



High surface area porous polymer frameworks: Potential host material for lithium–sulfur batteries



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ABSTRACT

Lithium–sulfur battery is one of the most promising energy storage systems for its high specific capacity. However, commercial development of lithium–sulfur batteries is severely hindered by the cathode host materials. To tackle this issue, we synthesized a new host material, high surface area, three-dimensional (3D) diamond-cage porous polymer frameworks PPN-13, to construct sulfur electrode by impregnating sulfur into its nano-pores. The PPN-13-S cathode delivers a specific discharge capacity up to 606.4 mA h/g over 100 cycles at 0.1 C with a high coulombic efficiency. It demonstrates that the 3D porous structure PPN-13 as host material shows the high performance and a remarkable positive effect on the capacity retention as cathode materials in lithium–sulfur batteries. Due to the unique features of the material, our research provides a new type of materials for tailoring cathode materials in lithium–sulfur batteries.

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1. Introduction

Lithium–sulfur batteries have attracted considerable attention from both the academic and industrial communities for their potential capability of meeting practical applications in new electrical energy storage [1]. Lithium–sulfur batteries have many conspicuous advantages, such as a high theoretical capacity of 1675 mA h/g, low cost, natural abundance and environmental friendliness, which making lithium–sulfur batteries become one of the most promising next-generation batteries [2]. Despite the prospect of lithium–sulfur batteries, a number of challenges still exist that prevents it from conquering the marketplace. A few scientific hurdles remain to be cleared, including the large volume expansion of S cathode, dissolution of intermediate lithium polysulfides (Li_2S_χ , $4 \leq \chi \leq 8$) in the electrolyte, and low ionic/electronic conductivity of both S and Li_2S [3,4].

In order to address the problems, various materials have been studied as matrix, such as porous carbons [5–7], graphene [8–10],

carbon nanofiber [11,12], hollow carbon spheres [13], conducting polymers [14,15], metal oxides [16,17], metal-organic frameworks (MOF) [18,19], and porous aromatic frameworks (PAF) [20,21], which have been developed as sulfur container. For example, Nazar et al. pioneered the concept of using a highly ordered CMK-3 to constrain S within its channels, which showed reversible capacity of over 1000 mA h/g at 0.1 C rate for 20 cycles [7]. Xiao et al. demonstrates that a novel Ni-based metal organic framework can remarkably immobilize polysulfides interactions at molecular level and improve the cycling stability [19]. Tarascon et al. confirmed the confinement effect of a porous material is more important than its conductivity as host material for lithium–sulfur [22]. The aforementioned works inspired us to explore the optimal host material for sulfur impregnation which should be lightweight, vast permanent nano-pores and with high surface area.

In the present work, we report a novel host material PPN-13 with high surface area and vast nano-pores for sulfur impregnation in lithium–sulfur battery. The host material PPN-13 exist vast nano-porous 3D diamond-cage structure [23], in which the abundant nano-pores can provide a large number of accessible voids for sulfur impregnating and thus considerably suppress the diffusive loss of soluble polysulfide intermediates. Despite its low electric conductivities, however, it was certified by Tarascon et al. that a

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suitable porous is more important than its conductivity for lithium–sulfur batteries [22]. In addition, PPN-13-S composite shows excellent chemical and thermal stabilities, also exhibits high capacity and excellent cycling stability in the lithium–sulfur battery. Hence, PPN-13 seems to be a potential host for sulfur in Li–S batteries.

2. Experimental

2.1. Preparation of PPN-13-S composite

PPN-13 was synthesized according to our previous papers [23]. PPN-13 powder and sublimed sulfur was mixed at weight ratio of (PPN-13/S) 2:3 and then grounded in a mortar, followed by heating at 155 °C for 15 h. At this temperature, the melt sulfur can easily diffuse into the pores of PPN-13. After cooling down, the PPN-13-S composite was obtained.

2.2. Materials characterization

Materials morphology was characterized by field-emission scanning electron microscopy (SEM, JSM-6700F) and field-emission transmission electron microscopy (TEM, JEM-2010). X-ray diffraction (XRD) was performed on a MiniFlexII diffractometer with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). Thermo-gravimetric (TG, STA449C) measurements were applied to characterize the content of the sulfur. N₂ sorption isotherms at 77 K were measured using a Micrometrics ASAP 2020-M surface area and pore size analyzer.

2.3. Electrochemical measurement

The sulfur cathode was prepared by mixing 40wt. % PPN-13-S, 40wt. % conductivity agent (BP2000) and 20wt. % PTFE (poly tetrafluoroethylene) into a paste and roll-pressing the paste into a film (ca. 0.4 mm), finally, pressing the electrode film on the surface of the aluminum foil. Then, the film was dried at 60 °C for 24 h before cut. All of the electrochemical tests for the sulfur cathode were carried out by using 2025 type coin cells, which were assembled in an argon filled glove box using lithium foil as the anode. The electrolyte used in this study was 1 M lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) dissolved in 1,3-dioxolane and 1,2-dimethoxyethane (DOL/DME = 1:1, V:V) containing LiNO₃ (1 wt.%) [24,25]. We used 150 μL of the electrolyte to assemble each cell.

