3D x-ray microtomography investigations on the bimodal porosity and high sulfur impregnation in 3D carbon foam for Li–S battery application

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Abstract
Lithium–sulfur (Li–S) batteries, regarded as one of the most promising alternatives to current state-of-the-art rechargeable Li-ion battery technologies, have received tremendous attention as potential candidates for next-generation portable electronics and the rapidly advancing electric vehicle market. However, substantial capacity decay, miserable cycle life, and meagre stability remain critical challenges. More specifically, shuttling of polysulfide (Li$_2$S$_x$; $3 < x \leq 8$) species severely hinders the cycle performance resulting in capacity fade and cycling instability. In the present work, a highly conducting three-dimensional (3D) carbon nanofiber (CNF) foam has been synthesized using the lyophilization method followed by thermal pyrolysis. The highly porous foam materials have a bimodal porosity distribution in the nano and micro regime and were successfully investigated to serve as a potential host for sulfur species intended for Li–S battery application. 3D x-ray microtomography was employed to estimate the nature of sulfur impregnation and distribution in the 3D porous networks. On utilizing the final product as cathode material, sulfur impregnated carbonized CNF foam and modified the separator with functionalized multiwalled carbon nanotubes delivered a specific capacity of $\sim$845 mAh g$^{-1}$ at 100 mA g$^{-1}$.

1. Introduction

Li–S batteries have emerged as promising next-generation energy storage systems owing to a substantially high theoretical specific capacity of $\sim$1675 mAh g$^{-1}$ and energy density of $\sim$2600 Wh kg$^{-1}$, which is approximately three to five times higher than the state of the art commercial Li-ion batteries [1–3]. High abundance, non-toxicity, low cost, and significantly high specific capacity make sulfur a promising cathode material [1–3]. However, the Li–S battery technology are practically impeded by the challenges such as (a) insulating nature of the sulfur ($5 \times 10^{-30}$ S cm$^{-1}$ at 25 °C), (b) significant volume expansion during lithiation ($\sim$79%) leading to capacity fade, (c) low sulfur utilization, (d) polysulfide shuttling which reduces the utilization of active materials in the electrode [1–4]. The electrochemical reaction of sulfur with lithium via two-electron transfer per sulfur atom first forms higher-order lithium polysulfides such as Li$_2$S$_6$, Li$_2$S$_8$, Li$_2$S$_{10}$, which are soluble in widely used ether-based electrolytes, leading to the loss of active sulfur from the cathode [3]. The soluble higher-order polysulfides migrate to the anode (generally referred to as 'shuttle...
effect) due to concentration gradient and reduce to insoluble and insulating Li$_2$S, resulting in the irreversible loss of active material and increase of cell resistance [5]. The shuttle effect has been addressed by applying several strategies, such as using different carbon materials, polar binding additives, and separator modification [6].

Various conductive carbon materials such as carbon nanofibers (CNFs) [7–10], carbon nanotubes (CNTs) [11–20], micro-mesoporous carbon [21–29], and graphene [4, 22, 28–31] have been utilized to either impregnate sulfur to design positive electrode or to trap polysulfides species for the Li–S batteries. High sulfur content and high mass loading are the crucial factors to obtain higher energy density, long cycle life and active utilization [16, 18, 32, 33]. The architecture and surface functionalities play a pivotal role to maximize sulfur loading in the carbonaceous host. Short diffusion path length for Li-ions and high electronic conductivity are also essential for the efficient cycling of Li–S batteries. Limited reports are available focusing on high sulfur loading (above 80% or so) in the carbon host to date. A systematically designed three-dimensional (3D) carbon with excellent conductivity can address some of these aforementioned challenges. Recently, 3D porous conducting networks have been explored to be an excellent sulfur host while offering a great deal of sulfur utilization due to the availability of large volumes. The impregnation of sulfur in various hosts is often linked with surface and morphological changes, resulting in a significant transformation in the properties of the host material. Researchers have recently shown immense interest in computational tomography as a high-resolution imaging and analytical tool for tracking the morphological changes in the Li–S battery systems. Guillaume et al utilized spatially resolved x-ray analysis coupled with absorption tomography to analyze the surface functionalities and morphological modification during a fully charged and discharged state [34]. In a recent publication, Guillaume et al have coupled operando in-situ analysis x-ray absorption tomography and x-ray computed tomography to track chemical and morphological information in Li–S coin cells [35]. Ruoyu et al have provided a visual demonstration of volume expansion in S@hollow carbon with porous shell/MnO$_2$ (S@HCS/MnO$_2$) based cathode during cycling with the help of computed microtomography [36]. Due to the chemical sensitivity and complexity of the system, most studies have been performed in an in-situ mode.

