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Abstract

Lithium sulfide (Li₂S), which has a theoretical capacity of 1166 mA h/g, is considered as a promising cathode material for the Li-S battery. The electrochemical performance of micro-sized Li₂S is impaired, however, by its low electrical conductivity as well as first cycle high activation potential problem. In this work, micro-sized Li₂S powder had been ball-milled with different carbon sources to synthesize Li₂S-C composites as well as to find the suitable carbon sources, which were then capillary-deposited in three-dimensional multi-layered Ni foam from a dioxolane-containing mixture to fabricate a binder-free Li₂S-C composite cathode. A large amount of active material (~5 mg/cm²) was loaded in each cathode with the help of conventional capillary deposition method. Scanning electron micrographs show that the Li₂S-C composite successfully fills the pores in the Ni foam through capillary action and maintains the integrity of the structure before and after cycling performance. Electrochemical performance testing shows that the capillary-deposited binder-free Li₂S-C composite showed excellent cycling performance along with superior rate capability. For further improvement of electrochemical performance, a single-walled carbon nanotube free-standing layer was inserted in between the cathode and the separator which minimized polysulfides shuttle phenomenon thus improved the discharge capacity and the capacity retention.

Keywords

active, material, li, battery, loading, high, cathode, composite, c, approach, li₂s, methodical, free, binder, fabrication

Disciplines

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A Methodical approach for Fabrication of Binder-free Li₂S-C composite Cathode with High Loading of Active Material for Li-S Battery

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Abstract

Lithium sulfide (Li_2S), which has a theoretical capacity of 1166 mAh/g, is considered as a promising cathode material for the Li-S battery. The electrochemical performance of micro-sized Li_2S is impaired, however, by its low electrical conductivity as well as first cycle high activation potential problem. In this work, micro-sized Li_2S powder had been ball-milled with different carbon sources to synthesize Li_2S -C composites as well as to find the suitable carbon sources, which were then capillary-deposited in three-dimensional multi-layered Ni foam from a dioxolane-containing mixture to fabricate a binder-free Li_2S -C composite cathode. A large amount of active material ($\sim 5 \text{ mg/cm}^2$) was loaded in each cathode with the help of conventional capillary deposition method. Scanning electron micrographs show that the Li_2S -C composite successfully fills the pores in the Ni foam through capillary action and maintains the integrity of the structure before and after cycling performance. Electrochemical performance testing shows that the capillary-deposited binder-free Li_2S -C composite showed excellent cycling performance along with superior rate capability. For further improvement of electrochemical performance, a single-walled carbon nanotube free-standing layer was inserted in between the cathode and the separator which minimized polysulfides shuttle phenomenon thus improved the discharge capacity and the capacity retention.

1. Introduction

It is now a great challenge to the scientific committee to improve the capacity of existing energy storage devices due to the advent of new electronic devices, electric cars, and hybrid electric vehicles. Commercially available rechargeable batteries show specific energy of 400 Wh kg⁻¹ which is almost to their theoretical limit but still falls far short of expectations for high energy applications [1, 2]. It seems impossible to increase the specific energy of these existing batteries due to the inherent capacity limitations of the materials. Therefore, it is necessary to introduce new materials for high energy battery applications.

Among all the promising rechargeable batteries, the Li/S system is considered a strong candidate to replace the currently available commercial batteries, due to its availability, low cost, and high performance. The poor electrical conductivity of sulfur, however, the dissolution of long chain polysulfides into electrolyte, and the expansion in volume during the sulfur to sulfide transformation are the limiting factors for sulfur-based battery systems [3]. Extensive research has been conducted to reduce the impact of these problems by applying different techniques to load sulfur onto carbon materials [4-9]. Engineered sulfur-based cathode materials [10-12], as well as different electrolytes, binders [13, 14], and additives [15-19], are also being meticulously studied to solve these problems, but yet to be successful. Moreover, in the Li/S system, it is necessary to achieve full lithiation of the sulfur during discharging to achieve higher discharge capacity. Unfortunately, this is unlikely to happen with elemental sulfur-based cathode, which negatively affects the performance of the Li/S cell. On top of that, the metallic lithium that has been used as anode for the Li/S system forms dendritic structures during operation, which penetrate through the separator and can cause short circuits and fire. Besides this major safety concern, metallic lithium is highly reactive, so it reacts with the electrolyte and degrades the cell performance. Considering all the shortcomings of elemental sulfur-based cathode, the performance and the safety concerns for the Li/S battery can be ameliorated by using prelithiated cathode, which helps to avoid the direct use of metallic lithium [20].

Lithium sulfide (Li_2S) has about four times higher theoretical capacity (1166 mAh/g) than that of commercial cathode materials, and also has a very high melting point (938 °C), which allows it to perform even at higher temperature. With the advantages of full lithiation of sulfur, Li_2S can also be paired with different anodes (e.g. tin, silicon, etc.) which eliminate dendrite formation and the safety issues of metallic lithium [21]. Moreover, Li_2S , which has a low density than sulfur, undergoes volumetric contraction rather than expansion during charging and discharging, resulting in less structural damage to the cathode. Although Li_2S has a number of advantages over sulfur, it also has some challenges to overcome. Unlike sulfur, Li_2S is very sensitive to moisture and needs to be activated when coupled with anodes. It is also electronically and ionically nonconductive and has very large particle sizes [22].

Few efforts have been directed towards mitigating the aforementioned shortcomings of Li_2S . Among them, Yang et al. [23] ball milled Li_2S and Al_2O_3 to reduce the size of the Li_2S particles and to increase the conductivity of the Li_2S . Similar ball-milling approaches along with cathode fabrication in inert environment (glove box), high 1st cycle activation voltage (~4V) were adopted by other groups [9, 22, 24] to fabricate Li_2S -C composites with different carbon sources, to prevent moisture absorption and to activate the active material. Besides mechanical mixing and grinding processes, *in-situ* chemical processes were also adopted to fabricate fine-grained Li_2S -C composite with increased conductivity [25, 26]. However, none of their works focused on suitable carbon material selection through ball milling method along with high active material content.

