

A Solid Polymer Electrolyte

References to Related Application

- 5 This application claims priority to Singapore application number 10202300468X filed with the Intellectual Property Office of Singapore on 23 February 2023, the contents of which is hereby incorporated by reference.

Technical Field

- 10 The present invention generally relates to a solid polymer electrolyte. The present invention also relates to a method of preparing a solid polymer electrolyte. The present invention further relates to a battery comprising the solid polymer electrolyte.

Background Art

- 15 All-solid-state rechargeable lithium-ion batteries (LiBs) hold great potential for electrifying vehicles due to their safety, high energy density and portability. A key component of the LiB is the electrolyte, in which Li ion transport occurs. Conventional LiBs consist of Li salts and liquid solvents. However, these suffer from poor mechanical strength, high flammability and poor cyclability/stability. The use of solid electrolytes (SEs) can resolve these issues.

- 20 Inorganic solid electrolytes, in general, face issues of poor mouldability, high interfacial resistance and complex fabrication process. Amongst less brittle inorganic electrolytes, sulfide-based SEs, despite their high ionic conductivities, suffer from poor electrochemical stability window and require a protective coating layer to be paired with high-voltage cathodes. In contrast, while halide SEs exhibit promising electrochemical stability, there are concerns over the synthesis protocols, high reactivity of halide ions and cycle life of halide-based all-solid-state batteries. 25 Additionally, these problems cannot be easily repaired upon battery failure.

- 30 As such, solid polymer electrolytes (SPEs), which are mechanically strong yet mouldable and can possess lower interfacial resistance and flammability, present an attractive option for all-solid-state LiBs. At present, there are few examples of all-solid-state rechargeable lithium-ion batteries based solely on solid polymer electrolytes. Most SPEs are based on poly(ethylene oxide) (PEO), which are run at temperatures where PEO is molten and typically have poor mechanical properties which may lead to wear and tear or dendrite formation. This may lead to shorting between the cathode and anode, causing battery failure and fire hazard. In addition, 35 the small electrochemical window of PEO renders it incompatible with high voltage cathodes.

Hence, a mechanically strong, reprocessable electrolyte is highly attractive as it can extend the service life of LiBs through on-demand repair. Reprocessable SPEs can

be achieved by incorporating dynamic, reversible cross-links into polymer networks to enable rapid bond reshuffling for crack healing. At present, there are a few examples of reprocessable cross-linked SPEs; however, due to their low ion conductivity, they are commonly used in conjunction with liquid electrolytes or inorganic electrolytes which could lower mechanical strength or increase interfacial resistance respectively. In addition, presently available reprocessable cross-linked SPEs cannot be used with high voltage cathodes.

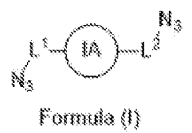
Thus, there is a need for mechanically strong, reprocessable SPEs for stable all-solid-state LiBs that are able to overcome, or at least ameliorate, one or more of the disadvantages described above.

There is also a need to provide a method for preparing such SPEs.

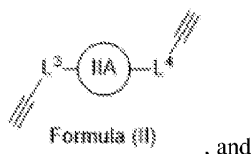
Summary

In one aspect, there is provided a solid polymer electrolyte comprising a plurality of metal cations M interspersed within a polymer comprising:

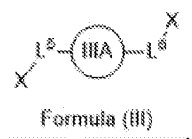
at least one monomer of Formula (I)



at least one monomer of Formula (II)



at least one monomer of Formula (III)



wherein

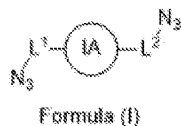
each of group IA, IIA and IIIA is independently a bivalent moiety derived from or polymerized from an ion-conducting oligomer or an ion-conducting polymer;

each X is independently a leaving group; and

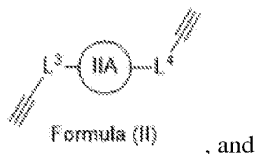
each of L^1 , L^2 , L^3 , L^4 , L^5 and L^6 is independently absent or a C_1 - C_6 alkylene.

In another aspect, there is provided a method of preparing a solid polymer electrolyte comprising the step of:

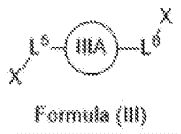
- 5 reacting a metal salt MZ_n with a polymer derived from or polymerized from at least one monomer of Formula (I)



at least one monomer of Formula (II)



at least one monomer of Formula (III)



10

at an elevated temperature,

wherein

M is a metal cation;

Z is a weakly coordinating anion;

- 15 n is suitably selected such that MZ_n is electrically neutral;

each of group IA, IIA and IIIA is independently a bivalent moiety derived from or polymerized from an ion-conducting oligomer or an ion-conducting polymer;

each X is independently a leaving group; and

each of L^1 , L^2 , L^3 , L^4 , L^5 and L^6 is independently absent or a C_1 - C_6 alkylene.

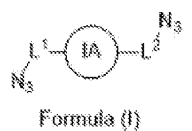
- 20 Advantageously, the method may form the solid polymer electrolyte in one step. This is more efficient than conventional methods for the synthesis of solid polymer

electrolytes and avoids the need for liquid electrolytes such as carbonates (e.g., ethylene carbonate) or ionic liquids.

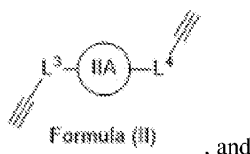
Further advantageously, the method may form a matrix of dynamic covalent bonds due to the reaction between azide moieties in the compound of Formula (I) and alkyne moieties in the compound of Formula (II). The azide moieties may react with the alkyne moieties to form triazole moieties, which may further react with the compound of Formula (III) to form triazolium moieties. Therefore, the solid polymer electrolyte may be regarded as a polytriazolium matrix, which is mechanically firm at operating temperatures yet reprocessable upon thermal activation.

Still further advantageously, the method may form the solid polymer electrolyte in situ in a battery.

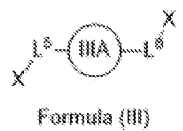
In another aspect, there is provided a solid polymer electrolyte obtainable by or obtained by reacting a metal salt MZ_n with a polymer derived from or polymerized from at least one monomer of Formula (I)



at least one monomer of Formula (II)



at least one monomer of Formula (III)



at an elevated temperature,
wherein

M is a metal cation;

Z is a weakly coordinating anion;

n is suitably selected such that MZ_n is electrically neutral;

each of group IA, IIA and IIIA is independently a bivalent moiety derived from or polymerized from an ion-conducting oligomer or an ion-conducting polymer;

each X is independently a leaving group; and

each of L^1 , L^2 , L^3 , L^4 , L^5 and L^6 is independently absent or a C_1 - C_6 alkylene,

wherein the solid polymer electrolyte comprises a cationic covalent adaptable network.

Advantageously, the present solid polymer electrolyte has improved electrical properties compared with conventional solid polymer electrolytes. This is due to the presence of both mobile metal cations and immobile triazolium cations, which can bind electrostatically to anions, in the solid polymer electrolyte. The solid polymer electrolyte may have a high lithium transference value of about 0.7 to about 0.9.

Further advantageously, the present solid polymer electrolyte has improved thermal stability compared to conventional solid electrolytes due to the presence of the crosslinked polytriazolium matrix. The present solid polymer electrolyte remains solid at cell cycling temperature and does not exhibit any melting transition unlike conventional solid polymer electrolyte e.g., PEO which is molten at cell cycling temperature. The present solid polymer electrolyte may be thermally stable at a high temperature of at least about 300 °C.

Still further advantageously, the present solid polymer electrolyte may be reprocessable upon thermal activation due to the presence of the triazole and triazolium moieties. As demonstrated in the present disclosure, the present solid polymer electrolyte may be reprocessed at a temperature of about 180 °C to about 220 °C, a pressure of about 10 bar for a duration of about 20 minutes.

In another aspect, there is provided a battery comprising the solid polymer electrolyte as described herein, a cathode and/or an anode. The solid polymer electrolyte may act as a separator, or as an ion-conducting phase in a cathode and/or anode.

Advantageously, the battery may retain at least about 99% coulombic efficiency after cycling for at least 60 cycles. This is due to the improved electrical, thermal and mechanical properties of the present solid polymer electrolyte compared with conventional solid polymer electrolytes.

Further advantageously, where the cathode is a high voltage cathode e.g., NMC, the battery may retain at least 90% coulombic efficiency after cycling for at least 60 cycles. The solid polymer electrolyte demonstrated improved cycling stability compared with conventional solid polymer electrolyte e.g., PEO which failed in less than 60 cycles.

Still further advantageously, as the present solid polymer electrolyte may act as a separator, an additional separator is not necessary.

Definitions

The following words and terms used herein shall have the meaning indicated:

As used herein, the term "alkyl group" includes within its meaning monovalent ("alkyl") and divalent ("alkylene") straight chain or branched chain saturated aliphatic groups having from 1 to 10 carbon atoms, e.g., 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 carbon atoms. For example, the term alkyl includes, but is not limited to, methyl,

ethyl, 1-propyl, isopropyl, 1-butyl, 2-butyl, isobutyl, tert-butyl, amyl, 1,2-dimethylpropyl, 1,1-dimethylpropyl, pentyl, isopentyl, hexyl, 4-methylpentyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 2,2-dimethylbutyl, 3,3-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 1,2,2-trimethylpropyl, 1,1,2-trimethylpropyl, 2-ethylpentyl, 3-ethylpentyl, heptyl, 1-methylhexyl, 2,2-dimethylpentyl, 3,3-dimethylpentyl, 4,4-dimethylpentyl, 1,2-dimethylpentyl, 1,3-dimethylpentyl, 1,4-dimethylpentyl, 1,2,3-trimethylbutyl, 1,1,2-trimethylbutyl, 1,1,3-trimethylbutyl, 5-methylheptyl, 1-methylheptyl, octyl, nonyl, decyl, and the like. For example, the term "alkylene" includes, but is not limited to methylene, ethylene, 1,2-propylene, 1,3-propylene, octylene, nonylene, decylene, and the like.

