

Full Length Article

Preparation of metal-organic framework-derived nitrogen-doped porous carbon and study of its supercapacitive performance in potassium citrate electrolyte

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ARTICLE INFO

Keywords:

Metal-organic frameworks
 Nitrogen-doped
 Potassium citrate electrolyte
 Energy density

ABSTRACT

As a new kind of power storage, supercapacitors have attracted much attention due to their short charge and discharge time, good cycle performance, large power density, and environmental friendliness. However, the main drawback of supercapacitors is lower energy density than batteries, as well as high cost per unit energy. Herein, the metal-organic frameworks compound $[\text{Zn}_3(\text{OH})(\text{BTC})_2(\text{C}_4\text{N}_2\text{H}_{11})(\text{H}_2\text{O})]_n$ was used as carbon precursor to prepare the nitrogen-doped porous carbon (ZMFC-T) by one-step carbonization process. We investigated the influences of carbonization temperature on the specific surface area, pore size distribution and electrochemical properties. The results show that the ZMFC-800 has a specific surface area of $1557 \text{ m}^2 \text{ g}^{-1}$, an average pore size of 3.85 nm, and nitrogen content of 5.25%. In the 1 M potassium citrate electrolyte solution, the stable voltage window is 2 V and the energy density is 65.28 Wh kg^{-1} . In potassium citrate electrolyte, ZMFC-800 has a strong charge storage capacity and high energy density. This work sheds a new light on the potential for developing superior nitrogen-doped porous carbon for energy storage devices.

1. Introduction

Supercapacitors, also known as electrical double-layer capacitors or pseudo-capacitors, have attracted considerable attention because of their pulse power supply, long cycle life, simple principle, and high dynamic of charge propagation [1–4]. However, the capacity per unit volume is relatively lower than the secondary batteries [5,6]. Therefore, under the premise of maintaining high power density, how to improve energy density has become the focus of research. There are mainly two aspects to improve the energy density of the supercapacitors: (1) the capacitance of the electrode materials, and (2) the stability of the super capacitor voltage window [7,8].

Carbon-based supercapacitors mainly used the electric double-layer to store energy in the interface between electrode and electrolyte [9]. The electric double-layer capacitance of porous carbon is related to its specific surface area, pore size distribution, carbon surface functional groups and other factors [10–13]. The capacitance is only closely related to the pores structure in the carbon structure, which allows electrolyte ions to pass [14–17]. For the electrolyte with larger ion diameter, internal resistance of the bigger micropores, slower diffusion speed of the electrolyte ions in the pores, and the mesopores are more conducive to the ion diffusion. They contribute to the electrical double-

layer capacitance. Therefore, for the larger diameter of the electrolyte, the utilization of mesopores is higher than micropores. The doping of heteroatoms (N, S) can improve the wettability and conductivity of the electrode and increase the capacitance [18].

Metal-organic frameworks, referred to as MOFs, are network framework structures formed via the connections of transition metals with oxygen- or nitrogen-containing organic ligands [19–23]. Most organic ligands are rich in carbon and contain heteroatoms such as N and P. MOFs play an important role in gas storage, catalytic activation, molecular and optical properties because of their special structure [24–32]. However, there are relatively few reports regarding the preparation and supercapacitive properties of porous carbon synthesized using MOFs as a carbon precursor [33].

The aqueous electrolytes have broad application because of their conductive ability, high specific capacitance, environment-friendly, etc. At present, the narrow voltage window of the aqueous electrolytes is the main reason that restricts the increase of energy density of supercapacitors [34,35]. In recent years, with the improvement of national environmental awareness, the development of the aqueous electrolytes has been become the research focus. Lee et al. used MnO_2 transition metal oxide as the electrode material, the specific capacitance in KCl electrolyte reached 200 F g^{-1} , the aforementioned studies generally

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illustrated that the inorganic alkali metal salt solution as an aqueous electrolytes displayed a superior electrochemical performance [36,37]. Luo et al. reported that the voltage window of 3 M LiNO₃ could be improved to 1.6 V [38]. The research on aqueous electrolytes of inorganic alkali metal salts with demonstrates low price, low corrosion, chemical stability and low pollution have important and realistic significance.

Here, [Zn₃(OH)(BTC)₂(C₄N₂H₁₁)(H₂O)]_n was synthesized via a hydrothermal method and used as a carbon precursor. ZMFC-T with hierarchical structure was then obtained from the precursor. The effect of different carbonization temperature on the structure of ZMFC-T was investigated. In the two-electrode system, the electrochemical properties of the ZMFC-800 as electrode material and different concentrations of potassium citrate as electrolyte were studied.

2. Experimental

2.1. Preparation of MOFs and nitrogen-doped porous carbon

Synthesis of [Zn₃(OH)(BTC)₂(C₄N₂H₁₁)(H₂O)]_n: Zn(NO₃)₂·6H₂O (0.604 g), 1,3,5-H₃BTC (0.828 g) and C₄H₁₀N₂ (1.188 g) were placed in a beaker, 40.0 mL of H₂O was added, the mixture was stirred further for 5 min. The resulting mixture was poured into a 100 mL autoclave reactor and placed in an oven. The reactor was heated in the oven to 150 °C at a rate of 10 °C h⁻¹, and then the temperature was maintained for 72 h. Pale yellow crystals of [Zn₃(OH)(BTC)₂(C₄N₂H₁₁)(H₂O)]_n were obtained after the temperature was cooled to room temperature at a rate of 10 °C h⁻¹.

