Confining Sulfur Species in Cathodes of Lithium-Sulfur Batteries: Insight into Nonpolar and Polar Matrix Surfaces

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Abstract

To alleviate polysulfides shuttle effect in lithium-sulfur batteries (LSBs), the use of a functionalized carbon matrix with polar surface has been widely reported to chemically bind the soluble polysulfides. However, whether and how such a polar carbon surface affects the overall cathode performance, particularly the initial discharge corresponding to the reduction of cyclooctasulfur (S_8), has not caught enough attention. By combining polar and nonpolar carbon matrix surfaces in different configurations through sandwiching sulfur species between two carbon matrix membranes, we found cells with dramatically different performance. The discharge process at different states, particularly the charge transfer resistances corresponding to nonpolar S_8 and polar polysulfide intermediates and the final Li_2S , were investigated. The experimental results, further supported by first-principles density functional theory calculations, indicate that the adsorption energy and barrier for electron transfer together affect the electrochemical performance of LSBs, and therefore a rational design that combines polar and nonpolar surfaces should be adopted.

TOC graphic

One severe challenge for development of lithium-sulfur batteries is the dissolution and diffusion problem of lithium polysulfides during charge and discharge cycles, giving rise to shuttle phenomenon, which causes irreversible loss of active materials, capacity fade, and self-discharge, among other detrimental effects.¹⁻⁶ With the concept of polysulfides confinement in a cathode matrix proposed,^{7,8} a variety of carbonaceous structures have been experimented with as the cathode conductive matrix to anchor the insulating sulfur species, and meanwhile, as a mesoporous maze to alleviate the shuttle effect of polysulfides by physically confining these soluble species.^{9,10} It was subsequently further realized that chemical binding of polysulfides onto the carbonaceous matrix with a polar surface, which is obtained through hetero-atom dopants or a second phase such as polymers, metal oxides or transition metal disulfides,¹¹⁻¹⁴ is much more effective in alleviating the shuttle effect.^{15,16} Therefore, a conductive, mesoporous and polar carbonaceous matrix, used to physically and chemically confine the otherwise soluble polysulfides, has dramatically boosted the LSB performance, particularly its capacity and cycling stability to an unprecedented level.

In contrast to significant interests in studying polar bonds in binding polysulfides, the role of nonpolar bonds for intimately binding S_8 has not caught enough attention.¹⁷ The electrochemistry of LSBs is based on a multiple electron transfer process.¹⁸⁻²¹ During discharge, S_8 experiences multi-step reduction, resulting first in formation of high-order lithium polysulfides, followed by their conversion into low-order lithium polysulfides, with the final product being Li_2S ; similarly, during charging, Li_2S converts back to S_8 in a reverse multi-step process. Lithium polysulfides and Li_2S_2/Li_2S are highly-polar materials, and a polar matrix surface will be expected to promote their binding, which has been a major interest of recent studies.^{17,22-26} However, S_8 has a nonpolar nature, and it remains unclear whether or not strongly polar host matrixes, particularly those based on amphiphilic molecule functionalization that favor polysulfides binding, are also able to facilitate the deposition of S_8 onto the host matrixes. An intimate contact between the highly insulating sulfur and the conductive matrix is indispensable, but as a probably overlooked factor, the strategy using chemically functionalized polar surface might increase the barrier for electron transfer at the sulfur/matrix interface leading to large polarization and capacity fading.

Combining first-principles density functional theory (DFT) calculations and experimental studies, this

work aimed to fundamentally reveal the polarity effects of the host matrix surface on S_8 and polysulfides binding, particularly the impact of different polarity configuration on charge-transfer resistance (R_{ct}) of the electrode at different charge or discharge states, and subsequently on the specific capacity and cycling stability of LSBs. Our studies reveal a critical but often neglected fact: in an attempt to minimize the shuttle effects of soluble polysulfides through a molecule-functionalized polar surface, one cannot neglect the adverse effect of this same polar surface on the increased barrier for electron transfer, and therefore an ideal cathode architecture design should have a surface that blends both polar and nonpolar characteristics together.

