Sandwiched Cathodes Assembled from CoS$_2$-Modified Carbon Clothes for High-Performance Lithium-Sulfur Batteries

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Structural design of advanced cathodes is a promising strategy to suppress the shuttle effect for lithium-sulfur batteries (LSBs). In this work, the carbon cloth covered with CoS$_2$ nanoparticles (CC-CoS$_2$) is prepared to function as both three-dimensional (3D) current collector and physicochemical barrier to retard migration of soluble lithium polysulfides. On the one hand, the CC-CoS$_2$ film works as a robust 3D current collector and host with high conductivity, high sulfur loading, and high capability of capturing polysulfides. On the other hand, the 3D porous CC-CoS$_2$ film serves as a multifunctional interlayer that exhibits efficient physical blocking, strong chemisorption, and fast catalytic redox reaction kinetics toward soluble polysulfides. Consequently, the Al@S/AB@CC-CoS$_2$ cell with a sulfur loading of 1.2 mg cm$^{-2}$ exhibits a high rate capability ($\approx$823 mAh g$^{-1}$ at 4 C) and delivers excellent capacity retention (a decay of $\approx$0.021% per cycle for 1000 cycles at 4 C). Moreover, the sandwiched cathode of CC-CoS$_2$@S/AB@CC-CoS$_2$ is designed for high sulfur loading LSBs. The CC-CoS$_2$@S/AB@CC-CoS$_2$ cells with sulfur loadings of 4.2 and 6.1 mg cm$^{-2}$ deliver high reversible capacities of 1106 and 885 mAh g$^{-1}$, respectively, after 100 cycles at 0.2 C. The outstanding electrochemical performance is attributed to the sandwiched structure with active catalytic component.

1. Introduction

To meet the requirement of developing rechargeable batteries with high energy density and long cycle life, lithium-sulfur batteries (LSBs) are regarded as one of the distinguished devices for next generation rechargeable batteries, owing to the natural abundance, low cost, high theoretical specific capacity of 1675 mAh g$^{-1}$ (five times the capacity of LiCoO$_2$), high gravimetric energy density of 2600 Wh kg$^{-1}$ and high volumetric energy density of 2800 Wh L$^{-1}$ of sulfur cathode.$^{[1–4]}$ However, the LSBs suffer from a series of intrinsic problems: 1) the severe “shuttle effect” caused by dissolution of intermediate lithium polysulfide (Li$_2$S$_n$, 4 $\leq$ n $\leq$ 8) species into electrolyte during the discharge/charge process, leading to a dramatic capacity loss and a low coulombic efficiency,$^{[5–8]}$ 2) the insulating nature of both sulfur (the active material, 10$^{-30}$ S cm$^{-1}$) and Li$_2$S (the product after discharge, 10$^{-14}$ S cm$^{-1}$),$^{[9–11]}$ and 3) the huge volumetric expansion of sulfur ($\approx$80%) upon lithiation owing to the density difference between sulfur (2.03 g cm$^{-3}$) and Li$_2$S (1.66 g cm$^{-3}$).$^{[12–14]}$ These issues become more serious in high sulfur loading LSBs. Moreover, some additional problems may occur: the thick active material film on the planar Al foil current collector is prone to crack and fall off during discharge/charge process$^{[15]}$ and the increasing thickness of active material layer blocks the Li$^+$ transport and increases the resistance, leading to deteriorated electrochemical performance.$^{[16]}$

To overcome the above-mentioned issues and improve the electrochemical performance of LSBs, many efforts have been devoted to developing advanced sulfur hosts and multifunctional separators.$^{[17–21]}$ The carbonaceous materials, such as mesoporous carbon (CMK-3),$^{[22–25]}$ reduced graphene oxide,$^{[26,27]}$ carbon nanotubes,$^{[28,29]}$ multichannel fibers,$^{[30–32]}$ were adopted as advanced sulfur hosts to reduce the capacity fading. These carbon-based host materials typically have essential characteristics of high electronic conductivity, large specific surface area, and porous structures, which can improve the conductivity, realize high sulfur loading and reduce the influence of volumetric expansion. However, the LSBs assembled from such...
carbonaceous hosts still suffer from poor rate capability and cycling performance, as the physical adsorption between the nonpolar carbonaceous materials and soluble polysulfides is usually insufficient to restrain the shuttle effect, inevitably causing low sulfur utilization.\textsuperscript{[33,34]} On the other hand, some polar metal compounds, such as metal organic frameworks,\textsuperscript{[35–37]} metal oxides,\textsuperscript{[38–40]} metal sulfides,\textsuperscript{[41–43]} metal nitrides,\textsuperscript{[44,45]} exhibit strong chemisorption of soluble polysulfides and are capable of capturing polysulfides species. Meanwhile, they can also function as an active catalyst which plays a key role in catalyzing polysulfide redox reactions (conversion of soluble Li2Sn to Li2S2/Li2S) and accelerating the reaction kinetics.\textsuperscript{[43]} Shuttling of polysulfide species can be effectively retarded when these polar metal compounds are introduced in the host and/or the separator.\textsuperscript{[19,41,42]} For example, cobalt sulfides have intensively investigated in host/interlayer/separator of LSBs. They can effectively capture polysulfides and promote their reversible redox kinetics, thereby resulting in improved electrochemical performance.\textsuperscript{[46–53]} Therefore, designing advanced cell configuration to integrate both physical confinement and chemical adsorption of polysulfides is a promising route to enhance electrochemical performance of LSBs, especially the high sulfur loading LSBs.

