



Infiltrating sulfur into a highly porous carbon sphere as cathode material for lithium–sulfur batteries



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ABSTRACT

Sulfur composite material with a highly porous carbon sphere as the conducting container was prepared. The highly porous carbon sphere was easily synthesized with resorcinol–formaldehyde precursor as the carbon source. The morphology of the carbon was observed with field emission scanning electron microscope and transmission electron microscope, which showed a well-defined spherical shape. Brunauer–Emmett–Teller analysis indicated that it possesses a high specific surface area of $1563 \text{ m}^2 \text{ g}^{-1}$ and a total pore volume of $2.66 \text{ cm}^3 \text{ g}^{-1}$ with a bimodal pore size distribution, which allow high sulfur loading and easy transportation of lithium ions. Sulfur carbon composites with varied sulfur contents were prepared by melt–diffusion method and lithium sulfur cells with the sulfur composites showed improved cyclability and long-term cycle life.

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1. Introduction

An increasingly diverse range of applications from microchips to electric vehicles require batteries with high energy density to meet the demands. As the energy density of current lithium ion batteries comes close to its ceiling, lithium–sulfur (Li–S) batteries with a high theoretical capacity of 1675 mAh g^{-1} and an energy density of 2600 Wh kg^{-1} have captured great attentions. Scientists have endeavored to improve the cyclability and life span of Li–S batteries for commercialization. Sulfur is abundant, inexpensive and environmentally friendly, making it one of the most promising cathode materials to power high energy storages [1]. However, several problems such as short life span, poor capacity retention and low rate capability still hinder the practical application of Li–S batteries. Sulfur and its intermediates polysulfides are naturally insulating, resulting in low active material utilization. Moreover, high ordered lithium polysulfides generated during the discharge process can be easily dissolved into the liquid electrolyte and migrated to the lithium anode, causing high self-discharge rate and

safety issues [2]. Several efforts have been made towards addressing these problems, among which confining sulfur into a porous carbon matrix showed great success [3]. The application of diverse-structured porous carbons with large specific surface area and total pore volume is proved to significantly enhance the electric conductivity of sulfur electrode and reduce active material loss. From then on, great achievements have been performed by confining sulfur in various structured porous carbons such as mesoporous carbons particles [4–6], graphene [7], carbon nanotubes [8,9] or conducting polymers [10–12] and oxide additives [13,14]. Enhanced capability and cycle stability have been obtained in Li–S batteries.

A wide range of methods have been applied to synthesize carbons with well-designed shapes and pore systems. For example, CMK was prepared with SBA-15 as the hard template and sucrose as the carbon source [3]; the conventional Stöber method was extended to prepare monodisperse carbon spheres with resorcinol–formaldehyde resin [15]. The use of these uniform porous carbon spheres is expected to increase the packing density of the electrode [16,17].

In this study, a highly porous carbon sphere (HPC) was prepared by a facile one-pot method using resorcinol–formaldehyde precursor as the carbon source. This HPC is characterized to be around 250 nm in size with a high surface area and large pore volume, which allows accommodation of large amounts of sulfur. Different amounts of sulfur were then encapsulated into HPC as the cathode

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material to investigate the electrochemical performance of Li-S cells. This porous carbon sphere significantly improved the distribution of sulfur, electric conductivity of the electrode and capacity retention.

2. Experimental

2.1. Chemicals

Tetraethyl orthosilicate (TEOS, 99.0%), formaldehyde (37 wt.%), hexadecyl trimethyl ammonium bromide (CTAB, 99.0%) and sublimed sulfur (99.5%) were purchased from Sigma-Aldrich. Aqueous ammonia solution ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 25–28 wt.%) and resorcinol (98%) were purchased from Daejung Chemicals & Metals Co., Ltd. Hydrofluoric acid (HF, 48.0–51.0%) was supplied by Avantor™ Performance Materials.

2.2. Synthesis of highly porous carbon sphere (HPC)

HPC was synthesized via a co-sol-gel process using TEOS as the template and resorcinol-formaldehyde (RF) resin as the carbon precursor [6]. 0.4 ml of ammonia solution and 0.3 g of resorcinol were sequentially mixed with 56 ml of ethanol/water solution (8/20, v/v) for 0.5 h. 0.4 g of CTAB was added and then stirred for another 0.5 h. 0.42 ml of formaldehyde and 2 ml of TEOS were added subsequently and stirred overnight. The mixture was heated at 80 °C for 24 h in a sealed and static condition for the polymerization of RF resin. The solid composite was collected by centrifugation and dried at 80 °C. The carbonization was carried out in a tubular furnace at 600 °C for 3 h with a heating rate of 3 °C min^{-1} under N_2 flow. The silica was etched away by immersing in 10 wt.% HF solution for 24 h. The HPC carbon obtained was filtered and rinsed with ethanol and water and then dried at 80 °C for further use.

