Int. J. Electrochem. Sci., 16 **(2021)** 210247, doi: 10.20964/2021.02.41

International Journal of
ELECTROCHEMICAL
SCIENCE
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Polyacrylonitile/Sulphur (PAN-S) cathode with KS6 Graphite as the conductive agent for Li-S battery

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Received: 28 September 2020 / *Accepted:* 15 November 2020 / *Published:* 31 December 2020

KS6 is selected as the conductive agent in this paper. Three kinds of PAN-S-KS6 composites with KS6 content of 5%, 10% and 20% are prepared by spray drying method. Than, the structure and electrochemical performance of the electrode are characterized, and the influence of different conductive content in the composite on the electrochemical performance of the composite electrode is also investigated by assembling lithium sulfur battery(Li-S battery). The results indicate that the ternary compounds with 10% KS6, 40% PAN and 50% elemental sulfur shows excellent electrochemical performance. The reason is that in PAN-S-KS6 composite, the appropriate amount of conductive agent provides good electron transport for the composite. Sufficient amount of PAN polymer can realize sulfur immobilization by complete bond of elemental sulfur, and form a complete conductive network on the surface layer of sulfur carbon composite, and the electrochemical performance of PAN-S composite electrode materials can be significantly improved.

Keywords: KS6; Conductive agent; Spray drying method; KS6-PAN-S composite; Li-S battery

1. INTRODUCTION

With the secondary batteries playing an increasingly important role in modern life, people are constantly exploring and developing energy storage systems with high energy density and low cost to satisfy the needs of secondary battery systems with higher energy density in the information age[1,2]. The theoretical specific energy of lithium sulfur battery is as high as 2600 Wh/Kg, which is more than 6 times of the traditional embedded lithium ion battery[3-5]. However, sulfur is the insulator of electrons

and ions, and the discharge intermediate product of sulfur electrode is easily soluble in organic electrolyte, and the intermediate product lithium polysulfide has the "shuttle effect" of positive oxidation - negative reduction in electrolyte, which results in poor cycling stability of sulfur electrode [6-10]. To solve such problems, Wang's group proposed a Polyacrylonitrile / sulfur (PAN-S) composite sulfur electrode [11-13]. Under heating conditions, sulfur participates in the cycleization reaction of polyacrylonitrile and is highly dispersed in polyacrylonitrile body structure in the form of chemical bonding. PAN-S composite electrode shows good cyclic stability in carbonate electrolyte solution with low solubility to polysulfide. However, as a polymer matrix material, PAN has poor electronic conductivity and lithium ion conductivity, and there are few S/e/Li^+ three-phase reaction sites in PAN-S composite materials, which restricts the improvement of sulfur electrochemical reaction activity[14,15]. Therefore, a new idea of developing sulfur electrode at high active sites was envisaged. The conductivity of PAN/S composite materials was improved by using strong conductive carbon as a conductive agent, and multiple composite sulfur electrodes with rich S/e/Li^+ three-phase reaction interfaces were constructed to realize efficient sulfur reaction in the complex network[16-20].

In this paper, KS6 was selected as the conductive agent, PAN-S-KS6 composites with KS6 content of 5%, 10% and 20% were prepared, and the electrochemical properties of various composite electrode materials were investigated to obtain the optimal composite ratio. On this basis, the effects of different conductive agent collection on the properties of the composite electrode were further studied.

2. EXPERIMENT

2.1 Material preparation

2.1.1 Preparation of PAN-S-KS6 composites

KS6 is a kind of conductive graphite commonly used in lithium ion batteries (ShenZhen BTR, China), which has very high conductivity. In the experiment, PAN-S-KS6 composite was prepared by mixing KS6 and elemental sulfur evenly and then covering with polyacrylonitrile. Elemental sulfur and KS6 were weighed according to a certain mass ratio and ground evenly. Planetary ball mill was used to grind them for 8 h to obtain evenly mixed sulfur-carbon compound under the protection of Ar. PAN was dissolved in DMF to prepare PAN solution with a mass fraction of 5%. PAN solution was mixed with the sulfur-carbon composite at a certain solid mass ratio, and the mixture is grinded by planetary ball mill for 10 h to disperse evenly. Then, the slurry was sprayed into distilled water by spray dryer at room temperature. PAN was quickly precipitated in water and contracted and coated on the surface of sulfur-carbon material. Fine powder products were obtained after filtering and drying. The product was placed in a sealed reaction kettle filled with Ar and heated at 300℃ for 6 h to make PAN cyclization. The PAN-S-KS6 composite with KS6 content of 5%, 10% and 20% and sulfur content of 50% were obtained.

