

A Composition And A Composite Material

References to Related Application

- 5 This application claims priority to Singapore application number 10202302665X filed with the Intellectual Property Office of Singapore on 21 September 2023, the contents of which is hereby incorporated by reference.

Technical Field

- 10 The present invention generally relates to a composition comprising an organo-ionic compound comprising at least one C=C double bond, a poly-thiol compound comprising a plurality of thiol groups and a bridging compound comprising a plurality of C=C double bonds. The present invention further relates to a composite material, a method of forming the same and an electrochemical device comprising the same.

Background Art

- 15 Recently, the proliferation of electric vehicles and electronic devices has witnessed an increase in the utilization of Li-ion batteries as energy storage devices.

- Conventionally, batteries found in commercial devices consist of a liquid electrolyte held within a pouch together with two electrodes. However, such conventional batteries are associated with shortcomings such as flammability issues associated with over-heating during operation, charging or short-circuit.
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- Another conventional technology used in batteries involves freestanding, structural battery electrode (SBE) systems, which may address the shortcomings of the liquid-based systems. SBE technologies can summararily be divided into two major divisions, namely, solid polymer electrolyte (SPE) and gel polymer electrolyte (GPE).

- 25 Conventional SPE systems consist of a highly flexible polymeric network that contains lithium salt dispersed within the matrix. These polymeric networks categorically contain large amount of ethoxy functional groups and these ethoxylations serve as "hopping" sites for Li-ion migration within the SPE systems. To further improve the Li-ion conductivities, high molecular weight PEGylated materials are dispersed within the matrix to increase the quantities of "hopping" sites.
- 30 However, this boost in ion conductivity comes at a price, as the storage modulus of these system degrades as the increased in ethoxy groups increase chain flexibility in the polymeric matrix, resulting in a tacky film. At elevated temperatures, the high molecular PEGylated materials would melt and plasticize the polymeric matrix, causing a reduction in storage modulus.
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As an alternative approach, conventional GPE systems consist of a polymeric network that serves as a binder to hold a liquid electrolyte within a uniform gel matrix

to serve as percolation channels for Li-ion conduction. While the GPE systems may deliver a higher ion conductivity, the formulation of GPE systems possess innate challenges. A GPE system with higher loading of liquid electrolyte would normally possess higher ion conductivity due to greater formation of continuous percolation channels within the gel but the resultant electrolyte film is mechanically weak as electrolyte molecules plasticize polymeric matrix.

Accordingly, there is a need for a composite material for use in electrochemical devices such as batteries that ameliorates one or more disadvantages mentioned above.

10 Summary

In one aspect, there is provided a composition comprising:

- (a) an organo-ionic compound comprising at least one C=C double bond;
- (b) a poly-thiol compound comprising a plurality of thiol groups; and
- (c) a bridging compound comprising a plurality of C=C double bonds.

15 Advantageously, the present composition may be readily polymerised to form a composite material in a one-pot manner.

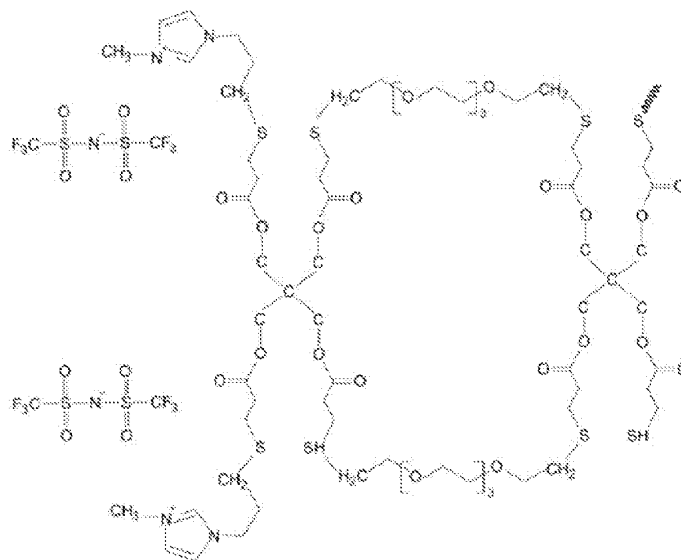
Further advantageously, the bridging compound may serve as an intermediary that facilitates binding of the poly-thiol compound to the organo-ionic compound.

20 In another aspect, there is provided a method of forming a composite material, comprising the steps of:

- (a) mixing an organo-ionic compound comprising at least one C=C double bond, a poly-thiol compound comprising a plurality of thiol groups and a bridging compound comprising a plurality of C=C double bonds to form a composition; and
- (b) curing the composition of step (a) to form the composite material.

25 Advantageously, the present method is easy to operate as it may be done in a one-pot manner.

In another aspect, there is provided a composite material comprising one or more moieties having a formula of:



In another aspect, there is provided a composite material obtained by or obtainable by the method as described herein.

Advantageously, the present composite material may have an ion conductivity of more than $10^{-5} \text{ S cm}^{-1}$ and an electrochemical stability window of more than 4 V. This is because of the use of the organo-ionic compound which is partially bound to a polymeric matrix and partially moving freely.

Further advantageously, the present composite material is formed from flexible organic materials. This allows the present composite material to conform to
10 challenging geometries.