Figure 1. (a) Schematic of the experimented LSB cell configuration, with sulfur species sandwiched between two conductive carbon membranes. SEM images of (b) CFP and (c) T-CFP (The insets show optical images of a water droplet on CFP and T-CFP, with water completely absorbed by the latter). (Scale bar = 10 μm)

We selected relatively simple host structures for this study, instead of using nano-architected matrix. The consideration is that a simple structure, even with a relatively low performance, can capture or even magnify the feature contrast between different polarity configurations, while these features might be obscured if a well-designed nanostructured electrode was used. To this end, carbonized filter paper (CFP) and Triton X-100 functionalized CFP (T-CFP) were used as the models of nonpolar and polar membrane surfaces, respectively. Four cathode configurations: Nonpolar/Nonpolar (N/N), Nonpolar/Polar (N/P), Polar/Nonpolar (P/N) and Polar/Polar (P/P) with sulfur species sandwiched between two carbonaceous

membranes were studied, as schematically shown in Figure 1a. The cathode with Nonpolar as the bottom carbonaceous membrane and Polar as the top membrane was denoted as N/P and the other three, N/N, P/N, P/P, by analogy. The commonly used laboratory filter paper (Fisherbrand Quantitative Q8) was pyrolyzed in argon environment at 800 °C for 2 hours. The obtained CFP is comprised of micrometer-scale carbon fiber mesh (Figure 1b). The structural and compositional measurements of CFP are presented in Figure S1~S3 in Supplementary Information (SI). With only trace amount of oxygen remaining, CFP exhibits a strongly hydrophobic or nonpolar surface characteristic (inset of Figure 1b), unfavorable for immobilizing polar polysulfides through strong binding, particularly considering that these polysulfides have a very large binding energy with the polar electrolytes.²⁷ Introduction of certain organic functional groups, such as ether groups or ester groups, has been proved capable of converting the nonpolar carbon surface to a polar surface, with chemical traps established on the matrix surface to bind soluble polysulfides.^{7,12,28-30} Triton X-100, or $C_{14}H_{22}O(C_2H_4O)_n$, is a nonionic surfactant with a hydrophilic polyethylene oxide chain and an aromatic hydrocarbon hydrophobic group, and therefore can graft on the hydrophobic carbon surface and render the latter with hydrophilic property. Thus, Triton X-100 functionalized carbon surface is capable of chemically binding polysulfides leading to minimized shuttling phenomenon.^{31,32} The morphology of Triton X-100 grafted CFP, T-CFP, is shown in Figure 1c, and its highly hydrophilic characteristic can be noticed from the inset where a water drop was completely absorbed with no droplet left on the surface. The cathode configuration shown in Figure 1a with sulfur species sandwiched between two carbon membranes was used to study and compare how nonpolar and polar matrix surfaces affect the specific capacity and cycling stability of the battery. To ensure the active materials uniformly distributed on both carbonaceous membranes, Li_2S_6 solution was used as the starting material instead of solid S_8 , since the initial inhomogeneous distribution of S_8 might obscure the observation of polar/nonpolar effect.

Figure 2. (a) Cycling performance of the N/N, N/P, P/N and P/P at 0.2 C. The galvanostatic C-D profiles of the (b) N/N, (c) N/P, (d) P/N and (e) P/P at 0.2 C within a potential window of 1.6-2.8 V versus Li^+/Li . (f) The specific capacities corresponding to the high plateaus of the N/N, N/P, P/N and P/P electrodes. (g) The ratio of the low plateau to the high plateau capacity of the N/N, N/P, P/N and P/P electrodes.