Table 1. The content of each component in PAN-S-KS6 composite

Samples	S (%)	PAN (%)	KS6 (%)
PAN-S-KS6-5%	50	45	5
PAN-S-KS6-10%		40	10
PAN-S-KS6-20%		30	20

2.1.2 Preparation of PAN-S cathode

The prepared composite material, conductive agent acetylene black and binder PTFE were evenly mixed at a mass ratio of 8:1:1. After mixing with isopropanol, the electrode membrane with a thickness of about 0.1mm was prepared by repeated roller pressing on a double-roller film press, and then vacuum dried at 60℃. The electrode plate is obtained by cutting a 1.0 cm diameter diaphragm and stamping it on the aluminum network. In this paper, the electrolyte composition is 1M $LiPF_6$/PC-EC-DEC(1:4:5,v/v).

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.% PAN-S-KS6 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 was 1 M $LiPF_6$/PC-EC-DEC (volume ratio of 1:4:5).

2.3.2 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. Therefore 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

3.1 Structure Analysis

The SEM images of conductive graphite KS6 and composite PAN-S-KS6-10% as prepared are shown in fig.1. As shown in Figure 1(a, b), the conductive graphite KS6 is composed of squamous carbon sheets with diameter 3~5 μm with smooth surface. KS6 was mixed with elemental sulfur and coated with PAN by cyclization. The morphology of the composite was shown in Figure 1(c, d). It can be seen that the composite is composed of large particles with particle size of 5 μm or more, which are agglomerated by small particles of 200~300 nm, and the lamellae structure of KS6 has completely disappeared. This could be the result of a planetary grinding and polymer coating in the preparation process. The results showed that KS6, as a conductive core, was coated by sulfur, and multiple KS6/S particles were coated by PAN and adhered together to form larger particles. Since the sulfur in the composite is sandwiched between the conductive core KS6 and the conductive PAN polymer in the outer layer, the electrochemical activity of the elemental sulfur is expected to be greatly improved.