Preparation of nitrogen-doped porous carbon: An appropriate amount of [Zn₃(OH)(BTC)₂(C₄N₂H₁₁)(H₂O)]_n crystals were placed in a tubular furnace and heated to 750, 800, 850, and 900 °C under an Ar atmosphere (99.999%) with a heating rate of 3 °C min⁻¹. The reactions were kept for 2 h at the according temperatures, and the resulting products were washed with 1 M hydrochloric acid and then rinsed with deionized water until the pH was neutral. Nitrogen-doped porous carbon was obtained after drying in vacuum at 80 °C for 12 h. Nitrogen-doped porous carbon was denoted as ZMFC-T, where ZMF represents [Zn₃(OH)(BTC)₂(C₄N₂H₁₁)(H₂O)]_n crystals, C represents nitrogen-doped porous carbon, and T represents the carbonization temperature.

2.2. Characterizations of structure and performance

Powder X-ray diffraction (XRD) patterns in the Bragg's angle (2θ) range of 10–90° were collected using a D/Max-2400 (Rigaku) diffractometer with monochromatic Cu Kα radiation of wave length λ = 0.1541 nm at a scanning speed of 15° min⁻¹. Raman spectra were recorded using a Horiva (JY-HR800 micro Raman) spectrometer. The excitation source is a laser at 532 nm with 25 mW power. The morphology of nitrogen-doped porous carbon was investigated by field-emission scanning electron microscopy (SEM; JSM-5600LV, JEOL) and high-resolution transmission electron microscopy (HRTEM; JEM-1200EX, JEOL). Surface elemental composition was determined by X-ray photoelectron spectroscopy (XPS) using a VG scientific ESCA-3000 spectrometer with non-monochromatized Mg Kα radiation (1253.6 eV). The structure performance of nitrogen-doped porous carbon was measured through nitrogen sorption isotherms obtained using a Micromeritics ASAP 2020 sorptometer. The apparent surface area (SBET) was calculated from the N₂ isotherms at relative pressures (P/P₀) from 0.06 to 0.20 through the Brunauer–Emmett–Teller (BET) method.

2.3. Electrochemical measurements

To prepare the working electrode, the ZMFC-800 were ground with super P (15 wt%) and polytetrafluoroethylene (5 wt%) and then pressed onto nickel foam (1 cm²) functioning as current collector. The total

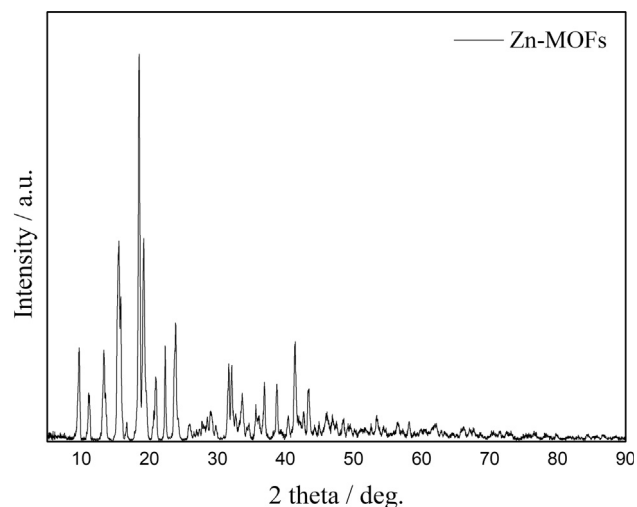


Fig. 1. XRD patterns of [Zn₃(OH)(BTC)₂(C₄N₂H₁₁)(H₂O)]_n.

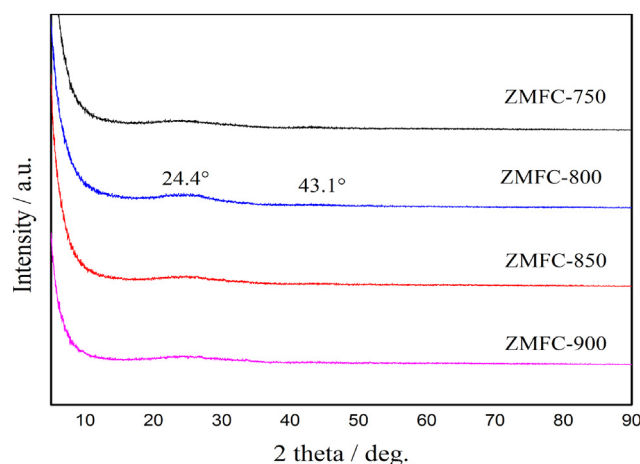


Fig. 2. XRD patterns of the ZMFC-T.

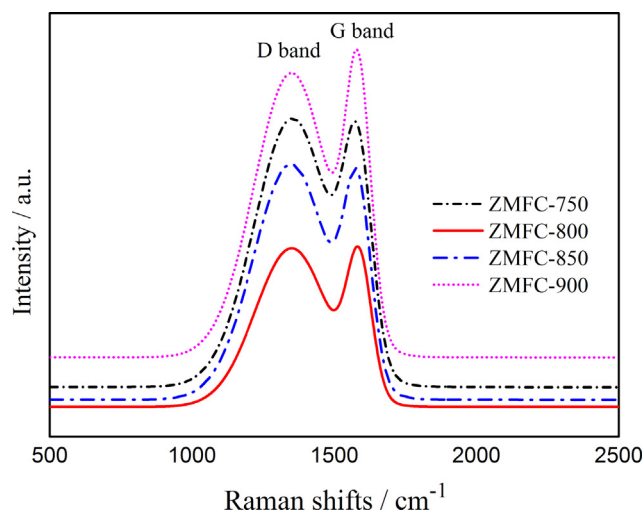


Fig. 3. Raman spectra of the ZMFC-T.

material loading on each electrode was approximately 3 mg. The working electrode was then dried in a vacuum at 80 °C for 12 h. Subsequently, the working electrode was pressed at 15 MPa for 1.5 min.

Electrochemical measurements including cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), and electrochemical impedance

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