The LSB cells with four different cathode polarity configurations behave differently with striking contrast, as shown by the galvanostatic charge-discharge cycling test at a representative 0.2 C rate. Figure 2a shows their discharge cycling performance. The N/P cell exhibits stable performance with a maximum discharge capacity, while the capacity of the P/N cell is initially much lower, and then approaches that of the N/P cell only after a few tens of cycles. The P/P cell, in spite of initially exhibiting large capacity close to that of the N/P cell, dramatically loses it to a half initial value in the first ten cycles, approaching the capacity value close to that of the N/N cell, which has a stable but lowest capacity. The cells have to experience several cycles before stabilizing and the data after the tenth cycle more clearly reflect the electrochemical performance of the LSBs.^{11,33} Therefore, we compare the electrochemical data of the four cells after 10 cycles. Figure 2b-e shows the C-D profiles of the four types of cells starting from 10th cycle. All the discharge curves are composed of a high plateau and a low plateau, corresponding to the reduction of S_8 to lithium polysulfide intermediates (Li_2S_4) and then to the final products $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$.³⁴ Similar is true for the charge curves, corresponding to oxidization of $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ to lithium polysulfides and then to S_8 .³³ The polarization decrease and capacity increase with cycling in the P/N and P/P cells might be caused by sulfur redistribution with repeating redox reaction and solid-liquid-solid phase change of sulfur species during cycling.

However, the discharge capacities corresponding to the high plateau (C_H) and to the low plateau (C_L) and their ratios are very different for the four cells. As summarized in Figure 2f, the N/N cell displays the largest C_H , the P/P cell exhibited the smallest C_H , and the P/N cell and the N/P cell have similar C_H , with the latter one slightly smaller. These data suggest that at least one nonpolar surface is essential for a large C_H , or to reduce S_8 to Li_2S_4 . On the other hand, the N/P cell has the largest and stable C_L , while the N/N cell has a trivial C_L value. The P/N cell initially has a smaller C_L , but gradually approaches that of the N/P

cell after approximately 50 cycles. Since capacity C_L is also correlated to C_H , or the amount of the available Li_2S_4 that was produced in the process corresponding to C_H , the ratio of C_L/C_H is more suitable to reflect the impact of the surface polarity, and it is plotted in Figure 2g. As can be noticed, the P/P and the N/P cells, both of which have the top membrane with a polar surface, offer the largest C_L/C_H , or have the best capability to reduce Li_2S_4 into the final $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ products, while the N/N cell, with both nonpolar surfaces, has a trivial capability to reduce Li_2S_4 .

Distinctive features seen in Figure 2 are summarized as: 1) The N/P and P/N mixed polar and nonpolar matrix structures, particularly the former one, provide a nearly doubled discharge capacity over that of N/N and P/P structures; 2) Of the two mixed polarity structures, the N/P is much better than the P/N, with the latter one achieving a high capacity only after a few tens of cycles; 3) Of the two single polarity structures, the P/P shows a large initial capacity, but it quickly fades away, resulting in only slightly better capacity than that of the N/N; 4) The high and low discharge plateaus and the corresponding capacity contributions as well as the contribution ratios are remarkably different for the four polarity configurations; 5) At least one nonpolar surface is needed for a large C_H , and the N/N nonpolar surfaces give the largest C_H ; and 6) A large C_L/C_H requires the top membrane having a polar surface. These results clearly indicate that the surface polarity of the electrode conductive matrix, and their relative position, i.e., N/P or P/N, have profound influences on the cell performance.

We attributed these influences to the binding capability of the conductive surface to the nonpolar S_8 and the polar Li_2S_n . To reveal the underlying mechanism that controls how the electrode surface polarity impacts the cell performance, we studied the charge transfer resistance in these cells at different discharge states through EIS measurements. Our assumption was that strong binding with a short charge transfer distance between the insulating solids (S_8 or $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$) and the conductive matrix will facilitate the charge carrier transfer and hence the redox reaction, while for the conductive but soluble lithium polysulfides, strong binding to the conductive matrix will also facilitate their redox reaction and inhibit their diffusion and shuttle effect.

Figure 3. (a) A typical C-D profile of LSB. (b) Nyquist plot of the four different cells measured at point A. Charge-transfer resistance measured at (c) point A, (d) point B and (e) point C.

