



# Insight into the loading temperature of sulfur on sulfur/carbon cathode in lithium–sulfur batteries



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## ABSTRACT

Lithium–sulfur batteries are highly desired because of their characteristics such as high energy density. However, the applications of Li-S batteries are limited because they exist dissolution of polysulfides into electrolytes. This study reports the preparation of sulfur cathodes by using bimodal microporous (0.5 nm and 0.8 nm to 2.0 nm) carbon spheres with high specific area ( $1992 \text{ m}^2 \text{ g}^{-1}$ ) and large micropore volume ( $1.2 \text{ g cm}^{-1}$ ), as well as the encapsulation of polysulfides via formation of carbon–sulfur bonds in a sealed vacuum glass tube at high temperature. Given that sulfur and polysulfides are well confined by the S–C bond, the shuttle effect is effectively suppressed. The prepared S/C cathodes with a sulfur loading of up to 75% demonstrate high sulfur activity with reversible capacity of  $1000 \text{ mA h g}^{-1}$  at the current density of  $0.1 \text{ A g}^{-1}$  and good cycling stability ( $667 \text{ mA h g}^{-1}$  after 100 cycles).

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## 1. Introduction

With rapid consumption of renewable resources and growing concern regarding climate, researchers have focused on the development of rechargeable lithium batteries with high capacity, high energy density, and low cost [1–9]. Lithium–sulfur batteries have been considered as promising energy storage devices for various practical applications because of their high energy density of  $2600 \text{ Wh kg}^{-1}$ , high capacity of  $1675 \text{ mA h g}^{-1}$  (achieved through two-electron conversion reaction between sulfur and metallic lithium), low cost, and natural abundance, as well as the non-toxicity of sulfur [10,11].

However, the use of Li-S batteries is currently limited to applications with low utilization of active material because of the poor intrinsic electronic conductivity of sulfur,  $\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$  as discharge product, low Coulombic efficiency, and fast capacity fading caused by high solubility of polysulfide intermediates in liquid electrolytes [12–16]. The most common strategy to improve cathode conductivity and alleviate dissolution of polysulfides is to incorporate sulfur into carbon substrates with porous structures [5,17], graphene/graphene oxide [18–21], and carbon nanotube [22]. Additionally, electrolyte additives ( $\text{LiNO}_3$ ,  $\text{P}_2\text{S}_5$ , etc.) [23–25] and new electrolytes (solid-state and ionic liquid) [26–29] are

introduced in Li-S cathodes. Previous studies have indicated that meso/microporous carbon/sulfur composites, particularly for microporous carbon with pore size of 0.5 nm, evidently demonstrate significantly improved electrochemical performance because of the fine confinement of carbon substrates on sulfur molecules and polysulfides [5]. However, given the small pore volume of micropores, sulfur loading of >50% is difficult to achieve. Low sulfur content results in decreased energy density of the cathode [21]. To achieve high sulfur loading, carbon substrates with large pore volume and pore sizes, such as mesoporous and macroporous carbon materials, are utilized as sulfur hosts in Li-S batteries. These mesoporous and macroporous carbon materials exhibit a high sulfur loading of >60%, accompanied with considerable polysulfide dissolution and fast capacity fading [30,31]. Therefore, micropores carbons with large pore volume and high specific surface area are suitable for Li-S batteries. In our previous work, a sulfur host carbon sphere with hierarchical micro-/mesoporous structure was prepared using a tunable KOH activation technique. The obtained carbon/sulfur composite exhibited a sulfur loading of 50%, but the specific surface area and pore volume of the optimized carbon sphere are only 828 and  $0.568 \text{ cm}^3 \text{ g}^{-1}$ , respectively [17]. Although the increase in KOH concentration can increase of the specific surface area and pore volume, excessive use of KOH results in carbon burn-off and wastage of reagents. In the present study, sulfur host carbon spheres, with bimodal microporous structure (0.5 and 0.8–2.0 nm), high specific surface area ( $1992 \text{ m}^2 \text{ g}^{-1}$ ), and large pore volume

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( $1.2 \text{ g cm}^{-1}$ ) were synthesized using an economical phosphoric acid activation method. Given the large pore volume, the sulfur loading can reach up to 75 wt%. Beyond that, the results show that the cycling stability and capacity retention of the sulfur-carbon composites would be further improved by increasing the sulfur loading temperature from  $155^\circ\text{C}$  to  $500^\circ\text{C}$  to form the S—C bond at  $500^\circ\text{C}$ . The in-situ formed C/S composite S/C-500 cathode (S/C-500 and S/C-155 refer to heated sulfur and carbon at  $155^\circ\text{C}$  and  $500^\circ\text{C}$ , respectively) exhibits high sulfur activity, reversible capacity of  $1000 \text{ mA h g}^{-1}$ , and good cycling performance ( $667 \text{ mA h g}^{-1}$  after 100 cycles) at the current density of  $0.1 \text{ A g}^{-1}$ .

