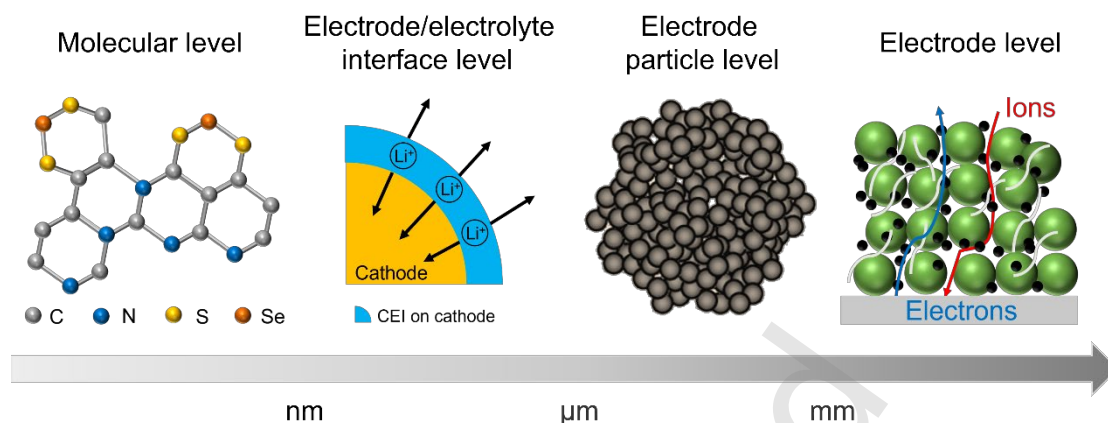


Graphical Abstract



A multiscale design of the pPAN/SeS₂ cathode is proposed to selenide at the molecular level to improve the kinetic performance. Fabrication of robust and stable CEIs to inhibit polysulfide shuttling and to probe the mechanism of action of polysulfide formation in ether electrolytes. Mesoscopic to microscopic conducting frameworks for continuous electron/ion conduction. As-fabricated Li–S full cell shows a superior cyclic stability even under high cathode mass loading of $\sim 7 \text{ mg cm}^{-2}$, low electrolyte/sulfur ratio of $\sim 2.9 \text{ }\mu\text{L mg}^{-1}$, and limited N/P ratio of 1.5.

Research Article

Multiscale design of organosulfur cathode with superior cycling stability in ether electrolytes under practical conditions by selenium co-doping

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Abstract

The sulfurized polyacrylonitrile (SPAN), featuring the sulfur atoms covalently anchored with the polyacrylonitrile, gives a chance to avoid the dissolution↔precipitation mechanism of the lithium polysulfides (LiPS) in traditional Li-S batteries. However, such a solid-solid conversion in SPAN cathodes is an electrolyte-dependent behavior, and current studies lack a detailed description of the dissolution mechanism of the covalently-bonded sulfur, which is important for understanding the sulfur reduction reaction (SRR) pathway in SPAN cathodes. In this work, interestingly, we discovered that the LiPS still dissolves from the SPAN matrix in the ether-based electrolytes, which may promote the SRR kinetics. It also

demonstrates that the sulfur-PAN bonds in the cathode-electrolyte interfaces are vulnerable to be attacked by the ether molecules. A selenization strategy was therefore introduced to further reinforce the bonding between the sulfur atoms and the SPAN matrix. Impressively, the as-designed cathode realizes rapid and stable lithium storage with 77% of capacity retention over 200 cycles under high mass loading of $\sim 7 \text{ mg cm}^{-2}$, low electrolyte/sulfur ratio of $\sim 2.9 \text{ } \mu\text{L mg}^{-1}$, and limited N/P ratio of 1.5. It is believed that the multiscale design strategy could pave a new avenue for fabricating stable organosulfur cathodes for next-generation energy storage.

Keywords: Li–S battery; Sulfurized polyacrylonitrile; Cathode electrolyte interface; High loading; Lean electrolyte

1.Introduction

Lithium-ion batteries (LIBs) have been dominating the global electrochemical energy storage market due to their advantages of high energy/power densities, lightweight, and environmental benignity [1-3]. However, the specific energy of the traditional LIBs based on the intercalation chemistries *e.g.* lithium transition metal oxides cathodes and graphite anodes are still hampered by their limited theoretical capacities, which could not fulfill the ever-growing demands for higher energy densities [4-6]. To break this limitation, the research community is pursuing alternative battery technologies with enhanced energy density. Among them, lithium-sulfur (Li–S) batteries featuring a 16-electron conversion chemistry of sulfur ($\text{S}_8 + 16\text{Li}^+ + 16\text{e}^- \leftrightarrow 8\text{Li}_2\text{S}$) have garnered extensive research attentions because of its ultrahigh theoretical specific capacity ($\sim 1675 \text{ mAh g}^{-1}$) and low raw material cost [7-9].

However, the sulfur chemistry still faces several challenges, especially from the full-cell viewpoint. The electronic/ionic insulating nature of the S_8 and Li_2S results in sluggish reaction kinetics during the sulfur reduction reaction (SRR) [10]. The SRR involves a complex reaction pathway with multiple intermediates — lithium polysulfides (LiPSs), which are soluble in organic electrolytes when e^- and Li^+ meet

together at the nanoscale junctions between S₈, carbon black and electrolytes. LiPSs act as redox mediators (RMs) to facilitate the kinetics, which is desired for a high sulfur utilization, but physically cross over the separator “poisoning” the reactive Li metal anode (LMA), so called the “shuttling effect”. Since Jiulin Wang [11] proposed an organosulfur cathode with S atoms covalent-bonded with polyacrylonitrile (PAN) in 2002, SPAN (sulfurized polyacrylonitrile) [12, 13] has attracted much attention as a new way to solve the shuttling effect in traditional nonbonded S₈ cathodes because the SRR can experience a “solid-solid” reaction (SSR) to avoid the generation of soluble RMs. While such SSR is often achieved in the carbonate-based electrolytes [14, 15], one may wonder if cathode-electrolyte interfaces (CEIs) are generated to seal the SPAN SSR “nanoreactors” because the carbonyl groups (–C=O) in the carbonate-based electrolytes, basically, can nucleophilic attack the LiPSs even when they meet together in the local CEI area. In other words, the SRR in SPAN cathodes should be an electrolyte-dependent reaction and the detailed mechanism of the LiPSs formation is essential to be validated. However, current studies lack a detailed description of such electrolyte-dependent mechanism along the SRR process, which is important for understanding the detailed reaction pathways in SPAN cathodes and thus helping pave the way for further improvement.