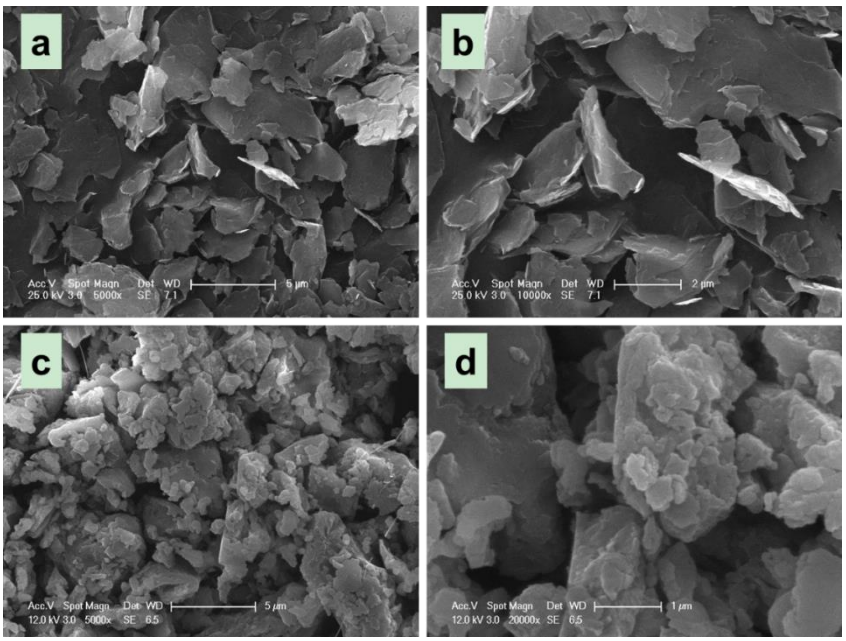

Figure 1. SEM images of KS6 (a, b) and PAN-S-KS6-10% composite material（c, d）

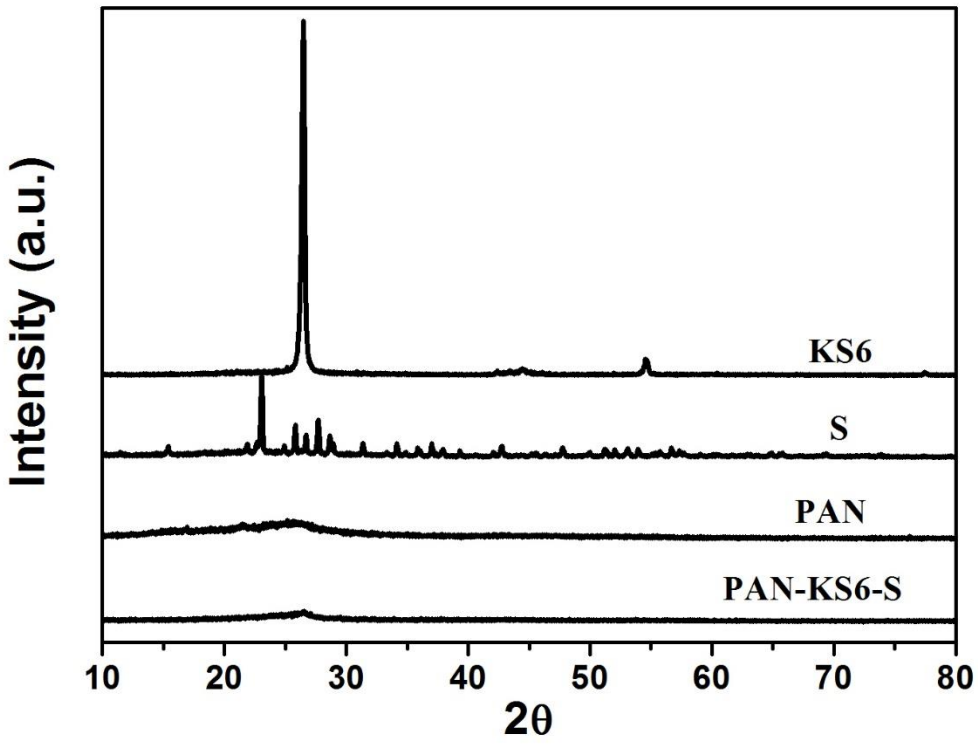

Figure 2. the XRD patterns of elemental sulfur, KS6, heat-cycled PAN and PAN-S-KS6-10% composite

The XRD patterns of the elemental sulfur, conductive graphite KS6, PAN cycled at 300℃, and PAN-S-KS6-10% composite materials are shown in Figure 2. It can be seen that the XRD pattern of the elemental sulfur shows a relatively sharp diffraction peak, indicating that the sulfur has a highly crystalline state[20]. Two strong characteristic peaks representing the graphite structure appeared near 2θ=~ 26.5° and 2θ=~ 55°, indicating that KS6 had a complete graphite crystalline phase[13]. A broad diffraction package 2θ=~ 26.5 ° appeared in cycled PAN, indicating that the cycled PAN has similar XRD properties to amorphous carbon[13]. The PAN-S-KS6-10% composite exhibited characteristic diffraction peaks corresponding to KS6 graphite structure around 26.5°, but its strength was significantly weakened, and the wider diffraction peak attributed to cycled PAN at ~26.5° also became significantly weaker. Meanwhile, the diffraction peak attributed to elemental sulfur completely disappears in the diffraction spectrum of the composite. The diffraction pattern indicated that the PAN formed a relatively complete coating layer on the surface of the sulfur-carbon composite.

