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A Li$^+$-conductive Porous Carbon/Polyacrylonitrile/Sulfur Composite for Li-S Batteries

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In this paper, we proposed a new Li$^+$- conductive porous carbon for polyacrylonitrile/sulfur (PAN/S) electrode to solve the problem of intermediates dissolution in Li-S batteries during the reaction process. The highly dispersed Li$^+$-conductive carbon (PANC@BP) was prepared by coating the high specific surface BP2000 with 10% polyacrylonitrile pyrolysis carbon. A composite sulfur electrode with a solid-solid reaction mechanism was constructed by dispersing PANC@BP into PAN/S composite. Electrochemical test results showed that the prepared PANC@BP had a realizable capacity of 50 mAh g^{-1} after 150 cycles with a voltage interval of 1.0-3.0 V at a current density of 100 mA g^{-1}. Based on the total mass of the composite material, the initial reversible specific capacity of the PANC@BP/PAN/S composite electrode was 745 mAh g^{-1}, maintained 701 mAh g^{-1} after 80 cycles, indicating an excellent cycling stability and a high reversible specific capacity. With oxidized β-cyclodextrin as binder and copper foil as the collecting conductor, the cycling performance of PANC@BP/PAN/S composite electrode had been significantly improved. The discharge specific capacity maintained 661 mAh g^{-1} after 300 cycles. Compared with discharge specific capacity of 948 mAh g^{-1} in the first cycle, electrode capacity retention was 72.0%, and compared with the reversible discharge specific capacity in the second cycle, the retention was 95.1%.

Keywords: Li$^+$-conductive carbon, Solid-solid reaction mechanism, polyacrylonitrile/sulfur electrode, Electrical properties

1. INTRODUCTION

The ever-increasing demand for electric energy storage, ranging from portable electronics to electric vehicles and to renewable power stations, stimulates the development of improved rechargeable lithium batteries with substantially enhanced energy density and greatly reduced cost1-3] 1. In this technology development, lithium-sulfur batteries (Li-S) are revisited as a promising candidate for large scale electric storage, because of its high theoretical energy density of 2600 Wh Kg^{-1} and particularly the natural abundance and low toxicity of sulfur[4]. Despite a great progress has been achieved, commercial development of Li-S batteries is still hindered by the insufficient cycle stability and low utilization of the electrode-active materials, which are given rise by the insulating nature of sulfur and the dissolution loss of the intermediates generated during discharge of sulfur4. In recent years, scholars and research institutions have carried out a lot of exploratory research work in the construction of sulfur electrode, and some results were obtained. For example, to immobilize sulfur by conductive polymer with chemical bond[7-9], and to slow down the dissolution and migration of polysulfide ions by porous carbon with physical adsorption 1112. At the same time, some new reaction mechanisms of sulfur electrode are proposed. Ai's group proposed a sulfur electrode based on the solid-solid reaction mechanism[13-16]. In this model, sulfur is highly dispersed in the pore structure of carbon matrix with lithium ion conductivity, and organic carbonates are used as electrolytes. Through the nucleophilic reaction between organic carbonates and polysulfide ions, a passivation film is formed on the surface of sulfur electrode. This passivation film can isolate the electrolyte from the bulk sulfur, so that lithium ions required for sulfur reduction can only be transferred to the sulfur/carbon interface through the porous carbon matrix, where in-situ electrochemical reduction and oxidation occur directly. This mechanism has been proved to be able to fundamentally avoid the problem of polysulfide dissolution and loss. And the key to realize this mechanism is to prepare carbon materials with reversible lithium implantation activity and good electronic conductivity at a high potential.

Polymer materials have been widely used for encapsulating and controlling the release of the reaction intermediate polysulfide polysulphide. Polyacrylonitrile (PAN)/S systems have been explored in rencent years[17]. It was reported that PAN became dehydrogenated and cyclized at 450 ° C, and all sulfur reacted with PAN to form a heterocyclic polymer interconnected with disulfide bonds on the side chain[18,19]. The chemically bonded sulfur showed good cycling retention of 90% up to 380 cycles[20], In order to obtain a sulfur electrode with high circulating capacity and good cycling performance. PAN/S system has been choosed in this study and the porous carbon with lithium ion conductivity was prepared for modification.

