

Carbon-coated Aluminum Foil as Current Collector for Improving the Performance of Lithium Sulfur Batteries

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Carbon-coated aluminum (Al) foil was employed as a current collector of sulfur cathode in lithium sulfur (Li-S) battery. The physical properties of different foils and prepared electrodes were characterized, and the effects of foil type on the electrochemical performance of the cell were investigated. The artificially designed carbon coating on Al foil enhances the adhesion of active material to the current collector, and reduces electrical resistivity of the sulfur electrode. When using carbon-coated Al foil, the electrochemical polarization of Li-S cell is obviously diminished and stable potential plateau can be held. Compared to common bare foil, the carbon-coated foil favors more sulfur utilization and better cycle capability. Especially the carbon-coated foil with a point-plane combined surface framework (DC foil) is preferable for the improvement of electrode properties and cell performance than that covered by merely carbon particle material. A high reversible capacity of 655 mAh g⁻¹ after 50 cycles is exhibited in the cell using DC foil, with low charge-transfer resistance.

Keywords: carbon-coated aluminum foil; current collector; sulfur cathode; lithium sulfur battery; electrochemical performance

1. INTRODUCTION

Rechargeable lithium ion batteries (LIBs) have been widely used in various portable devices, such as mobile phone, laptop and electric vehicle. However, the specific energy of commercialized LIB is hard to meet the ever-increasing market requirements due to the capacity restriction of conventional cathode materials. Elemental sulfur is an attractive active material by virtue of its low cost, no toxicity, high theoretical specific capacity of 1675 mAh g⁻¹ and high energy density of 2600

Wh kg^{-1} [1], assuming the complete reaction of lithium with sulfur to Li_2S . Therefore, lithium-sulfur (Li-S) batteries equipped with sulfur cathode have received extensive researches and attentions in recent years.

Most of Li-S batteries adopt bare aluminum foil (bare Al foil) as a current collector of sulfur cathode currently. This foil has limited contact area and weak adhesion ability to active material because of too smooth surface, which produces high contact impedance. Partial sulfur particles are inclined to separate from the bare foil at repeated charge-discharge cycles, causing capacity degradation of the cell. Besides, the bare foil is always easily corroded by the organic electrolytes [2, 3], which damages the electrochemical stability of the system and may give rise to self-discharge and safety issue [4]. To solve the problems, scientists have attempted various other metal or carbon based materials to substitute for bare Al foil, e.g., nickel foam, carbon foam, porous carbon paper, activated carbon fiber cloth, carbon nanotubes [5-9]. These current collectors have positive effects in cell performance. However, either complex manufacture process (accompanied by high cost) or difficulty of large-area fabrication impedes their practical applications. Besides, some alternatives have still a certain gap from the bare Al foil in conductivity. Therefore, it is necessary to further develop appropriate current collector materials for advanced Li-S batteries.

Recently, carbon-coated Al foil with a conductive carbon layer covered on the Al surface has been successfully introduced into conventional LIBs. The foil can not only reduce overall charge transfer resistance and improve adhesion at the active layer/current collector interface [10], but also prevent Al corrosion caused by organic electrolyte [11] and even alkaline slurry [12]. What's more, it has the merits of simple fabrication, convenient use and superior conductivity. Based on above reasons, some researchers have also attempted to employ the carbon-coated Al foils as current collector of Li-S batteries and obtained favorable results [13]. However, the detailed discussion on the sulfur electrode properties and cell performances boosted by the particular foil was seldom concerned, and the type of carbon-coated foil fit for Li-S cell system is still unclear.

In this paper, two kinds of commercialized carbon-coated Al foils were applied in Li-S batteries. The basic characteristics of the foils and prepared electrodes were studied. The effects of foil types on the electrochemical properties of the cell were investigated. The results suggest that the carbon-coated foils are in favor of the improvement of cell performance. The foil with the mixture of carbon black and layered graphite covered on the surface is more suitable for the current collector of sulfur cathode than other types of foils in this study, considering its contribution to capacity delivery and cycle stability.

