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(54) Title: COMPOSITION AND BATTERY

(57) Abstract: A composition comprising a crosslinked single-ion conducting polymer and a second polymer. The single-ion conducting polymer may be a crosslinked polymer. The second polymer may be a neutral conjugated polymer. The second polymer may be a single-ion conducting or neutral non-conjugated polymer. A metal battery or metal ion battery may contain a film formed from the composition.

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COMPOSITION AND BATTERY

BACKGROUND

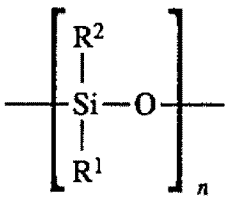
Embodiments of the present disclosure relate to metal batteries, in particular lithium batteries, and methods of forming the same.

Lithium metal batteries are known. However, secondary (i.e. rechargeable) lithium metal batteries have found limited application due in part to the tendency of lithium dendrites to form at the lithium anode during charging of the battery. Dendrite formation may result in a short circuit, with associated risks of combustion or explosion of the battery. Consequently, secondary lithium ion batteries are used more widely than secondary lithium batteries in applications where recharging of the battery is required.

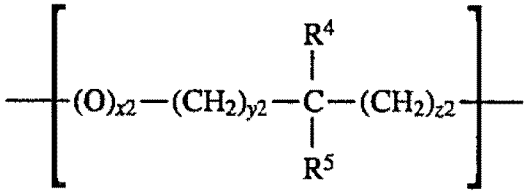
Single ion conducting polymer electrolytes are known.

Borzutzki et al, "Fluorinated polysulfonamide based single ion conducting room temperature applicable gel-type polymer electrolytes for lithium ion batteries" *J. Mater. Chem. A*, 2019, **7**, 188-201 discloses a blend of a fluorinated polysulfonamide single-ion conducting polymer and HVDF-HFP used as an electrolyte membrane after soaking in ethylene carbonate and propylene carbonate.

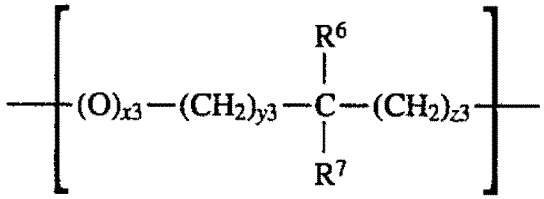
US 5548055 discloses single-ion conductive polymers having the structure of formula (I) or containing mer units of formulae (II) and (III) and combinations of these polymers with a liquid electrolyte and a PVDF plasticiser:



(I)

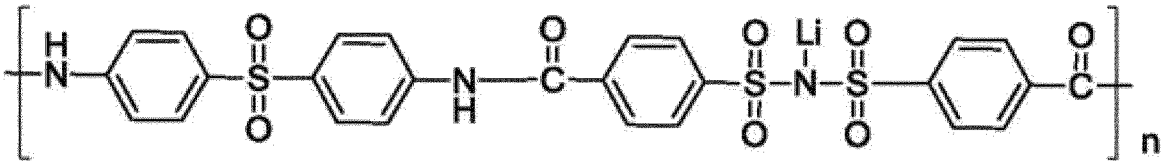


(II)



(III)

CN111081946 discloses a porous single-ion polymer electrolyte "PI-FPAS" for use with a liquid in which PI is polyimide and FPAS is:



Li et al, "Synthesis and Application of a Conjugated Polydianion-Based Single-Ion Conducting Polymer for High-Performance Solid Lithium-Ion Batteries" ChemElectroChem, Volume 6, Issue10, May 15, 2019 pages 2707-2714 discloses a PEO- poly(perfluoroalkylsulfonyl)diimide composite electrolyte.

Zhang et al, "Influence of Chemical Microstructure of Single-Ion Polymeric Electrolyte Membranes on Performance of Lithium-Ion Batteries" *ACS Appl. Mater. Interfaces* 2014, 6, 20, 17534–17542 discloses single ion polymer electrolytes blended with poly (vinylidene fluoride-hexafluoropropylene) (PVDF-HFP).

SUMMARY

In some embodiments, the present disclosure provides a composition comprising a crosslinked single-ion conducting polymer and a second polymer.

Optionally, the crosslinked single-ion conducting polymer comprises groups of formula (I):

$$[XO_4]^- \quad M^+ \qquad (I)$$

wherein X is B or Al; at least one of the O atoms of formula (I) is bound through an organic linking group L to another group of formula (I); and M+ is a metal cation.

Optionally, L is selected from groups of formula (IV):

$$-[(A^1)_p\text{-}Z]_q\text{-}(A^2)_r- \qquad (IV)$$

wherein:

A^1 and A^2 in each occurrence are independently selected from: unsubstituted or substituted arylene; unsubstituted or substituted heteroarylene; and CR^1_2 wherein R^1 in each occurrence is H or a substituent;

q is 0 or a positive integer;

if q is a positive integer then p is at least 1.

r is at least 1; and

Z is O, S, NR^4, $Si(R^5)_2$ SO_2, CO C=O, COO or $CONR^4$ wherein R^4 in each occurrence is independently H or a substituent and R^5 in each occurrence is a substituent.

Optionally, at least one of the O atoms of formula (I) is bound to a group of formula (IVa):

$$-(C_2R^1_4Z)n-(CR^1_2)_r-OH \qquad (IVa)$$

Optionally, the second polymer is a non-conjugated polymer, optionally a neutral, non-conjugated polymer.

Optionally, the second polymer is a neutral, conjugated polymer.

In some embodiments, the present disclosure provides a composition comprising a single-ion conducting polymer and a neutral conjugated polymer.

Optionally, the single-ion conducting polymer of the composition comprising the single-ion conducting polymer and the neutral conjugated polymer is selected from a polymer comprising groups of formula (I) and a polymer comprising groups of formula (II):

$$[XO_4]^- \qquad M^+ \qquad (I)$$

$$Si(OR^6)_uO_v \qquad (II)$$

wherein:

X is B or Al;

at least one of the O atoms of formula (I) is bound through an organic linking group L to another group of formula (I);

M^+ is a metal cation.

R^6 is an organic residue substituted with at least one group of formula $–An^-M^+$ wherein An^- is an anionic group;

u is 1 or 2;

v is 4-u;

and at least one of the v O atoms of formula (II) is linked by an organic linking group L to an O atom of another group of formula (II).

