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High performance nitrogen-doped carbon for supercapacitor obtained by carbonizing eco-friendly and cheap polyaspartic acid



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Guofu Ma^{a,*}, Yajuan Wu^a, Kanjun Sun^b, Hui Peng^a, Haiping Wang^a, Ziqiang Lei^a

^a Key Laboratory of Eco-Environment-Related Polymer Materials of Ministry of Education, Key Laboratory of Polymer Materials of Gansu Province, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, China ^b College of Chemistry and Environmental Science, Lanzhou City University, Lanzhou 730070, China

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ABSTRACT

Nitrogen-doped porous carbon is prepared by carbonizing polyaspartic acid under inertia atmosphere without template and activation. The powder X-ray diffraction, element analysis, scanning electron microscopy, and N_2 adsorption-desorption tests show that the morphologies and structures of the nitrogen-doped carbon samples deeply depend on carbonization temperature. Electrochemical measurements show that the specific capacitance of the PASP700 sample obtained at 700 $^{\circ}$ C is 166.1 F g⁻¹ at a current density of 1 A g^{-1} , and after 5000 charge/discharge cycles it still remains 97% which exhibits an excellent cycling stability.

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1. Introduction

Carbon materials are regarded as the most promising electrode materials for electrical energy storage devices due to their properties, such as high conductivity, heat, corrosion resistance, etc. [1]. It has reported that nitrogen doping seems to be the most promising method for enhancing capacity, surface wettability and electronic conductivity of the carbon materials [2]. Nitrogendoped carbon can be prepared through two primary pathways using nitrogen-containing precursor or post-treatment of carbon. For the latter, the carbon material is treated with ammonia [3] or urea [4] to introduce nitrogen-containing functional groups on its surface, which does not change the properties of the bulk material. In contrast, the first method is by in situ doping using precursors with affluent nitrogen, which can facilitate the uniform incorporation of nitrogen into the carbon material. Various nitrogen-containing precursors have been investigated to prepare nitrogen-doped carbon [5,6]. However, more or less-severe drawbacks, such as the complex process, low yields and high cost in the preparation still preclude widespread and practical use of nitrogen-doped carbon materials in commercial supercapacitors. Therefore, it is attractive and inspiring to find an easy method and a new precursor that is environmental friendly, cheap and high nitrogen content to make nitrogen-doped carbon materials.

* Corresponding author. E-mail addresses: magf@nwnu.edu.cn (G. Ma), leizq@nwnu.edu.cn (Z. Lei).

In the present work, biopolymer polyaspartic acid (PASP, extensively used in the agricultural fertilizer, and water treatment agent [7]), is used as a raw material to prepare nitrogen-doped carbon. The porous carbon with different nitrogen contents as electrode materials for supercapacitors in 2 M KOH aqueous electrolyte presents high electrochemical performance. The relationship between the morphologies and structures of the carbon electrode materials and its electrochemical performance are studied.

2. Experimental

Synthesis of nitrogen-doped porous carbon: In a typical process, 5 g of PASP was placed in a porcelain boat and put in a tube furnace. After vacuum extraction, the PASP was carbonized at the ultimate temperatures of 500, 600, 700 or 800 °C for 2.5 h, with a heating rate of 5 $^{\circ}$ C min⁻¹ in a slow N₂ flow. After cooling down to room temperature, the resulting sample was then thoroughly washed with HCl $(2 \text{ mol } L^{-1})$ to remove any inorganic salts, and then washed with distilled water until neutral pH and dried at 60 °C in ambient for 24 h. The samples at different carbonization temperatures were named as PASP500, PASP600, PASP700 and PASP800.

Characterization and electrochemical measurement: The morphologies and structures of the carbon samples were examined by a field emission scanning microscope (FE-SEM, JSM-6701F), and an X-ray diffractometer (XRD, D/Max-2400, Rigaku).





Fig. 1. XRD for the carbon samples.

The element content was measured by an Elementar CHNS analyzer model Vario EL III (Vario EL, Elementar Analyser systeme. GmbH, Hanau, Germany). The Brunauer–Emmett–Teller (BET) surface area (SBET) of the samples was analyzed by nitrogen adsorption in a Micromeritics ASAP 2020 nitrogen adsorption apparatus (U.S.A.).

The capacitive performances of the samples were investigated using a three electrodes system, similar to our previous reported literature [9]. Carbon rod and Hg/HgO electrode were used as counter and reference electrodes respectively. Working electrodes were fabricated by pressing a mixture of the carbon materials, acetylene black and PTFE binder with a weight ratio of 80:10:10 onto nickel foam at 20 MPa. The electrochemical tests were conducted on a CHI 660D electrochemical workstation using 2 M KOH aqueous solution as the electrolyte. The galvanostatic charge/ discharge and cycle-life stability measurement was performed using a computer controlled cycling equipment (LAND, CT2001A).



Fig. 2. SEM for the carbon samples: (a) PASP500; (b) PASP600; (c) PASP700; (d) PASP800; (e) adsorption-desorption isotherms of nitrogen at 77 K for the samples; (f) the corresponding pore size distribution for PASP700.

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