The term "alkynyl group" as used herein includes within its meaning monovalent ("alkynyl") and divalent ("alkynylene") straight or branched chain unsaturated aliphatic hydrocarbon groups having from 2 to 10 carbon atoms and having at least one triple bond anywhere in the carbon chain. Examples of alkynyl groups include but are not limited to ethynyl, 1-propynyl, 1-butyne, 2-butyne, 1-methyl-2-butyne, 3-methyl-1-butyne, 1-pentyne, 1-hexyne, methylpentynyl, 1-heptyne, 2-heptyne, 1-octyne, 2-octyne, 1-nonyl, 1-decynyl, and the like.

The term "aromatic group", or variants such as "aryl" or "arylene" as used herein refers to monovalent ("aryl") and divalent ("arylene") single, polynuclear, conjugated and fused residues of aromatic hydrocarbons having from 6 to 10 carbon atoms. Examples of such groups include phenyl, biphenyl, naphthyl, phenanthrenyl, and the like.

The term "heteroaromatic group" and variants such as "heteroaryl" or "heteroarylene" as used herein, includes within its meaning monovalent ("heteroaryl") and divalent ("heteroarylene"), single, polynuclear, conjugated and fused aromatic radicals having 5 to 10 atoms wherein 1 to 6 atoms are heteroatoms selected from O, N, NH and S. Examples of such groups include pyridyl, 2,2'-bipyridyl, phenanthroline, quinoline, thiophenyl, and the like.

The term "heteroatom" or variants such as "hetero-" as used herein refers to O, N, NH and S.

The term "leaving group" as used herein, refers to a functional group or atom that can be replaced by another functional group or atom in a nucleophilic substitution reaction. The leaving group can be any moiety known in the art that is useful in alkylating triazoles. Such leaving groups are well known in the art. The selection of which is well within the skill of a person of ordinary skill in the art. For example, the leaving group can be a halide, such as chloride, bromide, or iodide, or a weakly coordinating anion selected from the group consisting of bis(trifluoromethanesulfonyl)imide, bis(fluorosulfonyl)imide, (fluorosulfonyl)(trifluoromethanesulfonyl)imide, trifluoromethanesulfonate, toluenesulfonate, monohydrogen phosphate, dihydrogen phosphate,

hexafluorophosphate, perchlorate, tetrafluoroborate, and other borates e.g. bis(oxalato)borate, tetrakis(pentafluorophenyl)borate, tetrakis(3,5-bis(trifluoromethyl)phenyl)borate and combinations thereof.

- 5 The word “substantially” does not exclude “completely” e.g. a composition which is “substantially free” from Y may be completely free from Y. Where necessary, the word “substantially” may be omitted from the definition of the invention.

- 10 Unless specified otherwise, the terms “comprising” and “comprise”, and grammatical variants thereof, are intended to represent “open” or “inclusive” language such that they include recited elements but also permit inclusion of additional, unrecited elements.

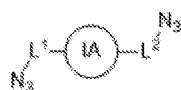
The term “about” as used herein typically means $\pm 5\%$ of the stated value, more typically $\pm 4\%$ of the stated value, more typically $\pm 3\%$ of the stated value, more typically, $\pm 2\%$ of the stated value, even more typically $\pm 1\%$ of the stated value, and even more typically $\pm 0.5\%$ of the stated value.

- 15 Throughout this disclosure, certain embodiments may be disclosed 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 disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as
20 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 sub-ranges 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, 3, 4, 5, and 6. This applies regardless of the breadth of the range.
- 25 Certain embodiments may also be described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the disclosure. This includes the generic description of the embodiments with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically
30 recited herein.

Detailed Disclosure of Embodiments

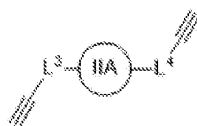
Exemplary, non-limiting embodiments of a solid polymer electrolyte will now be disclosed.

- 35 The solid polymer electrolyte comprises a plurality of metal cations M interspersed within a polymer comprising:
at least one monomer of Formula (I)



Formula (I)

at least one monomer of Formula (II)



Formula (II)

, and

at least one monomer of Formula (III)



Formula (III)

5

wherein

each of group IA, IIA and IIIA is independently a bivalent moiety derived from or polymerized from an ion-conducting oligomer or an ion-conducting polymer;

each X is independently a leaving group; and

- 10 each of L^1 , L^2 , L^3 , L^4 , L^5 and L^6 is independently absent or a C_1 - C_6 alkylene.

The solid polymer electrolyte may further comprise a quarternising agent of Formula R-Y, wherein

R is a C_1 - C_{10} alkyl, a C_1 - C_{10} heteroalkyl, a C_6 - C_{10} aryl or a C_5 - C_{10} heteroaryl, and

Y is a second leaving group.

- 15 In the solid polymer electrolyte, M may be selected from the group consisting of lithium, sodium, potassium, magnesium, calcium, aluminum, vanadium, zinc and combinations thereof.

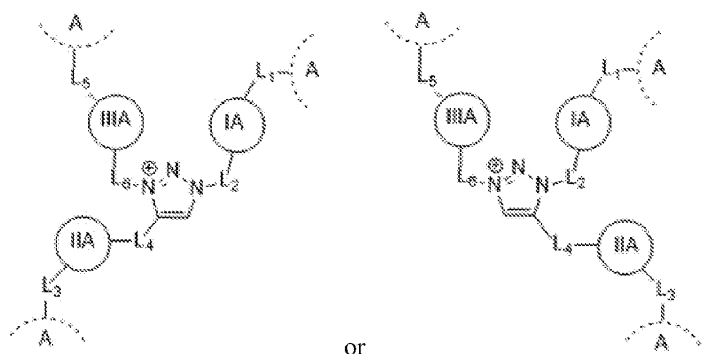
Each of the leaving group of X or the second leaving group of Y may be independently selected from a halide or a weakly coordinating anion.

- 20 The halide may be chloride, bromide or iodide. The halide may be bromide or iodide.

The weakly coordinating anion may be selected from the group consisting of bis(trifluoromethanesulfonyl)imide, bis(fluorosulfonyl)imide,

(fluorosulfonyl)(trifluoromethanesulfonyl)imide, trifluoromethanesulfonate, toluenesulfonate, monohydrogen phosphate, dihydrogen phosphate, hexafluorophosphate, perchlorate, tetrafluoroborate, bis(oxalato)borate, tetrakis(pentafluorophenyl)borate, tetrakis(3,5-bis(trifluoromethyl)phenyl)borate and combinations thereof.

The polymer may comprise a repeating unit of the formula:

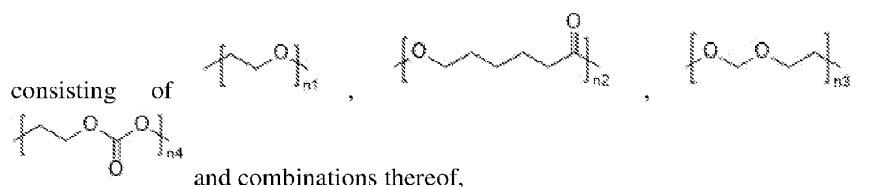


wherein when two or three repeating units are joined at A, A independently forms a triazole or a triazolium,

10 or a regioisomer thereof.

A may be a triazolium quarternised with a R group, where R is as defined above.

Each of group IA, IIA and IIIA may be independently selected from the group

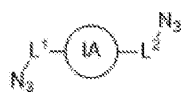


15 wherein each of n1, n2, n3 and n4 is independently a number in the range of 2 to 50.

Exemplary, non-limiting embodiments of a method of preparing a solid polymer electrolyte will now be disclosed.

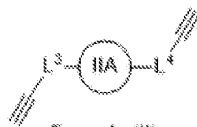
The method comprises the step of:

20 reacting a metal salt MZ_n with a polymer derived from or polymerized from at least one monomer of Formula (I)



Formula (I)

at least one monomer of Formula (II)



Formula (II)

, and

at least one monomer of Formula (III)



Formula (III)

5

at an elevated temperature,

wherein

M is a metal cation;

Z is a weakly coordinating anion;

10 n is suitably selected such that MZ_n is electrically neutral;

each of group IA, IIA and IIIA is independently a bivalent moiety derived from or polymerized from an ion-conducting oligomer or an ion-conducting polymer;

each X is independently a leaving group; and

each of L^1 , L^2 , L^3 , L^4 , L^5 and L^6 is independently absent or a C_1 - C_6 alkylene.

15 Each leaving group of X may be independently selected from a halide or a weakly coordinating anion.

Where each X is the halide, the method further comprises, before the reacting step, the step of first forming the polymer by heating a mixture comprising the at least one monomer of Formula (I), the at least one monomer of Formula (II), and the at

20 least one monomer of Formula (III) at the elevated temperature.

Where each X is the weakly coordinating anion, in the reacting step, the polymer may be formed in situ by heating a mixture comprising the at least one monomer of

Formula (I), the at least one monomer of Formula (II) and the at least one monomer of Formula (III) at the elevated temperature.

- Where each X is the weakly coordinating anion, the reacting step may be considered as a one-pot reaction where the metal salt MZ_n is mixed with the at least one monomer of Formula (I), the at least one monomer of Formula (II) and the at least one monomer of Formula (III), whereby the polymer is formed from the recited monomers and reacted with the metal salt MZ_n in situ.

The polymer may be further derived from a quarternising agent of Formula R-Y, wherein

- R is a C_1 - C_{10} alkyl, a C_1 - C_{10} heteroalkyl, a C_6 - C_{10} aryl or a C_5 - C_{10} heteroaryl, and Y is a second leaving group.

Advantageously, the quarternising agent may help to maintain a high ratio of cationic centers in the solid polymer electrolyte with a lower amount of the monomer of Formula (III) used.

- The second leaving group of Y may be selected from a halide or a weakly coordinating anion.

Where Y is the halide, the mixture of the forming step (which is before the reacting step) further comprises the quarternising agent.

- Where Y is the weakly coordinating anion, the mixture that is used to form the polymer in situ in the reacting step further comprises the quarternising agent.

The monomer of Formula (I) and the monomer of Formula (II) may have a molar ratio in the range of about 1:0.8 to about 1:1.2, about 1:1 to about 1:1.2 or about 1:0.8 to about 1:1.

- The monomer of Formula (I) and the monomer of Formula (III) may have a molar ratio in the range of about 1:0.1 to about 1:1.5, about 1:0.5 to about 1:1, about 1:0.75 to about 1:1, about 1:0.1 to about 1:0.75 or about 1:1 to about 1:0.5.