The non-destructive nature of the 3D x-ray tomography imaging technique has positioned itself as an indispensable tool in battery research [37]. Prior studies have underlined the potential of this technique which helps to perform non-destructive high resolution 3D imaging of batteries and their components at ambient and non-ambient environments [38–41]. Tomographic images of batteries before and after their ageing processes are compared to study the changes in micro-structure of electrode materials over a lifetime [42]. Analysis of these images helps to quantify the porosity of the electrodes and directly visualizes particle cracking, current collector corrosion, etc, which in turn can be further related to cell capacity and impedance [43].

Shearing et al [44–50], have extensively explored this x-ray imaging tool in battery research, ranging from multi-scale 3D in-situ approach to the derivation of effective transport parameters, employing both synchrotrons and lab-based tomography platforms. Studies on Li–S batteries revealed the evolution of micro-structures in sulfur cathode across multiple charge cycles, suggesting significant mass transport limitations, leading to sulfur agglomeration [45]. 4D studies on Li–S batteries visualized the 3D morphology of sulfur cathode as a function of the state of charge. They provided evidence towards the formation of sulfur clusters along preferred orthogonal orientations in the cathode in the subsequent charging cycles [46]. Nano computed tomography imaging of elemental sulfur electrode helps visualize its constituent phases and quantification of phase fractions along with particle size distributions [47, 48]. The crucial role of the intrinsic porosity of the carbon binder domain in enhancing Li-ion transport within the electrode was pointed out in this study [49]. Multi-scale tomography studies on rechargeable Mg–S batteries throw light on the micro-structural degradations in these batteries [50]. Dissolution and agglomeration of sulfur particles and densification of carbon binder after ten cycles has contributed immensely towards significant degradation of cell performance. These findings also demonstrate the indispensable role of non-destructive x-ray imaging techniques in the evolution of the battery research landscape.

In the present investigation, functionalized CNF has been chosen as the parental carbon source to produce 3D porous conducting CNF foam (CCNF-f), adopting a simple chemical process and lyophilization protocol followed by a thermal treatment. Mechanically robust and chemically stable CCNF-f host material was found incredibly efficient to impregnate with a high amount of S loading. We have utilized high-resolution x-ray microtomography imaging to visualize the S distribution in the host matrix. Furthermore, computational modeling was used to estimate the micro-scale porosity distribution in the CCNF-f host.
2. Experimental section

2.1. Materials
CNFs, resorcinol, glutaraldehyde, sodium tetraborate decahydrate, 1,2-dimethoxyethane (DME), 1,3-dioxolane (DOL), LiNO$_3$, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), N-methyl-2-pyrolidone (NMP), polyvinylidene difluoride (PVDF) were procured from Sigma Aldrich and used without further purification. Carbon black, Super P was procured from Alfa Aesar. Toluene (sulfur free) and HNO$_3$ were procured from Thomas Baker Chemicals Pvt. Ltd and was used as received. The coin cell (CR-2032) components were procured from Global Nanotech.

2.2. Synthesis of CNF-f
To synthesize 3D CNF-f, the CNFs from Sigma Aldrich were first refluxed in 3 M HNO$_3$ at 60 °C for 6 h, followed by washing with a copious amount of de-ionized (DI) water until the pH was neutral. Afterwards, the powder was washed with absolute ethanol and then dried in the oven at 80 °C for 12 h (the sample will be called f-CNF hereafter). The f-CNF and DI water were taken in a w/v ratio of 5:1 and subjected to ultrasonicication for proper dispersion. A precise amount of the glutaraldehyde, resorcinol, and sodium tetraborate decahydrate was added to the dispersion at a regular interval of 15 min. The resulting dispersion was frozen using liquid nitrogen and subjected to vacuum drying (0.120 mbar) at −80 °C to obtain the 3D CNF-f. Thus synthesized foam sample is referred to as CNF-f in the manuscript.

