



Oxygen and nitrogen co-doped porous carbons with finely-layered schistose structure for high-rate-performance supercapacitors



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ARTICLE INFO

Article history:

Received 20 February 2017

Received in revised form

17 May 2017

Accepted 2 July 2017

Available online 4 July 2017

Keywords:

Porous carbon

Ammonium citrate

O/N-doping

KOH activation

Supercapacitor

ABSTRACT

Heteroatom-doped porous carbons have currently been regarded as the promising materials for supercapacitors because of their outstanding contributions in Faradaic capacitance and electrolyte accessibility. In the present study, O/N co-doped porous carbons have been prepared by carbonization of ammonium citrate single precursor followed by KOH activation. The as-synthesized carbon (ACA-800) has a finely-layered schistose architecture together with a high surface O- and N-containing functionalities (6.82 at.% O and 1.37 at.% N), a high micropore surface area (1522 m² g⁻¹) and a balanced mesopore surface area (1138 m² g⁻¹). Due to their synergistic effects, the ACA-800 electrode displays high-rate capacitive performance with specific capacitance of 297 F g⁻¹ at 100 A g⁻¹, at least 85% of its capacitance (349 F g⁻¹) at 1 A g⁻¹. Moreover, symmetric supercapacitor assembled with such ACA-800 exhibits high energy density of 25.5 W h kg⁻¹ at 923 W kg⁻¹ as well as excellent cycling stability (only 4% of capacitance loss after 10000 cycles with a cell voltage of 1.8 V at a current load of 2 A g⁻¹). Considering the global abundance and low price of ammonium citrate, it can serve as a novel precursor for the mass production of O/N-enriched porous carbons for advanced supercapacitors.

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1. Introduction

The development of low-priced supercapacitor electrode materials with high electrochemical performance has always been and continues to be a huge challenge for the practical application of supercapacitors. Although supercapacitor (also known as electrical double-layer capacitors) has been under research and development for several decades, activated (porous) carbons are, perhaps, the most commonly used supercapacitor electrode materials due to their huge specific surface area (SSA), high physicochemical stability, and low cost [1–4]. Generally speaking, the capacitance of commercial activated carbons (ACs) based supercapacitors is usually around 100 F g⁻¹ in organic electrolytes with the working potential as high as 2.7 V. Although the capacitance can be doubled (200 F g⁻¹) in aqueous electrolytes, the working voltage, on the

contrary, decreases to 0.9 V [5,6]. Considering that the energy density ($E = 0.5CV^2$) of a supercapacitor is determined by its capacitance (C) and working potential (V), normally, the E values of the AC-based supercapacitors cannot exceed 10 W h kg⁻¹ in aqueous electrolytes [6]. One of the main reasons is that only part of their SAA can be electrochemically available due to the poorly-controlled pore size distribution, even though ACs prepared by chemical activation technique have a well-developed microporous structure with SSA up to 3000 m² g⁻¹ [7,8]. Another primary reason is that the distance of electrolyte ions transport and diffusion within the AC-based electrodes increases significantly and causes large IR drop at high current loads [9]. Put simply, the ACs-based supercapacitors commonly suffer from low energy density as well as poor rate performance, which cannot meet the requirements for practical applications.

To address the above-mentioned problems, heteroatom-doped (O, N, B, P) ACs with a proper ratio of micropore to mesopore should be very beneficial [10–14]. This is because heteroatom functionalities can give rise to Faradaic capacitance through electrochemical redox reactions on the one hand and can significantly enhance the wettability of ACs in aqueous electrolytes on the other

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[12,14]. Furthermore, mesopores can serve as reservoirs for electrolytes and thus considerably shorten the diffusion pathway of electrolyte ions [9,15]. In this way, both specific capacitance and charge-discharge rates can be elevated conspicuously for ACs-based supercapacitors via heteroatom doping. Among these doping heteroatoms, O/N co-doping was viewed as a promising strategy for the improvement of the electrochemical performance of the AC materials. The coexistence of oxygenated and nitrogenated groups promised many merits, in addition to the above-mentioned enhanced wettability in aqueous electrolytes and additional pseudocapacitance, but also improved electrical conductivity [16]. Recent researches on O-doped ACs have confirmed that oxygenated functionalities can substantially improve the surface hydrophilicity towards aqueous electrolytes [17,18], thus making micropores more accessible to electrolyte ions (contributing to electric double layer capacitance, EDLC), providing more active sites for rapid redox reactions (contributing to Faradaic capacitance), and guaranteeing excellent rate performance. N doping into ACs has been proved to possess electron-donating character, thereby leading to the shift of Fermi energy level and enhancing the specific capacitance [19]. In addition, N-doping of ACs in the form of graphitic-N can facilitate electron transfer and cause the enhancement of electrical conductivity [16]. In the form of pyridinic- and pyrrolic-N, they can induce Faradaic capacitance through redox reactions in aqueous electrolytes [20]. It is reasonable to expect that O/N co-doping of ACs can produce the synergistic effect and leads to further improvement of the electrochemical energy storage performance.