In this paper, a new porous carbon (labeled as PANC@BP) with highly dispersed Li^+- conductive properties was synthesized by coating on the surface of high specific surface BP2000 with a layer of polyacrylonitrile pyrolysis carbon (labled as PANC). The content of PANC in the carbon composite is 10%. Then, the as-prepared carbon sample was compounded with polyacrylonitrile/sulfur cathode material to construct a multiple composite sulfur electrode, which have a solid-solid reaction at the sulfur/carbon interface. With oxidized β-cyclodextrin as binder and copper foil as the collecting fluid, the cycling performance of the as-prepared composite electrode has been significantly improved.

2. EXPERIMENTAL

2.1 Materials preparation

A commercial microporous carbon, BP2000 (Black Pearls 2000, Cabot Corporation), with an average particle size of 12 nm, surface area of about 1300 m^2 g^{-1} and average pore size of 0.7 nm, was adopted as a porous matrix to fabricate the composite carbon with Li^+- conductive properties[14].

The composite carbon sample used in this study are prepared as follows: 0.17 g polyacrylonitrile(PAN, Mw=150000 Sigma Aldrich) was dissolved in 20 mL 0.54g N,N-Dimethylformamide (DMF, Alfa Aesar). 0.54 g BP2000 was added in the solution as prepared and grinded together by planetary milling for 6 h. Then, The PAN was precipitated from DMF with sufficient distilled water and deposited on the surface of BP2000. The mixture was dried at 60 ℃ for 6h, and then heated in a tubular furnace under argon flow at 280 ℃ for 2 h and 700 ℃ for 2 h. The prepared carbon matrix was labeled as PANC@BP. For comparison, pure polyacrylonitrile was pyrolyzed under the same conditions to obtain polyacrylonitrile pyrolysis carbon, labeled as PANC.

The sulfur cathode composite was mixed with a mass ratio of PANC@BP: PAN: S=1:10:50, and ball milling for 6 h in argon gas. then the mixture was heated in a tubular furnace under argon flow, 5 ℃ / min up to 300 ℃ for 8h. The prepared composite material was labeled as PANC@BP/PAN/S composite material. In order to compare, the PAN/S composite with a mass ration of PAN:S=10:50 without carbon matrix was prepared under the same conditions, which was labeled as blank PAN/S cathode material. In addition, with pure carbon black BP2000 as carbon matrix, the PAN/S composite electrode was prepared with a mass ration of BP2000:PAN:S=1:10:50 under the same conditions, which was labeled as BP/PAN/S composite material.

2.2 Structural characterization

The morphological and internal structural of the carbon material and the sulfur cathode compsite were characterized by scanning electron microscope (SEM, Quanta 200, FEI, Netherlands), transmission electron microscopy (TEM, JEOL JEM-2010FEF, Japan electronics co., LTD). X-ray diffractometer (XRD-6000, Shimadzu, Cu K alpha, Shimadzu) was used to characterize the structure of carbon materials, as well as the distribution pattern of sulfur in the pores of carbon matrix. The scan range was 10 ° to 80 °with a scan rate of 4 ° / min.

2.3 Electrochemical measurement

2.3.1 Electrode preparation

The sulfur cathode was prepared by mixing 80 wt.% PANC@BP/PAN/S composite material, 10 wt.% acetylene black and 10 wt.% PTFE(polytetrafluoroethylene) into a paste and roll-pressing the paste into about 0.1mm thick film, then, pressing the electrode film onto an aluminum mesh and vacuum drying at 60 ℃.

All electrochemical tests for the sulfur electrode were carried out using coin cells with lithium sheet as counter electrode. The organic carbonate electrolyte used in this study was 1 M $LiPF_6$ dissolved in a mixture of propylene carbonate(PC), ethylene carbonate (EC), and diethyl carbonate (DEC) in a volume ratio of 1:4:5. The electrolyte was purchased from Tianci Battery Material Co., Ltd. (Guangzhou, China). A microporous membrane (Celgard 2300) was used as the separator. The coin cells were assembled in an argon-filled glove box. The adding amount of the electrolyte in a single coin cell is ∼0.1 mL.

