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(71) Applicant: **MONASH UNIVERSITY** [AU/AU]; Wellington Road, Clayton, Victoria 3800 (AU).

(72) Inventors: **NISHSHANKE, Maleesha**; c/- Wellington Road, Clayton, Victoria 3800 (AU). **JOVANOVIC, Petar**; c/- Wellington Road, Clayton, Victoria 3800 (AU). **SHAIBANI, Mahdokht**; c/- Wellington Road, Clayton, Victoria 3800 (AU). **MAJUMDER, Mainak**; c/- Wellington Road, Clayton, Victoria 3800 (AU).

(74) Agent: **FPA PATENT ATTORNEYS PTY LTD**; Level 19, South Tower, 80 Collins Street, Melbourne, Victoria 3000 (AU).

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(54) Title: IMPROVED SULFUR CATHODES

(57) Abstract: Sulfur cathodes which include binding polymers, such as polyvinylpyrrolidone, which are capable of binding, or are bonded to, one or more of metal ions having a valency of two or more, halides, and polyhalogen anions are described. Electrochemical storage devices including the sulfur cathodes exhibit high C-rates over long cycle life.

Improved sulfur cathodes

Field of the disclosure

[0001] The present disclosure relates to sulfur cathodes and to electrochemical storage devices incorporating the sulfur cathodes, such as a lithium sulfur battery. The sulfur cathodes contain binding polymers which are capable of binding, or are bound to, one or more of metal ions, halides, and polyhalogen anions. Electrochemical storage devices including the sulfur cathodes exhibit high C-rates over long cycle life.

Background of the disclosure

[0002] Compared to lithium ion (Li-ion) battery technology, lithium sulfur (Li-S) batteries offer a number of potential advantages, including improved gravimetric energy density, reduced raw material cost due to the low cost of sulfur compared to the transition metals employed in Li-ion systems, and a reduced environmental impact of the cell materials.

[0003] Despite demonstrating excellent performance in coin cells and reaching promising energy densities at a pouch-cell level, Li-S batteries are still limited by the inherently sluggish reaction kinetics of sulfur and its intermediates, which can manifest in the form of higher-order soluble lithium polysulfides (LiPS) and lower order insoluble Li_2S_2 and Li_2S. Reaction kinetics in the discharge process are controlled by the conversion among soluble LiPS, and also the liquid to solid conversion of LiPS to Li_2S_2 and Li_2S, the latter being the rate limiting step in the discharge. Similarly, the kinetics of solid-liquid conversion represent a bottleneck in the charging process.

[0004] To date, an overwhelming majority of pouch cells are cycled at slow cycling rates of 0.05C or less. Even coin-cell studies typically limit rates to < 0.2C. A growing effort in Li-S battery development has been directed towards discovering improved material systems that could enable batteries at more practical rates (> 0.5C). Owing to the inherent trade-off between sulfur loading and rate, demonstrating fast batteries is usually achieved at impractically low sulfur loadings (below < 1.5 mg cm^{-2}) compromising a more realistic energy density. An unmet challenge in the field lies in identifying and realizing material systems that can sustain high C-rates over a long cycle life at practical sulfur loadings (> 3 mg/cm^2).

[0005] Reference to any prior art in the specification is not an acknowledgment or suggestion that this prior art forms part of the common general knowledge in any jurisdiction or that this prior art could reasonably be expected to be understood, regarded as relevant, and/or combined with other pieces of prior art by a skilled person in the art.

Summary of the disclosure

[0006] In one aspect the present disclosure provides a sulfur cathode comprising:

a) one or more sulfur containing materials;

b) one or more conductive materials;

c) one or more:

(i) metal cations having a valency of two or more;

(ii) halide anions;

(iii) polyhalogen anions;

or mixtures thereof; and

d) one or more binding polymers, said binding polymers being capable of binding one or more of metal cations having a valency of two or more, halide anions, or polyhalogen anions.

[0007] In another aspect the present disclosure provides a sulfur cathode comprising:

a) one or more sulfur containing materials;

b) one or more conductive materials;

c) one or more binding polymers having bound thereto one or more of:

(i) metal cations having a valency of two or more;

(ii) halide anions; or

(iii) polyhalogen anions.

[0008] In another aspect the present disclosure provides an electrochemical storage device comprising a lithium anode, a separator, the sulfur cathode according to any one of the herein disclosed aspects or embodiments, and electrolyte disposed between the anode and cathode.

[0009] In any one of the herein disclosed aspects or embodiments, the sulfur cathode further comprises one or more structural materials.

[0010] In any one of the herein disclosed aspects or embodiments, the one or more structural materials have higher mechanical strength and/or viscosity compared to the one or more binding polymers.

[0011] In any one of the herein disclosed aspects or embodiments, the one or more structural materials comprise one or more cellulose derivatives.

[0012] In any one of the herein disclosed aspects or embodiments, the one or more structural materials comprise one or more of carboxymethyl cellulose, anionically functionalised cellulose nanofibres, and alginate salts.

[0013] In any one of the herein disclosed aspects or embodiments, the one or more sulfur containing materials comprise one or more of elemental sulfur, Li_2S, MoS_2 and sulfurised polymers.

[0014] In any one of the herein disclosed aspects or embodiments, the one or more conductive materials comprise one or more of carbon black, graphite, graphene, activated carbon, carbon nanotubes, and carbon fibre.

[0015] In any one of the herein disclosed aspects or embodiments, the one or more metal cations having a valency of two or more comprise one or more of iron (III), iron (II), manganese (II), cobalt (III), copper (II), zinc (II), aluminium (III), nickel (II), and gallium (III).

[0016] In any one of the herein disclosed aspects or embodiments, the one or more halide anions comprise one or more of bromide and iodide.

[0017] In any one of the herein disclosed aspects or embodiments, the one or more polyhalogen anions comprise one or more of I_3^-, I_5^-, and Br_3^-.

[0018] In any one of the herein disclosed aspects or embodiments, the one or more binding polymers capable of binding, or having bound thereto, one or more of metal cations, halide anions, and polyhalogen anions comprise one or more of polyvinylpyrrolidone, poly(vinyl pyridine), poly(vinyl alcohol), polyether, and polysaccharide.

[0019] In any one of the herein disclosed aspects or embodiments, the one or more binding polymers capable of binding, or having bound thereto, one or more of metal cations, halide anions, and polyhalogen anions comprise polyvinylpyrrolidone, poly(vinyl alcohol), and poly(ethylene oxide).

[0020] For the avoidance of doubt, the sulfur cathodes according to any of the aspects or embodiments of the present disclosure may include:

(i) one or more metal cations having a valency of two or more; or

(ii) one or more halide anions; or

(iii) one or more polyhalogen anions; or

(iv) any combination of (i), (ii), and (iii).

[0021] In any one of the herein disclosed aspects or embodiments, the one or more binding polymers have a weight average molecular weight from about 2,500 Daltons to about 3,000,000 Daltons.

[0022] In any one of the herein disclosed aspects or embodiments, the one or more binding polymers have a weight average molecular weight from about 20,000 to about 2,500,000 Daltons.

[0023] In any one of the herein disclosed aspects or embodiments, the one or more binding polymers have a weight average molecular weight from about 20,000 to about 1,500,000 Daltons.

[0024] In any one of the herein disclosed aspects or embodiments, the one or more binding polymers have a weight average molecular weight from about 500,000 to about 2,500,000 Daltons.

[0025] In any one of the herein disclosed aspects or embodiments, the molar ratio of sulfur to one or more of metal cations having a valency of two or more, halide anions, and polyhalogen anions is from about 500 to about 10.

[0026] In some embodiments, the sulfur cathode comprises:

about 50 wt.% to about 80 wt.% of one or more sulfur containing materials;

about 10 wt.% to about 30 wt.% of one or more conductive materials;

about 0.1 wt.% to about 5 wt.% of one or more of metal cations having a valency of two or more, halide anions, and polyhalogen anions; and

about 2 wt.% to about 20 wt.% of one or more binding polymers capable of binding, or having bound thereto, one or more of metal cations, halide anions, and polyhalogen anions;

based on the total weight of the sulfur cathode.

[0027] In embodiments, the sulfur cathode further comprises about 2 wt.% to about 15 wt.% of one or more of structural materials. In embodiments, the one or more structural materials have higher mechanical strength and/or viscosity compared to the one or more binding polymers.

[0028] In some embodiments, the sulfur cathode comprises:

about 55 wt.% to about 75 wt.% of one or more sulfur containing materials;

about 15 wt.% to about 25 wt.% of one or more conductive materials;

about 1 wt.% to about 5 wt.% of one or more of metal cations having a valency of two or more, halide anions, and polyhalogen anions;

about 2 wt.% to about 20 wt.% of one or more binding polymers capable of binding, or having bound thereto, one or more of metal cations, halide anions, and polyhalogen anions;

based on the total weight of the sulfur cathode.

[0029] In embodiments, the sulfur cathode further comprises about 2 wt.% to about 15 wt.% of one or more of structural materials. In embodiments, the one or more structural materials have higher mechanical strength and/or viscosity compared to the one or more binding polymers.

[0030] In embodiments, the presently disclosed electrochemical storage device exhibits higher oxidation and/or reduction currents relative to a device absent the one or more of metal cations having a valency of two or more, halide anions, and polyhalogen anions.

[0031] In embodiments, the presently disclosed electrochemical storage device exhibits higher reduction peak potentials and/or lower oxidation peak potentials relative to a device absent the one or more of metal cations having a valency of two or more, halide anions, and polyhalogen anions.

[0032] In embodiments, the sulfur cathode of the presently disclosed electrochemical storage device adsorbs and promotes the conversion of soluble lithium polysulfides to solid lithium sulfur species.

[0033] In embodiments, the sulfur cathode of the presently disclosed electrochemical storage device promotes reduction of soluble lithium polysulfides to solid lithium sulfides (Li_2S/Li_2S_2) during discharge and promotes the reverse oxidation of the solid lithium sulphides to liquid lithium polysulfides during charge.

[0034] In embodiments, the sulfur cathode of the presently disclosed electrochemical storage device hinders the transport of soluble lithium polysulfides within the sulfur cathode.

[0035] In embodiments, during charging or discharging, the sulfur cathode of the presently disclosed electrochemical storage device promotes the transport of lithium ions within the sulfur cathode.

[0036] In embodiments, during charging or discharging, the sulfur cathode of the presently disclosed electrochemical storage device limits the diffusion of polysulfides from the sulfur cathode.

[0037] In embodiments, the presently disclosed electrochemical storage device exhibits improved C rate/current density relative to a device comprising a sulfur cathode

absent the one or more of metal cations having a valency of two or more, halide anions, and polyhalogen anions.

[0038] In any of the herein disclosed aspects or embodiments the electrochemical storage device is a lithium sulfur battery.

[0039] In another aspect the present disclosure provides use of the sulfur cathode according to any one of the herein disclosed aspects or embodiments in an electrochemical storage device.

[0040] In embodiments, the electrochemical storage device is a lithium sulfur battery.

[0041] In another aspect the present disclosure provides a binder for a sulfur cathode comprising:

one or more of metal cations having a valency of two or more, halide anions, and polyhalogen anions;

one or more binding polymers capable of binding, or having bound thereto, one or more of metal cations, halide anions, and polyhalogen anions; and

one or more structural materials.

[0042] In embodiments, the one or more structural materials have higher mechanical strength and/or viscosity compared to the one or more binding polymers

[0043] In embodiments, the one or more structural materials comprise one or more cellulose derivatives.

[0044] In embodiments, the one or more structural materials comprise one or more of carboxymethyl cellulose, anionically functionalised cellulose nanofibres, and alginate salts.

[0045] In another aspect the present disclosure provides a method of preparing a binder for a sulfur cathode comprising:

combining one or more of metal cations having a valency of two or more, halide anions, and polyhalogen anions, with one or more binding polymers capable of binding the one or more of metal cations, halide anions, and polyhalogen anions; and

combining the product of step a) with one or more structural materials.

[0046] In embodiments, the one or more structural materials have higher mechanical strength and/or viscosity compared to the one or more binding polymers

[0047] In embodiments, the one or more structural materials comprise one or more cellulose derivatives.

[0048] In embodiments, the one or more structural materials comprise one or more of carboxymethyl cellulose, anionically functionalised cellulose nanofibres, and alginate salts.

[0049] In embodiments, a particular advantage of the presently disclosed sulfur cathodes and batteries including the sulfur cathodes is that the binder systems promote both reduction and oxidation reaction kinetics without sacrificing sulfur mass loading in the cathode.

[0050] Any embodiment herein shall be taken to apply *mutatis mutandis* to any other embodiment unless specifically stated otherwise.

[0051] The present disclosure is not to be limited in scope by the specific embodiments described herein, which are intended for the purpose of exemplification only. Functionally-equivalent products, compositions and processes are clearly within the scope of the disclosure, as described herein.

[0052] Further aspects of the present disclosure and further embodiments of the aspects described in the preceding paragraphs will become apparent from the following description, given by way of example and with reference to the accompanying drawings.

Brief description of the drawings

[0053] Figure 1 illustrates UV-vis spectra of CMC/PVP-I, CMC/PVP and CMC binders.

[0054] Figure 2 illustrates Raman spectra of CMC/PVP-I, CMC/PVP and CMC binders.

[0055] Figure 3 shows SEM images of sulfur cathodes containing binder system, a) CMC/PVP-I, b) CMC/PVP, c) CMC, and d) elemental energy-dispersive x-ray mapping

across a sulfur cathode containing PVP-I in the binder system showing the initial uniform distribution of iodides.

[0056] Figure 4 shows cycling performance of coin cells with CMC/PVP-I, CMC/PVP and CMC containing sulfur cathodes with 3 mg cm^{-2} sulfur loading at 1C.

[0057] Figure 5 shows cycling performance of coin cells with CMC/PVP-I and CMC-I containing sulfur cathodes with 3 mg cm^{-2} sulfur loading at 1C.

[0058] Figure 6 shows cycling performance of coin cells with CMC/PVP-I, CMC/PVP and CMC containing sulfur cathodes with 3 mg cm^{-2} sulfur loading at 2C.

[0059] Figure 7 shows cycling performance of coin cells with CMC/PVP-I, CMC/PVP and CMC containing sulfur cathodes with 4 mg cm^{-2} sulfur loading at 0.5C.

[0060] Figure 8 shows CV profiles of Li–S cells with CMC/PVP-I, CMC/PVP and CMC containing cathodes 0.1 mV s-1 scan rate.

[0061] Figure 9 is a schematic diagram showing proposed reduction and oxidation reactions.

[0062] Figure 10 illustrates the cycling performance of 3mg cm^{-2} sulfur loaded PVP-Zn, PVP-Al, PVP-Fe, PVP-Cu and PVP-Ga cathodes at 0.5C rate.

[0063] Figure 11 illustrates the cycling performance of 3mg cm^{-2} sulfur loaded PVP-Zn, PVP-Al, PVP-Fe, PVP-Cu and PVP-Ga cathodes at 1C rate.

[0064] Figure 12 illustrates CV profiles of Li–S cells with PVP-Zn, PVP-Al, PVP-Fe, PVP-Cu, and PVP-Ga cathodes at 0.1 mV s^{-1} scan rate.

[0065] Figure 13 compares the cathodic peak currents *C1* and *C2* and anodic peak current *A1* of the metal cation binders with those of PVP-I.

[0066] Figure 14 illustrates the cycling performance of coin cells containing 3 mg cm^{-2} sulfur loaded PVP-Zn, PVP-Al, PVP-Fe, PVP-Cu and PVP-Ga cathodes in which 5 wt.% of the 20 wt.% conductive carbon was replaced by graphite.

[0067] Figure 15 illustrates the cycling performance of 3 mg cm^{-2} sulfur loaded (a) PVP-Zn/Fe (b) PVP-Al/Fe dual metal systems at 1C rate.

[0068] Figure 16 illustrates cycling performance of 3 mg cm^{-2} sulfur loaded PVP-Zn, PVP-Al, PVP-Fe, PVP-Cu and PVP-Ga cathodes at (a) 0.5C and (b) 1C rates using PVP with Mw: 360,000.

[0069] Figure 17 illustrates the cycling performance of PVP-Zn binder system with PVP of M_w 40,000, 360,000 and 1,300,000.

[0070] Figure 18 illustrates the cycling performance of 3 mg cm^{-2} sulfur loaded PVA-Zn, PVA-Al, PVA-Fe, PVA-Cu and PVA-Ga cathodes at (a) 0.5C and (b) 1C rates.

[0071] Figure 19 illustrates the cycling performance of 3 mg cm^{-2} sulfur loaded PVA*-Zn, PVP*-Zn, PEO*-Zn and PEO*-Fe cathodes at (a) 0.5C and (b) 1C rates without CMC in the binder system.

[0072] Figure 20 illustrates the cycling performance of 3 mg cm^{-2} sulfur loaded FeI/PVA* and FeI/PVP* cathodes at 0.5C and 1C rates without CMC in the binder system.

[0073] Figure 21 illustrates the cycling performance of 2 mg cm^{-2} sulfur loaded ZnI/PVA* and ZnI/PVP* cathodes at 0.5C and 1C rates without CMC in the binder system.

[0074] Figure 22 illustrates the cycling performance of PVP-I and PVA-I cathodes without CMC in the binder system: (a) coin cells configured with PVP-I and PVA-I at 0.5C rate; (b) coin cells configured with PVP-I at 1C rate.

Detailed description of the embodiments

[0075] It will be understood that the disclosure described and defined in this specification extends to all alternative combinations of two or more of the individual features mentioned or evident from the text or drawings. All of these different combinations constitute various alternative aspects of the disclosure.

Definitions

[0076] For purposes of interpreting this specification, terms used in the singular will also include the plural and vice versa.

[0077] As used herein, except where the context requires otherwise, the term "comprise" and variations of the term, such as "comprising", "comprises" and "comprised", are not intended to exclude further additives, components, integers or steps.

[0078] "About" as used herein when referring to a measurable value such as an amount, a temporal duration, and the like, is meant to encompass variations of ±20% or ±10%, in some instances ±5%, in some instances ±1%, and in some instances ±0.1% from the specified value, as such variations are appropriate to perform the disclosed methods.

[0079] Ranges: throughout this disclosure, various aspects of the invention can be presented in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the invention. Accordingly, the description of a range should be considered to have specifically disclosed all the possible subranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed subranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 2.7, 3, 4, 5, 5.3, and 6. This applies regardless of the breadth of the range.

[0080] As used herein the term “anionically functionalised cellulose nanofibres” refers to cellulosic materials as disclosed in applicant’s co-pending international application no. PCT/AU2023/050575, the entirety of which is incorporated herein by reference.

[0081] The present disclosure relates to new sulfur cathodes useful in electrochemical storage devices, such as lithium sulfur batteries. The cathodes contain binding polymers which are capable of binding, or are bound to, one or more of metal ions, halides, and polyhalogen anions. Lithium sulfur batteries incorporating the new sulfur cathodes possess a number of advantageous properties.

[0082] In an embodiment of the present disclosure the binding polymer comprises polyvinylpyrrolidone which when treated with iodide anion affords a useful binder

system for a sulfur cathode. Lithium-sulfur cells including such cathodes demonstrate accelerated reaction kinetics at every stage of cell cycling.

