Influence of C–S interactions on the electrochemical performance of –COOH functionalized MWCNT/S composites as lithium-sulfur battery cathode

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Abstract. Effective trapping of polysulfides within the carbon cathode host strongly depends on intrinsic C–S interactions. We report herein a systematic study of the influence of S-loading process on C–S interactions in MWCNT/S composites prepared by three commonly used industry-friendly methods, namely, mechanical solid-state mixing, infiltration method from a solution of S in CS₂, and chemical deposition by disproportionation reaction of sodium sulfide and sodium thiosulfate. FESEM and TEM studies reveal strikingly different morphologies of the resulting MWCNT/S composites. XPS and Raman studies indicate different extents of recovery of π bonds in MWCNT due to varying degrees of C–S interfacial interactions in the composites. Furthermore, it is found that the C/O atomic ratio in the composites plays a crucial role: the higher the C/O value the better is the S-confinement. These subtle physical changes induced by C–S interactions in the composites can be related to electrochemical performance when tested in Li-S coin cells. It is found that the best results (high initial capacity of 1143 mAh g^{−1} and better capacity retention) could be achieved when the solution infiltration method was used for S-loading. This conclusion is further validated by using activated carbon as S-host.

Keywords. Electrochemical energy storage; Li-S battery; carbon–sulfur interaction; XPS.

1. Introduction

Lithium-sulfur (Li-S) battery is emerging as the post-lithium-ion high energy density energy storage technology.^{1,2} Sulfur (S), an inexpensive and nontoxic material, is long known to be a good cathode material for various primary/secondary batteries owing to its high specific capacity (theoretical: 1675 mAh g^{−1} for the reaction, S₈ + 16 Li⁺ + 16 e[−] ↔ 8 Li₂S, considering the mass of S and 1166.5 mAh g^{−1} with respect to Li₂S).^{3,4} When S is coupled with high capacity Li (theoretical: 3862 mAh g^{−1}), very high energy density (theoretical: 2611 Wh kg^{−1}) could be achieved with respect to Li₂S as the end product.^{5–7} However, there are several major obstacles that hinder the practical application of the Li-S battery. First, the intrinsically insulating nature of elemental S limits charge transport. Second, the dissolution of intermediate polysulfides in the organic electrolyte

during the redox reactions (Li₂S_n, 4 ≤ n < 8) leads to loss of active material causing rapid capacity fading. Third, the dissolved lithium polysulfides diffuse to the Li anode and form solid precipitates (Li₂S or Li₂S₂) upon reduction. These reduced products may again diffuse back to the cathode forming long chain polysulfides during recharging. This repetitive parallel ‘shuttle phenomenon’ gradually lowers active material utilization leading to low Coulombic efficiency and short cycle life.^{8–10} Additionally, low sulfur utilization and large volume changes during the redox reactions cause severe performance degradation. It has long been recognized that developing a suitable sulfur host is the key to address these intriguing issues. Carbon materials having excellent conductivity, large surface area, pore volume and strong adsorption property have been proved to be effective cathode support. Therefore, carbon in various forms have been used to host S, e.g., carbon nanotubes,^{11,12} activated carbon,^{13,14}

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ordered mesoporous carbon,^{15,16} microporous carbon,^{17,18} porous hollow carbon spheres,^{19,20} porous carbon fibres etc.,²¹ as well as some mixed forms.^{22–24} Among these, multiwall carbon nanotube (MWCNT) is an attractive choice from a practical point of view for its unique structural, electrical, thermal and mechanical properties.^{12,25} Consequently, extensive research efforts have been focused on developing MWCNT/S cathodes for improving the S loading and utilization by using various methods of S loading and remarkable advancements have been made.^{23,24,26,27} For example, Chen *et al.* have obtained the specific capacity of 650 mAh g^{−1} after 200 cycles at 1 A g^{−1} from nanoscale core–shell functional MWCNT/S structure though the S content in the composite was low (58 wt%).²⁸ Yuan *et al.* could improve the S content to 80 wt% in S-coated-MWCNT and still obtained the reversible capacity of 670 mAh g^{−1} after 60 cycles at 100 mA g^{−1}.²⁹

