Electrochimica Acta 271 (2018) 49–57

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

N/P co-doped hierarchical porous carbon materials for superior performance supercapacitors

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ARTICLE INFO

Article history:
Received 7 February 2018
Received in revised form
21 March 2018
Accepted 21 March 2018
Available online 22 March 2018

Keywords:
N/P co-doping
Hierarchical porous carbon
Large surface area
Supercapacitors

ABSTRACT

The N/P co-doped hierarchical porous carbon materials are synthesized by SiO_2-template approach following potassium phosphate activation. Polyvinylidene fluoride is used as the carbon source, melamine as the nitrogen source and potassium phosphate as the phosphorus source and activator. The obtained porous carbon materials exhibit a hierarchical pore structure (~0.6 and ~4 nm), a large specific surface area (1431 $m^2 g^{-1}$) and a high nitrogen and phosphorus content. These predominant characteristics enable the CNP-5-800 sample to exhibit a superior specific capacitance of 337 F g^{-1} at 0.5 A g^{-1} and outstanding cycling stability of 97.8% retention after 10000 cycles in a three-electrode system. Even in the two-electrode system (an all-solid-state symmetric capacitor), this kind of materials still can deliver an energy density of 23.1 W h kg^{-1} to 12.4 W h kg^{-1} at power densities of 720.4 W kg^{-1} to 13950 W kg^{-1}, respectively, and a cycling property of 98.7% maintenance after 5000 cycles. Therefore, the practicable synthetic method and excellent electrochemical performance make CNP-*x*-*y* materials a potential candidate in supercapacitor application.

1. Introduction

Supercapacitors, as one of the most promising energy storage devices, have drawn increasing attention of researchers who have devoted to explore and improve their electrochemical performance, so that they can be widely and commercially applied. Based on the basic principles of supercapacitors, porous carbons are considered to be one of the most potential electrode materials because of their tremendous specific surface area, tunable pore structure, favourable conductivity, good stability and even more electrocatalytic active sites for a variety of redox reactions [1–4]. Additionally, the low cost and rich source of porous carbons further promote the development of carbon-based supercapacitors [5,6]. To fully take advantage of the superiority of porous carbons, heteroatoms are doped into the porous carbon matrix, which is proved to be a useful and popular approach. These heteroatoms (such as nitrogen, phosphorus and boron) in surface functional groups replace carbon atoms and notably improve the electrochemical property of porous carbons [7–10]. In a large number of quality literature, the nitrogen functional groups are always believed to be able to trigger pseudocapacitance because they offer electrochemical active sites for faradic redox reactions between electrode and electrolyte [11–14]. Additionally, they also make great contributions to interface wettability and electronic conductivity [15–18]. Some reports pointed out that nitrogen functional groups on carbon materials with unique electronegativity effectively promotes the distribution of electronic charge and spin density, so that the coped nitrogen helps electron transport through the carbon, particularly at high current loads [19,20]. Many researches have shown that the heteroatomic functional groups can affect the electron donor or acceptor characteristics of porous carbons. As for phosphorus dopants, they are regarded as having high electron-donating capability so that the phosphorus-containing functional groups can boost the charge reserve and delivery ability [21,22]. As one of the nitrogen-group elements, phosphorus can also affect the interface wettability more or less. Doping heteroatoms into carbon configuration can alter the energy and reactivity of surface. And generally, doping phosphorus is an effective strategy to enhance the chemical and physical activity of carbon surface [23,24]. Recently, Yang et al. reported a high specific capacitance and prominent energy density of phosphorus-doped hierarchical porous carbons in supercapacitors [25]. Phosphorus-doped porous carbons can also offer good electrochemical stability and wide potential window for supercapacitors, so that supercapacitors can possess longer cyclical life and higher energy density [26,27].

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https://doi.org/10.1016/j.electacta.2018.03.129

The introduction of onefold species heteroatom can enhance the capacitive performance of supercapacitors. Therefore, some researchers have started to consider the effect of dual- or multi-heteroatom doping. Most of related reports indicated that multi-doping can provide a synergetic effect, which can more roundly improve the electrochemical behaviour of supercapacitors [28–31]. In recent years, much more efforts have been made to study the P/N co-doped porous carbon materials for supercapacitors and the developments are obvious. For example, in 2013, Wang et al. directly carbonized phosphoric acid doped polyaniline and demonstrated that their P/N co-doped microporous carbons in supercapacitors possess 154.4 $F\,g^{-1}$ specific capacitance and outstanding stability [4]. In the next year, Yan et al. reported that they obtained the nitrogen/phosphorus co-doped carbons through the electrospinning of the polyacrylonitrile and phosphoric acid precursor solutions and subsequent thermal treatment, the obtained materials have the specific capacitance of 224.9 $F\,g^{-1}$ at 0.5 $A\,g^{-1}$ and 155.5 $F\,g^{-1}$ at 30 $A\,g^{-1}$ [32]. And recently, Jin et al. directly carbonized glucose containing N and P precursor and revealed that the P/N co-doped porous carbons in his paper show 265 $F\,g^{-1}$ at 0.5 $A\,g^{-1}$ specific capacitance and 94% capacitance retention after 5000 cycles [33]. In a world, many methods are emerging and promote the development of heteroatom coped carbon. In spite of the practical and effective heteroatom-doping method, incorporating appropriate pore structure is still very necessary and important. Therefore, exploring moderate porous construction and heteroatom content is the direction of our efforts.