From a viewpoint of full cell, especially when considering the energy density at a cell level [16, 17], extremely limited electrolyte and LMA should be guaranteed, yet called “practical conditions”, to achieve a high cell-level specific energy. The cell failure mechanism should also be evaluated under such conditions, *e.g.* controlled electrolyte to active material mass ratio (E/A) and negative to positive areal capacity ratio (N/P). In this scenario, the key is to construct stable electrolyte-LMA interfaces and to minimize the side reactions in a long-term manner (long time and large space). The ether-based electrolytes, featuring the *intrinsic* strong resistance against reduction of ether groups (–C–O–C–), enable stable electrolyte-LMA interfaces and high LMA reversibility [18]. Furthermore, they also show good chemical stability with the vulnerable LiPSs. Therefore, it is highly desirable to determine the detailed mechanism of the SRR process in the ether-based electrolytes and to construct a proper cathode

design to tailor LiPSs formation process.

To explore the LiPSs formation mechanism in the SPAN cathode, we propose the ether-based electrolytes, which are more stable with the LiPSs than the traditional carbonate-based electrolytes. In the SPAN cathode side, we also propose a multiscale design to tailor the electronic conductivity and the covalent bonds to tailor the LiPSs formation process in the ether-based electrolytes, which especially helps boost rapid and stable lithium storage under practical conditions. As shown in Fig. 1, the carbon framework of SPAN was first selenized at the molecular level to facilitate rapid Li^+ /electron conduction. Secondly, a uniform cathode electrolyte interphase (CEI) at the nanoscale is achieved by introducing LiNO_3 as a functional electrolyte additive. Thirdly, meso-to-macroscopic conductive frameworks are constructed to provide contiguous electronic/ionic pathways. Consequently, under practical conditions of high cathode mass loading ($\sim 7 \text{ mg cm}^{-2}$), lean electrolyte (E/S ratio of $\sim 2.9 \mu\text{L mg}^{-1}$), and limited lithium source (N/P=1.5), the as-designed polyacrylonitrile/selenium disulfide (pPAN/SeS₂) cathode enables Li-S cell to show improved cycling stability with 77% capacity retained over 200 cycles. The multiscale design strategy could offer a new avenue for fabricating stable organosulfur cathodes for next-generation energy storage.

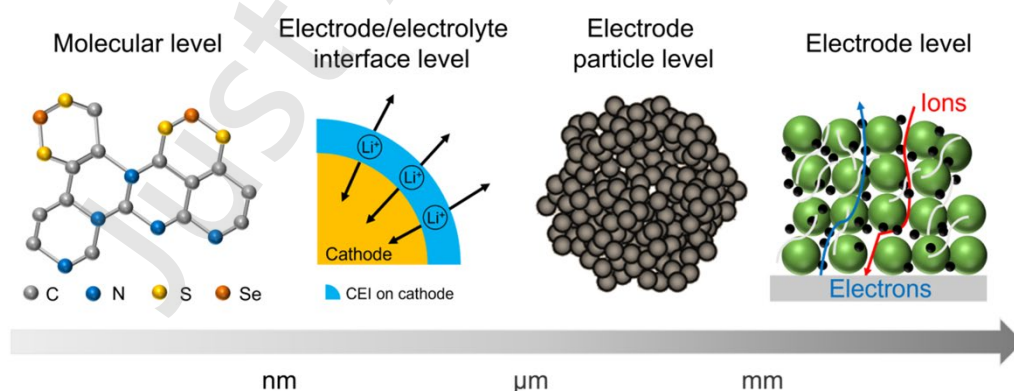


Fig. 1. Schematic illustration of the multiscale design of organosulfur cathodes.

2. Experimental section

2.1. Materials

PAN, sulfur, and SeS₂ powders were purchased from Sigma-Aldrich. Lithium

bis(trifluoromethane sulfonyl)imide (LiTFSI), anhydrous lithium nitrate (LiNO_3 , 99.9%, Alfa Aesar), 1,3 dioxolane (DOL), and 1,2-dimethoxyethane (DME) were purchased from TCI. Lithium foil (Li), aluminum foil (Al), copper foil (Cu), separator (Celgard 2400), carboxymethyl cellulose (CMC), styrene-butadiene rubber (SBR), and carbon black SUPER C45 were purchased from Hefei Kejing Material Technology Co., Ltd. All chemicals were used without purification.

2.2. Preparation of electrodes

PAN and SeS_2 powders (1:4 w/w) were sealed in glass containers and incubated at 380°C for 8 h under an argon atmosphere. As-obtained products were then placed in a porcelain boat, kept at 350°C under flowing nitrogen for 6 h to remove excess sulfur and selenium, and then naturally cooled to obtain pPAN/S and pPAN/ SeS_2 samples. The pPAN/S and pPAN/ SeS_2 cathode with a mass loading of 2 mg cm^{-2} or 7 mg cm^{-2} was prepared by slurry coating on Al foils. The mass ratio of active material, conductive agent, CMC, and SBR was controlled to be 80:10:5:5 or 75:15:5:5. After drying in a vacuum oven at 60°C for 24 h and calendaring for 3 times, the cathode films were punched into 12 mm discs for coin cell assembly.

2.3. Characterizations

X-ray diffraction (XRD) patterns were obtained from a SmartLab (9 kW) with a Cu $\text{K}\alpha$ source. X-ray photoelectron spectroscopy (XPS) tests were performed on ESCALAB 250. For the ex-situ XPS tests, the electrode films were obtained by disassembling the battery cells after charge-discharge cycles, washed by the DME solvent, and then fully dried before testing. Scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX) measurements were performed on a field emission SEM (Hitachi SU8000 FE-SEM). The conductivity of thick pPAN/ SeS_2 cathode film was measured by a four-probe method using an RTS9. The cathode and separator were cleaned by taking 200 μL of the corresponding ether-based or carbonate-based electrolyte to test ultraviolet–visible spectroscopy (UV-Vis). The mixture of Li_2S and S_8 with a molar ratio of 8:5 was added into the ether-based electrolyte to prepare Li_2S_6 solution. For the UV–vis tests, the solutions of 10 mM, 5 mM and 1 mM Li_2S_6

with 1.0 M LiTFSI-4wt% LiNO₃ in DOL/DME mixed solvent were prepared.