2.3. Thermal treatment to synthesize CCNF-f
As prepared, CNF-f was subjected to thermal treatment at 800 °C at a heating rate of 5 °C per min for 2 h in an inert (argon gas) atmosphere to convert the crosslinking network into conducting carbon framework without compromising the structure. This would be advantageous to enhance the performance of the Li–S battery through improvement in electronic conductivity. The thermally treated foam samples were collected and labeled as CCNF-f.

2.4. Sulfur impregnation into CCNF-f
Sulfur impregnation was carried out by placing 70 mg of the CCNF-f in an alumina boat and the CCNF-f was covered completely with 1.5 g of fine elemental sulfur powder (Sigma Aldrich). The alumina boat was placed inside a tubular furnace and heated to 350 °C at a heating rate of 5 °C min$^{-1}$ for 2 h under the continuous flow of argon gas. The set temperature in the furnace was 350 °C, but the measured temperature inside the tubular furnace was ~220 °C.

The sample was collected after the furnace reached room temperature and referred to as sulfur impregnated carbonized CNF foam (SCCNF-f). During the initial experimentations, an excessive S presence was observed on the surface of SCCNF-f. Therefore, SCCNF-f was washed with toluene to remove excess sulfur and dried in a vacuum oven at 55 °C for 12 h. The final product is labeled as SCCNF-f-AW. The same naming has been referred to in the manuscript. SCCNF-f-AW–CNT naming is given for the coin cells fabricated using the separator coated with functionalized multiwalled CNTs (f-MWCNTs).

2.5. Functionalization of MWCNTs
To functionalize, the MWCNTs were refluxed in a 3 M HNO$_3$ for 6 h at 60 °C in an oil bath. After cooling down to room temperature, washing was carried out with DI water till the pH reached neutral. Afterwards, the powder was washed with absolute ethanol and dried in the oven at 80 °C for 12 h.

2.6. Materials characterization
Powder x-ray diffraction (p-XRD) patterns were recorded on a Phillips PANalytical diffractometer. Raman spectra were carried out on an HR 800 Raman spectrometer (Jobin–Yvon, Horiba, France) using a 632.8 nm red laser. X-ray photoelectron spectroscopic (XPS) measurements were conducted on a VG Micro-Tech ESCA 3000 instrument. The nitrogen adsorption–desorption isotherm measurements were performed on a Quantachrome surface area analyzer; the samples' specific surface areas and pore size distributions (PSDs) were obtained by Brunauer–Emmett–Teller (BET) model and nonlocal density functional theory (NLDFT). Thermogravimetric analysis (TGA) was carried out using SDT Q600 DSC–TGA instrument.

2.7. 3D x-ray microtomography imaging and analysis of CNF-f
3D x-ray microtomography imaging (Xradia 510 Versa x-ray Microscope, Zeiss x-ray Microscopy, Pleasanton, CA, USA) was performed to investigate the morphology, porosity, and PSD of CNF-f. Specimens
were loaded onto the sample holder and placed between the x-ray source and the detector assembly. Detector assembly consists of a scintillator, 20 × optics and a charge-coupled device camera. X-ray source was ramped up to 80 kV and 7 W. The tomographic image acquisitions were completed by acquiring 7001 projections over 360° of rotation with a pixel size of 0.68 μms for a sample size of 0.7 × 0.7 × 0.7 mm³. In addition, projections without the samples in the beam (reference images) were also collected and averaged. The filtered back-projection algorithm reconstructs the projections to generate the two-dimensional (2D) virtual cross-sections of the specimens. Image de-noising, filtration, segmentation, and further processing were performed using the GeoDict software package (GeoDict®, 2018, Math2Market GmbH, Germany). 2D virtual cross-sections were further trimmed down to a sub-volume (100 × 100 × 100 voxels with 0.68 cubic microns per voxel), filtered to remove noise and segmented after OTSU threshold selection based on local minima from the grayscale histogram. The resultant 3D reconstructed model was used to estimate the pore characteristics such as porosity, PSD, etc., using the PoroDict® software package (GeoDict® 2018, Math2Market GmbH, Germany), where pore radius is determined by fitting spheres into the pore volume.

