MXene Based Self-assembled Cathode and Antifouling Separator for High-Rate and Dendrite-inhibited Li-S Battery

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Abstract

We demonstrate a novel strategy to enhance sulfur loading and rate performance for Li-S battery by synchronously coupling a nanostructured cathode with an antifouling separator via a facile electrostatic self-assembly approach. The assembly of two dimensional (2D) MXene and positively charged 1D CNT-Polyethyleneimine was observed to controllably address the key issues of sluggish ionic transport, and produce an integrate cathode with dynamic crosslinking network. Moreover, an antifouling separator is proposed by this strategy for the first time, which features well-organized inter-lamellar porosity, dual polarity and high conductivity. The antifouling separator is found to play a pivotal role in: 1) low-order polysulfide activation, 2) high

rate cyclability, and 3) Li dendrites inhibition. Our integrated design realizes a long-term capacity of 980 mAh g⁻¹ at 5 mA cm⁻² over 500 cycles (sulfur loading: 2.6 mg cm⁻²). Furthermore, a flexible self-assembled cathode with high loading (5.8 mg cm⁻²) and superb mechanical strength (13 MPa), demonstrates an appealing areal capacity of 7.1 mAh cm⁻² and rate performance at nearly 10 mA cm⁻².

Key words: Lithium–sulfur battery, 2D MXene, Antifouling separator, Self-assembled channels.

Introduction

The extremely high theoretical specific capacity (1675 mAh g⁻¹) coupled with the abundance and low cost of sulfur, had made Li-S battery a promising energy storage technology over the past decades [1–3]. However, their practical application have been hampered by several major obstacles including the inherent insulating nature of sulfur (10²⁴ Ω·cm) and discharged product Li₂S (10¹⁴ Ω·cm) [4], the well-known lithium polysulfide (LiPS) shuttle effect and uncontrolled Li dendrites growth. These challenges are associated to all the three vital parts of a Li-S battery, i.e., cathode, separator and Li anode, and hence need to be considered in an integrated way.

Various nanomaterials have been used to improve the cathode design, including conductive carbonaceous materials [5–10], polar metal oxides/nitrides [11–15] and metal organic frameworks [16–18]. These sulfur carriers could, to some extent, mitigate capacity loss. However, the long-term cycling stability achieved to date is still far from satisfactory, especially at high sulfur loading (>2 mg cm⁻²), due to the realization of a crafted cathode with both high conductivity and LiPS absorption capacity is still challenging.

For the separator design, 2D polar nanosheets, such as graphene oxide (GO) [19–21], black phosphorus [22], MoS₂ [23] and MOF membranes [24], have demonstrated better capability of blocking the flooded LiPS compared with open-structured 0D/1D coatings such as carbon nanotubes [25–27], nanofibers [28] or metal oxides particles [29,30]. However, it should be noted that such performance improvement is typically reported at relatively low current density ($<2\text{ mA cm}^{-2}$). The reason for this is that the common coating methods often lead to a dense laminar structure that is detrimental to the infiltration of electrolyte into the interior layer, which causes sluggish ions transport and high polarization during high rate cycling [19,20,31]. These issues have often been overlooked in previous studies, probably owing to the limited approach available for designing regular and expanded channels within 2D membranes. On the other hand, the functional coating on the separator suffers from electrical passivation due to accumulation of insulating Li₂S/Li₂S₂ species, which inevitably deteriorates the interfacial charge transfer and thus gradually leads to separator fouling [3,32,33]. Therefore, a proper design of separator with an “antifouling interface” is of considerable interest.

Recently, a new type of 2D transition metal carbides and nitrides named as MXenes, have shown both high metallic conductivity [34] and surface chemistry for LiPS chemisorption, which makes them a promising sulfur host [35]. However, common aggregation and restacking of the 2D flakes impede the access of electrolyte ions to the interspace ($<0.6\text{ nm}$), and active sites is thereby rather limited. More importantly, the previous anti-restacking methods are generally based on random physical mixing between 2D nanosheets and hybrid materials, which typically leads to non-directive distribution of interlayer spacers that does not efficiently prevent restacking owing to the lack of appropriate interactions [34,36,37].