2.4. Electrochemical measurements

Electrochemical measurements were performed by assembling CR2032 coin cells in an argon-filled glove box with both O₂ and H₂O content below 0.1 ppm. Celgard 2400 was used as the separator. Galvanostatic charge-discharge tests were performed on a LAND battery tester (Land CT2001A) in the voltage range of 1-3 V. The full cell tests were performed by using thin pPAN/SeS₂ cathodes and thin Li metal anodes. The Li anode was prepared by depositing Li metal on bare or modified copper current collectors at a certain capacity. The impedance spectroscopy (EIS) of the cells was performed on a PMC1000A electrochemical workstation with a frequency range of 100 mHz to 100 kHz and an AC oscillation amplitude of 5 mV. To investigate the Li⁺ diffusion of cathode, Galvanostatic Intermittent Titration Technique (GITT) curves were obtained via the method that the activated cells were repeatedly tested in the current density of 0.1 A g⁻¹ for 30 min, followed by an open-circuit stand for 30 min.

3. Results and discussion

3.1. Microstructure characterizations of pPAN/SeS₂

The phase composition and chemical information of pPAN/SeS₂ were characterized by XRD and XPS. As shown in Fig. 2a, SeS₂ exhibits good crystallinity with strong characteristic diffraction peaks. The XRD pattern of PAN displays a characteristic diffraction peak at 17° attributing to its (110) crystal plane. After polymerization, the above-mentioned diffraction peaks disappear and a broad peak at around 25° appears in the XRD pattern of pPAN/SeS₂, which should be ascribed to its amorphous carbon framework. The reason for the disappearance of the crystalline peak of SeS₂ may be the formation of chemical bonds with the amorphous PAN. XPS tests were further performed to investigate the chemical bonding in the pristine pPAN/SeS₂ sample and the pPAN/SeS₂ cathode after repeated charge-discharge cycles. In the pristine pPAN/SeS₂ sample, the deconvolution spectra of S 2p/Se 3p exhibit robust interaction between Se and S with S–Se bonding at 162.6 eV and Se–Se bonding at

163.9 eV (Fig. 2b). The C 1s spectrum can be deconvoluted by three peaks that correspond to C–C (284.8 eV), C=C/C–N (286.2 eV), and C–S/C–Se (288.7 eV) bonds (Fig. S1a), indicating the strong chemical bonding between C and S/Se [19]. The N 1s spectrum also confirms the C–N bonding in the carbon framework (Fig. S1b). The Se 3d spectrum exhibits characteristic Se-containing chemical environments, suggesting the coexistence of Se–S (54.4 eV) and Se–Se (56.3 eV) bonds (Fig. S2). These results indicate that Se is involved in the sulfurized PAN framework and participates in the formation of a Se-containing chalcogen network.

The morphology of pPAN/SeS₂ was revealed by SEM observations (Fig. 2c). It can be seen that pPAN/SeS₂ consists of particles with sizes in hundreds of nanometers, which agglomerate into micron-sized particles. In the EDS elemental mapping image, the carbon signal overlaps well with that of sulfur and selenium, indicating that Se and S are homogeneously distributed in the carbon matrix (Fig. 2d). The content of each element in pPAN/SeS₂ was quantitatively analyzed by elemental analysis. As summarized in Table S1, the as-prepared pPAN/SeS₂ contains 32.4 wt% C, 17.3 wt% N, 18.6 wt% S, and 31.7 wt% Se, and the active material content of pPAN/SeS₂ was determined to be 50.3 wt%.

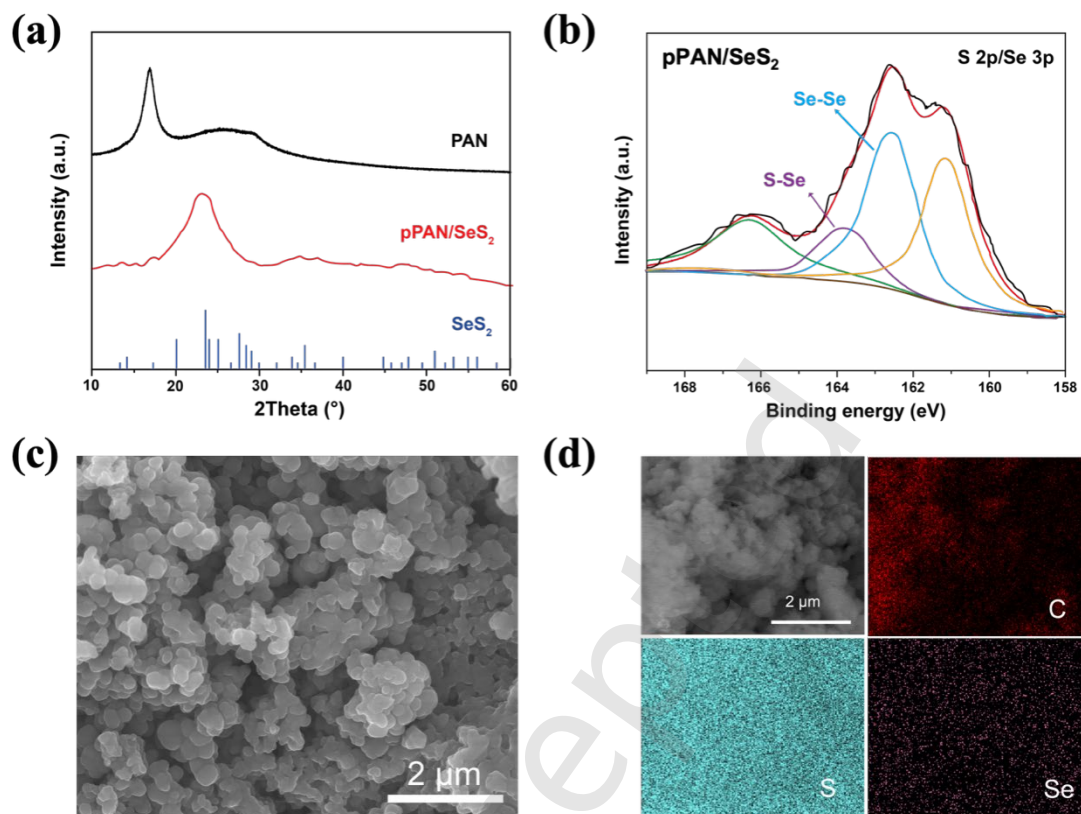


Fig. 2. (a) XRD patterns of PAN, SeS₂, and pPAN/SeS₂. (b) XPS spectrum of S 2p/Se 3p for the pristine pPAN/SeS₂. (c) SEM image of pPAN/SeS₂. (d) The EDS mappings of pPAN/SeS₂.

