Regulating Li^+ migration and Li_2S deposition by metal-organic framework-derived Co_4S_3 -embedded carbon nanoarrays for durable lithium-sulfur batteries

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ABSTRACT The shuttle effect of lithium polysulfides and the uncontrollable deposition of lithium sulfides (Li_2S) severely hinder the realization of high-performance lithium-sulfur (Li-S) batteries. Herein, we fabricated a carbon cloth (CC)-based self-supported interlayer (denoted as $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$), which is covered with Co_4S_3 -embedded porous carbon nanoarrays through a facile two-step method with cobalt-based metal-organic framework (Co-MOF) nanosheets as the template. The interconnected carbon network and the polar Co_4S_3 nanoparticles in the $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$ interlayer not only effectively suppress the polysulfide shuttle, but also significantly facilitate the lithium ion (Li^+) conduction with a considerable Li^+ transference number of 0.86. Besides, the rich interfaces between the polar Co_4S_3 nanoparticles and the conductive carbon substrate serve as reaction sites to accelerate the polysulfide conversion and guide the flower-like growth of Li_2S , which ultimately mitigates the interlayer surface passivation and improves the sulfur utilization. Therefore, the Li-S batteries with the $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$ interlayer deliver an excellent rate capacity ($368.7 \text{ mA h g}^{-1}$ at 10 C), a stable cycling performance (a low fading rate of 0.045% per cycle over 1400 cycles at 2.0 C), and a high initial areal capacity ($4.83 \text{ mA h cm}^{-2}$ at 0.2 C under a sulfur loading of 4.6 mg cm^{-2}). This work provides a perspective on the self-supported catalytic interlayer for the selective Li^+ conduction and Li_2S regulation toward high-performance Li-S batteries.

Keywords: metal-organic frameworks, self-supported interlayer, selective Li^+ conduction, flower-like Li_2S deposition, lithium-sulfur batteries

INTRODUCTION

Due to the ultrahigh theoretical specific energy (1675 mA h g^{-1}), remarkable energy density (2600 W h kg^{-1}) as well as environmental friendliness and low cost of sulfur, lithium-sulfur (Li-S) batteries hold promise as a next-generation battery system to sustain a low-carbon society [1,2]. Even so, many challenges still exist in the commercialization of high-performance Li-S batteries, such as the notorious shuttle effect and the sluggish sulfur

redox kinetics, which engender low sulfur utilization, low Coulombic efficiency (CE), fast capacity fading, and lithium corrosion/dendrites [3–6]. Therefore, as one key component of Li-S batteries, the commercial separator should be further functionalized to deal with the complex solution chemistry in Li-S batteries. So far, various nanostructure materials have been developed to construct an interlayer between the cathode and the separator for mitigating the shuttle effect of polysulfides [7–9]. In 2012, Manthiram's group [10] initially introduced a self-supported multi-walled carbon nanotube (MWCNT) interlayer which reduced the charge transfer resistance of Li-S batteries and improved the sulfur utilization. Hereafter, the self-supported interlayer has attracted much interest due to its binder-free property, easy functionalization, superior flexibility, and reasonable strength. Recently, Goodenough's group [11] reported a carbon cloth (CC)-based interlayer loaded with WS_2 for the high-performance Li-S batteries. The soluble polysulfides could be trapped by the WS_2 particles and then reutilized by the conducting CC membrane, which enabled the Li-S cell to harvest a capacity of 1000 mA h g^{-1} at 0.5 C after 500 cycles and deliver a high rate capacity of 750 mA h g^{-1} at 5.0 C. Li's group [12] also developed a binder-free ZIF-7@CC (ZIF-7 = zeolite imidazole framework-7) interlayer in 2021, offering massive sites for the physical/chemical adsorption and catalytic conversion of polysulfides in Li-S batteries. As a result, the cell with ZIF-7@CC achieved a high areal capacity of $4.75 \text{ mA h cm}^{-2}$ at 0.1 C under the sulfur loading of 5.5 mg cm^{-2} . Although functioning as an effective polysulfide barrier owing to their compact physical structure and abundant trapping-catalytic sites for polysulfides, the self-supported interlayers often suffer from the serious surface passivation by insulating lithium disulfides/sulfide ($\text{Li}_2\text{S}_{1/2}$) films during cycling, thus inevitably obstructing the lithium ion (Li^+) migration pathways and increasing the impedance of Li-S batteries. Besides, a low Li^+ transference number in typical Li-S batteries leads to the unfavorable concentration polarization and the large overpotential, which is detrimental to the rate capability [13]. Hence, it is very essential for functional interlayers to simultaneously regulate the Li^+ migration and the $\text{Li}_2\text{S}_{1/2}$ deposition behavior in Li-S batteries during cycling, however, both of which are often ignored by researchers.

