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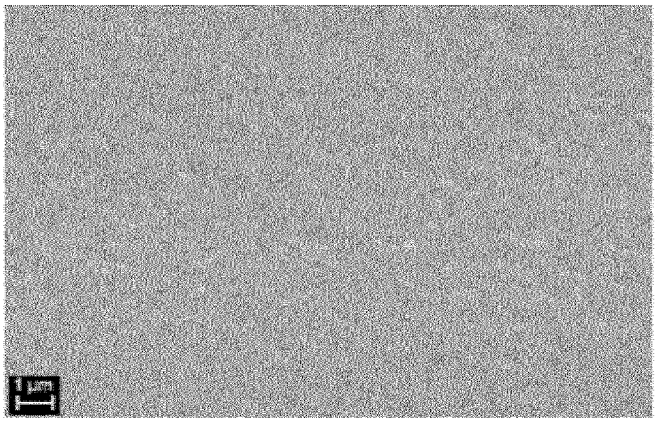

Figure 4a

(57) Abstract: The present invention pertains to a process for the preparation of a solid polymer electrolyte comprising at least fluoropolymer nanoparticles, inorganic nanoparticles having a negative zeta potential, at least a lithium salt and an ionic liquid; to the solid polymer electrolyte obtainable therefrom, and to its use in electrochemical devices.

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Description

A process for the preparation of a solid polymer electrolyte useful in batteries

Cross-reference to related applications

[0001] This application claims priority to European application No. 18305247.1 filed on 08 Mar 2018, the whole content of this application being incorporated herein by reference for all purposes.

Technical Field

[0002] The present invention pertains to a process for preparing a solid polymer electrolyte and to the thus obtainable electrolyte, as well as to electrochemical devices comprising this solid electrolyte.

Background Art

[0003] Liquid electrolytes have been applied for several decades in most commercial batteries. They comprise at least an ionically conducting salt and a non-aqueous solvent.

[0004] Liquid electrolytes are characterised by a high ionic conductivity and good wetting of the electrodes surface.

[0005] Liquid electrolytes may have though the drawback that leakage can occur, and even combustion at least for some organic liquid electrolytes.

[0006] Another drawback of the liquid electrolytes applied in lithium-ion batteries is the inevitable and hazardous formation in liquid solutions of lithium dendrites, which are microscopic fibres of lithium caused by uneven currents during repeated charge/discharge cycles.

[0007] As an alternative, solid polymer electrolytes, without liquid solvents, provide promising opportunity to tackle the safety issue and to avoid the growth of lithium dendrite. But, on the other side, the use of solid electrolytes has not yet reached commercial maturity due to issues linked to reduced conductivity.

[0008] Fluoropolymers are known in the art to be suitable for the manufacture of different components for use in electrochemical devices such as lithium-ion batteries, such as separators, binders and as polymer electrolytes too.

[0009] Polyvinylidenefluoride (PVdF) is one of the most widely used fluoropolymer in battery components, due to its high anodic stability and high dielectric constant, which favours the ionisation of lithium salts in lithium-ion batteries and enable the flow of ions thus improving the cell performance.

[0010] In order to further improve its performances, different copolymers of PVdF have been studied too; among these, polyvinylidenefluoride-co-hexafluoropropylene (PVdF-HFP) is receiving considerable attention due to its good compatibility with the electrodes, its low glass transition temperature and crystallinity, which enable improved ionic conductivity.

[0011] Besides co-polymerisation, also various kind of blending, cross-linking and addition of inorganic fillers, have been studied to modify the PVdF polymer to improve its electrochemical performances and effectively use it as electrolyte.

[0012] Due to the always-increasing demand for high-performance rechargeable batteries for use in portable electronic devices, as well as in electronic vehicles and in the emerging smart grids, the lithium-ion batteries are receiving much attention in order to maximise this battery performance in terms of cycle life, power density, reliability and in terms of safety too.

[0013] Accordingly, the need is highly felt for novel solid polymer electrolytes, particularly suitable for use in lithium-ion batteries, having improved conductivity over time that can be prepared by means of a scalable process, starting from easily available starting materials.

Summary of invention

[0014] It has been now surprisingly found by the inventors that mixing an ionic liquid comprising a lithium salt with a powder coming from drying a gel obtained by subjecting to high shear in a microchannel an aqueous dispersion of inorganic nanoparticles and a fluoropolymer, results in a mixture that yields, by a heat treatment, a solid polymer electrolyte having the desired properties described above. In particular, the thus obtained solid polymer electrolytes do improve the electrochemical properties of the

batteries where they are used, while preventing the electrolyte leakage phenomenon, thus also reducing the risk of corrosion of the batteries.

[0015] In a first aspect, this invention provides a process for the preparation of a solid polymer electrolyte comprising the steps of:

i) providing an aqueous dispersion of at least one fluoropolymer [polymer (FP)] in the form of nanoparticles, said polymer (FP) comprising recurring units derived from vinylidene fluoride (VDF) in an amount of at least 50% by mole with respect to the total moles of recurring units of polymer (FP), and recurring units derived from at least one fluorinated monomer (FM) different from vinylidene fluoride in an amount of at least 2.5% by mole with respect to the total moles of recurring units of polymer (FP);

ii) providing an aqueous dispersion of inorganic nanoparticles having a negative zeta potential;

iii) adding said dispersion of inorganic nanoparticles to said dispersion of polymer (FP) nanoparticles, and forming a gel subjecting the resulting mixture to intense shear;

iv) forming a dry powder from the gel coming from step iii);

v) mixing said dry powder with an ionic liquid wherein at least a lithium salt is dissolved, and submitting the resulting mixture to hot pressing.

[0016] In a further aspect, the present invention provides a solid polymer electrolyte comprising at least a fluoropolymer (FP) and inorganic nanoparticles, at least a lithium salt and an ionic liquid, obtainable by the above said process.

[0017] In still another aspect, the present invention provides electrochemical devices comprising the above said solid polymer electrolyte.

Brief description of drawings

[0018] Figure 1 is a schematic illustration of the microchannel

[0019] Figure 2 shows the distribution curves before and after one passage through the microchannel.

[0020] Figure 3 shows SEM pictures of two gels used in the examples (Figure 3a and Figure 3b, respectively), obtained by dispersion of inorganic

nanoparticles into the dispersion of polymer after a single passage in the microchannel.

[0021] Figure 4 shows SEM images at 20k magnitude and at 350k magnitude of the surface of films (Figure 4a and Figure 4b, respectively) obtained by compression moulding at 120°C and 10 kN for 5 minutes for a mixture of 30% FP/SiO_2 and 70% ionic liquid/Li salt.

Description of embodiments

[0022] By the term “recurring unit derived from vinylidene difluoride” (also generally indicated as vinylidene fluoride 1,1-difluoroethylene, VDF), is intended to denote a recurring unit of formula (I): CF_2=CH_2.

[0023] By the term “fluorinated monomer (FM)” it is hereby intended to denote an ethylenically unsaturated monomer comprising at least one fluorine atom.

