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(54) Title: CURABLE LIQUID FORMULATION AND USE THEREOF

(57) Abstract: The present invention relates to a curable liquid formulation comprising at least one lithium salt, at least one solvent for said lithium salt and a crosslinkable (per)fluoropolyether useful for the preparation of a gel electrolyte for electrochemical devices, such as secondary batteries and capacitors/super-capacitors.



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Description**Title**

[0001] **Curable liquid formulation and use thereof**

Cross-reference to related applications

[0002] This application claims priority to European application No. 16159100.3, filed on 8 March 2016, the whole content of these applications being incorporated herein by reference for all purposes.

Technical Field

[0003] The present invention relates to a curable liquid formulation useful for the preparation of a gel electrolyte for electrochemical devices, such as secondary batteries and capacitors/supercapacitors.

Background Art

[0004] In principle, a metal ion secondary battery is formed by assembling a metal (ion) or composite carbon anode, a ion conducting membrane and a composite cathode; the ion conducting membrane, often referred to as separator, plays a crucial role in the cell, as it must provide ion conductivity while ensuring effective separation between the opposite electrodes.

[0005] Basically, two types of separators can be used: either porous ones, wherein a solution of an electrolyte in a suitable solvent ("liquid electrolytes") fills the porosity of the separator, or non-porous ones, which are generally either pure solid polymer electrolyte (i.e. electrolyte dissolved in a high molecular weight polyether host, like PEO and PPO, which acts as solid solvent) or gelled polymer electrolyte system, which incorporates into a polymer matrix a liquid plasticizer or solvent capable of forming a stable gel within the polymer host matrix and an electrolyte.

[0006] Liquid electrolytes currently used are known to ensure good electrochemical performances and interfacial contacts with the electrodes. However, their potential leakage is of concern for both electrochemical performances and safety of the batteries.

[0007] In recent years, gelled electrolytes have been considered of interest for next-generation lithium secondary batteries and their research is worldwide promoted.

[0008] For example, US 20060222956 (NITTO DENKO CORPORATION)

discloses a gel electrolyte including a gel composition containing an electrolyte salt, a solvent for the electrolyte salt and a polymer matrix comprising a crosslinked polymer prepared by polymerizing bifunctional (meth)acrylate hydrogenated polymers.

- [0009] **NAIR, J.R., et al.** UV-induced radical photo-polymerization: a smart tool for preparing polymer electrolyte membranes for energy storage devices. *Membranes*. 2012, vol.2, p.687-704. discloses the preparation and the characterization of quasi-solid polymer electrolyte membranes based on methacrylic monomers and oligomers, with the addition of organic plasticizers and lithium salt. Although the membranes showed remarkable electrochemical performances, their mechanical resistance was not satisfying and hence, modified cellulose hand sheets were proposed as a reinforcement, to improve the mechanical behaviour of the membranes.
- [0010] Fluoropolymers, and in particular, vinylidene fluoride polymers, have been used with success in secondary batteries as raw materials for gelled polymer electrolytes, because of their high anodic stability and their high dielectric constant, which is of assistance in the ionic dissociation of used electrolytes.
- [0011] (Per)fluoropolyether polymers (PFPEs) have been disclosed in the art as additives for electrolytic compositions, for example in **US 20080127475** (AUSIMONT S.P.A.) .
- [0012] More recently, **WO 2014/062898** (THE UNIVERSITY OF NORTH CAROLINA AT CHAPEL HILL) disclosed both liquid and solid electrolyte composition for batteries. In some embodiments, the composition is a solid electrolyte composition comprising (a) a solid polymer comprising a crosslinked or the crosslinking product of a crosslinkable perfluoropolyether (PFPE) and a crosslinkable polyethylene oxide (PEO) and (b) an alkali metal ion salt dissolved in said polymer. The composition is made by combining perfluoropolyether and the polyethylene oxide with alkali metal salt and optionally a photoinitiator. The PFPE and the PEO can be crosslinked to form a solid polymer having the alkali metal dissolved therein. In other words, a copolymer of PFPE and PEO is obtained.

- [0013] JP 2007-182517 (SHINETSU CHEMICAL CO.) discloses a fluoropolyether rubber composition exhibiting semiconductivity when cured, the composition containing:
- (A) 100 pts.mass of a straight chain polyfluoro compound having two or more alkenyl groups in one molecule and a perfluoropolyether structure in the main chain,
 - (B) a fluorine-containing organo hydrogen siloxane having two or more hydrogen atoms directly bound with silicon atoms in one molecule as an Si-H group, in an amount of 0.5-3.0 moles to 1 mole of component (A),
 - (C) 0.1-500 ppm of a platinum group compound in terms of a platinum metal atom and
 - (D) 0.01-10 pts.mass of an ion conductivity imparting compound.
- [0014] However, gelled polymer electrolytes might not incorporate and retain the liquid electrolyte composition in an effective manner during both manufacturing of the battery and operation of the same and/or might not possess suitable mechanical properties as required for effective separation of the electrodes.

Summary of invention

- [0015] The Applicant faced the problem to provide a composition that can be easily processed into a uniform gel electrolyte, which can be operated in electrochemical devices, including notably secondary batteries or capacitors, in a wide temperature range.
- [0016] In addition, the Applicant faced the problem to provide a gel electrolyte that can be processed into a thin film or a membrane, which is flexible while showing good mechanical strength per se and which is endowed with high durability and low flammability.
- [0017] Thus, in a first aspect, the present invention relates to a curable liquid composition [composition C] comprising:
- a liquid electrolyte composition [composition (Ce)] comprising (i) at least one lithium salt and (ii) at least one solvent for said lithium salt;
 - a crosslinkable (per)fluoropolyether polymer [polymer (P)] comprising at least one (per)fluoropolyoxyalkylene chain [chain (R_{pf})] having two chain ends, wherein at least one chain end comprises at least one unsaturated

moiety [moiety U]; and

- optionally, one or more further ingredients.

[0018] Then, in a second aspect, the present invention relates to a gel electrolyte comprising:

(A) composition (Ce) as defined above and

(B) a polymeric matrix comprising a crosslinked polymer obtained by curing at least one polymer (P) as defined above.

[0019] Advantageously, in the gel electrolyte according to the present invention, the liquid electrolyte composition (Ce) is trapped within the polymeric matrix (or in other words within the network) obtained when curing said at least one polymer (P). Despite the large amount of the liquid electrolyte composition (Ce) contained in the polymeric matrix, the gel electrolyte according to the present invention is self-standing, i.e., when individualized or comprised in an electrochemical device, it possesses suitable mechanical properties for being handled and for withstanding mechanical stresses typical of the final intended use, for example in lithium batteries, capacitors or electro-chromic windows.

[0020] In a third aspect, the present invention relates to a process for the manufacturing of the gel electrolyte as defined above, the process comprising the steps of

(a) providing the composition (C) as defined above and

(b) curing said composition (C).

[0021] In a fourth aspect, the present invention relates to an assembly comprising

- at least one anode,

- at least one cathode and

- a gel electrolyte as defined above that is interposed between said anode and said cathode.

[0022] In a fifth aspect, the present invention relates to a process for the manufacture of the assembly as defined above, the process comprising the steps of:

(I-a) providing composition C as defined above;

(I-b) casting a film from said composition C onto a suitable support;

(I-c) curing said composition C thus obtaining a cured gel electrolyte onto

said support;

(I-d) optionally separating the cured gel electrolyte and the support; and

(I-e) contacting said cured gel electrolyte with an anode and/or a cathode.

[0023] Advantageously, said assembly is for use in an electrochemical device.

[0024] In a sixth aspect, the present invention relates to an electrochemical device comprising the assembly as defined above.

Description of embodiments

[0025] For the purpose of the present description and of the following claims:

- the use of parentheses around symbols or numbers identifying the formulae, for example in expressions like “polymer (P)”, etc., has the mere purpose of better distinguishing the symbol or number from the rest of the text and, hence, said parenthesis can also be omitted;
- the acronym “PFPE” stands for “(per)fluoropolyether” and, when used as substantive, is intended to mean either the singular or the plural form, depending on the context;
- the term “(per)fluoropolyether” is intended to indicate fully or partially fluorinated polyether;
- the adjective “continuous” when referred to a membrane, a film or a sheet is intended to indicate that the membrane, the sheet or the film is not interrupted and does not contain any cracks;
- the adjective “uniform” when referred to a membrane, a film or a sheet is intended to indicate that the membrane, the sheet or the film has the same thickness in all its length, as thinner areas could compromise mechanical strength and safety of the membrane, film or sheet when used in an electrochemical device;
- the term “separator” is intended to indicate a polymeric material, which electrically and physically separates electrodes of opposite polarities in an electrochemical cell and is permeable to ions flowing between them.

