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Asymmetric Cathode Membrane with Tunable Positive Charge Networks for Highly Stable Li–S Batteries

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Abstract

Freestanding cathodes with a high sulfur loading more than 4 mg cm^{-2} are essential for practical high-energy density Li-S batteries. However, Li^+ transport is sluggish and polysulfide shuttling is serious in thick cathodes, leading to rapid capacity loss and inferior rate performance. Herein, an asymmetric Li-S cathode threaded with positive charges networks was introduced by a facile phase separation strategy coupled with cationic-crosslinking method. This large-area and flexible cathode membrane shows a gradient distribution of pore structure with a skin sieving layer supported on a thick porous submatrix. This dual sulfur host reveals an inbuilt ability to suppress polysulfide shuttling in Li-S cells. Meanwhile, the positive charge networks derived from post-crosslinking endows the cathode frameworks with boosted S_n^{2-} trapping ability and enhanced ionic transport kinetics. Further adjustment of the cationic networks reveals its ionic exchange mechanism in accelerating the redox reactions at the positive charge interface. As a result, composite membrane with high sulfur loading (9.1 mg cm^{-2}) yields a capacity of over 8.1 mAh cm^{-2} for long-term cycling. This scalable and functional asymmetric cathode design presents an alternative route toward high energy density Li-S batteries.

Keywords: Freestanding asymmetric cathodes; Flexible porous membrane; Non-solvent phase inversion; Poly (2,6-dimethyl phenylene oxide); Lithium-sulfur battery.

1. Introduction

The high energy density (2600 Wh kg^{-1} in theory) coupled with the earth's abundance of sulfur, has made Li-S battery an attractive energy storage system over the past decades [1–3]. However, the complex intermediate redox and transport phenomena in Li-S cells still preclude its practical application. During charge–discharge cycles, the soluble lithium polysulfide (LiPS) is flooded inside the cell and shuttles between the electrodes, resulting in low sulfur utilization, inferior coulombic efficiency, and rapid capacity degradation [4–8]. Meanwhile, the sluggish Li^+ ion transport, especially in thick and freestanding electrodes, often causes poor rate capability [9–12].

To address these issues, researchers have focused on upgrading the cathode side through two main approaches, viz. physical confinement and chemical binding, to alleviate the shuttling of LiPS. From the earliest reported porous carbon-based confinement [13–16] to the latest polar absorbents like metal carbides/oxides/sulfides [17,18], heteroatom-doped carbon [19,20], and polymers [21–23], various materials have been explored and enhanced capacity has been demonstrated. Even then, when the sulfur loading is high in thick cathode film, the massive dissolved LiPS are hard to be trapped owing to the adsorption saturation [24,25], and capacity stability is far from satisfactory. Furthermore, a successful cathode that could exclusively trap shuttling S_n^{2-} anions, and ideally, has a functional interface to facilitate the synchronous flow of Li ions would be more appealing to long-term cyclability. On the other hand, building artificial coatings/interlayers on separators is also efficient in blocking/reusing the LiPS species. However, most of the techniques involved (e.g., vacuum filtration [26,27], freeze drying [28], and harsh conditions [29–31]) are time-consuming and can be barely scaled up. The increased polarization and decreased energy density due to the inserted thick interlayers may also impair

their merit of blocking effect in practical applications. Therefore, developing a facile fabrication route for a freestanding and high-loading cathode that could efficiently inhibit S_n^{2-} migration and regulate Li^+ transport is highly desired, but still remaining a challenge. In this regard, a new configuration is required to enrich this field, e.g., asymmetric structure.

Asymmetric structure is intriguing for its well-defined spatial morphologies and diverse chemical decorations [32,33]. Especially, asymmetric membranes often possess two distinct functions: the skin dense layer is specialized for selective molecular sieving, and the porous submatrix provides interconnected channels for fast mass transport. Such integrated structures with dual operation protocols make them highly attractive in cutting-edge applications such as nanofiltration [33], switchable ion transport [34], and flow battery separators [35]. Nevertheless, the exploration of asymmetric electrode in Li-S systems lags far behind.

With this in mind, we developed an asymmetric cathode membrane that is freestanding, positively charged, and scaled over meters. To realize this design, a robust poly (2,6-dimethyl phenylene oxide) (PPO) is introduced as an electrode skeleton for the first time, and a versatile non-solvent-induced phase separation (NIPS) is presented coupled with a post-cross-linking treatment. This strategy is simple and easily processable, with three notable merits. 1) The integral cathode is made of a skin polysulfide blocking layer and a nanoporous mass-transport sublayer, which could be well formed concurrently using the NIPS method; 2) the cross-linking of functional PPO with ionic liquid in the electrode generates a high-density imidazolium cationic charges, which makes the cathode mechanically strong and super-wetting toward electrolytes; 3) the anion metathesis mechanism between the mobile $TFSI^-$ tethered on functional PPO and S_n^{2-} endows the cathode frameworks with high S_n^{2-} trapping capacity and fast Li^+ diffusion. Therefore, bypassing the burden from separator coating or sophisticated cathode

engineering, this work may pave the way for a mass production of high-energy and stable Li-S cathodes.