In their methods, both the mechanical and the chemical processes, however, the electrodes were prepared by the conventional slurry casting method where a large proportion (~around 50%) of the slurry consists of binder (e.g., poly(vinylidene difluoride) (PVDF) and carboxymethyl cellulose (CMC)), solvents (e.g. N-methyl-2-pyrrolidone (NMP)), and other conductive additives which has no positive contribution on discharge capacity. In some cases, the active material content is reduced to 30-40 wt% to accommodate the various additives. It has been found that, among these inactive materials,

the binder has some adverse effects on cell performance. Most of the binders are insulating in nature and increase the internal resistance of the cell. Moreover, at high temperature, binders (e.g. PVDF) decompose into toxic compounds (e.g. hydrofluoric acid, fluorocarbons, etc.) [27, 28].

Eliminating the binder content is not the only way to increase the active material content and to achieve better capacity. A three-dimensional (3-D) interconnected metallic network such as nickel (Ni) foam has a large accessible surface area with high electrical conductivity, and can accommodate and utilize high amounts of active material. Researchers from all over the world [29-31] have focused their attention on 3-D network structures to load larger amounts of active material while maintain higher electrical conductivity, thermal stability, and structural integrity. They found that a 3-D interconnected network is an ideal means to allow the transport of electrons and ions during charging and discharging of a battery [32]. Very recently, some successful works have been conducted on 3-D Al-foam, Ni-foam and graphene aerogel, however, they used these 3-D network for impregnation of high amount sulfur rather than Li_2S [33-35].

Very few efforts have been directed independently towards the synthesis of Li_2S -C composite through ball milling, designing binder-free Li_2S -C composite, and applying 3-D network structures in the fabrication of Li_2S -C composite electrode. It is necessary, however, to develop a systematic approach to finding suitable carbon sources for fabrication of Li_2S -C composite through the ball-milling process. The usage of 3-D multi-layered Ni foam for encapsulation of Li_2S -C composite to produce high active material content binder-free 3-D-structured cathode is reported for the first time here. In this work, micro-sized Li_2S powder was ball milled with four different carbon sources to synthesize Li_2S -C composites, where smaller size Li_2S particles were mixed uniformly with conductive carbons. From physical and morphological examination, suitable carbon source was selected among the four carbons. The fabricated composites were then capillary-deposited in 3-D multi-layered Ni-foam from a dioxolane (DOL)-containing mixture with high amount active material. To facilitate the electrochemical activation of Li_2S -C composite by reducing the initial potential barrier, in the 1st cycle

the cells were charged to 3.5V with a very low current density. In addition, a conductive, single-walled carbon nanotube (SWCNT) free-standing layer with a refined, woven-like structure was inserted in between the cathode and the separator to improve the initial capacity and capacity retention. Finally, a comparative study was conducted to analyze the effects of binder and 3-D multi-layered Ni-foam.

2. Experimental:

2.1 Synthesis of Li₂S-Carbon Composite: Due to the sensitivity of Li₂S to moisture and air, the fabrication process and materials preparation were conducted inside an argon-filled glove-box. Commercial Li₂S was purchased from Sigma-Aldrich with larger mesh size (10-20 μm), and a carbon source were ball-milled together in a planetary ball mill at 100 rpm, with a 10:1 ball to Li₂S weight ratio, to synthesize the Li₂S-C composite. Same procedure and similar parameter were used for fabricating Li₂S-C composite for four different carbon sources. The other ball-milling parameters were chosen from our previous work on Li-S [36]. The ratio of Li₂S to carbon was 70:30. Four different carbon sources, carbon black (CB), activated carbon (AC), graphene (GP), and multi-walled carbon nanotube (MWCNT) were used for synthesizing four different Li₂S-C composites. Among the four carbon sources, GP was synthesized in our laboratory through a modified Hummers' method [37], and the other three are commercial grade purchased from Sigma Aldrich.

2.2 Fabrication of Li₂S-C composites encapsulated in 3-D Ni-foam electrode: First, the Ni foam was cut into circular disks with a diameter of 9.5 mm. The average areal weight of each Ni-foam disk is around 25 mg/cm². The disks were then washed with distilled water followed by ethanol. Then, the disks were put into an ethanol-containing beaker and sonicated for 10 minutes to remove all micro-sized contaminations. Then, the disks were dried at 80 °C for 24 hours under vacuum and transferred to the glove box. Before encapsulating the Li₂S-C composites in the Ni-foam disks, the weight of the each disk was measured, in order to calculate the amount of active material that was loaded into each disk. For encapsulation of the active material, a certain amount of Li₂S-C composite

was mixed with DOL in a mortar. Then, the disks were dipped into the slurry to encapsulate the active material. Through capillary action, the pores of the Ni foam were filled with active material-contained DOL which were later dried inside the glove box at room temperature. It should be noted that DOL, which is an organic compound, can sublime easily at room temperature. After the evaporation of DOL, the disks were mechanically pressed to entrap the active materials in the 3-D Ni-foam. Each 9.5 mm disk electrode contained ~5-6 mg of active materials ($\text{Li}_2\text{S-C}$). The sequence of active material loading into the Ni foam is shown in Figure S1 in the Supporting Information. For fabrication of $\text{Li}_2\text{S-C}$ composites with binder, polyvinylidene fluoride (PVDF) was added into the composite in such a way that the ratio of Li_2S to carbon to PVDF was kept at 60:30:10. A certain amount of mixture was mixed in a mortar with NMP to make slurry. When the PVDF was dissolved in the NMP, the disks were dipped into the mixture, which was followed by vacuum drying at 80 °C for 48 hours.

2.3 Fabrication of SWCNT free-standing layer: 15 mg SWCNT with 500 ml de-ionized water were poured into a beaker, and 500 mg Triton-X100 surfactant was added. Then, the solution was probe-sonicated for 1 h with a 2 s pause time, followed by vacuum filtration and washing with de-ionized water and ethanol. The polytetrafluoroethylene (PTFE) filter paper with the SWCNT layer was dried under vacuum overnight at 60 °C, and finally, the SWCNT layer was easily peeled off from the filter paper [38, 39].