[0026] Preferably, the composition C comprises said composition (Ce) in an amount of at most 99 wt.%, more preferably 95 wt.%, even more preferably 90 wt.%, still more preferably 85 wt.% based on the total weight of said composition C.

[0027] Preferably, the composition C comprises an amount of said composition

(Ce) of at least 50 wt.%, more preferably 55 wt.%, even more preferably 60 wt.% and still more preferably 65 wt.% based on the total weight of said composition C.

- [0028] Preferably, the composition C comprises an amount of said composition (Ce) of from 50 to 99 wt.%, more preferably from 55 to 95 wt.%, even more preferably from 60 to 90 wt.% and still more preferably from 65 to 80 wt.% based on the total weight of said composition (Ce).
- [0029] Preferably, said composition (Ce) contains the at least one lithium salt in a concentration of at least 0.01 M, more preferably 0.05 M. Preferably, said composition (Ce) contains the at least one lithium salt in a concentration of at most 2 M, more preferably 1.5 M. In a preferred aspect, said composition (Ce) contains the at least one lithium salt in a concentration of from 0.5 to 1.5 M.
- [0030] Preferably, said at least one lithium salt is selected in the group comprising LiPF_6 , LiBF_4 , LiClO_4 , lithium bis(oxalato)borate ("LiBOB"), $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$, $\text{M}[\text{N}(\text{CF}_3\text{SO}_2)(\text{R}_\text{F}\text{SO}_2)]_n$ with R_F being C_2F_5 , C_4F_9 , CF_3 , OCF_2CF_2 , LiAsF_6 , $\text{LiC}(\text{CF}_3\text{SO}_2)_3$ and combinations thereof.
- [0031] Preferably, said at least one solvent is a non-aqueous solvent and more preferably it is selected in the group comprising cyclic ester, such as ethylene carbonate (EC), dimethyl carbonate (DMC), propylene carbonate, butylene carbonate, γ -butyrolactone; cyclic or chain esters such as tetrahydrofuran and dimethoxyethane; and chain esters such as dimethyl carbonate, diethyl carbonate and ethylmethyl carbonate; and mixtures thereof. More preferably, said solvent is selected from cyclic ester, such as ethylene carbonate (EC), dimethyl carbonate (DMC), propylene carbonate, butylene carbonate. Good results have been obtained with mixtures of EC and DMC.
- [0032] Preferably, the composition C comprises an amount of polymer P of at least 1wt.%, more preferably 5 wt.%, even more preferably 10 wt.%, still more preferably 15 wt.% based on the total weight of said composition C.
- [0033] Preferably, the composition C comprises an amount of polymer P of at most 50 wt.%, more preferably 45 wt.%, even more preferably 40 wt.% and still more preferably 35 wt.% based on the total weight of said

composition C.

[0034] Preferably, the composition C comprises an amount of polymer P of from 1 to 50%, more preferably from 5 to 45%, even more preferably from 10 to 40% and still more preferably from 20 to 35 wt.% by weight based on the total weight of composition C.

[0035] Preferably, said chain (R_{pf}) is a chain of formula $-O-D-(CFX^{\#})_{z1}-O(R_f)(CFX^*)_{z2}-D^*-O-$

wherein

$z1$ and $z2$, equal or different from each other, are equal to or higher than 1;

$X^{\#}$ and X^* , equal or different from each other, are $-F$ or $-CF_3$,

provided that when $z1$ and/or $z2$ are higher than 1, $X^{\#}$ and X^* are $-F$;

D and D^* , equal or different from each other, are an alkylene chain comprising from 1 to 6 and even more preferably from 1 to 3 carbon atoms, said alkyl chain being optionally substituted with at least one perfluoroalkyl group comprising from 1 to 3 carbon atoms;

(R_f) comprises, preferably consists of, repeating units R° , said repeating units being independently selected from the group consisting of:

(i) $-CFXO-$, wherein X is F or CF_3 ;

(ii) $-CFXCFXO-$, wherein X , equal or different at each occurrence, is F or CF_3 , with the proviso that at least one of X is $-F$;

(iii) $-CF_2CF_2CW_2O-$, wherein each of W , equal or different from each other, are F , Cl , H ;

(iv) $-CF_2CF_2CF_2CF_2O-$;

(v) $-(CF_2)_j-CFZ-O-$ wherein j is an integer from 0 to 3 and Z is a group of general formula $-O-R_{(f-a)}-T$, wherein $R_{(f-a)}$ is a fluoropolyoxyalkene chain comprising a number of repeating units from 0 to 10, said recurring units being chosen among the following : $-CFXO-$, $-CF_2CFXO-$, $-CF_2CF_2CF_2O-$, $-CF_2CF_2CF_2CF_2O-$, with each of X being independently F or CF_3 and T being a C_1 - C_3 perfluoroalkyl group.

[0036] Preferably, $z1$ and $z2$, equal or different from each other, are from 1 to 10, more preferably from 1 to 6 and even more preferably from 1 to 3.

[0037] More preferably, D and D^* , equal or different from each other, are a chain of formula $-CH_2-$, $-CH_2CH_2-$ or $-CH(CF_3)-$.

[0038] Preferably, chain (R_f) complies with the following formula:

(R_f -I)

$-[(CFX^1O)_{g1}(CFX^2CFX^3O)_{g2}(CF_2CF_2CF_2O)_{g3}(CF_2CF_2CF_2CF_2O)_{g4}]$ -

wherein

- X^1 is independently selected from -F and -CF₃,
- X^2 , X^3 , equal or different from each other and at each occurrence, are independently -F, -CF₃, with the proviso that at least one of X is -F;
- g_1 , g_2 , g_3 , and g_4 , equal or different from each other, are independently integers ≥ 0 , such that $g_1+g_2+g_3+g_4$ is in the range from 2 to 300, preferably from 2 to 100; should at least two of g_1 , g_2 , g_3 and g_4 be different from zero, the different recurring units are generally statistically distributed along the chain.

[0039] More preferably, chain (R_f) is selected from chains of formula:

(R_f -IIA) $-[(CF_2CF_2O)_{a1}(CF_2O)_{a2}]$ -

wherein:

- a_1 and a_2 are independently integers ≥ 0 such that the number average molecular weight is between 400 and 10,000, preferably between 400 and 5,000; both a_1 and a_2 are preferably different from zero, with the ratio a_1/a_2 being preferably comprised between 0.1 and 10;

(R_f -IIB) $-[(CF_2CF_2O)_{b1}(CF_2O)_{b2}(CF(CF_3)O)_{b3}(CF_2CF(CF_3)O)_{b4}]$ -

wherein:

- b_1 , b_2 , b_3 , b_4 , are independently integers ≥ 0 such that the number average molecular weight is between 400 and 10,000, preferably between 400 and 5,000; preferably b_1 is 0, b_2 , b_3 , b_4 are > 0 , with the ratio $b_4/(b_2+b_3)$ being ≥ 1 ;

(R_f -IIC) $-[(CF_2CF_2O)_{c1}(CF_2O)_{c2}(CF_2(CF_2)_{cw}CF_2O)_{c3}]$ -

wherein:

$cw = 1$ or 2 ;

- c_1 , c_2 , and c_3 are independently integers ≥ 0 chosen so that the number average molecular weight is between 400 and 10,000, preferably between 400 and 5,000; preferably c_1 , c_2 and c_3 are all > 0 , with the ratio $c_3/(c_1+c_2)$ being generally lower than 0.2;

(R_f -IID) $-[(CF_2CF(CF_3)O)_d]$ -

wherein:

d is an integer > 0 such that the number average molecular weight is between 400 and 10,000, preferably between 400 and 5,000;

(R_f-IIE) -[(CF₂CF₂C(Hal*)₂O)_{e1}-(CF₂CF₂CH₂O)_{e2}-(CF₂CF₂CH(Hal*)O)_{e3}]-

wherein:

- Hal*, equal or different at each occurrence, is a halogen selected from fluorine and chlorine atoms, preferably a fluorine atom;

- e1, e2, and e3, equal to or different from each other, are independently integers ≥ 0 such that the (e1+e2+e3) sum is comprised between 2 and 300.