Where the quarternising agent is present in the mixture, the monomer of Formula (I) and the quarternising agent may have a molar ratio in the range of about 1:0.1 to about 1:2, about 1:1 to about 1:2 or about 1:0.1 to about 1:1.

- The reacting step may be undertaken in the presence of an organic solvent. The organic solvent is not particularly limited as long as it can dissolve the metal salt MZ_n . The organic solvent may be selected from the group consisting of acetonitrile, tetrahydrofuran, ethyl acetate, dimethylformamide, dimethylsulfoxide, dimethylsulfone or a combination thereof.

Where the organic solvent is present, the metal salt MZ_n may have a concentration in the range of about 0.01 M to about 2.0 M, about 1 M to about 2 M or about 0.01 M to about 1 M.

- 5 The elevated temperature used in the reacting step or the forming step (where present) may be a temperature in the range of about 40 °C to about 200 °C, about 100 °C to about 200 °C, about 150 °C to about 200 °C, about 40 °C to about 150 °C or about 100 °C to about 110 °C.

- 10 In the metal salt MZ_n , M may be selected from the group consisting of lithium, sodium, potassium, magnesium, calcium, aluminum, vanadium, zinc and combinations thereof. M may be lithium.

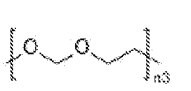
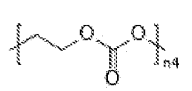
Where the leaving group of X or the second leaving group of Y is the halide, the halide may be chloride, bromide or iodide. The halide may be bromide or iodide.

- 15 In the metal salt MZ_n , Formula (III) or R-Y, the weakly coordinating anion (as Z or where present as the leaving group of X or the second leaving group of Y) is an anion that interacts weakly with cations due to delocalisation of the negative charge over a large area of non-nucleophilic and chemically robust moieties.

- 20 The weakly coordinating anion may be selected from the group consisting of bis(trifluoromethanesulfonyl)imide, bis(fluorosulfonyl)imide, (fluorosulfonyl)(trifluoromethanesulfonyl)imide, trifluoromethanesulfonate, toluenesulfonate, monohydrogen phosphate, dihydrogen phosphate, hexafluorophosphate, perchlorate, tetrafluoroborate, and other borates e.g. bis(oxalato)borate, tetrakis(pentafluorophenyl)borate, tetrakis(3,5-bis(trifluoromethylphenyl)borate and combinations thereof.

- 25 Each of group IA, IIA and IIIA may be independently derived from or polymerized from poly(ethylene glycol), polyester (e.g. poly(caprolactone)), poly(1,3-dioxolane) or polycarbonate (e.g. poly(ethylene carbonate)). Therefore, each of group IA, IIA

and IIIA may be independently selected from the group consisting of ,

, ,  and combinations thereof.

- 30 Each of n1, n2, n3 and n4 may be independently a number in the range of about 2 to about 50, about 10 to about 50, about 30 to about 50, about 2 to about 30 or about 2 to about 10.

The reacting step may be undertaken in an inert atmosphere. The reacting step may be undertaken in nitrogen, argon, or a combination thereof.

The reacting step or the forming step (where present) may be undertaken for a duration in the range of about 0.5 days to about 10 days, about 1 day to about 10 days, about 7 days to about 10 days, about 0.5 days to about 7 days, about 0.5 days to about 2 days or about 0.5 days to about 1 day.

- 5 The reacting step may be alternatively or additionally monitored by adding AgNO_3 to the solid polymer electrolyte. Where the adding of the AgNO_3 does not form any precipitate, the reacting step may be regarded as completed.

Where the reacting step is undertaken for a duration of more than 1 day, the mixture may be separated from the metal salt MZ_n and reacted with a new batch of the metal salt MZ_n every day.

10 The method may further comprise a step of hot pressing the solid polymer electrolyte.

In the hot pressing step, the solid polymer electrolyte formed in the reacting step may be treated at an elevated temperature and a nominal elevated pressure calculated based on the equation below.

$$\text{Nominal Elevated Pressure} = \text{Actual Pressure} - 1 \text{ bar}$$

The hot pressing step may be undertaken at a temperature in the range of about 100 °C to about 250 °C, about 150 °C to about 250 °C, about 200 °C to about 250 °C, about 100 °C to about 200 °C or about 100 °C to about 150 °C.

- 20 The hot pressing step may be undertaken at a nominal pressure in the range of about 0.1 bar to about 20 bar, about 10 bar to about 20 bar or about 0.1 bar to about 10 bar.

The method may further comprise a step of drying the solid polymer electrolyte after the reacting step or the hot pressing step (where present).

- 25 The drying step may be undertaken at a temperature in the range of about 50 °C to about 200 °C, about 100 °C to about 200 °C, about 150 °C to about 200 °C, about 50 °C to about 150 °C or about 50 °C to about 100 °C.

The drying step may be undertaken for a duration in the range of about 0.5 days to about 5 days, about 2 days to about 5 days or about 0.5 days to about 2 days. The drying step may be undertaken until the solid polymer electrolyte is free from or substantially free from moisture.

30 The drying step may be undertaken in vacuum.

Exemplary, non-limiting embodiments of a solid polymer electrolyte will now be disclosed.

The solid polymer electrolyte may be obtainable by or obtained by the method as described herein. Therefore, the solid polymer electrolyte may comprise a plurality of triazole moieties and/or triazolium moieties that are crosslinked by ion-conducting oligomers or polymers and impregnated with metal cations. The solid polymer electrolyte may comprise a cationic covalent adaptable network.

The solid polymer electrolyte may have a shape of a film.

The solid polymer electrolyte may be free-standing or exists as part of a composite.

The solid polymer electrolyte may have a structure as exemplarily shown in FIG. 1A or FIG. 1B.

Exemplary, non-limiting embodiments of a battery will now be disclosed.

The battery comprises the solid polymer electrolyte as described herein, a cathode and/or an anode. The solid polymer electrolyte may act as a separator, or as an ion-conducting phase in a cathode and/or anode or a combination thereof.

The anode may comprise lithium. The anode may be a foil of lithium metal.

The cathode may comprise lithium iron phosphate, lithium nickel manganese cobalt oxide or a combination thereof.

In the battery, the solid polymer electrolyte may be in a form of metal-ion, metal polymer, solid-state, metal-sulfide, or metal-air electrolyte.

Brief Description of Drawings

The accompanying drawings illustrate a disclosed embodiment and serves to explain the principles of the disclosed embodiment. It is to be understood, however, that the drawings are designed for purposes of illustration only, and not as a definition of the limits of the invention.

FIG. 1A

[FIG. 1A] shows a structure of cross-linked cationic vitrimeric polytriazolium solid polymer electrolyte synthesized without a quaternising agent.

FIG. 1B

[FIG. 1B] shows a structure of cross-linked cationic vitrimeric polytriazolium solid polymer electrolyte synthesized in the presence of a quaternising agent.

FIG. 2A

[FIG. 2A] shows the chemical structure of **TFSI-PEG-TFSI** of Example 2c.

FIG. 2B

[FIG. 2B] shows the ^1H spectrum of **TFSI-PEG-TFSI** of Example 2c.

FIG. 2C

[FIG. 2C] shows the ^{19}F NMR spectrum of **TFSI-PEG-TFSI** of Example 2c.

5 **FIG. 3**

[FIG. 3] is a schematic diagram showing a cross-section arrangement of PT-LiTFSI-based LiBs.

FIG. 4A

10 [FIG. 4A] shows the high resolution XPS spectra of N 1s of **PT-Br-5** of Example 2aii.

FIG. 4B

[FIG. 4B] shows the high resolution XPS spectra of Br 3d of **PT-Br-5** of Example 2aii.

FIG. 4C

15 [FIG. 4C] shows the high resolution XPS spectra of C 1s of **PT-Br-5** of Example 2aii.

FIG. 4D

[FIG. 4D] shows the high resolution XPS spectra of O 1s of **PT-Br-5** of Example 2aii.

20 **FIG. 4E**

[FIG. 4E] shows the wide-scan XPS spectra of **PT-Br-5** of Example 2aii.

FIG. 5A

[FIG. 5A] shows the high resolution XPS spectra of N 1s of **Pt-OTs-LiTFSI-1** of Example 2b.

25 **FIG. 5B**

[FIG. 5B] shows the high resolution XPS spectra of S 2p of **PT-OTs-LiTFSI-1** of Example 2b.

FIG. 5C

30 [FIG. 5A] shows the high resolution XPS spectra of C 1s of **PT-OTs-LiTFSI-1** of Example 2b.

FIG. 5D

[FIG. 5A] shows the high resolution XPS spectra of O 1s of **PT-OTs-LiTFSI-1** of Example 2b.

FIG. 5E

- 5 [FIG. 5E] shows the high resolution XPS spectra of Li 1s of **PT-OTs-LiTFSI-1** of Example 2b.

FIG. 5F

[FIG. 5F] shows the high resolution XPS spectra of F 1s of **PT-OTs-LiTFSI-1** of Example 2b.

- 10 **FIG. 5G**

[FIG. 5G] shows the wide-scan XPS spectra of N 1s of **PT-OTs-LiTFSI-1** of Example 2b.

FIG. 6A

- 15 [FIG. 6A] shows the high resolution XPS spectra of N 1s of **PT-Br-2-LiTFSI** of Example 3ai.

FIG. 6B

[FIG. 6B] shows the high resolution XPS spectra of Br 3d of **PT-Br-2-LiTFSI** of Example 3ai.

FIG. 6C

- 20 [FIG. 6C] shows the high resolution XPS spectra of C 1s of **PT-Br-2-LiTFSI** of Example 3ai.

FIG. 6D

[FIG. 6D] shows the high resolution XPS spectra of O 1s of **PT-Br-2-LiTFSI** of Example 3ai.

- 25 **FIG. 6E**

[FIG. 6E] shows the high resolution XPS spectra of S 2p of **PT-Br-2-LiTFSI** of Example 3ai.

FIG. 6F

- 30 [FIG. 6F] shows the high resolution XPS spectra of Li 1s of **PT-Br-2-LiTFSI** of Example 3ai.