2.4 Fabrication of cells: The CR 2032 coin-type cells were assembled in an Ar-filled glove box, where discs of Li foil were used as the counter electrode and reference electrode. The electrolyte was prepared by dissolving 1 M lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) and 0.1 M LiNO_3 in co-solvents of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME), with a volume ratio of 1:1 and the amount that was used for each coin cell was around 100-200 μL . A porous polypropylene film was used as the separator. A SWCNT free-standing layer with an areal mass of 1.5 mg/cm^2 and 1~3 μm thickness was inserted in between the cathode and the separator in some cells.

2.5 Characterization: To characterize the Li_2S -C composite and Li-S cells, different analytical tools were used. For physical and morphological characterization of the composite, X-ray diffraction (XRD, GBC MMA 017) and field emission scanning electron microscopy (SEM; JEOL: FESEM-7500) were used. A scanning electron microscope was also used for conducting large-area energy dispersive X-ray spectroscopy (EDS) mapping. For electrochemical performance evaluation of the Li-S cell, an automatic battery tester system (Land®, China) was used at various current densities at room temperature. For testing the cycling performance, the cell was activated by charging it to 3.5V with very low current density (C/200, 1 C = 1166 mAh/g $_{\text{Li}_2\text{S}}$). From the following cycle, a conventional voltage window (1.7-3 V) was applied. Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) measurements were performed on a Biologic VMP 3 electrochemical workstation over a frequency range of 10 mHz to 100 kHz, and the scan rate was 0.05 mV within a 1.5 V to 4 V voltage window.

3. Results and Discussion:

Figure 1: XRD patterns of Li_2S -C composites.

The X-ray diffraction (XRD) patterns of all Li_2S -C composites, along with commercial Li_2S , are shown in Figure 1, which clearly shows that all four composites exhibit characteristics peaks of Li_2S . As is well known, Li_2S has an antifluorite structure and has higher atomic packing density on the (111), (200), and (311) planes, and for this reason, all the major peaks for Li_2S come from the (111), (200), and (311) planes [40]. The intensity of the peaks for all four composites looks similar, however, except for Li_2S -MWCNT, where the peak intensities are much smaller than for the other composites, which means that, in Li_2S -MWCNT composite, Li_2S has less favorable condition to reflect the X-ray beams from those particular planes. In other words, it can be said that MWCNT, which has a very high aspect ratio (length to diameter ratio), managed to adhere and successfully cover the Li_2S particles, reducing the intensity. It should be mentioned that all the samples were covered with

Kapton tape before the XRD analysis due to the sensitivity to moisture and air of Li_2S . Figure S2 shows the XRD sample preparation using Kapton tape.

Field emission SEM (FESEM) micrographs of the four carbon sources are presented in Figure S3, which clearly shows the sizes and structures of the four different carbons. CB particles look spherical, whereas AC particles have an arbitrary flake shape. On the other hand, GP is in the form of agglomerated two-dimensional sheets, and MWCNT has a fiber-like structure with a very high aspect (length to diameter) ratio. These FESEM images were of help in analyzing the morphology of the ball-milled Li_2S -C composites that have been fabricated using those four carbon sources.

Figure 2: FESEM images of a) Li_2S , b) Li_2S -CB, c) Li_2S -AC, d) Li_2S -GP, and e, f) Li_2S -MWCNT composites (Scale bars are 1 μm for Figures-a, b, c, d, e and 100 nm for Figure-f).

Figure 2 shows the morphology of the ball-milled composites along with pristine Li_2S . It is clearly shown in Figure 2b and 2c that CB and AC are discretely dispersed and do not adhere to the Li_2S particles. This is because the CB and AC are much smaller in size compared to Li_2S , and the percentage of carbon that has been added into the composite, which is 30 wt%, is not sufficient to cover the larger size Li_2S particles. On the other hand, the same amounts (30 wt%) of GP and MWCNT not only firmly adhere to the Li_2S , but also covers the Li_2S particles, as is shown in Figure 2d and 2e. Moreover, the MWCNT covers each Li_2S particles completely because of its very high aspect ratio, which can reduce the insulation problem with Li_2S . From the FESEM micrograph, it can be predicted that the Li_2S -MWCNT composite should have better electrochemical performance compared to the remaining three composites. For further confirmation of the distribution of the Li_2S particles and the carbon sources in the composite, energy dispersive spectroscopy (EDS) analysis was carried out and is shown in Figure S4. EDS mapping clearly shows that both sulfur and carbon coexist in the composite, and in most cases, they are embedded in each other.

Before analyzing the electrochemical performance of Li_2S -C composites cathode, it is worthwhile to mention that conventional Li_2S -C composite cathodes are prepared from slurry which contains active materials, binder, solvent, and other ingredients. This slurry is then pasted onto a two dimensional aluminum foil current collector. It is worthwhile to mention here that the aluminum foil current collector is a two dimensional (2-D) sheet and can be loaded with only a very limited amount of active materials, and in most cases, it can be loaded with 1 mg or less of the active material. Moreover, it is mandatory to add binder and solvent to achieve a firm bonding between the 2-D current collector and the active materials. Sometimes other ingredients are also used to achieve better interfacial bonding between the current collector and the active materials, [24, 41] which not only reduces the active material content, but also increases the internal resistance of the cell. Furthermore, the binders, solvents, and other ingredients cost extra money, which could be a stumbling block for commercialization.

Table 1: Comparison of properties and performance of Li_2S -C composites for Li-S battery.

Table 1 tabulates the relationships among the active material content, current collector, binder content, and the discharge capacity in the most recent papers investigating Li_2S -C composite cathode. It clearly shows that, for fabrication of Li_2S -C composite cathode, different binders were used in almost every case and achieved allowable discharge capacity. It is also noticeable from Table 1 that, in all the works on Li_2S that are currently available from open sources, their conventional 2-D current collector can barely be loaded with 1.5 mg/cm^2 active materials. To increase the active material content, a 3-D network or framework needs to be considered. The use of 3-D conductive network materials in battery application is a promising feature that has already been used on several occasions. Xi et al. [27] used a 3-D graphene network to produce binder-free sulfur cathode. Zhao and Sa [42, 43] used 3-D Ni foam as a framework for the electrodeposition of sulfur materials and as current collector, respectively. All of them managed to achieve better electrochemical performance compared to that with a conventional 2-D Al-foil current collector.