[0040] Still more preferably, chain (R_f) complies with formula (R_f-III) here below:

(R_f-III) -[(CF₂CF₂O)_{a1}(CF₂O)_{a2}]-

wherein:

- a1, and a2 are integers > 0 such that the number average molecular weight is between 400 and 10,000, preferably between 400 and 5,000, with the ratio a1/a2 being generally comprised between 0.1 and 10, more preferably between 0.2 and 5.

[0041] Said moiety U is preferably selected in the group consisting of:

(U-I) -C(=O)-CR_H=CH₂

(U-II) -C(=O)-NH-CO-CR_H=CH₂

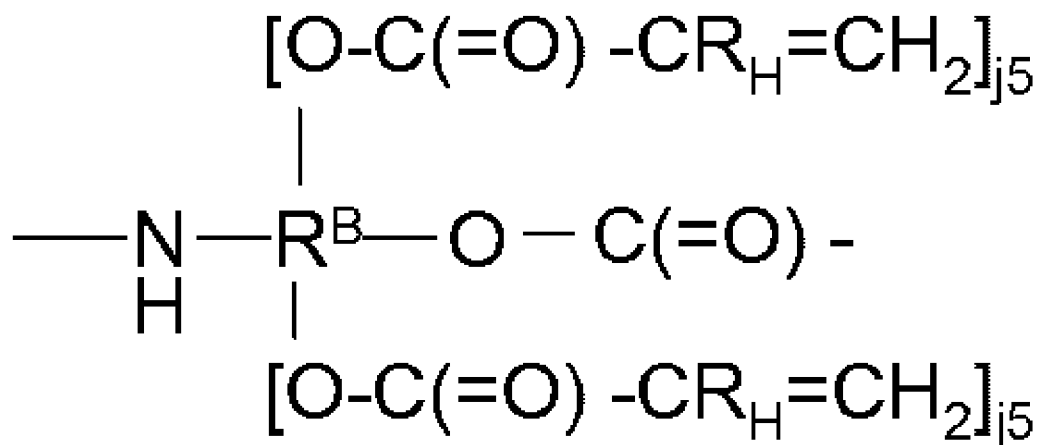
(U-III) -C(=O)-R^A-CR_H=CH₂

wherein

R_H is H or a C₁-C₆ alkyl group;

R^A is selected from the group consisting of (R^A-I) and (R^A-II):

(R^A-I)

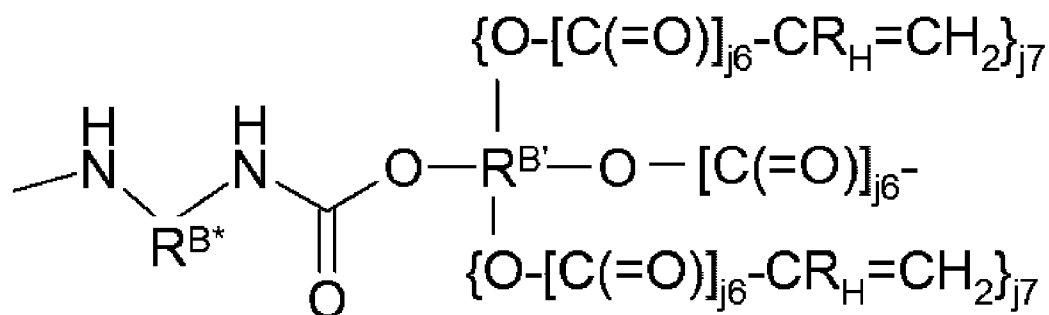


wherein

each of $j5$ is independently 0 or 1 and

R^B is a divalent, trivalent or tetravalent group selected from the group consisting of $\text{C}_1\text{-C}_{10}$ aliphatic group; $\text{C}_3\text{-C}_{12}$ cycloaliphatic group; $\text{C}_5\text{-C}_{14}$ aromatic or alkylaromatic group, optionally comprising at least one heteroatom selected from N, O and S;

($\text{R}^\text{A-II}$)



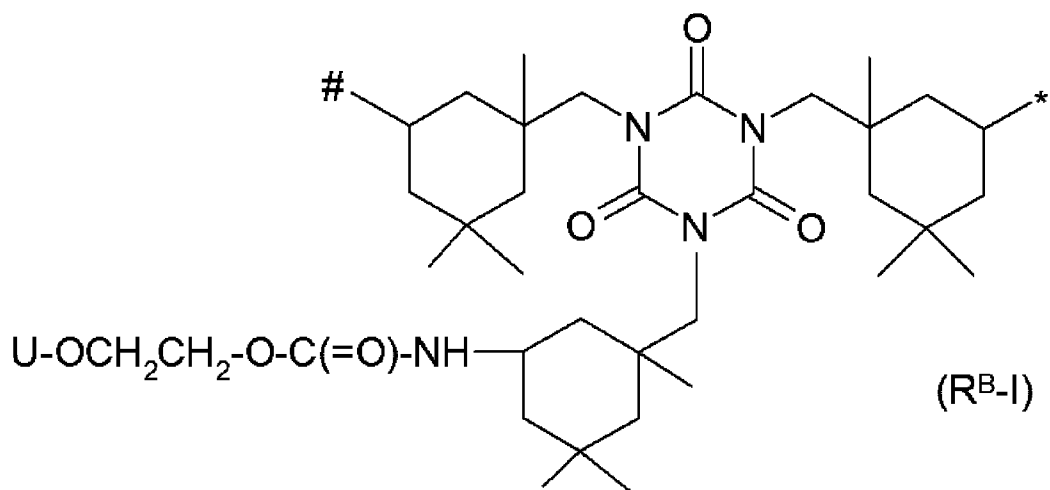
wherein

$j6$ is 0 or 1;

each of $j7$ is independently 0 or 1;

$\text{R}^\text{B'}$ is a divalent, trivalent or tetravalent group selected from the group consisting of $\text{C}_1\text{-C}_{10}$ aliphatic group; $\text{C}_3\text{-C}_{12}$ cycloaliphatic group; $\text{C}_5\text{-C}_{14}$ aromatic or alkylaromatic group, optionally comprising at least one heteroatom selected from N, O and S; and

$\text{R}^\text{B*}$ has the same meanings defined above for $\text{R}^\text{B'}$ or it is a group of formula ($\text{R}^\text{B-I}$):



wherein

U is selected from the groups (U-I) to (U-III) as defined above and

* and # indicate the bonding site to the nitrogen atoms in formula (R^A-II) above.

[0042] Preferably, said at least one moiety U is bonded to said chain (R_{pf}) via a sigma bond or via a (poly)oxyalkylene chain [chain (R_a)] comprising from 1 to 50 fluorine-free oxyalkylene units, said units being the same or different each other and being selected from -CH₂CH(J)O-, wherein J is independently selected from hydrogen atom, straight or branched alkyl or aryl, preferably hydrogen atom, methyl, ethyl or phenyl.

[0043] Preferably, chain (R_a) comprises from 2 to 50, more preferably from 3 to 40, even more preferably from 4 to 7 fluorine-free oxyalkylene units as defined above.

[0044] More preferably, said chain (R_a) is selected from:

(Ra-I) -(CH₂CH₂O)_{j1}-

(Ra-II) -[CH₂CH(CH₃)O]_{j2}-

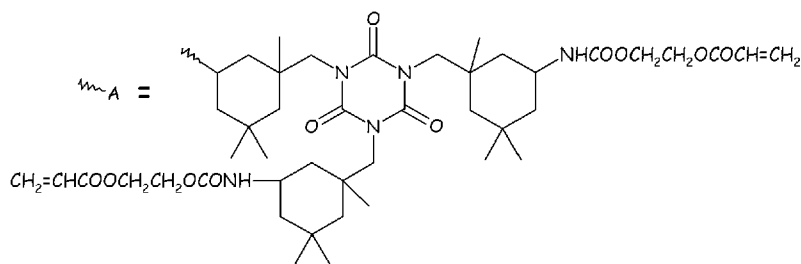
(Ra-III) -[(CH₂CH₂O)_{j3}-(CH₂CH(CH₃)O)_{j4}]_{j(x)}-

wherein

j₁ and j₂, each independently, are an integer from 1 to 50, preferably from 2 to 50, more preferably from 3 to 40, even more preferably from 4 to 15, and still more preferably from 4 to 7;

j₃, j₄ and j(x) are integers higher than 1, such that the sum of j₃ and j₄ is from 2 to 50, more preferably from 3 to 40, even more preferably from 4 to 15, and still more preferably from 4 to 7.