2. EXPERIMENTAL

2.1. Material, electrode and cell preparation

The sulfur/carbon (S/C) composites were prepared by a simple melting-infusion process. 75wt% of sulfur (Alfa Aesar, 99.5%) and 25 wt% of Ketjenblack ECP (Lion Specialty Chemicals Co.,

Ltd.) were mixed in an agate mortar for 30 min, then the obtained powder was put in a stainless-steel container, preserved at 155 °C for 12 hours, followed by another 2 hours at 250 °C.

For fabricating sulfur electrode, the prepared S/C composite, carbon black (Super P, Timcal) and poly(vinylidene fluoride) (PVDF, HSV900) (80: 10: 10 wt.) were mixed in N-methylpyrrolidone (NMP, Tianjin Kemiou) to form a homogeneous slurry. Then the slurry was spread onto a piece of Al foil and dried at 60 °C under vacuum overnight. There are three kinds of Al foils (provided by Shenzhen Perfect Power Technology Co., Ltd) employed in the experiment: D type carbon-coated foil (DC foil, with the mixture of Super P and layered graphite coated on Al foil), A type carbon-coated foil (AC foil, only Super P particles coated on Al foil) and common bare Al foil. Hence the fabricated electrode is marked as DC electrode, AC electrode and bare electrode, respectively, according to the foil type. The electrode was cut into disks with a diameter of ~14 mm and the sulfur mass on each disk is typically ~1.2 mg cm⁻².

The coin cells were assembled in an Ar-filled glove box (Mikrouna, with oxygen and water contents below 1 ppm), using above electrode as cathode, Li foil as anode, and Celgard 2400 as the separator. The electrolyte consisted of 1 mol L⁻¹ lithium bis(trifluoromethane sulfone)imide (LiTFSI, Aldrich) in solvent mixture of 1,2-dimethoxyethane (DME, Acros) and 1,3-dioxolane (DOL, Alfa) (1:1, volume ratio), containing 0.1 mol L⁻¹ lithium nitrate (LiNO₃, Acros) as additive. The ratio of electrolyte volume to sulfur mass on the cathode was controlled to be ~12 uL mg⁻¹.

2.2. Physical and electrochemical characterizations

The electrical resistivity of the foils and sulfur electrodes was measured by four-probe method (ST2258C). Each data presented in the paper is an average value based on three tests. The adhesion strength of active material to the foil was measured by tension tester (Instron5540) with a peeling rate of 300 mm min⁻¹. Generally, the tension force will reach a maximum rapidly and descend slightly subsequently. After that, a relatively stable value can be sustained, which was selected as the average adhesion strength. The surface and cross morphologies of the foils and electrodes were observed by scanning electron microscopy (SEM, FTSU8010).

The discharge/charge tests of Li-S cells were performed in the potential range of 1.7~2.8 V at a rate of 0.2 C under LAND CT2001A tester. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were conducted using an electrochemical workstation (CHI604E). The scanning rate and voltage range of CV tests were 0.1 mV s⁻¹ and 1.5~3.0 V, respectively. The frequency range of EIS measurements was 10⁵~0.1 Hz, with a perturbation amplitude of 5 mV.

After cycling, the sulfur cathode was carefully extracted from the cycled cell and washed with DME, then further dried in the glove-box for 2 h to remove residues. The cathode morphology was further investigated by SEM.