Figure 3: FESEM image of a) Ni-foam, and b, c) top view and side view images of Li₂S-MWCNT composite cathode, where the active material was loaded in Ni-foam through powder dispersion; d, e) top view and side view images of Li₂S-MWCNT composite cathode where the active material was loaded in Ni-foam through capillary deposition Scale bars for all the figures are 100 μm).

3-D Ni-foam, which consists of several layers and many micropores, can accommodate a large amount of active materials and can maintain its structural integrity after active material loading. Figure 3a presents a micrograph of the pristine Ni-foam where a microporous 3-D layered network structure is clearly visible. The lodgment of the active material in the foam has been done into two different ways, which are direct dispersion and capillary deposition. In both cases, the cathodes were pressed after the active material loading to achieve better mechanical confinement and interfacial bonding between the Ni-foam and the active material. Figure 3b and 3c respectively shows a top and side view of the morphology after direct active material dispersion (conventional dispersion method). From these two images, it is clear that the conventional deposition method is not suitable for loading high amount active material. The micro-sized Li₂S powder particles and carbon particles adhered to each other and failed to penetrate the Ni-foam pores. For this reason, most of the pores remained empty, and small amounts of active materials just adhered to the top of the Ni-foam surface. The side view (Figure 3c) shows that the materials cannot percolate to every layer, which reduces the active material content. On the other hand, the capillary deposition method can load more active material and provide better interfacial bonding. In the capillary deposition method, the active material can be loaded into each layer of the foam due to capillary action, which is unlikely to happen in the direct dispersion method. Figure 3d and 3e shows front and side views of a capillary deposited cathode and reveals that the active material is loaded into each layer of the foam. On top of that, due to capillary action, all the pores are completely filled by the active materials, which increased the active material content. It is important to mention here that DOL is an electrolytic compound that is used in the capillary deposition method as a solvent and is later evaporated, so that the active material is entrapped in the Ni-foam network. Moreover, DOL, which

is liquid at room temperature (25 °C) and pressure (1 atm) does not react with the cathode surface and active materials.

With the help of this capillary deposition method, large amounts of active materials were deposited in the Ni-foam, and in every case, 5 mg/cm² and more (5 to 6 mg/cm²) of the active materials were loaded in each electrode (9.5 mm diameter disk), which is the maximum amount compared to the all other results that are available from open sources. After the active material loading process, the electrochemical performance of the electrodes was evaluated for all four different carbon sources, and the best Li₂S-C composite was found among them. Unlike sulfur-carbon cathode, Li₂S-C cathode is fabricated in the discharged state and needs to be activated before measuring its electrochemical performance.

For activating the Li₂S-C cathode, an upper high cut-off voltage ($\sim 4 V_{Li}$) is usually applied by the researchers. They believed that the initial high cut-off voltage for charging promoted phase nucleation of the two-phase reaction between Li₂S and polysulfides [23]. At 4V, however, most of the ether-based electrolytes are not stable and start to dissociate. For this reason, researchers have tried to avoid a high cut-off voltage for the activation process [44]. They tried to use a redox-mediator in electrolyte, which can allow the recovery of most of the Li₂S theoretical capacity in the activation cycle at potentials as low as 2.9 V_{Li}.

Yang et al. [23] reported that the current density during first charging has a significant effect on the activation of the Li₂S-C cathode. They found a linear relationship between the overpotential and the current rate. They also claimed that the overpotential, which is the energy needed for phase nucleation to reduce the initial potential barrier, remains nearly constant and is quite small at low current. Inspired by their work, we used a very low current density (C/200) for the first cycle to activate the cathode. On top of that, we charged the cell to 3.5V instead of 4V for the first cycle. It is found that, in most cases Li₂S is activated at 3.5V when a very low current density is applied which

will protect the electrolyte from being dissociated. In the following cycles, the cathode need not be activated at 3.5V, and hence, a conventional voltage window (1.7-3 V) was applied.

Figure 4: (a) Charge discharge profile of first cycle for activation of Li_2S -MWCNT composite (b) Cycling performance of Li_2S -C composites at the 0.1 C rate.

The charge discharge profile of the activation process is shown in Figure 4a, where the cell was charged to 3.5 V with a current density of C/200. In the charging profile, it is seen that, the voltage is rapidly increased to 3.25V at the beginning of the charging and then dropped down to 3V followed by gradual increment to 3.5V. The initial rapid increment of voltage is known as the initial potential barrier of the cell which usually varies on the current density the charging. It is well known that the most suitable voltage window for ether-based electrolyte for the Li-S system is 1.5 V to 3 V, and Meini et al. [44] showed that the energy band gap between highest occupied molecular orbital (HUMO) and lowest unoccupied molecular orbital (LUMO) for ether-based electrolyte is around 4-4.5V but it can hardly be used this voltage window due to the formation of thick solid electrolyte interface (SEI). There is an inverse relationship between SEI thickness and electrolyte band gap. In most of the Li/S system, the SEI thickness is quite high which force to reduce the voltage window and beyond 3.6 V, the ether-based electrolyte in Li/S system starts to dissociate [45]. It is also shown in Figure 4a that, at 3.5 V upper cut-off voltages, the cell can achieve 990 mAh/g charge capacity, which is very close to Li_2S theoretical capacity (1166 mAh/g). So, it can be said from above discussion that, it is possible to activate Li_2S -C composites at 3.5V. This low voltage activation phenomenon has a substantial influence towards obtaining better discharge capacity.

Beside the activation charging profile, Figure 4a shows the discharge profiles of the Li_2S -C composites, and as expected, the discharge profiles of the Li_2S -C composites for both activation processes are similar to the discharge profile of the conventional Li-S cell. In the discharge curves, two plateaus are observed, with the first plateau related to the transformation from elemental sulfur to long chain lithium polysulfides (Li_2S_n , $n \geq 4$), and the second plateau representing the

reduction of long chain lithium polysulfides to short chain lithium polysulfides (Li_2S_n , $n < 4$). After the activation process, all four Li_2S -C composites were tested for cycling performance, and the results are shown in Figure 4b. Li_2S -AC and Li_2S -CB show higher initial capacity of 945 mAh/g and 906 mAh/g, respectively, compared to Li_2S -GP and Li_2S -MWCNT with 860 mAh/g and 888 mAh/g, respectively. Li_2S -MWCNT shows the highest capacity retention of 50.7%, however, followed by Li_2S -GP (40.9%), Li_2S -AC (25%), and Li_2S -CB (21.3%) after 100 cycles. It was expected from the morphology of this composite, where the Li_2S was fully covered and adhered to by MWCNT, that the Li_2S -MWCNT would exhibit better electrochemical performance compared to the other three composites. It is necessary to mention here that, compared to the other works on the Li_2S battery listed in Table 1, the discharge capacity has not significantly improved however, considering active material content which is 5 mg/cm²; this is the highest discharge capacity that is available when compared to reports in open sources. It can be concluded here that Li_2S -MWCNT composite has better characteristics in terms of morphological and electrochemical performance, and in the following part of this paper; we shall focus only on Li_2S -MWCNT composite for further characterization and improvement.

