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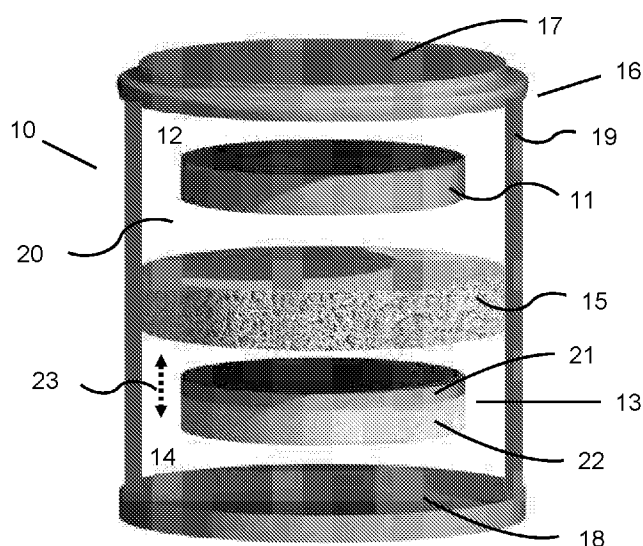
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(54) Title: LITHIUM-SULFUR ENERGY STORAGE CELL AND HYBRID CELL HAVING CAPACITIVE ENERGY STORAGE AND DISCHARGE CAPABILITY

Figure 1



(57) Abstract: The invention provides a rechargeable energy storage cell, the cell comprising: a lithium anode in an anodic portion of the cell; an oriented cathode in a cathodic portion of the cell, the cathode comprising: a sheet of impermeable material; and a cathodic material disposed on one side of the sheet, the cathodic material comprising sulfur, wherein the cathode is oriented with the sheet positioned between the cathodic material and the anode; and an electrolyte permitting lithium ion transport between the anodic portion and the cathodic portion, wherein the sheet forms a physical barrier that inhibits diffusion of electrolyte-soluble sulfides from the cathodic portion to the anodic portion during discharge and/or recharge of the cell.

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Lithium-sulfur energy storage cell and hybrid cell having capacitive energy storage and discharge capability

Technical Field

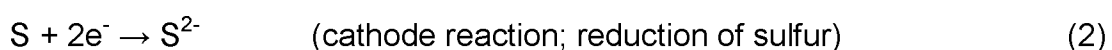
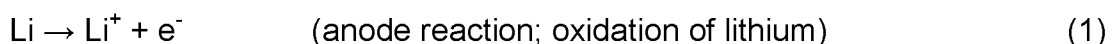
[1] The present invention relates to a rechargeable lithium-sulfur energy storage cell. In particular, the cell comprises a cathode having a sheet of impermeable material and a sulfur-containing cathodic material disposed on one side of the sheet. The cathode is oriented with the sheet positioned between the cathodic material and the anode, thus forming a physical barrier that inhibits diffusion of electrolyte-soluble sulfides during discharge and/or recharge of the cell.

10 Background of Invention

[2] Rechargeable batteries (or "secondary batteries") allow energy to be stored and consumed when required, and are central to the functioning of many products such as portable electronic devices and electric vehicles (EV). Lithium-ion (Li-ion) battery technology, based on lithium-ion intercalating electrode materials and organic electrolytes, is currently the most widespread commercial technology. However, despite considerable advances in Li-ion battery technology since the early discoveries in the 1980's, both cost and performance remain key constraints on the development of competitive battery powered technologies, particularly for EV and grid applications.

[3] In order to achieve the necessary step-change in performance, there is a need to develop alternative battery chemistries to commercial readiness. Lithium-sulfur (Li-S) batteries are a particularly promising candidate, due in part to the much high theoretical energy density relative to Li-ion batteries. Furthermore, sulfur is an abundant, low-cost and non-toxic material compared with many of the transition-metal containing inorganic electrode materials required for commercial Li-ion batteries.

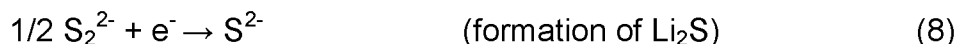
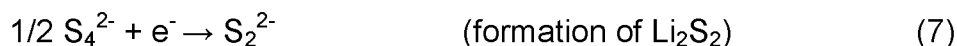
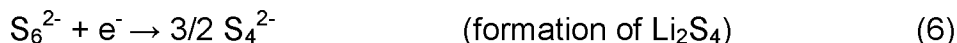
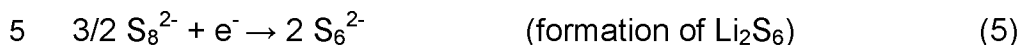
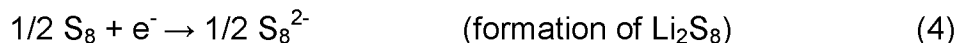
[4] The half reactions at the discharge of a Li-S cell are:



[5] Hence, the final discharge product is Li_2S and the overall discharge reaction of the Li-S battery is:



[6] The electrochemical reduction of elemental sulfur at the cathode during discharge is a multistep reaction, so that overall reaction (2) in fact consists of the series of reactions:



[7] The intermediates formed during reactions (4) to (7), having the general
10 formula Li_2S_x ($2 \leq x \leq 8$), are known as lithium polysulfides.

[8] There are a number of key challenges in realising the potential beneficial attributes of Li-S battery chemistry, in particular: (a) sulfur and its discharge products (Li_2S_x) are insulating, which limits the utilization of electrode active material; (b) a large volumetric expansion and contraction ($\approx 76\%$) associated with the
15 interconversion between elemental sulfur and Li_2S , resulting in disintegration of the cathode and rapid capacity fading upon cycling; and (c) the higher order polysulfides (Li_2S_x , $4 \leq x \leq 8$), which are highly soluble in common organic electrolytes, can migrate from the cathodic region of the cell, undergoing deleterious reactions at the anode which result in irreversible loss of active material, capacity degradation and low
20 coulombic efficiency. These challenges have been mitigated to an extent through the development of composite cathodes in which sulfur is dispersed in a conductive, porous matrix able to withstand the volumetric expansion. However, the loss of sulfur from the cathode to the anode due to the diffusion of soluble polysulfides remains a considerable issue to address.

[9] Previous attempts to address the polysulfide migration challenge include
25 the use of cathodic matrix materials with polar functionalities, such as graphene oxide and metal oxides. However, although such approaches may lessen capacity fading, barriers to ionic and electron transport typically reduce the effective sulfur utilisation, while processability challenges, increased mass (thus reducing energy density) and
30 high costs associated with these materials impose further practical limitations. Another reported strategy for reducing sulfur loss include positioning lithium ion-permeable interlayers between the cathode and anode, either as a non-conductive

“functional separator” to selectively inhibit polysulfide passage, or as a sulfide-retentive and conductive interlayer adjacent to the separator. Further approaches include protection of the lithium anode to minimise reactions with polysulfides and optimisation of the electrolyte composition.

5 [10] Despite progress to date, there is an ongoing need for new advances to improve one or more of the capacity utilisation and cycle life of Li-S energy storage devices, in particular by mitigating polysulfide losses from the cathodic region of the cell during successive discharge and charging cycles while preferably avoiding excessive weight addition, costly materials or complex manufacturing requirements.

10 [11] A reference herein to a patent document or other matter which is given as prior art is not to be taken as an admission that the document or matter was known or that the information it contains was part of the common general knowledge as at the priority date of any of the claims.

Summary of Invention

15 [12] We have now developed a rechargeable lithium-sulfur energy storage cell with a cathode configuration which affords excellent sulfur utilisation and capacity retention. It is believed that the orientation of the cathode suppresses migration of soluble polysulfides from the cathode to the anode, thereby reducing irreversible losses of active sulfur and/or suppressing redox shuttling reactions which
20 deleteriously affect coulombic efficiency.

[13] In a preferred embodiment, a sulfide-retentive composition in close proximity to the cathode further improves capacity utilisation and cycling performance. Where the sulfide-retentive composition comprises a conductive, porous, high surface area carbon, the cell may be capable of capacitive energy storage to complement its
25 faradaic energy storage capability.

[14] In accordance with a first aspect the invention provides a rechargeable energy storage cell, the cell comprising: a lithium anode in an anodic portion of the cell; an oriented cathode in a cathodic portion of the cell, the cathode comprising: a sheet of impermeable material; and a cathodic material disposed on one side of the
30 sheet, the cathodic material comprising sulfur, wherein the cathode is oriented with

the sheet positioned between the cathodic material and the anode; and an electrolyte permitting lithium ion transport between the anodic portion and the cathodic portion, wherein the sheet forms a physical barrier that inhibits diffusion of electrolyte-soluble sulfides from the cathodic portion to the anodic portion during discharge and/or
5 recharge of the cell.

[15] In accordance with a further aspect the invention provides a rechargeable energy storage cell capable of both capacitive energy discharge and faradaic energy discharge, the cell comprising: a lithium anode in an anodic portion of the cell; an oriented cathode in a cathodic portion of the cell, the cathode comprising: a sheet of
10 impermeable material; and a cathodic material disposed on one side of the sheet, the cathodic material comprising sulfur, wherein the cathode is oriented with the sheet positioned between the cathodic material and the anode; an electrically conductive and porous sulfide-retentive composition in the cathodic portion; and an electrolyte permitting lithium ion transport between the anodic portion and the cathodic portion,
15 wherein the sheet forms a physical barrier that inhibits diffusion of electrolyte-soluble sulfides from the cathodic portion to the anodic portion during discharge and/or recharge of the cell.

[16] In accordance with a further aspect the invention provides a battery comprising one or more rechargeable energy storage cells according to any one of
20 the embodiments disclosed herein.

[17] In accordance with a further aspect the invention provides an electrically powered device, powered by the battery according to any one of the embodiments disclosed herein.

[18] Where the terms “comprise”, “comprises” and “comprising” are used in the
25 specification (including the claims) they are to be interpreted as specifying the stated features, integers, steps or components, but not precluding the presence of one or more other features, integers, steps or components, or group thereof.

[19] Further aspects of the invention appear below in the detailed description of the invention.

Brief Description of Drawings

[20] Embodiments of the invention will herein be illustrated by way of example only with reference to the accompanying drawings in which:

[21] Figure 1 depicts a rechargeable energy storage cell capable of faradaic energy discharge, in accordance with an embodiment of the invention.

[22] Figure 2 depicts a rechargeable energy storage cell capable of both capacitive energy discharge and faradaic energy discharge, in accordance with an embodiment of the invention.

[23] Figure 3 is a schematic diagram of (a) a lithium-sulfur energy storage cell having a conventionally oriented cathode, as evaluated in Example 1; and (b) a lithium sulfur energy storage cell having an oriented cathode according to an embodiment of the invention, as evaluated in Example 2.

[24] Figure 4 is a graph which compares the cycling performance (discharge capacity and coulombic efficiency) for a lithium-sulfur energy storage cell having a conventionally oriented cathode, as evaluated in Example 1, and a lithium sulfur energy storage cell having an oriented cathode according to an embodiment of the invention, as evaluated in Example 2.

[25] Figure 5 is a schematic diagram of (a) a lithium-sulfur energy storage cell having a conventionally oriented cathode and a carbon-coated separator, as evaluated in Example 3; and (b) a lithium sulfur energy storage cell having an oriented cathode with the cathodic material facing a layer of carbon-coated carbon cloth, according to an embodiment of the invention, as evaluated in Example 4.

[26] Figure 6 is a graph which compares the cycling performance (discharge capacity and coulombic efficiency) at (a) 0.5 C cycling rate and (b) 0.2 C cycling rate, for a lithium-sulfur energy storage cell having a conventionally oriented cathode and a carbon-coated separator, as evaluated in Example 3; and a lithium sulfur energy storage cell having an oriented cathode with the cathodic material facing a layer of carbon-coated carbon cloth, according to an embodiment of the invention, as evaluated in Example 4.

[27] Figure 7 is a schematic diagram of a sulfur cathode-free cell having a layer of carbon-coated carbon cloth between the separator and the cathodic-end casing cover of the cell casing, as evaluated in Example 5.