2.3.1. Performance test

The charge and discharge tests were performed at a voltage interval of 1.0~3.0 V at a current density of 100 mA g^{-1} using a programmable computer-controlled battery charger (CT2001A Land Battery Testing System, Wuhan, China). The sulfur existed in the cyclic PAN in the form of bond, its content was difficult to accurately calibrate. Therefor the discharge specific capacity of PAN/S composite in this paper was calculated based on the total mass of the composite.

3. RESULTS AND DISCUSSION

The SEM images of PANC, BP2000, PANC@BP, PAN/S composite and PANC@BP/PAN/S composite as prepared are shown in fig.1.

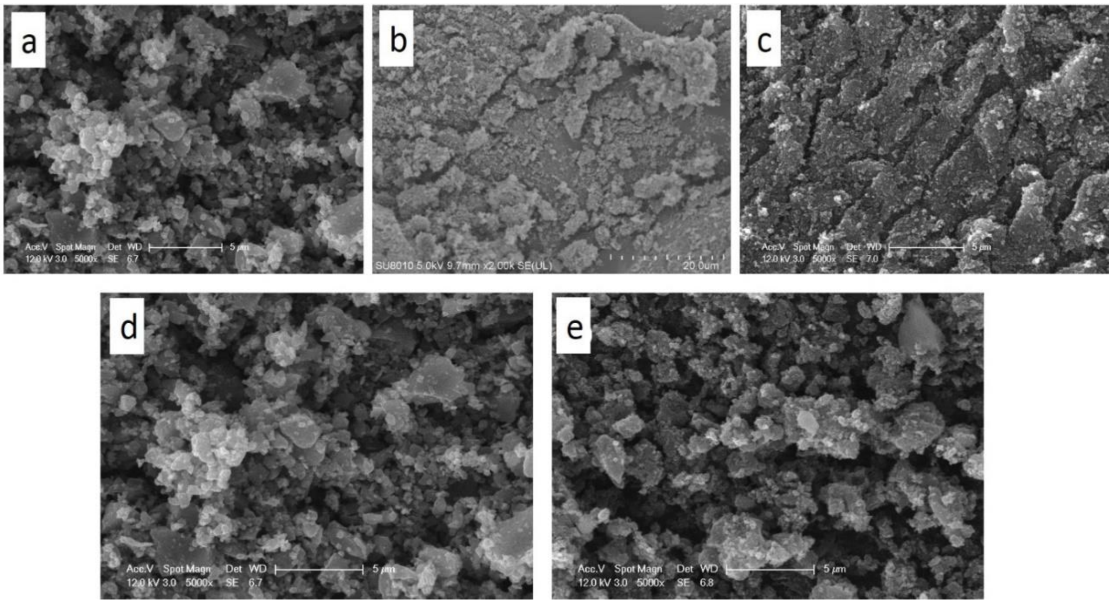

Figure 1. The SEM images of PANC(a), BP2000(b), PANC@BP(c), PAN/S(d) and PANC@BP /PAN/S(e).

The surface morphology of direct pyrolysis carbon of PAN is shown in fig.1(a) . It can be seen that the particle size of the pyrolysis carbon is about 0.5~2.0μm. Fig.1(b)and(c) are the SEM photos of commercial carbon black BP2000 before and after coated with 10%PANC respectively. It can be seen from the comparison that BP2000 has basically the same morphology characteristics before and after modification, all of which are loose powders with small particle size and relatively uniform distribution, indicating that the modification of a small amount of PAN has basically not affected the dispersion of BP2000. The SEM images of PAN/S composite and PANC@BP/PAN/S composite are shown in Fig.1(d) and (e). The morphology of the two composites is similar, and both are particles with a particle size of 1~3 μm. Further observation, it can be seen that after PANC@BP carbon is added, the surface of PAN/S composite material becomes relatively rough, indicating that PANC@BP carbon is uniformly adhered to the surface of PAN/S composite material and forming a coating layer.

