



# Synthesis and electrochemical performance of a simple and low-cost sulfur/porous carbon composite cathode for rechargeable lithium sulfur battery



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## ABSTRACT

The sugar and phenolic resin were used as source materials to prepare porous carbons labeled as PC1 and PC2 respectively, which were activated by chemical methods with  $\text{CaCO}_3$  as active agent. Sulfur/porous carbon composites were synthesized by thermally treating a mixture of sublimed sulfur and porous carbon. The morphology, structure, and electrochemical performance of the composite were investigated by scanning electron microscopy, Brunauer–Emmett–Teller, and a variety of electrochemical techniques. The electrochemical measurements show that the SPC2 electrode presents a more favorable electrochemical kinetics than the SPC1 electrode. In comparison with SPC1, it is shown that the rate of  $\text{Li}^+$  diffusion with SPC2 is significantly higher and the charge transfer resistance is much lower. The PC2 with high surface area ( $735.2 \text{ m}^2 \text{ g}^{-1}$ ) and large pore volume ( $1.56 \text{ cm}^3 \text{ g}^{-1}$ ) not only increases the electronic conductivity of composites, but also facilitates transfer of the Li ion in the composite electrode.

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## 1. Introduction

The lithium/sulfur system with a lithium metal anode and an elemental sulfur cathode that, on the basis of its electrochemical process,  $16\text{Li} + \text{S}_8 \rightarrow 8\text{Li}_2\text{S}$ , theoretically provides a significantly higher energy by mass than that offered by conventional lithium ion batteries, namely  $2600 \text{ W h kg}^{-1}$  vs.  $500 \text{ W h kg}^{-1}$  [1]. In addition, since sulfur is a cheap, abundant, and nontoxic material, Li/S cells are more eco-friendly and economical when compare to other secondary batteries. Thus, lithium/sulfur (Li/S) cells are ideally suited for high-energy applications. However, the practical development of the lithium/sulfur battery has been so far prevented by a series of issues which include: the insulating nature of sulfur and the solubility of redox reaction products in the electrolytes, resulting in poor performance of the battery. Over the past few years, many studies [1–19] have been performed to increase the energy density and the cycle life of the lithium/sulfur battery. Preparation of a sulfur/carbon composite is an alternative approach to enhance the electrical and ion conductivity of the sulfur cathode and retard the polysulfide shuttle phenomenon by using high surface area carbon adsorbents.

Various porous carbon materials, such as active carbon [7], acetylene black [8], carbon nanotubes [9–11], highly porous carbon [12,13], and ordered mesoporous carbon [14–17], have been applied to improve electrochemical properties of the sulfur cathode with conventional liquid electrolytes. Nazar and co-workers [12] reported that the composite electrode of sulfur and mesoporous carbon which was synthesized by a nanocasting method that used siliceous SBA-15 as a hard template exhibited extremely high reversible capacity. This composite accommodated up to 70 wt% sulfur and obtained a high utilization of sulfur cathode. Chen and co-workers [18] reported a composite material of sulfur and bimodal mesoporous carbon (5.6/2.3 nm) prepared through a triconstituent co-assembly method that exhibited an excellent high-current density performance as an electrode. Although mesoporous carbon is the most promising material for high performance sulfur cathode, a potential problem associated with their use is high preparation cost.

In our work, porous carbons (PC) were synthesized with different carbon sources (sucrose and phenolic resin, respectively) by activation methods with  $\text{CaCO}_3$  as active agent. The hierarchical sulfur/PC composites (SPC) were then prepared by a simple melt-diffusion method with optimized sulfur contents. The SPC composites were used as cathode for rechargeable Li/S batteries. As for the electrolyte, we used the  $\text{LiPF}_6 \text{ EC/DMC}$ , which is easy to get and has a relatively low cost. Wei et al. [20] and Xin et al. [21] reported excellent electrochemical performance of Li/S batteries with the

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electrolyte of 1M LiPF<sub>6</sub> EC/DMC. In addition, our previous work also got favorable outcomes by using the same electrolyte [22].

## 2. Experimental

### 2.1. Preparation of porous carbon

The sucrose/CaCO<sub>3</sub> composite was prepared according to the following procedure. 20 g of sucrose (AR-grade) was dissolved in 50 mL distilled water. 20 g CaCO<sub>3</sub> (AR-grade) was then added into the solution subsequently under vigorous stirring to obtain the homogeneous slurry at ambient temperature. The temperature of the slurry was then elevated to 110 °C to remove the excess water. Then the mixture was heated to 800 °C and held for 2 h under nitrogen flow to complete the pyrolysis and carbonization. The black carbonized composite was treated with 2M HCl solution at room temperature to remove the residual calcium. The carbon materials (designated as PC1) were ultimately obtained after filtration, washed with deionized water and dried overnight.

Another sample, which was prepared by introducing a certain amount of CaCO<sub>3</sub> into the phenolic resin and ethanol mixture, was labeled as PC2. The experimental conditions and structural parameters of porous carbon materials are shown in Table 1.

### 2.2. Preparation of S/C composite electrode

Sublimed sulfur and PC1 (or PC2) with the weight ratio of 3:1 were blended to prepare sulfur-based composite materials marked as SPC1 (or SPC2), which was blended by mechanical milling at room temperature, and heated to 155 °C to make elemental sulfur melt and this temperature was kept for 6 h for melted sulfur to diffuse into the pores of carbon under nitrogen flow. Then the temperature was enhanced to 300 °C and kept for 2 h so that the vaporized sulfur was coated onto the surface of pores. The structural parameters of SPC1 and SPC2 are shown in Table 1.

