

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property

Organization

International Bureau

(43) International Publication Date

31 May 2019 (31.05.2019)



(10) International Publication Number

WO 2019/101698 A1

(51) International Patent Classification:

H01M 4/134 (2010.01) H01M 4/62 (2006.01)
H01M 4/36 (2006.01) H01M 10/052 (2010.01)
H01M 4/38 (2006.01) H01M 6/14 (2006.01)

Published:

— with international search report (Art. 21(3))

(21) International Application Number:

PCT/EP2018/081824

(22) International Filing Date:

19 November 2018 (19.11.2018)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

17203413.4 23 November 2017 (23.11.2017) EP

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(81) Designated States (unless otherwise indicated, for every

kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every

kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

(54) Title: A MULTILAYER ASSEMBLY FOR ELECTROCHEMICAL CELLS

(57) Abstract: The present invention concerns a multilayer assembly comprising a metal electrode at least partially coated by a polymer composition, a process for its preparation and an electrochemical cell comprising this multilayer assembly as an anode, protected by the polymer composition from the rapid formation and growing of dendrites during the electrochemical cell operations.



Description**Title****A MULTILAYER ASSEMBLY FOR ELECTROCHEMICAL CELLS****Cross-Reference to Related Application**

This application claims priority to European application No. 17203413.4 filed on November 23, 2017, the whole content of this application being incorporated herein by reference for all purposes.

5 Technical Field

The present invention relates to a multilayer assembly comprising a metal layer at least partially coated by a polymer composition, a process for its preparation and an electrochemical cell comprising this multilayer assembly.

Background Art

10 Primary (non-rechargeable) batteries containing lithium metal or lithium compounds as an anode are very useful energy storage devices, which may find a variety of applications, ranging from a wide number of portable electronic devices to electrical vehicles.

Lithium (Li) metal would also be an ideal anode material for rechargeable (secondary) batteries due to its excellent electrochemical properties. Unfortunately, uncontrollable dendritic growth and limited Coulombic Efficiency (CE) during lithium deposition/stripping inherent in rechargeable batteries have prevented the practical applications and commercialisation of Li metal-based rechargeable batteries and related devices over the past 40 years (see XU, W., et al. "Lithium metal anodes for
15 rechargeable batteries". *Energy Environ. Sci.* 2014, vol.7, p.513-537, and references cited therein).

With the emergence of post-Li-ion batteries, safe and efficient operation of Li metal anodes is being regarded as an enabling technology which may determine the fate of energy storage technology for the next generation, including rechargeable Li-air
25 batteries, Li-S batteries, and Li metal batteries which utilize intercalation compounds as cathodes (see LIANG, Z., et al. "Polymer Nanofiber-Guided Uniform Lithium Deposition for Battery Electrodes". *Nano Lett.* 2015, vol.15, p.2910-2916, UMEDA, G.A., et al. Protection of lithium metal surfaces using tetraethoxysilane.

J. Mater. Chem., 2011, vol.21, p.1593, LOVE, C.A., et al. "Observation of Lithium Dendrites at Ambient Temperature". *ECS Electrochemistry Letters*, 2015, vol.4, no.2, p.A24-A27).

The main issue with the use of Li metal anodes in secondary batteries is linked to the
5 growth of lithium dendrites during repeated charge/discharge cycles, which ultimately lead to poor service life and potential internal short circuits.

Uncontrolled lithium dendrite growth results in poor cycling performance and serious safety hazards in lithium metal based batteries (see WU, H., et al. "Improving battery safety by early detection of internal shorting with a bifunctional separator".
10 *Nat. Commun.*, 2014, vol.5, p.5193). Upon electrochemical cycling, lithium ions diffuse toward the defects creating the so-called "hot spots". It is well recognized that Li dendrite growth is accelerated at these hot spots where the current density is locally enhanced dramatically. The resulting tree-like lithium metal dendrite will pierce through the separator and provoke internal short circuits, with risks of overheating, fire and
15 potential explosion of the device.

It was already proposed that the addition of a polymeric layer on lithium metal could prevent lithium dendrite growth. This layer should adhere homogeneously on lithium metal to get homogeneous deposition of lithium and should have also good mechanical properties to resist to dendrite growth, moderate swelling for long lifetime, good ionic
20 conductivity to avoid loss of performance and decrease of lithium concentration at the interface. However, coating compositions which are known in the art are not capable to suppress dendrite growth to a satisfactory level and lower the overall efficiency of the electrochemical cells.

In fact, the thickness and reactivity of these layers proved difficult to control, and the coatings may interfere with the battery functions, which eventually limit their practical
25 applications.

It is therefore still felt the need of having available durable, reliable and safe rechargeable electrochemical cell based on lithium metal anodes whereas adverse effects due to dendrite growths are avoided.

30 US2016/118638 discloses an electrode structure comprising: an electrode comprising lithium metal or lithium alloy; a polymer layer comprising a cross-linked polymeric material

formed by reaction of (aa) a polymeric material formed by reaction of (a) at least one polyimide selected from condensation products of: (a1) at least one polyisocyanate having on average at least two isocyanate groups per molecule; and (a2) at least one polycarboxylic acid having at least 3 COOH groups per molecule or an anhydride thereof;
5 and (b) at least one organic amine comprising at least one primary or secondary amino group, or a mixture of at least one organic amine comprising at least one primary or secondary amino group and at least one diol or triol; and (bb) at least one polyisocyanate having on average at least two isocyanate groups per molecule.

Summary of the Invention

10 The Applicant has now found that ionisable polymers having a low glass transition temperature (hereinafter referred to as " T_g "), when applied on a metal layer of an electrochemical cell's anode, are able to form a particularly effective coating that advantageously substantially lowers or even prevents the formation of dendrites during the cell's operation and hence advantageously improves the efficiency and stability of
15 the electrochemical cells comprising the same over performances of cells comprising uncoated metal anodes.

A subject of the present invention is therefore a multilayer electrode assembly for an electrochemical cell, said assembly comprising:

- a metal electrode (1) substantially consisting of at least one metal selected from the
20 group consisting of lithium metal, sodium metal, magnesium metal, and zinc metal, or substantially consisting of an alloy of one or more of lithium metal, sodium metal, magnesium metal, and zinc metal with silicon or tin, said metal electrode (1) comprising a first surface and a second surface;
- a coating layer (2), which adheres on at least a fraction of said first surface of said
25 metal electrode (1),

wherein (2) is a coating layer of a composition [composition (C)] comprising, and preferably consisting of:

- a) at least one polymer [polymer (P1)] comprising a polymer chain [chain (R)] consisting of a plurality of non-ionisable recurring units [units (U)], said chain
30 having two ends, each end comprising at least one ionisable acid group;
- b) at least one polymer [polymer (P2)] comprising a polymer chain [chain (R)]

consisting of a plurality of non-ionisable recurring units [units (U)], said chain (R) being equal or different from that of polymer (P1) and having two ends, each end comprising at least one ionisable amino group;

wherein:

5 said polymers (P1) and (P2) are amorphous and have a T_g lower than -35°C , preferably ranging from -35°C to -120°C ,

and where the ratio between the equivalents of polymer (P1) and the equivalents of polymer (P2) in said composition (C) preferably ranges from 1.4 to 0.6, more preferably from 1.2 to 0.8, most preferably from 1.1 to 0.9.

10 A further subject of the present invention is a process for the manufacture of a multilayer electrode assembly for an electrochemical cell as defined above, comprising the steps of:

i) providing a metal electrode (1) comprising a first surface and a second surface;
ii) providing a liquid mixture of a liquid medium [medium (L)] and of a composition
15 (C) comprising:

a) at least one polymer [polymer (P1)] comprising a polymer chain [chain (R)] consisting of a plurality of non-ionisable recurring units [units (U)], said chain having two ends, each end comprising at least one ionisable acid group;
and

20 b) at least one polymer [polymer (P2)] comprising a polymer chain [chain (R)] consisting of a plurality of non-ionisable recurring units [units (U)], said chain (R) being equal or different from that of polymer (P1) and having two ends, each end comprising at least one ionisable amino group;

wherein said polymers (P1) and (P2) are amorphous and have a T_g lower
25 than -35°C , and wherein the ratio between the equivalents of polymer (P1) and the equivalents of polymer (P2) in said composition (C) preferably ranges from 1.4 to 0.6, more preferably from 1.2 to 0.8, most preferably from 1.1 to 0.9,

iii) coating at least a fraction of said first surface of metal electrode (1) with the liquid mixture coming from step ii), to obtain a wet coated layer;

30 iv) drying said wet coated layer so as to obtain the multilayer electrode assembly.

In still further aspects, the invention relates to an electrochemical cell comprising the

multilayer electrode assembly as defined above, and to a method of making the same comprising assembling the multilayer electrode assembly as defined above with at least one of collector, separator, opposite electrode and an electrolyte.

Detailed Description of the Invention

5 According to a preferred embodiment of this invention, the metal electrode (1) of the multilayer assembly essentially consists of at least one of lithium metal and lithium metal alloys with tin or silicon, said preferred metal electrode being referred to as a lithium metal electrode. Advantageously, the lithium metal electrode can be further assembled to on another metal laminate, e.g. acting as reinforcing structure or
10 collector, preferably on copper, e.g. on a copper foil. When the lithium metal electrode is assembled to an additional metal laminate, this laminate is adhered to at least a fraction of the second surface of the lithium metal electrode, that is to say adhered on a surface of the electrode (1) that is not coated with the composition (C).

 In the present invention, by the term “consisting essentially of” is meant that a
15 composition or element comprises more than 95% by weight (with respect to the total weight of the composition) of a specific substance, e.g. lithium metal, or consists of such a substance, providing that it may include impurities and traces of other substances that are generally or inevitably present in such substance.

 Unless otherwise specified, in the context of the present invention, the amount of
20 a component in a composition is indicated as the ratio between the weight of the component and the total weight of the composition multiplied by 100 (also referred to in the following as “wt%”).

 As used herein, the terms “adhere” and “adhesion” indicate that two layers are permanently attached to each other via their surfaces of contact, e.g. classified as 5B
25 to 3B in the cross-cut test according to ASTM D3359, test method B. For the sake of clarity, multilayer compositions wherein a metal electrode (1) and a layer as described above for the coating layer (2) are assembled by contacting, e.g. by pressing (1) and (2) together without adhesion between the two layers, so that they can be separated/removed from each other by simply releasing pressure, are outside of the
30 context of this invention.

 By the term “electrochemical cell” it is hereby meant an electrochemical assembly

comprising two opposite electrodes, an electrolyte, and a separator ensuring physical separation between the said electrodes and enabling electrolyte to migrate from an electrode to the other electrode.

In the present invention, by the acronym "PFPE" is meant "(per)fluoropolyether",
5 i.e. fully or partially fluorinated polyether, i.e. wherein all or only a part of the hydrogen atoms of the hydrocarbon structure have been replaced by fluorine atoms so that a higher proportion of fluorine atoms than hydrogen atoms is contained in the structure. When this acronym is used as substantive in the plural form, it is referred to as "PFPEs".

10 The term "(per)haloalkyl" denotes a fully or partially halogenated straight or branched alkyl group.

Unless otherwise indicated, the term "halogen" includes fluorine, chlorine, bromine and iodine.

In the present invention, unless otherwise indicated, the following terms are to be
15 meant as follows:

- a "cycloalkyl group" is a univalent group derived from a cycloalkane by removal of an atom of hydrogen; the cycloalkyl group thus comprises one end which is a free electron of a carbon atom contained in the cycle, which able to form a linkage with another chemical group;

20 - a "divalent cycloalkyl group" or "cycloalkylene group" is a divalent radical derived from a cycloalkane by removal of two atoms of hydrogen from two different carbons in the cycle; a divalent cycloalkyl group thus comprises two ends, each being able to form a linkage with another chemical group;

- the adjective "aromatic" denotes any mono-or polynuclear cyclic group (or
25 moiety) having a number of π electrons equal to $4n+2$, wherein n is 0 or any positive integer; an aromatic group (or moiety) can be an aryl or an arylene group (or moiety);

- an "aryl group" is a hydrocarbon monovalent group consisting of one core composed of one benzene ring or of a plurality of benzene rings fused together by sharing two or more neighbouring ring carbon atoms, and of one end. Non-limitative
30 examples of aryl groups are phenyl, naphthyl, anthryl, phenanthryl, tetracenyl, triphenyl, pyrenyl, and perylenyl groups. The end of an aryl group is a free electron of

a carbon atom contained in a (or the) benzene ring of the aryl group, wherein an hydrogen atom linked to said carbon atom has been removed. The end of an aryl group is capable of forming a linkage with another chemical group;

- an "arylene group" is a hydrocarbon divalent group consisting of one core
5 composed of one benzene ring or of a plurality of benzene rings fused together by sharing two or more neighbouring ring carbon atoms, and of two ends. Non-limitative examples of arylene groups are phenylenes, naphthylenes, anthrylenes, phenanthrylenes, tetracenylenes, triphenylenes, pyrenylenes, and perylenylenes. An end of an arylene group is a free electron of a carbon atom contained in a (or the)
10 benzene ring of the arylene group, wherein a hydrogen atom linked to said carbon atom has been removed. Each end of an arylene group is capable of forming a linkage with another chemical group.