Figure 3a shows a typical C-D profile of the LSB, indicating the multistep process of S_8 reduction into the final Li_2S in discharging and the oxidation from Li_2S to S_8 in charging.³⁵ When the depth of charge (DOC) equals to 100 % or the depth of discharge (DOD) equals to 0, the sulfur species exist in the nonpolar form of S_8 (point A), while they present as the polar form of Li_2S (point C) when DOC equals to 0 % or DOD equals to 100 %. These active species would exist as lithium polysulfide intermediates or their mixture between point A and point C.³⁶⁻³⁹ We conducted the EIS measurement of the four cells for analyzing the difference in electrochemical performance. The mass loading of sulfur species in the four cells was the same during the EIS measurement.⁴⁰⁻⁴² Figure 3b shows EIS spectra, in the Nyquist plot, of the four different cells measured at point A, with others at point B and point C are presented in Figures S4 and S5. The Nyquist plots consist of a depressed semicircle in the high-frequency region and an inclined line at low

frequency. Based on the model in the inset of Figure 3b,^{33,34,43} the intercept at high frequency on the real axis indicates the ionic transport resistance of the electrolyte and the internal ohmic resistance of the battery (R_e). The diameter of the semicircle at high frequency to medium frequency corresponds to the charge-transfer resistance (R_{ct}), determined by the interface of the electrolyte and the electrode. The inclined line at low frequency represents Warburg impedance (W_o), which is associated with Li^+ diffusion into the porous electrode.⁴⁴ As shown in Figure 3b and S4-5, introducing of non-conductive Triton X-100 leads to a slight increase of the internal ohmic resistance R_e in the cells with polar membrane, suggesting a thin surface coating layer. Using the equivalent circuit (inset in Figure 3b) to fit the measurements, the extracted R_{ct} of the four types of cells measured at point A, B and C is shown in Figure 3c-e. The N/N cell has the smallest R_{ct} at point A, while it is the largest at point B and C. This is reasonable since at point A, nonpolar and insulating S_8 is the reactant, which must be intimately attached on a nonpolar surface for facile reduction reaction, while at points B and C, the polar polysulfides and Li_2S_2 and Li_2S require polar surface for intimate binding.¹⁷ Therefore, the P/P cell shows the smallest R_{ct} at point B and C, but the largest value at point A. The R_{ct} of the N/P and P/N cells falls in between the former two.

To confirm that active sulfur species do have very different binding energies on CFP and T-CFP; and therefore, the above experimental observations are truly rooted in the different nonpolar and polar nature of CFP and T-CFP, we explored the binding energy and charge transfer distance of S_8 and lithium polysulfides on non-polar and polar graphitic surfaces by performing DFT calculations. The non-polar CFP surface was modeled using a pristine graphene surface, and the polar T-CFP surface was simulated using the same graphene surface but functionalized with $\text{C}_{14}\text{H}_{22}\text{O}(\text{C}_2\text{H}_4\text{O})_2$ to model Triton X-100. Figure 4 shows the optimized structures along with the calculated adsorption energies of S_8 and LiS_x on these two different surfaces.

Figure 4. Density Functional Theory Calculations of binding energies of sulfur and lithium polysulfide on a graphitic surface. (a-d), structure of S_8 , Li_2S_8 , Li_2S_2 and Li_2S adsorption on a non-polar graphene surface. (e-h), structure of S_8 , Li_2S_8 , Li_2S_2 and Li_2S on a polar graphene surface functionalized with $C_{14}H_{22}O(C_2H_4O)_n$ ($n=2$) to model Triton X-100. The adsorption energies are also shown. (i) (x,y) plane-averaged electrostatic potential above the graphitic surface for adsorption of S_8 (dashed black), Triton/ S_8 (solid black) and Triton- Li_2S_8 (solid green). The positions of the graphene, Triton, S_8 and Li_2S_8 are schematically shown. The Li, S, C, H, O are colored green, yellow, cyan, white and red, respectively.

