# Multifunctional separator with porous carbon/ multi-walled carbon nanotube coating for advanced lithium-sulfur batteries

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# Abstract

An issue associated with lithium sulfur (Li-S) battery is the polysulfide dissolution, leading to the serious crossover of polysulfide to Li anode. To address this issue, this paper reports on a multifunctional separator prepared by introducing porous carbon / multi-walled carbon nanotube (PC/MWCNT) into a commercial one. It shows that the PC/MWCNT composite is able to enhance the interfacial interaction between coating and polysulfide and provide a large surface area for absorbing polysulfide, and thus improving the electrical conductivity. It has been demonstrated that the Li-S cell constructed with the PC/MWCNT composite separator results in a reversible capacity of as high as 659 mAh g<sup>-1</sup> after 200 cycles at 0.5 C, the average capacity fading rate of the cell is about 0.138% per cycle. The performance improvement is attributed to a reduction in the crossover rate of polysulfide through the composite separator as a result of the polysulfide absorption by PC/MWCNT layer.

## Introduction

In order to solve the growing environmental problems[1, 2], the development of new energy is imperative. Lithium sulfur (Li-S) battery is considered a very promising energy storage system, primarily because of its high theoretical energy density of 2600 Wh kg<sup>-1</sup> and specific capacity of 1675 mAh g<sup>-1</sup> at a safer operating potential ( $\approx 2.1$ V) [3-5], which are superior to the lithium-ion batteries [6-8]. In addition, the low price, environment-friendly, good safety and rich content of element sulfur make it more attractive to researchers and large-scale practical applications [9]. However, the widespread commercialization of Li-S battery is hampered by several technical challenges, such as low intrinsic conductivity (5×10<sup>-30</sup> S cm<sup>-1</sup> at 25 °C), low sulfur utilization and loading capacity, severe self-discharge and short cycle life [10-12]. Moreover, during the discharge/charge process, sulfur converts to polysulfide ( $Li_2S_x$ ,  $4 \le x \le 8$ ), which easily dissolve into the liquid electrolyte and diffuse through the separator to the lithium anode leading to the "shuttle effect" [13-15]. The unexpected reaction between polysulfide and the anode will cause the loss of active material, low coulombic efficiency and short cycle life [16, 17].

In order to address these issues, many approaches have been proposed over the past. One of the most effective methods is to capture polysulfide in the cathode by using adsorbing material, such as porous and hollow structure carbon [18-21], graphene [22-25], carbon nanotube [26, 27] and carbon nanofiber [28]. Besides, conductive polymers [29], metal oxide/sulfide such as MgO [30], Fe<sub>2</sub>O<sub>3</sub> [31], MoO<sub>2</sub> [32], CoS<sub>2</sub> [33] are also used to confine polysulfide in the cathode. Moreover, the LiNO<sub>3</sub> as an electrolyte additive has been added to protect the Li anode [13], thus enhance the electrochemical performance. Recently, a polysulfide adsorption layer between the separator and the cathode is considered to be a new strategy to improve the reversible capacity and stability of lithium-sulfur batteries [34, 35].

In a battery system, separator plays an important role in offering ion transport pathway and preventing electrons from passing through anode to cathode, the separator modification is an effective approach and receives ever increasing attention. The additives, such as conductive polymers [36], carbon materials like porous carbon [37], CNTs [38], graphene [39, 40] and functionalized graphene [41, 42] have been used to modify the separator. In order to strengthen the adsorption capacity of polysulfide, metal oxides [43-46] as another strategy for modifying the separator. However, an issue associated with the above mentioned materials is the trade-off among strong polysulfide adsorption ability, low cost, and high electrical conductivity.

