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Porous Carbon Derived From Pomelo Peels as Substrate for High Performance Lithium-Sulfur Batteries

Min Liu, Heliang Zhou, Hongliang Li*

Institute of Materials for Energy and Environment, College of Materials Science and Engineering, Qingdao University, Qingdao 266071, China

Abstract: **Porous carbon (PC) hasbeen obtainedby carbonizingthe natural pomelo peels and following a activation with KOH. Elemental sulfur has beenloaded to the micropores to form S/PC composite using a high pressure induced one-step impregnation technique. The resulted S/PC composite with a 60% sulfur loading has been used as cathodes for Li-S battery. The S/PC composite displayed an initial discharge capacity of 1281mAh g-1, excellent rate capability of 300 mAh g-1 at 2 C and good cycling stability of 771mAh g-1 after 100 cycles at 0.2C.**

Keywords: Carbonization; Pomelo peels; KOH; Lithium-sulfur battery

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*Corresponding Author: Hongliang Li

1. Introduction

The energy densities of lithium ion batteries are limited by the low capacity of currently applied cathode materials, which cannot meet the demand of electric vehicles. Elemental sulfur owns a high theoretical specific capacity of 1675mAh g^{-1}, which is nearly five times higher than that of existing transition metal oxide and phosphate materials [1, 2]. Besides, sulfur has an advantage of natural abundance, low cost, and environmental friendliness. Therefore, sulfur becomes a promising cathode material for the next generation of rechargeable batteries with high energy density. Carbonaceous materials are extensively used as electronic conductors in the battery industry, and play an important role in the sulfur electrode. Porous carbon (PC) materials derived from biomass usually show high surface area and pore volume, and are easily scalable with low cost. In this work, we present a 3D connected porous carbon derived from a natural resource of pomelo peels [3, 4]. The PC has been used as substrate for the sulfur cathode and demonstrated excellent electrochemical performance with good cycling performance, rate capability and the utilization of sulfur.

2. Experimental Section

2.1. Sample preparation

Commercially available pomelo peels was extensively washed by DI water, cutting into small pieces with diameter of 15mm and thickness of 3mm. After freeze-drying for 24h, and then carbonized at 400℃ for 1h under N_2 gas to form black carbon powders (CPs). The CPs were immersed in 1mol L−1 KOH aqueous solution for 12h with a KOH/CPs weight ratio of 1. After freeze-drying, the obtained product was then further pyrolyzed in a tubular furnace at 800℃ for 1h under N2 flow. Finally, the black sample was washed by water and dried at 80℃. The obtained PC was then utilized as matrices for the preparation of S/PC composite with sulfur loading contents of 60wt%. The mixture of sulfur and PC was loaded into a swagelokstructured stainless autoclave and cured at 155℃ for 6h, and then the temperature was increased to 300℃ and kept at this temperature for 5h to guarantee melted sulfur infiltrate into the pores of the porous carbon.

2.2. Characterization

X-ray power diffraction (XRD) patterns were recorded on a RigakuUltima IV X-ray diffractometer with Cu-Kα radiation (λ = 0.15418nm). The specific surface areas were estimated with the Brunauer-Emmett-Teller (BET) method with N2 adsorption data in the relative pressure range of P/P0 = 0.05-0.35. The pore size distributions were calculated using the Barrett-Joyner-Halenda (BJH) model applied to the desorption branch of the N2 isotherms. The morphologies and the microstructures of the samples were examined by using a JEOL JSM-7800F scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) and a JEOL JEM-2100Plus transmission electron microscope (TEM).

2.3. Electrochemical Measurements

The working electrodes were prepared by making a slurry consisting of 80wt% active material, 10wt% conductive agent (acetylene black) and 10wt% polyvinylidene fluoride (PVDF) as binder. The slurry was coated on an aluminum foil. After drying at 55 ℃ under vacuum overnight, the electrodes were punched to fit into 2016 coin-type cells in a glove box filled with Ar gas. Lithium metal was used as the counter electrode, a Cellgard 2400 microporous membrane was employed as the separator, and 50μL of 1M bis-(trifluoromethane) sulfonimide lithium (LiTFSI, Alfa Corp.) in a mixed solvent of dimethoxyethane (DME) and 1,3-dioxolane (DOL) (1:1,vol.%) as the electrolyte. The charge–discharge tests were carried out using a LAND Cell Test System (2001A, Wuhan, China) between cutoff voltage of 3V and 1.5V. Cyclic voltammetry (CV) measurements were conducted using a two-electrode

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coin-type cell performed between 1.5V and 3V at 0.1mVs-1 on a CHI760D electrochemical working station. Electrochemical impedance spectroscopy (EIS) profiles were recorded on a CHI760D electrochemical working station in the frequency range between 100kHz and 0.01Hz with amplitude of 5mV.

