A wet-laid carbon paper with 3D conductive structure as an interlayer for lithium-sulfur batteries

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Abstract

Using conductive interlayers to act as the ‘upper current collector’ is a common strategy to suppress the shuttle effect in lithium-sulfur batteries. However, the current widely used interlayers generally have the disadvantages of poor conductivity and complicated fabrication. Herein, we report a novel carbon paper prepared by simple wet laid method. The as-prepared carbon paper exhibits excellent conductivity of 11.9 S cm\(^{-1}\) and 3D conductive structure. Finally, the carbon paper as an interlayer for lithium-sulfur batteries displays an initial capacity of 1091 mAh g\(^{-1}\) at C/5 rate, and remains 631 mAh g\(^{-1}\) after 200 cycles with a decay rate of 0.21% per cycle.

1. Introduction

Significant improvements to the lithium-sulfur batteries have emerged in recent years, primarily due the high theoretical specific capacity (1675 mAh g\(^{-1}\)), low cost, abundance of sulfur and environment friendly of lithium-sulfur batteries [1]. Lithium-sulfur batteries now are widely considered as one of the promising candidate for next-generation electrochemical systems. However, there are still many problems that hinder the commercialization of lithium-sulfur batteries. Those problems can be summarized as: (1) poor ionic and electronic conductivities of sulfur and its various discharge products, (2) volume expansion of sulfur cathode, (3) the growth of lithium dendrites of lithium anode, and (4) the shuttle effect. Among these problems, the shuttle effect caused by soluble lithium polysulfides (LiPSs) is considered as the most intractable problem [2]. Soluble lithium polysulfides formed in the electrochemical process can dissolve into the organic solvent of electrolyte, which may cause irreversible capacity fade. Worse still, lithium polysulfides dissolved in electrolyte can migrate to the lithium anode side, and form Li2S2 or Li2S by reacting with lithium, leading to severe self-discharge [2–4].

In the past, many approaches have been proposed to solve the shuttle effect [5, 6]. One common strategy is using modified cathode materials, such as micro/mesoporous carbon or hierarchical carbon as host materials for sulfur. Porous carbon as host material can impart good conductivity to the sulfur cathode, thus overcoming the shortcomings of poor conductivity of sulfur. Meanwhile, porous structure not only can accommodate volume expansion of sulfur, but also confine the sulfur, therefore suppress the shuttle effect [7, 8]. Previous works indicate that modified sulfur cathode can significantly improve the electrochemical performance of lithium-sulfur batteries. However, low sulfur loading and complicated fabrication process hinder the large-scale application of these composite sulfur cathode materials.

Recently, using modified separator or interlayer to suppress the shuttle effect and improve the electrochemical performance of lithium-sulfur batteries is considered to be a viable approach [9]. Polypropylene separator modified with conductive carbon [10], porous carbon [11], metal [12], metal oxides [13], and sulfides [14] was reported. Among these strategies, the use of conductive carbon materials as interlayers has received extensive attention for they can effectively improve the performance of lithium-sulfur batteries both by absorbing and reactivating the LiPSs [15, 16]. Some methods were reported for preparing conductive carbon interlayers, such as microporous carbon films [17, 18], electrospinning carbon clothes [19], and carbonized carbon papers [20, 21]. Microporous carbon itself has no binding force, thus a large amount of binder is needed in the process of preparing the
microporous carbon film, which affects the conductivity of microporous carbon films, increases the cost and difficulty of preparation process. Electrospinning carbon clothes and carbonized carbon papers both need the high-temperature carbonization treatment of the raw materials, thus suffering low yield, high cost and poor strength. Worse still, the carbon materials produced by carbonization generally have the disadvantage of poor conductivity, unless further ultrahigh-temperature graphitization process is taken. Therefore, a simple and effective way for preparing the conductive carbon interlayer is currently urgently needed.