[0024] In the rest of the text, the expression “fluorinated monomers” is understood, for the purposes of the present invention, both in the plural and the singular, that is to say that they denote both one or more than one fluorinated monomers as defined above.

[0025] Should the fluorinated monomer (FM) comprise at least one hydrogen atom, it is designated as hydrogen-containing fluorinated monomer.

[0026] Should the fluorinated monomer (FM) be free of hydrogen atoms, it is designated as per(halo)fluorinated monomer.

[0027] The fluorinated monomer (FM) may further comprise one or more other halogen atoms (Cl, Br, I).

[0028] Non-limiting examples of suitable fluorinated monomers (FM) include, notably, the followings:

- C_2-C_8 perfluoroolefins such as tetrafluoroethylene and hexafluoropropylene (HFP);
- C_2-C_8 hydrogenated fluoroolefins such as vinyl fluoride, 1,2-difluoroethylene and trifluoroethylene;
- perfluoroalkylethylenes of formula CH_2=CH-R_{f0} wherein R_{f0} is a C_1-C_6 perfluoroalkyl;
- chloro- and/or bromo- and/or iodo-C_2-C_6 fluoroolefins such as chlorotrifluoroethylene;

- (per)fluoroalkylvinylethers of formula $CF_2=CFOR_{f1}$ wherein R_{f1} is a C_1-C_6 fluoro- or perfluoroalkyl, e.g. CF_3, C_2F_5, C_3F_7;
- $CF_2=CFOX_0$ (per)fluoro-oxyalkylvinylethers wherein X_0 is a C_1-C_{12} alkyl group, a C_1-C_{12} oxyalkyl group or a C_1-C_{12} (per)fluorooxyalkyl group having one or more ether groups, such as perfluoro-2-propoxy-propyl group;
- (per)fluoroalkylvinylethers of formula $CF_2=CFOCF_2OR_{f2}$ wherein R_{f2} is a C_1-C_6 fluoro- or perfluoroalkyl group, e.g. CF_3, C_2F_5, C_3F_7 or a C_1-C_6 (per)fluorooxyalkyl group having one or more ether groups such as $-C_2F_5-O-CF_3$;
- functional (per)fluoro-oxyalkylvinylethers of formula $CF_2=CFOY_0$ wherein Y_0 is a C_1-C_{12} alkyl group or (per)fluoroalkyl group, a C_1-C_{12} oxyalkyl group or a C_1-C_{12} (per)fluorooxyalkyl group having one or more ether groups and Y_0 comprising a carboxylic or sulfonic acid group, in its acid, acid halide or salt form;
- fluorodioxoles, preferably perfluorodioxoles.

[0029] The fluorinated monomer (FM) is preferably hexafluoropropylene (HFP).

[0030] At least another fluorinated monomer (FM2) different from (FM) and from VDF may be included in polymer (FP).

[0031] Such monomer (FM2) can include at least one conventionally used monomer copolymerizable with vinylidene fluoride, such as, but not limited to, vinyl fluoride, trifluoroethylene, trifluorochloroethylene (CTFE), tetrafluoroethylene (TFE), hexafluoropropylene (HFP), and fluoroalkyl vinyl ether and their mixtures.

[0032] The amount of monomer (FM2) in polymer (FP) is preferably below 10 mol%, more preferably below 2 mol% over the total number of moles of recurring units in polymer (FP).

[0033] In a preferred embodiment of the invention, (FP) is a copolymer of VDF with a fluorinated monomer, wherein the fluorinated monomer (FM) is comprised in an amount of between 2.5 % by mole and 12% by mole % with respect to the total moles of recurring units of polymer (FP). According to a particular embodiment of the present invention the

fluorinated monomer is comprised in an amount of at least 4.0% by mole with respect to the total moles of the recurring units of polymer (FP).

[0034] More preferably, the fluorinated monomer (FM) is hexafluoropropylene (HFP) and (FP) is a VDF-HFP copolymer.

[0035] The polymer (FP) in the form of nanoparticles is typically obtainable by emulsion polymerization or suspension polymerization of at least one vinylidene difluoride monomer and at least one fluorinated monomer (FM) and optionally at least one fluorinated monomer (FM2) different from (FM).

[0036] According to a preferred embodiment of this invention, the fluoropolymer in the aqueous dispersion is a core-shell polymer having a core of polymer (FP) as defined above and a shell comprising at least an acrylate, for instance selected from the group consisting of methyl methacrylate (MMA), methyl ester of methacrylic acid (MAA), ethyl hexyl acrylate (EHA), and mixtures thereof.

[0037] Aqueous dispersions comprising a core-shell polymer (FP) as above defined can be prepared by implementing the methods already described for example in JP 2003-171520 or in WO 2012/043580.

[0038] In step i), the polymer (FP) is dispersed in water typically at a concentration comprised between 15% wt and 40% wt, preferably between 20% wt and 30% wt.

[0039] Generally, the polymer (FP) possesses a primary particle average size of less than 1 μm. For the purpose of the present invention, the term "primary particles" is intended to denote primary particles of polymer (FP) deriving directly from aqueous emulsion polymerization, without isolation of the polymer from the emulsion (i.e. the latex). Primary particles of polymer (FP) are thus to be intended distinguishable from agglomerates (i.e. collection of primary particles), which might be obtained by recovery and conditioning steps of such polymer manufacture such as concentration and/or coagulation of aqueous latexes of the polymer (FP) and subsequent drying and homogenization to yield the respective powder.

[0040] The aqueous dispersion in step i) of the invention is thus distinguishable from an aqueous slurry that can be prepared by dispersing powders of a polymer in an aqueous medium. The average particle size of powders of a

polymer or copolymer dispersed in an aqueous slurry is typically higher than 1 μm, as measured according to ISO 13321.

[0041] Preferably, the primary particles average size of the particles of polymer (FP) in the aqueous dispersion in step i) is above 20 nm, more preferably above 30 nm, even more preferably above 50 nm, and/or is below to 600 nm, more preferably below 400 and even more preferably below 350 nm as measured according to ISO 13321.

[0042] As used herein, by the term “dispersion of inorganic nanoparticles having a negative zeta potential” is meant a dispersion of any inorganic nanoparticle having a pH higher than its isoelectric point (IEP).

[0043] Non-limiting examples of inorganic nanoparticles of possible use according to this invention are silicon dioxide (also referred to herein as “silica”), aluminium oxide, zirconium dioxide, cerium dioxide, vanadium oxide, titanium oxide, magnesium oxide and niobium oxide.

[0044] Preferably, the inorganic nanoparticles used in the process of this invention are silicon dioxide nanoparticles, and more preferably they are precipitated silica.

[0045] By "precipitated silica" it is meant herein a silica that is typically prepared by precipitation from a solution containing silicate salts (such as sodium silicate), with an acidifying agent (such as sulphuric acid).

[0046] Precipitated silica used in this invention may be prepared by implementing the methods already described in EP396450A, EP520862A, EP670813A, EP670814A, EP762992A, EP762993A, EP917519A, EP1355856A, WO03/016215, WO2009/112458, WO2011/117400, WO2013/110659, WO2013/139934, WO2008/000761.

