



Excellent Performance of Lithium-Sulfur batteries with Carbonized Porous Aromatic Framework Nanobeads as Support



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ABSTRACT

Carbonized porous aromatic framework (CPAF) nanobeads with 75 wt% S (SCPAF) were synthesized by a simple method. The surface areas of CPAF and SCPAF were $679.8 \text{ m}^2 \cdot \text{g}^{-1}$ and $2.0 \text{ m}^2 \cdot \text{g}^{-1}$ respectively, and the predominant micropores both centered at 0.46 nm. The spherical morphology guaranteed high tap density of Li-S batteries. After S loading, the SCPAF nanobeads exhibited excellent electrochemical performances. It showed high initial capacity of $1397.3 \text{ mAh} \cdot \text{g}^{-1}$ at 0.2C, which is 83.4% of the theoretical value of sulfur. And at 0.5C, it shows 0.074% decay rate per cycle over 1000 cycles. The good rate capability and long-term cycling stability indicated CPAF nanobeads composite is a promising sulfur support for Li-S batteries.

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1. Introduction

The ever-growing energy demands and the serious environmental problems induced by the excessive consumption of fossil energy have stimulated the pursuit of new energy storage systems to fit the requirements of electric vehicles as well as portable electronic appliances [1,2]. Although the conventional lithium-ion battery continues to progress and has achieved an energy density up to $200 \text{ Wh} \cdot \text{kg}^{-1}$ [3–5], this value is still far from the application requirements. Due to the eye-catching features of high theoretical capacity ($1675 \text{ mAh} \cdot \text{g}^{-1}$) and energy density ($2600 \text{ Wh} \cdot \text{kg}^{-1}$), low cost, natural abundance and environmental compatibility, lithium sulfur (Li-S) battery has been intensively revisited in the past decades and regarded as one of the most promising candidates for next generation electrochemical power sources [6–8]. However, the intrinsic disadvantages, such as the poor conductivity of elemental sulfur and discharge products, large volumetric change during lithiation and delithiation, as well as the shuttle effect that

is aroused by the intermediates of soluble polysulfides, direct to poor cycling stability and limit the practical application of Li-S batteries. Various strategies have been developed to improve the properties of Li-S battery, including composite cathodes [9–11], new electrolytes [12], lithium metal protection strategies [13], and modified separators [14]. However, only limited success has been achieved. Because the confinement effect has been confirmed more important for Li-S batteries, many efforts have been exerted on designing novel conductive nanostructured host materials to improve the electrochemical performances of sulfur cathodes. These conductive nanostructured host materials, including carbonaceous materials [15–20], conductive polymers [9,21] and metal oxides [11], graphene coated hybrid structures [22], afford numerous micro- and/or mesopores to confine highly dispersive sulfur particulates in the holes to improve the conductivity and alleviate the volumetric changes. Porous carbonaceous materials are particularly attractive due to their features of structural stability, excellent conductivity and inherently large surface area [23,24]. By using nanocarbon materials with controlled morphologies as the support [24–26], the encapsulation of sulfur in the pores inhibits the outflowing of the intermediate polysulfides into the electrolyte as well as the parasitic reactions with Li anodes. Various nanocarbon matrixes have been explored for sulfur storage, such as porous carbon [27–31], graphene/graphene oxide [19,32,33], and carbon nanotubes and nanofibers [18,34,35], with

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improved Li-S battery performances in terms of rate capability and cycling stability. However, the fabrication processes of the documented carbon supports, such as template method [20,25,36], chemical activation process [30,31] and freeze-drying [22,33], generally require expensive, stern and complicated synthetic conditions. In addition, these strategies usually have poor reproducibility. It is a paramount challenge to develop a simple and facile method to prepare porous carbon for high performance Li-S batteries.

Porous aromatic frameworks (PAFs) are a novel family of designable three-dimensional polymers with high surface areas, tuneable pore sizes and large internal volumes that are fabricated by linking phenyl-based monomers through covalent bonds to generate rigid diamond-like networks [37–39]. These features have attracted increasing interests for applications in gas separation and storage [39–43]. Otherwise, the phenyl rich structures supply plenty of conjugative benzyl groups that readily transform into conductive carbonaceous materials. Controlled heat treatments also possibly inherit the microporous features of the original PAFs. Ben et al. [44] proved that after direct carbonization of an ultrahigh surface area porous aromatic framework (PAF-1), the obtained microporous carbon possess excellent physicochemical stability, high surface area and narrow micropore size distribution, and show excellent carbon dioxide selectivity adsorption. The PAF-derived porous carbons show a lot of advantages. For example, their high surface area provide the possibility of formation of an electrostatic charge-separation layer, inherent optimized pore size facilitate ion migration, abundant micropores can absorb and accommodate active materials, and a highly ordered structure enables the formation of conductive paths. All these characteristics suggest that PAF-derived porous carbon is a class of promising electrochemical energy storage and conversion materials. Xiang et al. [45] use porous aromatic framework (PAF) as precursor to produce nitrogen-doped 3D carbon materials. N-PAF-Carbon based capacitor device is only 0.96 V equivalent series resistance low diffusive resistivity of the electrolyte ions within the pores and N-PAF-Carbon possesses not only large capacitance (385 F g^{-1}) but also excellent performance stability without any loss in capacitance after 9000 charge-discharge cycles. Furthermore, stronger

