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Optimized Preparation of Polyacrylonitrile/Sulfur Composite as Cathode for Lithium Sulfur Batteries

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The polyacrylonitrile/sulfur (PAN/S)composite was prepared by heating the mixture of polyacrylonitrile (PAN) and sulfur under sealed conditions. The effects of the ratio of raw materials, reaction temperature, reaction time and reaction container volume on the properties of the composite product were studied to optimize the preparation conditions of the PAN/S composite. The results showed that the PAN/S composite with the mass ratio of 1:1.5 had the best properties, which was prepared in a large container in a high temperature reaction kettle at 300℃-400℃ for 12 hours. Based on the total mass of the composite, the initial discharge capacity of the composite is 856 mAh g^{-1} and the reversible specific capacity is 678 mAh g^{-1}. After 100 cycles, the specific capacity of the composite is stable at 584 mAh g^{-1}, and the capacity retention rate is 86.1 %, showing a good application prospect.

Keywords: Li-S battery, sulfur cathode, PAN/S composites

1. INTRODUCTION

Elemental sulfur has a high theoretical capacity of 1675 mAh g^{-1} which is an order of magnitude higher than those of the insertion-oxide cathodes. Lithium-sulfur (Li-S) batteries are considered as a promising candidate for next generation rechargeable batteries due to their high theoretical energy density (2600 Wh kg^{-1}).[1,2] However, due to the electrical insulation of sulfur and the dissolution of reaction intermediates in sulfur electrode, it probably result in not only low electrochemical utilization but also poor cycle stability, and seriously restrict the application and development of sulfur electrode.

It is an effective way to develop high-performance sulfur electrode by applying conductive matrix with high specific surface area to disperse and load sulfur, meanwhile combined with physical adsorption or chemical bonding. Polymers are widely used in sulfur electrodes because of their simultaneous conductivity, physical adsorption and chemical bonding. According to their modes of action, polymers can be divided into three categories: (1) Directly dispersed and loaded sulfur as conductive matrix. For example, conductive polymers such as polythiophene, polypyrrole, polyaniline, PEDOT, etc.with good conductivity, are usually used as conductive substrate of sulfur.[3-5] (2) As the surface coating of carbon/sulfur composites which limits the loss of sulfur. Limited by the carbon pore volume, the content of sulfur in the carbon/sulfur composites is usually difficult to improve, and when to increase the sulfur capacity, it will inevitably aggravate the loss of active substances. Therefore, polymer modification is attempted to balance the contradiction between the increase of sulfur content and the aggravation of polysulfide dissolution. The addition of polymer as conductive modified layer can not only limit the dissolution of polysulfides and reduce the polysulfide shuttle effect, but also the flexible structure can buffer the volume change of sulfur during the cycle, thus reducing the capacity attenuation caused by structural collapse. [6-8] (3) Sulfur is chemically bonded to the polymer structure by the chemical reaction. Sulfurized polymer refers to the polymer/sulfur composite material which takes the polymer chain as the conductive skeleton and the side chain is bonded by polysulfide bonds at 280℃ and above. Sulfur is uniformly dispersed in the polymer conductive skeleton in the form of polysulfide bond, which not only improves the electrochemical activity of sulfur, but also improves the conjugation degree of polymer by cyclization[9].

Therefore, sulfide polymer composites show excellent electrochemical properties. At present, the vulcanized polymers mainly include vulcanized polyaniline, vulcanized polyacrylonitrile and so on[10-12]. Polyacrylonitrile/sulfur composites have attracted much attention in recent years because of their unique way of bonding fixed sulfur, in which may obtain high capacity, excellent cycle stability and high utilization rate of active substances (>90%). The properties of polyacrylonitrile/sulfur composites are closely related to preparation conditions and sulfur content. Wang obtained vulcanized polyacrylonitrile composites with sulfur content of 53 wt % by heating the mixture of excess sulfur and polyacrylonitrile. Although the complex has a high initial capacity due to its high sulfur content, the electrode capacity decays rapidly in subsequent cycles, and the capacity has decayed by 26 % at 50 weeks.[13] Aishuak Konarov has studied the influence of the mixing mode of sulfur and polyacrylonitrile on the product performance, and found that the performance of vulcanized polyacrylonitrile obtained by manual grinding mixture is better than that obtained by planetary grinding mixture. The possible reason is that planetary ball milling destroys the chain structure of polyacrylonitrile, resulting in short chain of polyacrylonitrile and poor conductivity[14]. Li has studied the effect of heat treatment temperature on the properties of vulcanized polyacrylonitrile. The results show that the composite sulfur electrode has the best electrochemical performance when heat treating at 350 ℃ . Further studies showed that the properties of polyacrylonitrile were greatly improved after the free elemental sulfur was removed by vacuum heating. After 100 cycles at the current density of 20 mA g^{-1}, the specific capacity of sulfide polyacrylonitrile electrode is still up to 1707 mAh g^{-1} (based on the mass of sulfur). It can be seen that the synthesis conditions and sulfur content are important factors affecting the properties of sulfide polyacrylonitrile. [15]

In this paper, the preparation process of polyacrylonitrile/sulfur composite is discussed. The effects of raw material ratio, reaction temperature, reaction time and reaction container volume on the properties of polyacrylonitrile/sulfur composite were studied to optimize the synthesis conditions, in order to prepare sulfur electrode materials with high capacity and high cycle stability.