[0047] Non-limiting examples of precipitated silica which could be used in the present invention are for instance Tixosil® 365 and Zeosil® 1085 GR, all commercially available from Solvay.

[0048] In step ii), the inorganic nanoparticles can be suitably dispersed in water by means of mechanical stirring or sonication, typically at concentration of at least 10% wt and at most 40% wt.

[0049] In step iii), the mixture resulting from the addition of the aqueous dispersion of step i) and the aqueous dispersion of step ii) suitably

contains inorganic nanoparticles having a negative zeta potential and polymer (FP) nanoparticles in a weight ratio as dry components that is comprised between 1:99 and 50:50, preferably between 5:95 and 40:60, more preferably between 10:90 and 20:80.

[0050] In step iii) the mixture resulting from the addition of the aqueous dispersion of step i) and the aqueous dispersion of step ii) is subjected to intense shear in order to provide a gel. The apparatus for making a gel from the aqueous dispersion of polymer (FP) and the aqueous dispersion of inorganic nanoparticles to provide a gel is not particularly limited,

[0051] In a preferred embodiment of the present invention, intense shearing is performed in a microchannel according to a microfluidic procedure; the operating pressure in the microchannel typically ranges from 80 to 160 bar; preferably the operating pressure is of approximately 120 bar.

[0052] For the purpose of the present invention, the term ”ionic liquid” is intended to denote a compound formed by the combination of a positively charged cation and a negatively charged anion in the liquid state at temperatures below 100°C under atmospheric pressure. As used herein, the term “ionic liquid” indicates a compound free from one or more solvents.

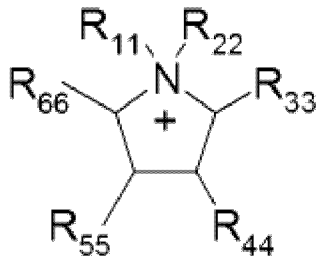
[0053] The ionic liquid typically contains:

- a positively charged cation selected from the group consisting of imidazolium, pyridinium, pyrrolidinium and piperidinium ions optionally containing one or more C_1-C_{30} alkyl groups, and
- a negatively charged anion selected from the group consisting of halides, perfluorinated anions and borates.

[0054] Non-limiting examples of C_1-C_{30} alkyl groups include, notably, methyl, ethyl, propyl, iso-propyl, n-butyl, isobutyl, sec-butyl, t-butyl, pentyl, isopentyl, 2,2-dimethyl-propyl, hexyl, 2,3-dimethyl-2-butyl, heptyl, 2,2-dimethyl-3-pentyl, 2-methyl-2-hexyl, octyl, 4-methyl-3-heptyl, nonyl, decyl, undecyl and dodecyl groups.

[0055] The positively charged cation of the ionic liquid is preferably selected from the group consisting of:

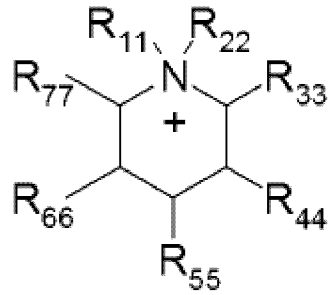
- a pyrrolidinium cation of formula (II):



(II)

wherein R_{11} and R_{22}, equal to or different from each other, independently represent a C_1-C_8 alkyl group and R_{33}, R_{44}, R_{55} and R_{66}, equal to or different from each other, independently represent a hydrogen atom or a C_1-C_{30} alkyl group, preferably a C_1-C_{18} alkyl group, more preferably a C_1-C_8 alkyl group, and

- a piperidinium cation of formula (III):

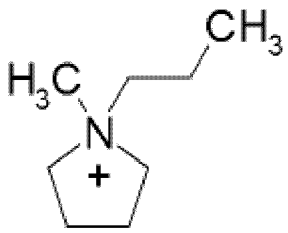


(III)

wherein R_{11} and R_{22}, equal to or different from each other, independently represent a C_1-C_8 alkyl group and R_{33}, R_{44}, R_{55}, R_{66} and R_{77}, equal to or different from each other, independently represent a hydrogen atom or a C_1-C_{30} alkyl group, preferably a C_1-C_{18} alkyl group, more preferably a C_1-C_8 alkyl group.

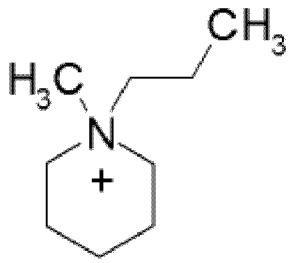
[0056] The positively charged cation of the ionic liquid is more preferably selected from the group consisting of:

- a pyrrolidinium cation of formula (II-A):



(II-A)

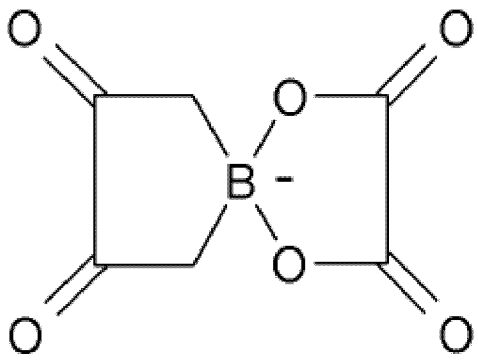
- a piperidinium cation of formula (III-A):



(III-A)

[0057] The negatively charged anion of the ionic liquid is preferably selected from the group consisting of:

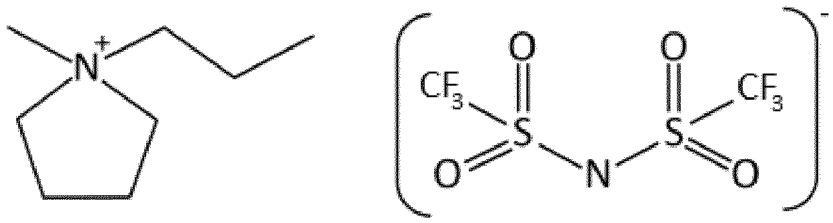
- bis(trifluoromethylsulphonyl)imide of formula $(SO_2CF_3)_2N^-$,
- hexafluorophosphate of formula PF_6^-,
- tetrafluoroborate of formula BF_4^-, and
- oxaloborate of formula:



[0058] The ionic liquid even more preferably contains a pyrrolidinium cation of formula (II-A) as defined above and a perfluorinated anion selected from the groups consisting of bis(trifluoromethylsulphonyl)imide of formula

$(SO_2CF_3)_2N^-$, hexafluorophosphate of formula PF_6^- and tetrafluoroborate of formula BF_4^-.

[0059] According to a particularly preferred embodiment of this invention the ionic liquid is N-propyl-N-methylpirrolidinium bis(trifluoromethylsulfonyl)imide (also indicated in the following by the commercial product reference Pyr1308), having the following formula:



[0060] In step v), the powder obtained by drying gel coming from step iii) is then mixed with an ionic liquid and Lithium salt, the resulting mixture submitted to a hot pressing.