## 2. Experimental

### 2.1. Preparation of S/C composites

All of the reagents were of analytical grade purity and used without any purification. Sulfur with a purity of  $>99.995\%$  purchased from Aldrich. Hydrothermal method was applied to synthesize the spherule-like carbon precursor as previous reported [17]. Then 1 g of carbon precursor was impregnated with 2 ml of phosphoric acid, followed by carbonization under Ar at  $800^\circ\text{C}$  for 1 h to yield the activated carbon. Sulfur and carbon were uniformly mixed with a weight ratio of 3:1 to form a black mixture. The mixture was then sealed in a glass tube under Ar with the pressure of 1 Pa under Ar and heated at  $155^\circ\text{C}$  and  $500^\circ\text{C}$  for 20 h to yield S/C composites.

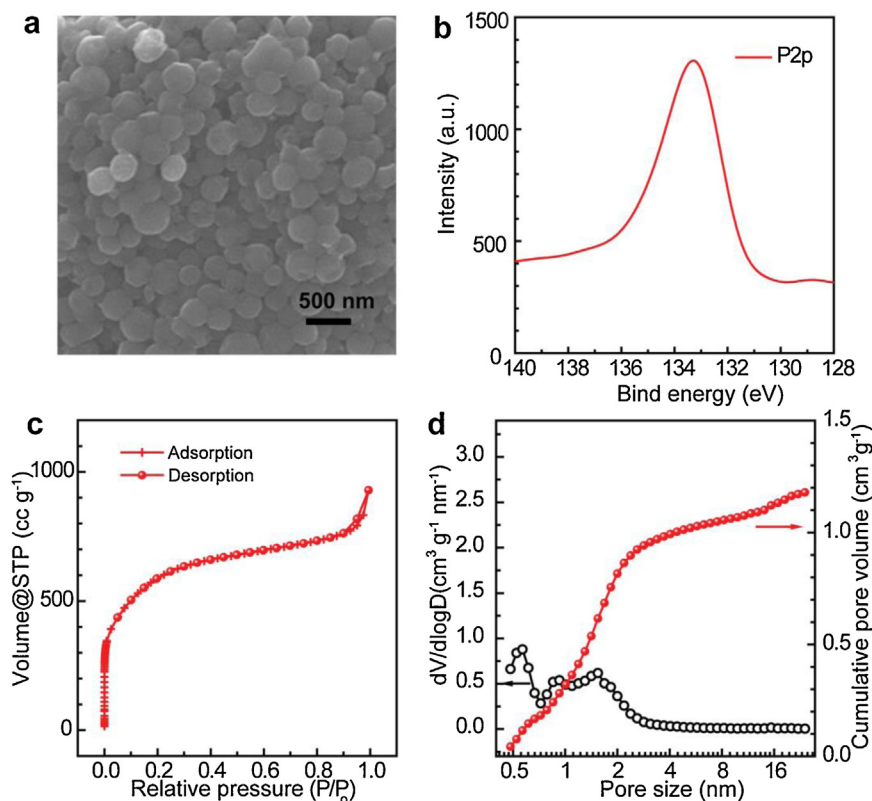
### 2.2. Structure characterizations

SEM (6701F, operating at 10 kV), TEM (Tecnai F20), high resolution TEM (Tecnai F20), EDX elemental mapping (Tecnai F20) were carried out to visualize the morphological

characteristics, sizes, microstructures, and elemental compositions of the as-obtained sample. TG analysis (TG/DTA6300) was performed to obtain the sulfur content in the S/C composite between  $25\text{--}800^\circ\text{C}$  at the speed of  $10^\circ\text{C}/\text{min}$  under the protection of nitrogen. XRD was conducted using a Philips PW3710 with filtered Cu  $K\alpha$  radiation (Rigaku D/max-2500,  $\lambda = 1.5405 \text{ \AA}$ ). The nitrogen adsorption/desorption isotherms were obtained at 77.3 K by using a Nova 2000e surface area pore size analyzer. An ESCALab220i-XL electron spectrometer (VG Scientific) with 300 W Al  $K\alpha$  radiation was performed to conduct XPS and analyze the elemental and valence.

### 2.3. Electrochemical measurements

Electrochemical measurements were carried out by using coin cells with metal lithium as the counter electrode and celgard microporous polypropylene/polyethylene/polypropylene composite film as a separator. The S/C cathode was prepared by mixing the active material S/C, ketjen black and polyvinidene fluoride at a weight ratio of 80:10:10 in N-methylpyrrolidone to form slurry. The slurry was pasted on aluminium foil and dried at  $50^\circ\text{C}$  for 12 h. The electrode was punched into circular disks with a diameter of 10 mm with active material loading of  $2 \text{ mg cm}^{-2}$ . An ether electrolyte of 1 M bis(trifluoromethane) sulfonamide lithium salt (LITFSI) in 1,3-dioxolane (DOL) and dimethoxymethane (DME) containing alpha-lipoic acid (4 wt%) was used. As reported, alphasulphonic acid as an electrolyte additive can form a polysulfide rejection layer on the cathode surface to improve the electrochemical performance [25]. The GDC cycling of the assembled cells was performed using a Land system a voltage at range of 1.0 V to 3.0 V (vs.  $\text{Li}^+/\text{Li}$ ). And all the capacity in parentheses based on the composite, and the one outside calculated on sulfur. Cyclic voltammetry (CV) was determined using an Autolab PG302N with



**Fig. 1.** Structural characterization of carbon spheres activated by phosphoric acid (a) SEM image. (b) P2p spectra. (c) Nitrogen adsorption/desorption isotherms at 77 K and (d) their pore size distributions.

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