2. EXPERIMENT

2.1 Preparation of Polyacrylonitrile/sulfur Composites

Polyacrylonitrile/sulfur (PAN/S) composites are prepared by heating under sealed conditions. The specific steps are as follows: grind and mix polyacrylonitrile (PAN) and sulfur (S) according to the mass ratios of 1:1, 1:1.2, 1:1.5, 1:1.8 and 1:2, ball mill at 450 rpm for 30 minutes to obtain a mixture of polyacrylonitrile and sulfur. Then, Put a certain amount of the mixture into the glass bottle, and transfer the glass bottle to the stainless steel lining of the 25 mL, 50 mL and 100 mL hydrothermal reaction kettle. Sealing with argon gas, the reactor is placed in muffle furnace and heated at a heating rate of 5°/min, and keep for 6-18 hours and obtain polyacrylonitrile/sulfur complex.

2.2 Preparation of Polyacrylonitrile/sulfur Composite Electrode

The prepared PAN/S composite, super P and sodium carboxymethylcellulose(CMC) were mixed evenly according to the mass ratio of 70:20:10, and the mixture was shaken in a micro oscillator (frequency: 35 Hz, shaking time: 15 min). Then, the slurry was evenly coated on the surface of carbon-coated aluminum foil. The obtained diaphragm is dried in vacuum drying oven at 60 ℃ for 12 hours, The electrode plate is obtained by cutting a 1.0 cm diameter diaphragm, which is used as the positive electrode to assemble CR2016 button battery. The electrolyte used is 1M $LiPF_6$/PC-EC-DEC (1:4:5, v/v/v).

3. RESULTS AND DISCUSSION

3.1 Optimization Ratio of Polyacrylonitrile and Sulfur

As shown in Figure 1, the SEM photos of PAN/S composites prepared with different raw material ratios are shown. It can be seen from the figure that the morphology of PAN/S composites prepared by different raw material ratios is basically the same, and the particle size is 0.2-1 μm.

In order to investigate the distribution of sulfur in the composites, we take PAN/S composites with raw material ratio of 1:1.5 as the research object, and scan them by energy dispersive spectroscopy (EDS). Figure 1 (d) is a high-power SEM photograph of the selected area. Figures 1 (e) and (f) show the distribution of corresponding carbon and sulfur elements, and the bright spots in the figure represent the scanned elements. From the photo, we can see that the sulfur element is evenly distributed in the whole region, so it can be considered that the sulfur is homogeneously dispersed in the composite product structure.

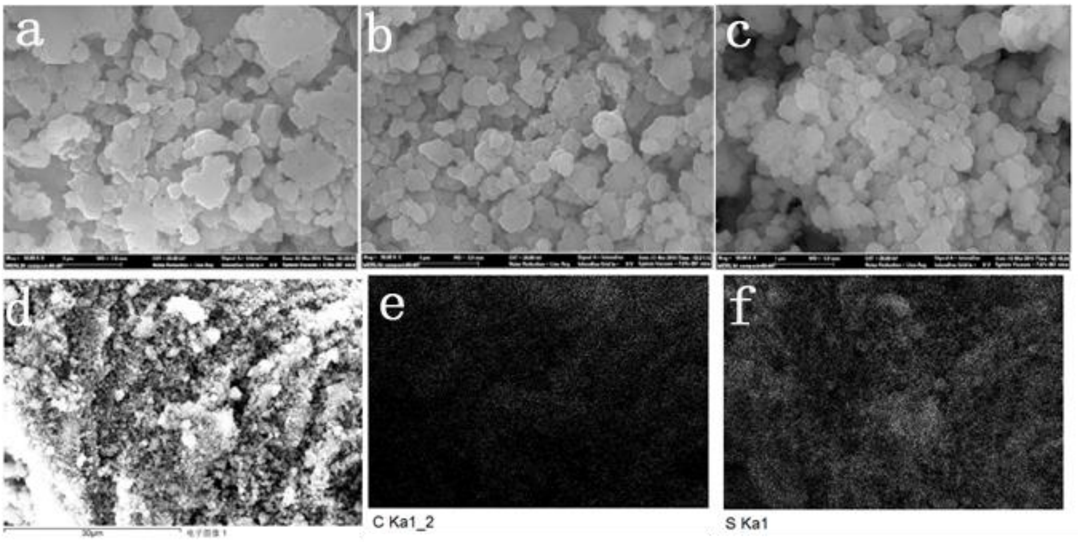

Figure 1. SEM photos of PAN/S composites based on different raw material ratio, (a) PAN: S=1:1, (b)PAN: S= 1:1.5, (c)PAN: S= 1:2, (d) SEM images of microzone and distribution images of carbon (e) and sulfur (f) in PAN/S composites with material ratio of 1:1.5

Figure 2 shows the X-ray diffraction spectra of PAN/S composites prepared with different raw material ratios, polyacrylonitrile (cPAN) cyclized in air at 300 ℃ and sublimated sulfur. It can be seen that the elemental sulfur has sharp diffraction peaks within the scanning range, indicating that the sublimated sulfur exists in crystalline form. cPAN only appears a broad diffraction peak which is located at 2θ of near 25°, indicating that cPAN exists in amorphous form. In the ratio range studied, the composites show similar diffraction characteristics to cPAN, but their diffraction peak intensity is weaker, and the characteristic diffraction peak of sulfur disappears, indicating that sulfur exists in amorphous form or highly dispersed in PAN/S composites structure in bonding form.

