



Preparation of lamellar carbon matrix for sulfur as cathode material of lithium-sulfur batteries



Xue-Bing Yang, Wen Zhu*, Ke Qin, Hui-Yong Wang

State Key Laboratory of Materials Processing and Die & Mould Technology, School of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan, Hubei 430074, China

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ABSTRACT

Sulfur is a promising cathode material for lithium batteries as it has high theoretical specific capacity and low cost. However, practical electrochemical performance of lithium-sulfur batteries needs to be improved. In this work, a new method is described to prepare carbon matrix for sulfur to improve electrochemical properties of sulfur electrodes. The carbon matrix is prepared by deoxidizing carbon precursor synthesized by carbonizing sucrose with concentrated sulfuric acid. Carbon matrix-sulfur composite has been characterized by scanning electron microscopy, transmission electron microscopy and Fourier transform infrared. Results indicate that carbon matrix-sulfur composite is composed of lamellas. The lamella contains a layer of carbon coating on the outside and chemical bonds of C-S. The formation of C-S bonds is promoted by deoxidizing carbon precursor. The carbon matrix-sulfur electrode exhibits improved discharge properties, which results from the appropriate structure. Carbon coating and C-S bonds confine sulfur and maintain contact between sulfur species and conductive carbon matrix.

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1. Introduction

Development of mobile multifunctional electric devices requires better performance of lithium batteries such as higher specific capacity. Used as cathode materials for commercial rechargeable lithium batteries, transition-metal oxides and phosphate have relatively low theoretical specific capacity [1,2]. As a cathode material for lithium batteries, sulfur has high theoretical specific capacity of 1672 mAh g⁻¹. And theoretical energy density of lithium-sulfur batteries reaches 2500 Wh Kg⁻¹ [3,4]. Moreover, sulfur is abundant, inexpensive and nontoxic. Thus, sulfur is a promising cathode material for secondary lithium batteries [5–7].

However, practical specific capacity of lithium-sulfur batteries is not high and cycle life is not long. There are several reasons for the low utilization rate of sulfur. The first reason is dissolution of lithium polysulfide (Li₂S_n (2 < n ≤ 8)) into organic liquid electrolyte, which leads to loss of sulfur species [8–11]. The second reason is agglomeration of insulated sulfur species. As products of discharge reactions, Li₂S₂ and Li₂S are nonconductive and insoluble in organic liquid electrolyte. They precipitate onto surface of sulfur electrodes and agglomerate [12–14]. The third reason is corrosion of lithium electrodes. The dissolved Li₂S_n passes through separator and

diffuses to the surface of lithium anodes. It reacts with lithium, which results in corrosion of lithium anodes [15].

Different solutions have been reported to improve the performance of lithium-sulfur batteries. The first kind of methods is to confine sulfur species to cathodes through adsorption. For example, porous carbon with different pore size is used to adsorb sulfur species to its surface [16–18]. Electrochemical tests have indicated that porous carbon increases the utilization rate of sulfur. The second type of means is to restrict sulfur species through envelopment. Conductive substances are utilized to wrap sulfur or sulfur-carbon composite. For instance, carbon materials such as carbon particles [19] and graphene [20–22] are used to envelop sulfur or sulfur-carbon composite to hinder the dissolution of polysulfide. Conductive polymers such as polypyrrole [23,24] and polyaniline [25] are utilized to wrap sulfur or sulfur-carbon composite to hinder the dissolution of sulfur species. Besides, nafion is used to envelop the entire sulfur electrode [26]. Results have shown that the method of wrapping is effective in improving electrochemical performance of lithium-sulfur batteries. The third kind of methods is to confine sulfur species through chemical bonds. Conductive substances are utilized to heat with sulfur to form chemical bonds. For example, carbyne is used to heat with sulfur to form C-S bonds. C-S bonds hinder the dissolution of sulfur species. The carbon-sulfur composite with C-S bonds exhibits good cycle stability [27].

In this work, envelopment and chemical bonding are combined to increase the utilization rate of sulfur. Lamellar carbon matrix has

* Corresponding author.

E-mail address: wennar@mail.hust.edu.cn (W. Zhu).

been prepared to wrap sulfur and form C-S bonds with sulfur. The structure is promising in improving the electrochemical properties of lithium-sulfur batteries.

2. Experimental

2.1. Synthesis of carbon-sulfur composite and characterization

The synthesis process of carbon-sulfur composite is shown in Fig. 1. Firstly, carbon precursor was prepared by carbonizing 0.8 g sucrose ($C_{12}H_{22}O_{11}$) with 5 mL concentrated sulfuric acid (H_2SO_4 , 98 wt %). Then, 0.3 mol dm^{-3} sodium thiosulfate ($Na_2S_2O_3$) solution was dropped into the carbon precursor sol to react with H_2SO_4 to synthesize sulfur. After filtration, the product of carbon precursor-sulfur was washed and then dispersed in solvent. Subsequently, sodium hydroxide (NaOH) solution and hydrazine hydrate ($N_2H_4 \cdot H_2O$) were dropped into the carbon precursor-sulfur sol to deoxidize carbon precursor to carbon matrix. Afterwards, the carbon matrix-sulfur sol was filtered. After washing for several times, the carbon matrix-sulfur composite was dried at 50°C for 10 h. Carbon matrix was obtained through no addition of $Na_2S_2O_3$ solution to the carbon precursor sol.