Herein, we design and fabricate advanced cathodes constructed from CoS\textsubscript{2} nanoparticles coated carbon cloth (CC-CoS\textsubscript{2}) for high-performance LSBs. The free-standing CC-CoS\textsubscript{2} can serve as a robust and flexible three-dimensional (3D) current collector with a good conductivity for fast electron transport, and the 3D structure with sufficient void space can not only increase the sulfur loading but also effectively buffer the volume expansion during the lithiation/delithiation process. On the other hand, owing to the small size and excellent polarity of the uniformly covered CoS\textsubscript{2} nanoparticles, the CC-CoS\textsubscript{2} provides strong localized chemical binding with lithium polysulfides and benefits for fast interfacial charge transfer. Therefore, the CC-CoS\textsubscript{2} film can be adopted as an efficient permeselective barrier that realizes multiple functions of efficient physical blocking, strong chemical adsorption, and rapid catalytic conversion of lithium polysulfides, as well as fast lithium-ion transport kinetics. As a result, the Al@S/AB@CC-CoS\textsubscript{2} cell with low sulfur loading of \(\approx 1.2 \text{ mg cm}^{-2}\) exhibits high rate capability and excellent capacity retention with a low decay of \(\approx 0.021\%\) per cycle for 1000 cycles at 4 C. Moreover, the sandwiched cathodes assembled from CC-CoS\textsubscript{2}@S/AB@CC-CoS\textsubscript{2} are also designed and fabricated for high sulfur loading LSBs (3.0–6.1 mg cm\(^{-2}\)) with significantly improved electrochemical performance.

2. Results and Discussion

The CC-CoS\textsubscript{2} was prepared by a simple one-pot hydrothermal synthesis of CoS\textsubscript{2} nanoparticles on a CC scaffold using CoSO\textsubscript{4}·7H\textsubscript{2}O and SCN(NH\textsubscript{2})\textsubscript{2} as the reactants, as shown in Figure 1a. Figure 1b–d shows typical scanning electron microscopy (SEM) images of the as-prepared CC-CoS\textsubscript{2}, which can well reserve 3D morphology of the bare CC built from carbon fibers (Figure S1, Supporting Information). However, the surfaces of the fibers become much rough and are uniformly covered by small CoS\textsubscript{2} nanoparticles with several tens of nanometers. Figure 1e displays a transmission electron microscopy (TEM) image of the CC-CoS\textsubscript{2} fiber, and corresponding energy dispersive X-ray spectroscopy (EDX) mappings of C, Co, S are shown in Figure 1f–h, respectively, which reveals that the CoS\textsubscript{2} nanoparticles are covered on surface of carbon fiber. Figure 1i presents a high-resolution TEM (HRTEM) image of the CoS\textsubscript{2} nanoparticle. The lattice fringes distance of 0.167 nm matches well with the (111) interplanar spacing of cubic CoS\textsubscript{2}, confirming formation of crystalline CoS\textsubscript{2} nanoparticles. X-ray diffraction (XRD) pattern of CC-CoS\textsubscript{2} is shown in Figure 1j. All diffraction peaks can be well indexed to those of CoS\textsubscript{2} (PDF#441-1471), except the two peaks marked with “*” corresponding to CC. The Raman spectrum in Figure S2, Supporting Information, has two resonance peaks at 290 and 390 cm\(^{-1}\), which agree with the previously reported values of CoS\textsubscript{2}.\textsuperscript{[54]} X-ray photoelectron spectroscopy (XPS) was also performed to further investigate the surface chemical composition of CoS\textsubscript{2}. Figure 1k shows the Co 2p region, where there are two prominent peaks at 778.9 and 794.0 eV corresponding to Co 2P\textsubscript{3/2} and Co 2P\textsubscript{1/2} of Co\textsuperscript{2+}, respectively.\textsuperscript{[46,56]} The appearance of satellite peaks at 780.1 and 802.6 eV also supports the presence of Co\textsuperscript{2+}.\textsuperscript{[57]} For the S 2p region in Figure 1l, a couple of peaks at 162.9 and 164.1 eV can be assigned to S 2P\textsubscript{1/2} and S 2P\textsubscript{3/2}, and a minor peak at 168.8 eV can be assigned to the sulfate impurity.\textsuperscript{[59]} Therefore, the above results demonstrate the formation of CoS\textsubscript{2} nanoparticles on CC surface.

To evaluate chemical adsorption capability of the CC-CoS\textsubscript{2} and bare CC for lithium polysulfides, visual adsorption tests were carried out. As shown inset of Figure 2a, the blank Li\textsubscript{2}S\textsubscript{6} solution has a brown color. When the CC was immersedin the Li\textsubscript{2}S\textsubscript{6} solution for 24 h, the color keeps unchanged, which indicates the weak adsorption capability of the nonporous CC. It is worth noting that the Li\textsubscript{2}S\textsubscript{6} solution after treatment with CC-CoS\textsubscript{2} for 24 h becomes almost transparent, thereby indicating the outstanding adsorption capability of CC-CoS\textsubscript{2} owing to the large polarity of CoS\textsubscript{2}. More precise analysis was achieved by the UV–vis spectroscopy. The blank Li\textsubscript{2}S\textsubscript{6} solution has an obvious absorption shoulder at 400–500 nm.\textsuperscript{[60]} The peak intensity is only slightly decreased for the Li\textsubscript{2}S\textsubscript{6} solution treated with CC-CoS\textsubscript{2}, however, the peak almost disappears for the Li\textsubscript{2}S\textsubscript{6} solution treated with CC-CoS\textsubscript{2}. This observation is in good agreement with visual adsorption test, indicating the strong adsorption capability of CC-CoS\textsubscript{2}.

Symmetrical cells constructed by two identical CC-CoS\textsubscript{2} (or CC) as electrodes and filled with the electrolyte of 0.2 M Li\textsubscript{2}S\textsubscript{6} in 1,3-dioxolane (DOL) and dimethyl (DMF) were fabricated to study catalytic activity of CC-CoS\textsubscript{2} (or CC) on polysulfide redox kinetics. Cyclic voltammetry (CV) curves of the symmetric cells of CC-CoS\textsubscript{2}||CC-CoS\textsubscript{2} and CC||CC are shown in Figure 2b. The CV curves exhibit four pronounced reduction/oxidation peaks, which can be assigned to the electrochemical redox reactions of polysulfides on the electrodes: Peak A arises from the reduction of Li\textsubscript{2}S\textsubscript{6} → Li\textsubscript{2}S; Peak B is the oxidation of Li\textsubscript{2}S → Li\textsubscript{2}S\textsubscript{2} and Peak C is the oxidation of Li\textsubscript{2}S\textsubscript{2} → Li\textsubscript{2}S\textsubscript{4} and Peak D can be attributed to the reduction of Li\textsubscript{2}S\textsubscript{4} → Li\textsubscript{2}S\textsubscript{6}.\textsuperscript{[61]} The redox peak current is larger in the CC-CoS\textsubscript{2}||CC-CoS\textsubscript{2} cell than that of the CC||CC one. This result suggests that CC-CoS\textsubscript{2} has a better catalytic activity than CC. The Nyquist plots of the two symmetric cells are shown in Figure 2c. Compared with the CC||CC cell, the CC-CoS\textsubscript{2}||CC-CoS\textsubscript{2} cell exhibits a much smaller semicircle in the high frequency range, revealing a significantly reduced charge transfer resistance (\(R_c\)) at the electrode-electrolyte interface. It indicates that the CoS\textsubscript{2} nanoparticles covered on the CC surface can serve as an active...
electrocatalyst and accelerate the conversion kinetics of polysulfides.