Figure 5: (a) Charge-discharge profiles, and (b) rate capability of Li_2S -MWCNT composite.

Figure 5a and 5b, respectively, shows representative charge-discharge profiles and the rate capability of Li_2S -MWCNT composite. The discharge plateau shows that there is no drastic voltage drop in the discharge profile, indicating very low polarization loss (both activation polarization and concentration polarization) along with internal impedance loss. The latter one can also be determined from electrochemical impedance spectroscopy (EIS), which will be discussed in a later part of the paper. Li_2S -MWCNT composite also shows high capacity at higher current density. The cells were tested at different current densities, varying from 0.1 C to 5 C, and the results show that, even at the 3C and 5C rates, the cells can exhibit a capacity of 300 mAh/g and 80 mAh/g, respectively. It is notable that, in most of the papers on Li_2S -C composite, the authors conducted

their testing with a maximum current density of 2 C, and in most of cases, our Li₂S-MWCNT composite shows much better rate capability than in other works [25, 46]. This exceptionally high rate performance may be achieved because of the structural benefit of the 3-D network of Ni-foam along with better carbon sources. This combination not only improved the conductivity of the composite, but also maintained a 3-D conductive network that acted as a better current collector, as well as helping to utilize a higher amount of active materials. In Figure-5b capacity fading seems violent when the current density is back to 0.1 C from 5C. However, it is not true in the real case and it can be explained in this way that, when there is sudden change of reaction time of Li⁺ ion which is 50 times increment (from 0.1 C from 5C), most of the Li⁺ ion can get back their own position and results higher reversible capacity than the usual cycling performance and from the next few cycles the capacity start to decay with the normal rate. To justify the above statement, Figure 4b and Figure 5b that show the cycling performance (at 0.1C) and rate capability (different current density) can be compared. The capacity gain after 35 cycles that shown in Figure-5b is almost similar to the capacity after 35 cycles in Figure-4b. This means that, the rapid capacity fading that has been observed when current density back to 0.1 C from 5C is due to high reversible capacity gain with sudden change Li⁺ movement rate.

Figure 6: a) Cyclic voltammetry (CV) curves for the first 4 cycles and b) electrochemical impedance spectra (EIS) of Li₂S-MWCNT composite. The inset to the EIS spectra is the Z-Fit equivalent circuit.

Table 2: Z-fitted EIS results for Li₂S-MWCNT composite.

Figure 6a shows cyclic voltammograms of Li₂S-MWCNT composite for the first 4 cycles with 0.05 mV s⁻¹ scan rate, in which two reduction peaks and one oxidation peak are observed. The first cycle shows a small oxidation peak at 3.5 V, however, along with a very sharp peak at 2.5 V. Yang et al. [23] showed that the peak at 3.5 V indicates the necessity of overpotential to overcome the initial barrier. The EIS results shown in Figure 6b are impedance spectra of Li₂S-MWCNT composite (with and without binder) as cathode, while the inset in Figure 6b shows the Z-fitted equivalent circuit

for the composite, where the resistance (R), constant phase element ($CPE \approx Q_2$), and Warburg impedance element (W) are included. R_e ($\sim R_1$) and R_{ct} ($\sim R_2$) represent the solution resistance of the electrolyte and the charge transfer resistance along with the surface resistance, respectively. Q_2 represents the CPE, which is related to the solid-state diffusion of Li^+ due to the formation of a double layer capacitor between the electrolyte and the cathode interface. W is the Warburg impedance element attributable to the diffusion of lithium ions in the active materials. The Z-fitted values of the EIS curves for Li_2S -MWCNT composite with binder and without binder are shown in Table 2. Both EIS curves show similar depressed semicircles with similar values of R_e and CPE. The charge transfer resistance (R_{ct}) and Warburg impedance (W), however, are much higher for Li_2S -MWCNT composite with binder than without binder. This is because the polymeric binders are electrical insulators, which impedes the Li ionic movement, as well as electron, movement inside the cell. This is because, linear-chain PVDF is a polar compound with a dipole moment of 2.1D and due to the high dipole moment, PVDF shows significant attraction to the positive Li ion which will impede Li -ion movement in the cathode material. It is important to mention here that the values of R_e and CPE remain the same for both cases, which is due to the structural benefit of the electrode. It is proposed that the 3-D Ni-foam network helps to diffuse Li^+ without increasing the thickness of the solid electrolyte interphase (SEI) and the double layer capacitor.

From Figure 4 and Figure 5, it is obvious that, as in the case of the Li -S cell, the capacity decay with cycle number is also an important issue for Li_2S -C composite. The main reason behind the capacity fading is the dissolution of polysulfide into the electrolyte, which causes the so-called shuttle phenomenon. To improve the initial capacity and the capacity retention, a free-standing layer (FSL) of single-walled carbon nanotube (SWCNT) was inserted in between the separator and the cathode, which can increase the conductivity of the sulfur results, high amount active material utilization. This novel approach was first introduced by Manthiram's group [47], and later, it was also adopted by other groups [48, 49] to achieve higher initial capacity and better capacity retention for the Li -S

battery. Although there are many similarities between elemental sulfur and Li_2S , this novel approach has not been used for Li_2S -C composite.

Figure 7: Cycling performance at the 0.1 C rate of Li_2S -MWCNT composite with binder and FSL.

