

Fabrication of conductive carbonaceous spherical architecture from pitch by spray drying



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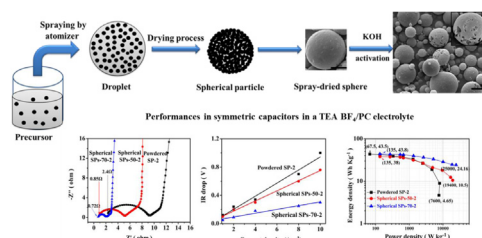
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HIGHLIGHTS

- Continuous synthesis of sulfonated pitch-based spherical nanocarbons.
- Spray drying is proved to be effective to improve carbon's electric conductivity.
- Spherical porous carbon makes higher utilization of inner-pores than powder ones.
- EDLCs exhibit not only low internal resistances but also good rate performances.
- High energy density and power density (24.16 W h kg⁻¹ even at 25 kW kg⁻¹).

GRAPHICAL ABSTRACT



Spraydrying hassignificant potentials for continuous fabrication of conductivecarbonaceous spherical architecture from amphiphilic pitch. It makes the resulted carbon have excellent electrical conductivity and high utilization of energy storage spaces, comparing with a typical carbon powder. As an electrode material for EDLCs, itexhibits low internal resistances and good rate performances simultaneously. Spherical SPs-70-2 has an energy density of 24.16 Wh kg⁻¹even at a power density up to 25 kW kg⁻¹in a TEABF₄/PC electrolyte.

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ABSTRACT

Continuous spray drying used to synthesize amphiphilic sulfonated pitch-based spherical nanoparticles was reported in this study. The spherical particles were further carbonized and activated by KOH to obtain porous spheres. N₂ adsorption–desorption, mercury porosimetry and Raman spectroscopy were used to investigate the pore structure and electron conductivity of the resulting spherical activated carbon particles. The results show that the porous spheres had a high specific surface area (e.g., up to 2550 m² g⁻¹) and a continuous pore size distribution that varied from micropores to macropores. This interconnected 3-D carbonaceous architecture efficiently improved the electrical conductivity and facilitated a better utilization of the inner-pores for energy storage. These two aspects combine together to guarantee a low internal resistance and a good rate performance to an EDLC using these spherical nanoporous carbons as the electrodes. In 1 M TEA-BF₄/PC solution, such EDLC showed a specific capacitance of 173 F g⁻¹ at 0.05 A g⁻¹ and 115 F g⁻¹ at 10 A g⁻¹. Its energy density gets to 43.8 W h kg⁻¹ and maintains at 24.16 W h kg⁻¹ even the power density rises up to 25 kW kg⁻¹.

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1. Introduction

Among the various carbon materials that are available today, spherical activated carbon particles have received considerable attention due to their various potential advantages compared to granular or powder-like activated carbons; these advantages include good packing, a high bulk density and a controllable pore size distribution (Liu

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et al., 1999). A number of preparation techniques for carbon spheres have been reported in the literature, including hydrothermal synthesis (Xia et al., 2012), chemical vapor deposition (Tosheva et al., 2005), and template methods (Zhang et al., 2014). However, long reaction times or complex preparation processes, particularly those not favorable for mass production, make these techniques unsuitable for industrialization. To be industrially relevant, a technique for producing carbon spheres must operate continuously to produce a stable quality of products; fortunately, spray drying has been developed to meet this demand. Spray drying is a well-developed technique that is initiated by atomizing/spraying suspensions into droplets, followed by a drying process, producing solid particles. The obtained particles are generally spherical but can be square, circular or another type of particle morphology in certain cases. The fabrication of micrometer-sized particles via spray drying has been reported previously by several authors. For example, Iskandar et al. (2003) used a spray drying method to produce ordered porous particles from colloidal silica. Kim et al. (2013) prepared ball-like particles for EDLCs by aerosol spray drying, which involved transforming a suspension of graphene oxide (G-O) into fine droplets that modified the G-O sheets in the suspension into crumpled and hollow G-O particles during evaporation. Okuyama and Wuled Lenggoro (2003) prepared spherical porous particles with nanoscale porosity; the zinc oxide quantum dots produced in the silica nanoparticle matrix by the spray drying method used a colloidal mixture as the precursor. In this study, we combined the spray drying technique with carbonization and KOH activation to prepare porous carbon spheres. When spray technology is used for carbon synthesis, the carbon precursor used must be well-dispersed in a solvent, which is ideally water to reduce the amount and severity of the resulting environment pollution. Based on previous works in our lab (Wang et al., 2011), sulfonated pitch (SP) was chosen as the carbon precursor in this study due to its amphiphilic characteristics and its carbonaceous nature.

