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Fabrication of the phosphorus doped mesoporous carbon with superior capacitive performance by microwave irradiation under ambient atmosphere: An ultra-facile and energy-efficient method

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ABSTRACT

This paper reports an ultra-facile and energy-efficient microwave irradiation method for fabrication of phosphorus doped mesoporous carbon under ambient atmosphere. The fabricated phosphorus doped mesoporous carbons exhibit high specific surface area (up to 2055 $m^2 g^{-1}$), large pore volume (up to 2.73 $cm^3 g^{-1}$) and good conductivity, which specific capacitance reaches up to 210 F g^{-1}, over 201 F g^{-1} of capacitance is retained even under a high current density of 20 A g^{-1}, and the capacitance retention arrives 97.39% after 10,000 times charge/discharge cycles. Comparative study reveals that similar morphology is obtained by microwave irradiation and traditional pyrolytic carbonization, but more developed porosity and higher graphitization degree are achieved under microwave irradiation. The carbonization process completes in 1–3 min under microwave irradiation, which generally spends more than 2 h at a high temperature of over 600 °C by traditional pyrolytic method. No dramatic increase for surface oxygen content is found even it was fabricated under ambient atmosphere. The samples fabricated under microwave irradiation are potentially cost-efficient and high-performance electrode material for commercial supercapacitors.

1. Introduction

In recent years, huge demand for electrochemical energy storage devices (EES), especially for lithium-ion batteries and supercapacitors, has aroused keen interest in advanced electrochemical energy storage materials [1,2]. For supercapacitors and anode of lithium-ion batteries, carbon materials seem to be an eternal topic due to its excellent physical and chemical stability, good electrical conductivity, large specific surface area, and environmental friendliness [2–4]. Various carbon materials, such as graphene [5,6], carbon nanotube [7,8], hollow carbon nanosphere [9,10] and mesoporous carbon [11–13], and their energy storage capability have been extensively investigated in the last decade. But the large-scale practical application of carbon materials for EES devices depends on its performance and cost. For example, the excellent electrochemical energy storage capability of graphene has been verified by theoretical and experimental researches, which theoretical specific capacity reaches 744 mAh g^{-1} (twice that of graphite) when using as anode of lithium-ion batteries, and a large theoretical double electric layer capacitance of 550 F g^{-1} also can be arrived when using as electrodes for supercapacitors[5,14].But the expensive cost and tedious preparation process seriously obstructs its large-scale practical application [15,16]. So, cost-effective porous carbon still is the primary choice for large-scale practical application for EES devices.

The cost advantage of porous carbons mainly owes to the easily available and cheap raw materials, especially for some biomass and industrial waste-based porous carbons [12,17–19]. Generally, pyrolysis carbonization of raw materials is a necessary process for fabricating the porous carbons, which need to be performed at high temperature under protection of inert atmosphere for several hours. Energy utilization efficiency in this process is extremely low, and the necessary inert atmosphere protection makes fabrication condition rigorous. Comparing traditional heating method, microwave heating converses energy by dipole rotation and ionic conduction inside the substances but not by conduction or convection, so microwave heating can be more energy-efficient due to its rapid, selective, and uniform heating [20]. Microwave irradiation has been wildly utilized for fabricating porous carbons [21–25]. For instance, A. U. Shaikh et al. reported a heteroatom doped mesoporous carbon with a specific surface area of 855 m^2 g^{-1}

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synthesized by microwave irradiating tannin cross-linked melamine [21]. An activated carbon with a specific surface area of 619 m^2 g^{-1} fabricated by microwave irradiating the mixture of cocoa shell, $ZnCl_2$ and $FeCl_3$ also was reported by C. Saucier et al. Even so, as far as our knowledge, one-step fabrication of the porous carbon by microwave irradiation under ambient atmosphere is rare reported. Actually, due to the severe oxidation reaction between carbon and oxygen under high temperature, it is a common challenge for fabricating carbon materials under ambient atmosphere.

Phosphoric acid, a normal liquid inorganic acid, is an ideal microwave absorbent due to its strong polar nature. Under microwave irradiation, phosphoric acid can be heated in high efficiency. Phosphoric acid molecules self-polymerize to form pyrophosphoric acid, and finally form polyphosphoric acid by intramolecular dehydration with the sharply increasing temperature [26]. Pyrophosphoric acid and its derivatives exhibit high thermal stability, especially for polyphosphoric acid, which boiling point reaches up to 856 °C. This temperature is high enough to carbonize the organic precursors. Therefore, organic precursors can be carbonized in phosphoric acid under microwave irradiation in a very short time, which provides a time-saving and energy-efficient carbonization method. Moreover, the produced carbon particles are coated by pyrophosphoric acid and its derivatives during the carbonization process, which suppresses the oxidation reaction between carbon and oxygen. And then, the fabrication can be performed under ambient atmosphere. Based on above facts, we developed an ultra-facile and energy-efficient method for fabrication of phosphorus doped mesoporous carbons by microwave irradiation under ambient atmosphere using inositol as precursor, phosphoric acid and water as microwave absorbent and pore-making agent. The fabricated samples exhibit high specific surface area (up to 2055 m^2 g^{-1}) and large pore volume (up to 2.35 cm^3 g^{-1}), which capacitance reaches up to 210 F g^{-1}, over 201 F g^{-1} of capacitance is retained even under a high current density of 20 A g^{-1}, and the capacitance retention arrives 97.39% after 10,000 times charge/discharge cycles. The samples fabricated under microwave irradiation and ambient atmosphere exhibit excellent textural parameters and superior capacitive performance, which is suggested as a cost-efficient and high-performance electrode material for commercial supercapacitors.