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Herein, a new self-supported interlayer ($\text{Co}_4\text{S}_3/\text{C}@\text{CC}$) was fabricated by assembling CC with cobalt-based metal-organic framework (Co-MOF)-derived Co_4S_3 -embedded carbon nanoarrays ($\text{Co}_4\text{S}_3/\text{C}$) through one-step sulfidation. This is a facile and controllable method to synthesize Co_4S_3 -embedded carbon materials, compared with their multi-step energy-intensive synthesis sometimes needing post-processing in the literature [14–17]. Besides, to our knowledge, there are no prospective studies on the application of Co_4S_3 -embedded carbon materials in Li-S batteries. The long-range interconnected architecture of CC and MOF-derived N-doped carbon nanoarrays can physically shield the polysulfide shuttle and shorten the Li^+ migration distance [17,18], while the polar Co_4S_3 nanoparticles can provide CC with a strong Li^+ affinity and meanwhile regulate the conversion kinetics and flower-like deposition of polysulfides [19,20]. Thus, the Li-S cell with $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$ exhibits a mitigated self-discharge behavior, a high specific capacity, an excellent rate capability, and a stable cycling performance. Specially, this cell can deliver an initial capacity as high as 959 mA h g^{-1} and a slow capacity decay of 0.045% per cycle over 1400 cycles at 2.0 C. Even under an areal sulfur loading of 4.6 mg cm^{-2} , the Li-S cell with $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$ can still harvest a high areal capacity of $4.21 \text{ mA h cm}^{-2}$ after 100 cycles at 0.2 C. This work demonstrates that the selective Li^+ migration and Li_2S regulation capacities of self-supported interlayers play an important role in realizing the durable Li-S batteries.

EXPERIMENTAL SECTION

Preparation of Co-MOF@CC precursors, $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$, and $\text{Co}/\text{C}@\text{CC}$ interlayers

Firstly, the CC ($2.5 \text{ cm} \times 5.0 \text{ cm}$) was cleaned with acetone, ethanol, and deionized water under ultrasonic treatments for 1 h, respectively. After that, the clean CC was treated by a mixed acid solution containing 10 wt% of concentrated HNO_3 and 10 wt% of concentrated H_2SO_4 (3:1 in volume) for 12 h, and then washed with deionized water for several times. The Co-MOF@CC precursor, prepared according to the literature [21], was loaded in the middle of the tube furnace, while sublimated sulfur was placed at upstream. The raw materials were then heated to 700°C with a ramp rate of 2°C min^{-1} , and kept for 3 h under Ar/H_2 (95%/5%) atmosphere (30 sccm, $1 \text{ sccm} = 1 \text{ mL}^3 \text{ min}^{-1}$) to yield $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$. $\text{Co}/\text{C}@\text{CC}$ was prepared under the same heating procedure but free of sublimated sulfur. The obtained products were further punched into circular interlayers for cell assembly.

Visualized adsorption tests

The Li_2S_6 solution was prepared by a method as reported in the previous study [22]. Afterwards, 50 mg of CC, $\text{Co}/\text{C}@\text{CC}$ or $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$ was, respectively, added into 3 mL of 2.25 mmol L^{-1} Li_2S_6 solutions and incubated for a while in an Ar-filled glove box. The ultraviolet-visible (UV-vis) absorption spectra were recorded by a Shimadzu UV-3600-plus spectrophotometer.

Assembly and measurements of Li_2S_6 symmetric cells

Two identical electrodes (CC, $\text{Co}/\text{C}@\text{CC}$ or $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$, $\Phi = 12 \text{ mm}$) were designated as the working and counter electrodes in a standard 2025 coin cell, respectively. And $60 \mu\text{L}$ of 0.3 mol L^{-1} Li_2S_6 electrolytes were added into the cell and a

Celgard 2500 membrane was used as the separator. Cyclic voltammetry (CV) measurements were carried out under the polarization of 1.0 V, and electrochemical impedance spectroscopy (EIS) tests were conducted within the range of 100 kHz to 0.01 Hz.

Potentiostatic intermittent titration technique (PITT) measurements

Li_2S_8 solutions (0.25 mol L^{-1}) were prepared by dissolving stoichiometric amounts of sulfur and lithium sulfides (Li_2S) into a tetraglyme solvent with 1 mol L^{-1} lithium bis(trifluoromethylsulfonyl)imide (LiTFSI). $\text{Li}/\text{CC}/\text{Li}_2\text{S}_8$, $\text{Li}/\text{Co}/\text{C}@\text{CC}/\text{Li}_2\text{S}_8$, and $\text{Li}/\text{Co}_4\text{S}_3/\text{C}@\text{CC}/\text{Li}_2\text{S}_8$ cells were assembled using CC, $\text{Co}/\text{C}@\text{CC}$, and $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$ ($\Phi = 12 \text{ mm}$) as the cathode collector, respectively, lithium foil (0.6 mm) as the anode, and Celgard 2500 membrane as the separator. Forty microlitre of $0.0625 \text{ mol L}^{-1}$ Li_2S_8 solution was used as the catholyte, while $5 \mu\text{L}$ of blank electrolyte without Li_2S_8 was applied as the anolyte. The total sulfur content in the cells was around 0.56 mg. For discharge PITT evaluation, the cells were firstly rested at open circuit voltage (OCV) for 2 h, and then subjected to the successive potential drop from 2.45 to 1.95 V at a rate of 50 mV per step, using a time cutoff of 10,000 s. For charge PITT test, the voltages of abovementioned cells continued to drop to 1.7 V at a rate of 0.05 C, and then maintained at 1.7 V for 10,000 s to guarantee the complete reduction of polysulfides. Similar steps were followed in the subsequent charge PITT evaluation, except that the voltage was successively increased from 2.2 to 2.5 V.