Still further advantageously, the present composite material has an onset of thermal degradation which is higher than 300 °C. This makes the present composite material better in thermal stability compared with conventional composite materials.

Still further advantageously, the present composite material may be considered as
15 “non-leaky”. This is due to the presence of a strong interaction between cationic
groups and anionic groups from the organo-ionic compound which prevents leaching
from the composite material, which is commonly faced in conventional composite
materials.

Still further advantageously, the present composite material may be regarded as a 20 free-standing or solid-state material. Therefore, it does not require an additional structural casing as support.

Still further advantageously, the present composite material may have a low fire hazard as it may not comprise flammable liquids.

In another aspect, there is provided an electrochemical device comprising the composite material as described herein.

Definitions

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

5 As used herein, the term “organo-ionic compound” refers to an organic compound comprising both cationic groups and anionic groups. Therefore, an organo-ionic compound may also be regarded as an organic salt of the cationic groups and anionic groups.

10 As used herein, the term “poly-thiol compound” refers to an organic compound comprising a plurality of thiol groups.

As used herein, the term “thiol group” refers to a terminal -SH group. Therefore, the term “thiol group” is interchangeable with -SH and sulfhydryl group.

15 As used herein, the terms “C=C double bond” and “C=C double bonds” refer to one or more groups comprising a C=C double bond. Non-limiting examples of the groups above include acrylic acid, acrylate, acrylamide, allyl, vinyl, ethylene, and the like.

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.

20 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.

25 The term “about” as used herein typically means +/- 5 % of the stated value, more typically +/- 4 % of the stated value, more typically +/- 3 % of the stated value, more typically, +/- 2 % of the stated value, even more typically +/- 1 % of the stated value, and even more typically +/- 0.5 % of the stated value.

30 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 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.

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- 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 recited herein.

Detailed Disclosure of Embodiments

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

The composition comprises:

- 10 (a) an organo-ionic compound comprising at least one C=C double bond;
- (b) a poly-thiol compound comprising a plurality of thiol groups; and
- (c) a bridging compound comprising a plurality of C=C double bonds.

- The present composition may be polymerised into a composite material which can be used as a polymer electrolyte. Therefore, the present composition may be regarded as or used as a precursor of a polymer electrolyte.

The organo-ionic compound may have a melting point that is lower than 20 °C. Therefore, the organo-ionic compound may be in a liquid state at 20 °C or room temperature and may serve as a solvent to dissolve other compounds in the composition.

- 20 The organo-ionic compound may comprise at least one cationic group and at least one anionic group. One of the at least one cationic group and the at least one anionic group may at least partially comprise the at least one C=C double bond. The at least one C=C double bond may be absent from the at least one cationic group or the at least one anionic group. Therefore, the at least one C=C double bond may not be
- 25 simultaneously present on both the at least one cationic group and the at least one anion.

- When the organo-ionic compound is incorporated into a polymeric matrix via the at least one C=C double bond, it will become partially bound to the polymeric matrix via the at least one C=C double bond and partially moving freely. For example, if the
- 30 at least one cationic group comprises the at least one C=C double bond, the at least one cationic group will be bound to the polymeric matrix and the at least one anionic group will be moving freely. If the at least one anionic group comprises the at least one C=C double bond, the at least one anionic group will be bound to the polymeric matrix and the at least one cationic group will be moving freely.

- 35 Advantageously, this allows the composition to be polymerised into a composite material with high ionic conductivity and electrochemical stability.

The organo-ionic compound may comprise an ionic liquid. Where the at least one cationic group comprises the at least one C=C double bond and the at least one anionic group comprises hydroxides, the organo-ionic compound may be regarded as an organo-hydroxide.

- 5 The organo-ionic compound may be selected from the group consisting of 1-ethyl-3-methylimidazolium aminoacetate (EMAM), 1-ethyl-3-methylimidazolium lactate (EML), 1-allyl-3-ethylimidazolium bis(trifluoromethanesulfonyl)imide (AEF), 1-allyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (AMF), 1-allyl-3-butylimidazolium bis(trifluoromethanesulfonyl)imide (ABF), vinyl-3H-imidazolium
 10 bis(trifluoromethanesulfonyl)imide, 1-allyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide, 3,3'-(butane-1,4-diyl)bis(1-vinyl-3-imidazolium) bis(trifluoromethanesulfonyl)imide, and combinations thereof.

- The organo-ionic compound may be AMF. Advantageously, AMF has a high solubility for metal salts, particularly lithium salts. Therefore, the composition may
 15 be readily homogenized upon addition of metal salts without any thermal treatments.

The poly-thiol compound may be selected from the group consisting of dipentaerythritol hexakis(3-mercaptopropionate) (DPHS), pentaerythritol tetrakis(3-mercaptopropionate) (PTS), 2,2'-(ethylenedioxy)diethanethiol, and combinations thereof.

- 20 The bridging compound may further comprise one or more C=O double bonds.