[28] Figure 8 is a graph which depicts the cycling performance (discharge capacity and coulombic efficiency) for a sulfur cathode-free cell having a layer of carbon-coated carbon cloth between the separator and the cathodic-end casing cover of the cell casing, as evaluated in Example 5.

[29] Figure 9 is a graph which depicts charge-discharge cyclic voltammetry profiles for a sulfur cathode-free cell having a layer of carbon-coated carbon cloth between the separator and the cathodic-end casing cover of the cell casing, as evaluated in Example 5.

Detailed Description

[30] The present invention relates to a rechargeable lithium-sulfur energy storage cell. The cell comprises a lithium anode, a cathode comprising sulfur-containing cathodic material disposed on one side of a sheet of impermeable material, wherein the cathode is oriented with the sheet positioned between the cathodic material and the anode; and an electrolyte. The cell may optionally contain a sulfide-retentive composition in the vicinity of the cathode, the sulfide-retentive composition preferably comprising porous, high surface area carbon.

Cell configuration

[31] As with conventional lithium-sulfur energy storage cells, the energy storage cell according to the invention comprises a lithium anode in an anodic portion of the cell, a sulfur-based cathode in a cathodic area of the cell and an electrolyte permitting lithium ion transport between the anodic portion and the cathodic portion. As used herein, the anodic portion of the cell is a portion of the cell comprising the anode and a portion of the electrolyte in contact with the anode (i.e. typically corresponding to the anodic half-cell). As used herein, the cathodic portion of the cell is a portion of the cell comprising the cathode and a portion of the electrolyte, the electrolyte being in contact with the cathode (i.e. typically corresponding to the cathodic half-cell).

[32] In some embodiments, the cell comprises a lithium ion-permeable separator which defines a boundary between the anodic portion and the cathodic portion. In some embodiments, the cell comprises a casing which encloses the anodic portion and the cathodic portion. The casing generally includes an electrically
5 conductive anodic-end cover in electrical communication with the anode, and an electrically conductive cathodic-end cover in electrical communication with the cathode, thus permitting the cell to be charged and discharged via an external circuit.

Lithium anode

[33] The rechargeable energy storage cell comprises a lithium anode in the
10 anodic portion of the cell. Any lithium anode suitable for use in lithium-sulfur cells may be used. In some embodiments, the anode is a metallic lithium anode. In other embodiments, a lithium alloy or lithium composite anode is used. The anode may be protected against redox shuttling reactions and hazardous runaway reactions by any of the methodologies reported in the art, for example by creating a protective layer on
15 the surface of the anode by chemical passivation or polymerisation.

Oriented cathode

[34] The rechargeable energy storage cell comprises an oriented cathode in the cathodic portion of the cell. The oriented cathode comprises a sheet of impermeable material and a sulfur-containing cathodic material disposed on one side of the sheet.
20 The cathode is oriented in the cell such that the sheet is positioned between the cathodic material and the anode, and thus forms a physical barrier capable of inhibiting diffusion of electrolyte-soluble sulfides from the cathodic portion of the cell to the anodic portion during discharge and/or recharge of the cell.

[35] Conventional lithium-sulfur energy storage cells may also include a
25 cathode comprising a sheet of impermeable material – generally the current collector – and a sulfur-containing cathodic material disposed on one side of the sheet. However, in these cells, the cathode is oriented with the cathodic material facing towards the anode, with the sheet thus positioned on the opposite side of the cathodic material from the anode. As such, the sheet is not able to form a barrier to polysulfide
30 diffusion from the cathodic portion of the cell to the anodic portion. In comparison

with the conventional cathode configuration, the oriented cathode of the present invention may be considered an “inverted cathode”.

Sheet of impermeable material

[36] The impermeable material of the sheet is substantially, and preferably
5 completely, impermeable to the electrolyte, and in particular to polysulphide ions dissolved therein. In some embodiments, the sheet as a whole is impermeable to the electrolyte, such that passage of electrolyte-soluble sulfides through the sheet is blocked. In other embodiments, a degree of ionic conductivity across the sheet is provided, for example via apertures in the sheet. Even in these embodiments,
10 however, the sheet as a whole inhibits or restricts the passage of electrolyte-soluble sulfides across the sheet as a result of the impermeable material. Since the cathode is oriented with the sheet positioned between the sulfur-containing cathodic material and the anode, the sheet forms a physical barrier that inhibits diffusion of electrolyte-soluble sulfides from the cathodic portion to the anodic portion during discharge
15 and/or recharge of the cell.

[37] Despite being positioned between the cathodic material and the anode, the sheet of impermeable material is configured to allow lithium ion transport between the anode and cathode during charging and discharging of the cell. Therefore, the sheet does not completely isolate the anode and the cathode from each other. One or more
20 electrolyte-permeable channels bypassing, or penetrating through apertures in, the impermeable face of the sheet must be provided to allow sufficient lithium ion flux between the anodic and cathodic portions of the cell. In some embodiments where the sheet is itself completely impermeable, such a channel may be provided through the annulus between the periphery of the sheet and the walls of the cell casing.

25 [38] Without wishing to be bound by theory, it is believed that the sheet of impermeable material inhibits diffusion of electrolyte-soluble polysulfides from the cathodic portion to the anodic portion by increasing the average diffusion distance required for migration from the cathodic material to the anode, where undesirable reactions (both reversible and irreversible) can take place. The longer pathway
30 increases the average retention time of soluble polysulfide intermediates in the cathodic portion of the cell during discharging and charging, allowing them to be

converted to the insoluble final discharge or charge products before escaping to the anodic portion of the cell.

[39] It will be appreciated by a person skilled in the art that the optimal dimensions of the sheet of impermeable material must balance competing imperatives: maximum impedance to polysulfide migration while nevertheless allowing sufficient lithium ion flux. A cell with an impermeable barrier extending across a high proportion of the interface between the anodic and cathodic portions of the cell may exhibit excellent capacity retention, due to enhanced confinement of polysulfides in the anodic portion. However, such a cell may have unacceptably high internal resistance due to reduced lithium ion flux. In general, therefore, the sheet should form a physical barrier across the highest proportion of the interface between the anodic and cathodic portions whereby lithium ion flux remains acceptable for charge-discharge cycling performance.

[40] Aside from this consideration, the specific shape and orientation of the sheet is not particularly limited, and will depend in part on the cell configuration. For example, the sheet may be substantially circular in a coin-type cell, and substantially rectangular in a pouch-type cell. As described herein, the surface of the sheet may be devoid of apertures, so that lithium ion flux occurs exclusively around the edges of the impermeable sheet. However, cathode geometries in accordance with the invention are also contemplated in which some or all of the required lithium ion flux is provided through apertures in the sheet. In some embodiments the sheet is substantially flat. However, it is not excluded that curved or other non-planar configurations may be used. In some preferred embodiments, the sheet is oriented in a plane that is substantially normal to a longitudinal axis of the cell, for example the axis intersecting the midpoints of the cathode and anode.

[41] The sheet may be of any suitable thickness. In order to maximise energy density of the cell, it is generally preferred that the sheet is as thin and light as possible. However, the sheet should be thick enough to provide sufficient mechanical robustness and to ensure that the material of the sheet is suitably impermeable. In some embodiments, the sheet has a thickness of from 1 micron to 200 microns,

preferably from 10 microns to 100 microns, more preferably from 10 microns to 30 microns.

[42] In some embodiments, a surface area of the sheet is smaller than an external surface area of a separator which defines a boundary interface between the anodic portion and the cathodic portion of the cell. As used herein, the surface area of the sheet is the impermeable area on one face of the sheet. The sheet is preferably in contact with and in parallel alignment with the separator. Accordingly, lithium ion flux between the anodic and cathodic portions of the cell is permitted only through regions of the separator which are not obstructed by the sheet. In some such embodiments, the surface area of the sheet is from 20% to 80%, preferably from 30% to 70% of the surface area of the separator. Such embodiments may achieve a desirable inhibition of polysulfide migration from the cathodic portion of the cell, while nevertheless permitting adequate lithium ion flux.

[43] In one embodiment, the sheet and the separator are coaxial discs, wherein a diameter of the sheet is smaller than a diameter of the separator. Sufficient lithium ion flux between the anodic and cathodic portions of the cell may thus be provided through the annulus between the periphery of the sheet and the casing. In another embodiment, the sheet and the separator are coaxial discs of the same diameter, with one or more apertures provided in the sheet to provide adequate lithium ion flux. Such configurations may be particularly suitable for coin-type cells.

[44] In some embodiments, the sheet of impermeable material is a current collector for the cathode, and the impermeable material is therefore electrically conductive and in electrical communication with the cathodic material disposed on one of its sides. In such embodiments, the sheet may be configured to be connected to an external circuit, for example, via an electrical connection provided between the conductive sheet and the cathode-end casing cover of the cell casing. In other embodiments, the impermeable material is non-conductive and/or the sheet is not configured to be electrically connected to an external circuit. In such embodiments, another means of collecting current and ensuring electrical connectivity between the cathodic material and an external circuit is generally provided. For example, the

cathodic material may be in contact with the conductive cathodic-end casing cover of the cell, which therefore acts as a current collector.

[45] The sheet of impermeable material may be an electrically conductive metallic foil, such as aluminium foil. In some embodiments, the sheet is a carbon coated aluminium foil. Carbon coating of the aluminium foil reduces the risk of hazardous runaway reactions between sulfur and aluminium at high temperatures, and may also improve adhesion of the cathodic material to the sheet. In other embodiments, the sheet of impermeable material may be a non-conductive film, for example a polymeric film.

10 Cathodic material

[46] Any suitable cathodic material comprising sulfur may be used, including those previously reported to be advantageous in lithium-sulfur cells. In some embodiments, the cathodic material is a composite material of sulfur dispersed in a conductive, porous matrix. The matrix should preferably provide conductive sites for faradaic reduction and oxidation reactions during discharge and charging, facilitate electrolyte penetration (and thus lithium ion conductivity) into the cathodic material, retain soluble polysulfide reduction intermediates within the structure of the cathodic material, and accommodate volume expansion of sulfur during reduction. Suitable porous matrices for sulfur-based cathodic materials include porous carbon, such as amorphous carbon, microporous carbon, mesoporous carbon, macroporous carbon, carbon nanotubes or nanofibers, carbon spheres, expanded graphite, graphene and reduced graphene oxide. In some embodiments, matrix materials comprising polar functionalities are used, for example graphene oxide, nitrogen-doped carbons, porous organic frameworks, metal oxides and conductive polymers.

[47] In a preferred embodiment, the cathodic material comprises sulfur impregnated mesoporous carbon. The cathodic material may be prepared using melt diffusion to incorporate sulfur into the porous network of the carbon matrix, as reported in *Nature Materials* 2009, 8, 500-506. Melt diffusion is preferably conducted at temperatures where molten sulfur has its lowest viscosity, such as between 140 and 170°C, preferably between 150 and 160°C. Alternatively, solution impregnation

or other suitable techniques may be used to impregnate the sulfur into the porous carbon matrix.

[48] Various performance-enhancing additives may be included in a composite cathodic material, including conductivity agents and binders to maintain structural integrity of the cathode as the sulfur phase dissolves into the electrolyte during discharge. In an embodiment, carbon black is included as a conductivity agent. In an embodiment, a binder such as polyvinylidene fluoride (PVDF), polyethylene oxide (PEO), polyacrylamide-co-diallyldimethylammonium chloride (AMAC), gelatin, sodium carboxymethyl cellulose, polyacrylic acid or Nafion is included. In a preferred embodiment, the binder comprises PVDF.

[49] As will be appreciated by a person skilled in the art, the energy density of the cell is increased as the sulfur mass fraction of the cathodic material increases. Electrochemically inactive components such as the porous matrix, conductivity agents and binders – while necessary in some embodiments for their functional properties – reduce the energy density, and should thus be minimised. In some embodiments, the cathodic material may comprise more than 20% sulfur, preferably more than 30% sulfur, most preferably more than 50% sulfur, still more preferably more than 65% sulfur, and most preferably more than 75% sulfur, such as approximately 80% sulfur.

[50] The cathodic material is disposed on one side of the sheet of impermeable material. In some embodiments, the cathodic material is coated onto the sheet, for example as a slurry in a liquid such as N-methyl-2-pyrrolidinone (NMP). The liquid may then be removed with heat and/or reduced pressure to leave a solid coating on the sheet.

