

RAPID CURING OF PHOSPHORUS ALLYL/VINYL COMPOUNDS FOR
FLAME RETARDANT POLYMERIC MATRIX

Cross-Reference to Related Application

- 5 [0001] This application claims the benefit of priority of Singapore Patent Application No. 10202302729Y, filed 26 September 2023, the content of it being hereby incorporated by reference in its entirety for all purposes.

Technical Field

- 10 [0002] The present disclosure relates to a method for forming a flame retardant polymer electrolyte. The present disclosure also relates to the flame retardant polymer electrolyte, such as a lithium-based flame retardant polymer electrolyte.

Background

- 15 [0003] With the increase in widespread utilization of electric vehicles (EVs) and electronic devices, lithium-ion (Li-ion) batteries as energy storage devices, may have experienced a gain in prominence. This may be due to Li-ion battery's technological maturity and the relative abundance and ease of excess to materials that may constitute the battery. Despite their popularity, Li-ion batteries may possess safety concerns, such as susceptibility to fire hazards. In recent years, there appears to be an increased in the
20 spate of Li-ion battery related fire accidents that may have resulted in loss of lives and injuries. To address this issue, developmental works may have been conducted to develop battery electrolytes with flame retardant (FR) capabilities. A traditional, industrial practice may be to mix a phosphorous-containing liquid state organic compound (e.g., triethyl phosphate, dimethyl methyl phosphonate) with the battery
25 electrolytes. In this regard, phosphonium-based ionic liquids (e.g., tributyl(methyl)phosphonium dimethyl phosphate) may be used as either the liquid electrolyte or mixed with other electrolytes as a flame retardant. However, the drawback of this approach tends to be that such compounds degrade the ion conductivity of the
30 battery, and the FR materials may be undesirably volatile.
- [0004] Another traditional approach to achieve FR battery electrolyte may be to introduce halogenated compounds (e.g., brominated, chlorinated) into the battery

electrolyte matrix. During combustion, the halogenated compound may form halogen radicals that may attack the $\cdot\text{H}$ and $\cdot\text{OH}$ radicals formed during combustion of electrolyte materials, thereby quenching the propagation of the fire.

[0005] In the case of other approaches, there seems to be a heightened interest in physical integration of phosphorous-based compounds (e.g., bis[2-(methacryloyloxy)ethyl] phosphate) within the battery electrolyte matrix as a means of imparting the electrolyte with FR capability. Like the halogenated FR compounds mentioned above, phosphorous-based compounds release $\text{PO}\cdot$ radicals during combustion, which attacks the $\cdot\text{H}$ and $\cdot\text{OH}$ radical formed during combustion of electrolyte materials, thereby quenching the combustion.

[0006] In one reported example, a battery gel polymer electrolyte (GPE) was prepared via polymerization of a synthesized 2-((bis((2-oxo-1,3-dioxolan-4-yl) methoxy) phosphoryl)oxy) ethyl acrylate monomer with triethyl phosphate as plasticizer, to achieve a FR electrolyte film with Li-ion conductivity of $5.65 \times 10^{-4} \text{ S/cm}$.

[0007] In another reported example, a FR GPE was fabricated via copolymerizing polyethylene glycol diacrylate with diethyl vinyl phosphonate to form an electrolyte with Li-ion conductivity of $6 \times 10^{-4} \text{ S/cm}$.

[0008] In another reported example, a battery electrolyte matrix material was prepared by first synthesizing dimethyl-p-vinyl benzyl phosphonate from p-vinyl benzyl chloride, followed by polymerization via thermally initiated free radical polymerization.

[0009] In all examples mentioned above, free radical polymerization tends to be utilized to bond the monomers to form the polymeric matrix. However, due to the relatively lower reactivity of allyl or vinyl groups, long thermal reaction durations (e.g., 10 hours to 12 hours) tend to be required to complete polymerization.

[0010] There is thus a need to provide for a solution that addresses one or more of the limitations mentioned above. The solution should at least address the processing disadvantage mentioned above.

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Summary

[0011] In a first aspect, there is provided a method for forming a flame retardant polymer electrolyte, the method comprising:

forming a mixture comprising a phosphorus compound having a terminal vinyl or allyl moiety, a thiol-based agent having two or more terminal thiol functional groups, and a polymerization initiator; and

subjecting the mixture to a stimulus to have the flame retardant polymer electrolyte formed in one hour or less.

[0012] In another aspect, there is provided a lithium-based flame retardant polymer electrolyte comprising:

a polymer network comprising phosphate or phosphonate groups crosslinked with a thiol-based agent via thioether linkages; and

5 a lithium salt,

wherein the phosphate or phosphonate groups, and the lithium salt, are present in an amount of at least 30 wt% of the lithium-based flame retardant polymer electrolyte.

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Brief Description of the Drawings

[0013] The drawings are not necessarily to scale, emphasis instead generally being placed upon illustrating the principles of the present disclosure. In the following description, various embodiments of the present disclosure are described with reference to the following drawings, in which:

15 **[0014]** FIG. 1A shows a flame retardant polymer electrolyte of the present disclosure and its polymeric network (i.e., polymeric matrix).

[0015] FIG. 1B shows the same flame retardant polymer electrolyte as FIG. 1A, except that FIG. 1B identifies the components (e.g., the vinyl or allyl moieties, the poly-thiol, the bridging compound) of the flame retardant polymer electrolyte. The poly-thiol and bridging compound in the polymeric matrix may be referred to as poly-thiol moiety and bridging compound moiety, respectively.