Cycloalkyl, cycloalkylene, aryl and arylene groups can be substituted with one or more straight or branched alkyl or alkoxy groups and/or halogen atoms and/or can
15 comprise one or more heteroatoms, like nitrogen, oxygen and sulphur, in the ring.

The use of parentheses "(...)" before and after names of compounds, symbols or numbers identifying formulae or parts of formulae like, for example "polymer (P1)", "chain (R)", etc..., has the mere purpose of better distinguishing those names, symbols or numbers from the rest of the text; thus, said parentheses could also be omitted.

20 The expression "average functionality (F)" denotes the average number of functional groups per polymer molecule and can be calculated according to methods known in the art. For example, the average functionality (F) of PFPE alcohols can be calculated following the method reported in EP 1810987 B (SOLVAY SOLEXIS SPA) 7/25/2007 or in S.Turri, E. Barchiesi, M. Levi Macromolecules 28, 7271, (1995). In
25 particular, the average functionality of polymers (P1) and (P2) according to the present invention was determined following the teaching of the latter reference.

When ranges are indicated, range ends are included.

The expression "as defined above" is intended to comprise all generic and specific or preferred definitions referred to by that expression in preceding parts of the
30 description, unless indicated otherwise.

The expression "ionisable amino group" and "ionisable acid groups" identify

amino or acid groups able to form ionic groups, namely cationic and anionic groups respectively. In greater detail, an ionisable amino group identifies a primary, secondary or tertiary amino group, while an “ionisable acid group” identifies an acid group comprising at least one hydroxyl function in its protonated form, i.e. a protic acid group.

5 The expression “non-ionisable recurring unit” identifies a chemical moiety that is not able to form an ionic group with the at least one ionisable amino group or the at least one ionisable acid group in each end of polymers (P1) and (P2).

POLYMER (P1)

Polymer (P1) can be represented with formula (P1) here below:

10 (P1) E1-R-E1'

wherein:

- R is a polymer chain consisting of a plurality of non-ionisable recurring units [units (U)], equal to or different from one another and
 - E1 and E1', equal to or different from one another, are end groups each comprising at
- 15 least one ionisable acid group. Recurring units (U) are hydrocarbon units, which can further comprise non-ionisable atoms or non-ionisable functional groups, including one or more of halogen atoms, preferably fluorine atoms, ethereal oxygen atoms, alkyl or alkoxy silane groups, carbonate, ester, urethane and acrylate groups.

Non limiting examples of polymers (P1) are those wherein chain (R) is

20 independently selected from a fully or partially fluorinated polyoxyalkylene chain, a polyalkylsiloxane chain, a polyoxyalkylene chain, a polycarbonate chain, a polyester chain, a polyacrylate chain and a polybutadiene chain, as described in greater detail here below.

Examples of chains (R)

25 *Fully or partially fluorinated polyoxyalkylene chains (R_F)*

As intended herein, a fully or partially fluorinated polyoxyalkylene chain [herein after otherwise referred to as “chain (R_F)”, “(per)fluoropolyether chain” or “PFPE chain”] comprises recurring units [units (U_F)] having at least one catenary ether bond and at least one fluorocarbon moiety; typically, chain (R_F) comprises repeating units (U_F)

30 selected from:

(U_F - i) -CFXO-, wherein X is F or CF₃;

(U_F - ii) -CFXCFXO-, wherein X, equal or different at each occurrence, is F or CF₃, with the proviso that at least one of X is -F;

(U_F - iii) -CF₂CF₂CW₂O-, wherein each of W, equal or different from each other, is F, Cl, H,

5 (U_F - iv) -CF₂CF₂CF₂CF₂O-;

(U_F - v) -(CF₂)_j-CFZ-O- wherein j is an integer from 0 to 3 and Z is a group of general formula -OR_f^{*}T, wherein R_f^{*} is a fluoropolyoxyalkene chain comprising a number of repeating units from 0 to 10, said recurring units being chosen among the followings : -CFX^{*}O-, -CF₂CFX^{*}O-, -CF₂CF₂CF₂O-, -CF₂CF₂CF₂CF₂O-, with each of each of X^{*} being independently F or CF₃ and T being a C₁-C₃ perfluoroalkyl group.

When recurring units [units (U_F)] are different from one another, they are randomly distributed along the chain.

Preferably, chain (R_F) complies with formula (R_F-I):



15 wherein:

- X₁ is independently selected from -F and -CF₃;

- X₂, X₃, 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;

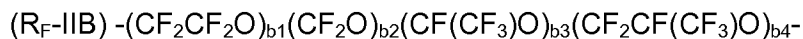
- g₁, g₂, g₃, and g₄, equal or different from each other, are independently integers ≥ 0, selected in such a way that the average number molecular weight (M_n) ranges from 400 to 10,000; should at least two of g₁, g₂, g₃ and g₄ be different from zero, the different recurring units are generally statistically distributed along the chain.

More preferably, chain (R_F-I) is selected from chains of formulae (R_F-IIA) - (R_F-IIE):

25 (R_F -IIA) -(CF₂CF₂O)_{a1}(CF₂O)_{a2}-

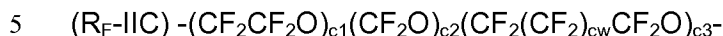
wherein:

- a₁ and a₂ are independently integers ≥ 0 such that the number average molecular weight (M_n) ranges from 400 to 10,000, preferably from 400 to 5,000; both a₁ and a₂ are preferably different from zero, with the ratio a₁/a₂ being preferably ranging from between 0.1 to 10;



wherein:

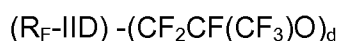
- b1, b2, b3, b4, are independently integers ≥ 0 such that the number average molecular weight (M_n) ranges from 400 to 10,000, preferably from 400 to 5,000; preferably b1 is 0, b2, b3, b4 are > 0 , with the ratio $b4/(b2+b3)$ being ≥ 1 ;



wherein:

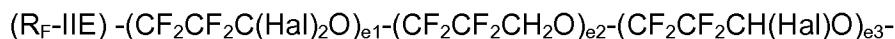
- cw is 1 or 2;

- c1, c2, and c3 are independently integers ≥ 0 such that the number average molecular weight (M_n) ranges from 400 to 10,000, preferably from 400 to 5,000; preferably c1, c2 and c3 are all > 0 , with the ratio $c3/(c1+c2)$ being generally lower than 0.2;



wherein:

- d is an integer > 0 such that the number average molecular weight (M_n) ranges from 400 to 10,000, preferably from 400 to 5,000;



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 selected in such a way that the $(e1+e2+e3)$ number average molecular weight (M_n) ranges from 400 to 10,000.

Still more preferably, chain (R_F) complies with formula (R_F-III) here below:



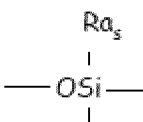
25 wherein:

- a1, and a2 are integers > 0 such that the number average molecular weight (M_n) ranges from 400 to 4,000, with the ratio $a2/a1$ generally ranging from 0.2 to 5.

Polyalkylsiloxane chains (R_S)

As intended herein, a polyalkylsiloxane chain [herein after otherwise referred to as chain (R_S)] comprises, preferably consist of recurring units [units (US)] of formula:

(U_S)



in which R_{a_s} and R_{b_s} , equal to or different from one another, are independently selected from hydrogen, straight or branched (halo)alkyl and aryl, with the proviso that at least one of R_{a_s} and R_{b_s} is not hydrogen.

Preferred R_{a_s} and R_{b_s} groups are straight or branched alkyl groups comprising from 1
5 to 4 carbon atoms; more preferably, both R_{a_s} and R_{b_s} are methyl, i.e. chain (R_s) is a polydimethylsiloxane chain [chain (R_{s-I})], which essentially consists of a sequence of recurring units of formula (U_{s-i}) here below:

(U_{s-i}): $-\text{OSi}(\text{CH}_3)_2-$.

Minor amount (e.g. < 1 % wt, based on the weight of chain (R_{s-I})) of spurious units,
10 defects or recurring unit impurities may be comprised in chain (R_{s-I}) without this affecting chemical properties of this chain.

Chain (R_s) has a number average molecular weight (M_n) typically ranging from 500 to 10,000, preferably from 500 to 5,000.

Polyoxyalkylene chains (R_{OA})

15 As intended herein, a polyoxyalkylene chain [herein after otherwise referred to as chain (R_{OA})] is a straight or branched polymer chain consisting of repeating hydrocarbon units comprising at least one catenary ether bond [units (U_{OA})]; non-limiting examples of chain (R_{OA}) are chains comprising, preferably essentially consisting of a sequence of units of formula $-\text{OR}_{OA}^-$, wherein each of R_{OA}^- , equal to or
20 different from each other, is, independently at each occurrence, an hydrocarbon divalent group, possibly comprising additional heteroatom(s), and preferably a divalent alkylene group, which may be linear or branched.

Preferred chains (R_{OA}) are polyoxyethylene chains comprising, preferably essentially consisting of recurring units of formulae (U_{OA-i}) as below detailed,
25 polyoxypropylene chains comprising, preferably essentially consisting of recurring units of formulae (U_{OA-ii}) - (U_{OA-iv}) here below, a polytetramethylene glycole chain, comprising, preferably essentially consisting of recurring units of formula (U_{OA-v}) here below, or a chain comprising, preferably essentially consisting of, a mixture of any of oxyethylene, oxypropylene, oxytetramethylene units (U_{OA-i}) - (U_{OA-v}):

30 (U_{OA-i}): $-\text{OCH}_2\text{CH}_2-$

(U_{OA-ii}): $-\text{OCH}_2\text{CH}_2\text{CH}_2-$

(U_{OA}-iii): -OCH(CH₃)CH₂-

(U_{OA}-iv): -OCH₂CH(CH₃)-

(U_{OA}-v): -OCH₂CH₂CH₂CH₂-.

The expression “essentially consisting of” when used in connection with chain
 5 (R_{OA}) is hereby understood to indicate that said chain (R_{OA}) may comprise, in addition
 to the listed recurring units, impurities, defects or spurious groups in a minor amount
 (e.g. < 5 % moles, wrt to total amount of recurring units), these impurities, defects or
 spurious groups having generally no peculiar effect on properties of chain (R_{OA}).

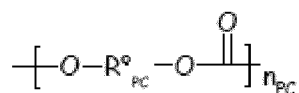
Preferred chains (R_{OA}) according to the invention are polyoxypropylene chains.

10 Chain (R_{OA}) has a number average molecular weight (M_n) typically ranging from
 500 to 10,000, preferably from 500 to 5,000.

Polycarbonate chains (R_{PC})

As intended herein, a polycarbonate chain [herein after otherwise referred to as
 chain (R_{PC})] consists of repeating units [units (U_{PC})] of formula:

15 (U_{PC})



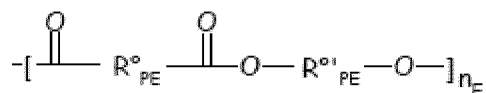
wherein R[°]_{PC} represents:

- a straight or branched alkylene chain, optionally comprising one or more cycloalkyl,
 divalent cycloalkyl group, aryl or arylene group as defined above, and wherein n_{PC} is an
 integer such that the polycarbonate chain has a number average molecular weight (M_n)
 20 typically ranging from 500 to 10,000, preferably from 500 to 5,000.

Polyester chains (R_{PE})

As intended herein, a polyester chain [herein after otherwise referred to as
 chain (R_{PE})] comprises recurring units [units (U_E)] of formula:

(U_E)



25 wherein each of R[°]_{PE} and R^{°'}_{PE}, equal to or different from one another, represents
 independently a straight or branched alkylene chain, optionally comprising one or more

cycloalkyl, divalent cycloalkyl group, aryl or arylene group as defined above, and wherein n_E is an integer such that the chain (R_{PE}) has a number average molecular weight (M_n) typically ranging from 500 to 10,000, preferably from 500 to 5,000.

According to a preferred embodiment, chain (R) of polymer (P1) is a chain (R_S) as defined above, preferably a chain (R_{S-I}).

Polybutadiene chains (R_{PBD})

As intended herein, a polybutadiene chain [herein after otherwise referred to as chain (R_{PBD})] is a chain comprising recurring units derived from 1,3-butadiene monomer, whereas the said recurring units may be formed by connecting the 1,3-butadiene monomers end-to-end, so-called 1,4-addition polymerisation, either in *cis* or *trans* configuration, yielding, respectively, 1,4-*cis* or 1,4-*trans* units, or by connecting 1,3-butadiene monomers via 1,2-addition polymerization, so providing 1,2-*vinyl* units.

The chain (R_{PBD}) may comprise recurring units derived from olefins and dienes other than 1,3-butadiene monomer, being nevertheless understood that chains (R_{PBD}) whereas 1,3-butadiene is the predominant monomer (e.g. at least 60 % moles, preferably at least 80 % moles, even more preferably 90 % moles) are preferred. Most preferably, chain (R_{PBD}) essentially consists of a sequence of recurring units derived from 1,3-butadiene.