Blocking of polysulfide diffusion by the CC-CoS$_2$ and CC films were carried out in an H-type glass, where the left chamber contains the Li$_2$S$_6$ in DOL/DME solution, and the right chamber is the transparent DOL/DME solution. The Celgard separator (i.e., CS), the Celgard separator with CC (i.e., CS+CC) and the Celgard separator with CC-CoS$_2$ (i.e., CS+CC-CoS$_2$) were employed in the middle of the two chambers, respectively. We took pictures and recorded color changes of the solutions after resting for different time (Figure 2d). As an increase in the resting time (0–24 h), the color of the right chamber solution gradually changes from transparent to yellow for both CS and CS+CC, indicating more polysulfides were diffused in. After resting for 24 h, however, the right chamber solution shows little change for CS+CC-CoS$_2$. Such an observation reveals CC-CoS$_2$ film can effectively retard the polysulfide diffusion and suppress the shuttle effect.

In order to investigate effect of CC-CoS$_2$ film as a barrier layer on improving electrochemical performance, LSBs without and with CC-CoS$_2$ and CC interlayer were fabricated by coating the active material (S) mixed with acetylene black (AB) on the traditional current collector of Al foils. The sulfur loading density on
Figure 2. a) UV–vis spectra of the $\text{Li}_2\text{S}_6$ in DOL/DME solutions before and after exposure to CC and CC-CoS$_2$ for 12 h, respectively; inset: the photographs of the three solutions. b) CV curves of the symmetric cells assembled from CC-CoS$_2$ and CC, respectively, in 0.2 m $\text{Li}_2\text{S}_6$ electrolyte scanned at 10 mV s$^{-1}$. c) Nyquist plots of the symmetric cells assembled from CC-CoS$_2$ and CC, respectively. d) Photographs of H-type glass cell filled with the lithium polysulfide ($\text{Li}_2\text{S}_6$) in DOL/DME solution (the left chamber) and the bare DOL/DME solvent (the right chamber), and separated by the bare Celgard separator (i.e., CS), the separator with a CC film (i.e., CS + CC), and the separator with a CC-CoS$_2$ film (i.e., CS + CC-CoS$_2$) taken after testing durations of 0, 6, 12, and 24 h.

the Al foils is $\approx$1.2 mg cm$^{-2}$. Figure 3a shows a schematic diagram of the Al@S/AB@CC-CoS$_2$ cathode, where the CC-CoS$_2$ film was covered on the surface of the active material layer. The rate capabilities of the Al@S/AB@CC-CoS$_2$, Al@S/AB@CC and Al@S/AB cells were evaluated by cycling under different current rates (0.1–4 C) (Figure 3b). The Al@S/AB cell delivers low discharge capacities of 805, 603, 390, 26, and 1 mAh g$^{-1}$ at the current rates of 0.1, 0.2, 0.5, 1, 2, and 4 C, respectively. Compared with the Al@S/AB cell, both the Al@S/AB@CC-CoS$_2$ and Al@S/AB@CC cells show significantly improved specific capacities in the wide current range (0.1–4 C), and the Al@S/AB@CC-CoS$_2$ cell exhibits the best rate performance. The reversible specific capacities of the Al@S/AB@CC-CoS$_2$ cell are as high as 1481, 1408, 1271, 1159, and 1031 mAh g$^{-1}$ at the current rates set for 0.1, 0.2, 0.5, 1, 2, and 4 C, respectively. The capacity recovers to 1333 mAh g$^{-1}$ when the current rate decreases from 4 to 0.2 C. Figure 3c shows the galvanostatic charge/discharge profiles of Al@S/AB@CC-CoS$_2$ from 0.1 to 4 C in the potential range of 1.7–2.8 V. There are two obvious reaction plateaus along with sloping regions in the various discharge curves. The plateau at $\approx$2.3 V is attributed to the conversion of $\text{S}_8$ to $\text{Li}_2\text{S}_6$ (4 $\leq n \leq 8$), and the lower plateau at $\approx$2.1 V is assigned to the reaction process of $\text{Li}_2\text{S}_6$ to $\text{Li}_2\text{S}_4$/$\text{Li}_2\text{S}_2$.[11] $Q_{\text{H}}$ represents the discharge capacities at the high discharge voltage plateaus ($\approx$2.3 V), and $Q_{\text{L}}$ represents the discharge capacities of the low voltage plateaus ($\approx$2.1 V).[59] As discharge current increases from 0.1 to 4 C, the large capacity loss (658 mAh g$^{-1}$) of Al@S/AB@CC-CoS$_2$ is mainly attributed to $Q_{\text{L}}$ loss, while $Q_{\text{H}}$ has little decay (24 mAh g$^{-1}$). Importantly, the two distinct discharge voltage plateaus for Al@S/AB@CC-CoS$_2$ cell can still be observed at high rate of 4 C, implying excellent electrochemical dynamic behavior. In contrast, the two discharge voltage plateaus at 4 C almost disappear for the Al@S/AB@CC cell (Figure S3, Supporting Information). Theoretically, $Q_{\text{H}}$ and $Q_{\text{L}}$ are 419 and 1256 mAh g$^{-1}$, respectively, corresponding to $Q_{\text{H}}$/$Q_{\text{L}}$ = 3.0.[59] The $Q_{\text{H}}$/$Q_{\text{L}}$ ratio reflects the capability of converting polysulfides.[62] Figure 3d displays charge/discharge profiles of Al@S/AB@CC-CoS$_2$, Al@S/AB@CC and Al@S/AB cells at a current density of 0.2 C. The $Q_{\text{H}}$ and $Q_{\text{L}}$ values of the three cells are calculated and presented in Figure 3e. The Al@S/AB@CC-CoS$_2$ cell has a $Q_{\text{H}}$/$Q_{\text{L}}$ ratio of 2.44, which is higher than those of Al@S/AB@CC cell (1.84) and Al@S/AB cell (1.63). It indicates the significantly promoted conversion of $\text{Li}_2\text{S}_n$ (4 $\leq n \leq 8$) to $\text{Li}_2\text{S}_4$/$\text{Li}_2\text{S}_2$ in the Al@S/AB@CC-CoS$_2$ cell. Furthermore, the charge/discharge profiles of Al@S/AB@CC-CoS$_2$ cell exhibit less polarization than those of Al@S/AB@CC and Al@S/AB cells.