2. Results and discussion

Fig. 1 Characterization of the asymmetric cathode membrane. (a) Schematic illustration of the preparation process for the asymmetric cathode using the NIPS method. (b) SEM images of the asymmetric membrane prepared from bromide PPO. (c, d) Cross section of the cathode and the

energy dispersive spectroscopy mappings. (e, f) Morphology of the surface layer and cross section of the cathode (scale bar: 500 nm). (g) Electrolyte contact angles of the electrode. (h, i) Digital photographs of the self-supporting cathode and the mechanical properties. (j) Pore-size distribution for the cathode fabricated by the NIPS (red line) and routine casting (black line) method. (k) The areal size of freestanding sulfur cathodes by various preparation methods that reported in the last 7 years, references [36–53].

Fig. 1a depicts the features of the asymmetric cross-linked cathode membrane using imidazolium functionalized PPO (ACImPPO) coupled with a phase inversion strategy (Fig. S1). The PPO is explored here as a promising starting material to weave the electrode membrane for excellent physiochemical stability (Fig. S2) and high mechanical strength [54]. Moreover, the two methyl groups in each unit enable the opportunity for a quantified modification. The PPO is first functionalized via bromination of the benzyl groups to obtain bromide PPO (BPPO) (Fig. S3), and then a slurry of CNT-S, BPPO, and NMP solvent is blade cast onto a flat plate. The BPPO polymer can be dissolved in NMP, while water is a nonsolvent. When the as-cast composited slurry is immersed into a coagulation bath of water, the NMP diffuses rapidly from the slurry surface to the water bath and induces a skin dense layer. The skin layer keeps a moderate convection rate between the water and NMP inside the membrane, and a sponge-like porous sublayer is then generated [55]. Next, the porous membrane is treated with an ionic liquid cross-linker of 1,1'-(1,6-hexanediyl)bisimidazole (Fig. S4, Fig. 2a). The nucleophilic reaction between BPPO and 1,1'-(1,6-hexanediyl)bisimidazole introduce highly cross-linked networks with massive imidazolium cations (detailed reaction mechanism see Fig. S5). As shown in Fig. 1b, the pristine BPPO membrane prepared by the NIPS method exhibits a typical thin skin layer of about 500 nm supported on a porous matrix. Similarly, the cathode composite membrane also

exhibits a gradient distribution of porosity over the cross section in Fig. 1c-d. More clearly, Fig. 1e, f reveals that the top layer is smooth without visible through-holes, while the cross section of the electrode is highly porous with interpenetrating nanochannels. The energy dispersive spectroscopy (EDS) in Fig. 1e,f found that there are small amount of sulfur content (~5.2 wt%) and large amount of carbon element (81 wt%) in the skin dense layer, while the sulfur content in the porous sub-matrix is up to ~48.5%. This gradient distribution confirms the asymmetric cathode that the crosslinked ImPPO is rich in the surface layer and the sulfur is well hosted in the sublayer. Another feature of the electrode, benefiting from the hydrophilic nature of cationic tethered PPO, is its strong affinity with electrolytes, as revealed by the low contact angle toward the electrolytes (Fig. 1g). The large-area flexible electrode is exhibited in Fig. 1h-i with superior mechanical robustness (tensile stress and strain above 20 MPa and 8%, respectively), and the distinct porosity distribution between 10-100 nm (Fig. 1j, Fig. S6) would benefit the ions transport desired for redox reaction. Moreover, electrode of over 2000 cm² could be easily prepared in this strategy, which is the largest in size among the recorded self-supporting cathodes (Fig. 1k).

Fig. 2 (a) Modification process of the PPO polymer and the corresponding ^1H NMR analysis. (b, c) XPS spectra of the N 1s signal for the cationic ImPPO polymer before and after the interaction with polysulfide. (d) Density functional theory calculation of the energy interactions between the cationic monomers and the typical Li₂S₄, Li₂S₆, and LiTFSI. (e) Electrolyte uptake and swelling ratio behavior of the prepared polymer and other different types of polymers used in Li-S cells.