[51] Any suitable mass loading of cathodic material on the sheet may be used, and may depend on the size and intended purpose of the cell. In some embodiments, the loading of cathodic material per unit area of the sheet is from 0.1 to 15 mg.cm⁻², preferably from 1 to 10 mg.cm⁻².

[52] In some embodiments, the cathodic material is a coating which substantially covers the entire surface of the one side of the sheet. However, it is

within the scope of the invention that the cathodic material covers only a fraction of the surface of one side of the sheet. In some preferred embodiments, the cathodic material disposed on one side of the sheet does not protrude beyond the peripheral edges of the sheet. However, it is not excluded that a fraction of the cathodic material
5 may extend laterally beyond the edges of the sheet, either in the cathode as fabricated or as a result of structural changes during discharge-charge cycling of the cell.

Electrolyte

[53] The rechargeable energy storage cell comprises an electrolyte that permits
10 lithium ion transport between the anodic portion and the cathodic portion of the cell. Any electrolyte suitable for use in lithium-sulfur cells may be used.

[54] In some embodiments, the electrolyte contains an organic solvent, which may optionally comprise a mixture of organic compounds. The organic solvent should be a good solvent for lithium salts, preferably including the polysulfide reduction
15 intermediates, and should preferably have low viscosity. Furthermore, the solvent is preferably resistant to chemical reactions with lithium metal and with polysulfide anions and radicals. In some embodiments, the solvent may comprise one or more ethers. In some embodiments, the solvent comprises at least one selected from dimethoxyethane (DME) and 1,3-dioxolane (DOL). In a preferred embodiment, the
20 solvent comprises a mixture of DME and DOL, such as a 50:50 (v/v) mixture.

[55] In other embodiments, the electrolyte comprises an ionic liquid. In some such embodiments, the electrolyte comprises an ionic liquid instead of an organic solvent. Room temperature ionic liquids advantageously have low flammability and volatility, and may furthermore provide performance advantages in energy storage
25 cells.

[56] In some embodiments, the electrolyte contains a soluble lithium salt to provide ionic conductivity between the anode and the cathode. The anion of the lithium salt is preferably resistant to chemical reactions with polysulfide anions and with common electrolyte solvents. In some embodiments, the lithium salt comprises
30 at least one selected from lithium bis(trifluoromethane)sulfonimide (LiTFSI) and

lithium trifluoromethanesulfonate, and preferably comprises LiTFSI. The lithium salt may be present in the electrolyte at concentrations between 0.1 and 5.0 M, preferably between 0.5 and 1.5 M, for example approximately 1.0 M.

[57] In some embodiments, the electrolyte comprises one or more additives, including additives previously disclosed to impart favourable properties in lithium-sulfur cells. In some embodiments, the electrolyte may comprise lithium nitrate (LiNO_3), which is reported to suppress redox shuttling reactions of polysulfides at the anode, thereby increasing the coulombic efficiency of the cell. In some embodiments, LiNO_3 may be present in the electrolyte in a concentration of between 0.05 and 0.5 M, for example 0.1 M. Other suitable additives may include one or more of P_2S_5 , LiBr, ionic liquids and viscosity modifying co-solvents.

Separator

[58] In some embodiments, the rechargeable energy storage cell comprises a lithium ion-permeable separator. The separator defines a boundary between the anodic portion and the cathodic portion of the cell. The role of the separator is to maintain physical separation of the cathode and the anode, thus preventing electrical short circuits in the cell. Any separators generally suitable for lithium-sulfur cells may be employed. In some embodiments, the separator is a porous membrane produced from nonwoven fibres (such as glass fibers), polymer films or other permeable materials. In some embodiments, the separator is a glass fiber separator. Although the separator is generally formed separately from the sheet, it is not excluded that the sheet of impermeable material may be integrally formed as part of the separator.

[59] In some embodiments, the separator is a functional separator designed to permit a suitably high flux of lithium ions while selectively inhibiting the passage of anionic polysulfides. For example, a lithiated Nafion ionomer separator may be employed, as reported in *Journal of Power Sources* 2012, 218, 163-167. In one embodiment, the separator is coated or impregnated with a permeable sulfide-retentive composition, such as porous carbon, which physically retains polysulfides while nevertheless permitting lithium ion transport through the separator. A suitable porous carbon for coating onto a separator, such as a glass fiber separator, is a microporous, graphitic carbon such as Black Pearl 2000, available from Cabot Co. It

is envisaged that such permeable functional separators may further inhibit polysulfide diffusion from the cathodic portion of the cell to the anodic portion, additionally to the effect provided by the oriented cathode of the present invention.

Rechargeable cell having faradaic energy storage capacity

5 [60] An embodiment of the invention is now described with specific reference to Figure 1. Rechargeable energy storage cell 10 comprises lithium anode 11 in anodic portion 12, oriented cathode 13 in cathodic portion 14, lithium-ion permeable separator 15 which defines a boundary between anodic portion 12 and cathodic portion 14, and casing 16 which encloses anodic portion 12 and cathodic portion 14. 10 Casing 16 comprises anodic-end casing cover 17, cathodic-end casing cover 18 and cylindrical casing wall 19. Cell 10 is depicted with co-axial disc-shaped components 17, 11, 15, 13 and 18 axially exploded for greater clarity; however it will be appreciated that these components are stacked in direct abutment in the embodiment described. Electrolyte 20 is contained within casing 16 in both anodic portion 12 and 15 cathodic portion 14, and provides lithium ion conductivity across separator 15 between anode 11 and cathode 13.

[61] Oriented cathode 13 comprises impermeable sheet 21 and cathodic material 22, with cathodic material 22 disposed on one side of impermeable sheet 21. Cathodic material 22 is a coating which covers the entire surface of one side of 20 impermeable sheet 21, but does not protrude beyond the periphery thereof. Cathode 13 is oriented in cell 10 such that impermeable sheet 21 is positioned between cathodic material 22 and anode 11, lying in a plane that is substantially normal to a longitudinal axis of cell 10 which intersects the midpoints of cathode 11 and anode 13. Impermeable sheet 21 has a smaller external surface area than separator 15 due 25 to its shorter diameter. Channel 23, depicted as a dashed arrow in Figure 1, is thus provided in the form of an annulus between the periphery of impermeable sheet 21 and casing wall 19. Channel 23 is permeable to electrolyte 20, and thus provides lithium ion conductivity between anode 11 and cathodic material 22 during charging and discharging of cell 10.

30 [62] Cathodic material 22 is in direct contact with conductive cathodic-end casing cover 18, which acts as a current collector for cathode 13. Additionally or

alternatively, impermeable sheet 21 may be conductive and electrically connected with cathodic-end casing cover 18 (connection not shown), such that impermeable sheet 21 acts as a current collector for cathode 13. Lithium anode 11 directly contacts and is thus electrically connected to anodic-end casing cover 17. Therefore, cell 10 may be discharged and charged via an external circuit (not shown) that is connected to anodic-end casing cover 17 and cathodic-end casing cover 18.

[63] During a complete discharge of charged cell 10, electrons released by lithium oxidation at anode 11 flow via the external circuit to cathode 13, reducing elemental sulphur in cathodic material 22 to a final insoluble discharge product (comprising Li_2S) via a series of electrolyte-soluble lithium polysulfide reduction intermediates. To balance the charge, lithium ions present in electrolyte 20 migrate from anodic portion 20 through separator 15 and along channel 23 into cathodic portion 14. As the lithium ions in electrolyte 20 migrate, they are replenished in anodic portion 12 via oxidation of lithium cathode 11, and incorporated into cathodic material 22 in the form of the lithium sulfide discharge products (both soluble and insoluble).

[64] Before reduction to the insoluble final discharge products, a fraction of the soluble polysulfide reduction intermediates diffuse through electrolyte 20, passing out of cathodic material 22. However, the soluble polysulfides are inhibited by impermeable sheet 21 from diffusing to anodic portion 12. Impermeable sheet 21 forms a physical barrier that requires polysulfides to migrate from cathodic portion 14 along channel 23 to enter anodic portion 12, thereby extending the average path distance for polysulfide migration.

Sulfide-retentive composition

[65] In some embodiments, the rechargeable energy storage cell comprises a sulfide-retentive composition in the cathodic portion. The sulfide-retentive composition may be provided as interlayer between the separator and the cathode, for example as reported in *Nature Communications* 2012, 3, 1166 or *ACS Nano* 2016, 10, 7768. However, in preferred embodiments, the sulfide-retentive composition forms a layer adjacent to the cathodic material, such that the cathodic material is sandwiched between the sheet of impermeable material and the sulfide-retentive

composition. The sulfide-retentive composition in such embodiments is typically disposed against the cathodic-end casing cover of the cell casing. In this configuration, the sulfide-retentive composition may further impede polysulfide migration from the cathodic portion of the cell to the anodic portion, since the polysulfides may be physically retained while diffusing through the layer of sulfide-retentive composition along the extended migration pathway established by the oriented cathode of the invention.

[66] In some embodiments, the sulfide-retentive layer is a non-conductive material, preferably a material with polar functional groups that improve polysulfide retention. An example of such a material is graphene oxide. However, in preferred embodiments, the sulfide-retentive composition is electrically conductive. The conductive sulfide-retentive composition is preferably configured to be electrically connected to the external circuit during discharging and charging of the cell. In some embodiments, the sulfide-retentive composition is thus a current collector for the cathode. The sulfide-retentive composition may be the primary current collector for the cathode, but alternatively it may form a second current collector, for example when the sheet is configured as a current collector. Generally, electrical connectivity to the external circuit is provided via the contact between the conductive sulfide-retentive composition and the cathodic-end casing cover of the cell casing. Advantageously, the conductivity of the sulfide-retentive composition and its electrical connectivity to the external circuit may enable retained polysulfides to remain electrochemically active without necessarily being reincorporated into the cathodic material of the cathode. This provides improved sulfur capacity utilisation in the cell.

[67] In some preferred embodiments, the sulfide-retentive composition is porous to the electrolyte. The high porosity may improve the retention and subsequent electrochemical reduction of electrolyte-soluble polysulfides within the sulfide-retentive composition. Furthermore, in embodiments where the sulfide-retentive composition forms a layer adjacent to the cathodic material, the porosity may improve lithium ion conductivity between the cathode and the anode due to the intimate contact between the electrolyte-saturated porous composition and the cathodic material. In especially preferred embodiments, the sulfide-retentive composition is both conductive and porous to the electrolyte.

[68] Suitable sulfide-retentive compositions may be, or comprise, high surface area carbon. In some embodiments, the high surface area carbon is selected from the group consisting of activated carbon, expanded graphite, graphene, carbon nanotubes, chemically reduced graphene oxide, electrochemically reduced graphene oxide, and e-beam reduced graphene oxide. In some embodiments, the sulfide-retentive composition comprises a microporous, graphitic carbon, such as Black Pearl 2000.

[69] In some embodiments, the sulfide-retentive composition comprises a high surface area carbon which is supported on, or is provided in the form of, a woven or non-woven carbon cloth. A suitable carbon cloth is AvCarb carbon fiber cloth, available from AvCarb Material Solutions, USA. In a preferred embodiment, the sulfide-retentive composition is a carbon-coated carbon cloth, which may be formed by coating a carbon cloth with a slurry of high surface area carbon and optionally a binder in a liquid such as N-methyl-2-pyrrolidinone (NMP). The liquid may then be removed with heat and/or reduced pressure to leave a solid carbon coating impregnated on the carbon cloth. The carbon-coated carbon cloth thus prepared is both porous and conductive. It has been found that the use of such a sulfide-retentive composition in combination with the oriented cathode of the invention provides a cell displaying excellent sulfur capacity utilisation, coulombic efficiencies and capacity retention, even at low discharge-charge cycling rates.

