



Mesoporous carbon spheres with tunable porosity prepared by a template-free method for advanced lithium–sulfur batteries

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ABSTRACT

Mesoporous carbon spheres (MCS) with tunable porosity are prepared by a mass-producible spray-drying process using chitosan as carbon precursor with ethanol as porosity tuning agent. By this template-free method, MCSs with different porosity are deduced by manipulating the volume ratio of ethanol in the solvent for chitosan. The resulted MCSs show controllable surface areas, pore volumes and bimodal pore size distribution. They are employed as substrates for the preparation of sulfur/carbon composite cathode. Electrochemical performance of the MCSs with 50 wt% sulfur loading is investigated. One of the S/MCS composite cathodes displays initial discharge capacity of 1163 mAhg⁻¹, excellent rate capability of 510 mAhg⁻¹ at 2 C and good cycling stability of 715 mAhg⁻¹ after 100 cycles at 0.2 C. The sulfur loading content could reach as high as 60%, while it still could deliver a capacity of 642 mAhg⁻¹ after 100 cycles at 0.2 C.

1. Introduction

Lithium-ion batteries have received great attention in recent years because of their potential applications to solve energy supplies shortage and global environment problems, nevertheless the limited energy capacity and low power density of present electrode materials is still not enough to meet the electric vehicle requirements for extended range [1,2]. Therefore, it is essential to explore new cathodes with higher specific capacity to increase the energy density of battery system [3,4]. Based on light-weight elements and multi-electron reactions, sulfur is one of the most promising candidates among all conventional cathode materials for Li secondary cells due to its high theoretical capacity (1675 mAhg⁻¹) [5], which is nearly five times higher than that of existing transition metal oxide and phosphate materials [6,7]. 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 high energy density rechargeable batteries. However, in spite of these advantages, there are several crucial technical problems to tackle [8–10]. First of all, a major hurdle is the electrical insulating nature of sulfur. The second one is the capacity degradation of the sulfur cathode upon cycling due mainly to the shuttle phenomenon. Third, the deposition of insulating Li₂S on

reaction interface during the discharge process increases the resistance of the cell.

To overcome these problems, many methods have been intensively investigated including surface coating [11–13], conductive substrates [14,15], multifunctional binders and novel electrolytes with inorganic additives [16–18]. Among the above strategies, carbon-based materials with controlled morphology and structure, particularly those derived from cheap sustainable sources constitute a rational solution for the preparation of practical carbon-sulfur composite electrodes [19,20]. In comparison with other carbon materials such as graphene [21] and carbon nanotubes [22], porous carbon materials was believed to be an ideal electrode material for lithium-sulfur batteries due to their interconnected porous structure, high specific surface area and pore volume [23–25]. Nowadays, many researchers focus on designing the composite by optimizing the porous structure of carbon. For example, Ye invented a series of uniform porous carbon spheres through a KOH activation process, and they claim that the pore structure of the carbon host can be easily controlled by adjusting the activation concentration of KOH [23], meanwhile, Zhao has reported the fabrication of novel-structured porous carbon microspheres with a controllable multi-modal pore size distribution, and they claimed that they can control the pore size by adding into silica sols with different particle sizes [26]. In most

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cases, researchers mainly concentrate on these two methods, but it always followed with high expenditure or complicated synthesis, which hinders the practical applications of mesoporous carbon in large scale.

Herein, mesoporous carbon spheres with tunable porosity have been prepared by a simple, cost-effective and template-free method, which then were employed to the design and fabrication of sulfur-impregnated porous carbon composite cathode materials for lithium-sulfur battery. In comparison with the traditional sulfur cathode and normal sulfur/carbon composite cathode, the novel S/MCS composite cathode shows several advantages. Firstly, the MCS was prepared through a spray drying process with chitosan as a precursor. The method is relatively simple, flexible and easily scalable for industrialization and the precursor is sustainable biomass. Secondly, the surface area, pore volume and the unique bimodal pore size distribution of the MCSs can be easily tuned by just mixing different volume ratio of ethanol into the suspension, and no pore directing agent or template is needed. Thirdly, an autogenetic pressure technique (APT) at high temperature based on a swagelok structured stainless autoclave was exploited for loading sulfur into the pores of the MCS spheres. By this autogenetic pressure technique, sulfur-impregnated mesoporous carbon spheres with controlled sulfur loading content were obtained efficiently and no extra heating process to remove the excess sulfur is required, avoiding high expenditure or complicated synthesis.