- [0045] When present, the recurring units having j^*1 and j^*2 as indexes can be either randomly distributed or they can be arranged to form blocks.
- [0046] Advantageously, said polymer P comprises at least one chain [chain R_{pf}] and at least two unsaturated moieties [moieties U] as defined above, more preferably from 2 to 6 moieties U, and even more preferably from 2 to 4 moieties U.
- [0047] More preferably, said at least two moieties U are bonded to opposite sides of said chain R_{pf} .
- [0048] Preferred polymers P according to the present invention comprise:
- one chain (R_{pf}) and
 - from 2 to 4 moieties U complying with formulae (U-I), (U-II) or (U-III) as defined above,
- wherein said moieties U are bonded to said chain (R_{pf}) via a sigma bond or a chain (R_a) of formula $-(CH_2CH_2O)_{j1}-$ wherein $j1$ is an integer from 4 to 7.
- [0049] In a preferred aspect, said moieties U are bonded to said chain (R_{pf}) via a sigma bond.
- [0050] Most preferred polymers (P) are selected from the group consisting of:
- (P-i)
- $$A-OCH_2CF_2(CF_2CF_2O)_{a1}(CF_2O)_{a2}CF_2CH_2O-A$$
- wherein
- $a1$ and $a2$ are as defined above and
- each A is a group of formula



- [0051] Polymer (P-i) above is commercially available from Solvay Specialty Polymers Italy S.p.A. as Fluorolink^(R) AD1700 PFPE.
- [0052] Further suitable ingredients can be added to the composition (C) depending on the nature of both the electrolyte composition (Ce) and the

polymer (P) used. The amounts of said further ingredients can be adjusted on a case by case basis by the person skilled in the art of electrochemical devices.

- [0053] Suitable further ingredients include for example photoinitiators and inorganic fillers.
- [0054] When present, photoinitiators are preferably used in an amount up to 2 wt.%, more preferably from 0.01 to 1 wt.% based on the weight of the polymer (P).
- [0055] Preferably, said photoinitiator is selected in the group comprising liquid alpha hydroxy ketones, blends of acyl phosphine oxide/alpha hydroxy ketones, benzophenones, phenylglyoxylates. Alpha hydroxy ketones are particularly preferred.
- [0056] When present, inorganic fillers are preferably used in an amount up to 5 wt.%, more preferably from 0.01 to 3 wt.% and even more preferably from 0.05 to 2 wt.% based on the total weight of said composition (C).
- [0057] Preferably, inorganic fillers are in the form of particles having an average particle size of 0.001 to 1000 μm .
- [0058] Suitable inorganic fillers are selected for example in the group comprising inorganic oxides, including mixed oxides, metal sulphonates, metal carbonates, metal sulphides and the like.
- [0059] Preferably, said composition C is prepared by mixing said liquid electrolyte composition (Ce) and said polymer P.
- [0060] Typically, the liquid electrolyte composition (Ce) is prepared by dissolving the lithium salt into at least one solvent as defined.
- [0061] Polymers P comprising one or more chain(s) (R_a) can be advantageously prepared starting from (poly)alkoxylated (per)fluoropolyether polymers [polymer P^*],
which comprise at least one (per)fluoropolyoxyalkylene chain [chain (R_{pf})]
having two chain ends [end (R_e)],
wherein at least one end (R_e) comprises a hydroxy-terminated
(poly)oxyalkylene chain (R_{a^*}) comprising from 1 to 50 fluorine-free
oxyalkylene units, said units being the same or different each other and
being selected from $-\text{CH}_2\text{CH}(\text{J})\text{O}-$ wherein J is independently selected

from hydrogen atom, straight or branched alkyl or aryl, preferably hydrogen atom, methyl, ethyl or phenyl; and the other end (R_e) bears a hydroxy-terminated (poly)oxyalkylene chain (R_{a^*}) as defined above or is a neutral group selected from $-CF_3$, $-C_2F_5$, $-C_3F_7$, $-CF_2Cl$, $-CF_2CF_2Cl$ and $-C_3F_6Cl$.

- [0062] When only one of said ends (R_e) comprises a hydroxy-terminated (poly)oxyalkylene chain (R_{a^*}) and the other end (R_e) bears a neutral group as defined above, the polymer is also referred to as "monofunctional polymer P^* ".
- [0063] When both said ends (R_e) comprises a hydroxy-terminated (poly)oxyalkylene chain (R_{a^*}), the polymer is also referred to as "bifunctional polymer P^* ". Preferably, the functionality of the bifunctional polymer P^* , i.e. the number of $-OH$ groups, is at least equal to 1.80, more preferably at least equal to 1.85 and still more preferably at least equal to 1.94. The functionality (F) can be calculated for example as disclosed in EP 1810987 A (SOLVAY SOLEXIS S.P.A.) .
- [0064] Said chain (R_{pf}) is as defined above. In a preferred embodiment, said chain (R_{pf}) comprises chain (R_f) complying with formula (R_f -III) as defined above.
- [0065] Preferably, said ends (R_e) comply with the following general formulae (R_e -I) to (R_e -III):
- $-(CH_2CH_2O)_{j1}-H$ (R_e -I)
 - $-(CH_2CH(CH_3)O)_{j2}-H$ (R_e -II)
 - $-[(CH_2CH_2O)_{j3}(CH_2CH(CH_3)O)_{j4}]_{j(x)}-H$ (R_e -III)
- wherein
- $j1$ and $j2$, each independently, are an integer from 1 to 50, preferably from 2 to 50, more preferably from 3 to 40, even more preferably from 4 to 15, and still more preferably from 4 to 7;
- $j3$, $j4$ and $j(x)$ are integers higher than 1, such that the sum of $j3$ and $j4$ is from 2 to 50, more preferably from 3 to 40, even more preferably from 4 to 15, and still more preferably from 4 to 7.
- [0066] More preferably, both said chain ends (R_e) comply with formulae (R_e -I) to (R_e -III) as defined above. Even more preferably, both ends (R_e) comply

with formulae (R_e -I) as defined above.

- [0067] Polymers P^* are commercially available from Solvay Specialty Polymers (Italy) and can be obtained according to the method disclosed in **WO 2014/090649** (SOLVAY SPECIALTY POLYMERS S.P.A.) .
- [0068] Polymers (P) comprising moiety(ies) U of formula (U-I), (U-II) and (U-III) wherein R^A is selected from the groups of formula (R^A -I) or (R^A -II) wherein R^B is different from the group of formula (R^B -I), can be advantageously prepared by a process comprising:
- (a*) reacting at least one polymer P^* as defined above with at least one compound comprising at least one α,β -unsaturated carbonyl group [compound (α,β)] .
- [0069] Suitable examples of said compounds (α,β) are those having the following general formulae:
- $X-C(O)-CR_H=CH_2$
 $X-C(O)-NH-C(O)-CR_H=CH_2$ and
 $X-C(O)-R^A-CR_H=CH_2$
- wherein
- X is halogen atom, preferably Cl,
- R_H has the same meaning defined above, more preferably it is hydrogen or methyl,
- R^A has the same meaning defined above, except that in formula (R^A -II) R^B is different from group (R^B -I), more preferably R^B is a divalent or trivalent group selected from C_1 - C_6 alkyl chain, C_5 - C_7 cycloaliphatic group, C_6 aromatic group, optionally comprising at least one heteroatom selected from N, O and S.
- [0070] Preferred compounds (α,β) are acryloyl chloride, methacryloyl chloride and the like.
- [0071] Preferably, step (a*) is performed in the presence of a suitable organic solvent, such as for example hydrofluoroethers, hexafluoroxylene, and chloro-hydrocarbons.
- [0072] Preferably, step (a*) is performed in the presence of a primary or secondary amine compound, such as for example di-isopropylamine, triethylamine and pyridine.