3.2. Enhanced lithium storage property by selenization

Selenization is beneficial to improve the lithium storage performance of the sulfurized polyacrylonitrile cathode. As shown in Fig. 3a, the pPAN/S and pPAN/SeS₂ cathodes deliver reversible specific capacities of 1162 and 1114 mAh g⁻¹ at a current density of 0.2 A g⁻¹, respectively. Although pPAN/S delivers a slightly higher gravimetric capacity at low current densities because of the higher theoretical specific capacity of sulfur, the pPAN/SeS₂ cathode exhibits superior capacity retention at elevated current densities and markedly improved cycling stability. As the current density increases, the specific capacity of the pPAN/S cathode decays rapidly. At the same time, it can be seen from the charge-discharge curves in Fig. S3 that the voltage polarization of the pPAN/S cathode increases significantly with the increase of the current density. In contrast, the specific discharge capacity of the pPAN/SeS₂ cathode shows a minor decrease with increasing current density. As the current density gradually increases to 2 A g⁻¹, the

contour of the charge-discharge curves and the corresponding voltage plateau do not change significantly, indicating its excellent rate capability (Fig. 3b). When it returns to 0.2 A g^{-1} , the specific capacity can be well recovered to the initial value (1108 mAh g^{-1}), demonstrating the excellent lithium storage reversibility.

To explore the rooting reason of improved rate performance by selenization, EIS were performed. Fig. 3c shows the Nyquist curves and simulated equivalent circuit diagrams of the pPAN/S and pPAN/SeS₂ cathodes. The Nyquist curve consists of a semicircle in the high-frequency region and an oblique line in the low-frequency region, which correspond to the charge transfer process and Li⁺ diffusion process in the electrode, respectively. The impedance values are summarized in Table S2. The ohmic impedances (R_{ohm}) of the pPAN/S and pPAN/SeS₂ cathodes do not show a big difference. However, the charge transfer resistance (R_{ct}) of pPAN/SeS₂ ($81.2 \text{ } \Omega$) is significantly lower than that of pPAN/S ($146 \text{ } \Omega$), indicating the enormously enhanced electrochemical reaction kinetics of the sulfurized polyacrylonitrile cathode after selenization.

Fig. 3d shows the cyclability of the pPAN/S and pPAN/SeS₂ cathodes. pPAN/SeS₂ delivers an initial specific discharge capacity of 1378 mAh g^{-1} , which rapidly decreases to 1126 mAh g^{-1} in the second cycle. Such initial capacity decay should be assigned to the irreversible reduction of short conjugated carbon bonds in the small pPAN/SeS₂ fragments and the formation of initial CEI [20]. The pPAN/S cathode delivers slightly higher initial and second discharge capacities of 1500 and 1170 mAh g^{-1} , respectively. However, it shows fast capacity decline after 80 cycles and maintains only 69% of its initial capacity after 150 cycles. In addition, severe polarization can be observed in the pPAN/S cathode after prolonged cycling. The distinct comparison further confirms the benefit of selenization toward more rapid and stable lithium storage. To demonstrate the advantage the reaction kinetics by Se substitution, galvanostatic intermittent titration technique (GITT) measurements were conducted on the Li||pPAN/SeS₂ and Li||pPAN/S cells during the first initial cycle. It is apparent that the overpotentials of the Li||pPAN/S cell (Fig. S4a) during charging and discharging are higher than that of the cell after Se substitution (Fig. S4b), which agrees well with our expectation. The

Li^+ diffusion coefficients over different voltages are also elucidated from the GITT results (Fig. S5). The diffusion coefficient of the pPAN/SeS₂ cathode ($2.09 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$) is significantly higher than that of the pPAN/S cathode ($1.82 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$) during the delithiation process, indicating that Se doping promotes the kinetics of the sulfur reduction reaction. Moreover, to probe the catalytic effect, CV was tested and Tafel slopes were calculated from the CV results. Fig. S6 illustrates the CV curve for a sweep rate of 0.1 mV s^{-1} within a 1–3 V voltage window. There is an anodic peak at around 2.2 V and a cathodic peak at 1.7–2.1 V. To precisely analyze the nucleation and dissociation reactions of Li₂S, Tafel curves of the corresponding redox peaks were plotted. (Fig. S7). For reduction peak corresponding to Li₂S nucleation, the fitted Tafel slopes for pPAN/SeS₂ (436 mV dec^{-1}) and pPAN/S (519 mV dec^{-1}). For the oxidation peak corresponding to Li₂S dissociation, the Tafel slopes are 169 mV dec^{-1} (pPAN/SeS₂) and 213 mV dec^{-1} (pPAN/S). The decrease in Tafel slopes for the pPAN/SeS₂ cathode indicates that Se doping has catalytic effect on the electrochemical process. Overall, Se doping plays a catalytic role and improves the sulfur reduction reaction kinetics.

In order to explore the LiPSs dissolution, UV-vis was performed on both the Li||pPAN/S and the Li||pPAN/SeS₂ cells after 60 cycles in the ether-based electrolyte (Fig. S8). In the ether electrolyte, both cells had trace amounts of LiPSs dissolved in the electrolyte, which is reflected by the characteristic peaks of S_4^{2-} and S_6^{2-} at concentrations below 5 mmol L^{-1} calibrated by the standard samples at 1, 5, 10 mM LiPSs concentrations (Fig. S8). The concentration of S_6^{2-} for the Li||pPAN/SeS₂ cell was lower than that for the Li||pPAN/S cell, demonstrating that the Se substitution could suppress the LiPSs shuttling. As expected, there was hardly LiPSs observed from the Li||pPAN/SeS₂ cell after cycling in the carbonate-based electrolyte (Fig. S9).