3. Results and discussion

PPN-13 is a porous polymer framework was synthesized from 3, 3', 5, 5'-tetraethynyl-2, 2',4, 4',6, 6'-hexamethylbiphenyl through highly efficient eglinton homocoupling [23]. The PPN-13-S composite was prepared by melt-diffusion strategy. As measured by nitrogen-absorption isotherms (Fig. 1), PPN-13 shows an exceptionally high BET surface area of 3420 m²/g with a total pore volume of 2.07 cm³/g and a pore size of 1.17 nm. As the pore size of PPN-13 is 1.6 times of S₈ (~0.7 nm), the aggregation of S₈ can be restricted in the channel. The nanoscaled pores of PPN-13 favors the intimate contact between sulfur and PPN-13. This characteristic is important for the high capacity performance of the sulfur cathode.

Fig. 1c shows the XRD patterns of elemental sulfur, PPN-13 and PPN-13-S composite. The powder X-ray diffraction (XRD) pattern of PPN-13 displays a broad peak at $2\theta = \sim 25^\circ$, which clearly demonstrates that the PPN-13 is an amorphous structure material. The sulfur shows very sharp diffraction peaks, indicating that it is in a crystalline state. After loading of sulfur into the micropores,

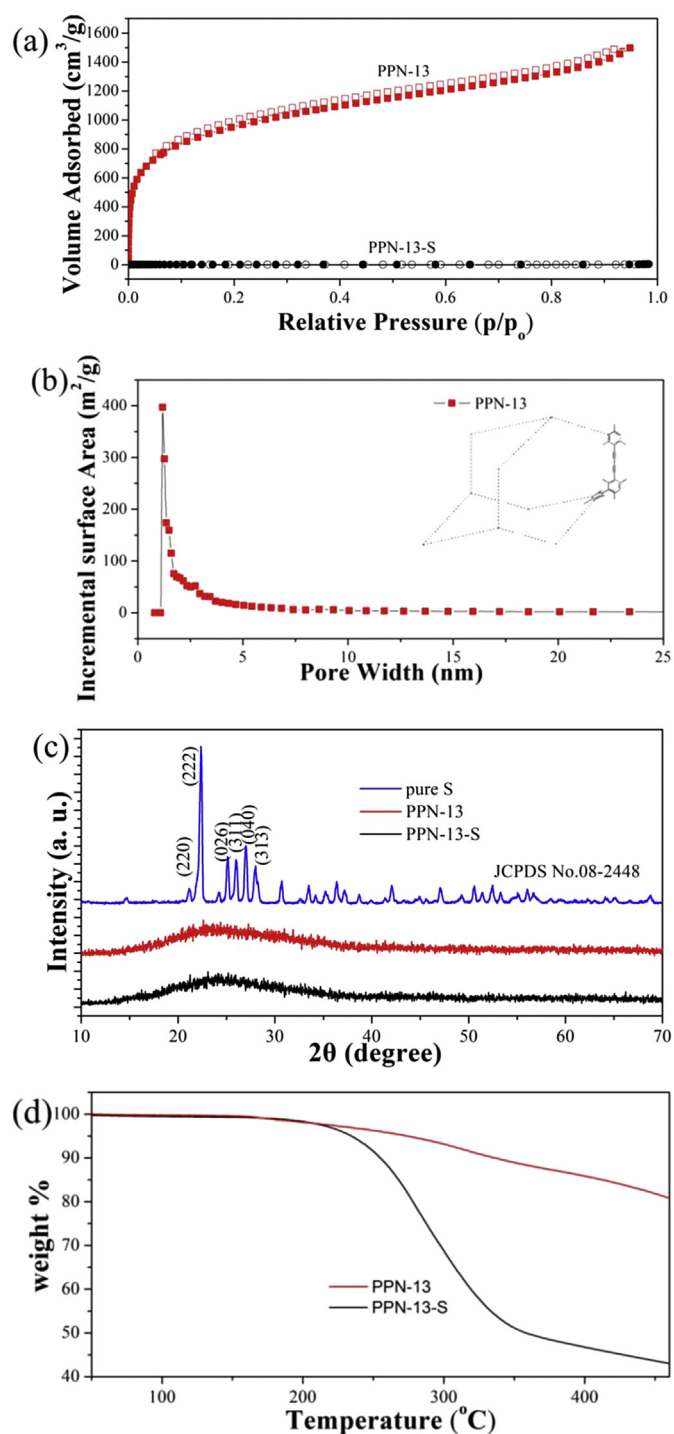


Fig. 1. (a) Nitrogen sorption isotherms; (b) the pore size distribution of PPN-13; (c) Powder X-ray diffraction patterns of S, PPN-13 and PPN-13-S composite; (d) TGA curves of PPN-13 and PPN-13-S composite recorded in N₂ atmosphere.

however, the sharp peaks corresponding to crystalline sulfur completely disappeared in PPN-13-S. Which indicates the sulfur is highly dispersed inside the PPN-13 at the nanoscale and sub-nanoscale level. Additionally, a sharp decrease in the specific surface area of PPN-13-S from 3420 m²/g to 15.74 m²/g, these data further confirmed that the sulfur has successfully diffused into the pores of PPN-13. Also this indicated that the pores are almost completely occupied by sulfur. Furthermore, thermal

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