- The bridging compound may be selected from the group consisting of dipentaerythritol hexaacrylate (DHL), tetrakis[dimethyl(vinyl)silyl] orthosilicate (ORP), trimethylolpropane ethoxylate triacrylate (TMET), trimethylolpropane triacrylate (TMPTA), trimethylolpropane triglycidyl ether, pentaerythritol
 25 tetraglycidyl ether, 1,2,4-trivinylcyclohexane (TVH), tri(ethylene glycol) divinyl ether (TDV), trimethylolpropane diallyl ether (TMPD), diallyl carbonate (DAC), pentaerythritol allyl ether, diallyl maleate, 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane, 2,4,6-trimethyl-2,4,6-trivinylcyclotrisiloxane, tetra allyl silane (TAL), polyethylene glycol dimethacrylate (PEGDMA), and combinations
 30 thereof.

- The plurality of C=C double bonds comprised in the bridging compound may not undergo homopolymerization under mild reaction conditions such as slight elevated temperature (e.g., about 25 to 40 °C) or short exposure (e.g., below about 10 seconds) to UV radiation. Therefore, the bridging compound may comprise one or more vinyl
 35 groups or allyl groups. The bridging compound may not comprise acrylate groups.

Advantageously, where the plurality of C=C double bonds comprised in the bridging compound do not undergo homopolymerization under mild reaction conditions, the composition may undergo less cross-linking upon exposure to UV radiation.

Therefore, the composition may have less chain rigidity and improved ionic conductivity.

As the plurality of C=C double bonds comprised in the bridging compound and the C=C double bond comprised in the organo-ionic compound are reactive towards thiol groups comprised in the poly-thiol compound, the bridging compound and the organo-ionic compound may be linked to the poly-thiol compound via thiol-ene reactions. Therefore, the poly-thiol compound may cross-link the bridging compound and the organo-ionic compound.

The composition may further comprise a lithium salt. As the organo-ionic compound may be in a liquid state at 20 °C or room temperature, the lithium salt may advantageously dissolve in the organo-ionic compound to form a homogenous mixture. Therefore, the composition may be formed into a lithium battery, where the lithium salt serves as conducting species.

The lithium salt may exemplarily be, but not limited to, lithium triflate (LiTRF), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), and a combination thereof.

The composition may further comprise a polymerisation initiator.

The polymerisation initiator may be a photo initiator or a thermal initiator.

The photo initiator may be selected from the group consisting of methyl benzoylformate, 2,2-dimethoxy-2-phenylacetophenone, 2,4,6-tris(dimethylaminomethyl)phenol, 4-thiophenyl phenyl diphenyl sulfonium hexafluoroantimonate (TPSHA), diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (DTPO), 4-(dimethylamino) pyridine, 2-hydroxy-2-methylpropiophenone (HMPP) and combinations thereof.

The thermal initiator may be selected from the group consisting of azobisisobutyronitrile, 1,5,7-triazabicyclo[4.4.0]dec-5-ene and combinations thereof.

Where a Type I photo initiator (e.g., 2,2-dimethoxy-2-phenylacetophenone or 2-hydroxy-2-methylpropiophenone) or a thermal initiator (e.g., azobisisobutyronitrile) is present, the composition may not comprise any acrylate or derivatives thereof.

Where the polymerisation initiator is a base or a nucleophile (e.g., 4-(dimethylamino) pyridine or DTPO) and one or more acrylates are present (e.g., in the bridging compound), the polymerisation initiator may advantageously force C=C double bonds present on the one or more acrylates to undergo Michael's Addition with the thiol groups instead of homo-polymerisation between acrylates. This may improve the present composition's reaction efficiency and yield.

In the composition, the number of thiol groups may be greater than the number of C=C double bonds. Therefore, when the thiol groups react with the C=C double bonds, there may be excess thiol groups that are unreacted. The excess thiol groups

may have an amount in the range of about 0.001 mole to about 0.003 mole, about 0.002 mole to about 0.003 mole or about 0.001 mole to about 0.002 mole.

Advantageously, where the number of thiol groups is greater than the number of C=C double bonds, the C=C double bonds will be completely reacted upon curing of the composition. Therefore, when the organo-ionic compound is incorporated into the polymeric matrix via the at least one C=C double bond, each molecule of the organo-ionic compound will be partially bound to the polymeric matrix. This may avoid the formation of a semi-solid electrolyte that is “leaky” due to elution of unbound molecules of the organo-ionic compound. A “leaky” electrolyte will lead to a loss of cation inventory and hence a degradation in material performance (e.g. if employed in a battery, a degradation in capacity).

In the composition, the organo-ionic compound may have a molar percentage in the range of about 12 mol% to about 37 mol%, about 20 mol% to about 37 mol%, about 30 mol% to about 37 mol%, about 12 mol% to about 30 mol% or about 12 mol% to about 20 mol%, based on the total number of moles of compounds in the composition.

The poly-thiol compound may have a molar percentage in the range of about 20 mol% to about 35 mol%, about 25 mol% to about 35 mol%, about 30 mol% to about 35 mol%, about 20 mol% to about 30 mol% or about 20 mol% to about 25 mol%, based on the total number of moles of compounds in the composition.

The bridging compound may have a molar percentage in the range of about 5 mol% to about 18 mol%, about 10 mol% to about 18 mol%, about 15 mol% to about 18 mol%, about 5 mol% to about 15 mol% or about 5 mol% to about 10 mol%, based on the total number of moles of compounds in the composition.