Groups E1 and E1'

End groups E1 and E1' typically comprise at least one carboxylic acid group, phosphonic acid group or sulfonic acid group, said at least one acid group comprising at least one hydroxyl group in its protonated form, so that it is capable to form an anionic group via acid/base reaction with the at least one ionisable amino group at one of the ends of polymer (P2). E1 and E1' can be equal to or different from one another. Preferably, E1 and E1' are equal to one another.

The polymer (P1) may comprise from two to six end groups or more. According to a preferred embodiment of the present invention, the polymer (P1) comprises four acid end groups as defined above.

Preferably, groups E1 and E1' comply with formula (E1-A) here below:

(E1-A) -B1-E_A

wherein:

- B1 represents a chemical bond or a straight or branched alkylene chain, said alkylene chain preferably comprising from 1 to 20 carbon atoms, and optionally bearing one or more halogen atoms, one or more further -E_A groups and/or optionally comprising one or more heteroatoms or moieties independently selected from:

- 5 - cycloalkylene and arylene groups as defined above, -O-, -S-, -OC(O)O-, -OC(O)NH-, -OC(O)S-, -SC(O)S-, -NHC(O)NH- and -NHC(S)NH

and

- E_A represents a -COOH, a -P(O)(OR_{EA})₂ or a -S(O)₂OH group, wherein one of R_{EA} is hydrogen and the other one is hydrogen or straight or branched alkyl, preferably C₁-C₄ alkyl.

In a preferred embodiment, E_A is a -COOH group.

POLYMER (P2)

Polymer (P2) can be represented with formula (P2) here below:



15 wherein:

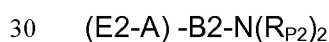
- R is a polymer chain as defined above and
- E2 and E2', equal to or different from one another, are end groups each comprising at least one ionisable amino group.

Groups E2 and E2'

20 End groups E2 and E2' typically comprise at least one ionisable primary, secondary or tertiary amino group. Groups E2 and E2' can be equal to or different from one another; preferably, groups E2 and E2' are equal to one another. "Ionisable primary, secondary or tertiary amino group" means that the amino group is in its free form, so that it is capable to form a cationic group via acid/base reaction with the at least one a ionisable acid group at one of the ends of polymer (P1).

The polymer (P2) may comprise from two to six or more end groups. According to a preferred embodiment of the present invention, the polymer (P2) comprises two amino end groups as defined above.

Preferably, groups E2 and E2' comply with formula (E2-A) here below:



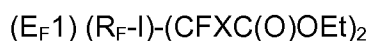
wherein:

- B2 represents a chemical bond or a straight or branched alkylene chain, said alkylene chain preferably comprising from 1 to 20 and optionally bearing one or more halogen atoms, one or more further $-N(R_{P2})_2$ groups and optionally comprising one or more heteroatoms or moieties independently selected from:

- 5 - cycloalkylene and arylene groups as defined above;
 $-N(R_{P2})_2$ wherein R_{P2} represents hydrogen or straight or branched alkyl, preferably C_1 - C_4 alkyl, more preferably methyl;
 $-O-$, $-S-$, $-OC(O)O-$, $-OC(O)NH-$, $-OC(O)S-$, $-SC(O)S-$, $-NHC(O)NH$ and $-NHC(S)NH$
 and
 10 - R_{P2} represents hydrogen or straight or branched alkyl, preferably C_1 - C_4 alkyl.

Polymers (P1) and (P2) wherein chain (R) is a chain (R_F) [herein after polymers (P_{F1}) and (P_{F2})]

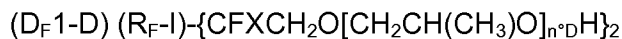
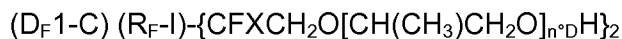
Polymers (P_{F1}) and (P_{F2}) can be prepared according to methods known in the art for the synthesis of PFPEs. In particular, the synthesis of polymers (P_{F1}) and (P_{F2})
 15 wherein chain (R_F) is a chain of formula (R_F-I) can be carried out by oxypolymerization of fluoroolefins, followed by conversion of a resulting $-CFXC(O)F$ terminated polymer ("acyl fluorideterminated polymer", wherein X is as defined above) into the corresponding ethyl ester of formula (E_{F1}):



20 Ester (E_{F1}) can be either hydrolyzed to provide an acid polymer (P_{F1}) wherein E and E' represent $-CFXC(O)OH$ [herein after (P_{F1-A})] or reduced to the corresponding PFPE diol ["diol (D_{F1})] of formula (R_F-I)-(CFXCH₂OH)₂ [herein after "PFPE diol (D_{F1-A})"]. The reduction of ester (E_{F1}) can be carried out according to methods known in the art, using reducing agents such as NaBH₄, or by catalytic hydrogenation,
 25 as disclosed, for example, in US 6509509 A (AUSIMONT S.P.A.) 7/5/2001, US 6573411 (AUSIMONT S.P.A.) 11/21/2002, WO 2008/122639 A (SOLVAY SOLEXIS S.P.A.) 10/16/2008.

Polymer (P_{F1-A}) can be used as such in the manufacture of compositions (C).

Diols (D_{F1-A}) can be reacted with alkylene oxides, typically ethylene oxide and
 30 propylene oxide, in the presence of a base, to provide further diols (D_{F1-B}) - (D_{F1-D}) of formulae:



wherein $n^{\circ}D$ is a positive number, preferably ranging from 1 to 10, more preferably
 5 ranging from 1 to 5. Diols (D_F1-B) - (D_F1-D) can also be used as precursors for
 polymers (P_F1) and (P_F2), as explained below in greater detail.

Diols (D_F1-A) and (D_F1-B) with a chain (R_F-III) and wherein in (D_F1-B) $n^{\circ}D$ ranges
 from 1 to 2 are available from Solvay Specialty Polymers Italy S.p.A. with the
 tradename Fomblin® Z DOL. Other diols (D_F1-B) - (D_F1-D) can be obtained following
 10 the teaching of WO2014090649 (SOLVAY SPECIALTY POLYMERS ITALY SPA).

Throughout the present application, ester (E_F1), diols (D_F1) and polymers (P_F1)
 and (P_F2) are visually represented as bifunctional compounds. However, it is known to
 a person skilled in the art that ester (E_F1) and diols (D_F1) such are always obtained as
 mixtures comprising the corresponding mono-functional and neutral esters or alcohols
 15 which form in the oxypolymerization reaction, i.e. compounds terminating with
 (per)haloalkyl groups at one or both ends, typically C_1 - C_3 perfluoroalkyl groups.
 Ester (E_F1) and diols (D_F1) are thus characterized by an average functionality (F) as
 defined above; the higher the average functionality, the higher the number of
 bifunctional species. As a consequence, polymers (P_F1) and (P_F2) obtained from
 20 ester (E_F1) or from diols (D_F1) are also in admixture with corresponding polymers
 wherein one end of chain (R_F) bears a (per)haloalkyl group and with neutral
 compounds present in the (E_F1) or diol (D_F1) used as starting material. Usually, neutral
 compounds that comprise (per)haloalkyl groups at both ends are present in an amount
 lower than 0.04% on a molar basis. For the purpose of the present invention,
 25 ester (E_F1), diols (D_F1) having an average functionality (F) higher than 1, preferably of
 at least 1.5 can be used.

PFPE ester (E_F1) and diols (D_F1) can be used as precursors for the synthesis of
 polymers (P_F1) and (P_F2) with suitable reaction partners, according to methods known
 in the art for the manufacture of PFPE derivatives.

For example, PFPE ester (E_F1) can be used as precursor for polymers (P_F1) or (P_F2) wherein groups ($E1-A$) and ($E2-A$) respectively comply with formulae ($E1-Aa$), ($E1-Ab$), ($E2-Aa$), ($E2-Ab$) herein below:

($E1-Aa$) $-CF_2C(O)NH-B1^*-E_A$

5 ($E1-Ab$) $-CF_2C(O)O-B1^*-E_A$

($E2-Aa$) $-CF_2C(O)NH-B2^*-N(R_{P2})_2$

($E2-Ab$) $-CF_2C(O)O-B2^*-N(R_{P2})_2$

wherein:

- E_A and R_{P2} are as defined above and

10 - $B1^*$ and $B2^*$ represent straight or branched alkylene chains, said alkylene chain preferably comprising from 1 to 10 carbon atoms and optionally bearing one or more halogen atoms, and/or optionally comprising one or more heteroatoms or moieties independently selected from:

- cycloalkylene and arylene groups as defined above;

15 -O-, -S-, -OC(O)O-, -OC(O)NH-, -OC(O)S-, -SC(O)S-, -NHC(O)NH and -NHC(S)NH-.

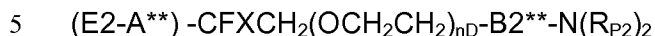
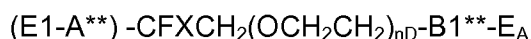
$B1^*$ may also comprise one or more further E_A groups, while $B2^*$ may also comprise one or more further $-N(R_{P2})_2$ groups.

$B2^*$ may also comprise one or more $-N(R_{P2})_2$ moieties.

Polymers (P_F1) or (P_F2) wherein groups ($E1-A$) and ($E2-A$) comply with formulae
20 ($E1-Aa$), ($E1-Ab$), ($E2-Aa$), ($E2-Ab$) as defined above can be manufactured by reacting ester (E_F1) with compounds of formulae $NH_2-B1^*-E_A$ and $HO-B2^*-N(R_{P2})_2$, wherein $B1^*$, E_A , $B2^*$ and $N(R_{P2})_2$ are as defined above.

Should $B1^*$ and $B2^*$ polymers (P_F1) or (P_F2) contain one or more of the
aforementioned heteroatoms or moieties, end groups ($E1-Aa$), ($E1-Ab$), ($E2-Aa$),
25 ($E2-Ab$) can also be build up by subsequent reactions of ester (E_F1) with suitable
reaction partners. For example, a polymer (P_F1) wherein group ($E1-Aa$) comprises a
-NHC(O) moiety can be obtained by reacting ester (E_F1) first with a diamine and then
with an acid comprising two E_A groups. A polymer (P_F1) wherein group ($E1-Ab$)
comprises one or more $-O-C(O)-NH$ moieties can be obtained by reacting ester (E_F1)
30 first with a diol and then with a diisocyanate.

PFPE diols (D_F1) can be used, for example, as precursors of polymers (P_F1) and (P_F2) wherein groups (E1-A) and (E2-A) respectively comply with the formulae listed below:



in which X, E_A and R_{P2} are as defined above and nD is 0 or a positive number, preferably from 1 to 10, more preferably from 1 to 5, while $B1^{**}$ and $B2^{**}$ represent a chemical bond or straight or branched alkylene chains, said alkylene chains preferably comprising from 1 to 10 carbon atoms and optionally bearing one or more halogen
10 atoms, and/or comprising one or more heteroatoms or moieties independently selected from:

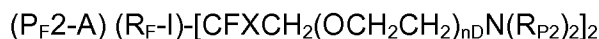
-cycloalkylene and arylene groups as defined above;

-O-, -S-, -OC(O)O-, -OC(O)NH-, -OC(O)S-, -SC(O)S-, -NHC(O)NH- and -NHC(S)NH-.

$B1^{**}$ may also comprise one or more further E_A groups, while $B2^{**}$ may also
15 comprise one or more further $-N(R_{P2})_2$ groups.

$B2^{**}$ may also comprise one or more $-N(R_{P2^*})$ - moieties.

For example, starting from a PFPE diol (D_F1-A) or (D_F1-B), polymers (P_F2) can be obtained complying with formula (P_F2-A):



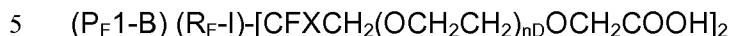
20 in which R_{F-I} , X, R_{P2} and nD are as defined above.

Conveniently, polymers (P_F2-A) can be obtained by converting a PFPE diol (D_F1-A) or (D_F1-B) into the corresponding sulfonic ester (like the trifluoromethanesulfonyl, perfluorobutylsulfonyl or p-toluenesulfonyl ester) and then reacting the sulfonic ester with an amine of formula $HN(R_{P2})_2$, following the procedure
25 disclosed in US 6984759 B (SOLVAY SOLEXIS SPA).

Amines (P_F2-A) can be used as such in the manufacture of compositions (C) or can be used as precursors of other polymers (P_F1) or (P_F2) by reaction with suitable reaction partners according to methods known in the art. For example, convenient polymers (P_F1) can be obtained by reaction of an amine(P_F2-A) with an aromatic
30 polycarboxylic acid or a derivative thereof able to form amido bonds, for example with trimellitic acid or a derivative thereof, such as trimellitic anhydride. Good results were

obtained using a polymer (P_{F1}) obtained by reacting an amine (P_{F2-A}) of formula (R_{F-III})-(CF₂CH₂NH₂)₂ with trimellitic anhydride.