It was found that at the early stage of discharge, pristine graphene and Triton-functionalized graphene show comparable binding to S_8 since the interfacial interaction is dominated by van der Waals interaction

(Figure 4a, e). This comparable binding agrees with previous experiments showing that both polysulfides and sulfur are preferentially deposited on a tin-doped indium-oxide-functionalized polar surface.²⁴ The wave function of adsorbed S_8 overlaps with that of the pristine carbon surface evidenced by a negative potential (with respect to Vacuum level) at the interface (Figure 4i dashed curve). The electrostatic potential of S_8 is shifted to a higher position (shown by a dashed arrow) indicating that S_8 is decoupled from the graphitic surface due to the presence of the Triton and the van-der-Waals-type interaction. Therefore, the electron transfer between S_8 and the carbon surface, which is critical for the discharge process, is hindered by the surface functionalization leading to increased ohmic resistance at the graphene/triton/ S_8 interface. The calculation result is consistent with EIS result in Figure 3.

Instead, Li_2S_8 prefers adsorption on the polar surface (Figure 4b, f) caused by a newly formed Li-O bond between Li_2S_8 and the O atoms in the hydrophilic polyethylene oxide chain in Triton (Figure S6). This Li-O bond not only stabilizes the Li_2S_x but also facilitates charge transfer at the graphene/Triton- Li_2S_x interface due to its covalent character, shown by a more negative electrostatic potential at the Triton- Li_2S_x interface than the Triton/ S_8 interface (Fig. 4i green curve). The interfacial binding on functionalized graphene is further enhanced for Li_2S_2 and Li_2S manifested by the increased adsorption energy (Figure 4g, h) and shorter bond lengths (Figure S6), whereas it becomes weaker on pristine graphene (Figure 4c, d). The latter is caused by reduced number of van der Waals pair interaction that dominates at the non-polar graphitic surface. It should be noticed that the present calculations only include a monolayer of Triton molecules on the surface, and one would expect further enhanced binding of Li_2S_x at a higher Triton coverage, since each Li atom can bind to an oxygen atom in the polyethylene oxide chain of Triton.

The DFT calculations thus suggest that at the beginning of the discharge, both non-polar and polar surfaces can provide favorable binding for S_8 , and non-polar surface is more desirable due to the shorter barrier for electron transfer. As discharge proceeds, polar surface becomes more desirable, because it provides both favorable binding for Li_2S_x and facilitated electron transfer through the Li-O covalent bonds at the interface.

The surface binding dependence on polarity and measurements of charge transfer resistance can well explain the observation of cell performance in Figure 2. To obtain a large C_H , nonpolar surface is essential

for efficient charge transfer and hence S_8 reduction, while for efficiently reducing soluble polysulfides for a large C_L/C_H , a polar surface, especially for the top membrane, is critical. The best combination of the bottom and top membranes therefore is the N/P pair. It deserves to be mentioned that the performance of the N/P cell exceeds the P/N cell, since the polar membrane between the sulfur species in the cathode and the lithium anode could capture and reuse a certain amount of soluble lithium polysulfides, which may otherwise diffuse to the lithium anode, alleviating the shuttle effect. We emphasize that this study is to show the surface polarity effect on the nonpolar S_8 and polar sulfides. To provide unambiguous evidences, the study is based on polarity surface at the macroscale with two membranes as the conductive matrix. It is envisioned that a better electrode matrix design could be a surface that has both polar and nonpolar regions at a microscale with a dimension suitable for on-surface or close-to-surface diffusion of the polar and nonpolar species. It requires further study in the future.

To briefly summarize, we consider the impact of the functional Triton X-100 molecules on conductive carbon surface is manifested in three aspects: 1) binding capability for both S_8 and polysulfides, 2) electron transfer, and 3) electrode conductivity. Their relative importance, from high to low, follow the 1), 2), 3) sequence. The most important positive impact of the functional surface is the enhanced binding capability for polar polysulfides. This will effectively reduce the shuttling effect of intermediate polysulfides and therefore enhance the capacity. Furthermore, this strong binding should also facilitate electron transfer through Li-O bonds at the interface. On the other hand, since binding to the nonpolar S_8 is dominated by van der Waals interaction, nonpolar surface and the functionalized polar surface have the same binding energy. However, the functional molecules unavoidably introduce an extra charge transfer barrier. Therefore, the electron transfer between S_8 and the carbon surface, which is critical for the discharge process, is hindered by the surface functionalization. This is the negative impact of the Triton X-100 functionalized surface. The impact on electrode conductivity is rather trivial. For example, from Fig. 3b, R_e values were approximately 5.5, 7.9, 9.6, and 10.1 Ω for N/N, N/P, P/N, and P/P, respectively. This is reasonable considering that for the electrode, the resistances from functional layer and from the carbon itself are predominantly in parallel connection. Therefore, this negative effect is trivial.

