

TRANSITION METAL SULFIDE-BASED MATERIAL FOR LITHIUM-SULFUR BATTERIES

5 Cross-Reference to Related Application

This application claims priority to Singapore Patent Application No. 10201807048V filed 20 August 2018, the entire contents of which are hereby incorporated by reference.

10 Field of the Invention

The present invention relates to a transition metal sulfide-based material, method of synthesizing transition metal sulfide-based material and method of preparing a transition metal sulfide-based electrode material. In particular, the present invention
15 relates to a transition metal sulfide-based carbon fiber material, method of synthesizing transition metal sulfide-based carbon fiber material and method of preparing a transition metal sulfide-based carbon electrode material.

Background

20

Global demand for energy is predicted to increase in the coming decades. While much progress has been made towards alternative sources for energy production in the past century, advancements in energy storage have arguably not kept up to pace. This is especially critical since most renewable energy sources (such as solar, wind,
25 hydroelectric) are periodic and intermittent. Therefore, there is a need for advanced storage systems capable of delivering this energy when required, from the batteries in small portable devices to high-energy grid-level storage systems. Amongst the various rechargeable battery systems with potential to overtake current lithium-ion batteries (LIBs), lithium-sulfur batteries (LSBs) have garnered the most attention since the
30 seminal work on a carbon-sulfur cathode described in the publication Xiulei Ji, *et al.*, *Nature Materials* 8, 500-506 (2009). The high theoretical specific capacity of sulfur cathodes (1673 mAh g^{-1}) is one order of magnitude larger than typical LIB cathodes and provides an energy density up to 2500 Wh kg^{-1} , which is several times higher than current LIBs. Sulfur is also cheap and abundant. Coupled with suitable cathode hosts

that can be mass-produced, LSBs can thus potentially be manufactured at a much lower cost.

Nevertheless, LSBs do not come without its own set of challenges. The challenges include the electrically insulating nature of both charge and discharge products that preclude complete utilisation of sulfur, and the volume expansion during discharge cycles that can cause structural damage to the cathode (Z.W. Seh, *et al.*, *CHEM. SOC. REV.*, 2016, 45, 5605-5634; L. Ma, *et al.*, *NANO TODAY*, 2015, 10, 315-338; L. Borchardt, *et al.*, *CHEM. EUR. J.*, 2016, 22, 7324-7351; Y. Yang, *et al.*, *CHEM. SOC. REV.*, 2013, 42, 3018-3032). Most importantly, however, the challenges include the loss of active sulfur by polysulfide dissolution through the polysulfide shuttling effect (Z. W. Seh, *et al.*, *CHEM. SOC. REV.*, 2016, 45, 5605-5634). Thus, suitable host materials must inhibit lithium polysulfide (LiPS) dissolution by providing either physical or chemical entrapment, but not at the expense of electrical conductivity.

It is therefore desirable to provide a transition metal sulfide-based material and a method for synthesizing the same that seeks to address at least one of the problems described hereinabove, or at least to provide an alternative.

Summary of Invention

In accordance with a first aspect of this invention, a method of synthesizing a transition metal sulfide-based carbon material for use as an electrode in lithium-sulfur battery is provided. The method comprising providing a solution containing group VI transition metal sulfide precursor and a solvent; immersing a carbon fiber material into the solution to form a mixture; subjecting the mixture to a temperature between 200°C to 300°C to allow loading of transition metal sulfide onto the carbon fiber material; and drying the loaded carbon fiber material to obtain a transition metal sulfide-based loaded carbon material.

In one embodiment, the transition metal sulfide precursor is selected from the group consisting of ammonium tetrathiomolybdate and ammonium tetrathiotungstate.

In one embodiment, the transition metal sulfide is selected from the group consisting of molybdenum disulfide and tungsten disulfide.

In one embodiment, the method further comprises annealing the transition metal sulfide-based loaded carbon material to form a semiconducting transition metal sulfide-based loaded carbon material.

5

In one embodiment, the method further comprises preparing an electrode for lithium-sulfur battery using the transition metal sulfide-based loaded carbon fiber material, wherein the preparation comprises mixing and heating sulfur with carbon black to obtain a sulfur-carbon black mixture; mixing the sulfur-carbon black mixture with a
10 binder and a solvent to obtain a sulfur-containing slurry; depositing the sulfur-containing slurry onto the transition metal sulfide-based loaded carbon material; and drying the transition metal sulfide-based loaded carbon material to obtain a sulfur-loaded transition metal sulfide-based carbon electrode.

15 In accordance with a second aspect of this invention, a transition metal sulfide-based carbon material is provided. The transition metal sulfide-based carbon material comprises a carbon fiber material and a group VI transition metal sulfide selected from the group consisting of molybdenum disulfide and tungsten disulfide, wherein the transition metal sulfide is loaded onto the carbon fiber material.

20

In accordance with a third aspect of this invention, a transition metal sulfide-based carbon electrode is provided. The transition metal sulfide-based carbon electrode comprises a transition metal sulfide-based carbon material of the present invention loaded with sulfur.

25

In accordance with a fourth aspect of this invention, a lithium-sulfur battery is provided. The lithium-sulfur battery comprises an anode and a cathode, wherein the cathode comprises a transition metal sulfide-based carbon material of the present invention loaded with sulfur.

30

Brief Description of the Drawings

The above advantages and features of a material and method in accordance with this invention are described in the following detailed description and are shown in the
35 drawings:

Figure 1 is a schematic illustration of the synthesis of the transition metal sulfide-based carbon material. The scheme illustrates phase and morphological control. Figure 1(a) shows unmodified interwoven carbon fiber; Figure 1(b) shows a metallic phase edge-oriented sheet; Figure 1(c) shows a semiconductor phase edge-oriented sheet; Figure 1(d) shows metallic phase basal plane-oriented nanoplatelets.

Figure 2 shows the X-ray diffraction patterns of 1T-Edge, 2H-Edge, and 1T-Basal (a) MoS_2 , and (b) WS_2 , with spectra normalized to the carbon (002) peak of unmodified carbon cloth for comparison.

Figure 3 shows the SEM images of (a) bare unmodified carbon fiber cloth, and the morphologies of structured (b-d) MoS_2 , and (e-g) WS_2 materials.