2.8. Electrode preparation and electrochemical characterization
The SCCNF-f-AW, carbon black (Super P) and PVDF were taken in 80:10:10 ratio and made a slurry by grinding using NMP as the solvent. Thus prepared slurry was coated on carbon-coated aluminum foil using the doctor-blade method and it was dried at 55 °C in a vacuum oven for 24 h. Electrochemical characterizations were performed on the coin cells (CR 2032) fabricated in the half-cell configuration. The coating was subjected to calendering and then cut into circular discs of 14 mm diameter. The average sulfur loading was 1.5 mg cm⁻². With these electrodes coin cells were fabricated using Li metal discs as counter electrodes, Celgard 2325 as separator and a freshly prepared electrolyte consisting of 1 M LiTFSI in 1:1 v/v mixture of DOL and DME with 0.4 M LiNO₃ as additive. The coin cells were assembled in an Ar-filled glove box with H₂O and O₂ levels less than 0.1 ppm. The cyclic voltammetry measurement were performed on a SP-300 EC Biologic potentiostat and the galvanostatic charge/discharge cycling were performed on Newark BTS4000 series battery testing system in a voltage window between 1.7 and 2.8 V.

3. Results and discussion
The steps involved in the preparation of SCCNF-f-AW foam is shown in scheme 1. The CNF-f was prepared by treating the CNFs first with HNO₃ and then preparing the 3D foam as described in the section 2. Transmission electron microscope images of the CNFs utilized are shown in figure S1 (available online at stacks.iop.org/JPEnergy/4/014003/mmedia) (supplementary information) and the optical photographs of the CNF-f in figure S2 (supplementary information). The 3D crosslinking network formed by polymerization between f-CNFs using resorcinol and glutaraldehyde contains carbon content [51, 52]. The stability of the 3D SCCNF-f is also crucial after carbonization and sulfur impregnation. To eliminate the possibility of excess sulfur deposition on the surface of SCCNF-f after S impregnation, which may cause increased interfacial resistance, the SCCNF-f was washed in toluene followed by drying in a vacuum oven at 55 °C for 12 h. To investigate sulfur impregnated 3D cross-linked carbon structure, the product was characterized with various techniques.

Figure 1 shows the p-XRD data and Raman spectrum of the CCNF-f and SCCNF-f-AW. Image in figure 1(a) represents the typical p-XRD spectrum of CCNF-f with the peaks for (002) and (100) planes appearing at 24.2° and 43°, respectively, corresponding to the partially graphitic nature of the sample [53, 54]. The broadness could be attributed to the cross-linked carbon resulting in amorphous carbonization of the resorcinol-glutaraldehyde crosslinkage. The p-XRD of the CNF-f is supplied as figure S3 (supplementary information). After the impregnation and successive washing, the p-XRD confirms the successful impregnation of sulfur into the foam. The diffraction peaks corresponding to sulfur in the SCCNF-f-AW match well with the JCPDS card (JCPDS 08-0247) for elemental sulfur. The peaks corresponding to CCNF-f could not be observed in the case of SCCNF-f-AW due to the high intensity and dominant diffraction peaks of x-rays from the sulfur compared to carbon. Figure 1(b) reports the Raman spectra comparison for CCNF-f and SCCNF-f-AW, indicating changes in the intensity and the I₃d/I₉g ratio. The results suggest the Raman spectrum of the CCNF-f consist of two major peaks corresponding to D and G bands with the slightly higher D band intensity. The I₉g/I₃d ratio is calculated using the area of D and G peaks by fitting them using the Gaussian function, which is shown in figure S4 (supplementary information). For CCNF-f this ratio is ~2.28, which indicates the high defective nature of the material. Further, I₉g/I₃d for SCCNF-f-AW is found to be 2.71, this increase in the I₉g/I₃d suggests an increase in defects on the materials after sulfur impregnation [55]. The defective nature of CCNF-f could be conducive for alleviating polysulfides’ dissolution and diffusion generated during the charge/discharge cycles. Furthermore, figure 1(b) shows the Raman spectra of SCCNF-f-AW, indicating some high intense peaks centered at 153,
217.6, 433.3, and 471 cm\(^{-1}\) corresponding to the sulfur presence along with the D and G bands of the host material. The presence of high-intensity peaks in the p-XRD and the Raman characterization confirms the successful impregnation of the sulfur in the host carbon foam [56].