[0083] In another embodiment of the present disclosure replacement of iodide with a metal cation having a valency of two or more in the sulfur cathode affords lithium-sulfur cells having similar reaction rate enhancement to that of iodide.

Binding polymers

[0084] Suitable binding polymers include polymers that are capable of forming interactions with metal cations, halide anions, or polyhalogen anions. The interactions may be in the form of covalent bonds, coordination bonds, or non-covalent interactions, such as hydrogen bonds. Other types of interactions are contemplated.

[0085] A feature of the interactions is that the binding polymer sufficiently interacts with the metal cations, halide anions, or polyhalogen anions so as to enhance the retention of these species within the binder system, and thus retention within sulfur cathodes which include the binder system. Moreover, the retention of these species within the sulfur cathode may be enhanced by the binding polymer during electrochemical cycling of a lithium-sulfur cell.

[0086] Suitable binding polymers may comprise one or more of polyvinylpyrrolidone, poly(vinyl pyridine), poly(vinyl alcohol), polyether, and polysaccharide. Other binding polymers are contemplated.

[0087] The one or more binding polymers may have a weight average molecular weight from about 2,500 to about 3,000,000 Daltons, or from about 500,000 to about 2,500,000 Daltons, or from about 600,000 to about 2,400,000 Daltons, or from about 700,000 to about 2,300,000 Daltons, or from about 800,000 to about 2,200,000 Daltons, or from about 900,000 to about 2,100,000 Daltons, or from about 1,000,000 to about 2,000,000 Daltons, or from about 20,000 to about 2,500,000 Daltons, or from about 30,000 to about 2,500,000 Daltons, or from about 40,000 to about 2,500,000 Daltons, or from about 50,000 to about 2,500,000 Daltons, or from about 60,000 to about 2,500,000 Daltons, or from about 70,000 to about 2,500,000 Daltons, or from about 800,000 to about 2,500,000 Daltons, or from about 90,000 to about 2,500,000 Daltons, or from about 100,000 to about 2,500,000 Daltons, or from about 150,000 to about 2,500,000 Daltons, or from about 200,000 to about 2,500,000 Daltons, or from about 250,000 to

about 2,500,000 Daltons, or from about 300,000 to about 2,500,000 Daltons, or from about 350,000 to about 2,500,000 Daltons, or from about 400,000 to about 2,500,000 Daltons, or from about 450,000 to about 2,500,000 Daltons, Other weight average molecular weight ranges within the 2,500 to 3,000,000 Dalton range are contemplated.

[0088] In embodiments, the one or more binding polymers may have a weight average molecular weight of about 20,000 Daltons, or about 30,000 Daltons, or about 40,000 Daltons, or about 50,000 Daltons, or about 60,000 Daltons, or about 70,000 Daltons, or about 80,000 Daltons, or about 90,000 Daltons, or about 100,000 Daltons, or about 150,000 Daltons, or about 200,000 Daltons, or about 250,000 Daltons, or about 300,000 Daltons, or about 350,000 Daltons, or about 400,000 Daltons, or about 450,000 Daltons, or about 500,000 Daltons, or about 550,000 Daltons, or about 600,000 Daltons, or about 700,000 Daltons, or about 800,000 Daltons, or about 900,000 Daltons, or about 1,000,000 Daltons, or about 1,100,000 Daltons, or about 1,200,000 Daltons, or about 1,300,000 Daltons, or about 1,400,000 Daltons, or about 1,500,000 Daltons, or about 1,600,000 Daltons, or about 1,700,000 Daltons, or about 1,800,000 Daltons, or about 1,900,000 Daltons, or about 2,000,000 Daltons, or about 2,100,000 Daltons, or about 2,200,000 Daltons, or about 2,300,000 Daltons, or about 2,400,000 Daltons, or about 2,500,000 Daltons. Other weight average molecular weights are contemplated.

Metal cations, halide anions, and polyhalogen anions

[0089] Without being bound by theory, it is envisaged that the metal cations, halide anions, or polyhalogen anions play a role in catalysing or promoting sulfur reaction kinetics within a lithium sulfur battery.

[0090] The metal cations have a valency of two or more. Suitable metal cations include one or more of iron (III), iron (II), manganese (II), cobalt (III), copper (II), zinc (II), aluminium (III), nickel (II), and gallium (III). Other metal cations of valency two or more are contemplated.

[0091] The weight ratio of binding polymer to metal cation may be from about 10:1 to about 0.1:1, or from about 9:1 to about 0.1:1, or from about 8:1 to about 0.1:1, or from about 7:1 to about 0.1:1, or from about 6:1 to about 0.1:1, or from about 5:1 to about 0.1:1, or from about 4:1 to about 0.1:1, or from about 3:1 to about 0.1:1, or from about

2:1 to about 0.1:1, or from about 1:1 to about 0.1:1, or from about 10:1 to about 0.2:1, or from about 10:1 to about 0.3:1, or from about 10:1 to about 0.4:1, or from about 10:1 to about 0.5:1, or from about 10:1 to about 0.6:1, or from about 10:1 to about 0.7:1, or from about 10:1 to about 0.8:1, or from about 10:1 to about 0.9:1, or from about 10:1 to about 1:1. In some preferred embodiments, the weight ratio of binding polymer to metal cation may be from about 10:1 to about 0.5:1, or from about 8:1, to about 1:1. Other ratios are contemplated.

[0092] The halide anion may be one or more of bromide and iodide.

[0093] In embodiments, the weight ratio of binding polymer to iodide may be from about 10:1 to 0.1:1, or from about 9:1 to about 0.1:1, or from about 8:1 to about 0.1:1, or from about 7:1 to about 0.1:1, or from about 6:1 to about 0.1:1, or from about 5:1 to about 0.1:1, or from about 4:1 to about 0.1:1, or from about 3:1 to about 0.1:1, or from about 2:1 to about 0.1:1, or from about 1:1 to about 0.1:1, or from about 10:1 to about 0.2:1, or from about 10:1 to about 0.3:1, or from about 10:1 to about 0.4:1, or from about 10:1 to about 0.5:1, or from about 10:1 to about 0.6:1, or from about 10:1 to about 0.7:1, or from about 10:1 to about 0.8:1, or from about 10:1 to about 0.9:1, or from about 10:1 to about 1:1. In some preferred embodiments, the weight ratio of binding polymer to iodide may be from about 10:1 to about 0.3:1, or from about 8:1, to about 0.5:1. Other ratios are contemplated.

[0094] When the halide anion is bromide, the ratios of binding polymer to bromide may be the same as for iodide, except for adjusting for the atomic weight difference between the halides.

[0095] In embodiments, a feature of the halide anion components in the presently disclosed binder systems is the formation of polyhalogen anions. For example, when PVP and iodide are combined the polyhalogen anion I_3^- forms. Without being bound by theory, it is envisaged that the I^-/I_3^- redox couple is immobilized by a stable polyvinylpyrrolidone (PVP) complex.

Sulfur cathodes

[0096] The sulfur cathodes according to the present disclosure comprise a mixture of one or more sulfur containing materials, one or more conductive materials, one or more binding polymers as disclosed herein, and one or more metal cations having a valency

of two or more, one or more halide anions, one or more polyhalogen anions, or mixtures thereof

[0097] The one or more sulfur containing materials include one or more of elemental sulfur, Li_2S, MoS_2, and sulfurised polymers. Other sulfur containing materials typically utilised in the construction of sulfur cathodes are contemplated.

[0098] In embodiments, the presently disclosed sulfur cathodes comprise from about 50 wt.% to about 80 wt.% of one or more sulfur containing materials, or from about 51 wt.% to about 80 wt.%, or from about 52 wt.% to about 80 wt.%, or from about 53 wt.% to about 80 wt.%, or from about 54 wt.% to about 80 wt.%, or from about 55 wt.% to about 80 wt.%, or from about 56 wt.% to about 80 wt.%, or from about 57 wt.% to about 80 wt.%, or from about 58 wt.% to about 80 wt.%, or from about 59 wt.% to about 80 wt.%, or from about 60 wt.% to about 80 wt.%, or from about 55 wt.% to about 79 wt.%, or from about 55 wt.% to about 78 wt.%, or from about 55 wt.% to about 77 wt.%, or from about 55 wt.% to about 76 wt.%, or from about 55 wt.% to about 75 wt.%, one or more sulfur containing materials.

[0099] The one or more conductive materials comprise one or more of carbon black, graphite, graphene, activated carbon, carbon nanotubes, and carbon fibre. Other conductive materials typically utilised in the construction of sulfur cathodes are contemplated.

[0100] In embodiments, the presently disclosed sulfur cathodes comprise from about 10 wt.% to about 30 wt.% of one or more conductive materials, or from about 11 wt.% to about 30 wt.%, or from about 12 wt.% to about 30 wt.%, or from about 13 wt.% to about 30 wt.%, or from about 14 wt.% to about 30 wt.%, or from about 15 wt.% to about 30 wt.%, or from about 15 wt.% to about 29 wt.%, or from about 15 wt.% to about 28 wt.%, or from about 15 wt.% to about 27 wt.%, or from about 15 wt.% to about 26 wt.%, or from about 15 wt.% to about 25 wt.% of one or more conductive materials.

[0101] In embodiments, the presently disclosed sulfur cathodes comprise from about 2 wt.% to about 15 wt.% of one or more structural materials, or from about 2 wt.% to about 12 wt.%, or from about 3 wt.% to about 10 wt.%, or from about 4 wt.% to about 10 wt.%, or from about 5 wt.% to about 10 wt.%, or from about 5 wt.% to about 9 wt.%, or

from about 5 wt.% to about 8 wt.%, or from about 5 wt.% to about 7 wt.%, of one or more structural materials.

[0102] The one or more structural materials may have higher mechanical strength and/or viscosity compared to the one or more binding polymers. In embodiments, the one or more structural materials comprise one or more cellulose derivatives.

[0103] Suitable structural materials include carboxymethyl cellulose, anionically functionalised cellulose nanofibres, and alginate salts. Other structural materials are contemplated.

[0104] The one or more structural materials may improve the longevity of the sulfur cathodes. In embodiments the one or more structural materials may enhance the mechanical strength of the cathode. Alternatively, or additionally, the structural material may limit volumetric expansion of the cathode during operation.

[0105] In embodiments, the presently disclosed sulfur cathodes comprise from about 0.1 wt.% to about 5 wt.% of one or more of metal cations having a valency of two or more, halide anions, and polyhalogen anions.

[0106] In embodiments, the sulfur cathodes comprise from about 0.2 wt.% to about 5 wt.% of one or more of metal cations having a valency of two or more, halide anions, and polyhalogen anions, or from about 0.3 wt.% to about 5 wt.%, or from about 0.4 wt.% to about 5 wt.%, or from about 0.5 wt.% to about 5 wt.%, or from about 0.6 wt.% to about 5 wt.%, or from about 0.7 wt.% to about 5 wt.%, or from about 0.8 wt.% to about 5 wt.%, or from about 0.9 wt.% to about 5 wt.%, or from about 1.0 wt.% to about 5 wt.%, or from about 1.1 wt.% to about 5 wt.%, or from about 1.2 wt.% to about 5 wt.%, or from about 1.3 wt.% to about 5 wt.%, or from about 1.4 wt.% to about 5 wt.%, or from about 1.5 wt.% to about 5 wt.%, or from about 0.3 wt.% to about 5 wt.%, or from about 0.3 wt.% to about 5 wt.%, or from about 0.1 wt.% to about 4 wt.%, or from about 0.1 wt.% to about 3 wt.%, or from about 0.1 wt.% to about 2 wt.%, or from about 0.5 wt.% to about 5 wt.%, or from about 0.5 wt.% to about 4 wt.%, or from about 0.5 wt.% to about 3 wt.%, or from about 0.2 wt.% to about 4 wt.%, or from about 0.2 wt.% to about 3 wt.%.

[0107] In embodiments, the presently disclosed sulfur cathodes comprise from about 2 wt.% to about 20 wt.% of one or more binding polymers capable of binding, or having bound thereto, one or more of metal cations, halide anions, and polyhalogen anions, or

from about 3 wt.% to about 19 wt.%, or from about 3 wt.% to about 18 wt.%, or from about 3 wt.% to about 17 wt.%, or from about 3 wt.% to about 16 wt.%, or from about 3 wt.% to about 15 wt.%, or from about 5 wt.% to about 15 wt.%.

[0108] In embodiments, the molar ratio of sulfur to one or more of metal cations having a valency of two or more, halide anions, and polyhalogen anions in the sulfur cathode is from about 500 to about 10, or from about 400 to about 20, or from about 300 to about 50.

Preparation of sulfur cathodes

[0109] The presently disclosed sulfur cathodes may be prepared by combining one or more binding polymers and one or more metal cations having a valency of two or more; halide anions; or polyhalogen anions.

[0110] In embodiments, the metal cations may in the form of nitrate salts although other sources of the metal cations are contemplated. The halide anions may be in the form of lithium salts, although other sources of halide ions are contemplated.

[0111] The combining may be typically performed in water, although other solvents may be utilised.

[0112] Optionally, one or more structural materials may be added so as to form a binder slurry.

[0113] To prepare the final cathode slurry, a source of sulfur and a conducting material are added.

[0114] Methods typically used in the art may be utilised to form the final sulfur cathode, for example they may be prepared by coating the cathode slurry on aluminium foil and drying. Optionally, the coated foil may be subjected to calendering.

Lithium sulfur batteries

[0115] The present disclosure provides a lithium sulfur battery comprising a lithium anode, a separator, the cathode according to any one of the herein disclosed embodiments, and electrolyte disposed between the anode and cathode.

[0116] Typical separators known in the art of lithium sulfur batteries may be employed.

[0117] Coin cells comprising the presently disclosed sulfur cathodes may deliver high areal capacities at 0.5C, 1C and 2C with sulfur loadings ≥ 3 mg/cm^2.

[0118] Coin cells comprising the presently disclosed sulfur cathodes may deliver an initial areal capacity of 6.7 mAh cm^{-2} at 0.5C at a sulfur loading of 7 mg/cm^2.

[0119] A pouch cell comprising the presently disclosed sulfur cathodes may be stable over 55 cycles at 0.3C.

Certain embodiments

[0120] Certain embodiments of the present disclosure include the following:

[0121] **Embodiment 1**: A sulfur cathode comprising:

a) one or more sulfur containing materials;

b) one or more conductive materials;

c) one or more:

(i) metal cations having a valency of two or more;

(ii) halide anions;

(iii) polyhalogen anions;

or mixtures thereof; and

(d) one or more binding polymers, said binding polymers being capable of binding one or more of metal cations having a valency of two or more, halide anions, or polyhalogen anions.

[0122] **Embodiment 2:** A sulfur cathode comprising:

a) one or more sulfur containing materials;

b) one or more conductive materials;

c) one or more binding polymers having bound thereto one or more of:

(i) metal cations having a valency of two or more;

(ii) halide anions; or

(iii) polyhalogen anions.

[0123] Embodiment 3: An electrochemical storage device comprising a lithium anode, a separator, the sulfur cathode according to embodiment 1 or embodiment 2, and electrolyte disposed between the anode and cathode.

[0124] Embodiment 4: The sulfur cathode according to embodiment 1 or embodiment 2, or the electrochemical storage device according to embodiment 3, wherein the sulfur cathode further comprises one or more structural materials

[0125] Embodiment 5: The sulfur cathode or the electrochemical storage device according to embodiment 4, wherein the one or more structural materials have higher mechanical strength and/or viscosity compared to the one or more binding polymers.

[0126] Embodiment 6: The sulfur cathode or the electrochemical storage device according embodiment 4 or embodiment 5, wherein the one or more structural materials comprise one or more cellulose derivatives.

[0127] Embodiment 7: The sulfur cathode or the electrochemical storage device according to embodiment 4 or embodiment 5, wherein the one or more structural materials comprise one or more of carboxymethyl cellulose, anionically functionalised cellulose nanofibres, and alginate salts.

[0128] Embodiment 8: The sulfur cathode according to any one of embodiments 1, 2, or 4 to 7, or the electrochemical storage device according to any one of embodiments 3 to 7, wherein the one or more sulfur containing materials comprise one or more of elemental sulfur, Li_2S, MoS_2, and sulfurised polymers.

[0129] Embodiment 9: The sulfur cathode according to any one of embodiments 1, 2 or 4 to 8, or the electrochemical storage device according to any one of embodiments 3 to 8, wherein the one or more conductive materials comprise one or more of carbon black, graphite, graphene, activated carbon, carbon nanotubes, and carbon fibre.

[0130] Embodiment 10: The sulfur cathode according to any one of embodiments 1, 2 or 4 to 9, or the electrochemical storage device according to any one of embodiments 3 to 9, wherein the one or more metal cations having a valency of two or more comprise one or more of iron (III), iron (II), manganese (II), cobalt (III), copper (II), zinc (II), aluminium (III), nickel (II), and gallium (III).

[0131] Embodiment 11: The sulfur cathode according to any one of embodiments 1, 2 or 4 to 10, or the electrochemical storage device according to any one of embodiments 3 to 10, wherein the one or more halide anions comprise one or more of bromide and iodide.

[0132] Embodiment 12: The sulfur cathode according to any one of embodiments 1, 2 or 4 to 11, or the electrochemical storage device according to any one of embodiments 3 to 11, wherein the one or more polyhalogen anions comprise one or more of I_3^-, I_5^-, and Br_3^-.

[0133] Embodiment 13: The sulfur cathode according to any one of embodiments 1, 2 or 4 to 12, or the electrochemical storage device according to any one of embodiments 3 to 12, wherein the one or more binding polymers comprise one or more of polyvinylpyrrolidone, poly(vinyl pyridine), poly(vinyl alcohol), polyether, and polysaccharide.

[0134] Embodiment 14: The sulfur cathode or electrochemical storage device according to embodiment 13, wherein the one or more binding polymers comprise polyvinylpyrrolidone.

[0135] Embodiment 15: The sulfur cathode or electrochemical storage device according to embodiment 13 or embodiment 14, wherein the one or more binding polymers have a weight average molecular weight from about 2,500 to about 3,000,000 Daltons.

[0136] Embodiment 16: The sulfur cathode according to any one of embodiments 1, 2 or 4 to 15, or the electrochemical storage device according to any one of embodiments 3 to 15, wherein the molar ratio of sulfur to one or more of metal cations having a valency of two or more, halide anions, and polyhalogen anions is from about 500 to about 10.

[0137] Embodiment 17: The sulfur cathode according to any one of embodiments 1, 2 or 4 to 16, comprising:

a) about 50 wt.% to about 80 wt.% of one or more sulfur containing materials;

b) about 10 wt.% to about 30 wt.% of one or more conductive materials;

c) about 0.1 wt.% to about 5 wt.% of one or more of metal cations having a valency of two or more, halide anions, and polyhalogen anions; and

d) about 2 wt.% to about 20 wt.% of one or more polymers capable of binding one or more of metal cations, halide anions, and polyhalogen anions.

