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RESEARCH PAPER

Preparation and modification of high performance porous carbons from petroleum coke for use as supercapacitor electrodes

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Abstract: As a byproduct of oil refining, petroleum coke with a high carbon content (about 90 wt%) has been shown to be a good raw material for porous carbons (PCs). PCs with high specific surface areas were derived from petroleum coke by KOH activation. The effect of KOH/coke mass ratio on the pore structure of the PCs and their electrochemical performance as electrodes of electric double layer capacitors were investigated. Results showed that the specific surface area and pore size distribution of the PCs could be efficiently controlled by the KOH/coke ratio. The pore sizes of the PCs increase with increasing KOH/coke ratio, and the largest specific surface area was as high as 2964 $m^2 \cdot g^{-1}$. A PC-5 electrode prepared with a KOH/coke ratio of 5:1 has a high specific surface area of 2 842 $m^2 \cdot g^{-1}$ and mesoporosity of 67.0 %, and has the largest specific capacitance at all investigated current densities among the PCs examined. This is ascribed to its high specific surface area and high mesoporosity. Hydrothermal modification of PC-3 (KOH/coke ratio at 3:1) in ammonia at 200 ^oC increases its specific capacitance, especially at high discharge current densities. This improved electrochemical performance can be attributed to nitrogen-doping that occurs during the process, and this can induce pseudo-capacitance and improve the hydrophilicity of the PC electrode to the electrolyte. KOH activation combined with ammonia hydrothermal modification is a simple yet efficient approach to prepare cost-effective PCs for supercapacitors with excellent electrochemical performance.

Key Words: Petroleum coke; Porous carbon; Supercapacitors; Ammonia hydrothermal modification; Nitrogen doping

1 Introduction

Electric double-layer capacitors (EDLCs) have attracted much attention as attractive energy storage devices owing to their high power density and excellent cycling stability[1-3]. EDLCs store energy mainly via forming electric double layers (EDLs) on the electrode/electrolyte interface, thus their electrochemical performance highly depend on the available surface area of electrode materials[4-6]. Porous carbons (PCs) have been widely used as electrode materials for commercial EDLCs owing to their relatively large specific surface area, good chemical stability, and a wide range of application temperatures [7-10].

Generally, the larger the specific surface area of the PC is, the higher specific capacitance will be obtained according to the equation below[11]:

$$C=\varepsilon A/d \qquad (1)$$

Where, A is the available surface area to electrolyte ions, ε is the electrolyte dielectric constant, and d is the separation between electrolyte ions and carbon surface. The values of A and d depend on the specific surface area and pore size of electrode materials. PCs with high specific surface areas usually have relatively low capacitance than expected, due to a lot of ultramicropores (smaller than 0.7 nm) inaccessible to form EDLCs. Although the pores larger than the size of the electrolyte ions and their solvation shell are required for high value of A, the larger pores will certainly decrease the total specific surface area of PCs and increase the value of d, leading to an impressive power density but a low energy density. Therefore, an appropriate pore size distribution is very important for electrode materials to have excellent electrochemical performance. Many studies focus on template methods to produce controllable pores in the range of 2 to 4 nm[12-14]. However, the complicated preparation procedure, high cost and low yield of PCs make the template methods difficult to achieve practical applications[15-17]. Moreover, the micropores larger than 0.7 nm are proved available for electro-adsorption of hydrated ions in aqueous electrolytes[11, 18]. Therefore, PCs having lots of mesopores and a certain amount of micropores prepared from inexpensive raw material via simple methods may have excellent electrochemical performance and promising applications in EDLCs. Besides

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the pore structure, the surface properties also play important roles in improving the electrochemical performance of PCs. As an effective method, nitrogen-doping has received much attention and is often used to enhance the specific capacitance of electrode based on PCs [19-22].

In this paper, petroleum coke was used as raw material to prepare PCs for EDLCs by KOH activation. Ammonia hydrothermal treatment on PCs was further used to improve the EDLC electrochemical performance. As a byproduct of oil refinery, petroleum coke has a high carbon content (about 90 wt%) and has been proved suitable raw material for PC preparation [23, 24]. The relationships among the KOH/coke ratio, the pore structure and the electrochemical performance were discussed. Ammonia hydrothermal treatment is an efficient approach to dope nitrogen on PCs and enhance the electrochemical performance of PC electrodes.