- [0073] Preferably, step (a*) is performed at a temperature of from 5 to 40°C, more preferably from 15 to 30°C.
- [0074] Polymers (P) comprising moiety(ies) U of formula (U-III) wherein R^A is the group of formula (R^A-II) wherein R^B is the group of formula (R^B-I) can be advantageously prepared by a process comprising:
- (a**) reacting at least one diisocyanate compound with a compound [compound CU*] bearing at least one unsaturated moiety of formula (U-III) wherein R^A is the group of formula (R^A-II) as defined above and R^B is the group of formula (R^B-I) or at least one unsaturated moiety of formula (U-V); and
- (b**) reacting the intermediate obtained in step (a) with at least one (per)fluoropolyether polymer P* as defined above.
- [0075] Suitable diisocyanate compounds include for example aliphatic and aromatic isocyanate, such as isophoronediiisocyanate (IPDI), hexamethylene diisocyanate (HDI), isomers of methylene-bis(cyclohexyl isocyanate) [also referred to as hydrogenated MDI] and mixtures thereof, isomers of methylene diphenyl diisocyanate (MDI) such as 2,2'-MDI, 2,4'-MDI and 4,4'-MDI and mixtures thereof, isomers of toluene diisocyanate (TDI) such as 2,4-TDI and 2,6-TDI, and mixtures thereof. Isophoronediiisocyanate is particularly preferred.
- [0076] Preferably, said compound CU* is selected from hydroxy-[C₁-C₆ alkyl]-acrylate derivatives, notably hydroxyethylacrylate, hydroxymethylacrylate, hydroxypropylacrylate; and alkyl-vinyl-ethers, notably ethylene glycol vinyl ether.
- [0077] Preferably, step (a**) is performed in the presence of a suitable organic solvent, such as for example butyl acetate, ethyl acetate and mixtures thereof.
- [0078] Preferably, step (a**) is performed in the presence of a catalyst, more preferably selected from tertiary amines, such as triethylendiamine, N-ethyl-ethylene-imine, tetramethylguanidine; organotin compounds, such as for example dibutyltin dioctanoate and dibutyltin-dilaurate. Good results have been obtained by using dibutyltin-dilaurate.
- [0079] Said catalyst are used in an amount not higher than 0.5 wt.% based on the

total weight of the reaction mixture.

- [0080] Preferably, step (a**) is performed using butylated-hydroxytoluene.
- [0081] Preferably, step (a**) is performed under heating at a temperature of from 35°C to 100°C. Preferably, heating is performed until the mixture turns limpid. The skilled person can determine the duration of the heating depending on the starting materials and on the reaction conditions.
- [0082] Preferably, step (b**) is performed in the presence of an organic solvent such as ethyl acetate, butyl acetate and mixtures thereof.
- [0083] Preferably, step (b**) is performed under heating at a temperature of from 40°C to 100°C. Preferably, heating is performed until the mixture turns limpid. The skilled person can determine the duration of the heating depending on the starting materials and on the reaction conditions.
- [0084] Preferably, the gel electrolyte according to the present invention is in the form of a membrane, i.e. a uniform and continuous self-standing film.
- [0085] Preferably, said membrane has a thickness of from 10 to 200 µm, more preferably from 75 to 150 µm.
- [0086] The membrane can be advantageously used as a separator in an electrochemical device.
- [0087] Thus, a further aspect of the present invention relates to a self-standing polymer electrolyte separator comprising:
- composition (Ce) as defined above and
 - a polymeric matrix comprising a crosslinked polymer obtained by curing at least one polymer (P) as defined above.
- [0088] The terms “curing” and “crosslinking” are used as synonyms within the present description.
- [0089] Typically, the curing conditions depend on the ingredients of said composition (C) and from the circumstances under which the curing process is carried out.
- [0090] Advantageously, the step of curing is performed by UV-curing.
- [0091] Any source of radiation can be used. The radiation does can be adjusted by the skilled persons as a function of the composition (C) that is used.
- [0092] Good results have been obtained by applying a radiation of from 200 to 750W. Preferably, when said step of curing is performed using UV, the

curing time is from 1 to 50 seconds, more preferably from 5 to 30 seconds.

[0093] Preferably, the self-standing polymer electrolyte separator is in the form of a membrane, i.e. a uniform and continuous self-standing film. More preferably, said membrane has a thickness of from 10 to 200 μm , more preferably from 75 to 150 μm .

[0094] Suitable active materials for the anode (negative electrode) are selected from the group consisting of:

- graphitic carbons able to intercalate lithium, typically existing in forms such as powders, flakes, fibers or spheres (for example mesocarbon microbeads) hosting lithium;
- lithium metal;
- lithium alloy composition, including notably those described in **US 6203944** (3M INNOVATIVE PROPERTIES) and/or in **WO 00/03444** (MINNESOTA MINING) ;
- lithium titanates, generally represented by formula $\text{Li}_4\text{Ti}_5\text{O}_{12}$; these compounds are generally considered as “zero-strain” insertion materials, having low level of physical expansion upon taking up the mobile ions, i.e. Li^+ ;
- lithium-silicon alloys, generally known as lithium silicides with high Li/Si ratios, in particular lithium silicides of formula $\text{Li}_{4.4}\text{Si}$;
- lithium-germanium alloys, including crystalline phases of formula $\text{Li}_{4.4}\text{Ge}$.

[0095] The anode may contain additives as will be familiar to those skilled in the art. Among them, mention can be made notably of carbon black, graphene or carbon nanotubes. As will be appreciated by those skilled in the art, the negative electrode may be in any convenient form including foils, plates, rods, pastes or as a composite made by forming a coating of the negative electrode material on a conductive current collector or other suitable support.

[0096] Representative cathode (positive electrode) materials for secondary batteries include composites comprising a polymer binder (PB), a powdery electrode material and, optionally, an electroconductivity-imparting additive and/or a viscosity modifying agent.

[0097] The active material for the positive electrode preferably comprises a

composite metal chalcogenide represented by a general formula of LiMY_2 , wherein M denotes at least one species of transition metals such as Co, Ni, Fe, Mn, Cr and V; and Y denotes a chalcogen, such as O or S. Among these, it is preferred to use a lithium-based composite metal oxide represented by a general formula of LiMO_2 , wherein M is the same as above. Preferred examples thereof may include: LiCoO_2 , LiNiO_2 , $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ ($0 < x < 1$), and spinel-structured LiMn_2O_4 .

[0098] As an alternative, in the case of forming a positive electrode for a lithium-ion secondary battery, the active material may comprise a lithiated or partially lithiated transition metal oxyanion-based electro-active material of formula $\text{M1M2}(\text{JO}_4)_f\text{E}_{1-f}$,

wherein

M1 is lithium, which may be partially substituted by another alkali metal representing less than 20% of the M1 metals,

M2 is a transition metal at the oxidation level of +2 selected from Fe, Mn, Ni or mixtures thereof, which may be partially substituted by one or more additional metals at oxidation levels between +1 and +5 and representing less than 35% of the M2 metals, including 0,

JO_4 is any oxyanion wherein J is either P, S, V, Si, Nb, Mo or a combination thereof,

E is a fluoride, hydroxide or chloride anion,

f is the molar fraction of the JO_4 oxyanion, generally comprised between 0.75 and 1.

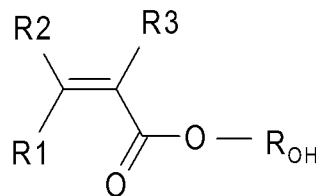
[0099] The $\text{M1M2}(\text{JO}_4)_f\text{E}_{1-f}$ electro-active material as defined above is preferably phosphate-based and may have an ordered or modified olivine structure.

[0100] More preferably, the active material is a phosphate-based electro-active material of formula $\text{Li}(\text{Fe}_x\text{Mn}_{1-x})\text{PO}_4$ wherein $0 \leq x \leq 1$, wherein x is preferably 1 (i.e. lithium iron phosphate of formula LiFePO_4).

[0101] When an active material showing a limited electron-conductivity, such as LiCoO_2 or LiFePO_4 , is used, the positive electrode preferably also contains an electroconductivity-imparting additive, in order to improve the conductivity of a resultant composite electrode. Examples of said electroconductivity-imparting additive may include: carbonaceous

materials, such as carbon black, graphite fine powder and fiber, and fine powder and fiber of metals, such as nickel and aluminum.

[0102] As per the polymer binder (PB), polymers well known in the art can be used including, preferably, vinylidene fluoride (VDF) polymers and even more particularly, VDF polymers comprising recurring units derived from VDF and from 0.01 to 5 % moles of recurring units derived from at least one (meth)acrylic monomer [monomer (MA)] of formula:



wherein

each of R1, R2, R3, equal or different from each other, is independently a hydrogen atom or a C₁-C₃ hydrocarbon group, and

R_{OH} is a hydrogen atom or a C₁-C₅ hydrocarbon moiety comprising at least one hydroxyl group.