Wet laid method is to uniformly disperse the fibers in the dispersion medium, followed by filtration and drying processes to achieve fabrics or films. Wet laid method is considered to be a simple, large-scale approach for preparing fibrous porous materials, which is widely used in the fabrication of paper, alkaline battery separator [22], lithium-ion battery separator [22–25], super capacitor separator [26] and fuel cell gas diffusion layer [27]. However, up to now no study focusing on using wet laid method to prepare conductive carbon paper as interlay for lithium-sulfur batteries was reported. Therefore, in this work, commercial carbon fiber was used and the simple fabrication of carbon paper via wet laid method was reported. The extremely high conductivity and 3D structure of the as-prepared carbon paper can effectively reduce the interface resistance and adsorb electrolyte. Thus, using as-prepared carbon paper as interlayer can effectively improve the electrochemical performance of the lithium-sulfur battery.

2. Experimental

2.1. Carbon paper fabrication

The Tenax™-A, HT C124 type commercial carbon fiber was purchased from Kumiai Chemical Industry CO.,Ltd with a cut length of 3 mm. The VPB 105–2 poly(vinyl alcohol) fiber was purchased from Kuraray China Co.,Ltd. The cut length and thickness of the poly(vinyl alcohol) is 4 mm and 1.17 dtex, respectively. The carbon paper was produced by the No.2542-A Automatic Sheet Former (Kumagai Riki Kogyo CO.,Ltd). Generally, 95% commercial carbon fiber and 5% poly(vinyl alcohol) fiber were uniformly mixed in an aqueous suspension, and randomly laid down on a 100 mesh screen belt. After filtration process, the as-prepared wet paper sheet was transferred and dried at 90°C using a plate dryer to make sure the poly(vinyl alcohol) fiber fully swelled in the water to act as the binder. The grammage of the as-prepared carbon fiber paper were measured to be 39.8 g m⁻².

2.2. Characterization

The morphology and the conductivity of the sample was characterized by scanning electron microscopy (SEM, Phenom) and four-probe method, respectively. The element mapping of carbon paper and separator was collected by energy dispersive spectrometer (EDS) Quantax400. Raman spectra were collected by LabRAM Aramis.

The thickness of the carbon paper was measured by Lorentzen and Wettre Micrometer 250 instrument. According to ISO standard 534–2005, by applying a pressure of 100 ± 10 kPa to the carbon paper, the thickness was measured by the sensor with an accuracy of 0.1 μm. The pore size of the carbon paper was tested using a capillary flow porometer (CFP100A, PMI, USA). The capillary flow porometer is based on liquid extrusion method. Generally, the carbon paper was first filled with the test liquid Porewick™, then subjected to gas pressure. As the pressure increases, the flow rate of the gas and the pressure date are simultaneously recorded. The pore size was calculated based on equation (1):

\[
D = \frac{4γ \cos θ}{p}
\]  

Where D is the pore diameter; γ is the surface tension of the test liquid; θ is the contact angle between fiber and test liquid; p is the pressure, respectively.

2.3. Battery assembly

Li–S batteries containing commercial separator (Celgard 2500) and carbon paper interlayer were assembled by using 2032 coin-type cells in a glove box. The sulfur slurry was prepared by mixing sulfur (70 wt%), conductive ketjen black (20 wt%) and polyvinylidene fluoride (PVDF 10 wt%) binder in N-methyl pyrrolidinone (NMP) solvent, the slurry was then coated onto the carbon-coated aluminum foil, following by dried at 60 °C overnight. The sulfur mass loading of the electrodes was about 1.7 mg cm⁻². The electrolyte was 1,2-dimethoxyethane (DME) and 1,3-dioxacyclopentane (DOL) with a volume ratio 1:1 containing 1 M LiTFSI and 0.1 M LiNO₃. The amount of electrolyte was about 30 μL mg⁻¹.

2.4. Performance evaluation

Galvanostatic charge/discharge tests were performed with a LAND CT2001A battery-testing instrument in the potential range of 1.7–2.6 V. The cyclic voltammetry (CV) test was conducted with a scan rate of 0.1 mV s⁻¹ in a
potential range of 1.5V–3.0 V using CHI660E electrochemical workstation. The electrochemical impedance spectroscopy (EIS) test was conducted using electrochemical workstation with an amplitude of 5 mV and the frequency range from $10^{-2}$ to $10^5$ Hz.