Coal tar pitch (CTP), the residue after removal of the liquid fraction by distillation during the processing of coal tar, is a kind of abundant industrial by-product and is known to everyone because of its low cost and high carbon content. Moreover, the CTP is used as a carbonaceous precursor apply to silicon/carbon anode of lithium ion battery [47]. To our surprise, the application of CTP in Li-S batteries has never been reported, and it has been recently demonstrated that the porous carbon (PC) with high specific surface area and large pore volume for improving the adsorption of polysulfide [48], in addition, multi-walled carbon nanotube (MWCNT) intrinsically offer a good polysulfide absorption capacity and a high electrical conductivity [38]. In this paper, therefore, we first develop a PC with high specific surface area and large pore volume prepared form CTP, and composite it with MWCNT to modify the separator of Li-S batteries. The PC/MWCNT composite synthesized via the heat treatment method, is deposited onto one side of a polypropylene (PP) separator by a slurry coated method. With the PC/MWCNT-coated separator, the initial capacity is increased from 541 mAh  $g^{-1}$  to 911 mAh  $g^{-1}$  at 0.5 C. And the capacity is enhanced more significantly at high current density.

# **Results and discussion**

For the cell configuration (Fig. 1), the coating facing the sulfur cathode, acts as a barrier to block the migration of polysulfide and functions as an alternative current collector to collect and supply electrons. Therefore, a high sulfur utilization and an effective active material reutilization can be accomplished.



**Fig. 1** Schematic configuration of Li-S cell with the PC/MWCNT-coated separator As shown in Fig. 2 (a), The original PP separator plays the basic function in the cell

that avoid the cathode direct contact with the anode, allow ions to pass through and electronically insulated. The scanning electron microscopy (SEM) structure of PC/MWCNT is presents in Fig. 2 (b), the porous carbon mix well with the MWCNT and is filled in the MWCNT gap, which is advantageous for contact with the electrolyte, thereby enhancing the absorption of polysulfide. The cross-sectional SEM (Fig. 2 c) shows that the PC/MWCNT composite coating layer with a thickness about 12  $\mu$ m is stacked well on the surface of the PP separator, which, however, is much thicker than the PC/MWCNT coating layer. Indicating that the addition of PC/MWCNT coating layer has little effect on the energy density of the battery.

In order to investigate the polysulfide adsorption capability, 10 mg PC/MWCNT composite is added to 200  $\mu$ L Li<sub>2</sub>S<sub>6</sub> solution in 5 mL DOL/DME (1:1 by volume). The vials are sealed and gently shaken and placed in the glove box, it can be seen from Fig. 2 (d), the color of the solution changes from bright yellow to nearly transparent after storing for 4 h, proving the obvious adsorption ability of PC/MWCNT for polysulfide



**Fig. 2** SEM images of original PP separator (a) and PC/MWCNT composite (b), crosssectional image of PC/MWCNT coated separator (c), polysulfide adsorption test of PC/MWCNT composite (d).

The contents of porous carbon in PC/MWCNT composite is checked by the thermalgravimetric analysis. With a scan rate of 5 °C min<sup>-1</sup> from room temperature to 1000 °C in Ar atmosphere, TG curves of the CTP shown in Fig. 3. When heating to 850 °C, the mass of carbonized CTP remains approximately 43.5%, and when take the MWCNT into account, PC accounted for 26.6% in the PC/MWCNT composite. However, the activation of KOH on PC will result in the weight loss of PC, so the contents of PC in PC/MWCNT composite should be less than the calculated value.



Fig. 3 Thermal gravimetric (TG) curves of CTP

Fig. 4 (a) presents the highresolution TEM image of PC. It shows an amorphous structure. The Raman spectroscopy (Fig. 4b) of PC shows two characteristic peaks: The G band and the D band, which corresponds to the hexagonal structure and the defects or disorders in the carbon matrix, respectively. the value of  $I_D/I_G$  is ~1.2, indicating that the structure of PC with more structural defects, which is in accordance with the TEM results. The BET surface area and pore structure of the PC/MWCNT composite are measured by nitrogen adsorption-desorption isotherm as shown in Fig. 4 (c). The BET specific surface area and the total pore volume of the PC/MWCNT are 83.4 m<sup>2</sup> g<sup>-1</sup> and 0.17 cm<sup>3</sup> g<sup>-1</sup>, respectively. Additionally, as revealed in Fig. 4 (d), the average pore diameter is less than 5 nm. Research has shown that porous carbon with high surface area, large pore volume and abundant micropores can strongly adsorb polysulfide, reduce the loss of active materials in the electrolyte [49].



