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High-capacity sulfur copolymer cathode with metallic fibril-based current collector and conductive capping layer†

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Highly conductive and porous current collectors that can provide favorable interfacial interaction with sulfur components play a critical role in the performance of lithium–sulfur (Li–S) batteries. Although three-dimensional (3D) porous textiles have emerged as promising current collector materials, most reported approaches have reached a limit in producing textiles with metal-like conductivity and do not effectively utilize the large surface area of textiles. Here, we introduce a Li–S copolymer cathode with high areal/specific capacity and good rate capability using a metallic cotton textile (CT)-based current collector that exhibits strong interfacial interaction with sulfur. To fabricate the metallic current collector, CT was first carbonized and subsequently electroplated with nickel (Ni). When a sulfur copolymer-based hybrid slurry and layer-by-layer-assembled conductive capping layer were deposited onto the Ni-electroplated CT, the resulting Li–S copolymer cathode displayed significantly enhanced areal capacity, specific capacity, and rate capability. These improvements were realized due to the full utilization of the large conductive surface area of Ni-electroplated CT as well as the effective chemical confinement of soluble lithium polysulfides by a conductive capping layer. The Li–S copolymer cathode prepared in this study outperforms previously reported sulfur copolymer-based cathodes and provides a basis for the development and design of future high-performance electrodes.

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1. Introduction

The recent explosive growth in the use of electric vehicles and various portable electronics has stimulated the development of high-energy and high-power rechargeable batteries.^{1–3} In particular, sulfur is a promising cathode material for rechargeable batteries due to its exceptionally high theoretical specific capacity of $\sim 1675 \text{ mA h g}^{-1}$ based on multielectron conversion reactions with Li ions. Moreover, the natural abundance and low toxicity of sulfur have increased economic interest in lithium–sulfur (Li–S) batteries. Despite their notable advantages, Li–S batteries have a few critical drawbacks that must be addressed prior to their commercial application. Specifically, the dramatic volume change ($\sim 80\%$) of sulfur

during charge/discharge cycling, the extremely low electrical conductivity ($\sim 5 \times 10^{-30} \text{ S cm}^{-1}$) of sulfur, and the shuttle effect of soluble lithium polysulfides (Li_2S_x , $4 \leq x \leq 8$) cause poor rate capability and rapid capacity decay, limiting the practical use of Li–S batteries.^{4,5}

To address these drawbacks, considerable research efforts have focused on the development of sulfur cathodes that allow efficient charge transfer while simultaneously reducing the dissolution of intermediate polysulfides. For example, nano-carbons, metal oxides, metal sulfides, and metal nitrides have been proposed as host materials of sulfur to trap polysulfides by physical confinement or chemical interaction.^{6–10} Despite improved cycling stability as a result of the trapping processes, these host materials restrict the areal mass density ($0.5\text{--}2 \text{ mg cm}^{-2}$) of active sulfur, limiting their overall areal capacity. Another approach is to use sulfur copolymers (S-copolys) synthesized from the free-radical copolymerization of elemental sulfur with carbon compounds, such as 1,3-diisopropenylbenzene (DIB).^{11–17} Strong chemical bonding (*i.e.*, C–S bonds) in the S-copolys can effectively suppress the shuttle effect of polysulfides, thereby improving cycling stability. Pyun and coworkers reported that a S-copoly cathode could provide a high specific capacity of 1100 mA h g^{-1} (with a sulfur areal mass density of 0.8 mg cm^{-2}) at 0.1C with cycling stability up to 100 cycles.¹¹ However, with higher current density (at 2C), the

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specific capacity of the S-copoly cathode sharply decreased to 400 mA h g^{-1} , indicating poor rate capability. Additionally, Hu *et al.* reported that a S-copoly/carbon nanotube hybrid cathode with a sulfur areal mass density of $1.9\text{--}2.5 \text{ mg cm}^{-2}$ exhibited a high specific capacity of 1300 and 880 mA h g^{-1} at 0.1C and 1C, respectively.¹³ Furthermore, amine (NH_2)-functionalized polymers such as poly(ethyleneimine) have been physically blended with S-copolys (or elemental sulfur) to prepare the cathodes that can trap polysulfides by chemical interaction.^{18–21} However, the presence of insulating polymers or polymer binders can significantly decrease the electrical conductivity of active materials, resulting in poor charge transfer within the cathodes.

Recent research efforts on Li–S batteries have been devoted to increasing the areal energy density using highly porous current collectors.^{22–25} As such, parameters including sulfur areal mass density (mg cm^{-2}) and areal capacity (mA h cm^{-2}) are considered important performance indicators. In most cases, the reported high specific capacity and long cycling operation have been achieved by both the relatively low areal mass density of sulfur or S-copolys ($<2 \text{ mg cm}^{-2}$) and the resultant low areal capacity ($<2 \text{ mA h cm}^{-2}$).^{25–27} Recently, porous textiles with large surface area have emerged as promising materials that can serve as both current collectors and sulfur-filling reservoirs for high areal capacity of electrodes. The electrical conductivity of insulating textiles has been improved through various approaches, such as high-temperature carbonization, blending with pristine multi-walled carbon nanotubes (MWCNTs), and chemical reduction of metal ions.^{28–32} However, these conductive textiles have not been able to achieve bulk metal-like conductivity due to the inferior electrical properties of carbon-based materials (mainly MWCNTs) or the organic impurities within chemically reduced metals, limiting improvements in the rate capability of electrodes. Additionally, they have had much difficulty in fully utilizing the large surface area of textiles due to poor interfacial interaction²⁸ and/or the formation of nonuniform structures³² such as agglomerates that can block pores. Furthermore, their areal and specific capacities were also significantly restricted due to the low utilization efficiency of sulfur.

Approaches involving metal electrodeposition onto porous carbon frames (e.g., commercial carbon paper or carbon cloth) have also been used for preparing highly conductive current collectors. For example, it was reported that metal oxide or metal layers could be electrodeposited (or electroplated) onto carbon frames to fabricate supercapacitor or lithium-ion battery electrodes.^{33–37} However, when hydrophobic carbon frames with a relatively dense fibril structure are used as conductive supports for metal electroplating, the hydrophilic metal ions are less likely to infiltrate into the interior of the hydrophobic carbon frames during electroplating process in an aqueous electrolyte solution,³⁵ and the electroplated metal layer is therefore formed mainly on the exterior surface of the carbon frames (the detailed explanation will be given in the latter part). Although these metal-electroplated carbon frames have been never applied to Li–S batteries to date, the above-mentioned phenomena can have an adverse effect on the coating quality

and sulfur loading over the entire region of porous current collectors for Li–S cathodes.

Therefore, if textile-based current collectors with uniformly electrodeposited metal layer can be prepared using a unique approach, they can exhibit a bulk metal-like conductivity, and additionally improve charge transfer within the Li–S cathodes. Particularly, considering that the Ni metal layer can effectively induce the rapid reduction/oxidation kinetics of soluble Li_2S_x ($4 \leq x \leq 8$) and the absorption/decomposition of Li_2S to enhance the utilization of sulfur,^{38,39} the Ni-electrodeposited textile-based current collectors can significantly alleviate the shuttle effect of soluble polysulfides. Furthermore, if the active sulfur compounds (specifically S-copolys) and conductive fillers can be deeply incorporated into the large-area textile-based current collector through favorable interfacial interaction, the areal capacity of the resultant Li–S cathode can be notably increased according to the loading mass of sulfur without a significant decay in specific capacity.

Herein, we introduce a S-copoly cathode with high areal/specific capacity values, rate capability, and cycling stability, using carbonization-induced Ni electroplating and interfacial interaction-controlled conductive capping layers (Fig. 1). In this study, a metallic cotton textile (CT) with an exceptionally low sheet resistance ($\sim 0.01 \Omega \text{ sq}^{-1}$) was prepared by carbonization at relatively low temperature (700°C ; for preventing the formation of carbonized CT (*i.e.*, C-CT) with extremely hydrophobic property) and subsequent Ni electroplating. The electroplated CT (*i.e.*, EP-CT) maintained a highly porous structure and large surface area without metal agglomeration at its surface. These properties are in stark contrast to those of electroless Ni-deposited (*i.e.*, chemically reduced Ni-coated) CT with blocked pores, metal agglomerates, and relatively high sheet resistance ($\sim 0.5 \Omega \text{ sq}^{-1}$). Additionally, the entire region (*i.e.*, all the carbonized cotton fibrils) ranging from the exterior to the interior of the EP-CT was uniformly covered with Ni layer. These EP-CTs can be used as an effective reservoir for the high loading of S-copolys, allowing strong chemical bonding between the electroplated Ni layer and the S-copolys.⁴⁰ That is, when the EP-CT is immersed into a hybrid slurry composed of S-copolys, carbon black, and NH_2 -modified MWCNTs (NH_2 -MWCNTs), the slurry is deeply embedded within the EP-CT. The inclusion of NH_2 -MWCNTs can compensate for the insulating property of S-copolys, and simultaneously induce the chemical confinement of polysulfides due to the high affinity between NH_2 groups and Li_2S_x .