3. RESULTS AND DISCUSSION

The surface and cross morphologies of various foils and as-prepared electrodes were compared in Fig.1. The bare foil (Fig.1a) owns a smooth and flat surface, so the cross section of bare electrode (Fig.1b) is only composed of two parts: active layer and Al foil layer. By contrast, the AC foil (Fig.1c) presents rough morphology, with plenty of nano-sized particles uniformly coated on it. These particles are mainly composed of the carbon black material--Super P. Therefore, an additional conductive layer with a thickness of 3~5 μm appears between active layer and Al foil layer when the AC foil was used as a current collector (Fig.1d). As for DC foil, it is found that some large-sized flake graphite is also located at the foil surface, besides those nano-sized carbon particles (Fig.1e). The close contact between the flake graphite and carbon black constitutes a highly conductive structure combining two characteristics of "point" and "plane". The DC foil is similar with AC foil on the thickness of the carbon layer (Fig.1f).

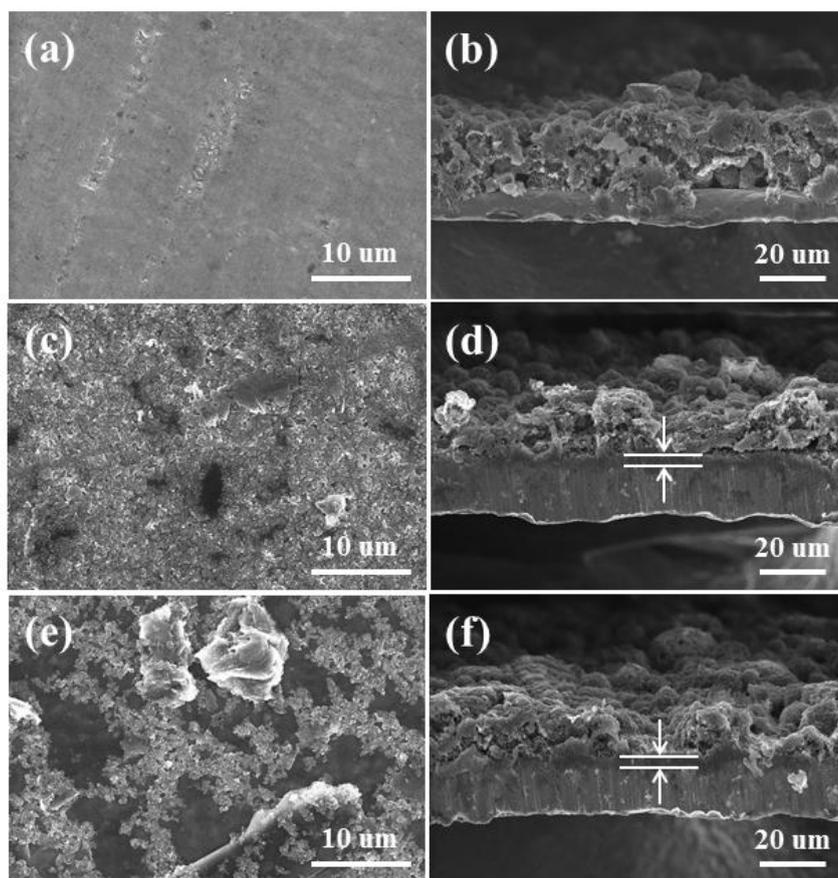


Figure 1. The surface morphology of (a) bare foil, (c) AC foil and (e) DC foil; the cross section of (b) bare electrode, (d) AC electrode and (f) DC electrode

The adhesion strengths of active material to different foils were listed in Table 1. The data in the table refers to the tolerable pressure limit on the unit area of the electrode piece. It can be seen that the active material can be easily separated from the bare foil. The weak combination between above two parts results from too smooth surface of the bare foil. When coated by conductive carbon, the

adhesion strength of the active material to the foil increases dramatically. The carbon coating on Al foil constructs a rough surface framework with rich holes, thus the contact area of active material and the current collector is increased [14], which is advantageous to stable attachment. In addition, it is believed that the improved adhesion of active material is associated with polarity variation of current collector surface [10]. The adhesion ability of DC foil to the active material is higher than AC foil, suggesting that the so-called “point-plane” combined surface provides better binding force compared to that covered by merely some particle materials.

