Covalent Triazine Frameworks Incorporating Charged Polypyrrole Channels for High Performance Lithium-Sulfur Batteries

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ABSTRACT: Organosulfur polymers have emerged as promising electrode materials for lithium-sulfur (Li-S) batteries, mainly due to their ability to incorporate and stabilize high sulfur contents. The low ionic and electronic conductivity of these polymers, however, limits their cycling performance at high active mass loadings. Moreover, Li-polysulfide (Li-PS) shuttling, a fatal phenomenon in the cyclability of Li-S batteries, can be mitigated *via* the entrapment of Li-PS by utilizing various supramolecular interactions. Here, we report a new approach that incorporates one-dimensional charged polypyrrole into a two-dimensional covalent triazine framework (cPpy-S-CTF) synthesized in the presence of elemental sulfur. The cPpy-S-CTF enabled sulfur loadings up to 83 wt% thanks to the perfluoroaryl‐elemental sulfur SNAr chemistry. Notably, the addition of charged polypyrrole, cPpy, triggered a 3D nanochannel formation in the cPpy-S-CTF with high-affinity anchoring sites towards Li-PS while achieving decent ionic and electronic conductivity. cPpy-S-CTF showed a remarkable electrochemical performance with a specific capacity of 1203.4 mAh g−1 at 0.05C, initial Coulombic efficiency of 94.1%, and capacity retention of 86.8% after 500 cycles. These results point to the fact that the incorporation of charged conducting polymers could be a universal strategy to boost the electrochemical performance of organosulfur polymers in Li-S batteries.

INTRODUCTION

The large-scale adaptation of renewable energy in households and public sectors as well as the timely and broad dissemination of electric vehicles necessitate the development of low-cost, high energy density energy storage systems. In this direction, lithium-sulfur (Li-S) batteries with the high theoretical specific energy density of 2600 Wh kg–1 and low-cost of raw materials has emerged as a promising candidate. In addition, the large-scale utilization of elemental sulfur is highly feasible considering the global supply surplus of sulfur due to its involuntary production from the purification of natural gas and oil by a process called “hydrodesulfurization”.1-3 Aside from these noticeable characteristics of Li-S batteries, there is still a significant gap for its broad practical use due to the fact that (1) Li-S chemistry is based on solid-liquid-solid transition that involves the insulating solid phases of elemental sulfur and Li2S, thus suffering from the interfacial resistance during charging and discharging, (2) the dissolution of lithium polysulfides (Li-PS) in the electrolyte results in an inevitable shuttling of lithiated reaction products that impairs the reversibility of discharge-charge in each cycle,4-8 and (3) volume expansion up to 80%, which makes it nontrivial to keep the mechanical stability of a sulfur electrode. In order to address these challenges, there have been two main approaches, namely, physical and chemical confinement of sulfur. The first approach involves the utilization of highly porous conducting hosts such as ordered mesoporous carbon (CMK-3),9 hierarchical porous carbon (HPC),9 carbon nanotubes,10 porous carbon fibers,11 carbon sphere,12 graphene, graphene oxide,13-16 covalent organic framework (COF),17-19 metal-organic framework (MOF),20-23 porous organic polymers,24 and conducting polymers25-27 as hosts for the physical confinement of elemental sulfur. Though these approaches have improved the cycling performance to large extents, the dissolution of Li-PS and its shuttling due to the lack of specific interactions and low binding energy between the host and Li-PS led to a capacity decay especially at high sulfur loadings.28 Recently, surface coating of a porous carbon host using a cationic polymer has been shown to alleviate Li-PS shuttling.29 In addition, in the context of physical confinement, the coating of a conductive layer on the separator30-33 or on the host material32,34 has been demonstrated to increase electronic and ionic conductivity.35,36 The second approach is the chemical confinement based on strong chemical bonding between sulfur and polymeric host. This approach is rather promising as it allows homogeneous distribution and efficient stabilization of sulfur.37-45 Having recognized the importance of strong bonding between sulfur and host material, inverse vulcanization strategy has been developed to form sulfur-rich copolymers by radicalic copolymerization of sulfur and organic monomers.46-49 While the chemical confinement approach enabled strong binding for sulfur along with high sulfur contents (> 80 wt%), it is still desired to have multiple conducting pathways involving anchoring sites i.e., the heteroatoms, and charged sites, to facilitate efficient ionic and electronic transport at substantial sulfur loadings.50 Recently, elemental sulfur mediated synthesis of a covalent triazine framework (CTF) *via* the trimerization of aromatic nitriles has been reported.51 This approach enabled the in-situ formation of a conjugated 2D polymeric host bearing nitrogen atoms as anchoring sites for Li+ while achieving homogeneous distribution of sulfur and its chemical impregnation onto the backbone thorough radical



**Figure 1.** Figure 1. Synthetic scheme for the elemental sulfur-mediated synthesis of cPpy-S-CTFs incorporating different amounts of cPpy *via* SNAr chemistry and inverse vulcanization.

C-H insertion reaction, leading to a sulfur content of 62 wt%. In order to further increase the sulfur content of the organosulfur polymers, perfluoroaryl‐elemental sulfur nucleophilic aromatic substitution reaction (SNAr) chemistry was introduced.52,53 The synthesis of the organosulfur polymer called SF-CTF was achieved by the trimerization of perfluorinated arylcyanides while sulfur is simultaneously impregnated, thus enabling sulfur contents >80 wt%. These examples clearly signify the importance of the chemistry of sulfur insertion to achieve a high sulfur content. Due to the limited conductivity of organosulfur polymers, however, further improvements in mass loading, specific capacity and cycling stability have been hindered.