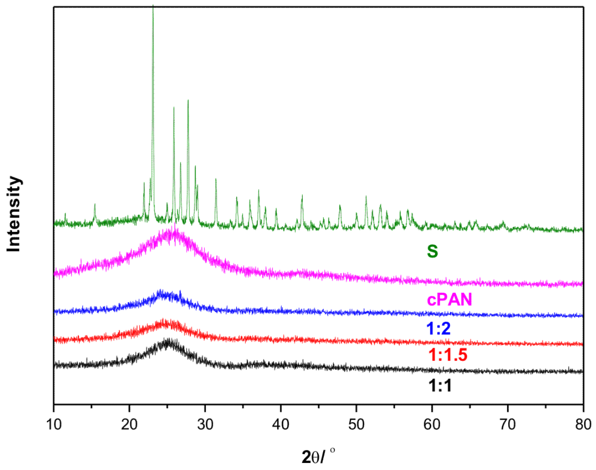

Figure 2. XRD patterns of sublimated sulfur, cyclized polyacrylonitrile (cPAN) and PAN/S composites based on different raw material ratios

Table 1 shows the elemental analysis results of PAN/S composites. The data in the table showed that sulfur content in PAN/S composites with raw material ratios of 1:1, 1:1.2, 1:1.5, 1:1.8 and 1:2 are 37.5 wt %, 40 wt %, 47.7 wt %, 52.3 wt % and 56.7 wt %, respectively. According to literature[16], the structure of PAN can be expressed as $(C3NH3)_n$, whose the nitrogen/carbon atom ratio is 1:3, but the ratio of nitrogen to carbon atoms in the composite is still 1:3 after heating, so it was believed that the polymer skeleton did not decompose during the composite process. By comparing the mole ratio of carbon to hydrogen of the composite with different ratio of raw materials, it was found that the hydrogen content in the reaction products decreased with the increase of sulfur content in the raw materials, indicating that sulfur partially replaced hydrogen on the polyacrylonitrile. When the initial ratio of raw materials was 1:1.8 and the sulfur content in the composite was 52.3wt%, the molar ratio of carbon to hydrogen in the reaction product reaches the maximum, indicating that the substitution of hydrogen does not increase with the increase of sulfur content, which proved to a certain extent that there are limited sites for bonding reaction on PAN. Excess shall be in the form of elemental sulfur exist in composite materials[17].

Table 1. Contents of elements in PAN/S composites prepared with different raw material ratios

PAN-S mixture ratio	Mass percentage of elements in Composites(%)				Molar ratio of elements in Composites(mol/mol)	
	S	C	N	H	C/N	C/H
1:1	37.5	44.8	16.4	1.45	3.187	2.575
1:1.2	40	42.8	16	1.15	3.121	3.101
1:1.5	47.7	37.5	14	0.78	3.125	4.006
1:1.8	52.3	34.1	12.9	0.69	3.084	4.118
1:2	56.7	31.1	11.6	0.63	3.128	4.114

In order to investigate the effect of raw material ratio on the properties of composites, we compared the cyclic voltammetry behavior, charge discharge behavior and cyclic properties of composites with different sulfur content.

Figure 3 showd the cyclic voltammetric curves of PAN/S composites with sulfur contents of 47.7 wt % (a) and 56.7 wt % (b) in 1 M $LiPF_6$/PC-EC-DEC electrolyte. It can be seen from figure 3 (a) that the composite with sulfur content of 47.7 wt % has a reduction peak at 1.4 V in the first week, and the corresponding electrochemical reaction is the breaking of polysulfide bond on the sulfide polyacrylonitrile chain segment to form pyridine ring polymers without sulfur bonding and lithium sulfide. Subsequently. There is an oxidation peak appears at 2.35 V, corresponding to the re formation of polysulfide bonds on the polymer segments. The redox reaction process is shown in figure 4. As the cycle continues, the reduction peak shifts forward and is divided into two peaks, corresponding to the electrochemical reaction process of sulfur conversion to $–S_xLi$ ($2<x\leq6$) and finally to Li_2S. In addition, the current of charge-discharge is almost unchanged, indicating that the electrode has good stability[18].