To investigate the functionalization process and the features of the positively charged networks (Fig. 2a), we analyzed the imidazolium tethered PPO (ImPPO) polymer. As shown in Fig. 2b, the stretching band at around 986 cm^{-1} is associated with the CH_2Br group in BPPO. After the cross-linking, the CH_2Br disappeared and a new characteristic peak emerged at 1562 cm^{-1} in ImPPO owing to imidazolium vibration, demonstrating the complete S_N^2 substitution and

the formation of imidazolium cations. The IEC (i.e., cationic concentration) in this polymer could be finely tuned by controlling the bromination degree and quantified on the basis of the ^1H NMR spectra (Fig. S3). To explore the interaction between ImPPO and polysulfide, a set of ImPPO with IEC values of 1.45, 2.51, and 3.68 mmol g $^{-1}$ were prepared. Both the visual observation and the UV-Vis measurement (Fig. S7–8) reveal that the polysulfide-capturing ability hinges on the IEC values, i.e., a higher cationic charge density leads to better absorption capability and, consequently, to higher capacity retention, as will be discussed later. To understand these phenomena, we performed an X-ray photoelectron spectroscopy analysis from ImPPO-TFSI. As shown in Fig. 2c, the peak at 401.8 eV and 399.1 eV corresponds to nitrogen atoms in the imidazolium ring (i.e., N_{cation}) and TFSI $^{-}$ (i.e., N_{anion}), respectively. The peak area ratio of $\text{N}_{\text{cation}}/\text{N}_{\text{anion}}$ is $\sim 2:1$, consistent with the signature of ImPPO-TFSI. However, the immersion of ImPPO-TFSI into polysulfide causes a near-complete loss of N_{anion} at 399.1 eV (Fig. 2d), revealing that there is an anion exchange process undergoing between the mobile TFSI $^{-}$ and the S_n^{2-} anions. This metathesis was also validated by the density functional theory (DFT) calculations in Fig. 2e. The binding energy of TFSI $^{-}$ anion to a monomer of ImPPO is 9.7 kcal mol $^{-1}$, while this value increases reach 11.5 and 13.7 kcal mol $^{-1}$ for Li_2S_4 and Li_2S_6 , respectively. Therefore, the driving force based on ionic exchange regulated the IEC-dependent polysulfide-capturing behavior.

In principle, an efficient electrolyte uptake is in favor of higher ion transfer and lower inner cell resistance in the cycling process; however, excessive swelling under high electrolyte uptake often leads to loss of mechanical and adhesive strength and, consequently, to cell failure because of large volume changes [56]. As illustrated in Fig. 2f, compared with the routine poly(vinylidene fluoride) (PVDF), linear-type poly(diallyldimethylammonium chloride)

(PDDA), and anion-tethered Nafion, ImPPO (IEC: 3.68 mmol g⁻¹) exhibited the highest electrolyte uptake (~98%) while maintaining a low swelling ratio of 25%. This means that the cross-linking networks enhance the electrolyte uptake and retain the anti-swelling property for electrode integrity at the same time.

When demonstrated in actual Li-S cells, the prepared cathode obtained an initial discharge capacity of over 1170 mAh g⁻¹ at 0.2 C (Fig. 3a), and a much improved cycling performance was achieved over 300 cycles (925 mAh g⁻¹) with a capacity retention of 83%. Moreover, for a more practical application, Li₂S₆ catholyte was introduced into a porous membrane, thereby increasing the sulfur loading from 2.5 to 5.3 mg cm⁻² (Fig. S9). The corresponding cyclic voltammetry (CV) showed typical Li-S redox characteristics at various scanning rates (Fig. 3b). The constant peak current and potential at 0.15 mV s⁻¹ indicated superb redox reversibility and stability. More clearly, the galvanostatic cycling profile (Fig. 3c) revealed that the electrode delivered a remarkably stable capacity from 30th (930 mAh g⁻¹) to 300th cycle (875 mAh g⁻¹), corresponding to a 94% capacity retention. Additionally, a high coulombic efficiency (CE) above 99.2% could be maintained throughout the cycling, although there was a catholyte injection, which has often been reported to cause serious polysulfide shuttling and low CE [57]. We also noted that, at a current of 0.05 C (Fig. 4b) the reversible capacity reached 1612 mAh g⁻¹, which indicates that almost 100% utilization of sulfur in the redox reactions. Therefore, the cycle performances from this functional asymmetric cathode were highly competitive in comparison with those of the recent freestanding electrodes such as graphene sandwich pure sulfur [37], metal compound cathodes [14,58], dual separator-coated LDH@CNT-S composites [49], and carbon-SiO₂ composite membranes [59] when considering the cyclability, sulfur loading, and capacity retention.

Fig. 3 (a) Cycling performance of the cell with the asymmetric cathode at 0.2 C. (b) CV profiles of the electrode at various scanning rates. (c) Galvanostatic charge-discharge profiles of the cathode at different cycles at 0.2 C. (d) Shuttle currents cells with an asymmetric cathode and a skin layer-removed cathode. (e) SEM images of the fresh PP separator. Back side (facing Li anode) of the PP separator paired with asymmetric cathode (f), and with the skin layer-removed cathode (g) after 100 cycles. (h) SEM images of fresh Li anode, (i) Li anode paired with asymmetric cathode, and (j) the skin layer-removed cathode after 100 cycles.

