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Metal organic frameworks templated sulfur-doped mesoporous carbons as anode materials for advanced sodium ion batteries

Xiaodong Shi [a, 1], Yuxiang Chen [a, 1], Yanqing Lai [a], Kai Zhang [a], Jie Li [a], Zhian Zhang [a, b, *]

[a] School of Metallurgy and Environment, Central South University, Changsha 410083, China
[b] Engineering Research Center of High Performance Battery Materials and Devices, Research Institute of Central South University in Shenzhen, Shenzhen 518057, China

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ABSTRACT

In this paper, we focus on an innovative sulfur doping method with MOF-5 and inorganic sulfur powders as templated carbon precursor and sulfur source, in which sulfur powders were firstly encapsulated into the abundant pore structure of MOF-5 and then sulfur doping process could be realized through further pyrolysis treatment. Based on the results of material characterization, sulfur-doped mesoporous carbon (SPC) holds an amorphous structure with an enlarged interlayer distance of 0.386 nm and a mesoporous size distribution of 3–6 nm, while sulfur atoms existing in SPC (2.5 at.%) are mainly in the form of thiophene-type bonds (C–S–C and C=S). Benefitting from the structural advantages, SPC electrode could display a long-term cycling stability with a reversible capacity of 173.7 mAh g^{-1} at 200 mA g^{-1} after 500 cycles and an outstanding rate capability of 104.9 and 90 mAh g^{-1} even the current raised up to 1.6 and 3.2 A g^{-1}, respectively. The enhanced electrochemical performances could be mainly attributed to the introduction of S atoms into carbon structure, which can effectively enlarge the interlayer distance, improve the electronic conductivity and promote the insertion/extraction process of sodium storage.

1. Introduction

Lithium ion batteries (LIBs), one of the most common rechargeable batteries, have a wide applications in portable devices, electric vehicles and smart wearable electrics for their high energy density and environmental benignity. However, the potential huge demands of LIBs may be gradually hindered by the deficient reserves and expensive extraction cost of lithium resources [1]. Thus, sodium ion batteries (SIBs) have been regarded as an alternative rechargeable battery system owing to the abundant reserves of sodium resources and similar chemical properties with lithium [2].

Compared with Li^+, Na^+ possesses a larger ionic radius and slower diffusion kinetics, making it complicated insert into or extract from the interlayer of conventional graphite materials ($d_{(002)}$ = 0.335 nm) [3], which has been widely applied in commercial anode materials of LIBs. Therefore, developing suitable anode materials with superior electrochemical performances is urgently desirable but remains a great challenge. In view of the dominant materials, carbonaceous materials have been supposed to be one of the prime candidates for SIBs as a result of their low potential (vs. Na/Na^+), cheap price, chemical stability, sustainability and stable cyclability. Generally, various kinds of carbon-based materials, such as carbon nanofibers [4–6], carbon nanowires [7], expanded graphite [8], carbon nanospheres [9–11], carbon nanosheets [12,13], and amorphous carbon derived from biomass [14], have been employed as anodes for SIBs. Unfortunately, these materials suffer from low specific capacity due to the finite graphite interlayer distance. In the previous reports, the energy barrier for Na ions intercalation would be low enough to conquer if the interlayer distance could enlarge to 0.37 nm [15]. Therefore, in order to promote the sodium storage capability of carbonaceous materials, an effective method is to guarantee the carbon materials with an interlayer distance over 0.37 nm. Meanwhile, an available approach to enlarge the interlayer distance is to introduce heteroatoms into carbon materials. Owing to the similar covalent radius of N (75 pm), B (82 pm) with C (77 pm), the introduction of N or B atoms could mainly generate extrinsic defects and enhance the

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* Corresponding author. School of Metallurgy and Environment, Central South University, Changsha 410083, China.
E-mail address: zhangzhian@csu.edu.cn (Z. Zhang).

[1] X. S. and Y. C. contributed equally to this work and should be considered as cofirst authors.

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electronic conductivity [16–21]. Meanwhile, sulfur atom holds a covalent radius of 102 pm, which is far larger than that of C, so that the introduction of sulfur atoms into carbon structure is a convenient route to significantly enlarge the interlayer distance [22], which could accommodate more sodium ions storage and promote the insertion/extraction process of Na^+. In 2012, Yang et al. [23] successfully realized sulfur doping process for the first time with graphene oxide and benzyl disulfide as carbon source and sulfur source, respectively. In 2015, Chen et al. synthesized sulfur-doped graphene through high temperature flash heat treatment with phenyl disulfide as sulfur dopant [24]. As an anode material for SIBs, it could display a reversible discharge capacity of 291 mAh g^{-1} at the current density of 50 mA g^{-1} and an excellent rate performance with a discharge capacity of 127 and 83 mAh g^{-1} at 2 and 5 A g^{-1}, respectively. Additionally, Huang and his co-workers reported a sulfur-doped carbon material with an enlarged interlayer distance of 0.386 nm [25], derived from the precursor of poly(3,4-ethylenedioxythiophene), which could exhibit a reversible capacity of 482.1 mAh g^{-1} under the current of 100 mA g^{-1}. Based on these sulfur doping methods, it can be detected that the previous reports always adopted sulfur-containing organics or polymers as sulfur sources, which usually have the disadvantages of toxicity, expensive price and inconvenience for large scale applications. Therefore, choosing a suitable sulfur sources with the advantages of low cost, nontoxicity and environmental friendly is also urgently desirable.