3. Results and discussion

The interactive force between conductive carbons are relatively low. Thus, a large amount of binders are needed to make conductive carbon films or papers, and these materials commonly suffers the disadvantage of poor foldability. However, the as-prepared carbon paper made of 95% carbon fiber and only 5% poly(vinyl alcohol) binder fiber shows good flexibility, which can be seen from the digital images (figure 1(a)). Generally, physical entanglement between carbon fibers and the excellent adhesion effect of poly(vinyl alcohol) fibers contributes to the good foldability of carbon paper. The surface and cross section SEM images of carbon paper (figures 1(b) and (c)) were collected to observe the microstructure of the carbon paper. It is seen from the SEM pictures that the carbon fiber is cylindrical with a diameter of 7 μm, and the poly(vinyl alcohol) fiber is flake-shaped which uniformly dispersed between carbon fibers. The thickness of the carbon paper observed from the cross section SEM image is about 450μm. And the thickness of the carbon paper measured by L&W micrometer is 322μm. Moreover, the porous carbon paper also has 3D conductive
structure and abundant pore structure. Which was also confirmed by the pore size distribution of the carbon paper, as shown in figure 1(d). The pore size of the carbon paper ranges from 1.51 to 78 μm, and the mean flow pore diameter is 30.95 μm. The Raman spectrum of the carbon paper (figure 1(e)) shows two peaks at about 1355 and 1590 cm⁻¹, corresponding to the D bond and G bond, respectively. The intensity ratio of I_D/I_G is 0.94, indicating the graphite structure of the carbon fiber. Which is further confirmed by the excellent electrical conductivity of the carbon paper of 11.9 S cm⁻¹, measured by four-probe method. The porous structure enables the carbon paper maintaining electrolyte and improving contact of the cathode side. Meanwhile, the 3D conductive network of carbon fibers promotes the electron transfer and reduce the reaction impedance of the sulfur cathode. Thus, the simple and easy fabrication carbon paper with porous structure and 3D conductive network is expected to be used in large-scale applications in lithium-sulfur batteries.

Figure 2(a) shows the cyclic voltammetry profile of the cell with carbon paper interlayer for the first five cycles. Two overlapped anodic peaks at around 2.39 V and 2.44 V, and two cathodic peaks at around 2.00 V and 2.32 V were observed, which refers to typical lithium-sulfur batteries. The cathodic peak located at 2.32 V corresponds to the reduction of sulfur to long-chain LiPS, and the peak located at 2.00 V attributes to the reduction of long-chain LiPS to Li₂S₂ and Li₂S. In addition, the overlapped anodic peaks at 2.39 V and 2.44 V are assigned to the oxidation of the Li₂S₂ and Li₂S to sulfur. The lower cathodic peaks were observed in the first cycle,
which may due to the rearrangement and migration of the active material [17]. The voltage gap of the cell with carbon paper is only 0.44 V, indicating excellent reactivity and little polarization of the cell. Furthermore, the curves for last four cycles are almost overlapped, indicating good cycle stability of the cell. Mainly due to the porous structure and 3D conductive network of carbon paper interlayer.

Figures 2(b) and (c) shows the galvanostatic charge-discharge curves of the lithium-sulfur batteries with or without carbon paper interlayer, respectively. Both curves have two typical discharge platforms at about 2.3 V and 2.05 V. Moreover, the initial discharge specific capacity of the cell with carbon paper interlayer is 1091 mAh g⁻¹, which is 161 mAh g⁻¹ higher than that of the battery without carbon fiber paper. The discharge capacity of the cell with carbon paper interlayer is retained of 694 mAh g⁻¹ after 100 cycles, whereas the capacity of the cell without carbon paper is only 480 mAh g⁻¹. Indicating that the use of carbon paper interlayer can significantly improve the utilization efficiency of sulfur, thus slow down the capacity attenuation.