To explore the performance gains originating from the asymmetric structure of the electrode, the thin skin layer was deliberately removed by plasma treatment (Fig. S10). As shown in Fig. 3d, after assembling with the skin layer-removed cathode, we found that the shuttle current, recorded at a potentiostatic charge of 2.38 V, increased almost 10-fold compared to that for the asymmetric cathode, reaching around $2.6 \times 10^{-2} \text{ mA cm}^{-2}$. This clearly reveals the polysulfide shuttling is significantly reduced for the asymmetric cathode. To further investigate this effect, we disassembled the cells and traced the separators and Li anodes after 100 cycles. As shown in Fig. 3f–i, for the cell without the skin-layer cathode, the separator across the surface is covered with the massive sulfur species (Fig. 3g, Fig. S11), and Li anode was seriously pulverized (Fig. 3j, Fig. S12c) due to parasitic reactions. While both the separator and Li metal paired with asymmetric cathode exhibited a well-retained surface without a distinct LiPS deposition (Fig. 3f, i). This observation is also consistent with the high coulombic efficiency ($\sim 86\%$), stable open-circuit voltage and improved capacity retention (Fig. S13-14) compared with the electrode in the absence of the skin blocking layer.

Fig. 4 (a) Galvanostatic intermittent titration profiles of the cell with the asymmetric cathode based on ImPPO and PPO at 0.1 C and (b) the rate performance. (c) Electrochemical impedance spectra of the ACImPPO cathode and PPO cathode (inset is the equivalent circuit). (d) Lithium ion diffusion coefficient of the two cathodes. (e-h) SEM images of the electrodes at the discharged and recharged state for (e-f) ACImPPO- and the (g-h) PPO-based cathode. Scale bar: 500 nm. (i) Illustration of the cathode with asymmetric structure and positive charges interface.

Aside from its structural advantages, the effects of the positively charged cross-linking networks that regulate the electrochemical kinetics were further investigated. As demonstrated by the experiment results and DFT calculations above, the S_n^{2-} anions blocked in the cathode side preferentially interact with the imidazolium cations from the ImPPO-TFSI moieties. Note that this anion metathesis is accompanied by the release of an equal molecular quantity of

LiTFSI, which enables high $[\text{Li}^+]$ accessibility where polysulfides are generated, as desired for rapid conversion kinetics [60–62]. Deeper insights are dynamically gleaned from galvanostatic intermittent titration and electrochemical impedance spectroscopy (EIS) analysis. For a fair comparison, an asymmetric electrode made from PPO was also tested. We observed that, upon application of a current pulse (Fig. 4a), the voltage penalty for initiating polysulfide reduction was higher for the PPO than that for the ACImPPO electrode, and the overpotential (potential difference between the quasi-equilibrium status and the current step) was also lower for the ACImPPO cell. This clearly reveals that the presence of cationic networks could enable a lower kinetic conversion barrier and not just act as exclusive sites for S_n^{2-} trapping. Furthermore, ion-transfer kinetics were evaluated based on the Randles–Sevcik equation [11] at series CV scanning rates (Fig. 4b, Fig. S15-16). Apparently, the lithium ion diffusion coefficients in the ACImPPO electrode (i.e., $D_A=2.5\times10^{-7}$, $D_{CI}=9.2\times10^{-8}$ $\text{cm}^2 \text{ s}^{-1}$) were much higher than those in the PPO electrode ($D_A=1.42\times10^{-7}$, $D_{CI}=5.1\times10^{-8}$ $\text{cm}^2 \text{ s}^{-1}$) at the anodic and cathodic peaks (Fig. 4d). This behaviors also agree with Nyquist plots (Fig. 4c, Table S2, Fig. S17). In the Nyquist plots (Fig. 4c), the ACImPPO exhibits the lower and stable charge-transfer resistance (R_{ct}) before and after cycling ($\sim 30 \Omega$) compared with the PPO cathode. These results demonstrate that the presence of positive charges enabled the formation of free [LiTFSI] where Li_2S_n anions was absorbed, which, on the one hand, facilitate Li^+ migration at the reaction interface and, on the other hand, decreased the polysulfide concentration in the electrolyte, further promoting the movement of Li-ions between electrodes. As expected, this superior kinetics helps to realize the much higher rate performance compared with the PPO-based counterpart, with over 800 mAh g^{-1} at 1.5C and high sulfur loading of 5.3 mg cm^{-2} (Fig. 4b, Fig. S18).