Fig. 4 (a) Highresolution TEM image and (b) Raman spectroscopy of CTP-derived PC,
(c) N<sub>2</sub> adsorption-desorption isotherms and (d) pore-size distribution of the PC/MWCNT

The electrochemical performance is tested to demonstrate the superiority of the PC/MWCNT-coated separator. Fig.5 (a) shows the charge/discharge curves PC/MWCNT-coated separator at the current density 0.2 C with a potential range between 1.7 V and 2.7 V. The discharge curve shows two different plateaus, representing the multi-step electrochemical reaction process from sulfur element to Li<sub>2</sub>S during discharge. The upper plateau around at 2.3 V is caused by the conversion of the element sulfur to the higher-chain polysulfide (Li<sub>2</sub>S<sub>x</sub>, 4 $\leq$ x $\leq$ 8) with a rapid kinetic process, the 2.1 V potential plateau is for high-chain polysulfide to low-chain polysulfide (Li<sub>2</sub>S<sub>2</sub> or Li<sub>2</sub>S) conversion [50, 51]. The first five cycles CV curves at 0.05 mV s<sup>-1</sup> of Li-S cell with PC/MWCNT-coated separator are presented in Fig. 5 (b). It

shows typical two different reduction peaks in the cathodic sweep and two overlapping oxidation peaks in the anodic sweep, which are coincide with the discharge/charge curves. The voltage of the first scan cycle is much lower than that of the 2-5 scan cycles, which may due to the contact of sulfur with the conductive carbon is not sufficient, leading to the polarization of the battery. And further result in the lower voltage. But after the first cycle, the electrical contact between active materials and conductive carbon is enhanced and most of the sulfur could be activated, so the polarization of the cell would be decreased. From the second cycle, the CV curves have an excellent consistency, reflecting a good cycle stability of PC/MWCNT-coated separator batteries.

Cycle performance tests are carried out at the current density of 0.5 C with the potential range between 1.7 V and 2.7 V (Fig. 5 c). the initial discharge capacity of the Li-S cell with the original separator shows a reversible capacity of 559 and 407 mAh g<sup>-1</sup>, whereas the cells with PC/MWCNT-coated separator have a higher capacity of 911 mAh g<sup>-1</sup>, remained at 659 mAh g<sup>-1</sup> after 200 cycles, respectively, equivalent to as low as 0.138% capacity fading for per cycle. The cell with the modified separator shows a great cycle performance, especially relatively higher specific capacity, which probably attributes to the polysulfide adsorption and block of the coating layer.



**Fig. 5** (a) Charge/discharge profiles and (b) CV curves of Li-S cells with the PC/MWCNT-coated separator, (c) Cycle performance of Li-S cell with PC/MWCNT-coated separator and original separator at 0.5 C.

To further illustrate the excellent performance of the PC/MWCNT composite separator. The Li-S cells are cycled from 0.1 to 2 C for rate performance testing. As is shown in Fig. 6 (a), The PC/MWCNT composite separator cell delivers the discharge capacity of 1258 mAh  $g^{-1}$  at 0.1 C. In addition, when the current density is increased to 0.2, 0.5, 1 and 2 C, the discharge capacities are 905, 784, 688, and 566 mAh  $g^{-1}$ , respectively. When current density returns to 0.1 C, the reversible capacity rise to 734 mAh  $g^{-1}$ . However, the capacity of the cell with original separator is 842, 639, 556, 250 and 106 mAh  $g^{-1}$  at 0.1, 0.2 0.5, 1 and 2 C, respectively. The performance improvement possibly owing to the polysulfide is successfully confined at the area between the

cathode and separator, due to the physical absorption and electrochemical deposition by the PC/MWCNT composite layer. Moreover, the promotion is noticeable at high current density, which means that the battery has a high conductivity, can promote the electrochemical reaction and improve the performance of the battery.