Li^+ transference number measurements

Symmetrical cells (CR2032) were assembled by sandwiching the Celgard separator without or with various interlayers (CC, $\text{Co}/\text{C}@\text{CC}$, and $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$) between two lithium electrodes. The Li^+ transference numbers (t_{Li^+}) in different symmetrical cells were measured with a constant step potential of 10 mV and were determined by the ratio of the steady-state current (I_s) to initial state current (I_0) based on the following equation:

$$t_{\text{Li}^+} = \frac{I_s}{I_0}. \quad (1)$$

Ionic conductivity measurements

Symmetrical cells (CR2032) were assembled by sandwiching the Celgard separator without or with various interlayers (CC, $\text{Co}/\text{C}@\text{CC}$, and $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$) between two stainless steel electrodes. The ionic conductivities of different symmetrical cells were calculated from EIS (0.01–100 KHz) measurements according to the following equation:

$$\sigma = \frac{L}{R_b A}, \quad (2)$$

where σ is the ionic conductivity (S cm^{-1}), L refers to the thickness of the separator (cm), A is the area of the stainless steel electrode (cm^2), and R_b represents the bulk resistance (Ω) determined by the intercept of Nyquist plots with the real axis.

Material characterizations

The phase purity, morphology, and elemental composition of all samples were measured on a Bruker AXS Advance diffractometer, a field-emission scanning microscope (SU70, Hitachi), and a JEOL JEM-2100 microscope, respectively. The chemical states were tested by an X-ray photoelectron spectro-

scope (XPS, Ulvac-Phi, Inc., Tokyo, Japan).

Electrochemical measurements

CR2032 coin cells were assembled in an argon-filled glove box (Shanghai Mikrouna Super: $O_2 < 0.1$ ppm, $H_2O < 0.1$ ppm). The S@CNTs disks were fabricated according to our previous work [23], and directly used as the cathodes with the areal sulfur loading within $1.1\text{--}1.5\text{ mg cm}^{-2}$. Lithium metal was employed as the anode and the separator was the Celgard 2500 membrane. The electrolyte contained 1 mol L^{-1} LiTFSI in 1,2-dimethoxyethane (DME)/1,3-dioxolane (DOL) (1:1 in volume) with 2 wt% $LiNO_3$, and the electrolyte/sulfur ratio remained at $30\text{ }\mu\text{L mg}^{-1}$ for the cathodes with a low sulfur loading and $8.6\text{ }\mu\text{L mg}^{-1}$ for a high sulfur loading (4.6 mg cm^{-2}). The galvanostatic charge/discharge tests were measured by a LAND CT 2001A charge/discharge system at 26°C after being rested for 4 h. CV and EIS measurements were performed on a CHI660E electrochemical workstation (CH Instruments Co., Ltd, Shanghai, China).

RESULTS AND DISCUSSION

A two-step synthesis strategy of $Co_4S_3/C@CC$ is given in Scheme 1. The Co-MOF nanosheets were vertically grown on the CC substrate via a facile solution method [21]. After that, this harvested Co-MOF@CC was transformed into $Co_4S_3/C@CC$ through annealing. During the annealing, the Co_4S_3 nanoparticles were formed from the sulfuration of Co^{2+} by H_2S and embedded into the MOF-derived carbon nanosheets. Field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) were conducted to survey the morphology and structure evolutions of the as-synthesized products. As illustrated in Fig. 1a, b, the routine CC shows the knitted structure with a smooth surface. After a precipitation reaction, abundant leaf-like nanosheets are grown on the CC surface, manifesting the successful introduction of Co-MOF (Fig. 1c) [24]. An enlarged SEM image further indicates that these nanosheets have a smooth surface, with leaf length, width and thickness being about $2.2\text{ }\mu\text{m}$, 600 nm and 80 nm , respectively (Fig. 1d). The corresponding energy-dispersive X-ray spectroscopy (EDS) spectrum illustrates the existence of Co, C, N, and O elements in Co-MOF@CC (Fig. S1). After annealing, these nanosheets still maintain a leaf-like structure but with a rough and twisted surface due to the Kirkendall effect (Fig. 1e–i) [17]. EDS analysis clearly reveals a uniform distribution of Co, S, C, N, O in $Co_4S_3/C@CC$ with a S/Co atomic ratio of 1.32 (Fig. 1j, k). As displayed in Fig. 1l, m, massive nanoparticles are embedded in the MOF-derived porous carbon nanosheets. A high-resolution TEM image (Fig. 1n) further shows that the

lattice fringe of 0.299 nm matches well with the (311) plane of Co_4S_3 . To further investigate the phase composition of these products, X-ray diffraction (XRD) technique was also used. As shown in Fig. S2, the XRD pattern of Co-MOF@CC is consistent with that of simulated Co-MOF, again indicating the successful growth of Co-MOF on the CC surface. According to the XRD patterns in Fig. 1o, the diffraction peaks located at 25.5° and 43.5° are corresponding to CC. After sulfidation, additional peaks at 29.9° , 31.1° , 39.5° , 47.6° , and 51.9° are attributed to the Co_4S_3 characteristic peaks (PDF# 02-1338). No metallic cobalt and Co-MOF peaks can be found in the diffractogram of $Co_4S_3/C@CC$, indicating a complete transformation from Co-MOF to Co_4S_3 after sulfidation. It should be noted that the Ar/H_2 sweeping rate during sulfidation would affect the residence time of the generated H_2S in the quartz tube, which determines the final phase composition of the as-prepared products. Specifically, the cobalt metal phase (Co/C@CC), cobalt sulfide phase ($Co_4S_3/C@CC$), and coexistence of two phases ($Co_4S_3/Co/C@CC$) are formed at high (200 sccm), medium (100 sccm), and low (30 sccm) sweeping rates, respectively (Fig. S3).