[0103] For electric double layer capacitors, the active substance preferably comprises fine particles or fibre, such as activated carbon, activated carbon fibre, carbon nanotubes, graphene, silica or alumina particles, having an average particle (or fibre) diameter of 0.05-100 μm and a specific surface area of 100-3000 m^2/g , i.e., having a relatively small particle (or fibre) diameter and a relatively large specific surface area compared with those of active substances for batteries.

[0104] The assembly according to the present invention is preferably formed by assembling a metal (ion) or composite carbon cathode, the gel electrolyte as above defined and a composite anode.

[0105] Preferably, in the process for the manufacture of the assembly, said step (I-b) is performed by spreading the composition C onto a support surface using a standard device, according to well-known techniques like doctor blade coating, metering rod coating, slot die coating, knife over roll coating, and the like.

[0106] A suitable support can be chosen in the group comprising: sheets made

from fluoropolymers, preferably polytetrafluoroethylene (PTFE), the anode or cathode active materials as defined above.

[0107] Preferably, the film obtained in step (I-b) has a thickness of from about 10 to 200 μm , more preferably from 75 to 150 μm .

[0108] Preferably, said step (I-c) is performed by UV-curing.

[0109] Any source of radiation can be used. The radiation does can be adjusted by the skilled persons as a function of the composition (C) that is used.

[0110] Good results have been obtained by applying a radiation of from 200 to 750W. Preferably, when said step of curing is performed using UV, the curing time is from 1 to 50 seconds, more preferably from 5 to 30 seconds.

[0111] Preferably, said step (I-e) is performed according to methods known in the art, for example by pressing the components together.

[0112] According to a first preferred embodiment, when the support is a sheet made from fluoropolymers, the process for the manufacture of the assembly according to the present invention comprises the following steps:

(I-a*) providing composition C;

(I-b*) casting a film from said composition onto the surface of a sheet made from a fluoropolymer, preferably polytetrafluoroethylene (PTFE);

(I-c*) curing said composition C thus obtaining a cured gel electrolyte onto said support;

(I-d*) separating the cured gel electrolyte from said support; and

(I-e*) contacting the cured gel thus obtained with an anode and a cathode, such that the gel is interposed between said anode and said cathode.

[0113] Preferably, the film obtained in step (I-b*) has the same thickness disclosed above in step (I-b).

[0114] Preferably, step (I-c*) is performed in the same conditions disclosed above for step (I-c).

[0115] Preferably, step (I-e*) is performed as disclosed above for step (I-e).

[0116] According to a second preferred embodiment, when the support is the anode or cathode active material, the process for the manufacture of the assembly according to the present invention comprises the following steps:

(I-a[#]) providing composition C;
(I-b[#]) casting a film from said composition onto the anode active material or the cathode active material;
(I-c[#]) curing said composition C thus obtaining a cured gel electrolyte onto the cathode active material or the anode active material; and
(I-e[#]) contacting the cured gel thus obtained with an anode active material or a cathode active material, respectively, such that the cured gel is interposed between said anode and said cathode.

[0117] Preferably, the film obtained in step (I-b[#]) has the same thickness disclosed above in step (I-b).

[0118] Preferably, step (I-c[#]) is performed by UV-curing as disclosed in step (I-c) above.

[0119] Preferably, step (I-e[#]) is performed as disclosed above for step (I-e).

[0120] Advantageously, the assembly of the present invention is for use in an electrochemical device, which is preferably selected from batteries, such as lithium batteries; electric double layer capacitors (also referred to as "super-capacitors"); and electro-chromic windows.

[0121] The invention will be herein after illustrated in greater detail by means of the Examples contained in the following Experimental Section; the Examples are merely illustrative and are by no means to be interpreted as limiting the scope of the invention.

[0122] Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of the present application to the extent that it may render a term unclear, the present description shall take precedence.

Experimental section

[0123] Materials

[0124] The following were obtained from Sigma-Aldrich:

ethylenecarbonate (EC)

dimethylcarbonate (DMC)

poly(ethylene glycol) methyl ether methacrylate (PEGMA-475) with Mn 475

bisphenol A ethoxylate (15 EO/phenol) dimethacrylate (BEMA) with Mn

1700

poly(ethylene glycol) dimethacrylate (PEO-DMA) with Mn 550

lithium trifluoromethanesulfonimide (LiTFSI)

[0125] The following were obtained from CIBA:

Darocur[®] 1173: 2-hydroxy-2-methyl-1-phenyl-propan-1-one, liquid photoinitiator

[0126] The following were obtained from Solvay Specialty Polymers Italy S.p.A.:

Fluorolink[®] MD 700 PFPE - perfluoropolyether (PFPE) urethane acrylate (neat polymer without solvents)

Fluorolink[®] AD 1700 PFPE - perfluoropolyether (PFPE) urethane acrylate (neat polymer without solvents)

Solef[®] 5130 PVDF – polyvinylidenefluoride

[0127] Example 1

[0128] 1.5 g of Fluorolink[®] AD1700 were mixed under stirring at room

temperature with 3.5 g of a solution containing lithium trifluoromethanesulfonimide (LiTFSI) 1M in

ethylenecarbonate(EC)/dimethylcarbonate (DMC) 1/1 w/w and 0.03 g of Darocur[®] 1173. A clear and homogeneous mixture was obtained.

The liquid formulation was then applied by tape casting on polytetrafluoroethylene (PTFE) sheets and UV cured with a UV lamp under the following conditions: 500 W, 15 seconds. A transparent and homogeneous membrane (herein after M1) with a thickness of 120 micron was thus obtained.

The ionic conductivity values of the above prepared membrane M1 were measured at different temperatures, in a sealed steel conductivity cell through electrochemical impedance spectroscopy (EIS) covering a frequency range from 200 mHz to 200 kHz with a perturbation amplitude of $\pm 5\text{mV}$.

The average values measured on three single cells for each temperature are reported in Table 1.

[0129] Example 2C (comparative)

[0130] Example 3 as disclosed in WO 2014/062898 (previously cited) was repeated.

[0131] 5.64 g of a mixture of poly(ethylene glycol) dimethacrylate (PEO-DMA) and Fluorolink[®] MD 700, in a ratio 80/20 by weight, was mixed under stirring at room temperature with 0.36 g of a solution containing lithium trifluoromethanesulfonimide (LiTFSI) 1M in ethylenecarbonate (EC) / di-methylcarbonate (DMC) 1/1 w/w and 0.12 g of Darocur[®] 1173.

The liquid formulation was then applied by tape casting on polytetrafluoroethylene (PTFE) sheets and UV cured with a UV lamp under the following conditions: 500 W, 15 seconds. The resulting film (herein after M4C) had a thickness of 120 micron and, at a visual inspection, appeared homogeneous but hazy.

The ionic conductivity values of the above prepared membrane M2C were measured at different temperatures, in a sealed steel conductivity cell through electrochemical impedance spectroscopy (EIS) covering a frequency range from 200 mHz to 200 kHz with a perturbation amplitude of $\pm 5\text{mV}$.

The average values measured on three single cells for each temperature are reported in Table 1.

Table 1

Sample	Thickness (micron)	Temperature (°C)	Specific conductivity (S/cm)
M1	120	55	2.4×10^{-3}
M1	120	25	7.0×10^{-4}
M1	120	4	4.5×10^{-4}
M2C(*)	120	55	$< 10^{-5}$
M2C(*)	120	25	$< 10^{-5}$
M2C(*)	120	4	$< 10^{-5}$

[0132] (*) comparative

[0133] The above results demonstrated that sample M1 had good conductivity properties also at low temperatures. Differently, comparative sample

M2C(*) in addition of being hazy, probably due to dishomogeneity and/or phase separation, showed inadequate and insufficient conductivity, such that it is not suitable for use in a lithium battery.

[0134] Example 3C (comparative)

[0135] The same procedure as disclosed in Nair et al. (previously cited) was repeated.