FIG. 6G

[FIG. 6G] shows the high resolution XPS spectra of F 1s of **PT-Br-2-LiTFSI** of Example 3ai.

FIG. 6H

- 5 [FIG. 6H] shows the wide-scan XPS spectra of N 1s of **PT-Br-2-LiTFSI** of Example 3ai.

FIG. 7A

[FIG. 7A] shows the high resolution XPS spectra of N 1s of **PT-Br-5-LiTFSI** of Example 3aai.

- 10 **FIG. 7B**

[FIG. 7B] shows the high resolution XPS spectra of Br 3d of **PT-Br-5-LiTFSI** of Example 3aai.

FIG. 7C

- 15 [FIG. 7C] shows the high resolution XPS spectra of C 1s of **PT-Br-5-LiTFSI** of Example 3aai.

FIG. 7D

[FIG. 7D] shows the high resolution XPS spectra of O 1s of **PT-Br-5-LiTFSI** of Example 3aai.

FIG. 7E

- 20 [FIG. 7E] shows the high resolution XPS spectra of S 2p of **PT-Br-5-LiTFSI** of Example 3aai.

FIG. 7F

[FIG. 7F] shows the high resolution XPS spectra of Li 1s of **PT-Br-5-LiTFSI** of Example 3aai.

- 25 **FIG. 7G**

[FIG. 7G] shows the high resolution XPS spectra of F 1s of **PT-Br-5-LiTFSI** of Example 3aai.

FIG. 7H

- 30 [FIG. 7H] shows the wide-scan XPS spectra of N 1s of **PT-Br-5-LiTFSI** of Example 3aai.

FIG. 8A

[FIG. 8A] shows the SEM image for **PT-Br-2-LiTFSI** of Example 3ai.

FIG. 8B

5 [FIG. 8B] shows the X-ray mapping of elements present for **PT-Br-2-LiTFSI** of Example 3ai.

FIG. 8C

[FIG. 8C] shows the SEM-EDX spectrum for **PT-Br-2-LiTFSI** of Example 3ai.

FIG. 8D

10 [FIG. 8D] shows the summary of detected elements present for **PT-Br-2-LiTFSI** of Example 3ai.

FIG. 9A

[FIG. 9A] shows the SEM image for **PT-Br-5-LiTFSI** of Example 3aii.

FIG. 9B

15 [FIG. 9B] shows the X-ray mapping of elements present for **PT-Br-5-LiTFSI** of Example 3aii.

FIG. 9C

[FIG. 9C] shows the SEM-EDX spectrum for **PT-Br-5-LiTFSI** of Example 3aii.

FIG. 9D

20 [FIG. 9D] shows the summary of detected elements present for **PT-Br-5-LiTFSI** of Example 3aii.

FIG. 10A

[FIG. 10A] shows the FTIR spectra of **PT-Br-2** (Top) and **PT-Br-2-LiTFSI** (Bottom).

FIG. 10B

25 [FIG. 10B] shows the FTIR spectra of **PT-Br-6** (Top) and **PT-Br-6-LiTFSI** (Bottom).

FIG. 11A

[FIG. 11A] is a schematic illustration of the reprocessibility of the **PT** of Example 2 and **PT-MZ** of Example 4 via dynamic covalent bonds.

FIG. 11B

- 5 [FIG. 11B] shows the triazolium dynamic covalent bond exchange.

FIG. 11C

[FIG. 11C] is a photo of **PT-Br-2-LiTFSI** demonstrating that it is a free-standing film.

FIG. 12

- 10 [FIG. 12] is an Arrhenius plot showing ionic conductivity of **PT-Br-2-LiTFSI** of Example 4ai in the temperature range of 20 to 80 °C.

FIG. 13

- 15 [FIG. 13] is a DC polarisation curve (24 hours) and Nyquist plots of impedance before and after polarization (inset figure) in a SS|**PT-Br-2-LiTFSI**|SS cell used to measure the lithium transference number of the **PT-Br-2-LiTFSI** of Example 4ai.

FIG. 14

[FIG. 14] is an Arrhenius plot showing ionic conductivity of **PT-Br-5-LiTFSI** of Example 4aii in the temperature range of 20 to 80 °C.

FIG. 15

- 20 [FIG. 15] is an Arrhenius plot showing ionic conductivity of **PT-OTs-LiTFSI-1** of Example 4b in the temperature range of 20 to 80 °C.

FIG. 16

- 25 [FIG. 16] shows charge-discharge capacity and coulombic efficiency plots of Li|**PT-Br-2-LiTFSI**|LFP (voltage range 2-4 V, current density of 0.15 C) at elevated temperature of 60 °C using Example 4ai as the solid polymer electrolyte.

FIG. 17

[FIG. 17] shows charge-discharge capacity and coulombic efficiency plots of Li|**PT-Br-2-LiTFSI**|NMC (voltage range 3-4.2 V) cell cycled at current density of 0.1 C at elevated temperature of 60 °C using Example 4ai as the solid polymer electrolyte.

30

FIG. 18

[FIG. 18] shows charge-discharge capacity and coulombic efficiency plots of Li|PEO-LiTFSI|NMC (voltage range 3-4.2 V) cell cycled at current density of 0.1 C at elevated temperature of 60 °C using PEO (MW=900k) - LiTFSI as the solid polymer electrolyte.

5 FIG. 19

[FIG. 19] shows charge-discharge capacity and coulombic efficiency plots of Li|PT-Br-5-LiTFSI|NMC (voltage range 3-4.2 V) cell cycled at current density of 0.1 C at elevated temperature of 60 °C using Example 4a as the solid polymer electrolyte.

FIG. 20

- 10 [FIG. 20] shows charge-discharge capacity and coulombic efficiency plots of Li|PT-OTs-LiTFSI-1|LFP (voltage range 3-4.2 V) cell cycled at current density of 0.1 C at elevated temperature of 60 °C using Example 4b as the solid polymer electrolyte.

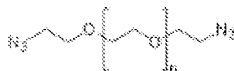
Detailed Description of Drawings

- 15 Referring to FIG. 1A, there is shown the reaction and structure of a cross-linked cationic vitrimeric polytriazolium solid polymer electrolyte synthesized without a quaternising agent according to one disclosed embodiment.

Here, the method of forming a solid polymer electrolyte comprises the steps of:

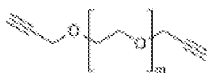
- a) reacting a mixture comprising a monomer of Formula (I)

20



Formula (I),

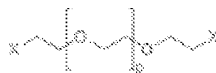
- a monomer of Formula (II)



25

Formula (II), and

a monomer of Formula (III)



Formula (III),

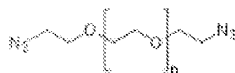
at 110 °C in an argon atmosphere to form a polymer, wherein m is about 2, n is about 44, p is about 2 and X is bromide; and

b) reacting a metal salt lithium bis(trifluoromethanesulfonyl)imide with the polymer in the presence of acetonitrile at 80°C to form the solid polymer electrolyte, wherein the metal salt has a concentration of about 0.15 M in acetonitrile.

Referring to FIG. 1B, there is shown the reaction and structure of a cross-linked cationic vitrimeric polytriazolium solid polymer electrolyte synthesized in the presence of a quaternising agent according to another disclosed embodiment.

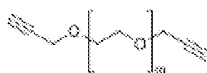
Here, the method of forming a solid polymer electrolyte comprises the steps of:

b) heating a mixture comprising a monomer of Formula (I)



Formula (I),

a monomer of Formula (II)



Formula (II),

a monomer of Formula (III)



Formula (III),

and a quaternising agent methyl bis(trifluoromethanesulfonyl)imide at 110 °C in an argon atmosphere to form a polymer, wherein m is about 2, n is about 44, p is about 2 and X is bromide; and

b) reacting a metal salt lithium bis(trifluoromethanesulfonyl)imide with the polymer in the presence of acetonitrile at 80°C to form the solid polymer

electrolyte, wherein the metal salt has a concentration of about 0.15 M in acetonitrile.

Examples

- Non-limiting examples of the invention will be further described in greater detail by reference to specific Examples, which should not be construed as in any way limiting the scope of the invention.

Example 1 – General Process Steps

Table 1 below outlines an example of general process steps for fabrication of a PT-LiZ battery.

10 **Table 1.** Process steps for fabrication of **PT-MZ** battery

Step	Process	Description
1	One-pot synthesis of cross-linked PEG-triazolium polymer (PT)	- Alkyne-PEG-alkyne + N₃-PEG-N₃ + X-PEG-X in ratio 1:1:y - PEG (poly(ethylene glycol)) chain length of each component can be varied. PEG may also be substituted by other ion-conducting oligomers/polymers such as poly(caprolactone) (PCL), poly(dioxolane) (PDOL), poly(carbonate) (PC), etc. - X = Br, I, OTs, TFSI 0 < y ≤ 1 - Quarternising agent (e.g. R-Y, where R = alkyl, heteroalkyl, aryl, heteroaryl; Y = Br, I, OTs, TFSI and need not be the same as the X-PEG-X) may also be added to quarternise any unreacted triazoles. The amount of R-Y (w) added may be between 0 < w ≤ 2(1-y) or it may be w > 2(1-y) if step 2 is undertaken. - Reacted under inert atmosphere (Ar or N₂) at 110 °C for 1 day. - If X is weakly coordinating and not reactive, e.g., TFSI, then the metal salt MZ_n may be added in this step and the swelling step (2) may be skipped.
2	Swelling of PT in metal salt MZ _n /organic solvent	- For (i) incorporation of Mⁿ⁺ cation and (ii) ion exchange of X⁻ anion to weakly coordinating anion Z. If X is a weaklycoordinating and non-reactive anion, then metal salt (MZ_n) can directly be added in step (1) and this step may be skipped. PT is soaked in a solution of metal salt (MZ) in organic solvent until ion exchange and Li incorporation is complete. - M = Li, Na, K, Mg, Ca, Al, etc. - Z = TFSI, FSI, OTf, H₂PO₄, B(C₂O₄)₂, B(C₆F₅)₄, etc. - Organic solvent may be acetonitrile, THF, EtOAc, etc. - Concentration of MZ_n solution may be 0.01 to 2.0 M - Ion exchange is complete when addition of AgNO₃ to an aliquot does not form a precipitate. - Ion exchange may take 1 to 7 days with fresh MZ_n solution each day
3	Hot-pressing of	PT-MZ_n film is hot-pressed to form a 100-300 μm film - temperature = 100-250 °C