The lithium salt (where present) may have a concentration in the range of about 1 M to about 1.5 M, about 1.2 M to about 1.5 M or about 1 M to about 1.2 M based on the total volume of the organo-ionic compound.

The polymerisation initiator (where present) may have a molar percentage in the range of about 0.5 mol% to about 5 mol%, about 3 mol% to about 5 mol% or about 0.5 mol% to about 3 mol%, based on the total number of moles of compounds in the composition.

Exemplary, non-limiting embodiments of a method of forming a composite material will now be disclosed.

The method comprises the steps of:

- (a) mixing an organo-ionic compound comprising at least one C=C double bond, a poly-thiol compound comprising a plurality of thiol groups and a bridging compound comprising a plurality of C=C double bonds to form a composition; and
- (b) curing the composition of step (a) to form the composite material.

The method may be undertaken in a one-pot system.

The composition may further comprise a polymerisation initiator to aid the curing step (b) where the composition is polymerised.

- 5 In the method, the curing step (b) may comprise curing the composition of step (a) thermally or via UV radiation.

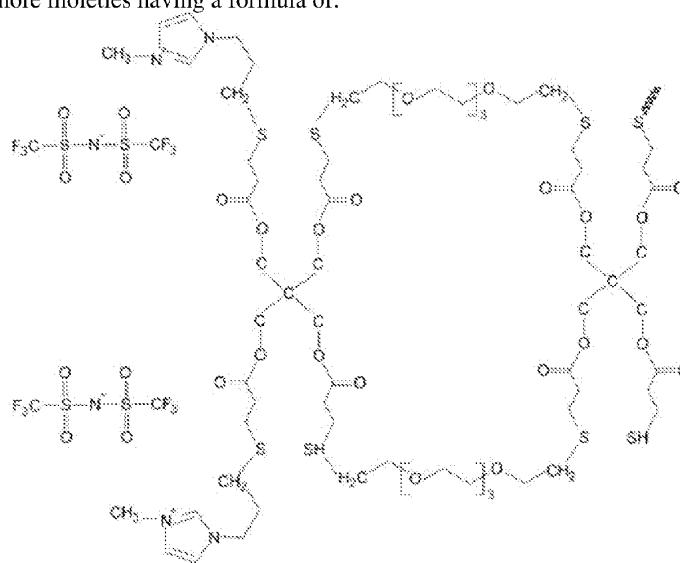
Where the curing step (b) comprises curing the composition of step (a) thermally, the curing step (b) may comprise heating the composition of step (a) at a temperature of at least about 70 °C for at least about 1 hour.

- 10 Where the curing step (b) comprises curing the composition of step (a) via UV radiation, the curing step (b) may comprise exposing the composition of step (a) to a UV source of at least about 30 mW in power for a duration of at least about 10 minutes.

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

- 15 The composite material comprises one or more moieties having a formula of:

one or more moieties having a formula of:



The composite material may be obtained by or obtainable by the method as described herein.

- 20 The composite material may be a free-standing material or a solid-state material.

The composite material may be in the form of a homogeneous gel film.

The composite material may be regarded as or used as a polymer electrolyte.

When the composite material is not voltage-stressed, cationic groups and anionic groups of the organo-ionic compound may adhere strongly to each other as well as to the remaining components that are cross-linked to form a polymeric matrix.

- 5 Therefore, the composite material may behave like a solid polymer electrolyte.

When a voltage is applied to the composite material, the part of the organo-ionic compound that is freely moving gains mobility and form pseudo-percolation channels that aid migration of lithium ions. Therefore, the composite material may have a higher ionic conductivity than conventional solid polymer electrolytes.

- 10 Further, the composite material may behave like a gel polymer when the voltage is applied due to the part of the organo-ionic compound that is bound to the polymeric matrix, which serves as shuttling sites for mobile ions. The composite material may then have an ionic conductivity between that of a conventional solid polymer electrolyte and a gel polymer electrolyte.

- 15 Where the bridging compound further comprise one or more C=O double bonds, the one or more C=O double bonds may serve as sites that facilitate Li-ion "hopping" in the composite material formed by the present composition. The presence of C=O bonds may cause a synergistic boost to conductivities of the composite material together with the pseudo percolations channels formed as described above.

- 20 The composite material may not comprise flammable liquids.

The composite material may have an ion conductivity of more than 10^{-5} S cm⁻¹.

The composite material may have an electrochemical stability window of more than 4 V.

- 25 The present composite material may have a high ionic conductivity and electrochemical stability window with a relatively low concentration of lithium salt (e.g., about 1 M) due to the use of the organo-ionic compound as described above. This is advantageous compared with conventional polymer electrolytes using polyethylene glycol (PEG). The conventional polymer electrolytes require very high concentrations of lithium salt (e.g., [EO]/[Li]=8-10) to achieve similar performances
30 which causes degradation of the polymer electrolytes' mechanical properties. This is because of the absence of cationic and anionic groups in the conventional polymer electrolytes, which are solely dependent on PEG groups for propagation of lithium ions.

- 35 Exemplary, non-limiting embodiments of an electrochemical device will now be disclosed.