Current approaches to preparing O/N co-doped ACs can be classified into two categories, namely direct pyrolysis [21,22] and post-synthesis [11]. The former method involved pyrolyzing O/N coenriched precursor [21] or the mixture of the O-rich and N-rich precursors at high temperature followed by chemical and/or physical activation [23–25]. The latter approach attempted to heat-treat O-rich ACs with N-enriched dopants [26], or alternatively, to heat-treat N-rich ACs with O-rich precursor [27]. Although the post-synthesis method preserved the bulk properties of ACs, it was difficult to homogeneously incorporate the O or N element into the ACs matrix. Moreover, the latter introduced O-containing or N-containing groups might block the accessibility of micropore to electrolytes and led to the deterioration of capacitive performance. Conversely, the direct pyrolysis method promised uniform doping of O/N elements into the ACs. More significantly, the versatility of O/N coenriched precursors (such as O/N-coenriched polymers [28,29], biomass [30,31], and small organic molecules [21,32]) provided another chance to fine-tune the final capacitive performance of the doped ACs. In this regard, the direct pyrolysis method is more practical, manoeuvrable, and efficient than the post-synthesis approach.

Considering the preparation cost and electrochemical performance of supercapacitor electrode materials, the preparation of O/N co-doped ACs starting from low-cost bioorganic compounds is of great significance. We herein report the preparation of O/N co-doped AC by pyrolyzing ammonium citrate single precursor followed by KOH activation. This choice was based on the fact that citric acid was mainly produced by fermentation with an annual output of several million tonnes, of which more than half was manufactured in China. Moreover, ammonium citrate can be simply produced by neutralization of citric acid with ammonia with a price as low as U.S. \$ 1000 per tonne. Although citrate salts of various metals (such as Na, K, Ca, Ba, Mg, Zn) have been applied to fabricate porous carbons [33–37], the utilization of ammonium citrate as single precursor for O/N co-doped porous carbon production was seldom reported in literature except where N-doped carbon dots have been fabricated by hydrothermal treatment of ammonium

citrate [38,39]. In the present study, the O/N-co-doped porous carbon synthesized under optimal conditions had a finely-layered schistose architecture, a high O and N contents as well as a high micropore surface area. Due to their synergistic effects, the as-synthesized O/N-co-doped porous carbon displays excellent rate capability and long-term stability in aqueous electrolyte as the electrode materials for supercapacitor.

2. Experimental

2.1. Preparation of O/N co-doped porous carbons

In a typical process, ammonium citrate (10 g) was directly carbonized at 600 °C in a tubular furnace under ultra-pure N₂ flow for 2 h. The obtained carbon (denoted as AC-600, the carbon yield was about 30 wt. % with elemental composition of 61.58 wt. % C, 25.81 wt.% O, and 10.12 wt.% N as determined by elemental analysis, Table S1, see Supporting Information, SI) was then mixed with KOH at a KOH/carbon mass ratio of 2/1 followed by activation at 750–850 °C for 2 h under N₂ atmosphere. The activated products were washed with 1 M HCl followed by water until pH = 7 and then dried at 100 °C. The obtained porous carbons are labeled as ACA-x and x represents the activation temperature, i.e., 750, 800, and 850. The carbon yield was about 21 wt. % for ACA-750, 16 wt. % for ACA-800 and 12 wt. % for ACA-850, respectively.

2.2. Characterization of O/N co-doped ACA carbons

Scanning electron microscopy (SEM, JEOL JSM-6610LV) and transmission electron microscopy (TEM, JEOL JEM-2010) were used to characterize the morphology and structure of the ACA carbons. X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, England) was applied to determine the surface elemental composition of the ACA carbon. Elemental analyzer (Vario EL, Elementar, Germany) was applied to analyze the bulk elemental compositions of the ACA carbons. Micromeritics surface area and porosity analyzer (Micromeritics TriStar II 3020) was used to characterize the textural properties of the ACA carbons.

2.3. Electrochemical tests

The ACA carbons were first separately mixed with carbon black and polytetrafluoroethylene (PTFE) at a weight ratio of 8: 1: 1 in ethanol. The obtained pastes were then separately coated onto square nickel foam with side length 1 cm. After compressing at 10 MPa for 5 min followed by drying at 100 °C for 12 h, the working electrodes were obtained. The mass of carbon material deposited on nickel foil was around 2.2 mg. The ACA carbon-based symmetric supercapacitor was assembled using the same two ACA carbon-based electrodes in 1 M Na₂SO₄ aqueous electrolyte in a stainless steel CR2032 coin cell with glassy fabric as the separator. The traditional three-electrode system was carried out in 6 M KOH aqueous solution at 25 °C using platinum wire and Hg/HgO electrode as the counter and reference electrodes, respectively. All electrochemical tests were performed in a CHI760D electrochemical workstation. Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) were used to evaluate the capacitive performance of the ACA carbon electrodes. The GCD tests were carried out at an extremely wide range of current density from 1 to 100 A g⁻¹. However, GCD test at current load above 100 A g⁻¹ is difficult due to the detection limit of the instrument. The energy density (*E*) of the ACA carbon-based supercapacitor was estimated by $E = 0.5C_{\text{cell}}V^2$, where *C*_{cell} is the gravimetric capacitance of the supercapacitor cell, *V* is the working voltage. The power density (*P*) was evaluated by

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