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doi: 10.3866/PKU.WHXB20112836

www.whxb.pku.edu.cn

花生壳制备微孔炭及其在电化学超级电容器中的应用

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摘要: 以未使用和使用氢氧化钠溶液处理的花生壳为碳源分别制备出微孔炭 PSC-1 和 PSC-2. PSC-1 和 PSC-2 的比表面积分别为 552 和 726 m²·g⁻¹, 其主要孔径都约为 0.8 nm. 用 PSC-1 和 PSC-2 制备的电极和对称型超级电容器的循环伏安曲线均接近矩形, 表明其具有良好的电容特性. 在以微孔炭电极为工作电极、铂电极为对电极和银/氯化银电极为参比电极组成的三电极体系测量表明, 在 0.1 A·g⁻¹ 的电流密度下, PSC-1 和 PSC-2 的比电容达到 233 和 378 F·g⁻¹. 经过 1000 次恒电流充放电循环后, 在三电极体系和超级电容器中电极均表现出良好的稳定性和电容保持率. 基于实验结果探讨了微孔炭的形成机理及其结构与电化学性质之间的联系.

关键词: 超级电容器; 电极; 微孔炭; 花生壳; 电容

中图分类号: O646

Preparation and Characterization of Peanut Shell-Based Microporous Carbons as Electrode Materials for Supercapacitors

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Abstract: Microporous carbons (PSC-1 and PSC-2) were obtained directly by the carbonization of peanut shells without and with NaOH solution pretreatment, respectively. Both samples have a main pore size of ~0.8 nm. The surface area increases from 552 m²·g⁻¹ for PSC-1 to 726 m²·g⁻¹ for PSC-2. Cyclic voltammograms (CVs) of the PSC-1 and PSC-2 electrodes and the symmetrical supercapacitors show almost rectangular shape indicating excellent capacitance features. The specific capacitances of PSC-1 and PSC-2 can reach 233 and 378 F·g⁻¹, respectively, at a current density of 0.1 A·g⁻¹ in a three-electrode system using porous carbon as the working electrode, a platinum electrode as the counter electrode and a Ag/AgCl electrode as the reference electrode. Furthermore, the electrodes in both three-electrode systems and supercapacitors show high stability and capacitance retainability after 1000 cycles. The formation mechanisms for the two microporous carbons and the relationship between the carbon materials and their electrochemical properties are discussed based on the experimental results.

Key Words: Supercapacitor; Electrode; Microporous carbon; Peanut shell; Capacitance

Received: July 18, 2011; Revised: September 26, 2011; Published on Web: October 13, 2011.

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The project was supported by the National Natural Science Foundation of China (20803037, 21143006), Foundation of Qingdao Municipal Science and Technology Commission, China (11-2-4-2-(8)-jch) and "Taishan Scholar" Program of Shandong Province, China.

国家自然科学基金(20803037, 21143006), 青岛市应用基础研究项目(11-2-4-2-(8)-jch)和“泰山学者”计划资助

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1 Introduction

Electrochemical double-layer capacitors (EDLCs) are promising power sources because the demand for energy storage devices is increasing as a result of the fast-growing market for portable electronic devices and hybrid electric vehicles.^{1–3} The capacitance of EDLCs comes from charge accumulation at the electrode/electrolyte interface, and is therefore strongly dependent on the pore size and the surface area of the electrode accessible to the electrolyte.^{4–6} Among the various electrode materials for EDLCs, porous carbons are the most popular because of their high surface area, low cost, good electrical conductivity, and excellent chemical stability.^{6–9}

There are several approaches to prepare porous carbon. One is the direct high-temperature carbonization of appropriate precursors.^{10,11} The other uses a template to prepare composites of the template and carbon precursor, and the mixed composites are then carbonized.^{6,7} Many researchers also use alkali/salt activation methods consisting of treating a mixture of the precursors and an alkali/salt at high temperature.^{12,13} For example, Béguin *et al.*¹⁰ reported that porous carbon derived directly by carbonization of sodium alginate had a capacitance as high as $200 \text{ F} \cdot \text{g}^{-1}$. Zhang *et al.*¹² reported that oxygen-rich activated carbons prepared from bituminous coal by a high-temperature activation method had a specific capacitance of $370 \text{ F} \cdot \text{g}^{-1}$. Recently, we have shown that the carbonization temperature has a significant effect on the electrochemical properties of chitosan-based porous carbons.¹¹