[70] In some embodiments, the sulfide-retentive composition in the cathodic portion of the cell is adapted for capacitive energy storage by ionic charge separation of the electrolyte. Thus, in addition to the improved cell performance due to polysulfide retention as discussed herein, the sulfide-retentive composition may itself contribute to the energy storage capacity of the cell. High surface area carbon is suitably conductive and porous to electrolytes to allow such energy storage when electrically connected to the external circuit. In such embodiments, the sulfide-retentive composition operates as a lithium ion capacitor. Lithium ion capacitors are hybrid energy storage devices, combining the intercalation mechanism of a lithium ion battery cathode and the electrostatic charge storage of an electric double-layer capacitor (EDLC).

[71] In some embodiments, a mass of the sulfide-retentive composition, such as a high surface area carbon, is sufficient relative to a mass of the sulfur such that the capacitive energy discharge capacity of the cell is at least 5%, or at least 10%, or at least 20%, or at least 30 % of the faradaic energy discharge capacity during a complete discharge of the cell.

[72] The capacitive energy storage provided by the sulfur-retentive composition will increase the overall energy storage capacity of the cell. More significantly, the power density of the cell is improved over at least a part of the cell discharge cycle, since energy stored in a capacitor may be rapidly discharged. The combination in one cell of both a capacitive energy storage capability (low energy density but high power density) and a faradaic energy storage capability (high energy density but low power density) may be useful for applications with high peak power demand. One application where a hybrid cell with both capacitive and faradaic energy storage capability may be advantageous is in electric vehicles, where separate supercapacitors have previously been used in combination with conventional batteries to improve energy recovery in regenerative braking, to improve peak power delivery, and to protect the battery from the stresses imposed by high charge / discharge rates.

Hybrid device

[73] In some preferred embodiments, therefore, the rechargeable energy storage cell is capable of both capacitive energy discharge and faradaic energy discharge. Such hybrid energy storage cells generally comprise: a lithium anode in an anodic portion of the cell, as described herein; an oriented cathode in a cathodic portion of the cell, as described herein, an electrically conductive and porous sulfide-retentive composition in the cathodic portion, as described herein; and an electrolyte permitting lithium ion transport between the anodic portion and the cathodic portion of the cell, as described herein. In such embodiments, the sulfide-retentive composition is generally configured in the cell to be electrically connected to an external circuit during discharging and charging of the cell, for example via contact with the cell casing.

[74] Preferably, the conductive sulfide-retentive composition comprises porous, high surface area carbon and is thus adapted for capacitive energy storage by ionic

charge separation as a lithium ion capacitor. Preferably, the conductive sulfide-retentive composition forms a layer adjacent to the cathodic material, such that the cathodic material is sandwiched between the sheet of impermeable material and the sulfide-retentive composition.

- 5 [75] In the preferred embodiment of the hybrid energy storage cell, the porous and conductive sulfide-retentive composition may perform one or more of, and preferably each of, the following advantageous roles: (a) physical retention of soluble polysulfides in the cathodic portion of the cell, thereby further improving capacity retention and coulombic efficiency; (b) providing conductive sites for reduction of the
10 retained polysulfide reduction intermediates, thereby ensuring that the polysulfides remain electrochemically available; (c) acting as a current collector for the cathode; (d) facilitating an intimate contact between the electrolyte and the cathodic material, thereby providing improved or adequate lithium ion conductivity between the cathode and the anode; (e) contributing to the total energy storage capacity of the cell; and (f)
15 providing capacitive energy storage capability to complement the faradaic energy storage capability provided by the sulfur-based cathode.

- [76] An embodiment of the invention is now described with specific reference to Figure 2. Rechargeable energy storage cell 10a, which is capable of both capacitive energy discharge and faradaic energy discharge, comprises lithium anode 11a in
20 anodic portion 12a, oriented cathode 13a in cathodic portion 14a, electrically conductive and porous sulfide-retentive composition 24a in cathodic portion 14a, lithium-ion permeable separator 15a which defines a boundary between anodic portion 12a and cathodic portion 14a, and casing 16a which encloses anodic portion 12a and cathodic portion 14a. Casing 16a comprises anodic-end casing cover 17a,
25 cathodic-end casing cover 18a and cylindrical casing wall 19a. Cell 10a is depicted with co-axial disc-shaped components 17a, 11a, 15a, 13a, 24a and 18a axially exploded for greater clarity; however it will be appreciated that these components are stacked in direct abutment in the embodiment described. Electrolyte 20a is contained within casing 16a in both anodic portion 12a and cathodic portion 14a, and provides
30 lithium ion conductivity across separator 15a between anode 11a and cathode 13a.

[77] Oriented cathode 13a comprises impermeable sheet 21a and cathodic material 22a, with cathodic material 22a disposed on one side of impermeable sheet 21a. Cathodic material 22a is a coating which covers the entire surface of one side of impermeable sheet 21a, but does not protrude beyond the periphery thereof.

5 Cathode 13a is oriented in cell 10a such that impermeable sheet 21a is positioned between cathodic material 22a and anode 11a, lying in a plane that is substantially normal to a longitudinal axis of cell 10a which intersects the midpoints of cathode 11a and anode 13a. Impermeable sheet 21a has a smaller external surface area than separator 15a due to its shorter diameter. Channel 23a, depicted as a dashed arrow
10 in Figure 2, is thus provided in the form of an annulus between the periphery of impermeable sheet 21a and casing wall 19a. Channel 23a is permeable to electrolyte 20a, and thus provides lithium ion conductivity between anode 11a and cathodic material 22a during charging and discharging of cell 10a.

[78] Sulfide-retentive composition 24a comprises high surface area carbon 25a
15 coated on carbon cloth 26a, and is porous to electrolyte 20a. Cathodic material 22a is in direct contact with conductive sulfide-retentive composition 24a, which is itself electrically connected to cathodic-end casing cover 18a and thus acts as a current collector for cathode 13a. Lithium anode 11a directly contacts and is thus electrically connected to anodic-end casing cover 17a. Therefore, cell 10a may be discharged
20 and charged via an external circuit (not shown) that is connected to anodic-end casing cover 17a and cathodic-end casing cover 18a.

[79] During a complete discharge of charged cell 10a, electrons released by lithium oxidation at anode 11a flow via the external circuit to cathode 13a, reducing elemental sulphur in cathodic material 22a to a final insoluble discharge product
25 (comprising Li_2S) via a series of electrolyte-soluble lithium polysulfide reduction intermediates. To balance the charge, lithium ions present in electrolyte 20a migrate from anodic portion 20a through separator 15a and along channel 23a into cathodic portion 14a. Lithium ion conductivity from electrolyte 20a to cathodic material 22a is facilitated by the porosity of sulfide-retentive composition 24a, which is saturated with
30 electrolyte 20a. As the lithium ions in electrolyte 20a migrate, they are replenished in anodic portion 12a via oxidation of lithium cathode 11, and incorporated into cathodic

material 22a in the form of the lithium sulfide discharge products (both soluble and insoluble).

[80] Before reduction to the insoluble final discharge products, a fraction of the soluble polysulfide reduction intermediates diffuse through electrolyte 20a, passing out of cathodic material 22a. However, the soluble polysulfides are inhibited by impermeable sheet 21a from diffusing to anodic portion 12a. Impermeable sheet 21a forms a physical barrier that requires polysulfides to migrate from cathodic portion 14a along channel 23a to enter anodic portion 12a, thereby extending the average path distance for polysulfide migration. Furthermore, a high proportion of polysulfides migrating out of cathodic material 22a diffuse into porous sulfide-retentive composition 24a, where they are physically retained on the internal surfaces of high surface area carbon 25a. This further impedes polysulfide migration via channel 23a to anodic portion 12a.

[81] Conductive sulfide-retentive composition 24a is electrically connected to the external circuit and acts as the current collector for cathode 13a. Therefore, polysulfides retained on high surface area carbon 25a remain electrochemically active, and are further reduced to final discharge products during discharge and re-oxidised to elemental sulfur during subsequent recharging of cell 10a.

[82] Furthermore, high surface area carbon 25a, being porous to electrolyte 20a and electrically connected to the external circuit, is adapted for capacitive energy storage by ionic charge separation of electrolyte 20a. Therefore, sulfide-retentive composition 24a, acting as a lithium ion capacitor, contributes to the total energy storage capacity of cell 10a. Cell 10a, when fully charged, is thus capable of both capacitive energy discharge and faradaic energy discharge.

25 Cell performance

[83] The performance of the rechargeable energy storage cells according to the invention may be assessed by standard electrochemical techniques such as cyclic voltammetry. In some embodiments, the rechargeable energy storage cell may provide improved performance (on one or more metrics such as capacity utilisation, capacity retention and coulombic efficiency) relative to previously reported cells when

evaluated in cyclic voltammetry discharge-charge cycling experiments. Cell cycling rates of from 0.1 C to 3.0 C may be used to simulate cell performance across a wide range of usage conditions.

[84] In some embodiments, the rechargeable energy storage cell according to the invention may provide improved performance relative to previously reported cells at relatively low cycling rates, such as below 0.5 C. Without wishing to be bound by theory, it is believed that deleterious polysulfide migration from the cathodic portion of the cell may be particularly prevalent during discharge at low cycling rates due to the increased time available for diffusion before the soluble polysulfide reduction intermediates are further reduced to insoluble species. Furthermore, cell performance is less likely to be constrained by barriers to lithium ion conductivity at low cycling rates. For both of these reasons, a rechargeable energy storage cell according to the invention may be of particular utility for applications requiring low discharge rates.

Batteries and electrically powered devices

[85] The rechargeable energy storage cells according to any of the embodiments disclosed herein may be provided in a battery. The battery may comprise one or more of the cells, optionally in combination with further energy storage cells not in accordance with the invention. In some embodiments, the battery comprises multiple cells according to any of the embodiments disclosed herein, which may be connected in series and/or in parallel. The battery thus provided may be used to power any electrically powered device, including devices conventionally powered by lithium-sulfur or lithium-ion batteries. Non-limiting examples of such devices include electric vehicles, consumer electronics, power tools and storage batteries for intermittent renewable energy, such as from solar and wind.

EXAMPLES

[86] The present invention is described with reference to the following examples. It is to be understood that the examples are illustrative of and not limiting to the invention described herein.

Materials

[87] N-methyl-2-pyrrolidinone (NMP), Bis(trifluoromethane)sulfonimide lithium salt (LiTFSI), Lithium nitrate (LiNO_3), Polyvinylidene fluoride (PVDF), 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) were purchased from Sigma-Aldrich and directly used without any further purification, except that LiNO_3 and LiTFSI were
5 evacuated overnight prior to use.

[88] Microporous carbon (Black Pearls 2000) was purchased from CABOT Co. Activated nanopowder carbon (NPC) is purchased from US Research Nanomaterials, Inc. Battery grade etched Al foil (30 μm thickness) was purchased from Japan Capacitor Industrial Co. Conductive carbon coated aluminum foil for battery cathode
10 substrate (18 μm thickness) was purchased from MTI corporation. Glass fiber BG03013 separator sheets (0.203 mm, max pore size= 15.5 μm) was purchased from Hollingsworth & Vose (H&V), USA. Circular discs with a diameter of 19 mm were cut out with a disc cutter for use in a cell. Carbon cloth (356 micron thickness at 1 psi) was purchased from AvCarb Material Solutions, USA. Lithium chip anodes (15.6 mm
15 diameter; 0.25 mm thickness) were purchased from MTI Corporation. Standard coin cell packages (CR2302) were purchased from Hohsen Corp (Japan).

Carbon coated separator

[89] A slurry of microporous carbon (90 wt. %) and PVDF (10 wt. %) in NMP was blade coated onto one side of a glass fiber separator sheet. The coated
20 separator was dried overnight at 100 $^{\circ}\text{C}$ under vacuum to remove all traces of the solvent. The loading was approximately 2 mg cm^{-2} , as determined using a microbalance with a weighing precision of 0.1 μg . Circular discs with a diameter of 19 mm were then cut out with a disc cutter for use in a cell.

Carbon-coated carbon cloth

[90] A slurry of microporous carbon (90 wt. %) and PVDF (10 wt. %) in NMP was blade coated onto the carbon cloth. The coated cloth was dried overnight at 100
25 $^{\circ}\text{C}$ under vacuum to remove all traces of the solvent. The loading was approximately 2 mg cm^{-2} , as determined using a microbalance with a weighing precision of 0.1 μg . Circular discs with a diameter of 19 mm were then cut out with a disc cutter for use in
30 a cell.