2.3. Synthesis of sulfur/carbon (S/HPC) composites

The S/HPC composite was synthesized by a melt-diffusion method. Sulfur and HPC were mixed with different weight ratios of 8:2, 7:3 and 6:4 and then heated at 155 °C in a sealed Teflon tube for 24 h. Sulfur content of the S/HPC composites was determined with thermogravimetric analyzer (TGA). S/HPC composites prepared with different ratios of sulfur/carbon mixture gave sulfur contents of 72, 63 and 52 wt.%, which were accordingly designated hereafter as S/HPC-72, S/HPC-63 and S/HPC-52, respectively.

2.4. Characterizations and electrochemical measurements

The morphologies of HPC and S/HPC composites were observed with field emission scanning electron microscope (FE-SEM, Philips XL30S FEG) and transmission electron microscope (TEM, JEM2010 JEOL). The specific surface area and pore volume of the carbon were measured with Brunauer-Emmett-Teller analysis (BET, ASAP 2010) and Barrett-Joyner-Halenda (BJH) method. X-ray diffraction (XRD) patterns of samples were recorded by X-ray diffractometer (XRD, D2 Phaser Bruker AXS). Thermogravimetric analyzer (TGA, Q50 TA Instruments) was used to determine the sulfur content by heating to 500 °C at 10 °C min^{-1} under N_2 flow.

To prepare the S/HPC cathodes, S/HPC composite, Super-P (SP) carbon black and poly(vinylidene fluoride) (PVdF) were mixed at a ratio of 8:1:1 in *N*-methyl-2-pyrrolidone (NMP) and cast on an aluminum current collector. Conventional sulfur cathode was prepared by ball milling elemental sulfur, SP carbon black and PVdF at a ratio of 50:30:20 in NMP for comparison and designated as S/SP-50. The stainless steel (SS) Swagelok® cells were assembled by stacking S/HPC or S/SP-50 cathode, Celgard® 2400 separator and Li anode in an argon-filled glove box. The electrolyte was 1 M bis(trifluoromethane) sulfonimide lithium salt (LiTFSI) in a mixed solvent of 1,3-dioxolane (DOL) and dimethyl ether (DME) at a volume ratio of 1:1. Cyclic voltammetry (CV) study of cells was

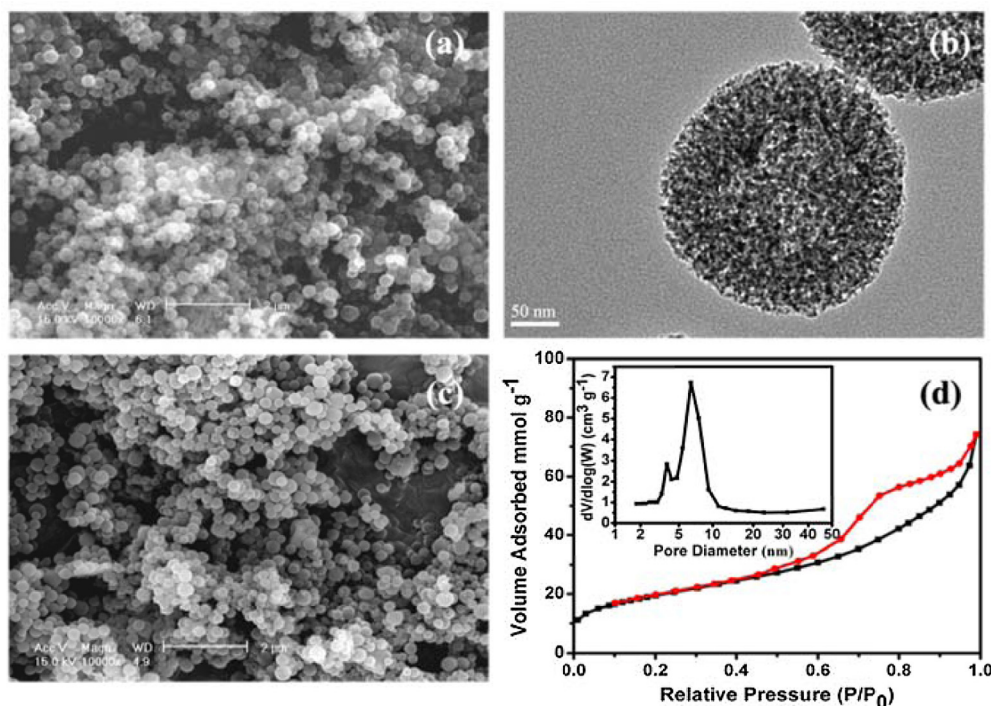


Fig. 1. The morphology of HPC observed by FE-SEM (a) and TEM (b); FE-SEM image of S/HPC composite prepared with a sulfur/HPC mixture at a weight ratio of 6:4 (c); N_2 sorption isotherms of HPC and its pore size distribution (inset) (d).

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