



Shaddock wadding created activated carbon as high sulfur content encapsulator for lithium-sulfur batteries



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ABSTRACT

In this work, a microporous and high surface area carbon material with excellent electron conductivity is synthesized through carbonizing and activation processes using waste shaddock wadding. Because of the unique multi-hole, thin sheets cluster and irregular wrinkled surface coexisting structure, the shaddock wadding carbon-sulfur (SWD-S) composite can be used as a kind of cathode material for rechargeable lithium-sulfur batteries by loading element sulfur into the shaddock wadding activated carbon via simple heat treatments. Because of the high specific surface area of SWD ($1637.3 \text{ m}^2 \text{ g}^{-1}$), the SWD-S composite has a sulfur content about 73.7 wt%, and delivers a high initial discharge capacity of 1050 mAh g^{-1} at a rate of 0.2C. Moreover, SWD-S composite exhibits a good rate capacity and excellent cycle ability. Over 200 cycles it achieves with a high columbic efficiency around 95%. After 200 cycles at 0.2C, it still remains a capacity of 599 mAh g^{-1} .

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1. Introduction

With the increasing demand for efficient and economic energy storage, Li-S batteries have become attractive candidates for the next generation high energy rechargeable Li batteries because of their high theoretical energy density and cost effectiveness [1]. The gravimetric capacity of sulfur is the highest of any solid cathode at 1675 mAh g^{-1} , correlating to theoretical energy densities of 2500 Wh kg^{-1} or 2800 Wh L^{-1} based on weight or volume, respectively [2]. Additionally, the advantages of the natural abundance, low cost and environmental friendliness of elemental sulfur make it attractive for large-scale practical applications [3,4]. However, the electrochemistry brings noticeable problems that hinder the practical application of the battery [5]. Firstly, elemental sulfur and its lithiated compounds (Li_2S) are intrinsically non-conducting, which makes it hard for them accept electrons from the current collector. Therefore, the theoretical capacity is rarely achieved due to the limited utilization of sulfur, even though conducting media is added. Moreover, electrochemical kinetics are affected by the large resistance of the electrode, leading to large polarization and inferior rate capability [6]. In addition, the dissolved polysulfides shuttle between the anode and

cathode during cycling, reacting with both the lithium metal anode and the sulfur cathode [7]. Furthermore, the electrochemical conversion of sulfur to lithium sulfides involves structural and morphological changes as well as repetitive dissolution and deposition of reactive species, which tend to passivate both the electrodes, leading to a significant increase in impedance. These issues result in a low utilization of the active material, poor cycle life and low system efficiency [8]. To offset these issues, many means have been used to improve the electrochemical performance of the sulfur cathode. One of the most effective way is to combine sulfur with other materials to construct composite materials with high conductivity and stable cycle ability. Because of the porous carbon has an excellent conductivity and adsorption property. It was widely used to encapsulate sulfur as a loader [9–22]. For example, in 2009 Nazar and co-workers developed a highly-ordered, mesoporous carbon sulfur cathode for use in lithium-sulfur batteries [9]. After using hydrophilic polyethylene glycol to modify the carbon surface, the CMK-3 carbon-sulfur cathode exhibited a high initial reversible capacity of 1320 mAh g^{-1} . Wang et al. [12] used microporous carbon to encapsulate sulfur and its species for a Li-S battery. He found a new type of SEI membrane, which improved the isolation of sulfur. Over 4020 cycles, the coulomb efficiency is still high at about 100%. In another paper, Co et al. [15] made porous nitrogen and phosphorous doped graphene that had been prepared by using a thermal annealing and subsequent hydrothermal reaction, and the graphene-

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sulfur composite was used as the interlayer between sulfur and anode. The battery with the interlayer performed a superior high initial capacity about $1158.3 \text{ mAh g}^{-1}$ at 1C and 633.7 mAh g^{-1} . Zhang et al. [16] used a versatile chemical vapor deposition (CVD) method to prepare a kind of hierarchical porous graphene. The as prepared graphene had microsized in-plane vacancies, mesosized wrinkled pore and macrosized strutted cavities. As an encapsulator for the sulfur cathode with superior rate capability, the initial capacity was as high as 656 mAh g^{-1} at a current rate of high 5C. Recently, Xiong et al. [19] prepared a microporous–mesoporous carbon nanotube–sulfur cathode for Li–S battery. The multi-layered structure promoted electron and ion transfer during the charge–discharge process, also suppressed PS dissolution efficiently. Even at a high current density of 1600 mA g^{-1} , capacity decay was only $\sim 0.13\%$ per cycle after 150 discharge–charge cycles. In addition, biologic materials can also be used in rechargeable batteries. Xu et al. [21] synthesized cellulose/polysulfonamide composite as separator for lithium-ion batteries by via a facile papermaking process. This kind of membrane exhibited stable charge–discharge capability even at 120°C . It was demonstrated that the composite separator possessed an enhanced thermal dimensional stability. Zhang et al. [22] who were inspired by Taichi used robust cellulose nonwoven as a matrix to hold solid electrolyte for high performance lithium batteries. This kind of new solid polymer electrolyte possessed comprehensive properties in high mechanical integrity strength, sufficient ionic conductivity (3×10^{-4}) at 60°C and improved dimensional thermostability (up to 160°C).