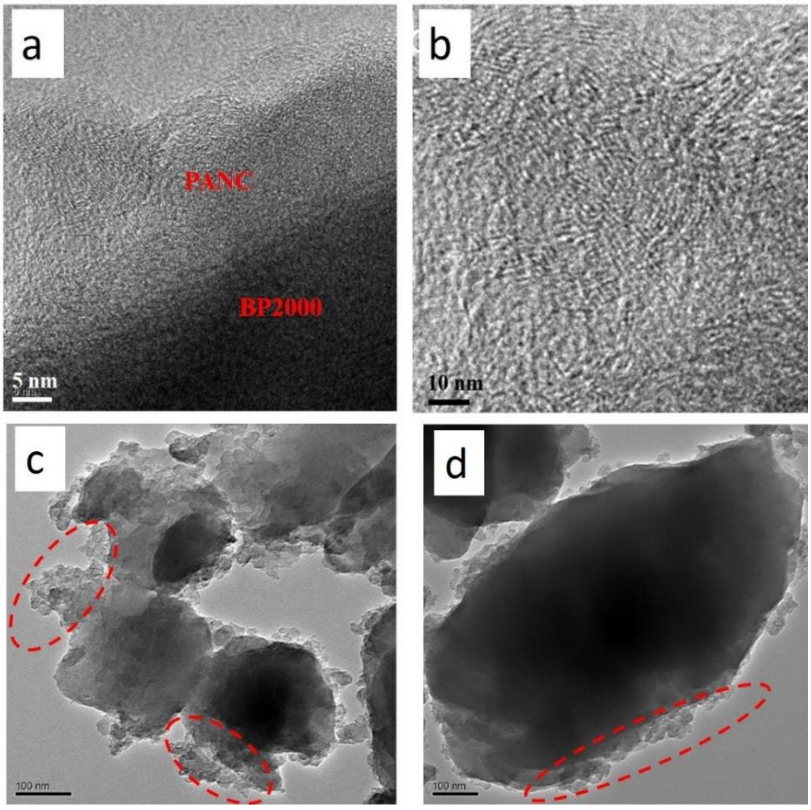

Figure 2. TEM (a) and HRTEM (b) images of PANC@BP, and TEM(c、 d) images of PANC@BP/PAN/S composite

Fig. 2 shows TEM (a) and HRTEM (b) images of PANC@BP. The TEM photo of composite carbon material is divided into two layers as shown in Fig.2(a). The inner layer is dark in color, which is amorphous carbon black BP2000[14]，the outer layer is light color and polyacrylonitrile pyrolysis carbon. From the HRTEM image in Fig.2(b), it can be seen that the polyacrylonitrile pyrolysis carbon on the surface has graphite lamellar structure, while the accumulation is relatively disordered. The TEM image in Fig. 2(c)and Fig. 2(d) shows that PANC@BP/PAN/S composite particle size is about 200 ~ 500 nm, the surface of the composite is a dense layer of PANC@BP carbon, as shown in red curve area. The carbon layer will provide lithium ion conduction channels for the reaction of sulfur/carbon solid-solid interface, which will be improve solid-solid sulfur electrode electrochemical performance[13].

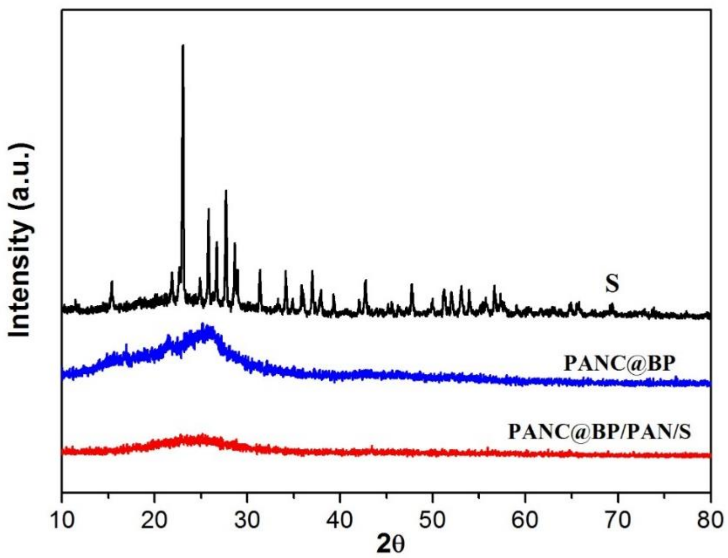

Figure 3. XRD patterns of sulfur, PANC@BP and PANC@BP/PAN/S composite

Figure 3 compares the X-ray diffraction (XRD) patterns of sulfur, PAN@BP and PANC@BP/PAN/S composites. The sharp diffraction peaks of sulfur demonstrate its presence in a highly crystalline state. A broad diffraction package 2θ=~ 26.5 ° appeared in as-prepared PANC@BP, indicating that the carbon exists in the form of crystalline and amorphous blending, which is consistent with the HRTEM image. In the case of the PANC@BP/PAN/S composite, it shows featureless diffractions with a broad and weak band at 2θ=~ 25 °, and the sharp diffraction peaks of sulfur, PANC@BP have disappeared, implying that sulfur is deeply embedded and well dispersed in the PANC@BP[14].