Furthermore, we demonstrate that interface control on the surface of hybrid slurry using layer-by-layer (LbL) assembly can reinforce the chemical confinement of polysulfides and facilitate charge transfer within the cathode. Specifically, hydrogen-bonding interaction-induced LbL assembly (H-LbL) between carboxylic acid-functionalized MWCNTs (COOH-MWCNTs) and NH_2 -MWCNTs is observed in the slurry-coated EP-CT. These LbL-assembled MWCNT multilayers can operate as a conductive capping layer (*i.e.*, an additional layer with a polysulfide trap) to restrict the dissolution of polysulfides and notably enhance the rate capability of the cathode. An EP-CT-based

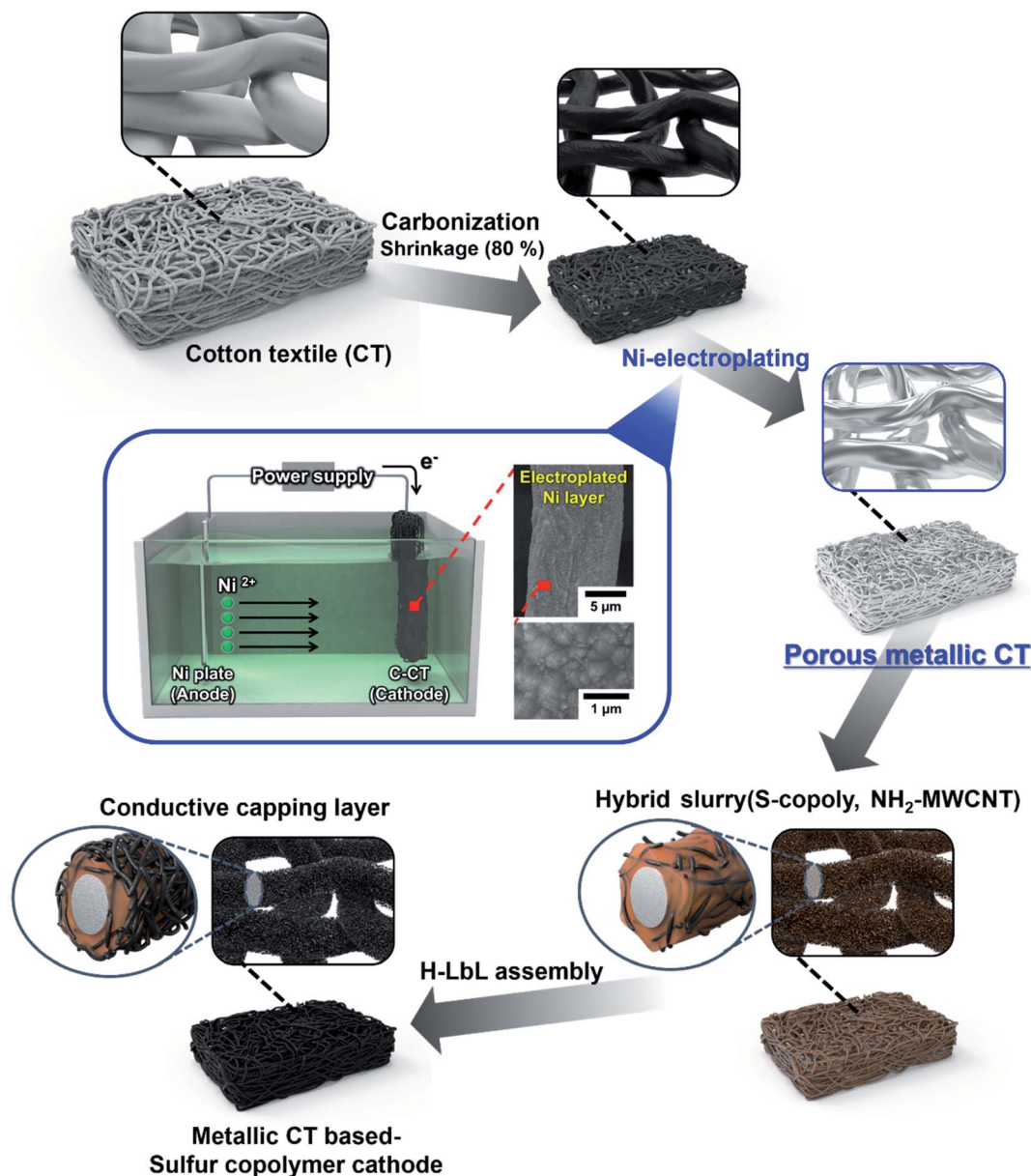


Fig. 1 Schematic illustration of the formation of the metallic textile-based S-copoly cathode using carbonization-induced metal electroplating and layer-by-layer-assembled conductive capping layer.

cathode with an areal mass density of $\sim 3 \text{ mg cm}^{-2}$ for S-copolys (containing 90 wt% sulfur) exhibited a high areal capacity of $\sim 4.4 \text{ mA h cm}^{-2}$ (specific capacity of $\sim 1618 \text{ mA h g}^{-1}$) and $\sim 2.8 \text{ mA h cm}^{-2}$ at 0.1C and 1C, respectively. Increasing the S-copoly areal mass density to $\sim 8 \text{ mg cm}^{-2}$ increased the areal capacity of the cathode to $\sim 5.1 \text{ mA h cm}^{-2}$ (specific capacity of $\sim 713 \text{ mA h g}^{-1}$), even after 100 cycles at 0.2C. Notably, the electrochemical performance of the EP-CT-based cathode with a conductive capping layer outperforms the C-CT-based cathode without Ni electroplating and the EP-CT-based cathode without a capping layer.

That is, we highlight that our approach using carbonization-induced Ni electroplating (for preparing porous current collector with a large surface area and metal-like conductivity)

and LbL-assembled conductive capping layer (for enhancing the electrochemical performance and operation stability of cathode) can generate a high-performance Li-S copolymer cathode with high areal/specific capacity, good rate capability, and stable operation. Furthermore, our approach can provide a basis for developing and designing a variety of high-performance electrochemical electrodes as well as Li-S cathodes.

2. Experimental section

2.1. Materials

All chemical reagents were purchased from Sigma-Aldrich and used without further purification. The CTs were purchased from

KohasiD Co., Ltd. (Republic of Korea) and the commercial Ni foam was purchased from Goodfellow Cambridge Ltd. (United Kingdom).

2.2. Preparation of the EP-CT

The EP-CT was prepared by Ni electroplating following the carbonization of the CT. The CT was first washed with deionized water and dried in an oven. The CT was then heated to 700 °C at a rate of 2 °C min⁻¹ and held for 3 h in a furnace under a flow of argon gas. After cooling to ambient temperature, the resulting C-CT was immersed in a Watt bath (45 g L⁻¹ NiCl₂, 240 g L⁻¹ NiSO₄, and 30 g L⁻¹ H₃BO₃).⁴¹ The C-CT was used as the cathode and a nickel plate as the anode. Electroplating was performed at a current density of 216 mA cm⁻² for 20 min using a power supply. The EP-CT was then washed with deionized water and dried in a vacuum oven.

2.3. Preparation of S-copolys with 10 wt% DIB

The S-copolys were synthesized in accordance with a previous study.⁴¹ The sulfur powder (4.50 g, 17.6 mmol) was heated to 185 °C in an oil bath. After an orange molten phase was formed, DIB (0.5 g, 3.16 mmol) was added to the molten sulfur with a syringe. The mixture was stirred for 10 min before cooling to ambient temperature.