The electrochemical device comprises the composite material as described herein.

The electrochemical device may be a battery.

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. 1

[FIG. 1] shows a moiety comprised in an embodiment of the composite material as described herein.

FIG. 2

[FIG. 2] shows an illustration of an embodiment of the composite material as described herein.

FIG. 3

[FIG. 3] shows a comparison of thermogravimetric analysis (TGA) profiles of various samples.

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 – Preparation of A Composite Material

Generally, an organo-ionic compound, a poly-thiol compound, a bridging compound, a polymerisation initiator and a lithium salt were blended mechanically in a one-pot system until the lithium salt was fully dissolved and the mixture was fully homogeneous to form a composition. The concentration of the lithium salt as dissolved in the organo-ionic compound (which was used as a solvent and an electrolyte) was kept at 1 M. The polymerization initiator was added at about 3 weight% based on the total weight of all chemicals used in the one-pot system. The composition was subsequently cast into a silicone mold, followed by curing either thermally (at about 70 °C for about 1 hour) or via UV initiation (using a UV radiation source which was more than 30 mW for about 10 minutes). An exact amount of reagents as provided in tables below) for each type of chemical was measured and reacted.

A list of the compounds used is provided below: Organo-ionic compound - 1-allyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (AMF, purchased from Sigma Aldrich, Singapore and Tokyo Chemical Industry Co, Tokyo, Japan), 1-allyl-3-butylimidazolium bis(trifluoromethanesulfonyl)imide (ABF, purchased from Sigma Aldrich, Singapore and Tokyo Chemical Industry Co, Tokyo, Japan).

Poly-thiol compound - dipentaerythritol hexakis(3-mercaptopropionate) (DPHS, purchased from Sigma Aldrich, Singapore and Tokyo Chemical Industry Co, Tokyo, Japan), pentaerythritol tetrakis(3-mercaptopropionate) (PTS, purchased from Sigma Aldrich, Singapore and Tokyo Chemical Industry Co, Tokyo, Japan).

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- Bridging compound - trimethylolpropane ethoxylate triacrylate (TMET, purchased from Sigma Aldrich, Singapore and Tokyo Chemical Industry Co, Tokyo, Japan), tri(ethylene glycol) divinyl ether (TDV, purchased from Sigma Aldrich, Singapore and Tokyo Chemical Industry Co, Tokyo, Japan), trimethylolpropane diallyl ether (TMPD, purchased from Sigma Aldrich, Singapore and Tokyo Chemical Industry
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- Co, Tokyo, Japan), diallyl carbonate (DAC, purchased from Sigma Aldrich, Singapore and Tokyo Chemical Industry Co, Tokyo, Japan), polyethylene glycol dimethacrylate (PEGDMA, purchased from Sigma Aldrich, Singapore and Tokyo Chemical Industry Co, Tokyo, Japan).

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- Polymerisation initiator - 2-hydroxy-2-methylpropiophenone (HMPP, purchased from Sigma Aldrich, Singapore and Tokyo Chemical Industry Co, Tokyo, Japan).

Lithium salt - lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, purchased from Sigma Aldrich, Singapore and Tokyo Chemical Industry Co, Tokyo, Japan).

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- To investigate the impact of the organo-ionic compound, the poly-thiol compound and the bridging compound on the ion conductivities (IC) and electrochemical stability window (ECV) of the composite material formed, a series of different experiments were conducted to elucidate their influences as set forth below. The lithium salt was exemplified using LiTFSI and the polymerization initiator was exemplified using HMPP in the experiments.

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Example 2 – Impact of Organo-Ionic Compound and Poly-Thiol Compound Loaded on Properties of Composite Material

Table 1a. Formulation of composite materials with different electrolytes and poly-thiol compound loaded

Code	Electrolyte type	Mole of chemical used		
		Electrolyte	Poly-thiol compound	TDV
D1	AMF	1.7×10^{-3}	7×10^{-4} (DPHS)	1.15×10^{-3}
D2	AMF	1.8×10^{-3}	7×10^{-4} (DPHS)	1.1×10^{-3}
D3	AMF	1.9×10^{-3}	7×10^{-4} (DPHS)	1.05×10^{-3}
D4	AMF	2.3×10^{-3}	7×10^{-4} (DPHS)	8.5×10^{-4}

D5	AMF	2.5×10^{-3}	7×10^{-4} (DPHS)	7.5×10^{-4}
A2	AMF	1.8×10^{-3}	1.05×10^{-3} (PTS)	1.1×10^{-3}
B2	ABF	1.8×10^{-3}	1.05×10^{-3} (PTS)	1.1×10^{-3}
VEC-2	VEC	1.8×10^{-3}	1.05×10^{-3} (PTS)	1.1×10^{-3}

Table 1b. Formulation of composite materials with different electrolytes and poly-thiol compound loaded