Recently, it has been recognized that enhancing interactions between carbon and sulfur is extremely important for effective S confinement within the host structure. Therefore, efforts have been made to restrict the dissolution of polysulfides and their diffusion by physical confinement through morphological designing such as porous carbon materials.^{30–33} Efforts have also been directed to prepare functionally modified carbon surfaces or incorporation of metal/metal oxides to introduce polar interactions^{34–37} or the thiosulfate mechanism for sulfide binding through chemical interactions.^{7,38} Additionally, low sulfur loading in the cathode support is another major hindrance for practical application. The degree of S loading would vary not only on the physical and morphological properties of MWCNT but also on the method of S incorporation. Several methodologies have been employed to prepare MWCNT/S cathodes, for example, melt diffusion,³⁹ ball milling,⁴⁰ solution mixing,⁴¹ liquid phase infusion,⁴² chemical deposition, etc.²³ Surprisingly, no systematic study is available to examine how different methods of preparation result in different morphologies and affect the extent of S loading. Besides loading, S confinement is also very crucial for practical application. The S confinement inside the carbon support would depend both upon morphology and C–S interactions. It is commonly believed that carbon being non-polar, physical mixing of C and S through mechanical solid-state mixing or solution infiltration route would lead to weak C–S interactions in comparison to chemical interactions through the thiosulfate mechanism for sulfide binding.^{7,43–45} However, no systematic study on the effect of different S loading processes on the same carbon material, particularly MWCNT with respect to C–S interactions and S-confinement is available.

Thus, in this work, we have endeavoured to undertake three common industry-friendly preparation techniques, namely, mechanical solid-state mixing, solution infiltration from 10% solution of S in carbon disulfide and chemical deposition by disproportionation reaction of sodium sulfide and sodium thiosulfate to develop MWCNT/S electrodes using commercially available –COOH-terminated MWCNT and evaluate the physical, morphological and electrochemical properties. The objective here is to understand how C–S interactions are influenced by the sulfur loading process. A comparison of the electrochemical performances of the MWCNT/S cathodes obtained by the three methods is also presented.

2. Experimental

2.1 Materials

–COOH-functionalized MWCNTs (purity 95%, ash content < 1.5%) were purchased from Cheap Tubes Inc. The outer diameter, length and surface area of the –COOH-functionalized MWCNTs (henceforth referred to as MWCNT) were <8 nm, 10–30 mm and 500 m² g^{−1}, respectively. Sulfur (≥99.5%) was obtained from Sigma-Aldrich.

2.2 Preparation of MWCNT/S composite cathodes

MWCNT/S composite cathodes were prepared by loading S onto MWCNT by three commonly used methods as described below:

2.2.1. Mechanical solid-state mixing: Sulfur and MWCNT were homogeneously mixed in the weight ratio of 4:1 by manual grinding with a mortar and pestle. The composite was named CSM.

2.2.2. Solution infiltration method: Sulfur was dissolved in carbon disulfide (CS₂; 99.9+%, Alfa Aesar) to form a 10 wt% solution. MWCNT was added to the sulfur-CS₂ solution and the mixture was made homogeneous by sonication for 15 min. It was then heated at 60 °C with constant stirring to evaporate CS₂. The resulting composite powder was named CSC.

2.2.3. Chemical deposition method: Sulfur was deposited by disproportionation reaction of sodium sulfide (Na₂S; 98.0% min, Alfa Aesar) and sodium thiosulfate (Na₂S₂O₃; 99%, Alfa Aesar) in acidic medium. The reaction can be described as:

The composite was named CSCH. The MWCNT/S composites were annealed separately in closed vessels in Ar atmosphere in two steps: first, at 155 °C for 12 h and then, at 200 °C for 2 h. The first annealing temperature was selected

Scheme 1. Schematic representation of three synthesis methods adopted for MWCNT/S composites.

as 155 °C because at this temperature, the viscosity of sulfur is the lowest and thus, sulfur could conformably diffuse to the surface of the MWCNT. In order to remove any superfluous sulfur as well as sulfur without any interaction with MWCNT surface further annealing at 200 °C was done.⁴⁶ A schematic representation of the three synthesis methods is shown in Scheme 1.

