Corncob-derived Porous Carbon as an Interlayer Coating to Improve the Performance of Lithium Sulphur Battery

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Porous activated carbon derived from corncob without further element-doping was employed as a coating interlayer on polypropylene (PP) separator in lithium sulphur (Li/S) battery. The highly electrically conductive activated carbon served as a pseudo current collector dramatically reducing the interface resistance and thus improved the reaction kinetics of the cell system. Furthermore, the mirco-/mesoporous structure and large pore volume of activated carbon provided an excellent environment to trap soluble polysulfide intermediates resulting in shuttle reaction and buffered the volume change of sulphur during cycling, prominently alleviating capacity fading. The cell with activated carbon coating layer maintained a high reversible specific capacity of 839.8 mA h g⁻¹ after 100 cycles at a current rate of 0.3 C (1 C = 1672 mA g⁻¹), comparing to 496.7 mAh g⁻¹ of the cell with only pristine PP separator. Extended cycle life test exhibited a discharge capacity of 648 mAh g⁻¹ after 350 cycles under 0.5 C. Moreover, thickness influence of activated carbon coating layer indicated that a thin layer of 29 μ m coating was sufficient enough to improve the electrochemical performance of Li/S battery. Thicker coating was only able to slightly improve the performance of battery.

Keywords: activated carbon, interlayer, Li/S battery, thickness

1. INTRODUCTION

The new generation of cost-efficient, high energy storage systems is essential for the rapid development of electric vehicles, renewable energy plants and smart grids [1]. Li/S battery is considered as one of the most promising candidates due to its high theoretical specific capacity (1672 mAh g^{-1}) and high energy density (2500 Wh k g^{-1}), which significantly surpasses the state-of-art lithium ion batteries [2-4]. Moreover, the wide-spread abundance, low cost and non-toxic nature of elemental sulphur predestines its large-scale applications. However, the commercialization of such a promising

system is still hindered by three major issues. (i) Sulphur and its discharge products (Li₂S₂, Li₂S) have low electrical conductivity which leads to a low electrochemical accessibility and low sulphur utilization ratio. So that additional conducting medium such as Super P and acetylene black is needed which reduces the content of active material. (ii) The density difference between sulphur and Li₂S leads to large volume change during charge-discharge process which results in the degradation of the sulphur cathode after cycling. (iii) High-order poly-sulfides (Li₂S_x, $4 \le x \le 8$) produced in the chargedischarge processes are soluble in normal organic electrolyte, causing so-called shuttle effect [5] and resulting in low sulphur utilization ratio and corrosion of the lithium anode, finally leading to a quick capacity decay and short battery life [6].

In order to overcome the aforementioned hurdles, different approaches have been explored by the researchers over the last several decades. One of the most effective strategies is to confine polysulfides inside the cathode by applying porous materials, including micro/meso-porous carbon materials and porous metal oxides [7-10]. So far various types of porous carbon materials have been employed to construct S/C cathode, especially biomass derived carbon materials such as pig bone [11], litchi shells [12], bamboo [13], etc. A typical synthesis process of such a biomass derived carbon includes a carbonization process and an activation process (physically or chemically). These activated carbons possess large surface area (SSA) and large pore volume (PV) so that they can efficiently absorb the polysulfides, leading to much improved capacity retention. Besides, the relatively simple and harmless synthesis procedure and using cheap biomass wastes as resources make this approach also scalable. However, different activated carbon derived from different biomass resources may lead to different properties when employed in the sulphur cathode. It is reported that the surface functional groups of the carbon play a key role when used in sulphur cathode [14-15]. Recently, our group [16] developed a corncob derived high surface area activated carbon to make S/C composite cathode for Li/S battery. However, the performance was not prominently improved as we thought. Although doping nitrogen into carbon matrix (through HNO₃ oxidation and NH₃ N-doping) to make N-doping carbon improved the electrochemical performance, the whole procedure got a lot more complicated and expensive.