2 Experimental

Petroleum coke from Daqing Oilfield of China was used as raw material to prepare PCs. The proximate and elemental analysis are listed in Table 1[25].

PCs were prepared from petroleum coke with particle diameter smaller than 100 μm by KOH activation, using a mass ratio of KOH to petroleum coke of 1 to 5. The carbonization and activation were carried out in a horizontal tube furnace, where the samples were heated from room temperature to 500 °C at 5 °C·min^{-1} and kept for 1 h, then heated to 850 °C at 5 °C·min^{-1}, and kept for 1.5 h. The above processes were performed under nitrogen flow of 60 mL· min^{-1} to protect the samples from oxidation. According to the mass ratio of KOH to petroleum coke ($m_{\mathrm{KOH}}/m_{\mathrm{petroleum\ coke}}$), the obtained samples were denoted as PC-1, PC-2, PC-3, PC-4 and PC-5.

In order to further increase the electrochemical performance of the PC electrodes, the PCs were hydrothermally treated in ammonia at different temperatures. PC-3 was mixed with ammonia, then placed into a hydrothermal reactor, and kept for 24 h at different temperatures. After the hydrothermal treatment, the samples were rinsed with distilled water, and then dried in an oven at 110 °C. According to the temperature of hydrothermal treatment, hydrothermal treated PC-3 samples were named as PC-3-RT (room temperature), PC-3-100 (100 °C), PC-3-150 (150 °C) and PC-3-200 (200 °C).

N_2 adsorption-desorption was carried out on a Micromeritics ASAP 2020 sorption analyzer (USA) to determine the BET specific surface areas and the pore size distributions of PCs. The crystal structures of samples were confirmed by X-Ray diffraction (XRD) (Rigaku RINT 2400, Japan). The surface morphology was characterized by scanning electron microscopy (SEM) (JEOL JSM-6360LV SEM, Japan) and transmission electron microscopy (TEM) (JEM-2100UHR, Japan). The temperature programmed desorption of carbon dioxide (CO_2-TPD) was conducted by a Catalyst Analyzer BELCAT-B (Japan) with a heating rate of 10 °C·min^{-1} to measure the intensity of basic sites of samples. X-ray photoelectron spectra (XPS) were recorded on a ESCALAB 250Xi spectrometer (Thermo Scientific, USA).

The electrodes were prepared from PCs by adding polytetrafluoroethylene emulsion (PTFE) as binder and acetylene black as conductive agent with a PC/acetylene black/PTFE mass ratio of 85/5/10. The mixture was pressed on the foam nickel with diameter of 12 mm at 20 MPa for 30 s, and then dried at 100 °C for 1 h in vacuum. Finally, button-type capacitor was assembled with two PC electrodes separated by a polypropylene membrane, using a 6 M KOH aqueous solution as an electrolyte. Galvanostatic charge/discharge analysis was carried out on a land cell tester (Land, CT-2001A, China). The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed on an electrochemical workstation (PARSTAT 4000, Princeton, USA). The potential range of CV was 0-1 V, and the Nyquist plot was recorded at the frequency from 100 kHz to 0.01 Hz. All electrochemical measurements were carried out at room temperature.

3 Results and discussion

The N_2 adsorption–desorption isotherms obtained at 77 K for PCs with different KOH/coke ratios are shown in Fig. 1a. PC-1 and PC-2 exhibit a typical type-I isotherm with a sharp increase in the amount of nitrogen adsorbed at low relative pressure until a plateau is formed and no obvious hysteresis loop is observed at high relative pressure. It is well known that the adsorption of microporous material at low p/p_0 is micropore filling. For PC-1 and PC-2, the plateaus are formed immediately following the quick increase. Compared to PC-1 and PC-2, the plateaus of PC-3, PC-4 and PC-5 are formed

Table 1 The basic properties of petroleum coke.

Raw material	Proximate analysis, (wt%)			Elementale analysis, (wt%)				
	A_d	V_{daf}	M_{ad}	C	H	S	N	O
Petroleum coke	0.21	12.49	1.20	90.30	4.26	0.81	1.79	2.84

*A_d: the ash content in petroleum coke on the dry basis; M_{ad}: the water content in petroleum coke on the air dry basis; V_{daf}: the volatile matter content in petroleum coke on dry and ash free basis