

# High-Capacity and Stable Sodium-Sulfur Battery Enabled by Confined Electrocatalytic Polysulfides Full Conversion

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The efficient polysulfide capture and reversible sulfur recovery during reverse charging process are critical to exploiting the full potential of room temperature Na–S batteries. Here, based on a core-shell design strategy, the structural and chemical synergistic manipulation of sodium polysulfides quasi-solid-state reversible conversion is proposed. The sulfur is encapsulated in the multi-pores of 3D interconnected carbon fiber as the core structure. The  $\text{Fe}(\text{CN})_6^{4-}$ -doped polypyrrole film serves as a redox-active polar shell to lock up polysulfides and promote complete polysulfide conversion. Importantly, the short-chain  $\text{Na}_2\text{S}_4$  polysulfides are reduced to  $\text{Na}_2\text{S}$  directly leaving with a small fraction of soluble intermediates as the cation-transfer medium at the core/shell interface, and freeing up formation of solid  $\text{Na}_2\text{S}_2$  incomplete product. Further, the redox mediator with open Fe species electrocatalytically lowers the  $\text{Na}_2\text{S}$  oxidation energy barrier and renders the high reversibility of electrodeposited  $\text{Na}_2\text{S}$ . The tunable quasi-solid-state reversible sulfur conversion under versatile polymer sheath greatly enhances sulfur utilization, affording a remarkable capacity of  $1071 \text{ mAh g}^{-1}$  and a stable high capacity of  $700 \text{ mAh g}^{-1}$  at  $200 \text{ mA g}^{-1}$  after 200 cycles. The confined electrocatalytic effect provides a strategy for tuning electrochemical pathway of sulfur species and guarantees high-efficiency sulfur electrochemistry.

$\text{LiMn}_2\text{O}_4$ , and  $\text{LiFePO}_4$ ) with optimized structures are approaching their upper capacity limits. In comparison, cathodes rely on conversion chemistry render the sulfur with overwhelming advantages, such as high theoretical discharge capacity of  $\approx 1672 \text{ mAh g}^{-1}$  (versus  $\text{LiCoO}_2$ ,  $137 \text{ mAh g}^{-1}$ ) and energy density of  $\approx 1274 \text{ Wh kg}^{-1}$  ( $\text{S}||\text{Na}$  versus  $\text{LiCoO}_2||\text{graphite}$ ,  $371 \text{ Wh kg}^{-1}$ ).<sup>[2]</sup> More importantly, the impressive progress achieved on Li–S technologies provides an attractive opportunity to directly integrate the stable metal anode and high capacity cathode chemistry into Na–S cells.<sup>[3]</sup> Nevertheless, Na–S batteries share a similar sulfur (de)sodiation mechanism to Li–S chemistry but face much more challenges, especially in terms of low reversible capacity and fast capacity fade during cycling.<sup>[2b,c,4]</sup>

To meet the capacity and durability targets for promising Na–S cell commercialization, many novel sulfur scaffolds including porous carbon,<sup>[5]</sup> metallic oxides,<sup>[2b,6]</sup> conductive polymers,<sup>[7]</sup> and metal-organic frameworks (MOFs)<sup>[8]</sup> have been investigated, and it has been revealed that the morphology, porosity, and polarity have a significant effect on intermediate trapping efficiency. The polar hosts exhibit intrinsic sulfiphilic property that could “lock-up” polysulfide through strong polar-polar interactions.<sup>[4a,9]</sup> Encapsulating sulfur with polar conductive carrier results in well

## 1. Introduction

Room temperature Na–S batteries, first reported in 2006, have drawn substantial attention due to low cost (\$300–500  $\text{kWh}^{-1}$ ) and abundance of resources, and are being considered as one of the most promising devices for large-scale adoptions.<sup>[1]</sup> Traditionally, the Li-based intercalative cathodes (e.g.,  $\text{LiCoO}_2$ ,

oxides,<sup>[2b,6]</sup> conductive polymers,<sup>[7]</sup> and metal-organic frameworks (MOFs)<sup>[8]</sup> have been investigated, and it has been revealed that the morphology, porosity, and polarity have a significant effect on intermediate trapping efficiency. The polar hosts exhibit intrinsic sulfiphilic property that could “lock-up” polysulfide through strong polar-polar interactions.<sup>[4a,9]</sup> Encapsulating sulfur with polar conductive carrier results in well

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confinement of polysulfide and efficient manipulation of the shuttling effect. However, insufficient emphasis was placed on accelerating the sluggish and incomplete reactivity of elemental sulfur with sodium metal. Furthermore, the slow redox kinetics of liquid-solid conversion between  $\text{Na}_2\text{S}_4$  and  $\text{Na}_2\text{S}$  is the rate-determining step of the electrochemical Na–S chemistry, and also the major limiting factor to achieve high-capacity and high-rate capability.<sup>[10]</sup> To this end, electrocatalysis concept and catalytic matrix were utilized to accelerate the conversion rates of short-chain sodium polysulfide into solid-phase  $\text{Na}_2\text{S}$ .<sup>[11]</sup> Specifically, various catalysts and redox mediator, such as Pt,<sup>[12]</sup> Au,<sup>[12]</sup> atomic cobalt,<sup>[13]</sup>  $\text{MnO}_2$ ,<sup>[6b]</sup> and MOF<sup>[6a]</sup> have been anchored on sulfur hosts to direct polysulfide electrochemical reduction path and lower the activation energy barrier of  $\text{Na}_2\text{S}$  same as in Li–S chemistry.<sup>[14]</sup> Moreover, unlike the rigid carbon framework, the integration of flexible conductive polymers could effectively alleviate the sulfur severe volumetric change during battery dynamic cycling.<sup>[7b,15]</sup> It was hypothesized that the designation of a core-shell structured sulfur host with a polar conductive

polymer film wrapping, could impede the shuttling effect and trap soluble polysulfides within inner carbon core. Additionally, embedding catalyst on the polymer framework would render strong interaction with sulfur components and further direct its sodiation pathway.