In some embodiments, the present disclosure provides a formulation comprising a composition as described herein dissolved or dispersed in one or more solvents.

In some embodiments, the present disclosure provides a metal battery comprising:

a metal anode;

an anode current collector in electrical contact with the anode;

a cathode;

a cathode current collector in electrical contact with the cathode;

a separator disposed between the anode and cathode; and

an anode protection layer disposed between the anode and the separator,

wherein the anode protection layer comprises a single-ion conductive polymer and an second polymer.

Optionally, the second polymer is a neutral polymer.

Optionally, the anode protection layer is a phase separated layer.

Optionally, the metal battery is a solid metal battery.

In some embodiments, the present disclosure provides a metal battery precursor comprising:

an anode current collector;

a cathode;

a cathode current collector in electrical contact with the cathode;

an anode protection layer disposed between the anode current collector and the cathode;

a separator disposed between the anode protection layer and the cathode,

wherein the anode protection layer comprises a single-ion conductive polymer and a second polymer.

In some embodiments, the present disclosure provides method of forming a metal battery as described herein comprising applying a bias across the metal battery precursor as described herein.

In some embodiments, the present disclosure provides a metal battery precursor as described herein comprising depositing a formulation comprising the single-ion conductive polymer and the inert polymer onto the anode current collector dissolved or dispersed in one or more solvents and evaporating the one or more solvents.

In some embodiments, the present disclosure provides a solid metal battery comprising:

a metal anode;

an anode current collector in electrical contact with the anode;

a cathode;

a cathode current collector in electrical contact with the cathode;

a layer disposed between the anode and cathode comprising a single-ion conductive polymer and a second polymer.

In some embodiments, the present disclosure provides a metal battery comprising:

a metal anode;

an anode current collector in electrical contact with the anode;

a cathode;

a cathode current collector in electrical contact with the cathode; and

a layer disposed between and in direct contact with the anode and cathode, the layer comprising a composition as described herein.

In some embodiments, the present disclosure provides a metal ion battery comprising:

an anode;

an anode current collector in electrical contact with the anode;

a cathode;

a cathode current collector in electrical contact with the cathode; and

a layer disposed between the anode and cathode comprising a composition as described herein.

DESCRIPTION OF DRAWINGS

Figure 1 is a schematic illustration of a battery according to some embodiments of the disclosure having a separator comprising a single-ion conductive network as described herein;

Figure 2 is a photoluminescence optical microscopy of a film of a single-ion conducting polymer and poly(9,9-dioctylfluorene-co-benzothiadiazole) (F8BT);

Figure 3 is a graph of current density vs. time generated in a galvanostatic cycling experiment using a film of a single-ion conducting polymer and F8BT; and

Figure 4 shows graphs of Coulombic efficiency vs cycle number for cells containing a copper anode coated with a composition of a single-ion conducting polymer and F8BT according to embodiments of the disclosure and a comparative battery having an uncoated copper anode.

The drawings are not drawn to scale and have various viewpoints and perspectives. The drawings are some implementations and examples. While the technology is amenable to various modifications and alternative forms, specific embodiments have been shown by way of example in the drawings and are described in detail below. The intention, however, is not to limit the technology to the particular implementations described. On the contrary, the technology is intended to cover all modifications, equivalents, and alternatives falling within the scope of the technology as defined by the appended claims.

DETAILED DESCRIPTION

Unless the context clearly requires otherwise, throughout the description and the claims, the words "comprise," "comprising," and the like are to be construed in an inclusive sense, as opposed to an exclusive or exhaustive sense; that is to say, in the sense of "including, but not limited to." Additionally, the words "herein," "above," "below," and words of similar import, when used in this application, refer to this application as a whole and not to any particular portions of this application. Where the context permits, words in the Detailed Description using the singular or plural number may also include the plural or singular number respectively. The word "or," in reference to a list of two or more items, covers all of the following interpretations of the word: any of the items in the list, all of the items in the list, and any combination of the items in the list. References to a layer “over” another layer when used in this application means that the layers may be in direct contact or one or more intervening layers are may be present. References to a layer “on” another layer when used in this application means that the layers are in direct contact.

The teachings of the technology provided herein can be applied to other systems, not necessarily the system described below. The elements and acts of the various examples described below can be combined to provide further implementations of the technology. Some alternative implementations of the technology may include not only additional elements to those implementations noted below, but also may include fewer elements.

These and other changes can be made to the technology in light of the following detailed description. While the description describes certain examples of the technology, and describes the best mode contemplated, no matter how detailed the description appears, the technology can be practiced in many ways. As noted above, particular terminology used when describing certain features or aspects of the technology should not be taken to imply that the terminology is being redefined herein to be restricted to any specific characteristics, features, or aspects of the technology with which that terminology is associated. In general, the terms used in the following claims should not be construed to limit the technology to the specific examples disclosed in the specification, unless the Detailed Description section explicitly defines such terms. Accordingly, the actual scope of the technology encompasses not only the disclosed examples, but also all equivalent ways of practicing or implementing the technology under the claims.

To reduce the number of claims, certain aspects of the technology are presented below in certain claim forms, but the applicant contemplates the various aspects of the technology in any number of claim forms.

In the following description, for the purposes of explanation, numerous specific details are set forth in order to provide a thorough understanding of implementations of the disclosed technology. It will be apparent, however, to one skilled in the art that embodiments of the disclosed technology may be practiced without some of these specific details.

In some embodiments, the single-ion conducting polymer is a crosslinked polymer and the second polymer may be an inert polymer. A polymer which is not a single-ion conductor is referred to hereinafter as an "inert" polymer. The second polymer may be selected according to desired properties of the composition comprising the crosslinked SIC polymer and the second polymer. For example, if the crosslinked polymer has a low extent of crosslinking, e.g. if the crosslinked polymer alone has low viscosity gel or liquid-like properties, then the second polymer may provide the composition with greater mechanical stability.

In some preferred embodiments, the second polymer is an inert conjugated polymer.

The SIC polymer : second polymer weight ratio is preferably in the range of about 60 : 40 – 99 : 1, preferably 70 : 30 – 90 : 10.

A film of the SIC polymer and the second polymer may comprise a scaffold of the second polymer and the SIC polymer disposed on the scaffold and / or in apertures defined by the scaffold. The film structure may be formed by bulk (lateral) phase separation of a mixture comprising the SIC polymer and the second polymer.