Figure 4 are charts showing the performance and characterization of 1T-Edge polytype MoS_2 -sulfur, and WS_2 -sulfur cathodes. (a) Galvanostatic charge/discharge curves and (b) cyclic voltammograms ($\nu = 0.05 \text{ mV} \cdot \text{s}^{-1}$) after initial stabilization, shown with the unmodified sulfur-loaded carbon cloth as control; key: MoS_2 -sulfur (dotted line), WS_2 -sulfur (dashed line), unmodified sulfur-loaded carbon cloth (solid line). (c) Lithium polysulfide adsorption, each with one cathode placed in 1 mM Li_2S_4 solution of DOL/DME. (d) Cycling study of 1T-Edge MoS_2 -sulfur (solid diamonds), WS_2 -sulfur (hollow circles), and the sulfur-loaded carbon cloth control (hollow squares), at $0.1 \text{ mA} \cdot \text{cm}^{-2}$ for the first five activation cycles followed by $0.2 \text{ mA} \cdot \text{cm}^{-2}$, in 1 M LiTFSI electrolyte dissolved in 1:1 (v/v) DOL/DME solution containing 2 wt% LiNO_3 additive.

Figure 5 shows a comparison of cathode performances between the structured MoS_2 -sulfur and WS_2 -sulfur, based on varying phase and morphology. Figures (a,c) Rate stabilities at increasing areal current; 1T-Edge (solid squares), 2H-Edge (solid diamonds), 1T-basal (hollow circles), unmodified (hollow squares). Figures (b,d) cyclic voltammograms of TMD-sulfur cathodes, shown with unmodified sulfur-loaded carbon cloth as control ($\nu = 0.05 \text{ mV} \cdot \text{s}^{-1}$); 1T-Edge (solid line), 2H-Edge (short-dashed line), 1T-basal (long-dashed line), unmodified (dotted line). Cycling performances of structured (e) MoS_2 -sulfur, and (f) WS_2 -sulfur cathodes.

Figure 6 shows the (a) Galvanostatic charge/discharge curves; and (b) cycling performance of 1T-Edge MoS₂-sulfur cathode at increased sulfur loading of 4.1 mg_(S)·cm⁻². Conditions: 0.5 mA·cm⁻² for the first five activation cycles and 1.0 mA·cm⁻² thereafter; 1 M LiTFSI electrolyte in 1:1 (v/v) DOL/DME solution containing 2 wt% LiNO₃ additive.

Figure 7 shows the cyclic voltammograms of control MoS₂ cathodes without sulfur loading. No reactions corresponding to the lithium sulfur system, nor MoS₂ intercalation/conversion reactions, were observed.

Figure 8 shows the electrochemical impedance spectra (Nyquist plots) of sulfur-loaded structured (a) MoS₂ and (b) WS₂ cathodes after charge/discharge cycling (forty cycles), obtained with a 10 mV amplitude at typical open circuit potential of ~2.3 V vs. Li/Li⁺.

Figure 9 shows the dependence of the obtained (a) specific capacity, and (b) areal capacity as a function of the applied current C-rate, on unmodified carbon cloth. (c) Rate stability of an unmodified carbon cloth with 4.6 mg_(S)·cm⁻² areal sulfur loading.

Detailed Description

In one aspect of the present invention, a method of synthesizing a transition metal sulfide-based carbon fiber material for use as an electrode in lithium-sulfur battery or cell is provided. The method comprises providing a solution containing a group VI transition metal sulfide precursor and a solvent; immersing a carbon fiber material into the solution to form a mixture and subjecting the mixture to elevated temperature between 200°C and 300°C to allow loading of transition metal sulfide onto the carbon fiber material. The loaded carbon fiber material is then dried to obtain the transition metal sulfide-based loaded carbon fiber material.

As used herein, group VI transition metal sulfide include sulfides from group VI transition metal selected from the group consisting of chromium (Cr), molybdenum (Mo), tungsten (W), and seaborgium (Sg).

In one embodiment, the group VI transition metal sulfide precursor is an ammonium tetrathiomallate selected from the group consisting of ammonium tetrathiomolybdate

and ammonium tetrathiotungstate. The solvent for dissolving the precursor can be of any suitable solvent or solvent combination so long as the solvent or solvent combination is capable of dissolving the precursor completely. Examples of suitable solvents include, but are not limited to, dimethylformamide (DMF), deionised water or a combination thereof.

In one embodiment, the carbon fiber material is a woven material having a multiplicity of interwoven carbon fibers. Any suitable types of carbon fibers and any suitable types of methods may be used to prepare the carbon fiber material. Example of such carbon fibers include, but are not limited to, carbon fibers produced from carbonization of extruded polyacrylonitrile or from other polymeric materials. Carbon fibers produced from carbonization of extruded polyacrylonitrile are preferred due to their high electrical conductivity (which is comparable to graphite, at approximately 10^2 to 10^5 S/m). Other suitable methods include, but are not limited to, electrospinning, followed by carbonization. In one embodiment, the woven material is prepared by weaving individual carbon fibers into a porous cloth-like material. The porous cloth-like material can have varying porosity as long as the cloth-like material is able to absorb the precursor solution substantially, if not fully. The cloth-like material can be in the form of a cloth, mesh, mat or web. In one embodiment, the carbon fiber material is a porous carbon cloth.

In some embodiments, the carbon fibers have an average single filament diameter of 5 μm to 10 μm . Thinner filaments having an average diameter of at least 100 nm can also be used. Preferably, the carbon fiber material has an overall thickness between 100 μm and 500 μm , with an upper limit of approximately 1 mm, as any thicknesses beyond 1 mm could prevent uniform loading of metal sulfide throughout the carbon fiber material. It will be appreciated that the carbon fiber material may be of any suitable size and shape. In an exemplary embodiment, the carbon fiber material has a size of 5 cm by 10 cm. While each of the dimensions are typically less than 15 cm, one skilled in the art will appreciate that other sizes of the carbon fiber material can also be employed as long as the carbon fiber material can be fully immersed into the solution when the solution is contained within an autoclave apparatus used for the synthesis.