[0061] The hot pressing in step v) of the present process is a treatment at a temperature ranging from 100 to 130°C, carried out by compression moulding.

[0062] The weight ratio of powder coming from step iii) and solution obtained dissolving Li salt in ionic liquid is advantageously comprised between 10:90 and 90:10, preferably between 20:80 and 80:20, more preferably between 30:70 and 60:40.By the term “electrochemical device”, it is hereby intended to denote an electrochemical cell comprising a positive electrode, a negative electrode and an electrolyte, wherein a monolayer or multilayer separator is adhered to at least one surface of one of said electrodes.

[0063] Non-limitative examples of suitable electrochemical devices include, notably, secondary batteries, especially, alkaline or alkaline-earth secondary batteries such as lithium ion batteries, and capacitors, especially lithium ion–based capacitors and electric double layer capacitors (“supercapacitors”).

[0064] For the purpose of the present invention, by “secondary battery” it is intended to denote a rechargeable battery. Non-limitative examples of

secondary batteries include, notably, alkaline or alkaline-earth secondary batteries.

[0065] In a first embodiment, the present invention encompasses an electronic device comprising a solid polymer electrolyte obtainable by the above said process.

[0066] The present solid polymer electrolyte is particularly suitable for use in lithium-ion batteries, which is preferably a separator-free secondary battery.

[0067] The term “separator-free batteries” refers to batteries having a negative electrode comprising an active material, which releases lithium ions when discharging and absorbs lithium ions when the battery is being charged, wherein a self-standing electrolyte is placed within said negative electrode and the positive electrode, without the need for a physical separator.

[0068] In the above said lithium-ion batteries the present solid polymer electrolyte can be placed preferably in the form of a film between the positive electrode and the negative electrode.

[0069] Should the disclosure of any patents, patent applications, and publications that 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.

[0070] The invention will be now described with reference to the following examples, whose purpose is merely illustrative and not intended to limit the scope of the invention.

[0071] EXPERIMENTAL PART

[0072] Materials

[0073] The following chemicals have been employed in the following examples without further treatments: Acetone (puriss. p.a.,≥99.5%), lithium hexafl uorophosphate solution (1M in Ethylene carbonate and Dimethyl carbonate 50/50 (v/v)) were purchased from Sigma-Aldrich; ionic liquid N-Propyl-N-Methylpyrrolidinium bis(trifluoromethanesulfonyl)-imide (Pyr1308b, purity 99.5%) from Solvionic; Sodium dodecyl sulphate (SDS, purity≥99%) from Apollo; Poly(vinylidenefluoride-co-hexafluoropropylene) (PVdF-HFP), fumed silica Tixosil® 365 and Zeosil® 1085 GR, bis(trifl

uoromethane)sulfonimide lithium salt (LiTFSI) were provided by Solvay Specialty Polymers Italia S.p.A. (Bollate, Italy). Ion-exchange resin (Dowex Marathon MR-3 hydrogen and hydroxide form) purchased from Sigma-Aldrich has been employed as received. Ultra-pure grade water was prepared by Millipore Synergy.

[0074] Preparation of the solid polymer electrolyte according to the invention

[0075] *The fluoropolymer (FP)*

[0076] The polymers (FP) in the form of aqueous nanoparticles dispersions used in the following were provided by Solvay Specialty Polymers Italia S.p.A. (Bollate, Italy). In particular the following products were used:

[0077] POLYMER A: VdF-HFP copolymer with about 11 wt.% or 5 mol% of HFP, obtained by emulsion polymerisation carried out using an anionic surfactant as stabiliser.

[0078] POLYMER B: core-shell structured polymer (70/30 wt.%) including a core of VdF-HFP copolymer (90/10 wt.%) and a shell of a mixture of acrylates.

[0079] The polymers described above contained quite high amounts of surfactants that were removed by using ion exchange resin DOWEX MR-3. This cleaning procedure was as follows:

- the resin was washed with deionised water and filtered with 100 µm mesh to remove small fragments;
- 30 wt.% of the washed resin was added with respect to the solid content of the polymer (FP);
- the mixture was left overnight under stirring at 80 rpm;
- the resin was then removed by filtering with a 100 µm mesh filter;
- this procedure was repeated multiple times, 3 for the POLYMER B polymer and 2 for the POLYMER A polymer.

[0080] To assess the number of repetitions of the aforementioned procedure needed to completely remove the surfactant, conductivity and surface tension were measured. The former was computed with Conductometer 712 from Metrohm at a concentration of 5 wt.% and 25°C, whereas surface tension measurements were performed with a Wilhelmy plate using DCAT 21 from Dataphysics at a concentration of 0.5 wt.% and 25°C. The solid content was assessed by spreading the sample over quartz sand

analysing the weight loss at 120°C using a HG53 Halogen Moisture Analyzer from Mettler-Toledo.

[0081] After the cleaning procedure, the conductivity of the polymer was < 10 µS/cm and its surface tension was close to that of deionised water, indicating that the colloidal system was free from SDS and from any other electrolyte.

[0082] *Inorganic nanoparticles*

[0083] Two batches of powder of precipitated SiO_2 of approximately 4 µm (TIXOSIL 365) and 0.5-10 mm (ZEOSIL 1085 GR) were provided by Solvay Silica. In order to be used in the intended application, the powder has to be effectively dispersed in water (final cluster size < 500 nm) and should be negatively charged on its surface to be stably mixed with the negatively charged polymer particles. Before use the powder was dispersed in water (final cluster size < 500 nm) and it was mixed with Millipore-grade water so that the solid content was the highest possible. The so obtained mixture was mechanically stirred and repeatedly sonicated using a Digital Sonifier from Branson. Finally, the dispersion was centrifuged at 2000 rpm for 10 minutes to remove the remaining large clusters. The average clusters size and the polydispersity index (PDI) were measured by dynamic light scattering (DLS) using Zetasizer Nano ZS from Malvern. By the same instrument the electrophoretic mobility of primary particles was measured too, and the Zeta potential was estimated through the Smoluchowski model (see Israelachvili J., *Intermolecular and surface forces*, Elsevier Academic Press, San Diego, 2011) at a concentration of 0.01 wt.% and 25°C with 10 mM NaCl. The solid content was measured using a HG53 Halogen Moisture Analyzer from Mettler-Toledo. The transmission electron microscopy (TEM) was used to verify the size of the dispersed clusters. The so-measured properties of the dispersions of SiO_2 nanoclusters prepared as described above are summarised in the following Table 1.

Table 1

	Average clusters diameter [nm]	PDI	Zeta potential [mV]	Solid fraction [wt.%]
TIXOSIL 365	160	0.19	-47.9	29.8
ZEOSIL 1085 GR	180	0.22	-42.6	19.7

[0084] The dispersed nanoclusters of SiO_2 obtained as described above were all lower than 200 nm in the pH range of 6-12, and they were negatively charged with the Zeta potential ranging from -48 to -42 mV.