In this work, we present a different and efficient approach to prepare N/P dual-doped hierarchical porous carbons by using polyvinylidene fluoride (PVDF) dissolved in *N,N*-dimethylformamide (DMF) as precursor, melamine as nitrogen source and potassium phosphate (K_3PO_4) as phosphorus source. To improve the porous architecture, nanoSiO_2 is wielded to introduce mesopores. The K_3PO_4 contents of the mixtures are compared and adjusted more than once for optimal phosphorus content. More importantly, the electrochemical performances of obtained carbon materials are tested and then comparatively investigated. The results show that nitrogen and phosphorus elements make a great contribution to the property of supercapacitors. The mesopore structure in nitrogen and phosphorus co-doped carbon materials also bring positive effects for supercapacitors.

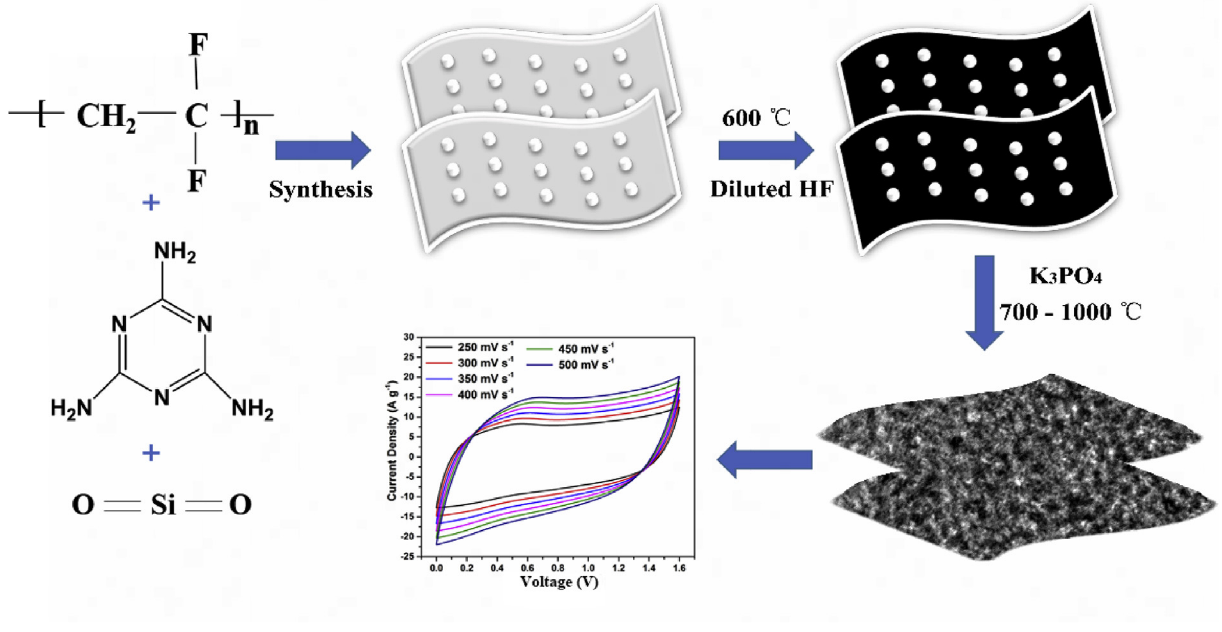
2. Experimental section

2.1. Chemicals

PVDF, melamine and K_3PO_4 were purchased from Adamas-Beta Inc. Nanosilicon dioxide (SiO_2, 20 nm) was from Aladdin Reagent (Shanghai) Co., Ltd. Hydrofluoric acid (HF), concentrated hydrochloric acid (HCl) and DMF were obtained from Sinopharm Chemical Reagent Co., Ltd. All reagents were used without any purification.

2.2. Synthesis

PVDF (8 g), melamine (4 g) and nanoSiO_2 (4 g) were added into DMF (100 g), and the mixture was stirred for 6 h at 70 °C in an oil bath. To remove the moisture and air bubbles from the semisolid mixture which has accomplished the sufficient stirring, it was placed in a 60 °C air-drying oven for approximately 4 h. Then, the semisolid mixture was made into membranes for subsequent uniform carbonisation. In a tubular furnace and under N_2 protection, these membranes were carbonized at 600 °C for 2 h. Subsequently, the obtained carbon was immersed in 50 wt% HF solution for 8 h and then washed several times with abundant deionised water to remove SiO_2. By drying the carbon material, we obtained the CN-600 sample. In the activation pre-treatment, CN-600 and K_3PO_4 were mixed with the weight ratio values of 1:3, 1:5 and 1:6 (CN-600: K_3PO_4) respectively. For homogeneous blending, a little of deionised water and absolute ethyl alcohol were used. After drying the above samples, hyperthermal activations were carried out at 700 °C, 800 °C, 900 °C and 1000 °C for 2 h under N_2 atmosphere respectively. Lastly, these activated carbons were immersed in HCl solution (1 M) twice with magnetic stirring for 12 h and washed with deionised water repeatedly. After drying and collection, we obtained the ultimate products named CNP-*x*-*y*, where *x* is the K_3PO_4/CN-600 mass ratio and *y* is the hyperthermal activation temperature. The schematic view of synthesizing CNP-*x*-*y* is shown in Scheme 1.



Scheme 1. The schematic diagram for the synthesis of P/N co-doped hierarchical porous carbon materials.