Figure 3f shows CV curves of the Al@S/AB@CC-CoS$_2$, Al@S/AB@CC, and Al@S/AB cells scanned at 0.1 mV s$^{-1}$. There
are two cathodic peaks and two overlapped anodic peaks. In comparison with the Al@S/AB@CC and Al@S/AB cells, the Al@S/AB@CC-CoS2 cell delivers higher current density and less polarization of the cathodic/anodic peaks, indicating its accelerated redox reaction kinetics. In order to further analyze the catalytic effects of the cathode reactions, both cathodic and anodic Tafel plots derived from the polarization curves (regions I and II in Figure 3f) are shown in Figure 3g,h, respectively. The Tafel slope at cathodic sweep is 39 mV dec$^{-1}$ for Al@S/AB@CC-CoS2, 45 mV dec$^{-1}$ for Al@S/AB@CC and 81 mV dec$^{-1}$ for Al@S/AB (Figure 3g). For the anodic sweep, the Al@S/AB@CC-CoS2 also has the smallest Tafel slope. The lower Tafel slope reveals the better catalytic activity. Therefore, Al@S/AB@CC-CoS2 exhibits the highest catalytic activity to accelerate the polysulfide conversion reactions.

To get a deep understanding of the improved electrochemical performance, electrochemical impedance spectroscopy (EIS) of the cells before and after cycling was performed. The Nyquist plots of the three cells before cycling are shown in Figure 3i. Each plot consists of a single semicircle in the high to medium frequency region and an inclined line at low frequency, which can be ascribed to the charge transfer resistance ($R_\text{ct}$) and diffusion resistance ($R_\text{d}$), respectively. The $R_\text{ct}$ value of the Al@S/AB@CC-CoS2 is 108 Ω, which is smaller than those of the Al@S/AB@CC (117 Ω) and Al@S/AB (140 Ω). The Nyquist plots of the cells recorded after 10 cycles at 0.5 C were also performed as shown in Figure S4, Supporting Information. It is obvious that all plots have an additional semicircle in the high frequency region which corresponds to the interfacial resistance ($R_\text{i}$) resulted from the irreversible Li$_2$S$_4$/Li$_2$S layer. $R_\text{i}$ value of Al@S/AB@CC-CoS2 cell (1.5 Ω) is smaller than that of Al@S/AB@CC cell (2.7 Ω). The Al@S/AB@CC-CoS2 cell after 10 cycles delivers a significantly decreased $R_\text{ct}$ (6.8 Ω), thus indicating improved electrolyte infiltration upon cycling. Compared with the Al@S/AB@CC cell, the Al@S/AB@CC-CoS2 cell delivers smaller $R_\text{ct}$ values before and after cycling, suggesting that the CC-CoS2 film contributes to faster charge transfer kinetics during the polysulfides conversion. These electrochemical results reveal the CC-CoS2 film can work as an excellent barrier to block polysulfide shuttle effect, and the polar CoS2 nanoparticles have high catalytic activity to accelerate the polysulfide conversion reactions.

The Li$_2$S precipitation test was carried out on surfaces of CC-CoS2 and CC hosts with addition of 0.1 m Li$_2$S$_8$ catholyte (20 µL) as the active material. The two cells were potentiostatically discharged at 2.0 V for 50 min, after they were galvanostatically discharged to 2.06 V. Figure 4a,b shows the time-dependent discharge current profiles of Li$_2$S deposition on the CC-CoS2 and CC surfaces, respectively. The deposition of Li$_2$S on CC-CoS2 surface is much faster with a higher peak current than on CC. The CC-CoS2 cell reaches the peak current of 0.53 mA with a time of 310 s, while the CC cell requires 537 s to achieve the peak current of 0.26 mA. Furthermore, the CC-CoS2 cell yields a precipitation capacity of 105 mAh g$^{-1}$, which is much larger than that (85 mAh g$^{-1}$) of the CC cell. This observation reveals the CC-CoS2 has the
better catalytic activity, which enables the more efficient utilization of lithium polysulfides\[67–69\]. The potentiostatic Li$_2$S dissolution tests were also performed (Figure 4c,d). The CC-CoS$_2$ cell exhibits a much larger dissolution capacity (143 mAh g$^{-1}$) than the CC cell (117 mAh g$^{-1}$). All these results further reveal that the CoS$_2$ nanoparticles covered on CC surface have a superior electrocatalytic activity to promote the deposition and dissolution of Li$_2$S.