Mixture of acetylene black and sulfur was prepared for comparison. At first, 0.35 g acetylene black and 0.65 g sulfur were mixed and ground for 2 h. Subsequently, the mixture was heated at 155°C for 4 h in the atmosphere of argon.

Morphology, element components and structure of materials were characterized by field emission scanning electron microscopy (FE-SEM, Sirion 200), energy dispersive X-ray spectroscopy (EDS, GENESIS) and X-ray diffraction (XRD, X Pert PRO). Microstructure of synthesized materials was analyzed through field emission transmission electron microscopy (FE-TEM, Tecnai G2 F30). Chemical bonds of materials were characterized by Fourier transform infrared spectroscopy (FT-IR, VERTEX 70) and Raman spectroscopy (LabRAM HR800) with laser wavelength of 532 nm. Content of sulfur in composite was obtained through thermo-gravimetric analysis (TG, Pyris1 TGA). Samples were tested in atmosphere of nitrogen and the heating rate was $10^\circ\text{C min}^{-1}$.

2.2. Assembly of batteries and tests of electrochemical properties

The first step was preparation of sulfur electrodes. Carbon-sulfur composite was mixed with acetylene black and polyvinylidene fluoride (PVDF) in mass ratio of 70:20:10 with N-methyl-pyrrolidone (NMP) as dispersant. The mixed slurry was coated onto aluminum foil ($20 \mu\text{m}$ in thickness) and was then dried at 60°C for 24 h. Subsequently, the prepared electrode was punched into circular disks. Mass density of materials for circular electrodes lay between 1.8 mg cm^{-2} and 2.3 mg cm^{-2} . The sulfur electrodes were used as cathodes of lithium-sulfur batteries.

The second step was assembly of batteries. Electrolyte consisted of lithium bis(trifluoromethanesulfonyl)imide (1 mol dm^{-3}) as solute and mixture of 1, 3-dioxolane (DOL) and 1, 2-dimethoxyethane (DME) with volume ratio of 1:1 as solvent. Lithium nitrate ($LiNO_3$, 0.1 mol dm^{-3}) was used as an additive in the electrolyte. Adopted anodes were lithium foils with thickness of $100 \mu\text{m}$. Separator between cathode and anode was microporous polypropylene film (Celgard 2300). Coin cells (CR2032) were assembled in a vacuum glove box (Lab2000) filled with purified argon.

The third step was tests of assembled lithium-sulfur batteries. Cyclic voltammetry tests were performed through electrochemical workstation with scanning rate of 0.1 mV s^{-1} . Cyclic discharge and charge capacity were tested by LAND CT2001A battery test system in galvanostatic mode. Current rates and specific capacity were calculated according to the mass of sulfur in sulfur electrodes. Alternating current impedance tests were carried out through electrochemical workstation with voltage amplitude of 5 mV and frequency between 0.1 Hz and 100 KHz.

3. Results and Discussion

X-ray diffraction patterns of carbon precursor, carbon matrix and carbon matrix-sulfur composite are shown in Fig. 2. In Fig. 2 (a), acetylene black exhibits obvious diffraction peak at 24.95° . The peak corresponds to the crystal plane of (002) [28]. The sharp peak indicates similar distance between graphitic layers. In comparison with acetylene black, both carbon precursor and carbon matrix exhibit wider diffraction peaks and lower diffraction angles. Wider

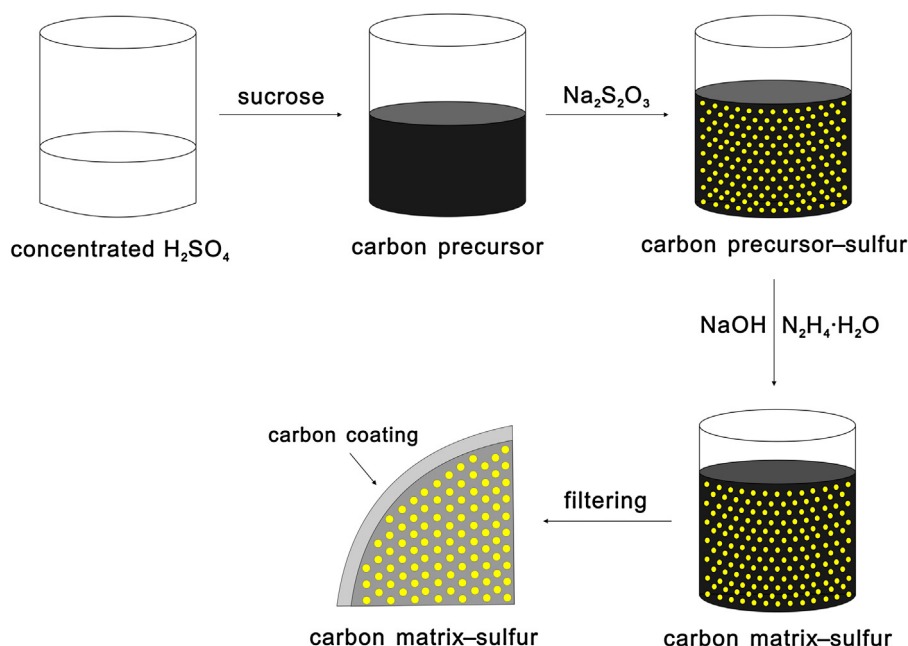


Fig. 1. Schematic illustration of the synthesis process of carbon-sulfur composite.

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