Here, we introduced a multifaceted strategy via one-pot self-assembly of MXene ($\text{Ti}_3\text{C}_2\text{T}_x$) with polyethyleneimine (PEI) functionalized CNT (T@CP), to tailor the design of both cathode and separator synergistically for the Li-S battery. The cathode prepared by this method had a robust 3D heterogeneous interlinked structure, which efficiently improved the LiPS adsorption capacity and interfacial reaction. The separator prepared by this strategy contained well-organized nanochannels, which afford better anti-fouling performance and high-rate cyclability. Moreover, the artificial interface with dual polarity and high electric conductivity ($4.8 \times 10^4 \text{ S m}^{-1}$) was found to accelerate low-order LiPS activation. As illustrated in Fig. 1a, compared to the fatal anode corrosion and uncontrolled Li dendrite growth due to flooded LiPS and inhomogeneous Li^+ flux in routine Li-S configuration, the new cell with integrated design showed substantial cathode stability and Li dendrite suppression, which promise the long cyclability and reliable capacity towards high rate and long-term battery applications.

Fig. 1. (a) Illustration for Li-S batteries with routine configuration and the proposed integrate configuration (b) Illustration of the fabrication of T@CP nanohybrids for sulfur cathode and modified separator. The CNT is omitted from the T@CP structure to highlight the MXene-polymer assembly and crosslinking. (c) Zeta potential of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet, CNT-PEI and T@CP composites. (d) Digital photographs of $\text{Ti}_3\text{C}_2\text{T}_x$, CNT-PEI suspension, and T@CP. (e) N_2

adsorption-desorption isotherms of $\text{Ti}_3\text{C}_2\text{T}_x$, T@C and T@CP composites. (f) HRTEM image of MXene nanosheet with SAED pattern in the inset (scale bar, 2 nm; inset, 2 nm^{-1}). (g) SEM image of the T@CP; scale bar: 5 μm . (h) TEM image of the T@CP nanohybrids; scale bar: 20 nm. (i) SEM images of T@CP-S cathode and corresponding elemental mappings; scale bar: 10 μm .

Results and discussion

Fig. 1b depicts the preparation process of a porous $\text{Ti}_3\text{C}_2\text{T}_x$ @CNT-PEI (T@CP) composite. First, the $\text{Ti}_3\text{C}_2\text{T}_x$ flakes were prepared using the MILD method (Fig. S1 in supplementary information) with high crystallinity (Fig. 1f). Owing to the existence of surface functional groups (e.g., $-\text{O}$, $-\text{OH}$, and $-\text{F}$), $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet is highly negatively charged with a zeta potential of -48 mV (Fig. 1c). Meanwhile, hyperbranched PEI, which has been used as a robust binder [38], was selected to be grafted on CNT due to its positive charge from the high density of amines. The resultant CNT-PEI exhibits a zeta potential of about $+40\text{ mV}$. As shown in Fig. 1d, both the MXene nanosheets and CNT-PEI could form a stable aqueous suspension. Upon dropwise addition of $\text{Ti}_3\text{C}_2\text{T}_x$ solution into the CNT-PEI suspension, the CNT-PEI was spontaneously attached to the surface of the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets driven by the electrostatic interaction. Consequently, coagulation occurred and a clear supernatant was observed (Fig. 1d, right), indicative of the successful self-assembly. On the other hand, the dynamic hydrogen bondings ($\text{N}-\text{H}\cdots\text{O}$, $\text{N}-\text{H}\cdots\text{F}$), originating from the $\text{N}-\text{H}$ group of PEI and the surface terminating oxygen or fluorine of $\text{Ti}_3\text{C}_2\text{T}_x$ (Fig. 1b), also assist in the assembly process. This was confirmed by FT-IR spectroscopy, as shown in Fig. S2. The stretching vibration at around 3470 cm^{-1} is related to the $-\text{OH}$ terminal group of MXene [36], which shifts to a higher wavenumber after assembly with CNT-PEI due to the strong hydrogen bond crosslinking [39]. After centrifugation and lyophilization, the T@CP composite was obtained. The weight ratio of CNT-PEI in the composite was controlled to be 20 wt%. For

comparison, pure CNTs were mixed with the $\text{Ti}_3\text{C}_2\text{T}_x$ solution in a similar way. The mixture, denoted as T@C, ended up with a CNT precipitation and a stable supernatant of the MXene nanosheets, confirming the important role of PEI in the self-assembly process.