Herein, we propose a confined electrocatalytic effect to manipulate reversible polysulfides full conversion. The bifunctional sheath of  $\text{Fe}(\text{CN})_6^{4-}$ -doped polypyrrole serves as cation reservoir to boost efficient ion transfer and redox mediator to facilitate reversible fast-kinetics conversion between short-chain  $\text{Na}_2\text{S}_4$  polysulfide and  $\text{Na}_2\text{S}$  or S, directing quasi-solid-state sulfur conversion within the carbon matrix. During the reverse charging process, the electrocatalytic redox Fe centers could lower the  $\text{Na}_2\text{S}$  activation energy barrier and facilitate the high reversibility of electrodeposited  $\text{Na}_2\text{S}$ . The synergistic effect of core-shell structure and redox-active mediator in the interconnected 3D freestanding network render the assembled Na–S cell with high reversible capacity and long cycling stability.

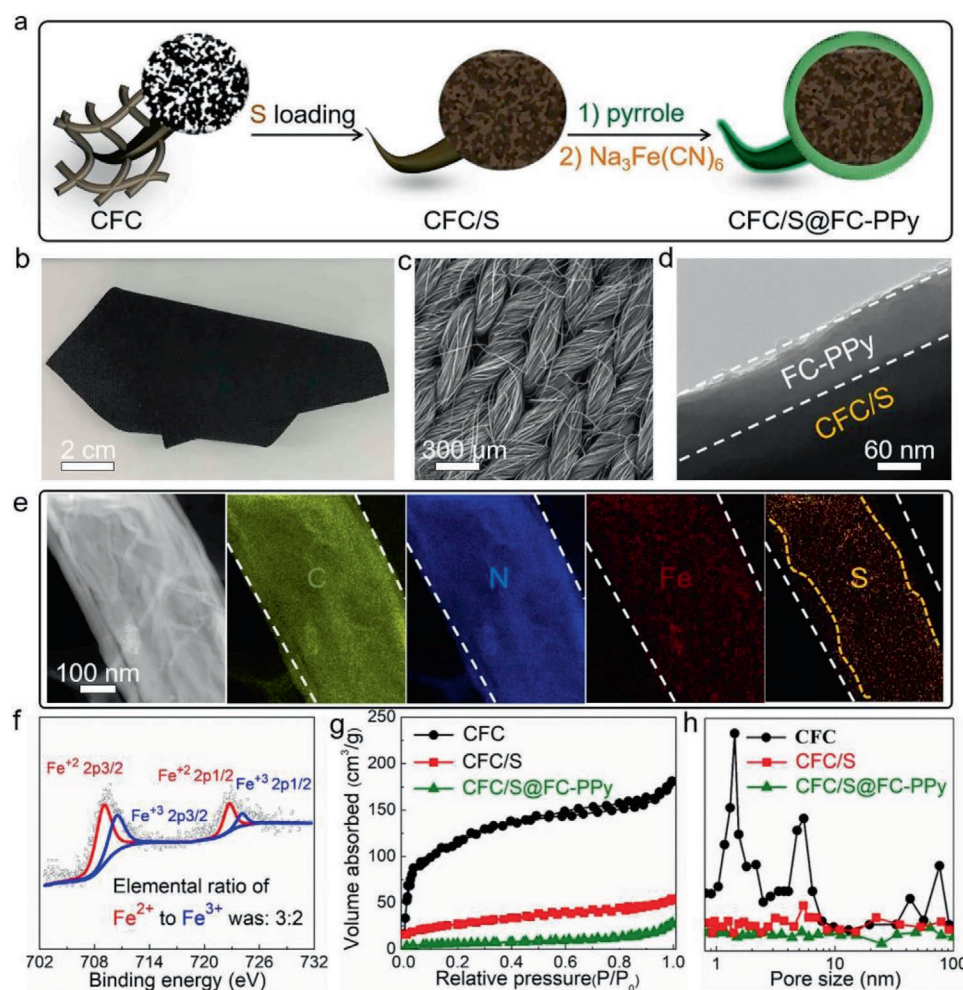


**Figure 1.** Illustration and structural characterization of freestanding sulfur cathode. a) Schematic showing the synthesis procedure for the core-shell structured flexible sulfur (CFC/S@FC-PPy) cathode with sulfur confined in the CFC micropores, and the sulfur-carbon is wrapped by flexible  $\text{Fe}(\text{CN})_6^{4-}$ -doped polypyrrole (FC-PPy) film; b) Photograph of as-prepared sulfur cathode showing its scalable preparation and good flexibility; c) SEM, d) TEM images, and e) EDS elemental mapping of CFC/S@FC-PPy; f) High-resolution XPS spectra of Fe 2p, g)  $\text{N}_2$  adsorption/desorption isotherms, and h) pore size distribution for the CFC/S@FC-PPy sample.