Further, the TGA was carried out to determine the percentage of sulfur impregnated into the CCNF-f foam, and the results are shown in figure S5 (supplementary information). The TGA shows that a very high content of about 95.6% of sulfur impregnation has been achieved into the CCNF-f.

BET analysis was carried out to understand the porous nature of prepared foam materials, and the resulting data is shown in figure 2. BET results are converted to the PSD curve shown in figure 2(a) for the test samples using the NLDFT slit pore model to analyze the porosity distribution. High volume adsorption for CCNF-f, for a pore diameter lesser than 2 nm, indicates the substantial presence of micropores. CCNF-f
also consists of the observable presence of mesopores having a diameter range between 2–5 nm and 8–14 nm. However, SCCNF-f-AW indicates a slight narrower presence of mesopores of the diameter in the 2–5 nm range. Figure 2(b) shows the $N_2$ adsorption–desorption isotherm for CCNF-f and SCCNF-f-AW. CCNF-f indicates the presence of type-I and type-IV BET isotherm with a sizeable microporosity and substantial presence of mesopores. However, SCCNF-f-AW consists of type-IV isotherm only, indicating the presence of mesopores only, thus complementing the PSD results. Multi point Brunauer–Emmett–Teller technique was used to estimate the surface area of CCNF-f and SCCNF-f-AW and found to be 310 and 23 m$^2$ g$^{-1}$ respectively. The results suggest that sulfur impregnation might be blocking the surface pores of SCCNF-f-AW for the $N_2$ adsorption resulting in the significant reduction of the surface area. The BET PSD and the isotherm of CNF-f sample are provided in the figure S6 (supplementary information).

XPS analysis was performed to analyze the elemental composition and bonding nature at the surface of CCNF-f, SCCNF-f-AW. The resulting spectra are shown in figure 3. Figure 3(a) represents the survey spectra of CCNF-f, and SCCNF-f-AW, confirming the additional elemental presence of S in the SCCNF-f-AW samples. Figures 3(b) and (d) depicts the high-resolution spectra of C 1s for the CCNF-f and SCCNF-f-AW samples, respectively. The XPS spectra indicates the presence of C–C and C=C, C=O, C=O, and O=C=O bonds in the CCNF-f. A similar composition has been observed for the SCCNF-f-AW except for a significant increase in the peak area around 285.7 eV, which is assigned to the C–O and C=S bonds. The increase in peak area indicates the additional formation of the C=S bond, which also have a closer BE to the C=O bond, and it is difficult to resolve them separately [17]. Figures 3(c) and (e) show the high-resolution spectra of O 1s for CCNF-f and SCCNF-f-AW, respectively. Both the materials indicate the dominance of presence of C=O, C=O and O=C=O bonds. Moreover, the high-resolution O 1s spectra of SCCNF-f-AW indicates the additional presence of S=O and C=O bonds with binding energy peak centered at 532.2 eV. The peak centered at 533.2 eV indicates the presence of C=O and S=O (in the form of sulfate ion) [9, 57, 58]. The binding energy of 534.89 eV corresponds to the presence of O=C=O bonds [57, 59]. The high-resolution spectrum of the S 2p peak for SCCNF-f-AW is shown in figure 3(f). With a peak splitting of 1.13 eV, both peaks 2p$^{3/2}$ and 2p$^{1/2}$ of S 2p indicate the significant presence of S in the SCCNF-f-AW [59].