To further prove the generality of our finding that a better sulfur cathode should pair nonpolar and polar electrode surface together and also to demonstrate a better electrode matrix structure, we used the combination of CFP and carbon nanofiber (CNF) membranes as the conductive matrix, and expected the large surface area of CNF would provide a better performance.⁴⁵ Two cells were tested, one with two nonpolar membranes (CFP/CNF), and the other using nonpolar CFP and polar Triton-treated CNF membrane (CFP/T-CNF). Figure 5a shows cycling performances of the two cells, tested under 0.2 C. The CFP/T-CNF cell shows an initial capacity of 1200 mA h g⁻¹, compared to an initial capacity of only 800 mA h g⁻¹ for the CFP/CNF cell. The former one also exhibits a better cycling stability, maintaining a capacity of 937 mA h g⁻¹ after 200 cycles. The over 400 mA h g⁻¹ capacity difference for the two cells for all testing cycles is due to both the larger C_H and C_L , as shown in Figure 5b. Furthermore, the CFP/T-CNF cell exhibits a lower charging voltage to transform Li₂S₂/ Li₂S to lithium polysulfides and then to S₈. To better demonstrate the difference in cycling performance between CFP/CNF and CFP/T-CNF, the discharge capacity was normalized to that of the 10th discharge capacity. The data from the 10th cycle is commonly selected to reflect the discharge characteristics at the beginning stage since a cell often requires a first few cycles for activation.¹¹ As shown in Figure 5c, the battery CFP/T-CNF shows better capacity retention than the CFP/CNF cell, with the former showing 85% capacity retention, while the latter is only 72% after 100 cycles. EIS spectra of the two cells are compared in Figure S8 and the corresponding R_{ct} is shown in Figure 5d. The CFP/T-CNF cell has a lower R_{ct} than the CFP/ CNF cell at point B and C, while they have very similar R_{ct} at point A. These results are consistent with our previous conclusion drawn from Figures 2-4.

Figure 5. (a) Cycling performances, (b) the third cycle galvanostatic charge/discharge profiles, (c) capacity retention and (d) charge-transfer resistance of the LSBs with the CFP/CNF and CFP/T-CNF electrodes.

In summary, a functionalized carbon matrix surface with a polar nature is important for binding polysulfides to minimize shuttle phenomenon, however, its adverse effect on intimate electronic contact of S₈ cannot be neglected. Using a sandwiched cathode structure with four different combinations of polar and nonpolar carbon matrixes, we have observed dramatic differences in their performance, and the best configuration had a nonpolar bottom membrane and a polar top membrane. The performance difference was explained by the charge transfer resistance and binding energy difference at different discharge states. Particularly, an intimate electronic contact between the highly insulating S₈ and a nonpolar conductive matrix is necessary for facile reduction of S₈ to achieve a high capacity in the high discharge plateau, while

a tight binding between polysulfides and a polar matrix is essential to alleviate the shuttle effect for a large capacity in the low discharge plateau. Therefore, an optimized design of the carbon matrix should consider both effects by integrating polar and nonpolar surfaces together. Our findings provide guidelines for design of a more desirable matrix material for sulfur cathodes used in LSBs.

Experimental Methods

Fabrication of carbon membranes

The commonly used laboratory filter paper (Fisherbrand Quantitative Q8) was carbonized in a tube furnace under argon flow of 50 sccm at 800 °C for 2 hours with a heating rate of 2.5 K/min to obtain CFP. Triton X-100 was dissolved in methanol to form a 5 wt% solution. The T-CFP was obtained by pipetting the prepared Triton X-100 solution uniformly on the CFP. The content of Triton X-100 in the T-CFP was controlled at around 0.2 mg cm⁻².