Code	Electrolyte type	Mole of S-H or C=C bonds		
		Electrolyte	Poly-thiol compound	TDV
D1	AMF	1.7×10^{-3}	4.2×10^{-3} (DPHS)	2.3×10^{-3}
D2	AMF	1.8×10^{-3}	4.2×10^{-3} (DPHS)	2.2×10^{-3}
D3	AMF	1.9×10^{-3}	4.2×10^{-3} (DPHS)	2.1×10^{-3}
D4	AMF	2.3×10^{-3}	4.2×10^{-3} (DPHS)	1.7×10^{-3}
D5	AMF	2.5×10^{-3}	4.2×10^{-3} (DPHS)	1.5×10^{-3}
A2	AMF	1.8×10^{-3}	4.2×10^{-3} (PTS)	2.2×10^{-3}
B2	ABF	1.8×10^{-3}	4.2×10^{-3} (PTS)	2.2×10^{-3}
VEC-2	VEC	1.8×10^{-3}	4.2×10^{-3} (PTS)	2.2×10^{-3}

- 5 **Table 1c.** Ion conductivities (IC) and electrochemical stability window (ECV) of the composite materials formed

Code	IC (S cm^{-1})	ECV (V)
D1	2.49×10^{-5}	-
D2	2.82×10^{-5}	5.3
D3	3.54×10^{-5}	-
D4	5.36×10^{-5}	-
D5	6.44×10^{-5}	4.8
A2	4.28×10^{-5}	4.9

B2	4.69×10^{-5}	-
VEC-2	3.79×10^{-6}	3

In the examples above, the bridging compound was fixed as tri(ethylene glycol) divinyl ether (TDV) to allow comparison of the electrolyte and the poly-thiol compound used. It could be observed from D1 to D5 in Table 1c that an increase in weight percentage of AMF loaded led to an increase in ionic conductivity of the resultant composite material. This observation could be explained by the increase in free volume brought about by the reduction in cross-linking density within the composite material, thus reducing the hinderance in ionic mobility, causing an increase in ion conductivity. A higher AMF loading also implies that a closer ionic liquid packing, leading to establishment of pseudo percolation channels within the electrolyte material, thus assisting the propagation of Li-ion within the composite material, causing an increase in ion conductivity.

By comparing samples A2, B2 and VEC-2 that were prepared with the same poly-thiol compound, PTS, it could be seen from the samples' respective ion conductivities that Li-ion conductivity for B2 was higher than that of A2, while VEC-2 had the lowest conductivity, i.e., ten-fold lower in ion conductivity measured as compared to A2. This demonstrated that ion conductivity of the electrolyte material was not solely dependent upon the free volume within the material, but also on the intrinsic structural characteristic of PBL.

Sample VEC-2 was prepared using a non-partially bounded electrolyte, vinyl ethylene carbonate (VEC); which could not form pseudo percolation channels within the material under a potential difference. This resulted in a severe degradation in ion conductivity.

Sample B2 was prepared with 1-allyl-3-butylimidazolium bis(trifluoromethylsulfonyl)imide (ABF) electrolyte, with a longer butyl side group attached to the imidazolium as compared to methyl group in 1-allyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (AMF). The longer dangling butyl chain has a greater plasticizing effect on the polymeric matrix, increasing mobility of the transmission of the Li-ion as compared to the shorter methyl group. This caused an increase in ion conductivity of ABF based electrolyte material.

By comparing samples D2 and A2, both samples were prepared with the same concentration of C=C double bonds and thiol functional groups but with different species of the poly-thiol compound. Sample A2 had a higher measured Li-ion conductivity. This phenomenon could be explained by sample D2 being constituted by DPHS possessing 6 thiol groups per DPHS molecules as compared to 4 thiol groups per molecule for PTS in sample A2. This implies that density of cross-linking per volume within the film was higher in D2 than A2, which resulted in an increase in polymeric matrix stiffness of the D2 battery electrolyte film as compared to A2. This further resulted in a reduction of Li-ion conductivity. Likewise, the higher density of cross-linking per volume of D2 also caused D2 to be more resilient to oxidative degradation as compared to A2, resulting in a higher ECV to be measured.

Sample D5 had a lower measured ECV as compared to D2. This could be due to AMF possessing a lower intrinsic ECV of 4.8V, and the D5 formula contained a higher

mole percentage of AMF, which resulted in an overall reduction in measured ECV. Sample VEC-2 had the lowest measured ECV, which could be attributed to the bond attaching the dangling carbonate to the vinyl functionality, being vulnerable to electrical degradation.

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- FIG. 1 shows a representative reactive bonding structure of A2, where the methylimidazolium ions served as “shuttling sites” which were more effective hopping sites for the ions of the lithium salt during diffusion under an applied potential as compared to C=O sites e.g., in Vinyl Ethylene Carbonate (VEC), a polar solvent frequently used in battery preparation.
- 10
- FIG. 2 shows an illustration of the arrangement of components within A2. PTS (202), TDV (204) and AMF (206) formed a cross-linked structure with channels housing lithium ions (208) and TFSI ions (210).