2. Experiment

2.1. Fabrication of the phosphorus doped mesoporous carbons by microwave irradiation

Phosphorus doped mesoporous carbons were fabricated by an ultra-facile and energy-efficient microwave irradiation method under ambient atmosphere. Briefly, 1.8 g of inositol (Sigma, > 99%) and 5.4 g of phosphoric acid (Sigma, > 85 wt%) were mixed in a quartz beaker, and then some distilled water was added to get a mixed aqueous solution containing 30–50 wt% H_2O, and then the mixed solution was directly heated in a household microwave oven (M1-231A, Midea, China) under a radiation power of 600–800 W for 1–3 min, followed by washing with distilled water until the pH of the filtrate was approximately 7, and drying under a radiation power of 500 W in microwave oven for 2 min. The final product designates as MPC-xW_t-y, where x refers to microwave power, t denotes the irradiation time, and y represents the wt. % of H_2O. Meanwhile, the samples fabricated under microwave irradiation are collectively referred to as MPC-W. The yield of the fabricated samples MPC-800W_1-50%, MPC-800W_2-50% and MPC-800W_3-50% is 35.0%, 32.2% and 26.1%, respectively.

2.2. Fabrication of the phosphorus doped mesoporous carbon by traditional pyrolytic carbonization

Phosphorus doped mesoporous carbon also was fabricated by traditional pyrolytic carbonization. Briefly, a mixture of 1.8 g of inositol, 5.4 g of phosphoric acid and 7.2 g of H_2O was placed in a tube furnace, and carbonized at 650 °C with a heating rate 5°Cper minute for 2 h under the protection of argon atmosphere. Afterwards, the sample was washed with distilled water until the pH of the filtrate was approximately 7, and dried at 105 °C for 12 h. The final product designates as MPC-H and the yield of prepared MPC-H is 18.61%.

2.3. Electrochemical measurements

Two-electrode coin cell type symmetric supercapacitors were assembled to evaluate capacitive performance of the fabricated materials using 6 mol L^{-1} KOH aqueous solution as electrolyte. Each carbon sample was mixed with acetylene black and polytetrafluoroethylene (PTFE) with a weight ratio of 8:1:1 and pressed onto nickel foam functioning as the current collector. Pieces of 1.2 cm in diameter were stamped and pressed under 10 MPa for 1 min. The electrode plates were then dried in a vacuum at 100 °C for 12 h. The total mass of each electrode was ca. 4.0 mg, and two electrodes with similar mass weight were selected for supercapacitor assembling. Symmetrical supercapacitor was assembled by sandwiching of the separator (PP/PE complex film) between two identical electrodes, followed by immersion in 6 M KOH aqueous solution. All electrochemical measurements of the assembled cells were performed in a two-electrode system configuration. The cycling voltammetry (CV), electrochemical impedance spectrum (EIS) and self-discharge were performed on a CHI 660E electrochemical analyzer (Shanghai CH Instruments Ins., China). The voltage window for the aqueous electrolyte was set to be 0–1 V. Galvanostatic charging-discharging curves (GCD), leakage current and cycle-life stability of the assembled supercapacitors were tested using a computer control supercapacitor testing system (NEWARE, Shenzhen China). The specific discharge capacitance (C) of the fabricated samples in symmetric supercapacitor was calculated from the galvanostatic discharge curves using the following equation:

$$C = \frac{4I}{m\mathrm{d}V/\mathrm{d}t} \quad (1)$$

where I is the applied discharge current (A), m (g) is the total mass of two electrodes, and $\mathrm{d}V/\mathrm{d}t$ (V s^{-1}) is the slope obtained by fitting a straight line to the discharge curve [27].

2.4. Material characterization

Nitrogen adsorption and desorption isotherms were obtained on an ASAP 2460 specific surface area and porosity analyzer (Micromeritics Inc., USA) at 77 K, all samples were degassed in a vacuum at 200 °C for 12 h prior to the measurements. The specific surface area was calculated by the Brunauere-Emmette-Teller (BET) method using the N_2 adsorption data. The total pore volume was determined by the amount of nitrogen absorbed at $p/p_0 = 0.99$. The according pore size distribution and pore volume were obtained by density functional theory (DFT) method for micropore, and Barrett-Joyner-Halenda (BJH) method for mesopore. Raman spectra was measured on a Horiba JY-HR800 Raman microscope (Japan) with an excitation wavelength of 532 nm at room temperature. X-ray photoelectron spectra (XPS) was collected on an Escalab 250Xi spectrometer (Thermo Scientific, USA), using an Al K*a* X-ray source. Hitachi S4800 field emission scanning electron microscope (FESEM, Japan) and JEOL JEM-2010 transmission electron microscopy (TEM, Japan) were applied to survey the surface morphology of the reported materials.

3. Results and discussion

Fig. 1 suggests the fabrication scheme for phosphorus doped mesoporous carbon by microwave irradiation·H_2O and phosphoric acid are ideal microwave absorbents due to strong molecular polarity, microwave energy can be efficiently converted into thermal energy, and