[0085] *Mixing of the polymer (FP) and silica nanoparticles*

[0086] The dispersion of silica prepared as described above was added dropwise to the dispersion of polymer particles prepared as described above. The amount of silica added was evaluated as mass percentage with respect to the mass of the polymer. Some SDS was also added (0.2% with respect to the solid content of the polymer).

[0087] *Aggregation of the polymer (FP) and silica nanoparticles*

[0088] The aggregation of the mixture of prepared as described above was performed by using a high-shear device HC-5000 from Microfluidics equipped with a L30Z microchannel with a width of 300 μm, a rectangular cross section of 5.26×10^{-8} m^2 and a length of 5.8 mm, as schematically illustrated in Figure 1. An operating pressure of 120 bar was chosen and a single passage of the mixture through the microchannel was performed. It has been verified that the silica nanoparticles were shear-inactive and thus they do not aggregate under intense shear, whereas the polymer nanoparticles are shear-active and form a compact gel. As the formation of the polymer network took place in this experiment in a very short time (i.e., less than 1 ms), the silica nanoparticles had no time to escape and remained entrapped in the fluoropolymer at a nanoscale level, yielding a compact gel after a single passage through the microchannel.

[0089] The so-obtained gel was redispersed in deionised water in the form of clusters and their average size and compactness in terms of fractal

dimension were measured using the small angle light scattering (SALS) Mastersizer 2000. Figure 2 shows the distribution curves before and after one passage through the microchannel. From these results it is clearly evident that, after a single passage through the microchannel, aggregation occurs producing clusters of few tens of micrometers.

[0090] In order to analyse the dispersion of silica particles inside the polymer matrix, SEM pictures of the gel obtained from the microchannel have been taken, and are illustrated in Figure 3. In particular, the two pictures of Figure 3 illustrates SEM pictures of the silica nanoparticles entrapped in the fluoropolymer after a single passage through the microchannel for POLYMER A + 10% SiO_2 (Figure 3a) and for POLYMER B + 10% SiO_2 (Figure 3b).

[0091] From the pictures in Figure 3 it is evident that the shear-induced aggregation was capable of dispersing uniformly and randomly the silica nanoparticles within the polymer matrix. The silica clusters indeed are clearly distinct with respect to the PVdF nanoparticles, being thus easily distinguishable (whiter and smaller clusters). The silica nanoparticles are moreover uniformly dispersed at the nanoscale level (i.e., the silica clusters are smaller than 500 nm). Moreover, it is possible to observe that the polymer primary particles of POLYMER B are interpenetrated, whereas those of POLYMER A maintain their original identity. This is due to the fact that the first presents a core-shell structure which facilitates the interpenetration, whereas the latter consists of just PVdF-HFP.

[0092] *Forming a dry powder of fluoropolymer and silica nanoparticles and mixing with ionic liquid*

[0093] The gel obtained as described above was dried in oven at 60°C to fully evaporate water, and then it was milled until a monodispersed powder was obtained. This powder was mixed with different percentages of ionic liquid, in which bis(trifluoromethane)sulfonimide lithium salt (LiTFSI) was previously dissolved in a concentration of 0.5 M.

[0094] *Heat treatment of the mixture FP/SiO_2/ionic liquid/Li salt*

[0095] The mixture of fluoropolymer, silica, ionic liquid and lithium salt prepared as described above was stirred for some minutes and placed between two

aluminium plates. The plates were then pressed at 5 or 10 kN for 5 minutes at 100-130°C and subsequently cooled down to room temperature with a cooling press. To avoid water absorption the so obtained samples were then stored under nitrogen atmosphere.

[0096] A continuous and homogeneous film was so obtained with an ionic liquid content varied from 40 to 70% of the total mass. In Figure 4a a SEM image at 20k magnitude is shown of the surface of a film obtained by compression moulding at 120°C and 10 kN for 5 minutes for a mixture of 30% FP/SiO_2 and 70% ionic liquid/Li salt. A SEM image of the same material but at 350k magnitude is shown in Figure 4b. It is evident from these images that the surface is rough and the structure looks quite homogeneous. No porosity or large aggregates are observed and silica nanoclusters cannot be distinguished from the polymer nanoparticles.

[0097] The so produced films were characterised in terms of ionic conductivity, mechanical properties and their charge/discharge capacities were evaluated by assembling and testing the solid polymer electrolytes in coin cells.

[0098] **Example 1**

[0099] A continuous film was obtained according to the process of the present invention, starting from a composite SiO_2:POLYMER A at ratio 10:90, wherein such composite is mixed with electrolyte solution (LiTFSI 0,5M in Pyr1308b) in ratio 30:70 and finally by hot pressing at 120°C.

[00100] Alternatively to compression moulding, another procedure was followed for mixing the polymer (or polymer/silica) clusters with the Pyr1308/LiTFSI mixture at the same concentration mentioned above by solution casting dissolving polymer and inorganic particles in acetone.

[0101] **Comparative Example 1**

[0102] A continuous film containing 30% of a composite SiO_2:POLYMER A at ratio 10:90and 70% of the electrolyte solution (LiTFSI 0.5M in Pyr1308b) in ratio 30:70, was obtained by solution casting starting from a solution prepared by mixing all components in acetone.

[0103] **Comparative Example 2**

[0104] A continuous film was prepared according to the process of present invention except for being without inorganic particles, thus containing 30% POLYMER A + 70% Pyr1308/LiTFSI, obtained by hot pressing at 120°C.

[0105] *Measurement of the ionic conductivity*

[0106] The ionic conductivity of the film was measured by AC impedance spectroscopy using a conductivity cell consisting of two stainless steel blocking electrodes. The resistance of the polymer electrolyte was measured and the ionic conductivity (σ) was obtained using the following equation:

$\sigma = d / (R \times S)$

wherein *d* is the thickness of the film, *Rb* the bulk resistance and *S* is the area of the stainless steel electrode.

Table 2

	σ (S/cm)				
T(°C)	24°C	40°C	55°C	70°C	80°C
Example 1	6.2E-04	9.6E-04	1.4E-03	1.8E-03	3.0E-03
Comparative Ex 1	1.5E-04	1.5E-04	2.7E-04	5.9E-04	9.1E-04

[0107] As shown in Table 2, the film obtained by the present process performs better than that a film having the same composition but prepared by a standard solution casting process at equal composition. This must be due to a better dispersion of inorganic particles.

[0108] *Tensile properties*

[0109] Mechanical properties of films obtained as described above were evaluated according to ASTM D-638 type V standard, by measuring tensile properties at room temperature.

Table 3

	Modulus [MPa]	Yield Stress [MPa]	Yield Strain [%]	Stress @ Break [MPa]	Strain @ Break [%]
Example 1	5	0.59	13	0.85	35
Comparative Ex 1	1	0.12	15	0.17	35

[0110] The data in Table 3 show that the membrane based on invention has an advantage also in terms of mechanical properties with a higher modulus.

[0111] *Cycling tests*

[0112] For the electrochemical performance, a battery was manufactured assembling the film so obtained with a positive electrode and a lithium metal foil as negative electrode.

