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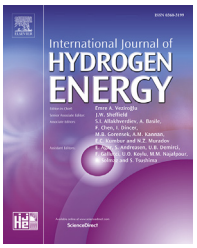

One-step synthesis of 3D sulfur-doped porous carbon with multilevel pore structure for high-rate supercapacitors

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ABSTRACT

In this work, three-dimensional (3D) interconnected S-doped porous carbon materials are fabricated using bio-waste sodium lignosulfonate as carbon and sulfur precursor by in situ carbonization and subsequent KOH activation process. The as-obtained S-PC-50 has high specific surface area of 1592 m^2 g^{-1}, high S weight percentage up to 5.2 wt% and interconnected porous framework consisting of micro-, meso- and macropores. As a result, the S-PC-50 exhibits a high specific capacitance of 320 F g^{-1} at 0.2 A g^{-1}, excellent rate performance with 76.5% capacitance retention after a current density increasing from 2 A g^{-1} (200 F g^{-1}) to 100 A g^{-1} (153 F g^{-1}) and 99% capacitance retention after 10,000 cycles at 5 A g^{-1}. Besides, the symmetric supercapacitor can deliver a high energy density up to 8.2 Wh kg^{-1} at 50 W kg^{-1}.

Introduction

Recently, supercapacitors have received significant attention because of higher power density with a long cycle life and faster charge/discharge capability than conventional dielectric capacitors [1]. That makes them applicable in a wide range of fields, such as consumer electronics and hybrid electric vehicles [2–6]. According to the energy storage mechanism, supercapacitors can be divided into two different types: electrical double-layer capacitors (EDLCs) and pseudocapacitors. The energy storage of EDLCs is achieved by the accumulation and release of electrostatic charge in the Helmholtz double layer formed at the electrode and electrolyte interface [7]. On the other hand, pseudocapacitors store energy through the reversible redox Faradic reaction between the electrode materials and the electrolyte.

Carbon materials, such as graphene [8], carbon nanotubes [9], carbon aerogels [10] and activated carbon [11], have been commonly used in EDLCs. Porous carbon is the most ideal electrode materials for commercial supercapacitor devices due to their high specific area, adjustable porous structure, stable physicochemical properties, sustainability and low cost [12]. The high surface area of the electrode is advantageous for the capacitance, especially the sufficient accessible surface with the electrolyte. Besides, the proper porosity of the electrode is also important for the ions transmission in short diffusion pathways during the charge/discharge process. In order to obtain excellent electrode materials, most researches only focus on their surface area but ignore the rationalisation of the pore structure. Although micropores can contribute to the high surface area and charge storage, transmission of electrolyte ions in electrode material will be restricted if the

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pore structure is too simple. This serious drawback can lead to an obvious reduction of specific capacitance and rate especially in high current densities [13]. It is one effective way to construct electrode materials of 3D connected multilevel pore structure which contain macropores, mesopores and micropores [14]. The mesopores can provide the shortest ion transporting pathways while macropores act as ion-buffering reservoirs [15,16], and the micropores will enhance the charge storage [17,18]. The cooperation of this 3D connected multilevel pore structure can reduce the ion transport resistance and ion diffusion distance for high-rate EDLCs.

Besides pore tuning, doping of heteroatoms into the carbon materials is also an effective way to improve the intrinsic chemical and electrical properties. Most researches have focused on the doping using single nitrogen, phosphorus, sulfur, and boron or dual heteroatoms [19–21]. Among those, sulfur has attracted more attention during the last few years. Different from nitrogen and boron, sulfur atoms protrude out of the carbon planar structure due to the larger radius than carbon. Sulfur, as the donor of electrons shows different changes at the electronic density of states which caused by the presence of the lone electron pairs after S-doping process. These changes can increase the local reactivity of S-doped carbon. Otherwise, the band gap of electronic structure will be opened after S-doping which due to the effect of π electrons in the carbon lattice by sulfur atom. Such changes might result in an increased electrode polarization in the application of supercapacitors [22]. S-doped carbon materials are also suitable for the nanoelectronic devices, since they are simple to vary the S-doped concentration into the lattice [23]. Until now, S-doped carbon materials have been used in many fields, such as the cathode catalysts [24], Li ion batteries [25,26], electrochemical capacitors [27], and H_2 storage [28].