2.3 Material characterization

X-ray powder diffraction patterns were recorded in the 2θ range of 10–70° at a scanning rate of 2° min^{-1} by a Rigaku Smart Lab X-ray diffractometer operating at 9 kW (200 mA; 45 kV) using Cu- $K\alpha$ radiation. Microstructure and morphology of the prepared MWCNT/S composites were examined by a field emission scanning electron microscope (FESEM) (ZEISS Supra 35) and a 300 kV transmission electron microscope (TEM) (Tecnai G2 30ST FEI). Thermogravimetric analyses (TGA) were carried out in the temperature range of 27–800 °C under argon flow at a heating rate of $5^\circ \text{ C min}^{-1}$ using Simultaneous Thermal Analyzer (STA 449F, Netzsch). Raman signals were recorded by a Renishaw In Via Reflex micro Raman spectrometer with excitation of argon ion (514 nm) laser with a resolution of 1 cm^{-1} by keeping the laser power low enough to avoid local heating of the sample. X-ray photoelectron spectroscopy (XPS) study of MWCNT/S composites was carried out by a PHI 5000 VersaProbe II spectrophotometer (Physical Electronics Inc.) using a monochromatized Al $K\alpha$ ($\sim 1486.6 \text{ eV}$) X-ray beam of size $\sim 100 \mu\text{m}$. Survey scans, as well as relevant high-resolution XPS scans, were recorded keeping the experimental conditions identical. The binding energies of all the high-resolution scans were calibrated using primary C 1s signal at 284.5 eV. High-resolution spectra were resolved into their respective Gaussian fits after removal of background

intensity. Elemental compositions and the ratios of carbon to oxygen (C/O) or sulfur to carbon (S/C) of all the composites were derived from integrated intensities of the relevant photoelectron peaks using the listed atomic sensitivity factors (ASF) for PHI 5000 VersaProbe II spectrophotometer.

2.4 Electrochemical characterization

The standard slurry casting procedure was followed for the preparation of the working electrodes. A homogeneous slurry, prepared by mixing 80 wt% of MWCNT/S composite, 10 wt% of Super-P (conducting agent) and 10 wt% of polyvinylidene fluoride (binder) in *n*-methyl pyrrolidinone (solvent), was coated onto Al foil (thickness $19 \mu\text{m}$) and dried at 60 °C under vacuum overnight. After calendaring the resulting film at 80 °C, circular disks of 15 mm in diameter were cut for use as an electrode. Sulfur loading in the electrode was typically within 1.1–1.3 mg/cm^2 and the corresponding S fraction was between 58 and 65 wt%.

2032-type coin cells were assembled in an Argon-filled glove box with MWCNT/S as a cathode, Li foil as an anode and Celgard 2300 as a separator. The electrolyte was 1 M lithium bis(trifluoromethanesulfonyl)-imide (LiTFSI, $\geq 98\%$, Alfa Aesar) dissolved in a mixture of 1,3-dioxolane (DOL, 99.8%, Acros Organics) and 1,2-dimethoxyethane (DME, $\geq 99\%$, Acros Organics) (1:1 vol%) containing 0.1 M lithium nitrate (LiNO_3 , $\geq 99\%$, Acros Organics).

Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) techniques were employed for electrochemical characterization of the composite cathodes. CVs were recorded with a galvanostat-potentiostat (PGSTAT302N, Autolab) in the potential range of 1.5–3.0 V at a scan rate of 0.1 mV s^{-1} . EIS experiments were performed by using the same galvanostat-potentiostat in the frequency range of 100 kHz to 0.1 Hz.

Figure 1. X-ray diffractograms of (a) MWCNT, (b) CSC, and (c) simulated pattern for S₈ (JCPDS Ref. no. 01-083-2283).

GCD measurements were carried out by using an automatic battery tester (BT2000, Arbin, USA) in the voltage range of 1.5–2.8 V at various current densities of 0.05 C–1.0 C (1 C = 1675 mA g^{−1}).

3. Results and Discussion

X-ray diffractograms of MWCNT and MWCNT/S composite (CSC) are shown in Figure 1. The diffractogram of MWCNT exhibits two characteristic broad peaks at ~25.7° and ~43.6° due to the (002) and (100) planes of graphitic carbon (Figure 1a). An additional broad hump, observed at ~53.1°, can be assigned to reflections from (004) planes of MWCNT. The X-ray diffractogram of CSC (Figure 1b) shows the presence of S in the highly crystalline state, the orthorhombic form of S₈ (space group *Fddd*) is in accordance with JCPDS File no. 01-083-2283. However, the diffraction peaks of MWCNTs in CSC are masked by the more intense S peaks. Similar X-ray diffractograms have also been observed for CSM and CSCH (Figure S1, Supplementary Information) indicating that none of the S-loading processes leads to any structural transformation of sulfur during the preparation of MWCNT/S composites.