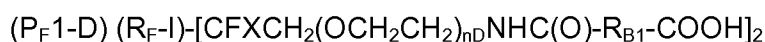
A further example of polymer which can be obtained from a PFPE diol (D_{F1}) is a polymer (P_{F1}) complying with formula (P_{F1-B}):



wherein (R_{F-I}), X and nD are as defined above by reaction of diol (D_{F1}) with an ester of a 2-halo-acetic acid, for example with 2-chloroethyl acetate. The reaction can be conveniently carried out as disclosed in US 7252740.

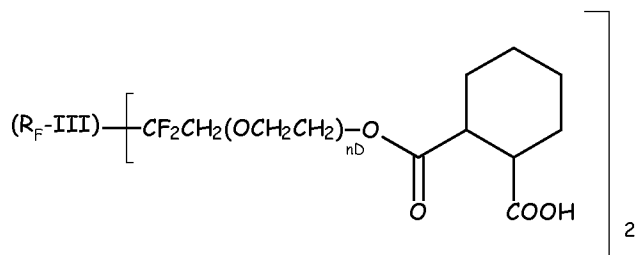
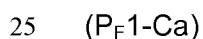
Polymer (P_{F1-B}) can be used as such in the manufacture of compositions (C) or it
10 can in turn be used as precursor for the manufacture of other polymers (P_{F1}) and (P_{F2}).

Further convenient polymers (P_{F1}) for the preparation of compositions (C) are those complying with the following formulae (P_{F1-C}) and (P_{F1-D}) herein below:



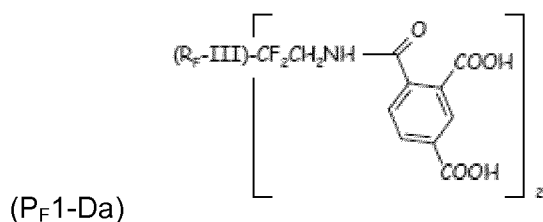
15 wherein R_{F-I}, X and nD are as defined above and R_{B1} is C₁-C₁₀ straight or branched alkylene, C₄-C₆ cycloalkylene as defined above or C₅-C₆ arylene as defined above, optionally comprising one or more -COOH groups. Preferably, chain (R_{F-I}) is a chain (R_{F-III}) as defined above, X is F, nD is 0 or ranges from 1 to 5 and R_{B1} is selected from *o*-, *m*-, *p*-cyclohexylene and *o*-, *m*-, *p*-phenylene. Polymers (P_{F1-C}) and (P_{F1-D}) can be
20 obtained from diols (D_{F1-A}), (D_{F1-B}) and from (P_{F2-A}) by reaction with a diacid of formula HOOC-R_{B1}-COOH wherein R_{B1} is as defined above or with a reactive derivative thereof, like a halide or an anhydride.

A convenient example of compound (P_{F1-C}) complies with formula (P_{F1-Ca}) here below:



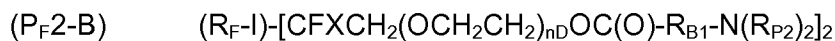
with group (R_{F-III}) and nD possessing the meaning as explained above.

A convenient example of polymer (P_{F1-D}) complies with formula (P_{F1-Da}) here below:

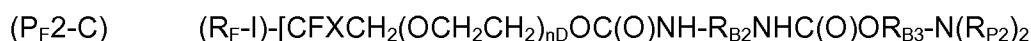


with group (R_{F-III}) possessing the meaning as explained above.

Further convenient examples of polymers (P2) for the preparation of compositions (C) are those complying with the following formulae (P_{F2-B}) and (P_{F2-C})



wherein R_{F-I}, X, nD and N(R_{P2})₂ and R_{B1} are as defined above.



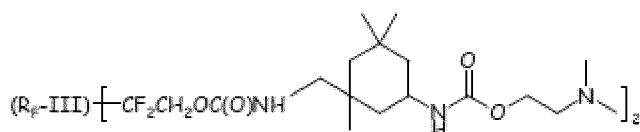
wherein R_{F-I}, X, nD and R_{P2} are as defined above, R_{B2} is straight or branched C₁-C₆ alkylene chain optionally comprising a C₄-C₆ cycloalkylene group as defined above or a C₅-C₆ arylene group as defined above and R_{B3} is C₂-C₁₀ straight or branched alkylene, optionally interrupted by one or more -N(RP2*)- groups as defined above.

Polymers (P_{F2-B}) can be obtained by reaction of a diol (D_{F1-A}) or (D_{F1-B}) with an amidoacid or with a reactive derivative thereof, such as a halide or anhydride.

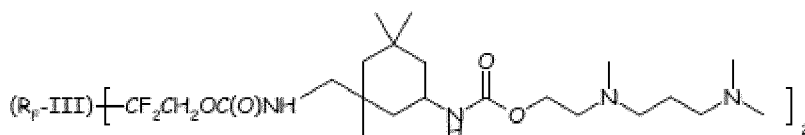
Polymers (P_{F2-C}) can be obtained by reaction of a diol (D_{F1-A}) or (D_{F1-B}) with a diisocyanate and an aminoalcohol.

Convenient examples of polymers (P_{F2-C}) comply with the formulae (P_{F2-Ca}) and (P_{F2-Cb}) here below:

(P_{F2-Ca})



(P_{F2-Cb})

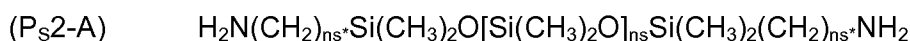


Polymers (P1) and (P2) wherein chain (R) is a chain (R_S) [herein after polymers

(P_{S1}) and (P_{S2})

Polymers (P_{S1}) and (P_{S2}) are available on the market, or can be obtained according to methods known in the art. In particular, polymers (P_{S1}) and (P_{S2}) wherein Ra_s and Rb_s are both methyl can be obtained by hydrolysis of dimethyl chlorosilane to provide a dihydroxy-terminated poly(dimethylsiloxane) and derivatization of the same according to methods known in the art for the manufacture of amines and acids.

A convenient example of polymer (P_{S2}) is a polydimethyl siloxane of formula (P_{S2}-A) here below:



in which ns is a positive number selected in such a way that the number average molecular weight (M_n) of the [Si(CH₃)₂O]_{ns} chain ranges from 500 to 10,000, preferably from 500 to 5,000 and ns* is 0 or a positive number equal to or higher than 1, preferably ranging from 1 to 10. Polymers (P_{S2}-A) wherein ns* is 3 is notably commercially available from Aldrich®, with various molecular weight (M_n) of the [Si(CH₃)₂O]_{ns} chain.

Polymer (P_{S2}-A) can be used as such in the manufacture of compositions (C) or can be used as precursor for the manufacture of other polymers (P_{S1}) and (P_{S2}).

For instance, convenient polymers (P_{S1}) complying with the following formula (P_{S1}-A) here below:

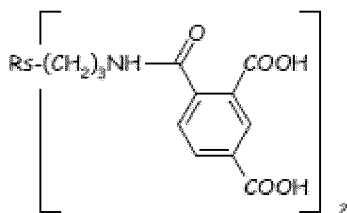


wherein ns* is 0 or a positive number equal to or higher than 1, preferably ranging from 1 to 10, and R_{B1} is a C₁-C₁₀ straight or branched alkylene, C₄-C₆ cycloalkylene as defined above or C₅-C₆ arylene, and preferably is selected from *o*-, *m*-, *p*-cyclohexylene and *o*-, *m*-, *p*-phenylene, as already defined above, and wherein R_S* is a chain of formula -Si(CH₃)₂O[Si(CH₃)₂O]_{ns}Si(CH₃)₂-, with ns is a positive number selected in such a way that the number average molecular weight (M_n) of the [Si(CH₃)₂O]_{ns} chain ranges from 500 to 10,000, preferably from 500 to 5,000, as defined above,

can be obtained by reaction of polymer (P_{S2}-A) with an acid of formula HOOC-R_{B1}-COOH, wherein R_{B1} is as defined above, or with a reactive derivative thereof, such as a halide or anhydride.

A convenient example of polymer (P_S1-A) is one complying with formula (P_S1-Aa) here below:

(P_S1-Aa)



wherein R_S is a chain of formula -Si(CH₃)₂O[Si(CH₃)₂O]_{ns}Si(CH₃)₂-, with ns is a positive
 5 number selected in such a way that the number average molecular weight (M_n) of the [Si(CH₃)₂O]_{ns} chain ranges from 500 to 10,000, preferably from 500 to 5,000, as defined above.

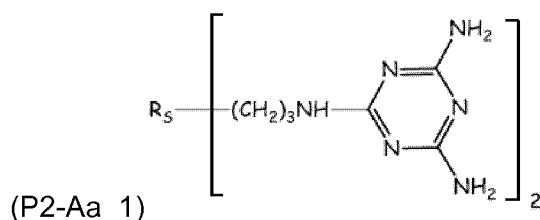
For instance, convenient polymers (P_S2-A) complying with the following formula (P_S2-Aa) here below:

10 (P_S2-Aa) R^{*}_S-[(CH₂)_{ns*}NH-R_{B2}-(NH₂)_{xb}]₂

wherein ns* is 0 or a positive number equal to or higher than 1, preferably ranging from 1 to 10, and R_{B2} is a C₁-C₁₀ straight or branched alkylene, C₄-C₆ cycloalkylene as defined above or C₅-C₆ arylene or heteroarylene, and preferably is selected from *o*-, *m*-, *p*-cyclohexylene and *o*-, *m*-, *p*-phenylene, as already
 15 defined above or from any of heteroarylene groups, e.g. divalent triazine, oxazole, benzoxazole, pyridine groups, xb is an integer of 1 to 3, preferably equal to 2, and wherein R^{*}_S is a chain of formula -Si(CH₃)₂O[Si(CH₃)₂O]_{ns}Si(CH₃)₂-, with ns is a positive number selected in such a way that the number average molecular weight (M_n) of the [Si(CH₃)₂O]_{ns} chain ranges from 500 to 10,000,
 20 preferably from 500 to 5,000, as defined above,

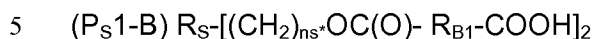
can be obtained by reaction of polymer (P_S2-A) with an halide of formula X-R_{B2}-(NH₂)_{xb}, wherein R_{B2} is as defined above.

A preferred example of polymer (P2-Aa) is one complying with formula (P2-Aa_1) here below:



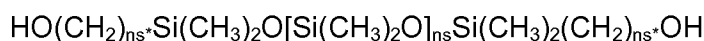
wherein R_S has the meaning as indicated above.

A further convenient example of polymer (P_{S1}) is a polymer complying with formula (P_{S1-B}):



wherein ns^* and R_{B1} are as defined above and R_S is a chain of formula $-\text{Si}(\text{CH}_3)_2\text{O}[\text{Si}(\text{CH}_3)_2\text{O}]_{ns}\text{Si}(\text{CH}_3)_2-$, with ns is a positive number selected in such a way that the number average molecular weight (M_n) of the $[\text{Si}(\text{CH}_3)_2\text{O}]_{ns}$ chain ranges from 500 to 10,000, preferably from 500 to 5,000, as defined above.

10 Polymer (P_{S1-B}) can be obtained by reaction of a dihydroxy-terminated silane precursor of formula:

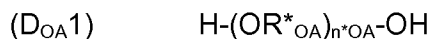


by reaction with an acid of formula $\text{HOOC}-R_{B1}-\text{COOH}$, wherein R_{B1} is as defined above, or with a reactive derivative thereof, such as a halide or anhydride.

15 Polymers ($P1$) and ($P2$) wherein chain (R) is a chain (R_{OA}) [herein after polymers ($P1_{OA}$) and ($P2_{OA}$)]

Polymers ($P1_{OA}$) and ($P2_{OA}$) are available on the market or can be obtained according to methods known in the art. Preferred examples of polymers ($P1_{OA}$) and ($P2_{OA}$) are those comprising a polyoxyethylene chain, a polyoxypropylene chain, a
20 polytetramethylene glycole chain, or a chain comprising a mixture of any of oxyethylene, oxypropylene, oxytetramethylene units.

For example, starting from a polyoxyalkylene diol of formula (D_{OA1}):

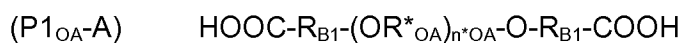


wherein each of R^*_{OA} , equal to or different from each other, is, independently at each
25 occurrence, a straight or branched alkylene divalent group, typically an ethylene, propylene or a tetramethylene group, and n^*_{OA} is an integer selected in such a way as the number average molecular way ranges from 500 to 5,000, polymers (P_{OA1}) and (P_{OA2}) can be obtained by methods know in in the art by reaction with suitable reaction

partners. A diol (D_{OA-1}) wherein R^*_{OA} is substantially at each occurrence an ethylene group is commercially available from Aldrich®.

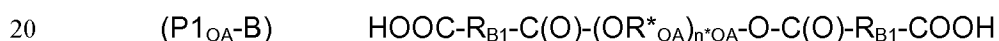
The expression "substantially at each occurrence" in connection with moieties R^*_{OA} of polymers ($P1_{OA}$) or ($P2_{OA}$) is meant to indicate that minor amounts (i.e. < 1 % in moles) of groups R^*_{OA} other than those specified may be present as impurities, defects or spurious components, being understood that these impurities, defects or spurious component may not substantially affecting the properties of chain R^*_{OA} .