## 2. Results and Discussion

Our strategy for synthesizing  $\text{Fe}(\text{CN})_6^{4-}$ -doped polypyrrole (FC-PPy) wrapped S/carbon core-shell structured composite is based on the  $\text{Fe}^{(\text{III})}(\text{CN})_6^{3-}$  initiated interfacial polymerization of pyrrole monomer on carbon fiber interface,<sup>[16]</sup> as schematically illustrated in **Figure 1a**. The  $\text{Na}_3\text{Fe}(\text{CN})_6$  was reduced to form the  $\text{Na}_4\text{Fe}(\text{CN})_6$  anchored on the framework of the flexible conductive PPy. Importantly, the intimate wrapping of carbon host renders a self-stabilized redox-active sheath within the free-standing cathode. Strong polysulfide adsorption and complete conversion of short-chain sodium polysulfide can be realized simultaneously. Optical and SEM images in **Figures 1b** and **1c** clearly show the scale synthetic approach to obtain the 3D interconnected sulfur cathode, strengthening the advantages of the constructed core-shell composite for practical Na–S batteries. As shown in **Figure 1d**, the image clearly showing the polymer film as noted was uniformly adhered to the carbon matrix with a thickness of about 100 nm. The energy dispersive X-ray (EDX) elemental mapping results (**Figure 1e**) demonstrate that the sulfur was uniformly encapsulated inside the FC-PPy shell. As the typical XPS spectra displayed in **Figure 1f**, the major peaks at 708.9 and 722.6 eV matched well with Fe 2p<sub>3/2</sub> and Fe 2p<sub>1/2</sub> signals of  $\text{Fe}^{2+}$  states. In addition, characteristic peaks at 710.2 and 723.9 eV were also determined and can be ascribed to  $\text{Fe}^{3+}(\text{CN})_6^{3-}$  component, indicating the co-existence of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  elements. According to the fitted curve, the average valence state of Fe anchored on polymer framework was 2.4 and the fraction of  $\text{Fe}(\text{CN})_6^{4-}$  was about 60%, suggesting the reduction and adsorption occurred at the same time with the polymerization of pyrrole monomer. Nitrogen adsorption-desorption isotherms were recorded (**Figure 1g,h**) to investigate the structural information of carbon matrix and sulfur cathode. As shown, the surface area of pristine carbon fiber cloth (CFC) was dramatically decreased from 427 to 77 m<sup>2</sup> g<sup>−1</sup> and typical microporous structures were also missed after infusing sulfur into the hierarchal pores of the scaffold.<sup>[2a,16a]</sup> According to the thermogravimetric analysis, the sulfur content encapsulated in the porous carbon host was about 58 wt% (**Figure S1**, Supporting Information).

To further explore the polysulfide adsorption and confinement capability of the polar composite matrix, soaking and beaker cell experiments were performed and quantified using UV detection at ≈624 nm.<sup>[17]</sup> As shown in **Figure 2a**, the physical and/or electrochemical interaction between polysulfide and matrix generates discoloration and the  $\text{Na}_2\text{S}_6$  adsorption on CFC@FC-PPy should be thermodynamically favorable compared with other two counterparts. In contrast, the  $\text{Na}_2\text{S}_6$  solution exhibited a characteristic peak with intensity of 0.63. Both solutions show quick color decay after immerse sulfur matrixes due to the adsorption of polysulfides, and the peak intensity was sharply decreased to 0.06 with the addition of CFC@FC-PPy scaffold because of the strong interaction and the possible formation of the chemical bond between polar film and intermediates, which in turn ensure the nearly complete adsorption (just 9.5% sulfur lost).<sup>[16a]</sup> However, the peak intensity was maintained at about 0.39 after interaction between CFC and  $\text{Na}_2\text{S}_6$ , indicating the limited polysulfide trapping ability (62% sulfur lost) just based on physical confinement.<sup>[18]</sup>

Aligning with our expectations, a stable Na–S cell can be obtained if certain sulfur host was designed. Intensity reduction and position shift of the retrieved sample in XPS spectra confirms the existence of chemical interaction (**Figure 2b**).<sup>[19]</sup> The main peak of Fe2p was shifted from 709.48 to 709.89 eV, suggesting the electron transfer between CFC@FC-PPy and  $\text{Na}_2\text{S}_6$  upon contact with each other. The partial oxidation of  $\text{Na}_4\text{Fe}^{(\text{II})}(\text{CN})_6$  to  $\text{Na}_3\text{Fe}^{(\text{III})}(\text{CN})_6$  could be ascribed to the cation transfer. Compared with the multistep sulfur redox process, the flexible polar interfacial layer served as sodium cation reservoir could ensure rapid chemical sodiation.<sup>[20]</sup> Sodium-ion intercalation within their conduction channels along with the  $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$  redox process facilitate cation transfer from saturated  $\text{Na}_4\text{Fe}(\text{CN})_6$  to long-chain sodium polysulfide intermediates and then direct its full reduction to  $\text{Na}_2\text{S}$ . The comparative outstanding stability of CFC/S@FC-PPy cathode was further evidenced in beaker cells (**Figure 2c**) and the corresponding UV–vis spectroscopy of the cycled electrolytes as noted was also recorded in **Figure 2d**. After fully discharge, the color of electrolyte changed from colorless to yellowish with CFC hosted sulfur cathode, while there is no obvious color change when employing CFC/S@FC-PPy cathode. The sharp contrast of visual observations and UV peak intensities (0.55, 0.24, and 0.09 for CFC/S, CFC/S@PPy, and CFC/S@FC-PPy cell at ≈420 nm) further confirm that the FC-PPy film is an effective shell to “lock-up” sulfur within the carbon inner core.