A. Manthiram [17] proposed a new idea of placing a bifunctional microporous carbon paper interlayer between the sulphur cathode and normal PP membrane. The interlayer acting not only as a physical barrier of polysulfides but also as an extra current collector reduces the internal impedance and shuttle effect, leading to better sulphur utilization and enhanced capacity retention. Since then, various carbon materials (Nano fibers [18-20], graphene [21-22], etc.), biomass derived carbons [19, 23-27] and metallic oxides [28-29] have been proved good choices as interlayers. However, few biomass derived carbon materials with high surface area and large pore volume are reported as interlayer so far because they are usually applied to make S/C composite cathode, due to the consideration of porous structure as an ideal structure to absorb polysulfide. But to make such a composite cathode, sulphur loading process is inevitably required (usually heating and melting load method) which makes the procedure more complicated and energy-costing.

Herein, we employed the activated carbon derived from corncob as an interlayer coating to improve the performance of the Li/S battery and investigated the influence of interlayer thickness to determine a suitable coating mass. It was proved that the large surface area and pore volume efficiently

absorbed the polysolfides and the coating layer reduced the internal resistance, resulting in a much improved capacity retention and longer cell life. It is worth noting that the same carbon without further N-doping proved not a good candidate for S/C cathode as we previously reported [16].

2. EXPERIMENTAL

2.1 Porous activated carbon-Coated Separator Preparation

Porous activated carbon was prepared by the same procedure as we described before [15]. In a typical synthesis process, dry corncob powders were carbonized at 673 K for 4 h in flowing nitrogen atmosphere. The obtained carbonized powders were then further ground into small particles by ball milling at the rate of 400 r min⁻¹. Then, the ball-milled powders were suspended in KOH saturated solutions (KOH/C ratio= 4:1) and magnetically stirred for 2 h at room temperature followed by drying under vacuum at 393 K for 12 h. Finally, the impregnated mixture was transferred to a muffle furnace and activated at 1073 K for 4 h. The final products were washed with hydrochloric acid and deionized water until the pH value reached about 7.0 and then dried at 393 K under vacuum. The as-prepared products were denoted as AC.

The AC carbon was mixed with Poly-vinylidene fluoride (PVDF) in a weight ratio of 9:1 in N-methyl-2-pyrrolido (NMP). Then the slurry was pasted onto a traditional polypropylene separator with molds of different thickness (50, 100 and 150 μ m) and dried at 70 °C for 12 h under vacuum. The average coating mass loading was around 1.70, 4.43 and 6.61 mg cm⁻² and the average thickness of the coating layer was 29, 79 and 92 μ m, respectively.

2.2 Pure Sulphur Cathode Preparation

The sulphur cathodes were prepared by conventional doctor blading method. The slurry was prepared by mixing 70 wt% element sulphur, 20 wt% Super P and 10 wt% PVDF in NMP. Then, the slurry was spread onto an aluminum current collector, dried at 70 $^{\circ}$ C for 4 h under vacuum and then cut into circular disks with a diameter of 12 mm. The sulphur loading was around 1.7-1.9 mg cm⁻².

2.3 Characterization

The textural properties of the AC were performed by N₂ sorption at 77 K using a Micromeritics ASAP 2020. The scanning electron microscopy (SEM, FEI SIRION 200/INCA, OXFORD) were used to determine the morphologies and texture of the samples. Specific surface areas were calculated at a relative pressure p/p0 = 0.05- 0.2 using the multipoint Brunauere-Emmette-Teller (BET) method while the total pore volume was determined at p/p0= 0.97. The pore size distributions were obtained using the Quenched Solid Density Functional Theory (QSDFT) equilibrium model. The thickness of the separator and carbon coating on the separator was determined by a Mitutoyo thickness gage (547-401).

2.4 Electrochemical Measurements

CR2032-type coin cells were assembled in an argon-filled glove box, in which the oxygen and water contents were less than 0.1 ppm. The electrolyte was 0.5 M $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ dissolved in a mixture of 1,3-dioxolane (DOL) / dimethoxyethane (DME) (1:1 volume ratio) containing 0.2 M LiNO₃.