Figure 7 shows the cycling performance of the FSL-containing Li_2S -MWCNT composite, where the FSL was inserted in between the cathode and the separator. Moreover, the cycling performances of Li_2S -MWCNT composite with binder (10 wt% binder) and the bare Li_2S -MWCNT composite are shown in the Figure for comparison to justify the EIS results that are shown in Table 2. The Figure shows that, with the insertion of a FSL, the initial capacity rises to 1146 mAh/g $_{\text{Li}_2\text{S}}$, and capacity of 571mAh/g $_{\text{Li}_2\text{S}}$ is retained after 100 cycles, which is almost 13% higher than without FSL. It is also shown in Figure 7 that the addition of binder makes no significant difference to the cycling performance of the Li_2S -MWCNT composite. In terms of capacity retention, however, Li_2S -MWCNT shows 7% more capacity under the same conditions than binder-containing Li_2S -MWCNT composite. Figure S5 presents a FESEM image of binder-free Li_2S -MWCNT composite cathode after 100 cycles, and it clearly shows that the cathode maintains its structural integrity even after 100 cycles. This Figure also shows that, unlike the pristine cathode, the active material of the cathode after cycling does not show cracking and agglomeration. The reason behind this phenomenon is that the continuous contraction and expansion of the active material during cycling and the percolation of electrolyte through the cracks disintegrates the active material, which increases the active surface area and facilitates the redox reactions, resulting in higher capacity. Hence, it can be said that the 3-D Ni-foam can not only hold a higher amount of active material, but also can maintain the structural integrity of the cathode with just its layered network structure, without the use of any binder.

4. Conclusion:

Binder-free Li_2S -C composites were synthesized through a high energy ball-milling process with different carbon sources. These composites were then capillary-deposited in 3-D Ni-foam networks.

Then, the composites were characterized physically, morphologically, and electrochemically. From the characterizations, it is found that Li_2S -MWCNT composite shows much better morphology and performances than those of other composites. Later, the performance of the Li_2S -MWCNT composite was further improved by inserting a vacuum-filtrated SWCNT free-standing layer in between the cathode and the separator. After insertion of the FSL, the initial capacity of the Li_2S -MWCNT composite was raised to $1146 \text{ mAh/g}_{\text{Li}_2\text{S}}$, which is equivalent to $1646 \text{ mAh/g}_\text{s}$ for the Li-S system. Besides superior cycling performance, another important phenomenon is achieved in this work which is the loading of large amount active material ($\sim 5\text{-}6 \text{ mg/cm}^2$) into the 3-D Ni-foam electrode. The amount of active material that was loaded into each cathode was at least five times higher than that of conventional electrode with a 2-D aluminum-foil current collector. Furthermore, the structural integrity of the 3-D Ni-foam cathode without binder shows similar morphology compare to with binder 3-D Ni-foam cathode, even after 100 cycles.

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References

- [1] Armand M, Tarascon JM. Building better batteries. *Nature*. 2008;451(7179):652-7.
- [2] Ji X, Lee KT, Nazar LF. A highly ordered nanostructured carbon-sulphur cathode for lithium-sulphur batteries. *Nat Mater*. 2009;8(6):500-6.

- [3] Bruce PG, Freunberger SA, Hardwick LJ, Tarascon J-M. Li-O₂ and Li-S batteries with high energy storage. *Nat Mater.* 2012;11(1):19-29.
- [4] Moon S, Jung YH, Jung WK, Jung DS, Choi JW, Kim DK. Encapsulated Monoclinic Sulfur for Stable Cycling of Li-S Rechargeable Batteries. *Adv Mater.* 2013;25(45):6547-53.
- [5] Zu C, Manthiram A. Hydroxylated Graphene-Sulfur Nanocomposites for High-Rate Lithium-Sulfur Batteries. *Advanced Energy Materials.* 2013;3(8):1008-12.
- [6] Wang L, Dong Z, Wang D, Zhang F, Jin J. Covalent Bond Glued Sulfur Nanosheet-Based Cathode Integration for Long-Cycle-Life Li-S Batteries. *Nano Lett.* 2013;13(12):6244-50.
- [7] Lin Z, Liu ZC, Fu WJ, Dudney NJ, Liang CD. Lithium Polysulfidophosphates: A Family of Lithium-Conducting Sulfur-Rich Compounds for Lithium-Sulfur Batteries. *Angew Chem Int Edit.* 2013;52(29):7460-3.
- [8] Ji LW, Rao MM, Aloni S, Wang L, Cairns EJ, Zhang YG. Porous carbon nanofiber-sulfur composite electrodes for lithium/sulfur cells. *Energ Environ Sci.* 2011;4(12):5053-9.
- [9] Cai KP, Song MK, Cairns EJ, Zhang YG. Nanostructured Li₂S-C Composites as Cathode Material for High-Energy Lithium/Sulfur Batteries. *Nano Lett.* 2012;12(12):6474-9.
- [10] Wang L, Wang D, Zhang F, Jin J. Interface Chemistry Guided Long-Cycle-Life Li-S Battery. *Nano Lett.* 2013;13(9):4206-11.
- [11] Liang X, Zhang M, Kaiser MR, Gao X, Konstantinov K, Tandiono R, et al. Split-half-tubular polypyrrole@sulfur@polypyrrole composite with a novel three-layer-3D structure as cathode for lithium/sulfur batteries. *Nano Energy.* 2015;11(0):587-99.
- [12] Liang X, Kaiser M, Konstantinov K, Tandiono R, Wang Z, Liu H-K, et al. High performance pure sulfur honeycomb-like architectures synthesized by a cooperative self-assembly strategy for lithium-sulfur batteries. *Rsc Adv.* 2014;4(69):36513-6.