20 **[0016]** FIG. 1C shows non-limiting examples of one or more monomers of the poly-thiol compound, an allyl-based bridging compound (e.g., a diallyl), and the vinyl-based or allyl-based compound, used to form a flame retardant polymer electrolyte of the present disclosure.

25 **[0017]** FIG. 2A is a table showing the compositional details of formulations used to prepare different flame retardant polymer electrolytes of the present disclosure, samples

are named using a code label, for example, D1, E1, D1 (35), etc. These flame retardant polymer electrolyte samples may be referred to as poly-thiol assisted curing of VAP-based flame retardant GPE systems. "Mol" denotes the measurement unit for mole(s). DEAP denotes diethyl allylphosphonate, DEV denotes diethyl vinyl phosphonate, DALP denotes diethyl allyl phosphate, TMET denotes trimethylolpropane ethoxylate triacrylate, DPHS denotes dipentaerythritol hexakis(3-mercaptopropionate), PTS denotes pentaerythritol tetrakis(3-mercaptopropionate).

[0018] FIG. 2B is a table showing the compositional details of formulations used to prepare different flame retardant polymer electrolytes of the present disclosure. Samples are named using a code label, for example, T3 and T4. These flame retardant polymer electrolyte samples may be referred to as poly-thiol (EDT) assisted curing of TRAP-based FR GPE systems. TRAP denotes tri-allyl phosphate. EDT denotes 2,2'-(ethylenedioxy)diethanethiol. "Mol" denotes the measurement unit for mole(s).

[0019] FIG. 3 is a table listing the ionic conductivities (IC), mechanical storage modulus (M), electrochemical stability window (ECV), and the time taken for the lit sample to be completely extinguish divided by sample mass (referred to as the Self-Extinguishing Time (SET)). Samples are named using a code label, for example, D1, E1, D1 (35), etc.

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Detailed Description

[0020] The following detailed description refers to the accompanying drawings that show, by way of illustration, specific details and embodiments in which the present disclosure may be practiced.

[0021] Features that are described in the context of an embodiment may correspondingly be applicable to the same or similar features in the other embodiments. Features that are described in the context of an embodiment may correspondingly be applicable to the other embodiments, even if not explicitly described in these other embodiments. Furthermore, additions and/or combinations and/or alternatives as described for a feature in the context of an embodiment may correspondingly be applicable to the same or similar feature in the other embodiments.

[0022] The present disclosure relates to a method for forming a flame retardant polymer electrolyte and the flame retardant polymer electrolyte. The flame retardant polymer

electrolyte may be a lithium-based flame retardant polymer electrolyte in various non-limiting embodiments and examples.

[0023] The proliferation of EVs, PMDs (personal mobility devices), electronic devices may have undesirably increased fire safety concerns for their associated battery electrolytes. To address this, traditionally, P-based (phosphorus-based) liquid reagent/ionic liquids may be mixed with the battery electrolyte, but this may adversely reduce Li-ion conductivity and imparts undesirable volatility (relatively high vapor pressure). Another traditional approach was to introduce P-atoms (phosphorus atoms) within electrolyte polymeric matrix via co-polymerization of P-based reagents with matrix forming reagents (e.g., vinyl-phosphorus), but this tends to be less successful or has drawbacks due to low reactivity of vinyl group, extremely long reaction time (e.g., 10 to 12 hours even at 70°C).

[0024] The present method and flame retardant polymer electrolyte address one or more limitations mentioned above. The present method and flame retardant polymer electrolyte present an advantageous technique and material that facilitates rapid curing of allyl/vinyl P-based compounds for FR applications.

[0025] The method is advantageous for rapid curing of vinyl/allyl based phosphorous (VAP) compounds, particularly VAP molecule/oligomer with mono C=C double bond site, to form a solid polymeric matrix with FR capability.

[0026] The method could be applied to bridge mono-functional molecules to form a solid-state macro-molecule matrix.

[0027] The method may involve homo-polymerization of acrylate terminals of the bridging element (i.e., the bridging compound), which facilitates a higher loading of VAP while still maintaining film mechanical stiffness, allowing better FR capability to be achieved.

[0028] The method drastically reduces curing time (10 minutes with ultraviolet (UV) light or 1 hours at 70°C), which in turn renders the method economically favorable.

[0029] The flame retardant polymer electrolyte, from the present method, is non-leaky. The term “non-leaky” in the context of the flame retardant polymer electrolyte means any liquid electrolyte within a solid gel does not leach out. The term “non-leaky” in various instances may mean that the inventory of salt (which contributes to the capacity of the cell) does not get lost. If a cell is leaky, the cell may suffer from loss of electrolyte,

and in turn the loss of salt (and hence cation inventory). The resultant flame retardant polymer electrolyte may be free standing/solid state (i.e., does not require a structural casing as support). The flame retardant polymer electrolyte reduces fire hazard potential (lack of flammable liquids).

