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Lithium battery using sulfur infiltrated in three-dimensional flower-like hierarchical porous carbon electrode

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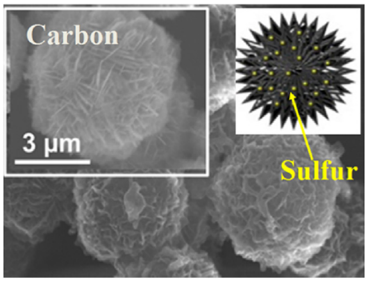
HIGHLIGHTS

- Sulfur electrode basing on activated, flower-like hierarchical porous carbon is reported.
- Defined micrometric morphology and a sulfur content as high as 66% are obtained.
- Lithium sulfur cell using the composite exhibits remarkable performances.
- A specific capacity of about 1000 mAh g^{-1} is obtained at high current rate.
- The resulting Li/S battery has relevant energy content.

GRAPHICAL ABSTRACT



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ABSTRACT

Three dimensional, flower-like hierarchical porous carbon (FPC) and its CO_2-activation (AFPC) are reported as sulfur-hosting matrixes in Li/S battery. The composites are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), nitrogen adsorption-desorption isotherms as well as by galvanostatic cycling and electrochemical impedance spectroscopy (EIS) in lithium-cell. Both samples show well defined micrometric morphology and a sulfur content as high as 66% expected to reflect into rather high practical energy density of the electrode in lithium-sulfur battery. The lithium sulfur cell using the FPC-S composite exhibits at 25 °C a moderate cycling stability with delivered capacity ranging from 1000 to about 610 mAh g^{-1} upon 50 cycles at 100 mA g^{-1}. The AFPC-S composite reveals increased cycling stability and delivers a capacity ranging from 1000 to 680 mAh g^{-1}. Improved capacity is achieved by slightly increasing the temperature, as demonstrated by cycling the FPC-S at 35 °C using a current as high as 500 mA g^{-1}. The excellent rate capability of the electrode is associated to the carbon texture and morphology that significantly lower the cell resistance, as indeed demonstrated by EIS measurement upon cycling.

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1. Introduction

Although Li-ion batteries have changed the portable electronic market [1], there is still need for increased energy storage to meet

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the large demand for emerging markets such as hybrid and electric vehicles (HEVs, EVs) [2,3]. Lithium sulfur battery, due to a capacity as high as 1675 mAh g^{-1} and corresponding energy density of 2500 Wh kg^{-1}, represents a possible alternative theoretically storing five times higher energy than Li-ion one [3,4]. Furthermore, sulfur shows important advantages such as abundance, low cost and environmental compatibility. However, the insulating nature of sulfur (~5×10^{-30} S cm^{-1} at 25 °C) and other drawbacks such as the intermediate polysulfides dissolution in organic electrolytes and volume changes during the cell operation still hinder its commercialization [5]. The use of conductive carbon matrixes represents the common solution to overcome poor electronic conductivity and volume stress of the sulfur-based electrodes, due to the relevant conductive and mechanical properties of these porous materials [6–8]. Moreover, carbon hosts may efficiently trap the polysulfide species formed during the cell operation in their cavities, thus mitigating loss of active material and shuttle effects. Several porous carbons, such as microporous carbons [9–11], mesoporous carbons [12–17] and hierarchical porous carbons [18–23] prepared by hard and soft template methods [24,25] have been proposed as suitable materials for application in lithium-sulfur cell. Three-dimensional hierarchical porous carbon has been used in supercapacitors due to high specific surface area and particular structure, consisting of interconnected micropores, mesopores and macropores [26–29]. The latter carbon may be of potential interest also for applications in Li/S batteries [30,31]. Indeed, 3D flower-like hierarchical porous carbon has shown high specific surface area and excellent interconnected pore structure that ensure not only intimate contact between active material and electrolyte, but also facilitate the ions transport. Two methods have been reported to prepare 3D flower-like hierarchical porous carbons (FPC), i.e., by employing ZnO-template [27] or nickel acetate catalyst as graphitization and pore-forming agent [28].

Herein, we study a composite electrode developed by impregnating sulfur in 3D flower-like carbon synthesized by ZnO-template and further activated by CO_2-treatment. The carbon activation by CO_2 treatment represents a clean, fast, cheap and less aggressive technique if compared to those basing on chemical treatment (e.g., by using KOH, H_3PO_4). Indeed, CO_2 reacts with the carbon at around 800 °C according to the Boudouard reaction ($C + CO_2 \rightarrow 2CO$). This process develops porosity by removing carbon atoms from the surface and it is therefore considered a “large-scale” method to produce active carbons. The increase in the surface area and porosity of the carbon is expected to improve the sulfur retention into the S–C composite, thus enhancing its electrochemical behavior in lithium cell. The resulting sulfur composite reveals high sulfur content and relevant characteristics in terms of capacity, cycling stability and rate capability in Li/S cell. Therefore, the 3D flower-like carbon-sulfur material is proposed as suitable electrode for application in a new generation of energy storage systems.

