

Research on super capacitance properties of modified activated carbon in sodium sulfate electrolyte

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Abstract: In order to improve the specific capacity and energy density of activated carbon electrode materials, activated carbon was modified by surface treatment using hydrogen peroxide. The modified carbons were characterized the changes of pore structure and functional groups before and after modification by N₂ adsorption-desorption isotherms and FTIR spectroscopy. The three electrode system was assembled with modified activated carbon as electrode materials and Na₂SO₄ as the electrolyte. The influence of surface modification on the performance of EDLCs was studied by galvanostatic charge-discharge, cyclic voltammetry, and alternating current impedance. The results show that the surface chemistry of the modified activated carbon material has changed, the specific surface area has changed and the pore size has not changed much with the introduction of new oxygen-containing functional groups. The specific capacity of the activated carbon material modified by 5h is 75F/g, which is 86.1% higher than that before the modification. It can be seen that the change of functional group after the modification of activated carbon can help to increase the specific capacity.

Introduction

Supercapacitors have received wide attention as an efficient, environmentally friendly, and renewable energy device. The traditional capacitor has low power density, short cycle life, slow charge and discharge speed, which makes the application market shrink compared with supercapacitors. Electrolyte and electrode materials are important components of supercapacitors and critical to the performance of capacitors^[1-3]. As an important electrode material, activated carbon material has the advantages of larger specific surface, excellent thermal, electrical conductivity, good chemical corrosion

resistance, small thermal expansion coefficient, low cost, easy availability and easy industrialization^[4-8]. The pore structure and surface chemistry of carbon materials have an important influence on the formation of electric double layers^[9-13].

In this paper, the activated carbon was modified with 30% H₂O₂. The modified activated carbon was used as the electrode material of the supercapacitor. Physical characterization was carried out by Fourier transform infrared spectroscopy and N₂ adsorption-desorption method. Activated carbon was used as the electrode material. The cyclic voltammetry, galvanostatic charge and discharge characteristics of activated carbon with different modification time were measured in 1mol/L

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Na₂SO₄ electrolyte, the specific capacity of the activated carbon was calculated and the effects of different modification conditions on the capacitance properties of carbon materials were investigated.

1 Experimental

1.1 Materials and reagents

activated carbon (AC), PTFE emulsion (PTFE), acetylene black, foam nickel, 30% H₂O₂, Na₂SO₄, absolute ethanol, etc. All reagents are analytical grade.

1.2 Activated carbon modification

The activated carbon for the study was prepared by SUNRISE POWER. A carbon (AC-0.5-AC-6) was prepared through oxidation of AC (1 g) with 50 mL of 35 wt% H₂O₂ solution under stirring for 0.5h-6h at room temperature. Recorded as AC-0.5, AC-1, AC-2, AC-3, AC-4, AC-5 and AC-6, untreated activated carbon is recorded as AC-0. The resultant material was extensively rinsed with distilled water. Then they were dried in a vacuum drying oven.

1.3 Performance characterization

1.3.1 Fourier transform infrared spectrometer (FTIR)

FTIR was carried out by KBr tableting method. The appropriate KBr and activated carbon before and after modification were mixed, grinded and tableted. The TENSOR 27 Fourier infrared spectrometer was used to analyze the changes in surface functional groups of carbon materials, with wavelength range of 250~4000cm⁻¹.

1.3.2 Nitrogen adsorption and desorption experiment

The nitrogen (N₂) isotherm adsorption/desorption test is one of the methods for testing parameters such as specific surface area and pore size distribution of materials. The specific surface area and pore distribution of the material were tested using a Micromeritics ASAP 2000 specific surface area tester, vacuum pretreatment at 393K, absorption/desorption at liquid nitrogen

temperature (-196°C), and data was recorded and analysed by computer.

1.3.3 Electrochemical characterization

Electrodes (1cm diameter) were pressed from a mixture of the studied carbons (80 wt%), PTFE(10 wt%), carbon black (10 wt%). Three-electrode with Hg/Hg₂SO₄ as a reference electrode comprised the studied carbon and Pt electrode as working and counter electrodes, respectively. Cyclic voltammetry and galvanostatic charge/discharge cycling were measured by a CHI660D electrochemical workstation in 1mol/L Na₂SO₄ electrolyte solution. The specific capacitance (C_s) can be calculated according to the following equation:

$$C_s = It/mU \quad (1)$$

where in I (A), t (s), m (g) and U (V) represent the discharge current, discharge time, mass of active material and window potential, respectively.

2 Results and discussion

2.1 Infrared spectroscopy

In order to investigate the Changes in oxygen-containing functional groups on the surface of activated carbon. Fourier transform infrared (FTIR) spectroscopy was conducted. The result is shown in Figure 1.