Supramolecular chemistry in general can play a major role in Li-S batteries, in particular, for suppressing the Li-PS shuttling by engineering specific binding sites targeting Li+, Sn2– or both. In this direction, N, O-doped porous organic polymers, N-doped carbon materials,54-56 O-doped mesoporous carbon,57 Lewis and acid-base interaction58-60 and covalent organic frameworks based on boronate-ester formation have been explored.61 However, the ability of these systems in impeding the Li-PS shuttling was limited mainly due to the moderate binding strength between Li-PS and anchoring sites. In addition, limited sulfur loading and difficulty of fine control in the doping levels further limit the application of these systems. In an effort to mitigate the shuttling effect of Li-PS, one can benefit from the hard and soft acid-base theory (HSAB), which allows to predict which acids and bases prefer to interact.62 Specifically, the most favorable acid-base interactions are from hard-hard and soft-soft pairs. The Li-PS contains a hard acid, Li+, and a soft base, Sn2–, thus targeting Sn2– with a soft acid such as organic cations would be a good direction. All in all, an ideal host material is desired to have 1) high affinity binding sites towards Li-PS, 2) high ionic/electronic conductivity, 3) sufficient void space to compensate volume expansion, 4) a high sulfur content (i.e., > 80 wt%). With these specifications in mind, herein, we demonstrate the integration of 1D charged polypyrrole (cPpy) to a 2D CTF (referred to as cPpy-S-CTF) formed upon the trimerization of tetrafluoroterephthalonitrile in the presence of elemental sulfur and simultaneous sulfur insertion *via* perfluoroaryl‐elemental sulfur SNAr chemistry as well as radicalic C-H insertion onto the cPpy backbone. The choice of cPpy was based on its unique properties that allow to have 1) decent electronic and ionic conductivity, 2) the ability to bind with Li-PS *via* the HSAB theory, and 3) the capability of releasing the stress of a sulfur composite electrode at high sulfur loadings. The incorporation of cPpy63-65 within the 2D CTF led to the formation of 3D interconnected nanochannels with abundant cationic sites i.e., quaternary nitrogen atoms, as soft acids for efficient Sn2– binding as well as high ionic and electronic conductivity. Notably, cPpy-S-CTF showed a high sulfur content of 83 wt%. The incorporation of only 2.5 wt% cPpy improved electrochemical performance significantly, such as the specific capacity of 1203 mAh g−1 at 0.05C, 94.1% initial Coulombic efficiency (ICE) and 86.8% capacity retention after 500 cycles. Also, such robust capacity retention of cPpy-S-CTF was maintained for a high sulfur loading of 4.0 mgsulfur cm–2.

EXPERIMENTAL SECTION

**Materials.** Tetrafluoroterephthalonitrile was purchased from TCI, Japan. 1,3-dioxolane (DOL), dimethyl ether (DME), elemental sulfur, lithium nitrate (LiNO3), lithium bis(trifluoromethane)sulfonamide (LiTFSI), polyvinylidene difluoride (PVDF, Mw = 560,000), and polypyrrole were purchased from Sigma-Aldrich, USA. *N*-methyl-2-pyrrolidone (NMP) was purchased from Junsei Chemical, Japan. All materials were used without further purification.

**Synthesis of cPpy-S-CTFs with varying polypyrrole ratio.** cPpy was incorporated into the perfluorinated CTFs to form cPpy-S-CTFs by reacting cPpy, tetrafluorophthalonitrile and elemental sulfur while the mass ratio of tetrafluorophthalonitrile and cPpy together to elemental sulfur was fixed at 1:3. cPpy content was varied with respect to tetrafluorophthalonitrile content in the mass ratios of 1:99, 2.5:97.5, 5:95, and 10:90. For example, in the case of cPpy-S-CTF 2.5%, 5 mg of cPpy, 0.195 g (0.97 mmol) of tetrafluorophthalonitrile and 0.6 g of elemental sulfur were transferred into a 10 mL pyrex ampoule. The ampoule was purged with Ar and kept under vacuum while being sealed. The ampoule was heated to 160 oC with a dwelling time of 20 h at a ramping rate of 1 oC min–1 in order for the SNAr reaction and trimerization of tetrafluorophthalonitrile to take place. The temperature was raised to 400 oC with dwelling time of 20 h at a ramping rate 1 oC min–1 to initiate the inverse vulcanization. The ampoule was then cooled down to room temperature producing black powder to be used for chemical and electrochemical characterization.

**Synthesis of cPpy-CTFs.** Sulfur-free cPpy-CTF 0, 2.5, and 10% were prepared for control experiment according to the literature80 with modified procedures. In a typical synthesis, cPpy and terephthalonitrile (mass: mass = 0:100, 1:99, 2.5:97.5, 5:95, 10:90) were homogenously mixed with ZnCl2 keeping the mass ratio of 1:5 (cPpy/terephthalonitrile : ZnCl2) and then transferred into a 10 mL pyrex ampoule. The ampule was sealed under vacuum and heated at 400 oC for 40 h with a ramping rate of 1 oC min–1. Next, the ampoule was cooled down to room temperature. The produced black powder was sequentially washed with DI water, 1 M HCl, acetone and ether to remove reaction residues. The obtained powder was kept in a vacuum oven at 120 oC overnight for further analyses.

**Material characterization.** Fourier transform infrared spectroscopy (FT-IR) analysis was carried out using TENSOR27 (Bruker, Germany). X-ray photoelectron spectroscopy (XPS) spectra were recorded on an Axis-Supra (KRATOS, United Kingdom) spectrometer. Raman spectra were attained from a LabRAM HV Evolution (Horiba, Japan) spectrometer. Thermogravimetric analysis (TGA) was performed on Mettler Toledo with ramping 5 °C min−1 under N2 atmosphere in a range of 25 °C to 600 °C. Field emission scanning electron microscopy (FESEM) analysis was carried out on Tescan Mira3 LM FE. Brunauer–Emmett–Teller (BET) analysis was performed on a Micrometrics 3flex system and the surface areas were estimated from N2 adsorption-desorption isotherms using the BET model. The pressure ranges were obtained from the Rouquerol plots. The pore size distributions were calculated using the Nonlocal Density Functional Theory (NLDFT) method. Ultraviolet-visible (UV-Vis) spectroscopy analysis was performed using a Lambda 35 UV/vis spectrometer (PERKIN ELMER Instruments, USA).