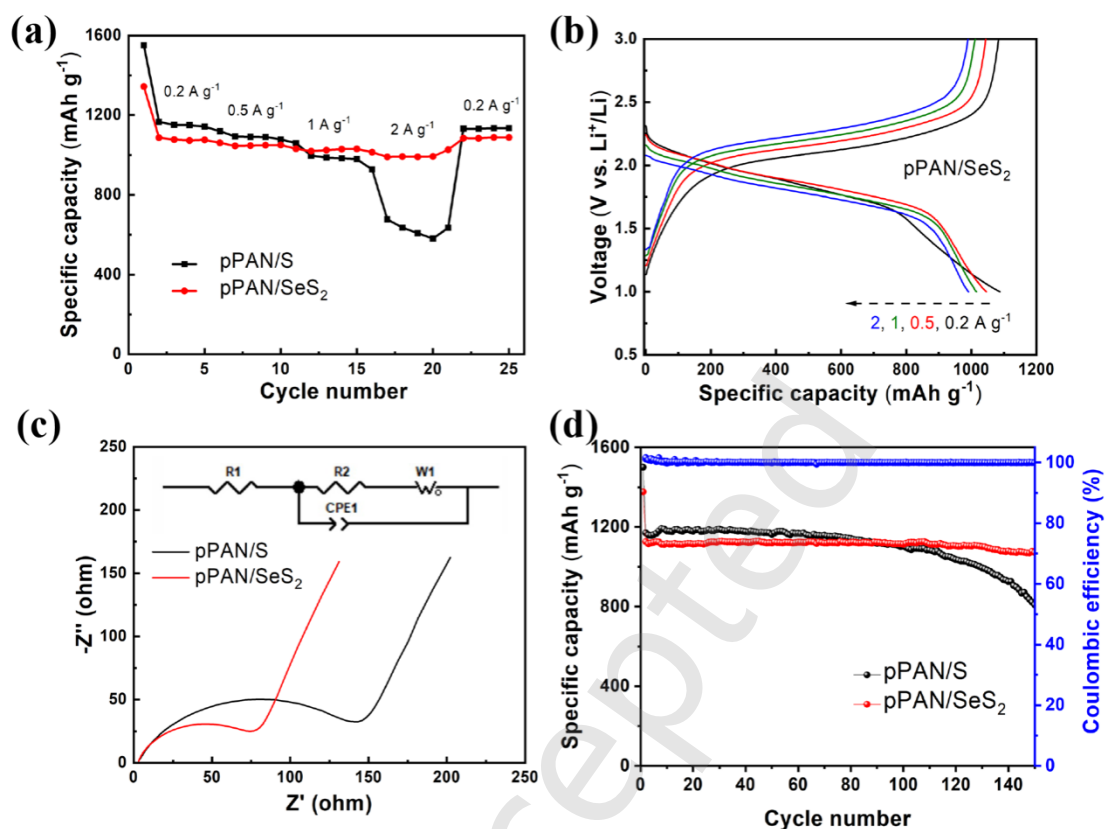


Fig. 3. (a) Rate performances of pPAN/S and pPAN/SeS₂ cathodes. (b) Charge-discharge curves of the pPAN/SeS₂ cathode at different cycles. (c) Nyquist plots of pPAN/S and pPAN/SeS₂ cathodes. The inset shows the corresponding equivalent circuit diagram. (d) Cyclic performances of pPAN/S and pPAN/SeS₂ cathodes at a current density of 0.2 A g⁻¹.

3.3. Tailored CEI for stable lithium storage

LiNO₃ has been widely reported to improve the cycle performance of lithium-sulfur batteries [21, 22]. Here we gradually increase the amount of LiNO₃ added in the ether electrolyte 1 M LiTFSI DOL/DME until near saturation (4 wt%). As shown in Fig. 4a, when using a LiNO₃-free electrolyte, the specific capacity of pPAN/SeS₂ decreases rapidly, with only 35% capacity retained over 120 cycles and low coulombic efficiencies of ~98%. Meanwhile, the voltage polarization became more pronounced over prolonged cycling (Fig. S10a). After 10 cycles, yellow substances appeared on the separator in the disassembled cell, which suggests the dissolution of Li₂Se_xS_y species in the ether electrolyte (Fig. S10b). It is worthy to note that unlike our pPAN/SeS₂

compound where the sulfur molecules are covalence-bonded with the PAN and Se, the classic carbon/sulfur cathodes could not be charged in the LiNO_3 -free electrolyte due to severe shuttling effect by LiPSs. In other words, our multiscale design can obviously suppress the LiPS shuttling effect. In stark contrast, those electrolytes with 1 wt% and 2 wt% LiNO_3 addition demonstrate much slower capacity decay with $\sim 90\%$ capacity retention after 120 cycles. And that with 4 wt% LiNO_3 addition shows further boosted reversibility with almost no capacity decay over 120 cycles and high coulombic efficiencies of nearly 100%. Meanwhile, the charge-discharge curves overlap very well over cycling (Fig. S11a) and no yellow substances can be detected on the separator (Fig. S11b), indicating effectively inhibited shuttling of $\text{Li}_2\text{Se}_x\text{S}_y$. After prolonged 300 cycles, it remains 87.2% of the initial specific capacity, corresponding to a quite low-capacity decay rate of 0.04% per cycle (Fig. S12).