3. Results and discussion

3.1. Structure and Morphology

Figure 1 shows the SEM images of the S/PC composite. The 3D connected sponge-like structure of the peel is well inherited without any breakage. It displays irregular monolithic morphologywith macropores of several tens of micrometers.It is found that the S/PC is composedof connected flakes with wrinkled surface [1].

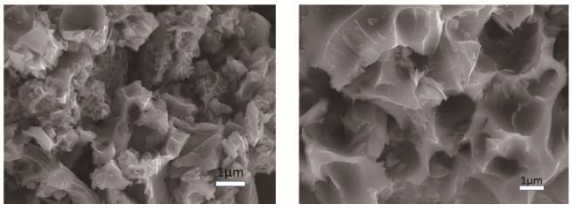

Figure 1. SEM images of the S/PCunder different magnifications.

Figure 2(a) shows the XRD patterns of the S/PC sample. For the S/PC, the strong peak at two theta of 22.0 °indicates the presence of graphitic domains while the small peak at two theta of 44.0 ° represents the quasi-amorphous nature of the hard carbon. To confirm the sulfur loading efficiency by the high pressure process and the exact sulfur loading content in the composite spheres, TGAs were conducted in an Ar flow. Fig. 2(b) shows the typical TGA curve of S/PCcomposites. As can be seen from the curve, the S/PC sample displays a weight loss of 59.7wt% in the temperature range between 180 and 450℃, and the weight losses are closed to the sulfur contents as set in their raw materials[3-4].

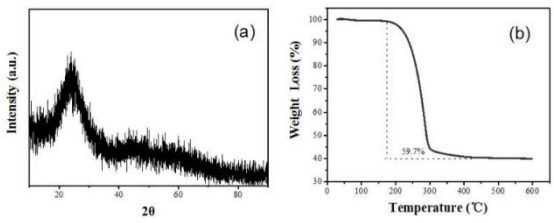

Figure 2. (a)XRD patterns of S/PC composite;(b) TGA curve of the S/PC composite.

The N2adsorption and desorption isotherms of PC and S/PC measured at 77K is shown in Fig. 3. Both samples display obvious hysteresis loops, which indicate the existenceof mesopores. The curve shows ansteep absorption below P/P0 = 0.2, indicating the presenceof abundant micropores in the PC. The BET surface area of samples PC andS/AC were of 1286.48and 21.394m2 g-1,and the pore volumes of 0.062 and 0.04respectively. The BET surface areadecreases significantly due to the impregnation of sulfurinto the micro/meso pores. It is found that the PC have a large amount ofmicropores with diameter around 2nm and some amount of mesopores around 3.5nm, indicating a bimodal pore size distribution character (see Fig.3a). The pore size distribution of S/PCcomposite indicatesthat most micropores and mesopores are filled with sulfur, resulting significant decrease of specific surface area and pore volume.

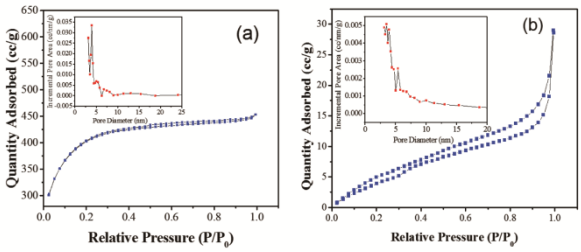

Figure 3. (a)Nitrogen adsorption and desorption isotherms and BJH pore size distribution curves of PC before sulfur loading; (b) Nitrogen adsorption and desorption isotherms and BJH pore size distribution curves of S/PC composite.

3.2 Electrochemical Performance

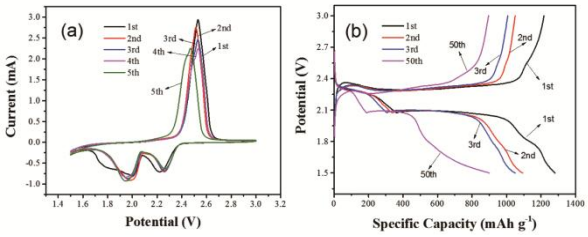

Figure 4.(a) CV curves ofS/PC compositeelectrodes at a scan rate of 0.2mV s−1; (b) GCD curves of S/PC composite at the 1st, 2nd, 3rd and 50thbetween 1.5 and 3.0V at a current density of 0.2C.