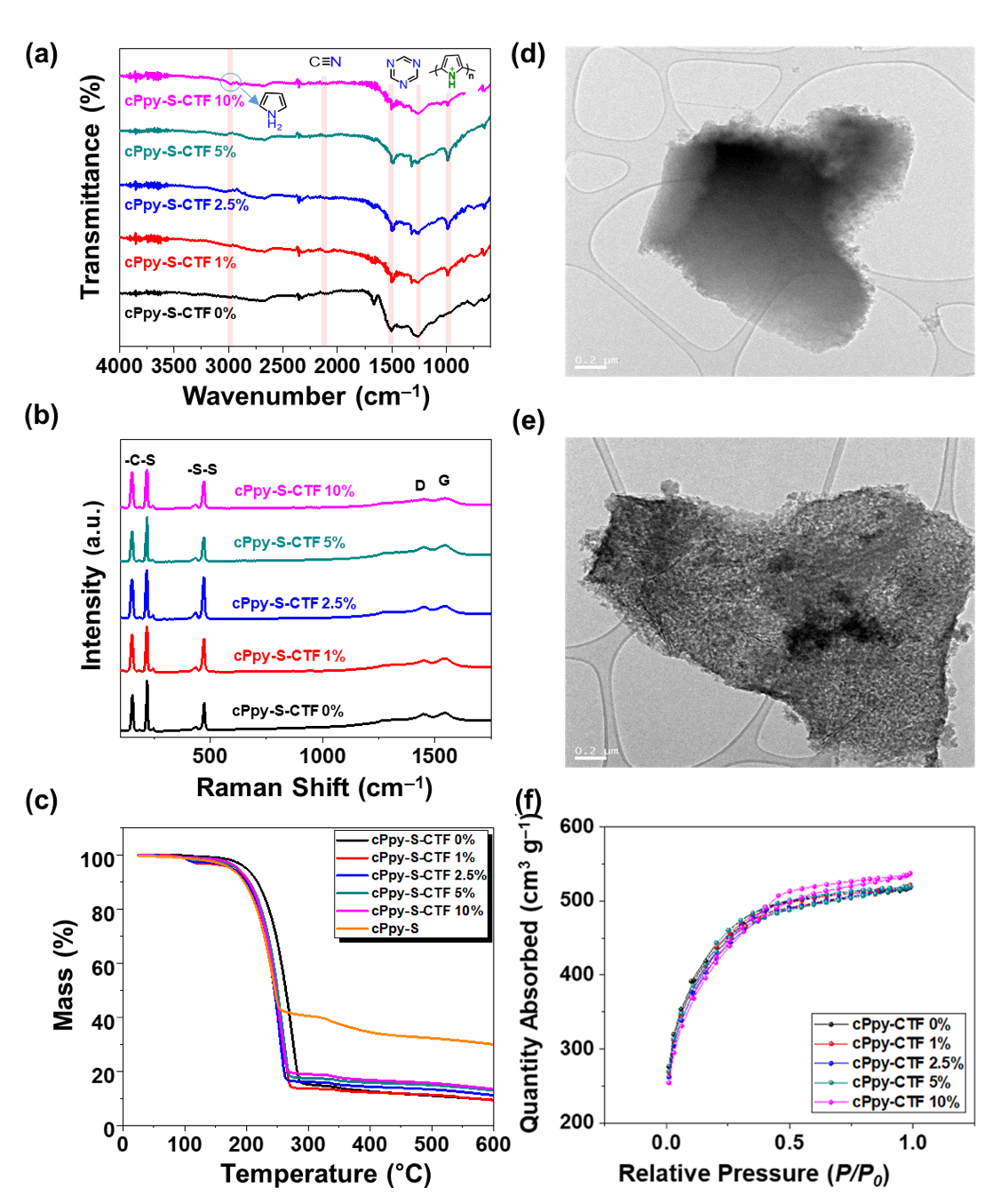
**Polysulfide adsorption test.** To prepare 50 mM Li2S6 solution, stoichiometric amounts of Li2S and elemental sulfur were dissolved in 1,3-dioxolane /1,2-dimethoxyethane solution (1:1 in volume ratio) and stirred at 80 oC for 72 h. The Li2S6 solution was then diluted to 3 mM for adsorption tests. All the cPpy-CTFs were dried under vacuum at 60 oC overnight prior to the adsorption tests.

**Electrochemical characterization of cPpy-S-CTFs.** All battery cells were tested in the form of CR2032-type coin cells. The synthesized composites were ground and mixed with carbon black and PVDF binder in NMP (70:20:10 in a mass ratio) to form slurries. The prepared slurries were coated onto aluminum foil (20 m, Hohsen, Japan) using the doctor blade technique and dried overnight in a convection oven at 60 oC. Each coin cell was assembled in an Ar-filled glove box and a Li metal disc was used as the counter and reference electrode. The electrolyte was LiTFSI (1.0 M) and LiNO3 (0.2 M) dissolved in solvent mixture of 1: 1 (v / v) DOL / DME. The polypropylene membrane (Celgard 2400) was used as the separator. The ratio of electrolyte: sulfur was ~15 mLelectrolyte gsulfur–1 for all measurements. The galvanostatic tests were programed by a PEBC050.01 battery cycler (PNE solution, South Korea). The cycling measurements were performed over a voltage range of 1.8–2.7 V *vs*. Li / Li+ and the EIS analysis was conducted in the frequency range of 1 MHz–0.01 Hz with an amplitude of 10 mV at open circuit potential using VSP (Bio-Logic, France). Cyclic voltammetry (CV) measurements were conducted between 1.8–2.7 V *vs*. Li / Li+ at a scan rate of 0.05–0.5 mV s–1 by using a WBCS 3000 battery cycler (Wonatech, South Korea). The current densities and specific capacities were all calculated based on sulfur weight only.