In one embodiment, the carbon fiber material is immersed in the solution for sufficient period of time to allow complete wetting of the carbon fiber material in the solution. The

carbon fiber material together with the solution are then transferred to an autoclave apparatus. In the autoclave apparatus, the mixture is subjected to elevated temperature, between 200°C and 300°C for a predetermined period of time to allow loading of the transition metal sulfide onto the carbon fiber material. Under the elevated temperature process, the transition metal sulfide precursor decomposes and deposits itself as metal sulfide on the surface of the carbon fiber material. The deposited metal sulfide forms a coating on the carbon fiber material. The mixture is then allowed to cool and the loaded carbon fiber material is removed and rinsed before the material is dried to obtain the desired transition metal sulfide-based loaded carbon material.

In one embodiment, the transition metal sulfide is selected from the group consisting of molybdenum disulfide and tungsten disulfide. The transition metal sulfide deposited or loaded onto the carbon fiber material is crystalline in nature and the crystals can be in an edge orientation or basal plane orientation.

The term "edge orientation" as used herein refers to an orientation whereby the crystal structures of the transition metal sulfide are arranged in a vertical position, substantially perpendicular to the surface of the carbon fiber material.

The term "basal orientation" as used herein refers to an orientation whereby the crystal structures of the transition metal sulfide are arranged in a horizontal position parallel to the surface of the carbon fiber material.

In some embodiments, the transition metal sulfide-based loaded carbon material is loaded with edge-oriented molybdenum disulfide or basal plane-oriented molybdenum disulfide. In other embodiments, the transition metal sulfide-based loaded carbon fiber material is loaded with edge-oriented tungsten disulfide or basal plane-oriented tungsten disulfide.

The loaded carbon material may be dried using any suitable methods. The drying is carried out to remove residual solvents. Some examples of such drying methods include, but are not limited to, heating the loaded carbon material at elevated temperature in an oven at ambient pressure, or in vacuum under reduced pressure, or a combination of both elevated temperature and reduced pressure. In one embodiment,

the loaded carbon material is dried under vacuum at a temperature in the range of about 40°C to 100°C, preferably 50°C to 70°C.

5 In another embodiment, the carbon fiber material is immersed in the solvent contained in the solution prior to the step of providing the solution containing group VI transition metal sulfide precursor and the solvent. In this embodiment, the solvent comprises cetyltrimethylammonium bromide dissolved in deionised water. The transition metal sulfide-based loaded carbon material obtained in this embodiment is loaded with basal plane-oriented molybdenum disulfide.

10

The transition metal sulfide-based loaded carbon material formed by the method of the present invention is in metallic-phase. The metallic-phase loaded carbon material can be converted to semiconducting phase and this is done by annealing the transition metal sulfide-based loaded carbon material under suitable conditions to form a
15 semiconducting transition metal sulfide-based loaded carbon material. Any suitable annealing conditions may be employed in this step. In one embodiment, the annealing includes thermal annealing of the transition metal sulfide-based loaded carbon material in a furnace under argon gas flow, heated at a rate of 0.5°C/min to 10°C/min, preferably at a rate of 3°C/min. In various embodiments, thermal annealing is carried
20 out at a temperature in the range of 250°C to 400°C, preferably 280°C to 350°C, for about 1 to 3 hours, preferably 1.5 to 2.5 hours to form the semiconducting phase.

The method of the present invention may further comprise preparing an electrode for lithium-sulfur battery using the transition metal sulfide-based loaded carbon material
25 synthesized by the present method. The preparation comprises mixing sulfur and a carbon black with heating at a temperature between 150°C and 180°C, preferably between 155°C and 160°C to form a sulfur-carbon black mixture. The sulfur-carbon black mixture is further mixed with an organic solvent and a binder to form a sulfur-containing slurry. Any suitable organic solvents may be used to prepare the sulfur-
30 containing slurry. Suitable solvents include, but are not limited to, N-methyl-2-pyrrolidone, or similar solvents. Any suitable binders may be used to prepare the sulfur-containing slurry. Examples of such binders include, but are not limited to, polymers such as polyvinylidene fluoride. While polyvinylidene fluoride and N-Methyl-2-pyrrolidone are a preferred binder/solvent combination, other binder/solvent
35 combinations can also be employed so long as the binder is soluble in the solvent.

The method further comprises depositing the sulfur-containing slurry onto the transition metal sulfide-based loaded carbon material; and drying the transition metal sulfide-based loaded carbon material to obtain a sulfur-loaded transition metal sulfide-based carbon electrode. In one embodiment, the sulfur-loaded transition metal sulfide-based carbon electrode is for use as a cathode in lithium-sulfur battery.

The method may further include a further heating step to remove excess surface sulfur from the sulfur-carbon black mixture, before the sulfur-containing slurry is produced and deposited onto the transition metal sulfide-based loaded carbon material. In one embodiment, excess surface sulfur is removed by heating the sulfur-carbon black mixture at a temperature between 160 to 300°C in argon flow for about 2 to 4.5 hours.

The method further comprises repeating the steps of deposition and drying several times to obtain the desired areal sulfur loading. This step allows areal sulfur loading to be adjusted to desired level. In the present invention, the areal sulfur loading can be adjusted between $1.5 \text{ mg}\cdot\text{cm}^{-2}$ and $5.5 \text{ mg}\cdot\text{cm}^{-2}$ by increasing the number of deposition-drying cycles.

In a second aspect of the present invention, a transition metal sulfide-based carbon material prepared by a method according to the first aspect is provided. The transition metal sulfide-based carbon material comprises a carbon fiber material and a group VI transition metal sulfide selected from the group consisting of molybdenum disulfide and tungsten disulfide, wherein the transition metal sulfide is loaded onto the carbon fiber material. The transition metal sulfide is loaded onto the carbon fiber material by forming nanocrystals on the surface of the carbon fiber material.

In various embodiments, the carbon fiber material is a woven material having a multiplicity of interwoven carbon fibers. The woven material is porous. In one embodiment, the woven material is a porous cloth-like material. The cloth-like material can be in the form of a cloth, mesh, mat or web. In one embodiment, the carbon fiber material is a porous carbon cloth.