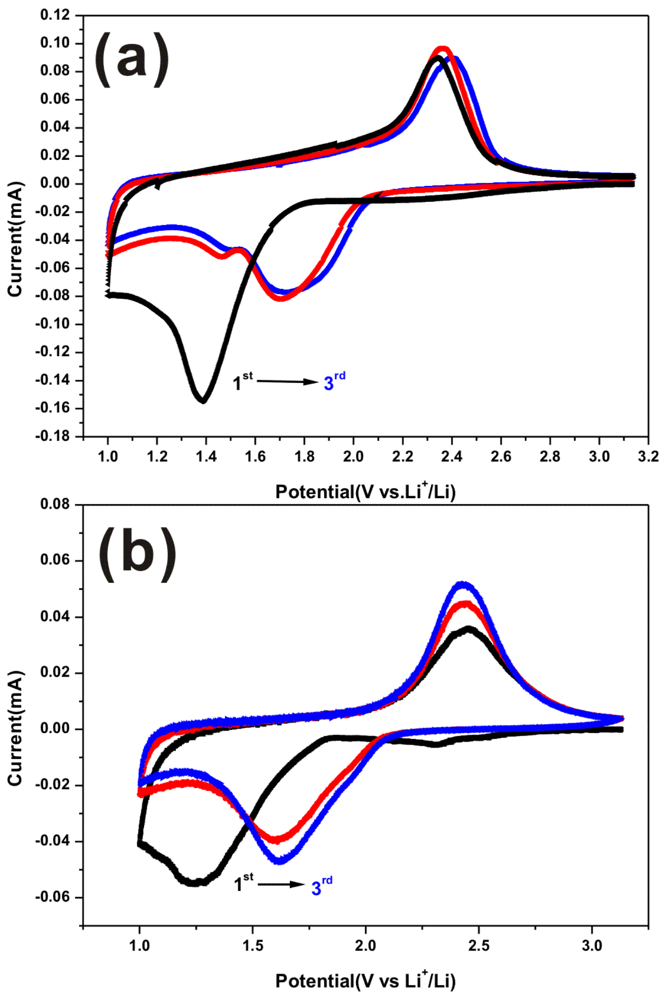

Figure 3. Cyclic voltammetry curves of PAN/S composites with sulfur content of 47.7 wt % (a) and 56.7 wt % (b), Electrolyte: 1 M $LiPF_6$/PC-EC-DEC, Scanning potential range: 1-3 V, Scanning rate: 0.1 mV/s

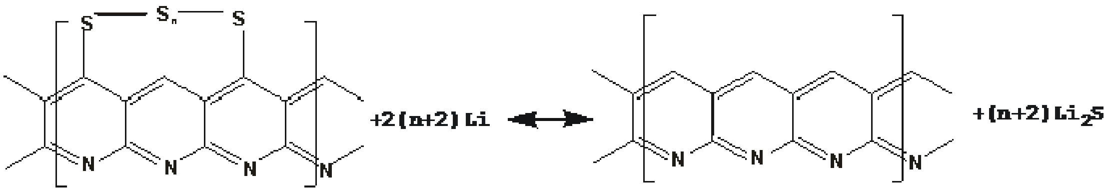

Figure 4. Electrochemical reaction mechanism of PAN/S composites

As can be seen from figure 3 (b), the composite with sulfur content of 56.7 wt% shows a cyclic voltammetric behavior different from that shown in figure 3 (b). In the first cycle, the reduction peak potential is lower at 1.25 V, and the oxidation potential is higher at 2.45 V, indicating that the electrochemical polarization of the composites with 56.7 wt % sulfur content is greater. In addition, during the first week of cathode scanning, a new reduction peak appeared at 2.3 V, corresponding to the reduction of surface elemental sulfur in the composite. Therefore, it is believed that in the composite with sulfur content of 56.7 wt%, sulfur exists in both bonded form and elemental sulfur form[19].

Figure 5 shows the charge-discharge curve (figure 5 a-e) and cycle performance (figure 5 f) of PAN/S composites with different sulfur content. It can be seen that the discharge behavior of PAN/S composites is different from that of carbon/sulfur composites. There is no obvious platform during charge-discharge, and the first discharge voltage is low, the capacity is mainly distributed below 1.8 V, and the charging voltage platform is about 2.1 V. From the second cycle, the discharge voltage increased significantly and the charging voltage platform decreased slightly. As the cycle continues, the voltage of the charge-discharge platform remains basically stable. The reason for the low voltage of first cycle discharge may be that the composites need higher activation energy to break the sulfur bonds and produce greater polarization[20].

Comparing the first cycle discharge curves of composites with different sulfur content (except 56.7 wt %), it can be seen that with the increase of sulfur content, the first cycle discharge voltage platform gradually increases from 1.5 V to 1.8 V, while the charging voltage platform basically remains at 2.1 V, indicating that the polarization of the composite electrode gradually decreases during the first cycle charge-discharge process. The possible reason is that with the increase of sulfur content, the cyclization degree and conjugation degree of the composite are higher, so the conductivity of the composite is improved and the polarization of the corresponding electrode is reduced. As can be seen from Figure 5 (e), for the composite with sulfur content of 56.7 wt %, a short platform appears at about 2.3 V during the first cycle discharge, which corresponds to the electrochemical reduction of surface elemental sulfur in the composite, which is consistent with its cyclic voltammetry scanning results[19]. Therefore, we believe that when the sulfur content is higher than 56.7 wt %, there is more elemental sulfur on the surface of the composite. As can be seen from Figure 5 (f), PAN/S composite with sulfur content of 47.7 wt % has both high specific capacity and high cycle stability. At 100 mA g^{-1} current density, the first cycle discharge specific capacity is 856 mAh g^{-1} and the charging capacity is 678 mAh g^{-1}(calculated by the total mass of the composite). After 50 cycles, the reversible capacity remained at 629 mAh g^{-1}. The reversible capacity is 584 mAh g^{-1} after 100 cycles, and the corresponding capacity retention rate was as high as 86.1%.

With the increase of sulfur ratio in raw materials, the composites show higher reversible capacity, but the cycle stability decreases significantly. The specific discharge capacity of the composite with sulfur content of 52.3 wt % in the first cycle is 843 mAh g^{-1}, and the electrode is basically stable in the first 20 cycles. However, the specific capacity of the composite decreases to 523 mAh g^{-1} after 50 cycles. When the sulfur content is 56.7 wt %, the first cycle discharge specific capacity of the composite is 819 mAh g^{-1} and the reversible capacity is 525 mAh g^{-1}. As the cycle continues, the specific capacity of the composites increases gradually at first and then basically stabilizes. After 50 weeks of cycle, the capacity is 588 mAh g-1. The main reason for the above charge-discharge behavior is that when the sulfur content in the raw material ratio is high, part of the sulfur fails to participate in the cyclization, but is deposited on the surface of the composite in the form of elemental sulfur. After the surface sulfur consumption is completed in the electrochemical reaction process, the PAN/S composite with good electrical contact begins to be utilized. However, as the cycle continues, the free elemental sulfur is easy to break away from the conductive structure and enter the electrolyte during the cycle, increasing the viscosity of the electrolyte and hindering the transmission of lithium ions. Therefore, the specific capacity of the composite increases first and then decreases[21].