The XPS measurement was performed to study the chemical states of $Co_4S_3/C@CC$. As shown in Fig. 2a, the wide-scan XPS spectrum of $Co_4S_3/C@CC$ clearly shows the presence of C, O, N, Co, and S elements. The C 1s spectrum can be fitted by three peaks located at 284.8, 285.6, and 287.4 eV, which should be corresponding to the C–C/C=C, C–O/C–N, and C=O bonds, respectively (Fig. 2b) [25]. The high-resolution N 1s spectrum can be fitted with three subpeaks corresponding to pyridinic N (399.4 eV), pyrrolic N (400.7 eV), and graphitic N (402.7 eV), respectively (Fig. 2c) [25]. These Co-MOF-derived N-containing groups not only improve the electronic conductivity of the carbon composites, but also are conducive to forming a strong chemical affinity with polysulfides [26,27]. The O 1s spectrum can be deconvoluted into two peaks at 533.3 and 532.2 eV, respectively (Fig. 2d). The peak at 532.2 eV is assigned to C–O/C=O, whereas the other peak at 533.3 eV is originated from the adsorbed OH or H_2O [28]. In the Co 2p region (Fig. 2e), three peaks at 778.7, 782.3, and 786.3 eV can be attributed to Co $2p_{3/2}$ of Co_4S_3 , and the others at 794.0, 798.6, and 803.9 eV should be assigned to Co $2p_{1/2}$ [14,17]. The high resolution S 2p spectrum (Fig. 2f) shows that the doublets at 163.8 and 162.6 eV can be indexed to S $2p_{1/2}$ and S $2p_{3/2}$ of Co_4S_3 . In addition, the peaks located at 169.3 and 170.5 eV can be identified as the oxidized sulfur species [29].

To assess the ability of the pristine Celgard and various interlayers to shield polysulfides, the Li_2S_6 permeation experiments were firstly performed using an H-type device (Fig. 3a). A

Scheme 1 Schematic diagram of the synthesis process of $Co_4S_3/C@CC$.

Figure 1 SEM images of (a, b) CC, (c, d) Co-MOF@CC, (e, f) Co/C@CC, and (g–i) Co₄S₃/C@CC (the insets show digital photos of the corresponding interlayers). (j, k) EDS elemental mapping of Co₄S₃/C@CC. (l, m) TEM and (n) high-resolution TEM images of Co₄S₃/C@CC. (o) XRD patterns of Co/C@CC and Co₄S₃/C@CC.

2.25 mmol L⁻¹ Li₂S₆ solution was poured into the left side of the H-type device, and the blank DME/DOL solution was injected into the other side. After 24 h, there is almost no color change in the right glass tube for the Co₄S₃/C@CC interlayer, indicating that the polysulfide shuttle is effectively controlled by the Co₄S₃/C@CC interlayer. This result is also supported by the corresponding UV-vis absorption spectra in which the blank solution in the right glass tube for Co₄S₃/C@CC experiences a much lower light absorbance after permeation tests (Fig. 3b). Furthermore, visualized static adsorption experiments were employed using a 2.25 mmol L⁻¹ Li₂S₆ solution. After being rested for five days (Fig. S4), the Li₂S₆ solution color gets lighter with the assistance of Co/C@CC or Co₄S₃/C@CC, demonstrating that Co/C@CC and Co₄S₃/C@CC have a stronger affinity for Li₂S₆ than CC, which is also verified by the corresponding UV-vis analysis. The interaction between Co₄S₃/C@CC and Li₂S₆ was finally investigated by XPS measurements. As shown in Fig. S5a, the Co–S peak intensity in the Co 2p spectrum of Co₄S₃/C@CC increases after the Li₂S₆ adsorption, associated with the reduction in the Co–O peak intensity. It indicates the generation of Co–S bonds between Co₄S₃ and Li₂S₆ [23,30]. Similar changes

are also observed in the Co 2p spectrum of Co/C@CC after Li₂S₆ adsorption (Fig. S5c). In addition, the peak located at 54.8 eV in the Li 1s spectrum of Co₄S₃/C@CC–Li₂S₆ should be affiliated with Li–S bonds, which shifts toward a lower binding energy compared with that (56.3 eV) of the pristine Li₂S₆, further emphasizing the robust adsorption capability of Co₄S₃/C@CC toward polysulfides (Fig. S5b) [31]. By comparison, the Li 1s spectrum of Co/C@CC after Li₂S₆ adsorption shows a depressed Li–S peak located at a higher binding energy (55.7 eV), indicating its poorer adsorption capability of polysulfides (Fig. S5d). Therefore, the Co₄S₃/C@CC interlayer can act as a reliable reservoir to significantly alleviate the shuttle effect of polysulfides due to its physical and chemical anchoring effects on polysulfides. Besides the polysulfide regulation, the Li⁺ migration capacities among various interlayers were also estimated by the t_{Li^+} and σ values using symmetric cells. Noticeably, the calculated t_{Li^+} value in the cell with Co₄S₃/C@CC is 0.86 (Fig. 3c), much higher than that in the cells with Celgard (0.68), CC (0.80), and Co/C@CC (0.69), which suggests that the Li⁺ cations dominate the ionic conduction in the electrolyte whereas the anion migration is significantly suppressed [19]. This may be related to

Figure 2 (a) Wide-scan spectrum, (b) C 1s, (c) N 1s, (d) O 1s, (e) Co 2p, and (f) S 2p XPS spectra of $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$.