Cycling performance of the Al@S/AB@CC-CoS$_2$, Al@S/AB@CC and Al@S/AB cells were evaluated. Figure 3j displays the cycling performance of the three cells at 0.5 C rate. The specific capacity of the Al@S/AB@CC-CoS$_2$ cell stabilizes at 1150 mAh g$^{-1}$ after 100 cycles at 0.5 C. In a distinct contrast, the Al@S/AB@CC and Al@S/AB cells yield respectively lower reversible specific capacities of 777 and 271 mAh g$^{-1}$ after 100 cycles. Cycle stability of the Al@S/AB@CC-CoS$_2$ cell was further investigated by analyzing the evolution of $Q_L/Q_H$ ratio at representative cycles (Figure S5, Supporting Information). $Q_L$ (QL) is 408 (847) mAh g$^{-1}$ at the 2nd cycle, and slightly decreases to 399 (834) mAh g$^{-1}$ at 20th cycle, to 378 (815) mAh g$^{-1}$ at 60th cycle, and to 352 (793) mAh g$^{-1}$ at 100th cycle, corresponding to a capacity retention of 98% (98%), 93% (96%), and 86% (94%), respectively. The high retention rates indicate that the shuttle effect has been effectively suppressed. Importantly, $Q_L/Q_H$ ratio increases from 2.08 (2nd) to 2.09 (20th), 2.16 (60th), and 2.25 (100th). The increase in $Q_L/Q_H$ ratio indicates improved catalytic conversion of polysulfides during cycling process, which is responsible for the well-preserved capacity.

After cycling for 100 cycles at 0.5 C, the three cells were disassembled to observe color change of the diaphragms, owing to soluble polysulfide diffusion. The separator of the Al@S/AB cell becomes yellowish obviously, while the Al@S/AB@CC-CoS$_2$ and Al@S/AB@CC cells show a separator with little color change (Figure S6, Supporting Information). This observation also reveals the shuttle effect of polysulfides is significantly suppressed and loss of active material is effectively prevented by incorporating CC-CoS$_2$ barrier in LSBs. XPS spectra of the CC-CoS$_2$ after cycling were recorded to gain a better understanding of the chemical adsorption and catalytic effect of CoS$_2$ on polysulfides. The XPS peaks of Co 2p exhibit a slight shift to lower binding energy (794.0 eV $\rightarrow$ 793.3 eV, 778.9 eV $\rightarrow$ 778.6 eV) relative to those before cycling, suggesting the Co$\rightarrow$S$_2$$^{-}$ interaction (Figure S8a, Supporting Information). The S 2p peak at 162.7 eV corresponding to CoS$_2$ also shows a shift of 0.2 eV to lower binding energy (Figure S8b, Supporting Information). These shifts are considered to be resulted from the interaction between CoS$_2$ nanoparticles and negatively charged polysulfides.\[61\] The polythionate (168.8 eV), thiosulfate (167.1 eV), Li$_2$S$_4$ (163.8 eV), and Li$_2$S$_2$ (161.8 eV) are also detected from the S 2p spectrum as shown in Figure S8b, Supporting Information. These peaks can be ascribed to the catalytic reactions of long-chain polysulfides with CoS$_2$ to form intermediate thiosulfate and short-chain polysulfides.\[70\]

To further investigate the synergistic effect of physical blocking, chemical absorption and catalytic conversion, a long-term cycling test of the Al@S/AB@CC-CoS$_2$ cell was carried out with a high current rate of 4.0 C. As shown in Figure 3k, the Al@S/AB@CC-CoS$_2$ cell displays a discharge capacity of 775 mAh g$^{-1}$ after the activation at 0.2 C for the initial three cycles. The capacity increases to 874 mAh g$^{-1}$ after following 200 cycles and then remains at 610 mAh g$^{-1}$ after 1000 cycles. The average decay rate of specific capacity is only 0.021% per cycle at 4 C rate, thereby indicating the excellent operation stability.
of the Al@S/AB@CC-CoS₂ cell. Therefore, the Al@S/AB@CC-CoS₂ cell with a low sulfur loading is demonstrated with superior electrochemical performance as indicated by the high specific capacity, excellent rate capacity, and unexpected long-term cycling stability.

CV measurements at various scan rates from 0.1 to 1.0 mV s⁻¹ were conducted on Al@S/AB@CC-CoS₂, Al@S/AB@CC, and Al@S/AB cells to study the Li⁺ diffusion coefficients (Figure 5a-c). The peak current of the oxidation peak and two reduction peaks at different potentials increases with the accelerated scan rate for the three cells. Figure 5d-f shows the linear curves obtained by fitting the peak current related to the scanning rate, according to the Randles–Sevcik equation:

\[
I_p = 2.69 \times 10^5 \cdot n^{1/2} \cdot A \cdot D_{Li}^{1/2} \cdot C_{Li} \cdot v^{1/2}
\]

where \(I_p\) is the peak current, \(n\) represents the number of transferred electrons (\(n = 2\) in LSB), \(A\) stands for the electrode area (\(\approx 1.13\) cm²), \(D_{Li}\) corresponds to the diffusion coefficient of Li⁺ (cm² s⁻¹), \(v\) indicates the scan rate, and \(C_{Li}\) means the Li⁺ concentration in the electrolyte (mol cm⁻³). Therefore, \(D_{Li}\) values can be evaluated based on the slopes of the fitted curves. The Al@S/AB@CC-CoS₂ cell has the largest slopes of \(k = 0.603\) for peak I, \(k = 0.229\) for peak II, and \(k = 0.232\) for peak III. These values can be evaluated as follows:

\(D_{Li} = \frac{2.69 \times 10^5 \cdot n^{1/2} \cdot A \cdot C_{Li} \cdot v^{1/2}}{I_p} \cdot \frac{1}{v^{1/2}} \cdot \frac{1}{C_{Li}} \cdot \frac{1}{A}\)

The \(D_{Li}\) values are calculated to be \(38.2 \times 10^{-10}\), \(5.51 \times 10^{-10}\), and \(5.64 \times 10^{-10}\) cm² s⁻¹ for peaks I, II, and III, respectively. These values are nearly 5–6 times higher than those of Al@S/AB@CC cell (6.05 \(\times 10^{-10}\), 1.09 \(\times 10^{-10}\), and 1.25 \(\times 10^{-10}\) cm² s⁻¹). The Al@S/AB cell has the lowest \(D_{Li}\) values (0.44 \(\times 10^{-10}\), 0.22 \(\times 10^{-10}\), and 0.23 \(\times 10^{-10}\) cm² s⁻¹). These data mean that the Li⁺ diffusion rate is significantly accelerated for the Al@S/AB@CC-CoS₂ cell by incorporating the CC-CoS₂ film. The accelerated \(D_{Li}\) values of the Al@S/AB@CC-CoS₂ cell were also proved by galvanostatic intermittent titration technique (GITT) as shown in Figure S7, Supporting Information. The 3D porous CC-CoS₂ film can selectively sieve Li⁺ ions while effectively suppress undesired polysulfides migration to the anode side. The fast Li⁺ diffusion at various stages in the Al@S/AB@CC-CoS₂ cell indicates outstanding redox reaction kinetics during polysulfide conversion.