The sulfur content in each of the MWCNT/S composites was determined from the respective TGA profiles where sharp weight losses are observed in the temperature region of ~250 to 370 °C due to the evaporation of S (Figure 2). It is observed that loss of sulfur occurs

Figure 2. TGA profiles for CSM, CSC and CSCH.

in CSCH at a temperature lower than that for CSC or CSM. There is a difference of ~22 °C. The reason for this is not clear, but probably can be assigned to relatively weaker C–S physical interactions in CSCH. The respective wt% of S are 79.1, 80.8 and 57.1 for CSM, CSC and CSCH. It is interesting to note that while both mechanical solid-state mixing and solution infiltration method result in high S loading, the chemical deposition produces a composite with a relatively lower S loading. However, it is possible that in addition to the S₈ form, some of the S deposited in CSCH may reside in chemically bound form e.g., as sulfate (as confirmed later on by XPS results).

For obtaining further structural information, Raman spectra of MWCNT and MWCNT/S composites were recorded in the range 100–3250 cm^{−1} and are shown in Figure 3. In the Raman spectrum of MWCNT, the peak at ~1351 cm^{−1} (D band) can be assigned to defects and disorder in the carbon matrix while the peak at ~1585 cm^{−1} (G band) can be associated with the coplanar vibrations of sp²-bonded carbon atoms (E_{2g} phonons).^{47–49}

The intensity ratio between D-band and G-band (I_D/I_G) is a measure of the degree of disorder in carbonaceous materials. An I_D/I_G ratio of ~1.0 is found for CSC indicating the presence of an almost equal amount of disordered carbon and graphitic carbon (Table S1, Supplementary Information). This partially graphitized carbon matrix may benefit the electron transportation from/to the poorly conducting S. Interestingly, the FWHM of the D band is the lowest for CSC and the nanographitic domain size (L_a) is the highest indicating more C–S interactions in CSC in comparison with CSM or CSCH (Table S1, Supplementary Information). The 2D band between 2500 and 2750 cm^{−1} is a pointer of the quality of graphitic carbon and its position can be qualitatively linked to the number of graphene layer stacking:

Figure 3. Raman spectra of MWCNT, CSM, CSC and CSCH. (a) in the range, 100–3250 cm^{-1} showing both C and S peaks; (b) in the range 1200–1800 cm^{-1} showing D and G bands of C; and (c) in the range 100–600 cm^{-1} showing the S peaks.

the characteristic positions of the 2D-band for single graphene and bulk graphite being $\sim 2680 \text{ cm}^{-1}$ and $\sim 2730 \text{ cm}^{-1}$, respectively.⁵⁰ Therefore, an up-shifting of the 2D band position reflects an increase in the number of graphene layer re-stacking. In the present case, the 2D band for MWCNT is observed at $\sim 2698 \text{ cm}^{-1}$ indicating stacking of few layers of graphene. No significant change in the 2D band is observed for CSM, but a slight up-shifting to $\sim 2703 \text{ cm}^{-1}$ is noticed for CSC and CSCH (Table S1, Supplementary Information). As shown in Figure 3, five characteristic bands of S are observed in the Raman spectra of CSM, CSC and CSCH: three strong bands at ~ 471 , ~ 217 and $\sim 151 \text{ cm}^{-1}$ and two relatively weak bands at ~ 437 and $\sim 244 \text{ cm}^{-1}$, consistent with the crystalline S_8 form.^{51,52} Apparently, the Raman peaks of S appear to be more intense for CSC compared to those for CSM or CSCH. However, the relative intensities should be calculated by comparing the intensity ratio of the major peaks at $\sim 152 \text{ cm}^{-1}$ (E_2) and the peaks at ~ 218 and 472 cm^{-1} (A_1). It is found that $\text{I}_{\text{E}_2}/\text{I}_{\text{A}_1}$ is similar for all three composites.