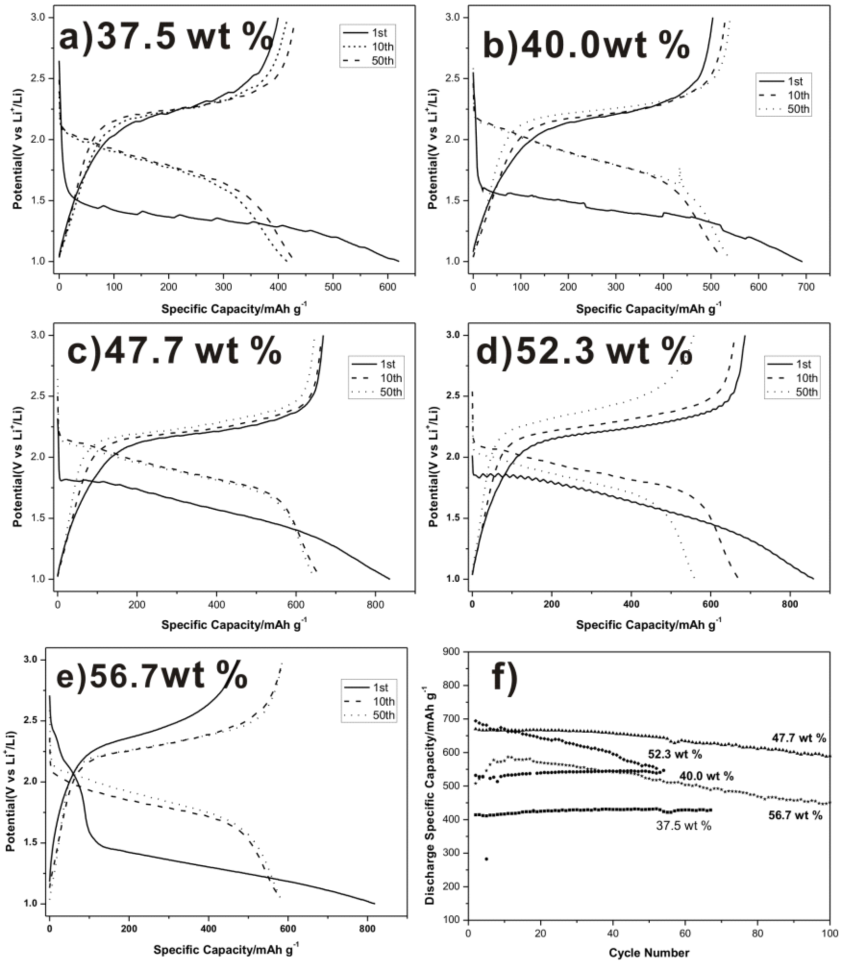

Figure 5. Charge-discharge curve (a-e) and cycle performance curve (f) of PAN/S composite electrode with different sulfur content, electrolyte: 1 M $LiPF_6$/PC-EC-DEC, current density: 100 mA g^{-1}

The above results show that the increase of sulfur content in raw material ratio is conducive to the cyclization of PAN and promote the utilization of active substances. However, the remaining free elemental sulfur has a certain passivation effect on the electrochemical utilization of the composites. Therefore, it is very important to select the appropriate raw material ratio to ensure both the full cyclization and vulcanization, and reduce the influence of elemental sulfur on the electrochemical properties of the composites. According to the above research results, we believe that the mass ratio of PAN to S is 1:1.5, which is the optimal raw material ratio.

3.2 Reaction Temperature Optimization

It can be seen from the previous introduction that the vulcanization cyclization of polyacrylonitrile is a complex reaction process[22]. In this work, PAN/S composites are prepared by sealed heating, so the dual effects of reaction temperature on chemical reaction rate and equilibrium movement need to be considered. When the temperature increases, the cyclization reaction rate is accelerated, which is beneficial to the cyclization reaction. However, with the increase of temperature, the partial pressure of H_2S in the reaction product gradually increases, and the equilibrium moves in the opposite direction, which is not conducive to the cyclization reaction. In order to achieve the best cyclization effect, we investigated the effect of reaction temperature on the structure and properties of the composites. The specific method is to select the PAN/S mixture with raw material ratio of 1:1.5 and react at 250 ℃, 300 ℃, 350 ℃, 400 ℃ and 450 ℃ respectively for 12 hours in a sealed high-temperature reactor to obtain PAN/S composites at different temperatures, and characterize the structure and properties of the composites.

The effect of reaction temperature on the electrochemical properties of the composites was investigated. Figure 6 shows the charge-discharge curves and cycle performance of PAN/S composites prepared at different reaction temperatures in 1 M $LiPF_6$/PC-EC-DEC electrolyte. As can be seen from figure 6 (a-e), the charge-discharge curves of the composites are basically the same, a discharge platform appears at about 1.5 V during the first cycle of discharge, corresponding to the electrochemical reduction of bonded sulfur. The corresponding charging voltage platform is 2.25 V. As the cycle continues, the charging voltage is basically unchanged, and the discharge voltage gradually increases to 2.1 V. After 50 cycles, the charge discharge curve remains basically stable.