Figure 4 (a) and (b) shows the electrochemical behaviors of PANC@ BP between 1 V and 3 V. It can be seen that the carbon material as prepared displayed a reversible Li^+ insertion–extraction behavior with a realizable capacity of~50 $mAhg^{-1}$ after 150 cycles, indicating a feasible Li^+ storage and transport in the carbon. According to the solid–solid redox mechanism proposed above, PANC@ BP carbon is one choice for sulfur electrode[9,10]. Because polyacrylonitrile pyrolysis carbon in PANC@ BP is only 10 wt. %, if the specific capacity of composite carbon is all attributed to the lithium storage on the surface of polyacrylonitrile pyrolysis carbon, the reversible lithium capacity of polyacrylonitrile pyrolysis carbon can reach about 500 $mAhg^{-1}$. Sufficient lithium ions were provided for the electrochemical reduction of sulfur in the PAN/S composite, enabling the sulfur electrode reaction to be carried out directly at the interface of sulfur and carbon, ensuring a high electrochemical utilization rate of the active material.The conclusion has been verified in our previous study.[13,14]

As shown in Figure 4 (c), in the carbonate electrolyte, the PANC@BP/PAN/S electrode exhibited a single discharge plateau at 1.87 V with the discharge capacity of 850 $mAhg^{-1}$. In the subsequent charging process, the voltage plateau was about 2.25V, and the specific charging capacity was 656 $mAhg^{-1}$. Since the second cycle, the discharge plateau gradually increased to 2.2V and remained basically unchanged with the discharge capacity of 645 $mAhg^{-1}$, indicating that the electrode has a high electrochemical activity and good cycling stability. The charging and discharging behavior of this electrode is consistent with the behavior of PAN/S electrode reported in literature[18,19].