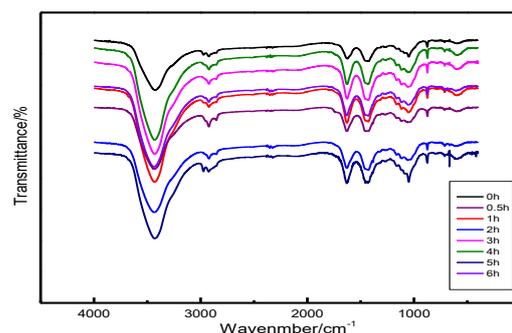


Figure 1. FTIR spectra of activated carbons before and after modification

Figure 1 is a FTIR spectrum of a carbon material before and after surface modification. It can be seen from the figure that after H₂O₂ modification treatment, the -COO-anti-extension peak of AC-0 at 1570 cm⁻¹

disappears after modification, and the -OH stretching vibration peak of the carbon material modified by H₂O₂ is obviously enhanced at 3430 cm⁻¹, especially the AC enhancement with the modification time of 5h is most obvious. The C-O stretching vibration and O-H out-of-plane bending occurred at 1264cm⁻¹ and 669cm⁻¹ respectively, and the carbonyl stretching vibration peak appeared at 1640cm⁻¹, indicating that the modified CO content may increase, and the surface of the carbon material was introduced with -OH [14-18]. It can be seen that the surface modification has a great influence on the surface chemistry of the carbon material. Through the modification of hydrogen peroxide, some functional groups and groups are introduced on the surface of the activated carbon, which is beneficial to improve the capacitance performance of the activated carbon electrode.

2.2 N₂ adsorption-desorption isotherm

Fig.2 is nitrogen adsorption-desorption isotherms of activated carbons. It can be seen from the figure that the activated carbon which was modified that the adsorption amount of N₂ was changed at different extents, but the shape of the adsorption curve and the desorption curve did not change substantially. All adsorption isotherms are classic V-type isotherms. The adsorption capacity in the low pressure is very low and slowly increases. The relative pressure at 0.9 is a significant lag in the desorption curve. According to the trend of the adsorption isotherm and the hysteresis loop, it can be seen that all activated carbon is a mesoporous or microporous material.

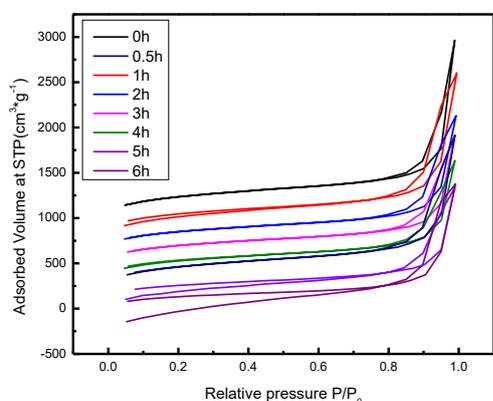


Figure 2. Nitrogen adsorption-desorption isotherms of activated carbons

The changes in specific surface area and pore structure parameters of carbon materials before and after modification are displayed in table 1. The modification treatment did not change in the pore structure of the micropores and mesopores of the activated carbon, and the sample still retained the characteristics of the microporous material. However, the specific surface area of the carbon material are decreased at different modification times. The total pore volume and micropore volume of carbon materials are reduced. The average pore size of the modified carbon material is decreased slightly. The results of different modification time modification treatments, except for a certain decrease in specific surface area, other pore structure parameters did not change much.

Table1. Specific surface area and pore diameter of active carbon

S _{BET} (m ² /g)	D (nm)
1593.241	3.345
1513.394	3.335
1458.420	3.365
1313.478	3.366
1296.835	3.354
1261.308	3.376
1143.590	3.360
1069.074	3.036

2.3 Electrochemical properties

To compare the electrochemical properties of carbon materials before and after modification. CV and galvanostatic charge-discharge measurements were performed. CV curves of AC-5 obtained at different scan rates and CV curves obtained at a scan rate of 20 mV/s for different treatment time are shown in Fig. 3 and Fig.4.

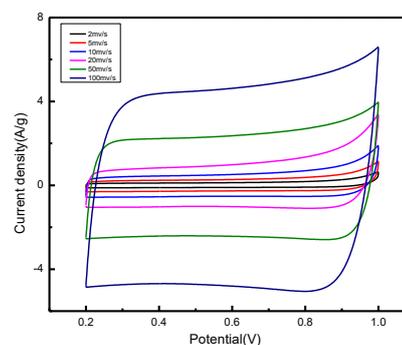


Figure 3. AC-5 CV curves obtained at different scan rates

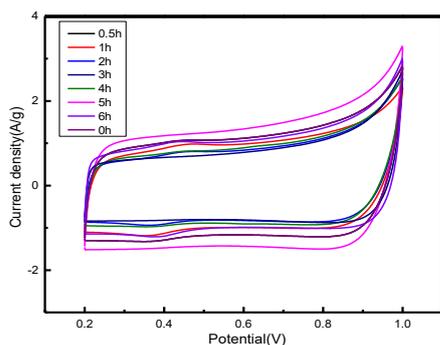


Figure 4. AC-5 CV curves obtained at a scan rate of 20 mV/ s for different treatment time