Deposition morphologies of the sulfur electrode after cycling may further explain the difference. As recorded in Fig. 4e-f, we note that at both discharge and recharge state, a relatively smooth surface and porous structure is well retained for ACImPPO electrode after 100 cycles, on which the active sulfur species are more uniformly deposited (Fig. S19). This indicates the positive charge interface has a strong distribution capability for sulfur species. The detailed analysis of XPS, XRD and TEM for the cycled cell at recharged state were shown in Fig. S20. These results could further account for the faster kinetics of the ACImPPO cell due to the more contact area and charge transfer sites with polysulfides. As for the PPO electrode, instead of growing into a smooth morphology, ubiquitous spherical-shaped discharged particles were observed (Fig. 4g). This large discharge particles would not benefit the charge transfer due to limited contact interface between the Li_2S islands and the electrode matrix. This behavior may explain the generally inferior sulfur utilization in pristine carbon cathode without rational designed interface [25,63]. After recharge the porous channels were clogged by aggregated oxidized products (Fig. 4h), which also delays the oxidation process (larger overpotential in Fig. 4a). Based on the above observation, we suggest that the ACImPPO is efficient in supporting stable capacity retention by suppressing polysulfide shuttling, facilitating transfer kinetics and delaying the electrode passivation, as shown in Fig. 4i.

Fig. 5 (a) Galvanostatic charge/discharge profiles of the ACImPPO electrode with various ionic exchange capacity (IEC) values. (b) Overpotential and capacity retention vs. IEC values in the prepared cell after 200 cycles. (c) Cycling performance of the cathode with an IEC value of 3.68 mmol g⁻¹ under sulfur loadings of 5.3, 7.5, and 9.1 mg cm⁻², respectively. (d) Battery stability versus sulfur loading in this work and recent reports. (e) Areal capacity of ACImPPO cathode at 0.1 C (1.5 mA cm⁻²), the sulfur loading is 9.1 mg cm⁻².

Furthermore, taking advantage of the ease of chemical modification, we tuned the degree of bromination for PPO from 21.5% to 48.6% and 72.2%, with theoretical IEC values of 1.45, 2.51, and 3.68 mmol g⁻¹, respectively. In this way, we cycled the three different cells and noticed that the overpotential between the discharge/charge plateaus was lower at a higher IEC value (Fig. 5a). The oxidation of Li₂S_x also experienced enhanced conversion kinetics at a higher IEC, as traced in the voltage profile in the initial charge state (Fig. 5a, insert). Therefore, the increase of IEC from 1.45 to 3.68 mmol g⁻¹ contributed to a 25.1% decrease in overpotential (179 vs. 143 mV) and to a 33% increase in reversible capacity retention (Fig. 5b, Fig. S21). It is thus

suggested that, with the benefit from the enriched cationic charges at the reaction interface, more LiPS could be trapped and faster diffusion kinetics could be realized, thereby obtaining high performance and stability, even with high sulfur loadings of 7.5 and 9.1 mg cm⁻² (Fig. 5c-d, Fig. S22). The ACImPPO cathode retained an areal capacity of 6.5 mAh cm⁻² after 100 cycles, and 5.8 mAh cm⁻² after 200 cycles at 0.1 C with a high loading of 9.1 mg cm⁻², which is consistently superior to that of the state-of-the-art Li-ion battery (Fig. 5e). Therefore, the critical coupling of the asymmetric structure with the targeted chemistry modification offers advantages that have a promising application in Li-S batteries.

3. Conclusions

In summary, a new type of asymmetric Li-S cathode was demonstrated to enhance the battery performance for the first time. A built-in skin dense layer is efficient in blocking the polysulfide immigration while the porous submatrix provide open pathways for liquid electrolyte permeation and ionic transport in Li-S chemistry. Furthermore, we found that the implementation of cationic networks greatly enhances the S_n²⁻ absorption ability, facilitate redox conversion and regulate polysulfide deposition, which allows the capacity to remain high and stable throughout the cycling. Considering the dual advantages of the asymmetric structure and the versatility of interface modification, this work may advance its emerging research on other metal-sulfur or organic Na/K-ion batteries as well as in the field of membrane separation.

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Conflicts of interest

The authors declare no competing financial interests.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/xx.xxxx/j.ensm.2018.xx.xxx>.

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Supplementary Information

Asymmetric Cathode Membrane with Tunable Positive Charge Networks for Highly Stable Li-S Batteries

Experimental section

Materials. Poly (2,6-dimethyl-1,4-phenylene oxide) (PPO), N-Bromosuccinimide (NBS), 2,2'-azobis-isobutyronitrile (AIBN), 1,6-dibromohexane, 1-methylimidazole and sulfur and electrolyte solvents were purchased from Sigma-Aldrich. Lithium metal chip (0.45 mm thick) was received from MTI. AIBN was recrystallized from CHCl_3 before use. The 1,1'-(1,6-Hexanediyl) bisimidazole (HBIm) was synthesized according to the previous method [1]. All other reagents were obtained from Sigma-Aldrich and used as received.