2.4. Preparation of COOH-MWCNTs and NH₂-MWCNTs

Pristine MWCNTs were oxidized in a mixture of H₂SO₄/HNO₃ at 70 °C for 3 h to prepare COOH-MWCNTs. Then, the COOH-MWCNT suspension was stirred with ethylenediamine (8.0 mL) and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide methiodide (800 mg) for 6 h to prepare NH₂-MWCNTs. The suspension was then dialyzed (MWCO: 12 000–14 000) for 3 days to remove any undesired byproducts or residuals.

2.5. Preparation of the EP-CT/slurry/capping layer cathode

A homogeneous hybrid slurry was prepared by mixing 65 wt% S-copoly, 25 wt% carbon black, and 10 wt% NH₂-MWCNTs in *N*-methyl-2-pyrrolidone (NMP). The slurry was then sonicated for 1 h at high-power. The EP-CT was immersed into the slurry and shaken for 10 min. After shaking, the EP-CT was removed from the slurry and dried in a vacuum oven at 60 °C overnight. The S-copoly loading was controlled by the viscosity of the slurry, which was tailored by the amount of NMP added to the initial mixture. EP-CT/slurry cathodes with a S-copoly loading of 3–8 mg cm⁻² (sulfur loading of 2.7–7.2 mg cm⁻²) were obtained. For the H-LbL assembly of conductive capping layer, COOH-MWCNTs (20 mg) and NH₂-MWCNTs (20 mg) were each separately mixed with carbon black (10 mg) in ethanol (20 mL). Then, the COOH-MWCNT and NH₂-MWCNT solutions were alternately filtered into the EP-CT/slurry using a vacuum filtration-assisted H-LbL assembly. The EP-CT/slurry/capping layer was dried in a vacuum oven at 60 °C overnight. The loading of the H-LbL-assembled MWCNT multilayers was ~3 mg cm⁻².

2.6. Materials characterization

Raman spectra were collected to determine the structure of the C-CTs using a LabRam Aramis IR2 (Horiba Jobin Yvon). X-ray diffraction (XRD) patterns were obtained using a SmartLab instrument (Rigaku) with Cu K α radiation. The surface/cross-sectional morphologies and energy-dispersive X-ray spectroscopy (EDS) elemental mapping images of the samples were characterized by field-emission scanning electron microscopy (FE-SEM; Quanta 250 FEG, FEI). X-ray photoelectron spectroscopy (XPS) analysis was conducted using an X-TOOL (ULVAC-PHI) equipped with Al K α radiation. Mercury porosimetry analysis was conducted with a MicroActive AutoPore V 9600 mercury porosimeter (Protechkorea Inc.). Water contact angle measurements were performed using a Phoenix-300 instrument with Surfaceware 8 (Surface Electro Optics Co., Ltd.). Thermogravimetric analysis (TGA; Q50, TA Instruments) was performed in an argon atmosphere with a heating rate of 5 °C min⁻¹ from room temperature to 900 °C. The sheet resistance of the C-CTs and EP-CTs was measured by a standard four-probe method using a Loresta-GP MCP-T610 (Mitsubishi Chemical Analytech). Temperature-dependent electrical conductivity measurements were performed using a physical property measurement system (PPMS-9, Quantum Design) in the range 300–10 K.

2.7. Electrochemical measurements

The EP-CT/slurry/capping layer cathode was assembled in an argon-filled glove box into a 2032 coin cell architecture with a Celgard 2325 separator, a lithium foil anode, and a nickel-foam spacer. The size of the electrode was 0.9 cm $\times$ 0.9 cm (0.81 cm²). The electrolyte was 0.2 M LiNO₃ (99.9%) and 1 M lithium bis(trifluoromethane)sulfonimide (LiTFSI) dissolved in 1 : 1 (v/v) 1,3-dioxolane/1,2-dimethoxyethane (Panax Etec Co., Ltd.). The electrolyte (60 μ L) was added into the cell. The assembled cell was allowed to rest for 12 h at 25 °C before conducting electrochemical measurements. The electrochemical measurements were carried out between 1.7–2.8 V vs. Li/Li⁺ using a WBCS3000 multichannel workstation. The C-rate was calculated based on the theoretical specific capacity of sulfur (1C = 1675 mA h g⁻¹). Electrochemical impedance spectroscopy (EIS) measurements were conducted in the frequency range of 0.1 MHz to 0.1 Hz with an amplitude of 10 mV at the open-circuit potential.

3. Results and discussion

To prepare CT-based current collectors for Li-S cathodes, the natural CTs composed of cellulose fibrils were first carbonized at 700 °C in an inert atmosphere. In this case, the electrical conductivity and sheet resistance of C-CTs were measured to be ~0.04 S cm⁻¹ and 361 Ω sq⁻¹, respectively. The diameter of fibrils within the CT notably decreased from ~21 to 12 μ m, and the resultant total area and volume of the CT shrank by ~66 and 80%, respectively (Fig. S1†). However, in spite of thermal-induced chemical and structural transformation, the C-CT

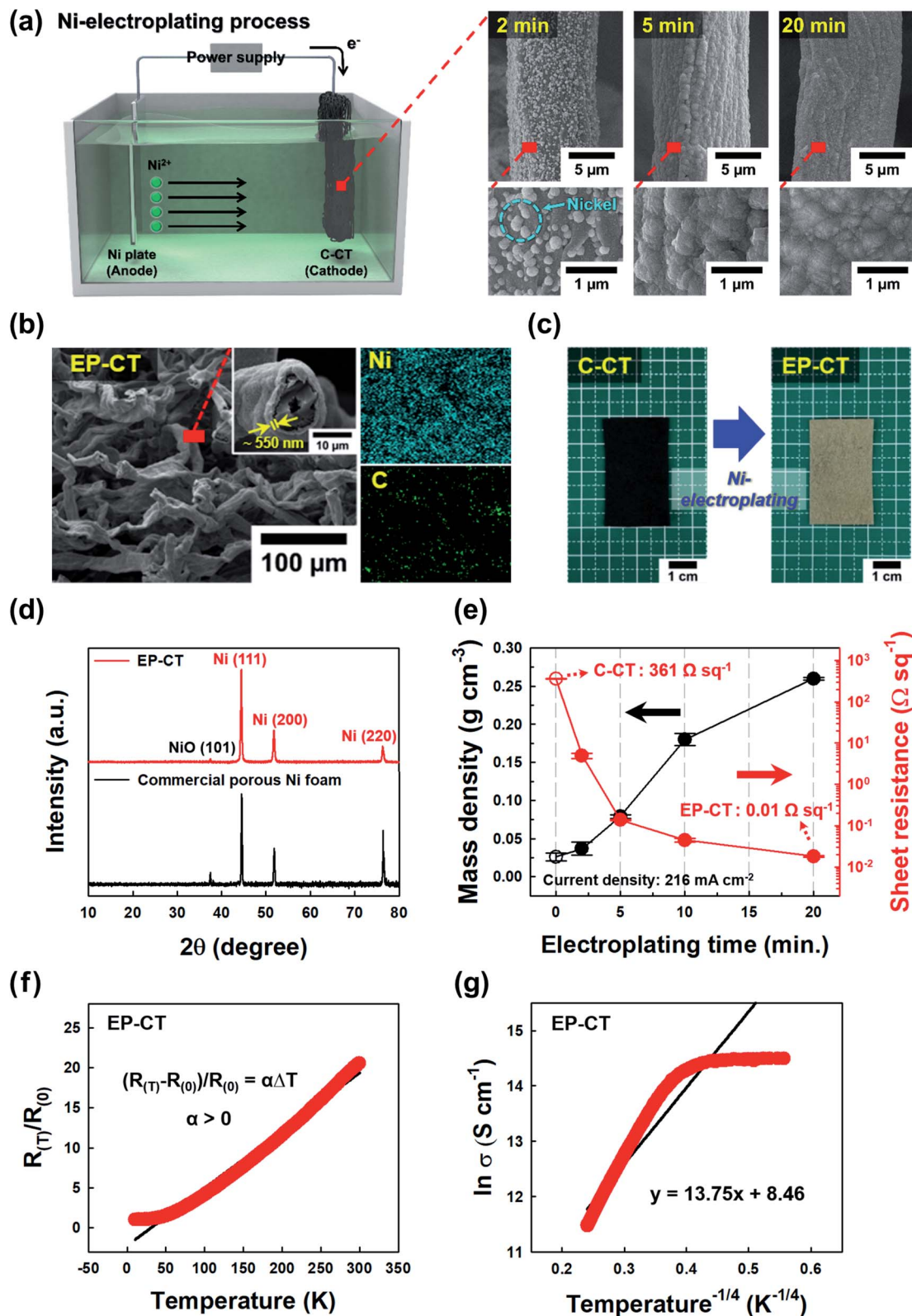


Fig. 2 (a) Schematic diagram of Ni-electroplating process and FE-SEM images of the resulting Ni layer on the surface of the C-CT fibrils as a function of electroplating time at 216 mA cm^{-2} . (b) Cross-sectional FE-SEM images of the EP-CT with corresponding EDS maps. The inset in the FE-SEM image shows the thickness of the electroplated Ni layer. (c) Photographic images of the C-CT and EP-CT. (d) XRD spectra for the EP-CT and commercial porous Ni foam. (e) Mass density and sheet resistance for the EP-CT as a function of electroplating time at 216 mA cm^{-2} . (f) Plot of resistance change ($R_{(T)}/R_{(0)}$) vs. temperature (K) for the EP-CT. (g) Plot of conductivity ($\ln \sigma$) vs. temperature ($\text{K}^{-1/4}$) (to describe the hopping mechanism) for the EP-CT.

showed stable electrical conductivity under repeated mechanical stresses (Fig. S2†).