	PT-MZ_n SPE	○ nominal pressure = 0.5-20 bar
4	Prepare all-solid-state energy storage device	• Drying the PT-MZ_n SPE to remove any trace of moisture • In this example of Li-ion battery: ○ Preparation of cathode material with LiFePO₄ (LFP) and LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂ (NMC 622) as active materials ○ Coin cell assembly with Li foil as anode, PT-LiZ SPE as electrolyte and LFP or NMC as cathode

Example 2 – Step 1: One-Pot Synthesis of Cross-linked PEG-Triazolium Polymer (PT)

Preparation of polymer **N₃-PEG-N₃**

- 5 30.1 g of poly(ethylene glycol) ($M_n=2050$, 14.7 mmol, 1 eq., purchased from Sigma-Aldrich, Singapore) was added to a round bottom flask and dried in a vacuum oven at 90 °C for 1 day. The round bottom flask was evacuated and filled with argon. 110 mL of 1M thionyl chloride in dichloromethane (purchased from Tokyo Chemicals Industry, Singapore) was added and the mixture was refluxed at
- 10 50 °C for 1 day. Solvent was reduced in vacuo. Polymer was reprecipitated in diethyl ether (purchased from Fisher Scientific, Singapore) and dried to obtain 28.6 g **Cl-PEG-Cl** ($M_n=2087$, 13.7 mmol). In a round bottom flask, **Cl-PEG-Cl**, 2.99 g of sodium azide (46.0 mmol, 3.4 eq., purchased from Fluka, Singapore) and 100mL of dimethylsulfoxide (purchased from Kanto Chemicals, Singapore) was added into
- 15 a round-bottom flask. The mixture was evacuated, filled with argon and sealed. It was heated at 80 °C over two days. Reaction mixture was cooled and extracted with dichloromethane 3 times. Organic layer was collected and washed with deionized water 3 times. Organic layer was collected and dried with magnesium sulfate (purchased from Kanto Chemical, Singapore) and filtered. Solvent was reduced in
- 20 vacuo and reprecipitated in diethyl ether (purchased from Fisher Scientific, Singapore). 21.9 g of **N₃-PEG-N₃** was collected as a white powder.

Example 2a: Br-PEG-Br as crosslinker

- The following samples shown in Table 2 were prepared using **Br-PEG-Br** ($X = \text{Br}$) as the crosslinker, optionally with quarternising agent MeTFSI. Different samples
- 25 of **PT-Br** were prepared with varying Br-PEG-Br and MeTFSI ratios. Increasing the amounts of Br-PEG-Br increased both the crosslinking density and the quarternisation of triazoles, while increasing the amounts of MeTFSI only increased the quarternisation of triazoles.

- 30 Crosslinker diethylene glycol bis(2-bromoethyl) ether, **Br-PEG-Br** ($X = \text{Br}$) was prepared.

3.28 g of tetraethylene glycol bis(p-toluenesulfonate) (6.54 mmol, 1 eq., purchased from Tokyo Chemical Industry, Singapore), 2.46 g of sodium bromide (23.9 mmol,

4 eq., purchased from Alfa Aesar, Singapore), 10 mL of dimethylsulfoxide (purchased from Kanto Chemicals, Singapore) and 11 drops of 15-crown-5 (purchased from Tokyo Chemicals Industry, Singapore) was added to a round-bottom flask and filled with argon. Mixture was stirred and heated at 60 °C overnight. The mixture was cooled to room temperature and dichloromethane and deionized water was added. The solution was washed 3 times with saturated brine and organic layer was collected. The organic layer was dried with magnesium sulfate (purchased from Kanto Chemicals, Singapore) and filtered. Filtrate was dried in vacuo to obtain yellow oil.

10 **Table 2.** Different samples of **PT-Br** prepared: Gel fractions of polymer networks formed from varying ratios of Br-PEG-Br and MeTFSI with respect to N₃-PEG-N₃

Sample	Br-PEG-Br ratio	MeTFSI ratio	Gel Fraction / %
PT-Br-1	1	0	87
PT-Br-2	0.75	0	85
PT-Br-3	0.5	0	79
PT-Br-4	0.3	0	60
PT-Br-5	0.5	0.5	73
PT-Br-6	0.75	0.25	87
PT-Br-7	0.5	1	85

Example 2ai: **PT-Br-2**

The synthesis method for **PT-Br-1** to **PT-Br-4** was similar. As a representative example, the synthesis method for **PT-Br-2** is described below. A summary of the reactants is shown in Table 3.

Table 3. Reactants for preparing **PT-Br-2**

alkyne-PEG-alkyne	N ₃ -PEG-N ₃	X-PEG-X	ratio
diethylene glycol bis(2-propynyl) ether	N ₃ -PEG-N ₃ (M _n =2095)	diethylene glycol bis(2-bromooctyl) ether	1:1:0.75

20 504.6 mg of N₃-PEG-N₃ (M_n=2095, 0.240 mmol, 1 eq.) was weighed in a 20 mL screw cap vial and dried in a vacuum oven at 90 °C overnight and subsequently filled with argon. 43 µL of diethylene glycol bis(2-propynyl) ether (0.240 mmol, 1 eq., purchased from Tokyo Chemicals Industry, Singapore) and 58.0 mg of

diethylene glycol bis(2-bromoethyl) ether (0.181 mmol, 0.75 eq.) were added. The scaled vial kept in argon was heated to 110 °C and stirred for 1 day.

Gel fraction test was performed on 30 mg of the resulting polymer. The sample was heated in acetonitrile at 70 °C for 1h. Thereafter, the resulting gel was washed 3
5 times with acetonitrile, dried and weighed.

$$\text{Gel fraction} = (\text{final mass} - \text{initial mass}) / \text{initial mass} \times 100\%$$

The gel fraction indicates the extent of crosslinking of the solid polymer electrolyte upon formation. Any unreacted monomer or short-chain oligomers are washed away during the gel fraction step. Hence, gel fraction also represents the yield of the
10 reaction. The higher the gel fraction, the higher the yield of the cross-linked polymer.

Since the undissolved gel has a mass that is >70% of the original mass, the reaction is successful and can proceed to the next step where ~15 mL of acetonitrile (purchased from Sigma-Aldrich, Singapore) was added to the vial and heated at 60
15 °C for 1 hour. The swelled polymer was washed 3 times with acetonitrile and then dried.

Example 2a: **PT-Br-5**

For **PT-Br-5** to **PT-Br-7**, the synthesis steps were similar. As a representative example, the synthesis method for **PT-Br-5** is described below. A summary of the
20 reactants is shown in **Table 4**.

Table 4. Reactants for preparing **PT-Br-5**

alkyne-PEG-alkyne	N ₃ -PEG-N ₃	X-PEG-X	R-Y	ratio
diethylene glycol bis(2-propynyl) ether	N ₃ -PEG-N ₃ (M _n =2095)	diethylene glycol bis(2-bromoethyl) ether	methyl bis[(trifluoromethyl)sulfonyl] imide (McTFSI)	1:1:0.5:0.5

505.7 mg of **N₃-PEG-N₃** (M_n=2095, 0.241 mmol, 1 eq.) was weighed in a 20 mL screw cap vial and dried in a vacuum oven at 90 °C overnight and subsequently
25 filled with argon. 43 µl of diethylene glycol bis(2-propynyl) ether (0.241 mmol, 1 eq.) was added and stirred in argon at 110°C overnight. In two separate 4 mL vials, 38.85 mg of diethylene glycol bis(2-bromoethyl) ether (0.121 mmol, 0.5 eq.) and 36.38 mg of methyl bis[(trifluoromethyl)sulfonyl] imide (0.123 mmol, 0.5 eq., purchased from Sigma-Aldrich, Singapore) was diluted with 1 mL of acetonitrile
30 (purchased from Sigma-Aldrich, Singapore) each. The solutions were transferred to the 20 mL screw cap vial. Excess acetonitrile was blown away with argon. Subsequently, the vial was sealed in argon and reacted at 110°C for 1 day. After

performing successful (>70%) gel fraction test on 30 mg of the resulting polymer, ~15 mL of acetonitrile was added to the vial and heated at 60 °C for 1 hour. The swelled polymer was washed 3 times with acetonitrile and then dried.

Example 2b: TsO-PEG-OTs as crosslinker with LiTFSI added in situ to skip the swelling / ion exchange step (step 2 in Table 1).

The following samples shown in Table 5 were prepared using **TsO-PEG-OTs** (X = OTs) as the crosslinker with lithium salt LiTFSI added in situ. Different samples of **PT-OTs-LiTFSI** were prepared with varying ratios of crosslinker and LiTFSI.

Table 5. Different samples of **PT-OTs-LiTFSI** prepared: Estimated gel fractions (excluding mass of LiTFSI) of polymer networks formed from varying ratios of TsO-PEG-OTs with respect to N₃-PEG-N₃ and LiTFSI with respect to EO groups.

Sample	TsO-PEG-OTs ratio	EO:LiTFSI ratio	Gel fraction / %
PT-OTs-LiTFSI-1	1	18	99
PT-OTs-LiTFSI-2	1	15	97
PT-OTs-LiTFSI-3	1	12	95

For **PT-OTs-LiTFSI-1** to **PT-OTs-LiTFSI-3**, the synthesis steps were similar. As a representative example, the synthesis method for **PT-OTs-LiTFSI-1** is described below. A summary of the reactants is shown in Table 6.