5 **[0030]** The method is advantageous, as it involves rapid curing of vinyl-based or allyl-based (abbreviated as vinyl/allyl) phosphorous compounds in the synthesis of a flame retardant (FR) polymeric material usable as an electrolyte in batteries (i.e., flame retardant polymer electrolyte). The flame retardant polymer electrolyte may have a flame retardant polymeric matrix. Particularly, advantages of the method include
10 polymerization of vinyl-based or allyl-based phosphorous compounds completed within an hour. For brevity, the vinyl-based or allyl-based phosphorous compounds may be abbreviated as “VAP” in the present disclosure.

[0031] The method may involve, for example, a poly-thiol compound or oligomer, or a mixture thereof, and optionally a bridging compound or oligomer which may help in
15 further chemically bonding the phosphorous-based compound to form a flame retardant polymeric network. The bridging compound or oligomer, in the context of the present disclosure, refers to a reagent with two or more double bonds (e.g., carbon double bonds). The poly-thiol compound or oligomer, in the context of the present disclosure, refers to a reagent with three or more thiol (S-H) functional groups. In non-limiting
20 examples, for a VAP with more than one vinyl/allyl moiety (e.g., triallyl phosphate), the bridging compound or oligomer may be optional. In non-limiting examples where the VAP is with only one vinyl/allyl moiety, the total concentration of the thiol functional groups may be in excess to the total concentration of double bonds in the VAP and of the bridging compound or oligomer.

25 **[0032]** Generally, as a non-limiting example, to prepare the rapid curing FR polymer electrolyte of the present disclosure, the VAP, a poly-thiol compound or oligomer, a lithium salt, and optionally the bridging compound or oligomer, together with a reaction initiator (i.e., polymerization initiator) may be mixed till homogeneity. Rapid polymerization of the mixture may then be triggered via two treatment processes, either
30 thermally or ultraviolet (UV) light. For UV initiated systems, a type I photo-initiator may be used, while for thermally initiated systems curing can be performed at 70°C for 1 hour or less. Total weight percentage of the lithium salt and the VAP in various

instances may be at least 30 weight percent (wt%) of the total FR polymer electrolyte mass to achieve flame retardancy.

[0033] Details of various embodiments of the flame retardant polymer electrolyte and method for forming the flame retardant polymer electrolyte, and advantages associated with the various embodiments are described below. Where the embodiments and advantages are described in the examples section further hereinbelow, they shall not be iterated for brevity.

[0034] The present disclosure provides for a method for forming a flame retardant polymer electrolyte. The method may comprise forming a mixture, and subjecting the mixture to a stimulus. The mixture may comprise a phosphorus compound having a terminal vinyl or allyl moiety, a thiol-based agent having two or more (e.g., three or more) terminal thiol functional groups, and optionally a polymerization initiator. Subjecting the mixture to a stimulus may be to have the flame retardant polymer electrolyte formed in one hour or less (e.g., within one hour).

[0035] In various embodiments, the method may further comprise mixing a lithium salt and the mixture prior to subjecting the mixture to the stimulus, or mixing a lithium salt solution and the mixture after subjecting the mixture to the stimulus, wherein the lithium salt solution comprises a lithium salt. In various embodiments, mixing the lithium salt solution and the mixture may comprise mixing the lithium salt with an ionic liquid or an organic solvent to form the lithium salt solution. Any suitable ionic liquid or organic solvent capable of forming a lithium salt solution may be used. In various non-limiting examples, the ionic liquid or the organic solvent may comprise 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide or propylene carbonate.

[0036] In various embodiments, the lithium salt may comprise lithium triflate or lithium dis(trifluoromethanesulfonyl)imide.

[0037] In various embodiments, forming the mixture may comprise mixing the phosphorus compound, the thiol-based agent, and the polymerization initiator to form the mixture.

[0038] In various embodiments, forming the mixture may comprise adding the poly-thiol agent and the polymerization initiator to the phosphorus compound in the presence of the lithium salt. For example, (i) the lithium salt may be first dissolved in the ionic liquid or the organic solvent prior to addition of the poly-thiol agent and the

polymerization initiator in the mixture, which may better aid lithium salt dissolution, or (ii) the lithium salt may be directly added (e.g., at the same time as the poly-thiol agent and/or the polymerization initiator) to the mixture, which helps reduce number of separate steps. In various embodiments, the method may further comprise blending the mixture at a temperature of 40°C to 45°C, after adding the poly-thiol agent and the polymerization initiator, until the mixture becomes homogeneous (e.g., clear and/or transparent).

[0039] In various embodiments, the mixture may further comprise a bridging agent.

[0040] In various embodiments, the bridging agent may comprise dipentaerythritol hexaacrylate, tetrakis(dimethyl(vinyl)silyl) orthosilicate, trimethylolpropane ethoxylate triacrylate, trimethylolpropane triacrylate, 1,2,4-trivinylcyclohexane, tri(ethylene glycol) divinyl ether, trimethylolpropane diallyl ether, diallyl carbonate, pentaerythritol allyl ether, diallyl maleate, 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane, polyethylene glycol dimethacrylate, and/or vinyl methacrylate.

[0041] In various embodiments, subjecting the mixture to the stimulus may comprise heating the mixture at a temperature of 60°C to 80°C (e.g., 60°C to 70°C, 70°C to 80°C) to have the mixture thermally cured, or exposing the mixture to ultraviolet light for 15 minutes or less (e.g., 10 minutes or less, 5 minutes or less) to have the mixture photo-cured.