Table 1. Adhesion strength of active material to the foil measured by tension tester

Type	Adhesion strength (N cm^{-1})
Bare Electrode	0.04
AC Electrode	2.00
DC Electrode	3.11

Table 2 presents the electrical resistivity on different foils and sulfur electrodes. The bare foil surface could form an aluminum oxide film in the presence of oxygen [10, 12, 15], and the passivation film has a negative effect on the conductivity of Al foil. The measured resistivity of bare foil is up to $28.17 \Omega\cdot\text{cm}$. After the bare foil was covered by active materials, the resistivity is further increased, because the contacts within active material particles and between these particles and Al foil generate contact resistances. In contrast, the resistivities of two electrodes using carbon-coated foils are significantly lower than that of bare foil. It may depend mainly on the following aspects: 1) the Al surface needs to be treated by acids and the native passivation film will be removed before the carbon layer is introduced, which directly improves conductivity of the foil substrate itself; 2) the designed highly conductive carbon layer also favors rapid electron transfer; 3) carbon-coated layer enhances the binding force between the active material and current collector (as discussed in Table 1), reducing contact resistances between them [16]. Compared with AC foil, DC foil has preferable carbon layer design and better adhesion ability to active material, thus resulting in lower electrical resistivity.

Table 2. Electrical resistivity of the foil and sulfur electrode measured by four-probe test

Type	Resistivity ($\Omega\cdot\text{cm}$)
Bare Foil	28.17
AC Foil	14.33
DC Foil	5.25
Bare Electrode	30.30
AC Electrode	16.11
DC Electrode	6.77

The effects of foil type on electrochemical characteristics of Li-S batteries were further investigated. The CV curves of the cells were shown in Fig.2a. Two cathodic peaks in negative scan are related to the transformation of elemental sulfur to soluble polysulfides (Li_2S_n , $4 \leq n \leq 8$) and the formation of insoluble $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$, respectively. And one typical anodic peak during subsequent positive scan represents the multistep oxidation of $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$, eventually forming oxidized Li_2S_8 or S [17]. In contrast to bare foil, the carbon-coated foils allow two cathodic peaks located at higher potential region and oxidation peak at lower value, indicating better redox reversibility and less cell polarization. This is mainly attributed to the decrease of electrode resistivity by additional carbon layer. The various charge/discharge plateaus appearing in the potential profiles of the cells (Fig. 2b) are corresponding to those anodic/cathodic peaks of CV curves. The fact that the cells using two carbon-coated foils have higher discharge plateaus than that using bare foil is well consistent with the CV results.

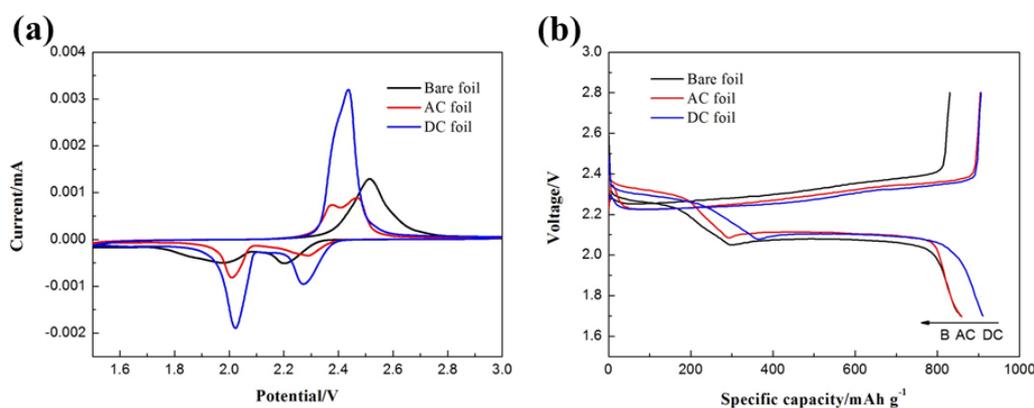


Figure 2. (a) CV curves and (b) potential profiles of the Li-S cells using different foils