The cathode slurry was made by mixing 80 wt% SPC1 (or SPC2), 10 wt% acetylene black and 10 wt% polyvinylidene fluoride (PVDF) binder in N-methyl-pyrrolidinone (NMP) solvent. The slurry was then spread onto aluminum foil substrates, dried in vacuum at 60 °C for 24 h. The electrode was punched into discs of 14 mm in diameter and the composite loading was about 1.7 mg cm<sup>-2</sup>. CR2032-type coin cells were assembled in an Argon atmosphere glove box (Universal5641101, Dellix, Chengdu, China) with H<sub>2</sub>O and O<sub>2</sub> content below 1 ppm. Metallic lithium foil was used as counter electrode. The electrolyte was 1M LiPF<sub>6</sub> dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v/v) and Celgard 2400 polyethylene was used as the separator.

### 2.3. Properties measurement

The specific surface area analysis of the porous carbon and sulfur/carbon composite was performed by nitrogen BET adsorption

**Table 1**  
Physical properties of porous carbons derived from sugar and phenolic resin and sulfur/porous carbon cathode.

Sample	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	Vol (cm <sup>3</sup> g <sup>-1</sup> )	Pore size <sup>a</sup> (nm)	Electrical conductivity (S cm <sup>-1</sup> )
PC1	598.3	0.76	7	
PC2	735.2	1.56	4	
SPC1	34.7	0.06		6.49
SPC2	68.2	0.28		4.74

<sup>a</sup> Average pore diameters calculated from desorption branches by using the BJH model.

measurements (BET, Micromeritics ASAP2020). The electrical conductivities of the sulfur/carbon composites were tested by a Four-probe Conductivity Analyzer (Kenpo Electronic Instrument Co. Ltd. Shanghai). The sulfur content in the composite was measured by the Carbon Sulfur Analyzer (CS-902, Wanlianda Xinke, Beijing, China). The morphology of the porous carbon and the composites were investigated by SEM using a Shimadzu JSM-5900LV microscope (Japan Electronics Co. Ltd.). The XRD patterns were taking place on a PW1730 X-ray diffraction using Cu K $\alpha$  radiation.

The galvanostatic discharge and charge test was conducted at various current densities from 100 to 600 mA g<sup>-1</sup>-sulfur at room temperature using a LAND CT2001 (Neware Co. Ltd.). The unit cell was typically cycled in a voltage range of 1.0–2.8 V vs. Li/Li+. The AC impedance measurements were performed with amplitude of 5 mV over a frequency range of 10<sup>5</sup>–10<sup>-2</sup> Hz using a Frequency Response Analyzer (FRA) technique on a Autolab Electrochemical Workstation (Gammy Instruments Ins.). The cyclic voltammetry (CV) tests were performed on a CHI660B electrochemical workstation.

## 3. Results and discussion

SEM images of the porous carbon and sulfur/porous carbon composites are shown in Fig. 1. Fig. 1a and b illustrate the typical SEM images of PC1 and PC2, respectively. Fig. 1c and d are the SEM images of SCP1 and SCP2, respectively. From Fig. 1a and b, the porous carbon has an irregular morphology in shape and widely distributed in size. The as-prepared porous carbons show highly developed porous structure. The developed porous structure is favorable for the diffusion of melt sulfur and the access connection of the electrolyte throughout the porous carbon. As shown in Fig. 1c and d, the surface roughness and the particle size of SPC1 are increased more evidently than that of the SPC2, and the Fig. 1d depicts more uniform particle morphology of SPC2, which suggests that the sublimed sulfur could diffuse into the mesopores or micropores of the porous carbon and be restricted. This can be further confirmed by the BET analysis shown in Table 1 that the pore volume of PC1 (0.76 cm<sup>3</sup> g<sup>-1</sup>) is much smaller than that of PC2 (1.56 cm<sup>3</sup> g<sup>-1</sup>), which means that PC2 has stronger potential for sulfur loading. As a result, the SPC2 possesses a higher sulfur content (58.12 wt%) than SPC1 (33.76 wt%). Besides, the specific surface area of SPC1 composite is sharply reduced to 34.7 m<sup>2</sup> g<sup>-1</sup> from initial 598.3 m<sup>2</sup> g<sup>-1</sup> of PC1 and 68.2 m<sup>2</sup> g<sup>-1</sup> for SPC2 from initial 735.2 m<sup>2</sup> g<sup>-1</sup> of PC2, respectively, which indicates that the porous structure is reduced seriously. In addition, the electronic conductivities of sulfur/carbon composites are also presented in Table 1, which are 6.49 S cm<sup>-1</sup> for SPC1 and 4.74 S cm<sup>-1</sup> for SPC2 respectively. A dramatic improvement of conductivity has been obtained in the composite compared with pure sulfur (5 × 10<sup>-28</sup> S cm<sup>-1</sup>).

Fig. 2 shows the XRD patterns of sublimed sulfur as well as porous carbon and the sulfur/carbon composite. The XRD pattern of sublimed sulfur is identical to standard one of PDF 74-1465 of S<sub>8</sub> molecules, and the broad diffraction peaks of the porous carbon at 2 $\theta$  = 24° and 45° depict a typical graphite structure. As for sulfur/carbon composite, the XRD pattern is similar to the porous carbon, presenting an amorphous state. That means sulfur has been well dispersed into the inner pores of porous carbon rather than aggregated and crystallized on the surface of porous carbon particles [23].

Fig. 3 shows cyclic voltammograms for the first charge/discharge cycle of lithium/sulfur cells tested with 0.1 mV s<sup>-1</sup> scan rate. As seen from Fig. 3, cathode for either SPC1 or SPC2 shows an oxidation peak at about 1.7–1.8 V as well as a reduction peak

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