[0042] In various embodiments, the phosphorus compound may comprise diethyl allylphosphonate, diethyl allyl phosphate, diethyl vinyl phosphonate, tri-allyl phosphate, dimethyl vinyl phosphonate, and/or tetraisopropyl vinylidenediphosphonate.

[0043] In various embodiments, the thiol-based agent may comprise dipentaerythritol hexakis(3-mercaptopropionate), pentaerythritol tetrakis(3-mercaptopropionate), and/or 2,2'-(ethylenedioxy)diethanethiol.

[0044] In various embodiments, the polymerization initiator may be a photo-initiator. That is to say, the polymerization initiator may be a compound which activates the polymerization in the presence of an optical stimulus, such as ultraviolet light.

[0045] In various embodiments, the polymerization initiator may comprise methyl benzoylformate, 2,2-dimethoxy-2-phenylacetophenone, 2,4,6-

tris(dimethylaminomethyl)phenol, azobisisobutyronitrile, 4-thiophenyl phenyl diphenyl sulfonium hexafluoroantimonate, diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide, and/or 2-hydroxy-2-methylpropiophenone.

[0046] The present disclosure describes a flame retardant polymer electrolyte (e.g., a lithium-based flame retardant polymer electrolyte), wherein its method of forming is described in various aspects and embodiments of the present disclosure. Embodiments and advantages described for the method can be analogously valid for the flame retardant polymer electrolyte described herein, and vice versa. Where the various embodiments and advantages have already been described above and in the examples section further hereinbelow, they shall not be iterated for brevity.

[0047] The present disclosure also provides for a lithium-based flame retardant polymer electrolyte, which may comprise a polymer network that may comprise phosphate or phosphonate groups crosslinked with a thiol-based agent via thioether linkages, and a lithium salt, wherein the phosphate or phosphonate groups, and the lithium salt, are present in an amount of at least 30 wt% (e.g., at least 40 wt%, at least 50 wt%) of the lithium-based flame retardant polymer electrolyte.

[0048] In various embodiments, the polymer network may be derived from a phosphorus compound having a terminal vinyl or allyl moiety. The phosphorus compound may comprise diethyl allylphosphonate, diethyl allyl phosphate, diethyl vinyl phosphonate, tri-allyl phosphate, dimethyl vinyl phosphonate, and/or tetraisopropyl vinylidenediphosphonate.

[0049] In various embodiments, the thiol-based agent may comprise dipentaerythritol hexakis(3-mercaptopropionate), pentaerythritol tetrakis(3-mercaptopropionate), and/or 2,2'-(ethylenedioxy)diethanethiol.

[0050] In various embodiments, the lithium-based flame retardant polymer electrolyte may further comprise a bridging moiety chemically coupled to the thiol-based agent. The bridging moiety may be derived from a bridging agent comprising dipentaerythritol hexaacrylate, tetrakis[dimethyl(vinyl)silyl] orthosilicate, trimethylolpropane ethoxylate triacrylate, trimethylolpropane triacrylate, 1,2,4-trivinylcyclohexane, tri(ethylene glycol) divinyl ether, trimethylolpropane diallyl ether, diallyl carbonate, pentaerythritol allyl ether, diallyl maleate, 2,4,6,8-tetramethyl-2,4,6,8-

tetravinylcyclotetrasiloxane, polyethylene glycol dimethacrylate, and/or vinyl methacrylate.

[0051] In various embodiments, the lithium salt may comprise lithium triflate or lithium dis(trifluoromethanesulfonyl)imide.

5 **[0052]** In various embodiments, the lithium-based flame retardant polymer electrolyte may be a gel polymer electrolyte or a solid polymer electrolyte.

[0053] In summary, the method advantageously involves rapid curing of vinyl/allyl based phosphorous compounds to form a flame-retardant polymeric matrix and a unique class of FR polymeric material. The FR polymeric material may include three
10 components, a poly-thiol (e.g., 3 or more -SH bonds within each compound), optionally a bridging compound or oligomer (2 or more double bonds within each compound), and a vinyl/allyl phosphorous (VAP) based reagent (1 or more double bond within each compound) (e.g., phosphate, phosphonate). In various embodiments, the total moles of thiol bonds may be in slight excess to the moles of double bonds. In various
15 embodiments, the total wt% of lithium salt and VAP may be at least 30 wt% of total electrolyte mass. The method may be a one-pot formulation. The method may involve wet casting of formulation with curing (e.g., 10 mins, UV at 125 W/cm² or 1 hour at 70°C).

[0054] The word “substantially” does not exclude “completely” e.g. a composition
20 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 present disclosure.

[0055] In the context of various embodiments, the articles “a”, “an” and “the” as used with regard to a feature or element include a reference to one or more of the features or elements.

25 **[0056]** In the context of various embodiments, the term “about” or “approximately” as applied to a numeric value encompasses the exact value and a reasonable variance.

[0057] As used herein, the term “and/or” includes any and all combinations of one or more of the associated listed items.

[0058] Unless specified otherwise, the terms “comprising” and “comprise”, and
30 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.

Examples

[0059] The flame retardant polymer electrolyte and method for forming the flame
5 retardant polymer electrolyte are described in further details, by way of non-limiting
examples, as set forth below.

[0060] Example 1A: General discussion of method

[0061] The examples of the present disclosure are not intended to be limiting but for
the purpose of demonstrating the flame retardant polymer electrolyte and its synthesis
10 so as to give a better understanding.