The cyclic voltammetry (CV) curves of the Na–S cells at the scan rate of 0.05 mV s<sup>−1</sup> in the potential range of 1.0–2.5 V (versus Na) are compared in **Figure 3a**. Both sulfur cathodes exhibited two couples of cathodic and anodic peaks. During the cathodic scan, the first reduction peak at approximately 1.85 V was attributed to the reduction of elemental sulfur to soluble sodium polysulfides  $\text{Na}_2\text{S}_x$  ( $4 \leq x \leq 8$ ). The second reduction peak centered at around 1.60 V results from the subsequent  $\text{Na}_2\text{S}_4$  sodiated to  $\text{Na}_2\text{S}$ .<sup>[4a,10a]</sup> In the successful anodic scan, the two oxidation peaks at ≈1.90 and ≈2.00 V corresponded to the reverse conversion of  $\text{Na}_2\text{S}$  to sodium polysulfides and further oxidized to  $\text{S}_8$ . Compared with CFC/S and CFC/S@PPy, the CFC/S@FC-PPy shows the largest redox current with good reversibility, demonstrating the facile polysulfide intermediate conversion and lower energy barrier, owing to the synergistic effect of 3D interconnected core-shell structure, and redox-active center endowed confined electrocatalytic effect. Notably, the CFC/S@FC-PPy exhibited distinguished second reduction peak at 1.65 V, which is the rate-determining step in Na–S chemistry during the electrochemical sodiation process. While there is just a broad hump and shift to 1.47 V in CFC/S cathode under the same testing condition, indicating the doped polymer shell can manipulate the complete conversion of  $\text{Na}_2\text{S}_4$  to S with faster electrochemical kinetics.<sup>[10a]</sup> In addition, the doped polymer also features a pair of redox peaks at 2.2 and 2.3 V indicates the reversible  $\text{Fe}^{(\text{II})}/\text{Fe}^{(\text{III})}$  conversion accompanying the intercalation of Na<sup>+</sup> ions.<sup>[16b]</sup> As demonstrated in **Figure S2**, Supporting Information, the incorporated functional polymer shell facilitates the formation of an efficient 3D interconnected charge transfer route, resulting in a relatively lower charge-transfer resistance (66 Ω cm<sup>2</sup>, 121 Ω cm<sup>2</sup> for CFC/S electrode). The momentary electrochemical response of  $\text{Na}_x[\text{Fe}(\text{CN})_6]^{3/4-}$  redox center was proved to be useful in

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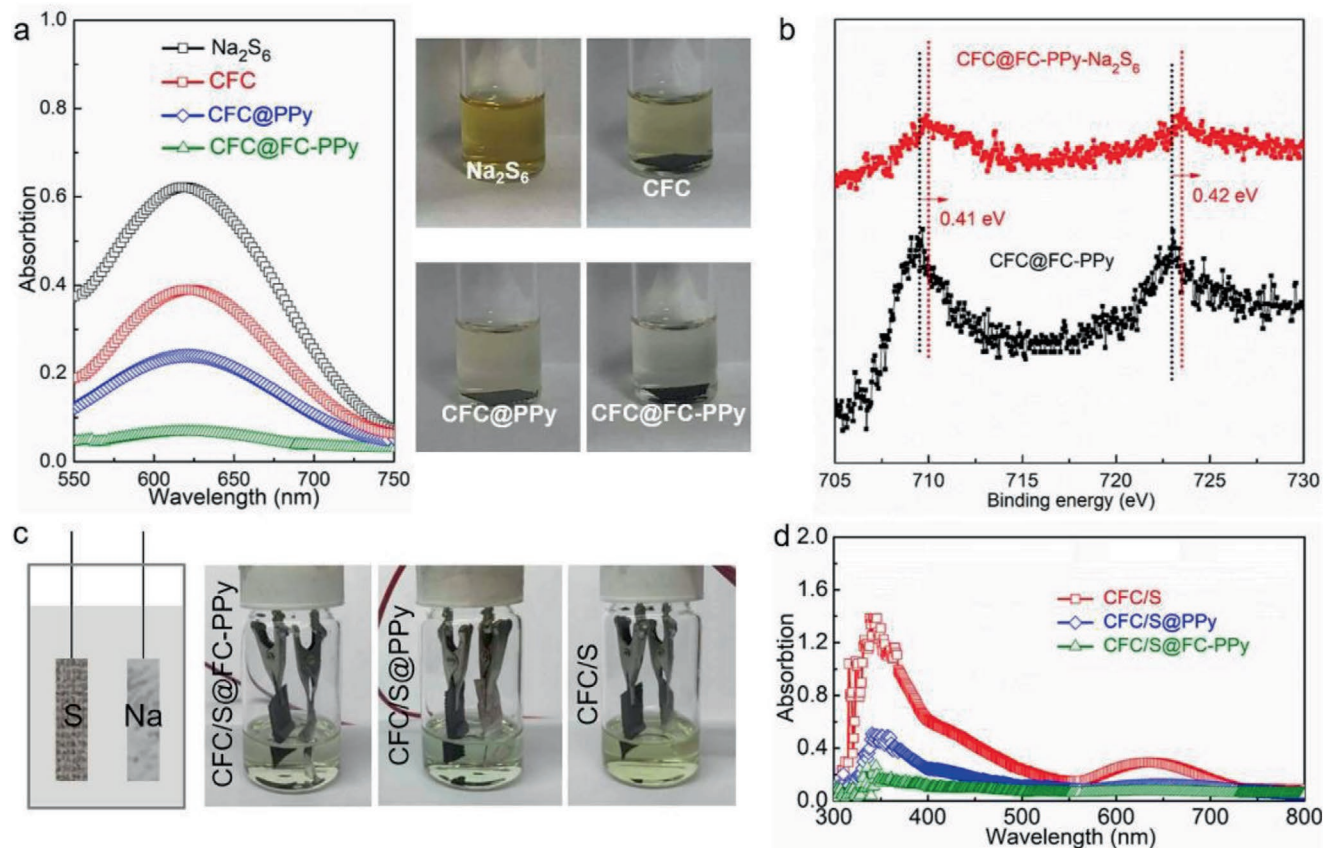