Fig. 6 (b) shows the charge/discharge curves of two cells fabricated with original separator and PC/MWCNT-coated one at the current density 0.1, 0.2 and 0.5 C in a potential range between 1.7 V and 2.7 V. The data from the charge/discharge curve at 0.1 C at 50% depth of discharge (DOD) shows a potential polarization ( $\Delta E$ ) of 221 mV for the Li-S cell with original separator, while the  $\Delta E$  for the Li-S cell with PC/MWCNT-coated separator presents a glower value of 157 mV. Moreover, as the current increased, the  $\Delta E$  of original separator increases more than that of the PC/MWCNT-coated separator, demonstrating a faster redox reaction kinetics for those cells with a PC/MWCNT-coated separator.

In order to understand the resistance of the fresh Li-S cells with the two separator samples. Electrochemical impedance spectroscopy (EIS) measurements are carried out with frequency from 0.01 Hz to 100 KHz. Fig. Fig. 6 (c) shows the Nyquist plots for both types of cells. The intercept at high frequency corresponds to the resistance of the electrolyte ( $R_s$ ), semicircle at high frequency region indicates the charge transfer resistance ( $R_{ct}$ ) of the cathode, and the Warburg impedance (Wo) is represented by an inclined line at low frequency. Based on the relevant equivalent circuit model, the  $R_{ct}$ decline from 96.2  $\Omega$  to 24.5  $\Omega$  after the PC/MWCNT-coated separator applied. Due to the high conductivity and contact well with electrolyte of the PC/MWCNT composite interlayer, thereby reducing the resistance of the cells. And an excellent cycle and rate performance achieved.

The advantage of PC/MWCNT-coated separator is further testified by the cycle performance of the Li-S cells at 1 and 2 C. As shown in Fig. 6 (d), the battery presents the initial capacity of 893 mAh g<sup>-1</sup> and remains 582 mAh g<sup>-1</sup> after 100 cycles at 1 C. Even at a higher current density of 2 C, the cell still maintains a capacity of 511 mAh g<sup>-1</sup>, demonstrating good cycle stability at high current density.



**Fig. 6** (a) rate performance, (b) Charge/discharge profiles at different current density and (c) Nyquist plots curve of Li-S cells with PC/MWCNT-coated separator and original separator, (d) Cycling performance at 1 and 2 C with PC/MWCNT-coated separator.

The SEM and corresponding energy-dispersive X-ray spectroscopy (EDX) elemental analysist results of the composite separator after cycling are shown in Fig. 7.

After the battery is disassembled, the PC/MWCNT-coated separator is washed several times with DOL/DME (1:1 v/v) solution and placed in glove box overnight to remove the DOL/DME solution. According to the elemental mapping of the PC/MWCNT-coated separator after 50 cycles at 0.5 C, sulfur is distributed homogeneously in the coating layer, inferring that the migrating active polysulfide is adsorbed and captured during the electrochemical cycling, confirming the trapping polysulfide during cycling.



**Fig. 7** SEM image of the PC/MWCNT-coated separator (toward the cathode side) and elemental mapping of C and S after 50 cycles at 0.5 C.

# Conclusion

In summary, the multifunctional PC/MWCNT composite material with high specific surface area and excellent electronic conductivity is developed for Li-S batteries. With 70% pure sulfur in the cathode, the Li-S cell of PC/MWCNT-coated separator deliver an excellent performance with a reversible capacity of 659 mAh g<sup>-1</sup> after 200 cycles, which is much higher than the cell with original separator. The

performance improvement is attributed to the PC/MWCNT coating layer, which not only captures the dissolved polysulfide, but also acts as an alternative current collector electron transmission and enhance rate capability. Besides, this work using CTP as the carbonaceous precursor, makes industrial by-products regain value, which provides a meaningful way of sustainable development.