Fig. 1g shows the SEM image of the T@CP composite which exhibits a highly porous architecture with a 3D percolating network. Detail observation by TEM in Fig. 1h, reveals that the MXene nanosheets are interconnected by the CNT-PEI web. Energy dispersive spectroscopy (EDS) (Fig. S3) demonstrates that the T@CP composite has a homogeneous structure. In sharp contrast, the T@C composites show a distinct phase separation in Fig. S4, where the MXene nanosheets and CNTs tend to agglomerate separately due to incompatibility between the hydrophilicity of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets and hydrophobicity of CNTs. The N_2 adsorption-desorption isotherms in Fig. 1e shows that the surface area of pure $\text{Ti}_3\text{C}_2\text{T}_x$ is only $25.8 \text{ m}^2 \text{ g}^{-1}$ —in agreement with the previous report [40–41], which increases to $165 \text{ m}^2 \text{ g}^{-1}$ for the T@C composite, and, notably, to $268 \text{ m}^2 \text{ g}^{-1}$ for the assembled T@CP matrix. Additionally, the pore size distribution for T@CP matrix is in the broad range of 10–80 nm (Fig. S5), while the stacked $\text{Ti}_3\text{C}_2\text{T}_x$ lacks pores in this size range. These results indicate that all the MXene, CNT and PEI have played important roles in the assembling process. A cathode T@CP-S was prepared by loading sulfur into the T@CP matrix. Fig. 1i shows the structure of T@CP-S composite with sulfur content of 70.2 wt% (Fig. S6). The sulfur loading was controlled around 2.6 mg cm^{-2} . EDS elemental mapping indicates that sulfur was well anchored into the T@CP host without apparent aggregation. For comparison, T@C-S cathode was also fabricated with similar sulfur loading.

Fig. 2. (a) Color changes of the Li_2S_x solution (A) exposure to CNT-PEI (B), $Ti_3C_2T_x$ (C) and T@CP (D) for 6 h. (b) The UV-Vis spectra of Li_2S_x solution after absorption. (c) High resolution XPS of C 1s of CNT-PEI; (d–f) Ti 2p, S 2p and N 1s peaks of T@CP- Li_2S_x composites.

To evaluate the adsorption capacity of LiPS, samples of T@CP, CNT-PEI and bare $Ti_3C_2T_x$ were immersed in Li_2S_6 solution at equal amounts. Visual inspection of the LiPS solution in Fig. 2a clearly suggests that T@CP is much more efficient in trapping LiPS than CNT-PEI or bare-MXene. UV-Vis spectra (Fig. 2b) also showed that the solution after T@CP absorption demonstrated substantially weaker LiPS peak intensity. Based on the UV-Vis calibration curve, the absorption capacity of T@CP was estimated to be 0.649 g g^{-1} , which is much higher than that of the pristine $Ti_3C_2T_x$ (0.294 g g^{-1}), CNT-PEI (0.107 g g^{-1}), and other reported hosts (Fig. S7). The interaction mechanism was further investigated by XPS. First, the covalent grafting of PEI to CNT was confirmed by the peak at 287.9 eV in Fig. 2c, which is associated with the $-N-C=O$ amide linkage between PEI and $-COOH$ functionalized CNT. In the Ti 2p spectra of the absorbed T@CP complex, characteristic Ti-C, Ti(II), Ti(III) and Ti-O peaks could be clearly assigned (Fig.