The electrochemical impedance spectroscopy (EIS) data were obtained with an impedance analyzer (SI 1287 and 1260, Solartron) from 1 MHz to 0.1 Hz with an AC voltage amplitude of 5 mV. The charge–discharge voltage profiles and cyclability data were collected with a programmable battery cycler (LANHE CT2001A, LAND) at 1.8- 2.7 V (*vs.* Li⁺/Li). For galvanostatic test, the cells were discharged and charged at a current rate of 0.05 C (1 C = 1672 mA g⁻¹) for the first cycle and then switched to the designated rate (for example 0.3 C, 0.5 C and 1 C) from the second cycle. The cyclic voltammetry (CV) test was conducted between 1.7 V and 2.8 V for 3 cycles at a scan rate of 0.1 mV s⁻¹.

3. RESULTS AND DISCUSSIONS



Figure 1. (a) Nitrogen physisorption isotherm of AC particle and (b) the corresponding pore size distribution plot obtained by employing the N₂-DFT equilibrium model

Porous activated carbon was synthesized through the same procedure as previous report [15]. The textural properties were assumed to be the same. To validate it, texture of the AC powder was examined by BET test (Figure 1). Distinct type I isotherm (Figure 1a) was observed, indicating the presence of micro-pores and meso-pores between 2-10nm in the carbon material, which was similar to the previous report [15]. The AC possessed high specific surface area (SSA) of 2645 m² g⁻¹ and pore volume (PV) of 1.54 cm³ g⁻¹ as shown in Figure 1b. It also shared the same pore size distribution (PSD) feature, ranging from 0.5 and 4nm.

The pure AC carbon was proved not a good candidate for S/C composite cathode mainly due to its surface functional groups. However, the large pore volume is able to absorb and trap the

intermediate polysulfide products of charge-discharge process and carbon-coating on the traditional membrane could act as an additional current collector which leads to a better utilization of the active material.

Figure 2 presents the morphology of AC powder and AC-coating layer. As shown in Figure 2a, the AC powders showed irregular particle morphology with a diameter between 2 to 10 um. The activated carbon was coated on one side of PP separator by doctor blading method. It was observed that AC-coating was distributed homogenously on the PP surface and presented a compact layer (Figure 2b), while the cross-sectional SEM image of the AC coating (Figure 2c) revealed a compact carbon layer with a thickness of about 30 μ m.



Figure 2. SEM images of (a) pristine corncob derived activated carbon particles, (b) carbon coating on PP separator and (c) cross-sectional view of the carbon coating layer

The successfully fabricated AC-coated separator was used as normal separator and the ACcoating was put on the cathode side. It is expected that the addition of the AC-coating is able to enhance the electrochemical performance of the Li/S batteries through (i) increasing the electrical conductivity of system and decreasing the internal resistance, (ii) trapping the soluble polysulfides, and thus, effectively improving the reutilization of the active sulphur material [1]. To validate the conductivity improvement, EIS measurements were first carried out to determinate the impact on cathode resistance of the fresh Li-S cells with or without AC coating. Figure 3 shows the Nyquist plots for both types of cells. It was quite obvious that each plot displayed a single semicircle at high-to-medium frequency range and an inclined line at low frequency range, which was respectively related to charge transfer resistance and mass transfer resistance [30]. However, the diameter of the semicircles differed. The profile of the cell with AC-coated PP separator exhibited a much smaller diameter, suggesting a lower charge transfer resistance. This improvement could be ascribed to the high electrical conductivity of the AC-coating which acted as an additional current collector, reducing the internal resistance of the cell [17]. Moreover, it is worth noting that the interlayer was made without any conductive carbon additives (e.g. Super P), which would highlight the electrical conductivity of the activated carbon.