Summing up the above, porous carbon materials have a positive effect to adsorb the polysulfides to suppress them from dissolving into the electrolyte, therefore this kind of carbon material as a sulfur encapsulator could enhance the cycle performance of Li–S batteries. Herein, we report a novel coexisting structured shaddock wadding carbon (SWD) material with high surface area ($1637.3 \text{ m}^2 \text{ g}^{-1}$) synthesized by carbonizing and activation process. Then the shaddock wadding carbon–sulfur (SWD–S) composite is prepared by simple heating treatments. Moreover, we use the pure sulfur cathode as a comparison to reach a decision that the SWD–S has advantages in electrochemical performance.

2. Experimental section

2.1. Preparation of microporous materials from shaddock wadding

The fresh shaddock wadding was collected and cut into small pieces, and then cleaned using ultrapure water and dried at 90°C for 36 h under air environment. The dried shaddock waddings were pre-carbonized at 300°C for 3 h with a heating rate of 1°C min^{-1} in the tube furnace. The obtained shaddock waddings were lapped and mixed with KOH (w/w = 1:1) in alcohol. The mixture was stirred for 12 h at room temperature, and dried in the beaker with the temperature to 75°C . Then the mixture was carbonized and activated in a tube furnace at 900°C for 1.5 h with a heating rate of 5°C min^{-1} under an argon atmosphere. The obtained mixture carbon materials were reacted with 1 M HNO_3 solution for three times, and washed several times with ultrapure water until the PH = 7.0 and vacuum dried at 120°C for 24 h. The obtained materials was named as SWD. The fabrication process is exhibited in the Scheme 1.

2.2. Synthesis of SWD–sulfur (SWD–S) composites

The SWD–S composite was prepared by simple heat treatments. Firstly, the as-prepared SWD and pure sulfur were mixed evenly with the weight ratio of 1:2 (SWD: S = 1:2). Then the mixture was heated at 155°C for 10 h in a sealed glass tube with a heating rate of 3°C min^{-1} . While, in order to vaporize the needless sulfur on the



Scheme 1. Schematic plot for the fabrication of SWD–S composite.

outer surface of carbon matrix, the as-prepared composite was heated at 600°C in the tube furnace under an argon atmosphere for 6 h.

2.3. Materials characterization

The composites were characterized using X-ray diffraction (Rigaku, model D/max2500 system at 40 kV and 100 mA of Cu Ka). In order to determine the sulfur content in the SWD–S composite, thermogravimetric analysis (TGA, Mettler Toledo TGA II STAR System) was used in the measuring process. A high-resolution field emission scanning electron microscopy (SEM, HITACHI S-4800) was used to observe the morphology of the samples. The pore size distribution and specific surface area of the samples were tested by a Brunauer Emmett–Teller (BET, BEL LAPAN, INC. Belsorp2).

2.4. Electrochemical measurements

Electrochemical tests were performed via CR2016 coin cell with lithium foil as the anode electrode. As for the cathode electrode, it was prepared by mixing 80 wt% SWD–S, 10 wt% super P and 10 wt% PVDF as a binder dissolved in 1-methyl-2-pyrrolidinone (NMP) solution. The cathodic slurry was coated onto an aluminum foil and dried at 50°C for 4 h in an ordinary oven and then 70°C in a vacuum oven for 24 h. The polypropylene (PP) film (Celgard-2400) was used as a separator. The electrolyte was a solution of 1 M lithium bis-trifluoromethanesulfonylimide (LiTFSI) in 1:1 v/v 1,2-dimethoxyethane and 1,3-DOL containing LiNO_3 (1 wt%). For comparison, the pure sulfur electrode was prepared by mixing sulfur with super P, and the sulfur content was nearly the same as the SWD–S electrode.

A multi-channel current static system Land (LAND CT2001A) was used to test the electrochemical performance of CR2016 coin cells. Charge–discharge measurements were carried out in a voltage between 1.7 V and 2.8 V at different current densities (0.2C, 0.5C, 1C) under room temperature. Cyclic voltammetry (CV) were recorded on a Series G750TM Redefining Electrochemical Measurement (USA GMARY Co.) between 1.5 V and 3.0 V at a scan rate of 0.2 mV s^{-1} to probe the redox behavior and the kinetic reversibility

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