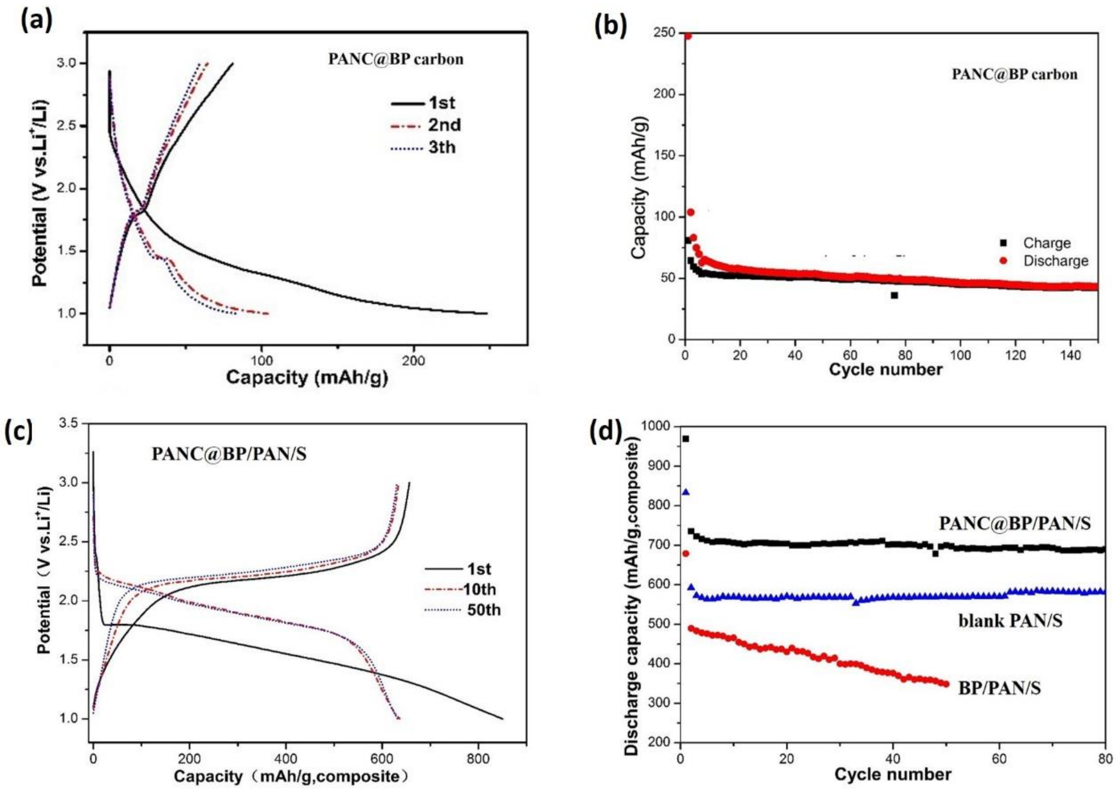

Figure 4. (a) The cycling performance and (b) the discharge and charge curves of the PANC@BP; (c) The discharge and charge curves and (d) Cycling performance of the of PANC@BP/PAN/S, blank PAN/S and BP/PAN/S

polyacrylonitrile pyrolysis carbon is the main component with Li^+-conductive function in PANC@BP, while BP2000 plays a dispersal effect, which is also verified by HRTEM photos above. In order to prove the lithium ion conductive effect of PANC@BP, Figure 4 (d) compared the cycling performance of PANC@BP/PAN/S, blank PAN/S and BP/PAN/S as prepared. At a current density of 100 mA g^{-1}, the PANC@BP/PAN/S composite showed a reversible capacity of 972 mAh g^{-1} and 745 mAh g^{-1} at 1^{st} and 2^{nd} cycle respectively, then maintained steadily 701 mAh g^{-1} at subsequent cycles, showing a stable cycling performance. The blank PAN/S electrode had the similar cycling stability, but with a reversible capacity of only ~570 mAh g^{-1} after 80 cycles. It can be seen that the reversible capacity of BP/PAN/S composite was 490 mAh g^{-1} at 2nd cycle, which decreased to 350 mAh g^{-1} after 50th cycle. Therefore, the PANC@BP/PAN/S composite has a good cycling performance and a high reversible capacity, implying that the PANC@BP carbon with the function of lithium ion conductive has a remarkable effect on improving the electrochemical properties of the composites.

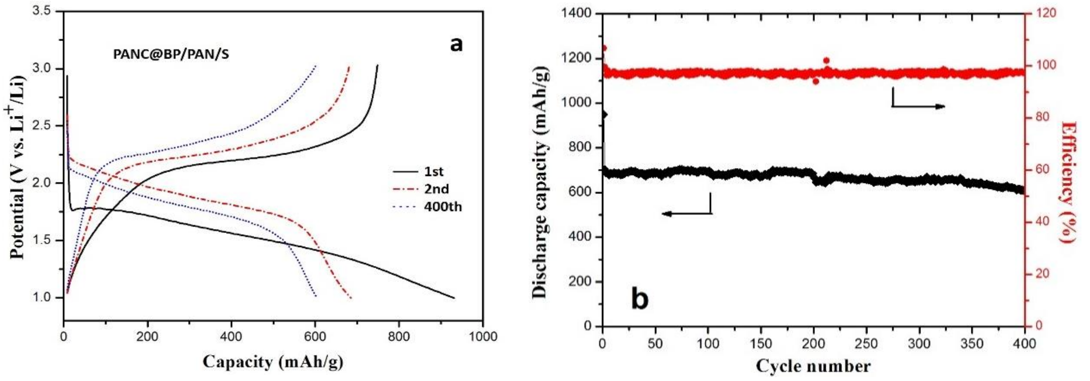

Figure 5. The charge-discharge curve(a) and cycling performance curve(b) of PANC@BP/PAN/S composite sulfur electrode, current density: 100 mA g^{-1}, voltage range: 1 V- 3 V