Figure 3 (a) Li_2S_6 permeation measurements using an H-type device with pristine Celgard, CC, $\text{Co}/\text{C}@\text{CC}$, and $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$ interlayers, and (b) the corresponding UV-vis absorption spectra of Li_2S_6 solutions in the right glass tube. (c) I - t curves and (d) EIS plots of symmetric cells with pristine Celgard, CC, $\text{Co}/\text{C}@\text{CC}$, and $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$ interlayers.

the following two aspects: the crossed conductive matrix of CC and carbon nanosheets provides continuous channels for the Li^+ migration through the Celgard membrane [18]; the Co_4S_3

nanoparticles may promote the dissociation of Li^+ cations due to their strong Li^+ affinity [19]. Moreover, the ionic migration resistance and conductivity were obtained from the EIS plots. As

shown in Fig. 3d, the symmetric cell with $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$ exhibits a relatively small resistance of $2.18\ \Omega$ and a larger Li^+ conductivity of $8.7\ \text{mS cm}^{-1}$. These results demonstrate that $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$ has a high Li^+ selectivity and an excellent Li^+ conductivity, which could facilitate the polysulfide conversion and enable the high-rate Li-S batteries.

To explore the catalytic ability of $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$ toward the polysulfide conversion, the Li_2S_6 symmetric cell technique was employed without the interference of lithium-metal anodes [32]. Compared with the control cells, the CV profiles of the $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$ -based symmetric cell always show a sharper redox current at scan rates of $1.0\text{--}5.0\ \text{mV s}^{-1}$ under the polarization of $1.0\ \text{V}$ (Fig. 4a and Fig. S6), illustrating the boosted liquid-liquid conversion kinetics of polysulfides on $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$. Meanwhile, the redox peaks in the CV profiles of $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$ -based symmetric cells are highly overlapped after the first cycle, implying that the polysulfide redox reaction at the $\text{Co}_4\text{S}_3/\text{C}@\text{CC}/\text{Li}_2\text{S}_6$ electrolyte interfaces is fully reversible and stable (Fig. 4b). These results are also supported by the EIS plots that point out a much reduced charge transfer resistance (smaller semicircle diameter) in the $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$ -based symmetric cell (Fig. 4c). To quantitatively estimate the electrocatalytic effects of various interlayers on the $\text{Li}_2\text{S}_{1/2}$ deposition and dissolution, PITT tests were conducted [32–35]. Typically, the PITT discharge profiles of the Li_2S_8 catholyte are composed of two parts: one is the liquid-liquid conversion process between the dissolved polysulfides, and the other is the liquid-solid conversion process from the short-chain polysulfides to insoluble $\text{Li}_2\text{S}_{1/2}$. In the liquid-liquid conversion region ($2.45\text{--}2.05\ \text{V}$), the sharp current responses against voltage pulses occur with an immediate current drop within 200 s, followed by a steady plateau (Fig. 4d). The higher current response in the $\text{Li}|\text{Co}_4\text{S}_3/\text{C}@\text{CC}/\text{Li}_2\text{S}_8$ cell suggests the faster liquid-liquid conversion kinetics at the $\text{Co}_4\text{S}_3/\text{C}@\text{CC}/\text{Li}_2\text{S}_8$ electrolyte interfaces. In the liquid-solid conversion region, the distinct current peaks emerge at $2.0\ \text{V}$ for each cell, indicating the occurrence of the electrochemical liquid-solid phase transi-

tion from polysulfides to $\text{Li}_2\text{S}_{1/2}$. The better $\text{Li}_2\text{S}_{1/2}$ deposition behavior in the $\text{Li}|\text{Co}_4\text{S}_3/\text{C}@\text{CC}/\text{Li}_2\text{S}_8$ cell can be evidenced by the maximum current response and the highest $\text{Li}_2\text{S}_{1/2}$ deposition capacity ($212\ \text{mA h g}^{-1}$) (Fig. 4d, f), indicating that the abundant conductive and polysulfide-adsorptive interfaces in $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$ could guide the more effective $\text{Li}_2\text{S}_{1/2}$ deposition. The PITT charge profiles (Fig. 4e), on the contrary, aim to explore the $\text{Li}_2\text{S}_{1/2}$ dissolution behavior under the mediation of different electrocatalysts. The solid-liquid conversion from $\text{Li}_2\text{S}_{1/2}$ to Li_2S_x ($x > 4$) can also be significantly propelled by the $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$ electrocatalysts, which is confirmed by the uppermost current hump at $2.25\ \text{V}$ in the PITT charge profiles. Also, the calculated $\text{Li}_2\text{S}_{1/2}$ dissolution capacity of the $\text{Li}|\text{Co}_4\text{S}_3/\text{C}@\text{CC}/\text{Li}_2\text{S}_8$ cell is $300\ \text{mA h g}^{-1}$, which is higher than that of the cells with CC and $\text{Co}/\text{C}@\text{CC}$ (Fig. 4f). The more favorable $\text{Li}_2\text{S}_{1/2}$ dissolution on the surface of $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$ should be attributed to the strong chemical interaction between the isolated Li ion and the sulfur atom in Co_4S_3 lowering the $\text{Li}_2\text{S}_{1/2}$ decomposition barrier [31]. Therefore, both the $\text{Li}_2\text{S}_{1/2}$ deposition and dissolution processes can be significantly promoted by the $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$ electrocatalysts, resulting in the increased capacities throughout both processes.