Figure 3. Nyquist plots of Li-S cells with pure PP separator and AC-coated separator, frequency ranges from 1 MHz to 0.1 Hz with an AC voltage amplitude of 5 mV

The cyclic voltammetry test was also carried out to investigate the electrochemical behaviors of the two types of cells. As is shown in Figure 4, for the cell with AC-coated PP separator, two well-defined reduction peaks at about 2.3 V and 2.0 V correspond to the reduction of element sulphur to soluble lithium polysulfides (Li_2S_n , 4< n< 8) and further conversion of these lithium polysulfides to insoluble Li_2S_n (n = 1, 2), respectively [16], indicating the multistep reduction process of elemental sulphur. On the other hand, the oxidation curve presented two continuous plateaus around 2.4 V (~2.35 V and ~2.43 V), which correspond to reversible oxidation reactions of Li_2S_2/Li_2S to into high-

order soluble polysulfides and further into S_8/Li_2S_8 [31]. Noticeably, there are only slight changes for CV peaks in subsequent cycles (Figure 4a), confirming the good electrochemical reversibility and excellent stability of sulphur cathode. However, for the cell with pure PP separator (Figure 4b), there was only one distinct reduction peak at ~2.25 V, one wide reduction peak near 1.7 V and one major oxidation peak at ~2.47 V. Combing EIS results, we come to a conclusion that the good electrical conductivity of the coated AC layer greatly reduces the internal resistance of the cell, leading to a much less polarization of the electrochemical system. On the other hand, due to the absence of carbon composite and large sulphur mass loading (1.7-1.9 mg cm⁻²), the polarization of the cell with pure PP separator is much worse that of the ordinary Li/S battery [32-33], resulting in much bigger reduction/oxidation peak shift.



Figure 4. Cyclic voltammogram scans of Li–S cells with (a) AC-coated separator and (b) pristine separator, scan rate of 0.1 mV s⁻¹ and voltage range of 1.7-2.8 V

The electrochemical cycling performance of Li/S cells was investigated by galvanostatic charging-discharging cycling and are presented in Figure 5. The testing program applied in this paper was slightly different from other groups [33-34]. The cells were first discharged and charged at a current rate of 0.05 C for one cycle to fully activate the active material, and then the testing rate was switched to 0.3 C in subsequent cycles. Figure 5a presents the charge-discharge voltage profiles of the cells and they were acquired during the 1st, 2nd, 10th, 20th, 50th and 100th cycles. Generally, for the cell with AC-coated separator, the profile exhibits two plateaus around 2.3 V and 2.0 V during discharge process, which are considered to represent the conversion of elemental sulphur (S₈) to soluble long-chain polysulfides (Li₂S_x, 4< x< 8) and their further reduction to short-chain polysulfides (Li₂S_x, 1<x<4) and Li₂S, respectively [1], in accord with CV results (Figure 4). The plateau length of different cycles changed slightly reflecting the good reversibility and redox reaction kinetics of the cell system [20, 35-36]. However, for the cell without AC coating, although the profile is similar to the one with AC coating in the 1st cycle, dramatic change in the 2nd and 10th cycles was observed. In these cycles, the discharge plateau is much shorter compared to their counterparts and polarization is also more

serious. The major reason of this odd phenomenon is due to the absence of polysulfide trappable AC and the poor electrical conductivity. Moreover, due to the large thickness of the sulphur layer, it is difficult for the electrolyte to infiltrate into the sulphur cathode, further lowering the utilization rate of sulphur in the first few cycles.



Figure 5. Galvanostatic charge-discharge test of cells with pristine PP and AC-coated separators (voltage range of 1.7-2.8 V): (a-b) charge-discharge voltage profiles at 0.3 C, (c) cycling performance for 100 cycles at 0.3 C, (d) cycling performance for 100 cycles at 0.5 C and 1 C, (e) long-term cycling performance of cell with AC-coated separator for 350 cycles at 0.5 C.