Currently, there is increasing interest in using porous carbon with 3-D architecture in electrochemical double-layer capacitors (EDLCs) due to their unique structures, high stability and high conductivity (Wan et al., 2014; Yang et al., 2014; He et al., 2014; Sun et al., 2014; He et al., 2012; Chen et al., 2015). Among the properties of the carbon materials used in EDLCs, high conductivity is required in carbon electrode material research to reduce the intrinsic electron resistance of an electric double-layer capacitor (EDLC) electrode. Based on previous reports (Rose, 1988; Biniak et al., 2001), the electrical resistance of a packed carbon electrode is a function of both the intrinsic (i.e., intra-particle) and the contact (i.e., inter-particle) resistances. These two resistances are highly dependent on the surface chemistry, morphologies and structures (e.g., size, shape and aggregation) of the carbon particles. The σ -conductivities of carbon materials can be improved by changing their structures and morphologies.

In this study, we investigate the effect of the physical structures and morphologies of the carbon materials on their conductivities by comparing two types of SP-based porous carbons (i.e., spheres and powders) with comparable specific surface areas. To describe the use of these materials in electrodes, the importance of their conductivities were investigated in depth by using them to create symmetric capacitors and characterizing their resulting electrochemical performances.

2. Experimental

2.1. Preparation of sulfonated pitch-based porous spheres and powders

SP is a commercial product purchased from Originchem Co., Ltd. A SP-1500 spray dryer (Shanghai Sunyi Tech. Co., Ltd, China) was used for the spray granulation experiments. In the

experiments, an aqueous solution of SP (50 g L^{-1}) was continuously supplied to the spray dryer in a peristaltic pump at a speed of 400 mL h^{-1} . The spray-dried powder was collected by a collection bottle and denoted as SPs-X, where X represents the inlet spray drying temperature (e.g., either 50 or 70°C). The obtained spheres were then carbonized at 500°C for 2 h at a heating rate of 2°C min^{-1} under a nitrogen atmosphere, which maintained their spherical structures. Then, the particles were activated by KOH (KOH/SPs mass ratio=2:1) at 800°C for 2 h under a flow of nitrogen. The obtained porous spheres were denoted as SPs-50-2 and SPs-70-2, respectively. For comparison, a nanoporous carbon powder denoted as SP-2 was prepared with the method reported in our previous work (Guo et al., 2014), which can be described as follows: SP was added to the KOH solution (KOH/SPs mass ratio=2:1) and stirred for 1 h. The mixtures were dried in air at 80°C for 12 h and then transferred into a tube furnace and heat-treated at 800°C for 2 h under a flow of nitrogen.

2.2. Sample characterization

Scanning electron microscopy (SEM, Nano SEM 430, FEI, America) was used to observe the spherical porous carbon surface morphologies. Raman spectra were measured using a Renishaw MKI-2000 Raman microscope with an Ar ion laser (532 nm) as the excitation source. N_2 adsorption-desorption isotherms were measured at 77 K using a Micrometrics ASAP 2020 instrument. The specific surface areas were calculated using the Brunauer-Emmett-Teller (BET) theory. The total pore volumes (V_{tot}) were calculated from the amount of N_2 adsorbed at a relative pressure (P/P_0) of 0.99. The micropore volumes were calculated using the t -plot method, and the surface areas and pore volumes of the mesopores were analyzed based on the Barrette-Joynere-Halenda (BJH) method. The pore size distributions were studied using the density functional theory (DFT) model. The macropore volumes (V_{mac}) and porosities were measured using an AutoPore IV 9510 mercury porosimetry analyzer from the Micrometrics Company.

2.3. EDLCs fabrication and electrochemical measurements

The synthesized SP materials were used to fabricate symmetric capacitors and their electrochemical performances were then studied. The electrodes were prepared by mixing the obtained carbon material (80 wt%), acetylene black (10 wt%) and poly(tetrafluoroethylene) (10 wt%) onto a nickel foam current collector or aluminum foil. Either 6 M KOH or 1 M TEA-BF₄/PC was used as the electrolyte. Cyclic voltammetry (CV) and galvanostatic charge-discharge tests were performed using a Princeton PARSTAT2273 electrochemical workstation and an Arbin battery test instrument, respectively. When 6 M KOH was used as the electrolyte, the CV sweep rates were varied from 5 to 400 mV s^{-1} , and the galvanostatic charge-discharge tests were performed at current densities ranging from 0.05 to 100 A g^{-1} . When 1 M TEA BF₄/PC was used as the electrolyte, the CV sweep rates were varied from 5 to 200 mV s^{-1} , and the galvanostatic charge-discharge tests were performed with current densities ranging from 0.05 to 10 A g^{-1} . The specific capacitances of the EDLCs were calculated using the formula $C = I\Delta t / \Delta V_m$, where C is the gravimetric specific capacitance (F g^{-1}) or the volumetric specific capacitance (F cm^{-3}), I is the current (A), Δt is the discharge time, ΔV is the potential change (V) during the discharge process and m is the mass of carbon (g) in a single electrode or the volume (cm^3) of the electrode. The energy density (E) and the average power density (P) of the capacitor were calculated using the equations $E = C_g V^2 / 2$ and $P = E / \Delta t$, respectively. Electrochemical impedance spectroscopy (EIS) was conducted using

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