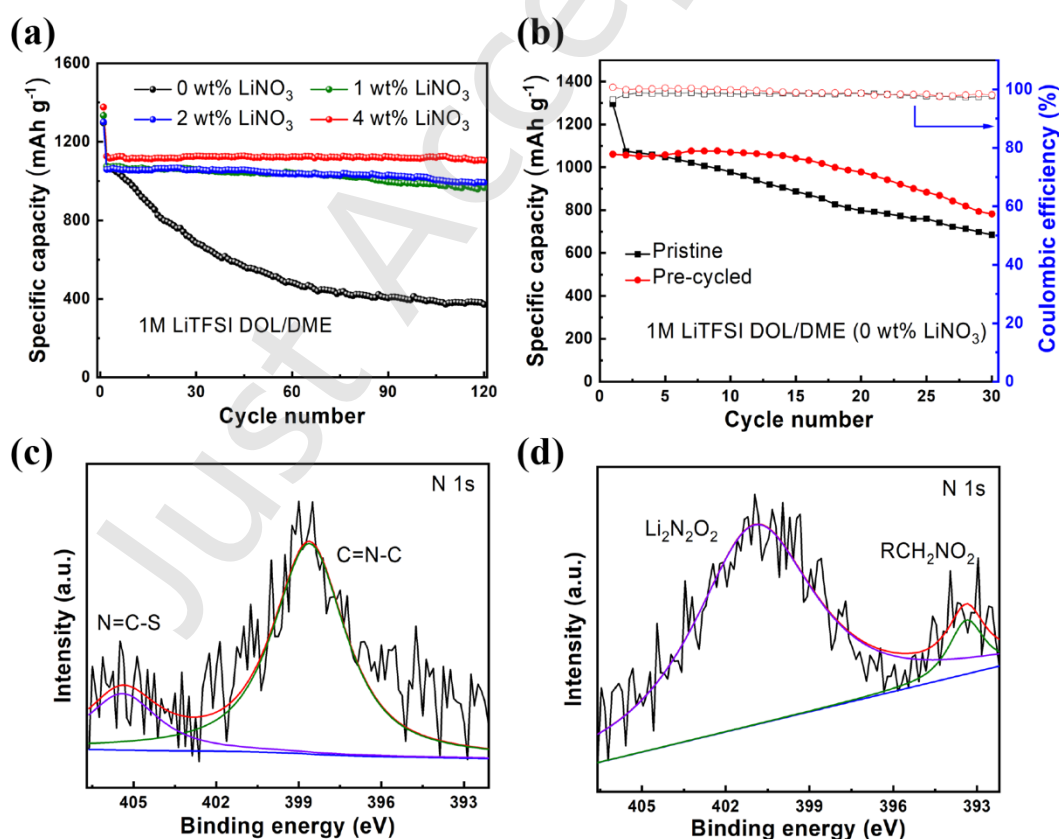


Fig. 4. (a) Cycling performance of the pPAN/SeS₂ cathode in different ether electrolytes at a current density of 0.2 A g⁻¹. (b) The cycling performance of the pPAN/SeS₂ cathode in the LiNO_3 -free electrolyte and that pre-cycled in the ether electrolyte (4 wt% LiNO_3)

for five charge-discharge cycles. (c) The N 1s XPS spectra of the pre-cycled pPAN/SeS₂ cathode after subsequent 30 cycles in the LiNO₃-free electrolyte. (d) The N 1s XPS spectra of the pPAN/SeS₂ cathode after subsequent 30 cycles in the electrolyte with 4 wt% LiNO₃.

The role of LiNO₃ in Li-S batteries is currently under debate. Zhang et al. reported that LiNO₃ helps form a protective SEI layer on the surface of lithium metal anode against corrosion reactions by dissolved polysulfides [23], and meanwhile, it catalyzes the conversion of polysulfides into elemental sulfur [24, 25]. Studies also reported that LiNO₃ facilitates to build a CEI layer at the cathode side, which prevents the shuttling of soluble polysulfides [26]. Here, comprehensive electrochemical and microstructural tests were performed for a better understanding of the critical role of LiNO₃. A Li||pPAN/SeS₂ cell underwent charge-discharge tests for five cycles in the ether electrolyte with 4 wt% LiNO₃ (Fig. S13a). The pre-cycled pPAN/SeS₂ cathode was paired with a fresh Li metal anode to assemble a new half-cell using the LiNO₃-free electrolyte. As can be seen in Fig. 4b, the pre-cycled pPAN/SeS₂ cathode shows almost no capacity decay in the initial ten cycles, with the charge-discharge curves well overlapping over cycling (Fig. S13b). After that, the abrupt capacity decline can be observed. The retained specific capacity after 30 cycles approach that of the electrode constantly cycled in the LiNO₃-free electrolyte.

To investigate the reason for such capacity change, XPS spectra of the electrode after being pre-cycled in the electrolyte with 4 wt% LiNO₃ and after subsequent 30 charge-discharge cycles in the LiNO₃-free electrolyte were measured and shown in Fig. 4c and Fig. S14, S15. After 30 cycles in the LiNO₃-free electrolyte, the O 1s spectrum of the pPAN/SeS₂ cathode shows two strong peaks centered at 531.9 eV and 528.8 eV (Fig. S16), corresponding to organic ROCO₂Li and ROLi phases [27], respectively. Additionally, the N 1s spectrum in Fig. 4d shows two peaks centered at 398.5 eV and 405.2 eV corresponding to C=N-C and N=C-S bonds [28] in the carbon framework of pPAN/SeS₂, respectively. And the characteristic peak ascribed to inorganic LiN_xO_y vanishes, indicating the decomposition of the inorganic dominant protective CEI after

prolonged cycling. The comparison between C 1s, and Li 1s spectra in Fig. S14, S15 also confirms the above assertion. In contrast, after repeated charge-discharge cycles in the electrolyte with 4 wt% LiNO₃, two new peaks centered at 393.7 eV and 399.3 eV appear, which should be assigned to organic RCH₂NO₂ and inorganic Li₂N₂O₂, respectively (Fig. 4d). It well reveals the formation of a surface protective CEI layer derived from the decomposition of LiNO₃ [29]. Li₂N₂O₂ is a good Li⁺ conductor, which favors rapid Li⁺ transfer through the CEI [26]. To further verify the interfacial stabilization effect of LiNO₃ under practical operating conditions, SEM characterization was performed after cycling (see Fig. S17). The LiNO₃-containing electrode exhibits a more preserved surface morphology with reduced structural degradation compared with the control electrode, indicating that the LiNO₃-derived interphase effectively maintains electrode integrity during repeated high-capacity conversion reactions.

3.4. Electrode microstructure tuning for rapid and stable lithium storage

High sulfur loading and lean electrolyte usage are the prerequisites for achieving high-energy-density Li-S batteries. The electrochemical properties of ether electrolytes under high sulfur loading were further investigated. As shown in Fig. S18, the low-loading electrode exhibits an active material layer thickness of approximately 18 μm, while the high-loading electrode reaches approximately 116 μm. The substantially increased electrode thickness confirms the successful preparation of thick electrodes with elevated active material loading, which better represents the practical requirements of high-energy-density sulfur-based batteries. In this study, it was found that when the mass ratio of active material, conductive additive, and binder was controlled to be 8:1:1, the pPAN/SeS₂ cathode with high mass loading (~7 mg cm⁻²) and lean electrolyte (electrolyte/active material ratio of 2.9 μL mg⁻¹) showed poor cycling stability. As shown in Fig. 5a, the specific capacity at a current density of decays rapidly in the LiNO₃-free electrolyte, and the cell completely failed after 35 cycles. Even with the addition of 4 wt% LiNO₃, an abrupt capacity decline to 894 mAh g⁻¹ within 10 cycles can be observed. Voltage fluctuations appeared at the 53rd cycle (Fig. 5b) and

deteriorated at the 60th cycle (Fig. S19), which can be ascribed to gradually enhanced local short circuits in the battery cell.

To explore the failure mechanism, the cycled cell was disassembled. The massive yellow substances on the separator (Fig. S20a) indicate the prominent dissolution of $\text{Li}_2\text{Se}_x\text{S}_y$ in the electrolyte, which easily causes severe side reactions with Li metal anode, the growth of dendrites, and local short circuit. As the mass loading increases, the charge transfer resistance of the pPAN/SeS₂ cathode increases (see Fig. S21). The final lithiation product thus tends to deposit more unevenly, leading to structural instability and easy breakage of as-generated CEI film. The continuous growth of CEI results in increased internal resistance over cycling, which was confirmed by the EIS spectra plotted in Fig. S22. Meanwhile, the sluggish kinetics of the conversion reaction also causes more dissolution and shuttling of $\text{Li}_2\text{Se}_x\text{S}_y$.