Besides working as an excellent barrier, the CC-CoS₂ film can also serve as a promising 3D current collector in LSBs with a higher sulfur loading. To highlight the advantages of CC-CoS₂ as a current collector in buffering volume expansion, promoting catalytic conversion reaction and slowing shuttle effect, electrochemical performances of LSBs using CC-CoS₂, CC, and Al foil as current collectors were compared. Figure 6a shows the schematic diagram of three different structure cells of Al@S/AB@CC-CoS₂, CC@S/AB@CC-CoS₂, and CC-CoS₂@S/AB@CC-CoS₂. The rate capabilities of Al@S/AB@CC-CoS₂, CC@S/AB@CC-CoS₂, and CC-CoS₂@S/AB@CC-CoS₂ cells with a sulfur loading of 2.0 mg cm⁻² were evaluated by cycling at different current rates from 0.2 to 1 C (Figure 6b). Significantly, the CC-CoS₂@S/AB@CC-CoS₂ cell yields high reversible specific capacities of 1471, 1353, and 1209 mAh g⁻¹ at the current rates of 0.2, 0.5, and 1 C. After the rate performance test, the CC-CoS₂@S/AB@CC-CoS₂ cell maintains a high specific capacity 1150 mAh g⁻¹ at 0.5 C after following 100 cycles, indicating good cycling stability. In comparison, the rate performances of both CC@S/AB@CC-CoS₂ and Al@S/AB@CC-CoS₂ cells at all rates are much lower than those of CC-CoS₂@S/AB@CC-CoS₂ cell.

Figure 6c shows the galvanostatic charge/discharge profiles of the three cells at 0.5 C. The capacities contributed by the higher-discharge plateau (Q₁₄₁) and the lower-discharge plateau (Q₁₄) are clearly revealed. The Al@S/AB@CC-CoS₂ cell has a relatively low Q₁₄ and Q₁₄ values of 332 and 497 mAh g⁻¹, corresponding to a Q₁₄/Q₁₄ ratio of 1.50. The Q₁₄/Q₁₄ ratio slightly increases to 1.59
Furthermore, the CC-CoS$_2@$S/AB@CC-CoS$_2$ cell exhibits the highest initial specific capacity of 1278, 1181, 1048, and 878 mAh g$^{-1}$ at 0.1 C. The average reversible specific capacities of the CC-CoS$_2@$S/AB@CC-CoS$_2$ cell are estimated to be 1278, 1181, 1048, and 878 mAh g$^{-1}$ at 0.1 C. The CC-CoS$_2@$S/AB@CC-CoS$_2$ cell exhibits lower specific capacities of 1029, 986, 916, and 653 mAh g$^{-1}$ at 0.1 C. The two cells with a sulfur loading of 3.0 mg cm$^{-2}$ were cycled at 0.2 C and 1 C, respectively. The rate performance of the two cells with a sulfur loading of 3.0 mg cm$^{-2}$ was further investigated.

Figure 7a shows the schematic diagram of a sandwiched structure of the CC-CoS$_2@$S/AB@CC-CoS$_2$ and the CC@S/AB cell as a control sample. The rate performance of the two symmetrical cells with a sulfur loading of 3.0 mg cm$^{-2}$ is presented in Figure 7b. The CC-CoS$_2@$S/AB@CC-CoS$_2$ cell yields a higher initial specific capacity than the CC@S/AB cell at 0.1 C. The average reversible specific capacities of the CC-CoS$_2@$S/AB@CC-CoS$_2$ cell are estimated to be 1278, 1181, 1048, and 878 mAh g$^{-1}$ at 0.1 C. The specific capacity can be well recovered to 1045 mAh g$^{-1}$ at 0.5 C, to 1156 mAh g$^{-1}$ at 0.2 C, and to 1232 mAh g$^{-1}$ at 0.1 C as the discharge current decreases. As comparison, the CC@S/AB cell exhibits lower specific capacities of 1029, 986, 916, and 653 mAh g$^{-1}$ at 0.1 C. The two cells with a sulfur loading of 3.0 mg cm$^{-2}$ were cycled at 0.2 C (Figure 7c). The CC-CoS$_2@$S/AB@CC-CoS$_2$ cell exhibits lower specific capacities of 1029, 986, 916, and 653 mAh g$^{-1}$ at 0.1 C. The two cells with a sulfur loading of 3.0 mg cm$^{-2}$ were cycled at 0.2 C (Figure 7c). The CC-CoS$_2@$S/AB@CC-CoS$_2$ cell exhibits lower specific capacities of 1029, 986, 916, and 653 mAh g$^{-1}$ at 0.1 C. The two cells with a sulfur loading of 3.0 mg cm$^{-2}$ were cycled at 0.2 C (Figure 7c). The CC-CoS$_2@$S/AB@CC-CoS$_2$ cell exhibits lower specific capacities of 1029, 986, 916, and 653 mAh g$^{-1}$ at 0.1 C. The two cells with a sulfur loading of 3.0 mg cm$^{-2}$ were cycled at 0.2 C (Figure 7c). The CC-CoS$_2@$S/AB@CC-CoS$_2$ cell exhibits lower specific capacities of 1029, 986, 916, and 653 mAh g$^{-1}$ at 0.1 C. The two cells with a sulfur loading of 3.0 mg cm$^{-2}$ were cycled at 0.2 C (Figure 7c).
cycles are achieved for both cells (Figure S10, Supporting Information). The performance is among the best of high sulfur loading LSBs as shown in Table S1, Supporting Information. The CC-CoS$_2$@S/AB@CC-CoS$_2$ cell can light up 46 light-emitting diode (LED) lamps at the same time (Figure 7h), showing a great potential for practical applications.