In some embodiments, the transition metal sulfide-based carbon material is loaded with edge-oriented molybdenum disulfide or basal plane-oriented molybdenum

disulfide. In other embodiments, the transition metal sulfide-based carbon material is loaded with edge-oriented tungsten disulfide or basal plane-oriented tungsten disulfide. The transition metal sulfide-based carbon material may be used as an electrode in energy storage devices such as battery or cell.

5

In a third aspect, a transition metal sulfide-based carbon electrode is provided. The transition metal sulfide-based carbon electrode comprises a transition metal sulfide-based carbon material of the present invention loaded with sulfur.

10 In a fourth aspect, a lithium-sulfur battery comprising the transition metal sulfide-based carbon material of the present invention is provided. The lithium-sulfur battery comprises an anode and a cathode, wherein the cathode comprises a transition metal sulfide-based carbon material of the present invention loaded with sulfur.

15 The method of the present invention is developed for controlled syntheses of group VI transition metal disulfides on carbon fiber material using a "bottom-up" approach. The transition metal sulfide-based carbon material produced by the method of the present invention can be applied as cathode material in lithium-sulfur batteries or cells for increased areal sulfur loading and capacity. In the method of the present invention,
20 there are three principal properties of the material that can be controlled and these include: (1) the phase of the carbon material (metallic or semiconducting); (2) morphology (edge-oriented or basal plane-oriented of the transition metal disulfide with respect to the surface of the carbon fiber material); and (3) the element composition loaded onto the carbon fiber material (molybdenum sulfide-based or tungsten sulfide-based).
25

The synthesized transition metal sulfide-based carbon material can be employed as cathodes in lithium-sulfur batteries or cells, where phase, morphology, and composition of the transition metal disulfide host material demonstrates an overall
30 positive effect on polysulfide entrapment, thereby enhancing the long term cyclability of the batteries or cells. The rate stability can also be preserved at increased currents due to high electrical conductivity of the metallic phases. The batteries or cells (for metallic edge-oriented molybdenum sulfide (MoS_2)) produced using the transition metal sulfide-based carbon material of the present invention show excellent long term
35 cycling performance, above 95% coulombic efficiency and $930 \text{ mAh}\cdot\text{g}^{-1}$ capacity after

100 cycles at $0.2 \text{ mA}\cdot\text{cm}^{-2}$. The batteries or cells are also able to maintain stability at higher current loads, with specific capacity above $1000 \text{ mAh}\cdot\text{g}^{-1}$ at $2.0 \text{ mA}\cdot\text{cm}^{-2}$. The method of the present invention further allows sulfur loadings to be increased to enhance areal capacities, achieving capacities of $4.0 \text{ mAh}\cdot\text{cm}^{-2}$, at $4 \text{ mg}_{(\text{S})}\cdot\text{cm}^{-2}$ loadings and $1 \text{ mA}\cdot\text{cm}^{-2}$ current discharge. The method of the present invention is unique in that the transition metal disulfide (TMD) host is distinct from the loaded-sulfur. This is unlike those systems available in the state of the art where exfoliated TMD nanosheets are physically mixed with sulfur and applied directly as cathode on aluminium foil or where molybdenum disulphide (MoS_2) nanosheets are used to physically encapsulate sulfur particles. Moreover, the use of the carbon fiber material ensures a long-range conduction path for both electrons and Li ions, circumventing the insulating natures of sulfur and Li_2S , while its flexibility prevents structural damage during expansion (discharge) cycles. This highlights a paradigm shift where physical encapsulation of sulfur was once paramount.

Advantageously, the technology presented in the present invention combines and exploits the individual benefits of: (1) the use of metal sulfide hosts for polysulfide entrapment, and thereby enhances the lifetime and performances of lithium-sulfur battery cathodes; (2) the use of porous carbon fiber material as a means to increase the areal sulfur loading, and consequently the areal capacity, over conventional methods of slurry-based cathodes on aluminium foil. With the use of a bottom-up solvothermal synthesis method, the method of the present invention is suitable for larger-scale industrial production of the transition metal sulfide-based carbon fiber material. The method of the present invention confers full control and tuning of physical properties (phase, morphology, and composition) in the synthesis of the transition metal sulfide, which the same level of control cannot be achieved from using a top-down approach known in the state of the art.

To facilitate a better understanding of the present invention, the following examples of specific embodiments are given. In no way should the following examples be read to limit or define the entire scope of the invention. One skilled in the art will recognize that the examples set out below are not an exhaustive list of the embodiments of this invention.

EXAMPLES

Example 1

Synthesis of metallic phase edge-oriented transition metal disulfide (TMDs)

- 5 A metallic 1T-Edge oriented molybdenum disulphide (MoS_2) and tungsten disulphide (WS_2) samples were synthesized through a one-pot solvothermal synthesis method (see Figure 1, Scheme 1a-1b).

Ammonium tetrathiomolybdate ($(\text{NH}_4)_2\text{MoS}_4$, 375 mg) was dissolved in a 2:1 (v/v)
10 mixture of dimethylformamide (DMF) and deionized water (70 mL) by stirring to give a reddish-brown solution. A 5×10 cm piece of carbon cloth was immersed into the solution with brief sonication. The solution was stirred slowly for 30 min to ensure complete wetting of the carbon cloth with the solution. The mixture was then transferred to a PTFE-lined stainless steel autoclave and the mixture was maintained
15 at a temperature of 200°C for about 12 hours. After cooling naturally to room temperature, the metallic-edge MoS_2 carbon cloth was removed, rinsed with deionized water and ethanol five times, and consequently dried at 60°C in vacuum overnight. The sample obtained is labelled as MoS_2 1T-Edge.

- 20 For synthesis of metallic-edge tungsten disulphide (WS_2), ammonium tetrathiotungstate ($(\text{NH}_4)_2\text{WS}_4$, 375 mg) was dissolved in DMF (70 mL) instead, with all other procedures kept constant. The sample obtained is labelled as WS_2 1T-Edge.

Average masses are approximately $2 \text{ mg} \cdot \text{cm}^{-2}$ for MoS_2 and WS_2 . Prior to synthesis,
25 all carbon cloths were first washed sequentially in ethanol, deionized water, and acetone with sonication for about 10 mins each, and dried at 60°C in vacuum overnight.