Example 3 – Impact of Bridging Compound Loaded on Properties of Composite Material

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- To determine the impact of bridging compounds on the properties of the composite material, different formulations utilizing trimethylolpropane ethoxylate triacrylate (TMET), diallyl carbonate (DAC), trimethylolpropane diallyl ether (TMPD) and polyethylene glycol dimethacrylate (n=9) were prepared as stated in Table 2a and their properties (IC, ECV) are listed in Table 2b.
- 20
- Table 2a.** Formulation of composite materials with different bridging compounds loaded

Code	Bridging compound type	Number of reactive sites	Mole of chemical used		
			AMF	DPHS	Bridging compound
TMPD	TMPD	2	2.5×10^{-3}	7×10^{-4}	7.5×10^{-4}
DAC	DAC	2	2.5×10^{-3}	7×10^{-4}	7.5×10^{-4}
PEGDMA	PEGDMA (n = 9)	2	2.5×10^{-3}	7×10^{-4}	7.5×10^{-4}
TMET	TMET	3	2.5×10^{-3}	7×10^{-4}	5×10^{-4}

Table 2b. Ion conductivities (IC) and electrochemical stability window (ECV) of the composite materials formed

Code	IC (S cm ⁻¹)	ECV (V)
TMPD	5.94×10^{-5}	4.2
DAC	6.93×10^{-5}	4.3
PEGDMA	1.87×10^{-5}	4.2
TMET	3.14×10^{-5}	4.4

It could be observed from Table 2b that despite all samples in Table 2a were prepared with the same molar concentrations of C=C double bonds and thiol functionalities, the measured IC values were starkly different. Sample DAC had the highest measured IC and this was accounted for by the presence of C=O bonds in the carbonate functionalities, which were known to be sites that facilitate Li-ion “hopping”. The presence of C=O bonds caused a synergistic boost to the Li-ion conductivity on top of the pseudo TFSI percolations channels.

Sample TMPD had a lower measured IC as compared to D5. This demonstrated that the ethylene oxide functionalities in TDV compound had a bigger impact on IC of electrolyte than the plasticizing effect of dangling methyl group of TMPD compound. Samples PEGDMA and TMET had a very much lower measured IC. This could be due to the increase in stiffness of the sample as a result of homo-polymerization of the bridging compound, causing an increase in chain rigidity of the polymeric matrix, reducing the Li-ions’ “hopping” capability, causing a reduction in IC. By comparing the measured ECV of the samples prepared with different bridging compounds, sample DAC possessed the highest Li-ion conductivity while still retaining a reasonably high ECV of 4.3V.

A side benefit of samples prepared with DAC and TMPD as bridging compounds is that they are biodegradable (e.g., broken down into smaller chain segments), as these bridging compounds serve as environmental degradation sites for soil-based degradation.

Example 4 – Thermal Analysis of Composite Materials

Samples A2, D2, D4, D5, VEC-2 were chosen to be analysed via thermogravimetric analysis (TGA) technique to determine the impact of various battery electrolyte structural designs on the thermal degradation stability. A small piece of each sample was heated to 100 °C and held for 5 minutes to remove moisture within the test piece, followed by heating the composite material to 600 °C at a ramping rate of 10 °C/minute in air. FIG. 3 shows the weight of the sample tested with respect to test chamber temperature derived from TGA test.

It could be observed from the TGA profiles in FIG. 3 that the onset of thermal degradation for VEC-2 was much lower than samples that contained the organo-ionic compound AMF as electrolyte. The onset temperature increased with the increase in AMF loading within the sample. This was due to the dangling cyclic carbonate present in the polymeric matrix requiring lower energy content to overcome, leading to a lower degradation temperature.

It could also be observed that D5 possessed a slightly higher onset temperature as compared to D2. Sample D5 was prepared with a significantly higher loading of AMF as compared to D2. AMF as an ionic liquid had innate higher thermal degradation temperature, which led to more energy required to degrade the polymeric network. The higher requirement of energy led to an increase in degradation temperature for D5.

By comparing A2 and D2, it could be observed that the onset temperature was lower for A2 despite both samples being prepared with the same moles of C=C double bond and thiol functionality content. Sample D2 was prepared with DPHS which possessed 6 thiol functionalities as compared to 4 thiol functionalities in PTS for A2. This led

to a higher cross-linking per volume of electrolyte film for D2 as compared to A2. Therefore, more energy and higher temperature was required to overcome the bonds in D2, leading to a higher degradation temperature. In summary, the TGA profiles demonstrated that AMF-DPHS-TDV based battery electrolyte system was thermal-tolerant for high temperature applications.

The onset of thermal degradation temperature of the present composite material is greater than 300 °C due to the ionic nature of the present composite material, thus allowing the present composite material to be used in demanding environment (e.g., high temperature).

10 Industrial Applicability

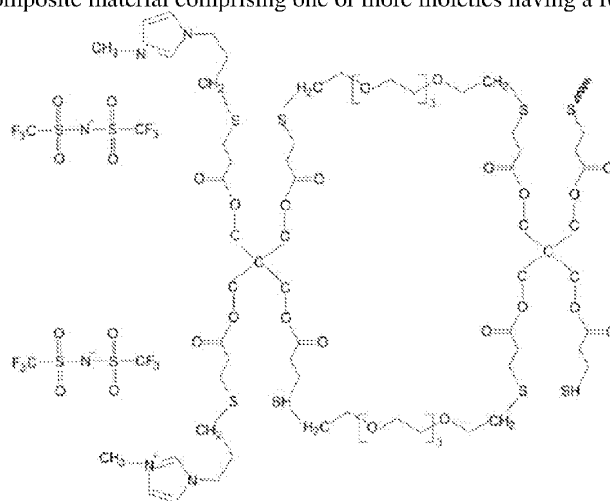
The composition and composite material of the disclosure may be used in a variety of applications such as electric vehicles, personal mobility devices, mobile phones, maritime, rail systems, micro-batteries, wearables or ion exchange membranes. Due to the resilience of the material to thermal degradation, this material is especially suitable for higher temperature environments.