Peanuts are widely planted in China, and the total amount can reach 14 million tons per year. Some of the peanut shells are used as animal feed and for cultivation of edible fungi, but a large proportion of the shells are unused. It is necessary to explore possible applications of peanut shells as well as other waste biomass.^{14–21} Recently, peanut shells have been used to fabricate porous carbons, which show many potential applications,^{14–16} for example as sorbents for metal ions¹⁴ and as Li-ion battery electrode materials.¹⁶ The activation method is usually used to fabricate activated carbons from peanut shell based on the solid mixture of the precursors and KOH or ZnCl_2 ,^{10–13} however, peanut shells are pretreated using aqueous NaOH solution before carbonization in our work. It is found that the pretreatment process has a strong effect on the physical and electrochemical properties of the peanut-shell-based microporous carbons. The electrochemical properties of the samples are characterized by cyclic voltammetry (CV), galvanic charge-discharge, and cycling experiments.

2 Experimental

2.1 Materials

Peanut shells were obtained from peanuts purchased at Qingdao market. NaOH and KOH (AR grade) were purchased from the Sinopharm Chemical Reagent Company. Acetylene carbon black (99.99%) and polytetrafluoroethylene (PTFE, with mass fraction of 60%) latex were purchased from Strem Chemicals

and Aldrich, respectively. All chemicals were used without further purification.

2.2 Preparation of porous carbons

The peanut shells were rinsed with water, dried, and then cut into small pieces (PS-1). Some peanut shells had been pretreated in an aqueous NaOH solution ($1 \text{ mol} \cdot \text{L}^{-1}$) at 80°C for 12 h, and then the treated peanut shells were washed with water, dried and cut into pieces (PS-2). Porous carbons were obtained by carbonization of the peanut shells in a tube furnace at 800°C for 90 min under a nitrogen flow. The heating rate was $10^\circ\text{C} \cdot \text{min}^{-1}$. The obtained black solid was then immersed into HF (20%, mass fraction) solutions for 48 h. Finally, the solid was filtered with water and dried at 60°C for 6 h. The samples referred to as PSC-1 and PSC-2 were derived from PS-1 and PS-2, respectively.

2.3 Characterization of porous carbons

The pore structures of the samples were investigated by physical adsorption of nitrogen at liquid nitrogen temperature (77 K) on an automatic volumetric sorption analyzer (NOVA 1100, Quantachrome). The specific surface area was determined by the Brunauer-Emmett-Teller (BET) method. Pore size distribution was evaluated by the Barrett-Joyner-Halenda (BJH) method. Elemental analyses were performed on a VARIO EL III elemental analyses system (Elementar Analysensysteme GmbH, Hanau, Germany). Fourier transform infrared (FTIR) spectra were recorded on a Thermo Nicolet 5700 spectrophotometer. X-ray powder diffraction (XRD) measurements were determined using a Bruker D8 advanced X-ray diffractometer equipped with Cu K_α radiation ($\lambda=0.15418 \text{ nm}$).

2.4 Fabrication of porous carbon electrodes

The electrochemical measurements were performed on an Autolab PGSTAT302N in an aqueous KOH solution ($6 \text{ mol} \cdot \text{L}^{-1}$) at room temperature using a three-electrode cell with porous carbon as the working electrode, a platinum electrode as the counter electrode, and an Ag/AgCl electrode as the reference electrode. The porous carbon electrodes were obtained by pressing a well-mixed slurry (80% (mass fraction) carbon, 15% acetylene carbon black, and 5% PTFE) onto a nickel foam grid ($1 \text{ cm} \times 1 \text{ cm}$) at $1.25 \times 10^7 \text{ Pa}$. The typical mass load of each electrode material was about 5 mg. The electrodes were vacuum dried at 110°C . Symmetrical sandwich-type supercapacitors made of two carbon pallets separated by fibrous paper and the electrode materials composed of 80% carbon (10 mg), 10% acetylene carbon black, and 10% PTFE.