The PAN/S composites prepared at different temperatures are named PAN/S-250, PAN/S-300, PAN/S-350, PAN/S-400 and PAN/S-450 respectively. It can be seen from figure 6 that the specific discharge capacity of PAN/S-250 composite in the first cycle is 751 mAh g^{-1} and the reversible specific capacity is 514 mAh g^{-1}. After 50 cycles, the specific capacity remains at 467 mAh g^{-1}. The specific discharge capacity of PAN/S-300 is 723 mAh g^{-1} in the first cycle and remains at 505 mAh g^{-1} after 50 cycles. The specific discharge capacity of PAN/S-350 composite is 725 mAh g^{-1} in the first cycle, and remains at 506 mAh g^{-1} after 50 cycles. The specific discharge capacity of PAN/S-400 is up to 810 mAh g^{-1} in the first cycle, and remains at 579 mAh g^{-1} after 50 cycles. The specific discharge capacity of PAN/S-450 composite is 586 mAh g^{-1} in the first cycle, and remained at 412 mAh g^{-1} after 50 cycles. Figure 6 (f) shows the cyclic properties of PAN/S composites prepared at different temperatures. It can be seen from the figure that the composites prepared under all temperature conditions show excellent cycle stability. However, as for the specific capacity, the specific capacity of the composite increases with the increase of temperature. When the temperature reaches 400 ℃, the composite has the highest specific capacity. However, when the temperature rises to 450 ℃, the specific capacity of the complex begins to decrease again. The reason for this phenomenon may be that with the gradual increase of temperature, the internal pressure of high-temperature reactor increases gradually, which speeds up the cyclization reaction rate of PAN. When the temperature is 450 ℃, the increase of internal pressure of reaction product at the same time the partial pressure of H_2S is also obvious increase, resulting in a decline in cyclization degree and thus results in the decrease of the capacity of the composite materials[22].

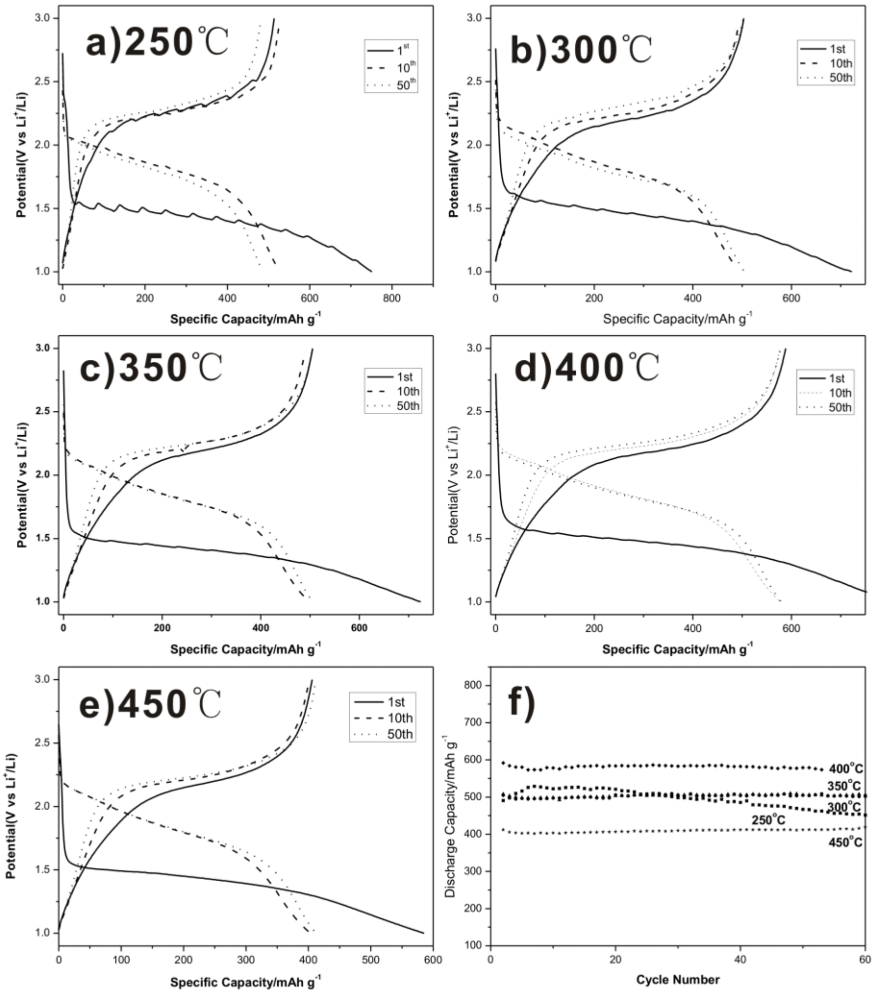

Figure 6. Charge-discharge curves (a-e) and cycle performance (f) of composites prepared at different temperatures, a-e correspond to 250 ℃, 300 ℃, 350 ℃, 400 ℃ and 450 ℃ respectively

In conclusion, the reaction temperature has a dual effect on the reaction rate and equilibrium of the reaction system. The results show that in the sealed autoclave, the optimal reaction temperature of PAN and S is 400 ℃. Considering the design temperature of high-temperature hydrothermal reactor, we still choose 300 ℃ as the reaction temperature in the following research.

