenge to prepare hierarchically porous carbon by a simple and environmentally friendly method [4].

In this work, hierarchical porous carbons were prepared using water-soluble pitch with potassium acetate activation. The high solubility of water-soluble pitch in potassium acetate solution not only avoids the use of organic solvent, but also ensures the uniform dispersion of activation agent in the carbon precursor. The results showed that the product had good electrochemical properties due to the significant activation effect of potassium acetate.
2. Experimental

2.1. Synthesis
The preparation process of the material is shown in Fig. 1. In a round flask, water-soluble pitch was mixed with potassium acetate (mass ratio of 1:3) and stirred at 60 °C until completely dissolved. After evaporation at 85 °C for 6 h, the mixture were treated at 700-900 °C for 1 h with a heating rate of 5 °C \text{min}^{-1} under pure N\textsubscript{2} atmosphere. The samples were finally washed with deionized water and dried overnight at 120 °C for 12 h. The final samples were designated as HPC-T, where T (700, 800, 900) refers to the annealing temperature.

2.2. Characterizations
SEM, TEM and XRD were used to investigate the morphologies and structural properties. Elemental analysis were carried out using X-ray photoelectron spectroscopy (XPS). The porous characteristics were collected using a Micromeritics ASAP 2020 sorptometer. The electrochemical evaluation was carried out using a two-electrode system in 6 mol L\textsuperscript{-1} KOH. The gravimetric capacitance was calculated according to the charge-discharge (GCD) curves.

3. Results and discussion
Fig. 2a and 2b shows the SEM images of the HPC-900 at different magnifications. Fig. 2a indicates that interconnected honeycomb hierarchically pores are distributed in the carbon matrix. Pores with diameters of tens of nanometers to hundreds of nanometers can be seen in a high magnification SEM image in Fig. 2b. The TEM image of HPC-900 (Fig. 2c) shows that small-mesopores (diameter less than 10) can be observed. XRD was employed to further characterize the crystallite structure of the samples (Fig. 2d). The XRD patterns of all the samples present the characteristics of amorphous carbons with entirely disordered graphite ribbons, two broad diffraction peaks at 2\theta \approx 23^\circ and 43^\circ, corresponding to the characteristic of (002) and (101) diffraction peaks, respectively [5]. The peak intensity at 2\theta \approx 43^\circ tends to increase with the increase of carbonization temperature, indicating the improvement of the degree of graphitic nature at higher pyrolysis temperature [6].
Nitrogen adsorption-desorption curves were used to characterize the pore structure of the samples (Fig. 3). The HPC-700 shows a type I adsorption-desorption, indicating the microporous characteristics. The increasingly obvious hysteresis loop (HPC-800 and HPC-900) with the pyrolysis temperature demonstrates the type II adsorption-desorption isotherm, which is evidence for the existence of mesopores and macropores [7]. The results are in good agreement with the TEM observations. The above analysis is also well proved by the pore-size distributions (Fig. 3b) and porous properties (Table 1). The pore size of HPC-700 is mostly concentrated in 1 and 2 nm, while the HPC-800 and HPC-900 have well-developed mesopores (2-10 nm and 20-50 nm) and a few macropores (50-80 nm). Due to intense activation at high temperature, the HPC-900 owns the largest BET surface area ($S_{BET}$) of 1108 m$^2$ g$^{-1}$ (Table 1). Surface element composition also has an important influence on the electrochemical properties of the material. The XPS measurements clearly show that all samples consist of C, O, S and N. As listed in Table 1, with temperatures rising, the contents of O, S and N gradually decrease, while the proportion of C increases. The result is due to the instability of N, O and S functional groups at high temperature. According to many previous studies, these functional groups can greatly improve electrical conductivity and capacitance properties [8].

Fig. 2 (a, b) SEM images of HPC-900 with different magnifications, (c) TEM image of HPC-900, (c) XRD of the samples.

Fig. 3 (a) N$_2$ adsorption-desorption isotherms; (b) Pore size distributions.
Table 1. Porous properties and chemical compositions of the prepared carbons.

| Samples     | $S_{BET}$ (m$^2$ g$^{-1}$) | $V_{total}$ (cm$^3$ g$^{-1}$) | XPS (at.%)      |
|-------------|----------------------------|-------------------------------|-----------------|
|             |                            |                               | C        | N        | O        | S        |
| HPC-700     | 856                        | 0.41                          | 73.53    | 2.12     | 22.13    | 0.22     |
| HPC-800     | 1009                       | 0.72                          | 78.79    | 1.49     | 19.62    | 0.10     |
| HPC-900     | 1108                       | 0.91                          | 84.70    | 0.65     | 14.56    | 0.09     |

$^a$ $V_{total}$, total pore volume calculated at $P/P_0 = 0.99$.

The electrochemical performance is measured in 6 mol L$^{-1}$ KOH with a two-electrode system. All samples appear the rectangular-like CV curve at 50 mV s$^{-1}$, suggesting the ideal EDLC characteristic (Fig.4a). As shown in Fig.4b, even when the scan rate increases to 100 mV s$^{-1}$, the CV curve of HPC-900 still maintains a rectangular-like shape with little polarization. When the scan rate increases, the capacitance decreases very slowly, implying good rate performance [9, 10]. The specific capacitances ($C_{SP}$) calculated from galvanostatic discharge curves at different current densities are shown in Fig.4c. The carbon prepared at higher annealing temperature presents a higher capacitance retention ratio at enhanced current loads, suggesting better rate capability. For example, as the current density increases from 0.05 A g$^{-1}$ to 20 A g$^{-1}$, the capacitance retention of HPC-900 is about 69.5%, much higher than that of the other samples. The HPC-900 possesses the highest $C_{SP}$ (208 F g$^{-1}$, 0.05 A g$^{-1}$) due to its highest $S_{BET}$. The electrochemical stability of HPC-900 was tested by the charge-discharge measurement at 2 A g$^{-1}$, as shown in Fig. 4d. The 96.3% capacitance retention after 10000 charge-discharge cycles confirms the superior stability of HPC-900 based supercapacitor. The last 10 nearly symmetric charge and discharge curves reveal an excellent reversibility of HPC-900 [11].

Fig. 4 Electrochemical performance of HPCs measured in a two-electrode system in 6 mol L$^{-1}$ KOH electrolyte: (a) CV curves at 50 mV s$^{-1}$, (b) CV curves of HPC-900 at different scan rates, (c) CSP at different current densities (d) The cycling performance of HPC-900 at the current density of 2 A g$^{-1}$, the inset depicts charge-discharge curves.
4. Conclusion
In this work, we successfully obtained hierarchical porosity carbon using water-soluble pitch as carbon source. The use of water-soluble pitch effectively avoids the harm of organic solvents. The resulting carbon exhibits a large surface area (1108 m² g⁻¹) and a high specific capacitance (208 F g⁻¹), as well as an excellent rate capability and considerable cycling stability. This work proposed a good potential material in supercapacitor applications.

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