Pyrolytic cyanobacteria derived activated carbon as high performance electrode in symmetric supercapacitor

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A B S T R A C T

Cyanobacteria, as a renewable source of carbon, was used to prepare activated carbon electrodes in supercapacitors. The activation includes a pre-carbonization at 400 °C followed by KOH heat treatment at 800 °C, leading to efficient and high degree of graphitization. The activated carbon electrode consisted primarily of carbon and oxygen, and possessed a large specific surface area of 2184 $m^2\,g^{-1}$, with pore size centered at 27 nm. In 6 mol L^{-1} KOH electrolyte, the electrode exhibited superior specific capacitance of 271 F g^{-1} and 222 F g^{-1} at a charge/discharge current density of 0.1 A g^{-1} and 5.0 A g^{-1}, respectively. The results demonstrated that the activated carbon derived from cyanobacteria can serve as promising electrode material for electrical double-layer capacitors.

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1. Introduction

Carbon materials are widely used as electrode materials in EDLC (electric double layer capacitors) [1], due to their high electric conductivity and excellent tolerance to various electrolytes. EDLC, stores energy by reversible adsorption of ions at the interface between electrolyte and active electrode materials. Currently, carbon black, single and multiwall carbon tubes and graphene are the predominant materials used in EDLC [2,3]. However, these materials have several drawbacks, such as low SSA (specific surface area) and high cost, which limit their potential applications. The capacitance of EDLC is closely related to three factors: i) accessible SSA of the electrode; ii) type of the electrolyte; and iii) effective thickness of the double layer. These factors are illustrated in the formula below [4]:

$$C = \frac{\varepsilon_r \varepsilon_0 A}{d} \qquad (1)$$

where C (F) is the capacitance of the EDLC, ε_r (F m^{-1}) is the dielectric constant of electrolyte, ε_0 (F m^{-1}) is the dielectric constant of vacuum, d (m) is the effective thickness of the double layer, and A (m^2) is the electrode surface area. It should be noted that only the surfaces that are accessible to the electrolyte ions can contribute to charge storage. Therefore, optimization of the pore size, pore structure, surface properties and conductivity of the electrode materials is required [4].

Carbon materials derived from biomass are promising candidates for EDLC electrodes due to their materials' abundance, low cost, sustainability and possible large SSA. Activated carbon produced from biomass can be divided into two groups: physically activated and chemically activated. Physically activated carbon is obtained by treating biomass with steam or CO_2 under a prescribed temperature, while chemically activated carbon is prepared by exposing biomass to activating agent (e. g. KOH, H_3PO_4, $ZnCl_2$) at high temperatures [5—8]. Physical activation typically results in activated carbon with larger SSA. Chemical activation typically results in activated carbon with greater amount of surface functional groups. Both of these characteristics would enhance EDLC performance. Therefore, various naturally abundant biomass and biowaste have been studied for supercapacitor electrodes [9,10].

Cyanobacteria are phototrophic bacteria that exist in many ecosystems across the planet. They have existed on Earth for

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approximately 3.5 billion years, and are a key contributor to global photosynthesis. However, not all cyanobacterias are beneficial to environment and human health; some cyanobacteria grow and expand too fast, destroying fresh water and creating toxins [11]. In recent years, the rapid and efficient photosynthetic system of cyanobacteria has been re-directed by metabolic engineering to produce third-generation biofuels and long-chain hydrocarbon intermediates [12,13]. Furthermore, cyanobacteria has been recognized as the most promising source of biomass for producing next generation biofuel because it can be easily grown in recirculating photobioreactors fed with CO_2 and powered by sunlight [14,15] without competing for crop land and fresh water [16]. In most current and proposed cyanobacteria bioenergy or biofuel platforms, cyanobacteria biomass is left as waste after harvesting lipid based biodiesel or volatile biofuels. Therefore, utilization of cyanobacteria biomass as feedstock for advanced materials or other high value products must be developed. Due to the abundance and accessibility of cyanobacteria, it is attractive to verify the suitability of converting this biomass into active carbon for energy storage. To our knowledge, no research has been attempted to use cyanobacteria for supercapacitors electrodes but seaweeds and microalgae [17,18]. The goal of this work was to evaluate cyanobacteria as a renewable source of carbon to create EDLC electrodes and transform the waste into efficient energy storage materials. In this work, we first activated cyanobacteria biomass *via* KOH chemical treatment, and then used the activated carbon to prepare EDLC electrode. We systematically evaluated the materials structures and properties (*e. g.* SSA, pore size, electric conductivity, and surface functional groups) that accounted for the promising EDLC performance.