Sulfur powder, with a wide applications in lithium sulfur batteries, holds abundant reserves of resources on the earth, which is usually confined into porous carbon materials to prepare sulfur-carbon composites [26] and treated as an ideal sulfur source to prepare sulfur-doped mesoporous carbon. Meanwhile, metal organic frameworks-5 (MOF-5), constructed by Zn ions and organic ligands has been widely applied in the field of catalysts, hydrogen storage and semiconductor due to its large specific surface area and tunable structure [27]. To make full use of the open channels and abundant pore structure, MOF-5 has been employed as the templates and precursors to prepare hierarchically porous carbon material under inert gas condition, in which Zn ions could be completely reduced to metal zinc and removed from the framework, inheriting a certain extent of porosity structure. In the related works of our research group, we also made efforts to the application of MOF-5 precursor in lithium-sulfur batteries [28] and lithium-selenium batteries [29]. Based on the previous literature and research foundations, we propose a novel and effective strategy to prepare sulfur-doped mesoporous carbon with MOF-5 and inorganic sulfur powders as templated carbon precursor and sulfur source, in which sulfur powders were firstly encapsulated into the porous channel of MOF-5 through melt-diffusion method just similar to sulfur-containing composites for lithium-sulfur batteries and then the sulfur doping process could be realized through further pyrolysis treatment.

Herein, sulfur-doped mesoporous carbon (SPC) material has been prepared through a two-step method, in which MOF-5 precursor was firstly synthesized by solvent thermal method and pyrolyzed with sulfur powder as dopants under Ar atmosphere. In this paper, the results of material characteriztions could detect the existence of C—S bands, confirming the introduction of sulfur atoms into SPC, which holds a disordered carbon structure with an enlarged interlayer distance of 0.386 nm and a mesoporous size distribution of 3–6 nm. When employed as anodes for SIBs, SPC electrode could present a stable cyclability with reversible capacities of 266.8 mAh g^{-1} at 50 mA g^{-1} after 150 cycles. Even the current was raised up to 3.2 A g^{-1}, it also could exhibit an excellent rate capability of 90 mAh g^{-1}. The superior electrochemical property is mainly due to the enlarged interlayer distance, the improved electronic conductivity and enhanced insertion/extraction process of sodium storage resulting from the introduction of S atoms.

2. Experimental

2.1. Preparation of MOF-5

MOF-5 was synthesized by a solvent thermal method reported in previous literature [30–32]. In details, 3 mmol zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, Aladdin, AR) and 1 mmol terephthalic acid (H_2BDC, Sinopharm Chemical Reagent, AR) were added into 150 ml dimethylformamide (DMF, Aladdin, AR). The above mixture was kept stirring for 1 h and heated at 105 °C for 24 h in a Teflon-lined stainless steel autoclave. Subsequently, the resultant suspensions were filtered and washed three times with DMF and dichloromethane (CH_2Cl_2, Aladdin, AR), alternately. The final white powders were obtained after drying in a vacuum oven at 150 °C for another 24 h to remove the solvent molecules.

2.2. Preparation of sulfur-doped mesoporous carbon

In order to synthesize sulfur-doped mesoporous carbon, the as-prepared MOF-5 was firstly mixed with sulfur powder (Sigma-Aldrich, AR) under the mass ratio of 1:1 and ground homogeneously in an agate mortar. Secondly, the mixture was heated at 155 °C for 6 h under Ar atmosphere to make sulfur fully encapsulated into the porous channel of MOF-5 (composite sample in this step is labeled as MOF-5@S). Thirdly, the sample was further pyrolyzed at the temperature of 950 °C with a heating rate of 5 °C min^{-1} and kept for another 4 h to promote the removement of zinc metal and sulfur doping process. Finally, the obtained black powder of sulfur-doped mesoporous carbon was washed several times with dilute hydrochloric acid (HCl, Aladdin, AR) and deionized water, respectively, abbreviated as SPC in the whole paper. For comparison, porous carbon was prepared by pyrolyzing MOF-5 precursor under the same condition just without adding sulfur powder, labled as PC throughout the paper.

2.3. Materials characterizations

Scanning electron microscopy (SEM, Nova NanoSEM 230) and transmission electron microscopy (TEM, TecnaiG220ST) were employed to investigate the microstructures and morphologies. X-ray powder diffraction (XRD, Rigaku3014), Quantachrome instrument (Quabrasorb SI-3MP) and Thermogravimetric analysis (TGA, SDTQ600) were adopted to identify the crystalline phases, porous structure and thermal decomposition behavior of the samples, respectively. Meanwhile, X-ray photoelectron spectroscopy (XPS, Thermo-FisherESCALAB250xi), Raman (Renishaw-INVIA) and Fourier transform infrared spectrometer (FTIR, Nicolet6700) were carried out to characterize surface functional groups and bond characteristics of SPC and PC.

2.4. Electrochemical measurement

The resultant samples of PC or SPC, sodium alginate (Aladdin, AR) and Super P (TIMCAL) were firstly dispersed into deionized water to form black slurry at the weight ratio of 8:1:1. Secondly, the black slurry was coated on the rough surface of copper film and dried for 12 h at 60 °C. Thirdly, the copper foil was cut into pellets with a diameter of 1 cm and dried at 60 °C for another 6 h. Finally, 2025-type coin cells were fabricated in a vacuum glove box (MIKROUNAUniversal-2440-1750) with metal sodium (Aladdin, 99%) as counter electrode, Celgard 2400 as the separator membrane and 1 M $NaClO_4$ (Aladdin, AR) dissolved in the mixture of ethylene