[0136] 0.92 g of poly(ethylene glycol) methyl ether methacrylate (PEGMA-475) and 2.07g of bisphenol A ethoxylate (15 EO/phenol) dimethacrylate (BEMA) were mixed under stirring at room temperature with 7.0 g of a solution containing lithium trifluoromethanesulfonimide (LiTFSI) 1M in ethylenecarbonate(EC)/dimethylcarbonate (DMC) 1/1 w/w and 0.03 g of Darocur[®] 1173. A clear and homogeneous mixture was obtained. The liquid formulation was then applied by tape casting at different thickness (from 100 to 200 microns) on polytetrafluoroethylene (PTFE) sheets and UV cured with a UV lamp (500w). The films thus obtained appeared not homogeneous at a visual inspection and were too fragile to be characterized in terms of conductivity.

[0137] Example 4

[0138] The membrane M1 prepared as disclosed in Example 1 above was tested as separator in a Li/LiFePO₄ battery.

A LiFePO₄ electrode (thickness 50 microns, 0.51 mAh/cm²) was prepared by mixing 82% LiFePO₄, 10% conductive carbon and 8% Solef[®] 5130 PVDF as binder. Circular electrodes (diameter 12 mm) were cut and tested in coin cells using lithium metal as counter electrode, without addition of liquid electrolyte.

A test protocol was applied increasing progressively C-rate from C/20 to C/2, at T= 55°C. Cut offs were 4.0 – 2.5 V vs. Li.

The results are reported in Table 2.

Table 2

Cycle No.	Discharge C-rate	Specific discharge capacity (mAh/g)	Coulombic efficiency (%)
2	C/20	170	100
4	C/10	157	100
6	C/4	144	100
8	C/2	127	100

[0139] C-rate is a measure of the rate at which a battery is discharged relative to its maximum capacity. For example, "C/20" rate means that the discharge current will discharge the entire battery in 20 hours.

[0140] Specific discharge capacity is the ratio between the capacity output of a battery and the weight of LiFePO_4 in the assembled electrode, at a certain discharge current (specified as C-rate) from 100 percent state-of-charge to the lower cut-off voltage. The coulombic efficiency is the ratio of the output of charge by battery (discharge step) to the input of charge (charge step).

[0141] The above results showed good performances of the batteries prepared with the gel electrolyte according to the present invention, with a discharge capacity well above 100 mAh/g.

Claims

1. A curable liquid composition [composition C] comprising:
 - a liquid electrolyte composition [composition (Ce)] comprising
 - (i) at least one lithium salt and
 - (ii) at least one solvent for said lithium salt;
 - a crosslinkable (per)fluoropolyether polymer [polymer (P)] comprising at least one (per)fluoropolyoxyalkylene chain [chain (R_{pf})] having two chain ends, wherein at least one chain end comprises at least one unsaturated moiety [moiety U]; and
 - one or more further ingredients.
2. The composition according to claim 1, wherein said composition C comprises an amount of polymer P of at least 1wt.%, more preferably 5 wt.%, even more preferably 10 wt.%, still more preferably 15 wt.% based on the total weight of said composition C.
3. The composition according to claim 1 or 2, wherein said composition C comprises an amount of polymer P of at most 50 wt.%, more preferably 45 wt.%, even more preferably 40 wt.% and still more preferably 35 wt.% based on the total weight of said composition C.
4. The composition according to any one of the preceding claims, wherein said composition C comprises an amount of polymer P of from 1 to 50%, more preferably from 5 to 45%, even more preferably from 10 to 40% and still more preferably from 20 to 35 wt.% by weight based on the total weight of composition C.
5. The composition according to claim 1, wherein said chain (R_{pf}) is a chain of formula:

$$-O-D-(CFX^{\#})_{z1}-O(R_f)(CFX^*)_{z2}-D^*-O-$$
 wherein
 - $z1$ and $z2$, equal or different from each other, are equal to or higher than 1;
 - $X^{\#}$ and X^* , equal or different from each other, are -F or -CF₃,

provided that when z_1 and/or z_2 are higher than 1, $X^\#$ and X^* are -F;
 D and D^* , equal or different from each other, are an alkylene chain comprising from 1 to 6 and even more preferably from 1 to 3 carbon atoms, said alkyl chain being optionally substituted with at least one perfluoroalkyl group comprising from 1 to 3 carbon atoms;

(R_f) comprises, preferably consists of, repeating units R° , said repeating units being independently selected from the group consisting of:

- (i) -CFXO-, wherein X is F or CF_3 ;
- (ii) -CFXCFXO-, wherein X, equal or different at each occurrence, is F or CF_3 , with the proviso that at least one of X is -F;
- (iii) - $CF_2CF_2CW_2O$ -, wherein each of W, equal or different from each other, are F, Cl, H;
- (iv) - $CF_2CF_2CF_2CF_2O$ -;
- (v) - $(CF_2)_jCFZO$ - wherein j is an integer from 0 to 3 and Z is a group of general formula - $O-R_{(f-a)}-T$, wherein $R_{(f-a)}$ is a fluoropolyoxyalkene chain comprising a number of repeating units from 0 to 10, said recurring units being chosen among the following : -CFXO-, - CF_2CFXO -, - $CF_2CF_2CF_2O$ -, - $CF_2CF_2CF_2CF_2O$ -, with each of X being independently F or CF_3 and T being a C_1 - C_3 perfluoroalkyl group.

6. The composition according to claim 5, wherein said chain (R_f) complies with the following formula:

(R_f-I)

- $[(CFX^1O)_{g1}(CFX^2CFX^3O)_{g2}(CF_2CF_2CF_2O)_{g3}(CF_2CF_2CF_2CF_2O)_{g4}]$ -

wherein

- X^1 is independently selected from -F and - CF_3 ,
- X^2 , X^3 , equal or different from each other and at each occurrence, are independently -F, - CF_3 , with the proviso that at least one of X is -F;
- g_1 , g_2 , g_3 , and g_4 , equal or different from each other, are independently integers ≥ 0 , such that $g_1+g_2+g_3+g_4$ is in the range from 2 to 300, preferably from 2 to 100; should at least two of g_1 , g_2 , g_3 and g_4 be different from zero, the different recurring units are generally statistically distributed along the chain.

7. The composition according to any one of the preceding claims, wherein said moiety U is selected in the group consisting of:

(U-I) $-\text{C}(=\text{O})-\text{CR}_\text{H}=\text{CH}_2$

(U-II) $-\text{C}(=\text{O})-\text{NH}-\text{CO}-\text{CR}_\text{H}=\text{CH}_2$

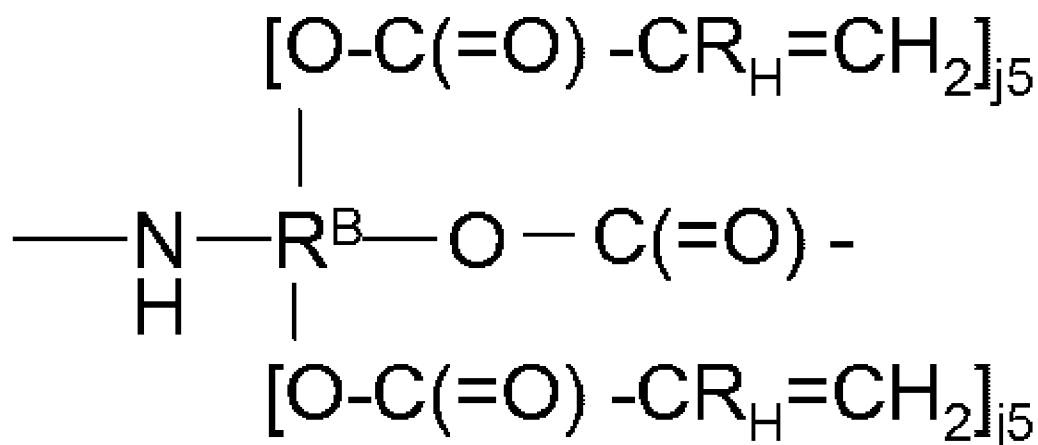
(U-III) $-\text{C}(=\text{O})-\text{R}^\text{A}-\text{CR}_\text{H}=\text{CH}_2$

wherein

R_H is H or a C_1 - C_6 alkyl group;

R^A is selected from the group consisting of (R^A -I) and (R^A -II):

(R^A -I)