2. Experimental section

2.1. Preparation of S/MCS composites

The high porosity MCSs were prepared through a spray drying process with chitosan as a precursor. In a typical preparation, 4 g chitosan was dissolved in 200 ml acetic acid solution using water/ethanol mixture with different volume ratio (e.g. 10 vol% and 20 vol% ratio of ethanol) as solvent for the solution. The solution of chitosan was stirred for 2 h, and it was then sprayed into the chamber of the spray dryer at 180 °C using hot air as carrier gas, and dried composite samples were simultaneously collected by a connected cyclone separator. Then, the obtained chitosan spheres were firstly cured at 400 °C for 2 h and then was carbonized at 900 °C for 5 h under a high purity nitrogen atmosphere. Three samples, designated as MCS-0, MCS-10 and MCS-20 were prepared with different ethanol/water volume ratios in the mixed solvent for dissolving chitosan, namely 0:100, 10:100 and 20:100. The obtained MCS-0, MCS-10, and MCS-20 spheres were then utilized as matrices for the preparation of S/MCS composite spheres with different sulfur loading contents, e.g. 50 and 60 wt%. The mixture of sulfur and MCS was loaded into a swagelok structured stainless autoclave and cured at 155 °C for 6 h, and then the temperature was increased to 300 °C and kept at this temperature for 5 h to guarantee melted sulfur infiltrate into the pores of the porous carbon spheres. Finally, when the autoclave was cooled to room temperature, S/MCS composite spheres named as S/MCS-0-50, S/MCS-10-50 and S/MCS-20-50 were collected (where -50 stands for the loading content of sulfur in the composite spheres). Similarly, sample of S/MCS-20-60 was prepared by the same process with 60 wt% sulfur content. A proposed formation mechanism of the sulfur-impregnated mesoporous carbon composite spheres is illustrated in Scheme 1.



Scheme 1. Illustration for the formation process of the S/MCS composite spheres.

2.2. Characterization

X-ray diffraction (XRD) patterns were collected on a Rigaku Ultima IV X-ray diffractometer with Cu-K α radiation ($\lambda = 0.15418$ nm) as the X-ray source. The thermo gravimetric analysis (TGA) was performed on a Mettler Toledo TGA-2 thermal gravimetric analyzer under Ar atmosphere with a heating rate of 10 °C min⁻¹. X-ray photoelectron spectroscopy (XPS) data were accumulated on a PHI VersaProbe III (ULVAC-PHI INC.) X-ray photoelectron spectrometer with a monochromatized Al K α standard X-ray source and the binding energies were calibrated by referencing the C1s to 283.8 eV. Nitrogen adsorption/desorption isotherms were measured using a Quantachrome Autosorb-IQ-MP/XR. 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 morphology and structure of the samples were examined by a JEOL JSM-7800F field emission scanning electron microscope (FESEM) and a JEOL JEM-2100plus transmission electron microscope (TEM).

2.3. Electrochemical measurement

The working electrodes were prepared by making a slurry consisting of 80 wt% active material, 10 wt% conductive agent (acetylene black) and 10 wt% polyvinylidene fluoride (PVDF) as binder. The slurry was coated on an aluminum foil. After drying at 55 °C 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 50 μ L of 1 M bis-(trifluoromethane) sulfonamide 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 3 V and 1.5 V. Cyclic voltammetry (CV) measurements were conducted using a two-electrode coin-type cell performed between 1.5 V and 3 V at 0.1 mVs⁻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 100 kHz and 0.01 Hz with amplitude of 5 mV.

3. Results and discussion

Fig. 1(a) shows the XRD patterns of the sublimed sulfur, MCS-20, S/MCS-0-50, S/MCS-10-50, and S/MCS-20-50 samples. The XRD pattern of elemental sulfur exhibits several sharp and intensive peaks throughout the entire diffraction range, indicating a well-defined crystal structure. For the carbon sphere of MCS-20, 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 [27–29]. However, typical crystallized sulfur diffraction peaks in S/MCS-10-50 and S/MCS-20-50 disappear entirely, indicating that most of the sulfur is incorporated into the interior of the pore structure and homogeneously dispersed therein. Differently, for S/MCS-0-50 sample the intensity of crystalline sulfur peaks grows to be detectable in the XRD patterns. It can be proposed that the excessive

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