#### **Experimental Section**

#### Synthesis of the PC/MWCNT composite

CTP and MWCNT suspension (6% solid content) in the weight ratio of 1:20 mixed homogeneously by ball-milling for 3 h. The resulting mixture (CTP/MWCNT) was dried at 80 °C for 6 h. To carbonized CTP, the CTP/MWCNT was transferred to a tube furnace and heated at 850 °C for 3 h under argon atmosphere with a heating rate of 5 °C min<sup>-1</sup>. Then the material was cooled to room temperature, mixed with twice KOH (by mass) and heated at 750 °C for 1.5 h in argon atmosphere with a heating rate of 5 °C min<sup>-1</sup>. Finally, the as-prepared composite was washed to a neutral pH with hydrochloric acid and deionized water, and then dried at 80 °C for 12 h to obtain PC/MWCNT composite.

## PC/MWCNT coated separator and Li<sub>2</sub>S<sub>6</sub> solution preparation

A mixture of 90 % PC/MWCNT and 10 % polyvinylidene fluoride (PVDF) was dissolved in N-methylpyrrolidinone (NMP, aladdin) to form a slurry and coated on commercial PP separator (Celgard 2400). The PC/MWCNT composite separator was punched into a diameter of 18 mm circular disk after dried 6 h at 60 °C under vacuum, and the mass loading of the coating was about 0.51 mg cm<sup>-2</sup>.

The polysulfide  $Li_2S_6$  solution (0.05 M) was prepared by chemically reacting elemental sulfur and  $Li_2S$  (5:1, by mol) in DOL/DME (1:1 v/v) solution, followed by heating at 50°C with magnetic stirring overnight in an Ar-filled glove box.

# Li-S cell assembly

The sulfur cathode was fabricated using a slurry coating method. The cathode slurry was made of 70% sulfur ( $\geq$ 99.98%, Sigma Aldrich), 20% carbon black and 10% LA132 in deionized water and normal propyl alcohol (1:3, by volume). The cathode slurry was spread onto aluminium foil by a doctor blade and dried 12 h at 60 °C under vacuum. The weight of sulfur in the cathode was 1.6-1.7 mg cm<sup>-2</sup>. The electrolyte contains a mixture of 1,3-dioxolane (DOL) and 1,2-dime-thoxyethane (DME) (1:1 v/v), with 1 M bis (trifluoromethane) sulfonamide lithium salt (LiTFSI) and 0.1M LiNO<sub>3</sub> dissolved in it. Lithium sheet was used as anode electrode. The original PP and PC/MWCNT composite separator was used in assembling the 2025 cells.

## Characterization

Morphologies characterization and elemental mapping of the PC/MWCNT before and after cycling were conducted by scanning electron microscopy (FEI Quanta-200). The weight loss of CTP was tested by the thermal gravimetric analysis (TGA) at the scan rate of 5 °C min<sup>-1</sup> from room temperature to 1000 °C. The Brunauer-Emmett-Teller (BET) was used for pore structure and specific surface area characterizing of PC/MWCNT composite.

#### Electrochemical measurements

The CHI600E electrochemical measurement system was used for cyclic

voltammetry (CV) and electrochemical impedance spectrometry (EIS) measurement. CV was obtained at the scan rate of  $0.05 \text{ mV s}^{-1}$  in the potential window from 1.7 V to 2.8 V. The EIS were recorded in the frequency range between 0.01 Hz and 100 kHz. The cells were charge/discharge in the potential range from 1.7 V to 2.7 V under NEWARE BTS 4000. All experiments were carried out and analyzed at room temperature.

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