The first several cycles of cell with normal PP separator acted like some sort of activation process and the discharge plateau length rebounded to a relatively normal level (but still much shorter than the cells with AC-coated separator). In the first cycle, thanks to ultralow discharge rate (0.05 C), the poor conductivity has a relatively low impact on the system. But the impact was amplified when the test rate was back 0.3 C, leading to serious polarization of the system. The average voltage polarizations (Δ E) (which is also associated to the reversibility and the redox reaction kinetics of the cell system [20]) obtained from the 20th, 50th and 100th cycles at 50% depth of discharge (DOD) [1] revealed a Δ E of 240 mV for the Li/S cell with AC-coated separator, in comparison with 421 mV (Figure 5a and b, highlighted with blue arrows) of the conventional Li/S cell. Much lower ΔE demonstrates less polarization for the cells with an AC-coated separator. The cell with AC-coated delivered a high initial specific discharge capacity of 1425.1 mAh g⁻¹, which means that a high sulphur utilization ratio of 85.8% was achieved. The specific capacity of the second cycle reached 1067.4 mAh g^{-1} . Even after 100 cycles it still remained 839.8 mAh g^{-1} with a high coulombic efficiency of 99.2%, indicating a low capacity fading rate of 0.79% per cycle (Figure 5a). In contrast, the cell with normal PP separator exhibited an initial specific discharge capacity of 973.9 mAh g⁻¹, but dropped to 321.3 mAh g⁻¹ in the second cycle (Figure 5b). After 100 cycles, the cell had a capacity retention of 496.7 mAh g⁻¹, which is much lower than the counterpart with AC-coated separator. And the same result also came out with larger current rate of 0.5 C and 1 C (Figure 5d). Cells with pristine PP separator delivered a capacity less than 200 mAh g⁻¹ at both rates while the AC-coated ones still kept a capacity retention of 834.6 and 652.5 mAh g⁻¹ respectively. Especially at the rate of 0.5 C, the cell still delivered a capacity of 648 mAh g⁻¹ after 350 cycles with a high coulombic efficiency of 96.43%, achieving a low capacity fading rate of 0.17% per cycle since the second cycle (Figure. 5e).

Table 1 summarizes the reported biomass-derived carbon and their application as interlayers in Li/S cells so far. For comparison, the results obtained in this work was listed as well. It is found that the Li/S cell with corncob-derived carbon interlayer showed better performances in terms of capacity and sulphur content. The initial discharge capacity of Li/S cell employing corncob-derived active carbon interlayer is higher than most cases and is only lower than the counterparts using cassavaderived carbon (1067.4 vs. 1318 mAh g⁻¹) at 0.5 C (cell using carbonized sucrose-coated eggshell membrane was tested under 0.1 C and was not compared here). Considering the fact that the current rate of first cycle was 0.05 C and thus the second discharge capacity was adopted in our work, the "real" initial discharge capacity should be higher than 1067.4 mAh g⁻¹ and is possibly even higher than the Li/S cell adopting cassava-derived carbon. On the other hand, the cycled discharge capacity (100th or more than 300th) of Li/S cell employing corncob-derived active carbon interlayer is apparent superior to many other cases. Only Li/S cell using natural carbonized leaf delivered comparable capacity (in the same consideration, cell using carbonized sucrose-coated eggshell membrane was tested under 0.1 C and was not compared here). We attributed these significant increase on electrochemical performance to the unique structure of corncob-derived carbon. It is filled with microporous structure which is hard for the polysulfide intermediates to infiltrate along with the mesopores to absorb the polysulfide intermediates. Although cell adopting carbonized bacterial cellulose is able to endure higher sulphur content cathode while cell using bamboo carbon fiber membrane could

provide similar discharge capacity even under higher C-rate (1C). Corncob-derived carbon is still quite attractive due to its abundant resource and biomass waste feature.

Biomass source	SSA (m2 g- 1)	$\begin{array}{c} PV \\ (cm^3 g^{-1}) \end{array}$	Initial capacity (mAh g ⁻¹)	Cycle capacity (mAh g ⁻¹)	Current rate (C)	S in cathode (wt.%)	Ref.
Cassava	13.8	0.015	1318	811/100th	0.5	60	23
Fungi	305.4	0.1	~970	650/100th	0.5	60	24
Sucrose-coated eggshell membrane	429	0.36	1327	1000/100th	0.1	3.2 mg cm ⁻²	25
Leaf	390	0.34	~1000	829/100th	0.5	70	26
Bamboo stick	776	0.33	907	605/300th	1	70	19
Bacterial cellulose	375	5.29	976	620/300th	0.48	81	27
Corncob	2645	1.54	1067.4/2nd	827.9/100th 648/350th	0.5	70	This work

Table 1. Electrochemical performance of Li–S cells based on different biomass carbon