Fig.3a and 3b exhibit the cycle performances of Li-S cells. The capacity fades rapidly in the cell using bare foil. After 50 cycles, the reserved capacity and capacity retention is only 560 mAh g^{-1} and 65.8 %, respectively. Moreover, the discharge plateau descends step by step during cycling (Fig.3c), suggesting the cell polarization increases gradually. When carbon-coated foil was chose as current collector, the cycle capability of the cell is improved remarkably. Especially for DC foil, a high reversible capacity of 655 mAh g^{-1} after 50 cycles is obtained (capacity retention reaches ~72 %), accompanied by quite stable discharge plateau over the whole cycle period (Fig.3d). The obtained electrochemical property owing to the unique foil is comparable with previous reports adopting other novel current collectors [18, 19]. The carbon-coated foil not only promotes the electronic conduction of the electrode, but also enhances the adhesion of active material towards current collector (restricting the removal of active material from the electrode). These factors together make more sulfur species electrochemically active over repeated cycles, so high utilization of active material is achieved. In addition, it is considered that the carbon coating can avoid direct contact of Al substrate with organic electrolyte, consequently preventing the metallic corrosion and maintaining the stabilization of current collector, which may be an important reason for the excellent performance as well.

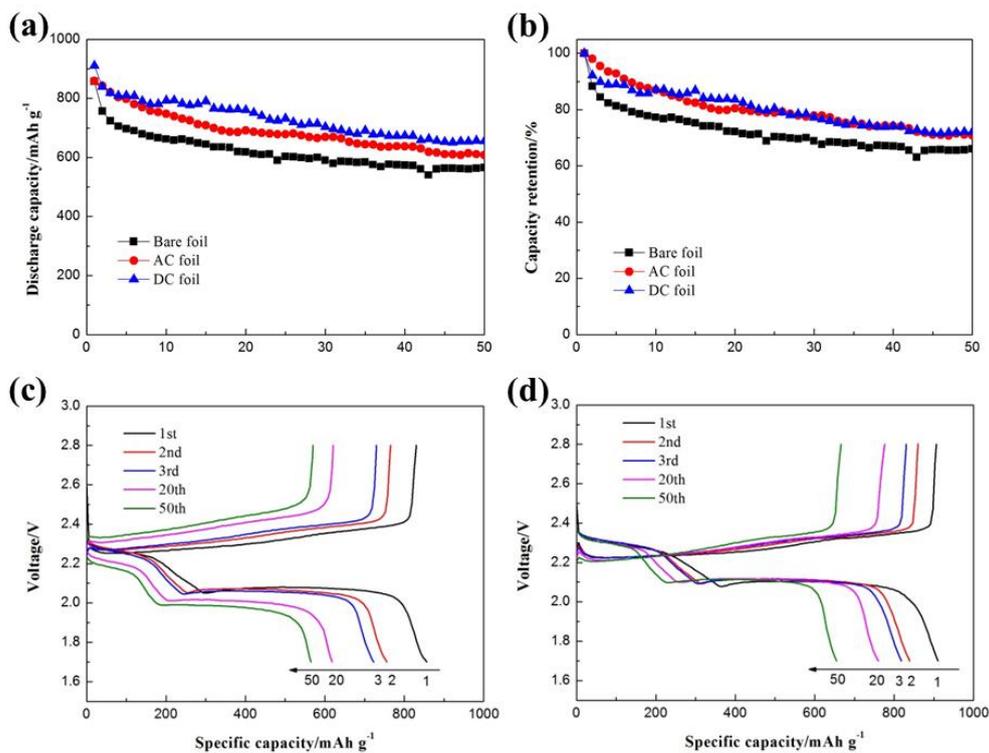


Figure 3. (a) Discharge capacity and (b) capacity retention of Li-S cells using different foils during cycling at a rate of 0.2 C; Charge-discharge curves of the cell using (c) bare foil and (d) DC foil

