



Sulfur impregnated in tunable porous N-doped carbon as sulfur cathode: effect of pore size distribution \diamond



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ABSTRACT

A novel porous N-doped carbon microsphere (polymer-dopamine derived carbon, PDA-C) with high specific surface area was synthesized as sulfur host for high performance of lithium-sulfur batteries. We used KOH to adjust the pore size and surface area of the PDA-C materials, and then impregnated sulfur into the PDA-C samples by vapor-melting diffusion method. Effects of pore size of the PDA-C samples on the electrochemical performance of the PDA-C@sulfur cathodes were systematically investigated. Raman spectra indicated an enhanced trend of the degree of graphitization of the PDA-C samples with increasing calcination temperature. The surface area of the PDA-C samples increases with amount of the KOH in the pore-creating process. The graphitized porous N-doped carbon provides the high electronic conductive network. Meanwhile, the PDA-C with high surface area and uniform micropores ensures a high interaction toward sulfur as well as the high dispersion of nanoscale sulfur layer on it. The microporous PDA-C@S cathode material exhibits the excellent high rate discharge capability (636 mA h g^{-1} at 2.0 C) and good low/high-rate cycling stability (893 mA h g^{-1} (0.5 C) and 608 mA h g^{-1} (2.0 C) over 100 and 300 cycles). Cyclic voltammogram curves and electrochemical impedance plots show that both the impedance and polarization of the cells increase with decreasing pore size.

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1. Introduction

Lithium-ion rechargeable batteries are developed as portable power sources with increasing demand for electric vehicles [1]. However, the specific energy of existing lithium ion batteries is still insufficient for many applications because of the relatively low charge capacity of cathodes [2], such as LiCoO_2 , LiMn_2O_4 , and LiFePO_4 . Among cathode materials for secondary lithium batteries, sulfur is a lightweight and abundant material. It has the highest theoretical capacity of 1675 mA h g^{-1} against lithium, which is at least 7–8 times greater than that of commercially used transition-metal phosphates and oxides [3]. Recently, lithium sulfur batteries have been studied as one of the most promising systems for the next generation high-energy rechargeable lithium batteries. However, the fast-capacity fading from polysulfide dissolution

into the electrolyte and rate capability from the insulation of sulfur ($5 \times 10^{-30} \text{ S cm}^{-1}$) remains as crucial challenges for the practical applications of the self-sustaining Li-S batteries [4,5].

Various efforts have mainly focused on the new design of conductive sulfur host materials to retain polysulfide at the cathode side. Lu and co-workers [6] reported a high-performance graphene-sulfur composite cathode with a capacity of 800 mA h g^{-1} over 100 cycles. Kim and co-workers [7] synthesized a mesoporous graphene- SiO_2 composite with a initial discharge capacities of 970 and 820 mA h g^{-1} at 0.2 C and 0.5 C, respectively.

Sulfur infiltrated mesoporous host or coated with conductive shell can delay the diffusion of polysulfide out of the cathode structure to a certain extent. However, the weak interaction of sulfur/polysulfide with porous host can still lead to a gradual loss of active sulfur in the cathode during cycling. In order to further enhance the interactions between sulfur and carbon, some research on pore size and functional groups modification have been proposed to design novel sulfur host materials. Ji and co-workers [8] reported a chemical approach to immobilize sulfur and lithium polysulfides via the reactive functional groups (e.g. epoxy and hydroxyl groups) on graphene oxide, which shows the reversible capacity of about $950\text{--}1400 \text{ mA h g}^{-1}$ at 0.1 C over

\diamond Supplementary Materials available: Structure, sulfur content and electrochemical characterization of the PDA-C@S composite results. Temperature programmed desorption (TPD) spectra of sulfur on the PDA-CM@S.

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50 cycles. Song and co-workers [9] used a mesoporous N-doped carbon and Moreno and co-workers [10] used activated carbon as the sulfur hosts to enhance affinity with sulfur and sulfide species. Thus, it can be seen pore size of the host is a critical factor to the electrochemical properties of the sulfur cathodes, especially in their cycling ability. Despite this progress, there are still few reports on pore size effects on electrochemical properties of sulfur cathode systematically.

Recently, a novel N-doped carbon with rich C sp^2 was reported by using bio-molecule dopamine as the carbon resource [11]. In contrast to other porous carbon materials, the containing rich sp^2 C atoms can enhance the electro-conductivity for electrochemical reaction [12]. Furthermore, the pyridinic N can promote adsorption interaction towards sulfur and polysulfide species [13]. In this work, the poly-dopamine derived carbon materials (PDA-C) were synthesized and chosen as carbon hosts for sulfur composite cathodes. We used KOH activator to adjust pore size of the PDA-C materials, and then infiltrated sulfur element by vapor-melting method to obtain sulfur/carbon composite. Effects of PDA-C pore size distribution on the electrochemical performance of Li-S batteries (such as capacity cycling, rate performance as well as electronic conductivity of the whole composite cathode materials) were systematically investigated.

