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Three-dimensional porous hollow microspheres of activated carbon for high-performance electrical double-layer capacitors

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ABSTRACT

As energy storage and delivery devices, electrical double-layer capacitors (EDLCs) with nanostructured activated carbon electrodes from natural organic precursors have attracted considerable attention, particularly for high-performance commercial EDLCs. Conventional methods for synthesizing activated carbons offer limited control on their morphology and structure. In this work, microspheres of activated carbon were synthesized by employing lotus pollens as both the carbon source and self-template combined with CO₂ activation. The prepared activated carbon microspheres (ACMs) own porous (pore size mainly in 1–3 nm) hollow structure with three-dimensional nanorod network constructed shell. EDLCs with the unique ACMs as electrodes showed high specific capacitance (244 F g⁻¹ at 0.1 A g⁻¹ in 1 M H₂SO₄ electrolyte), superior rate capability (83% retention at 20 A g⁻¹), remarkable frequency response and excellent charge–discharge cycling stability (no capacitance fading during 10,000 charge–discharge cycles). The ACMs are very attractive as electrode material for high-performance EDLC applications.

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1. Introduction

Electrical-double layer capacitors (EDLCs), as one type of supercapacitors, store the charge electrostatically by charging the electrochemical double-layer. The charge separation occurs through polarization at the electrode–electrolyte interface by using electrochemically stable and high specific surface area (SSA) materials as electrodes [1]. Owing to the charge storage mechanism, EDLCs offer a high power delivery or uptake, sub-second charging and ultra-long cycle life, which make them attractive for a wide range of applications, including consumer electronics, memory back-up systems, uninterruptable power supplies, smart grid systems, hybrid electric vehicles (HEVs), load-leveling applications and so on. The demanding applications require further increase in the energy density of EDLC technology, decrease in cost and enhancement in safety, at the same time maintaining their high power capacity [2,3].

The energy density of an EDLC is proportional to the specific capacitance and operational voltage according to the energy

equation ($E = 1/2 CV^2$). Since the operational voltage is determined by the electrolyte used in real applications, the specific capacitance of EDLCs plays a vital role in achieving high energy density. The key to reach high specific capacitance by charging the double-layer capacitors is to use high SSA and electronically conducting electrode materials with an optimized porosity [4].

Carbon-based active materials with high surface area, high electrical conductivity, good electrochemical stability and open porosity satisfy all the requirements for EDLCs and have been extensively studied, including activated carbons, templated carbons, carbide-derived carbons, carbon fabrics/fibers, carbon nanotubes, carbon onions, carbon aerogel, graphene and graphene-based materials [5]. Among them, activated carbons [6,7] due to their high SSA, relatively low cost, great cycle stability, well-developed manufacturing technologies and easy production in large quantities have been the most widely used electrode materials in commercial EDLCs today. Templated carbons [8,9] and carbide-derived carbons [10–12] offer tight pore size control and high surface area, but their preparation processes need to use toxic chemicals (such as high corrosive HF acid and Cl₂ gas) to etch templates or remove metal from carbides, and employ multi-step purification procedures. Hence these technologies are difficult to achieve the mass production required for the EDLC manufactures. Carbon fabrics/fibers [13] after activation can reach the same

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capacitance as activated carbon powders, since they have similar SSA, but the high price limits their use to specialty applications. Carbon nanotubes [14–16], carbon onions [17,18] and carbon aerogels [19,20] with large mesopores and macropores commonly offer high rate property, but relatively low gravimetric and volumetric specific capacitances. Graphene [21–25] possessing a high theoretical surface area ($2630 \text{ m}^2 \text{ g}^{-1}$) and superior electrical conductivity, however, due to the unavoidable aggregation of graphene nanosheets during processing, the real surface area of graphene is far below the theoretical one. In addition, due to its very high pore volume and thus low density, graphene electrodes commonly offer limited gravimetric capacitance and especially volumetric capacitance. Activation of graphene [26,27] can improve its performance but still not yet match the performances of the most advanced activated, template and carbide-derived carbons. Therefore, activated carbons will remain the material choice and keep dominating the EDLC market in the near future. By choosing appropriate carbon sources, developing novel synthesis methods and well-controlling the structure and porosity properties of activated carbon materials are of demands for the further development of commercial EDLC technology.