For example, polymers ($P1_{OA}$) complying with formula ($P1_{OA-A}$):



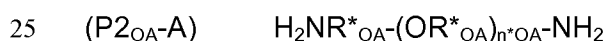
wherein R_{B1} , R^*_{OA} and n^*_{OA} are as defined above, can be obtained by reaction of a diol (D_{OA1}) with a halo-alkyl or haloalkylene acid $X^\circ-R_{B1}-COOH$ wherein X° is halogen and R_{B1} is a C_1 - C_{10} straight or branched alkylene, C_4 - C_6 cyloalkylene as defined above or C_5 - C_6 arylene, and preferably is selected from *o*-, *m*-, *p*-cyclohexylene and *o*-, *m*-, *p*-phenylene, as already defined above, or with a corresponding halide or ester. For example, a polymer ($P1_{OA-A}$) wherein R_{B1} is $-CH_2-$ can be obtained by reaction of diol (D_{OA1}) with a 2-halo acetic acid or halide or ester thereof, such as with 2-chloroacetic acid ethyl ester. A polymer ($P1_{OA-A}$) wherein R^*_{OA} is substantially at each occurrence an ethylene group and R_{B1} is $-CH_2-$ is available from Aldrich®.

Polymers ($P1_{OA}$) complying with formula ($P1_{OA-B}$):



can be obtained by reaction of a diol (D_{OA-1}) with a diacid of formula $HOC(O)-R_{B1}-COOH$, wherein R_{B1} is as defined above, or with a reactive derivative thereof, such as an halide or anhydride.

Polymers ($P2_{OA}$) complying with formula ($P2_{OA-A}$):



wherein R^*_{OA} and n^*_{OA} are as defined above can be obtained from a diol (D_{OA1}) by conventional reactions for the replacement of the hydroxyl group into an amino group. A polymer ($P2_{OA-A}$) wherein R^*_{OA} is substantially at each occurrence a propylene group of formula $-CH_2-CH_2-$ is available on the market from Aldrich®.

According to an embodiment of the invention, at least one of the following conditions (preferably both conditions) are satisfied:

(1) polymer (P1) complies with formula (P1_{OA}-A);

(2) polymer (P2) complies with formula (P2_{OA}-A)

wherein:



in which:

- each of R^{*}_{OA}, equal to or different from each other, is, independently at each occurrence, a straight or branched alkylene divalent group, typically an ethylene, propylene or a tetramethylene alkylene group,

10 - n^{*}_{OA} is an integer selected in such a way as the number average molecular weight ranges from 500 to 5,000, and

- R_{B1} is C₁-C₁₀ straight or branched alkylene, C₄-C₆ cycloalkylene or C₅-C₆ arylene, optionally comprising one or more -COOH groups.

Preferably, the polymer (P1) and (P2) in composition (C) have respectively the
15 formulae (P1_{OA}-A) and (P2_{OA}-A) as defined above, R^{*}_{OA} is substantially at each occurrence a propylene group of any of formulae -CH₂CH₂CH₂-, -CH₂-CH(CH₃)- and -CH(CH₃)-CH₂-, and R_{B1} comprises one -COOH group.

Polymers (P1) and (P2) wherein chain (R) is a chain (R_{PC}) [herein after polymers (P1_{PC}) and (P2_{PC})]

20 Polymers (P1_{PC}) and (P2_{PC}) can be manufactured by reaction of a diol of formula (D^o_{PC1}):

(D^o_{PC1}) HO-(R^o_{PC})-OH wherein (R^o_{PC}) is a straight or branched alkylene chain, preferably a C₂ - C₁₀ alkylene chain, optionally comprising ethereal oxygen atoms; and a carbonate, typically diphenylcarbonate, to provide a dihydroxy-terminated
25 polycarbonate of formula (D_{PC1}):



wherein R^o_{PC} and n_{PC} are as defined above; followed by subsequent reaction with suitable reactive compounds according to methods known in the art to provide polymers (P1_{PC}) and (P2_{PC}).

Dihydroxy-terminated polycarbonates (D_{PC1}) having an average number molecular weight (M_n) ranging from 500 to 3,000 are notably commercially available, for example, from UBE as Ethernacoll® PH.

For example, convenient polymers ($P1_{PC}$) can be obtained by reaction of (D_{PC1})
 5 with a halo-alkyl or haloalkylene acid ester, preferably with an acid of formula $X^\circ-R_{B1}-COOH$ wherein X° is halogen and R_{B1} is as defined above, or an ester thereof, for example with 2-chloro acetic acid ethyl ester.

Further convenient polymers ($P1_{PC}$) [polymers ($P1_{PC-B}$)] can be manufactured by reaction of diol (D_{PC1}) with an acid of formula $HOOC-R_{B1}-COOH$ wherein R_{B1} is as
 10 defined above, or with a reactive derivative thereof, such as a halide or an anhydride.

Convenient polymers ($P2_{PC}$) complying with formula ($P2_{PC-A}$):



wherein R_{P2} , R°_{PC} and n_{PC} are as defined above can be manufactured from diol (D°_{PC1})
 by converting the terminal hydroxyl groups into amino groups according to methods
 15 known in the art.

Polymers ($P2_{PC-A}$) wherein at least one of R_{P2} is hydrogen can be used as precursors of further polymers ($P1_{PC}$) and ($P2_{PC}$). For example, polymers of formula ($P1_{PC-C}$):

($P1_{PC-C}$) $HOOC-R_{B1}(O)C-R_{P2}N-R^\circ_{PC}-O[C(O)O-R^\circ_{PC}O]_{n_{PC}-1}R^\circ_{PC}-NR_{P2}C(O)R_{B1}-COOH$
 20 can be obtained by reaction with a diacid of formula $HOOC-R_{B1}-COOH$ wherein R_{B1} is as defined above or with a reactive derivative thereof, such as a halide or anhydride.

Polymers (P1) and (P2) wherein chain (R) is a chain (R_{PE}) [herein after polymers ($P1_{PE}$) and ($P2_{PE}$)"]

Polymers ($P1_{PE}$) and ($P2_{PE}$) can be prepared according to methods known in the
 25 art starting from a polyester diol [diol (D_{PE1})]. Diols (D_{PE1}) can be obtained by polycondensation of dicarboxylic acids or lactams and diols. Polyester diols are commercially available; for example, polycaprolactone diols are available from Perstop under the tradename Capa™. Convenient polymers ($P1_{PE}$) can be obtained by reaction of a diol (D_{PE1}) with a halo-alkyl or haloalkylene acid ester, preferably with an acid of
 30 formula $X^\circ-R_{B1}-COOH$ wherein X° is halogen and R_{B1} is as defined above, or an ester thereof, for example with 2-chloro acetic acid ethyl ester. Further convenient

polymers (P_{PE1}) can be obtained by reaction of a diol (D_{PE1}) with an acid of formula $HOOC-R_{B1}-COOH$ wherein R_{B1} is as defined above, or with a reactive derivative thereof, such as a halide or anhydride

Polymers (P_{PE2}) with $-N(R_{P2})_2$ end groups can be obtained from diols (D_{PE1}) according to methods known in the art for the replacement of the hydroxyl group with an amino group. Polymers (P_{PE2}) thereby obtained can be in turn used as precursors for other polymers (P_{PE1}) or (P_{PE2}) by reaction with suitable precursors according to methods known in the art.

Polymers (P1) and (P2) wherein chain (R) is a polybutadiene chain (R_{PBD}) [herein after "polymers (P_{PBD1}) and (P_{PBD2})"]

Polymers (P_{PBD1}) and (P_{PBD2}) can be obtained from dihydroxy terminated polybutadienes according to methods disclosed in the art.

Such polybutadienes are available, for example, from Cray Valley; one of them is marketed as Poly bd[®] R-45HTLO.

Convenient polymers (P_{PBD1}) can be obtained by reaction of a dihydroxy terminated polybutadiene [diol (D_{PBD1})] with a halo-alkyl or haloalkylene acid ester, preferably with an acid of formula $X^\circ-R_{B1}-COOH$ wherein X° is halogen and R_{B1} is as defined above, or an ester thereof, for example with 2-chloro acetic acid ethyl ester. Further convenient polymers (P_{PBD1}) can be obtained by reaction of a dihydroxy terminated polybutadiene with an acid of formula $HOOC-R_{B1}-COOH$ wherein R_{B1} is as defined above, or a reactive derivative thereof.

Polymers (P_{PBD2}) with $-N(R_{P2})_2$ end groups can be obtained from a dihydroxy terminated polybutadiene (D_{PBD1}) according to methods known in the art for the replacement of the hydroxyl groups with an amino group. Polymers (P_{PBD2}) thereby obtained can be in turn used as precursors for other polymers (P_{PBD1}) or (P_{PBD2}) by reaction with suitable precursors according to methods known in the art.

Composition (C) and preparation thereof

The composition (C) for preparing the coating layer (2) of the present multilayer electrode assembly comprises the ionisable amorphous polymers having a low T_g described above, i.e. at least one polymer (P1) and at least one polymer (P2).

By "low T_g " according to this invention is meant a T_g lower than -35°C , preferably

ranging from -35°C to 120°C.

T_g is measured according to ASTM D3418 at midpoint by differential scanning calorimetry (DSC) with a scan rate at 20°C/min.

Such T_g is a critical feature for enabling the three-dimensional network formed by polymer (P1) and polymer (P2) to cope with the requirements of an adaptative coating for preventing damages due to dendrites formation in the metal electrode layer.

The equivalent ratio between polymer (P1) and polymer (P2) is advantageously such to maximize ionic bonding between acid groups of polymer (P1) and amine groups of polymer (P2). The composition (C) will hence comprise an overall amount of acid groups of polymer (P1) and an overall amount of amine groups of polymer (P2) which is substantially similar. In other terms, the ratio between the equivalents of polymer (P1) and the equivalents of polymer (P2) in said composition (C) will tend to be close to unitary, and will preferably range from 1.1 to 0.9. Most preferably the equivalent ratio is about 1.

For the avoidance of doubt, the ratio between the equivalents of polymer (P1) and the equivalents of polymer (P2) is referred to the acid/base reaction between the at least one ionisable acid group in each end group of polymer (P1) and the at least one ionisable amino group in each end of polymer (P2).

By the term “at least a polymer (P1)” is meant in the present invention that only one or more polymers (P1) may be used in the preparation of the present composition (C). “More polymers” means that polymers (P1) can be used differing from one another in the nature of units (U) of the chain (R), in the nature of end groups (E1) and (E1’), in the molecular weight, or in a plurality of the said features.

By the term “at least a polymer (P2)” is meant in the present invention that only one or more polymers (P2) may be used in the preparation of the present composition (C). “More polymers” means that polymers (P2) can be used differing from one another in the nature of chain (R), in the nature of end groups (E2) and (E2’), in the molecular weight, or in a plurality of the said features.

According to a preferred embodiment of the present invention one polymer (P1) and one polymer (P2) are used in the manufacture of the composition (C); chain (R) of polymer (P1) can be the same or different from chain (R) of polymer (P2). Notably,

chain (R) of polymer (P1) may comprise recurring units of same nature as chain (R) of polymer (P2) and may possess same, similar or different molecular weight.

According to a preferred embodiment, chain (R) of both polymer (P1) and polymer (P2) is a polyoxyalkylene chain as defined above, preferably a chain
5 polyoxypropylene, as defined above.

According to a preferred embodiment of the present invention, the compositions (C) comprise one polymer (P1) and one polymer (P2) wherein one of them comprises two ionisable end groups and the other one comprises four end groups.

10 According to one of most preferred embodiments, the present compositions (C) comprise one polymer (P1) having four acidic end groups and one polymer (P2) having two amino end groups.

According to other preferred embodiments of the present invention, the compositions (C) comprise one polymer (P1) and one polymer (P2), wherein both of
15 them comprise four ionisable end groups.

According to another one of most preferred embodiments, the present compositions (C) comprise one polymer (P1) having four acidic end groups and one polymer (P2) having four amino end groups.

Convenient compositions (C) for preparing the coating layer (2) of the present
20 multilayer assembly comprise one polymer (P1) of formula (P1_{OA}-A) as defined above and a polymer (P2) of formula (P2_{OA}-A) as defined above, wherein each of R*_{OA} is substantially at each occurrence a propylene group, and R_{B1} comprises one -COOH group.

Other convenient compositions (C) for preparing the coating layer (2) of the
25 present multilayer assembly comprise one polymer (P1) of formula (P_s1) as defined above and a polymer (P2) of formula (P_s2) as defined above, and preferably one polymer (P1) of formula (P_s1-A) and especially of formula (P_s1-Aa) as defined above and a polymer (P2) of formula (P_s2-Aa) as defined above.