**Figure 2.** The core-shell structured CFC@FC-PPy framework has outstanding capability in adsorbing and trapping sodium polysulfide. a) Visual discrimination of CFC- $\text{Na}_2\text{S}_6$ , CFC@PPy- $\text{Na}_2\text{S}_6$ , and CFC@FC-PPy- $\text{Na}_2\text{S}_6$  in TEGDME after 20 min, and UV-vis adsorption spectra of the solutions after adsorption test; b) Comparison of high-resolution XPS spectra of Fe2p for CFC@FC-PPy and CFC@FC-PPy- $\text{Na}_2\text{S}_6$ ; c) Schematic of the Na-S beaker cell and change of electrolyte color after initial fully discharge at 50 mA  $\text{g}^{-1}$ , and d) UV-vis adsorption spectra of the electrolyte in (c).

constructing cation reservoir layer and 4 times increase of the diffusion kinetics of  $\text{Na}^+$  ( $9.1 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  versus  $2.2 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  for CFC/S). The discharge/charge profiles of CFC/S, CFC/S@PPy, and CFC/S@FC-PPy cathodes are shown in Figure 3b. It could be clearly seen that the reversible discharge capacity of CFC/S@FC-PPy is 1071 mAh  $\text{g}^{-1}$  at 100 mA  $\text{g}^{-1}$ , which is about 1.32 and 1.88 times larger than the capacity of CFC/S@PPy (814 mAh  $\text{g}^{-1}$ ) and CFC/S (570 mAh  $\text{g}^{-1}$ ) cathodes, and closer to the theoretical discharge capacity of S (1672 mAh  $\text{g}^{-1}$ ). The pristine carbon cloth is not a good substrate to support sulfur and the activation process facilitates the formation of 3D hierarchical interconnected porous scaffold (Figure S3, Supporting Information). The dramatic capacity difference may stem from different sulfur conversion route and sodiation depth.<sup>[12]</sup> Further, the initial charging period was highlighted, the lower overpotential suggests the confined electrocatalytic FC-PPy center could lower the  $\text{Na}_2\text{S}$  activation energy barrier and the electrodeposited  $\text{Na}_2\text{S}$  have much higher electrochemical activity.<sup>[13,22]</sup> As compared in Figure S4, Supporting Information, it is evident that the capacity increase of sulfur cathodes with varied carbon substrates was mainly contributed by sulfur redox process and strong interaction of active component with the doped functional sheath. The capacitive and pseudocapacitive contributions of CFC and

CFC@FC-PPy were 35.8 and 79.5 mAh  $\text{g}^{-1}$  at 100 mA  $\text{g}^{-1}$ , respectively, and 20.7 and 67.3 mAh  $\text{g}^{-1}$  at 1000 mA  $\text{g}^{-1}$ . To investigate the improvements on electrochemical sulfur conversion kinetic by the polymer shell confined electrocatalytic process and the corresponding mechanism, in situ Raman, ex situ XRD, and ex situ XPS analysis were performed. As illustrated in Figure 3c, when the CFC/S@FC-PPy||Na cell is discharged from 1.7 to 1.0 V, the long-chain and short-chain polysulfides Raman vibrational peaks were diminished and just one peak at  $\approx 428 \text{ nm}$ , indexed to the  $\text{Na}_2\text{S}$  characteristic peak, was generated at the fully discharged state.<sup>[4a,6a,18a]</sup> This means that FC-PPy can catalyze  $\text{Na}_2\text{S}_4$  complete conversion. While some irreversible  $\text{Na}_2\text{S}_2$  was reflected in the XRD patterns in CFC/S@PPy electrode (see Figure 3d), indicating that the confined intermediates are more fully reduced to the final discharged product in CFC/S@FC-PPy than in CFC/S@PPy and CFC/S, agreeing well with CV and GCD results above. In addition, after one cycled fully discharge and charge process of CFC/S@FC-PPy, its Raman peaks at charged state are almost identical with the fresh sulfur impregnated cathode, demonstrating the fully reversible sulfur conversion within the inner core. And the entire quasi-solid-state sulfur reduction within FC-PPy wrapped carbon carrier can be written as:  $\text{S} \leftrightarrow \text{Na}_2\text{S}_{8,6} \leftrightarrow \text{Na}_2\text{S}_4 \leftrightarrow \text{Na}_2\text{S}$ . The polymer shell confined sulfur

