



Mesoporous carbon with large pore volume and high surface area prepared by a co-assembling route for Lithium-Sulfur Batteries



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ABSTRACT

Mesoporous carbon (MC) materials with large pore volume and high surface area have been synthesized as the conductive matrix in the sulfur cathode for the lithium sulfur (Li/S) batteries using a simultaneous templating and carbonization method. The magnesium citrate is used as the precursor of the carbon and provides nanometer sized MgO particles template. Wide-angle X-ray diffraction (WA-XRD), high-resolution transmission electron microscopy (HR-TEM) and N₂ sorption analysis show that the resultant carbon material possesses mesopores structure (about 6.5 nm), high surface area (1432 m² g⁻¹), and large pore volumes (2.894 cm³ g⁻¹) after pyrolysis (1000 °C). Elemental maps confirm that sulfur is homogeneously dispersed in the MC framework after encapsulation. Electrochemical measurements performed on this mesoporous carbon used as an electrode material for Li/S batteries show excellent discharge capacity (1083.6 mAh g⁻¹) at current density 200 mA g⁻¹. The mesopores with large volume and high surface area are crucial in loading insulated sulfur, which provide enough space and good conducting networks for active materials. Meanwhile, mesoporous structure with high adsorption capacity can both effectively accommodate the polysulfide anions and improve the electrochemical performance of Li/S batteries.

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1. Introduction

Advance energy storage devices with higher energy density are critical for powering future society [1]. Many efforts have been focused on batteries having prospected energy density such as lithium/sulfur (Li/S), lithium/air and aluminum/air, while the lithium/air and aluminum/air are still in a very initial stage of R&D, the Li/S batteries are the most promising devices applying in the next generation of high density energy storage systems due a more advanced state of development. That can be attributed to the high theoretical specific capacity of sulfur cathodes (1675 mAh g⁻¹, near 6, 10 and 11 times compared to LiCoO₂, LiFePO₄ and LiMn₂O₄) and the high specific energy density (2600 Wh Kg⁻¹) [2]. However, there are still many significant technical limitations that hinder the commercialization of Li/S batteries. Firstly, nature sulfur is highly electrically and ionically insulating, which leads to low utilization and poor rate capability. Secondly, Li₂S and other insoluble compounds will deposit on Li anode during cycling, which could block the approaching of lithium ions. Thirdly, the soluble S_{n-x}²⁻ lower

order polysulfides will diffuse back to the cathode by charging and be reoxidized to S_n²⁻ higher order forms, creating the so-called internal “shuttle mechanism” [3,4].

Several approaches have been applied to address the challenges described above, including the use of metal sulfides [5], organic sulfides [6,7], metal oxides [8,9]. Although these methods are helpful in improving the electrochemical performances, the security issues and semiconducting or insulating nature of these compounds inevitably slow down cathode reaction kinetics. Then, Nazar et. al found that sulfur particles embedded in nanopores of the conductive carbon matrix could increase both the electrical and ionic conductivity of the sulfur cathode, while retarded the polysulfide shuttle phenomenon. Hence, efforts have focused on porous carbon with high surface area and good electrical conductivity [10,11], such as active carbon [12,13], nanotubes/nanofibers [14,15], graphene/graphene oxide [16,17], mesoporous carbon [18,19], microporous carbon [20], and hierarchical porous carbon [21]. Among them, mesoporous carbon hold many advantages like high surface area, large pore volume, and small pores size. Nazar et. al firstly succeeded in immobilizing sulfur in 3 nm ordered carbon pores and achieved promising cycle stability over 20 cycles and high initial discharge capacities of 1005 mAh g⁻¹ at 0.1 C rate [22]. Various mesoporous carbons prepared using soft or hard templates

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have been reported. An ordered mesoporous carbon with large surface area ($2102 \text{ m}^2 \text{ g}^{-1}$), pore volume of $2.0 \text{ cm}^3 \text{ g}^{-1}$, and bimodal mesoporous structure (5.6/2.3 nm) has been synthesized using a tri-constituent co-assembly method, with 60 wt% sulfur loading, the composite has high initial capacity and capacity retention [23]. Another MC (2/7.3 nm) synthesized using a soft-template approach and KOH activation has a relatively small pore volume ($0.56 \text{ cm}^3 \text{ g}^{-1}$) and maximum sulfur loading of 37.1 wt% [24]. However, sulfur utilization has been limited by relatively low load of sulfur (less than 60 wt% in their composites) [25] and complicated preparation process. Therefore, the development of mesoporous carbon with simple preparation method and large pore volume is necessary for realizing Li/S technology.

In this work, highly specific surface area porous carbon with good conductivity was synthesized by a simple situ MgO template method, which was a one-step process (simultaneous template and carbonization) without metal catalyst and activation processes [26,27]. Magnesium citrate was used as the precursor of the carbon and provides nanometer sized MgO particles template. This material had a wealth of mesoporous which contain large pore volume and high surface area, the mesopores acted as solvent restricted reactors for sulfur lithiation and provide sufficient electrochemical reaction sites, the interconnected nanochannels and defects provided good conducting networks for both Li-ion and electron. The mesoporous carbon/sulfur composites were then prepared by a melt-diffusion method with optimized sulfur contents, which were used as cathode for rechargeable Li/S batteries. MC was proved to be an effective candidate to improve the sulfur utilization and restrained the solubility of lithium polysulfides due to its excellent conductivity, large surface area, large pore volume and low cost.