Preparation of Cathode Membrane. Before preparation of the cathode, BPPO with different bromination degree (DB) was synthesized according to the previous report. BPPO was then dissolved in NMP (25 wt%) to form a stable polymer solution. Then sulfur impregnated CNT (CNT-S) composite were mixed into the BPPO solution to get homogeneous slurry, which was blade casted on clean glass plate followed by immersing in ultrapure water as coagulation bath. Once the phase inversion was completed, the freestanding composite membrane was peeled from the support and vacuum dried overnight. Following this, the electrode was treated with 1,1'-(1,6-Hexanediyl) bisimidazole to induce the crosslinking reaction, and then immersed in excess 1M LiTFSI aqueous solution for anion metathesis to obtain the electrode with cationic crosslinking networks. The other electrodes using different DB of BPPO as the polymeric precursor were also

fabricated through the similar process. Skin-layer removed cathode could be obtained by treating the prepared electrode with oxygen plasma (Femto plasma cleaner, 100W) for 15 min.

Benzylic Bromination of PPO (BPPO). The synthesis of BPPO as follows: To a solution of 6 g PPO (100 mmol) in chlorobenzene (50 mL) solution was added 4 g NBS and 0.21 g 2,2'-azobisisobutyronitrile (AIBN). The reaction was carried out at 135 °C for 4 h. Upon cooling to room temperature, the solution was poured into ethanol to precipitate the product. The resultant polymer was then filtrated, washed with methanol several times, and vacuum drying overnight to get the light yellow BPPO powder (yield: ~93%). The degree of bromination (DB) is 21%. The DB is defined as the ratio of the brominated methyl groups (CH_2Br) to the methyl groups on average, which could be calculated based on ^1H NMR. All of the other BPPO polymer with different DB could be facilely obtain by using different amount of NBS according to the above procedure.

Materials characterization: was performed by SEM (FESEM, Nova Nano), Brunauer-Emmett-Teller (BET) (ASAP-2420), ^1H NMR spectra (Avancell 500 MHz, Bruker), FTIR (is10), contact angles (KRUSG GmbH), thermo-gravimetric analysis (TGA, SDT Q600) and UV-vis (thermos evolution 600). The mechanical properties of the membranes were tested on DMA 800. Electrolyte uptake and swelling ratio of the polymer membrane were evaluated as followed: the dried membranes with recorded length (L_{dry}) and weight (W_{dry}) from different type of polymers were immersed in the electrolyte for 24 hours. Afterwards, the excess electrolyte on the surface was wiped away with tissue paper. The length and mass of the wetted membrane were measured (L_{wet}) and W_{wet}). Electrolyte uptake= $(W_{wet}-W_{dry})\times 100/ W_{dry}$. The swelling ratio= $(L_{wet}-L_{dry}) \times 100/ L_{dry}$. The ionic exchange capacity (IEC) of the imidazolium functionalized PPO (ImPPO) was measured using the typical Mohr method [2]. First, the ImPPO with recorded weight was

immersed and stirred in a 0.5 M NaNO₃ aqueous solution for 24 hours. The solution was then titrated with 0.05 M standard AgNO₃ aqueous solution with K₂CrO₃ as indicator. The IEC was

$$\text{calculated as follows: } IEC(\text{mmol/g}) = \frac{V_{\text{Ag}^+}(\text{ml}) \times 0.05 \text{ mol/l}}{W(\text{g})}$$

V_{Ag^+} is the volume of AgNO₃ solution consumed in the titration process, and W is the weight of the sample.

Polysulfide preparation and absorption test: Li₂S₆ solution was prepared by dissolving stoichiometric amounts of elemental sulfur and Li₂S (molar ratio, 1:5) in DOL:DME (1:1, v/v). After stirring at 70 °C for 24 h, a homogeneous dark-red Li₂S₆ solution was formed. The above solution was then diluted to 0.05 M for absorption experiment. The imidazolium functionalized PPO with different IEC was immersed in the above polysulfide solution for 24 h, the upper dispersion was collected and diluted to 10 times for UV-vis measurement in sealed cuvette.

Shuttle current was measured according to the previous method [3]. Specifically, the cells were firstly cycled three times at 0.1 C rate. Then, the cells were charged to 2.7 V and rested in an open-circuit state for 30 min. Subsequently, the cell voltage was maintained at the open-circuit voltage, and the current applied to the cell was recorded for at least 2 h during which a steady-state value was reached. This steady-state current was recorded as the shuttle current.

The binding energy between the typical polysulfide of Li₂S₆ and Li₂S₄ or LiTFSI and the monomer of ImPPO-TFSI was calculated by employing the B3LYP level [4, 5] of hybrid DFT functional with 6-31g(d) basis set [6]. The Grimme's D3 correction was employed to describe the vdW interactions between different particles [7]. The terminal atoms are saturated by hydrogen. The binding energy, E_b , was calculated through $E_b = E_{\text{tot}} - E_1 - E_2$.