Figure 4 shows the SEM images of the CCNF-f (a), (b) and the SCCNF-f-AW (c) and (d) samples. Figures 4(a) and (b) indicate that CCNF-f consists of a 3D interconnected structure of CNFs formed by polymerization between the f-CNF using resorcinol and glutaraldehyde crosslinker. Figures 4(c) and (d) shows the FESEM images of SCCNF-f-AW after sulfur impregnation in CCNF-f and washing with toluene. The SEM image confirms that pore of the CCNF-f are filled with the impregnated sulfur whilst retaining the 3D network. The elemental mapping of the SCCNF-f-AW is shown in the images (e)–(h). Figure 4(e) reports the SEM image, and the overlay image (f) shows the presence of carbon and sulfur in the samples. Figures 4(g) and (h) show the distribution of carbon and sulfur in the 3D foam. The pores of the CCNF-f are filled with the impregnated sulfur, as it is evident from the elemental mapping.

3D x-ray microtomography imaging was used to investigate the morphology and porous nature of CNF-f samples. Volume-rendered high-resolution 3D microtomography images of the CCNF-f and SCCNF-f-AW are shown in figure 5. Figure 5(a) shows the 3D porous arrangement of CCNF-f, which retains its interconnecting stacked layers after carbonization at 800 °C. The structure of CCNF-f also exhibits an...
enhancement in the porosity of the foam after carbonization. The as-prepared CNF-f is found to have a porosity of 70%, which further increases to 80% for CCNF-f due to the shrinkage of the crosslinking carbon network as a result of thermal treatment. Figure 5(b) exhibits a volume-rendered tomography image of SCCNF-f-AW to map the presence of impregnated S in the host. A very high sulfur loading is observable without disturbing the CCNF-f structure after impregnation. The tomographic image of the as-prepared CNF-f is provided in the figure S7 (supplementary information) comparing it with CCNF-f in figure 5(a) and SCCNF-f-AW in figure 5(b) it is evident that the 3D network structure of the foam is retained with an increase in micron-sized porosity after the carbonization process and successive sulfur impregnation followed by washing. The increase in porosity after carbonization is attributed to the conversion of the crosslinking network into the carbon.

Figure 6 shows the PSD after image segmentation and 3D x-ray tomography images of the CNF-f and CCNF-f. The PSD observed in microtomography analysis is in the micrometer size as the instrument’s true spatial resolution limit is 1 µm. The pores in CNF-f (figure 6(a)) have an average pore size of around 4 µm, which further increased to about approximately ∼7 µm for CCNF-f (figure 6(b)) after the thermal treatment. The BET results of CCNF-f shows a collective porosity distribution in the micro-mesoporous range (nano regime). At the same time, computational microtomography estimation provides a porosity distribution in micro regime with 7 µm pore contributing to maximum volume fraction for CCNF-f. From the results it can be established that the CCNF-f foam has a bimodal porosity distribution in the micro and nano regime, making it an ideal host candidate for high sulfur loading as observed in TGA. Figures 6(c)–(e) show the tomographic images of CNF-f, CCNF-f and the color coded PSD of CCNF-f. The color scale on the right side of figure 6(e) depicts the PSD range of the concerning colors in the image. Red corresponds to pore sizes on the higher side while blue for the lower side.
Figure 4. Scanning electron micrographs of the CCNF-f (a) and (b), SCCNF-f-AW (c) and (d). (e) SEM image of the SCCNF-f-AW taken for the mapping. (f) The overlay image of the mapping showing the distribution of carbon and sulfur in the sample, (g) and (h) shows the color-coded images of carbon and sulfur, respectively.

The coin cells of SCCNF-f-AW samples were assembled with the composition of 80:10:10 ratio of the SCCNF-f-AW:PVDF:conducting carbon. Figure 7 shows the electrochemical investigations of the coin cells. Figure 7(a) represents the cyclic voltammogram recorded at a scan rate of 0.1 mV s$^{-1}$. The cyclic voltammogram exhibits characteristic peaks corresponding to the typical Li–S battery electrochemical behavior with reversible reduction and oxidation processes. The reduction process occurs in two steps, with the first peak appearing $\sim 2.3$ V due to the reduction of $S_8$ to long-chain polysulfides ($Li_2S_n$, $4 \leq n \leq 8$) at high potential and the peak at $\sim 2.0$ V appears due to further reduction of long-chain polysulfides to short-chain polysulfides ($Li_2S_n$, $1 \leq n < 4$) [58]. The oxidation peak associated with the reversible formation of short-chain polysulfides to long-chain polysulfides and then to $S_8$ is observed at 2.46 V [58]. Except for the first cycle, the following cycles overlap, exhibiting excellent electrochemical reversibility [60]. Figure 7(b)
Figure 5. 3D volume rendered x-ray tomography images of (a) CCNF-f, (b) SCCNF-f-AW.