[0062] The examples of the present disclosure relate to a synthesis method that
advantageously cures liquid state vinyl-based or allyl-based phosphorous compounds
(VAP) to form a flame retardant (FR) polymeric matrix, that can be used to form a
unique class of flame retardant polymeric material (e.g., a flame retardant polymer
15 electrolyte usable in a battery). The method allows polymerization of the VAP to be
completed in an hour or less. The method involves a poly-thiol compound or oligomer,
or a mixture thereof, with or without a bridging compound or oligomer, to allow the
VAP to be physically linked to form a FR polymeric network. The bridging compound
or oligomer in the present disclosure refers to a reagent with two or more carbon double
20 bond sites. The poly-thiol compound or oligomer in the present disclosure refers to a
reagent with three or more thiol (S-H) functional groups. For VAP with more than one
vinyl or allyl moiety (e.g., triallyl phosphate), usage of the bridging compound or
oligomer is optional. For VAP with only one vinyl moiety or allyl moiety, the total
concentration of the thiol groups can be in excess to the total concentration of double
25 bonds in the VAP and in the bridging compound or oligomer.

[0063] In non-limiting examples, to prepare the rapid curing flame retardant polymeric
material, the VAP, poly-thiol compound or oligomer, and optionally the bridging
compound or oligomer, together with a reaction initiator (i.e., polymerization initiator)
may be first mixed till a homogeneous mixture.

30 [0064] Rapid polymerization of the mixture can then be triggered either thermally or
by ultraviolet (UV) light. For UV initiated systems, type I photo-initiator may be used,
while a thermally cured system may be performed at about 70°C for 1 hour. A type I

photo-initiator refers to an initiator molecule that can undergo homolytic fission upon exposure to UV light to form two radicals.

[0065] In various examples, a lithium salt can then be dissolved in an ionic liquid or organic solvent (about 20 wt% to 40 wt%) before mixing with the resultant flame polymeric material system to achieve a battery gel polymer electrolyte (GPE). Said differently, the lithium salt can be dissolved in the ionic liquid or organic solvent and then mixed into the mixture, prior to curing the mixture.

[0066] In various examples, the lithium salt can be directly dispersed in homogenous mixture before curing (i.e., polymerization) to achieve a battery solid polymer electrolyte (SPE).

[0067] The total wt% of the lithium salt and VAP may be as low as 30 wt% (at least 30 wt%) of the flame retardant polymer electrolyte, for conferring flame retardancy to the flame retardant polymer electrolyte.

[0068] Example 1B below describes a non-exhaustive list of chemicals that were usable for preparing the quick curing VAP polymeric material for FR applications. FIG. 1A and FIG. 1B show the chemical structure of a poly-thiol and a bridging compound incorporated to assist in bonding within the allyl phosphorous compounds via thiol Michael addition reactions.

[0069] **Example 1B: Non-Limiting examples of reagents used to prepare rapid curing VAP-based polymer electrolyte**

[0070] The following materials are non-limiting examples for demonstrating a flame retardant polymer electrolyte of the present disclosure.

[0071] Vinyl-based or allyl-based phosphorous compound: diethyl allylphosphonate (DEAP), diethyl allyl phosphate (DALP), diethyl vinyl phosphonate (DEV), tri-allyl phosphate (TRAP), dimethyl vinyl phosphonate, tetraisopropyl vinylidenediphosphonate.

[0072] Poly-thiol compound or oligomer (i.e., thiol-based agent): dipentaerythritol hexakis(3-mercaptopropionate) (DPHS), pentaerythritol tetrakis(3-mercaptopropionate) (PTS), 2,2'-(ethylenedioxy)diethanethiol (EDT).

[0073] Bridging agent (i.e., bridging compound or oligomer): dipentaerythritol hexaacrylate (DHL), tetrakis(dimethyl(vinyl)silyl] orthosilicate (ORP), trimethylolpropane ethoxylate triacrylate (TMET), trimethylolpropane triacrylate

(TMPTA), 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, polyethylene glycol dimethacrylate (PEGDMA), vinyl methacrylate (VMA).

5 [0074] Polymerization initiator: 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), 2-hydroxy-2-methylpropiophenone (HMPP).

10 [0075] Lithium Salt: lithium triflate (LiTRF), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI).

[0076] Organic solvent or ionic liquid: propylene carbonate (PC), 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMITFSI). The organic solvent and/or ionic liquid may be retained within the resultant flame retardant polymer electrolyte.

15 [0077] The stoichiometrically weighted mass of reagents are prepared by heated blending of all weighed components in a one-pot system at final step and cured either thermally (thermal initiator systems, 60°C to 80°C (e.g., 70°C) for 1 hour or less) or via UV initiation (e.g., about 8 to 12 mins (e.g., 10 mins) at UV radiation source of more than 30 mW). The blending may be carried out at ambient temperature (e.g., 20°C to 40°C). If blending is performed at higher temperatures, and/or if a thermal initiator is used, one or more of aforesaid components may run the risk of being decomposed, prematurely forming radicals before curing begins.

20 [0078] **Example 2A: Examples of Chemicals (and Reagents) used in some experiments**

[0079] For the purpose demonstration and not to limit the present disclosure, the following chemicals and reagents are experimented on as examples apart from many others. The following chemicals and reagents do not constitute an exhaustive list.