2. Experimental

2.1. Materials

Mesoporous carbon (MC) was prepared through simultaneous templating and carbonizing magnesium citrate (Tianjin Guangfu Fine Chemical Research institute). The magnesium citrate was used as the precursor of the carbon and also provided nanometer sized MgO particles template. The magnesium citrate was heated to 1000°C under nitrogen flow (60 mL/min) with a heating rate of 5°C/min , and maintained at this temperature for 1 h. Subsequently, carbon powder was collected by filtration, washing, and drying after the carbon-coated MgO powder was leached with a 1 mol/L HCl aqueous solution, and finally dried at 120°C for 12 h under vacuum.

Mesoporous carbon/sulfur (MC/S) composites were prepared by melt diffusion method. MC was mixed with the high-purity sulfur (99.99% Aladdin) in Agate mortar with different weight ratios of 1:1, 1:2, 1:3.352, 1:4, 1:5, denoted MC/S-x ($x = 1, 2, 3, 4, 5$, respectively), and ground into uniformity. Then, the composite was heated at 160°C for 5 h in a special sealed container filled with nitrogen gas. At this temperature, the melted sulfur had its lowest viscosity (7.09 mPa s) [30] which could diffuse into the pores of the mesoporous carbon easily. Finally, the temperature was increased to 300°C and was maintained for 3 h to vaporize the superfluous sulfur covering the surface of mesoporous carbon, and allowed it to diffuse into the mesoporous carbon nanopores.

2.2. Structure characterization

Morphological characterizations were carried out with a Hitachi-S4800 Scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDX). X-ray diffraction patterns (XRD) were obtained with a D8-Focus diffractometer using $\text{CuK}\alpha$

radiation (40 kV , 100 mA , $\lambda = 1.54056 \text{ \AA}$). Nitrogen adsorption isotherm was measured at 77 K with an Autosorb-iQ adsorption analyzer (Quantachrome). The specific surface areas and pore size distribution (PSD) were calculated according to Brunauer-Emmett-Teller (BET) method and Barrett – Joyner – Halenda (BJH) model, respectively. Total pore volumes were calculated from the amount adsorbed at a relative pressure P/P_0 of 0.994. High resolution transmission electron microscopy (HR-TEM) analyses were carried out with a TecnaiG220S-Twin equipment operating at 200 kV , and coupled with an energy dispersive X-ray spectrometer (EDX). The sample for HR-TEM analysis was prepared by dropping an ethanol droplet of the products on carbon-coated copper grids and drying at room temperature. Thermogravimetric analysis (TGA) data was collected with a Perkin-Elmer TGA 7 thermogravimetric analyzer at a heating rate of $10^\circ\text{C min}^{-1}$ from 25 to 600°C with an air flow of 20 mL min^{-1} .

2.3. Cell assemble and characterization

The working electrode consisted of active material (MC/S composite), conductive agent (carbon black Super P), carboxymethyl cellulose (CMC) as thickener, and water soluble binder styrene-butadiene rubber (SBR) at a ratio of 80:10:5:5 by weight. The mixture was prepared as slurry in water and spread onto Al foils using a common doctor-blade coating method. After drying under vacuum over night, the electrodes were incorporated into CR2430 coin type cells in a glove box filled with Ar gas using lithium metal as the counter electrode, polypropylene microporous membrane as separator and of 1 M bis-(trifluoromethane sulfonimide lithium (LiTFSI, Alfa Corp.) in a mixture solution of dimethoxyethane (DME, aladdin) and 1,3-dioxolane (DOL, aladdin) (1:1, vol.%) as the electrolyte. The batteries were rested for 12 h before testing. The galvanostatic charge-discharge test was conducted at a voltage interval of 1.0 to 3.0 V using a LAND CT-2001A instrument (Wuhan, China). The specific capacity was calculated on the basis of the active sulfur material. Cyclic voltammetry (CV) experiments were conducted using a CHI 660D potentiostat at a scan rate of 0.1 mV s^{-1} . Electrochemical impedance spectra (EIS) of the composites were measured before initial discharge using a Zahner IM6ex electrochemical workstation over a frequency ranges of 10 kHz to 10 mHz.

3. Results and discussion

3.1. Materials characterization

MC was prepared through one step pyrolysis of magnesium citrate material, as illustrated in Scheme 1. The XRD patterns of MC before and after sulfur incorporation are shown in Fig. 1. The sharp diffraction peaks suggested that sulfur existed in a crystalline state, while the broad diffraction peak appeared at about 24° indicated the amorphous characteristic of MC. After encapsulating sulfur into the mesoporous of MC, the sharp diffraction peaks of bulk crystalline sulfur disappeared entirely (MC/S-1, MC/S-2, and MC/S-3) or only a weak sulfur signal (MC/S-4, MC/S-5), further demonstrating that sulfur exists as a highly dispersed state inside the MC framework effectively suppressing the crystal growth of sulfur particles due to the high amount of mesopores. Such a highly dispersed state may also benefit good electric conductivity.

TGA (Fig. 2) analyses were carried out to measure the accurate ratio of carbon/sulfur composites. It was obvious that weight loss starts at about 200°C . At 300°C , the curves showed the fastest weight loss due to the existence of capillary force of mesopores. A steady state was achieved above 400°C due to the fully sublimated of sulfur, which indicates that the mesoporous carbon has a strong

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