3 Results and discussion

Nitrogen sorption isotherms were recorded to determine the pore properties of the peanut-shell-based porous carbons (Fig.1). It can be seen that the data for PSC-1 and PSC-2 are almost the same, except that the surface area of PSC-2 is larger than that of PSC-1. At low pressure, the initial step region ascends abruptly and then follows a plateau (Fig.1A), indicating that adsorption has virtually stopped because of the pore wall

Fig.1 Nitrogen adsorption-desorption isotherms (A) and pore size distribution (B) of PSC-1 and PSC-2

multilayer. Both isotherms are type IV isotherm curves. It can be seen from Fig.1B that for both porous carbons the major pore size of particles is ~ 0.8 nm, with a minor part of ~ 1.3 nm. However, the surface area increases from $552 \text{ m}^2 \cdot \text{g}^{-1}$ for PSC-1 to $726 \text{ m}^2 \cdot \text{g}^{-1}$ for PSC-2. These changes are ascribed to the pretreatment with NaOH solution, which may enable some pectin and hemicelluloses (lignin, and wax like substances) to separate from the peanut shell and contribute to the increase in the specific surface area and pore volume.²² This will be further confirmed by the FTIR results. The pore sizes of PSC-1 and PSC-2 are suitable for EDLC;^{1,23} they allow ion migration of inorganic electrolytes and electronic adsorption because the diameters of K^+ and OH^- in the KOH solution are smaller than 0.4 nm .²⁴

FTIR spectroscopy can give direct structural information in the peanut shells during various chemical treatments. It can be seen from the FTIR spectra of PS-1 and PS-2 (Fig.2) that most of the absorption peaks are not shifted. For example, the absorption peaks at 3420 cm^{-1} , ascribed to the OH group, and the peaks in the fingerprint regions at 1424 , 1158 , and 1054 cm^{-1} , attributed to the cellulose structure, are virtually unchanged in both peanut shell samples.²² The absorption band at 1635 cm^{-1} , ascribed to asymmetric COO^- stretching, and the bands at 1458 and 1378 cm^{-1} , assigned to the CH_2 and CH symmetric bending modes, are also unchanged. However, the vibrational peak at 1738 cm^{-1} in the PS-1 spectrum, which is ascribed to C=O stretching of the methyl ester and carboxylic acid groups in pectin, or the acetyl group in the hemicelluloses, disap-

Fig.2 FTIR spectra of PS-1 and PS-2

peared from the PS-2 spectrum. This indicates that pectin and hemicelluloses can be successfully extracted by a simple alkaline solution treatment.²² A new band at 877 cm^{-1} in the PS-2 spectrum, ascribed to an epoxy compound, gives further information on the efficiency of the pretreatment. Furthermore, the mass contents (%) of C, N, S, and H, based on the elemental analyses data, are 92.13, 0.79, 0.36, and 1.01 for PSC-1, and 92.30, 0.48, 0.36, and 0.81 for PSC-2.

Fig.3 shows the CV curves of PSC-1 and PSC-2 based electrodes in three-electrode systems or symmetrical supercapacitors at different scan rates. Fig.3(A, C) displays that the CV curves of the electrodes in three-electrode systems have an almost rectangular shape, even at high scan rates, indicating that electrodes based on PSC-1 and PSC-2 have good capacitance⁴⁻⁷ and fast charge-discharge switching.²⁵ PSC-1 and PSC-2 electrodes all have large specific currents. Furthermore, the specific currents for the PSC-2 electrode are larger than those of the PSC-1 electrode, indicating that the PSC-2 electrode has a lower resistance and higher capacitance than that of the PSC-1 electrode.³ For symmetrical supercapacitors (Fig.3(B, D)), all the CVs of the composites at a scan rate of $50 \text{ mV} \cdot \text{s}^{-1}$ are nearly rectangular. However, the shape of the CVs are somewhat tilted at $80 \text{ mV} \cdot \text{s}^{-1}$. The shape evolution of the CVs at different scan rates indicates that the ohmic resistance of the carbon electrodes is large at high scan rates.²⁶

Galvanostatic charge-discharge is a commonly used method for studying electrochemical capacitors; much information, such as the capacitance and the long cycle capability of electrode materials, can be obtained from the experiments.²⁷ The charge-discharge curves of the PSC-2 based electrodes and supercapacitors are shown in Fig.4. The coulombic efficiency of carbon electrodes is nearly 100%, although the charge/discharge curves are not exactly linear.²⁸ The specific capacitance can be calculated from the equation $C = It_d / (m \cdot \Delta V)^{-1}$,^{12,29} where I is the current in the galvanostatic charge-discharge measurement, m is the mass of the active materials, t_d is the variance metric of charge or discharge time, and ΔV is the potential window during the discharge process after IR drop. As depicted in Fig.4A, the PSC-2 electrode had a capacitance of $378 \text{ F} \cdot \text{g}^{-1}$ at a current density of $0.1 \text{ A} \cdot \text{g}^{-1}$, and the capacitances decreased