RESULTS AND DISCUSSION

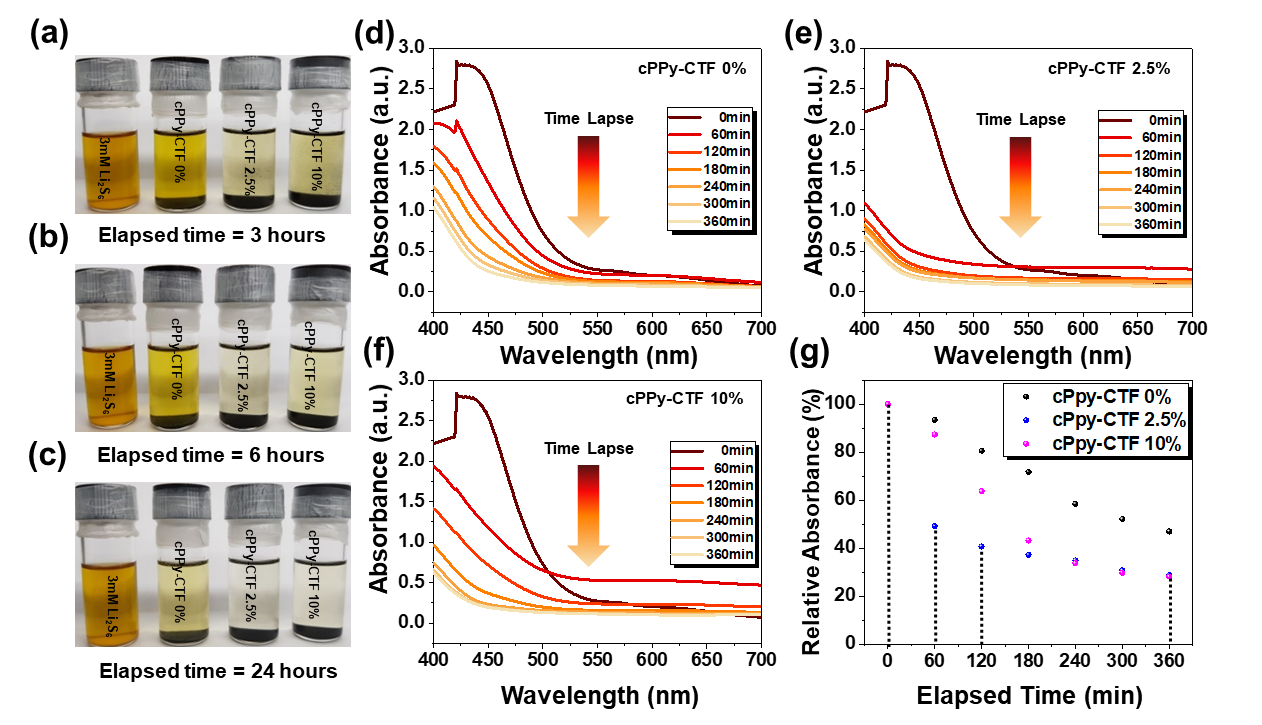
Elemental sulfur mediated synthesis of covalent triazine frameworks (S-CTF and SF-CTF) enabled in-situ growth of a conjugated polymeric host while simultaneously leading to homogenous distribution of sulfur and its chemical immobilization to the backbone. The limited conductivity of CTFs synthesized at 400 oC and the presence of heteroatoms with moderate binding affinity towards Li+ through ion-dipole interactions limit the electrochemical performance of these systems. The conductivity issue of CTFs can be lessened markedly by in-situ growth of conductive polymer during the synthesis of CTFs, which also enables its uniform distribution within the CTF network. In this sense, we identified cPpy as a conductive polymeric additive due to its high ionic and electronic conductivity and the presence of quaternary N+ sites offering high binding affinity with Sn2–. The synthesis of cPpy-S-CTF was accomplished (Figure 1) *via* a simple one-step route, that is, reacting tetrafluoroterephthalonitrile and elemental sulfur initially at 160 °C and afterwards at 400 °C in the presence of different cPpy amounts of 0, 1, 2.5, 5, and 10 wt% with respect to tetrafluoroterephthalonitrile weight. Sulfur-to-cPpy/monomer ratio was fixed to be 3:1 for all cPpy-S-CTFs. The formation of CTF backbone through the trimerization of tetrafluoroterephthalonitrile was accompanied by the homogeneous distribution of sulfur and its insertion to both CTF backbone and cPpy *via* perfluoroaryl‐elemental sulfur SNAr chemistry and radicalic C-H insertion, respectively. As a control experiment, we also synthesized sulfur-free cPpy-CTF by synthesizing CTF in the presence of different cPpy amounts of 0, 1, 2.5, 5, and 10 wt% (with respect to the weight of terephthalonitrile) under ionothermal reaction conditions at 400 oC for 40 h using ZnCl2.