Without being bound to theory, it is believed that when a polymer (P1) and a
30 polymer (P2) are mixed together in the above described equivalent ratio, they form an infinite ionic network characterised by a much higher viscosity than that of the pure

components. The closer to 1 the equivalent ratio between polymer (P1) and polymer (P2) is, the higher is the efficiency in this network formation. Moreover, when at least one of the polymers (P1) or (P2) comprises more than two ionisable end groups, it is believed that a three-dimensional, cross-linked network can be formed, resulting in a higher stability of the polymer coating in the assembly. At the same time, the formation of reversible, non-covalent bonds amongst the polymer molecules in the coating layer can accommodate the volume variation of the metal occurring during charge and discharge of the batteries. Furthermore, without being bound to theory, it is believed that the presence of ionic sites distributed in the polymer coating, promotes the ionic conduction and allows a homogeneous distribution of the ionic charge of the metal, e.g. Li⁺, on the metal electrode surface, thus limiting the dendrite formation.

Process for the preparation of the multilayer assembly

The composition (C) of the layer (2) coated at least a fraction of the first surface of the metal electrode (1) may be prepared by mixing the polymer (P1) with a liquid medium, then adding the polymer (P2) or vice versa. The added polymer may be incorporated as such or pre-mixed in a same or different liquid medium before addition to a liquid medium comprising the other polymer. A liquid medium comprising components of the composition (C) is thus obtained that can be used in accordance with step iii) of the present process for preparing the coating layer (2) in the present multilayer assembly, as described below.

Any conventional mixing techniques, operated by appropriate mixing equipment, may be used to achieve mixing the aforementioned components of the present composition (C). The preparation of this liquid mixture of liquid medium and composition (C) is typically carried out at room temperature.

In the liquid medium obtained in step ii) of the process of the invention, polymer (P1) and polymer (P2) may be, independently from each other, at least partially solubilized in the said medium (L). Otherwise, said polymer (P1) and polymer (P2) may be, independently from each other, dispersed in the said medium (L).

Generally, the medium (L) is a solvent medium, that is to said that medium (L) comprises one or more than one organic solvent as major liquid medium. The

medium (L) typically comprises one or more organic solvents selected from the group consisting of:

- aliphatic, cycloaliphatic or aromatic ethers, more particularly, diethyl oxide, dipropyl oxide, diisopropyl oxide, dibutyl oxide, methyltertbutylether, dipentyl oxide, diisopentyl oxide, ethylene glycol dimethyl ether, ethylene glycol diethyl ether, ethylene glycol dibutyl ether benzyl oxide; dioxane, tetrahydrofuran (THF),
 - glycol ether esters such as ethylene glycol methyl ether acetate, ethylene glycol monoethyl ether acetate, ethylene glycol monobutyl ether acetate,
 - ketones such as acetone, methylethylketone, methylisobutyl ketone, diisobutylketone, cyclohexanone, isophorone,
 - linear or cyclic esters such as methyl acetoacetate, dimethyl phthalate, γ -butyrolactone,
 - linear or cyclic carboxamides such as N,N-dimethylacetamide (DMAC), N,N-diethylacetamide, dimethylformamide (DMF), diethylformamide or N-methyl-2-pyrrolidone (NMP),
 - organic carbonates for example dimethyl carbonate, diethyl carbonate, dipropyl carbonate, dibutyl carbonate, ethylmethyl carbonate, ethylene carbonate, propylene carbonate, vinylene carbonate;
 - organosulfur solvents, such as dimethyl sulfoxide (DMSO) and sulfolane (tetramethylene sulfone);
 - diesters of formula (I_{de}), esteramides of formula (I_{ea}) and diamides of formula (I_{da}):

$$R^1O(O)C-Z_{de}-C(O)OR^2 \text{ (I}_{de}\text{)}$$

$$R^3O(O)C-Z_{ea}-C(O)NR^4R^5 \text{ (I}_{ea}\text{)}$$

$$R^5R^4N(O)C-Z_{da}-C(O)NR^4R^5 \text{ (I}_{da}\text{)}$$
- wherein:
- R¹ and R², equal to or different from each other, are independently selected from the group consisting of C₁-C₃ hydrocarbon groups,
 - R³ is selected from the group consisting of C₁-C₂₀ hydrocarbon groups, and
 - R⁴ and R⁵, equal to or different from each other, are independently selected from the group consisting of hydrogen and C₁-C₃₆ hydrocarbon groups, optionally substituted, being understood that R⁴ and R⁵ might be part of a cyclic moiety including the nitrogen

atom to which they are bound, said cyclic moiety being optionally substituted and/or optionally comprising one or more heteroatoms, and mixtures thereof, and - Z_{de} , Z_{ea} and Z_{da} , equal to or different from each other, are independently linear or branched C_2 - C_{10} divalent alkylene groups.

5 Preferred media (L) are tetrahydrofuran (THF), dimethyl sulfoxide (DMSO) and 1,4-dioxane; and alkylene carbonates, such as ethylene carbonate, propylene carbonate and vinylene carbonate. A further preferred liquid medium is THF. Any person with ordinary skills in the art will select the most appropriate liquid medium depending on the polymers (P1) and (P2) to be used, provided that the selected
10 medium is not reactive with the metal electrode (1).

To the sake of ensuring suitable coated weight on the substrate, the liquid mixture of medium (L) and composition (C) generally possesses a liquid viscosity of at least 100, preferably at least 250, more preferably at least 500 mPa.sec, when measured at 22°C, using a Brookfield viscometer operating at 10 rpm.

15 Conversely, in order to ensure acceptable liquid processability during coating via different coating techniques, it is generally preferred for the liquid mixture of medium (L) and composition (C) to possess a liquid viscosity of at most 5000 mPa.sec, at most 4700mPa.sec, when measured at 22° C, using a Brookfield viscometer operating at 10 rpm.

20 When a liquid mixture of a medium (L) and composition (C) is used, the amount of polymers (P1) and (P2) in the said liquid mixture may range from 1 to 10% by weight with respect to the total weight of the medium (L) and polymer (P1) and (P2).

From the so obtained liquid mixture of the composition (C) a film coating on the metal electrode (1) may be obtained by known techniques in the art, typically by
25 casting followed by drying of the solvent.

When the liquid mixture of medium (L) and composition (C) is processed by casting, it is typically applied on the metal electrode (1) by spreading onto the metal electrode using standard devices, according to well-known techniques, such as doctor-blade coating, metering rod (or Meyer rod) coating, slot die coating, knife over roll
30 coating, "gap coating", spin coating and the like.

The coating formed on the metal electrode may be then dried by evaporation of

the liquid medium (L) at room temperature and/or by heating until complete evaporation.

The thus obtained final coating film may have a thickness ranging from 0.1 μm to 100 μm , preferably from 0.5 to 50 μm , most preferably from 0.5 to 10 μm , as measured by a micrometer. Particularly preferred are thicknesses of less than 10 μm , so as to minimize adverse barrier to ionic conductivity of the metal electrode.

In a further aspect, this invention provides an electrochemical cell comprising the multilayer electrode assembly as defined above. Preferably, this electrochemical cell is a primary or secondary (rechargeable) lithium battery, most preferably it is a secondary lithium battery.

In still another aspect, the invention relates to a method of making an electrochemical cell comprising assembling the multilayer electrode assembly as defined above with at least one of collector(s), separator, a second electrode, and an electrolyte.

The multilayer electrode assembly can be advantageously assembled as a negative electrode (anode) in combination with a positive electrode (cathode).

The separator may be a polymer gel separator, comprising in a gelled state in the polymer matrix a solution in an organic solvent able to swell the said polymer matrix of an electrolyte. A vinylidene fluoride polymer matrix has been found particularly advantageous for polymer gel separators. As an alternative, the separator may be a porous polymeric structure, possibly a composite porous polymer separator, e.g. based on a polyolefin porous film possibly coated with another polymer matrix (e.g. a vinylidene fluoride polymer coating) which may be soaked with a solution in an organic solvent of an electrolyte.

The electrolyte will be selected depending upon the nature of the multilayer electrode assembly used. When the metal electrode is a lithium electrode, the electrolyte may be selected from the group consisting of LiBF_4 , LiBF_6 , LiClO_4 , LiPF_6 , Lithium trifluoromethanesulfonate (LiCF_3SO_3), Lithium bis(trifluoromethanesulfonyl)imide ($\text{LiC}_2\text{F}_6\text{NO}_4\text{S}_2$ or LiTFSI), lithium trifluoroacetate (LiCF_3CO_2), LiAsF_6 , LiSbF_6 , $\text{LiB}_{10}\text{Cl}_{10}$, lower aliphatic lithium carboxylates, LiAlCl_4 , LiCl , LiBr , LiI , chloroboran lithium, and lithium tetraphenylborate. These electrolytes may be

used either individually or in combinations of two or three or more. In particular, electrolyte for lithium electrode is selected from the group consisting of LiTFSI, LiCF₃SO₃, LiClO₄, LiBF₄ or LiBF₆ and/or LiPF₆.

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.

The invention is described in greater detail in the following experimental section by means of non-limiting examples.

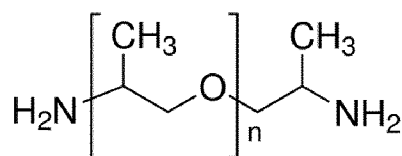
10 EXPERIMENTAL SECTION

Materials and methods

Materials

Triethylamine (TEA), dimethylformamide (DMF), 4-Dimethylaminopyridine (DMAP), trimellitic anhydride were purchased from Aldrich® and used as received.

15 Poly(propyleneglycol)-bis(2-aminopropylether) (Mn 2120, EW 1060) [herein after (P_{PPO}-Am)] was purchased from Aldrich® and was used as received. It is a low viscous liquid characterized by a T_g of -70°C, it contains to amine groups per molecule, and complies with formula:



20 Mn as detailed above. with n being an integer so as to provide for the

Poly(propyleneglycol) (Mn 2000) [herein after (P_{PPO}-OH)] was purchased from Aldrich® and was used as received.

LiCu metal electrode laminate consisting of a Lithium metal electrode assembled on a Copper metal foil was supplied from Honjo Metal Co. Ltd.; it possesses an overall thickness of 30 μm (20 μm of Li metal and 10 μm of Cu foil)

THF Tetrahydrofuran (Sigma Aldrich®) > 99.9%

VC Vinylene Carbonate (Sigma Aldrich®)

NMC Lithium nickel manganese cobalt oxide type TX7Ta was supplied from UMICORE

SuperC65 is a conductive carbon black supplied from Imerys[®] (carbon content > 99.5 % wt)

A solution of LiPF₆ 1M in a mixture of ethylene carbonate/ dimethyl carbonate 1:1 vol:vol was used (Sigma Aldrich[®]) as electrolyte solution.

5 Methods

Analytical procedure for the titration of acid polymers (P1) (direct acid/base titration)

Sample: 1- 3 g (exactly weighed)

Solvent: HFX/IPA 50 /10 ml

10 Titrating agent: tetramethylammonium hydroxide TMAH 0.1M in CH₃OH

Electrode: DG115SC Mettler Toledo

Analytical procedure for basic polymers (P2) (direct acid/base titration)

Sample: 1 -3 g (exactly weighed)

Solvent: HFX/IPA 50 /10 ml

15 Titrating agent: HCl 0.1M in IPA

Electrode: DG115SC Mettler Toledo

Viscosity

Rheological measurements were carried out with a “Dynamic mechanical spectrometer Rheometric ARES” Instrument

20 Geometry: Cone & Plate (25 mm)

Mode: Steady rate sweep test

Shear rate: from 1x10⁻⁰² to 1x10⁺⁰³ (1/s)

Temperature: 25°C

Calorimetry (T_g analysis)

25 The glass transition temperature (T_g) was determined according to ASTM D3418, by means of a Perkin-Elmer DSC 2C Instrument, and reported as midpoint by scans between -160°C and 20°C at a scanning speed of 20°C/min; the low temperature range was calibrated with reagent grade n-hexane.

¹⁹F and ¹H NMR

30 The number average molecular weight (M_n) of the polymers (P1) and (P2), used to calculate the reaction stoichiometry, and polymer structures were determined by

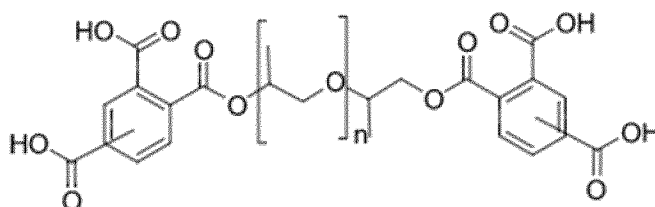
^{19}F -NMR end group analysis. ^{19}F -NMR spectroscopy was also used to determine the a1/a2 ratio. The assignments and the equations used for such determination were those set out in S.Turri, E. Barchiesi, M. Levi, *Macromolecules* 28, 7271 (1995).

GPC

5 Gel permeation Chromatography (GPC) was carried out with a Waters Model 5900 instrument equipped with a set of "Ultrastyrigel" columns using THF at 40°C as solvent (elution rate 1 ml/min).