Figure 4(a) shows the cyclic voltammetry (CV)profiles of S/PC composite for the 1st, 2nd, 3rd, 4th, and 5th cycles at a scanrate of 0.2mV s-1.During the first cathodic scan, two remarkable reduction peaks at 1.95 and 2.25V can be observed. The upper plateau at 2.25V corresponds to the reduction of elemental sulfur (S8) or highly oxidized polysulfides such as Li2S8 and Li2S6 to Li2S4 [5-7]. While, the lower plateau at 1.95V represents the reduction of Li2S4 or lower sulfides to Li2S2 or Li2S. In the anodic scan, only one sharp oxidation peak is observed at 2.55V, which corresponds to the oxidation process of Li2S [8, 9]. At the same time, the integral area intensity is almost unaffected in the following charge-discharge cycles, indicating that the S/PC composite electrode has excellent electrochemical reversibility. Figure 4(b) shows the GCD of the S/PC composite electrodes after 1st, 2nd, 3rd and 50thcycles at a current density of 0.2C in the voltagerange of 1.5-3.0V.The S/PC compositeelectrode shows the

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highest specific capacity and the initial discharge capacity is 1281mA h g-1 at 0.2C.In the following severalcycles, reversible capacity around 1000mAh g-1is obtained, which is about 60% of the theoretical capacity of 1675mAh g-1. The subsequent cycles show stable capacity, indicating the good cycling performance of the sample

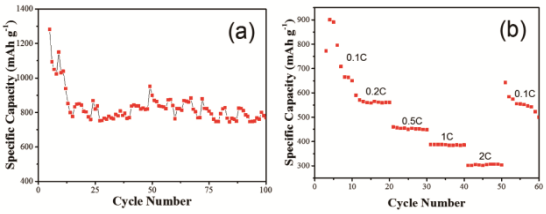

Figure 5. (a) Cycling performance at 0.2C rate and (b) rate capability of the S/PC composite electrode.

Figure 5.(a) shows the cycling performance at 0.2C rate. The capacity decays rapidly in the first five cycles from 1281 to 1100mAh g−1, which could be attributed to the loss of residual sulfur on the external surface of PC. After that, the capacity decreases slightly, probably due to partial dissolution of the polysulfides and their escape from the micro/mesopores of PC. Figure 5(b) depicts the discharge and charge curves of S/PC composites cathodes at different current rates. It can be seen when the rate is increased to 2C, the cell still delivers a capacity of more than 300mAh g-1. One can see that the discharge capacities decrease gradually as the rate increased from 0.1 to 2C. It can be explained by the probable formation of a thin S layer on the external surface of the activated carbon owing to the strong affinity of sulfur to carbon.

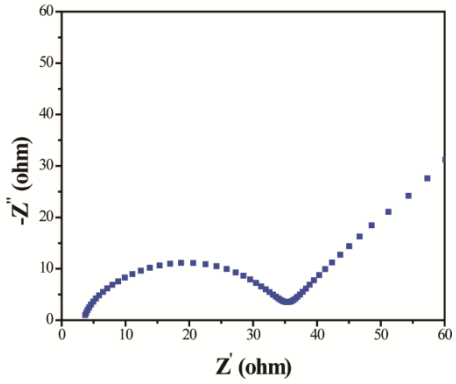

Figure 6. Nyquist plots of the S/PCcomposite electrodes before cycle.

To verify further the improved electrochemical performance, the electrochemical impedance spectroscopy (EIS) measurements of the S/PCcomposite electrodesbefore and after cycles have been carried out. As can be seen from Figure 6, the impedance plots are composed of a semicircle in the high frequencydomain corresponding to the charge transfer impedance andinterfacial impedance, and the slope lineat low frequency corresponds to the Warburg Impendence [10]. It is obvious that the S/PCcomposite electrode exhibited a low charge transferresistance, which shows high conductivity. In addition, this impedanceevolution matches well the excellent electrochemical performance of S/PCcomposite electrode with a high reversible cycle capacity.

4. Conclusions

Porous carbon (PC) with three dimensional connected structures was prepared by carbonizing of pomelo peels and following an activation procedure. Element sulfur was loaded into the PC through a high temperature approach with a closed cell toform S/PC composites. The S/PC composite show superior electrochemical performance when used as cathodes material for Li-S batteries. The results show that the porouscarbon with 3D connected structure could be promisingconductive substrates for rechargeable Li-S battery withhigh specific energy.

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