[0138] Embodiment 18: The sulfur cathode according to any one of embodiments 1, 2 or 4 to 16, comprising:

a) about 55 wt.% to about 75 wt.% of one or more sulfur containing materials;

b) about 15 wt.% to about 25 wt.% of one or more conductive materials;

c) about 0.1 wt.% to about 5 wt.% of one or more of metal cations having a valency of two or more, halide anions, and polyhalogen anions; and

d) about 2 wt.% to about 20 wt.% of one or more polymers capable of binding one or more of metal cations, halide anions, and polyhalogen anions,

[0139] Embodiment 19: The sulfur cathode according to embodiment 17 or embodiment 18, further comprising about 2 wt.% to about 15 wt.% of one or more structural materials.

[0140] Embodiment 20: The sulfur cathode according to embodiment 19, wherein the one or more structural materials have higher mechanical strength and/or viscosity compared to the one or more binding polymers.

[0141] Embodiment 21: The sulfur cathode according to embodiment 19 or embodiment 20, wherein the one or more structural polymers comprise one or more cellulose derivatives.

[0142] Embodiment 22: The sulfur cathode according to embodiment 19 or embodiment 20, wherein the one or more structural polymers comprise one or more of

carboxymethyl cellulose, anionically functionalised cellulose nanofibres, and alginate salts.

[0143] Embodiment 23: The electrochemical storage device according to any one of embodiments 3 to 16, wherein the device exhibits higher oxidation and/or reduction currents relative to a device absent the one or more of metal cations having a valency of two or more, halide anions, and polyhalogen anions.

[0144] Embodiment 24: The electrochemical storage device according to any one of embodiments 3 to 16 or 23, wherein the device exhibits higher reduction peak potentials and/or lower oxidation peak potentials relative to a device absent the one or more of metal cations having a valency of two or more, halide anions, and polyhalogen anions.

[0145] Embodiment 25: The electrochemical storage device according to any one of embodiments 3 to 16, 23 or 24, wherein the sulfur cathode adsorbs and promotes the conversion of soluble lithium polysulfides to solid lithium sulfur species.

[0146] Embodiment 26: The electrochemical storage device according to any one of embodiments 3 to 16, or 23 to 25, wherein the sulfur cathode promotes reduction of soluble lithium polysulfides to solid lithium sulfide (Li_2S/Li_2S_2) during discharge and promotes the reverse oxidation of the solid lithium sulphides to liquid lithium polysulfides during charge.

[0147] Embodiment 27: The electrochemical storage device according to any one of embodiments 3 to 16, or 23 to 26, wherein, during charging or discharging, the sulfur cathode hinders the transport of soluble lithium polysulfides within the sulfur cathode.

[0148] Embodiment 28: The electrochemical storage device according to any one of embodiments 3 to 16, or 23 to 27, wherein, during charging or discharging, the sulfur cathode promotes the transport of lithium ions within the sulfur cathode.

[0149] Embodiment 29: The electrochemical storage device according to any one of embodiments 3 to 16, or 23 to 28, wherein, during charging or discharging, the sulfur cathode limits the diffusion of polysulfides from the sulfur cathode.

[0150] Embodiment 30: The electrochemical storage device according to any one of embodiments 3 to 16, or 23 to 29, wherein the device exhibits improved C rate/current

density relative to a device comprising a sulfur cathode absent the one or more of metal cations having a valency of two or more, halide anions, and polyhalogen anions.

[0151] **Embodiment 31**: Use of the sulfur cathode according to any one of embodiments 1, 2 or 4 to 16, in an electrochemical storage device.

[0152] **Embodiment 32**: The use according to embodiment 31, wherein the electrochemical storage device is a lithium sulfur battery.

[0153] **Embodiment 33**: A binder for a sulfur cathode comprising:

a) one or more of metal cations having a valency of two or more, halide anions, and polyhalogen anions;

b) one or more binding polymers, said binding polymers being capable of binding, or having bound thereto, one or more of metal cations, halide anions, and polyhalogen anions; and

c) one or more structural materials.

[0154] **Embodiment 34**: A method of preparing a binder for a sulfur cathode comprising:

a) combining one or more of metal cations having a valency of two or more, halide anions, and polyhalogen anions, with one or more binding polymers capable of binding the one or more of metal cations, halide anions, and polyhalogen anions; and

b) optionally combining the product of step a) with one or more structural materials.

Examples

Materials

[0155] Elemental sulfur was purchased from Sigma-Aldrich. Conductive carbon powder as CABOT black pearl 2000 was purchased from Shandong Gelon LIB Co., LTD, China. Carboxymethylcellulose (CMC) structural material, polyvinylpyrrolidone (PVP) (average M_w ~1,300,000 - ~40,000), polyvinyl alcohol (PVA) M_w 89,000 – 98,000, poly(ethylene oxide) (PEO) M_w 100,000, binding polymers, aluminium (III) nitrate

nonahydrate, copper (II) nitrate trihydrate, zinc (II) nitrate hexahydrate, gallium (III) nitrate hydrate, iron (III) nitrate nonahydrate, and lithium iodide were purchased from Sigma-Aldrich. Carbon-coated glass fibre interlayer comprised of carbon (ASAC30, Adven Industries Inc., Canada), Gum Arabic (HawkinsWatts) and glass fibre (BG03013 separator, Hollingsworth & Vose, USA). Bis (trifluoromethane) sulphonamide lithium salt and lithium nitrate were purchased from Sigma-Aldrich and directly used without any further purification. DME and DOL solvent was purchased from Sigma-Aldrich. Li_2S was purchased from Alfa Aesar for lithium polysulfide synthesis. Battery-grade Al foil was purchased from Japan Capacitor Industrial Co. Celgard 2730 separator was purchased from Celgard Inc., USA. Lithium chips (16*0.2 mm) were purchased from Shandong Gelon LIB Co., LTD, China.

Example 1: Preparation of binders with PVP-iodide

[0156] A number of polyvinylpyrrolidone iodide (PVP-I) complexes were prepared by combining PVP and LiI, followed by addition of carboxymethylcellulose (CMC) structural material to afford CMC/PVP-I binders.

[0157] For example, 5 wt.% polyvinylpyrrolidone; Mw ~1,300,000 (PVP) was dissolved in 3 ml of deionized (DI) water. After the PVP was fully dissolved in DI water, 5 wt.% LiI was added to the solution to produce a PVP-I complex. The solution changed colour from colourless to dark orange upon addition of the LiI. Next, 5 wt.% carboxymethylcellulose (CMC) was added to the PVP-I solution and stirred for 1h to afford the final binder solution.

[0158] Further CMC/PVP-I binders were prepared by varying the PVP/LiI weight ratio. Additionally, control binders of CMC alone, CMC/PVP and CMC-I were also prepared for comparison with the CMC/PVP-I binders. Table 1 collects the composition details. For each composition, the balance to 100 wt.% is deionised water (DI).

Table 1

	Component (wt.%)		
	CMC	**PVP**	**LiI**
CMC/PVP-I	5	5	5
CMC/PVP-I	5	6.5	3.3
CMC/PVP-I	5	7.5	2.5

Table 1			
	Component (wt.%)		
	CMC	PVP	LiI
CMC/PVP (Control)	10	5	0
CMC (Control)	15	0	0
CMC-I (control)	10	0	5

Example 2: Preparation of sulfur cathodes

[0159] Sulfur (65 wt%) and conductive carbon (20 wt%) were mixed for 24 hours using a magnetic stirring bar, followed by adding each binder solution of Example 1 (600 rpm, about 22°C). The resulting slurry was stirred for another 24 hours to make a homogenous slurry (each binder system in 3 ml of DI water was used for 1 g of dry components in the final slurry for all slurries). The slurries were coated by the doctor blade technique on a battery-grade Al foil and dried at room temperature for about 10 hours, followed by 12 h drying in a vacuum at 80°C. Table 2 collects the composition details of the cathodes.

Table 2					
Cathode	Cathode composition (wt.%)				
	CMC	PVP	LiI	Sulfur	Carbon
CMC/PVP-I	5	5	5	65	20
CMC/PVP-I	5	6.6	3.3		
CMC/PVP-I	5	7.5	2.5		
CMC/PVP (Control)	10	5	0		
CMC (Control)	15	0	0		
CMC/LiI (control)	10	0	5		

Example 3: Characterisation of polymer-halide binders

[0160] Several comparative tests were performed to confirm the existence of iodide and the polyhalogen anions I_3^- and I_5^- in the CMC/PVP-I binder system. Ultraviolet-visible spectra were measured for the CMC/PVP-I, CMC/PVP and CMC binder solutions and these are illustrated in **Figure 1**. UV-Vis spectra of the CMC/PVP-I binder

confirmed the presence of I^- and I_3^- with absorbance peaks at 291 and 361nm corresponding to I_3^- and an absorbance peak at 226 nm corresponding to I^-. Further, each binder solution was drop cast on a glass slide, dried and collected for Raman analysis. Raman spectra were obtained for each binder using a Renishaw Confocal micro-Raman Spectrometer equipped with Ar-ion 514 nm laser excitation operating at 10% power. Extended scans with an accumulation time of 30 s were performed between 100 and 600 cm^{-1} range with a laser spot size of 1 μm.

[0161] Raman spectra (**Figure 2**) showed the characteristic vibrations of polyiodides, with peaks located between 110 and 120 cm^{-1} assigned to the symmetric stretching mode of I_3^-, while a peak between 150 and 160 cm^{-1} was assigned to the linear symmetric stretching mode of I_5^-. All of these peaks in the UV-Vis and Raman spectra were not present in the spectra of CMC or CMC/PVP.

[0162] **Figure 3** shows SEM images for three different cathode compositions of Table 2. As evident in Figure 3a, discrete fine particles with minimal binder coverage are present in CMC/PVP-I containing cathode. In contrast, CMC/PVP (Figure 3b) and CMC (Figure 3c) containing cathodes have large, segregated clusters with highly localized and continuous binder coverage which reduces the electrolyte diffusion in the cathodes. Energy dispersive X-ray (EDX) mapping of the CMC/PVP-I containing cathode (Figure 3d) illustrated the initial uniform distribution of iodide species.

Example 4: Assembly of coin cells

[0163] Coin cells were assembled under argon atmosphere in a glove box. A lithium foil was used as a counter electrode and a Celgard membrane (Celgard 2730, 20 μm thickness, 16 mm diameter, 1 μm pore size, and 43% porosity) was used as the separator. A glass fibre interlayer was coated with an aqueous slurry of activated carbon (80 wt. %) and Gum Arabic (20 wt. %), followed by overnight drying at 100°C under a vacuum to remove all traces of water, and was used as a conductive layer on sulfur cathodes (prepared as in Example 2). 0.25 M Bis (trifluoromethane) sulphonamide lithium and 0.75 M lithium nitrate in 1:1 by a volume mixture of 1,3-dioxolane and dimethoxymethane was used as the electrolyte. The sulfur loading for the coin cell cathode (1 cm × 1 cm) was from 3 mg cm^{-2} to 7 mg cm^{-2}. The electrolyte-to-sulfur ratio (E/S ratio) ranged from 11–20 $\mu L mg^{-1}$, depending on the sulfur loading. For example, a cathode with sulfur loading of 3 mg cm^{-2},15 μL of electrolyte was used to

wet the cathode. To wet the carbon-coated glass fibre and Celgard separator, 45 µL of electrolyte was used. For cathodes with sulfur loading of 4 to 7 mgcm^{-2}, 20 µL of electrolyte was used to wet the cathode. To wet the carbon-coated glass fibre and Celgard separator, 60 µL of electrolyte was used. Typically, an E/S ratio larger than 20 µLmg^{-1} is defined as electrolyte-flooded conditions and E/S ratio lower than 5 µLmg^{-1} is defined as lean-electrolyte conditions.

Example 5: Testing of coin cells

[0164] To assess the electrochemical performance of the coin cells, cathodes with CMC/PVP-I binder were compared with controls containing CMC/PVP and CMC binders. Cells were cycled at 0.5C, 1C, 1.5C and 2C with with sulfur loadings from 3 to 7 mg cm^{-2}.

[0165] At a high rating of 1C, the cell containing the CMC/PVP-I binder system and 3 mg cm^{-2} sulfur loading delivered an initial discharge capacity of 1031.81 mAh g^{-1} with CE above 99% (**Figure 4**) (1C =1675 mA g^{-1}). This cell maintained 80% capacity retention after 200 cycles, indicating electrochemical stability of CMC/PVP-I containing cathodes at high sulfur loading. In contrast, the cell with CMC/PVP and CMC containing cathodes delivered lower initial capacities of 863.77 and 756.54 mAh g^{-1}, respectively. The performance of coin cells with CMC/PVP-I binders with varying PVP to LiI mass ratio (1:1, 2:1 and 3:1) were also tested at a 1C rate. While all coin cells performed well, the cell containing the binder with a PVP to LiI weight ratio of 2:1 exhibited the best performance.

[0166] To analyse the role of PVP in the binder system, CMC-LiI cathodes were also constructed. The CMC/LiI cell exhibited low capacities at 1C rate and the results are illustrated in **Figure 5**. Without being bound by theory it is hypothesised that without the anchoring role of PVP in the binder system, rapid iodide shuttling may be prevalent and the iodine species may lose efficacy in the absence of being intimately held within the cathode structure.

[0167] Even at a very high rating of 2C, CMC/PVP-I containing cathodes delivered a discharge capacity of 736.93 mAh g-1 for coin cells with 3 mg cm^{-2} sulfur loading (at a high areal current of 10 mA cm^{-2}), as shown in **Figure 6**. This cell showed 70% capacity retention after 200 cycles at 2C with a CE of > 99%. This performance indicated that the

CMC/PVP-I binder system had an excellent ability to improve polysulfide redox kinetics and facilitate high C rates in Li-S batteries. In contrast, the CMC/PVP containing cathodes exhibited a 469.88 mAh g^{-1} discharge capacity at a 2C rate, and CMC containing cathodes delivered only 203.09 mAh g^{-1}. CMC containing cathodes could not maintain the charge-discharge plateaus at a 2C rate and could not deliver more than 200 mAh g^{-1} after only one cycle.

[0168] At a sulfur loading of 5 mg cm^{-2}, CMC/PVP-I containing coin cells delivered initial discharge capacities of 1084.3 mAh g^{-1} and high areal capacities of 5.5 with 100 stable cycles at 0.5C. When increasing the sulfur loading to 7 mg cm^{-2}, the cell still delivered a specific capacity of 956.9 mAh g^{-1} (6.7 mAh cm^{-2}), indicating that the CMC/PVP-I containing cathode had a high-capacity retention with increasing sulfur loading, even at high current densities. Moreover, at 4 mg cm^{-1} sulfur loading, the CMC/PVP-I containing cathodes maintained 100% capacity retention after 250 cycles at 0.5 C rate, as shown in **Figure 7**.

[0169] A rate capability test of CMC/PVP-I, CMC/PVP and CMC containing cathodes at 0.1C to 2C (sulfur loadings of 3 mg cm^{-1}) was conducted. The CMC/PVP-I containing cathode delivered excellent rate capability performance compared to CMC and CMC/PVP containing cathodes. When increasing the C rate from 0.1C to 1C and 1C to 2C, CMC/PVP-I containing cathodes maintained 73% and 69% of high discharge capacity. The CMC/PVP containing cathodes maintained a moderate discharge capacity of 67% when increasing the C rate from 0.1C to 1C, and 52% when increasing the C rate further, from 1C to 2C. The CMC cathodes maintained 68%, and a very low discharge capacity of 31 % when increasing the C rates from 0.1C to 1C and 1C to 2C respectively. These results indicated the inability of CMC cathodes to run at increasing current densities. However, compared with the CMC binder system, the CMC/PVP binder system showed significantly improved rate capability.

[0170] From the coin cell performance, it can be concluded that that the CMC/PVP-I binder system had combined metrics of specific capacity, areal capacity, and cycle life at high current densities, which has to date been difficult to achieve in Li-S batteries.

Example 6: Pouch cell preparation

[0171] For sulfur cathode preparation, a cathode slurry (as prepared in Example 2) was coated on both sides of Al foil, with a sulfur loading of 3 mg cm^{-2}. Double-side electrodes (5 cm × 3cm) were used for pouch cell fabrication and the Al tab was welded on the sulfur cathode. Next, a carbon-coated thin glass fiber interlayer (5.2 cm × 3cm) was stuck to the double-sided cathode, followed by stacking with a Celgard separator. The sack was then transferred to a glovebox to place Li-anodes on the Celgard separator's other side. For the Li anode, 0.05 mm thickness Li was used in 0.3 C pouch, and 0.1 mm thickness Li was used in 0.1 C and 0.2 C pouch. The Li anode was also cut into the same size as the sulfur cathode, 5 cm × 3cm. A two-spot welder was used to bond Ni tab onto the anode. The desired amount of electrolyte was injected into the stack and the pouch cell package was sealed under the vacuum inside the glove box. All pouch cells were assembled in an Ar-containing glove box (<0.1 ppm H_2O and (<0.1 ppm O_2).

Example 7: Pouch cell testing

[0172] Double-sided cathodes with 3 mg/cm^2 sulfur on each side were assembled in three and one-layer pouches with a total sulfur content of 95 mg and 275 mg, respectively. The pouches were cycled at 0.3C after five activation cycles at 0.1C. This pouch cell showed initial discharge capacities of 1197.9 at 0.1C and 938.0 mAh g^{-1} at 0.3C, with a capacity retention of 90% at 0.3 C over 55 cycles and CE >98%. The cell maintained typical charge-discharge curves of the two recognized plateaus, indicating that the profiles were well-developed and maintained even at 0.3 C. The three-layer pouches with an energy density of 213.29 Wh Kg^{-1}, provided a high specific discharge capacity of 1144.8 mAh g^{-1}, CE more than 95%, with a capacity retention of 81% after 50 cycles at 0.1C rate. The pouch cells cycled at 0.1 and 0.3C delivered an impressive areal capacity (single side) of 3.5 and 3 mAh cm^{-2}, respectively.

Example 8: Electrochemical characterisation of CMC/PVP-I binder

[0173] The electrochemical behaviour of the CMC/PVP-I containing cathode was studied to determine the influence of a CMC/PVP-I binder on cell reaction kinetics. Coin cells were analyzed by cyclic voltammogram (CV), lithium-ion diffusion coefficient (D_{Li^+})

measurements, electrochemical impedance spectroscopy (EIS), and galvanostatic charge-discharge.

[0174] A Li-S battery has a two-step reduction process wherein the first reduction peak at ~ 2.4 V (C_1) represents the reduction of sulfur to liquid Li_2S_8 and its further reduction to other soluble higher-order polysulfides, Li_2S_n ($4 \leq n < 7$), as shown in **Figure 8**. The reduction of these higher-order polysulfides to solid Li_2S_2 and Li_2S can be observed at a second peak at a ~ 2 V (C_2). An oxidation peak (A) around 2.2 to 2.6 V is observed during the anodic scan. As shown in **Figure 8**, the CMC/PVP-I containing cathode exhibited enhanced currents in the second reduction peak (C_2) and anodic peak (A), which may be explained by accelerated kinetics in the liquid-solid-liquid transition of sulfur and LiPS during the discharge and charge process. More importantly, the CMC/PVP-I containing cathodes exhibited higher reduction peak potentials and lower oxidation peak potentials than CMC/PVP and CMC containing cathodes. Therefore, the CMC/PVP-I binder appears to lower the polarization by facilitating enhanced polysulfide conversion kinetics and providing a low charge transfer barrier.