[0113] As positive electrode, a lithium iron phosphate electrode was used, having following composition: 82% LiFePO4, 10% super C65 carbon powder, 8% SOLEF® 5130 PVDF, and loading = 0.4 mAh/cm^2. This positive electrode was dried during one night under vacuum at 130°C.

[0114] The film was then placed between the positive electrode and the lithium metal in a coin cell and it was tested at 60°C.

[0115] The relative discharge capacity values (%) of the coin cells so obtained at different discharge rates are set forth in table here below. The C rate is the current needed to discharge the nominal capacity of the cell in 1 hour.

[0116] The relative discharge capacity values (%) are the discharge capacity values normalized by the discharge capacity obtained at C/10. The results are shown in Table 4.

Table 4

C-Rate		Relative Discharge capacity (%)	
		Ex 1	Comp Ex 2
0.1	Discharge C/10	100%	100%
0.2	Discharge C/5	98%	97%

0.5	Discharge C/2	95%	95%
1	Discharge C	91%	92%
2	Discharge 2C	84%	80%
0.2	Discharge C/5	100%	98%

[0117] The C-rate performance of the film obtained by the present process are good in lithium battery up to 2C.

Claims

Claim 1. A process for the preparation of a solid polymer electrolyte comprising the steps of:

i) providing an aqueous dispersion of at least one fluoropolymer [polymer (FP)] in the form of nanoparticles, said polymer (FP) comprising recurring units derived from vinylidene fluoride (VDF) in an amount of at least 50% by mole with respect to the total moles of recurring units of polymer (FP), and recurring units derived from at least one fluorinated monomer (FM) different from vinylidene fluoride in an amount of at least 2.5% by mole with respect to the total moles of recurring units of polymer (FP);

ii) providing an aqueous dispersion of inorganic nanoparticles having a negative zeta potential;

iii) adding said dispersion of inorganic nanoparticles to said dispersion of polymer (FP) nanoparticles, and forming a gel subjecting the resulting mixture to intense shear;

iv) forming a dry powder from the gel coming from step iii);

v) mixing said dry powder with an ionic liquid wherein at least a lithium salt is dissolved, and submitting the resulting mixture to a heat treatment.

Claim 2. The process according to claim 1, wherein said polymer (FP) has a core-shell structure having a core of polymer (FP) as defined above and a shell comprising at least an acrylate, preferably selected from the group consisting of methyl methacrylate (MMA), methyl ester of methacrylic acid (MAA), ethyl hexyl acrylate (EHA), and mixtures thereof.

Claim 3. The process according to any one of the preceding claims, wherein said fluorinated monomer (FM) is selected from the group consisting of:

- C_2-C_8 perfluoroolefins such as tetrafluoroethylene and hexafluoropropylene (HFP);
- C_2-C_8 hydrogenated fluoroolefins such as vinyl fluoride, 1,2-difluoroethylene and trifluoroethylene;
- perfluoroalkylethylenes of formula CH_2=CH-R_{f0} wherein R_{f0} is a C_1-C_6 perfluoroalkyl;
- chloro- and/or bromo- and/or iodo-C_2-C_6 fluoroolefins such as

chlorotrifluoroethylene;

- (per)fluoroalkylvinylethers of formula $CF_2=CFOR_{f1}$ wherein R_{f1} is a C_1-C_6 fluoro- or perfluoroalkyl, e.g. CF_3, C_2F_5, C_3F_7;

- $CF_2=CFOX_0$ (per)fluoro-oxyalkylvinylethers wherein X_0 is a C_1-C_{12} alkyl group, a C_1-C_{12} oxyalkyl group or a C_1-C_{12} (per)fluorooxyalkyl group having one or more ether groups, such as perfluoro-2-propoxy-propyl group;

- (per)fluoroalkylvinylethers of formula $CF_2=CFOCF_2OR_{f2}$ wherein R_{f2} is a C_1-C_6 fluoro- or perfluoroalkyl group, e.g. CF_3, C_2F_5, C_3F_7 or a C_1-C_6 (per)fluorooxyalkyl group having one or more ether groups such as $-C_2F_5-O-CF_3$;

- functional (per)fluoro-oxyalkylvinylethers of formula $CF_2=CFOY_0$ wherein Y_0 is a C_1-C_{12} alkyl group or (per)fluoroalkyl group, a C_1-C_{12} oxyalkyl group or a C_1-C_{12} (per)fluorooxyalkyl group having one or more ether groups and Y_0 comprising a carboxylic or sulfonic acid group, in its acid, acid halide or salt form;

- fluorodioxoles, preferably perfluorodioxoles.

Claim 4. The process according to any one of the preceding claims, wherein the fluorinated monomer (FM) is hexafluoropropylene (HFP).

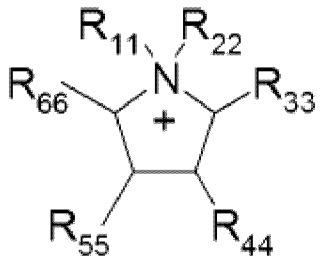
Claim 5. The process according to any one of the preceding claims, wherein said inorganic nanoparticles having a negative zeta potential are selected from the group consisting of silicon dioxide, aluminium oxide, zirconium dioxide, cerium dioxide, vanadium oxide, titanium oxide, magnesium oxide and niobium oxide.

Claim 6. The process according to any one of the preceding claims, wherein said inorganic nanoparticles are nanoparticles of precipitated silica.

Claim 7. The process according to any one of the preceding claims, wherein in step iii) the mixture is subjected to intense shear in a microchannel.

Claim 8. The process according to any one of the preceding claims, wherein said ionic liquid is a compound which is in the liquid state at temperatures below 100°C under atmospheric pressure, said compound being formed by the combination of a positively charged cation selected from the group consisting of:

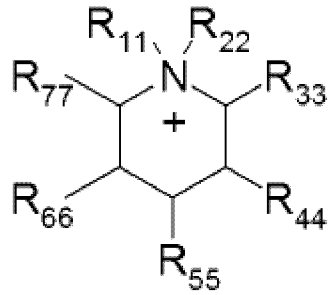
- a pyrrolidinium cation of formula (II):



(II)

wherein R_{11} and R_{22}, equal to or different from each other, independently represent a C_1-C_8 alkyl group and R_{33}, R_{44}, R_{55} and R_{66}, equal to or different from each other, independently represent a hydrogen atom or a C_1-C_{30} alkyl group, preferably a C_1-C_{18} alkyl group, more preferably a C_1-C_8 alkyl group, and

- a piperidinium cation of formula (III):

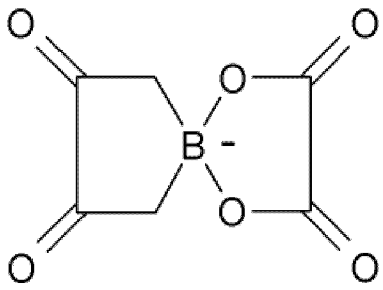


(III)

wherein R_{11} and R_{22}, equal to or different from each other, independently represent a C_1-C_8 alkyl group and R_{33}, R_{44}, R_{55}, R_{66} and R_{77}, equal to or different from each other, independently represent a hydrogen atom or a C_1-C_{30} alkyl group, preferably a C_1-C_{18} alkyl group, more preferably a C_1-C_8 alkyl group.