3.3 Reaction Time Optimization

In the process of PAN cyclization, with the extension of reaction time, on the one hand, the cyclization is more thorough, on the other hand, continuous heating may destroy the polymer chain segments, thus affecting the properties of the composites. Therefore, we investigate the effect of reaction time on the electrochemical properties of the composites. In the experiment, the mixture with raw material ratio of 1:1.5 is used, and the corresponding composites are obtained by holding for 6 h, 12 h and 18 h at 300 ℃ in a high-temperature hydrothermal reactor. Figure 7 (a-c) shows the charge-discharge curves of composites prepared at different heat treatment time. It can be seen that the reaction time does not affect the shape of the charge-discharge curve.

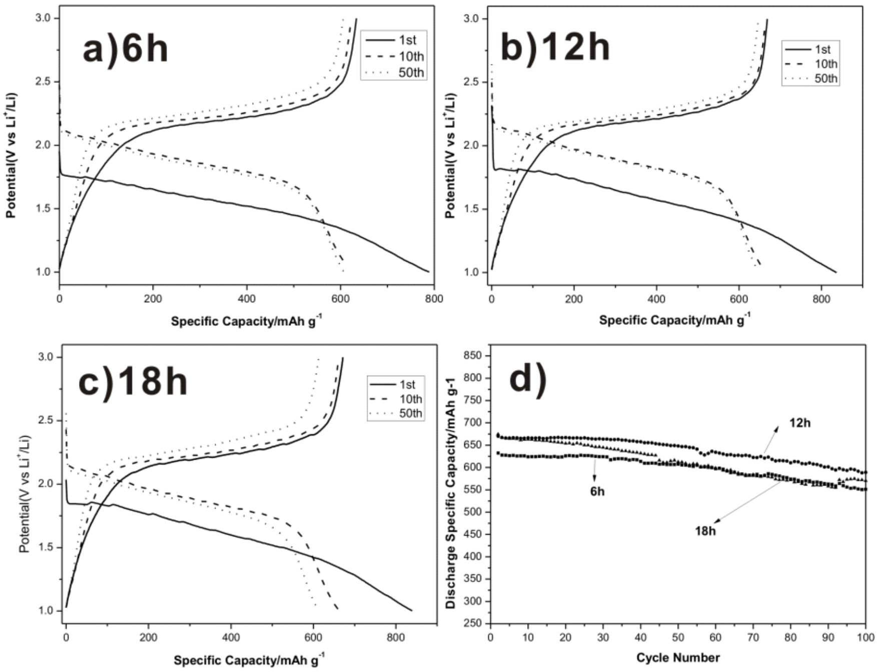

Figure 7. Charge-discharge curves (a-c) and cycle performance (d) of PAN/S composites prepared at different heat treatment times, a-c corresponds to the heat treatment temperature of 6 h, 12 h and 18 h respectively

Figure 7 (d) shows the cycle performance of composites prepared at different heat treatment time. The composites prepared with heat treatment time of 6 h, 12 h and 18 h are expressed as PAN/S-6, PAN/S-12 and PAN/S-18 respectively. The specific discharge capacity of the composite PAN/S-6 in the first cycle is 789 mAh g^{-1}, and the specific capacity remains 607 mAh g^{-1} after 50 cycles. The specific discharge capacity of PAN/S-12 is 836 mAh g^{-1} in the first cycle and 648 mAh g^{-1} after 50 cycles. The specific discharge capacity of PAN/S-18 is 840 mAh g^{-1} in the first cycle, and remained 612 mAh g^{-1} after 50 cycles. The above results show that the specific capacity of the composites increases first and then decreases with the extension of heat treatment time. When the reaction time is 12 h, the composites show both high specific capacity and high cycle performance. It may be because the heat treatment time is short and the cyclization is insufficient, so part of the sulfur cannot be utilized. When the heat treatment time is too long, although the specific capacity of the electrode is high in the first cycle, that is, the utilization rate of sulfur is high, the cycle performance of the electrode is poor due to the reduced stability of the chain structure of PAN/S composite[23]. The above results show that the optimal heat treatment time is 12 h.

3.4 Volume Optimization of Reaction Vessel

When the mass of reactants and reaction temperature are fixed, the volume of reaction vessel directly affects the pressure of reaction system. Therefore, it is an important factor affecting the rate and equilibrium of polyacrylonitrile cyclization. In order to explore the effect of the volume of the reaction vessel on the electrochemical properties of the composite products, we use the PAN-S mixture with the ratio of 1:1.5 to react in 25 ml, 50 ml and 100 ml high-temperature hydrothermal reactors at 300 ℃ for 12 hours to obtain the corresponding composites. The sulfur contents of the three products are 50.1 wt %, 47.7 wt % and 47.6 wt %, respectively.

Figure 8 shows the charge-discharge curves (a-c) and cycle performance (d) of the composite prepared in different volume containers. The composites prepared in 25 mL, 50 mL and 100 mL containers are expressed as PAN/S-25, PAN/S-50 and PAN/S-100 respectively. It can be seen from Figure 8 (a-c) that the charge-discharge curves of composite materials PAN/S-50 and PAN/S-100 are basically the same as those described above. During the first cycle discharge of composite PAN/S-25, a discharge platform appears at about 1.6 V, and the first cycle charging voltage platform is about 2.25 V. When entering the second cycle of charge and discharge, the charging voltage is basically unchanged, and the discharge voltage gradually increases to 2.1 v. As the cycle continues, the charging voltage increases and the discharge voltage decreases, indicating that the polarization of PAN/S-25 composites is becoming more and more serious, accompanied by the rapid attenuation of capacity.

