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Rod-shape porous carbon derived from aniline modified lignin for symmetric supercapacitors

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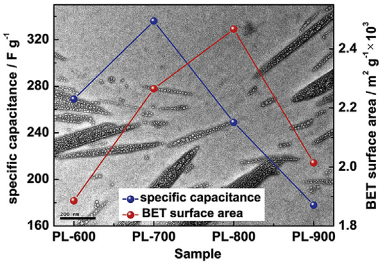
HIGHLIGHTS

- Rod-shape porous carbon derived from aniline modified lignin was prepared.
- High SSA, structured pores and good electrical conductivity were displayed.
- Excellent specific capacitance of up to 336 F g^{-1} was obtained.

GRAPHICAL ABSTRACT



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ABSTRACT

Rod-shape porous carbon was prepared from aniline modified lignin *via* KOH activation and used as electrode materials for supercapacitors. The specific surface area, pore size and shape could be modulated by the carbonization temperature, which significantly affected the electrochemical performance. Unique rod-shape carbon with massive pores and a high BET surface area of 2265 m^2 g^{-1} were obtained at 700 °C in contrast to irregular morphology created at other carbonization temperatures. In 6 mol L^{-1} KOH electrolyte, a specific capacitance of 336 F g^{-1}, small resistance of 0.9 Ω and stable charge/discharge at current density of 1 A g^{-1} after 1, 000 cycles were achieved using rod-shape porous carbon as electrodes in an electrical double layer capacitor.

1. Introduction

Supercapacitors, also known as electrochemical capacitors have received considerable attention because of their high power density, fast charge/discharge capability and long cycle life [1–3]. Supercapacitors can be classified into two major categories based on the energy storage mechanism: electrical double layer capacitor

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(EDLC) and pseudocapacitor [4]. Energy stored in an EDLC is proportional to the electrostatic charge accumulated at the electrode/electrolyte interface. Therefore, the specific capacitance depends on the electrode surface area accessible to the electrolyte. On the other hand, pseudocapacitors store energy *via* the Faradaic reactions that occur between the electrode materials and electrolyte. Pseudocapacitors usually use metal oxides/hydroxides (e.g. MnO_2, NiO, $Ni(OH)_2$, Co_3O_4) electrodes and possess higher specific capacitance than EDLCs that use carbon as electrode materials [5–9]. Pseudocapacitors are expected to find broader applications if their cycle stability can be improved, electrical conductivity can be increased, and the material cost can be reduced [10,11].

Carbon-based materials are the primary electrode materials for EDLC. Porous carbon, such as activated carbon (AC), mesoporous carbon and graphene [12–14] have been commonly used in EDLC. EDLC electrode materials should possess the following characteristics: i) high specific surface area that provides sufficient accessible surface to the electrolyte; ii) proper pore size that allows the electrolyte ions to transfer smoothly with short diffusion pathways; iii) excellent electrical conductivity to minimize resistive loss during charge/discharge; iv) sustainable and wide availability with low cost. The preparation of mesoporous carbon usually involves complex synthetic procedures in most cases, while graphene suffers from high cost although it could be obtained in labs after a series of harsh chemical treatments. Alternatively, activated carbon derived from abundant, renewable biomass feedstock can be produced sustainably at low cost [15]. So far, carbon materials derived from biomass such as rice husk, coffee grounds, grape seed, cornstalk, banana peel [16–20], have been explored as electrode materials in EDLC and promising electrochemical performance has been demonstrated.

Recent research showed that introducing nitrogen into activated carbon could induce additional pseudo-capacitance *via* reversible redox reactions and improve the wettability between the electrodes and electrolytes [21]. As a result, the capacitance performance of EDLC was greatly promoted. Therefore, biomass derived carbon materials with nitrogen may be promising electrode materials for EDLC. Since biochar typically contains low nitrogen content, we hypothesize that combination of nitrogen rich compounds with biomass will lead to biochar with high nitrogen content. Furthermore, there may be opportunities to tune the physicochemical properties of the nitrogen rich biochar, such as morphology, surface area, and conductance. Regarding the source of nitrogen, aniline appears a promising candidate because it is easy to polymerize, and the polymer can be grown into different shapes such as wires, tubes and spheres [22–24] by controlling the synthetic conditions.