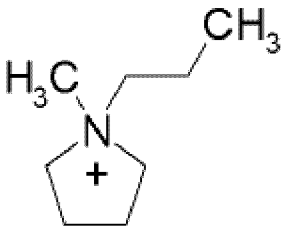
and of a negatively charged anion selected from the group consisting of:

- bis(trifluoromethylsulphonyl)imide of formula $(SO_2CF_3)_2N$-,
- hexafluorophosphate of formula PF_6^-,
- tetrafluoroborate of formula BF_4^-, and
- oxaloborate of formula:



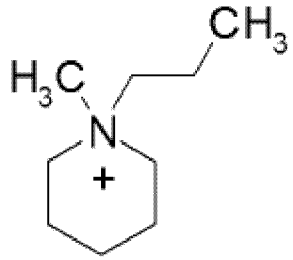
Claim 9. The process according to claim 8, wherein said positively charged cation of the ionic liquid is selected from the group consisting of:

- a pyrrolidinium cation of formula (II-A):



(II-A)

- a piperidinium cation of formula (III-A):



(III-A)

Claim 10. The process according to claim 9, wherein said ionic liquid contains a pyrrolidinium cation of formula (II-A) and a perfluorinated anion selected from the group consisting of bis(trifluoromethylsulphonyl)imide of formula $(SO_2CF_3)_2N^-$, hexafluorophosphate of formula PF_6^- and tetrafluoroborate of formula BF_4^-.

Claim 11. The process according to any one of the preceding claims, wherein said ionic liquid is N-propyl-N-methylpirrolidinium bis(trifluoromethylsulfonyl)imide.

Claim 12. The process according to any one of the preceding claims, wherein said lithium salt is selected from between lithium hexafluorophosphate and bis(trifluoromethane)sulfonimide lithium salt.

Claim 13. The process according to any one of the preceding claims, wherein said heat treatment in step v) is at a temperature ranging from 100 to 130°C and is selected from hot compression moulding and casting followed by heating.

Claim 14. A solid polymer electrolyte comprising at least a fluoropolymer (FP), inorganic nanoparticles, at least a lithium salt and an ionic liquid, obtainable by the process according to anyone of claims 1 to 13.

Claim 15. An electronic device comprising a solid electrolyte according to of claim 14.

Claim 16. An electronic device according to claim 15, which is a lithium-ion battery.

Claim 17. An electronic device according to claim 16, wherein the solid electrolyte is placed in the form of a film between the positive electrode and the negative electrode of said lithium-ion battery.

Claim 18. An electronic device according to any of the claims 15 to 17, which is a separator-free secondary battery.

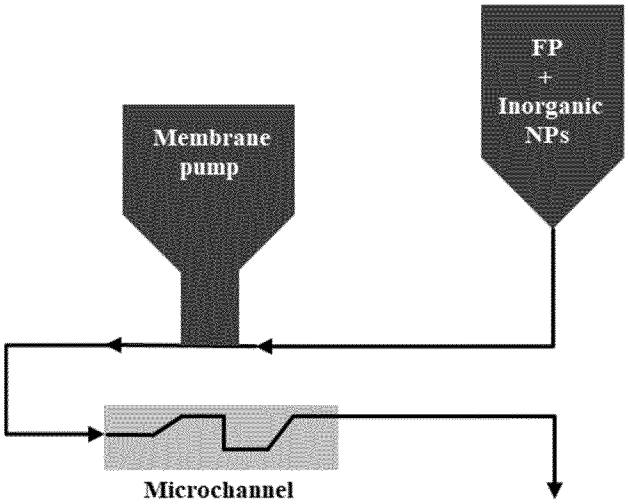


Figure 1

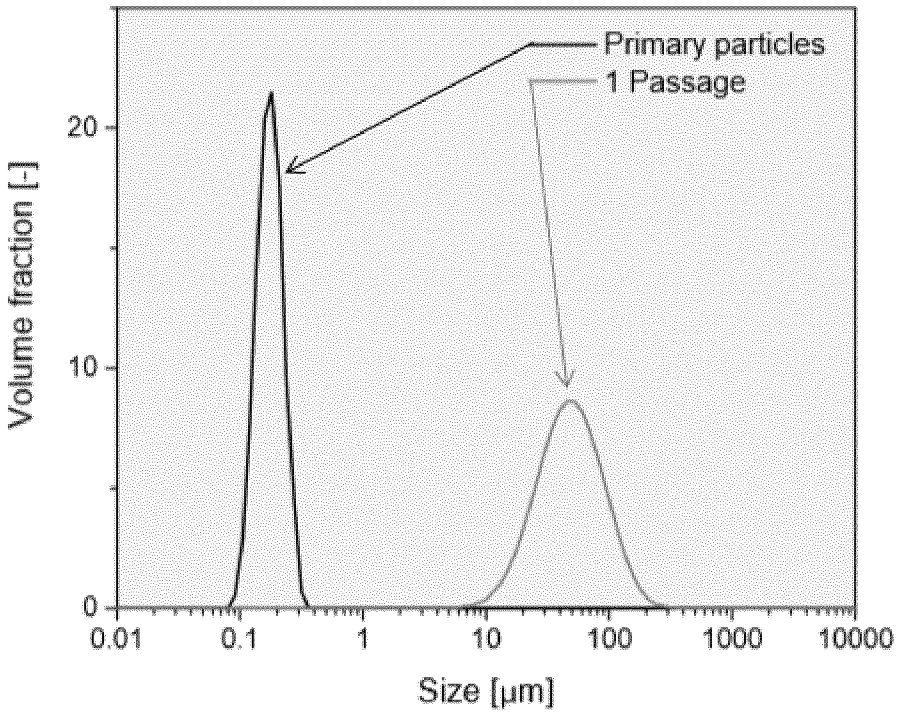

Primary particles
1 Passage
Volume fraction [-]
20
10
0
0.01
0.1
1
10
100
1000
10000
Size [µm]