In some embodiments, the amount of the SIC polymer as a mass percent of the SIC polymer + second polymer mass is substantially uniform (e.g. ± 10 %) across the thickness of the anode protection layer.

In some embodiments, the anode protection layer has a non-zero concentration gradient across its thickness. According to these embodiments, a mixture comprising the SIC polymer and the second polymer may undergo vertical phase separation, optionally both bulk and vertical phase separation.

SIC polymer

SIC polymers as described herein comprise anionic groups covalently bound to the polymer and a free metal cation. The SIC polymer may be any SIC polymer known to the skilled person including, without limitation, SIC polymers as disclosed in Zhenan Bao et al, "A Dynamic, Electrolyte-Blocking, and Single-Ion-Conductive Network for Stable Lithium-Metal Anodes" Joule, Volume 3, Issue 11, 20 November 2019, Pages 2761-2776, the contents of which are incorporated herein in their entirety.

Preferably, the SIC polymer is a crosslinked polymer. A crosslinked SIC polymer may comprise anionic aluminate or borate groups bound into the polymer structure, e.g. a polymer comprising groups of formula (I):

$$[XO_4]^- \quad M^+ \quad (I)$$

wherein X is B or Al; at least one of the O atoms of formula (I) is bound through an organic linking group L to another group of formula (I); and M+ is a metal cation.

Formation of the polymer comprising groups of formula (I) may comprise reacting a metal borohydride or metal tetrahydroaluminate of formula $XH_4^- M^+$ with an alcohol having at least 2 hydroxyl groups and, optionally, with a monohydric alcohol.

It will be understood that an alcohol having n hydroxyl groups may react with up to n compounds of formula $XH_4^- M^+$ to form the crosslinked polymer.

If no monohydric alcohol is used, then substantially all O atoms of formula of formula (I), e.g. 95 mol% of groups of formula (I), may be linked via an organic linking group L to an O atom of another group of formula (I).

If a monohydric alcohol is used then the groups of formula (I) may include groups in which all O atoms are linked via an organic linking group L to an O atom of another group of formula (I) and groups of formula (I) in which 1, 2 or 3 of the O are linked via an organic linking group L to an O atom of another group of formula (I), the remaining O atom or atoms being linked to an alkoxy group formed by reaction of the monohydric alcohol which is not directly linked to another group of formula (I). In this way, the extent of crosslinking within the SIC polymer may be controlled.

If a monohydric alcohol is used then a molar ratio of the alcohol having at least 2 hydroxyl groups : monohydric alcohol may be selected to control the degree of interlinking between groups of formula (I) within the SIC polymer. The molar ratio may be in the range of 1 : 99 to

99 : 1. Limiting the degree of interlinking within may increase the softness or liquid-like characteristics of the SIC polymer which may increase the metal ion mobility within the SIC polymer. The second polymer may be selected so as to provide a composition having greater mechanical strength as compared to the interlinking-limited SIC polymer alone.

The SIC polymer may be a crosslinked polymer comprising silicate substituted with an anionic group, for example a SIC polymer comprising groups of formula (II):

$$Si(OR^6)_uO_v \qquad (II)$$

wherein R^6 is an organic residue substituted with at least one group of formula $-An^-M^+$ wherein An^- is an anionic group, preferably $-SO_3^-$ and M^+ is a cation;

u is 1 or 2, preferably 1;

v is 4-u;

and at least one of the v O atoms is linked by an organic linking group L to an O atom of another group of formula (II).

Formation of the polymer comprising groups of formula (II) may comprise reacting a compound of formula $Si(OR^6)_uY_v$ with an alcohol having at least 2 hydroxyl groups and, optionally, with a monohydric alcohol. Y is a leaving group, preferably a halide, more preferably Br, Cl, or I, most preferably Cl.

The use of a monohydric alcohol may limit the degree of linking between groups of formula (II), as described with respect to formula (I).

Optionally, the alcohol having two or more hydroxyl groups is a compound of formula (III):

$$HO\text{-}L\text{-}OH \qquad (III)$$

L is a divalent organic group.

Preferably, L is selected from groups of formula (IV):

$$-[(A^1)_p\text{-}Z]_q\text{-}(A^2)_r- \qquad (IV)$$

A^1 and A^2 in each occurrence are independently selected from: unsubstituted or substituted arylene; unsubstituted or substituted heteroarylene; and CR^1_2 wherein R^1 in each occurrence is H or a substituent.

q is 0 or a positive integer.

If q is a positive integer then p is at least 1.

In a preferred embodiment, q is at least 1, more preferably 1-6 and each A^1 is CR^1_2. According to these embodiments, p is preferably 2.

r is at least 1, preferably 1 or 2.

Z is O, S, NR^4, $Si(R^5)_2$ SO_2, CO C=O, COO or $CONR^4$ wherein R^4 in each occurrence is independently H or a substituent and R^5 in each occurrence is a substituent.

In a preferred embodiment, r is 1 and A^2 is an arylene or heteroarylene group.

In another preferred embodiment each A^2 is CR^1_2. According to these embodiments, r is preferably 2.

Preferably, R^1 in each occurrence is selected from:
H;
F; and
a linear, branched or cyclic alkyl, optionally a C_{1-20} alkyl, wherein one or more non-adjacent, non-terminal C atoms may be replaced with O, S, NR^4, $Si(R^5)_2$ SO_2, CO, COO or $CONR^4$ and one or more H atoms may be replaced by F wherein R^4 in each occurrence is independently H or a substituent and R^5 in each occurrence is a substituent;
an anionic substituent; and
a photocrosslinkable group.

By "non-terminal C atom" of an alkyl group as used herein is meant a C atom of the methyl group or groups at the chain end or chain ends of a linear or branched alkyl, respectively.

The presence of an anionic substituent R^1 may increase one or more of ionic conductivity of the network; solubility of the network in polar organic solvents or water; and adhesion as compared to a network in which the aluminate or borate groups formed following reaction of the compound of formula (I) are the only anionic groups of the network.

Exemplary anionic substituents are C_{1-12} alkyl, aryl (e.g. phenyl) or C_{1-12} alkylenearyl substituted with one or more anionic groups, wherein one or more non-adjacent, non-terminal C atoms of the C_{1-12} alkyl or alkylene may be replaced with O, S, NR^4, $Si(R^5)_2$, SO_2, CO, COO or $CONR^4$. The anionic substituent may be a sulfonate ($-SO_3^-$) group or a substituent carrying one or more sulfonate groups, for example an alkylene sulfonate substituent. It will be understood that the charge of the anion is balanced with a cation M^+ which is preferably the same as the cation M^+ of formula (I), more preferably Li^+.