Table 6. Reactants for preparing **PT-OTs-LiTFSI-1**

alkyne-PEG-alkyne	N ₃ -PEG-N ₃	X-PEG-X	ratio	EO:Li ratio
diethylene glycol bis(2-propynyl) ether	N ₃ -PEG-N ₃ (M _n =2095)	tetraethylene glycol di(<i>p</i> -toluenesulfonate)	1:1:1	18:1

1181.8 mg of N₃-PEG-N₃ (M_n=2095, 0.564 mmol, 1 eq.) was weighed in a 20 mL screw cap vial and dried in a vacuum oven at 90 °C overnight and subsequently filled with argon. 101 µL of diethylene glycol bis(2-propynyl) ether (0.241 mmol, 1 eq.) was added and stirred in argon at 110°C overnight. In a separate 4 mL vial, 225 µL of tetraethylene glycol di(*p*-toluenesulfonate) (0.564 mmol, 1.0 eq., purchased from Tokyo Chemicals Industry, Singapore) was diluted in 2.26 mL of acetonitrile (purchased from Sigma-Aldrich, Singapore). In yet another 20 mL vial, 459 mg of lithium bis[(trifluoromethyl)sulfonyl] imide (1.60 mmol, purchased from Tokyo Chemicals Industry, Singapore) was diluted with 6.4 mL of acetonitrile (purchased from Sigma-Aldrich, Singapore). The solutions were transferred to the original 20

mL screw cap vial. Excess acetonitrile was blown away with argon. Subsequently, the vial was sealed in argon and reacted at 110°C for 1 day.

Gel fraction test was performed on 30 mg of the resulting polymer. The sample was heated in acetonitrile at 70 °C for 1h. Thereafter, the resulting gel was washed 3 times with acetonitrile, dried and weighed.

As the polymer contains LiTFSI which is expected to be washed off with acetonitrile, we could only estimate the gel fraction by excluding the mass of LiTFSI based on this assumption.

Estimated gel fraction = (final mass – initial mass) / (initial mass – mass of LiTFSI) x 100%

Example 2c: TFSI-PEG-TFSI as crosslinker

Crosslinker *N,N'*-(((oxybis(ethane-2,1-diyl))bis(oxy))bis(propane-3,1-diyl))bis(1,1,1-trifluoro-*N*-((trifluoromethyl)sulfonyl)methanesulfonamide), **TFSI-PEG-TFSI** (X = TFSI) was prepared. This crosslinker may be used to form the PT-TFSI with LiTFSI salt added in situ to skip the swelling / ion exchange step (step 2 in Table 1).

100 µl of 4,7,10-trioxa-1,13-tridecanediamine (0.46 mmol, 1 eq. purchased from Sigma-Aldrich, Singapore), 623 µL of diisopropyl ethyl amine (3.65 mmol, 8 eq., purchased from Tokyo Chemical Industry, Singapore) and 1.9 mL of anhydrous dichloromethane (purchased from Acros Organics, Singapore) were added to a 30 mL vial. The mixture was stirred and cooled using a NaCl (purchased from VWR, Singapore)/ice bath. A 4 mL vial, in argon, was filled with 0.62 mL of trifluoromethanesulfonic anhydride (3.65 mmol, 8 eq., purchased from Sigma-Aldrich, Singapore) and 0.9 mL anhydrous dichloromethane. The trifluoromethanesulfonic anhydride solution was stirred and added dropwise to the cooled vial. Once added, the NaCl/ice bath was removed, and reaction mixture was stirred for 1 hour. Subsequently, the solution was washed once with saturated sodium bicarbonate solution (purchased from VWR Chemicals, Singapore), once with 1M hydrochloric acid solution (purchased from Honeywell, Singapore) and once with deionized water. The aqueous phases were back-extracted and the organic phases were combined. The organic phase was dried with magnesium sulfate, filtered and the solvent was removed. NMR spectrum: ¹H NMR (400 MHz, CDCl₃) δ 4.15 – 4.04 (m, 8H), 3.69 – 3.50 (m, 12H), 2.13 – 2.02 (m, 8H); ¹⁹F NMR (376 MHz, CDCl₃) δ -71.95.

The ¹H and ¹⁹F NMR spectrum of **TFSI-PEG-TFSI** are shown in FIGs. 2B and 2C, respectively.

The following sample of PT-TFSI-LiTFSI was prepared using TFSI-PEG-TFSI (X = OTFSO) as the crosslinker with lithium salt LiTFSI added in situ. A summary of the reactants is shown in Table 7.

Table 7. Reactants for preparing **PT-TFSI-LiTFSI-1** and the estimated gel fraction (excluding mass of LiTFSI) obtained

alkyne-PEG-alkyne	N ₃ -PEG-N ₃	X-PEG-X	ratio	EO:Li ratio	Gel Fraction / %
diethylene glycol bis(2-propynyl) ether	N ₃ -PEG-N ₃ (M _n =2095)	TFSI-PEG-TFSI	1:1:1	18:1	77

203.15 mg of N₃-PEG-N₃ (M_n=2095, 0.097 mmol, 1 eq.), 17.3 µl of diethylene glycol bis(2-propynyl) ether (0.097 mmol, 1 eq., purchased from Tokyo Chemicals Industry, Singapore), 72.16mg of TFSI-PEG-TFSI (0.096mmol, 1 eq.) and 1.832mL of 0.15M LiTFSI in acetonitrile solution was added into a 4 mL vial. The vial was evacuated and filled with argon and acetonitrile was blown away. The vial was sealed and reaction mixture was heated to 110 °C overnight.

10 **Example 3 – Step 2: Swelling of PT in Metal Salt (MZ_n) / Organic Solvent**

LiTFSI was used as the lithium salt and MeCN was used as the solvent with a concentration of 0.15 M.

Example 3ai

390.5.0 mg of **PT-Br-2** was hot pressed at 160 °C under nominal pressure of 5 bar and placed in a screw-cap bottle. 20 mL of 0.15M LiTFSI/MeCN was added to the bottle and heated to 60 °C for one day. The next day, the LiTFSI solution was removed, and the polymer was rinsed 3 times with acetonitrile. Another 15 mL of 0.15M LiTFSI/MeCN was added, and the vial was again heated to 60 °C for another day. Finally, the polymer was rinsed 3 times with acetonitrile and dried in a vacuum oven at 80 °C overnight. 386.83 mg of **PT-Br-2-LiTFSI** was obtained.

Example 3aai

150.10 mg of PT-Br-5 was hot pressed at 180 °C, under nominal pressure of 5 bar (10 min heating, 10 min press) and placed in a screw-cap bottle. 25 mL of 0.15M LiTFSI/MeCN was added to the bottle and heated to 70 °C for one day. The next day, the LiTFSI solution was removed, and the polymer was rinsed 3 times with acetonitrile. Another 15 mL of 0.15M LiTFSI/MeCN was added, and the vial was again heated to 70 °C for another day. Finally, the polymer was rinsed 3 times with acetonitrile and dried in a vacuum oven at 85 °C overnight. 206.51 mg of PT-Br-5-LiTFSI was obtained.

Example 4 – Step 3: Hot-pressing of PT-MZ_n Solid Polymer ElectrolyteExample 4ai

- 5 **PT-Br-2-LiTFSI** of Example 3ai was placed between two stainless steel plates lined by a PTFE film in a hot press. The plates were heated to 220 °C for 10 minutes before being pressed at nominal pressure of 10 bar for 20 minutes. The **PT-LiTFSI** SPEs were then dried at 110°C under vacuum for 48 hours followed by drying under vacuum at 80°C for > 20 hours to remove any trace of moisture before transferring to an Ar-filled glovebox.

Example 4aii

- 10 **PT-Br-5-LiTFSI** of Example 3aii was placed between two stainless steel plates lined by a PTFE film in a hot press. The plates were heated to 180 °C for 15 minutes before being pressed at nominal pressure of 10 bar for 45 minutes. The **PT-Br-5-LiTFSI** SPEs were then dried at 110°C under vacuum for 24 hours followed by drying under vacuum at 80°C for > 20 hours to remove any trace of moisture before transferring to Ar-filled glovebox.

Example 4b

- 20 **PT-OTs-LiTFSI-1** of Example 2b was placed between two stainless steel plates lined by a PTFE film in a hot press. The plates were heated to 180 °C for 30 minutes before being pressed at nominal pressure of 10 bar for 45 minutes. The **PT-OTs-LiTFSI-1** SPEs were then dried at 110°C under vacuum for 24 hours followed by drying under vacuum at 80°C for > 20 hours to remove any trace of moisture before transferring to Ar-filled glovebox.

Example 5 – Step 4: Preparation of All-Solid-State Energy Storage Device

- 25 Coin cells with lithium foil (purchased from AOT Battery Technology Co., LTD, China) as anode, **PT-LiTFSI** solid polymer electrolyte (**PT-LiTFSI** SPE) of Examples 4ai, 4aii and 4b, with LiFePO₄ (LFP) (purchased from ANR Technologies Pte Ltd, Singapore) and/or LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂ (NMC 622, (purchased from ANR Technologies Pte Ltd, Singapore)) as cathode active materials were fabricated. All the steps of cell fabrication are handled in an argon filled glovebox (O₂<0.1 ppm; H₂O<0.1 ppm). PEO-LiTFSI (EO:Li = 10) was used as ion conducting phase in the electrode. The loadings of active material in the cathode were 2 ± 0.2 mg cm⁻² and 2.5 ± 0.2 mg cm⁻² for Li|**PT-LiTFSI**|LFP and Li|**PT-LiTFSI**|NMC622 cells, respectively. The cell was pressed at a pressure of 50 kg/cm².

- 35 The cells with Example 4ai and 4 aii were cycled under constant current density at 60 °C. For Li|**PT-Br-LiTFSI**|LFP (voltage range 2-4 V, 0.15C) and for Li|**PT-Br-LiTFSI**|NMC (voltage range 3-4.2 V, 0.1C).

The cells with Example 4b were charged under constant current density of 0.1 C at 60 °C in the voltage range of 2-4 V for Li|**PT-OTs-LiTFSI-1**|LFP cells.

The cross-section arrangement of the PT-LiTFSI-based LiBs is shown in FIG. 3. The anode was made of Li. The cathode was made of LiFePO₄ (LFP) or LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂ (NMC 622) as the cathode active materials, carbon (Super C-65), PVDF binder and PEO-LiTFSI as the ion conducting phase. Solid polymer electrolyte (PT-LiTFSI SPE) was placed between the cathode and anode.

Example 6 – Characterisation of Solid Polymer Electrolyte PT-LiTFSI

Example 6a: XPS

X-ray photoelectron spectroscopy (XPS) was performed on the Kratos Axis Supra+ to characterize **PT-Br-5**, **PT-OTs-LiTFSI-1**, **PT-Br-2-LiTFSI**, and **PT-Br-5-LiTFSI**.