2. Experimental

2.1. Synthesis of polydopamine spheres (PDA)

PDA carbon spheres were prepared by using the previously reported method [11,13]. In a typical synthesis of PDA spheres with a size of about 380 nm, ammonia aqueous solution (NH_4OH , 0.75 mL, 28–30%) was mixed with ethanol (40 mL) and deionized water (90 mL) under mild stirring at room temperature (see Fig. 1, Step I). Then, 0.5 g dopamine hydrochloride (Sigma Aldrich, > 98%) was dissolved in 10 mL deionized water. This solution was injected into the ammonia solution previously made to initiate the polymerization reaction. The color of the solution turned to pale brown immediately and changed to dark brown gradually. The reaction was allowed to proceed for 30 h. The PDA nano-spheres were obtained after filtration and washing by deionized water for 4–5 times followed by drying in vacuum oven at 333 K.

2.2. Preparation of porous PDA-based carbon (PDA-C)

The obtained PDA spheres were firstly calcined [11] at 1073 K in Ar atmosphere. The temperature was raised from room temperature to

1073 K at a rate of 5 K min^{-1} and kept at 1073 K for 1.0 h (see Fig. 1, Step II). After the PDA spheres were cooled down to room temperature, they were mixed with solid KOH at a mass ratio of 1:(4–6). Then, the mixture was heated to 1043 K at Ar atmosphere at a rate of 5 K min^{-1} and kept at 1043 K for 1.0 h. The obtained mixture was taken out after it was cooled down to room temperature, and then washed with HCl (1 M) solution to remove the unreacted KOH until the pH = 7. Finally, the porous PDA-C was obtained after drying in vacuum oven at 333 K for 12 h (see Fig. 1, Step III). PDA-C with different pore sizes and specific surface area can be achieved by adjusting the mass ratio of PDA spheres to KOH. In this work, three PDA-C samples with small-, medium- and large-micropores (labeled as PDA-CS, PDA-CM, and PDA-CL) were obtained with a PDA:KOH mass ratio of 1:4, 1:5 and 1:6, respectively.

2.3. Preparation of PDA-C@S composite materials

The PDA-C@S (PDA-CS@S, PDA-CM@S and PDA-CL@S) composites were prepared by using the vapor-melt diffusion method as we previously reported [14]. And the weight ratio of sulfur to the PDA-C was 1:2. (see Fig. 1, Step IV). The prepared PDA-C@S composites were then vaporized by heating at 473 K for 30 min [8] to vaporize the sulfur deposited on the outside surface of the composite.

2.4. PDA-C/sulfur composites characterization

The structures and morphologies of the PDA-C and PDA-C@S were analyzed by field emission scanning electron microscopy (SEM, JEOL 6300F scanning electron microscope), powder X-ray diffraction (XRD, Bruker D8 ADVANCE powder diffraction using Cu $K\alpha$ radiation at 40 kV and 40 mA at a step of 0.02). BET and pore size of the precursor PDA spheres and the porous PDA-C materials were estimated from the N_2 adsorption/desorption isotherms at 77 K using a Micromeritics ASAP 2020. The structure of the samples was tested by Raman spectrometer (Jobin-Yvon Lab RAM HR-800, Horiba). The thermal stability of PDA-C and the sulfur content in the PDA-C@S were measured by a thermogravimetric analyzer (TGA-Q50, TA) performed at a scan rate of 5.0 K min^{-1} from room temperature to 873 K with a N_2 flow rate of 30 mL min^{-1} .

2.5. Temperature programmed desorption of sulfur on the PDA-C samples

Temperature programmed desorption (TPD) for the PDA-C/sulfur composites were carried out on the thermogravimetric

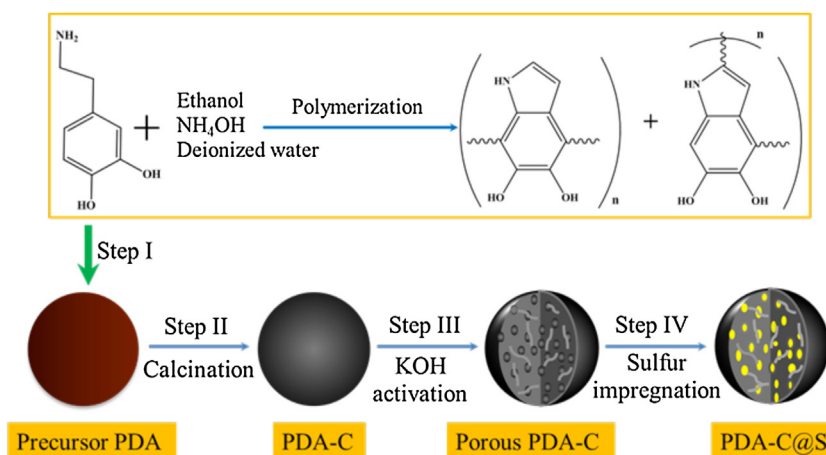


Fig. 1. Synthesis procedure of the PDA-C@S composites.

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