2. Experimental

2.1. Preparation of activation and original carbon

All reagents were purchased from Fisher Scientific Incorporation. Cyanobacteria cell mass was obtained from Biology and Microbiology department of South Dakota State University. To prepare the activated carbon, 10 g dried cyanobacteria powder was heated to 400 °*C* for 1 h in a muffle furnace (1100 box furnace, Lindberg/Blue M, Thermo Scientific Inc.) using N_2 as inert carrier gas (flow rate was 96 ml min^{-1}) to complete the pre-carbonization. After the carbonized material was cooled to room temperature, it was mixed with activation agent KOH in a mass ratio of 1:3 in a steel crucible. To obtain a uniform mixture, 30 mL deionized water was also added. The mixture was left in the crucible and dried in an oven with stirring every 20 min at 110 °*C* for 24 h. Then, the crucible was transferred into a muffle and annealed at 800 °*C* for 1 h under a N_2 flow rate of 96 mL min^{-1}. Afterwards, the activated carbon was washed with deionized water to remove the extra KOH for several times till pH equals 7. After this, the sample was hydrothermally treated with 0.1 mol L^{-1} HCl at 110 °*C* for 1 h in a 50 mL PTFE (polytetrafluoroethylene) autoclave to remove the residual KOH and other impurities. Finally, the material was washed several times with deionized water again till to pH stabilized at 7. The obtained material was dried at 105 °*C* for 12 h in an oven and denoted as AC (activated carbon). For comparison, the OC (original carbon) materials were also prepared in the same way, except the KOH treatment was omitted.

2.2. Preparation of electrodes

Electrodes were prepared by mixing 80 *wt*% AC or OC with 10 *wt*% acetylene black (that to improve the conductivity), and 10 *wt*% PTFE served as binder, and then pressing onto nickel foam current

collector (EQ-bcnf-16m, MTI Corp.) of a surface area of 1 cm^2. The electrodes were dried at 60 °C overnight in an oven. Afterwards, a sandwich structure was formed placing two pieces of microporous PP (Polypropylene) separator celgard-3501 between two electrodes in a cell 2032 coin-type system. Finally, the cell was pressed under a pressure of 1000 kg cm^{-2} to finish the assembly.

2.3. Physical characterization

XPS (X-ray photoelectron spectra) was obtained using a SSX-100 system (Surface Science Laboratories, Inc.) equipped with a monochromated AlK_α X-ray source, a HSA (hemispherical sector analyzer) and a resistive anode detector. 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 spectrum was obtained on a Horiba LABRam confocal Raman microscopean with excitation wavelength at 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 BET (Brunauer–Emmett–Teller) method and the pore size distribution was calculated by the DFT (density functional theory) method using NLDFT (non local density functional theory) analysis for carbon with slit pore model (Micromeritics Inc.) TEM (Transmission Electron Microscope) (Talos F200X, FEI Inc.) equipped with EDX (energy-dispersive X-ray spectroscopy) was used to study the morphology, microstructure, and elemental mapping of the materials at an acceleration voltage of 80 kV.

2.4. Electrochemical characterization

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

To evaluate the specific capacitance in the two-electrode system, the following equation [19] was used:

$$C = \frac{2I\Delta t}{m\Delta v} \tag{2}$$

where C (F g^{-1}) is the specific capacitance, I (A) is the charge/discharge current, Δt (s) is the corresponding charge or discharge time, m (g) is the mass of active materials on single electrode, and Δv(V) is the total corresponding potential change.

3. Results and discussion

Fig. 1a shows the N_2 sorption–desorption isotherms of AC and pore size distribution in the inset. The AC exhibited an extremely large BET SSA (up to 2184 m^2 g^{-1}) and desirable pore structure. The large SSA means there is a large accessible surface area for the electrolyte, while the narrow pore size distribution (which concentrates at 27 nm) can serve as ion-buffering reservoir and allow the smooth transform of ions [20]. Fig. 1b presents the Raman spectra of AC. Two featured peaks correspond to *D* band (1340 cm^{-1}) and *G* band (1585 cm^{-1}) and these were relate to i) the breaking of the A_{1g} symmetry caused by structural disorder and defects and ii) the in-plane bond –stretching motion of a pair of sp^2 carbon atoms with E_{2g} symmetry, respectively [21].

XPS survey was employed to confirm the contained elements and corresponding existing forms. As shown in Fig. 1c, the signals of C and O were detected. The high-resolution XPS spectra of the C 1s region is illustrated in Fig. 1d. The different binding energies