interactions between the carbonized PAFs are desirable because all-carbon-scaffold networks can be expected to create strong polarity on the frameworks' surface [46], which imparts the networks with a strong affinity toward polar polysulfide.

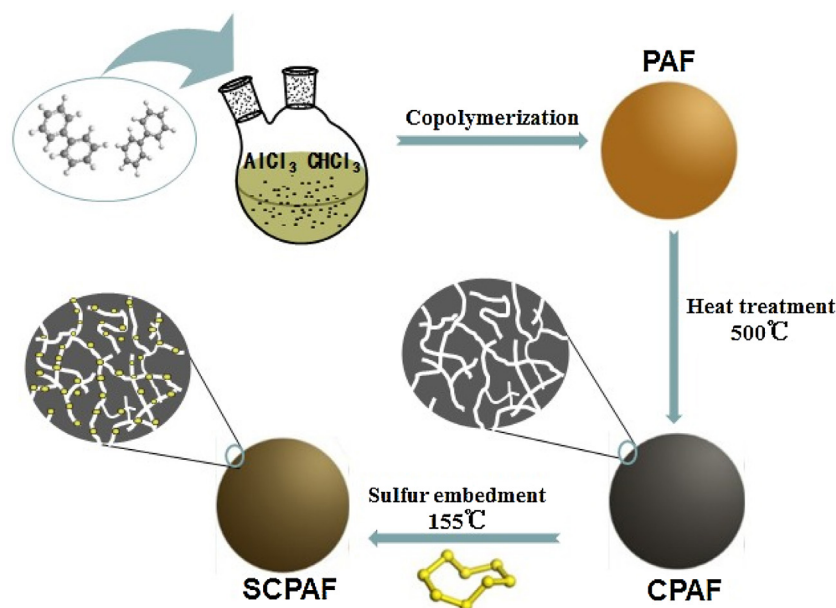
On the basis of these previous studies, we propose that PAF-derived porous carbons are good candidates for the sulfur support that will enhance the Li-S battery performances. Also, organic synthetic route is easily scale-up and guaranties the reproducibility. With this viewpoint, herein, microporous carbon materials are fabricated from porous aromatic frameworks. The modified synthetic procedure affords a facile, up-scalable, low cost and low temperature route to fabricate stable porous carbon networks with high surface areas and interconnected pore architectures. The carbon-sulfur composites with high sulfur loading (75 wt.%) deliver a high specific capacity of $1211 \text{ mAh}\cdot\text{g}^{-1}$ at the first cycle and exhibit excellent long-term cycling stability over 1000 cycles with a low average decay rate of 0.074% per cycle at 0.5C and improved rate performances.

2. Experimental Section

2.1. Materials Fabrication

The crude PAF powders were synthesized according to a recent reference [42] with simplified procedures in a nitrogen atmosphere. Scheme 1 illustrates the synthesis procedure of the CPAF-S composite. Firstly, 2.5 g anhydrous aluminium chloride and 40 mL dried chloroform were added into a 250 mL round flask under vigorous stirring. After the mixtures were heated at 100°C for 2 h, 1.0 g diphenyl in 30 mL CHCl_3 was added into the system. The mixtures were stirred at 100°C for 20 h. After cooled to room temperature, the crude product was obtained by filtration, washed with 1 M hydrochloric acid, ethanol, and water to remove the unreacted monomers and catalyst residues, and dried at 100°C in a vacuum oven for 8 h. Afterward, the crude PAF powders were carbonized at 500°C with a heating rate of $5^\circ\text{C}\cdot\text{min}^{-1}$ for 5 h under an argon flow. The carbonized products were denoted as CPAF.

The carbon sulfur composites were fabricated via a melt infiltration method. Firstly, mixtures of 0.1 g CPAF and 0.3 g sulfur



Scheme 1. Schematic of Synthetic Procedure for Sulfur-carbonized porous aromatic framework (SCPAF) composites.

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