Electrochemical measurement: The prepared ACImPPO membrane was used as cathode with skin blocking layer facing polypropylene separator with lithium chip used as counter electrodes, which was assembled with CR2032 cells in glove box. The electrolyte is 1 M LiTFSI in 1,2-dimethoxyethane (DME) and 1, 3-dioxolane (DOL) (1:1, v/v) with 0.4 M LiNO₃. To prepared high loading cathode, polysulfide modified electrolyte was prepared and injected into the cathode matrix. The catholyte could be prepared by adding 8.613 g LiTFSI and 0.827 g LiNO₃ into the prepared fresh Li₂S₆ (0.5M) solution (30 mL) and stirred overnight. The cell performance were tested on Neware test system and potentiostat BioLogic VMP3a CHI 660D electrochemical workstation. The lithium ion diffusion (D_{Li}) is evaluated based on the classical Randles Sevcik equation:

$$I_p = (2.69 \times 10^5) n^{1.5} A D_{Li}^{0.5} C_{Li} v^{0.5}$$

Where I_p is the peak current, n is the charge transfer number, A is the electrode area, D_{Li} refers to the lithium ion diffusion coefficient, C_{Li} is the Li⁺ concentration change, and V is the scan rate. The peak currents are linear fitted with the $V^{1/2}$. Combining the linear relationship of I_p and $V^{1/2}$ and the above Equation, the D_{Li} could be estimated and show in Fig. 4d.

Fig. S1. Schematic representation of ternary phase diagram for asymmetry porous membranes [8] (left) and the solvent/non-solvent exchange through the surface (right).

Fig. S2. CV curves of ImPPO/CNT (1:1, w/w) at a scan rate of 0.1 mV s^{-1} . The CV scans shows that the imidazolium tethered PPO is electrochemically stable in the voltage range of 1.5–3.0V (vs Li^+/Li).

Fig. S3. ^1H NMR spectra of the PPO and BPPO in CDCl_3 . The peak 3 and peak 2 at around 4.3 ppm and 2.1 ppm corresponds to CH_2Br group and methyl group, respectively. The average degree of bromination could be determined by comparing the integral of CH_2Br groups and the remaining methyl groups.

Table S1 Degree of bromination and corresponding IEC values of the functionalized polymers.

Sample	Degree of bromination (DB)	IEC (titration, mmol/g)
PPO	0	0
BPPO-1	0.21	1.45
BPPO-2	0.48	2.51
BPPO-3	0.72	3.68

Fig. S4. ^1H NMR spectra of the 1,1'-(1,6-Hexanediyl) bisimidazole in $d\text{-DMSO}$.^[1]

Fig. S5. The nucleophilic reaction mechanism of the BPPO with 1,1'-(1,6-Hexanediyl) bisimidazole. Here, 1,1'-(1,6-hexanediyl)bisimidazole is nucleophile (donor of an electron pair) because the nitrogen atom has unshared pairs of electrons. The carbon atom of CH_2Br is electrophilic because it is bonded to an electronegative Br atom. Electron density is drawn away from carbon by the halogen atom, giving the carbon atom a partial positive charge. The imidazole with the electron pair attacks the back side of the electrophilic carbon atom, donating a pair of electrons to form a new bond and the resulting imidazolium cations.

Fig. S6. N_2 adsorption–desorption isotherm of the cathode prepared by the NIPS method (black) and routine blade casting method.

Fig. S7. UV-vis spectra analysis of LiPS trap ability of the cationic ImPPO with various IEC values (1.45, 2.51 and 3.68 meq g⁻¹, respectively).

Fig. S8. Digital images of the Li₂S₆ trapping by the ACImPPO cathode in DOL/DME (1:1, v/v) solution after 24 h.

Fig. S9. TGA curve of the composite cathode. Based on the TGA curve, the sulfur and ImPPO fraction is determined to be about 40.6% and 30.2%, respectively. By introducing the Li_2S_6 catholyte, the sulfur loading in the Li-S cell could be controlled at around 5.3, 7.5 and 9.1 mg cm^{-2} , respectively.

Fig. S10. SEM images of the electrode membrane top surface after plasma treatment.

Fig. S11. (a) Illustration of Li-S batteries with routine cathode (left) and asymmetric cathode (right). (b-e) Photographs of the separators and Li metal anodes after 100 cycles in cells with no-asymmetric cathode (b, c) and with an asymmetric cathode (d, e).

Fig. S12. (a) SEM images of the surface of fresh Li anode, (b) Li anode paired with asymmetric cathode, and (c) Li anode paired with the skin layer-removed cathode after 100 cycles.