Density functional theory (DFT) calculation was conducted to investigate the binding energies of lithium polysulfides on CoS$_2$ and CC surfaces. The optimized structures of the various lithium polysulfides and S$_8$ molecules are shown in Figure S11, Supporting Information. The adsorption configurations of these sulfur species on the CoS$_2$ (111) plane and the carbon basal plane are presented in Figure 8a and Figure S12, Supporting Information, respectively. The binding energies of soluble polysulfides (Li$_2$S$_n$, $n =$ 4, 6, and 8) on CoS$_2$ are $-1.26$, $-1.12$, and $-1.06$ eV, which are much higher than those on carbon (Figure 8b). The higher binding energy indicates the stronger chemical anchoring of soluble Li$_2$S$_n$. The calculations match well with the visual adsorption test in Figure 2a, confirming the improved adsorption capability by coating CoS$_2$ on CC. The charge density of soluble Li$_2$S$_n$ absorbed on CoS$_2$ and carbon are quite different owing to their diverse electrostatic affinities. A pronounced charge accumulation and redistribution between Li$_2$S$_n$ and CoS$_2$ substrate occurs. Abundant electrons transfer to the Li–S bond, producing stable adsorption of Li$_2$S$_n$ on CoS$_2$, at a molecular level. On the contrary, less electron distribution is found on carbon surface, which results in weak atomic interaction and inferior binding energy of Li$_2$S$_n$ on carbon. In the discharge process, it involves the reduction of S$_8$ with Li$^+$ to form the various intermediate lithium polysulfides of Li$_2$S$_8$, Li$_2$S$_6$, Li$_2$S$_4$, and Li$_2$S$_2$, and the final product of Li$_2$S. The Gibbs free energies were evaluated for the above reactions on CoS$_2$ and carbon surfaces as displayed in Figure 8c. According to the calculated Gibbs free energy changes, the reaction from S$_8$ to Li$_2$S$_8$ is spontaneous and the conversion from Li$_2$S$_8$ to Li$_2$S$_6$/Li$_2$S$_4$ is nearly thermodynamic equilibrium on both CoS$_2$ and carbon surfaces. The reduction of Li$_2$S$_4$ to Li$_2$S$_2$/Li$_2$S has the obviously positive free energy changes ($0.97$ and $1.13$ eV) on carbon, implying that this conversion of Li$_2$S$_2$ to Li$_2$S is the rate-controlling step in the discharge process. In contrast, the same transformation happens spontaneously with large negative free energy changes ($-6.43$ and $-0.78$ eV) on CoS$_2$ surface. These calculations indicate that the reduction of polysulfides species is
more thermodynamically favorable on CoS₂ surface than that on carbon surface.

3. Conclusions

In summary, we reported an effective strategy to fabricate high-performance LSBs by using the as-prepared CC-CoS₂ film as both current collector and physicochemical barrier for capturing soluble lithium polysulfides and promoting their redox reactions. The CC-CoS₂ has the advantages of 3D porous structure, high conductivity, strong chemisorption, high catalytic activity, efficient physical blocking, and fast Li⁺ transport kinetics. Theoretical calculations reveal that catalytic reduction of sulfide species is thermodynamically more favorable on CoS₂ surface than on carbon. Compared with the pristine CC, the CC-CoS₂ exhibits improved physical confinement, enhanced chemical adsorption, and accelerated redox reaction kinetics of polysulfide species. Benefitting from these merits, the LSBs assembled from CC-CoS₂ exhibit significant improvements in discharge capacity, rate capability, and cycling stability. The discharge capacity at 1 C increases from 200 mAh g⁻¹ for Al@S/AB to 700 mAh g⁻¹ for Al@S/AB@CC and 1159 mAh g⁻¹ for Al@S/AB@CC-CoS₂. The Al@S/AB@CC-CoS₂ cell also shows high rate capability and long cycling stability. Furthermore, the symmetrically sandwiched cathode of CC-CoS₂@S/AB@CC-CoS₂ is beneficial for high sulfur loading LSBs. The CC-CoS₂@S/AB@CC-CoS₂ cell with a sulfur loading of 3.0 mg cm⁻² has initial discharge/charge capacities of 1328/1357 mAh g⁻¹ with a coulombic efficiency of 97.86% at 0.2 C, which are much better than those of the CC@S/AB@CC cell. Significantly, no capacity loss is observed for the CC-CoS₂@S/AB@CC-CoS₂ cells with high sulfur loadings of 4.2 and 6.1 mg cm⁻² after 100 cycles at 0.2 C, indicating their excellent cycling stability. This symmetrically sandwiched cathode based on high catalytic metal chalcogenides modified CC opens up a new door for developing high-performance LSBs with a high sulfur loading.

4. Experimental Section

Materials: Cobaltous sulfate (CoSO₄·7H₂O, AR 99.5%), sublimed sulfur (S, AR 99.5%), AB, N-Methyl-2-pyrrolidone (NMP, 99.5 wt%), polyvinylidene fluoride (PVDF, 99.5 wt%), lithium sulfide (Li₂S, AR 99.9%), lithium bis (trifluoromethanesulfonyl) imide (LITFSI, 99.95 wt%) and lithium nitrate (LiNO₃, 99.99 wt%) were purchased from Aladdin. Carbon cloth (CC, HCP330N) was purchased from HESEN. 1,3-dioxolane (DOL, AR 99.5%), dimethyl ether (DME, AR 99.5%), and thiourea (CS(NH₂)₂, AR 99%) were obtained from Macklin.