Based on these results, the conductive C-CT (carbonized at 700 °C) was electroplated with Ni at a current density of 216 mA cm⁻² for 20 min to produce EP-CT (Fig. 2a and S3†). With increasing the electroplating time from 2 to 20 min, the deposited Ni rapidly evolved from a few hundred nanometer-sized Ni particles to a dense Ni layer with a protuberant structure (Fig. 2a). As confirmed by FE-SEM, EDS, and photographic images, the resultant electroplated Ni layer (after electroplating for 20 min) was uniformly deposited onto the surface of fibrils and the porous structure of the C-CT was preserved without the formation of metal agglomerates and/or additional shrinkage (Fig. 2a–c and S4†). The thickness of the electroplated Ni layer reached approximately 550 nm after 20 min (Fig. 2b). In contrast to the highly uniform surface morphology observed for the EP-CT, the Ni layer that was electroless deposited (*i.e.*, chemically reduced) onto the C-CT (hereinafter, electroless deposited Ni layer-coated C-CT is designated as EL-CT) was not evenly coated onto the fibrils, which resulted in Ni agglomeration and pore plugging (Fig. S5†). It should also be noted that it is difficult to control the electroless chemical reduction process because of its complex process variables, including metal precursor concentration, reducing agent concentration, and/or reaction time.

Additionally, the commercial carbon paper and cloth could be directly Ni-electroplated with no carbonization process. However, the Ni layer was not evenly deposited on the inner surface of the carbon paper and cloth, generating a number of nonuniform electroplating region (Fig. S6†). These phenomena were mainly caused by the dense fibril structure and hydrophobic properties of carbon paper and cloth. That is, the metal ion precursors or electrolytes for Ni electroplating had much difficulty in being deeply infiltrated into the interior of carbon frames, which was confirmed by both EDS images (Fig. S7†) and water contact angle measurements (Fig. S8†). On the other hand, it should be noted that the C-CT prepared at a relatively low carbonization temperature (700 °C) has a larger amount of hydrophilic moieties and a larger pore structure compared to the above-mentioned carbon frames.^{42,43} By virtue of these chemical and structural uniqueness of the C-CT, all carbonized fibrils in the entire region from the exterior to the interior of C-CT could be almost completely converted to the metallic fibrils.

The electroplated Ni layer on the EP-CT was further analyzed using XRD. The XRD pattern for the EP-CT exhibited characteristic (111), (200), and (220) reflection peaks for face-centered cubic (fcc) Ni with a minor (101) peak attributed to NiO. The XRD pattern for the EP-CT was nearly identical to that for the commercial porous Ni foam (Fig. 2d).^{44,45} These results imply that insulating cotton fibrils can be converted into bulk Ni-like conductive fibrils through carbonization and Ni electroplating. In order to confirm this, the electrical properties of the EP-CT were investigated. The sheet resistance of the EP-CT was substantially lower ($\sim 0.01 \Omega \text{ sq}^{-1}$) than that of the EL-CT ($\sim 0.5 \Omega \text{ sq}^{-1}$), which contained large amounts of organic impurities, and of the C-CT ($\sim 361 \Omega \text{ sq}^{-1}$) (Fig. 2e). The EP-CT, in particular, exhibited a typical metallic conduction behavior when its

electrical resistivity was measured as a function of temperature. That is, as the temperature decreased from 300 to 10 K, the electrical resistivity of the EP-CT gradually decreased, indicating a positive temperature coefficient (α) of metallic conduction behavior (Fig. 2f). Furthermore, the natural log electrical conductivity *vs.* inverse temperature plots of the EP-CT did not exhibit a linear dependence for hopping (Fig. 2g) or tunneling (Fig. S9†) mechanism of semiconducting behavior (see the detailed explanation in Fig. S9†).^{46,47} Additionally, the electrical conductivity remained stable in the EP-CT with repeated mechanical bending at a curvature radius of 0.4 cm (Fig. S10†).

The specific surface area and porosity of the EP-CT were also investigated using mercury porosimetry. The specific surface area of the EP-CT, having a mass density of $\sim 0.26 \text{ g cm}^{-3}$, was found to be $\sim 0.158 \text{ m}^2 \text{ g}^{-1}$, which is 4.5 times higher than that of commercial porous Ni foam ($\sim 0.035 \text{ m}^2 \text{ g}^{-1}$) having a mass density of $\sim 0.71 \text{ g cm}^{-3}$ (Fig. S11†). Additionally, the porosities of the EP-CT and commercial porous Ni foam were estimated to be approximately 83 and 53%, respectively. These results strongly suggest that a lightweight and highly porous current collector having bulk metal-like conductivity can be easily prepared from metal electroplating onto carbonized textiles. Although the highly porous EP-CT-based current collector can induce relatively low tap density and/or volumetric energy density, it should be noted that the areal energy density, which is considered an important index in practical use, can be significantly enhanced by sufficiently accommodating a large amount of active sulfur compounds. Additionally, the EP-CT-based cathodes are mechanically compressed during the assembly of coin cells, which also increases the volumetric energy density compared to that of the initial cathodes before mechanical compression.

A Li–S cathode was prepared by infiltrating the porous EP-CT with hybrid slurry composed of S-copolys, carbon black, and NH₂-MWCNTs in an organic medium (NMP; see the Experimental section). For this goal, S-copolys were synthesized by the copolymerization of elemental sulfur with DIB, as previously reported.¹¹ TGA showed that the S-copolys consisted of $\sim 90 \text{ wt}\%$ sulfur and XPS confirmed the formation of stable C–S bonds (per the characteristic peak at 162.6 eV) (Fig. S12†).¹³ As mentioned previously, NH₂-MWCNTs, which served as conductive binders with carbon black, can restrict the shuttle effect of soluble polysulfides due to the high affinity (*i.e.*, Li–N bonding) between Li₂S_x and NH₂ groups bound to the surface of the MWCNTs. This means that additional insulating polymer binders containing NH₂ moieties are not required. Additionally, it should be noted that our NH₂-MWCNTs contained uniformly distributed NH₂ groups on the surface of the MWCNTs as a result of the acid treatment-based chemical process. It has been previously reported that NH₂-MWCNTs could be directly prepared from ethylenediamine (EDA) or poly(ethyleneimine) (PEI) and pristine MWCNTs due to the affinity between NH₂ groups in EDA or PEI and partial defect moieties (*i.e.*, OH and C=O groups) in MWCNTs.²⁰ However, this approach does not uniformly distribute NH₂ groups onto the surface of pristine MWCNTs. Furthermore, this approach imposes limits on the amount of sulfur-based active materials that can be loaded. In

this report, pristine MWCNTs were first converted to COOH-MWCNTs using an acid treatment, and then the COOH-MWCNTs were reacted with EDA to form NH₂-MWCNTs through the formation of amide bonds between the NH₂ groups in the EDA and the COOH groups in the MWCNTs as confirmed by the XPS analysis (Fig. S13†).