[0175] Rate-dependent CV curves indicated that CMC/PVP-I and CMC/PVP containing cathodes exhibited nearly similar peak currents in the first cathodic peak, indicating the likely role of PVP in adsorbing and promoting the conversion of higher-order LiPS. However, in the second reduction peak, C_2, and the oxidation peak, A, the CMC/PVP-I containing cathode showed significantly higher currents than CMC/PVP and CMC containing cathodes, emphasizing the contribution of I^-/ I^{3-} redox couple in promoting liquid-to-solid reaction kinetics during reduction and solid-to-liquid reaction kinetics during oxidation.

[0176] Rate-dependent CV curves were used to calculate the lithium-ion diffusion coefficient (D_{Li^+}) using the Randles-Sevick equation. The CMC/PVP-I containing cathode gave an improved D_{Li^+} value of 1.07×10^{-7}, 4.5×10^{-7} and 6.3×10^{-7} $cm^2\ s^{-1}$ for C_1, C_2 and A peaks respectively. In contrast, CMC/PVP and CMC containing cathodes gave D_{Li^+} values of 1.02×10^{-7}, 3.1×10^{-7} and 4.9×10^{-7}, and 0.71×10^{-7}, 3.0×10^{-7} and 4.0×10^{-7} $cm^2\ s^{-1}$ for C_1, C_2 and A peaks respectively, the trend being consistent with the CV studies. In summary, the PVP-I component of the binder accelerated the full range of redox kinetics in the Li-S batteries.

[0177] EIS was performed at fully charged states before and after 100 cycles at 1C rate. The CMC/PVP-I containing cathode exhibited smaller semi-circles compared to the control samples and yielded lower charge transfer resistance (R_{ct}) before the cycling process and even after intense cycling at a 1C rate. This may be attributed to the accelerated reaction kinetics of CMC/PVP-I containing cathodes, which limited polysulfide shuttling and solid Li_2S/Li_2S_2 precipitation and dissolution, paving pathways to enhanced ionic conduction and charge transfer.

[0178] In the galvanostatic charge-discharge profile a first plateau observed at around 2.4 V, and a following ramp until ~ 2 V, was associated with the liquid-liquid transition of higher-order LiPS. In comparison, a second plateau at 2.1 V and a ramp until 1.8V were associated with the liquid-solid transition of LiPS to Li_2S. It was apparent that a significantly lower polarization was observed for CMC/PVP-I containing cathodes (0.31V) compared to CMC/PVP (0.37V) and CMC (0.38V) containing cathodes at 1C.

[0179] The onset of the second plateau for CMC/PVP-I containing cathodes is at a higher discharge capacity of 398.33 mAh g^{-1} than the other two binder systems, supporting the notion that PVP-I enhances liquid-liquid reaction kinetics. The CMC/PVP-I system has an extended lower plateau of 633.5 mAh g^{-1} at 1C, compared to CMC/PVP and CMC which are 500.22 and 436.71 mAh g^{-1} respectively. These results also supported the hypothesis that the CMC/PVP-I binder offers a favorable interface and improved liquid-solid phase transitions. In the charging process, the CMC/PVP-I containing cathodes exhibit a lower potential barrier, explaining the lower overpotential compared to other binder systems in converting solid Li_2S back to LiPS. Moreover, the CMC/PVP-I system also improved the Li^+ transfer, representing higher upper and lower plateau voltages. Importantly, the charge-discharge curves at 2C indicated that the CMC/PVP-I containing cathodes maintained the discharge curve with two plateaus throughout the cycling whereas cathodes with CMC absent PVP-I failed to develop a second plateau.

Example 9: Mechanisms in promoting sulfur kinetics

[0180] Li_2S_6 solution was prepared following a literature method (Liao, K. et al. Stabilization of polysulfides via lithium bonds for Li–S batteries. J. Mater. Chem. A 4, 5406–5409 (2016)). Elemental sulfur and Li_2S powder were mixed in a solvent of DOL and DME solvent (DOL/DME 1:1 v/v) at 50 °C for 36 h under stirring in an argon glove

box and with a molar ratio of 8:5 ($8Li_2S+5S_8 \rightarrow 8Li_2S_6$). The product was centrifuged at 3610.7 × g for 10 minutes to remove particles, and the remaining red-brown solution contained Li_2S_6.

[0181] 50 mg of PVP and CMC were each soaked in 6 ml of Li_2S_6 solution. The supernatants were collected, diluted and analysed by UV-Vis spectroscopy. The concentration of Li_2S_6 was 2mmol/L in DOI/DME (1:1 v/v) after the dilution.

[0182] When Li_2S_6 solution was mixed with PVP a dark brown precipitate formed. Such a precipitate did not form when Li_2S_6 was mixed with CMC. The LiPS species may be enclosed within the PVP polymer structure as indicated by UV-Vis adsorption studies of the supernatants, where the presence of PVP showed high Li_2S_6 adsorption. FTIR studies of the precipitate sample of PVP+Li_2S_6, showed S-S peaks at 490-495cm^{-1} attributed to S_6^{2-} and peak at 480 cm^{-1} is attributed to S_3^{2-} species, indicating that PVP provides an energetically suitable interface for LiPS reactions due to the high affinity of LiPS towards PVP. FTIR was performed using an attenuated total reflectance FTIR spectrometer (PerkinElmer, USA) in the range of 400–4000 cm^{-1} at an average of 32 scans.

[0183] Without being bound by theory it is proposed that the polyiodides influence the Li-S reaction kinetics through the following pathways,

$$S_n^{2-} + 3I^- \rightleftharpoons S^{2-} / S_2^{2-} + I_3^- \qquad (4 \leq n < 8)$$

$$S_n^{2-} + 5I_3^- \rightleftharpoons S^{2-} / S_2^{2-} + 3I_5^- \qquad (4 \leq n < 8)$$

[0184] During the reduction of a Li-S cell, I^- is oxidized to I_3^- and I_5^-, and promotes the formation of solid Li_2S_2 /Li_2S from sulfur and other higher-order LiPS by the forward reactions in Eq. (1 and 2), enhancing cell capacity and reversibility. During oxidation, polyiodides promote the conversion of solid Li_2S/ Li_2S_2 back to liquid LiPS and sulfur, lowering the high potential barrier in the charging process and reducing the cell overpotential via the backward reactions in Eq (1 and 2).

[0185] To evidence the hypothesis of an alternative, lower-energy reaction pathway for liquid-solid reactions in Li-S batteries, *ex-situ* Raman spectroscopy analysis on the cathodes were performed, focusing on the iodine species at different points along the

charge and discharge curve. **Figure 9** is a schematic diagram of the contribution of the CMC/PVP-I binder system to improving fast charging capability.

[0186] Coin cells with CMC/PVP-I and CMC/PVP binder systems were discharged to 2.8 (OCV), 2.4, 2.3, 2.1, 1.9 and 1.8 V. Another set of coin cells from each binder system was first discharged to 1.8 V and then charged back to 2.2V, 2.4V and 2.8V. These cells were opened, and their cathodes were removed after washing with DOL/DME (1:1 v/v) solution, followed by drying. Raman spectra were obtained for each cathode using a Renishaw Confocal micro-Raman Spectrometer equipped with Ar-ion 514 nm laser excitation operating at 10% power. Extended scans with an accumulation time of 30 s were performed between 100 and 600 cm^{-1} range with a laser spot size of 1 μm.

[0187] Discharging from full charge 2.8V to the first plateau at 2.3V (**Figure 9**, Region 1), peaks for S_8 at 150, 219, 474 cm^{-1} and S_4^{2-} at 246 and 439 cm^{-1} were observed in agreement with literature values. The peaks for I_3^- or I_5^- were not observed between 2.8V to 2.3V, and cells with CMC/PVP-I binder and control cells had similar Raman spectra. This is likely because I^- is more dominant than I_3^- or I_5^- in this voltage limit. The other possible reason is that iodine species are in very low concentration (~3%) in the CMC/PVP-I binder system compared to active material, sulfur (65%) in the cathode. Hence, the high-intensity sulfur peaks in Region 1, may hinder the observation of iodine species in this voltage limit 2.8V to 2.3V.

[0188] In Region 2, at the second plateau, starting at 2.1V, the S_8 peaks at 150 cm^{-1} and 470 cm^{-1} were reduced into other LiPS and Li_2S. The peaks for Li_2S, S_6^{2-}, S_2^{2-} and S^{3-} appear at 370, 394, 449 and 520 cm^{-1} continue until the lowest discharge voltage, 1.8V. Interestingly, a sharp peak between 110 cm^{-1} and 120 cm^{-1} emerged, indicating the symmetric stretching mode of the I_3^- in the second plateau at 2.1V. This I_3^- peak continues until 1.8V, supporting the hypothesis of I^- to I_3^- oxidation while the sulfur is reduced to lower-order LiPS. This I_3^- peak was clearly visible in Region 2 due to the high concentration of I_3^- formed via the forward reaction in Eq (1). It was also observed that the S_8 peak at 150 cm^{-1} experienced a peak shift and became more prominent in region 2, at 2.1 V to 1.8V. Hence, this shifted peak in the CMC/PVP-I containing cell was possibly due to the overlap of the linear symmetric stretching mode of I_5^- with the S_8 peak. This could be further confirmed by observing control cells without PVP-I, where the S_8 peak at 150 cm^{-1} had almost disappeared and no peak shift was observed in

Region 2. The peak trends continued until full discharge at 1.8V, while the peaks for lower-order polysulfides became more pronounced in CMC/PVP-I containing cells, in contrast to the CMC/PVP containing cell. The CMC/PVP containing cell showed peaks for higher-order polysulfides, S_6^{2-}, S_4^{2-}+ S_5^{2-} and S_7^{2-}+ S_8^{2-} at 328, 415 and 484 cm^{-1} even at full discharge 1.8V. These polysulfides peaks were absent in the CMC/PVP-I containing cells, indicating improved conversion of higher-order LiPS to lower-order LiPS, due to the presence of iodide species. The control cathodes containing PVP/CMC and CMC showed no peaks in the polyiodide region of the Raman spectra. The results suggested that iodide was oxidized to I_3^- and further oxidized to I_5^-, promoting the formation of liquid to solid reaction kinetics via the forward reactions in Eq 1 and 2 during the reduction of the cell.

[0189] To test the reversibility of the forward reactions in Eq (1) and (2), ex-situ Raman studies were performed on the charge process. In Region 3, the charging region, the peaks for sulfur reappeared at 2.4 to 2.8 V with the disappearance of polyiodide peaks of I_3^- and I_5^- in CMC/PVP-I containing cathodes. The absence of polyiodide peaks implied that polyiodides are converted back to I^- in the charging process. This makes the Raman spectra of CMC/PVP-I containing cathodes similar to control cathodes containing PVP/CMC in the charging process. These observations provided evidence for the promotion of solid-to-liquid reaction kinetics by the CMC/PVP-I binder due to the occurrence of the reverse chemical redox reaction in Eq (1) and (2).

[0190] The UV-Vis adsorption spectra of PVP-I, Li_2S_6+PVP-I and Li_2S+PVP-I in DOL/DME solutions were further analysed to validate the reaction in Eq (1). For the Li_2S evolution experiment, 200 mg of Li_2S powder was dissolved in a 6ml DOl/DME (1:1 v/v) solution. 50mg of PVP-I was added to Li_2S solution and the supernatant liquid was removed for UV-Vis spectroscopic analysis. For the Li_2S_6 evolution experiment, 50 mg of PVP-I was soaked in 6 ml Li_2S_6 solution. The supernatant liquid was collected and diluted for the UV-Vis measurement. The final concentration of Li_2S_6 was 2mmol/L in DOl/DME (1:1 v/v) after dilution. The peak associated with I^- at 220 nm disappeared and both I_3^- peak intensities at 280 and 390 nm increased with the addition of LiPS into PVP-I, further supporting the forward reaction in Eq (1). In contrast, when an excess amount of Li_2S was added to PVP-I, the I_3^- peaks at 280 and 390 nm almost disappeared, supporting the reverse reaction in Eq (1).

[0191] The FTIR spectra for PVP-I before and after adding Li_2S_6 further supported the hypothesis of iodide-mediated sulfur reactions. No peaks were present in the S-S bond region 450 – 520 cm^{-1} for pure PVP-I. This precipitate exhibited S-S peaks for S_4^{2-} at 487 cm^{-1} and S_3^{2-} at 480 cm^{-1} and S_2^{2-} at 472 cm^{-1} representing the formation of Li_2S_4, Li_2S_3, and lower order polysulfide Li_2S_2 and in agreement with literature values. However, a peak observed for PVP+Li_2S_6 at around 495cm^{-1}, attributed to Li_2S_6, disappeared with PVP-I. Therefore, the absence of Li_2S_6 and the presence of Li_2S_2 further confirmed that iodides can reduce higher-order LiPS via Eq (1) and (2).

[0192] Kinetic experiments using symmetric cells were performed to further support the notion that PVP-I promotes liquid-liquid LiPS conversion in Region 1 and accelerates liquid-solid reaction kinetics and solid-liquid reaction kinetics in Region 2 and Region 3, respectively.

[0193] Li_2S_6 symmetric cells were analysed to further explore the high affinity of PVP towards higher-order LiPS in Region 1. The function of each binder system towards Li_2S_6 conversion was evaluated by assembling symmetric cells using two identical electrodes composed of carbon and binder, where Li_2S_6 solution serves as the electrolyte.

[0194] To assemble the symmetrical cells two identical electrodes (1 cm × 1 cm) and a Celgard membrane separator were used. 10 μL of 0.5 M Li_2S_6 and 15 μL of 0.25 M LiTFSI and 0.75 M $LiNO_3$ in DOL and DME (1:1, v/v) was used as the electrolyte to wet each electrode. Carbon and binder systems (CMC/PVP-I, CMC/PVP, CMC) were mixed with a 3:1 dry weight ratio to prepare the slurries for symmetric cell electrodes, followed by the same coating and drying method as for the sulfur cathodes. CV measurements were performed in the voltage window between -0.8 and 0.8 V under scan rates of 10 mV s^{-1}.

[0195] The symmetric cells with the CMC/PVP-I binder system showed a higher CV current response and peak area than control cells, PVP and CMC. The CMC/PVP-I binder had two distinct peaks in reduction and oxidation, representing the reduction of S_8 to Li_2S_6 and Li_2S_6 to Li_2S, respectively, and their reverse oxidization. It should be noted that the CMC/PVP symmetrical cell gave a higher current response than CMC owing to the high affinity of LiPS towards PVP in Region 1, illustrating fast redox reaction kinetics in higher-order LiPS conversion. The EIS spectra of symmetric cells

directly corresponded to the properties of the electrode-LiPS interface due to the absence of Li anode. In agreement with the CV results, the CMC/PVP-I binder system exhibited a significantly lower R_{ct} value than CMC/PVP and CMC, indicating enhanced Li_2S_6 reaction kinetics by the CMV/PVP-I binder system.

[0196] The Li_2S nucleation in Region 2 and dissolution in Region 3 is a key index in Li-S batteries as they have rate-limiting, sluggish reaction kinetics. For instance, precipitation of Li_2S from liquid LiPS requires more energy, and efficient transformation is required to reach the full potential of the Li-S cell, as this contributed to three-quarters of the theoretical capacity during the reduction. On the other hand, there is a larger energy barrier in converting solid Li_2S to LiPS during oxidation. Potentiostatic discharge-charge experiments were performed for three binder systems, using symmetric cell cathodes and Li_2S_8 catholyte.

[0197] Li_2S_8 solution was prepared following a literature method (Hong et al., Electrolyte with Low Polysulfide Solubility for Li–S Batteries ACS Appl. Energy Mater. 2018, 1, 6, 2608–2618). 0.92 g Li_2S and 4.48 g sulfur were dissolved in DOL: DME 1:1 (v/v) solvent under continuous stirring at 55°C for 48 h to form 0.5 M Li_2S_8 solution.

[0198] To assemble the cells CMC/PVP-I, CMC/PVP, CMC electrodes used in symmetric cell experiments were used as cathodes (1 cm × 1 cm). A lithium foil was used as a counter electrode and a Celgard membrane (Celgard 2730, 20 µm thickness, 16 mm diameter, 1 µm pore size, and 43% porosity) was used as the separator. As the catholyte and anolyte 15 µL of Li_2S_8 solution (0.5 $molL^{-1}$) and 15 µL of DOL/DME (v/v = 1/1) solution was used respectively. For Li_2S nucleation experiments, the cells with each binder system were first galvanostatically discharged at 0.05 C until the potential reached 2.09 V to consume most high-order LiPS. Then, to kinetically evaluate the nucleation and growth of Li_2S, cells were potentiostatically discharged at 2.08 V until the current decreased to 10^{-5} A. For the Li_2S dissolution experiments, the cells were first galvanostatically discharged at 0.05 C until the voltage decreased to 1.8 V to generate solid Li_2S. Then, to induce dissolution of Li_2S into higher-order LiPS, the cells were potentiostatically charged at 2.4 V until the current was below 10^{-5} A.

[0199] The CMC/PVP-I binder provided a sharp Li_2S nucleation peak with a much higher nucleation capacity of 241.3 $mAhg^{-1}$ than CMC/PVP binder (202.5 $mAhg^{-1}$) and CMC binder (183.34 $mAhg^{-1}$). Notably, a higher peak current response in a shorter

period was observed in the potentiostatic charge for the CMC/PVP-I system, which corresponds to fast Li_2S decomposition. Also, CMC/PVP-I binder generated a significantly high specific capacity of 603.0 $mAhg^{-1}$ in Li_2S decomposition. The CMC/PVP and CMC binders exhibited broader decomposition peaks with low capacities of 503.6 and 98.6 $mAhg^{-1}$, respectively. Hence, these results also gave insight into how the CMC/PVP-I binder system promotes solid-liquid-solid reaction kinetics in Li_2S dissolution and precipitation, which enables cycling Li-S cells even at high C rates.

[0200] In summary, *Ex-situ* Raman, UV-vis. and FTIR spectroscopies and symmetric cells studies revealed the important role of a CMC/PVP-I binder system in accelerating the slow redox kinetics and performing within the working voltage limit of Li-S batteries by lower energy reaction pathways via Eq (1) and (2).

Example 10: Ex situ post-mortem studies

[0201] The effect of acceleration of Li-S reaction kinetics on the lithium anode and sulfur cathodes was further characterised by ex-situ post-mortem examination of the electrodes by Scanning Electron Microscopy (SEM) after intense 100 cycles at 1C.