30 [0080] Diethyl Allylphosphonate (DEAP), Diethyl Allyl phosphate (DALP), Diethyl Vinyl Phosphonate (DEV), Tri-Allyl Phosphate (TRAP), Diallyl Carbonate (DAC), 2-Hydroxy-2-methylpropiophenone (HMPP), Lithium Bis(trifluoromethanesulfonyl)imide (LiTFSI), Tri(ethylene glycol) divinyl ether

(TDV), Trimethylolpropane ethoxylate triacrylate Mw=428 (TMET), Pentaerythritol tetrakis(3-mercaptopropionate) (PTS), Dipentaerythritol Hexakis(3-mercaptopropionate) (DPHS), Trimethylolpropane ethoxylate triacrylate (TMPTA), Ethylene Glycol Dimethacrylate (EGD).

5 **[0081] Example 2B: Experiments and characterizations of samples based on chemicals and reagents of non-limiting example 2A**

[0082] The weighted VAP and acrylate-based bridging agent are blended with LiTFSI until full dissolution and homogeneity. The concentration of LiTFSI dissolved in VAP or VAP/VEC mixture is kept in the range of 1 mol dm⁻³ to 1.5 mol dm⁻³. VEC denotes
 10 vinyl ethylene carbonate (which was used in a non-limiting example to prepare a control sample that has an agent with no phosphorus atom in it). The poly-thiol and initiator are then added and blended till a fully uniform mixture is formed. If the resultant mixture is slightly cloudy, stir the mixture at range of 40 to 45°C for 10 minutes till homogeneity. The amount of UV initiator used is 0.015 wt% HMPP. The heated
 15 mixture is cast into a silicone mold, and then subjected to UV radiation curing (~125 mW/cm²) in ambient (e.g., atmospheric pressure and 20°C to 40°C) for 10 mins to form the eventual solidified GPE film. UV curing may ideally be performed in an inert environment. The GPE films are then characterized for their ion conductivities (IC), mechanical storage modulus (M) and electrochemical stability window (ECV). To
 20 determine the impact of number of C=C double bonds per bridging compound on the Li-ion conductivity and mechanical properties of FR GPE films, formulations with same C=C and S-H bonds concentrations with different types of bridging compounds are tested. FIG. 2A lists the formulations used to prepare poly-thiol assisted curing of different VAP and bridging compound-based FR GPE films. The LiTFSI concentration
 25 of these FR GPE films are kept at 1 M with respect to the volume of VAP present in the formulation. FIG. 2B lists the formulations used to prepare poly-thiol assisted curing of TRAP based FR GPE films. The ionic liquid solvent used for preparing the FR GPE is 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI) and it constituted 30 wt% of the total weight of electrolyte film and 40 wt% for the T-series
 30 GPE films, while concentration of LiTFSI is kept at 1 M with respect to volume of EMITFSI. Sample D1 (35) contains 35 wt% of EMITFSI IL solvent within the FR GPE film. To determine the FR efficacy of the GPEs samples, the samples are subjected to

a FR test. A GPE sample with the dimensions of Length x Width x Thickness (mm) = 60 x 18 x 1 is clamped vertically at top end. A lit tea light is then placed into contact with the unclamped end for 3 seconds and immediately removed. The time taken for the lit sample to be completely extinguished divided by sample mass is referred to as the Self-Extinguishing Time (SET). The burn test is conducted on three individual test pieces for each chemical formulation entry and average SET is recorded under SET column in FIG. 3. FIG. 3 lists the respective IC, M, SET and selective ECV measured of FR GPE systems.

[0083] Example 3: Discussion of results from example 2B

10 **[0084]** By comparing samples D1, D2 & D3, these samples possess relatively similar storage moduli (e.g., less than 1 MPa) and ion conductivities. However, their ECV and SET results are vastly different. The SET result of D2 is significantly lower than that of D1 and D3. This difference may be due to D2 being prepared with a FR reagent with lower molecular weight, DEV, as compared to D1 and D3 being prepared with FR reagents with higher molecular weight, DEAP and DALP, respectively. This results in sample D2 possessing a higher weight percentage content of phosphorus, rendering a faster quenching of the propagating flame and a lower measured SET. By comparing samples D1 and E1, it can be recognised that the bridging agent has an impact on properties of the GPE film. Sample E1 possess a lower storage modulus, a longer SET value but also a higher ionic conductivity. This difference could be due to the ionic liquid EMITFSI and the Lithium salt forming coordination with the ethoxy groups within TMET, thus causing the EMITFSI/LiTFSI to have a less plasticizing effect on the polymeric matrix of D1 as compared to E1, thus causing the storage modulus of E1 to be lower than D1. Likewise, this coordination effect between EMITFSI/LiTFSI and the ethoxylation, impedes the “hopping” of the ions within EMITFSI/LiTFSI, thus reducing the ionic conductivity of D1 as compared to E1. Sample D1-2 has a slightly higher DEAP and lower TMET content as compared to D1. It could be observed from the table that D1-2 have a slightly higher ionic conductivity and lower SET, and lower M as compared to D1. This could be attributed to sample D1-2 possessing a lower TMET content, resulting in lower amount of cross-linking within the polymeric matrix, thus allowing more inter-connected EMITFSI channels to be established within the D1-2 GPE, thus rendering the higher ionic conductivity. The higher DEAP content within

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sample D1-2 also renders reduction in SET, which could also be explained by higher concentration of P (i.e., phosphorus) within the polymeric matrix, resulting in higher P· radical quenching of propagating flames. Samples P1 (35) and D1 (35) are prepared within 35 wt% of EMITFSI as compared to the other samples with 30 wt% EMITFSI.