Fig. 3a and b show that the hybrid slurry, having an S-copoly areal mass density of ~ 3 and 5 mg cm^{-2} , respectively, was evenly deposited onto and into the highly porous EP-CT using a simple immersion process. In particular, the cross-sectional FE-SEM and elemental mapping images clearly revealed that the slurry was homogeneously coated from the exterior to the interior of the EP-CT. Although the slurry was more densely deposited onto the EP-CT having a S-copoly areal mass density of $\sim 5 \text{ mg cm}^{-2}$, the porous structure of the slurry-coated EP-CT

(i.e., EP-CT/slurry) was still preserved. Then, a conductive capping layer was prepared by alternately infiltrating the EP-CT/slurry (i.e., EP-CT/slurry/capping layer) with COOH-MWCNTs and NH₂-MWCNTs using a vacuum filtration-assisted H-LbL assembly (Fig. 3c). This capping layer, along with the NH₂-MWCNTs within the slurry, can further induce the chemical confinement of soluble polysulfides and enhance charge transfer within the cathode.

The electrochemical performance of the EP-CT/slurry/capping layer cathode having a S-copoly areal mass density of $\sim 3 \text{ mg cm}^{-2}$ was investigated using cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and EIS measurements. CV scans were first taken to examine the electrochemical reaction mechanism at a scan rate of 0.03 mV s^{-1} with a potential window of 1.7 to 2.8 V *versus* Li/Li⁺ (Fig. 4a). The steady-state CV

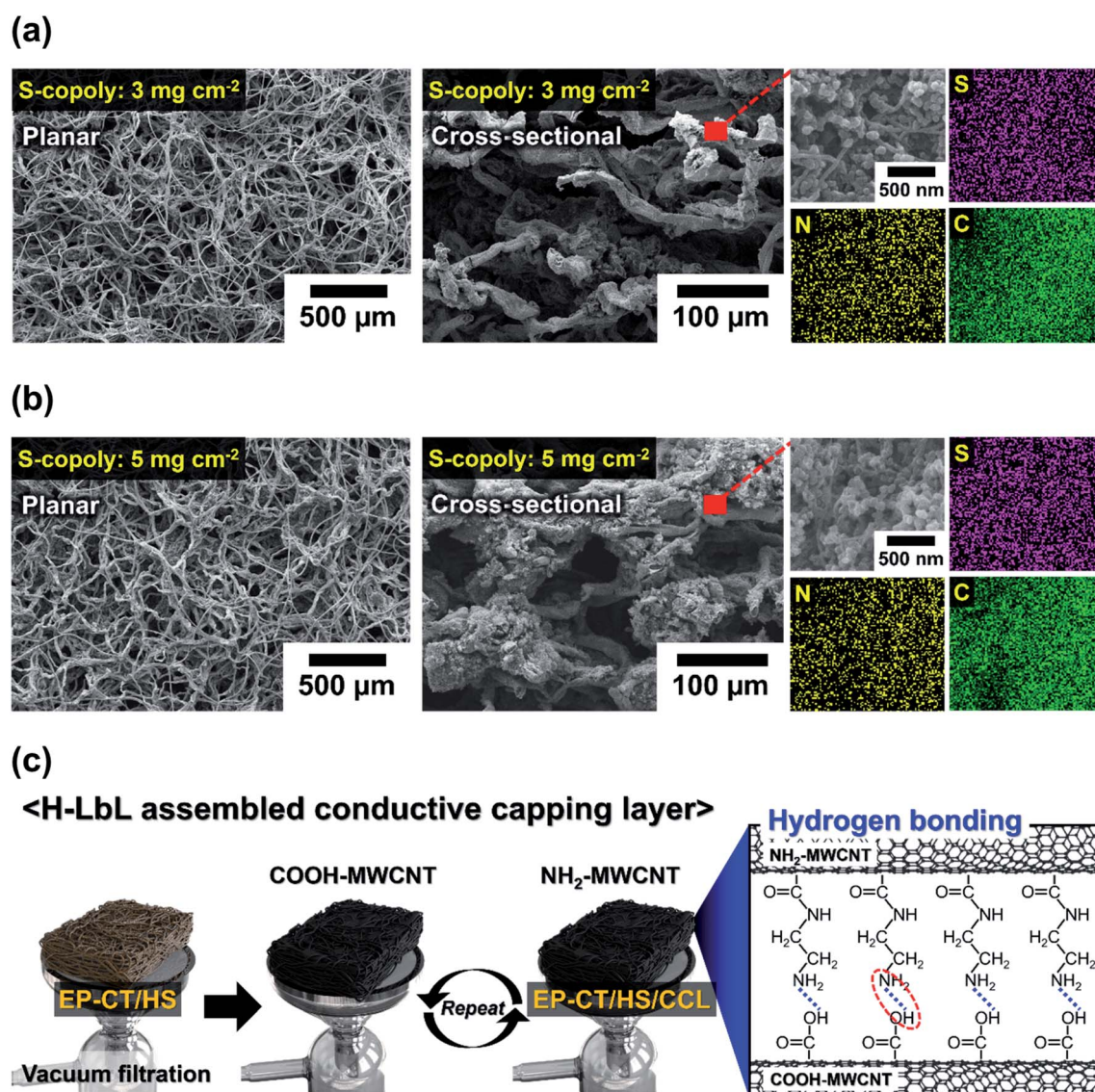


Fig. 3 Planar/cross-sectional FE-SEM images and corresponding EDS maps for the EP-CT/slurry having S-copoly areal mass densities of (a) ~ 3 and (b) 5 mg cm^{-2} . (c) Schematic diagram of the process for depositing conductive capping layer on the EP-CT/slurry using vacuum filtration-assisted H-LbL assembly. Herein, the abbreviations of HS and CCL in the figures refer to (hybrid) slurry and (conductive) capping layer, respectively.