2d). It should be noted that the Ti–S peak is hard to distinguish here due to its overlapping with the Ti–C peak [42]. On the other hand, in the S 2p spectra in Fig. 2e, the observed peaks at 164.1 and 165.3 eV correspond to the $2p_{1/2}$ and $2p_{3/2}$ species of bridging S–S, and the peaks at around 162.3 eV could be assigned to the terminal sulfur species [43,44], which shift to a higher binding energy compared with previous pure Li_2S_6 spectra due to the interaction between MXene and LiPS. Meanwhile, two sulfate and thiosulfate humps at 168.9 eV and 167.3 eV are formed due to *in situ* oxidation of LiPS on the exposed Ti sites, which could act as a further protective layer for LiPS immobilization [35]. Furthermore, N 1s signal was observed in T@CP (Fig. 2f) and underwent a slight positive shift after contact with LiPS, identifying a strong N–Li interaction. These results confirmed that the superb adsorption of T@CP towards LiPS results from the synergetic effect of the massive amine groups from PEI, and the highly exposed active sites from $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets.

Fig. 3. SEM image of the top surface and corresponding cross-sections of different separators: (a–c) $\text{Ti}_3\text{C}_2\text{T}_x$ separator, (d–f) T@C separator, and (g–i) T@CP separator; scale bars: 2 μm (a, d, b, e, h) and 500 nm (c, g, f, i). Electrolyte contact angles for $\text{Ti}_3\text{C}_2\text{T}_x$ (j) and T@CP separator (k).

The merits of T@CP as a sulfur host were first evaluated by cyclic voltammetry (CV). As shown in Fig. S8, both the T@CP-S and T@C-S cathodes exhibited typical two cathodic peaks (~ 2.35 and 2.05 V) and one anodic peak (~ 2.30 V), but the former one exhibits notably smaller potential hysteresis and higher current density. Furthermore, the CV curves from T@CP-S cathode in the initial 10 cycle scans were well overlapped compared with that of the T@C-S cathode. Considering the similar sulfur loading for the two cathodes, the performance difference observed

in the CV measurement is believed to be resulted from the chemical coupling between MXene and CNT-PEI, which could ultimately enable massive active species anchoring onto the conductive and polar interface to trigger the kinetically efficient reactions. Consequently, the T@CP-S cathode delivered a considerably higher capacity of 1325 mAh g⁻¹ at 0.2 C (1C=1675 mAh g⁻¹) and better cyclability (Fig. S8).

Apart from cathode optimization, the pursuit of high Li-S battery stability and fundamental limitations originating from high sulfur loadings have inspired us to explore the separator part further. Specifically, we sonicated and then filtrated the as-prepared T@CP solution on a commercial glass fiber (GF) separator to obtain the T@CP separator. Likewise, bare MXene nanosheets and T@C composites were also employed as functional coatings for comparison. Interestingly, we found that the three kind of separators have totally different structures. As shown in Fig. 3a-c, upon filtration, the directional flow guided the gathering of MXene nanosheets to form a layer-by-layer stacking structure, yielding a pure MXene film with a typical densely packed morphology in the cross-section image. The T@C separator exhibited a clearly phase separated structure (Fig. 3d-f), in which the MXene and CNTs are packed separately. In striking contrast, for the T@CP separator, a much more uniform assembly is observed in both top surface and cross-section (Fig. 3g-h) images. Fig. 3i clearly reveals that the CNT-PEI, are intercalated between individual MXene nanosheets as conductive linkers and lithiophilic pillars, creating a nano-sandwich motif and accessible channels. The free access of electrolytes into the separator was validated through the contact angle test (Fig. 3j-k), where the contact angle of electrolyte on T@CP separator is much smaller than that of the bare MXene separator, indicating the stronger electrolyte affinity and accessibility.

The electrical conductivity of the bare MXene film was measured to be around $4 \times 10^5 \text{ S m}^{-1}$ by the four-point probe method, and was reduced to $4.8 \times 10^4 \text{ S m}^{-1}$ for the T@CP separator (Fig. S9), and this value is much higher than that of the reduced GO and MoS₂ counterparts [45,46]. Moreover, for the first time to the best of our knowledge, we fabricated the dual sulfiphilic and lithiophilic membrane with a nano-sandwich motif, which is supposed to endow the T@CP separator with highly polar channels for facile LiPS anchoring and homogeneous Li⁺ transport.