2. Experimental

2.1. Synthesis of the FPC and AFPC

All chemicals (Sigma-Aldrich, analytical grade) were used without further purification. The carbon sample was synthesized using flower-like ZnO as template and resorcinol-formaldehyde resin (RF) as the carbon source. The synthesis differed by the one already reported by Wang et al. [27] in principal by the carbon source. The flower-like ZnO template was prepared by dissolving 0.74 g of $Zn(NO_3)_2 \cdot 6H_2O$ and 1.76 g of $Na_3C_6H_5O_7 \cdot 2H_2O$ in 50 mL of water. Subsequently, 10 mL of NaOH 1.25 M was stepwise added and the solution stirred for 2 h until a white suspension was obtained. The flower-like ZnO was achieved upon filtration and drying the precipitate in oven at 100 °C for 12 h. The porous carbon was obtained by dispersing 0.4 g of flower-like ZnO template in 60 mL of tetrahydrofurane (THF) under vigorous stirring. Then 0.05 g of RF resin was dissolved in 20 mL of THF by sonication for 1 h, added stepwise to the dispersion and stirred for 5 h. The mixture was evaporated at 60 °C to remove the solvent and heated at 800 °C in a tubular furnace for 3 h under a N_2 atmosphere. The flower-like porous carbon (FPC) was finally obtained by ZnO removal using HCl. An activated sample of this carbon (AFPC) was achieved by heating the above FPC in tubular furnace under CO_2 atmosphere (50 mL min^{-1}). The samples were heated for 3 h at a temperature of 900 °C achieved by following a heating rate of 1 °C min^{-1}.

2.2. Synthesis of the carbon –sulfur composites

The C–S composites were prepared by in situ sulfur deposition from an aqueous solution of sodium thiosulfate acidified with hydrochloric acid in a mass ratio of 1:2 (C:S) under the following conditions: $Na_2S_2O_3$ $5H_2O$ (1.55 g) was dissolved in H_2O (80 mL) to which 2 mL of an aqueous solution of 1% Triton X-100 (Sigma-Aldrich, laboratory grade) was added. Simultaneously, the carbon (0.1 g) was suspended in 100 mL H_2O and soaked for 1 h, then added into above solution under magnetic stirring. The mixture was heated to 70 °C in an oil bath and HCl (8 mL, 12 M) was stepwise added. The system was cooled to room temperature and kept under magnetic stirring for 24 h. The product was filtered and washed several times with water, ethanol and acetone. Finally, the carbon-sulfur composites were dried in an air-oven at 50 °C overnight. A schematic representation of the synthesis is reported in Fig. 1.

2.3. Materials characterization

The structural properties of carbon flowers and composites were studied by a Siemens D5000 X-ray diffractometer. The sulfur content was determined by thermogravimetric analysis using a Mettler Toledo-TGA/DSC with heating rate of 5 °C min^{-1} from 25 to 600 °C under nitrogen atmosphere. The SEM/EDAX analysis of the samples was performed by using a JEOL JSM 6300 scanning electron microscope equipped by microanalysis system Inca Energy 250. The textural properties were determined by a Micromeritics ASAP 2020 system using nitrogen as adsorbent. Pore size distribution was calculated by the density functional theory (DFT) method applied to the adsorption branch of the isotherms.

2.4. Cell assembly and electrochemical characterization

The electrodes were prepared by mixing the composite with Super P carbon conductor and polyvinylidine fluoride (PVDF) binder (80:10:10 mass ratio) in N-methylpyrrolidone (NMP) solution. The slurries were coated onto an Al foil current collector by doctor blade deposition. Disks of 14 mm in diameter ($\approx$1.5 mg cm^{-2} of active material) were cut and dried in a vacuum oven at 50 °C for 3h before cell assembling. The electrochemical measurements were performed on CR2032 coin cells assembled inside an Ar-filled glove box (M-Braun, H_2O and O_2 below 1 ppm) with Li metal foil as the counter electrode. The electrolyte used was LiTFSI 1 M and $LiNO_3$ 0.4 M in 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1 v/v) soaked in a celgard polyethylene separator. The electrolyte amount was around 20 μL. The cycling tests were performed using a Maccor Series 4000 Battery Test System and an Arbin BT2143 in a voltage range of 1.8–2.8 V at various current rates. The EIS measurements were carried out using a VSP (Biologic Instruments) by applying a 10 mV signal amplitude in a 75 kHz–100 mHz frequency range.

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