Herein, we present aniline modified lignin as the raw materials to prepare rod-shape porous carbon as EDLC electrode materials. It is shown that the chemical activation plays a key role in achieving large specific surface area, uniform pore size distribution and good conductivity, which lead to excellent electrochemical performance.

2. Experimental

2.1. Preparation of activated carbon

Solvent lignin (3 g), aniline (1.5 ml) and 30 ml ethanol were added into a flask with 30 ml ethanol, followed by stirring at 80 °C until the ethanol was evaporated. Then the mixture was heated at 400 °C for 1 h with a heating rate of 10 °C min^{-1} for 1 h in a muffle furnace (1100 box furnace, Lindberg/Blue M, Thermo Scientific Inc.) under the protection of nitrogen (flow rate was 96 ml min^{-1}). After the precarbonized material was cooled to room temperature, it was mixed with potassium hydroxide (KOH, Fisher Scientific Inc.) in a mass ratio of 1:3, in a steel crucible also containing 30 mL deionized water. The crucible was placed in an oven and dried at 110 °C for 24 h. Then, the crucible was transferred into a muffle and activated at 600–900 °C for 1 h with a heating rate of 10 °C min^{-1} under N_2 protection (flow rate was 96 ml min^{-1}). Afterwards, the carbonized solids were washed with 30 mL 0.1 mol L^{-1} HCl (Fisher Scientific Inc.) at 110 °C for 1 h in a 60 mL polytetrafluoroethylene (PTFE) autoclave to remove the residual KOH and impurities. Finally, the carbon solid was washed several times with deionized water until the pH stabilized at 7. The material was then dried at 105 °C overnight in an oven. The carbonized samples were denoted as PL-600, PL-700, PL-800 and PL-900, corresponding to the activation temperature of 600 °C, 700 °C, 800 °C, and 900 °C, respectively. In addition, the carbon material derived from lignin (L) with the same method at 700 °C but without KOH was used as control sample.

2.2. Preparation of electrodes

Electrodes were prepared by mixing the activated carbon PL-600, PL-700, PL-800, PL-900 and L (80 *wt%*) with acetylene black (10 *wt%*) and PTFE (10 *wt%*), and then pressing onto a surface area of 1 cm^2 nickel foam (EQ-bcnf-16m, MTI Corp.). The electrodes were dried at 60 °C overnight in an oven. Afterwards, a sandwich structure was formed by placing two pieces of microporous PP separator celgard-3501 between two electrodes in a coin cell 2032 type system. Finally, the cell was pressed under a pressure of 1000 kg cm^{-2} to finish the assembly.

2.3. Physical characterization

X-ray photoelectron spectroscopy (XPS) was performed on an SSX-100 system (Surface Science Laboratories, Inc.) equipped with a monochromated Al K_α X-ray source. For high resolution data, the lowest binding-energy C 1s peak was set at 285.0 eV and used as the reference for all of the other elements. Raman spectra were obtained on a Horiba LABRam confocal Raman microscopean with excitation wavelength of 532 nm from a diode pumped solidstate laser. Isothermal adsorption analyses with N_2 were carried out at 77 K (liquid nitrogen bath), using Tristar 3000 Micropore analyzer. The specific surface area was determined by the Brunauer–Emmett–-Teller (BET) method and the pore size distribution was calculated according to the density functional theory (DFT) method [25] using non local density functional theory (NLDFT) analysis for carbon with slit pore model (Micromeritics Inc.). Elemental analysis was conducted using Perkin Elmer 2400 II for C, H and N analysis and LECO Tru Spec Micro was used to analyze O with oxygen module. A transmission electron microscope (TEM) (JEM-2100 LaB6, JEOL) equipped with energy-dispersive X-ray spectroscopy (EDX) was used to study the morphology, microstructure, and elemental mapping of the materials at an acceleration voltage of 80 kV. Additionally, a Technai Spirit G2 Twin (FEI Company) TEM operating at 120 kV was used to acquire some of the micrographs.

2.4. Electrochemical characterization

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy tests were measured on an electrochemical work station (SP-150, BioLogical, France) in 6 mol L^{-1} KOH electrolyte. The galvanostatic charge/discharge curves were obtained from a battery test system (BTS series, NEWARE, China).

3. Results and discussion

TEM images of PL-700 with different magnifications are shown in Fig. 1. In contrast to the chunk shape for the L sample (Fig. S1a),