Electrochimica Acta 271 (2018) 599–607

Contents lists available at ScienceDirect

Electrochimica Acta

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

Ultrahigh-content nitrogen-decorated nanoporous carbon derived from metal organic frameworks and its application in supercapacitors

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ARTICLE INFO

Article history:
Received 9 January 2018
Received in revised form
6 March 2018
Accepted 31 March 2018
Available online 3 April 2018

Keywords:
Ultrahigh nitrogen-decorated
Supercapacitor
MOF-Derived

ABSTRACT

Single electric double-layer capacitors cannot meet the growing demand for energy due to their insufficient energy density. Generally speaking, the supercapacitors introduced with pseudo-capacitance by doping heteroatoms (N, O) in porous carbon materials can obtain much higher capacitance than electric double-layer capacitors. In view of above merits, in this study, nanoporous carbon materials with ultrahigh N enrichment (14.23 wt%) and high specific surface area (942 $m^2\ g^{-1}$) by in situ introduction of N-doped MOF (ZTIF-1, Organic ligands 5-methyltetrazole/$C_2H_4N_4$) were produced. It was found that as supercapacitors' electrode materials, these nanoporous carbons exhibit a capacitance as high as 272 $F\ g^{-1}$ at 0.1 $A\ g^{-1}$, and an excellent cycle life (almost no attenuation after 10,000 cycles.). Moreover, the symmetric supercapacitors were assembled to further investigate the actual capacitive performance, and the capacitance shows up to 154 $F\ g^{-1}$ at 0.1 $A\ g^{-1}$. Such excellent properties may be attributed to a combination of a high specific surface area, ultrahigh nitrogen content and hierarchically porous structure. The results shown in this study fully demonstrate that the nanoporous carbon materials containing ultrahigh nitrogen content can be used as a potential electrode material in supercapacitors.

1. Introduction

Supercapacitor devices, also known as electric double-layer capacitors (EDLCs), store charges by the adsorption of electrolyte ions onto the surface of electrode materials. Compared to traditional batteries, supercapacitors have higher power density and longer cycle life. However, the traditional carbon-based EDLCs show a low capacitance due to the confine of specific surface area (SSA), a single pore structure as well as a bad conductivity on the electron desorption-adsorption surface [1]. Thus, fabricating carbon materials with high SSA, hierarchically porous and good conductivity has become the key for improving the supercapacitor capacitance.

Nanoporous carbon materials derived from metal–organic frameworks (MOFs) that contain metal ions and organic ligands have abundant nanoscale cavities [2,3] that can provide high surfaces for electron desorption-adsorption. Such nanoporous carbon materials have been used as electrode materials for supercapacitors [4–6]. Liu et al. first reported a nanoporous carbon materials (SSA up to 2872 $m^2\ g^{-1}$) prepared from MOF (PFA/MOF-5 composite) [7]. The electrode materials show a high capacitance up to 258 $F\ g^{-1}$ at a current density of 0.25 $A\ g^{-1}$. By using ZIF-8-derived nanoporous carbon electrodes, Chaikittisilp et al. obtained a high-capacitance (214 $F\ g^{-1}$ at 5 $mV\ s^{-1}$) using a 0.5 M H_2SO_4 as the electrolyte [8]. Moreover, Hu et al. obtained a nanoporous carbon material with ultrahigh SSA (5500 $m^2\ g^{-1}$) by direct carbonization of Al-PCP at 800 °C [9]. Lately, the MOF-derived nanoporous carbon was also reported in energy storage [10–13]. Although commonly nanoporous carbon materials derived from MOFs show a good performance, they still cannot meet the demand for energy storage.

In recent years, nanoporous carbon materials with pseudocapacitive behavior have been reported [14–16]. The introduction of heteroatoms, such as nitrogen (N), phosphorus (P) and oxygen (O), into carbon materials can effectively improve the specific

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https://doi.org/10.1016/j.electacta.2018.03.200
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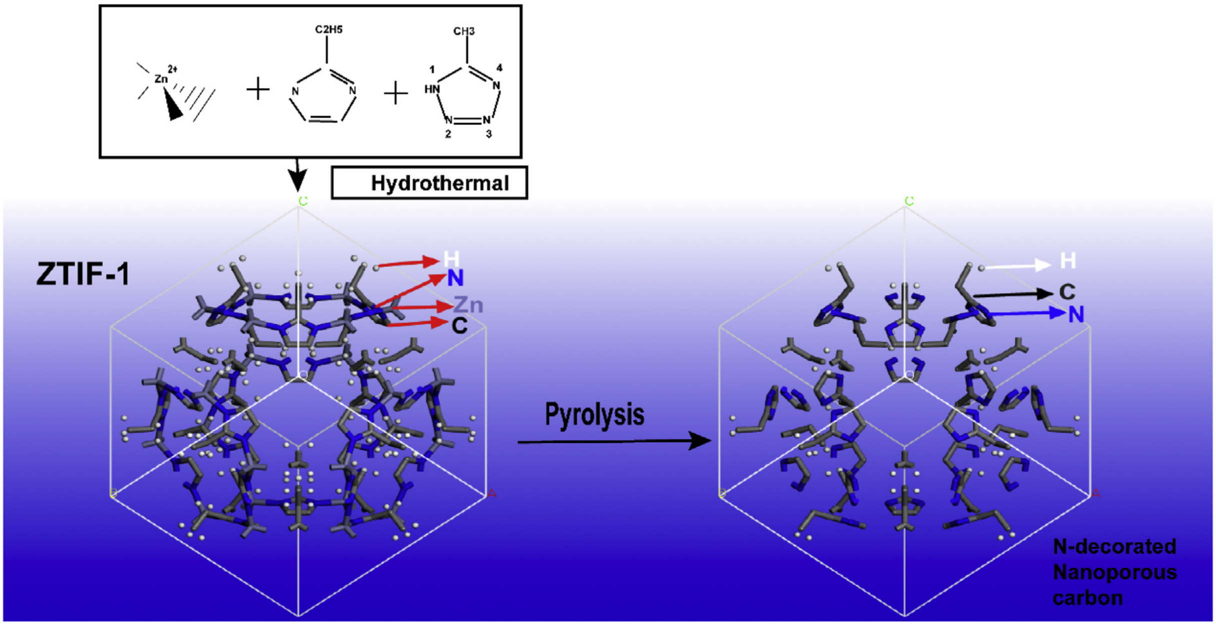