Figure 2

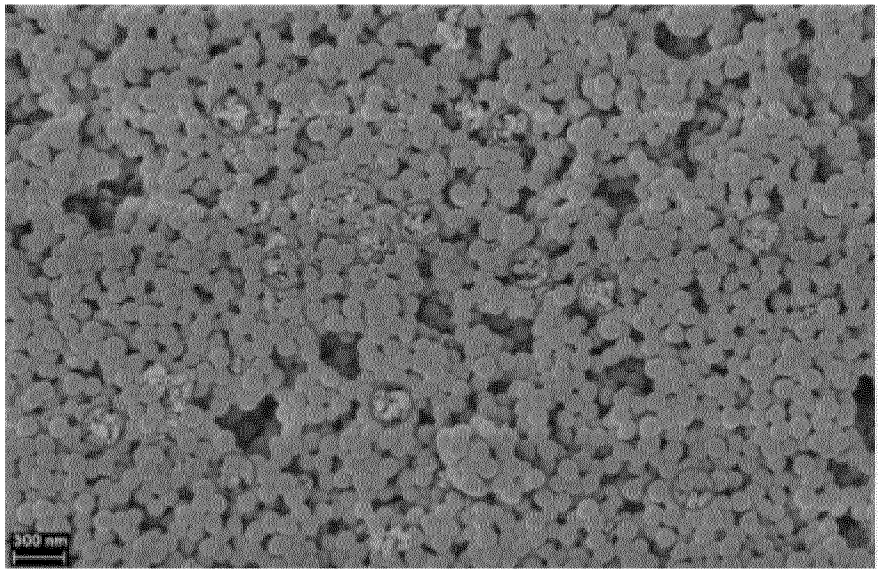


Figure 3a

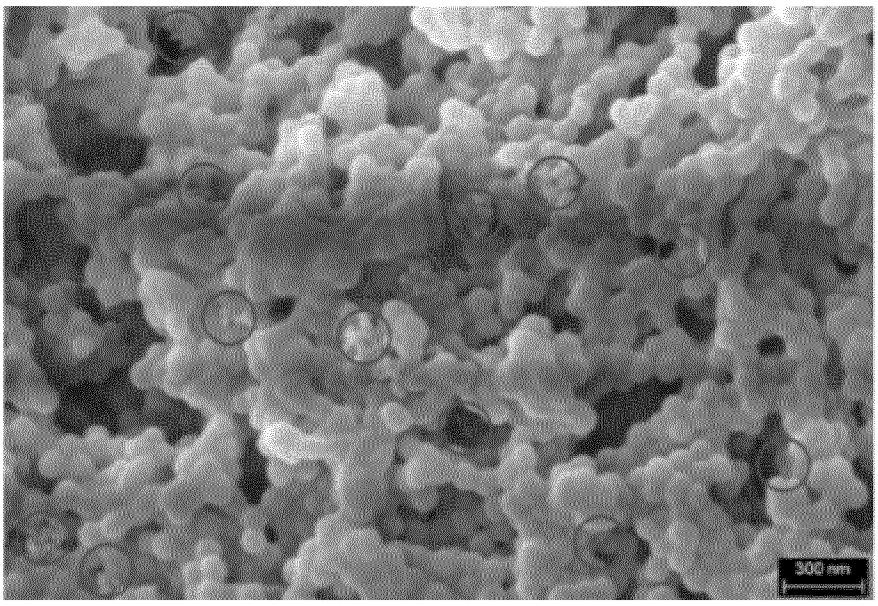


Figure 3b

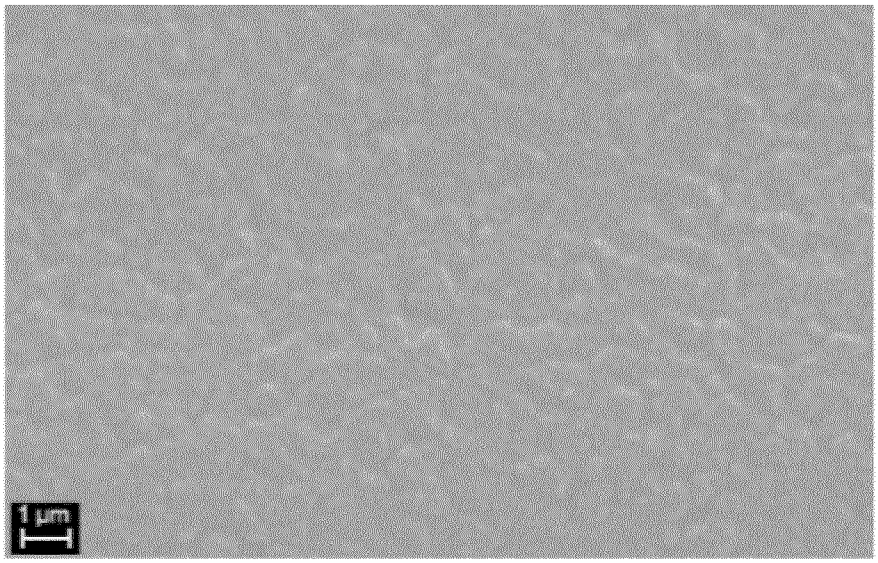


Figure 4a

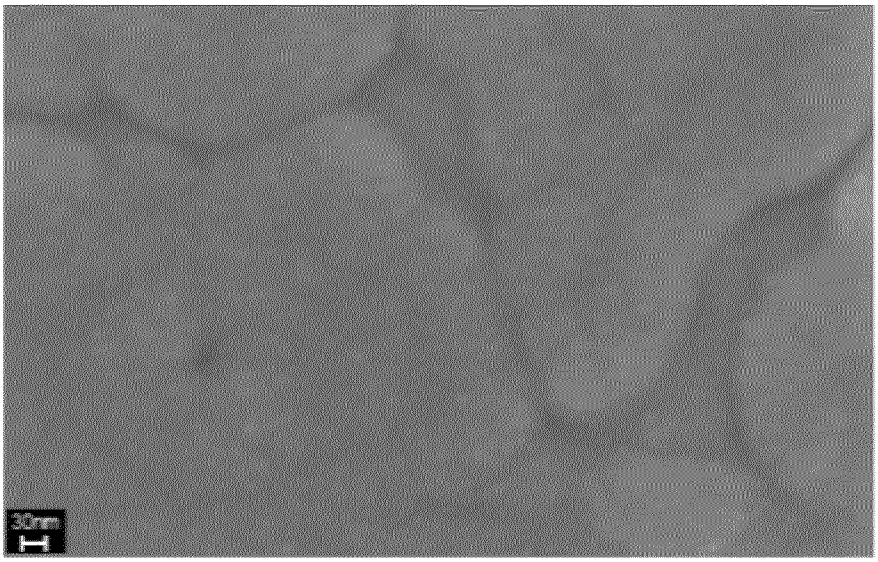


Figure 4b

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/055477

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01M10/0525 H01M10/0565
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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2015/020947 A1 (STANGA MILENA [IT] ET AL) 22 January 2015 (2015-01-22) paragraph [0021] - paragraph [0026] paragraph [0201] - paragraph [0204] claims 1-20	1-18
Y	WO 2017/067948 A1 (SOLVAY SPECIALTY POLYMERS IT [IT]) 27 April 2017 (2017-04-27) paragraph [0025] - paragraph [0032]; claims 1-11	1-18
Y	US 2017/125868 A1 (KIM KIHYUN [KR] ET AL) 4 May 2017 (2017-05-04) paragraph [0054] - paragraph [0073]	1-18

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"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	Date of mailing of the international search report
9 April 2019	18/04/2019

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Götz, Heide

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2019/055477

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		US 2015020947 A1	22-01-2015
		WO 2013120858 A1	22-08-2013
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		CN 108140782 A	08-06-2018
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