- [13] Hagen M, Dörfler S, Fanz P, Berger T, Speck R, Tübke J, et al. Development and costs calculation of lithium–sulfur cells with high sulfur load and binder free electrodes. *J Power Sources*. 2013;224(0):260-8.
- [14] Jeddi K, Sarikhani K, Qazvini NT, Chen P. Stabilizing lithium/sulfur batteries by a composite polymer electrolyte containing mesoporous silica particles. *J Power Sources*. 2014;245(0):656-62.
- [15] Song M-K, Zhang Y, Cairns EJ. A Long-Life, High-Rate Lithium/Sulfur Cell: A Multifaceted Approach to Enhancing Cell Performance. *Nano Lett*. 2013;13(12):5891-9.
- [16] Li G-C, Li G-R, Ye S-H, Gao X-P. A Polyaniline-Coated Sulfur/Carbon Composite with an Enhanced High-Rate Capability as a Cathode Material for Lithium/Sulfur Batteries. *Advanced Energy Materials*. 2012;2(10):1238-45.
- [17] Wang J, Chew SY, Zhao ZW, Ashraf S, Wexler D, Chen J, et al. Sulfur-mesoporous carbon composites in conjunction with a novel ionic liquid electrolyte for lithium rechargeable batteries. *Carbon*. 2008;46(2):229-35.
- [18] Wang JZ, Lu L, Choucair M, Stride JA, Xu X, Liu HK. Sulfur-graphene composite for rechargeable lithium batteries. *J Power Sources*. 2011;196(16):7030-4.
- [19] Wang J, Chen J, Konstantinov K, Zhao L, Ng SH, Wang GX, et al. Sulphur-polypyrrole composite positive electrode materials for rechargeable lithium batteries. *Electrochim Acta*. 2006;51(22):4634-8.
- [20] Lin Z, Liu ZC, Dudney NJ, Liang CD. Lithium Superionic Sulfide Cathode for All-Solid Lithium-Sulfur Batteries. *Acs Nano*. 2013;7(3):2829-33.
- [21] Hayashi A, Ohtsubo R, Ohtomo T, Mizuno F, Tatsumisago M. All-solid-state rechargeable lithium batteries with Li_2S as a positive electrode material. *J Power Sources*. 2008;183(1):422-6.

- [22] Takeuchi T, Sakaebe H, Kageyama H, Senoh H, Sakai T, Tatsumi K. Preparation of electrochemically active lithium sulfide-carbon composites using spark-plasma-sintering process. *J Power Sources*. 2010;195(9):2928-34.
- [23] Yang Y, Zheng GY, Misra S, Nelson J, Toney MF, Gui Y. High-Capacity Micrometer-Sized Li₂S Particles as Cathode Materials for Advanced Rechargeable Lithium-Ion Batteries. *J Am Chem Soc*. 2012;134(37):15387-94.
- [24] Guo JC, Yang ZC, Yu YC, Abruña HD, Archer LA. Lithium-Sulfur Battery Cathode Enabled by Lithium-Nitrile Interaction. *J Am Chem Soc*. 2013;135(2):763-7.
- [25] Nan CY, Lin Z, Liao HG, Song MK, Li YD, Cairns EJ. Durable Carbon-Coated Li₂S Core-Shell Spheres for High Performance Lithium/Sulfur Cells. *J Am Chem Soc*. 2014;136(12):4659-63.
- [26] Zheng SY, Chen Y, Xu YH, Yi F, Zhu YJ, Liu YH, et al. In Situ Formed Lithium Sulfide/Microporous Carbon Cathodes for Lithium-Ion Batteries. *Acs Nano*. 2013;7(12):10995-1003.
- [27] Xi K, Kidambi PR, Chen R, Gao C, Peng X, Ducati C, et al. Binder free three-dimensional sulphur/few-layer graphene foam cathode with enhanced high-rate capability for rechargeable lithium sulphur batteries. *Nanoscale*. 2014;6(11):5746-53.
- [28] Wang C, Wang X, Yang Y, Kushima A, Chen J, Huang Y, et al. Slurryless Li₂S/Reduced Graphene Oxide Cathode Paper for High-Performance Lithium Sulfur Battery. *Nano Lett*. 2015;15(3):1796-802.
- [29] Dang L, Wei C, Ma H, Lu Q, Gao F. Three-dimensional honeycomb-like networks of birnessite manganese oxide assembled by ultrathin two-dimensional nanosheets with enhanced Li-ion battery performances. *Nanoscale*. 2015;7(17):8101-9.
- [30] Mao S, Lu G, Chen J. Three-dimensional graphene-based composites for energy applications. *Nanoscale*. 2015;7(16):6924-43.

- [31] Lingappan N, Van NH, Lee S, Kang DJ. Growth of three dimensional flower-like molybdenum disulfide hierarchical structures on graphene/carbon nanotube network: An advanced heterostructure for energy storage devices. *J Power Sources*. 2015;280(0):39-46.
- [32] Rolison DR, Long JW, Lytle JC, Fischer AE, Rhodes CP, McEvoy TM, et al. Multifunctional 3D nanoarchitectures for energy storage and conversion. *Chem Soc Rev*. 2009;38(1):226-52.
- [33] Cheng X-B, Peng H-J, Huang J-Q, Zhu L, Yang S-H, Liu Y, et al. Three-dimensional aluminum foam/carbon nanotube scaffolds as long- and short-range electron pathways with improved sulfur loading for high energy density lithium–sulfur batteries. *J Power Sources*. 2014;261:264-70.
- [34] Cheng JJ, Zhu JT, Pan Y, Ma ZS, Song HJ, Pan JA, et al. Sulfur-Nickel Foam as Cathode Materials for Lithium-Sulfur Batteries. *ECS Electrochemistry Letters*. 2015;4(2):A19-A21.
- [35] Rehman S, Guo S, Hou Y. Rational Design of Si/SiO₂@Hierarchical Porous Carbon Spheres as Efficient Polysulfide Reservoirs for High-Performance Li–S Battery. *Adv Mater*. 2016: doi:10.1002/adma.201506111.
- [36] Kaiser MR, Wang J, Liang X, Liu H-K, Dou S-X. A systematic approach to high and stable discharge capacity for scaling up the lithium–sulfur battery. *J Power Sources*. 2015;279(0):231-7.
- [37] Li X, Wang X, Zhang L, Lee S, Dai H. Chemically Derived, Ultrasoft Graphene Nanoribbon Semiconductors. *Science*. 2008;319(5867):1229-32.
- [38] Chew SY, Ng SH, Wang JZ, Novak P, Krumeich F, Chou SL, et al. Flexible free-standing carbon nanotube films for model lithium-ion batteries. *Carbon*. 2009;47(13):2976-83.