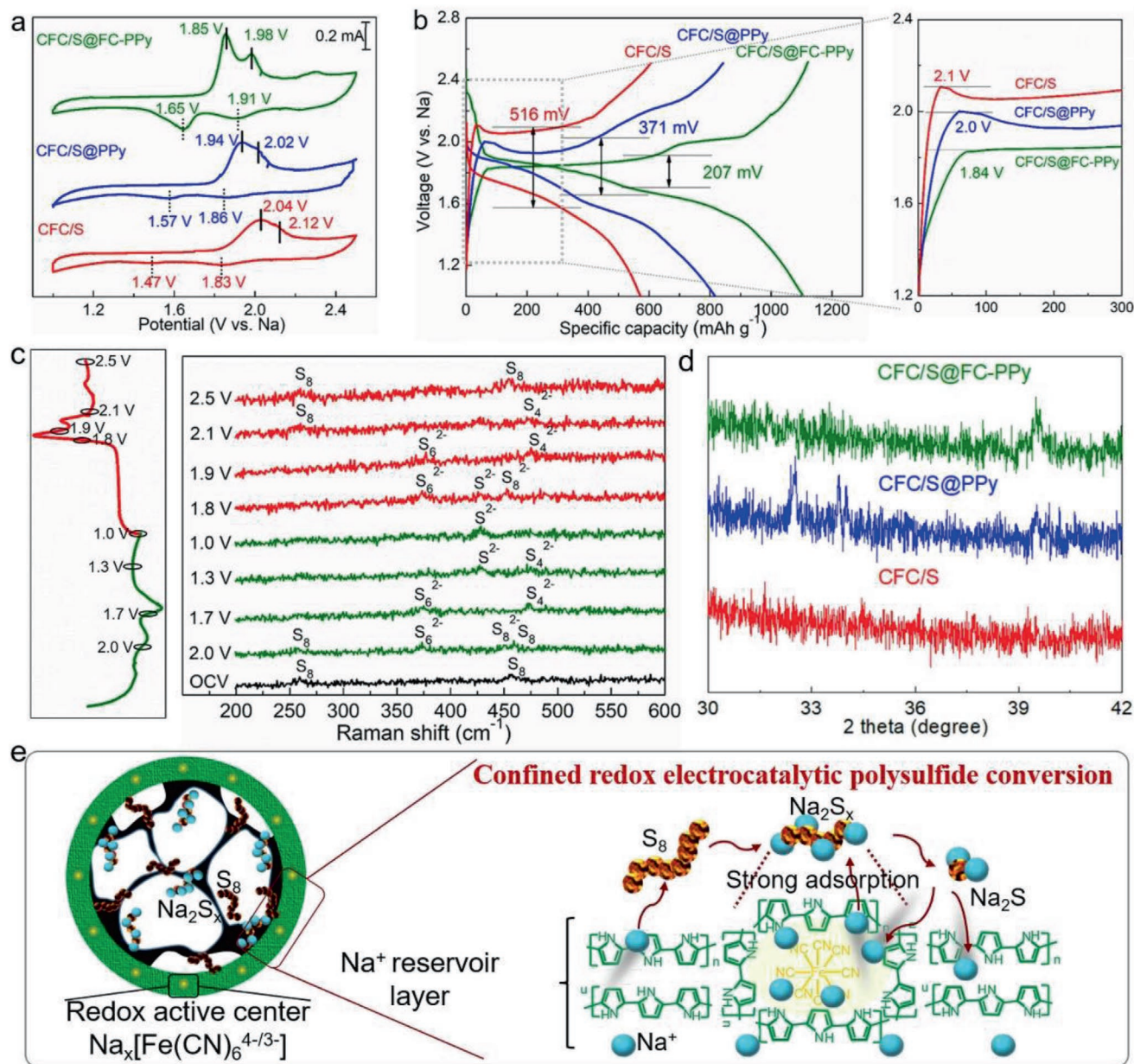


**Figure 3.** Mechanistic investigation of confined electrocatalytic quasi-solid-state reversible sulfur conversion. a) Comparison of CV of sulfur impregnated in different hosts as noted, the scan rate is 0.05 mV s<sup>-1</sup>; b) Voltage profiles of different sulfur cathodes at 100 mA g<sup>-1</sup>, the electrochemical activation behaviors for Na<sub>2</sub>S decomposition are highlighted; c) Cyclic voltammogram with the test potentials for analysis and in situ Raman spectra of CFC/S@FC-PPy; d) XRD patterns of different fully discharged sulfur cathodes; e) Scheme presenting the confined electrocatalytic polysulfide conversion during sodiation.

reduction path and polysulfide immobilization process are schematically illustrated in Figure 3e. Remarkably, the strong polysulfide adsorptivity and Na<sub>4</sub>Fe<sup>(II)</sup>(CN)<sub>6</sub>/Na<sub>3</sub>Fe<sup>(III)</sup>(CN)<sub>6</sub> redox mediator (see high-resolution Fe2p spectra at charged and discharged states, Figure S5, Supporting Information) facilitate cation transfer from Na<sub>4</sub>Fe(CN)<sub>6</sub> to sodium polysulfide and enable the facile depth fully sodiation of soluble intermediates.