To boost the conversion reaction kinetics of the pPAN/SeS₂ cathode, the content of conductive additive was further increased to 15 wt%. For high-loading sulfur electrodes, the insufficient electronic conductivity of sulfur species and lithiation products represents a critical limitation because the increased electrode thickness leads to prolonged electron transport pathways and heterogeneous reaction environments. Therefore, increasing the conductive additive content is adopted here to construct a more continuous electronic conduction network, which facilitates uniform sulfur conversion and reduces polarization during prolonged cycling (see Fig. S23). The accompanying modification of electrode architecture may further contribute to improved electrolyte accessibility and structural stability. As shown in Fig. 5c, the 75:15:10 cathode presents far superior cycling stability to the 80:10:10 counterpart. After 100 cycles at 0.1 A g⁻¹, it still delivers a high specific capacity of 958 mAh g⁻¹ with a low-capacity decay rate of 0.05% per cycle and charge-discharge curves well overlapping over prolonged cycles (Fig. 5d). The disassembled cells demonstrate almost no yellow substances on the separator, indicating the well-inhibited polysulfide shuttling (Fig. S20b). Additionally, the charge transfer resistance after charge-discharge cycles shows little change (Fig. S24), again confirming the structural stability of the cathode film even under high mass loading and lean electrolyte.

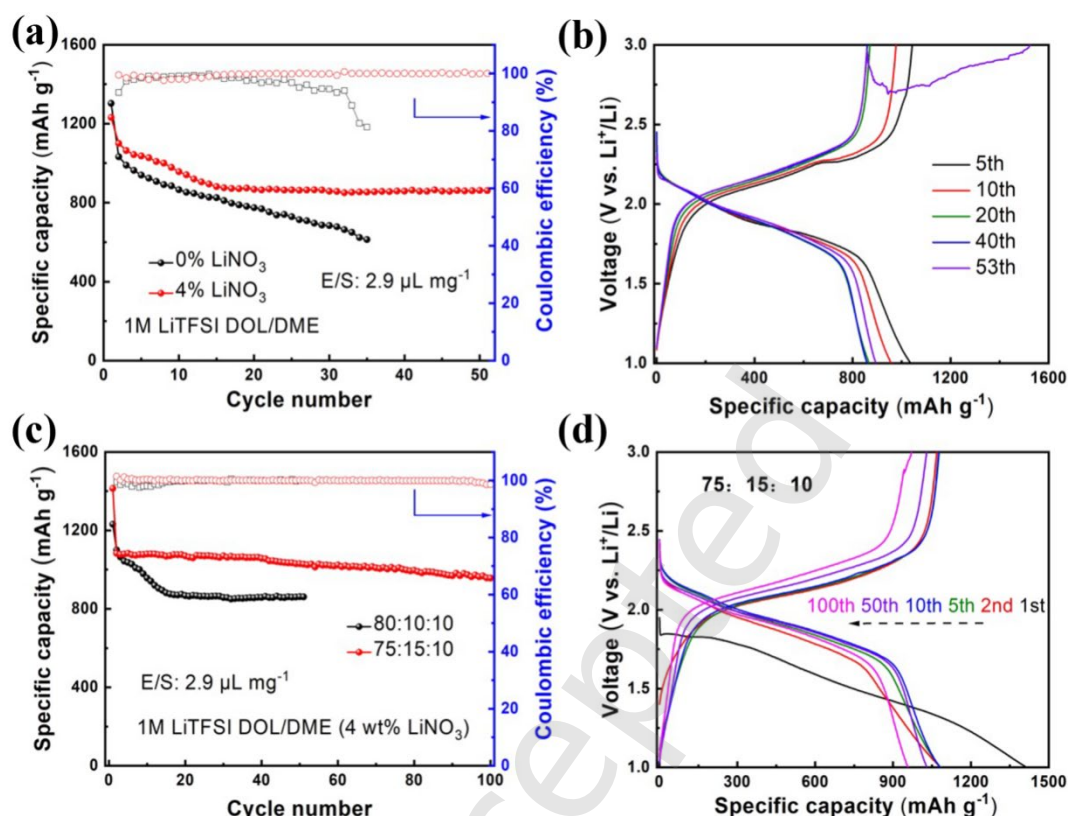


Fig. 5. (a) Cycling performance of the pPAN/SeS₂ cathode at a high mass loading in ether electrolytes. (b) The corresponding charge-discharge curves of high-mass-loading pPAN/SeS₂ cathode in the ether electrolytes with 4 wt% LiNO₃. (c) Cycling performance of high-mass-loading pPAN/SeS₂ cathodes with different conductive additive content. (d) The charge-discharge curves of the high-mass-loading pPAN/SeS₂ cathode with a mass ratio of 75:15:10 over prolonged cycling.

3.5. Electrochemical performances of Li-S full cells under practical conditions

To achieve a high full-cell energy density for practical applications, high sulfur loading, low electrolyte/sulfur (E/S) ratio and low negative/positive (N/P) electrode mass ratio are critical for Li-S batteries [15]. Hence, a Li-S cell with a high cathode mass loading of ~7 mg cm⁻², lean electrolyte (E/S ratio of 2.9 μL mg⁻¹) and thin Li metal anode (N/P ≤ 1.5) was constructed to verify the potential of our pPAN/SeS₂ cathode with multiscale design (Fig. 6a). A ZnF_x(OH)_y modified copper foil (*m*-Cu) was used as the current collector as reported in our previous work, which promotes more uniform Li deposition than the bare copper foil and helps improve the stability of Li