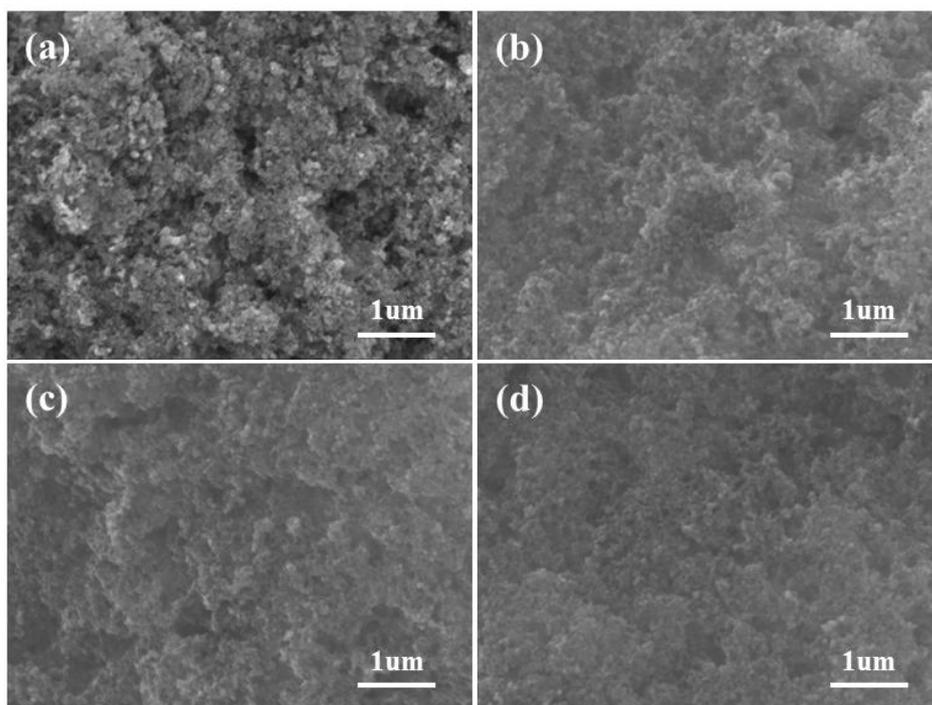


Figure 4. SEM images of (a) bare electrode before cycle and (b) bare electrode, (c) AC electrode, (d) DC electrode after cycles

To get further insight into the reason why the carbon-coated foil is capable of boosting cell performance, the morphologies of different sulfur electrodes were characterized. It can be seen that the typical electrode shows a porous morphology before cycle (Fig.4a). After cycles, the pore space is occupied by some solid particles and the porous characteristic of the electrode is no longer obvious. This is mainly involved with the deposition of insoluble reaction products ($\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$) on the electrode [20]. It should be noted that the surface morphology using carbon-coated foil (Fig.4c and 4d) looks more uniform and regular than that using bare foil (Fig.4b). As carbon-coated foil has a good adhesion to the active material, the random accumulation of insoluble products in the charge-discharge process would be limited to some extent. Meanwhile, carbon-coated foil is conducive to rapid charge transfer within the whole electrode, decreasing the possibility of forming non-active region in local position [21]. Hence those inevitable deposits can be well-distributed in the electrode. It will serve as sufficient utilization of active species and structural stabilization of the sulfur electrode.