Example 2

- 30 Synthesis of semiconducting phase edge-oriented TMDs

Figure 1, Scheme 1b-1c illustrates a phase conversion of the transition metal sulfide-based carbon material from metallic 1T-Edge polytype to semiconducting polytype (denoted as 2H-Edge).

Metallic 1T-Edge oriented molybdenum disulphide (MoS_2) and metallic 1T-Edge oriented tungsten disulphide (WS_2) were each annealed in a tube furnace under argon gas flow heated at a rate of $3^\circ\text{C}/\text{min}$, and held at 300°C for about 2 hours to form the semiconducting phase before cooling to room temperature. The samples obtained were labelled as MoS_2 2H-Edge and WS_2 2H-Edge, respectively.

Example 3

Synthesis of metallic phase basal plane-oriented TMDs

Metallic 1T-Basal plane-oriented molybdenum disulphide (MoS_2) was prepared through a surfactant-assisted hydrothermal synthesis of MoS_2 .

Cetyltrimethylammonium bromide (CTAB, 1.275 g , 50 mmol L^{-1}) was first dissolved in deionized water (70 mL) with rapid stirring. A $5\times 10\text{ cm}$ piece of carbon cloth was immersed into the solution and stirred slowly for 30 mins to allow uniform coating. Ammonium tetrathiomolybdate ($(\text{NH}_4)_2\text{MoS}_4$, 375 mg) was then added and dissolved with stirring. Finally, hydrazine monohydrate ($\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$, 1.6 mL) was added dropwise and further stirred for 30 mins. The mixture was then transferred to a PTFE-lined stainless steel autoclave and maintained at 200°C for about 12 hours. The mixture was cooled to room temperature, followed by rinsing with deionized water and ethanol five times, before drying at 60°C in vacuum overnight. The sample obtained was labelled as MoS_2 1T-Basal.

Metallic 1T-Basal plane-oriented tungsten disulphide (WS_2) was prepared through a modified one-pot solvothermal synthesis. For the synthesis of 1T-Basal WS_2 , only ammonium tetrathiotungstate ($(\text{NH}_4)_2\text{WS}_4$, 375 mg) was dissolved in a 2:1 volume mixture of DMF:water (70 mL), before introducing of a $5\times 10\text{ cm}$ piece of carbon cloth into the solution. The mixture was similarly transferred to a PTFE-lined autoclave and maintained at 200°C for about 12 hours, followed by cooling the mixture, rinsing the mixture with deionized water and ethanol five times, and drying the mixture at 60°C . The sample obtained was labelled as WS_2 1T-Basal.

Example 4

Coin Cell Preparation and Electrochemical Testing

35

Consequently, the prepared MoS₂ and WS₂ polytypes with their varying morphologies were applied and tested as sulfur hosts in full lithium-sulfur cells.

Sulfur was first loaded into carbon black (Ketjenblack) using a melt-diffusion method at 160°C to form a sulfur-carbon black mixture. Excess sulfur on the surface of the sulfur-carbon black mixture was removed by further heating the sulfur-carbon black mixture to 200°C in argon flow for 4 hours. The sulfur-carbon black mixture, consisting of 90 wt% sublimed sulfur in conductive carbon black (Ketjenblack), was then used to prepare a sulfur-containing slurry. The sulfur-containing slurry was prepared by mixing the sulfur-carbon black mixture with N-methyl-2-pyrrolidone (NMP) and 10 wt% polyvinylidene fluoride (PVDF).

This unique method of sulfur-loading first into porous carbon black (Ketjenblack) and not directly on MoS₂ or WS₂ allows proper study of their true polysulfide adsorption/catalytic effects to be carried out, as dissolved polysulfides are chemically adsorbed onto exposed TMD surfaces, and not physically confined by them.

Sulfur-loaded TMD-carbon cloth cathodes (5×5 cm) were then formed by blade deposition of the sulfur-containing slurry in direct contact with the carbon cloth materials, dried at 60°C and then in dynamic vacuum overnight. Areal sulfur loadings can be adjusted between 1.5 mg·cm⁻² and 5.5 mg·cm⁻² by increasing the number of deposition-drying cycles. The final sulfur-loaded carbon cloth materials were subsequently cut to fix 12.7 mm diameter cathodes.

Standard 2032-type coin cells were used for cell cycling and stability tests. Assembly was done in an argon-filled glovebox, with the respective sulfur-loaded TMD-carbon cloth material (12.7 mm diameter) used directly as the cathode, pure lithium foil as the anode/reference electrode separated by a Celgard membrane with 1 M LiTFSI electrolyte in a 1:1 volume mixture of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME), with 2 wt% LiNO₃. The minimum electrolyte amount was 12-15 μL mg_(S)⁻¹ to ensure complete wetting. Galvanostatic charge-discharge cycling was done using a LAND CT2001 battery tester (Lanhe), between 1.6 V to 2.8 V vs. Li/Li⁺ and the results obtained are as shown in Figure 4(a). Cyclic voltammograms were obtained at a scan rate of 0.05 mV s⁻¹ and the results obtained are as shown in Figure 4(b). Electrochemical impedance spectra was done with a 10 mV amplitude at open circuit

potential, between a frequency range of 1 MHz to 0.01 Hz on an M204 Autolab potentiostat (Metrohm) fitted with a frequency response analyser module.

Lithium Polysulfide Adsorption

5 Lithium Polysulfide (LiPS) adsorption studies were done using a 1 mM Li_2S_4 solution prepared by reacting stoichiometric amounts (1:3) of Li_2S and elemental sulfur in a 1:1 mixture of DOL and DME (v/v), at 60°C under inert atmosphere with stirring for one week to ensure complete dissolution. Respective TMD/carbon cloth cathodes (each
10 12.7 mm diameter) were then immersed in 2 mL aliquots of the Li_2S_4 solution and left to stand overnight.

Example 5

Structure Characterisation and Performance Testing

15 Field emission scanning electron microscopy (SEM) was performed on a JSM-7400F (JEOL), with energy-dispersive X-ray spectroscopy (EDS) (Oxford Instruments) obtained at an accelerating voltage of 30 kV. X-ray diffraction (XRD) was done on a D8 ADVANCE (Bruker) with a Cu $\text{K}\alpha$ source, thermogravimetric analysis (TGA) on a Pyris
20 1 TGA (PerkinElmer), and both survey and high- resolution core-level X-ray photoelectron spectroscopy (XPS) performed on an ESCALAB 220i-XL (VG Scientific) with an Al $\text{K}\alpha$ X-ray source, calibrated to the carbon 1s signal at 284.4 eV.