Electrolyte

[91] The electrolyte was prepared as a 1.0 M Lithium LiTFSI/0.1 M LiNO₃ solution in a mixed solvent of DOL and DME (1:1, v/v).

Preparation of cathodes

[92] Nano powder carbon-sulfur composite (NPC-S powder) was prepared (following the procedure disclosed in *Nature Materials* 2009, 8, 500-506) by mixing nanopowder carbon and sulfur in a ratio of 50:50 wt % and heating at 155 °C for 10 h under N₂. A homogeneous slurry was then prepared by mixing 70 wt % NPC-S powder, 20 wt % Super P carbon black (printex-55), and 10 wt % PVDF in NMP. The slurry of composite cathodic material was then coated on Al foil (18 µm thickness for Examples 1, 2 and 4; 30 µm thickness for Example 3) and dried at room temperature for 48 h, followed by overnight drying at 40 °C under vacuum to remove all traces of the solvent. The sulfur mass loading in the composite cathodes thus formed was in the range of 1-1.2 mg cm⁻² (total cathodic material mass loading of 2.8-3.4 mg cm⁻²). Circular discs with a diameter of 11 mm were then cut out with a disc cutter for use in a cell.

Cell assembly

[93] Battery cells were assembled in a coin cell package in an argon-filled glove box with zero ppm oxygen and moisture. The cathode active material was wet with 20 µl of the electrolyte, while the separator was wet with 60 µl of the electrolyte.

Battery experiments

[94] Cyclic voltammetry (CV) experiments were performed with a BioLogic Potentiostat. All cycling experiments were carried out at ambient conditions. CV plots are generated by the EC-Lab software and are plotted as current vs. potential. All the electrochemical experiments were repeated at least three times to examine the reproducibility of the electrochemical data.

Example 1 (comparative)

[95] A conventional Li-S cell was assembled as schematically represented in Figure 3(a), using an unmodified glass fiber separator and with the cathode oriented such that the active cathodic material is disposed between the separator and the impermeable Al foil current collector.

[96] The cycling performance of the conventional cell was monitored at a cycling rate of 0.5 C (in the voltage range of 1.7 – 2.8 V relative to Li^+), and is presented in Figure 4. It is evident that the cell displays low initial sulfur utilisation (discharge capacity) and experiences a dramatic decrease in the current response, losing half its initial capacity after 25 cycles as a result of sulfur loss from the cathode.

Example 2

[97] A “inverted cathode” cell was assembled as schematically represented in Figure 1 and Figure 3(b), using an unmodified glass fiber separator and with the cathode oriented such that the impermeable Al foil current collector is adjacent to the separator, and thus positioned between the separator and the active cathodic material.

[98] The cycling performance of the “inverted cathode” cell was monitored at a cycling rate of 0.5 C (in the voltage range of 1.7 – 2.8 V relative to Li^+), and is presented in Figure 4. It is evident that that the degradation rate is much lower compared to the conventional cell assembly of Example 1. Without wishing to be bound by any theory, it is believed that the non-porous Al current collector acts as a physical barrier which retains the soluble polysulfides in the cathodic portion of the cell, while nevertheless allowing sufficient clearance around the edges to allow lithium ion transport between the cathodic and anodic regions of the cell. The initial low capacity, which increases to a maximum over the first c.a. 20 cycles, is believed to originate from diffusion limitations that prevent the electrolyte carrying the Li ions from penetrating into the bulk of the inverted cathode. A number of activation cycles are thus required to achieve maximum utilization of the sulfur.

Example 3 (comparative)

[99] “Carbon-interlayer” cells were assembled as schematically represented in Figure 5(a), with a permeable carbon layer coated onto the separator, adjacent to the composite cathodic material of a conventionally oriented cathode.

[100] The cycling performance of the conventional cathode cell with carbon coated separator was monitored at a cycling rate of 0.5 C (in the voltage range of 1.8 – 2.8 V relative to Li^+), and is presented in Figure 6(a). Improved capacity utilisation

and capacity retention of sulfur is evident in this experiment (compared with experiment 1) as a result of the carbon interlayer. Without wishing to be bound by any theory, it is believed that – at the high cycling rate of this experiment – a high proportion of the soluble polysulfides is physically retained in the carbon layer during discharge for long enough to be further reduced to insoluble sulfides on the conductive carbon network. Therefore, irreversible loss of active sulfur material from the cathodic region of the cell is mitigated.

[101] The cycling performance of a cell with carbon coated separator was then monitored at a more realistic cycling rate of 0.2 C (in the voltage range of 1.8 – 2.8 V relative to Li^+), and is presented in Figure 6(b). At this lower cycling rate, much higher loss of capacity was evident, particularly after the first discharge cycle. Without wishing to be bound by any theory, it is believed that – a such a slow discharge rate – the physical absorption of soluble polysulfides in the carbon interlayer's porosity is insufficient to prevent their migration through the separator before they are fully reduced to an insoluble form. Furthermore, the coulombic efficiency of the discharge is poor as a result of redox shuttling reactions at the lithium anode.

Example 4

[102] “Inverted cathode – carbon-coated carbon cloth” cells were then assembled as schematically represented in Figure 2 and Figure 5(b), using an unmodified glass fiber separator and with the cathode oriented such that the impermeable Al foil current collector is adjacent to the separator, and thus between the separator and the active cathodic material. A carbon-coated carbon cloth (wet with 80-100 μl of electrolyte) was positioned between the cathode and the cathodic-end cover of the battery case, with the composite cathodic active material thus sandwiched between the Al foil and the porous carbon coating of the cloth.

[103] The cycling performance of this cell was monitored at a cycling rate of 0.5 C (in the voltage range of 1.8 – 2.8 V relative to Li^+), and is presented in Figure 6(a). The performance may thus be directly compared against the “carbon interlayer cell” of Experiment 3 (with conventional cathode arrangement and a carbon interlayer interposed between the cathode and the separator). Superior performance is evident in the inverted cathode configuration, with notably less capacity fading in the first five cycles compared with the conventional cathode arrangement. This resulted in a

sustained performance advantage over the duration of the experiment. Furthermore, the coulombic efficiency of the discharge is greatly improved, indicating that redox shuttling reactions at the lithium anode are much less prevalent than in Experiment 3.

[104] Without wishing to be bound by any theory, it is believed that the non-porous Al current collector acts as a physical barrier which retains the soluble polysulfides in the cathodic portion of the cell, while nevertheless allowing sufficient clearance around the edges to allow lithium ion transport between the cathodic and anodic regions of the cell. In particular, it is believed that the soluble polysulfides are retained within the porous and electrically conductive structure of the carbon coating on the carbon cloth during the discharging of the cell for long enough that they are fully reduced to the final insoluble discharge species. The sulfur species thus retained on the electrolyte-porous and electrically conducting cloth remain electrochemically active, ensuring excellent effective retention of capacity in the cell.

[105] The cycling performance of the inverted cathode cell with carbon-coated carbon cloth was also monitored at a more realistic cycling rate of 0.2 C (in the voltage range of 1.8 – 2.8 V relative to Li^+), and is presented in Figure 6(b). An even more substantial performance advantage over the conventional configuration is evident at this lower cycling rate. Whereas the slow cycling rate allows high levels of polysulfide migration directly through the carbon layer in the conventional cathode configuration with carbon interlayer (i.e. Experiment 3), it is believed that the combination of the physical confinement by the impermeable Al foil and the absorptive retention by the microporous carbon acts cooperatively to retain the sulfur active phase in the cathodic region of the cell even under these demanding operating conditions.

Example 5 (comparative)

[106] A “cathode free” cell was assembled as schematically represented in Figure 7, using an unmodified glass fiber separator and a carbon-coated carbon cloth (wet with 80-100 μl of electrolyte) positioned between the separator and the cathodic-end cover of the battery case, with the porous carbon coating of the cloth directly adjacent to the separator.

[107] The cycling performance of this cell was monitored at the same current density as for the 0.5 C cycling experiments with sulfur cathode cells (in the voltage range of 1.8 – 2.8 V relative to Li), and is presented in Figure 8. Charge-discharge CV profiles (cycles 10-13) of the cell are presented in Figure 9. It is evident that the carbon-coated carbon cloth is itself capable of electrochemical energy storage. Without wishing to be bound by theory, it is believed that the charge storage capacity is provided by a combination of the intercalation mechanism of a lithium ion battery electrode and the electrochemical capacitive charge storage of an electric double-layer capacitor (EDLC), i.e. it acts as a lithium-ion capacitor (LIC). The rectangular CV profile shown in Figure 9 is characteristic of a LIC device.

[108] The carbon-coated carbon cloth is thus making a contribution to the total discharge capacity measured for the invert cathode cell of Experiment 4, as shown in Figure 6(a). The cell with an inverted cathode and a carbon-coated carbon cloth may thus be thought of as a hybrid device, having both capacitive energy storage capacity and faradaic energy storage capacity.

[109] Nevertheless, the capacitive storage contribution from the carbon-coated carbon cloth is not sufficient to account for the improved performance due to the inverted cathode configuration evident in Figure 6(a) and Figure 6(b). This is true even under the limiting assumption that the carbon interlayer of the conventional cathode cell of Experiment 3 has a negligible capacity as an LIC, and that all of the energy storage in Experiment 3 was due to faradaic Li-S energy storage capacity.

Claims

1. A rechargeable energy storage cell, the cell comprising:

a lithium anode in an anodic portion of the cell;

an oriented cathode in a cathodic portion of the cell, the cathode comprising:

5 a sheet of impermeable material; and

a cathodic material disposed on one side of the sheet, the cathodic material comprising sulfur,

wherein the cathode is oriented with the sheet positioned between the cathodic material and the anode; and

10 an electrolyte permitting lithium ion transport between the anodic portion and the cathodic portion,

wherein the sheet forms a physical barrier that inhibits diffusion of electrolyte-soluble sulfides from the cathodic portion to the anodic portion during discharge and/or recharge of the cell.

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2. The rechargeable energy storage cell of claim 1, further comprising a lithium ion-permeable separator which defines a boundary between the anodic portion and the cathodic portion, wherein a surface area of the sheet is smaller than a surface area of the separator.

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3. The rechargeable energy storage cell of claim 2, wherein the surface area of the sheet is from 20% to 80% of the surface area of the separator.

4. The rechargeable energy storage cell of claim 2 or claim 3, wherein the sheet of the cathode is in contact with and in parallel alignment with the separator.

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5. The rechargeable energy storage cell of any one of claims 2 to 4, wherein the sheet and the separator are coaxial discs, wherein a diameter of the sheet is smaller than a diameter of the separator.

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6. The rechargeable energy storage cell of any one of claims 1 to 5, wherein the sheet comprises one or more apertures for lithium ion flux between the anodic and cathodic portions.

7. The rechargeable energy storage cell of any one of claims 1 to 6, wherein the sheet is a current collector for the cathode.
- 5 8. The rechargeable energy storage cell of any one of claims 1 to 7, wherein the sheet of impermeable material comprises a metallic foil.
9. The rechargeable energy storage cell of any one of claims 1 to 8, further comprising a sulfide-retentive composition in the cathodic portion.
- 10 10. The rechargeable energy storage cell of claims 9, wherein the sulfide-retentive composition comprises high surface area carbon.
11. The rechargeable energy storage cell of claim 10, wherein the high surface area
15 carbon is selected from the group consisting of activated carbon, expanded graphite, graphene, carbon nanotubes, chemically reduced graphene oxide, electrochemically reduced graphene oxide, and e-beam reduced graphene oxide.
12. The rechargeable energy storage cell of claim 9 or claim 10, wherein the high
20 surface area carbon is supported on and/or in the form of a woven or non-woven carbon cloth.
13. The rechargeable energy storage cell of any one of claims 9 to 12, wherein the sulfide-retentive composition is porous to the electrolyte.
- 25 14. The rechargeable energy storage cell of any one of claims 9 to 13, wherein the sulfide-retentive composition is electrically conductive.
15. The rechargeable energy storage cell of any one of claims 9 to 14, wherein the
30 sulfide-retentive composition forms a layer adjacent to the cathodic material, wherein the cathodic material is sandwiched between the sheet and the sulfide-retentive composition.