Based on the T@CP-S cathode, the lithium diffusion coefficients (D_{Li^+}) of the three types of separators were measured based on Randles–Sevcik equation at series CV scanning rates (Fig. 4a, Fig. S10–11). As shown in Fig. 4b, the D_{Li^+} of the T@CP separator are 1.97×10^{-7} , 6.1×10^{-8} and $5.5 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ at, respectively, A₁, C₁ and C₂ peaks, which are about 6 and 3 times of that of the bare MXene and T@C separators, respectively. The ionic conductivity of T@CP separator, evaluated based on EIS in Fig. 4c, is 3.08 mS cm^{-1} , comparable to that of the pristine GF separator (4.18 mS cm^{-1} ; reported value: 3.83 mS cm^{-1} [47]) and almost one order of magnitude higher than that of the bare MXene separator and other reported 2D separators [23,48]. These results confirmed that the well-organized micro/nanofluidic channels in T@CP separator plays a vital role in realizing high ionic conductivity and affording high rate performance. Accordingly, Fig. 4d shows the CV scans of the cells based on the T@CP-S cathode and three types of separators. Among the three types of cells, the T@CP cell has the smallest redox peak separation. This trend is also in agreement with the GCD curves in Fig. S12, where the voltage hysteresis for T@CP (120 mV) is much smaller than that of T@C (164 mV) and Ti₃C₂T_x (228 mV) cells. The difference is much more distinct at high current density. As shown in Fig. 4e and Fig. S13, increasing current density from 0.87 mA cm^{-2} to 2.18, 4.4, 10.9 and 17.4 mA cm^{-2} (corresponding to current rate of 0.25 C, 0.5 C, 1 C, 2.5 C and 4 C, respectively) causes colossal potential gap for T@C and bare MXene

cells. This is also commonly observed in other reported 2D coatings [22,23,49] due to the sluggish transport kinetics through dense layers. Those issues, however, are absent with T@CP separator, as demonstrated by the stable voltage plateaus even at 10.9 mA cm^{-2} (Fig. 4f). The boosted redox kinetics at high current density mainly benefit from the enhanced ion transport capability through the expanded pillars, and the inherent metallic conductivity of MXene.

Fig. 4. (a) CV curves of the T@CP-S cathode with a T@CP separator at various scan rates (b) Li^+ ion diffusion coefficient for the three separators. (c) Ionic conductivities of different separators. (d) CV scans of T@CP-S cell with different separators. (e) The potential gap for three separators at various current densities. (f) GCD profiles of T@CP-S|T@CP cell at various rates. (g) Rate

performances of T@CP-S cathode with different separators. (h) Cycling at 0.25 C for T@CP cathode with different separators.

The high-rate performance in Fig. 4g further demonstrates such advantages. Compared with the formidable capacity loss for the T@C and bare MXene cells when the discharge rate was increased, the cell with T@CP separator showed impressive high-rate capacities of 1110, 1035 and 950 mAh g⁻¹ at 0.5 C, 1 C and 2.5 C, respectively. Long-term cycling performance shows that the T@CP cell with sulfur loading of 2.6 mg cm⁻² maintained nearly 1100 mAh g⁻¹ after 200 cycles (89.6% retention) at 0.25 C (Fig. 4h). Whereas, the capacity of the bare MXene cell quickly decayed to 565 mAh g⁻¹, which is even worse than that of the bare GF separator (Fig. S14). Also the effect of T@CP loading on separator is investigated in Fig. S15. Considering that the T@CP separator exhibited lower electronic conductivity than that of the bare MXene, the EIS analyses and the rate performances give a strong indication that the facile ionic transport through the regular nanochannels of the T@CP separator is the main contributors to the battery performance gains.

Fig. 5. (a–d) SEM images of different Li metal anodes from: (a) T@C-S|GF and (b) T@CP-S|GF cell after 100 cycles, (c, d) from T@CP-S|T@CP cell after 100 and 200 cycles. (e) Voltage-time profiles of Li stripping/plating in Li//Li symmetric cells with 1 mAh cm^{-2} at step-increased current densities. (f–h) GCD profiles of T@CP-S cathode with $\text{Ti}_3\text{C}_2\text{T}_x$ (f), T@C (g), and T@CP (h) separators at 0.25 C. (i) Illustration of the interlamellar nanofluidic channels for LiPS interaction mechanism within the T@CP membrane. (j) Performance of T@CP-S|T@CP system at 1 C, sulfur loading is 2.6 mg cm^{-2} .