Figure 4a shows rate capability of the CFC/S@FC-PPy cathode at varied current densities. When cycled at 100, 200, 300, 1000, and 2000 mA g<sup>-1</sup>, the cathode delivers reversible

capacities of 1071, 962, 803, 555, and 441 mAh g<sup>-1</sup>. As summarized in Figure 4b, when the current density increased 20 times from 100 to 2000 mA g<sup>-1</sup> (Figure S6, Supporting Information), the initial discharge capacity retention was 41.2%, 13.7% (111 mAh g<sup>-1</sup>), and 11.6% (66 mAh g<sup>-1</sup>) for CFC/S@FC-PPy, CFC/S@PPy, and CFC/S, respectively. The CFC/S@FC-PPy also shows the smallest average polarization of 248 mV among the three cells during 200 cycles, indicating the high energy efficiency and fast redox kinetics.<sup>[18b]</sup> After 200 cycles at 200 mA g<sup>-1</sup>, the CFC/S@FC-PPy cell still maintains a reversible capacity of 700 mAh g<sup>-1</sup>, corresponding to

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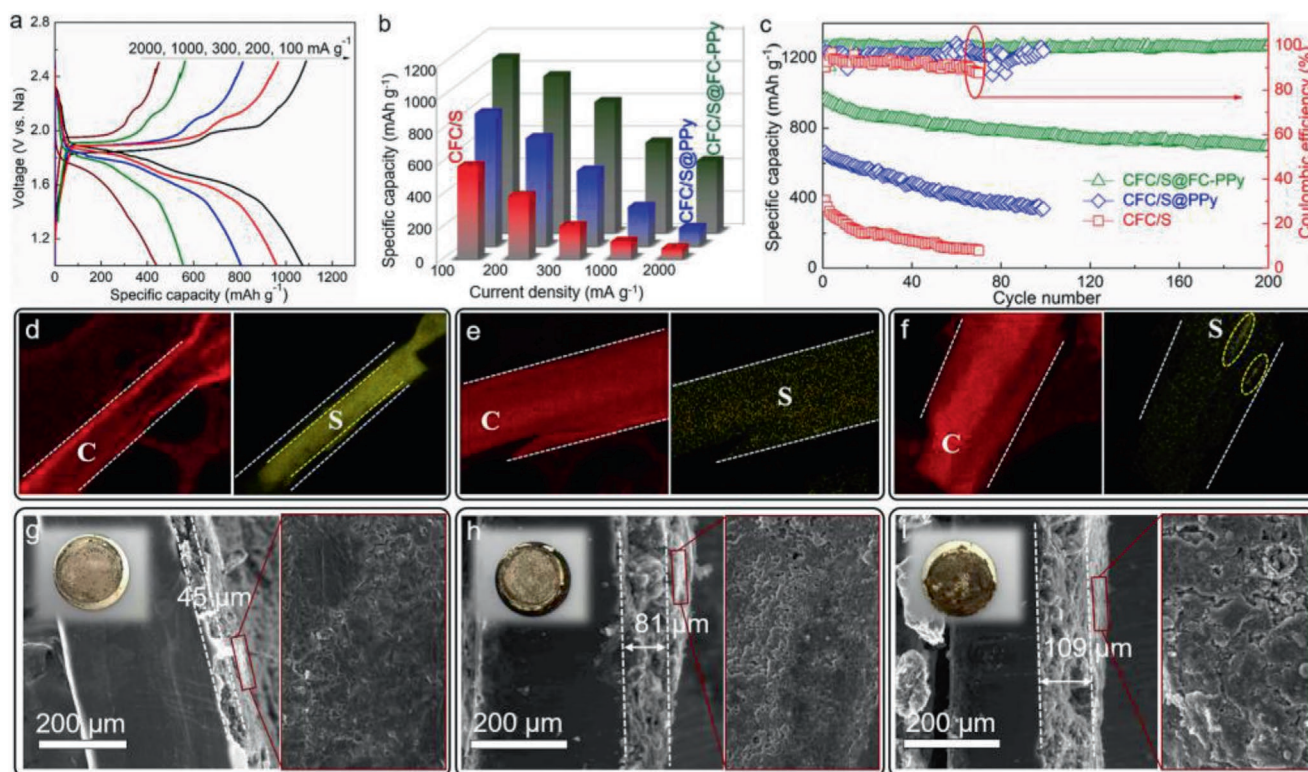


**Figure 4.** Electrochemical performance and degradation mechanism of the Na–S cell. a) Charge–discharge curves of the CFC/S@FC-PPy cathode; b) Rate performance and c) cycling stability of different cathodes for Na–S cells; EDS elemental mapping of d) CFC/S@FC-PPy, e) CFC/S@PPy, and f) CFC/S electrodes after 40 cycles in (c); Cross-section and top-view SEM images of Na metal anodes after 50 cycles paired with g) CFC/S@FC-PPy, h) CFC/S@PPy, and i) CFC/S cathodes, insets are photographs of cycled Na metal anodes.