16. The rechargeable energy storage cell of claim 15, wherein the sulfide-retentive composition is a current collector for the cathode.
- 5 17. The rechargeable energy storage cell of any one of claims 9 to 16, wherein the sulfide-retentive composition is adapted for capacitive energy storage by ionic charge separation.
- 10 18. The rechargeable energy storage cell of claim 17 wherein a mass of the sulfide-retentive composition is sufficient relative to a mass of the sulfur such that a capacitive energy discharge capacity is at least 10% of a faradaic energy discharge capacity during a complete discharge of the cell.
- 15 19. The rechargeable energy storage cell of any one of claims 1 to 18, wherein the cathodic material comprises a porous carbon matrix impregnated with the sulfur.
- 20 20. The rechargeable energy storage cell of any one of claims 1 to 19, wherein the cathodic material is a coating which substantially covers an entire surface of the one side of the sheet.
21. The rechargeable energy storage cell of any one of claims 1 to 20, further comprising a casing which encloses the anodic portion and the cathodic portion.
22. A rechargeable energy storage cell capable of both capacitive energy discharge and faradaic energy discharge, the cell comprising:
- 25 a lithium anode in an anodic portion of the cell;
 an oriented cathode in a cathodic portion of the cell, the cathode comprising:
 a sheet of impermeable material; and
 a cathodic material disposed on one side of the sheet, the cathodic material comprising sulfur,
- 30 wherein the cathode is oriented with the sheet positioned between the cathodic material and the anode;
 an electrically conductive and porous sulfide-retentive composition in the cathodic portion; and

an electrolyte permitting lithium ion transport between the anodic portion and the cathodic portion,

wherein the sheet forms a physical barrier that inhibits diffusion of electrolyte-soluble sulfides from the cathodic portion to the anodic portion during discharge and/or recharge of the cell.

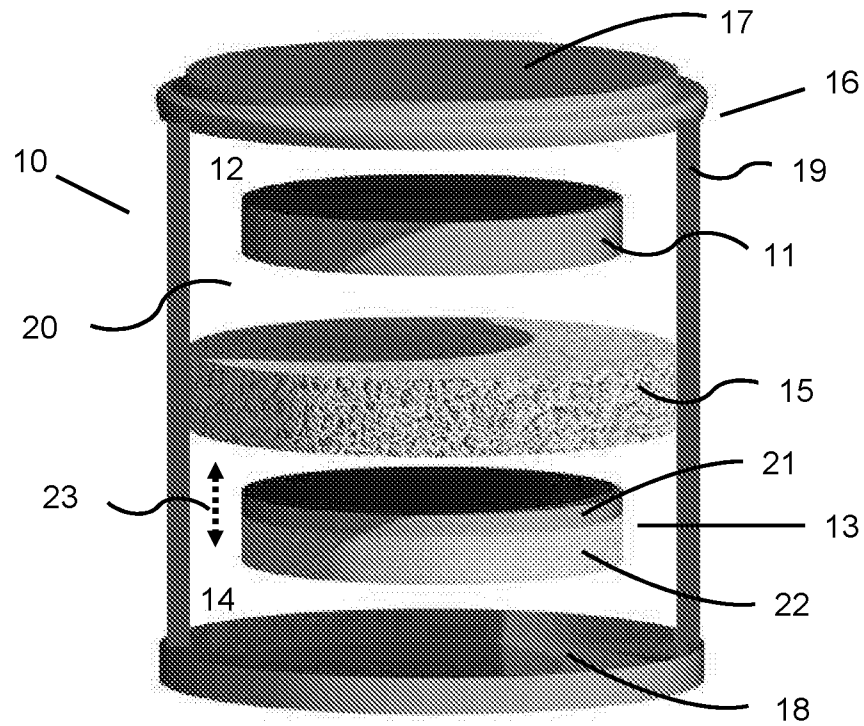
5

23. A battery comprising one or more rechargeable energy storage cells according to any one of claims 1 to 22.

10 24. An electrically powered device, powered by the battery of claim 23.

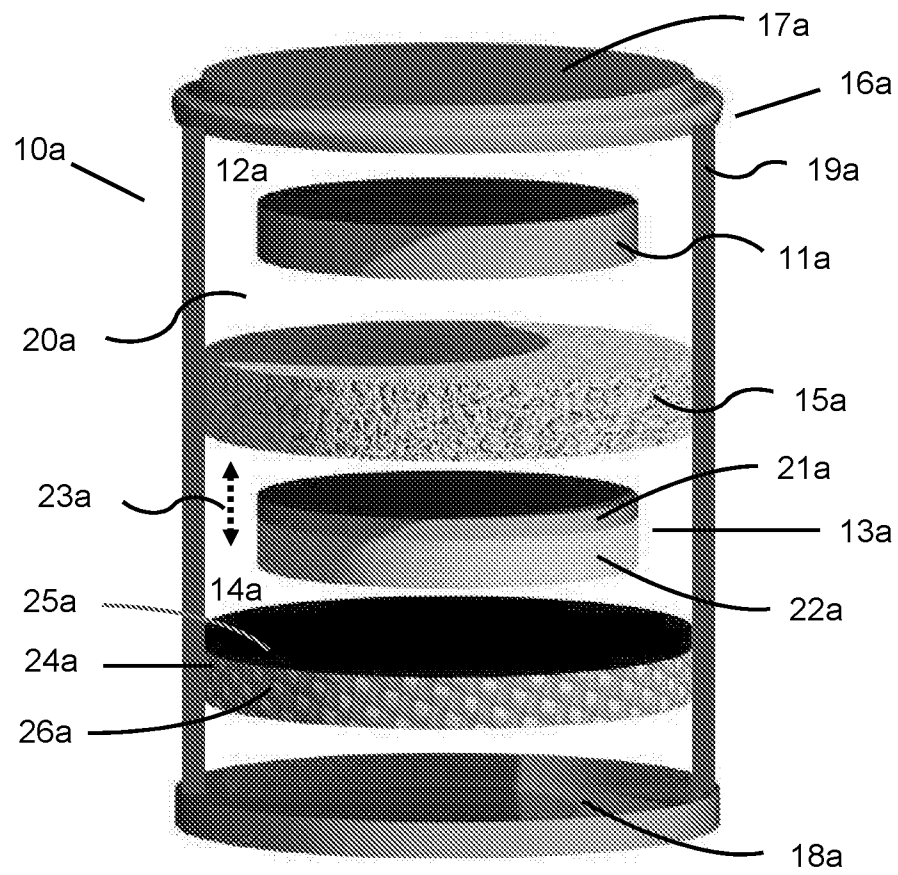
1/9

Figure 1



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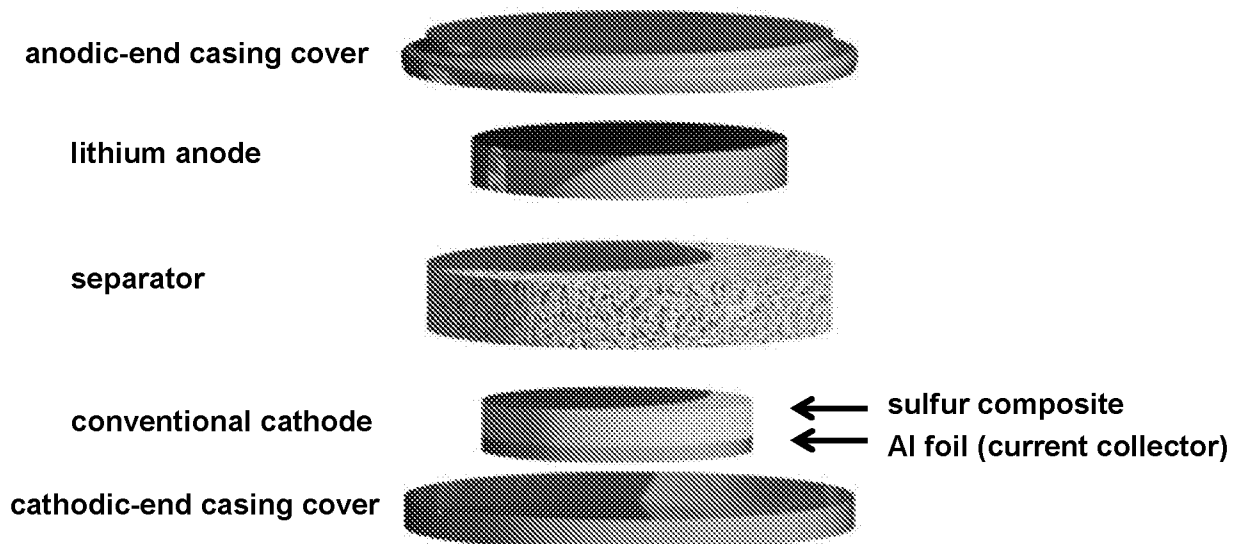
Figure 2



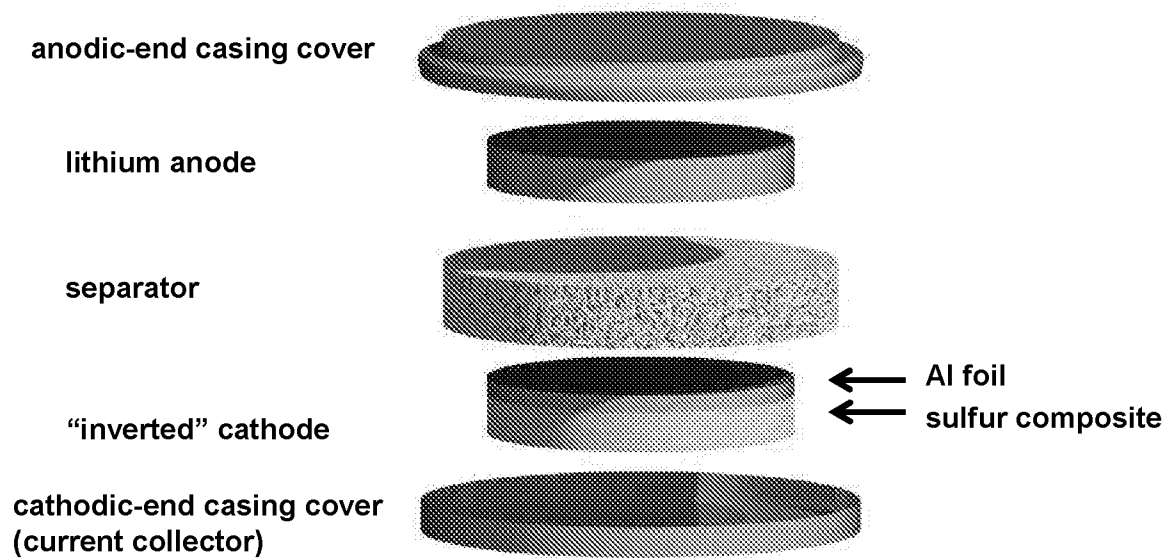
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Figure 3

(a)