In order to investigate the formation of cPpy-S-CTF, FT-IR analysis was conducted (Figure 2a). The disappearance of nitrile stretching band at 2218 cm–1 along with the appearance of triazine bands at 1321 and 1509 cm–1 supports the designated synthesis of cPpy-S-CTFs.66 The successful integration of cPpy in cPpy-S-CTF was verified by the existence of the quinonoid bipolaron structure of doped cPpy at 973 cm–1, 67-69 which is absent for the S-CTF without cPpy. Moreover, with increasing cPpy content, the stretching vibration of N–H was observed at 2986 cm–1 which further proves the addition and structural integrity of cPpy. Importantly, these data collectively suggest that the presence of cPpy in the reaction mixture did not interrupt the formation of 2D CTF. Dispersive Raman analysis was performed (Figure 2b) to probe the formation of 2D CTF. The



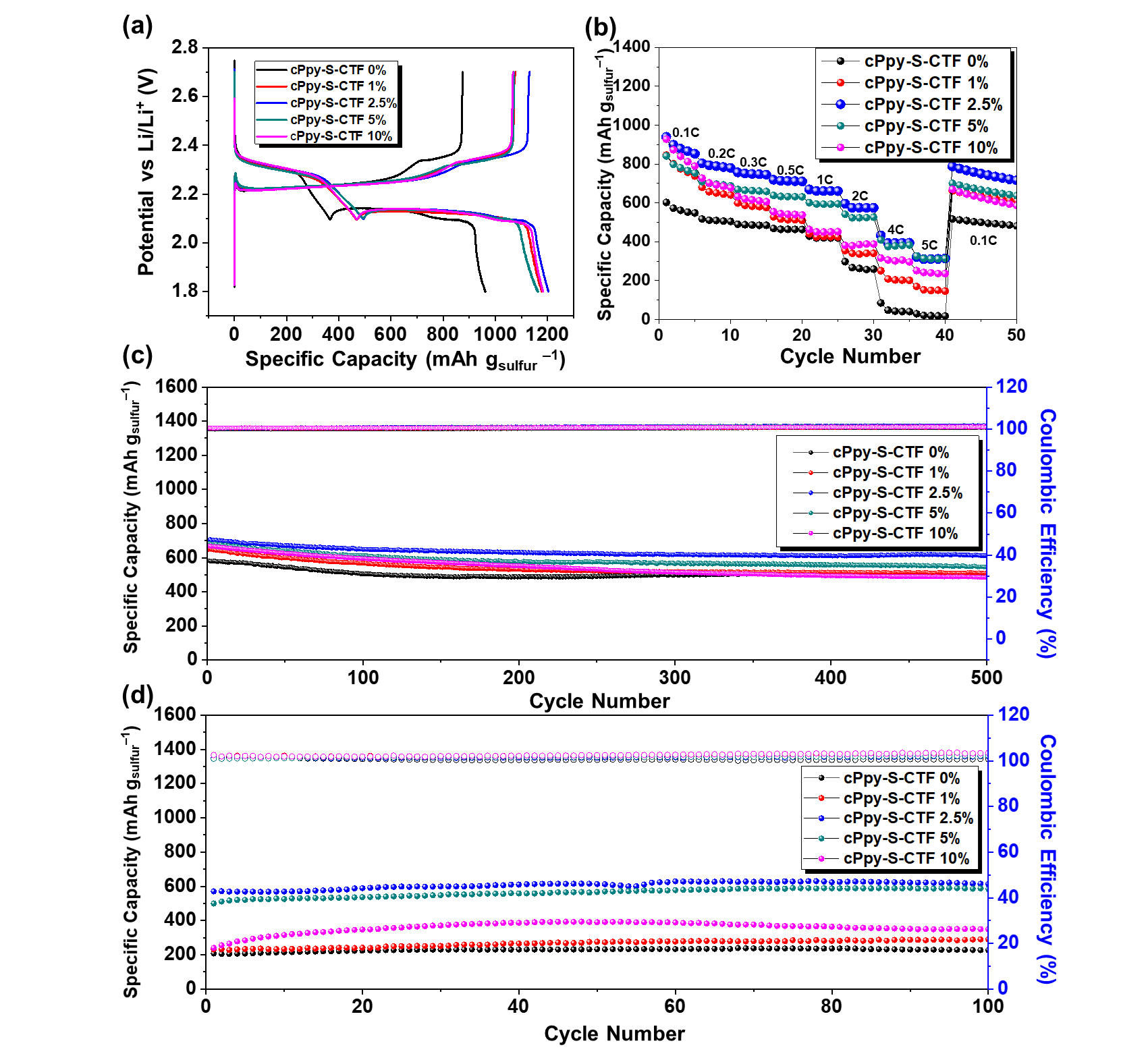
**Figure 2.** Structural analysis of various cPpy-S-CTFs. (a) FT-IR spectra. (b) Raman spectra. (c) TGA curves obtained under N2 atmosphere. TEM images of (d) cPpy-S-CTF 0% cPpy and (e) cPpy-S-CTF 2.5% cPpy. (f) N2 adsorption-desorption isotherms measured at 77 K.