It can be seen from Fig.3 and Fig.4 that the cyclic voltammetry curves all show an approximately rectangular shape and do not contain obvious redox peaks, indicating that electrostatic physical adsorption is the main energy storage method for electrode materials. However, due to the existence of a large number of micropores in the activated carbon, the electrolyte infiltration and the positive and negative ions penetrate the pores in different ways, resulting in different equivalent series resistance (ESR), and the cyclic voltammetry deviates from the ideal rectangular shape to some extent. As the scanning speed increases, the response current increases proportionally, indicating that the electrolyte ions migrate faster and have less resistance in the activated carbon tunnel. The cyclic voltammetry curve is basically rectangular, indicating good reversibility.

The galvanostatic charge/discharge characteristics of AC-0-AC-6 in 1mol/L Na_2SO_4 were recorded in Fig.5.

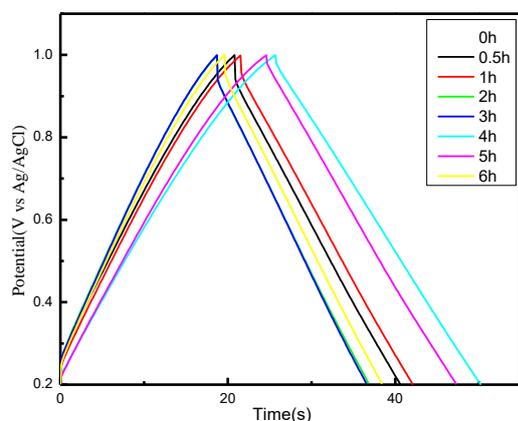


Figure 5. The charge-discharge curves obtained at 2A/g for sample AC-0-AC-6 in 1mol/L Na_2SO_4

It can be seen from Fig.5 that the charge-discharge curve has a relatively symmetrical isosceles triangle shape,

indicating that the capacitor has good capacitance characteristics, and at the moment of charging and discharging, the potential drop is small, indicating that the internal resistance of the activated carbon electrode is small. According to the charge-discharge curve, the specific capacitance value of the activated carbon electrode can be calculated. Fig.6 shows the specific capacitance of different samples calculated from their discharge processes at different current densities.

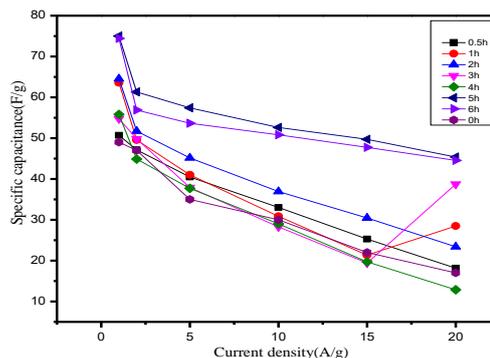


Figure 6. The specific capacitance of AC-0-AC-6 at different current densities

It can be seen from Fig.6 that the variation rules of activated carbon at different modification times are not much different. Before the modification time 5h, the specific capacity gradually increased, and reached the maximum at the modification time of 5h. When the modification time is 6h, the specific capacity does not continue to increase, it is slightly smaller than the modification time of 5h, indicating that the electrochemical performance of the activated carbon is the best at 5h.

3 Conclusion

(1)The modification treatment leads to large changes in the surface chemistry of the carbon, and the original $-\text{COO}-$ content is reduced. Functional group $=\text{CO}$ and $-\text{OH}$ on the carbon surface are increased. the specific capacity of the carbon materials are increased, thereby improving the electrochemical performance of the electrode.

(2)By comparing the relationship between capacitance and structure of activated carbon materials with different modification times, due to the pore structure, surface chemistry and wettability of carbon materials, with the increasing of the specific surface area, the specific

capacitance is not increasing always. There is no direct correlation between the specific capacity of activated carbon materials and the change in specific surface area.

(3) It has been shown by both galvanostatic charge/discharge and cyclic voltammetry experiment that the surface functional groups introduced by the modification of carbon materials can effectively increase their specific capacity. By comparing the activated carbon electrode materials with different modification time, the specific capacity of activated carbon with the modification time of 5h is the highest. When the current density is 1A/g, the specific capacity is the largest, which is 75F/g compared to the modification time of 0h (specific capacity 40.3 F/g) increased by 86.1%, and it was found that the modification time was not as long as possible.

Acknowledgement

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