3.2 Electrochemical performance

The effects of different conductive agent contents (including 5%, 10% and 20%) on the electrochemical properties of the composite were investigated. Figure 3 shows the charge-discharge cycle performance of the three kinds of composites between 1.0 and 3.0V at a current density of 100

mA g^{-1}, and an obvious difference in the cycling performances. It can be seen that the discharge capacity of the PAN-S-KS6-5% composite is 1180 mAh g^{-1} in the first cycle. However, it attenuates to 480 mAh g^{-1} in the second cycle, and with a capacity of 270 mAh g^{-1} after 50 cycles. The cycle performance of PAN-S-KS6-10% composite material is relatively high. The curve shows that discharge capacity is 1701 mAh g^{-1} in the first cycle and 1200 mAh g^{-1} in the second cycle, and remains above 1000 mAh g^{-1} after 50 cycles. The discharge capacity of PAN-S-KS6-20% composite material is 1281 mAh g^{-1} in the first cycle and 878 mAh g^{-1} in the second cycle, and only 500 mAh g^{-1} after 50 cycles. The above results show that the PAN-S-KS6-10% composite with 10% KS6 content and 40% PAN content has the highest specific capacity and the best cycling performance. It was indicated that the proper addition of KS6 will improve the dispersion and conductivity of sulfur. At the same time, The sufficient PAN can form a complete coating layer on the surface of the KS6-S composite[20].

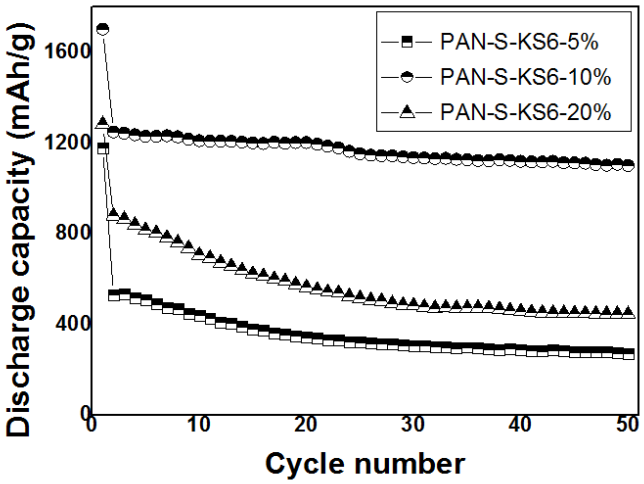

Figure 3. The cyclic performance curves of PAN-S-KS6-5%, PAN-S-KS6-10% and PAN-S-KS6-20%.

Figure 4 shows the charge-discharge characteristics of the PAN-S-KS6-5%, PAN-S-KS6-10% and PAN-S-KS6-20% at a voltage interval of 1.0~3.0 V and a current density of 100 mA g^{-1}. It can be seen that the charge and discharge curves of the three kinds of composites are similar to those of the PAN-S composite in the carbonate electrolyte[13,21]. The discharge plateau is mainly under 1.8V in the first cycle, and increased significantly from the second cycle. The charging voltage platform is about 2.3V and decreased slightly in the following cycles. It indicates that the polarization phenomenon in the discharge process is obviously decreased. The greater polarization should be caused by the bonding of PAN to sulfur during the first discharge process. As the destruction of PAN-S bond need to overcome the additional activation energy, resulting in a loss of potential response [22,23]. In addition, comparing the charge-discharge curves of the three kinds of composites, it can be found that the polarization of PAN-S-KS6-10% composite was minimal. It was indicated that the proper addition of KS6 will improve the dispersion and conductivity of sulfur, and provid more S/e/Li^+ three-phase reaction sites for PAN-S composite[16,20].