To study the LiPS shuttle behaviors of different separators and their effects to the Li anode, the cells were disassembled after 50 cycles, and then the separators and Li anode were characterized by SEM and EDS. As shown in Fig. S16, a clear sulfur signal on the back side of bare GF separator (anode side) suggested free migration of LiPS through the separator. However, a negligible sulfur signal was detected when the T@CP separator was inserted. The constantly lower shuttle current for T@CP cell further demonstrated its excellent capability of suppressing “shuttle effect” (Fig. S17). Furthermore, as shown in Fig. 5a–b, the Li anodes in the cells with bare GF separator showed massive Li dendrites after 100 cycles, while comparatively, Li anodes in the cells with T@CP separator displayed much smooth and compact surfaces over 100 and 200 cycles at 0.25 C (Fig. 5c, d), indicating a distinguished anode protection of the T@CP separator.

Furthermore, the Li/Li symmetric cells were also cycled to elucidate the effect of T@CP layer on controlling the growth of Li dendrite. For the cell with blank GF separator, an initial overpotential around 40 mV was observed at 1 mA cm^{-2} (Fig. S18), which failed to maintain a stable overpotential after 160 h stripping/plating, implying the uncontrolled Li anode interface [50,51]. The bare MXene separator (Fig. 5e) exhibited a pretty high overpotential in the initial stage and quickly reached beyond 200 mV at 1 mA cm^{-2} due to the high barrier for lithium diffusion. In the case of T@CP separator, the initial overpotential showed a slight fluctuation and gradually reached to a low plateau less than 25 mV at 0.5 mA cm^{-2} for 100 h. Moreover, the cell could still keep a smooth plateaus over 400 cycles when the current densities step-increase to 5 mA cm^{-2} . This confirms that the T@CP separator rich in 3D ordered channels and lithiophilic PEI pillars can guide the homogeneous Li^+ flux and lithium electrodeposition [50,52]. The enhanced coulombic efficiency (CE) in Cu |Li cell (Fig. S19) also confirm the virtue of the T@CP separator in controlling the lithium dendrite growth.

Fouling is an inevitable problem in any type of membrane processes, including ultrafiltration, nanofiltration and desalination applications. The foulants adsorption and pore blockage during operation will gradually cause interface deterioration and flux decline. The fouling behaviors of the separators were studied by Nyquist plots before and after cycling. As plotted in Fig. S20, for T@C and bare MXene cells, the charge transfer resistances (R_{ct}) at low frequency were much larger. Moreover, a huge surge of R_{ct} was observed for the bare MXene cell after 50 cycles at 0.25 C. An additional semicircle is appeared at middle frequency due to deposition of insulating discharge products on the impermeable interlayer [23,53], a sign of separator fouling. Conversely, the stable R_{ct} value at low frequency for the T@CP separator implies unhindered ion diffusion and insulating layer inhibition. Hence, the T@CP separator has an “antifouling nature”, which is different from other reported separators [48,54,55]. This antifouling behavior was further supported by analyses of the adsorbed foulants on the separator. As shown in Fig. S21, insoluble and aggregated discharge products on the MXene separator (cathode side) could be observed, similar to previous observations of uncontrollable deposition of discharge product on lamellar layers [19,32]. In contrast, the T@CP interlayer shows a smooth surface without bulk “dead S”. These observations suggested that an efficient transformation between solid sulfide and liquid intermediates was realized within the T@CP nanoporous channels, which is the key to fully reuse the escaped active species and to avoid separator fouling.

This antifouling property was further found to play a critical role in discharge plateau behavior. As shown in Fig. 5f–h, we found that the three cell configurations exhibit a relatively stable high plateau capacity (Q_H) (referring to soluble polysulfides blocking). However, the low plateau capacity (Q_L) retention for T@CP-S|Ti₃C₂T_x (72%) and T@CP|T@C are much lower than that of T@CP-S|T@CP system (94%) after 200 cycles. Such a capacity improvement means that the

T@CP motif not only addresses the shuttling issue, but also ensures the reversible activation of the intercepted low-order sulfur species. With these benefits, T@CP-S|T@CP presents an capacity of 980 mAh g⁻¹ after 500 cycles (88.5% capacity retention) at 1 C rate (Fig. 5j), with an low decay rate of 0.021% and high CE approaching 100%.