the capacity retention of 72.8% at nearly 100% stable Coulombic efficiency (Figure 4c). In contrast, the CFC/S@PPy cathode exhibited a stable capacity of  $340 \text{ mAh g}^{-1}$  with capacity retention of 51.4% after 100 cycles. And the CFC/S cathode showed the discharge capacity of  $100 \text{ mAh g}^{-1}$  with a capacity retention of 25.8% after 70 cycles under the same testing conditions. To verify the degradation mechanism of Na–S cells during long-term cycling, cycled sulfur cathodes and Na metal anodes were tested separately. Based on the ex situ EDX mapping results in Figure 4d–f, the doped polymer shell could trap soluble polysulfide without dissolution and confine the sulfur elements within the inner carbon cores even underwent 40 deep cycles in Figure 4c. With the help of polar polymer film wrapping, the polysulfide dissolution could be alleviated at some content, and sulfur components could also transfer from the inner core to the pores of polymer shell (Figure 4e). Significantly, EDX data for the CFC/S electrode just present the trace of sulfur component and almost colorless in carbon host, and the majority of sulfur elements were dissolved into the electrolyte and its discharge capacity obviously decreased (Figure 4f). The polysulfide content dissolved in electrolyte after 50 cycle test was further analyzed. As shown in Figure S7, Supporting Information, the sharp contrast of UV peak intensities (0.61, 0.32, and 0.18 for CFC/S, CFC/S@PPy, and CFC/S@FC-PPy cell at  $\approx 430 \text{ nm}$ ) confirms the slow dissolution of the sulfur within the CFC@FC-PPy matrix. As well known, the dissolved sulfur

components could react with sodium metal and accelerate the corrosion of metallic anode.<sup>[4a,8]</sup> Noticeably, the metal anode in CFC/S@FC-PPy cell shows a relatively dense and thin SEI layer and exhibits prolonged stability compared with other two control cells (Figure 4g–i). As clearly shown in the optical image (inset, Figure 4i), serious interfacial pulverization was observed of sodium anode paired with CFC/S cathode along with porous and thick SEI film. In comparison, the cycled CFC/S@FC-PPy||Na cell reassembled with a fresh Na metal anode, stable high discharge capacity was realized again, highlighting the importance of utilizing a stable anode to reach high stability (Figure S8, Supporting Information). Furthermore, over cycling, the CFC/S@FC-PPy electrode showed a much smaller charge transfer resistance ( $R_{ct}$ ,  $112 \Omega \text{ cm}^2$ ) even after 200 cycles compared with CFC/S@PPy ( $R_{ct}$ ,  $197 \Omega \text{ cm}^2$ ) after 100 cycles and CFC/S ( $R_{ct}$ ,  $558 \Omega \text{ cm}^2$ ) after 70 cycles, therefore further confirming more effective polysulfides confinement of the CFC@FC-PPy matrix (Figure S9, Supporting Information). The comparison of typical electrochemical performances for this work with recently reported Na–S cell is listed in Figure S10, Supporting Information, demonstrating the superiority of building the core-shell structured sulfur cathode with confined electrocatalytic effect.<sup>[1d,10a,23]</sup> Cathode with high areal sulfur mass loading of  $6.4 \text{ mg cm}^{-2}$  was also fabricated to verify the superiority of the core-shell structured sulfur host. As shown in Figure S11, Supporting Information, high discharge capacity of  $588 \text{ mAh g}^{-1}$  was also realized

at scarified battery cycling stability with a capacity retention of 43.9% after 100 cycles. Therefore, to further prolong the cycle life of Na–S cell, stable sodium metal anode should be designed through 3D designation and stable artificial layer preformation,<sup>[24]</sup> and the constructed CFC/S@FC-PPy cathode herein may be a reasonable choice for high-performance Na–S batteries.

### 3. Conclusions

Overall, a stable high-capacity Na–S battery was reported by using a 3D freestanding core-shell structured sulfur cathode. Effective polysulfides confinement was realized within the carbon channel under flexible polymer shell with Fe<sup>(II/III)</sup>(CN)<sub>6</sub> redox-active center anchored on its framework. In this context, the confined redox electrocatalytic effect was demonstrated as its chemical origin. The resultant Na–S cell presents high reversible capacity of 1071 mAh g<sup>-1</sup>, long cycling stability with a capacity retention of 72.8% after 200 cycles, and high rate capacity (441 mAh g<sup>-1</sup> at 2000 mA g<sup>-1</sup>). The functional redox mediator facilitates the Na<sub>2</sub>S<sub>4</sub> to be completely reduced to Na<sub>2</sub>S during battery discharge process, and lowers the activation energy barrier of Na<sub>2</sub>S decomposition during reverse charging process. The high-reversible quasi-solid-state sulfur conversion mechanism was confirmed by in situ and ex situ spectroscopic results. The combination of the proposed cathode and stable metal anode could lead to a promising high-energy Na–S battery chemistry.

### Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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### Conflict of Interest

The authors declare no conflict of interest.

### Data Availability Statement

Research data are not shared.

### Keywords

confined electrocatalysis, core-shell structures, Na–S batteries, polysulfide manipulation, reaction kinetics

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