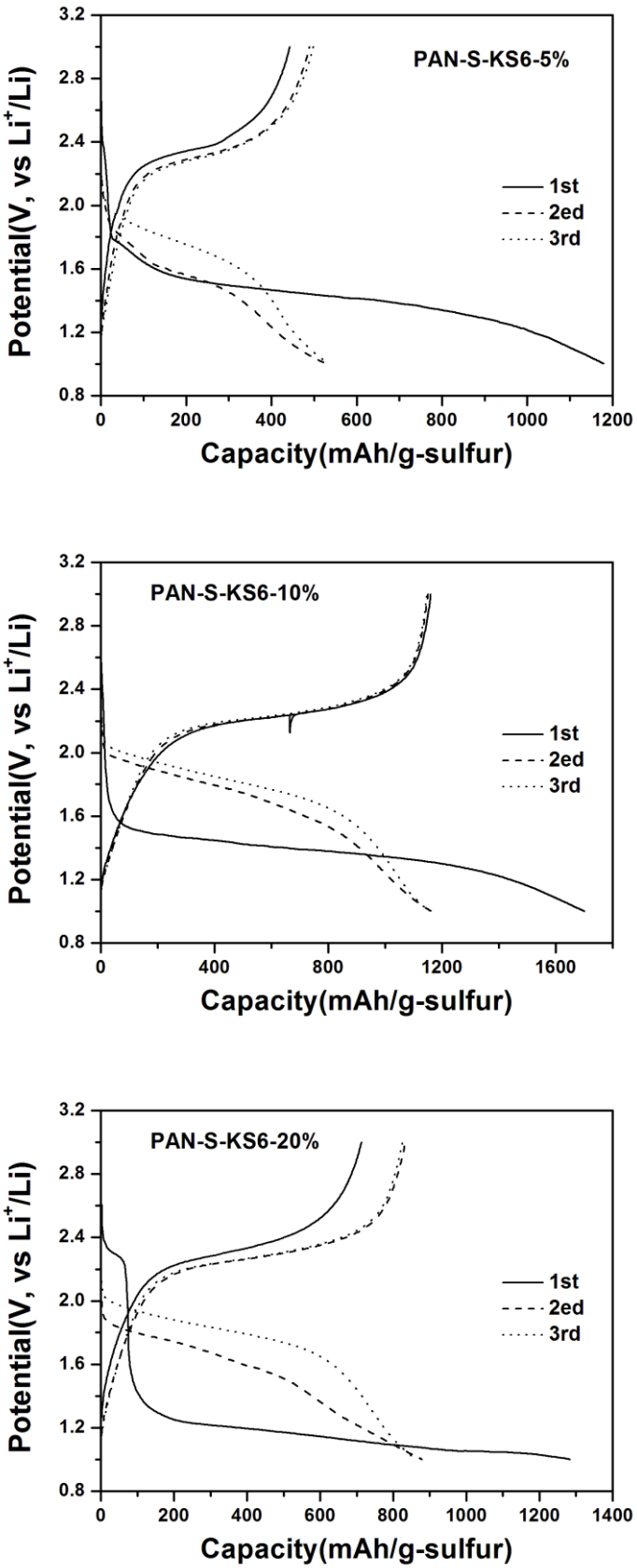

Figure 4. The charge and discharge curves of PAN-S-KS6-5%, PAN-S-KS6-10% and PAN-S-KS6-20%.

The effects of different conductive agents on the electrochemical properties of the composite was investigated. The conductive agents used in the experiment are MCMB, VGCF and KS6. The content of conductive agent was 10%, PAN was 40% and elemental sulfur was 50% in the PAN-S-carbon composite. As shown in Figure 5, the electrochemical properties of the composites of the three conductive agents are significantly different. The composite material with KS6 as the conductive agent shows that the discharge capacity is 1701 mA g^{-1} in the first cycle and a reversible capacity of 1162 mA g^{-1} in the second cycle, and the capacity maintained above 1000 mA g^{-1} after 100 cycles. The composite with MCMB as the conductive agent has a discharge capacity of 1641 mA g^{-1} in the first cycle and a reversible capacity of 622 mA g^{-1} in the second cycle. After 50 cycles, the discharge capacity maintained 340 mA g^{-1}. The third kind of composite with VGCF as the conductive agent, which has a discharge capacity of 1141 mA g^{-1} in the first cycle and a reversible capacity of 511 mA g^{-1} in the second cycle. After 50 cycles, the capacity maintained 211 mA g^{-1}. By comparison, it can be found that the composite with KS6 as the conductive agent has higher specific capacity and better cycling performance. The possible reason is that KS6 is a scale-like structure, and it is easy to disperse elemental sulfur on both sides of the scales through ball grinding, so that sulfur carbon can get better contact. It will improve the dispersion and conductivity of sulfur[24]. The MCMB has a spherical structure with a smooth and hard surface, which cannot be mixed thoroughly by the ball grinding[25]. Due to VGCF has fibrous structure and high toughness, a similar problem exists with VGCF fibers, which do not disperse easily and are difficult to mix uniformly with elemental sulfur even through ball milling. Therefore, MCMB and VGCF cannot provide sufficient electron transport for the compostie, resulting in poor electrochemical performance.