[0202] The Li anode of the CMC/PVP-I cathode had a homogeneous surface consisting of coalesced plating sites and was absent high surface area lithium deposits such as mossy growth or dead lithium even after intense cycling of 100 cycles at 1C. In contrast, both CMC/PVP and CMC exhibited high surface area lithium growths. High surface area lithium is associated with capacity fading due to electrolyte consumption. Without being bound by theory it is believed that the sluggish reaction kinetics of CMC/PVP and CMC cells cause the deposition of dead Li_2S on the anode surface, inducing Li dendrite growth. The solid-to-liquid reaction kinetic enhancement of the CMC/PVP-I binder system reduced the dead and insulating Li_2S deposition in CMC/PVP-I cathodes, limiting the corrosion of the anode surface.

[0203] To elucidate the role of the environment of the PVP-I versus an iodide only environment, the lithium anode of a CMC/LiI cell was compared to the lithium anode of the CMC/PVP-I cell. The direct addition of LiI into the cathodes without the PVP causes iodide shuttling over the cell. It induced pronounced corrosion of the Li anode. In contrast, the CMC/PVP-I binder system retained or slowed down the transportation of

iodides from the cathode side, limiting anode corrosion. This was evidenced by the more homogenous Li anode post-mortem studies of CMC/PVP-I cells.

Example 11: Preparation of binders with PVP-metal cation

[0204] 5 wt.% Polyvinylpyrrolidone; Mw ~1,300,000 (PVP) was dissolved in 2 ml of deionized (DI) water. After the PVP was fully dissolved, 3.75 wt.% $Al(NO_3)_3 \cdot 9H_2O$ was added to the solution to produce a PVP-Al complex. Next, 6.25 wt.% carboxymethylcellulose (CMC) was added to the PVP-Al solution and stirred for 1h to afford the final binder solution. This procedure was repeated by replacing $Al(NO_3)_3 \cdot 9H_2O$ with $Fe(NO_3)_3 \cdot 9H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$ and $Ga(NO_3)_3 \cdot xH_2O$ to make PVP-Fe, PVP-Cu, PVP-Zn and PVP-Ga binder systems respectively. This procedure was repeated by keeping the weight percentage of metals and binding polymers PVP having M_w of 40,000 or 360,000, PVA having an M_w of 89,000 – 98,000 and PEO having an M_w of 100,000, between 0.6-1.8 wt.% and 4.5 wt.%, respectively. Further variants were prepared by mixing a 1:1 weight ratio of metal cations with I^- as LiI. Still further variants were prepared absent CMC structural material by keeping the weight percentage of metals and binding polymers PVP having M_w of 360,000, PVA having an M_w of 89,000 – 98,000 and PEO having an M_w of 100,000, between 0.6-1.8 wt.% and 8-11 wt.% respectively. Even further variants were prepared by replacing part of the carbon in the cathode with 5 wt.% graphite.

Example 12: Preparation of sulfur cathodes

[0205] Sulfur cathodes using the PVP-metal cation binders were prepared following the method of Example 2.

Example 13: Assembly and testing of coin cells

[0206] Coin cells were assembled as in Example 4. Coin cells were cycled at high rates of 0.5C and 1C, with practical sulfur loadings of 3 mg cm^{-2}. As shown in **Figure 10**, cathodes composed of PVP-Zn and PVP-Al binder systems exhibited higher discharge capacities to the PVP-I binder system, with initial discharge capacities of 1287.17 and 1335.35 mAh g^{-1} at 0.5C rate. The discharge capacities of PVP-Fe, PVP-Ga and PVP-Cu were similar to the discharge capacities to the PVP-I system at 0.5C rate. When increasing the C rating to 1C (**Figure 11**), PVP-Zn and PVP-Al also exhibited higher discharge capacities of 1198.71 and 1073.72 mAh g^{-1}, respectively.

Cathodes composed of PVP-Fe, PVP-Cu and PVP-Ga showed moderately high discharge capacities at 0.5C, but lower capacities at 1C compared to PVP-I. Overall, the capacities of the PVP-metal cation complexes delivered high areal capacities in mAh cm^{-2}, given the high rates. The cathodes comprised of PVP-Al, PVP-Zn and PVP-Fe binder systems show high areal capacities, similar to the PVP-I system.

[0207] In order to further study the effect of the metal cation binder on sulfur electrochemical redox processes, CV curves were obtained and are compared in **Figure 12** at a scan rate of 0.1 mV s^{-1}. The cells composed of each binder show elevated peak currents. The PVP-Fe, PVP-Al and PVP-Zn cathodes exhibit higher reduction peak potentials and lower oxidation peak potentials, similar to the PVP-I system, indicating effective sulfur utilization, low polarization and rapid conversion kinetics. The cathodic peak currents C_1 and C_2, and anodic peak current A_1, of each catalytic binder system were compared with the peak currents of the PVP-I system as shown in **Figure 13.** The peak C_1 in each binder system shows comparable peak currents with the PVP-I system, showing improved affinity towards higher-order lithium polysulfides (LiPS) by PVP-metal cation binder systems, except for the PVP-Cu binder system. The peak C_2 at ~ 2 - 1.8 V represents the conversion of higher-order LiPS to lower-order Li_2S. The improved kinetics in this step are extremely important as it contributes to two-thirds of the theoretical capacity in Li-S batteries. As shown in **Figure 13,** PVP-Al, PVP-Fe, PVP Ga and PVP-Zn cathodes exhibted higher peak currents at peak C_2 than the PVP-I system, indicating accelerated reaction kinetics in liquid-to-solid sulfur reactions. The PVP-Al and PVP-Fe cathodes had high anodic peak "A" magnitudes at ~ 2.4 - 2.6 V, demonstrating enhanced kinetics in solid-to-liquid reactions in the oxidation of Li-S batteries.

Example 14: Conductive carbon/graphite cathodes

[0208] The cycling performance of coin cells containing 3 mg cm^{-2} sulfur loaded PVP-Zn, PVP-Al, PVP-Fe, PVP-Cu and PVP-Ga cathodes in which 5 wt.% of the 20 wt.% conductive carbon was replaced by graphite were evaluated. The results indicated that the incorporation of graphite improved stability of the cells over 150 cycles at a high C rate. The capacity retention of PVP-Zn, PVP-Al, PVP-Fe, PVP-Cu and PVP-Ga cathodes at 1C rates were 70, 100, 77, 98 and 83% respectively. The PVP-Zn binder system still delivered the highest discharge capacity of 1020.01 mAh g^{-1}, and the PVP-Cu binder system showed the lowest discharge capacity of 665.47 mAh g^{-1}, similar to

cathodes containing conductive carbon as the sole carbon source. The results are illustrated in **Figure 14**.

Example 15: Dual metal containing cathodes

[0209] PVP cathodes were prepared containing two different metal cations. PVP-Al/Fe and PVP-Zn/Fe coin cells showed lower discharge capacities than their comparative single metal systems, **Figures 15 a-b**. However, capacity retention increased with the dual metal systems. For example, PVP-Zn and PVP-Fe exhibited 71% and 77% capacity retention over 150 cycles, while PVP-Zn/Fe dual catalytic system showed 90% capacity retention (**Figure 15a**).

Example 16: Variation of PVP molecular weight

[0210] Li-S coin cells were assembled using PVP with M_w: 360,000 (**Figure 16**). Unlike the cells composed of PVP M_w 1,300,000, PVP-Cu and PVP-Al cells delivered excellent discharge capacities at 0.5 and 1 C rates. The PVP-Cu system showed the highest discharge capacity of 1232 and 1092 mAh g^{-1} at 0.5 and 1 C, respectively. Further, both cells composed of PVP-Al and PVP-Ga catalytic binders exhibited high cell stability over 150 cycles with capacity retention of 82.5 and 81.4%, respectively, at a 1C rate. In contrast to binders composed of high M_w PVP (360,000-1,300,000), cathodes manufactured with lower M_w PVP (40,000) showed lower discharge capacities at 1C rate in a PVP-Zn binder system (**Figure 17**).

Example 17: Polyvinyl alcohol (PVA) based binder

[0211] The cycling performance of coin cells containing 3 mg cm^{-2} sulfur loaded PVA-Zn, PVA-Al, PVA-Fe, PVA-Cu and PVA-Ga based cathodes at 0.5C and 1C rates were evaluated. The cells showed enhanced cycling performance. The binders were synthesized by immobilizing the metal species using the complexation agent PVA.

[0212] At a high C rating of 0.5C and 1C, the cell containing the PVA-Cu binder system and 3 mg cm^{-2} sulfur loading delivered the highest discharge capacities of 1311.02 and 1166.74 mAh g^{-1} respectively with CE above 99% (**Figure 18 (a) and (b)**). In contrast, the cell with the PVA-Al binder system delivered the lowest initial discharge capacities among all the PVA-based metal binder systems of 924.05 and 855.31 mAh g^{-1} at 0.5C

and 1C, respectively. Overall, Li-S coin cells with PVA-metal based cathodes deliver high capacities and coulombic efficiencies at high C rates.

Example 18: Cathodes absent structural material

[0213] The cycling performance of coin cells containing 3mg cm^{-2} sulfur loaded PVA*-Zn, PVP*-Zn, PEO*-Zn and PEO*-Fe cathodes at 0.5C and 1C rates without CMC in the binder system were evaluated. (PEO; Poly(ethylene oxide)). The asterisk indicates a system absent structural material.

[0214] Even in the absence of structural material (CMC) to enhance the mechanical strength during intense cycling, Zn-binder species PVA*-Zn, PVP*-Zn, PEO*-Zn and PEO*-Fe delivered higher cycling performance between 800-1000 mAh g^{-1} at 0.5C and 1 C rates (**Figure 19 a and b**). It should also be noted that the cells were stable for 250 cycles at 1C rate with the PVP-Zn and PVA-Zn binder systems.

Example 19: Polymer/metal halide based cathodes

[0215] Coin cell performance was evaluated by preparing sulfur cathodes containing metal halides as a single source of metal cation and halide. Discharge capacities around 800 mAh g^{-1} and coulombic efficiencies over 99% at 0.5C and 1C rates were obtained by complexing FeI with PVP* and PVA* polymer binding agents (**Figure 20**). For ZnI-polymer complexes, the ZnI-PVP system delivered superior initial discharge capacities of 844.57 and 835.46 mAh g^{-1} at 0.5 and 1C to the ZnI-PVA binder system, which delivered initial discharge capacities of 798.01 and 771.61 mAh g^{-1} at 0.5 and 1C respectively (**Figure 21**). This performance was obtained in the absence of CMC in the binder system.

Example 20: PVP-I and PVA-I based cathodes absent structural material

[0216] The cycling performance of coin cells containing PVP-I and PVA-I cathodes without CMC in the binder system was evaluated. The PVP-I and PVA-I systems' cycling performances were evaluated without structural polymer (CMC) typically added to support intense cycling at high C rates. However, both PVP-I and PVA-I systems still delivered high initial discharge capacities of 1007.73 and 1002.46 mAh g^{-1} at 0.5 C rate. At 1C rate, the PVP-I cell exhibited 973.64 mAh g^{-1} initial discharge capacity but the cell was stable for only 100 cycles. See **Figure 22 a and b**.

Analysis and measurement techniques

Electrochemical measurements:

[0217] A multichannel battery testing system (Neware, China) was used to get the galvanostatic charge-discharge data between 1.8-2.8 V. Cyclic voltammetry was carried out between scan rate of 0.05 to 0.1 mV s^{-1} from 1.8 to 2.8 V (vs. Li+/Li) at room temperature. Electrochemical impedance spectroscopy (EIS) tests were conducted by potentiostatic signal with 1 mHz to 1 MHz frequency range, 6 data points per decade of frequency, 10 mVrms alternating currents (AC) voltage and 2.8 V vs Eref direct current (DC) voltage.

Scanning electron microscopy imaging and EDX mapping:

[0218] The morphology of the fabricated cathodes was characterized by scanning electron microscopy (SEM) by mounting fresh cathodes on an Al stub with a conductive carbon tap. Thermo Scientific Verios 5 UC FEGSEM and Nova 450 field emission scanning electron microscope (FESEM) were used for secondary electron imaging and energy dispersive spectroscopy mapping (EDX).

CLAIMS

1. A sulfur cathode comprising:

   a) one or more sulfur containing materials;

   b) one or more conductive materials;

   c) one or more:

      (i) metal cations having a valency of two or more;

      (ii) halide anions;

      (iii) polyhalogen anions;

      or mixtures thereof; and

   d) one or more binding polymers, said binding polymers being capable of binding one or more of metal cations having a valency of two or more, halide anions, or polyhalogen anions.

2. A sulfur cathode comprising:

   a) one or more sulfur containing materials;

   b) one or more conductive materials;

   c) one or more binding polymers having bound thereto one or more of:

      (i) metal cations having a valency of two or more;

      (ii) halide anions; or

      (iii) polyhalogen anions.

3. An electrochemical storage device comprising a lithium anode, a separator, the sulfur cathode according to claim 1 or claim 2, and electrolyte disposed between the anode and cathode.

4. The sulfur cathode according to claim 1 or claim 2, or the electrochemical storage device according to claim 3, wherein the sulfur cathode further comprises one or more structural materials

5. The sulfur cathode or the electrochemical storage device according to claim 4, wherein the one or more structural materials comprise one or more cellulose derivatives selected from carboxymethyl cellulose, anionically functionalised cellulose nanofibres, and alginate salts.

6. The sulfur cathode according to any one of claims 1, 2, 4, or 5, or the electrochemical storage device according to any one of claims 3 to 6, wherein the one or more sulfur containing materials comprise one or more of elemental sulfur, Li_2S, MoS_2, and sulfurised polymers.

7. The sulfur cathode according to any one of claims 1, 2 or 4 to 6, or the electrochemical storage device according to any one of claim 3 to 6, wherein the one or more conductive materials comprise one or more of carbon black, graphite, graphene, activated carbon, carbon nanotubes, and carbon fibre.

8. The sulfur cathode according to any one of claims 1, 2 or 4 to 7, or the electrochemical storage device according to any one of claims 3 to 7, wherein the one or more metal cations having a valency of two or more comprise one or more of iron (III), iron (II), manganese (II), cobalt (III), copper (II), zinc (II), aluminium (III), nickel (II), and gallium (III).

9. The sulfur cathode according to any one of claims 1, 2 or 4 to 8, or the electrochemical storage device according to any one of claims 3 to 8, wherein the one or more halide anions comprise one or more of bromide and iodide.

10. The sulfur cathode according to any one of claims 1, 2 or 4 to 9, or the electrochemical storage device according to any one of claims 3 to 9, wherein the one or more polyhalogen anions comprise one or more of I_3^-, I_5^-, and Br_3^-.

11. The sulfur cathode according to any one of claims 1, 2 or 4 to 10, or the electrochemical storage device according to any one of claims 3 to 10, wherein the one or more binding polymers comprise one or more of polyvinylpyrrolidone, poly(vinyl pyridine), poly(vinyl alcohol), polyether, and polysaccharide.

12. The sulfur cathode or electrochemical storage device according to claim 11, wherein the one or more binding polymers have a weight average molecular weight from about 2,500 to about 3,000,000 Daltons.

13. The sulfur cathode according to any one of claims 1, 2 or 4 to 12, or the electrochemical storage device according to any one of claims 3 to 12, wherein the molar ratio of sulfur to one or more of metal cations having a valency of two or more, halide anions, and polyhalogen anions is from about 500 to about 10.

14. The sulfur cathode according to any one of claims 1, 2 or 4 to 13, comprising:

a) about 50 wt.% to about 80 wt.% of one or more sulfur containing materials;

b) about 10 wt.% to about 30 wt.% of one or more conductive materials;

c) about 0.1 wt.% to about 5 wt.% of one or more of metal cations having a valency of two or more, halide anions, and polyhalogen anions;

d) about 2 wt.% to about 20 wt.% of one or more polymers capable of binding one or more of metal cations, halide anions, and polyhalogen anions.

15. The sulfur cathode according to claim 14, further comprising about 2 wt.% to about 15 wt.% of one or more structural materials.

16. The sulfur cathode according to claim 15, wherein the one or more structural materials comprise one or more cellulose derivatives selected from carboxymethyl cellulose, anionically functionalised cellulose nanofibres, and alginate salts.

17. Use of the sulfur cathode according to any one of claims 1, 2 or 4 to 16, in an electrochemical storage device.

18. The use according to claim 17, wherein the electrochemical storage device is a lithium sulfur battery.

19. A binder for a sulfur cathode comprising:

a) one or more of metal cations having a valency of two or more, halide anions, and polyhalogen anions;

b) one or more binding polymers, said binding polymers being capable of binding, or having bound thereto, one or more of metal cations, halide anions, and polyhalogen anions; and

c) one or more structural materials.

20. A method of preparing a binder for a sulfur cathode comprising:

a) combining one or more of metal cations having a valency of two or more, halide anions, and polyhalogen anions, with one or more binding polymers capable of binding the one or more of metal cations, halide anions, and polyhalogen anions; and

b) combining the product of step a) with one or more structural materials.