S-doped carbon materials have been synthesized by several approaches. Most of them including the complex procedure that mixing of the sulfur-containing and carbon precursors. Worse is the sulfur-containing precursors, such as benzyl disulfide [29], hydrogen sulfide [30], and carbon disulfide [21] are toxic.

Herein, we proposed one novel environmental friendly way to synthesize S-doped porous carbon. Abundant sodium lignosulfonate as non-valuable bio-wastes after the pulping process are always combusted for energy and result in serious air pollution [31]. However, sodium lignosulfonate can provide both carbon and sulfur precursors without toxicity. The S-doped highly porous carbon (S-PC) can be obtained via simple pyrolysis of sodium lignosulfonate with potassium hydroxide. The electrodes obtained by S-PC have been electrochemically characterized and show higher specific capacitance as well as excellent cycling stability due to the multilevel pore structure.

Experimental

Regents and materials

Sodium lignosulfonate was purchased from aladdin (Shanghai, China). Potassium hydroxide, ethanol and 37% HCl were purchased from Kermel (Tianjin, China). Other reagents were used as received without further treatment. All solutions were prepared with deionized water throughout all the experiments.

Preparation of S-doped porous carbon (S-PC)

In a typical procedure, sodium lignosulfonate (LS, 2.0 g) was transferred to a vial with 10 ml deionized water and then stirred for about 0.5 h until the LS completely dissolved. Subsequently, different amounts of potassium hydroxide (0, 33, 55 wt%, relative to LS) was added to the above solution under stirred until the potassium hydroxide dissolved. The mixture was transferred into a porcelain boat and dried at 110 °C for 10 h to evaporate deionized water. After flushing with N_2 for 0.5 h, the obtained solid mixture was placed in a tube furnace and carbonized at 900 °C for 3 h at a heating rate of 5 °C min^{-1} under N_2 protection. Afterwards, the carbon was washed with deionized water three times until the pH was 7. The washed carbon material was then dried at 80 °C for 24 h in an oven. The obtained samples were labeled as S-PC-0, S-PC-33, and S-PC-50 for different KOH adding. The entire preparation process of S-doped porous carbon material is shown in Scheme 1.

Preparation of electrodes

Electrodes were prepared by mixing the obtained porous carbon with acetylene black and polytetrafluoroethylene solution (30 wt%) in ethanol at a mass ratio of 8:1:1. The slurry was stirred until the ethanol was completely evaporate. The obtained paste was then pressed into a piece of thin film and cut into disks with same area. The disk was pressed onto nickel foam at 10 MPa and dried at 80 °C for 24 h in an oven. The cells were formed by placing two same mass of electrodes in a coin cell with Glassy fibrous films and 6 M KOH aqueous solution as separator and electrolyte, respectively. Finally, the cell assembly was completed after being pressed at 5 MPa pressure for 3 s.

Material characterization

The morphology of the prepared S-doped porous carbon were characterized using Carl Zeiss Ultra55 field-emission scanning electron microscope (FE-SEM, Germany). The JEM-2100F field-emission transmission electron microscope (FE-TEM, Japan) equipped with energy-dispersive X-ray spectroscopy was also used to investigate the morphology, micropores and elemental mapping of the porous carbon. The nitrogen adsorption-desorption curve was collected using the Micromeritics 2460 N_2 adsorption apparatus. Brunauer–Emmett–Teller (BET) surface area and pore size distribution were calculated using non local density functional theory [32]. Raman spectra were obtained on a Lab-RAM Aramis Raman spectrometer (HORIBA Jobin Yvon, France) with excitation wavelength of 532 nm. X-ray photoelectron spectroscopy (XPS) were performed on a Kratos Axis Ultra DLD spectrometer with an Al Kα X-ray source (Kratos, UK). X-ray diffraction (XRD) patterns were obtained using a Rigaku D diffractometer (Rigaku, Japan) with Cu Kα radiation.

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