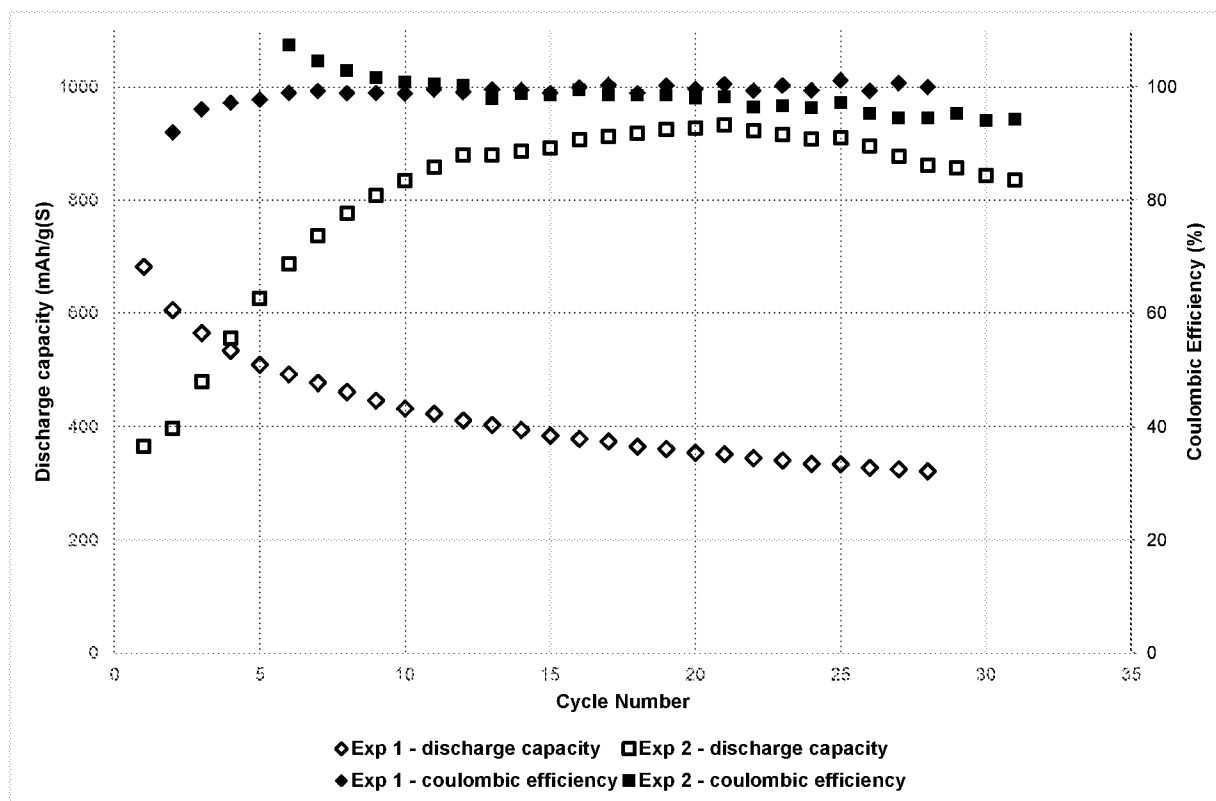


(b)



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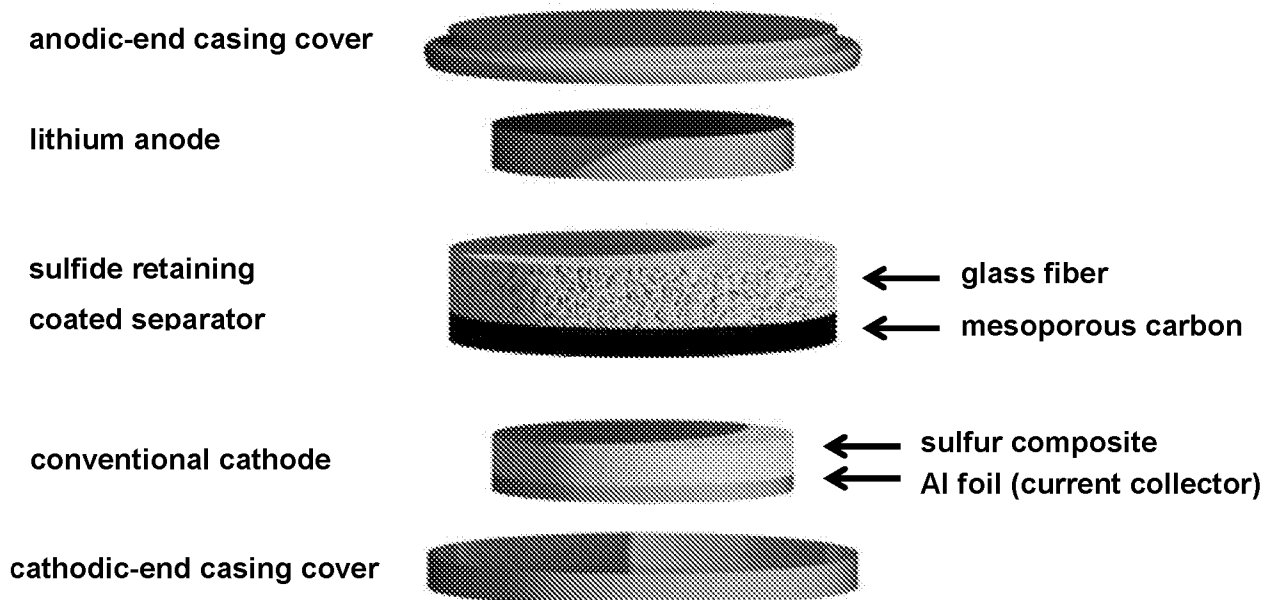
Figure 4



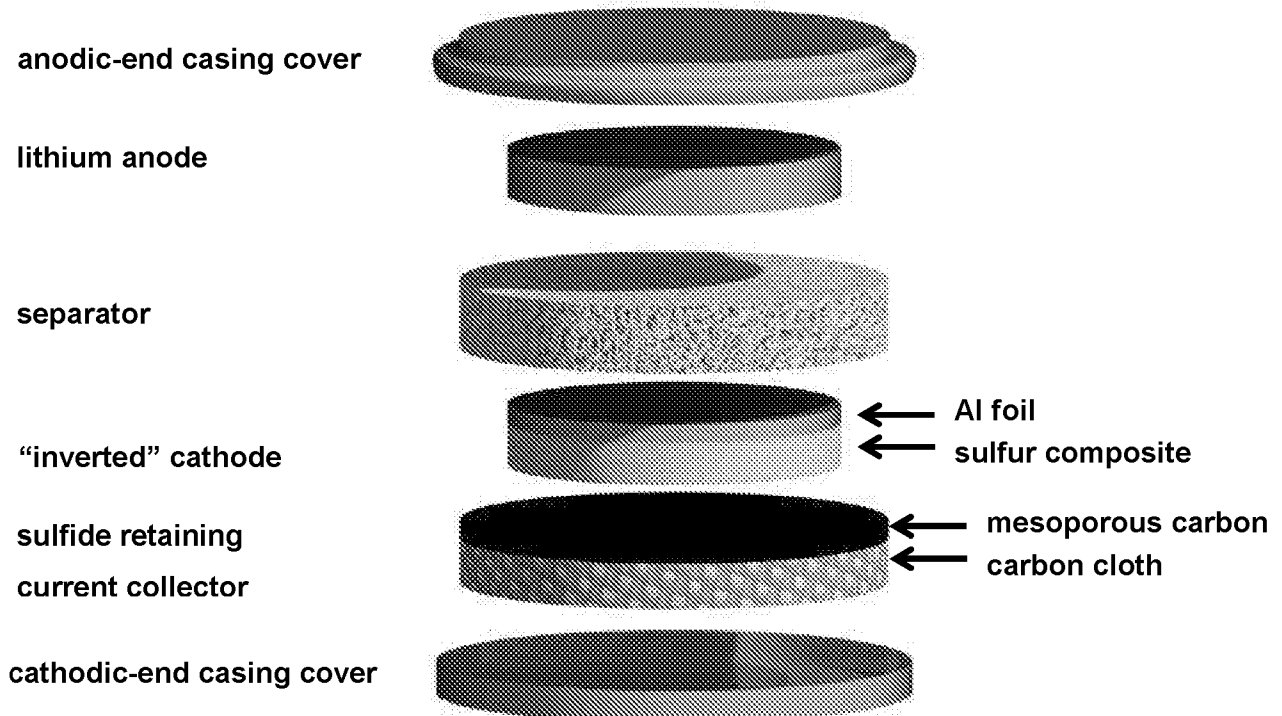
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Figure 5

(a)

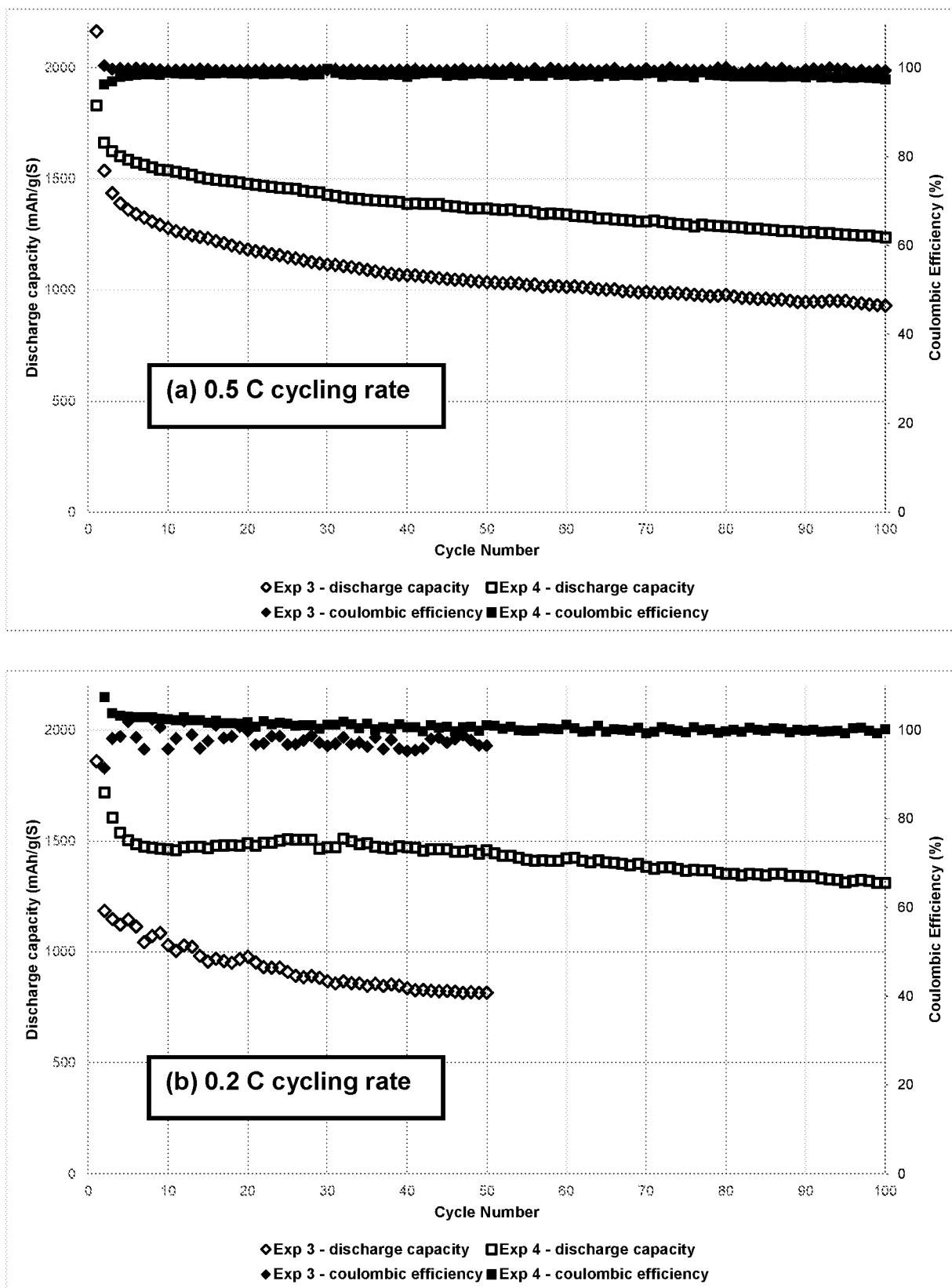


(b)