FIGURE 1

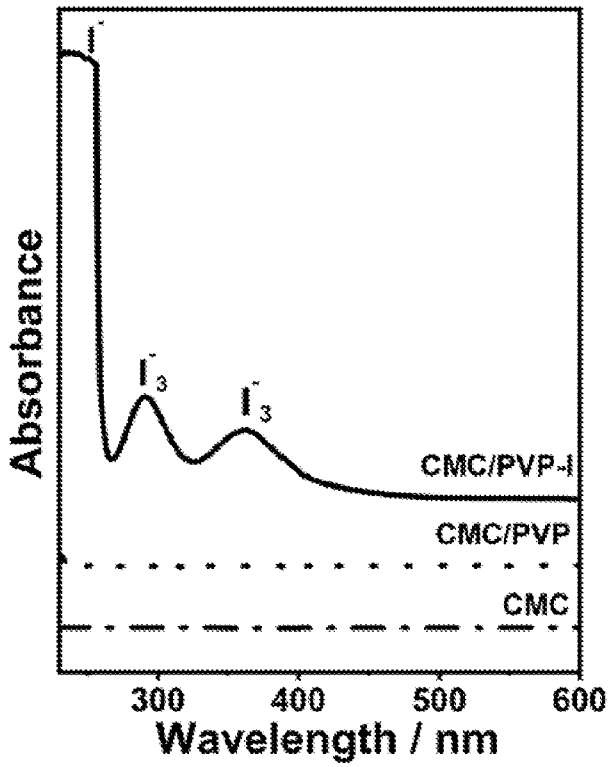


FIGURE 2

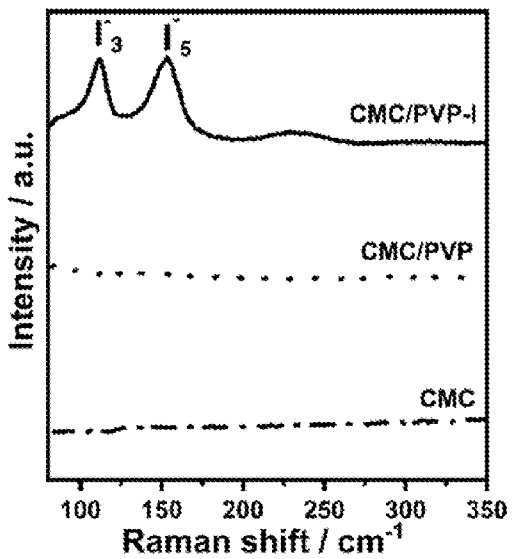


FIGURE 3

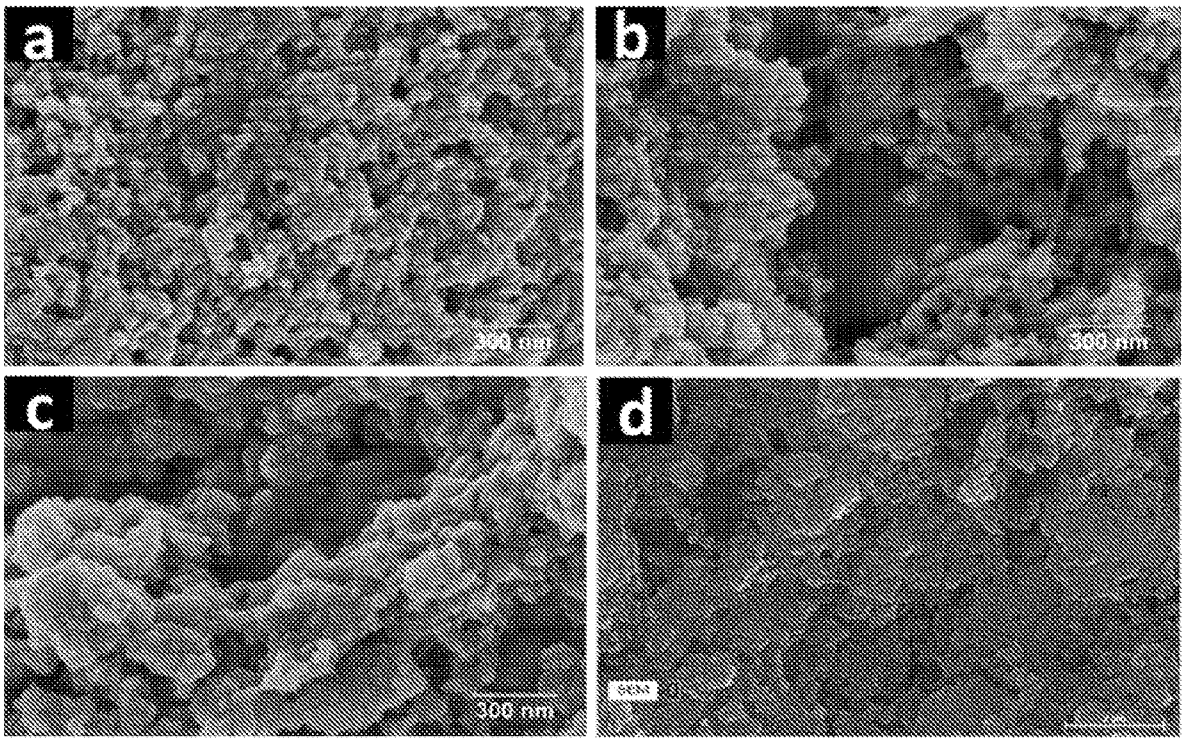


FIGURE 4

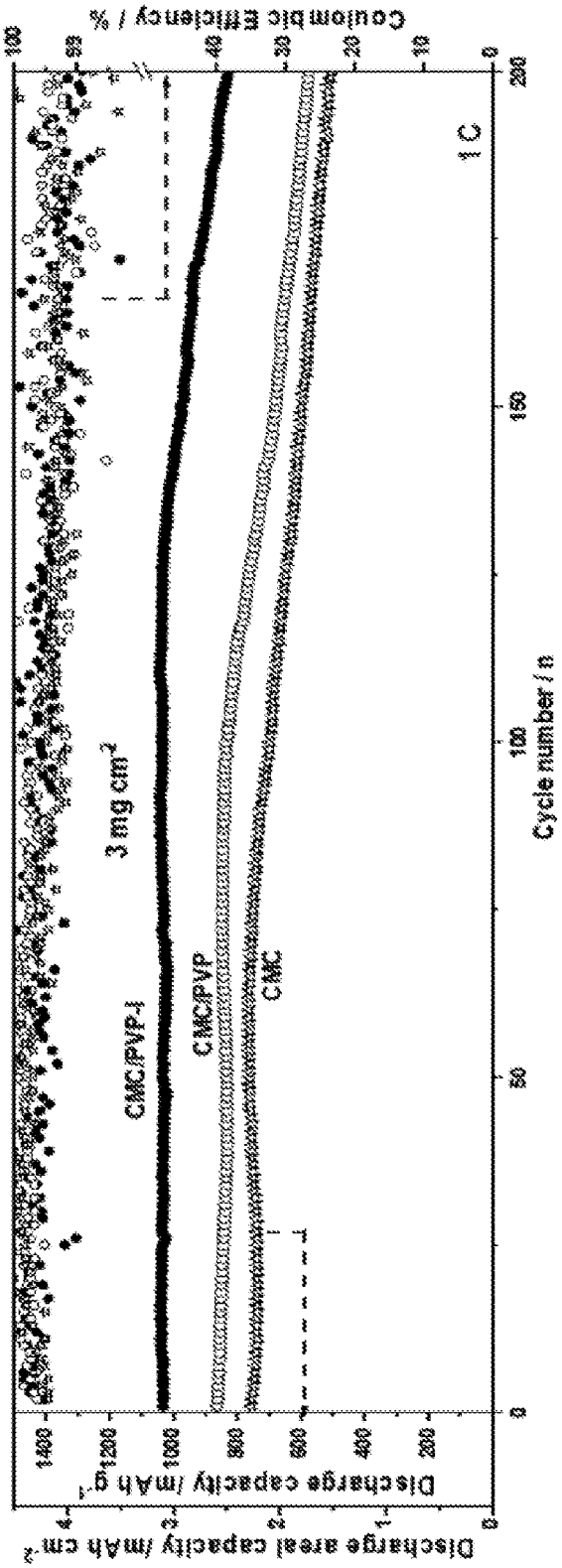

Coulombic Efficiency / %
Discharge areal capacity /mAh cm-2
Discharge capacity /mAh g-1
Cycle number / n
1 C
3 mg cm-2
CMC/PVP-I
CMC/PVP
CMC

FIGURE 5

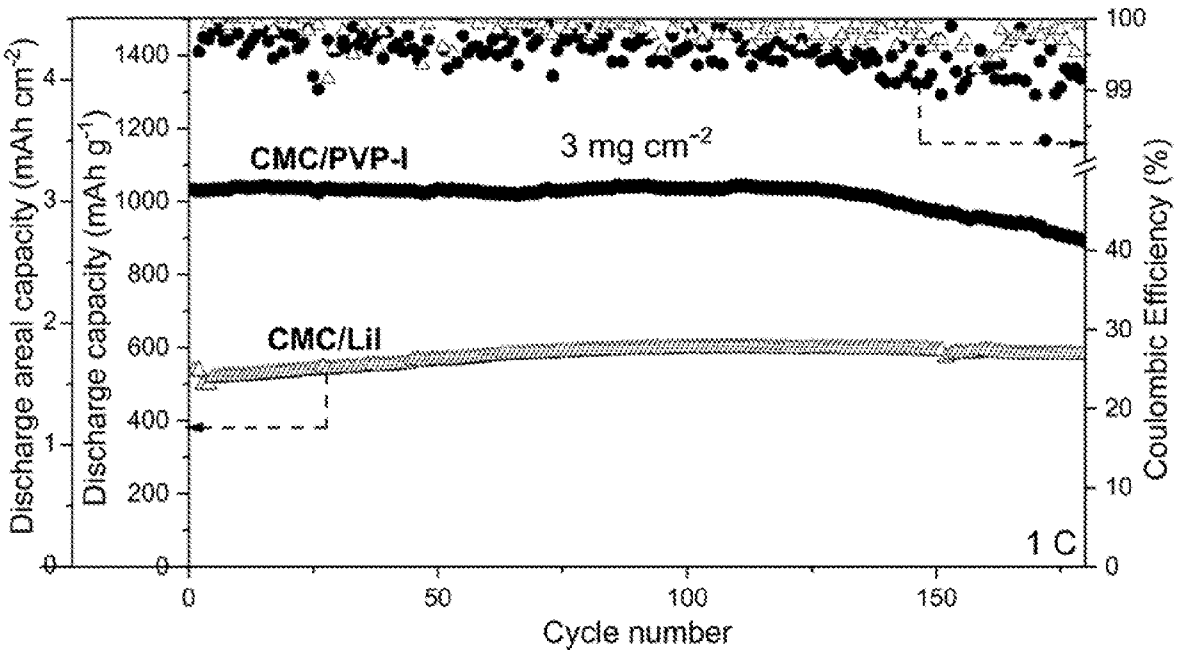


FIGURE 6

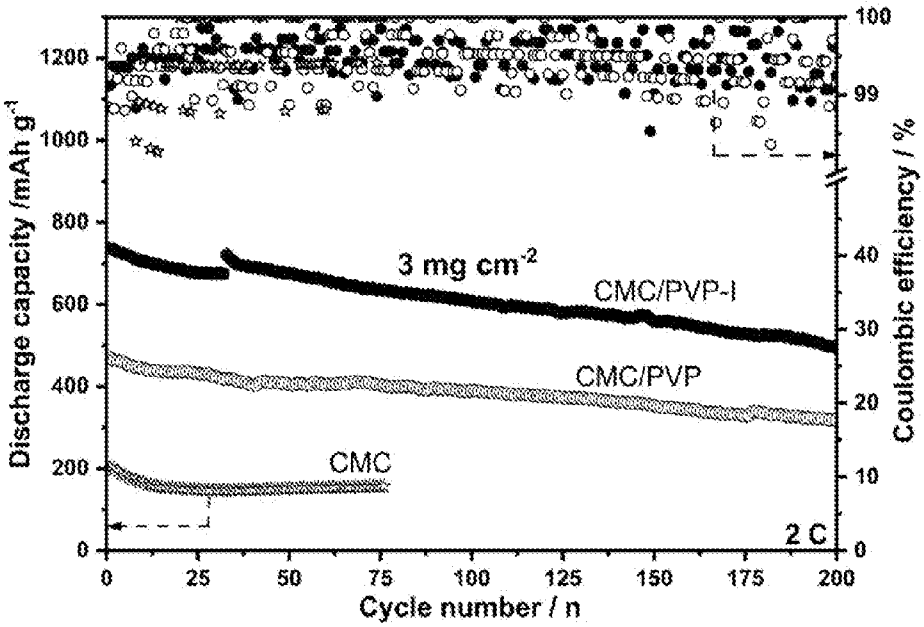


FIGURE 7

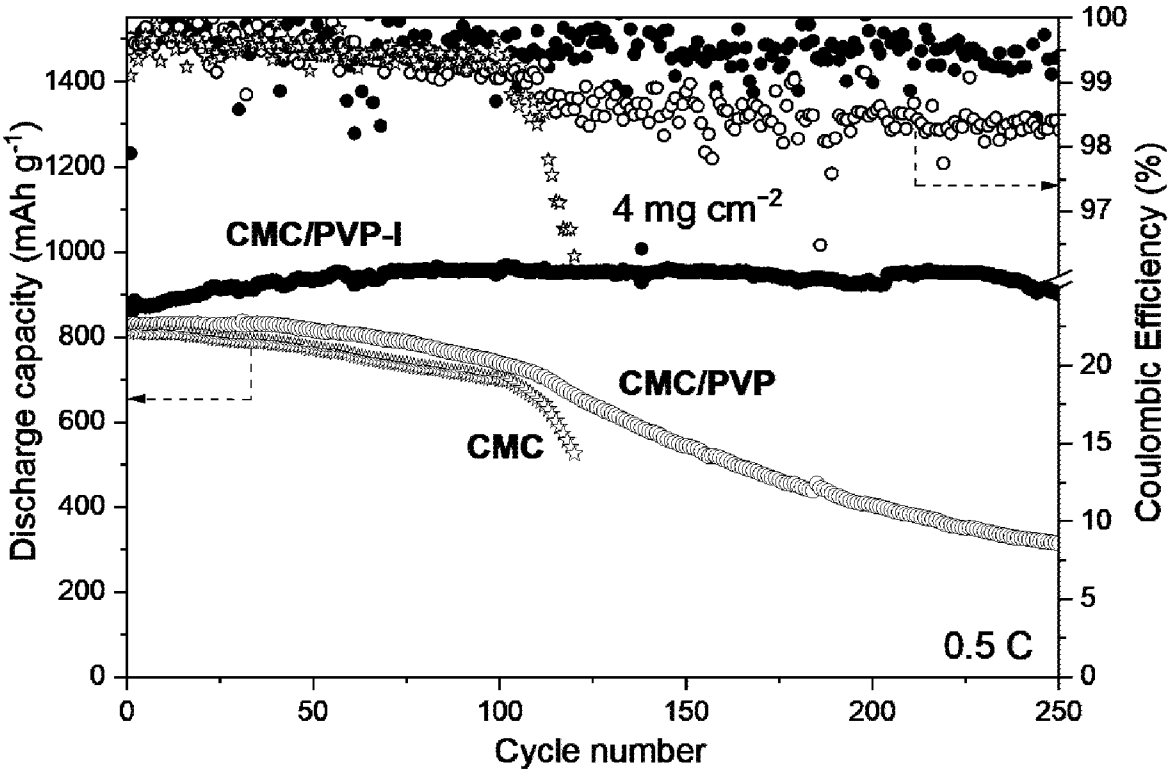


FIGURE 8

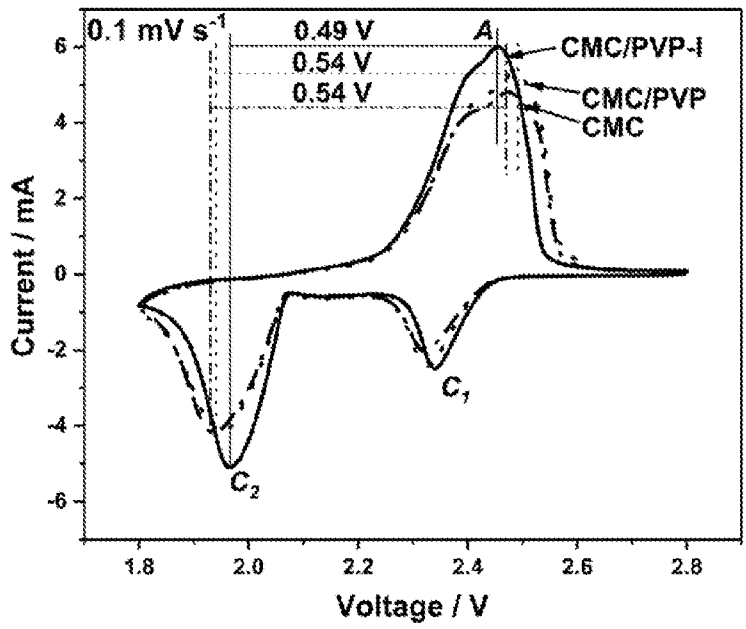


FIGURE 9

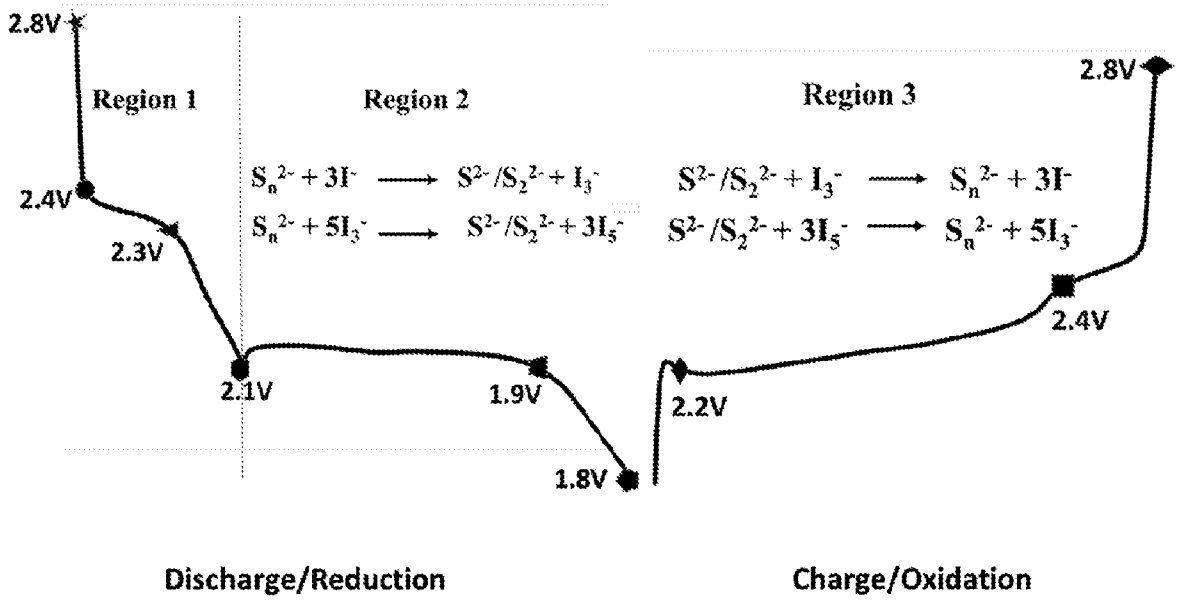

2.8V
Region 1
Region 2
Region 3
$S_n^{2-} + 3I^- \longrightarrow S^{2-}/S_2^{2-} + I_3^-$
$S_n^{2-} + 5I_3^- \longrightarrow S^{2-}/S_2^{2-} + 3I_5^-$
$S^{2-}/S_2^{2-} + I_3^- \longrightarrow S_n^{2-} + 3I^-$
$S^{2-}/S_2^{2-} + 3I_5^- \longrightarrow S_n^{2-} + 5I_3^-$
2.4V
2.3V
2.1V
1.9V
1.8V
2.2V
2.4V
2.8V
Discharge/Reduction
Charge/Oxidation