The photocrosslinkable group may, following reaction of the first, second and third compounds, be crosslinked to increase the degree of crosslinking within the single-ion conductive network. Exemplary photocrosslinkable groups are groups comprising an azide.

Preferably, each R^1 is independently H or F.

A preferred arylene or heteroarylene group A^1 or A^2 is phenylene.

An arylene or heteroarylene group A^1 or A^2 may be unsubstituted or substituted with one or more substituents selected from F; CN; NO_2; and linear, branched or cyclic C_{1-12} alkyl wherein one or more non-adjacent, non-terminal C atoms may be replaced with O or COO and one or more H atoms may be replaced by F.

Optionally, R^4 in each occurrence is selected from H or a linear, branched or cyclic C_{1-12} alkyl wherein one or more non-adjacent C atoms other than the C atom bound to N or a terminal C atom may be replaced with O, S, CO or COO and one or more H atoms may be replaced by F or an anionic group, e.g. SO_3^-.

Each R^4 is preferably selected from H or a linear, branched or cyclic C_{1-12} alkyl wherein one or more non-adjacent C atoms other than the C atom bound to N or a terminal C atom may be replaced with O and one or more H atoms may be replaced by F.

Optionally, R^5 in each occurrence is selected from H or a linear, branched or cyclic C_{1-12} alkyl wherein one or more non-adjacent C atoms other than the C atom bound to Si or a terminal C

atom may be replaced with O, S, CO or COO and one or more H atoms may be replaced by F or an anionic group, e.g. SO_3^-.

Each R^5 is preferably selected from H or a linear, branched or cyclic C_{1-12} alkyl wherein one or more non-adjacent C atoms other than the C atom bound to Si or a terminal C atom may be replaced with O and one or more H atoms may be replaced by F.

Exemplary alcohols having two or more hydroxyl groups are diols, more preferably compounds of formula (IIIa):

$$HO\text{-}(C_2R^1{}_4Z)n\text{-}(CR^1{}_2)_r\text{-}OH \quad (IIIa)$$

wherein:
Z is O, S, NR^4, $Si(R^5)_2$ SO_2, CO C=O, COO or $CONR^4$ wherein R^4 and R^5 are as described above; n is at least 1, optionally 1-6; r is at least 1, preferably 1 or 2; and each R^1, Z, R^4 and R^5 are as defined above.

Each R^1 is preferably H or F. Each Z is preferably O.

Exemplary compounds of Formula (IIIa) include:

$$HO\text{-}CH_2CF_2\text{-}(OC_2F_4)_2\text{-}CF_2CH_2\text{-}OH$$

Optionally, the monohydric alcohol is a compound of formula (V):

$$HO\text{-}L\text{-}R^3 \quad (V)$$

wherein L is as described above and R^3 is selected from F and H.

Exemplary monohydric alcohols are compounds of formula (Va):

$$HO\text{-}(C_2R^1{}_4Z)_q\text{-}(CR^1{}_2)_r\text{-}R^3 \quad (Va)$$

wherein q, r, Z and R^1 are as described above and R^3 is H or F.

Exemplary compounds of Formula (Va) include:

$HO\text{-}CH_2CF_2\text{-}(OC_2F_4)_2\text{-}CF_2\ CF_2CF_3$

$HO\text{-}CH_2CF_2\text{-}(OC_2F_4)_2\text{-}CF_2CF_3$

$HO\text{-}CH_2CF_2\text{-}(OC_2F_4)_2\text{-}CF_3$

In some embodiments, the anode protection layer described herein contains only one SIC polymer.

In some embodiments, the anode protection layer described herein may contain two or more SIC polymers.

Second polymer

An inert second polymer as described herein is suitably a non-ionic polymer.

The second polymer may be selected from a wide range of polymers known to the skilled person in order to provide the composite comprising the SIC polymer and the second polymer with the desired mechanical properties.

Exemplary second polymers include, without limitation, non-conjugated, neutral polymers and conjugated, neutral (non-ionic) polymers.

The second polymer is preferably a linear polymer, i.e. an unbranched polymer. The second polymer is preferably not crosslinked.

The second polymer may be a conjugated polymer or a non-conjugated polymer. A conjugated polymer comprises repeat units in the backbone of the polymer which are conjugated to adjacent repeat units. The entire backbone of the polymer may be conjugated or conjugation along the backbone may be interrupted by one or more non-conjugating repeat units.

Conjugated polymers include, without limitation, polymers containing one or more of C_{6-40} arylene repeat units and heteroarylene repeat units with 5-40 C atoms; and arylenevinylene repeat units.

Exemplary arylene repeat units include, without limitation, phenylene, fluorene, spirofluorene, indenofluorene, naphthalene, anthracene or phenanthrene repeat units, each of which may be unsubstituted or substituted with one or more substituents.

Exemplary heteroarylene repeat units include, without limitation, thiophene, benzothiadiazole, furan, dibenzothiophene, dibenzofuran, dibenzosilole and carbazole, each of which may be unsubstituted or substituted with one or more substituents.

Substituents of arylene, heteroarylene or arylenevyinylene repeat units may be selected from, without limitation:

F; CN; NO_2; C_{1-20} alkyl wherein one or more non-adjacent, non-terminal C atoms may be replaced with O, S, COO or CO and one or more H atoms of the alkyl may be replaced with F; and a group of formula $-(Ar^1)_p$ wherein Ar^3 in each occurrence is independently an aryl or heteroaryl group, preferably phenyl, which is unsubstituted or substituted with one or more substituents and p is at least 1, optionally 1, 2 or 3. Substituents of Ar^3, where presently, may be selected from F, CN, NO_2 and C_{1-12} alkyl wherein one or more non-adjacent, non-terminal C atoms may be replaced with O, S, COO or CO.

In a preferred embodiment, the repeat units of the conjugated polymer comprise or consist of an arylene repeat unit and a heteroarylene repeat unit, for example a copolymer of a fluorene repeat unit and a benzothiadiazole repeat unit.

Exemplary non-conjugated polymers include, without limitation, neutral polymers including partially or per-fluorinated polymers for example PVDF or PVDF-HFP; poly(ethylene oxide); polystyrene; and acrylates or methacrylates, for example PMMA.