Synthesis examples

Preparative Example 1 – Synthesis of a polymer ($P_{\text{PPO-Ac}}$) of formula:



10

A glass reactor was charged with trimellitic anhydride (144.1 g, 759 mmoles) dissolved in dehydrated DMF (200 ml) under nitrogen atmosphere. Triethylamine (165 ml) and DMAP (9.2g, 75mmoles) were introduced to the solution and the mixture stirred for 30 min at room temperature (25°C). Poly(propyleneglycol) ($P_{\text{PPO-OH}}$), as specified
 15 above, (250g, 125 mmoles) was dissolved in DMF (200ml) and added dropwise to the mixture over a period of 30 min. The temperature was increased at 80°C and the reaction was pursued for 48 hr, until complete conversion of hydroxyl groups of ($P_{\text{PPO-OH}}$) (by NMR). Then the mass was cooled at room temperature and diluted with dichloromethane 500 ml and washed with aqueous 1N HCl solution (3 x 200 ml)
 20 followed by brine (2 x 200ml), and finally with water (500 ml). The organic phase was separated and concentrated /dried to give the target product in 100%yield. (M_n 2470, carboxylic equivalent weight 618). The product contained 4 carboxylic groups per molecule, and its T_g was found to be of -70°C.

25

Preparation of the compositions (C) of the invention and application on metal electrodes

0.32 g of ($P_{\text{PPO-Am}}$) was added to 9.50 g of THF anhydrous at room temperature. The mixture was stirred until dissolution of the polymer. Then 0.18 g of the ($P_{\text{PPO-Am}}$)

polymer prepared as described above in Preparative Example 1 were added, and the resulting solution was maintained under stirring overnight at room temperature. This solution, having an overall polymers amount of 5% by weight, was introduced in a glove box and casted on the lithium surface of a lithium copper metal electrode using doctor blade technique, with a blade opening set at 80 μm . A wet coating layer on the lithium metal surface having a thickness of about 80 μm was obtained. The wet-coated electrode was maintained for 30 minutes on the coating table at room temperature, and then dried for 30 minutes at 80°C to remove the solvent. A 5 μm homogeneous and transparent dry coating, referred to in the following as Coating (54), was thus obtained on the Li surface of the lithium-copper metal electrode.

A Coating (58) was obtained by using the same polymers and THF as the solvent, also following the same procedure described above, with the only difference that a 2% solution of the polymers in THF was prepared and applied on the Li-surface of the lithium-copper metal electrode at 60 μm of thickness of the wet coating. A thickness of 4 μm of the polymer coating in the multilayer assembly was obtained after drying under the same conditions described above.

Tests on the multilayer assemblies

The multilayer assemblies with the polymer coatings of the invention, prepared as described above, have been tested in an electrochemical cell in parallel with a same cell comprising an uncoated lithium metal electrode to evaluate:

- Li stripping / plating test, to measure the efficiency of lithium deposition and dissolution during cycling;
- Cell cycling test, to evaluate the stability of coating layer during battery performances;

As showed in detail in the following, it was thus found that, compared to the uncoated metal electrodes, the present coated layers had improved efficiency and stability. Moreover, it was also observed for the present coatings the compatibility with the electrolytes used, with no dissolution of the coating when in the battery.

Manufacture of a lithium metal battery

A battery was manufactured using the multilayer electrode assemblies prepared as described above as the negative electrode (anode), and assembling the same with a separator, an electrolyte and a positive electrode (cathode).

5 As separator, a microporous membrane from Tonen[®] was used, type F20BMU. It was dried at 80°C under vacuum a night before being used in the battery.

As positive electrode, a nickel-manganese-cobalt electrode was used, having following composition: 95% NMC, 3% super C65 carbon powder, 2% SOLEF[®] 5130 PVDF, and loading = 3.1 mAh/cm². This positive electrode was dried during one night
10 under vacuum at 130°C.

The electrodes and the separator were placed under argon atmosphere (no oxygen, 0% humidity); 150 µL of electrolyte solution (LiPF₆ 1M solution in ethylene carbonate/ dimethyl carbonate 1:1 vol:vol) with 2% vinyl carbonate was injected into the separator. The soaked separator was then placed between the positive electrode
15 and the coated lithium-copper metal electrode in a coin cell and was tested at room temperature in the following tests. Each test was carried out in parallel with a same battery under the same conditions but using an uncoated lithium-copper metal electrode as the negative electrode.

C-rate performance test

20 The coin cell prepared as described above was cycled between 2.8 V and 4.2 V. After a step of 2 cycles at 0.1 Charge rate (C) – 0.1 Discharge rate (D), the test protocol was carried out according to successive series of 2 cycles at 0.2C – 0.2D, 0.2C – 0.5D, 0.2C – 1D, 0.2C – 2D, 0.2C – 5D.

The discharge capacity values of the coin cell under different discharge rates
25 were then obtained and compared with an identical assembly but with only a Li-Cu foil without any coating, resulting in a good performance observed for both the coated electrodes of this invention.

In the following Table 1 the average discharge capacity for one of the coated multilayer assembly of the invention and for the same uncoated assembly at different
30 C-rates:

Table 1

C-Rate (discharge)	Average Discharge Capacity – Coating (54) [mAh/g]	Average Discharge Capacity – Uncoated Li [mAh/g]
0.1	141	144
0.2	140	138
0.5	134	131
1	127	124
2	114	115
5	45	58

It is evident from these values that the polymer coating exhibits good ionic conductivity in contact with the liquid electrolyte, thus not limiting the diffusion of lithium ions, so that the battery can work at different C-rates as in the case of uncoated lithium.

5 Stability test

After the C-rate performance test, the coin cell was continuously cycled at 1C-1D until a drop of performance superior to 80% with respect to the initial performance. It was observed an improvement of the cycling stability of the lithium battery for both the assemblies coated with the Coating (58) and with the Coating (54). In the following
10 Table 2 are the values obtained for the battery with an uncoated assembly and for the battery with a lithium assembly coated with Coating (54):

Table 2

	Li with Coating (54)	Li uncoated
Average Discharge capacity after 2nd cycle (mAh/g)	126	128
Number of cycles to reach 80% of the discharge capacity after 2nd cycle	24	12

The uncoated lithium battery showed a much shorter cycling stability, proving that the polymer coating described herein allowed postponing the lithium dendrite growth by
15 providing a uniform and adaptive interface with the lithium metal electrode.

Lithium efficiency test in an electrochemical cell

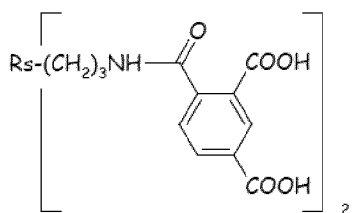
An electrochemical cell was assembled using a thin lithium metal electrode (coated with Coating (54) or uncoated), a separator, an electrolyte and a thick lithium metal electrode. This cell with two lithium electrodes was used to investigate the
20 cycling performance of Li during plating/stripping repeated cycles. The two electrodes had different Li amounts: a limited 20 μm electrode (working electrode) and an excess 380 μm electrode (counter/reference electrode). The separator was a 260 μm thick

glass fiber membrane Whatman®. The separator was dried at 250°C under vacuum during one night before assembling. 200 µL of electrolyte solution (ethylene carbonate/dimethyl carbonate 1:1 vol LiPF₆ 1M) with 2% vinyl carbonate was added to the separator. The separator membrane was then placed between the thick lithium metal and the coated lithium metal electrode in a coin cell, and was tested at 24°C. Galvanostatic tests were performed at 0.8 mA/cm² with cut-off voltage of 3 V and the current was reversed every 190 minutes in order to always remove and/or deposit the same quantity of lithium, substantially corresponding to the Li in the limited electrode. The tests were stopped when the voltage reached cut off, due to limited electrode depletion or it was arbitrarily stopped after 50 cycles. The number of cycles were correlated to lithium deposition/stripping efficiency using the equation: efficiency = N/(N+1) where N=number of charge/discharge cycles before cut-off.

The lithium efficiency resulted far improved for the battery including the thin lithium metal coated with the polymer Coating (54) prepared as said above, compared to the same battery including the thin lithium metal uncoated. A stable lithium deposition/stripping was indeed observed for the battery with the coated multilayer assembly of the invention over more than 50 cycles against the results for the uncoated battery for which the lithium was exhausted already after 26 cycles, due to non-uniform deposition of lithium and formation of dead mossy lithium.

Preparation of the composition (C_{PDMS}) of the invention and application on metal electrodes

Preparative Example 2 – Synthesis of a polymer (P_{PDMS-Ac}) of formula

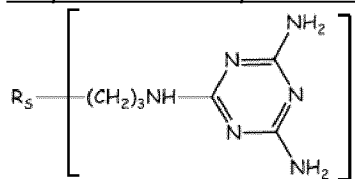


wherein Rs is a poly(dimethylsiloxane) chain

A glass reactor was charged with polymer NH₂-(CH₂)_{ns}-Rs-(CH₂)_{ns}-NH₂ with Rs being a poly(dimethylsiloxane) chain (100 g, 33.33 mmol, Mn 3000) and dried under vacuum for two hours under mechanical stirring at 70 °C. 1,4-dioxane (100 ml) and trimellitic anhydride (15.95 g, 83 mmol) were added to the reactor and stirred at 100 °C for 18 hours. The reaction completion was monitored by ¹H-NMR. The NMR analyses

confirmed the obtainment of title product, with purity higher than 99%, and its T_g was found to be of less than -120°C .

Preparative Example 3 – Synthesis of a polymer ($P_{\text{PDMS-Am}}$) of formula:



5 ^{2} wherein R_s is a poly(dimethylsiloxane) chain

A glass reactor was charged with 2-chloro-4,6-diamino-1,3,5-triazine (14.553 g, 99.99 mmol), KHCO_3 (10.033 g, 99.99 mmol), 2-propanol (300 mL) and water (150 mL) and the so obtained reaction mixture was warmed up to 70°C . Polymer $\text{NH}_2(\text{CH}_2)_{\text{ns}}\text{-R}_s\text{-(CH}_2)_{\text{ns}}\text{-NH}_2$ with R_s being a poly(dimethylsiloxane) chain (100 g, 33.33 mmol, M_n 3000) was added to the reaction mixture and stirred at 90°C . The completion of the reaction was monitored by $^1\text{H-NMR}$. The solvent was evaporated under reduced pressure and the polymer was purified by selective impurity precipitation in ethyl acetate solvent. All analyses confirmed the obtainment of the title product, with purity higher than 99%, and its T_g was found to be of less than -120°C .

15 Preparation of the compositions (C_{PDMS}) of the invention and application on metal electrodes

8.35 g of polymer ($P_{\text{PDMS-Ac}}$) was added to 17 g of TBME at room temperature. 6.08 g of ($P_{\text{PDMS-Am}}$) was added and the mixture was stirred until dissolution of the polymer. The ratio between the equivalents of polymer ($P_{\text{PDMS-Ac}}$) and the equivalents of polymer ($P_{\text{PDMS-Am}}$) is 1.

The resulting solution was maintained under stirring overnight at room temperature. 0.864 g of the so obtained solution has been diluted adding 5.28 g of TBME and mixed for few minutes. This solution, having an overall polymers amount of 12% by weight, was introduced in a glove box and casted on the lithium surface of a lithium copper metal electrode using doctor blade technique, with a blade opening set at $30\ \mu\text{m}$. A wet coating layer on the lithium metal surface having a thickness of about $30\ \mu\text{m}$ was obtained. The wet-coated electrode was dried for 60 minutes at 120°C to remove the solvent. A $3.4\ \mu\text{m}$ homogeneous dry coating, referred to in the following as Coating (C_{PDMS}), was thus obtained on the Li surface of the lithium-copper metal electrode.

Manufacture of a lithium metal battery

A battery was manufactured using the multilayer electrode assemblies prepared as described above as the negative electrode (anode), and assembling the same with a separator, an electrolyte and a positive electrode (cathode).

5 As separator, a microporous membrane from Tonen[®] was used, type F20BMU. It was dried at 80°C under vacuum a night before being used in the battery.

As positive electrode, a nickel-manganese-cobalt electrode was used, having following composition: 95% NMC, 3% super C65 carbon powder, 2% SOLEF[®] 5130 PVDF, and loading = 3.1 mAh/cm². This positive electrode was dried during one night
10 under vacuum at 130°C.

The electrodes and the separator were placed under argon atmosphere (no oxygen, 0% humidity); 150 µL of electrolyte solution (LiPF₆ 1M solution in ethylene carbonate/ dimethyl carbonate 1:1 vol:vol) with 2% vinyl carbonate was injected into the separator. The soaked separator was then placed between the positive electrode
15 and the coated lithium-copper metal electrode in a coin cell and was tested at room temperature in the following tests. Each test was carried out in parallel with a same battery under the same conditions but using an uncoated lithium-copper metal electrode as the negative electrode.

C-rate performance test

20 The coin cell prepared as described above was cycled between 2.8 V and 4.2 V. After a step of 2 cycles at 0.1 Charge rate (C) – 0.1 Discharge rate (D), the test protocol was carried out according to successive series of 2 cycles at 0.2C – 0.2D, 0.2C – 0.5D, 0.2C – 1D, 0.2C – 2D, 0.2C – 5D.