- [39] Kaiser MR, Liang X, Konstantinov K, Liu H-K, Dou S-X, Wang J-Z. A Facile Synthesis of High-Surface-Area Sulfur–Carbon Composite for Li/S Batteries. *Chemistry – A European Journal*. 2015;n/a-n/a.
- [40] Bahloul B, Amirouche L, Dekhira A, Bentabet A. Ab initio study of the structural, electronic and elastic properties of anti-fluorite Li_2X ($\text{X}=\text{S}$ and Te) compounds under pressure effect. *Computational Materials Science*. 2014;86(0):49-56.
- [41] Nagao M, Hayashi A, Tatsumisago M. High-capacity Li_2S -nanocarbon composite electrode for all-solid-state rechargeable lithium batteries. *J Mater Chem*. 2012;22(19):10015-20.
- [42] Zhao Q, Hu X, Zhang K, Zhang N, Hu Y, Chen J. Sulfur Nanodots Electrodeposited on Ni Foam as High-Performance Cathode for Li–S Batteries. *Nano Lett*. 2015;15(1):721-6.
- [43] Sa Q, Wang Y. Ni foam as the current collector for high capacity C–Si composite electrode. *J Power Sources*. 2012;208(0):46-51.
- [44] Meini S, Elazari R, Rosenman A, Garsuch A, Aurbach D. The Use of Redox Mediators for Enhancing Utilization of Li_2S Cathodes for Advanced Li-S Battery Systems. *J Phys Chem Lett*. 2014;5(5):915-8.
- [45] Goodenough JB, Park K-S. The Li-Ion Rechargeable Battery: A Perspective. *J Am Chem Soc*. 2013;135(4):1167-76.
- [46] Seh ZW, Wang HT, Hsu PC, Zhang QF, Li WY, Zheng GY, et al. Facile synthesis of Li_2S -polypyrrole composite structures for high-performance Li_2S cathodes. *Energ Environ Sci*. 2014;7(2):672-6.
- [47] Su YS, Manthiram A. A new approach to improve cycle performance of rechargeable lithium-sulfur batteries by inserting a free-standing MWCNT interlayer. *Chem Commun*. 2012;48(70):8817-9.

- [48] Wang XF, Wang ZX, Chen LQ. Reduced graphene oxide film as a shuttle-inhibiting interlayer in a lithium-sulfur battery. *J Power Sources*. 2013;242:65-9.
- [49] Jeong T-G, Moon YH, Chun H-H, Kim HS, Cho BW, Kim Y-T. Free standing acetylene black mesh to capture dissolved polysulfide in lithium sulfur batteries. *Chem Commun*. 2013;49(94):11107-9.

Figures

Figure 1: XRD patterns of Li₂S-C composites.

Figure 2: FESEM images of a) Li₂S, b) Li₂S-CB, c) Li₂S-AC, d) Li₂S-GP, and e, f) Li₂S-MWCNT composites (Scale bars are 1 μ m for Figures-a, b, c, d, e and 100 nm for Figure-f).

Figure 3: FESEM image of a) Ni-foam, and b, c) top view and side view images of Li_2S -MWCNT composite cathode, where the active material was loaded in Ni-foam through powder dispersion; d, e) top view and side view images of Li_2S -MWCNT composite cathode where the active material was loaded in Ni-foam through capillary deposition (Scale bars for all the figures are 100 μm).

Figure 4: (a) Charge discharge profile of first cycle for activation of Li_2S -MWCNT composite (b) Cycling performance of Li_2S -C composites at the 0.1 C rate.

Figure 5: (a) Charge-discharge profiles, and (b) rate capability of Li_2S -MWCNT composite.

Figure 6: a) Cyclic voltammetry (CV) curves for the first 4 cycles and b) electrochemical impedance spectra (EIS) of Li₂S-MWCNT composite. The inset to the EIS spectra is the Z-Fit equivalent circuit.

Figure 7: Cycling performance at the 0.1 C rate of Li₂S-MWCNT composite with binder and FSL.

Supporting Information

A Methodical approach for Fabrication of Binder-free Li₂S-C composite Cathode with High Loading of Active Material for Li-S Battery

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Figure S1: Encapsulation of active materials in 3-D Ni foam.

Figure S2: Sample prepared for XRD analysis.

Figure S3: FESEM images of a) carbon black (CB), b) activated carbon (AC), c) graphene (GP), and d) multi-walled carbon nanotube (MWCNT) (Scale bars for all the figures are 1 μm).

Figure S4: EDS mapping of a-d) Li₂S-CB, e-h) Li₂S-AC, i-l) Li₂S-GP, and m-p) Li₂S-MWCNT (Scale bars for all the figures are 20 μm).

Figure S5: FESEM image of Li₂S-MWCNT composite confined in Ni-foam after cycling.

Table 1: Comparison of properties and performance of Li₂S-C composites for Li/S battery.

Discharge capacity (mAh/g Li ₂ S)	Binder use	Active material (wt%)	Active material (mg/cm ²)	Current collector	Reference
250 after 50 cycles	Yes	60	NA	2-D Aluminum foil	[39]
650 after 80 cycles	Yes	NA	1.0	Carbon nano fiber	[40]
380 after 20 cycles	Yes	38	NA	Copper composite	[21]
600 after 100 cycles	Yes	60	1.0-1.5	2-D Carbon paper	[25]
550 after 400 cycles	Yes	60	NA	2-D Aluminum foil	[41]
650 after 150 cycles	Yes	NA	1.0	2-D Aluminum foil	[42]
500 after 50 cycles	Yes	40	1.0	2-D carbon paper	[23]
550 after 150 cycles	Yes	NA	1.0	2-D Aluminum foil	[26]
620 after 100 cycles	No	NA	1.0	MWCNT paper	[43]
300 after 95 cycles	Yes	55	0.96	2-D Aluminum foil	[44]
320 after 20 cycles	Yes	49	1.1-1.4	2-D Aluminum foil	[45]
450 after 150 cycles	No	NA	0.8-1.5	Graphene oxide	[28]

				layer	
437 after 100 cycles	No	70	5.0-6.0	3-D Nickel foam	This work

Table 2: Z-fitted EIS results for Li₂S-MWCNT composite.

	Impedance values	R_e (Ω)	R_{ct} (Ω)	CPE (μ F)	W ($\Omega.S^{-0.5}$)
Li ₂ S-MWCNT composite	Without binder	7.993	93.51	21.43	19.12
	With binder	7.322	154.8	21.98	45.35