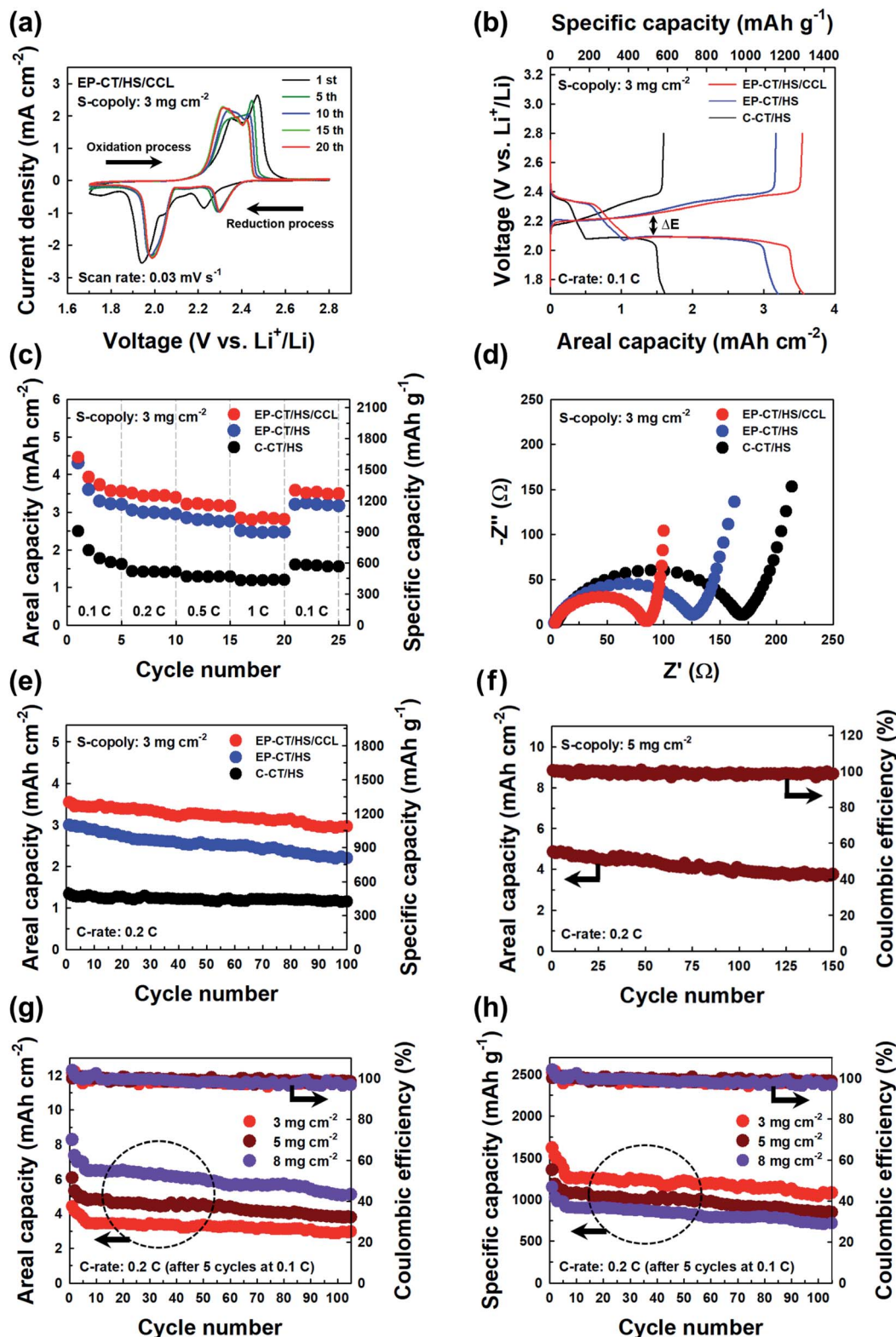


Fig. 4 (a) CV curves for the EP-CT/slurry/capping layer cathode taken at a scan rate of 0.03 mV s⁻¹ up to 20 cycles. (b) GCD profiles for the C-CT/slurry, EP-CT/slurry, and EP-CT/slurry/capping layer cathodes at 0.1C. (c) Areal and specific capacities taken from 0.1 to 1C for the C-CT/slurry, EP-CT/slurry, and EP-CT/slurry/capping layer cathodes with a S-copoly areal mass density of ~3 mg cm⁻². (d) Nyquist plots and (e) cycling stability at 0.2C for the C-CT/slurry, EP-CT/slurry, and EP-CT/slurry/capping layer cathodes. (f) Cycling stability and coulombic efficiency of the EP-CT/slurry/capping layer cathode with a S-copoly areal mass density of ~5 mg cm⁻² at 0.2C. According to (g) areal capacity and (h) specific capacity, cycling stability and coulombic efficiency of the EP-CT/slurry/capping layer cathodes with S-copoly areal mass densities of ~3, 5, and 8 mg cm⁻² at 0.2C (after 5 cycles at 0.1C). Herein, the abbreviations of HS and CCL in the figures refer to (hybrid) slurry and (conductive) capping layer, respectively.

scans showed two cathodic peaks centered at ~ 2.28 and 1.98 V that were attributed to (1) the reduction of the S-copolys to organosulfur DIB with shortened oligosulfur units and lithium polysulfides (Li_2S_x , $4 \leq x \leq 8$) and (2) the conversion of the S-copolys to fully discharged organosulfur DIB products and insoluble lithium sulfides (Li_2S_2 and Li_2S), respectively.¹² In the anodic scans, two peaks appeared at ~ 2.31 and 2.42 V, which were both ascribed to the conversion of the fully discharged short-chain organosulfur DIB to long-chain S-copolys. The positive shift in the cathodic peaks and the negative shift in the anodic peaks with increasing cycle number reflected the decreased polarization and increased redox kinetics. In addition, the negligible change in the CV shapes over 20 cycles suggested that the EP-CT/slurry/capping layer cathode exhibited good electrochemical reversibility.

The GCD profiles for the C-CT/slurry, EP-CT/slurry, and EP-CT/slurry/capping layer cathodes with a S-copoly areal mass density of ~ 3 mg cm^{-2} at 0.1C ($1\text{C} = 1675$ mA h g^{-1}) displayed two discharge plateaus, consistent with the CV results (Fig. 4b). The GCD curves exhibited significantly longer second discharge plateaus and smaller potential gaps (polarization, ΔE) for the EP-CT/slurry (~ 1.9 mA h cm^{-2} and ~ 165 mV, respectively) and EP-CT/slurry/capping layer (~ 2.1 mA h cm^{-2} and ~ 156 mV, respectively) than for the C-CT/slurry (~ 1 mA h cm^{-2} and ~ 210 mV, respectively) (Fig. S14†).^{48,49} The areal capacity was higher and the polarization was lower in the EP-CT/slurry and EP-CT/slurry/capping layer cathodes than in the C-CT/slurry cathode. To investigate these phenomena in more detail, the electrochemical activity of the C-CT/slurry and EP-CT/slurry cathodes was examined using CV over a potential window of 1.7 – 2.8 V and at a scan rate of 0.03 mV s^{-1} . As shown in Fig. S15,† both cathodes exhibited two cathodic peaks and two anodic peaks. In both cases, the cathodic peak at the higher potential was attributed to the reduction of S-copolys to Li_2S_x ($4 \leq x \leq 8$) and the cathodic peak at the lower potential to the formation of Li_2S . When a reverse potential was applied to the cathodes, two anodic peaks were observed, indicating the oxidation of Li_2S . In this case, the EP-CT/slurry cathode exhibited an upshift in the two cathodic peaks and a downshift in the two anodic peaks, implying a lower polarization and faster redox rates in electrochemical reactions compared to the C-CT/slurry cathode. These behaviors were mainly attributed to the facile charge transfer by the highly conductive and porous EP-CT. However, we also cannot exclude the possibility that the electroplated Ni layer on the EP-CT can be partially related to the effective reduction/oxidation of polysulfides.^{38,39} Recently, Zheng and coworkers reported that the Ni layer could accelerate the redox kinetics of soluble Li_2S_x ($4 \leq x \leq 8$) and efficient absorption/decomposition of insoluble Li_2S .³⁸

The rate capabilities of the C-CT/slurry, EP-CT/slurry, and EP-CT/slurry/capping layer cathodes were further evaluated at various C-rates (Fig. 4c). The S-copoly areal mass density for all cathodes was adjusted to ~ 3 mg cm^{-2} (sulfur loading of ~ 2.7 mg cm^{-2}) and the specific capacity was calculated on the basis of sulfur loading. The EP-CT/capping layer cathode without S-copolys had a negligible areal capacity of ~ 0.15 mA h cm^{-2} at 0.1C (Fig. S16†). The initial areal capacity of

the C-CT/slurry cathode was ~ 2.5 mA h cm^{-2} at 0.1C (with a sulfur utilization efficiency of $\sim 54\%$ and a specific capacity of ~ 909 mA h g^{-1}). The average areal capacities were ~ 1.6 , 1.4 , 1.3 , and 1.2 mA h cm^{-2} (corresponding specific capacities of ~ 588 , 516 , 468 , and 432 mA h g^{-1}) at 0.1 , 0.2 , 0.5 , and 1C , respectively. Overall, the poor rate performance of the C-CT/slurry cathode was due to the low electrical conductivity and nonpolar surface of the C-CT. A significant enhancement in the rate performance was observed for the EP-CT/slurry cathode. The EP-CT/slurry cathode exhibited an initial areal capacity of ~ 4.3 mA h cm^{-2} at 0.1C , a sulfur utilization efficiency of $\sim 92\%$, and a specific capacity of ~ 1546 mA h g^{-1} . The average areal capacities were ~ 3.2 , 3.0 , 2.8 , and 2.5 mA h cm^{-2} (corresponding specific capacities of ~ 1151 , 1078 , 1007 , and 889 mA h g^{-1}) at 0.1 , 0.2 , 0.5 , and 1C , respectively. These results confirm the role of the electroplated Ni layer in improving the utilization efficiency of sulfur and reaction kinetics. The results also demonstrate that the rate performance is improved due to the high electrical conductivity of the EP-CT. Moreover, the effect of NH_2 -MWCNTs was investigated in the EP-CT/slurry cathode by substituting slurry containing pristine MWCNTs for slurry containing NH_2 -MWCNTs (Fig. S17†). The EP-CT/slurry with NH_2 -MWCNTs exhibited enhanced capacities compared to the EP-CT/slurry with pristine MWCNTs at all C-rates. This confirms that faster redox rates and higher sulfur utilization are achieved in the EP-CT/slurry with NH_2 -MWCNTs due to the chemical interaction between polar NH_2 -MWCNTs and polar polysulfides.