Fig.3 CV curves of PSC-1 (A, B) and PSC-2 (C, D) based electrodes (A, C) and supercapacitors (B, D)

to 322 and 310 $\text{F} \cdot \text{g}^{-1}$ at 0.5 and 1 $\text{A} \cdot \text{g}^{-1}$, respectively. However, the capacitance of the PSC-2 electrode dropped to 233 $\text{F} \cdot \text{g}^{-1}$ at a current density of 0.1 $\text{A} \cdot \text{g}^{-1}$ and decreased to 208 and 205 $\text{F} \cdot \text{g}^{-1}$ at current densities of 0.5 and 1 $\text{A} \cdot \text{g}^{-1}$, respectively. For symmetrical supercapacitors,^{29,30} the capacitances were 130, 109, and 75 $\text{F} \cdot \text{g}^{-1}$ for PSC-2 at current densities of 0.2, 0.5, and 1 $\text{A} \cdot \text{g}^{-1}$ (Fig.4B), respectively, while the capacitance was 102 $\text{F} \cdot \text{g}^{-1}$ for PSC-1 at 0.2 $\text{A} \cdot \text{g}^{-1}$ and decreased to 74 and 52 $\text{F} \cdot \text{g}^{-1}$ at current densities of 0.5 and 1 $\text{A} \cdot \text{g}^{-1}$, respectively. These results indicate that the pore sizes of PSC-1 and PSC-2 are suitable for rapid diffusion of ions, similar to those of carbide-derived microporous carbons.¹⁻³ The difference in the capacitances of PSC-1 and PSC-2 is mainly caused by variations in the specific surface areas.

The electrochemical stabilities of the active materials and their repeatability were also investigated by galvanostatic

charge-discharge measurement. Fig.5 shows the results of a cycling performance test on the PSC-2-based electrodes and supercapacitors. For the PSC-2 based symmetric supercapacitor, the capacitance retention was over 90.0% at a current density of 0.5 $\text{A} \cdot \text{g}^{-1}$ after 1000 cycles (Fig.5A). After 1000 cycles, the specific capacitance of the PSC-2 electrode at a current density of 2 $\text{A} \cdot \text{g}^{-1}$ was maintained more than 94.5% of the original value (Fig.5B). These results indicate that the peanut shell-based carbon electrodes and supercapacitors have good stability and capacitance retainability.

The excellent electrochemical performances of PSC-1 and PSC-2 can be attributed to their unique micropore structure and appropriate surface areas which afford a large enough electrode/electrolyte interface for charge accommodation. It should be noted that no products were obtained when solid mixtures of peanut shells and NaOH were undergone the same calcina-

Fig.4 Galvanostatic charge-discharge curves of PSC-2-based electrodes (A) and supercapacitors (B)

Fig.5 Cycling performance of the PSC-2-based supercapacitors (A) and electrodes (B)

tion procedure. The new procedure consisting of sample pretreatment with alkaline solutions increases the specific surface areas while the pore structure can be maintained. FTIR spectra showed that the peak at 1738 cm^{-1} in the PS-1 spectrum, ascribed to the $\text{C}=\text{O}$ stretching of the methyl ester and carboxylic acid groups in pectin, or the acetyl group in hemicelluloses, disappeared from the PS-2 spectrum. This indicates that pectin and hemicelluloses can be successfully extracted by a simple alkaline solution treatment. And thus microporous carbons with superior electrochemical properties from peanut shells are produced.

4 Conclusions

The alkaline solution activation method has been used to fabricate peanut-shell-based microporous carbons. It is found that PSC-2 derived via the activation method displays a higher surface area than that of PSC-1 produced by a non-activation method. The pore size distribution is unchanged. The CV curves of the samples in three-electrode systems and supercapacitors display rectangular shapes denoting the fast charge-discharge switching. The PSC-2 electrode shows a specific capacitance as high as $378\text{ F}\cdot\text{g}^{-1}$ and good cycle stability. These results suggest that microporous carbon electrodes made from peanut shells have a potentially broad application as electrochemical capacitor electrode materials.

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