The rate performance of cells using corncob-derived carbon interlayer was also investigated. The cells were discharged at a rate of 0.1 C, 0.3 C, 0.5 C, 1 C and 2 C for 10 cycles at each rate respectively and then the rate was switched back to 0.3 C for 20 cycles. The charge rate was kept steady at 0.1 C to make sure the cells were fully charged before each discharge process. As is shown in Figure 6, for the cell with AC coated separator, the specific capacity was 1067.8, 906.4, 840.3, 765.4 and 687.9 mA g⁻¹ at 0.1, 0.3, 0.5, 1, 2 C respectively, and rebounded to 837.8 mAh g⁻¹ at 0.3 C, showing great high-rate performance and capacity retention which is attributed to the conductivity improvement due to the addition of AC coating on the separator. In comparison, the cell with ordinary PP separator exhibited the same activation process during the first several cycles at 0.1 C, but the specific capacity dropped to less than 200 mAh g⁻¹ at a higher discharge rate and did not rebound since then. It is worth noting that the capacity dropped since the rate of 0.3 C which is not consistent with previous galvanostatic charge-discharge test. This could be attributed to too many activation cycles at 0.1 C which is possible to result in severe shuttle effect and precipitation of active sulphur on the lithium anode and causes irreversible failure of the cell system.

To understand the influence of coating thickness on the electrochemical behavior of the cell system and find the suitable coating mass, three different doctor blade mold were employed and were noted as AC-1, AC-2 and AC-3, which had an average coating thickness of 29, 79 and 92 μ m respectively. The average coating mass loading was 1.7, 4.43 and 6.61 mg cm⁻² respectively. The cycling performance at 0.3 C are presented in Figure 7.



Figure 6. Rate performance of cells with PP separator and AC-coated separator (1.7-2.8 V) charged at 0.1 C for all cycles and discharged at 0.1 C, 0.3 C, 0.5 C, 1 C, 2 C for 10 cycles at each rate and then switched back to 0.3 C



Figure 7. Galvanostatic performance at 0.3 C with different carbon coating thickness: AC-1 of 29 μ m; AC-2 of 79 μ m; AC-3 of 92 μ m

Apparently, a thicker coating layer lead to an improved cycling performance (839.8 mAh g⁻¹ of AC-1 *vs.* 949.5 mAh g⁻¹ of AC-2, after 100 cycles). But further increase of thickness brought no recognizable improvement on capacity while the overall specific capacity decreased. Furthermore, comparing the cycling performance at a higher rate of 1 C, there was also slight improvement with a thicker coating (694.8, 771.3 and 800.3 mAh g⁻¹ respectively after 200 cycles). The results above

indicate that a thin layer of carbon coating on the separator is enough to greatly improve the electrochemical performance of Li/S battery. Thick coating layer has limited impact on further improvement and will decrease overall specific capacity on the contrary.

4. CONCLUSION

In summary, an activated porous carbon derived from corncob without further atomic doping was used as an interlayer coating of the Li/S battery. The high electrical conductivity of the activated carbon served as a pseudo current collector, reducing the resistance and thus improving the reaction kinetics of the battery system. Besides, the mirco-/mesoporous structure and large pore volume of the carbon provides an excellent environment to trap soluble polysulfides and buffer the volume change of sulphur. The cell maintained a high reversible specific capacity of 839.8 mAh g^{-1} after 100 cycles at a charge rate of 0.3 C, comparing to 496.7 mAh g^{-1} of the cell with pristine PP separator. And the cell with AC coating had a long battery life, maintaining a capacity of 648mAh g^{-1} after 350 cycles. Moreover, the thickness impact of the coating layer was studied and indicated that a thin layer of coating is sufficient to improve the electrochemical behavior of Li/S battery. Thicker coating is only able to slightly improve the specific capacity of sulphur cathode and will decrease the capacity of the whole system. Overall, the corncob-derived activated carbon used as coating interlayer of Li/S battery is able to improve the electrochemical performance of battery system, and the simple fabrication process together with abundance of corncob makes this approach a promising strategy for future rechargeable lithium batteries.

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