Film formation

A film comprising the SIC polymer and the second polymer may be formed by deposition of a formulation containing the SIC polymer and the second polymer dissolved or dispersed in a

solvent or solvent mixture followed by evaporation of the solvent or solvents. Phase separation may occur during evaporation. Phase separation may be controlled by, without limitation, solvent selection and / or drying conditions.

Exemplary solvents include, without limitation, chlorinated solvents, for example chloroform and ethers, preferably solvents with two or more ether groups for example dimethoxyethane and dioxane.

In some embodiments, a metal battery precursor may be formed wherein the anode protection layer is formed by deposition as described herein onto an anode current collector and a separator is disposed between the anode protection layer and a cathode supported on a cathode current collector. If the metal battery precursor is a solid device then it may be sealed without introduction of any liquid electrolyte. In other embodiments, liquid electrolyte is introduced into the structure prior to sealing or is present in the separator.

Application of a bias across the anode current collector and the cathode current collector causes lithium ions to migrate across the anode protection layer, thus forming the lithium battery having anode layer. The presence of the anode protection layer may result in a smooth lithium film, limiting the growth of "mossy" or dendritic lithium.

Electrolyte

In some embodiments, the metal battery is a solid metal battery, i.e. the metal battery does not contain a liquid electrolyte, for example an ionic liquid or a salt dissolved in a solvent.

In some embodiments, the metal battery contains a liquid electrolyte. The liquid electrolyte may be absorbed in the anode protection layer and / or, if present, a separator.

The electrolyte may comprise an organic solvent or a blend of organic solvents. The solvent is optionally an alkyl carbonate or a mixture of organic carbonates, for example propylene carbonate, ethylene carbonate, dimethyl carbonate, ethylmethyl carbonate, fluoroethylene carbonate, vinylene carbonate, acetonitrile, adiponitrile, dimethylsulfoxide, dimethylformamide, nitromethane, N-methylpyrrolidone, ionic liquids, deep eutectic solvents and mixtures thereof.

A salt having a metal cation, may be dissolved in the electrolyte solvent, for example lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) or lithium hexafluorophosphate Li

bis(fluorosulfonyl)imide (LiFSI), $LiAsF_6$, $LiSbF_6$, $LiClO_4$, Li bisoxalatoborane, $LiBF_4$, $LiNO_3$, Li halides, Li dicyanamide and combinations thereof.

Cathode

The cathode may be any cathode known to the skilled person capable of releasing and reabsorbing metal ions for example, in the case of a lithium battery,$LiCoO_2$, $LiNi_xMn_yCo_z$ (e.g. NMC 622 and 811), $LiFePO_4$ (LFP), $LiMnO_2$, $LiNiCoAlO_2$, V_2O_5, sulfur, and (in the case of a lithium-air battery) oxygen.

Applications

The composition as described herein may be used to form a layer of a metal battery, for example an anode protection layer and / or separator of a metal battery as described herein.

Figure 1 illustrates a battery, preferably a metal battery, comprising an anode current collector 101carrying an anode 103 on a surface thereof; a cathode current collector 109 having a cathode 107 disposed on a surface thereof; a separator 105 disposed between the anode and cathode; and an anode protection layer 111 disposed between anode and the separator. The separator may comprise or consist of a single-ion conductive network as described herein or may be any other separator known to the skilled person, for example a porous polymer having a liquid electrolyte absorbed therein. The anode protection layer comprises or consist of a composition as described herein. The anode protection layer may prevent or retard formation of lithium metal dendrites of a metal battery.

In other embodiments, a metal ion battery may comprise a layer comprising a composition as described herein, for example a separator of a metal ion battery. The anode and cathode of a metal ion battery may be selected from anodes and cathodes known to the skilled person.

A metal or metal ion battery as described herein is preferably a lithium or lithium ion battery, respectively. The metal or metal ion battery as described herein is preferably a secondary metal or metal ion battery.

The metal or metal ion battery as described herein may be used in a wide variety of applications including, without limitation, portable electronic devices such as phones, tablets and laptops; vehicles including cars, electric motorbikes, electric bicycles and drones; medical devices;

wearable electronic devices; and energy storage for storage of energy from renewable energy sources such as solar, wind or hydroelectric power sources.

EXAMPLES

SIC polymer formation

1.23g of 1H,1H,11H,11H-perfluoro-3,6,9-trioxaundecane-1,11-diol (FTEG) was dissolved in anhydrous THF (9 ml) under nitrogen in a Schlenk flask. 1.5 ml of 1M $LiAlH_4$ was added dropwise under nitrogen, under continuous stirring, using a dry ice cooling bath. The mixture was left for reaction at room temperature overnight, to obtain a ~140 mg/ml solution of SIC polymer in THF.

SIC polymer – F8BT blend

Solutions of the SIC with poly[(9,9-di-*n*-octylfluorenyl-2,7-diyl)-*alt*-(benzo[2,1,3]thiadiazol-4,8-diyl)] (F8BT) were prepared in a nitrogen filled glovebox.

Solution 1 containing F8BT (28 mg) and the SIC polymer (112 mg) in 10 ml of THF (20:80 F8BT : SIC polymer weight ratio) was formed, having a concentration of 1.6 w/v.

Solution 2 was formed by mixing 42 mg of F8BT with 1200 microlitres of the SIC polymer solution (~140 mg/ml in THF) and diluted with anhydrous THF to final concentrations of 2.4 w / v %.

The blend solutions were deposited by spin coating onto copper foil in a nitrogen-filled glovebox to obtain layers with thicknesses of 140 nm formed from Solution 1 and 210 nm formed from Solution 2.

Characterisation with Optical Microscopy

Photo luminescence (PL) optical microscopy of a 120 nm F8BT:SIC 20:80 blend film on glass is shown in Figure 2, which shows the presence of a ramified network-like substructure of photoluminescent F8BT polymer (white in Figure 2) where the SIC polymer phase (black in Figure 2) is disposed in the pores of the F8BT sub-structure, or underneath the F8BT sub-structure.

The F8BT sub-structure provides a solid scaffold for enhanced mechanical properties as compared to the SIC polymer, while the SIC polymer phase provides lithium ion conductivity.

Galvanostatic Cycling Efficiency in Coin Cells

Coulombic efficiency (CE = charge "OUT" / charge "IN") of metal stripping and plating was determined by electrochemical methods.