100 mg of carbon nanofiber powder (Sigma-Aldrich) was dispersed in 200 ml isopropyl alcohol and deionized water (1:1 by volume). The solution was then stirred for 2 hours. CNF was coated on a Celgard 2400 separator via vacuum filtration with 15 ml of the prepared solution for an area of 10 cm². Then, CNF-coated Celgard 2400 separator was dried at 50 °C for 12 hours to detach the CNF membrane from the separator. To prepare T-CNF membrane, the solution was made of 80 mg carbon nanofiber powder and 20 mg Triton X-100 dispersed in 200 ml isopropyl alcohol and deionized water (1:1 by volume).

Material characterization

The morphology of the CFP, T-CFP, CNF and T-CNF was characterized using a field emission scanning electron microscope (FE-SEM). X-ray powder diffraction (XRD) was conducted through a Siemens/Bruker AXS D5005 X-ray diffractometer. X-ray photoelectron spectra (XPS) were measured using a PHI 5000 VersaProbe X-ray photoelectron spectrometer. The photoelectrons were excited by monochromatic Al K_α radiation (1486.6 eV). Raman spectra were recorded using a Bruker SENTERRA dispersive Raman microscope spectrometer with an excitation laser beam wavelength of 532 nm.

Cell assembly

The used electrolyte is a solution of lithium bis (tri-fluoromethanesulfonyl)imide (1 M) in 1, 2-

dimethoxyethane (DME) and 1, 3-dioxolane (DOL) solvents (volume ratio 1:1), which further contains 1 wt % LiNO_3 . Li_2S_6 catholyte (0.25 M) was prepared by chemically reacting sulfur (99.999%, Acros Organics) and Li_2S (99.9%, Alfa Aesar) in the electrolyte. The prepared CFP, T-CFP, CNF and T-CNF membranes were cut to circular pieces with a diameter of 1 cm. 2032-type coin cells were assembled in an argon-filled glove box. 40 μL of Li_2S_6 catholyte was sandwiched between two CFP or T-CFP membranes to form the cathode of LSB with different polar and nonpolar configurations. To ensure that the catholyte was uniformly distributed on both of the membranes, 20 μL of Li_2S_6 catholyte was dropped on the bottom carbonaceous membrane and 20 μL on the top one. Then the top one was turned upside down and overlaid on the bottom one to form a sandwich-like structure, with the catholyte diffusion into two membranes. The sulfur loading of the cathode was 2.45 mg cm^{-2} . Lithium foil was used as the anode, which was separated from the cathode by a Celgard 2400 separator soaked with 20 μL electrolyte. CFP/CNF and CFP/T-CNF based cells were assembled in a similar method.

Electrochemical measurements

Electrochemical impedance spectroscopy (EIS) of the assembled cells was measured by an electrochemical workstation (EC-Lab SP-150, BioLogic Science Instruments). EIS spectra were taken by applying 5 mV alternative signal versus the set voltage in the frequency range of 1 MHz to 0.1 Hz. The cells were discharged to 2.0 V for EIS measurement at point B, then discharged to 1.6 V for measurement at point C, and subsequently were charged to 2.8 V to characterize at point A. The scan rate was 0.05 mV s^{-1} . Galvanostatic charge–discharge cycling was carried out using a LAND CT-2001A instrument (Wuhan, China) from 1.6 to 2.8 V versus Li^+/Li . Specific capacity values were calculated based on the mass of sulfur loaded in the cathode.

Density functional theory calculation method

The DFT calculations were carried out using the VASP package.⁴⁶ The PBE-GGA exchange-correlation potential⁴⁷ was used, and the electron-core interactions were treated in the projector augmented wave method.^{48,49} The van der Waals interaction has been taken into account through the DFT-D3 semi-empirical method.^{50,51} All the calculations have been performed using a graphene supercell containing 160 C atoms embedded in a 15 Å of vacuum space. Structures have been optimized using a single Γ point of the Brillouin

zone with a kinetic cut off energy of 400 eV. All the atoms were fully relaxed until the atomic forces were smaller than 0.01 eV Å⁻¹.

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Supporting Information Available: (XRD, Raman and XPS results, Nyquist plots, calculated Li-O bond length, and optical images).

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