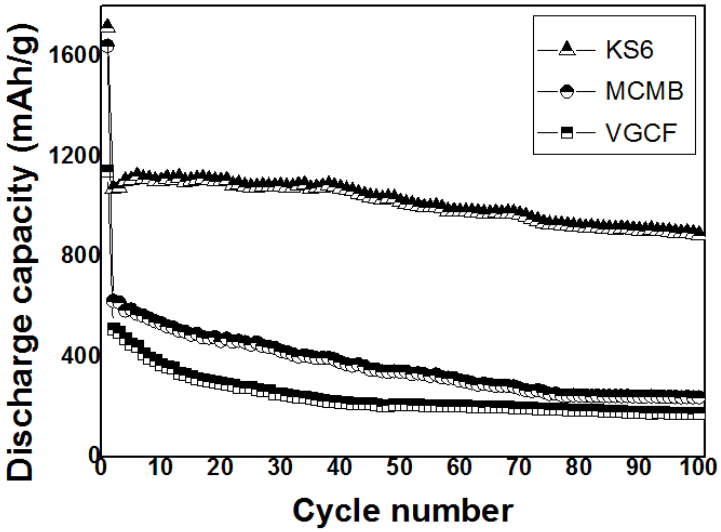

Figure 5. Cycle performance of KS6, MCMB and VGCF as conductive agents

Table 2. Comparison of electrochemical performance of sulfur electrodes

Cathode	The calculation of specific capacity	Initial discharge capacity(m Ahg^{-1})	Stable discharge capacity after 50 cycles($mAhg^{-1}$)	Rate	Refer ence
PAN-S	Composite mass	~860	~610	0.2 $mAcm^{-2}$	[12]
PAN-S-KS6-10% (as prepared)	Composite mass	~1700	~1050	100 mAg^{-1}	This work

As shown in Table 2, the PAN-S-KS6-10% composite prepared by dispersing the S-KS6 composite in the PAN solution and spray drying. The PAN-S composite prepared by heating at 300℃ without conductive agent [14]. The performance of two composites were compared. The specific capacity of two composites is calculated in terms of the total mass of the composite. The discharge capacity of PAN-S composite is 860 $mAhg^{-1}$ in first cycle and 610 $mAhg^{-1}$ after 50 cycles. However, The discharge capacity of PAN-S-KS6-10% composite is 1700 $mAhg^{-1}$ in first cycle and 1050 $mAhg^{-1}$ after 50 cycles. This is mainly due to the addition of KS6 conductive agent. KS6 can improve the conductivity of PAN-S and provid more $S/e/Li^+$ three-phase reaction sites for PAN-S composite[16-20]. It indicates that KS6 graphite can improve the electrochemical performance of PAN-S composite electrode materials.

4. CONCLUSION

In this paper, three kinds of PAN-S-KS6 composites with KS6 content of 5%, 10% and 20% were prepared by spray drying method. The structure and electrochemistry of the electrode were characterized, and the effects of different conductive carbon on the electrochemical performance of the composite electrode were also investigated. The results showed that the ternary compounds with 10% KS6, 40% PAN and 50% elemental sulfur showed excellent electrochemical performance. Due to the appropriate amount of conductive agent in PAN-S-KS6 composite materials, the composite provides good electron transport. Sufficient amount of PAN polymer can immobilize the elemental sulfur and form a complete conductive network on the surface of the sulfur-carbon composite. And the above reasons improve the electrochemical performance of PAN-S composite electrode materials.

ACKNOWLEDGEMENTS
This work was supported by the National Natural Science Foundation of China [grant number 21603093, 21702090, 62041406], Technology Plan of Department of Education of Jiangxi [grant number GJJ151139], Jiangxi Province Key Laboratory of Precision Drive and Control (grant number PLPDC-KFKT-201614)and Jiangxi science and technology support plan
(grant number 20171BAB206040).

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