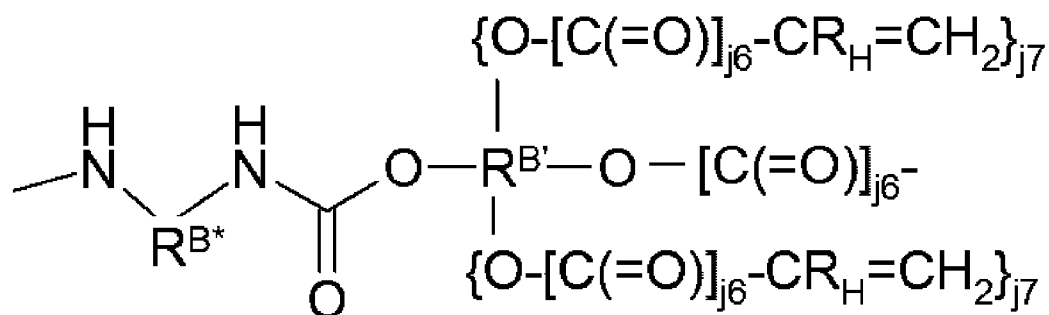


wherein

each of $j5$ is independently 0 or 1 and

R^B is a divalent, trivalent or tetravalent group selected from the group consisting of C_1 - C_{10} aliphatic group; C_3 - C_{12} cycloaliphatic group; C_5 - C_{14} aromatic or alkylaromatic group, optionally comprising at least one heteroatom selected from N, O and S;

(R^A -II)



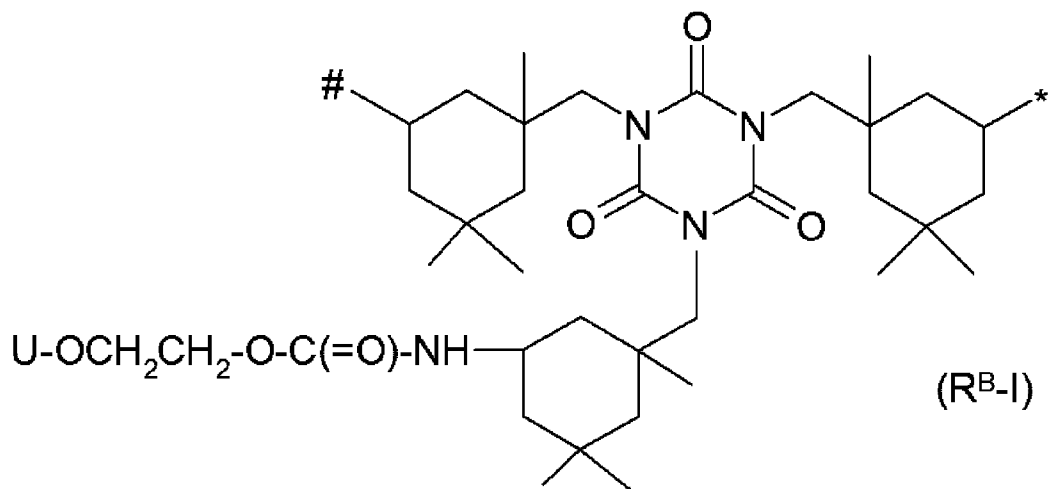
wherein

j6 is 0 or 1;

each of j_7 is independently 0 or 1;

R^{B'} is a divalent, trivalent or tetravalent group selected from the group consisting of C₁-C₁₀ aliphatic group; C₃-C₁₂ cycloaliphatic group; C₅-C₁₄ aromatic or alkylaromatic group, optionally comprising at least one heteroatom selected from N, O and S; and

R^{B^*} has the same meanings defined above for $R^{B'}$ or it is a group of formula (R^{B-I}):



wherein

U is selected from the groups (U-I) to (U-III) as defined above and

* and # indicate the bonding site to the nitrogen atoms in formula (R^A-II) above.

8. The composition according to any one of the preceding claims, wherein said at least one moiety U is bonded to said chain (R_{pf}) via a sigma bond or via a (poly)oxyalkylene chain [chain (R_a)] comprising from 1 to 50 fluorine-free

oxyalkylene units, said units being the same or different each other and being selected from $-\text{CH}_2\text{CH}(\text{J})\text{O}-$, wherein J is independently selected from hydrogen atom, straight or branched alkyl or aryl, preferably hydrogen atom, methyl, ethyl or phenyl.

9. A gel electrolyte comprising:
 - (A) a liquid electrolyte composition [composition (Ce)] comprising
 - (i) at least one lithium salt and
 - (ii) at least one solvent for said lithium salt; and
 - (B) a polymeric matrix comprising a crosslinked polymer obtained by curing at least one crosslinkable (per)fluoropolyether polymer [polymer (P)] comprising at least one(per)fluoropolyoxyalkylene chain [chain (R_{pf})] having two chain ends, wherein at least one chain end comprises at least one unsaturated moiety [moiety U].
10. The gel electrolyte according to claim 9, wherein said polymer (P) is as defined in any one of claims 5 to 8.
11. The gel electrolyte according to claim 9, which is a self-standing polymer electrolyte separator.
12. A process for the manufacturing of the gel electrolyte according to claim 9, said process comprising the steps of:
 - (a) providing a curable liquid composition [composition C] comprising:
 - a liquid electrolyte composition [composition (Ce)] comprising
 - (i) at least one lithium salt and
 - (ii) at least one solvent for said lithium salt;
 - a crosslinkable (per)fluoropolyether polymer [polymer (P)] comprising at least one(per)fluoropolyoxyalkylene chain [chain (R_{pf})] having two chain ends, wherein at least one chain end comprises at least one unsaturated moiety [moiety U] and
 - optionally, one or more further ingredients; and
 - (b) curing said composition (C).

13. An assembly comprising
- at least one anode,
 - at least one cathode and
 - the gel electrolyte according to claim 9,
- said gel electrolyte being interposed between said anode and said cathode.
14. A process for the manufacture of the assembly according to claim 13, the process comprising the steps of:
- (I-a) providing a curable liquid composition [composition C] comprising:
- a liquid electrolyte composition [composition (Ce)] comprising
 - (i) at least one lithium salt and
 - (ii) at least one solvent for said lithium salt;
 - a crosslinkable (per)fluoropolyether polymer [polymer (P)] comprising at least one(per)fluoropolyoxyalkylene chain [chain (R_{pf})] having two chain ends, wherein at least one chain end comprises at least one unsaturated moiety [moiety U]; and
 - optionally, one or more further ingredients;
- (I-b) casting a film from said composition C onto the surface of a support;
- (I-c) curing said composition C thus obtaining a cured gel electrolyte onto the surface of said support;
- (I-d) optionally separating the cured gel electrolyte and the support; and
- (I-e) contacting said cured gel electrolyte with an anode and/or a cathode.
15. The process according to claim 14, wherein said support is a sheet made from a fluoropolymer and the process comprises the steps of:
- (I-a*) providing composition C;
- (I-b*) casting a film from said composition onto the surface of a sheet made from a fluoropolymer, preferably polytetrafluoroethylene (PTFE);
- (I-c*) curing said composition C thus obtaining a cured gel electrolyte onto said support;
- (I-d*) separating the cured gel electrolyte from said support; and
- (I-e*) contacting the cured gel thus obtained with an anode and a cathode,

such that the gel is interposed between said anode and said cathode.

16. The process according to claim 14, wherein said support is the cathode active material or the anode active material and said process comprises the steps of:
- (I-a[#]) providing composition C;
 - (I-b[#]) casting a film from said composition onto the anode active material or the cathode active material;
 - (I-c[#]) curing said composition C thus obtaining a cured gel electrolyte onto the cathode active material or the anode active material; and
 - (I-e[#]) contacting the cured gel thus obtained with an anode active material or a cathode active material, respectively, such that the cured gel is interposed between said anode and said cathode.
17. An electrochemical device comprising the assembly according to claim 13.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/055134

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01M10/0565 H01M10/052 H01G9/15
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01M H01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2014/062898 A1 (UNIV NORTH CAROLINA [US]) 24 April 2014 (2014-04-24) cited in the application claim 13; example 3 -----	1-17
A	JIJEESH R. NAIR ET AL: "UV-Induced Radical Photo-Polymerization: A Smart Tool for Preparing Polymer Electrolyte Membranes for Energy Storage Devices", MEMBRANES, vol. 2, no. 4, 17 October 2012 (2012-10-17), pages 687-704, XP055295591, DOI: 10.3390/membranes2040687 cited in the application page 697; figure 1; table 1 -----	1-17



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2014062898 A1	24-04-2014	DE 13847827 T1	10-03-2016
		EP 2909886 A1	26-08-2015
		US 2015288028 A1	08-10-2015
		WO 2014062898 A1	24-04-2014