Figure 6. Pore size distribution obtained from tomography analysis for (a) CNF-f and (b) CCNF-f, (c) and (d) segmented 3D x-ray tomography images of CNF-f and CCNF-f, respectively. (e) Color coded 3D visualization of pores in CCNF-f with respect to their pore size and corresponding color scale on the right side.

shows the impedance spectroscopic measurements before and after the cyclic voltmometry (CV). The fitted equivalent circuits are shown in the figure S8(a) (supplementary information). The porous carbon material more often exhibits combined impedance response in one or two elongated semicircle due to overlapping of frequency bands and hence it become very difficult to predict separate impedance response on the basis of contributor in final electrochemical impedance spectroscopy curve. The Nyquist plot for SCCNF-f-AW in figure 7(b) indicates the presence of an elongated semicircle which is fitted with two separate time constants. On separating the two time constants and realizing a simplified circuit, results in series connection of two constant phase elements (CPEs) in parallel with one charge transfer resistance (Rct) to each, in series with an equivalent series resistance (ohmic resistance at high frequency) and a Warburg element (diffusion resistance at low frequency) [61, 62]. The two charge transfer resistances may arise from the contribution of solid electrolyte interphase (SEI) layer, separator or charge transfer resistance at the electrode interface. However after CV, the fitted data (subset data) indicates similar impedance characteristics but the charge transfer
Figure 7. (a) Cyclic voltammogram at a scan rate of 0.1 mV s$^{-1}$, (b) electrochemical impedance spectra before and after the CV measurement, (c) cycling stability at a current density of 100 mA g$^{-1}$ and (d) specific capacity versus potential plot for the sample SCCNF-f-AW.

resistance decreases substantially, indicating the conducive SEI layer formation and conducting channel formation for Li ion transport.

Figure 7(c) represents the cycling data of the SCCNF-f-AW. The cell was first discharged at a lower current density of 50 mA g$^{-1}$ in order to favor the formation of SEI and then further charging/discharging cycles were carried out at 100 mA g$^{-1}$. In figure 7(c) only the cycling data at 100 mA g$^{-1}$ is shown for the sake of clarity. The cell delivered an initial discharge capacity of $\sim$694 mAh g$^{-1}$ which decreases to 228 mAh g$^{-1}$ after 50 cycles. Figure 7(d) shows the plot of specific capacity vs potential, which displays two distinct charge–discharge plateaus associated with the oxidation-reduction reactions between Li and S, which is a characteristic feature of the Li–S battery. These plateaus match well with the redox peaks appearing in the CV curves. The formation of soluble long-chain lithium polysulfides is recognized by the appearance of a discharge plateau at a higher potential. The discharge plateau at lower potential is ascribed to the reduction of long-chain polysulfides to short-chain polysulfides.

The electrochemical performance of the CNF-f and CCNF-f (SCNF-f and SCCNF-f after S impregnation) were also studied and the data is shown in figures S9 and S10 (supplementary information) respectively. However, CNF-f suffers from poor conductivity due to the presence of polymeric crosslinkages formed during foam synthesis process. The cell fabricated without washing the sample (SCCNF-f) exhibited significant shift in the position of successive CV peaks as it can be observed from figure S10(a) (supplementary information). After washing the sample (SCCNF-f-AW), did not show significant shift in the position of successive peaks in the CV curves as it can be seen from the figure 7(a). Hence, although capacity and stability of SCCNF-f are slightly better than SCCNF-f-AW, by carrying out the washing step, significant polarization was reduced. Figures S11(a) and (b) show the calculated overpotential for the 1st and 20th cycles of SCCNF-f and SCCNF-f-AW respectively. Washing the sample also resulted in reduction of the overpotential (the gaps between charge–discharge plateaus). The increasing polarization will eventually lead to a larger overpotential which will result in faster capacity fading; hence washing was an important step to reduce the polarization observed in without washing the sample (SCCNF-f).