Finally, the EP-CT/slurry/capping layer cathode presented a much higher rate capability than the C-CT/slurry or EP-CT/slurry cathodes. The initial areal capacity at 0.1C for the EP-CT/slurry/capping layer cathode was ~ 4.4 mA h cm^{-2} (with a sulfur utilization efficiency of $\sim 97\%$ and a specific capacity of ~ 1618 mA h g^{-1}) (Fig. S18†). Additionally, when the specific capacity of the cathode was evaluated based on S-copoly loading (~ 3 mg cm^{-2}), it was found to be ~ 1456 mA h g^{-1} . The average areal capacities of the EP-CT/slurry/capping layer cathode were ~ 3.6 , 3.4 , 3.2 , and 2.8 mA h cm^{-2} (corresponding specific capacities of ~ 1299 , 1252 , 1169 , and 1028 mA h g^{-1}) at 0.1 , 0.2 , 0.5 , and 1C , respectively. When the current density was cycled from 1 to 0.1C , the areal capacity recovered to ~ 3.5 mA h cm^{-2} (specific capacity of ~ 1287 mA h g^{-1}), indicating excellent electrochemical reversibility. This superior electrochemical performance of the EP-CT/slurry/capping layer cathode demonstrates the positive effect of the capping layer as a polar conductive network composed of NH_2 -MWCNTs and COOH -MWCNTs.

EIS analysis was performed to further understand the electrochemical performance of the prepared cathodes using an equivalent circuit for simulating the model of Li-S cells (Fig. 4d and S19†). The Nyquist plots followed a half-circle configuration in the high-to-mid-frequency region with sloped lines at low frequencies. The two regions were ascribed to the charge transfer resistance (R_{ct}) and mass transfer processes, respectively. The EP-CT/slurry/capping layer cathode revealed a lower R_{ct} value (~ 84 Ω) than the C-CT/slurry ($R_{\text{ct}} \sim 168$ Ω) and EP-CT/slurry ($R_{\text{ct}} \sim 126$ Ω) cathodes, indicating a much faster charge transfer capability. These results

clearly demonstrate that the EP-CT/slurry/capping layer cathode enabled fast redox kinetics and benefited from improved charge transfer due to the metallic EP-CT host and conductive capping layer.

Furthermore, the EP-CT/slurry/capping layer cathode with a S-copoly areal mass density of $\sim 3 \text{ mg cm}^{-2}$ displayed excellent cycling stability with high coulombic efficiency ($>97\%$) at 0.2C (Fig. 4e and S20†). The areal capacity was found to be $\sim 3.5 \text{ mA h cm}^{-2}$ (specific capacity of $\sim 1293 \text{ mA h g}^{-1}$). An areal capacity of $\sim 3 \text{ mA h cm}^{-2}$ (specific capacity of $\sim 1082 \text{ mA h g}^{-1}$) was maintained after 100 cycles, with a capacity retention of $\sim 84\%$. In contrast, the C-CT/slurry and EP-CT/slurry cathodes with the same S-copoly areal mass density ($\sim 3 \text{ mg cm}^{-2}$) showed lower areal capacities of $\sim 1.1 \text{ mA h cm}^{-2}$ (specific capacity of $\sim 419 \text{ mA h g}^{-1}$) and $\sim 2.2 \text{ mA h cm}^{-2}$ (specific capacity of $\sim 788 \text{ mA h g}^{-1}$) at 0.2C after 100 cycles, with capacity retentions of ~ 81 and 73% , respectively. Particularly, the EP-CT/slurry/capping layer cathode exhibited a good areal capacity of $\sim 2.5 \text{ mA h cm}^{-2}$ (specific capacity of $\sim 909 \text{ mA h g}^{-1}$) even after 150 cycles (Fig. S20†). These results further imply that the outstanding electrochemical performance of the EP-CT/slurry/capping layer cathode results from both the metallic EP-CT host that allows high sulfur utilization and the conductive capping layer that alleviates the dissolution of polysulfide due to its chemical confinement as Li–N and Li–O interactions.^{19,50} In the case of EP-CT/slurry/capping layer with a S-copoly areal mass density of $\sim 5 \text{ mg cm}^{-2}$ (sulfur loading of $\sim 4.5 \text{ mg cm}^{-2}$), upon cycling at 0.2C up to 150 cycles, the areal capacity decreased from $\sim 4.8 \text{ mA h cm}^{-2}$ (specific capacity of $\sim 1080 \text{ mA h g}^{-1}$) to $\sim 3.8 \text{ mA h cm}^{-2}$ (specific capacity of $\sim 838 \text{ mA h g}^{-1}$) with high coulombic efficiency over 97% (Fig. 4f and S21†).

Based on these results, we further investigated the high-loading performance of the EP-CT/slurry/capping layer cathode as a function of S-copoly areal mass density. Specifically, three different samples (*i.e.*, S-copoly loading of ~ 3 , 5 , and 8 mg cm^{-2} corresponding sulfur loading of ~ 2.7 , 4.5 , and 7.2 mg cm^{-2}) delivered high initial areal capacities of ~ 4.4 , 6.1 , and 8.3 mA h cm^{-2} (corresponding specific capacities of ~ 1617 , 1355 , and 1149 mA h g^{-1}) at 0.1C, respectively (Fig. 4g and h). Moreover, the areal capacities at 0.2C (after 5 cycles at 0.1C) were ~ 3.5 , 4.8 , and 6.6 mA h cm^{-2} (corresponding specific capacities of ~ 1293 , 1080 , and 915 mA h g^{-1}) and exhibited good capacity retention, with areal capacities of ~ 3 , 4 , and 5.1 mA h cm^{-2} (corresponding specific capacities of ~ 1081 , 874 , and 713 mA h g^{-1}) after 100 cycles (Fig. S22†). The coulombic efficiencies were observed to be $>96\%$. Although Li–S cathodes with higher sulfur loading than our S-copoly cathode were reported using carbon-based current collectors (Table S1†), the reported cathodes were based on elemental sulfur and exhibited relatively low specific capacity at high areal capacity. Additionally, the EP-CT/slurry/capping layer cathode with high areal/specific capacity outperforms previously reported S-copoly cathodes (Table S2†) due to its highly porous structure, favorable interfacial interaction, and metal-like conductivity of the chemically modified EP-CTs with a conductive capping layer.

4. Conclusion

We demonstrated that a metallic cotton textile-based S-copoly cathode with high areal/specific capacity values, rate capability, and cycling stability can be prepared with an approach using carbonization, metal electroplating, and LbL assembly of conductive capping layer. The large surface area and bulk metal-like conductivity of the EP-CT significantly enhanced the areal mass density of S-copolys and facilitated charge transfer within the cathode. The H-LbL assembly of conductive capping layer onto the EP-CT/slurry cathode further suppressed the shuttle effect of soluble polysulfides through chemical confinement. The electrochemical performance of the EP-CT/slurry/capping layer cathode was superior to that of previously reported S-copoly cathodes, as well as the EP-CT/slurry and C-CT/slurry cathodes investigated herein. Given that our novel design approach can be effectively applied to prepare Li–S cathodes, which require (1) a large specific surface area, (2) a high electrical conductivity, (3) facile charge transfer between active materials, and (4) effective suppression of soluble polysulfides, we believe that it can provide a basis for the development and design of a variety of high-performance textile-based electrodes.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- 1 M. Armand and J.-M. Tarascon, *Nature*, 2008, **451**, 652–657.
- 2 X. Ji, K. T. Lee and L. F. Nazar, *Nat. Mater.*, 2009, **8**, 500–506.
- 3 Y. Yang, G. Zheng and Y. Cui, *Chem. Soc. Rev.*, 2013, **42**, 3018–3032.
- 4 J. Liang, Z.-H. Sun, F. Li and H.-M. Cheng, *Energy Storage Mater.*, 2016, **2**, 76–106.
- 5 Y.-S. Su and A. Manthiram, *Nat. Commun.*, 2012, **3**, 1166.
- 6 X. Ji and L. F. Nazar, *J. Mater. Chem.*, 2010, **20**, 9821–9826.
- 7 A. Manthiram, Y. Fu, S.-H. Chung, C. Zu and Y.-S. Su, *Chem. Rev.*, 2014, **114**, 11751–11787.
- 8 H. Wang, Y. Yang, Y. Liang, J. T. Robinson, Y. Li, A. Jackson, Y. Cui and H. Dai, *Nano Lett.*, 2011, **11**, 2644–2647.
- 9 Y. Yang, G. Zheng and Y. Cui, *Chem. Soc. Rev.*, 2013, **42**, 3018–3032.
- 10 S.-J. Kim, K. Kim, J. Park and Y.-E. Sung, *ChemCatChem*, 2019, **11**, 2373–2387.
- 11 W. J. Chung, J. J. Griebel, E. T. Kim, H. Yoon, A. G. Simmonds, H. J. Ji, P. T. Dirlam, R. S. Glass, J. J. Wie, N. A. Nguyen, B. W. Guralnick, J. Park, A. Somogyi, P. Theato, M. E. Mackay, Y.-E. Sung, K. Char and J. Pyun, *Nat. Chem.*, 2013, **5**, 518.