For **PT-Br-5** of Example 2a, (FIGS. 4A to 4E), XPS spectra showed the presence of elements N, Br, C and O in the system. C and O can be primarily attributed to the ethylene glycol (-CH₂CH₂O-) units of the polymer backbone, while the N can be attributed to the triazole/triazolium moiety and the Br its counteranion. The high resolution scan of the N 1s XPS spectrum revealed the presence of both triazolium (2 peaks in 2:1 ratio at >402 eV) and triazole (3 peaks in 1:1:1 ratio at ≤402 eV).

For **PT- OTs-LiTFSI-1** of Example 2b (FIGS. 5A to 5G). XPS spectra showed the presence of elements N, S, C and O from the polymer network and elements S, Li, F and N from the LiTFSI. The high resolution scan of the N 1s XPS spectrum revealed the presence of both triazolium (2 peaks in 2:1 ratio at >402 eV) and triazole (3 peaks in 1:1:1 ratio at ≤402 eV), as well as TFSI (<400eV).

For **PT-Br-2-LiTFSI** of Example 3a (FIGS. 6A to 6H) and **PT-Br-5-LiTFSI** of Example 3a (FIGS. 7A to 7H) XPS spectra showed the presence of elements N, C and O from the polymer network and elements S, Li, F and N from the LiTFSI. Along with the absence of element Br, this indicated that swelling **PT-Br** in LiTFSI solution achieved both incorporation of LiTFSI and removal of Br⁻ anions in **PT-Br-LiTFSI**. The high resolution scan of the N 1s XPS spectrum revealed the presence of both triazolium (2 peaks in 2:1 ratio at >402 eV) and triazole (3 peaks in 1:1:1 ratio at ≤402 eV), as well as TFSI (<400eV).

Example 6b: SEM-EDX

Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) was performed on a JEOL JSM-7600F SEM to characterize **PT-Br-2-LiTFSI** and **PT-Br-5-LiTFSI**.

For **PT-Br-2-LiTFSI** of example 3a (FIGS. 8A to 8D) and **PT-Br-5-LiTFSI** of Example 3a (FIGS. 9A to 9D), EDX mapping showed the presence of elements N, C and O from the polymer network. C and O can be primarily attributed to the ethylene glycol (-CH₂CH₂O-) units of the polymer backbone while the N can be attributed to the triazole/triazolium moiety. While Br is also present, it is found in trace amounts, indicating that almost all Br⁻ anions from **PT-Br** was removed.

Furthermore, the presence of TFSI anion can be confirmed due to the presence of elements S and F; element Li cannot be detected by the instrument.

Example 6c: FTIR

5 Fourier-transform infrared spectroscopy (FTIR) analysis was performed on the Bruker Vertex 80v to characterise **PT-Br-2** and **PT-Br-2-LiTFSI** (FIG. 10a), as well as **PT-Br-6** and **PT-Br-6-LiTFSI** (FIG. 10b). Absence of azide stretching peak ($2220\text{--}2260\text{ cm}^{-1}$) in all 4 samples indicate that the starting azide material was fully reacted.

10 For the samples after swelling in LiTFSI solution, **PT-Br-2-LiTFSI** and **PT-Br-6-LiTFSI**, additional S=O ($\sim 1180\text{ cm}^{-1}$) and C-F stretch ($\sim 1350\text{ cm}^{-1}$) from TFSI anion were observed. These peaks were not present in their respective **PT-Br** samples before swelling, thus their presence in the samples after swelling indicate the successful incorporation of LiTFSI into the **PT-Br-LiTFSI** samples.

Example 6d: Reprocessability

15 The **PT-Br** of Example 2ai and 2a ii could be reprocessed at $160\text{--}220\text{ }^{\circ}\text{C}$, while **PT-LiTFSI** SPE of Example 4ai, 4ai and 4b could be reprocessed at $180\text{--}220\text{ }^{\circ}\text{C}$ at under nominal pressure of 10 bar for 20-45 minutes as shown in FIG. 11A via exchange of the triazolium dynamic covalent bonds shown in FIG. 11B. Reprocessing is successful when the SPE can be remoulded to form a film of a
20 desired and different form factor (e.g., shape, size, thickness) without decomposition. The dynamic covalent bonds allow the network to be reprocessed at a lower temperature as compared to crosslinked samples with permanent covalent bonds, which are typically not reprocessable at all.

25 After reprocessing, the **PT-LiTFSI** SPE is a free-standing film as shown in FIG. 11C.

Example 6c: Thermal properties

Thermogravimetric analysis (TGA) was performed on TA Instruments TGA Q500. Procedure involves (i) temperature ramp $20^{\circ}\text{C}/\text{min}$ to $100\text{ }^{\circ}\text{C}$; (ii) isothermal at 100°C for 10 min and (iii) temperature ramp $20^{\circ}\text{C}/\text{min}$ to $700\text{ }^{\circ}\text{C}$. Decomposition temperature
30 ($T_{d,98\%}$) and estimated LiTFSI content can be determined from the TGA spectra. The LiTFSI content can only be estimated due to the overlap in decomposition of LiTFSI salt and polymer backbone.

Differential scanning calorimetry (DSC) was performed on TA Instruments Q100. Prior to testing, the sample was dried in a vacuum oven at $90\text{ }^{\circ}\text{C}$ and crimped in the glovebox.
35 Procedure is as follows: (i) ramp $20^{\circ}\text{C}/\text{min}$ to 200°C ; (ii) isothermal for 1 min; (iii) ramp $20^{\circ}\text{C}/\text{min}$ to -80°C ; (iv) isothermal for 1 min and (v) ramp $20^{\circ}\text{C}/\text{min}$ to 200°C . Phase transition temperatures, glass transition temperature (T_g) and melting temperature (T_m), can be determined from DSC spectrums. For PT-LiTFSI samples, T_m is not present.

- 5 **PT-LiTFSI** samples of Examples 4a were stable up to ~ 300 °C, with decomposition temperatures ($T_{d,98\%}$) ranging between 295 °C to 331 °C. Differential scanning calorimetry of the networks showed a glass transition temperature (T_g) of around -29.8 °C to -15.6°C. The solid polymer electrolyte remains solid at cell cycling temperature and does not exhibit any melting transition (T_m), unlike conventional solid polymer electrolyte e.g. PEO which is molten at cell cycling temperature.

Table 8. Thermal decomposition temperature and transition temperatures of **PT** and **PT-LiTFSI** samples

Sample	PT			PT-LiTFSI		
	$T_{d,98\%}$ ^a /°C	T_g ^b /°C	T_m ^b /°C	$T_{d,98\%}$ ^a /°C	Est. LiTFSI ^a (wt%)	T_g ^b /°C
PT-Br-1	240.7	-14.3	47.7	319.2	47.6	-29.8
PT-Br-2	254.0	-14.3	49.2	322.1	32.0	-28.0
PT-Br-3	278.8	-14.3	49.4	319.1	32.7	-15.6
PT-Br-4	TBC	-27.5	41.8	324.2	49.3	-17.0
PT-Br-5	286.2	-41.1	48.7	295.1	32.5	-28.0
PT-Br-6	250.7	-41.1	47.2	331.4	32.5	TBC

^a Decomposition temperature and estimated LiTFSI content is determined via TGA; ^b Phase transition temperatures (T_g and T_m) are determined via DSC; ^c TBC indicates data has yet to be collected.

10 **Example 6f: Ionic conductivity and Li transference**

The cationic polytriazolium SPE **PT-Br-2-LiTFSI** of Example 4ai had an ionic conductivity of $2.0 \pm 0.1 \times 10^{-4}$ S/cm (FIG. 12) and a Li⁺ transference value of 0.89 (FIG. 13) at 60 °C.

- 15 The cationic polytriazolium SPE **PT-Br-5-LiTFSI** of Example 4aai had an ionic conductivity of 2.2×10^{-4} S/cm (FIG 14)

The cationic polytriazolium SPE **PT-OTs-LiTFSI-1** of Example 4b had an ionic conductivity of 1.4×10^{-4} S/cm at 60°C (FIG 15).

Example 7 – Performance of PT-Br-2-LiTFSI All-Solid-State Battery

Example 7a: In a Li|PT-Br-2-LiTFSI|LFP cell

- 20 The cells with **PT-Br-2-LiTFSI** of Example 4ai as solid polymer electrolyte and LFP as active cathode material were successfully cycled under current density of 0.15 C at elevated temperature of 60 °C. The cell delivered an initial discharge capacity of 160 mAh/g. Stable charge and discharge plateaus were achieved for 60

cycles with capacity retention of > 94 % and coulombic efficiency of > 99% (FIG. 16).

Example 7b: In a Li|PT-Br-2-LiTFSI|NMC cell

- 5 The cells with **PT-Br-2-LiTFSI** of Example 4ai as solid polymer electrolyte and high voltage cathode of NMC622 as active cathode material were successfully cycled under current density of 0.1 C at elevated temperature of 60°C. Stable charge and discharge plateaus were achieved over 25 cycles with coulombic efficiency of > 97% (FIG. 17). The cell delivered a capacity of 140 mAh/g (after stabilization of electrolyte interphase) and retained 75% of this capacity for 60 cycles. This capacity fading could be attributed to the decomposition of PEO as conducting phase in the cathode.

Example 8 – Performance of Conventional Solid Polymer Electrolyte PEO - LiTFSI All-Solid-State Battery with NMC Cathode

- 15 In comparison, a similar cell was assembled with conventional solid polymer electrolyte PEO (MW=900k) – LiTFSI (EO:Li = 12) and high voltage cathode of NMC622 as active cathode material. The cells were cycled under current density of 0.1 C at elevated temperature of 60°C, but failed in less than 60 cycles (FIG. 18) due to instability of PEO at higher voltages.

Example 9 – Performance of PT-Br-5-LiTFSI All-Solid-State Battery

- 20 The cells with **PT-Br-5-LiTFSI** of Example 4aii as solid polymer electrolyte and high voltage cathode of NMC622 as active cathode material were successfully cycled under current density of 0.1 C at elevated temperature of 60°C. Stable charge and discharge plateaus were achieved for more than 30 cycles with coulombic efficiency of > 99% (FIG. 19). The cell delivered an initial capacity of about 115 mAh/g and retained > 96% of this capacity for 30 cycles.