Modifying separator with the coating of MWCNTs helps in the retention of capacity due to the binding of polysulfides with the functional groups on the surface of MWCNTs [18–20, 60]. In the present work, to improve capacity retention and mitigate the polysulfide dissolution the separator was coated with f-MWCNT. The f-MWCNTs were coated on the separator by making slurry of f-MWCNTs and PVDF binder (9:1) in NMP. The cells were fabricated such that the f-MWCNT coated side of the separator faces the
Figure 8. (a) Cyclic voltammogram at a scan rate of 0.05 mV s\(^{-1}\), (b) electrochemical impedance spectra before and after the CV measurement, (c) cycling stability at a current density of 100 mA g\(^{-1}\) and (d) specific capacity versus potential plot for the SCCNF-f-AW-CNT.

cathode. The electrochemical results with modified separator are shown in figure 8. Figure 8(a) shows the CV carried out at a scan rate of 0.05 mV s\(^{-1}\) exhibiting two distinct reduction peaks, the first peak at 2.25 V corresponds to the formation of long-chain polysulfides Li\(_{2}\)S\(_n\) (4 ≤ n ≤ 8) and the second peak at ~2.0 V corresponds to the further reduction of long-chain polysulfides to the short-chain Li\(_2\)S\(_2\)/Li\(_2\)S \[19, 24, 29, 58, 59\]. The oxidation peak at 2.5 V is attributed to the formation of long-chain polysulfides from the short-chain polysulfides and then to form the S\(_8\). Figure 8(b) shows the fitted impedance spectrum before and after the CV measurements. The equivalent circuit for the same is provided in the figure S8(b) supplementary information. Figure 8(b) indicates that for SCCNF-f-AW-CNT initially charge transfer resistance is less which further increases after performing CV. The circuit fitting of SCCNF-f-AW-CNT indicates a parallel contribution from a CPE, and an associated charge transfer resistance which is in series with two CPEs and Rcts and a Warburg element as shown in figure S8(b). The circuit has been drawn on the basis of best fitted curve. However, after CV the impedance behavior becomes rather simplified but the overall charge transfer resistance increased. The binding of polysulfides to the MWCNTs coated on the separator after initial cycling may increase the resistance contribution from the separator. Figure 8(c) shows the cycling data at a current density of 100 mA g\(^{-1}\). Before doing cycling at 100 mA g\(^{-1}\) the cell was cycled at a current density of 10 mA g\(^{-1}\) and 25 mA g\(^{-1}\), respectively for one cycle each to ensure proper SEI formation. At 100 mA g\(^{-1}\), an initial discharge capacity of ~845 mAh g\(^{-1}\) was achieved and it reaches to ~567 mAh g\(^{-1}\) after 46 cycles, with significant improvement in the capacity retention as a result of separator modification. Figure 8(d) depicts the plot of specific capacity versus potential showing two distinct plateaus in the discharge curves corresponding to the reduction of S\(_8\) to Li\(_2\)S\(_n\) (4 ≤ n ≤ 8) and then to Li\(_2\)S\(_2\)/Li\(_2\)S. These short-chain polysulfides are further converted to long-chain polysulfides and then to S during the charging process. The separator modification helps in the retention of capacity values by reducing the polysulfide shuttling by binding them to the functional groups on the MWCNTs.

4. Conclusion

In conclusion, the present investigation presents a simple chemical and lyophilization technique followed by thermal pyrolysis to prepare 3D CNF foam with a high surface area of ~310 m\(^2\) g\(^{-1}\) and bimodal porosity with micro-mesopores below 5 nm and micron-sized pores in the range of ~7 µm. The suitability of the as prepared foam was investigated as a potential sulfur host for the Li–S battery cathode. The
SCCNF-f-AW-CNT delivered an initial specific capacity of $\sim 845 \text{mAh g}^{-1}$, showing significant capacity retention.

**Data availability statement**

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

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**Ethical statement**

This material is the authors’ own original work, which has not been previously published elsewhere.

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