FIGURE 10

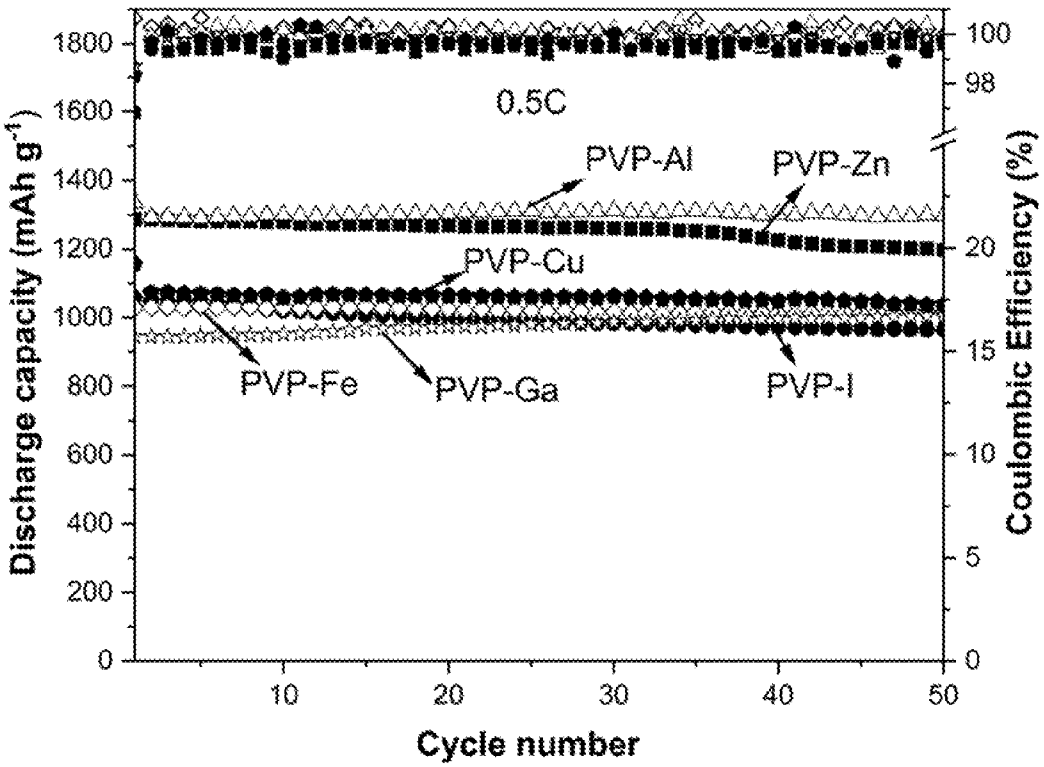


FIGURE 11

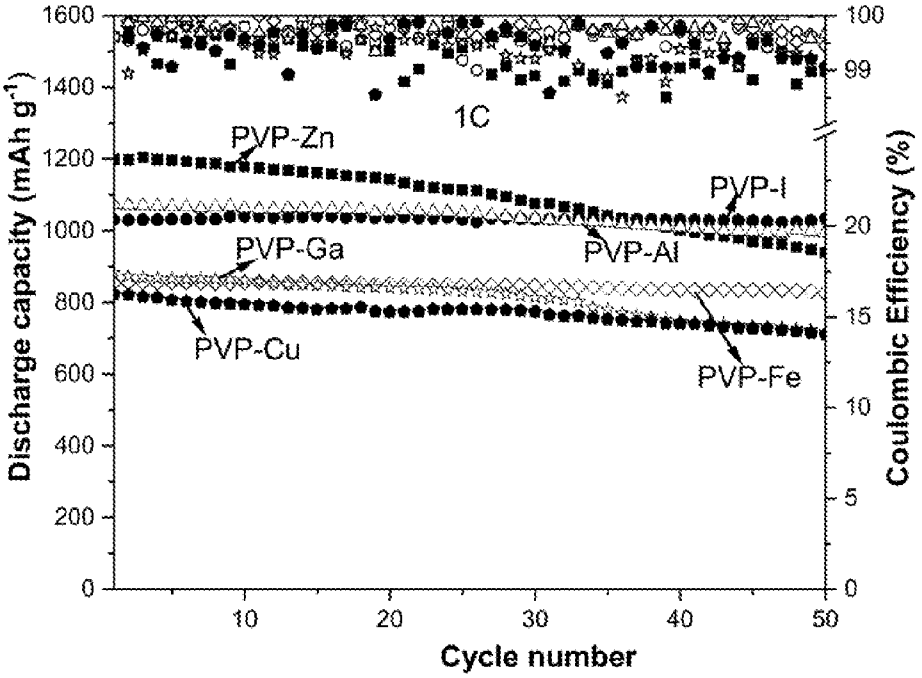


FIGURE 12

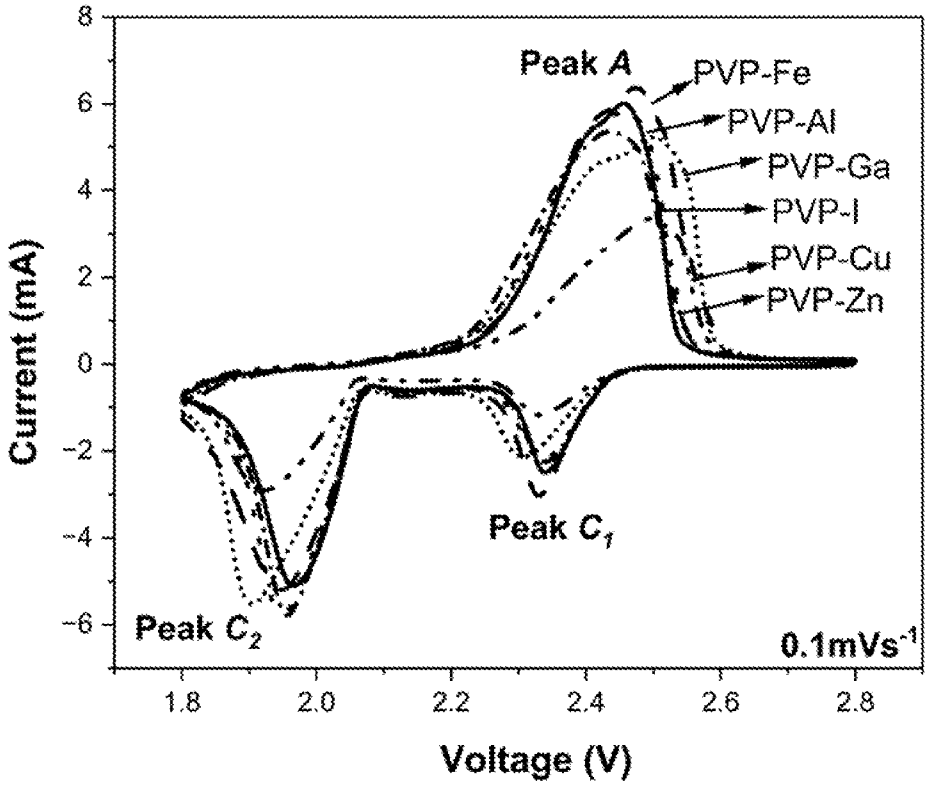


FIGURE 13

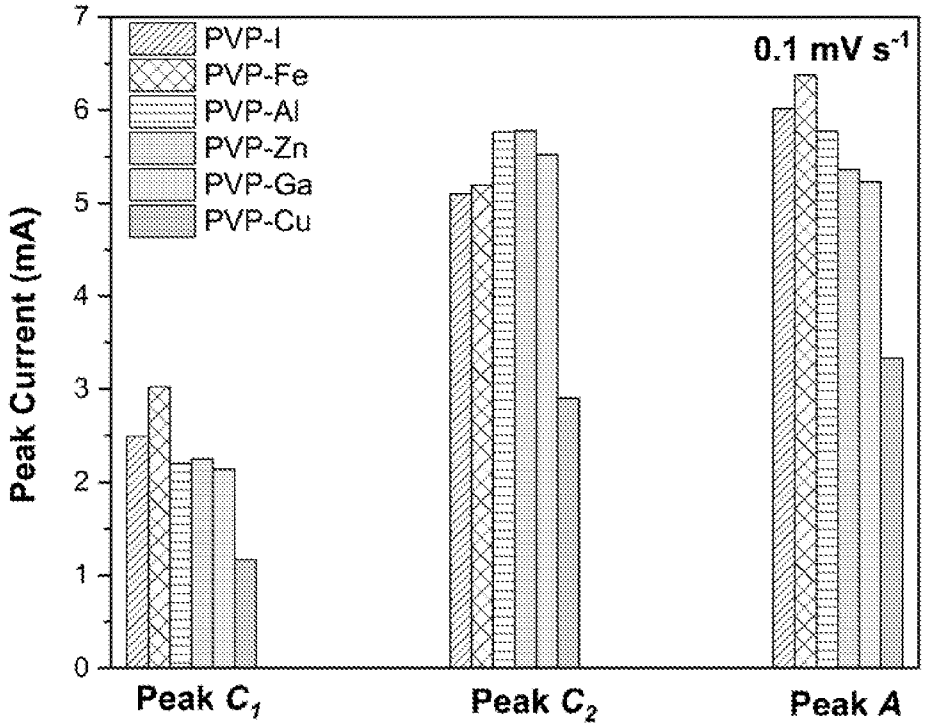


FIGURE 14

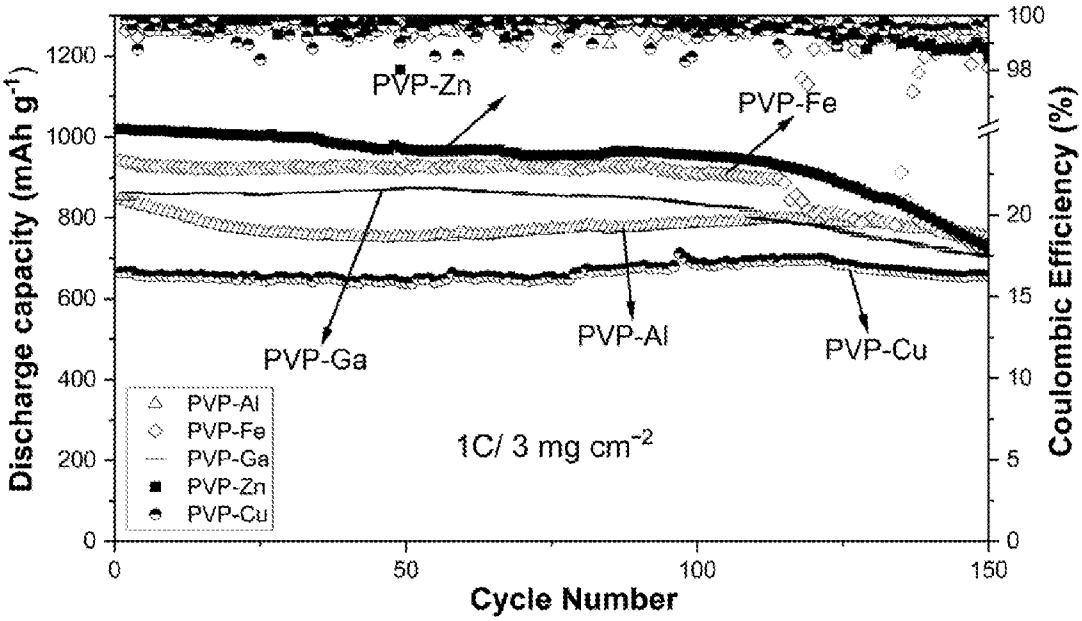
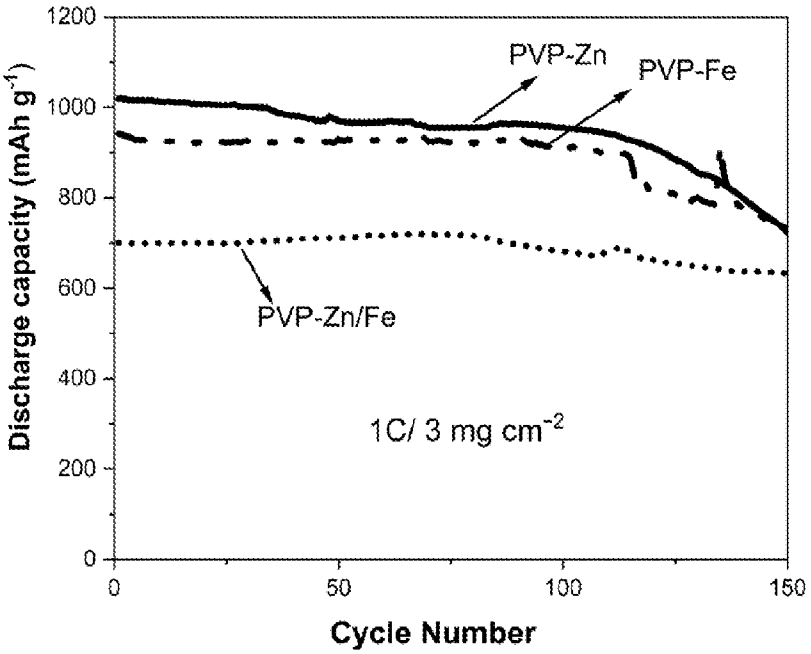

Discharge capacity (mAh g^{-1})
Coulombic Efficiency (%)
Cycle Number
PVP-Zn
PVP-Fe
PVP-Ga
PVP-Al
PVP-Cu
1C/ 3 mg cm^{-2}
PVP-Al
PVP-Fe
PVP-Ga
PVP-Zn
PVP-Cu
0
200
400
600
800
1000
1200
0
5
10
15
20
98
100
0
50
100
150

FIGURE 15

(a)


1200
1000
800
600
400
200
0
0
50
100
150
Discharge capacity (mAh g-1)
Cycle Number
PVP-Zn
PVP-Fe
PVP-Zn/Fe
1C/ 3 mg cm-2

(b)

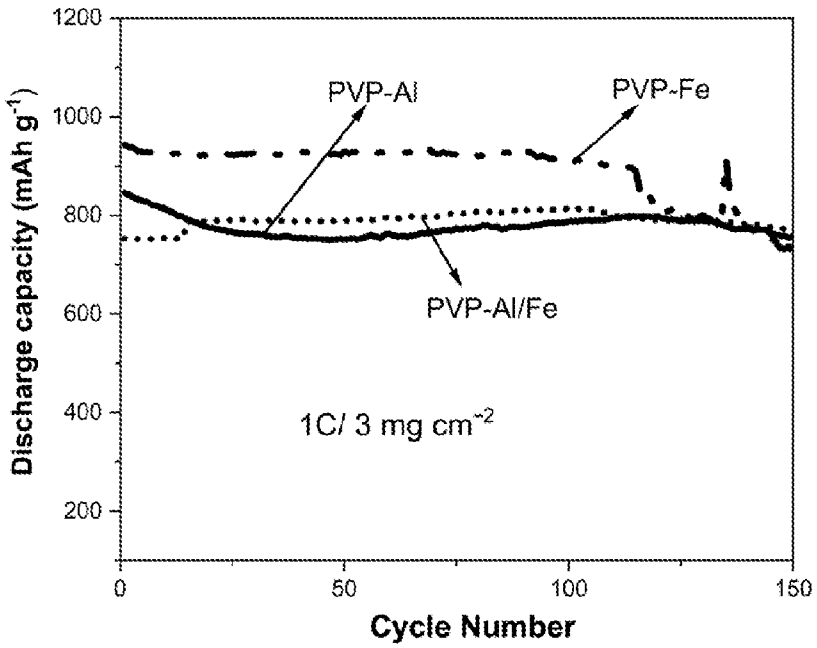
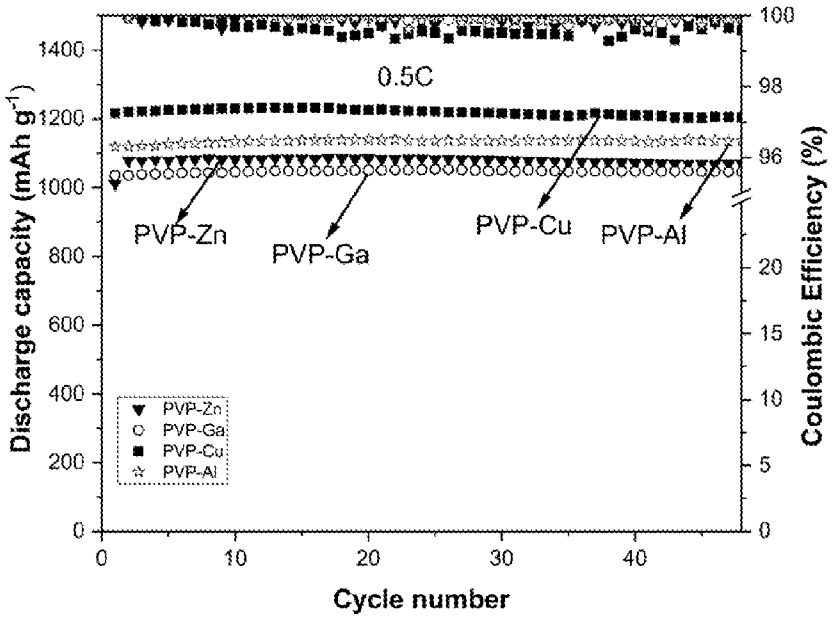

1200
1000
800
600
400
200
0
50
100
150
Discharge capacity (mAh g-1)
Cycle Number
PVP-Al
PVP-Fe
PVP-Al/Fe
1C/ 3 mg cm-2

FIGURE 16

(a)


0.5C
PVP-Zn
PVP-Ga
PVP-Cu
PVP-Al
Discharge capacity (mAh g-1)
Coulombic Efficiency (%)
Cycle number
0
200
400
600
800
1000
1200
1400
0
5
10
15
20
96
98
100
0
10
20
30
40

(b)

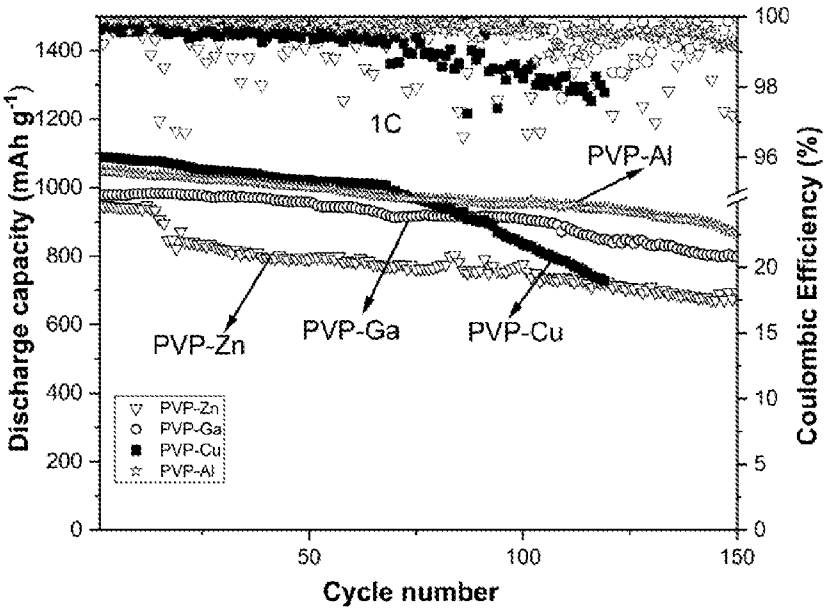

1C
PVP-Al
PVP-Zn
PVP-Ga
PVP-Cu
Discharge capacity (mAh g-1)
Coulombic Efficiency (%)
Cycle number
0
200
400
600
800
1000
1200
1400
0
5
10
15
20
96
98
100
50
100
150