Morphology and microstructure of the composites were examined by FESEM and TEM. Strikingly different morphologies are observed for CSM, CSC and CSCH as depicted by the FESEM micrographs, shown in Figure 4 and also in Figure S2 (Supplementary Information). While the mechanically mixed composite

(CSM) shows a porous structure having a uniform agglomeration of S wrapped around MWCNT (Figure 4a), the morphology of the composite prepared by solution infiltration method (CSC) shows a 3D interconnected network with channel-like voids (Figure 4b). On the other hand, the chemically deposited composite (CSCH) shows a completely different morphology where large near-spherical agglomerates of diameter 2–4 μm are observed with protruding spikes of MWCNT (Figure 4c). Presence of network structure and abundant pores/channels would provide the electrolyte ease of access to the active sites resulting in a better utilisation of S in CSC or CSM compared to CSCH. The microstructural features of the composites were further investigated by TEM (Figure 5a–c). The high-resolution TEM images clearly reveal the deposit of S_8 nanoparticles in the carbon matrix without agglomeration for all three composites (Figure 5d–f). It appears from the TEM images that the MWCNTs are open-ended. However, whether S would go inside MWCNT or not would primarily depend on the diameter of open-ended MWCNT which may vary from $<8 \text{ nm}$ to $>50 \text{ nm}$. The diameter of MWCNT used in the present study is $<8 \text{ nm}$, which is also corroborated by high-resolution TEM image (Figure S3, Supplementary Information). It is known that S_8 may form clusters of size 10 nm or more.⁵³ Also, the phase diagram of S_8 shows that there is no structural

Figure 4. FESEM micrographs of (a) CSM, (b) CSC, and (c) CSCH.

change for temperatures of ~ 200 °C, though there might be phase changes. Therefore, it is highly unlikely that S_8 clusters would go inside MWCNT through the openings. Rather, the S_8 clusters reside primarily on the outer surface of carbon through physical interactions similar to MWCNT/S composites reported earlier where it is shown that outer surfaces of well dispersed MWCNT network can act as adhesion points for sulfur binding.^{54,55} This conclusion is further supported by the observation of a single-step S evaporation starting at ~ 220 °C in TGA (Figure 2) indicating that sulfur is mainly located on the outer surface of the MWCNT. If a fraction of S resides inside, then there would have been a second stage of evaporation of S at a higher temperature (> 300 °C) similar to mesoporous carbon/S composites.⁵⁶ Therefore, it may be concluded that S

resides primarily on the surface of carbon through physical interactions.

In order to investigate the interaction between S and MWCNT as a function of processing methods, XPS studies were undertaken. For this, survey scans, as well as relevant high-resolution XPS scans, were recorded for the composite materials (CSM, CSC, CSCH) as well as for MWCNT by keeping the experimental conditions identical. Figure 6 shows the XPS survey-scans of MWCNT and MWCNT/S composites before and after 3 minutes of Ar^+ sputtering. As expected, the $-COOH$ terminated MWCNT shows the presence of carbon with only a minute amount of oxygen (Figure 6d1 & 6d2) while surfaces of the as-prepared MWCNT/S composites exhibit the presence of carbon, sulfur and oxygen (Figure 6a1–c1). However, interesting observations can be made in the survey scans after 3 min of Ar^+ sputtering (corresponding to a depth of approximately 25 nm) which effectively removes the possible surface contaminants. While no significant change is noticed for MWCNT (Figure 6d2), the carbon content decreases significantly for all the composites (Figure 6a2–c2). Along with carbon, the oxygen content also decreases substantially in CSM and CSC (Figure 6a2–b2). On the contrary, CSCH shows an overall increase in oxygen content signifying the presence of additional chemically bound oxygen (Figure 6c2).

The asymmetric tailing observed in high-resolution C 1s spectrum (Figure 7a) suggests the existence of functional groups at the surface of MWCNT. Therefore, in order to determine the composition and to identify the functional groups in MWCNT, high-resolution XPS spectra of C 1s and O 1s, recorded after Ar^+ sputtering, were deconvoluted into their respective Gaussian components (Figure 7a–b). The flatness of differential intensity profile, i.e., the difference between an experimental profile and the sum of all the Gaussian fits, represented by a dotted line along the background line in Figure 7 signifies the merit of the peak fitting protocol undertaken to resolve the high resolution XPS spectra. The resolved components of C 1s spectrum of MWCNT centred at ~ 284.5 , 285.1, 285.6 and ~ 286.45 eV (Figure 7a) correspond to graphitic sp^2 -hybridized carbon ($C=C$), deformed or lattice order distorted graphitic carbon, sp^3 carbon ($C-C$, $C-H$) and hydroxyl ($C-OH$) functional group, respectively.^{57–59} Though MWCNTs are mechanically robust, it is probable that chemical or thermal cycles during material processing may induce the formation of defective graphitic carbon originating from graphitic sp^2 -hybridized carbon.⁵⁷ The two resolved components of O 1s profile of MWCNT at ~ 531.7 and 533.8 eV may be attributed to oxygen atoms attached to carbon in $C=O$ and $C-O$ ($C-OH$) forms,

Figure 5. TEM images of (a) CSM, (b) CSC, and (c) CSCH. The corresponding high resolution images are shown in (d), (e) and (f), respectively.

respectively.^{59,60} The relative concentrations of four types of C-species and C/O atomic ratio in MWCNT and the composites as estimated from XPS analysis are presented in Table 1.