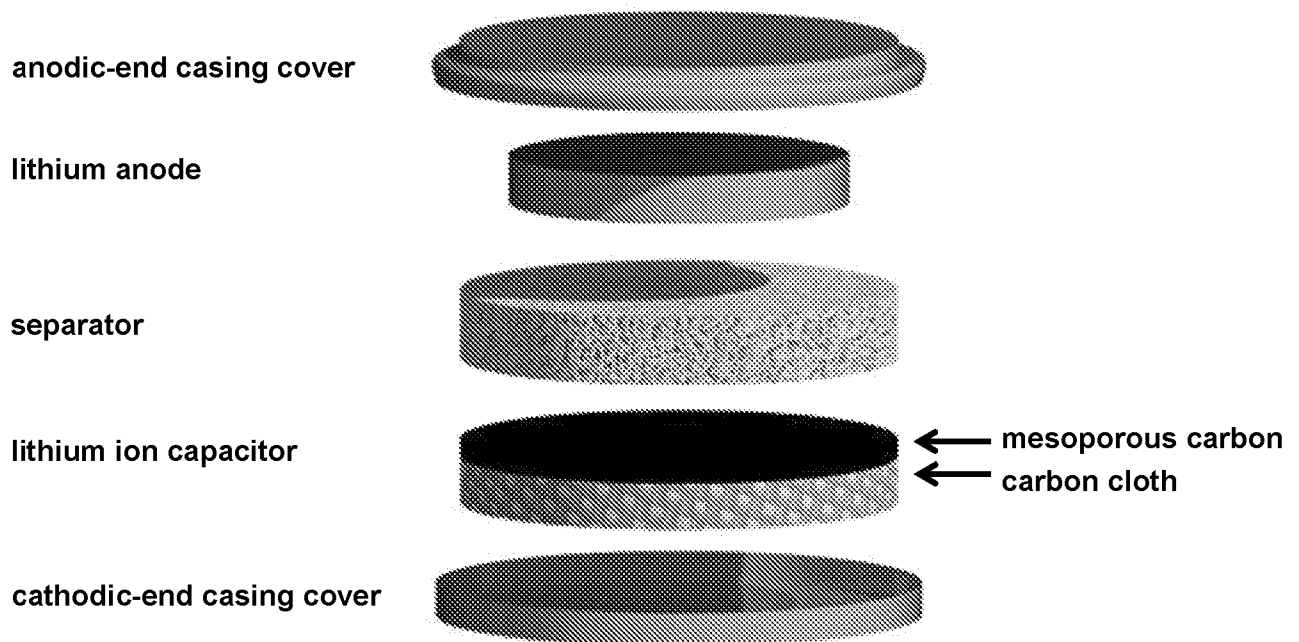
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Figure 6



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Figure 7



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Figure 8

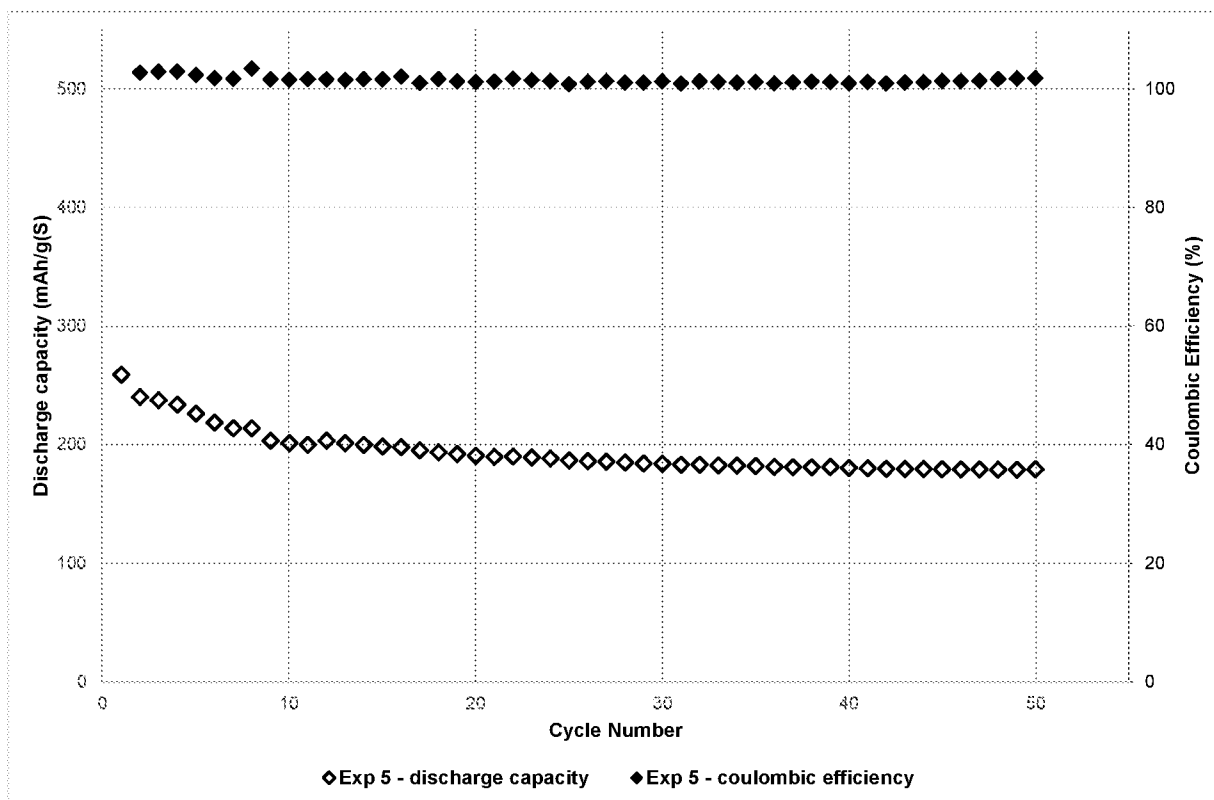
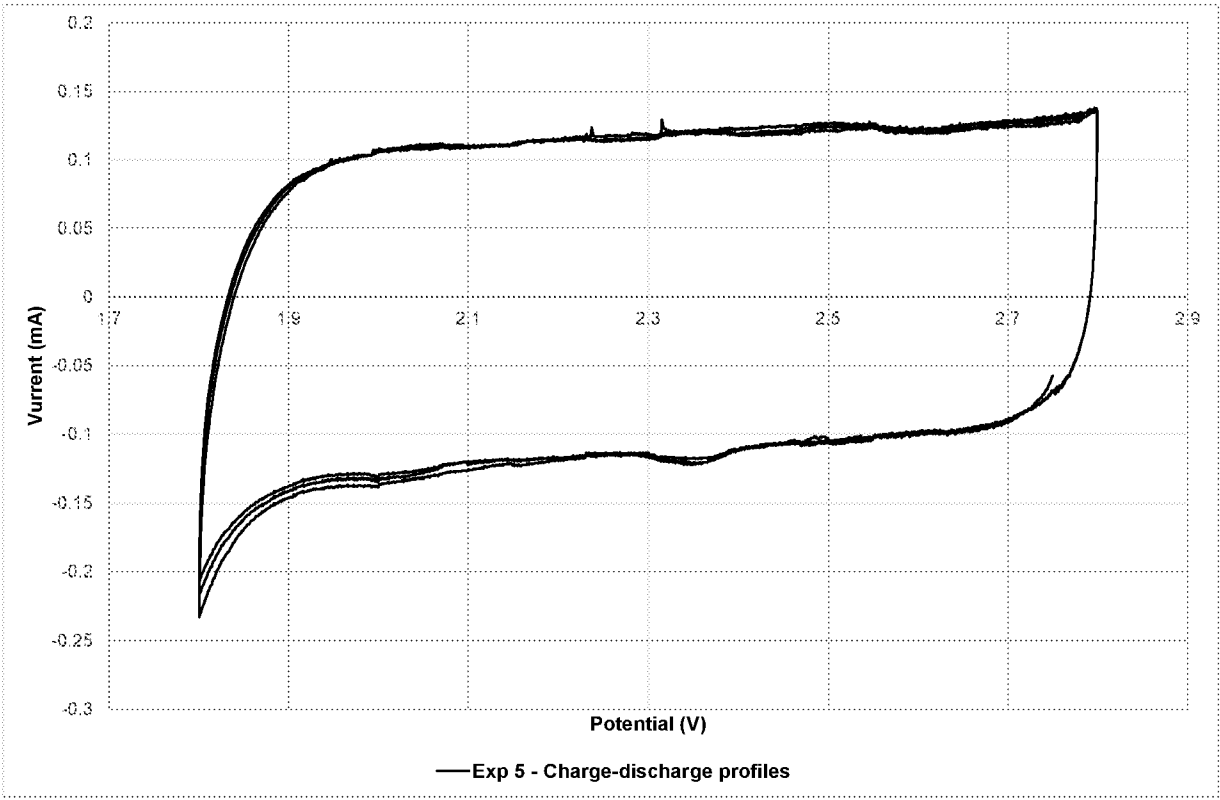


Figure 9



INTERNATIONAL SEARCH REPORT

 International application No.
PCT/AU2017/051292

A. CLASSIFICATION OF SUBJECT MATTER

H01M 4/38 (2006.01) H01M 4/58 (2010.01) H01M 4/1393 (2010.01) H01G 11/32 (2013.01) H01M 4/80 (2006.01)
H01M 4/583 (2010.01) H01G 11/24 (2013.01) H01G 11/26 (2013.01) H01M 10/04 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PATENW, Espacenet, Auspat, Google Patents and Google

IPC/CPC: H01M4/382, H01M4/13, H01M4/405, Y02T10/7011, Y02E60/122, H01M10/052, H01M4/5815, H01M4/1393, H01M4/625, H01G11/32, H01M4/133, H01G11/06, H01G11/50, H01M2004/021, H01M4/667, H01M4/765, H01G11/70, H01M4/80, H01M4/668, H01M4/583, H01M2/1606, H01M2/14, H01M4/045, H01M4/0404, H01G11/24, H01G11/26, H01M10/0477, H01M10/643, H01M10/0422

Keywords: lithium, sulfur, sulphur, sulfide, sulphide, battery, cell, impermeable, capacitive, faradaic, inverted, electrode, shuttle effect, current collector, membrane, hybrid, porous, activated, cloth, carbon, graphene, graphite, impermeable, impassable, foil and similar

Applicant/Inventor: Monash University, SHAIBANI, Mahdokht, MAJUMDER, Mainak

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	



Further documents are listed in the continuation of Box C



See patent family annex

* "A"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 19 February 2018	Date of mailing of the international search report 19 February 2018
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustalia.gov.au	Authorised officer Dominique Wisniewski AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. 0399359626

INTERNATIONAL SEARCH REPORT		International application No.
C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		PCT/AU2017/051292
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 20160190561 A1 (LG CHEM, LTD.) 30 June 2016 Paragraphs 2, 12, 18, 21, 28, 31, 34, 37, 50, 61-63, 73-74, fig.2	1-6, 8-24
X	Niu, S. et al., 'Electrostatic-spraying an ultrathin, multifunctional and compact coating onto a cathode for a long-life and high-rate lithium-sulfur battery', Nano Energy, 28 September 2016, Vol. 30, pages 138-145 Introduction, pages 138-139, experimental section, page 139, fig. 1, b	1-5, 7-11, 13-14, 16-24
X	Su, Y. et al., 'A new approach to improve cycle performance of rechargeable lithium-sulfur batteries by inserting a free-standing MWCNT interlayer', Chemical Communications, 2012, Vol. 48, pages 8817-8819 Scheme 1, b, page 8817 right column, page 8818, right column, abstract	1-9, 13-14, 16-18, 21-24
A	Caban-Huertas, Z. et al., 'Capacitive vs Faradaic Energy Storage in a Hybrid Cell with LiFePO ₄ /RGO Positive Electrode and Nanocarbon Negative Electrode', 'Journal of The Electrochemical Society, 22 November 2016, Vol. 164, pages A6140-A6146 Page A6140	1-24
A	Li, X. et al., 'Mesoporous carbon/sulfur composite with N-doping and tunable pore size for high performance Li-S batteries', Journal of Solid State Electrochemistry, 12 November 2016, Vol. 21, issue 4, pages 1101-1109 Abstract	1-24

INTERNATIONAL SEARCH REPORT Information on patent family members		International application No. PCT/AU2017/051292	
This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.			
Patent Document/s Cited in Search Report		Patent Family Member/s	
Publication Number	Publication Date	Publication Number	Publication Date
US 20160190561 A1	30 June 2016	US 2016190561 A1	30 Jun 2016
		CN 105453308 A	30 Mar 2016
		EP 3016181 A1	04 May 2016
		JP 2016527699 A	08 Sep 2016
		KR 20150020144 A	25 Feb 2015
		KR 101615017 B1	22 Apr 2016
		TW 201523987 A	16 Jun 2015
		TW I553947 B	11 Oct 2016
		WO 2015023154 A1	19 Feb 2015
End of Annex			
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001. Form PCT/ISA/210 (Family Annex)(July 2009)			