5 It could be concluded from the table (e.g., FIG. 3) that the SET values of both samples increased as compared to the rest of the samples, while the ionic conductivities are also increased. The increase in SET values could be due to increase in EMITFSI content, a combustible liquid by nature, rendering the increased resultant flammability of the samples. The higher ionic conductivity measured in sample P1 (35) as compared to D1
10 (35) could be attributed to PTS possessing 4 cross-linking as compared to 6 in DPHS, causing the cross-linking content to be lower in sample P1 (35) as compared to sample D1 (35). More interconnected EMITFSI percolation channels could be established in sample P1 (35), leading to a higher ionic conductivity. Samples T3 and T4 had very much lower ionic conductivities and higher measured storage moduli as compared to
15 the rest of the samples. This may be due to the FR reagent TRAP, possessing 3 cross-linking sites, causes the resultant polymeric matrix to be more highly cross-linked and less inter-connected percolation channels to be achieved, thus reducing the ionic conductivities and increasing the storage modulus. Generally, an increase in cross-linking leads to increase in mechanical strength and a reduction in ionic conductivity.
20 However, samples T3 and T4 have lower loading of ionic liquid as compared to samples D1 (35) and P1 (35), hence the lower conductivity of samples T3 and T4.

[0085] In addition to the rapid curing process feature, phosphorous-based FR GPEs prepared via the present method possesses some unique advantages over current reported techniques. (1) The high polarity of the liquid state VAP (dipole moment of
25 about 2.9 D, wherein D denotes Debye) serves as an ideal solvent for the dissolution and solvation of lithium salts. Unlike traditional SPE films that require an auxiliary polar solvent to dissolve the lithium salts to achieve a homogeneous dispersion of the salt within the polymeric matrix and the eventual removal of this solvent via thermal evaporation. Such additional processes and reagent are not required in the reaction
30 processes of the present method. High polarity of the VAP also implies that a higher concentration of Lithium salt (e.g., more than 1 M) could be dissolved within the polymeric matrix, resulting in further increment of Li-ion conductivity and flame

retardancy in SPE systems. (2) The high reactivity of the acrylate terminals of the bridging compounds results in homo-polymerization of the bridging molecules before reacting with thiol functionality. This homo-polymerization phenomenon assists in stiffening the polymeric matrix thus allowing lower molar content of bridging agents to be used. Conversely, this can imply that the molar content of VAP within the formulation increased, thus allowing the Li-ion conductivity and FR capability to increase.

[0086] Example 4: Summary

[0087] The present method and flame retardant polymer electrolyte have the following advantages, which include rapid curing as compared to traditional free radical polymerization (e.g., 60 to 80°C for 12 hours), 10 minutes UV cure at 400 W/125 mW/cm² radiation and 1 hour at 70°C for thermal curing process., good ion conductivity (e.g., sample P1(35) of about 2.2×10^{-4} S cm⁻¹), high electrochemical stability window (more than about 5.1-5.4V), and low Self-Extinguishing Time (less than 20 s g⁻¹).

[0088] The present disclosure describes for a synthesis technique to facilitate rapid curing of vinyl/allyl based phosphorous (VAP) compounds, particularly VAP molecule/oligomer with mono C=C double bond site, to form a solid polymeric matrix with FR capability. The technique involves bridging compound/oligomer with two or more C=C double bond sites (e.g., acrylate terminal) as intermediary between VAP-Poly-Thiol oligomers. Homo-polymerization of acrylate terminals of the bridging compound or oligomer facilitates a higher loading of VAP while still maintaining film mechanical stiffness, allowing better FR capability to be achieved.

[0089] Despite the solvent being bounded to the polymeric matrix, the mechanical strength is still lower than 100 MPa, which may be desirable for applications that require such mechanical strength. In any case, this can be overcome by reinforcing it with carbon fibre matrix. Said differently, carbon fiber fabric can be used as a scaffolding agent to increase the strength of the electrolyte gel. The incorporation can be achieved via infusion through vacuum bagging technique.

[0090] The present technology can be applied to machinery, vehicles, or devices, that require electrical energy storage such as, electric vehicles, personal mobility devices, mobile phones, maritime, rail-systems, FR coating, and battery encapsulation.

[0091] While the present disclosure has been particularly shown and described with reference to specific embodiments, it should be understood by those skilled in the art that various changes in form and detail may be made therein without departing from the spirit and scope of the present disclosure as defined by the appended claims. The

5 scope of the present disclosure is thus indicated by the appended claims and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced.