To further demonstrate the outstanding advantages of the $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$ interlayer on the polysulfide shielding, the selective Li^+ conduction, and the regulation of polysulfide conversion, the electrochemical performances of Li-S cells with/without interlayers were tested. As illustrated in Fig. 5a, the fabricated interlayer is inserted between the Celagrd 2500 separator and the cathode, and CR2032 coin cells with a sulfur loading of $1.1\text{--}1.5\ \text{mg cm}^{-2}$ were assembled to compare the electrochemical performances. Fig. 5b shows the CV profiles of the cells with Celgard, CC, $\text{Co}/\text{C}@\text{CC}$, and $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$ at $0.1\ \text{mV s}^{-1}$. Obviously, the cell with $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$ displays the highest current density and the smallest polarization when compared with the control cells, demonstrating its enhanced electrochemical reaction kinetics during both the cathodic and anodic sweeping

Figure 4 (a) CV profiles of symmetric cells of CC, $\text{Co}/\text{C}@\text{CC}$, and $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$. (b) CV profiles of symmetric cells of $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$ in the first five cycles. (c) EIS curves of symmetric cells. PITT (d) discharge, (e) charge profiles, and (f) quantitative $\text{Li}_2\text{S}_{1/2}$ deposition and dissolution of $\text{Li}|\text{CC}/\text{Li}_2\text{S}_8$, $\text{Li}|\text{Co}/\text{C}@\text{CC}/\text{Li}_2\text{S}_8$, and $\text{Li}|\text{Co}_4\text{S}_3/\text{C}@\text{CC}/\text{Li}_2\text{S}_8$ cells.

Figure 5 (a) Schematic diagram of a Li-S battery. (b) CV profiles and (c) EIS plots of the Li-S cells with Celgard, CC, Co/C@CC, and Co₄S₃/C@CC. (d) Rate performances of the Li-S cells with Celgard, CC, Co/C@CC, and Co₄S₃/C@CC. (e) Galvanostatic discharge-charge profiles of the cell with Co₄S₃/C@CC at different current densities. (f) Cycling performances at 0.2 C. (g) Long-term cycling performances and (h) the corresponding galvanostatic discharge profiles at 2.0 C.

processes. Fig. S7 shows the CV profiles of Li-S cells with various interlayers at different scan rates and the corresponding linear relationships between the peak current values and the square root of scan rates. The slopes of the curves in Fig. S7e–h are proportional to the Li⁺ diffusivity. At the peak c1, the long-chain polysulfides dissolved in the electrolyte can be trapped by the polar Co₄S₃/C@CC interlayer, thus reducing the electrolyte viscosity and leading to the better Li⁺ diffusion capability. At the peak c2 involving the Li₂S_{1/2} deposition, the Co₄S₃/C@CC interlayer with the high Li⁺ conductivity can guide more effective Li₂S_{1/2} deposition, which relieves the interlayer passivation and results in the facile Li⁺ migration [31,36]. These observations again indicate that the Co₄S₃/C@CC interlayer can significantly facilitate the Li⁺ migration in the sulfur redox process. EIS plots of the cells with different interlayers were also measured under the OCV condition. As shown in Fig. 5c, there are one semicircle in the high-frequency area and a straight line in the low-frequency area appearing in all Nyquist plots, which should mean the charge transfer resistance and the Li⁺ diffusion impedance in the cells, respectively. The cell with Co₄S₃/C@CC shows the smallest semicircle in the EIS curves than the cells with Celgard, CC, and Co/C@CC. This suggests that the Co₄S₃/

C@CC interlayer can significantly reduce the charge transfer resistance among the separator, Co₄S₃/C@CC, and cathode. Rate capabilities of the cells with various interlayers are presented in Fig. 5d. The cell with Co₄S₃/C@CC delivers discharge capacities of 1886.9, 1311.9, 1206.1, 1078.1, 917.4, 790.2, 621.0, and 368.7 mA h g⁻¹ at 0.1, 0.2, 0.5, 1.0, 2.0, 3.0, 5.0, and 10 C, respectively, superior than the cells with Celgard, CC, and Co/C@CC. When the current returns to 0.1 C, the cell with Co₄S₃/C@CC can still harvest a high reversible capacity of 1165 mA h g⁻¹, indicating the durable sulfur electrochemistry during cycling. The additional capacity exceeding 1675 mA h g⁻¹ at 0.1 C may be contributed by the porous interlayer, as also reported in the literature [37,38]. Furthermore, two well-defined discharge plateaus can be maintained in the cell with Co₄S₃/C@CC even at a high-current density up to 5.0 C (Fig. 5e), which should be related to the favorable Li⁺ transference number and the reduced Li⁺ migration resistance of Co₄S₃/C@CC. In addition, the Li|Co₄S₃/C@CC cell without any sulfur was also tested to determine the additional capacity contributed by the Co₄S₃ nanoparticles. As shown in Fig. S8, the Co₄S₃ nanoparticles show a negligible lithiation/delithiation behavior within the working voltage range of Li-S batteries, hence providing an