FIGURE 17

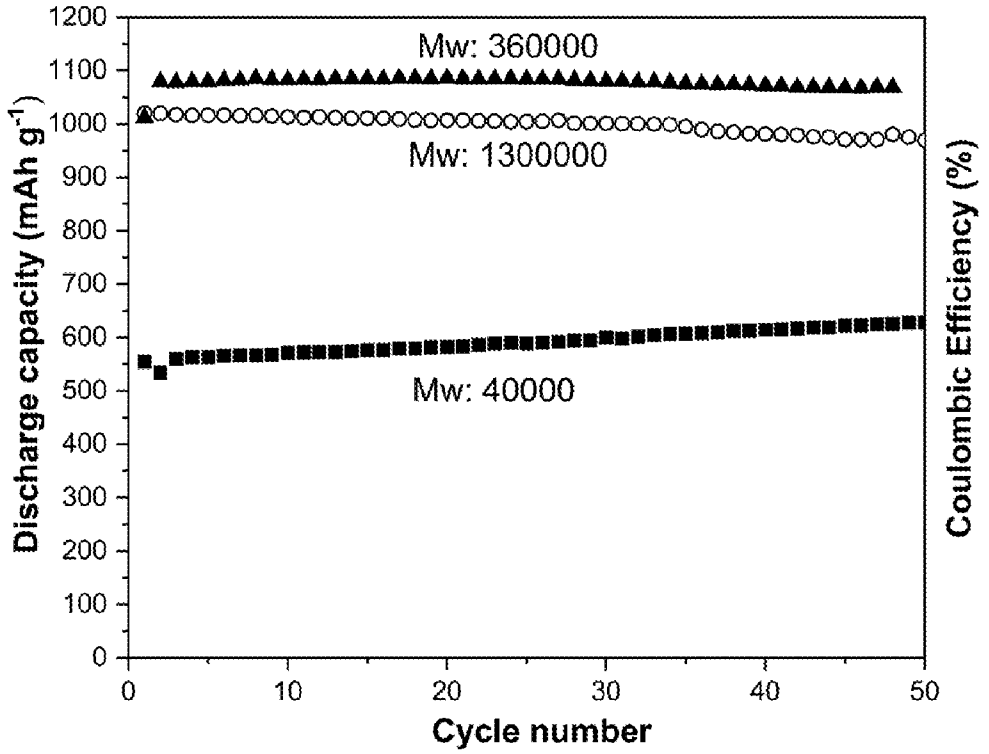
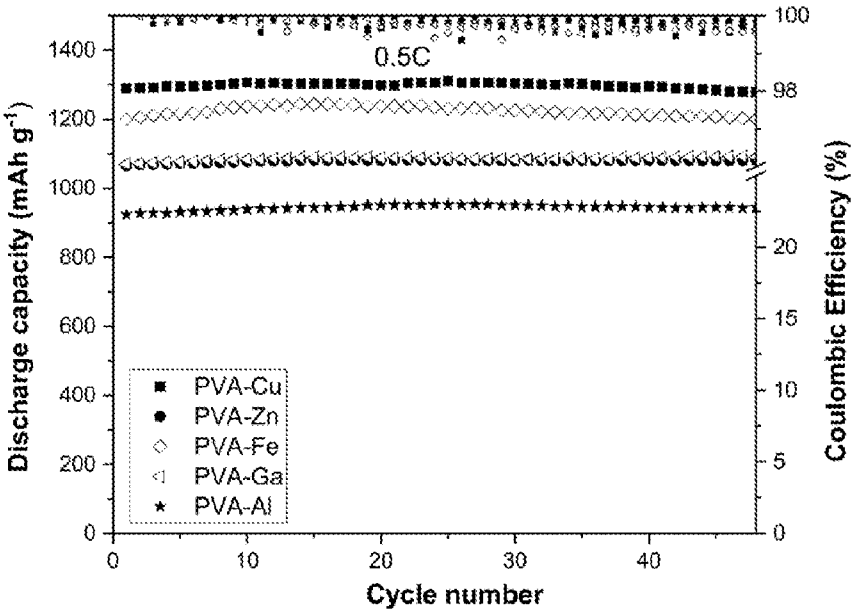

Mw: 360000
Mw: 1300000
Mw: 40000
Discharge capacity (mAh g-1)
Coulombic Efficiency (%)
Cycle number
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
0
10
20
30
40
50

FIGURE 18

(a)


0.5C
Discharge capacity (mAh g^{-1})
Coulombic Efficiency (%)
Cycle number
PVA-Cu
PVA-Zn
PVA-Fe
PVA-Ga
PVA-Al

(b)

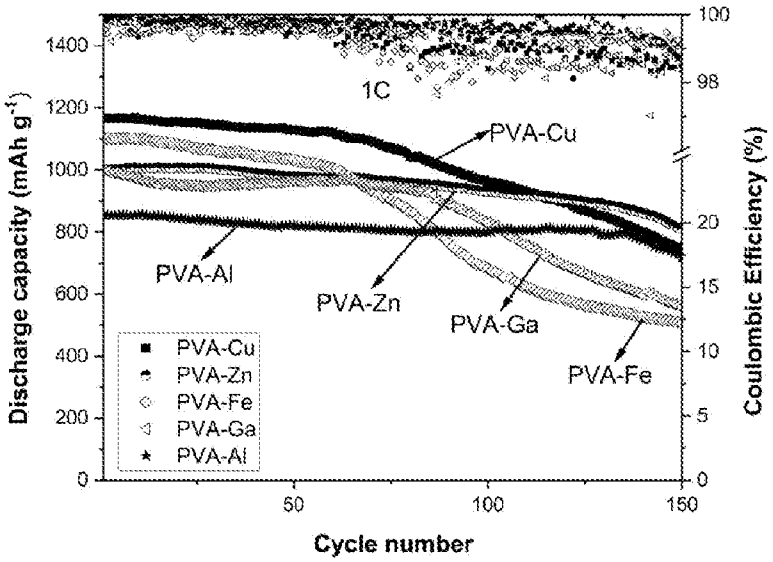
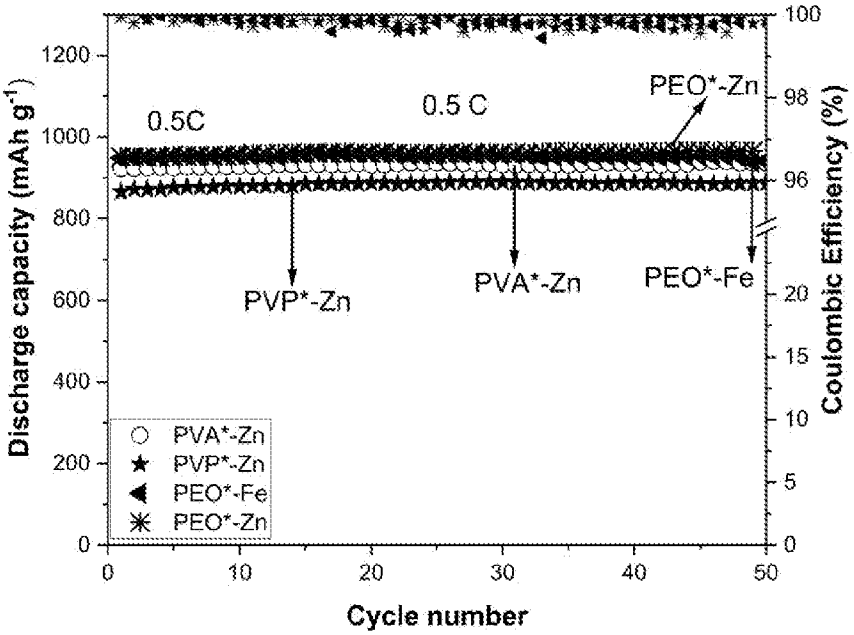

1C
PVA-Cu
PVA-Al
PVA-Zn
PVA-Ga
PVA-Fe
Discharge capacity (mAh g^{-1})
Coulombic Efficiency (%)
Cycle number

FIGURE 19

(a)


Discharge capacity (mAh g-1)
Coulombic Efficiency (%)
Cycle number
0.5C
0.5 C
PEO*-Zn
PVP*-Zn
PVA*-Zn
PEO*-Fe
PVA*-Zn
PVP*-Zn
PEO*-Fe
PEO*-Zn

(b)

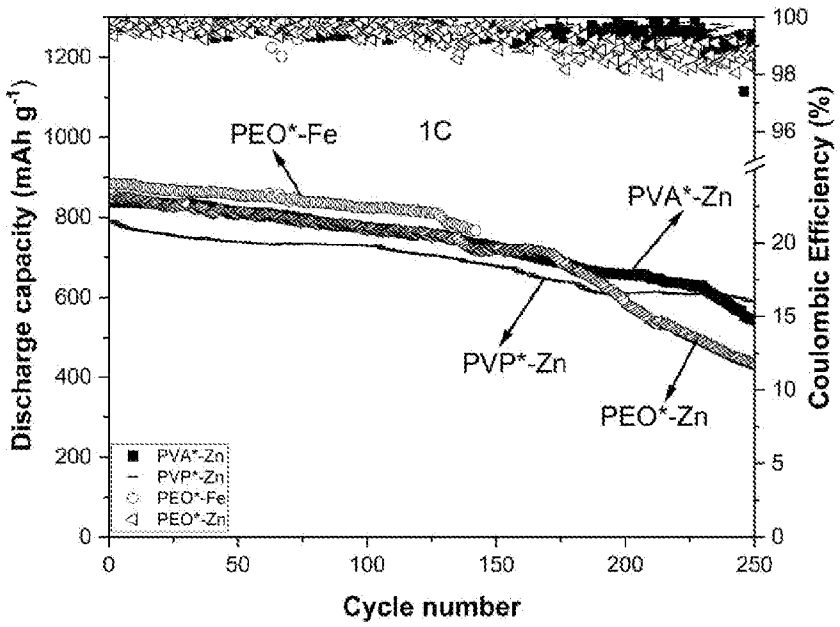

Discharge capacity (mAh g-1)
Coulombic Efficiency (%)
Cycle number
PEO*-Fe
1C
PVA*-Zn
PVP*-Zn
PEO*-Zn
PVA*-Zn
PVP*-Zn
PEO*-Fe
PEO*-Zn

FIGURE 20

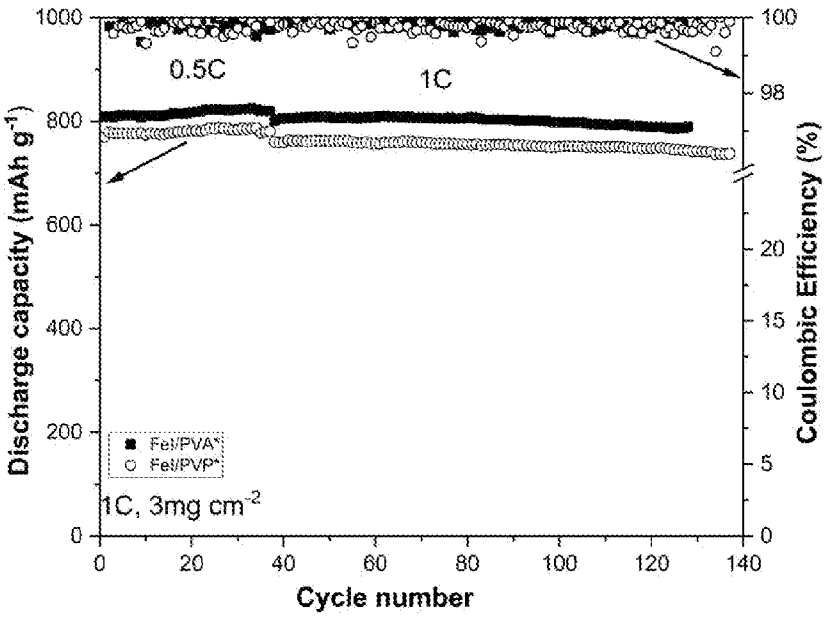


FIGURE 21

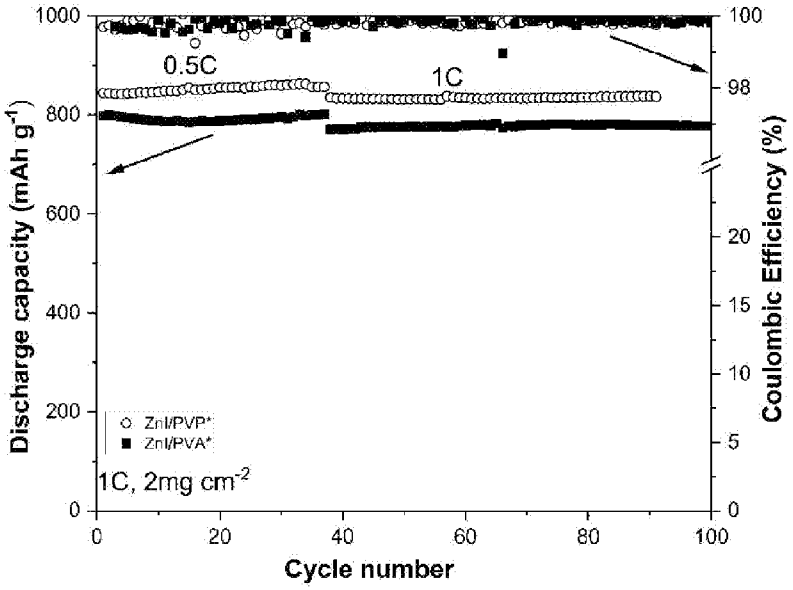
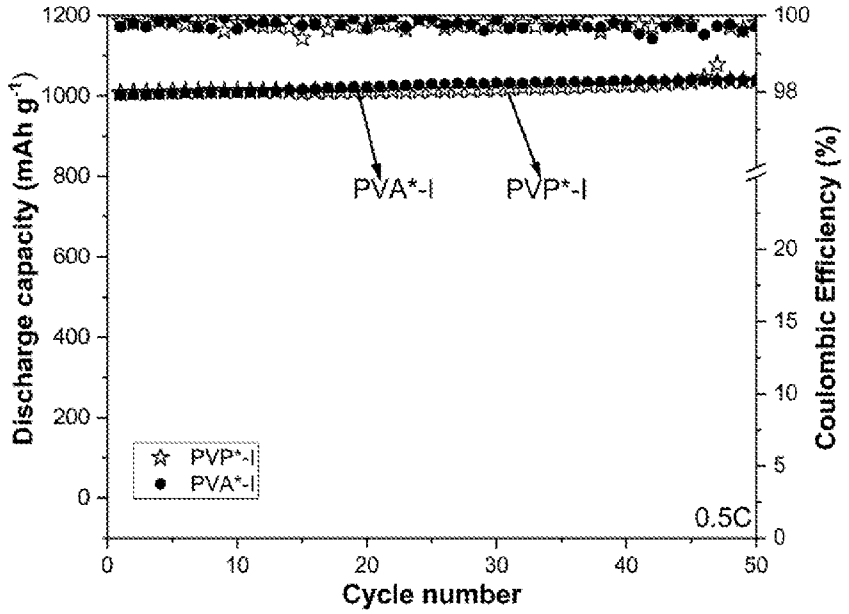
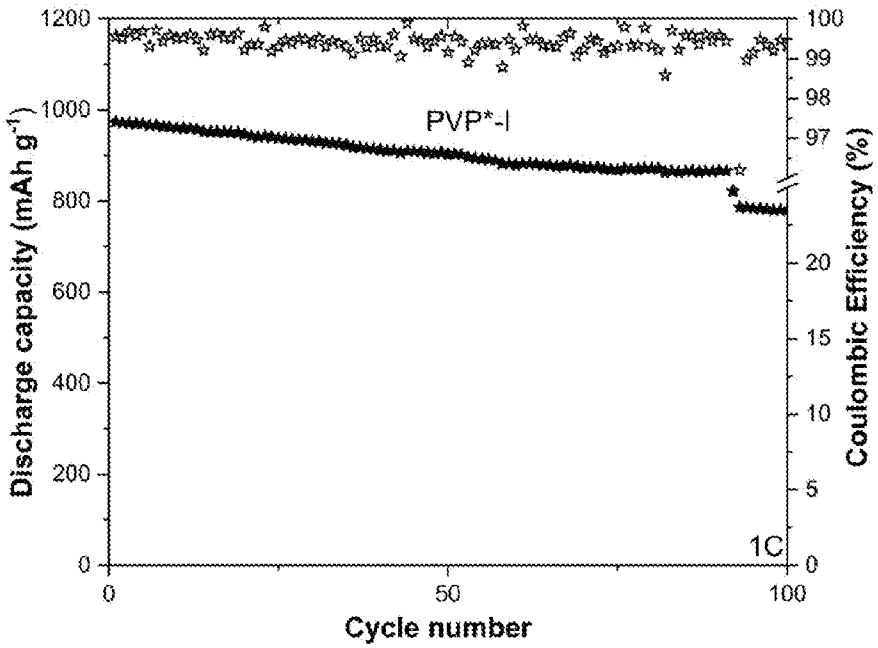


FIGURE 22

(a)


Discharge capacity (mAh g-1)
Coulombic Efficiency (%)
Cycle number
PVA*-I
PVP*-I
PVP*-I
PVA*-I
0.5C

(b)


Discharge capacity (mAh g-1)
Coulombic Efficiency (%)
Cycle number
PVP*-I
1C

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2024/051384

A. CLASSIFICATION OF SUBJECT MATTER

H01M 4/62 (2006.01) H01M 4/02 (2006.01) H01M 4/1315 (2010.01) H01M 4/50 (2010.01) H01M 4/505 (2010.01) H01M 4/52 (2010.01) H01M 10/052 (2010.01)

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: IPC/CPC marks and keywords such as H01M4/622, H01M4/58, H01M4/50, H01M4/52, H01M4/1315, H01M4/625, H01M2004/026 and keywords such as sulphur cathode, halogen, polyhalogen, bromide, iodide, polyvinyl pyrrolidone, pvp, PVOH, polyvinyl alcohol, starch, cmc, carboxymethyl cellulose, aluminium, manganese, zinc, gallium, cobalt, iron, ferrous, ferric and same keyword search through Google Patents and Espacenet and applicant/inventor name search through IP Australia internal databases and DOCDB and DWPI.

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	

[X] Further documents are listed in the continuation of Box C

[X] See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"E" earlier application or patent but published on or after the international filing date

"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)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

"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

"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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 March 2025	19 March 2025
Name and mailing address of the ISA/AU	**Authorised officer**
AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustralia.gov.au	Heramb M Bal AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. +61 2 6283 7966

INTERNATIONAL SEARCH REPORT C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		International application No. **PCT/AU2024/051384**
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2023/136612 A1 (LG ENERGY SOLUTION LTD) 20 July 2023 & English equivalent US 2024/0339601 A1 (LG ENERGY SOLUTION LTD) 10 October 2024 abstract, paragraphs 0002, 0003, 0011, 0053-0058, 0060, 0064-0065	1-20
A	US 11367895 B1 (LYTEN INC) 21 June 2022 abstract	1-20

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/AU2024/051384**

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**
WO 2023/136612 A1	20 July 2023	WO 2023136612 A1	20 Jul 2023
		CN 117678100 A	08 Mar 2024
		EP 4358219 A1	24 Apr 2024
		JP 2024537211 A	10 Oct 2024
		KR 20230108580 A	18 Jul 2023
		US 2024339601 A1	10 Oct 2024
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		CN 114725656 A	08 Jul 2022
		CN 114725656 B	13 Oct 2023
		CN 114788039 A	22 Jul 2022
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		CN 117063314 A	14 Nov 2023
		CN 117999667 A	07 May 2024
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		EP 4107518 A1	28 Dec 2022
		EP 4315458 A1	07 Feb 2024
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		EP 4491572 A2	15 Jan 2025
		EP 4491573 A2	15 Jan 2025
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