To further improve the performance of the sulfur electrode as prepared, we introduced oxidized β-cyclodextrin as the binder and used copper foil instead of aluminum mesh as the current collector. The oxidized β-cyclodextrin has a special ring structure, with hydrophilic external cavity and hydrophobic inner cavity[20-22]. The sulfur electrode was prepared according to the mass ratio of 8:1:1 of active material, conductive agent and binder. The lithium sheet was used as negative electrode, and the carbonate electrolyte 1 M $LiPF_6$/ PC-EC-DEC (1:4:5,v/v/v) was selected as electrolyte to assemble battery. The galvanostatic charge–discharge behaviors and cycling performance of perpared sulfur electrode was shown in Fig.5. Fig.5(a) shows the charge-discharge curve of PANC@BP/PAN/S composite sulfur electrode when oxidized β-cyclodextrin and copper foil are selected. During the discharge process, a discharge voltage platform appears at 1.8V in the first cycle, and rises to 2.0V after the second cycle. During the charging process, a voltage platform appeares near 2.2V, and the voltage platform rises only slightly with the increase of cyclic numbers. These show typical charge-discharge characteristics of sulfur electrodes. Fig.5(b) shows the cycling performance curve of PANC@BP/PAN/S composite sulfur electrode. According to the figure, the specific discharge capacity of the electrode in the first cycle reached 948 mAh g^{-1} at the current density of 100 mA g^{-1}. From cycle 2 to 200, the discharge specific capacity was relatively stable, maintained at about 700 mAh g^{-1}. After 200 cycles, the discharge specific capacity attenuated and decreased to 661 mAh g^{-1} in the 300th cycle. Compared with discharge specific capacity of 948 mAh g^{-1} in the first cycle, electrode capacity retention was 72.0%, and compared with the reversible discharge specific capacity in the second cycle, the retention was 95.1%. After 400 cycles, the electrode discharge specific capacity was 612 mAh g^{-1}, and the capacity retention was 87.6%. From the charge-discharge efficiency curve in the figure, it can be seen that the coulomb efficiency is close to 100% from the second cycle, indicating that the composite electrode has good electrochemical reversibility. The results showed that PANC@BP/PAN/S composite had excellent cycling performance when oxidized β-cyclodextrin was used as binder and copper foil as collecting fluid. This might be due to the coating of oxidized β-cyclodextrin on the electrode material during charge and discharge, which inhibits the volume expansion of the electrode material. The better electrical contact between the electrode and copper foil provides more active sites for the electrode material, which further improves the specific capacity of the electrode and the stability of the circulation[23,24].

Table 1. Comparison of electrochemical performance of sulfur electrodes

Cathode	The calculation of specific capacity	Initial discharge capacity(mAhg^{-1})	Stable discharge capacity after 400 cycles(mAhg^{-1})	Rate (mAg^{-1})	Reference
S/BP2000/PAN	Sulfur content (53%)	1183	~790	200	[14]
PANC@BP/PAN/S (as prepared)	Composite mass	948	~610	100	This work

Table 1 compared the performance of S/BP2000/PAN composites nanofibers prepared by electrospinning the dispersion of the S/C composite in a PAN/DMF solution and PANC@BP/PAN/S composites prepared by coated a Li$^+$-conductive carbon on the PAN/S composite. [14]. The specific capacity of PANC@BP/PAN/S composites prepared in this paper is calculated in terms of the total mass of the complex. If the sulfur content of the composite is calculated, the specific capacity of the prepared electrode will be higher, which shows outstanding performance, cyclic stability and capacity retention rate.

4. CONCLUSION

The highly dispersed lithium ion transport conductor PANC@BP carbon was prepared by coating the high specific surface of BP2000 with 10% polyacrylonitrile pyrolysis carbon. By dispersing PANC@BP carbon into PAN/S composites, a composite sulfur electrode with a solid-solid reaction mechanism was constructed. Electrochemical test results showed that PANC@BP/PAN/S composite electrode had high specific capacity and excellent cycling stability. Based on the total mass of the composite material, the initial reversible specific capacity was about 745 mAh g^{-1}, and the specific capacity maintained 701 mAh g^{-1} after 80 cycles. With oxidized β-cyclodextrin as binder and copper foil as the collecting conductor, the cycling performance of PANC@BP/PAN/S composite electrode had been significantly improved. The discharge specific capacity maintained 661 mAh g^{-1} after 300 cycles. Compared with discharge specific capacity of 948 mAh g^{-1} in the first cycle, electrode capacity retention was 72.0%, and compared with the reversible discharge specific capacity in the second cycle, the retention was 95.1%.

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