Galvanostatic cycling experiments were conducted on 2032-type coin cell (casings purchased from Cambridge Energy Solutions) devices having either a bare Cu electrode or a Cu electrode coated with a layer of a SIC polymer - F8BT-DSN blend of 140 nm or 210 nm thickness, a parafilm with a hole (SigmaAldrich), a porous Pervio separator (Sumitomo), a glass microfibre separator (Whatman) with 1 M LiTFSI (Solvionic) in propylene carbonate electrolyte (SigmaAldrich) for both of the separators and a Li metal disc counter electrode.

The electrolyte and all coin cell devices were prepared or assembled in a rigorously dry and oxygen-free Ar-filled MBraun glovebox.

The electrochemical measurement was performed on Arbin battery testing system (Arbin Instruments). Cycling Coulombic efficiency was determined by calculating the ratio of the charge passed during stripping to the total charge passed during plating.

The galvanostatic cycling experiment was carried out following steps 1-13 below, and as illustrated in Figure 3

1. Applying a plating current density of -0.1 mA·cm−2 to the working electrode (referred to hereafter as plating) for 60 minutes …

2. Application of a stripping current density of 0.1 mA·cm−2 to a cut-off voltage of 1 V versus the Li/Li+ redox couple (referred to hereafter as stripping) or for 60 minutes, whichever occurs first.

3. 60 minutes rest, when no current was applied.

4. Repeating steps 1-3 twice.

5. A 30 minute plating.

6. 20 minutes rest.

7. Another 30 minute plating.

8. Stripping for up to 30 minutes.

9. 20 minutes rest.

10. Another stripping for up to 30 minutes.

11. 20 minutes rest.

12. Steps 5-11 were repeated twice.

13. Steps 1-12 were repeated 54 times.

With reference to Figure 4, a comparison of the cycling Coulombic efficiencies of cells containing bare Cu foil electrode and Cu foil electrode coated in SIC polymer – F8BT shows that the incorporation of the polymer blend increases the cycling Coulombic efficiencies of the cells.

After about 220 cycles Coulombic efficiencies of the exemplary cells containing the polymer blend cells reached 89% for 140 nm film thickness, and 85% for 210 nm thickness.

In comparison, the Coulombic efficiency of the comparative cell with bare Cu degrades to 56% after 220 cycles.

CLAIMS

1. A composition comprising a crosslinked single-ion conducting polymer and a second polymer.

2. The composition according to claim 1 wherein the crosslinked single-ion conducting polymer comprises groups of formula (I):

$$[XO_4]^- \quad M^+ \quad (I)$$

wherein X is B or Al; at least one of the O atoms of formula (I) is bound through an organic linking group L to another group of formula (I); and M+ is a metal cation.

3. The composition according to claim 2 wherein L is selected from groups of formula (IV):

$$-[(A^1)_p\text{-}Z]_q\text{-}(A^2)_r- \quad (IV)$$

wherein:

A^1 and A^2 in each occurrence are independently selected from: unsubstituted or substituted arylene; unsubstituted or substituted heteroarylene; and CR^1_2 wherein R^1 in each occurrence is H or a substituent;

q is 0 or a positive integer;

if q is a positive integer then p is at least 1.

r is at least 1; and

Z is O, S, NR^4, $Si(R^5)_2$ SO_2, CO C=O, COO or $CONR^4$ wherein R^4 in each occurrence is independently H or a substituent and R^5 in each occurrence is a substituent.

4. The composition according to claim 2 or 3 wherein at least one of the O atoms of formula (I) is bound to a group of formula (IVa):

$$-(C_2R^1_4Z)n\text{-}(CR^1_2)_r\text{-}OH \quad (IVa)$$

5. The composition according to any one of the preceding claims wherein the second polymer is a neutral, non-conjugated polymer.

6. The composition according to any one of claims 1-4 wherein the second polymer is a neutral, conjugated polymer.

7. A composition comprising a single-ion conducting polymer and a neutral conjugated polymer.

8. The composition according to claim 7 wherein the single-ion conducting polymer is selected from a polymer comprising groups of formula (I) and a polymer comprising groups of formula (II):

$$[XO_4]^- \quad M^+ \qquad (I)$$

$$Si(OR^6)_uO_v \qquad (II)$$

wherein:

X is B or Al;

at least one of the O atoms of formula (I) is bound through an organic linking group L to another group of formula (I);

M^+ is a metal cation.

R^6 is an organic residue substituted with at least one group of formula $–An^-M^+$ wherein An^- is an anionic group;

u is 1 or 2;

v is 4-u;

and at least one of the v O atoms of formula (II) is linked by an organic linking group L to an O atom of another group of formula (II).

9. A formulation comprising the composition according to any one of the preceding claims dissolved or dispersed in one or more solvents.

10. A metal battery comprising:

a metal anode;

an anode current collector in electrical contact with the anode;

a cathode;

a cathode current collector in electrical contact with the cathode;

a separator disposed between the anode and cathode; and

an anode protection layer disposed between the anode and the separator,

wherein the anode protection layer comprises a single-ion conductive polymer and an second polymer.

11. The metal battery according to claim 10 wherein the anode protection layer is a phase separated layer.

12. The metal battery according to claim 10 or 11 wherein the metal battery is a solid metal battery.

13. A metal battery precursor comprising:

an anode current collector;

a cathode;

a cathode current collector in electrical contact with the cathode;

an anode protection layer disposed between the anode current collector and the cathode;

a separator disposed between the anode protection layer and the cathode,

wherein the anode protection layer comprises a single-ion conductive polymer and a second polymer.

14. A method of forming a metal battery according to any one of claims 10-12 comprising applying a bias across the metal battery precursor according to claim 13.

15. A method of forming a metal battery precursor according to claim 13 comprising depositing a formulation comprising the single-ion conductive polymer and the inert polymer onto the anode current collector dissolved or dispersed in one or more solvents and evaporating the one or more solvents.

16. A solid metal battery comprising:

a metal anode;

an anode current collector in electrical contact with the anode;

a cathode;

a cathode current collector in electrical contact with the cathode;

a layer disposed between the anode and cathode comprising a single-ion conductive polymer and a second polymer.

17. A metal battery comprising:

a metal anode;

an anode current collector in electrical contact with the anode;

a cathode;

a cathode current collector in electrical contact with the cathode; and

a layer disposed between and in direct contact with the anode and cathode, the layer comprising a composition according to any one of claims 1-8.