extremely low capacity of 8.1 mA h g^{-1} at 0.1 C . So the faster sulfur redox kinetics and the mitigated shuttle effect in the cell with $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$ promise an increased discharge capacity and an outstanding rate performance. The cycling performances of various cells were firstly investigated at 0.2 C (Fig. 5f). A high initial capacity of $1392.7 \text{ mA h g}^{-1}$ can be realized in the cell with $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$, and the capacity stabilizes at $1073.3 \text{ mA h g}^{-1}$ after 100 cycles. When the current density increases to 2.0 C , an excellent cycle lifespan can still be achieved by the cell with $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$. The cell with $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$ displays an initial capacity of 959 mA h g^{-1} with the smaller polarization, and maintains a capacity of $360.6 \text{ mA h g}^{-1}$ after 1400 cycles with a low fading rate of 0.045% per cycle (Fig. S9), whereas the cells with Celgard, CC, and $\text{Co}/\text{C}@\text{CC}$ suffer from the premature failure and the huge polarization (Fig. 5g, h). As shown in Fig. S10, the cell with $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$ also has the lowest ohmic resistance after cycling, reflecting the lower polysulfide viscosity in the electrolyte and the mitigated $\text{Li}_2\text{S}_{1/2}$ passivation on the interlayer [39]. The lower polysulfide viscosity and the more effective $\text{Li}_2\text{S}_{1/2}$ deposition can alleviate the shuttle effect of polysulfides and accelerate the Li^+ migration, hence boosting the battery performance.

To further find out the degradation mechanism of the cells with Celgard, CC, $\text{Co}/\text{C}@\text{CC}$, and $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$, these cells cycled at 2.0 C were disassembled for further analyses. As shown in Fig. 6a, the separator color of the cell with $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$ keeps

almost unchanged after cycling, while the other three separators more or less encounter coloring by polysulfides. When the $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$ interlayer was immersed in a clean dimethyl carbonate (DMC) solution, the solution color still remained almost transparent (Fig. 6b). By contrast, the DMC solution changed from colorless to yellow after contacting with Celgard, CC, or $\text{Co}/\text{C}@\text{CC}$ in which there are many unreacted polysulfides during the discharge. These observations show that the dissolved polysulfides can be completely transformed into the solid $\text{Li}_2\text{S}_{1/2}$ with $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$ as the interlayer in the discharge process, hence guaranteeing the alleviated polysulfide shuttle and the effective sulfur utilization. The cycled CC, $\text{Co}/\text{C}@\text{CC}$, and $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$ interlayers were also subjected to XRD and SEM investigations. XRD results in Fig. 6c show that the cycled $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$ interlayer remains the characteristic diffraction peaks of Co_4S_3 , with its crystal structure highly stable during cycling. As a contrast, the disappearance of the characteristic peaks of metal cobalt in $\text{Co}/\text{C}@\text{CC}$ indicates that cobalt may participate in the side reaction to form the amorphous cobalt-based compounds in the electrochemical process, thus resulting in the inactivated electrocatalytic sites and deteriorating the cycling performance. According to the SEM images (Fig. 6d, e), a relatively smooth $\text{Li}_2\text{S}_{1/2}$ film covers on the CC surface, which passivates the conductive CC surface and leads to the poor reaction kinetics as well as the low discharge capacity [13]. For the cell with $\text{Co}/\text{C}@\text{CC}$, there are many large $\text{Li}_2\text{S}_{1/2}$ agglomerates on the surface

Figure 6 (a) Photographs of the cathodes, interlayers, separators, and Li-metal anodes after cycling. (b) Photographs of the DME solutions containing Celgard, CC, $\text{Co}/\text{C}@\text{CC}$, and $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$. (c) XRD patterns of the cycled $\text{Co}/\text{C}@\text{CC}$ and $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$ interlayers. SEM images of the cycled (d, e) CC, (f, g) $\text{Co}/\text{C}@\text{CC}$, and (h, i) $\text{Co}_4\text{S}_3/\text{C}@\text{CC}$ interlayers.

of Co/C@CC (Fig. 6f, g). This three-dimensional (3D) growth mode is consistent with the observations in the literature and can reduce the surface passivation on Co/C@CC [40]. Interestingly, a flower-like 3D structure composed of $\text{Li}_2\text{S}_{1/2}$ nanoflakes can be clearly observed on the surface of $\text{Co}_4\text{S}_3/\text{C@CC}$ (Fig. 6h, i), which may result from the rapid polysulfide conversion due to the low $\text{Li}_2\text{S}_{1/2}$ formation barrier on the $\text{Co}_4\text{S}_3/\text{C@CC}$ surface, although it still needs to be confirmed by the theoretical calculation. Such interlaced nanosheet architecture can favor a fast charge transport and provide a larger surface area favorable for the subsequent $\text{Li}_2\text{S}_{1/2}$ deposition, further relieving the surface $\text{Li}_2\text{S}_{1/2}$ passivation on interlayers, and thus achieving a higher discharge capacity as well as a longer cycle life [41–43]. Besides, the Li-anode surfaces of the Celgard-, CC-, and Co/C@CC-based cells suffer severe damages after cycling, and lithium-dendrites can be obviously found (Fig. S11). On the contrary, the Li surface of the $\text{Co}_4\text{S}_3/\text{C@CC}$ -based cell is smooth and intact, suggesting that the $\text{Co}_4\text{S}_3/\text{C@CC}$ interlayer can effectively suppress the polysulfide shuttle and regulate the homogeneous Li^+ flux, accordingly protecting the Li-metal anode.