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 appended claims.

Claims

1. A composition comprising:
 - (a) an organo-ionic compound comprising at least one C=C double bond;
 - (b) a poly-thiol compound comprising a plurality of thiol groups; and
 - (c) a bridging compound comprising a plurality of C=C double bonds.
2. The composition of claim 1, wherein the organo-ionic compound has a melting point that is lower than 20 °C.
3. The composition of claim 1 or 2, wherein the organo-ionic compound comprises at least one cationic group and at least one anionic group, and wherein one of the at least one cationic group and the at least one anionic group comprises the at least one C=C double bond.
4. The composition of any one of claims 1 to 3, wherein the organo-ionic compound is selected from the group consisting of 1-ethyl-3-methylimidazolium aminoacetate (EMAM), 1-ethyl-3-methylimidazolium lactate (EML), 1-allyl-3-ethylimidazolium bis(trifluoromethanesulfonyl)imide (AEF), 1-allyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (AMF), 1-allyl-3-butylimidazolium bis(trifluoromethanesulfonyl)imide (ABF), vinyl-3H-imidazolium bis(trifluoromethanesulfonyl)imide, 1-allyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide, 3,3'-(butane-1,4-diyl)bis(1-vinyl-3-imidazolium) bis(trifluoromethanesulfonyl)imide, and combinations thereof.
5. The composition of any one of claims 1 to 4, wherein the organo-ionic compound is AMF.
6. The composition of any one of claims 1 to 5, wherein the poly-thiol compound is selected from the group consisting of dipentaerythritol hexakis(3-mercaptopropionate) (DPHS), pentaerythritol tetrakis(3-mercaptopropionate) (PTS), 2,2'-(ethylenedioxy)diethanethiol, and combinations thereof.
7. The composition of any one of claims 1 to 6, wherein the bridging compound is selected from the group consisting of dipentaerythritol hexaacrylate (DHL), tetrakis(dimethyl(vinyl)silyl) orthosilicate (ORP), trimethylolpropane ethoxylate triacrylate (TMET), trimethylolpropane triacrylate (TMPTA), trimethylolpropane triglycidyl ether, pentaerythritol tetraglycidyl ether, 1,2,4-trivinylcyclohexane (TVH), tri(ethylene glycol) divinyl ether (TDV), trimethylolpropane diallyl ether (TMPD), diallyl carbonate (DAC), pentaerythritol allyl ether, diallyl maleate, 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane, 2,4,6-trimethyl-2,4,6-trivinylcyclotrisiloxane, tetra allyl silane (TAL), polyethylene glycol dimethacrylate (PEGDMA), and combinations thereof.
8. The composition of any one of claims 1 to 7, further comprising a lithium salt.
9. The composition of claim 8, wherein the lithium salt is selected from the group consisting of lithium triflate (LiTRF), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), and a combination thereof.

10. The composition of any one of claims 1 to 9, further comprising a polymerisation initiator.
11. The composition of claim 10, wherein the polymerisation initiator is selected from the group consisting of methyl benzoylformate, 2,2-dimethoxy-2-phenylacetophenone, 2,4,6-tris(dimethylaminomethyl)phenol, azobisisobutyronitrile, 4-thiophenyl phenyl diphenyl sulfonium hexafluoroantimonate (TPSHA), diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (DTPO), 4-(dimethylamino) pyridine, 1,5,7-triazabicyclo[4.4.0]dec-5-ene, 2-hydroxy-2-methylpropiophenone (HMPP), and combinations thereof.
12. The composition of any one of claims 1 to 11, wherein the number of thiol groups in the composition is greater than the number of C=C double bonds.
13. The composition of any one of claims 8 to 12, wherein the lithium salt has a concentration in the range of about 1 M to about 1.5 M based on the total volume of the organo-ionic compound.
14. The composition of any one of claims 10 to 13, wherein the polymerisation initiator has a molar percentage in the range of about 0.5 mol% to about 5 mol% based on the total number of moles of compounds in the composition.
15. A method of forming a composite material, comprising the steps of:
 (a) mixing an organo-ionic compound comprising at least one C=C double bond, a poly-thiol compound comprising a plurality of thiol groups and a bridging compound comprising a plurality of C=C double bonds to form a composition; and
 (b) curing the composition of step (a) to form the composite material.
16. The method of claim 15, wherein the mixing step (a) is undertaken in a one-pot system.
17. A composite material comprising one or more moieties having a formula of:



18. A composite material obtained by or obtainable by the method of claim 15 or 16.
19. The composite material of claim 17 or 18, which has an ion conductivity of more than $10^{-5} \text{ S cm}^{-1}$.
- 5 20. The composite material of any one of claims 17 to 19, which has an electrochemical stability window of more than 4 V.
- 10 21. An electrochemical device comprising the composite material of any one of claims 17 to 20.