Figure 2(d) presents the cycling stability performance of Li-S batteries with or without carbon paper interlayer at C/5 rate up to 200 cycles. The cell with carbon paper interlayer delivered a discharge capacity of 631 mAh g⁻¹ after 200 cycles at C/5 rate, which is 52% higher than that of the cell without carbon paper interlayer. Meanwhile the decay rate of the cell with carbon paper interlayer is only 0.21% per cycle. It indicates that the carbon paper interlayer can significantly improve the cycling performance. Mainly due to the 3D conductive structure of the carbon paper allows electrons to move freely between the cathode and the interlayer, significantly reducing the interface resistance of the cathode [28].

Figure 2(e) shows the rate performance of the cell with and without carbon paper interlayer. Both cells presented similar capacity at C/10, C/5, C/2 rate, but the cell with carbon paper interlayer exhibited better capacity retention at 1 C and 2 C rate. Which may due to the excellent conductivity of the carbon paper improves the conversion kinetics of the LiPSs [15]. Figure 2(f) shows the electrochemical impedance spectra of the cells with and without carbon paper interlayer. The smaller impedance of the cell with carbon paper interlayer is generally caused by the porous structure which helps maintain electrolyte and the 3D conductive network which helps improving kinetics for the conversion of active materials.

The SEM images and corresponding EDS element maps of carbon paper and separator after 100 cycles at 1 C and stopped at charged state are shown in figure 3. The carbon paper still retains pore structure after 100 cycles, meanwhile the sulfur element signal is spread all over the carbon paper and distributed homogenously, which guarantees a superior utilization of sulfur. Simultaneously, the sulfur element signal of the separator from the
Table 1. Some conductive interlayers researched in recent years and their electrochemical properties.

| Interlayer                        | S loading mg/cm² | Initial capacity mAh/g⁻¹ | Cycle number | Capacity retention mAh/g⁻¹ | Decaying rate %/per cycle | Rate/C | Reference  |
|-----------------------------------|------------------|--------------------------|--------------|----------------------------|----------------------------|--------|------------|
| Carbonized filter paper           | —                | 1500                     | 50           | 810                        | 0.92                        | 0.2    | [21]       |
| Carbonized regenerated silk nanofiber | 2.0             | 1164                     | 200          | 799                        | 0.16                        | 0.2    | [29]       |
| Free-standing MWCNT paper         | —                | 1446                     | 50           | 962                        | 0.67                        | 0.2    | [15]       |
| Treated Toray carbon paper        | —                | 1651                     | 50           | 900                        | 0.91                        | 0.2    | [28]       |
| Carbonized waste cotton cloth     | 2.0              | 1112                     | 200          | 743                        | 0.17                        | 0.2    | [30]       |
| Carbonized waste newspaper        | 3.0              | 1295                     | 100          | 770                        | 0.83                        | 0.1    | [31]       |
| Carbonized cellulose paper        | —                | 961                      | 130          | 830                        | 0.10                        | 0.2    | [32]       |
| Carbon paper                      | 1.7              | 1091                     | 200          | 631                        | 0.21                        | 0.2    | This work  |
cell with carbon paper interlayer after 100 cycles is clearly less than the separator from the cell without carbon paper interlayer. The less sulfur element signal occurred on the separator from the cell with carbon paper interlayer also demonstrate the inhibition function of the shuttle effect by the carbon paper. Table 1 shows some conductive interlayers researched in recent years and their electrochemical properties. The carbon paper provided in this paper has a lower capacity retention, but it has a relatively lower decaying rate. Otherwise, the carbon paper prepared by papermaking method has advantages of low cost, easy to fabricate, and high conductivity. Therefore, using the carbon paper prepared by papermaking method as an interlayer is still a promising approach for improving lithium sulfur batteries.

4. Conclusion

In summary, a novel carbon paper with excellent electrical conductivity of 11.9 S cm$^{-1}$ has been successfully prepared through simple wet-laid method. The use of the carbon paper as interlayer for lithium-sulfur batteries can achieve high initial capacity of 1091 mAh g$^{-1}$ at C/5, and maintain of 631 mAh g$^{-1}$ after 200 cycles (0.21% capacity fade per cycle). The excellent conductivity of the carbon paper can effectively reduce the interface impedance of lithium-sulfur batteries. Therefore, the carbon paper can significantly improve the performance of lithium-sulfur batteries, providing a new strategy for the development of lithium-sulfur batteries.

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