The self-discharge behavior and the high sulfur loading are of great significance to the practical Li-S batteries, and these two

key parameters were also evaluated accordingly [44,45]. As represented in Fig. 7a, after being rested for 48 and 168 h intermittently, the cell with $\text{Co}_4\text{S}_3/\text{C@CC}$ shows a more stable cycling performance at 0.2 C. Precisely, the OCV curves of the $\text{Co}_4\text{S}_3/\text{C@CC}$ -based cell stay flat during the rest, with the OCV values remaining at 2.39 and 2.37 V after being rested for 48 and 168 h, respectively, superior to those of the cells with Celgard, CC, and Co/C@CC (Fig. 7b–d). These results indicate the concentration gradient-driven polysulfide shuttle can be effectively suppressed by the $\text{Co}_4\text{S}_3/\text{C@CC}$ interlayer, thus bringing about the less active material loss and the higher capacity retention during the rest. Moreover, the $\text{Co}_4\text{S}_3/\text{C@CC}$ -based cell with a sulfur loading of 4.6 mg cm^{-2} delivers an initial areal capacity of $4.83 \text{ mA h cm}^{-2}$, and the areal capacity maintains at $4.21 \text{ mA h cm}^{-2}$ after 100 cycles at 0.2 C (Fig. 7e), which is comparable to that of the previously reported studies in Table S1. By comparison, the cell with the CC interlayer can experience only a few cycles with a quite low initial areal capacity of $1.49 \text{ mA h cm}^{-2}$ at 0.2 C.

CONCLUSIONS

In summary, we fabricated a novel CC-based interlayer with Co_4S_3 -embedded porous carbon nanoarrays *via* a template

Figure 7 (a) Cycling performances of the Li-S cells with Celgard, CC, Co/C@CC, and $\text{Co}_4\text{S}_3/\text{C@CC}$ at 0.2 C before and after the rest. (b, c) Self-discharge profiles during two and seven days of rest. (d) Voltage retention capacities after two and seven days of rest. (e) Areal capacities and cycling performances of the cells with CC and $\text{Co}_4\text{S}_3/\text{C@CC}$ at 0.2 C for 100 cycles under a sulfur loading of 4.6 mg cm^{-2} .

method. The Li-S batteries with the $\text{Co}_4\text{S}_3/\text{C}/\text{CC}$ interlayer exhibit excellent electrochemical performances. On one hand, the $\text{Co}_4\text{S}_3/\text{C}/\text{CC}$ interlayer realizes the effective shielding of the polysulfide shuttle and significantly facilitates the Li^+ migration. On the other hand, the embedded Co_4S_3 nanoparticles with robust stability against cycling tremendously accelerate the conversion kinetics of polysulfides and regulate the flower-like growth of $\text{Li}_2\text{S}_{1/2}$ around the interlayer. Accordingly, the $\text{Co}_4\text{S}_3/\text{C}/\text{CC}$ -based cell delivers an excellent rate capability of $368.7 \text{ mA h g}^{-1}$ at 10 C and an outstanding long-term cycling performance with a low capacity fade rate of 0.045%/cycle over 1400 cycles at 2.0 C. Hence this work provides an effective approach for simultaneously regulating the polysulfide and Li^+ migration and guiding the 3D $\text{Li}_2\text{S}_{1/2}$ deposition in durable Li-S batteries.

Received 29 July 2021; accepted 27 September 2021;
published online 18 November 2021

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Acknowledgements This work was financially supported by the National Natural Science Foundation of China (51871188 and 51931006).

Author contributions Xie RJ, Peng DL, and Liu J conceived and designed the project, wrote and revised the paper; Liu J was primarily responsible for the experiments; Song Y and Lin C helped perform the experiments; Xie Q provided the useful suggestions. All authors contributed to the general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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金属-有机框架衍生的 Co_4S_3/C 纳米阵列调控锂硫电池中锂离子迁移和硫化锂沉积

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摘要 多硫化锂的飞梭效应与不可控硫化锂(Li_2S)的沉积现象严重阻碍了高性能锂硫电池的实现。在本研究中,我们制备了一种负载有 Co_4S_3/C 多孔纳米阵列的自支撑碳布(CC)基夹层($Co_4S_3/C@CC$),其中 Co_4S_3/C 多孔纳米阵列是以钴基金属-有机框架(Co-MOF)纳米片为模板制备而成的。 $Co_4S_3/C@CC$ 夹层中相互连接的碳网络和极性 Co_4S_3 纳米粒子不仅能有效地抑制多硫化物飞梭,而且能显著地促进锂离子(Li^+)的传导,其 Li^+ 迁移数高达0.86。此外,极性 Co_4S_3 纳米粒子与导电碳基底之间丰富的界面能够作为反应中心以加速多硫化物的转化与引导 Li_2S 的花状生长,最终减轻 Li_2S 对夹层表面的钝化以及提高硫的利用率。因此,载有 $Co_4S_3/C@CC$ 夹层的锂硫电池可以提供出色的倍率容量(在10 C时比容量为 368.7 mA h g^{-1})、稳定的循环性能(在2.0 C下1400周循环过程中衰减率为0.045%)以及高初始面容量(在0.2 C且硫含量为 4.6 mg cm^{-2} 时面容量达到 4.83 mA h cm^{-2})。这项工作展现了自支撑催化夹层对高性能锂硫电池中选择性 Li^+ 传导和 Li_2S 沉积的调控能力。