The cells were cycled under lean electrolyte conditions to probe the potential application in practice. As shown in Fig. S22, at electrolyte (ml)/sulfur (g) ratio (E/S) of 12 ml g⁻¹, the cell could maintain a capacity of $\approx$ 1100 mAh g⁻¹ in 5 cycles and 880 mAh g⁻¹ after 60 cycles, and a 920 mAh g⁻¹ capacity could be still realized as the E/S was controlled to be 5. This performance is pretty competitive to the recent reports [56-57] in terms of low electrolyte amount applied. A further decrease of E/S ratio to be 3.5 leads to relatively poor performance, mainly because the polysulfide transformation kinetics under lean electrolyte condition is limited. Also the issues of electrolyte consumption in the cell stand out during the continuous cycling. Future work could focus on optimizing lean-electrolyte cyclability through the control of electrolyte consuming/evaporation and exploring the solid-phase Li-S transformation [58].

Electrodes with higher sulfur loading were also demonstrated. As shown in Fig. 6a–b, a free-standing cathode was fabricated by infiltration of sulfur into a thick T@CP membrane followed by an annealing process, and the sulfur loading is up to 5.8 mg cm⁻². Note that the freestanding electrode exhibits prominent mechanical integrity and flexibility and could be bent repeatedly without cracking. Further mechanical tests showed a high tensile strength (13.5 MPa) and Young's modulus (Fig. 6c), despite the heavy sulfur content. This mechanical robustness is thought to be related to the crosslinking of the integrated T@CP skeletons (Fig. S23) and assist in conquering drastic volume changes of cathode materials.

Fig. 6. (a) Cross-sectional SEM images of the thick T@CP-S cathode and the corresponding elemental mappings. (b) Photographs of the flexible cathode film. (c) Stress-strain curve of the T@CP-S film. (d) Open circuit voltage of T@CP-S cathodes (sulfur: 5.8 mg cm⁻²) with T@CP separator and bare GF separator. (e) Cycling performance of the freestanding T@CP electrode with T@CP separator at 2.4 mA cm⁻² and 9.7 mA cm⁻², and with bare GF separator at 2.4 mA cm⁻², respectively. (f) Sulfur loading versus capacity loss per cycle for this work and recent relevant report.

When cycled at 0.25 C (2.4 mA cm⁻²), as shown in Fig. 6e, the initial discharge capacity was 1184 mAh g⁻¹ (6.87 mAh cm⁻²), and remained at 845 mAh g⁻¹ after 100 cycles for the prepared freestanding cathode. When configured with a T@CP separator, the freestanding T@CP-S|T@CP had a more stable open circuit voltage (Fig. 6d) and a capacity of 7.1 mAh cm⁻² (Fig. 6e) was reached after 100 cycles. It is worth noting that when the current density was increased to 9.7 mA cm⁻², a decent capacity above 4.0 mAh cm⁻² could be still maintained. As listed in Fig. 6f, these results clearly highlight the advantages of T@CP-S|T@CP system towards high loading, high rate Li-S applications.

Conclusions

We have demonstrated comprehensive cell design aimed at upgrading the sulfur host and functional separator through a versatile electrostatic self-assembly approach. The robust, inter-linked cathode host benefiting from the synergetic effects of $\text{Ti}_3\text{C}_2\text{T}_x$ frameworks and lithiophilic CNT-PEI spacer, resolved the key issues of restacking and maximized exposure of dual polar sites towards polysulfide interaction. Meanwhile, we suggest that the routine 2D lamellar type interlayer, even though possessing high electric conductivity, may not be suitable for high rate Li–S performance. Alternatively, the antifouling separator here, coupled by metallic, and sulfiphilic nanosheet and lithiophilic pillars, bridges a suitable gap between metal anode and cathode, which provide: 1) rapid electrolyte ions transport, 2) efficient LiPS activation, and 3) Li anode protection for high rate cyclability and long service life. As a result, the integrated T@CP-S|T@CP system demonstrated high loading and high rate capacity Li–S application.

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