appearance of D and G bands at 1446 and 1535 cm−1, respectively, indicates the graphitic nature of CTF, which was also reflected in the ID/IG ratios close to 1 (Table S1). Interestingly, since the ID/IG ratio was unaffected by the addition of cPpy, it further indicates the inert nature of cPpy to the formation of CTF. In addition, C-S stretching bands were observed at 234 and 162 cm−1 and S-S band at 464 cm−1, confirming the covalent bonding of sulfur chains to the cPpy and CTF backbones. We also performed (Figure 2c) TGA under N2 atmosphere to assess the sulfur contents of cPpy-S-CTFs with different amounts of cPpy. In all the cPpy-S-CTF series with cPpy contents of 0-10 wt%, the sulfur contents were found to be in the narrow range of 81 to 83 wt%, which points to the insertion of sulfur to the cPpy backbone. TGA analysis of S-cPpy synthesized under the same experimental conditions by reacting cPpy and elemental sulfur showed a relatively low sulfur content of 57 wt% indicating the importance of SNAr chemistry to accomplish the high sulfur loadings of cPpy-S-CTFs. Powder X-ray diffraction (PXRD) analysis (Figure S1) elucidated the presence of physically trapped crystalline sulfur domains within the framework.70 Furthermore, the bonding nature of cPpy-S-CTFs was examined (Figure S2, S3) by XPS over a range of binding energies corresponding to the C 1s and N 1s. The C 1s spectra of the cPpy-S-CTFs exhibited C−C bonding peaks of the phenyl and pyrrole moieties at 284.8 eV.71 Their C 1s spectra also showed C−S and triazine peaks at 285.6 and 286.5 eV, respectively.52 On the other hand, the C 1s spectrum of cPpy showed C−C, C−N−H bond and π−π\* satellite peaks at 284.8, 286.2 and 290.4 eV, respectively, which were also observed in cPpy-S-CTFs.72 In addition, the N 1s spectra of cPpy-S-CTFs revealed triazine N=C−N, pyrrolic N−H and C−N+ peaks at 398.4, 399.8 and 401.7 eV, respectively.68,73-75 These data verify the coexistence of CTF and cPpy in the cPpy-S-CTFs. FE-SEM analysis was performed (Figure S4) in order to elucidate the effect of cPpy on the morphology of cPpy-S-CTFs. Notably, even with the addition of 1 wt% cPpy, significant changes in the morphology of cPpy-S-CTFs were observed. In particular, cPpy-S-CTF 2.5%



**Figure 3.** Visual effects of the 3 mM Li2S6 in DOL/DME (1:1 v/v) solution when exposed to various cPpy-CTFs over 3, 6 and 24 h (a, b, c). Time dependent UV–Vis absorption spectra of cPpy-CTF 0 (d), 2.5 (e), and 10% (f) in 3 mM Li2S6 in DOL/DME (1:1 *v*/*v*) solution. (g) Plots of UV–Vis absorbance changes with time.

showed the most integrated morphology, which is likely to be attributed to homogeneous distribution of cPpy. However, direct analysis of the distribution of cPpy was infeasible because the signal of cPpy in energy dispersive X-ray spectroscopy (EDX) was weak. By contrast, cPpy-S-CTFs with other contents of cPpy displayed particulate or island-like morphology. The formation of the 3D interconnected structure was verified (Figure 2d, e) by transmission electron microscopy (TEM) analysis; while cPpy-S-CTF 0% showed a plain lamella structure reflective of 2D morphology of S-CTF, cPpy-S-CTF 2.5% cPpy revealed certain contrast indicating its porous morphology owing to the formation of nanochannels mediated by cPpy. We have also measured (Figure 2f) the surface areas of cPpy-CTFs 0, 1, 2.5, 5 and 10% using N2 adsorption isotherms measured at 77 K. The surface areas were in the range of 1483–1561 m2 g−1 for all cPpy-CTFs (Figure S5-S9, Table S2) while they all showed type I isotherms pointing to the dominant presence of micropores. Interestingly, we also observed growth of H4 hysteresis for cPpy-CTFs with an increase in the cPpy content, which indicates the increased mesopores. This feature was not observed in the absence of cPpy (cPpy-CTF 0%) due to the efficient stacking of 2D CTF layers. As expected, increasing cPpy content slightly decreased the surface area and the micropore content, accompanied by an increase in the mesopore content. The pore size distribution analysis using NLDFT also revealed (Figure S10) gradual increase in the mesopore content with increasing cPpy amount. In order to probe the impact of cPpy on the Li-PS affinity of the framework, we performed (Figure 3) a polysulfide absorption test by monitoring the time-dependent change in the PS concentration using the UV–Vis spectroscopy. The cPpy-CTF (7 mg) 0, 2.5, and 10% were added to 3 mM Li2S6 in 1,3-dioxolane (DOL) / 1,2-dimethoxyethane (DME) (1:1 *v*/*v*) solution and monitored for 3, 6 and 24 h (Figure 3a–c). Notably, the presence of cPpy in cPpy-CTFs substantially improved the Li-PS uptake kinetics (Figure 3d–f) originating from strong ionic interactions between a soft acid, quaternary nitrogen, and a soft base, Sn2–. The Li-PS uptakes of cPpy-CTFs 1 and 5% were also compared (Figure S11 a–g) with those of cPpy-CTFs 0, 2.5, and 10%. Remarkably, cPpy-CTF 2.5% showed almost 50% Li-PS uptake in 1 h, whereas the cPpy-CTFs 0, 1, 5 and 10% showed only 7%, 2%, 18% and 13% Li-PS uptake, respectively, after the same time duration (Figure 3g and Figure S11 g). This result is rather significant as it shows that there is an optimal spot in the amount of cPpy to realize efficient interactions with the Li-PS. We speculate that the faster uptake kinetics of cPpy-CTF 2.5% originates from low aggregation and homogeneous dispersion of cPpy within the polymer network. Interestingly, the Li-PS uptake of cPpy itself was (Figure S11 f, g) lower than those of all the cPpy-CTFs pointing to the synergistic effect between cPpy and CTF and also the detrimental role of aggregation of cPpy chains in the Li-PS uptake.



**Figure 4.** Electrochemical performance of various cPpy-S-CTFs. (a) Comparison of the first discharge-charge profiles of cPpy-S-CTFs at 0.05C in the potential range 1.8–2.7 V (1C=1675 mA g–1). (b) Rate performance of cPpy-S-CTFs (0–10%) evaluated at various C-rates (0.1–5C). (c) Cycling performance and Coulombic efficiencies of cPpy-S-CTFs at 0.5C and 0.8 mgsulfur cm–2 for 500 cycles. (d) Cycling performance and Coulombic efficiencies of cPpy-S-CTFs at 0.2C and 4.0 mgsulfur cm–2 condition for 100 cycles.