It can be seen from Figure 8 (d) that the specific discharge capacity of PAN/S-25 in the first cycle is 831 mAh g^{-1} and 392 mAh g^{-1} after 29 cycles. The specific discharge capacity of PAN/S-50 is 836 mAh g^{-1} in the first cycle, 648 mAh g^{-1} after 50 cycles and 589 mAh g^{-1} after 100 cycles. The specific discharge capacity of PAN/S-100 is 794 mAh g^{-1} in the first cycle and 585 mAh g^{-1} after 100 cycles. The results in the figure show that with the increase of the volume of the reaction vessel, the specific capacity of the composite first increases and then basically remains unchanged, but the cycle stability gradually improves. The reason may be that with the increase of the volume of the reaction vessel, the partial pressure of H_2S in the reaction product decreases, and the vulcanization reaction balance moves to the right, which promotes the reaction between sulfur and polyacrylonitrile chain segment, so that the product has richer sulfur-carbon bonds and sulfur-sulfur bonds. Therefore, the cycle performance of the composite sulfur electrode can be significantly improved. When the volume of the reaction vessel continues to increase to 100 mL and the cycle cycle is long, it can be found that the specific capacity of PAN/S-50 and PAN/S-100 tends to be the same, which may be because the PAN of the two systems has reached the fully cyclized state, so the cycle stability of the two composites is almost the same[23].

In conclusion, the volume of reaction vessel affects the properties of composite products by changing the equilibrium of vulcanization reaction. The experimental results show that increasing the volume of the container can improve the cyclic stability of the reaction products to a certain extent.

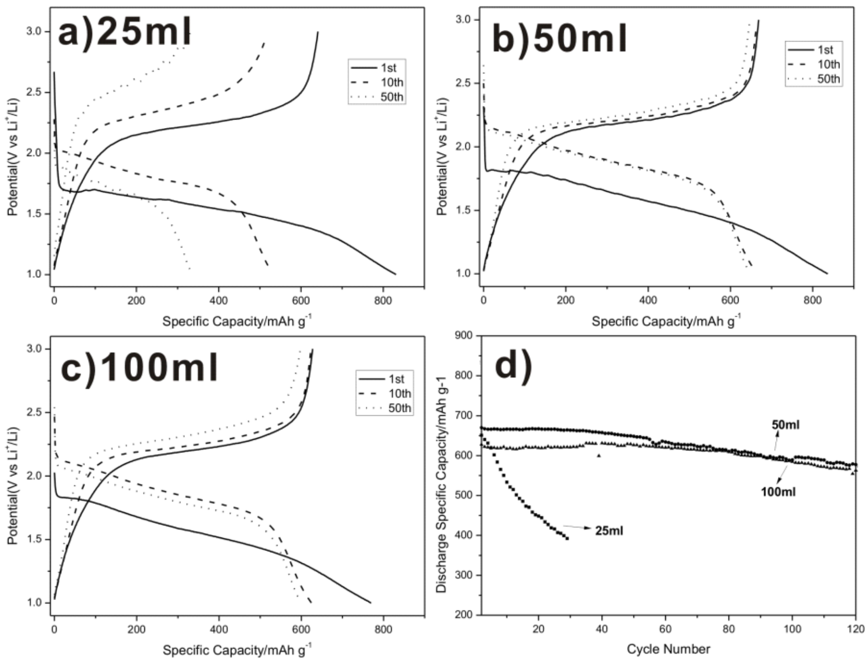

Figure 8. Charge-discharge curves (a-c) and cycle performance (d) of the composites prepared in reaction vessels of different volumes, the corresponding container volumes of a-c are 25 mL, 50 mL and 100 ml respectively

Table 2. Comparison of electrochemical performance of sulfur electrodes

Cathode	The calculation of specific capacity	Initial discharge capacity(mAhg^{-1})	Stable discharge capacity after 50 cycles(mAhg^{-1})	Rate (mAg^{-1})	Reference
PAN-S	Composite mass	~850	~600	0.2 mAcm^{-2}	[24]
PAN-S (as prepared)	Composite mass	~856	~628	100	This work

As shown in Table 2, the PAN-S composite prepared by PAN-S mixture with raw material ratio of 1:1.5 and holding at reaction temperature of 300 ℃- 400 ℃ for 12 hours in large volume of reaction vessel. The PAN-S composite prepared by heating at 300℃ for 6h[24]. 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 composite as prepared is 836 mAhg^{-1} in first cycle and 648 mAhg^{-1} after 50 cycles. This is mainly due to the optimization of preparation conditions. It indicates that optimization of raw material ratio, treatment temperature and time, the volume of reaction vessel can improve the electrochemical performance of PAN-S composite electrode materials.

4. CONCLUSION

In this work, the effects of raw material ratio, reaction temperature, reaction time and reaction vessel volume on the structure and properties of PAN/S composites are studied. The results show that PAN/S composites prepared by PAN-S mixture with raw material ratio of 1:1.5 and holding at reaction temperature of 300 ℃ - 400 ℃ for 12 hours in a high-temperature reactor with 50mL vessel have the best properties. Based on the total mass of the composite, the initial discharge specific capacity of the composite is 856 mAh g^{-1} and the reversible specific capacity is 678 mAh g^{-1}. After 100 cycles, the specific capacity is stable at 584 mAh g^{-1}, and the capacity retention rate is 86.1%.

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