To elaborate on the difference in the surface chemistry that prevails purely from the sample processing aspects, high-resolution XPS spectra of C 1s, O 1s and S 2p, recorded with Ar⁺ sputtered CSM, CSC and CSCH, were resolved into their respective Gaussian fits and compared (Figure 8). The overall elemental compositions of all the carbon-sulfur composites are shown in Table 1. Similar to MWCNT, C 1s spectra

of the C–S composites (Figure 8a1–a3) were also found to be composed of four components corresponding to graphitic sp²-hybridized carbon (BE $\sim 284.5 \pm 0.05$ eV), deformed graphitic carbon (BE $\sim 285.1 \pm 0.05$ eV), sp³ carbon (BE $\sim 285.6 \pm 0.05$ eV) and hydroxyl (BE ~ 286.45 eV) group although their relative concentrations are different (Table 1). From Table 1, it is also evident that the carbon to oxygen atomic ratio is maximum (C/O ~ 27) for CSC while it is minimum (C/O ~ 3) for CSCH. Thus, the mechanism of sulfur incorporation into the host carbon matrix and its content appears to be dependent on the sulfur loading method. As can

Figure 6. Survey scans of XPS spectra recorded from CSM, CSC, CSCH and MWCNT specimens (a1–d1) before and (a2–d2) after 3 min of Ar⁺ sputtering.

Figure 7. High-resolution XPS spectra of (a) C 1s, and (b) O 1s recorded with MWCNT after 3 min of Ar⁺ sputtering.

be seen in Figure 8b1, b2, S 2p profiles of CSM and CSC, except for the photoelectron line intensity, look very similar which suggests that the chemical bonding of sulfur atoms within the carbon matrix is identical but the amounts of S-loading are different. The positions of the resolved S 2p_{3/2} and S 2p_{1/2} spin-orbit doublets of CSM and CSC composites at $\sim(163.8 \pm 0.05)$ and $\sim(165 \pm 0.05)$ eV in binding energy scale signifies the existence of sulfur in the carbon matrix as elemental

sulfur (S⁰), i.e., in the form of S–S type bonding^{61–64} and/or as sulfur atom bonded with carbon directly by a C–S bond probably in thiophenic arrangement.^{65–70} However, in the case of CSCH, sulfur is observed to exist in two distinct forms within the host C-matrix (Figure 8c1–c3). While first pair of S 2p spin-orbit doublet (S 2p_{3/2} ~ 163.9 ; S 2p_{1/2} ~ 165.1 eV) confirms the presence of S–S and/or C–S type of bonding, second pair (S 2p_{3/2} ~ 168.5 ; S 2p_{1/2} ~ 169.7 eV) suggests the formation of sulfate [(SO₄)^{2–}] species where S-atoms exist in oxidation state VI.^{64,71,72} The ratio of sulfur as S–S/C–S and as sulfate [(SO₄)^{2–}] form in CSCH was estimated to be about 1.34 ($\sim 57\%$: 43%). Thiophene-S atoms are known to form C–S bond either with defective sp² graphitic carbon located in the BE range of 284.8–285.3 eV^{65,70} or with sp³ carbon located in the BE range of 285.6–285.7 eV.^{69,71} In the present study, it has been observed that the binding energy positions of all the resolved C 1s components (graphitic sp²-hybridized-C, defective sp² graphitic-C, sp³-C, hydroxyl-C) of CSM, CSC and CSCH composites are almost identical to that of MWCNT. The absence of significant core-level binding energy shifts in C 1s components of composites suggest that no or negligible charge transfer occurs between the sulfur and carbon atoms. This is quite likely because the electronegativity of sulfur (2.58) and carbon

Table 1. Analytical results of MWCNT, CSM, CSC and CSCH as obtained from XPS analyses.