X-ray diffraction (XRD)

25 Characterization was performed to confirm that correct phases of the TMDs were obtained, starting with X-ray diffraction (XRD) as the standard for identification of the exact polytype. Figure 2a displays the XRD patterns of the prepared MoS_2 , with peaks correlated to native 2H- MoS_2 (JCPDS card no.37-1492). The unmodified carbon cloth
30 shows two broad peaks at $2\theta = 25^\circ$ and 44° , corresponding respectively to the (002) and (100)/(101) planes of graphite, which suggest a mixture of pristine graphitic planes interspersed with small amounts of disordered carbons. X-ray photoelectron spectroscopy (XPS) further confirms the majority of carbon to be sp²-hybridized at 284.4 eV and a very low amount of surface oxygen (Table 1). The 1T-Edge MoS_2
35 shows a sharp (002) peak at 9.1° , corresponding to an interlayer spacing of $\sim 9.7 \text{ \AA}$

and in excellent agreement with previous reports of 1T-MoS₂ materials between 9.0 Å to 9.8 Å. This occurs together with a (004) second-order diffraction peak at about 18.2°. More importantly, the intensity of the (002) peak also suggests a strong vertical orientation of the MoS₂ sheet edges.

5

The semiconducting 2H-polytype was then obtained after annealing at 300°C, demonstrating complete disappearance of the 9.1° peak with a new (002) peak at 13.9°. This confirms conversion to the 2H-polytype with an interlayer spacing of 6.3 Å, close to the expected 6.15 Å separation of bulk 2H MoS₂. In contrast, the 1T-Basal material exhibited a diffused (002) peak centered at 8.6°, indicating greater disorder in sheet arrangement and a slightly larger interlayer separation of 10.3 Å.

Likewise, XRD patterns of the structured WS₂ materials were similarly compared to 2H-WS₂ (JCPDS card no. 08-0237), with both 1T-Edge and 1T-Basal polytypes presenting (002) peaks at ca. 9.2°, and their second-order diffractions at 18.3°. Interlayer separations thus are estimated at 9.6 Å and are similar to prior reports of 9.43 Å for 1T-WS₂. Again, the intensity of the (002) peak is enhanced for the 1T-Edge material compared to the 1T-Basal indicative of a greater edge orientation. Annealing was similarly done in inert atmosphere to convert the 1T-Edge to the 2H-Edge polytype, with shift of the (002) peak to 11.6°. In this case, the separation of 7.6 Å is notably larger than the expected 6.16 Å for 2H-WS₂, and the broad FWHM is also likely due to increased randomness the sheet stacking.

Further analyses were then carried out to ascertain the chemical nature of the synthesized materials. Wide scan XPS was first performed to obtain surface elemental compositions, and their values tabulated in Table 1 below. It is interesting to note that the surface was slightly sulfur-deficient in all materials with a metal:sulfur ratio little under the theoretical 1:2 stoichiometry. This phenomenon was nonetheless observed with other TMDs prepared, and is potentially beneficial in several electrocatalytic reactions previously reported. In contrast to the surface specific sensitivity of the XPS technique, energy-dispersive X-ray spectroscopy (EDS) was also employed to study the bulk composition. In this case, the materials all showed stoichiometries closer to the expected 1:2 ratio, indicating that sulfur-deficiencies are only limited to the exposed top surfaces.

35

EDS mapping further confirm that the synthesized TMDs are well distributed across the carbon fibers. High resolution XPS scans of the Mo 3d region show both 1T-polytype MoS₂ materials with slightly lower 3d_{5/2} and 3d_{3/2} binding energies of approximately 228.6 eV and 231.9 eV respectively, as compared to bulk 2H-MoS₂ at 229.4 eV and 232.5 eV. With annealing, binding energies are upshifted again to the 2H-polytype at 229.1 eV and 232.3 eV. Sulfur similarly experienced a small upshift after annealing, from the initial 161.5 eV for the 2p_{3/2} peak. For the tungsten sulfides, XPS of both 1T-polytypes show the W 4f_{7/2} and 4f_{5/2} peaks at ca. 31.8 eV and 33.9 eV, similar to reported positions for the 1T-phase. However, the upshift in binding energies that occurred with annealing was observed to be less than expected. An additional pair of oxidized W(VI) peaks were also noted at 35.5 eV and 37.8 eV. This is not uncommon with either exfoliated or synthesized WS₂ nanosheets due to their higher surface susceptibility for oxidation and may thus account for the lack of a distinct upshift after annealing.

Table 1: Surface elemental compositions of structured-MoS₂ and WS₂ carbon cloth cathodes, based on X-ray photoelectron spectroscopy.

Phase/Morphology	C (at.%)	O (at.%)	Mo/W (at.%)	S (at.%)	Surface Composition (M ₅)
MoS ₂ 1T-Edge	31.6	16.4	18.9	33.1	MoS _{1.25}
MoS ₂ 2H-Edge	30.5	12.3	22.3	34.8	MoS _{1.56}
MoS ₂ 1T-Basal	52.1	6.4	16.0	25.5	MoS _{1.39}
WS ₂ 1T-Edge	29.3	17.4	19.0	34.3	WS _{1.81}
WS ₂ 2H-Edge	31.1	24.0	17.2	27.7	WS _{1.61}
WS ₂ 1T-Basal	42.2	14.8	16.1	27.0	WS _{1.68}
Unmodified	97.9	2.1	-	-	-

Scanning Electron Microscopy (SEM)

With confirmation of composition and TMD-polytypes based on the three characterization methods, we subsequently move to determine the morphology of the materials using scanning electron microscopy (SEM). Bare unmodified carbon fibers are as displayed in Figure 3a, with thin longitudinal ridges along the surface, but are otherwise smooth and interwoven into a lattice structure as shown in the upper-right panel. In comparison, both 1T-Edge MoS₂ and WS₂ polytypes (Figures 3b, 3e) appear as vertically-oriented angular sheets, with growth perpendicular to the surface of the carbon fiber material, correlating well with the previous observation of intense (002)

XRD peaks. Individual WS₂ platelets are also noted to be larger at approximately 200-300 nm in length compared to MoS₂ with a smaller and denser network. There were also no obvious morphological changes observed after annealing to the 2H-Edge (Figures 3c, 3f). This is opposed to 1T-Basal polytypes of MoS₂ and WS₂ which have preferential sheet/platelet orientations parallel to the carbon fiber surface (Figures 3d, 3g). Interestingly, individual WS₂ platelets were again larger at up to 300 nm across, versus MoS₂ with diameters which were typically 100 nm or less.