Example 10 – Performance of PT-OTs-LiTFSI-1 All-Solid-State Battery

- 30 The cells with **PT-OTs-LiTFSI-1** of Example 4b as solid polymer electrolyte and LFP as active cathode material were successfully cycled under current density of 0.1 C at elevated temperature of 60 °C. The cell delivered an initial capacity of 169 mAh/g. with capacity retention of > 75 % and coulombic efficiency of > 98% over 50 cycles (FIG. 20).

Industrial Applicability

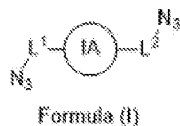
- 35 The solid polymer electrolyte of the disclosure may be used in a variety of applications such as coin cells, pouch batteries, cylindrical batteries, prismatic batteries, structural batteries, energy storage devices, wearables, biosensors, implantable devices or organic microelectronics.

It will be apparent that various other modifications and adaptations of the invention will be apparent to the person skilled in the art after reading the foregoing disclosure without departing from the spirit and scope of the invention and it is intended that all such modifications and adaptations come within the scope of the

5 appended claims.

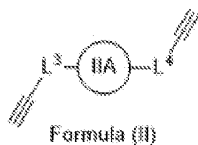
Claims

1. A solid polymer electrolyte comprising a plurality of metal cations M interspersed within a polymer comprising:
at least one monomer of Formula (I)



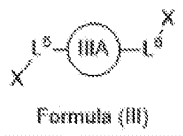
5

at least one monomer of Formula (II)



, and

at least one monomer of Formula (III)



10

wherein

each of group IA, IIA and IIIA is independently a bivalent moiety derived from or polymerized from an ion-conducting oligomer or an ion-conducting polymer;
each X is independently a leaving group; and
each of L¹, L², L³, L⁴, L⁵ and L⁶ is independently absent or a C₁-C₆ alkylene.

15

2. The solid polymer electrolyte of claim 1, further comprising a quarternising agent of Formula R-Y, wherein
R is a C₁-C₁₀ alkyl, a C₁-C₁₀ heteroalkyl, a C₆-C₁₀ aryl or a C₅-C₁₀ heteroaryl, and
Y is a second leaving group.

20

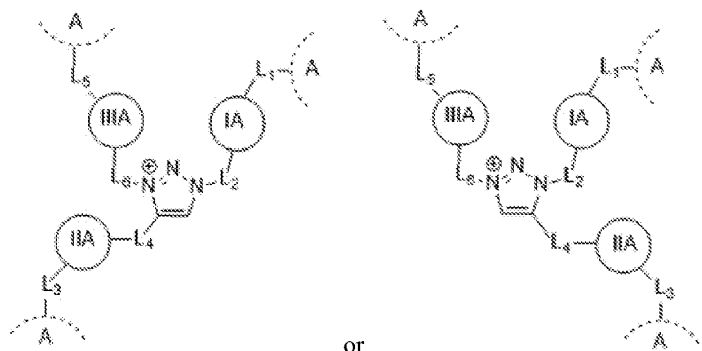
3. The solid polymer electrolyte of claim 1 or 2, wherein M is selected from the group consisting of lithium, sodium, potassium, magnesium, calcium, aluminum, vanadium, zinc and combinations thereof.

25

4. The solid polymer electrolyte of any one of claims 1 to 3, wherein each of the leaving group of X or the second leaving group of Y is independently a halide or a weakly coordinating anion.

30

5. The solid polymer electrolyte of any one of claims 1 to 4, wherein the polymer comprises a repeating unit of the formula:



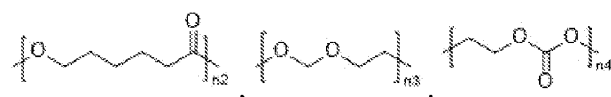
wherein when two or three repeating units are joined at A, A independently forms a triazole or a triazolium, or a regioisomer thereof.

5

6. The solid polymer electrolyte of claim 5, wherein A is triazolium quarternised with a R group, wherein R is a C₁-C₁₀ alkyl, a C₁-C₁₀ heteroalkyl, a C₆-C₁₀ aryl or a C₅-C₁₀ heteroaryl.

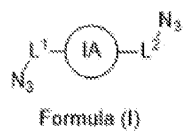
10 7. The solid polymer electrolyte of any one of claims 1 to 6, wherein each of group

IA, IIA and IIIA is independently selected from the group consisting of ,

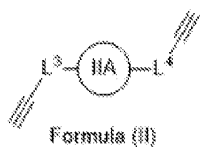


wherein each of n1, n2, n3 and n4 is independently a number in the range of 2 to 50.

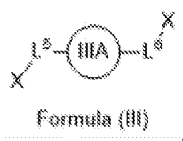
15 8. A method of preparing a solid polymer electrolyte comprising the step of:
reacting a metal salt MZ_n with a polymer derived from or polymerized from at least one
monomer of Formula (I)



at least one monomer of Formula (II)



at least one monomer of Formula (II),
 at least one monomer of Formula (III)



at an elevated temperature,

wherein

M is a metal cation;

5 Z is a weakly coordinating anion;

n is suitably selected such that MZ_n is electrically neutral;

each of group IA, IIA and IIIA is independently a bivalent moiety derived from or polymerized from an ion-conducting oligomer or an ion-conducting polymer;

each X is independently a leaving group; and

10 each of L^1 , L^2 , L^3 , L^4 , L^5 and L^6 is independently absent or a C_1 - C_6 alkylene.

9. The method of claim 8, wherein each leaving group of X is independently a halide or a weakly coordinating anion.

15 10. The method of claim 8, wherein when each leaving group of X is the halide, the method further comprises, before the reacting step, the step of forming the polymer by heating a mixture comprising the at least one monomer of Formula (I), the at least one monomer of Formula (II) and the at least one monomer of Formula (III) at the elevated temperature.

20 11. The method of claim 9, wherein when each leaving group of X is the weakly coordinating anion, in the reacting step, the polymer is formed in situ by heating a mixture comprising the at least one monomer of Formula (I), the at least one monomer of Formula (II) and the at least one monomer of Formula (III) at the elevated temperature.

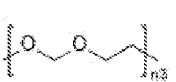
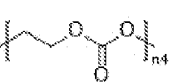
25 12. The method of any one of claim 8 to 11, wherein the polymer is further derived from or polymerized from a quarternising agent of Formula R-Y, wherein R is a C_1 - C_{10} alkyl, a C_1 - C_{10} heteroalkyl, a C_6 - C_{10} aryl or a C_5 - C_{10} heteroaryl, and Y is a second leaving group.

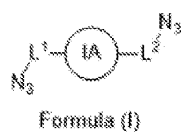
30 13. The method of any one of claims 8 to 12, wherein the monomer of Formula (I) and the monomer of Formula (II) have a molar ratio in the range of about 1:0.8 to about 1:1.2.

35 14. The method of any one of claims 8 to 13, wherein the monomer of Formula (I) and the monomer of Formula (III) have a molar ratio in the range of about 1:0.1 to about 1:1.

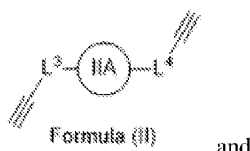
40 15. The method of any one of claims 8 to 14, wherein the monomer of Formula (I) and the quarternising agent have a molar ratio in the range of about 1:0.1 to about 1:2.

45 16. The method of any one of claims 8 to 15, wherein the elevated temperature is a temperature between about 50 °C to about 200 °C.

17. The method of any one of claims 8 to 16, wherein M is selected from the group consisting of lithium, sodium, potassium, magnesium, calcium, aluminum, vanadium, zinc and combinations thereof.
18. The method of any one of claims 8 to 17, wherein each second leaving group of Y is independently a halide or a weakly coordinating anion.
19. The method of any one of claims 8 to 18, wherein each of group IA, IIA and IIIA is independently selected from the group consisting of , , , , and combinations thereof, wherein each of n1, n2, n3 and n4 is independently a number in the range of 2 to 50.
20. The method of any one of claims 8 to 19, wherein the reacting step is undertaken in an inert atmosphere.
21. The method of any one of claims 8 to 20, wherein the reacting step is undertaken for a duration in the range of 0.5 days to 10 days.
22. The method of any one of claims 8 to 21, further comprising a step of hot pressing the solid polymer electrolyte.
23. The method of claim 22, wherein the hot pressing step is undertaken at a temperature in the range of 100 to 250 °C.
24. The method of claim 22 or 23, wherein the hot pressing step is undertaken at a nominal pressure in the range of 0.5 to 20 bar.
25. The method of any one of claims 8 to 24, further comprising a step of drying the solid polymer electrolyte.
26. A solid polymer electrolyte obtainable by or obtained by reacting a metal salt MZ_n with a polymer derived from or polymerized from at least one monomer of Formula (I)



- at least one monomer of Formula (II)



- at least one monomer of Formula (III)



Formula (III)

at an elevated temperature,

wherein

M is a metal cation;

5 Z is a weakly coordinating anion;

n is suitably selected such that MZ_n is electrically neutral;

each of group IA, IIA and IIIA is independently a bivalent moiety derived from or polymerized from an ion-conducting oligomer or an ion-conducting polymer;

each X is independently a leaving group; and

10 each of L^1 , L^2 , L^3 , L^4 , L^5 and L^6 is independently absent or a C_1 - C_6 alkylene, wherein the solid polymer electrolyte comprises a cationic covalent adaptable network.

27. The solid polymer electrolyte of claim 26, wherein the solid polymer electrolyte is free-standing or exist as part of a composite.

15

28. A battery comprising the solid polymer electrolyte of any one of claims 1 to 7, 26 and 27, a cathode and/or an anode.

29. The battery of claim 28, wherein the solid polymer electrolyte acts as a separator, or as an ion-conducting phase in a cathode and/or anode or a combination thereof.

20

30. The battery of claim 28 or 29, wherein the solid polymer electrolyte is in a form of metal-ion, metal polymer, solid-state, metal-sulfide, or metal-air electrolyte.

25