- 12 A. G. Simmonds, J. J. Griebel, J. Park, K. R. Kim, W. J. Chung, V. P. Oleshko, J. Kim, E. T. Kim, R. S. Glass, C. L. Soles, Y.-E. Sung, K. Char and J. Pyun, *ACS Macro Lett.*, 2014, **3**, 229–232.
- 13 G. Hu, Z. Sun, C. Shi, R. Fang, J. Chen, P. Hou, C. Liu, H.-M. Cheng and F. Li, *Adv. Mater.*, 2017, **29**, 1603835.
- 14 J. Park, E. T. Kim, C. Kim, J. Pyun, H.-S. Jang, J. Shin, J. W. Choi, K. Char and Y.-E. Sung, *Adv. Energy Mater.*, 2017, **7**, 1700074.
- 15 J. Liu, M. Wang, N. Xu, T. Qian and C. Yan, *Energy Storage Mater.*, 2018, **15**, 53–64.
- 16 J. Key, Y. Feng, J. Shen, P. Wang, H. Wang, H. Liang, R. Wang and S. Ji, *J. Electrochem. Soc.*, 2020, **167**, 020530.
- 17 J. Shen, Y. Feng, P. Wang, G. Qiu, L. Zhang, L. Lu, H. Wang, R. Wang, V. Linkov and S. Ji, *ACS Sustainable Chem. Eng.*, 2020, **8**, 10389–10401.
- 18 P. Bhattacharya, M. I. Nandasiri, D. Lv, A. M. Schwarz, J. T. Darsell, W. A. Henderson, D. A. Tomalia, J. Liu, J.-G. Zhang and J. Xiao, *Nano Energy*, 2016, **9**, 176–186.
- 19 W. Chen, T. Lei, T. Qian, W. Lv, W. He, C. Wu, X. Liu, J. Liu, B. Chen, C. Yan and J. Xiong, *Adv. Energy Mater.*, 2018, **8**, 1702889.
- 20 M. Yan, H. Chen, Y. Yu, H. Zhao, C.-F. Li, Z.-Y. Hu, P. Wu, L. Chen, H. Wang, D. Peng, H. Gao, T. Hasan, Y. Li and B.-L. Su, *Adv. Energy Mater.*, 2018, **8**, 1801066.
- 21 L. Ma, H. L. Zhuang, S. Wei, K. E. Hendrickson, M. S. Kim, G. Cohn, R. G. Hennig and L. A. Archer, *ACS Nano*, 2016, **10**, 1050–1059.
- 22 N. Kang, Y. Lin, L. Yang, D. Lu, J. Xiao, Y. Qi and M. Cai, *Nat. Commun.*, 2019, **10**, 4597.
- 23 W. Kou, X. Li, Y. Liu, X. Zhang, S. Yang, X. Jiang, G. He, Y. Dai, W. Zheng and G. Yu, *ACS Nano*, 2019, **13**, 5900–5909.
- 24 Q. Zhao, X. Hu, K. Zhang, N. Zhang, Y. Hu and J. Chen, *Nano Lett.*, 2015, **15**, 721–726.
- 25 Y. Hu, W. Chen, T. Lei, Y. Jiao, J. Huang, A. Hu, C. Gong, C. Yan, X. Wang and J. Xiong, *Adv. Energy Mater.*, 2020, **10**, 2000082.
- 26 M. Xiang, H. Wu, H. Liu, J. Huang, Y. Zheng, L. Yang, P. Jing, Y. Zhang, S. Dou and H. Liu, *Adv. Funct. Mater.*, 2017, **27**, 1702573.
- 27 G. Hu, C. Xu, Z. Sun, S. Wang, H.-M. Cheng, F. Li and W. Ren, *Adv. Mater.*, 2016, **28**, 1603–1609.
- 28 F. Wu, E. Zhao, D. Gordon, Y. Xiao, C. Hu and G. Yushin, *Adv. Mater.*, 2016, **28**, 6365–6371.
- 29 B. Yao, J. Zhang, T. Kou, Y. Song, T. Liu and Y. Li, *Adv. Sci.*, 2017, **4**, 1700107.
- 30 S.-H. Chung, C.-H. Chang and A. Manthiram, *ACS Nano*, 2016, **10**, 10462–10470.
- 31 A. Sahasrabudhe, H. Dixit, R. Majee and S. Bhattacharyya, *Nat. Commun.*, 2018, **9**, 2014.
- 32 L. Liu, Y. Yu, C. Yan, K. Li and Z. Zheng, *Nat. Commun.*, 2015, **6**, 7260.
- 33 H. Zhang, H. Ning, J. Busbee, Z. Shen, C. Kiggins, Y. Hua, J. Eaves, J. Davis, T. Shi, Y.-T. Shao, J.-M. Zuo, X. Hong, J. Liu and P. V. Braun, *Sci. Adv.*, 2017, **3**, e1602427.
- 34 W. Fu, E. Zhao, X. Ren, A. Magasinski and G. Yushin, *Adv. Energy Mater.*, 2018, **8**, 1703454.
- 35 Y. An, Z. Hu, B. Guo, N. An, Y. Zhang, Z. Li, Y. Yang and H. Wu, *RSC Adv.*, 2016, **6**, 37562–37573.
- 36 S. Ni, X. Lv, T. Li, X. Yang and L. Zhang, *J. Mater. Chem. A*, 2013, **1**, 1544–1547.
- 37 K. Chen, R. Pathak, A. Gurung, K. M. Reza, N. Ghimire, J. Pokharel, A. Baniya, W. He, J. J. Wu, Q. Qiao and Y. Zhou, *J. Mater. Chem. A*, 2020, **8**, 1911–1919.
- 38 J. Chang, J. Shang, Y. Sun, L. K. Ono, D. Wang, Z. Ma, Q. Huang, D. Chen, G. Liu, Y. Cui, Y. Qi and Z. Zheng, *Nat. Commun.*, 2018, **9**, 4480.
- 39 Z. Wang, J. Shen, J. Liu, X. Xu, Z. Liu, R. Hu, L. Yang, Y. Feng, J. Liu, Z. Shi, L. Ouyang, Y. Yu and M. Zhu, *Adv. Mater.*, 2019, **31**, 1902228.
- 40 J.-H. Wang and M. Liu, *Electrochem. Commun.*, 2007, **9**, 2212–2217.
- 41 O. P. Watts, *Trans. Am. Electrochem. Soc.*, 1916, **29**, 395–403.
- 42 S. Y. Cho, Y. S. Yun, S. Lee, D. Jang, K.-Y. Park, J. K. Kim, B. H. Kim, K. Kang, D. L. Kaplan and H.-J. Jin, *Nat. Commun.*, 2015, **6**, 7145.
- 43 Z. Wang, Z. Zheng, S. Zheng, S. Chen and F. Zhao, *J. Power Sources*, 2015, **287**, 269–275.
- 44 X. Wang, X. Li, X. Sun, F. Li, Q. Liu, Q. Wang and D. He, *J. Mater. Chem. A*, 2011, **21**, 3571–3573.
- 45 S. Ni, X. Lv, T. Li, X. Yang and L. Zhang, *J. Mater. Chem. A*, 2013, **1**, 1544.
- 46 Y. Song, D. Kim, S. Kang, Y. Ko, J. Ko, J. Huh, Y. Ko, S. W. Lee and J. Cho, *Adv. Funct. Mater.*, 2019, **29**, 1806584.
- 47 B. T. Zhang, C. J. Sheehan, J. Zhai, G. Zou, H. Luo, J. Xiong, Y. T. Zhu and Q. X. Jia, *Adv. Mater.*, 2010, **22**, 3027–3031.
- 48 S.-H. Chung, P. Han, R. Singhal, V. Kalra and A. Manthiram, *Adv. Energy Mater.*, 2015, **5**, 1500738.
- 49 J. Wang, G. Yang, J. Chen, Y. Liu, Y. Wang, C.-Y. Lao, K. Xi, D. Yang, C. J. Harris, W. Yan, S. Ding and R. V. Kumar, *Adv. Energy Mater.*, 2019, **9**, 1902001.
- 50 G. Xu, Q. Yan, A. Kushima, X. Zhang, J. Pan and J. Li, *Nano Energy*, 2017, **31**, 568–574.