Performance and Characterization of 1T-Edge polytype MoS₂-sulfur and WS₂-sulfur cathodes

A first comparison was made between the 1T-Edge polytype of MoS₂-sulfur and WS₂-sulfur cathodes (see results in Figure 4). Galvanostatic charge and discharge measurements (Figure 4a) demonstrated a stable average specific capacity of 1410 mAh·g⁻¹ and 1320 mAh·g⁻¹ for 1T-Edge MoS₂ and WS₂, respectively at current density of 0.2 mA·cm⁻² (which at a sulfur loading of approximately 1.5 mg(S)·cm⁻² translates to a C-rate of approximately 0.1 C; 1 C = 1673 mA·g⁻¹ based on the molecular weight of sulfur). Characteristic two-plateau discharge curves representative of the lithium-sulfur system were observed at 2.33 V vs. Li/Li⁺ for the conversion of sulfur/Li₂S₈ to Li₂S₄, followed by a second plateau at 2.10 V. Capacities of both plateaus were also close to the theoretical 25:75 ratio, indicating complete discharge and conversion of dissolved intermediate polysulfides to the final solid Li₂S product.

Further characterization by cyclic voltammetry shown in Figure 4b revealed enhanced peak currents for both 1T-Edge MoS₂ and WS₂ over the unmodified carbon cloth for sulfur reduction (discharge) and subsequent Li₂S oxidation (charge) processes, representative of polysulfide electrocatalysis. A larger peak current for MoS₂ than WS₂ is also observed. Polysulfide adsorption tests (Figure 4c) each with a single MoS₂ and WS₂ edge-grown cathode demonstrate good adsorption of Li₂S₄, with their solutions turning clear as compared to the yellow-brown solution for unmodified carbon cloth. It is also important to emphasize that additional control experiments for TMD-cathodes *without* loaded sulfur exhibited none of the polysulfide redox reactions. See Figure 7 which shows that there are no peaks corresponding to sulfur-polysulfide conversion. Neither was any inherent activity of TMD materials seen as no distinct peaks were observed that could correspond to intercalation reactions, such as the MoS₂

intercalation and conversion reactions which thermodynamically, occur outside the potential range of LSBs. These therefore confirm that the TMD host itself does not contribute to the obtained capacity in any manner, which solely arises from the sulfur/polysulfide redox reaction. Cycling stabilities of the cathodes were also investigated, with the 1T-Edge MoS₂ cathode maintaining a specific capacity of 927 mAh·g⁻¹ after 100 cycles, and WS₂ at 830 mAh·g⁻¹. This is in contrast to the unmodified carbon cloth at only 611 mAh·g⁻¹ (Figure 4d) after 100 cycles, and which experienced a large capacity loss after the first discharge cycle due to the lack of any polysulfide-confining ability on carbon surfaces. Furthermore, 1T-Edge MoS₂ cathodes were noted to reach stable capacities after roughly forty cycles, while a gradual decrease continued for the WS₂ case. Coulombic efficiencies also remained high throughout cycling, above 95% for MoS₂, and WS₂ marginally lower at 93%. Although both the voltammetric and cycling studies suggest a slight performance advantage of 1T-Edge MoS₂ over its WS₂ counterpart. This may however be well explained by the lower observed charge transfer resistances (R_{ct} ; width of semicircle) of 1T-Edge MoS₂ at typically 10 Ω or less, compared to that for WS₂ at 18 Ω seen from the Nyquist plots of electrochemical impedance spectroscopy (see Figure 8). The lower R_{ct} values of 1T-Edge MoS₂ in turn correlate well with their smaller platelet sizes and increased density of edge sites, which are reported to have enhanced selectivity for polysulfide adsorption/electrocatalysis.

Effects of both TMD phase and morphology on lithium-sulfur battery (LSB) performance

With the different performances of 1T-Edge MoS₂ and WS₂ cathodes identified, we now turn our attention to the dramatic effects of both TMD phase and morphology on LSB performance.

Figure 5a illustrates the vastly different rate stabilities of MoS₂ cathodes based on phase and morphology. At the highest areal current density of 2.0 mA·cm⁻² close to 1 C, 1T-Edge MoS₂ performed best with a specific capacity of 1024 mAh·g⁻¹; the unmodified carbon control material offered only 645 mAh·g⁻¹. Furthermore, the capacity recovered back to a high of 1205 mAh·g⁻¹ upon decrease of the current density back to 0.2 mA·cm⁻². Contrastingly, the 2H-Edge MoS₂ cathode showed a substantially poorer capacity of 359 mAh·g⁻¹ at the same high current density, despite