18. A metal ion battery comprising:

an anode;

an anode current collector in electrical contact with the anode;

a cathode;

a cathode current collector in electrical contact with the cathode; and

a layer disposed between the anode and cathode comprising a composition according to any one of claims 1-8.

FIGURE 1

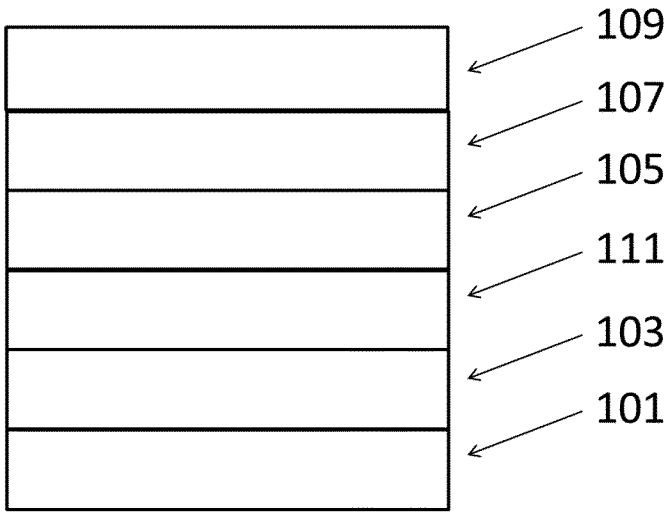


FIGURE 2

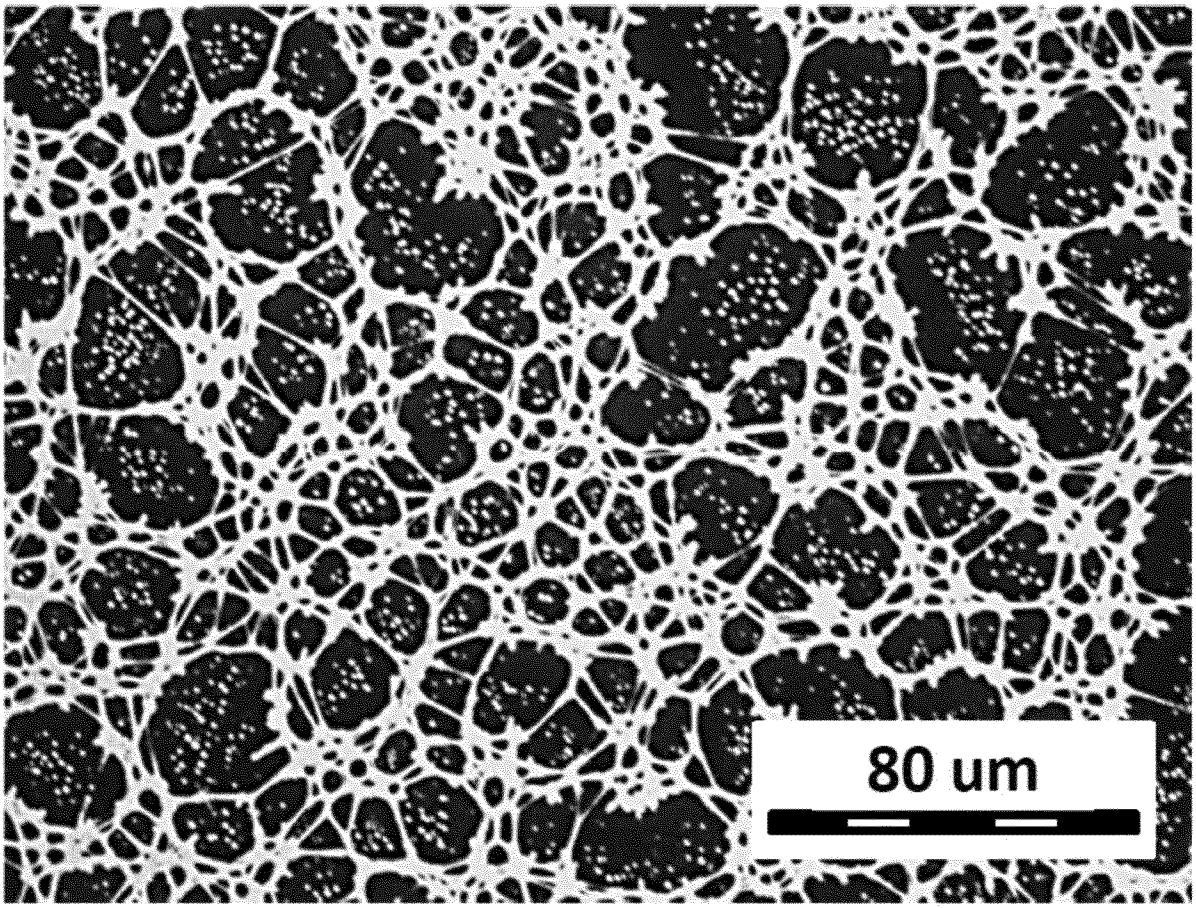


FIGURE 3

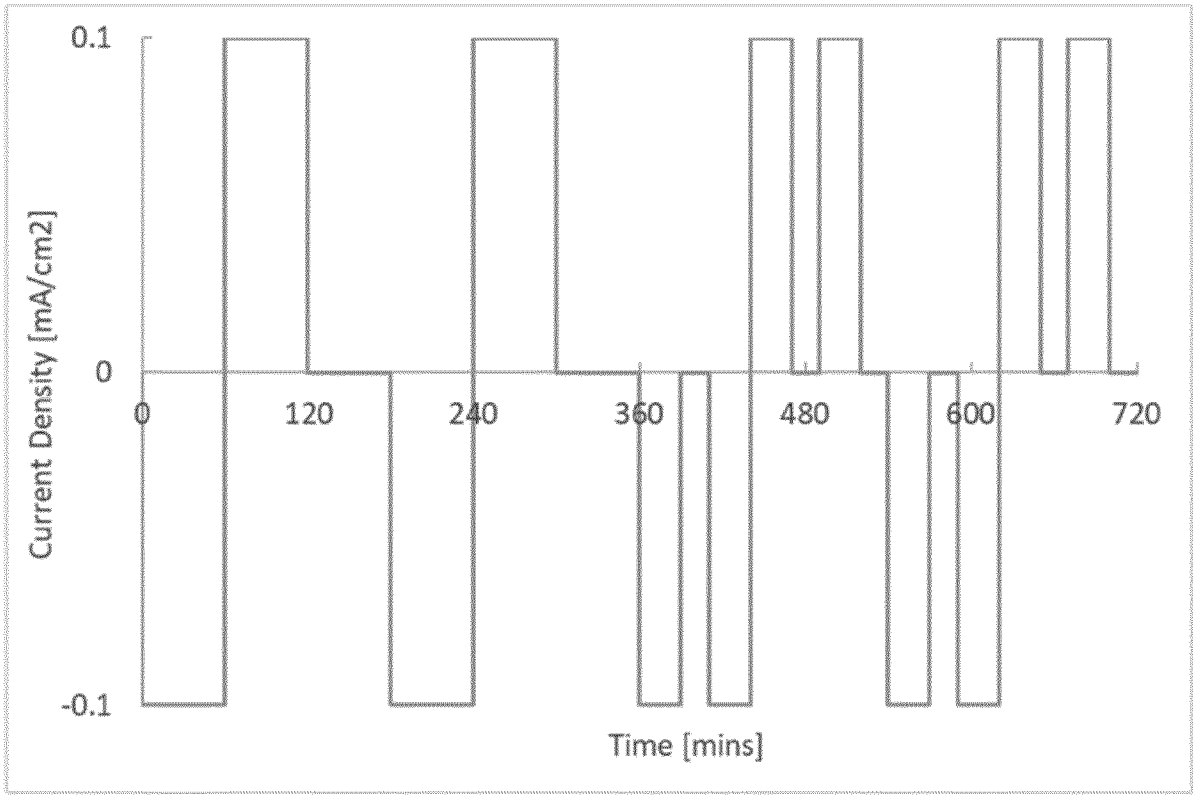
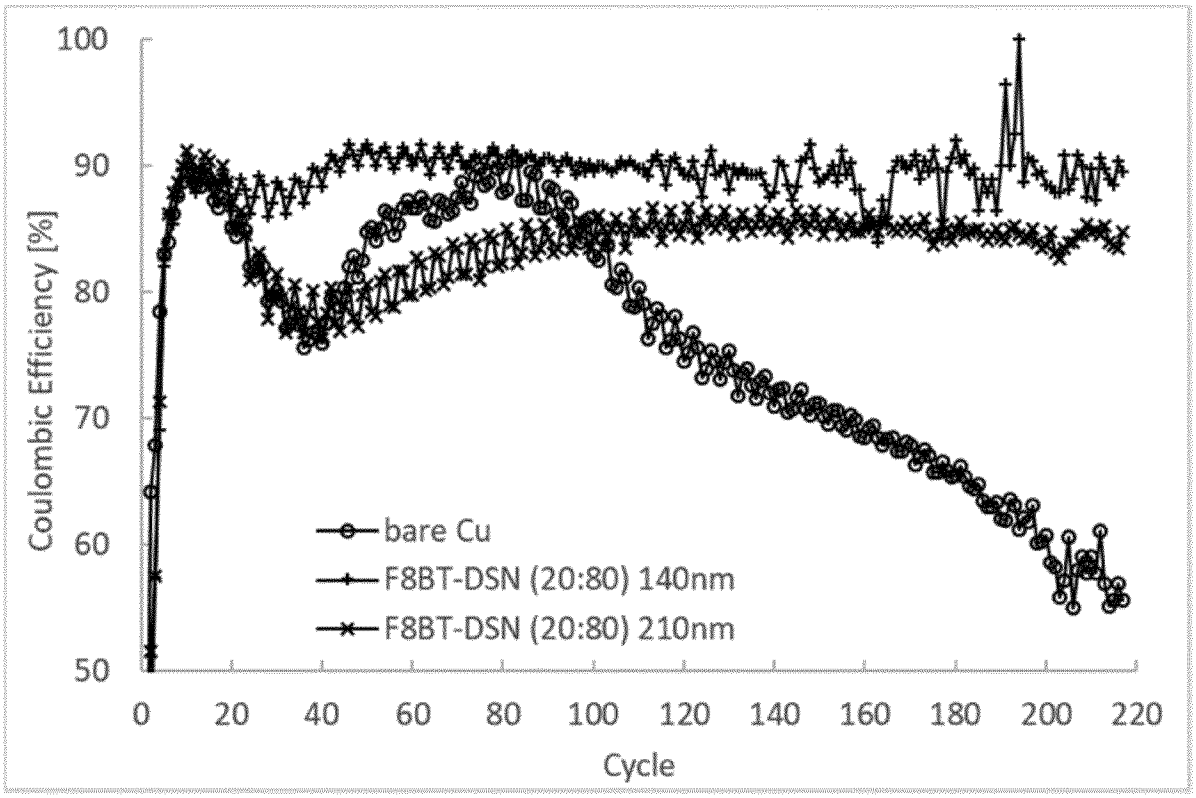


FIGURE 4



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2022/063593

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01M4/04 H01M4/131 H01M4/1391 H01M10/0525 H01M50/403
H01M50/414
ADD.
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)
H01M

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)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 111 748 095 A (UNIV NORTHEAST) 9 October 2020 (2020-10-09)	1,5,9
A	claims 1,7,8,10; examples	2-4,6-8, 10-18

A	BORZUTZKI K. ET AL: "Fluorinated polysulfonamide based single ion conducting room temperature applicable gel-type polymer electrolytes for lithium ion batteries", JOURNAL OF MATERIALS CHEMISTRY A, vol. 7, no. 1, 1 January 2019 (2019-01-01), pages 188-201, XP055962030, GB ISSN: 2050-7488, DOI: 10.1039/C8TA08391F abstract	1-18

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

[x] See patent family annex.

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"&" 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 September 2022	27/09/2022

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2022/063593

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	LI DAN ET AL: "Synthesis and Application of a Conjugated Polydianion-Based Single-Ion Conducting Polymer for High-Performance Solid Lithium-Ion Batteries", CHEMELECTROCHEM, vol. 6, no. 10, 15 May 2019 (2019-05-15), pages 2707-2714, XP055962032, Chichester ISSN: 2196-0216, DOI: 10.1002/celc.201900553 Retrieved from the Internet: URL:https://onlinelibrary.wiley.com/doi/full-xml/10.1002/celc.201900553> abstract -----	1-18

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2022/063593

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CN 111748095 A	09-10-2020	NONE	