The EIS results of the prepared cells using different foils were shown in Fig.5. The impedance plots before cycle are composed of a semicircle in high frequency and an inclined line in the low frequency (Fig.5a), corresponding to the charge-transfer resistance (R_{ct} , occurring at the electrolyte/electrode interface) and Warburg impedance (W_o , relating to Li^+ diffusion in the electrode), respectively. The high-frequency intercept on the real axis represents ohmic resistance (R_o), consisting of the ionic resistance of the electrolyte, the contact resistance between active material and current collector and the intrinsic resistance of active materials. After cycles, an additional semicircle appears in the impedance responses (Fig.5b), relating to Li^+ migration through the solid electrolyte interface films (R_s) [22]. The plots were fitted by the ZView software and the insets display the corresponding equivalent circuits. The fitted resistance data are shown in Table 3.

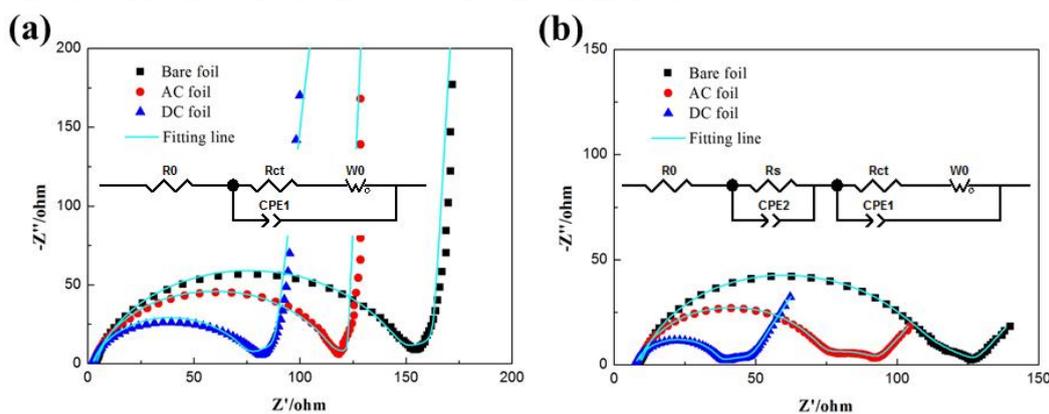


Figure 5. Nyquist plots of the prepared cells using different foils (a) before cycle and (b) after cycles

The slight increase in R_o with cycle illustrates that charge-discharge process causes the bulk resistance to become larger. However, the values in the cells using two carbon-coated foils are always smaller than the bare foil, ascribing to better electric contact between active material and carbon-coated foil and higher conductivity of the current collector. The decline of R_{ct} after cycling is probably attributed to the redistribution of sulfur in the electrode and continuous penetration of the electrolyte into the electrode [22, 23]. The DC foil with “point-plane” combined surface contributes to lowest R_{ct} ,

suggesting that it is strongly in favor of rapid electron/ion transport due to the overall improvements of electrode properties. While the uniform surface morphology of sulfur cathode using carbon-coated foil (as discussed in Fig.4) could facilitate Li^+ migration thus resulting in relatively low R_s value.

Table 3. Fitted resistances data from the equivalent circuit

Type	Stage	$R_0(\Omega)$	$R_s(\Omega)$	$R_{ct}(\Omega)$
Bare Foil	before cycle	3.8	/	142.1
	after cycles	8.7	90.8	27.5
AC Foil	before cycle	2.7	/	112.1
	after cycles	8.3	64.1	20.5
DC Foil	before cycle	2.1	/	71.7
	after cycles	7.3	29.3	11.5

4. CONCLUSIONS

Significant effects of current collector type on the basic properties of sulfur electrode and electrochemical performance of Li-S cell have been demonstrated in this study. The carbon-coated Al foil with rough surface morphology is favorable for strong adhesion of active material and excellent conductivity within the electrode. Compared to widely-used bare foil, higher capacity delivery, better cycle stability and less polarization impedance are achieved in the cell using carbon-coated foil. Besides, it is found that the carbon-coated Al foil with point- plane combined surface structure is more advantageous in improving electrode quality and cell capability than another carbon-coated foil covered by merely some particle materials. This work is beneficial to better understand the roles carbon-coated Al foil played in Li-S battery system.

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