We investigated (Figure 4) the electrochemical performance of cPpy-S-CTFs as active cathode materials in Li–S batteries through galvanostatic measurements. For these tests, CR2032-type coin cells were prepared by using Li metal as the counter/reference electrode. The first discharge–charge voltage profiles of cPpy-S-CTF 0, 1, 2.5, 5, and 10% are shown in Figure 4a when tested at a current density of 0.05C (1C=1675 mA g–1) with 0.8 mgsulfur cm–2 loading. We observed discharge capacities of 961.2, 1177.6, 1203.4, 1162.9, and 1182.6 mAh g–1 and initial coulombic efficiency (ICE) values of 91.1, 91.5, 94.0, 92.2, and 90.3%, for cPpy-S-CTF 0, 1, 2.5, 5, and 10%, respectively. Considering the unique properties of cPpy in cPpy-S-CTFs, namely, high ionic and electronic conductivity as well as ability to bind with polysulfide anions, we investigated (Figure 4b) their rate performance by invoking different C-rates from 0.1C to 5C and compared the performance of cPpy-S-CTF 0, 1, 2.5, 5, and 10%. The impact of cPpy addition was conspicuous as the rate capability of cPpy-S-CTF 2.5, 5% was clearly superior to that of cPpy-S-CTF 0, 1, and 10%. The distinct capacities observed at high C-rates represent a kinetically efficient (de)lithiation process in cPpy-S-CTFs engaging cPpy.

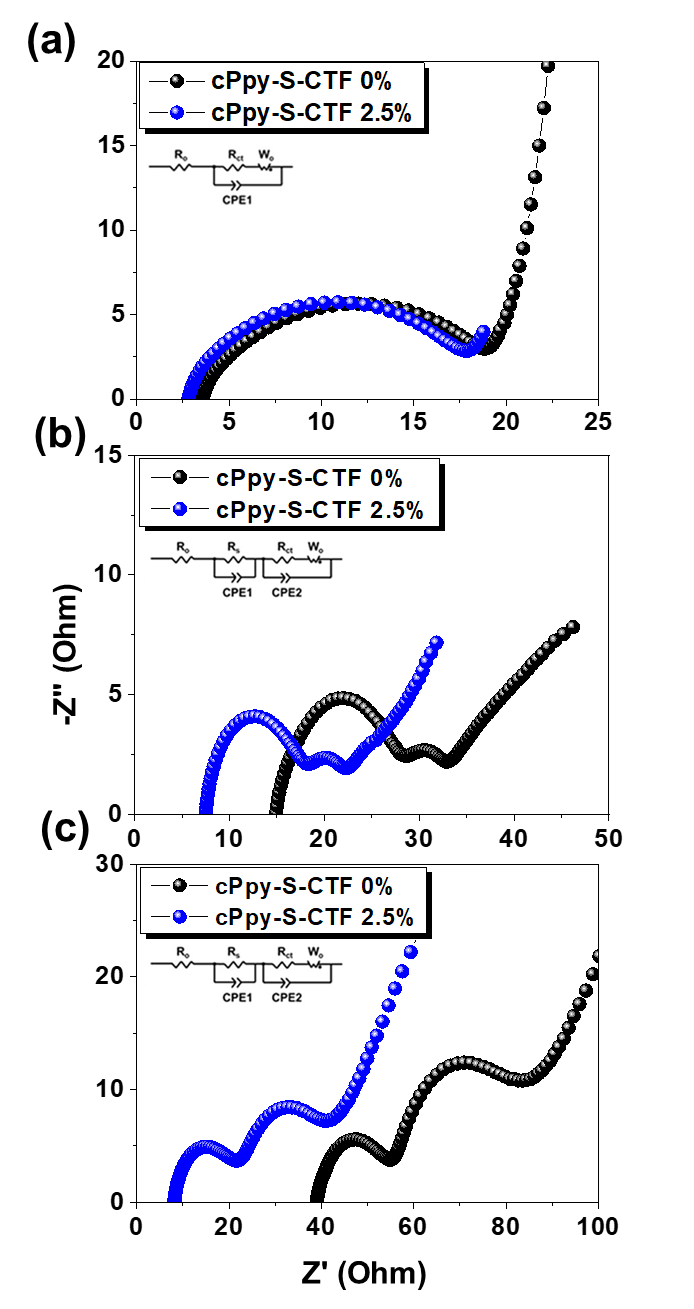
In an attempt to elucidate the effect of cPpy on the cycling performance of cPpy-S-CTFs, these electrodes with 0.8 mgsulfur cm–2 loading were cycled at 0.5C. Accordingly, the initial discharge capacities of cPpy-S-CTFs 0, 1, 2.5, 5, 10% were found (Figure 4c) to be 582.2, 647.2, 702.9, 683.3, and 667.9 mAh g–1 along with capacity retentions of 86.1, 78.5, 86.8, 79.8, and 72.5% after 500 cycles, respectively. Notably, the cycling performance of cPpy-S-CTF 2.5% was better than that of all the other samples due to the homogeneous distribution of cPpy and also the accessibility of cationic binding sites for the polysulfide anions, in perfect agreement with the Li-PS uptake experiments. In an effort to see the cycling stability at higher C-rates, cyclability tests were carried out (Figure S12) at 1C and 2C for all cPpy-S-CTFs with 0.8 mg cm–2 of sulfur loading. Notably, cPpy-S-CTF 2.5% achieved the highest discharge capacities of 699.4 and 631.2 mAh g–1, respectively, in the initial cycles at 1C and 2C. cPpy-S-CTF 2.5% also exhibited superior capacity retentions of 97.6% and 96.7% after 500 and 300 cycles at 1C and 2C, respectively. In order to test electrochemical performance of cPpy-S-CTFs at a higher mass loading, we increased the sulfur loadings to 4.0 mgsuflur cm–2 and cycled it at 0.2C. The initial discharge capacities of 207.8, 232.2, 570.5, 499.9, and 240.8 mAh g–1 were lower compared to those at the lower sulfur loading of 0.8 mgsulfur cm–2 for cPpy-S-CTF 0, 1, 2.5, 5 and 10% cPpy, respectively. Nevertheless, cPpy incorporation of 2.5 wt% resulted in superior performance to all other samples tested, thus reconfirming the beneficial role of cPpy regardless the loading of active material. The capacity retention was measured after 100 cycles under the same conditions (Figure 4d). The discharge capacities of the cPpy-S-CTF 0, 1, 2.5, 5, and 10% cPpy after 100 cycles were 227.6, 290.0, 612.9, 583.8, and 348.6 mAh g–1, respectively. Poor electrochemical performance of cPpy alone (Figure S13) verifies the synergistic effect between cPpy and CTF backbone.