The discharge capacity values of the coin cell under different discharge rates
25 were then obtained and compared with an identical assembly but with only a Li-Cu foil without any coating, resulting in a good performance observed for both the coated electrodes of this invention.

In the following Table 3 the average discharge capacity for one of the coated multilayer assembly of the invention including coating (C_{PDMS}) and for the same
30 uncoated assembly at different C-rates:

Table 3

C-Rate (discharge)	Average Discharge Capacity – Coating (C_{PDMS}) [mAh/g]	Average Discharge Capacity – Uncoated Li [mAh/g]
0.1	142	142
0.2	137	138
0.5	129	131
1	119	126
2	94	110
5	21	28

It is evident from these values that the polymer coating exhibits good ionic conductivity in contact with the liquid electrolyte, thus not limiting the diffusion of lithium ions, so that the battery can work at different C-rates as in the case of uncoated lithium.

5 Stability test

After the C-rate performance test, the coin cell was continuously cycled at 0.33C-0.33D until a drop of performance superior to 80% with respect to the initial performance. It was observed an improvement of the cycling stability of the lithium battery for the assembly coated with the Coating (C_{PDMS}). In the following Table 4 are the values obtained for the battery with an uncoated assembly and for the battery with a lithium assembly coated with Coating (C_{PDMS}):

Table 4

	Li with Coating (C_{PDMS})	Li uncoated
Average Discharge capacity after 2nd cycle (mAh/g)	134	134
Number of cycles to reach 80% of the discharge capacity after 2nd cycle	16	13

The uncoated lithium battery showed a shorter cycling stability, proving that the polymer coating described herein allowed postponing the lithium dendrite growth by providing a uniform and adaptive interface with the lithium metal electrode.

CLAIMS

Claim 1. A multilayer electrode assembly for an electrochemical cell, said assembly comprising:

- a metal electrode (1) substantially consisting of at least one metal selected from the group consisting of lithium metal, sodium metal, magnesium metal, and zinc metal, or substantially consisting of an alloy of one or more of lithium metal, sodium metal, magnesium metal, and zinc metal with silicon or tin, said metal electrode (1) comprising a first surface and a second surface;
- a coating layer (2), which adheres on at least a fraction of said first surface of said metal electrode (1),

wherein (2) is a coating layer of a composition [composition (C)] comprising, and preferably consisting of:

- a) at least one polymer [polymer (P1)] comprising a polymer chain [chain (R)] consisting of a plurality of non-ionisable recurring units [units (U)], said chain having two ends, each end comprising at least one ionisable acid group;
- b) at least one polymer [polymer (P2)] comprising a polymer chain [chain (R)] consisting of a plurality of non-ionisable recurring units [units (U)], said chain (R) being equal or different from that of polymer (P1) and having two ends, each end comprising at least one ionisable amino group;

wherein:

said polymers (P1) and (P2) are amorphous and have a T_g lower than -35°C , preferably ranging from -35°C to -120°C ,

and where the ratio between the equivalents of polymer (P1) and the equivalents of polymer (P2) in said composition (C) preferably ranges from 1.4 to 0.6, more preferably from 1.2 to 0.8, most preferably from 1.1 to 0.9.

Claim 2. The multilayer assembly according to claim 1, wherein said polymer (P1) and said polymer (P2) have the following formulae:

(P1) E1-R-E1'

(P2) E2-R-E2'

wherein:

-E1 and E1', equal or different from one another, are end groups each comprising at

least one ionisable acid group;

-E2 and E2', equal or different from one another, are end groups each comprising at least one ionisable amino group.

Claim 3. The multilayer assembly according to claim 1 or 2, wherein said chain (R) of the polymer (P1) and polymer (P2) is independently selected from a fully or partially fluorinated polyoxyalkylene chain, a polyalkylsiloxane chain, a polyoxyalkylene chain, a polycarbonate chain, a polyester chain and a polybutadiene chain.

Claim 4. The multilayer assembly according to claim 3, wherein chain (R) of at least one of polymers (P1) and (P2), and preferably of both polymers (P1) and (P2) is a polyoxyalkylene chain selected from the group consisting of chains comprising, preferably essentially consisting of, a sequence of units of formula $-\text{OR}^{\sim}_{\text{OA}}-$, wherein each of $\text{R}^{\sim}_{\text{OA}}$, equal to or different from each other, is, independently at each occurrence, an hydrocarbon divalent group, possibly comprising additional heteroatom(s), and preferably a divalent alkylene group, which may be linear or branched.

Claim 5. The multilayer assembly according to any one of the previous claims, wherein at least one (preferably both) of following conditions are satisfied:

(1) polymer (P1) complies with formula (P1_{OA}-A);

(2) polymer (P2) complies with formula (P2_{OA}-A)

wherein:

(P2_{OA}-A) $\text{H}_2\text{NR}^*_{\text{OA}}-(\text{OR}^*_{\text{OA}})_{n^*_{\text{OA}}}-\text{NH}_2$

(P1_{OA}-A) $\text{HOOC}-\text{R}_{\text{B1}}-(\text{OR}^*_{\text{OA}})_{n^*_{\text{OA}}}-\text{O}-\text{R}_{\text{B1}}-\text{COOH}$

in which:

- each of R^*_{OA} , equal to or different from each other, is, independently at each occurrence, a straight or branched alkylene divalent group, typically an ethylene, propylene or a tetramethylene alkylene group,

- n^*_{OA} is an integer selected in such a way as the number average molecular weight ranges from 500 to 5,000, and

- R_{B1} is C₁-C₁₀ straight or branched alkylene, C₄-C₆ cycloalkylene or C₅-C₆ arylene, optionally comprising one or more -COOH groups.

Claim 6. The multilayer assembly according to claim 3 to 5, wherein the polyoxyalkylene chain is a polyoxypropylene chain comprising, preferably essentially consisting of recurring units of formulae (U_{OA}-ii) - (U_{OA}-iv):

(U_{OA}-ii): -OCH₂CH₂CH₂-

5 (U_{OA}-iii): -OCH(CH₃)CH₂-

(U_{OA}-iv): -OCH₂CH(CH₃)-

Claim 7. The multilayer assembly according to claim 5, wherein the polymer (P1) and (P2) have respectively the formulae (P1_{OA}-A) and (P2_{OA}-A) as defined in Claim 5, wherein R*_{OA} is substantially at each occurrence a propylene group of any of formulae
10 -CH₂CH₂CH₂-, -CH₂CH(CH₃)- and -CH(CH₃)CH₂-, and R_{B1} comprises one -COOH group.

Claim 8. The multilayer assembly according to any one of claims 1 to 3, wherein at least one (preferably both) of following conditions are satisfied:

(3) polymer (P1) complies with formula (Ps1-A);

15 (4) polymer (P2) complies with formula (Ps2-Aa)

wherein:

(Ps1-A) $R^*_S-[(CH_2)_{ns^*}NHC(O)-R_{B1}-COOH]_2$

(Ps2-Aa) $R^*_S-[(CH_2)_{ns^*}NH-R_{B2}-(NH_2)_{xb}]_2$

wherein ns* is 0 or a positive number equal to or higher than 1, preferably
20 ranging from 1 to 10, R_{B1} is a C₁-C₁₀ straight or branched alkylene, C₄-C₆ cycloalkylene or C₅-C₆ arylene, and preferably is selected from *o*-, *m*-, *p*-cyclohexylene and *o*-, *m*-, *p*-phenylene, and R_{B2} is a C₁-C₁₀ straight or branched alkylene, C₄-C₆ cycloalkylene or C₅-C₆ arylene or heteroarylene, and preferably is selected from *o*-, *m*-, *p*-cyclohexylene and *o*-, *m*-, *p*-phenylene, or
25 from any of heteroarylene groups, e.g. divalent triazine, oxazole, benzoxazole, pyridine groups, xb is an integer of 1 to 3, preferably equal to 2, and wherein R*_S is a chain of formula -Si(CH₃)₂O[Si(CH₃)₂O]_{ns}Si(CH₃)₂-, with ns is a positive number selected in such a way that the number average molecular weight (M_n) of the [Si(CH₃)₂O]_{ns} chain ranges from 500 to 10,000, preferably from 500 to 5,000.

30 **Claim 9.** The multilayer assembly according to any one of the claims 1-8, wherein said metal electrode (1) is a lithium metal electrode essentially consisting of at least one of

lithium metal and lithium metal alloys with tin or silicon.

Claim 10. A process for the manufacture of a multilayer electrode assembly for an electrochemical cell according to anyone of claims 1 to 9, comprising the steps of:

- v) providing a metal electrode (1) comprising a first surface and a second surface;
- 5 vi) providing a liquid mixture of a liquid medium [medium (L)] and of a composition (C) comprising:
 - c) at least one polymer [polymer (P1)] comprising a polymer chain [chain (R)] consisting of a plurality of non-ionisable recurring units [units (U)], said chain having two ends, each end comprising at least one ionisable acid group;
 - 10 and
 - d) at least one polymer [polymer (P2)] comprising a polymer chain [chain (R)] consisting of a plurality of non-ionisable recurring units [units (U)], said chain (R) being equal or different from that of polymer (P1) and having two ends, each end comprising at least one ionisable amino group;
- 15 wherein said polymers (P1) and (P2) are amorphous and have a T_g lower than -35°C , and wherein the ratio between the equivalents of polymer (P1) and the equivalents of polymer (P2) in said composition (C) preferably ranges from 1.4 to 0.6, more preferably from 1.2 to 0.8, most preferably from 1.1 to 0.9,
- vii) coating at least a fraction of said first surface of metal electrode (1) with the
20 solution coming from step ii), to obtain a wet coated layer;
- viii) drying said wet coated layer so as to obtain the multilayer electrode assembly.

Claim 11. The process according to claim 10, wherein said liquid medium (L) is selected from the group consisting of tetrahydrofuran (THF), dimethyl
25 sulfoxide (DMSO), 1,4-dioxane and alkylene carbonates selected from ethylene, vinylene and propylene carbonate.

Claim 12. An electrochemical cell comprising the multilayer electrode assembly according to anyone of claims 1 to 9, wherein preferably, this electrochemical cell is a primary or secondary (rechargeable) lithium battery, most preferably it is a secondary
30 lithium battery.

Claim 13. A method of making an electrochemical cell comprising assembling the multilayer electrode assembly according to anyone of claims 1 to 9 with at least one of collector(s), separator, a second electrode, and an electrolyte.

Claim 14. The method of claim 13, wherein said multilayer electrode assembly is
5 assembled as a negative electrode (anode) in combination with a positive electrode (cathode).

Claim 15. The method of claim 13 or 14, wherein said multilayer electrode assembly is assembled with a separator which is a polymer gel separator, comprising in a gelled state in the polymer matrix a solution in an organic solvent able to swell the said
10 polymer matrix of an electrolyte, or which is a porous polymeric structure soaked with a solution in an organic solvent of an electrolyte; and/or wherein the metal electrode is a lithium electrode, and the electrolyte is selected from the group consisting of LiBF_4 , LiBF_6 , LiClO_4 , LiPF_6 , Lithium trifluoromethanesulfonate (LiCF_3SO_3), Lithium bis(trifluoromethanesulfonyl)imide ($\text{LiC}_2\text{F}_6\text{NO}_4\text{S}_2$ or LiTFSI), lithium trifluoroacetate
15 (LiCF_3CO_2), LiAsF_6 , LiSbF_6 , $\text{LiB}_{10}\text{Cl}_{10}$, lower aliphatic lithium carboxylates, LiAlCl_4 , LiCl , LiBr , LiI , chloroborane lithium, and lithium tetraphenylborate.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/081824

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	H01M4/134 H01M6/14	H01M4/36 H01M4/38 H01M4/62 H01M10/052
ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) H01M		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2016/118638 A1 (GRONWALD OLIVER [DE] ET AL) 28 April 2016 (2016-04-28) paragraphs [0002], [0007] - [0014], [0022] - [0027], [0034], [0035], [0038], [0039], [0041] - [0056], [0059], [0066], [0067], [0070], [0073] paragraphs [0075] - [0079], [0116], [0120], [0130] examples	1-15
A	US 2016/276656 A1 (OSHIMA HIROKI [JP] ET AL) 22 September 2016 (2016-09-22) paragraphs [0010] - [0018], [0021], [0025], [0027] - [0028], [0032], [0033] examples ----- -/-	1-15
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 7 January 2019		Date of mailing of the international search report 24/01/2019
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Duval, Monica

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2018/081824

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2017/140649 A1 (SOLVAY SPECIALTY POLYMERS IT [IT]) 24 August 2017 (2017-08-24) paragraphs [0002], [0010] - [0014], [0023], [0026], [0032], [0044] - [0046], [0050] examples -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2018/081824

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 2016118638	A1	28-04-2016	NONE	

US 2016276656	A1	22-09-2016	DE 112014006944 T5	01-06-2017
			US 2016276656 A1	22-09-2016
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			EP 3417501 A1	26-12-2018
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			WO 2017140649 A1	24-08-2017