Synthesis of the CC-CoS₂: The CC-CoS₂ was obtained using a one-step hydrothermal synthesis. A carbon cloth (2×2 cm⁻²) was pretreated in hydrochloric acid (≈37%) for 1 h and then washed with deionized (DI) water. For the synthesis, 0.6 mmol of CoSO₄·7H₂O and 1.8 mmol of CS(NH₂)₂ were dissolved in 35 mL DI water under vigorous stirring to form a homogeneous solution, and then the solution was transferred to a 50 mL Teflon-lined stainless steel autoclave, then the cleaned carbon cloth (2×2 cm⁻²) was immersed in the solution and kept at 180 °C for 24 h. After cooling down to ambient temperature, the carbon cloth covered with CoS₂ nanoparticles was obtained and washed with DI water and dried at 60 °C for 12 h.

Characterization: XRD patterns were obtained from an X-Pert PRO MPD diffractometer with a Cu Kα radiation. SEM images were recorded on a field-emission SEM (Philips XL30 FEG). TEM and HRTEM images were obtained from a JEM-2100 electron microscope at an accelerating voltage of 200 kV. XPS measurement was carried out by using a VG ESCALAB 220i-XL UHV system with an Al Kα X-ray source (1486.6 eV). Raman spectra were recorded on a Lab RAM HR spectroscope with a 532 nm excitation. The UV-vis analysis was obtained from an ultraviolet visible near infrared spectrophotometer (CARY 5000) to evaluate the adsorption capability of different anchor materials.

Preparation of Sulfur Electrodes: An electrode slurry was made by mixing 60 wt% sublimed sulfur, 30 wt% AB, and 10 wt% PVDF in NMP. The...
slurry was then coated onto the CC-CoS$_2$ and dried at 60 °C for 12 h under vacuum to obtain the CC-CoS$_2@$S/AB electrode. The sulfur loading density of the CC-CoS$_2@$S/AB electrode is tunable in the range of 2–6 mg cm$^{-2}$. The slurry was coated onto the Al foil to obtain the Al@S/AB electrode with a sulfur loading of ≈1.2 mg cm$^{-2}$. These sulfur electrodes were punched into disks with 12.0 mm in diameter for assembling coin cells.

Fabrication of Coin Cells: The CR2032 cells were assembled in an Ar-filled glove box (H$_2$O < 0.1 ppm and O$_2$ < 0.1 ppm). The Li foil (diameter of 15.6 mm) and the Celgard 2400 sheets (diameter of 16.0 mm) were used as the anode and the separator, respectively. The electrolyte was prepared by dissolving 1 m LiTFSI in a mixed solution of DOL and DME (1:1 in volume) with addition of 1 wt% LiNO$_3$. The CC-CoS$_2@$S/AB@CC-CoS$_2$ battery was assembled by covering the CC-CoS$_2$ on the CC-CoS$_2@$S/AB electrode as the cathode, while the Al@S/AB@CC-CoS$_2$ battery was fabricated by covering the CC-CoS$_2$ on the Al@S/AB electrode as the cathode. The parameters of areal sulfur loading, electrolyte amount, and electrolyte/sulfur ratio in each cell were listed in Table S2. Supporting Information.

Fabrication of the CC-CoS$_2||$CC-CoS$_2$ and the CC||CC Symmetrical Cells: Symmetrical cells were fabricated to verify catalytic effect of the pristine CC and the CC-CoS$_2$. The pristine CC or the CC-CoS$_2$ was cut into circular disks with a diameter of 12 mm. CR2032 coin cells were assembled in an Ar-filled glove box by using two identical electrodes, a Celgard 2400 separator, and 40 µL electrolyte of 1 m LiTFSI and 0.2 m Li$_2$S in 1:1 (v/v) DOL/DME.

Electrochemical Measurements: The electrochemical performances of the various samples were measured by assembling CR2032 coin cells. Galvanostatic discharge/charge tests and GITT were carried out on a Neware BTS2300 system (Shenzhen, China) at 25 °C in voltage range of 1.7 to 2.8 V. CV measurements scanned at rates from 0.1 to 1 mV s$^{-1}$ and EIS measurements conducted from 100 kHz to 0.1 Hz with potentiostatic amplitude of 5 mV were carried out on a CHI660E (Shanghai, China) electrochemical workstation.

Lithium Poly sulfide Adsorption Tests: The Li$_2$S$_n$ solution (2 mmol L$^{-1}$) was prepared by stoichiometric amounts of sulfur and lithium sulfide (Li$_2$S) with a molar ratio of 5:1 dissolving in DOL/DME (1:1 in volume) mixture and stirring at room temperature in an Ar-filled glove box. The CC-CoS$_2$ (24 mg) and the pristine CC (20 mg) were added in the Li$_2$S$_n$ solution (4 mL), respectively. The adsorption capability of the CC-CoS$_2$ and the CC to Li$_2$S$_n$ was investigated by UV–vis spectroscopy.

Theoretical Calculations: All calculations were carried out by spin-polarized DFT as implemented in Vienna Ab initio Simulation Package (VASP). The Perdew–Burke–Ernzerhof generalized gradient approximation (GGA) was used for the exchange-correlation functional. A supercell of graphite containing 5 × 5 unit cells was employed to model carbon system. As for CoS$_2$ system, 2 × 2 unit cells of (111) plane with terminated sulfur atoms was used. The cutoff energy was set as 420 eV after cutoff testing and the k-points were set to be 3 × 3 × 1 for geometry optimization for CoS$_2$ and carbon optimization. The electronic energy and forces were converged to within 1 × 10$^{-5}$ eV and 0.02 eV Å$^{-1}$, respectively. For charge density and frequency calculations, the energy was converged to within 10$^{-6}$ and 10$^{-7}$ eV, respectively. The van der Waals interactions were considered by the method of the Grimme (DFT-D3). The effect of water was taken into consideration using VASP implicit solvent model. For quantitatively measuring the interaction between the substrates and Li$_2$S$_n$, we defined the binding energy $E_b$ as follows:

$$E_b = E_{\text{Total}} - E_{\text{Sub}} - E_{\text{Li}_2\text{S}_n}$$

(2)

where $E_{\text{Sub}}$, $E_{\text{Li}_2\text{S}_n}$, and $E_{\text{Total}}$ represent the total energies of the substrate, the Li$_2$S$_n$ cluster, and the adsorption pair of the substrate and Li$_2$S$_n$, respectively.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

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