Sample	Relative Concentration (%)				Overall Composition (at%)	Atomic Ratio	
	sp ² -C (C=C)	Defective sp ² carbon	sp ³ -C (C-C/C-H)	C-O/C-OH (ether/hydroxyl)		C/O	S/C
MWCNT	73	11	9	8	C:O ~95.8:4.2	~23	-
CSM	53	6	24	7	C:O:S ~53.8:2.4:43.8	~22	~0.8
CSC	56	18	18	8	C:O:S ~62.2:2.3:35.5	~27	~0.6
CSCH	61	7	17	15	C:O:S ~63.8:25.0:11.2	~2.6	~0.2

Figure 8. High-resolution XPS spectra of (a) C 1s, (b) O 1s and (c) S 2p recorded for CSM, CSC, CSCH after 3 min of Ar⁺ sputtering.

(2.55) are almost the same on the Pauling scale. Hence, it is quite logical to believe the existence of sulfur (S 2p_{3/2} ~ 163.8 eV; S 2p_{1/2} ~ 165 eV) within the carbon matrix as elemental sulfur (S⁰ or S–S). Also, the much higher extent of S-loadings observed particularly in CSM and CSC composites corroborate the above notion. Resolved Gaussian components of O 1s spectra of the composites at ~531.5, 532.6±0.2 and 534 eV may be ascribed to S–O, hydroxyl (C–OH) and C–O–C linkages, respectively.^{67,69} In the case of CSCH, the amounts of S and O estimated from S-contribution due to the second pair of S 2p spin-orbit doublet [~S 2p_{3/2} ~ 168.5; S 2p_{1/2} ~ 169.7 eV; due to sulfate [(SO₄)²⁻] and O-contribution due to the first O 1s component (~531.5 eV) was found to be about 23 at% and 77 at%, respectively. The closeness of the observed S and

O atomic percentages to that of the stoichiometric values (S = 20 at% and O = 80 at%) of sulfate [(SO₄)²⁻] further confirms the existence of sulfate in the CSCH composite.

Electrochemical properties of CSM, CSC and CSCH were evaluated in coin cells vs Li⁺/Li. Figure 9 shows the first three successive cyclic voltammetry scans recorded for each of these composite cathodes. Essentially, all the composites show very similar cathodic behaviour with two clear peaks at ~2.3 V and 2.0 V indicating a multistep reduction of sulfur.^{56,73,74} The first peak can be assigned to the formation of Li₂S₈ whereas the second peak is a signature for deep reduction of higher order polysulfides (Li₂S_x; 4 < x < 8) to lower order polysulfides (Li₂S_x; x ≤ 2). However, the anodic scans show a markedly different behaviour for

Figure 9. First three successive cyclic voltammograms for (a) CSM, (b) CSC, and (c) CSCH.

CSCH compared to CSM and CSC. The first anodic peak due to the conversion of lower order polysulfides into higher order polysulfides occurs at ~ 2.4 V in all cases. But, the second oxidation peak appears as a shoulder at ~ 2.5 V for CSCH while for CSM and CSC it appears as a broad hump centered at ~ 2.7 V. This indicates a gradual rearrangement process of orthogonal sulfur from the original sites to more stable sites in CSM and CSC.^{56,74,75} However, in all cases, a good reversibility is indicated as the positions of the respective redox peaks remain unchanged in subsequent scans.^{76,77}

The initial galvanostatic charge-discharge profiles exhibit two distinct plateaus (Figure 10a). A relatively low ΔE of ~ 0.28 – 0.33 is indicative of good reversibility of the redox processes. However, of the

three composites, CSC shows the lowest ΔE of ~ 0.28 . The respective initial discharge/charge capacities are found to be 997.4/967.8, 1143.0/1141.2 and 1044.7/1024.3 mAh g⁻¹ for CSM, CSC and CSCH with corresponding Coloumbic efficiencies of 97.0, 99.8 and 98.0%. As expected, CSC shows the highest initial capacity as well as highest initial Coloumbic efficiency utilising 68% of S. The rate performance study also shows a superior performance of CSC with average capacity values of 941, 755, 607 and 401 mAh g⁻¹ at current densities of 0.1 C, 0.2 C, 0.5 C and 1.0 C, respectively (Figure 10b). Again, when the current rate was reduced to 0.1 C, about 76.7% of capacity is restored. The cycling performances of all three composites were tested at a current density of 0.5 C for 100 cycles. It is found that all the composites show a gradual fading in capacity, but the capacity retention after 100 cycles is the highest for CSC (67%) compared to those for CSM (47.8%) or CSCH (55.6%) (Figure 10c). A plot of capacity vs. cycle number has also been made for CSM, CSC and CSCH where the mass of both S and MWCNT are taken into account (Figure S4, Supplementary Information). It is observed that the obtained capacity values are still reasonable: 510 mAh g⁻¹ (initial) & 235 mAh g⁻¹ (100th cycle) for CSM, 581 mAh g⁻¹ (initial) & 389 mAh g⁻¹ (100th cycle) for CSC, and 354 mAh g⁻¹ (initial) & 205 mAh g⁻¹ (100th cycle) for CSCH.