Fig. S13. (a) Cyclic performance of the electrode without asymmetric structure at 0.2C for 200 cycles. The specific capacity of the non-asymmetric cathode decreases rapidly because the flooded catholyte could easily diffuse from the cathode side to lithium anode without the protective skin layer. This further results in serious loss of irreversible sulfur species and low columbic efficiency compared with the ACImPPO cathode in Fig. S11 (b).

Fig. S14. Open-circuit voltage profiles of the cells with the asymmetric ACImPPO cathode and non-asymmetric cathode.

Fig. S15. CV profiles of the PPO-based cathode at various scanning rates.

Fig. S16. Linear fits of the peak current of the cathode with ImPPO and PPO for different peaks.

(a) anodic oxidation peak, (b) cathode reduction peaks at around 2.01 V and (c) at 2.32 V.

Fig. S17. Discharge/charge curve of a Li-S battery (a), with each point representing an EIS measurement in (b) and (c).

Fig. S (a-c) show the first discharge and charge curves of the Li-S battery and the points at which EIS spectra were recorded. As the cell was discharge to point A (2.38 V), a depressed semicircle appeared in the middle frequency region, indicating “lithiation” of solid sulfur into soluble long-chain lithium polysulfides⁹. Meanwhile the ohmic resistance (inset of Fig. S b) increased slightly also indicating the increased electrolyte resistance from the soluble polysulfdes. As the cell was discharged to point B (2.28 V), the semicircle in the middle frequency region enlarged due to the increased soluble polysulfdes at this stage. When discharging continuously to point C (2.03 V), the ohmic resistance further increased, and the semicircle in the middle

frequency is maximum. This conforms that the amount of soluble lithium polysulfides should reach a maximum at the end of the first plateau. At point D and E, the semicircle in middle frequency disappeared, and ohmic resistance decreased slightly, this suggests that the soluble long-chain polysulfide was further lithiated into short-chain and insoluble polysulfides ($\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$). During the charge step, an overall decrease in the absolute values of the resistance elements is observed. The maximum value of electrolyte ohmic resistances occur at point G, where the concentration of polysulfides in the electrolyte is maximum, indicating the $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ has been delithiated to high order polysulfides, which were finally converted into sulfur at point I.

Table S2. Nyquist plots fitting results of the batteries with different cathode in Fig. 4c.

Cathode	R_0 / Ω	R_{ct} / Ω	R_{int} / Ω
ACImPPO fresh cell	3.1	34.2	18.6
PPO fresh cell	3.6	55.2	32.8
ACImPPO 50 cycles	3.9	27.6	10.9
PPO 50 cycles	3.8	81.5	30.4

Fig. S18. Rate performance of the cell with ACImPPO cathode.

Fig. S19. SEM images of the ACImPPO cathode after 100 cycles at discharge state. (a–d) cross-section of the electrode membrane and the EDS mappings. (e–f) surface and cross-section morphology of the electrode.

Fig. S20. Characterization of the cell at charged state. (a) XPS S 2p spectra of the cycled electrode. (b) XRD of the electrode, the ImPPO and sulfur. (c) TEM images of the electrode at cycled state.

As shown below, the XPS S 2p spectra exhibit three main twin-peaks. The peak at 163.9 and 165.1 eV is related to the $2p_{1/2}$ and $2p_{3/2}$ of bridging elemental sulfur (S-S), and the peaks at around 162.1 eV could be assigned to the terminal sulfur species². Meanwhile, the main peaks at 169.8 and 168.6 eV are attributed to the sulfur signal in TFSI⁻ anion. This indicates that in charge state, the short-chain polysulfide species were converted into elemental sulfur, and the TFSI⁻ was tethered with the cationic networks. In the XRD patterns, only one broad peak was observed for the cationic ImPPO networks, revealing amorphous morphology of ImPPO. For the cycled

electrode, the main broad peak from the ImPPO networks was also observed, meanwhile the sulfur signals also appeared, indicating the polysulfide was delithiated into elemental sulfur at the charged state. TEM measurement was also conducted at charging state. It could be observed that there are element sulfur nanoparticles, which are surrounded by the conductive CNT and the cationic ImPPO, suggesting the positive charge interface induced deposition of oxidized sulfur at the conductive electrode.

Fig. S21. Cycling performance the ACImPPO cathode functionalized with different IEC (i.e., 3.68, 2.51, and 1.45 mmol g⁻¹) with sulfur loading of 4.5 mg cm⁻².

Fig. S22. Discharge/charge profiles of the cells employing the ACImPPO cathodes with high sulfur loading at 0.1 C.

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Asymmetric Cathode Membrane with Tunable Positive Charge Networks for Highly Stable Li-S
Batteries Energy Storage Materials

Conflict of Interest

The authors declare no competing financial interests.