plating/stripping cycles [30]. The *m*-Cu substrate provides an additional interfacial regulation strategy, contributing to the improved full-cell performance together with the optimized cathode design. As can be seen in Fig. 6b, at an N/P ratio of 1:1, Li/Cu||pPAN/SeS₂ exhibits rapid capacity fading, retaining only 296 mAh g⁻¹ after 100 cycles. In contrast, the Li/*m*-Cu||pPAN/SeS₂ cell still delivers a high specific capacity of 652 mAh g⁻¹ with a low capacity decay rate of 0.33% per cycle. As the N/P ratio increases from 1:1 to 1.5:1, the cycling stability was much improved. It maintains a high specific capacity of 970 mAh g⁻¹ at the 100th cycle and 846 mAh g⁻¹ at the 200th cycle, with a high capacity retention ratio of 77% and capacity decay rate of only 0.06% per cycle (Fig. 6c). The Li/*m*-Cu||pPAN/SeS₂ full cell achieved an average CE of 99.8% (Fig. S25). And the charge-discharge curves of the full cell over prolonged cycling demonstrate little shape change and voltage polarization. Polarization at the 100th revolution was 231 mV, while at the 200th revolution it was only 255 mV (Fig. S26). It should be noted that under high sulfur loading conditions, the cycle life of the full cell is not solely determined by the cathode stability. The cathode morphology remained intact after cycling (Fig. S27). The increased areal capacity requires repeated high-capacity lithium plating/stripping, which significantly amplifies the influence of irreversible lithium loss. Furthermore, a cathode with a high surface area implies an increase in current density on the lithium metal side, which will significantly affect the cycling stability of the lithium metal (Fig. S28). Therefore, under a limited N/P ratio, the lithium metal anode becomes increasingly critical for long-term operation. Even when compared with those previously-reported advanced Li-S battery systems [31-35], our Li/*m*-Cu||pPAN/SeS₂ cell shows great advantages. Such improved electrochemical performance under practically relevant conditions highlights the potential of our rationally designed pPAN/SeS₂ cathode for stable sulfur-based battery operation. The proposed multiscale design strategy offers new guidelines for fabricating advanced organosulfur cathodes for next-generation energy storage.

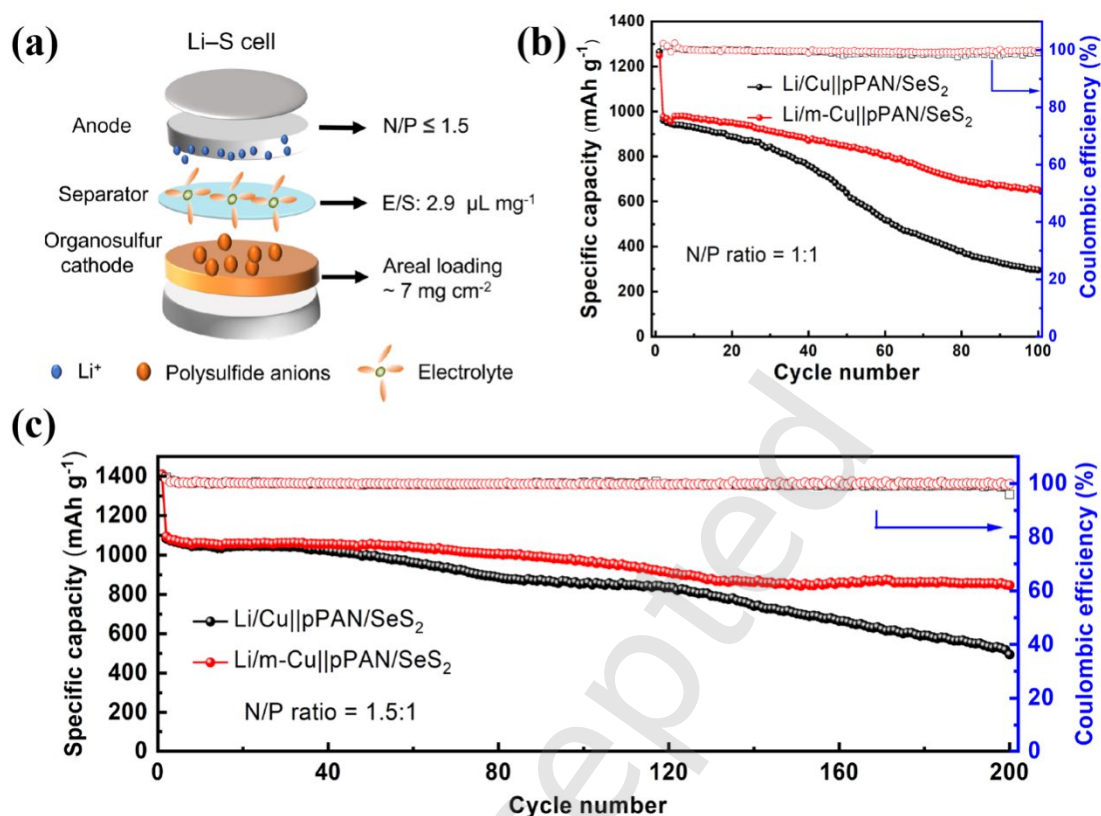


Fig. 6. (a) Schematic of the Li-S full cells under practical conditions of high cathode mass loading, low E/S ratio, and low N/P ratio. Cycling performances of Li-S full cells under different N/P ratios: (b) N/P=1:1 and (c) N/P=1.5:1.

4. Conclusions

In summary, a multiscale design of pPAN/SeS₂ cathode has been proposed to achieve rapid and stable lithium storage in ether electrolytes. Selenization in SPAN at the molecular level facilitates the rapid conversion of polysulfides and charge transfer. A robust and stable CEI constructed by LiNO₃-assisted decomposition at the nanoscale well inhibits the dissolution of polysulfides in ether electrolytes. Additionally, the meso-to-macroscopic conductive frameworks at the particle/electrode level provide contiguous electronic/ion pathways, which are particularly important for fast and uniform deposition of the final lithiation products under high mass loading and lean electrolyte. As a result, both lithium storage kinetics and stability are enhanced in as-fabricated pPAN/SeS₂ cathode. The as-constructed Li-S full cell shows superior cyclic stability with 77% capacity retained over 200 cycles, even under high cathode mass

loading of $\sim 7 \text{ mg cm}^{-2}$, low electrolyte/sulfur ratio of $\sim 2.9 \text{ } \mu\text{L mg}^{-1}$, and limited N/P ratio of 1.5. This work provides important guidelines for the multiscale design of advanced organosulfur cathodes in Li-S batteries for next-generation energy storage.

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Author contribution statement

Ting Ma: Writing-Original draft preparation, Methodology. **Wanming Teng:** Writing-Original draft preparation, Conceptualization. **Xiaoliang Yu:** Data curation, Validation, Writing - Review & Editing. **Yibo Xiao** and **Haixia Yue:** Investigation, Formal analysis. **Jun Liu:** Validation, Supervision. **Na Huang:** Validation, Supervision. **Jian-Gan Wang:** Writing- Reviewing and Editing, Supervision. **Chunguang Wei:** Writing- Reviewing and Editing, Supervision. **Ding Nan:** Writing- Reviewing and Editing, Supervision, Resources. All the authors have approved the manuscript.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Use of AI statement

None.

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