For in-depth understanding of the effect of cPpy on the Li+ ion diffusion in the framework, we performed CV measurements (Figure S14) on cPpy-S-CTF 0, 2.5 and 5% cPpy at a scan speed from 0.05 to 0.5 mV s–1. Both cathodic and anodic peak currents were proportional to the square root of the scan speeds, which obeys the following Randles-Sevcik equation (Equation 1):76

(1)

(*Ip* = peak current, *n* = number of electrons per reaction, *a* = active electrode area, *D* = diffusion coefficient of Li+, *υ* = scan velocity, *ΔCo* = Li-ion concentration gradient during the electrochemical reaction)

Since *n*, *a*, and *ΔCo* are constant values, the peak current *Ip* and the square root of the scan velocity, *υ*0.5 are proportional to each other and the slope is associated with the square root of the diffusivity of the Li ion (Figure S14 a–c). Markedly, cPpy-S-CTF 2.5% exhibited the highest slope values for all of the cathodic and anodic reactions, which implies that the Li+ diffusion at this cPpy content is most facile.



**Figure 5.** Nyquist plots of cPpy-S-CTF 0 and 2.5%. (a) Before cycling, (b) after 100th charge, and (c) after 100th discharge.

We also performed (Figure 5a–c) electrochemical impedance spectroscopy (EIS) measurements on cPpy-S-CTF 0% and cPpy-S-CTF 2.5%. The Nyquist plots of the two electrodes prior to cycling showed semicircles in the high and mid-frequency regimes and sloping lines in the low-frequency regime (Figure 5a). The high-frequency intercept of the real axis represents the bulk resistance (*Ro*) of the cell composed of the electrolyte and electrode resistance.77 The semicircle in the middle to the high-frequency regime represents the interface charge transfer resistance (*Rct*),78 and the sloping line in the low-frequency regime relates to Li-ion diffusion at the cathode, called Warburg impedance (*Wo*). Prior to cycling, *Rct* of cPpy-S-CTF 2.5% cPpy was slightly lower than that of cPpy-S-CTF 0%. After 100 cycles (Figure 5c), cPpy-S-CTF 0% showed drastically increased bulk resistance compared to that of cPpy-S-CTF 2.5% cPpy (40.3 *vs*. 8.7 Ω). This phenomenon is attributed to the fact that polysulfides adsorption by cPpy prevents27,79 from increasing the viscosity of the electrolyte by Li-PS dissolution more effectively compared to the case of cPpy-S-CTF 0%. Moreover, after cycling, the semicircles of both cells were split into two small semicircles, both of which were clearly smaller for cPpy-S-CTF 2.5%. The semicircle in the high-frequency regime relates to surface resistance (*Rs*) corresponding the deposition on the surface of the electrode and the agglomeration of Li2S2 / Li2S layer.80 The semicircle in the intermediate frequency regime relates to the charge transfer process at the conductive interface.81 Thus, the smaller semicircles of cPpy-S-CTF 2.5% reflect its lower *Rs* and *Rct* during cycling than that of cPpy-S-CTF 0%. In order to study the effect of the cPpy concentration more comprehensively, the EIS data of cPpy-S-CTFs with varying cPpy contents were compared (Figure S15). Notably, cPpy-S-CTF 2.5% exhibited (Table S3) the lowest bulk (*Ro*) and interfacial (*Rs* + *Rct*) resistance among all the cPpy contents tested. These results demonstrate that 2.5% cPpy is the optimal condition for achieving the facile electronic and ionic transport.

CONCLUSIONS

In summary, we have introduced a 3D hybrid polymer composite in which 1D charged conducting polymer is blended with sulfur-embedded 2D conjugated porous polymer network. The in-situ formation of CTF backbone in the presence of elemental sulfur facilitated the homogeneous distributions of sulfur domains alongside cPpy and also enabled high sulfur contents above 80% through the perfluoroaryl‐elemental sulfur SNAr chemistry. Notably, cPpy incorporation presented not only high affinity cationic anchoring sites for Li-PS but also well-defined conducting pathways to expedite the Li-ion and electron transport. The homogenous distribution of 2.5 wt% cPpy in the new framework were found to be optimal in realizing the efficient binding between soft acid N+ and soft base Sn2–. In a broader context, this study reveals the potential of supramolecular chemistry in Li-S batteries, wherein the optimal binding affinity for polysulfide anions as well as the accessibility of the binding sites are critical in sustaining electrode frameworks and achieving long-term cyclability. In addition, the present strategy represents a major leap for organosulfur polymers suffering from low electronic/ionic conductivity at substantial sulfur mass loadings. Beyond sulfur cathodes, the findings in this study are generally applicable to post-LIB electrodes that undergo large volume change and unwanted dissolution of reaction products.

ASSOCIATED CONTENT

**Supporting Information**.

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Notes  
The authors declare no competing financial interest

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