Scheme 1. Schematic illustration for the preparation of NNPC.

capacitance, because the N, P, O-functional groups can induce pseudocapacitive effects or improve the wettability of carbon materials to electrolyte solution [17–19], especially the introduction of N element. Moreover, N doping can improve the electronic conductivity of nanoporous carbon materials [14,20]. Thus, the capacitance of nanoporous carbon materials can be enhanced by heteroatom doping.

N-doped carbon materials were prepared by treating carbon materials with ammonia, amines, or urea during the calcination process, or with the direct carbonization of the N-rich precursor, such as polymers, biomass materials [21]. However, the traditional method could only provide either low N content or low SSA. Thus, developing an approach to obtain high SSA and N content is highly desired.

In this study, a simple route was used to fabricate nitrogen-decorated nanoporous carbon (NNPC) materials with high SSA (942 $m^2 g^{-1}$), hierarchically porous and ultrahigh N content (14.23 wt%) by carbonizing ZTIF-1. Furthermore, the NNPC material was used as electrode materials for supercapacitors and shows an excellent electrochemical performance. A capacitance as high as 272 $F g^{-1}$ at 0.1 $A g^{-1}$ was obtained when the precursor was calcined at 800 °C based on the measurement of a 3-electrode configuration. Moreover, the symmetric supercapacitor was assembled to further investigate the actual capacitive performance, and the capacitance shows up to 154 $F g^{-1}$ at 0.1 $A g^{-1}$. These results indicate that NNPC materials can be used in supercapacitors for energy storage.

2. Experimental

2.1. Materials

Zinc acetate ($Zn(CH_3CO_2)_2$), ethanol and 5-methyltetrazole were purchased from Macklin. N,N′-dime-thylformide (DMF) was purchased from Sigma Aldrich. 2-ethylimidazole was purchased from TCI. The metal organic framework (ZTIF-1) was prepared by modifying the method reported in Ref. [22]. The mixture of $Zn(CH_3CO_2)_2$) (10 mmol, 1.83 g), 5-methyltetrazole (5-mtz, 10 mmol, 0.86 g), and 2-ethylimidazole (2-eim, 10 mmol, 0.96 g) in DMF (40 ml) and ethanol (40 ml) was sealed in a 150 ml vial and heated to 120 °C for 72 h, and then cooled to room temperature. The yellow polyhedral crystals (ZTIF-1) were obtained, washed with ethanol, and dried at room temperature.

2.2. The synthesis of NNPC

Firstly, the dried ZTIF-1 was carbonized under Ar flow at 700 °C, 800 °C and 900 °C for 2 h with a rate of 10 °C min^{-1}, respectively. Secondly, the NNPC materials were washed by hydrochloric acid to remove the Zn. These samples were named as NNPC-700, NNPC-800 and NNPC-900, respectively.

2.3. Characterization

Field emission scanning electron microscopy (FESEM) images were captured by a Hitachi SU-70 FESEM instrument, and transmission electron microscopy (TEM) was conducted via a FEI Tecnai G^2 F30 facility. Elemental analysis was acquired using a Vario EL cube elemental analyzer. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 advance powder X-ray diffractometer using Cu Kα radiation. The specific surface areas were determined by the gas sorption technique using a Micromeritics ASAP 2020 based on the Brunauere-Emmette-Teller (BET) method. Laser Raman spectroscopy was performed on a Renishawin Via Spectrometer. X-ray photoelectron spectroscopy (XPS) was investigated on a ULVAC-PHI 1800 spectrometer. The electrochemical properties were examined on an electrochemistry workstation (CHI660E).

2.4. The fabrication of electrode and electrochemical measurements

The NNPC electrodes were prepared by mixing 85 wt% active materials, 10 wt% acetylene black and 5 wt% polytetrafluoroethylene with ethanol to form a slurry that was then spread onto a nickel foam with a coating area of 1 cm^2. This coated foam was dried at 100 °C under vacuum 24 h and then pressed under a pressure of 10 MPa to completely adhere to the electrode materials. The loading mass of active materials on the prepared working electrode is approximately 3 $mg cm^{-2}$.