that reasonable capacities were still obtained at low current densities ($1038 \text{ mAh}\cdot\text{g}^{-1}$ at $0.2 \text{ mA}\cdot\text{cm}^{-2}$), marginally lower than the 1T-Edge polytype. In consideration of the edge-oriented morphological similarities of these cathodes, we can thus conclude that the lower conductivity of the 2H-semiconducting polytype must have resulted in the drastic drop in capacity at high current density. Indeed, a comparison of the impedance spectra establishes a twice large charge-transfer resistance (19Ω) of the 2H-polytype, and an increased uncompensated/solution resistance possibly due to increased polysulfide dissolution into the electrolyte. This negative effect is even more pronounced in the cyclic voltammogram of 2H-Edge MoS_2 which demonstrated significant increases in onset and peak potentials of all redox processes (Figure 5b). Of note is the considerably larger overpotential for the initial sulfur/ Li_2S_8 discharge. The drawn-out redox waves, increased overpotentials, and reduced peak currents are all characteristic of kinetically slower reactions, which arise from sluggish heterogeneous electron transfers at the semiconducting surface. Comparatively, the 1T-Basal MoS_2 cathode exhibited a capacity of $791 \text{ mAh}\cdot\text{g}^{-1}$ at the highest current density of $2.0 \text{ mA}\cdot\text{cm}^{-2}$ that is moderately lower than the 1T-Edge material, thus reiterating the importance of achieving high electrical conductivity by phase-engineering. Both 1T-polytypes further demonstrate similar R_{ct} values due to their similar metallic nature. With only slightly larger peak currents of 1T-Basal MoS_2 over unmodified carbon, we obtain a second conclusion of the preferential edge morphology. After extended cycling (Figure 5e), capacities of $927 \text{ mAh}\cdot\text{g}^{-1}$, $872 \text{ mAh}\cdot\text{g}^{-1}$, and $742 \text{ mAh}\cdot\text{g}^{-1}$ were attained at the 100th cycle for 1T-Edge, 1T-Basal, and 2H-Edge MoS_2 in that order. It was also noted that the capacity decrease was most gradual in 1T-Basal MoS_2 . Therefore, the observed "electrocatalysis" can be attributed to the combined effects of high electrical conductivity and preferential LiPS adsorption capacity of 1T-Edge MoS_2 , and the overall trend in decreasing order of LSB performance is 1T-Edge > 1T-Basal > 2H-Edge.

The overall trend of the structured WS_2 cathodes is analogous to that of MoS_2 . The 1T-Edge WS_2 gave a $1019 \text{ mAh}\cdot\text{g}^{-1}$ capacity at the highest current density, and recovered up to $1232 \text{ mAh}\cdot\text{g}^{-1}$ upon current reduction (Figure 5c). For the case of WS_2 cathodes however, the negative effect of the 2H-semiconducting polytype is less pronounced. 2H-Edge WS_2 had a capacity of $743 \text{ mAh}\cdot\text{g}^{-1}$ at the highest $0.2 \text{ mA}\cdot\text{cm}^{-2}$ current; $1045 \text{ mAh}\cdot\text{g}^{-1}$ on recovery to $0.2 \text{ mA}\cdot\text{cm}^{-2}$. Although there still were larger overpotentials and reduced peak currents similar to the MoS_2 case, the use of semiconducting WS_2

was less detrimental (Figure 5d). This can however be largely expected from the comparable R_{ct} of both 1T and 2H-polytypes of WS_2 at about $20\ \Omega$ in each (see Figure 8b). Most importantly, from these results, we may nonetheless gather that the polytype is a more crucial factor for rate stability than morphology, similar to MoS_2 . The inventors also observed from the cycling data in Figure 5f capacities of $830\text{ mAh}\cdot\text{g}^{-1}$, ca. $820\text{ mAh}\cdot\text{g}^{-1}$, and $729\text{ mAh}\cdot\text{g}^{-1}$, for the 1T-Edge, 1T-Basal, and 2H-Edge WS_2 polytypes respectively after 100 cycles.

Areal Capacity

In considering practical considerations required for adoption of LSBs, TMD-carbon fiber material system in terms of areal capacity is also examined. Higher areal capacities can be achieved with a higher areal sulfur load, as demonstrated in Figure 6 for the best performing 1T-Edge MoS_2 polytype at $4.1\text{ mg}_{(S)}\cdot\text{cm}^{-2}$ loading. A high initial specific capacity of $1200\text{ mAh}\cdot\text{g}^{-1}$ ($4.9\text{ mAh}\cdot\text{cm}^{-2}$) was obtained, and stabilized at a capacity of about $900\text{ mAh}\cdot\text{g}^{-1}$ over forty cycles at $1.0\text{ mA}\cdot\text{cm}^{-2}$ (0.15 C). The equivalent stable areal capacity achieved was $3.7\text{ mAh}\cdot\text{cm}^{-2}$, compared to traditional lithium-ion batteries at approximately $2\text{ mAh}\cdot\text{cm}^{-2}$, and recent reports of full-cell lithium-ion battery systems at 3.1 to $3.4\text{ mAh}\cdot\text{cm}^{-2}$. While the present invention has also achieved higher initial areal capacities of $6\text{ mAh}\cdot\text{cm}^{-2}$ on the current system with sulfur-loadings beyond $5\text{ mg}_{(S)}\cdot\text{cm}^{-2}$, it is observed that an upper limit on the applied current can be drawn from the cells, and thus it is determined that at a sulfur loading of approximately 4.5 to $5.0\text{ mg}_{(S)}\cdot\text{cm}^{-2}$, a reasonable compromise between overall areal capacity and current/C-rate can be reached (see Figure 9).

In the present invention, the inventors present a systematic approach in the application of structured Group VI transition metal sulfides (MoS_2 and WS_2) on carbon fiber material as lithium sulfur battery cathodes. Primarily, the effects of phase, morphology and composition were investigated towards polysulfide confinement and the electrocatalytic observations reported in previous studies. In the examples set forth hereinabove, the inventors have identified a clear trend in both MoS_2 and WS_2 , where the polytype/phase was the dominant factor followed by their sheet orientations. 1T-Edge polytypes outperformed all others due to the combination of its metallic character and preferential edge-oriented morphology. The best-performing 1T-Edge MoS_2 was also seen to deliver enhanced battery cycling performance over its WS_2 counterpart,

which the inventors attribute to its higher density of catalytically-active edges. Considering the potential use of lithium-sulfur cathodes in larger scale battery systems, increased areal capacities were also demonstrated with a stable areal capacity of approximately $4 \text{ mAh}\cdot\text{cm}^{-2}$, greater than the average commercial lithium-ion battery.

5 Thus, from the above results, we can see that transition metal sulfide-based loaded carbon fiber material can be exploited to achieve increased areal capacities required for commercial adoption of lithium sulfur batteries. The important insights gained from the above investigations also contribute to the possibility of customizing the design of sulfur cathodes based on morphology and phase engineering of the selected element
10 composition.

Although an embodiment of the present invention have been shown and described, the present invention is not limited to the described embodiments. Instead, it would be appreciated by those skilled in the art that changes may be made to the embodiments
15 without departing from the scope of the invention, the scope of which is set forth in the following claims.