CLAIMS

1. A method for forming a flame retardant polymer electrolyte, the method comprising:
 - 5 forming a mixture comprising a phosphorus compound having a terminal vinyl or allyl moiety, a thiol-based agent having two or more terminal thiol functional groups, and a polymerization initiator; and
 - subjecting the mixture to a stimulus to have the flame retardant polymer electrolyte formed in one hour or less.
- 10 2. The method of claim 1, further comprising:
 - mixing a lithium salt and the mixture prior to subjecting the mixture to the stimulus; or
 - mixing a lithium salt solution and the mixture after subjecting the mixture to the
 - 15 stimulus, wherein the lithium salt solution comprises a lithium salt.
3. The method of claim 2, wherein mixing the lithium salt solution and the mixture comprises mixing the lithium salt with an ionic liquid or an organic solvent to form the lithium salt solution.
- 20 4. The method of claim 3, wherein the ionic liquid or the organic solvent comprises 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide or propylene carbonate.
- 25 5. The method of any one of claims 2 to 4, wherein the lithium salt comprises lithium triflate or lithium dis(trifluoromethanesulfonyl)imide.
6. The method of any one of claims 1 to 5, wherein forming the mixture comprises mixing the phosphorus compound, the thiol-based agent, and the polymerization
- 30 initiator to form the mixture.

7. The method of any one of claims 2 to 5, wherein forming the mixture comprises adding the poly-thiol agent and the polymerization initiator to the phosphorus compound in the presence of the lithium salt.
- 5 8. The method of claim 7, further comprising:
blending the mixture at a temperature of 40°C to 45°C, after adding the poly-thiol agent and the polymerization initiator, until the mixture becomes homogeneous.
9. The method of any one of claims 1 to 8, wherein the mixture further comprises
10 a bridging agent.
10. The method of claim 9, wherein the bridging agent comprises dipentaerythritol hexaacrylate, tetrakis[dimethyl(vinyl)silyl] orthosilicate, trimethylolpropane ethoxylate triacrylate, trimethylolpropane triacrylate, 1,2,4-trivinylcyclohexane,
15 tri(ethylene glycol) divinyl ether, trimethylolpropane diallyl ether, diallyl carbonate, pentaerythritol allyl ether, diallyl maleate, 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane, polyethylene glycol dimethacrylate, or vinyl methacrylate.
- 20 11. The method of any one of claims 1 to 10, wherein subjecting the mixture to the stimulus comprises:
heating the mixture at a temperature of 60°C to 80°C to have the mixture thermally cured; or
exposing the mixture to ultraviolet light for 15 minutes or less to have the
25 mixture photo-cured.
12. The method of any one of claims 1 to 11, wherein the phosphorus compound comprises diethyl allylphosphonate, diethyl allyl phosphate, diethyl vinyl phosphonate, tri-allyl phosphate, dimethyl vinyl phosphonate, or tetraisopropyl
30 vinylidenediphosphonate.

13. The method of any one of claims 1 to 12, wherein the thiol-based agent comprises dipentaerythritol hexakis(3-mercaptopropionate), pentaerythritol tetrakis(3-mercaptopropionate), or 2,2'-(ethylenedioxy)diethanethiol.
- 5 14. The method of any one of claims 1 to 13, wherein the polymerization initiator comprises methyl benzoylformate, 2,2-dimethoxy-2-phenylacetophenone, 2,4,6-tris(dimethylaminomethyl)phenol, azobisisobutyronitrile, 4-thiophenyl phenyl diphenyl sulfonium hexafluoroantimonate, diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide, or 2-hydroxy-2-methylpropiophenone.
- 10 15. A lithium-based flame retardant polymer electrolyte comprising:
a polymer network comprising phosphate or phosphonate groups crosslinked with a thiol-based agent via thioether linkages; and
a lithium salt,
15 wherein the phosphate or phosphonate groups, and the lithium salt, are present in an amount of at least 30 wt% of the lithium-based flame retardant polymer electrolyte.
16. The lithium-based flame retardant polymer electrolyte of claim 15, wherein the
20 polymer network is derived from a phosphorus compound having a terminal vinyl or allyl moiety, wherein the phosphorus compound comprises diethyl allylphosphonate, diethyl allyl phosphate, diethyl vinyl phosphonate, tri-allyl phosphate, dimethyl vinyl phosphonate, or tetraisopropyl vinylidenediphosphonate.
- 25 17. The lithium-based flame retardant polymer electrolyte of claim 15 or 16, wherein the thiol-based agent comprises dipentaerythritol hexakis(3-mercaptopropionate), pentaerythritol tetrakis(3-mercaptopropionate), or 2,2'-(ethylenedioxy)diethanethiol.
- 30 18. The lithium-based flame retardant polymer electrolyte of any one of claims 15 to 17, further comprising a bridging moiety chemically coupled to the thiol-based agent, wherein the bridging moiety is derived from a bridging agent comprising

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dipentaerythritol hexaacrylate, tetrakis[dimethyl(vinyl)silyl] orthosilicate, trimethylolpropane ethoxylate triacrylate, trimethylolpropane triacrylate, 1,2,4-trivinylcyclohexane, tri(ethylene glycol) divinyl ether, trimethylolpropane diallyl ether, diallyl carbonate, pentaerythritol allyl ether, diallyl maleate, 2,4,6,8-tetramethyl-
5 2,4,6,8-tetravinylcyclotetrasiloxane, polyethylene glycol dimethacrylate, or vinyl methacrylate.

19. The lithium-based flame retardant polymer electrolyte of any one of claims 15 to 18, wherein the lithium salt comprises lithium triflate or lithium
10 dis(trifluoromethanesulfonyl)imide.

20. The lithium-based flame retardant polymer electrolyte of any one of claims 15 to 19, wherein the lithium-based flame retardant polymer electrolyte is a gel polymer electrolyte or a solid polymer electrolyte.

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