The capacity fading of Li-S cells is generally related to a decrease in the conductivity of the electrolyte due to the dissolution of lithium polysulfides formed during the electrochemical reactions.⁷⁸ In order to understand the internal changes in the cell, electrochemical impedance spectroscopy studies on CSC at various cycling intervals (as-assembled, after initial cycle and after 100 cycles) were carried out. The Nyquist plots in Figure 10d show a typical semicircle the diameter of which represents the charge transfer resistance (R_{CT}) followed by a straight line inclined at $\sim 45^\circ$ to the X-axis (Warburg resistance).⁷⁹ The electrolyte resistance (R_s) can be determined by extrapolation of the Nyquist plot to an infinitely large frequency in the X-axis.⁸⁰ The impedance data were fitted using appropriate equivalent circuit models (shown in the inset of Figure 10d) and the obtained parameters are listed in Table S2, Supplementary Information. It is found that R_s increases from 1.3 Ω in the as-assembled state to 2.8 Ω in the initial cycle and to 3.1 Ω after 100 cycles. Such a small increase in the electrolyte resistance during 100 numbers of charge-discharge cycles indicates a low extent of polysulfide dissolution and confirms good S-confinement in CSC. On the other hand, R_{CT} decreases from 81.0 Ω in the as-assembled state to 41.7 Ω after the 1st cycle due to better wetting of the electrode and further decreases

Figure 10. Comparison of electrochemical properties of CSM, CSC and CSCH: (a) First cycle galvanostatic charge-discharge profiles; (b) Rate performance at various current densities of 0.1 C to 1.0 C; (c) Cycling performance at 0.5 C; and (d) Nyquist plots in the frequency range 0.1 Hz to 100 kHz.

to 36.6Ω after 100 cycle. It is to be noted that during the 1st discharge, a surface SEI layer is formed due to which appearance of two semicircles is observed in the Nyquist plots of CSC after the 1st cycle. Interestingly, R_{SL} and C_{SL} do not change significantly even after 100 cycles indicating good stability of the electrode.

The superior electrochemical performance of CSC compared to those of CSM or CSCH can be correlated to Raman and XPS results. Among the composites, CSC has the highest proportion (18%) of deformed graphitic carbon (defective $\text{sp}^2\text{-C}$) compared with only 6–7% in CSM or CSCH along with the highest nanographitic domain size (4.36 nm) which offers a greater degree of C–S interactions through the disorder or defect sites (Table 1). Secondly, a higher C/O value in CSC reflects a greater degree of C–S interactions through the functional groups. On the other hand, the relatively poor performance of CSCH can largely be attributed to the presence of sulfate. These results validate the notion that for good electrochemical performance chemical irregularities or defects are essential.⁴⁴ That similar electrochemical results were obtained with activated carbon/sulfur composite cathodes prepared by the three methods further confirms the superiority of the solution

infiltration method from 10 wt% of S solution in CS_2 (Figure S5, Supplementary Information).

4. Conclusions

In summary, we have made a systematic study on MWCNT/S composites prepared by three industry-friendly S loading processes with the objective of understanding the C–S interactions in each of these composites. Significant variation in the electrochemical performance is noticed depending upon the S-loading method which could be attributed to different degrees of recovery of π bonds in MWCNT due to a varying extent of C–S interactions. Further, the loading method influences the atomic ratio of C and O which plays a crucial role in electrochemical performance – a higher C/O value yielding a better performance. The solution infiltration method provides the most favourable guest–host interaction. CSC shows the highest initial capacity, as well as highest initial Coulombic efficiency utilising 68% of S. This observation, is validated by using activated as host. The results could be useful for adopting suitable preparation methods for C/S composites for practical applications.

Supplementary Information (SI)

Additional material characterization data (XRD, FESEM, Raman), and electrochemical data data (GCD, rate performance, cycling, impedance) are given. Supplementary Information is available at www.ias.ac.in/chemsci.

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