Activated carbons are derived from carbon-rich precursors by high-temperature pyrolysis (carbonization) in an inert atmosphere with subsequent selective oxidation by chemical (such as in KOH, H_3PO_4 or ZnCl_2) or physical (such as in CO_2 or water vapor) activation to increase the SSA and pore volume [6]. Petroleum coke, pitch and coal used to be the most common carbon sources for activated carbon productions. Considering the global growing energy consumption and environmental issues caused by fossil fuel combustion, natural and sustainable organic precursors from agricultural and forest residues, such as coconut shell [28,29], apricot shell [30], cherry stone [31], rice husk [32], sun flower seed shell [33], banana fibers [34], potato starch [35], melaleuca barks [36], beer lees [37], corn grain [38], sugar cane bagasse [39], coffee grounds [40], wheat straw [41] and pollens [42], have been explored as carbon sources to prepare activated carbons for supercapacitors. However, all of these precursors were carbonized and activated *via* chemical activation (in KOH, NaOH or ZnCl_2), resulting in relatively high SSA and large mesopores, which is in favor of getting good rate performance. In addition, after the activation step, the activated carbons present almost the morphology and structure of irregular shaped fragments, subsequent ball milling or grinding to lower the particle size is normally necessary. Compared with chemical activation, physical activation using CO_2 or steam as activation agent, does not need post-processing to remove metal ions in the activated carbons introduced by activation agents, thus it does not lead into impurities, and is a low cost, simple and environmentally friendly process. More importantly, physical activation does not change the original morphology and structure of carbon targets. It contributes to maintain the featured morphology as one expected, and at the same time, increases the SSA and pore volume of the carbon targets [43].

In this work, we utilized biological resource, lotus pollens, as carbon precursors, which are abundant, regenerative and inexpensive. Lotus pollens possess a kind of mono-dispersed microspherical structure with life-related substances in the core and distinctive micro/nano architecture on the shell. By employing lotus pollens as both the carbon source and self-template, hollow activated carbon microspheres with three-dimensional (3D) porous shell were fabricated; the morphology and structure of lotus pollens were almost ideally preserved. To the best of our knowledge, up to now there are only two works [42,44] related to pollen-derived materials as electrode for supercapacitors. Zhang et al. [42] used various pollens as carbon sources to produce activated carbon for EDLCs. However, after hydrothermal carbonization and

chemical activation (KOH) treatment, they just got solid irregular shaped activated carbon particles, which showed the highest capacitance of 207 F g^{-1} in EMIMBF₄ electrolyte. Very recently, Li et al. [44] synthesized hollow MnO_2/C composite by utilizing lotus pollens as template. But without high-temperature carbonation and activation, the MnO_2/C composite possesses relatively low electrical conductivity and specific surface area. With the contribution of pseudocapacitance induced by MnO_2 nanosheets, supercapacitors with the MnO_2/C electrodes showed specific capacitance of 257 F g^{-1} in 1 M Na_2SO_4 electrolyte, yet lower rate capability and cycle stability than those of EDLCs with activated carbons electrodes. We are confident that the porous hollow microspheres of activated carbon would provide an ideal model of electrode materials for EDLCs to investigate the relationship between the special porous structure and the electrochemical performances.

2. Experimental

2.1. Preparation of activated carbon microspheres

2.1.1. Pre-treatment of lotus pollens

Firstly, the purchased lotus pollens (10 g) were immersed into acetone solution (70 ml) with ultrasonic treatment for 2 h. Next, they were filtered and washed with ethanol and deionized water, then dried in an oven at $70 \text{ }^\circ\text{C}$ for 12 h. The above process could clean impurities on the exine and remove the core substances in pollen grains, such as proteins, amino acids, vitamins and nucleic acids. Afterward, the cleaned lotus pollens were heated in an oven at $300 \text{ }^\circ\text{C}$ in air for 6 h. This process could fix the morphology of lotus pollens, and avoid the structural collapse in the following high-temperature heat-treatment.

2.1.2. Carbonization and activation of pre-treated lotus pollens

After calcination at $300 \text{ }^\circ\text{C}$ in air, the pre-treated lotus pollens were transferred into a tube furnace and heated to $700 \text{ }^\circ\text{C}$ at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ in Ar gas (250 ml min^{-1}) for 2 h. After cooling to room temperature, carbonized black powders were obtained. The powders were subsequently heated to $900 \text{ }^\circ\text{C}$ at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ in an Ar flow (250 ml min^{-1}) and then activated using a pure CO_2 gas (150 ml min^{-1}) for 2–6 h. After activation, the samples were cooled down in Ar to minimize the possible formation of surface groups at elevated temperatures. These activated carbon samples are tagged as ACM-2h, ACM-4h and ACM-6h with reference to different activation hours.

2.2. Characterization of activated carbon microspheres

The morphology of the prepared activated carbon microspheres was observed by a Sirion 200 (FEI Corporation, Netherlands) field emission scanning electron microscope (FE-SEM). The surface and pore characterization of activated carbon microspheres were characterized by N_2 adsorption/desorption measurements at $-196 \text{ }^\circ\text{C}$ using an ASAP 2020 surface area and porosity analyzer (Micromeritics Instrument Corporation, USA). Before analyzing, the activated carbon microspheres were degassed at $300 \text{ }^\circ\text{C}$ using the VacPrep 061 degasser (Micromeritics Instrument Corporation, USA) to remove moisture and adsorbed contaminants. The SSA of activated carbon microspheres are calculated from N_2 adsorption isotherms using the Brunauer–Emmett–Teller (BET) equation in the range of relative pressures from 0.1 to 0.3. Porosity distributions were calculated by the nonlocal density functional theory (NLDFT) analysis of N_2 adsorption in carbon slit pores. Raman spectra were recorded using LabRAM HR800 spectrometer (HORIBA Jobin Yvon Corporation, France). The source of radiation was a Nd:YAG laser

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