



(51) International Patent Classification:

H01G 9/042 (2006.01) *H01M 4/62* (2006.01)
H01G 9/20 (2006.01) *H01M 10/0569* (2010.01)
H01G 9/155 (2006.01)

(21) International Application Number:

PCT/EP2013/051397

(22) International Filing Date:

25 January 2013 (25.01.2013)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

12305094.0 25 January 2012 (25.01.2012) EP

(71) Applicants: SOLVAY SA [BE/BE]; Rue de Ransbeek, 310, B-1120 Bruxelles (BE). CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE [FR/FR]; Rue Michel-Ange, 3, F-75794 Paris Cedex 16 (FR). UNIVERSITE D'ORLEANS [FR/FR]; Château de la Source - BP 6749, F-45067 Orléans Cedex 2 (FR).

(72) Inventors: BÉGUIN, François; 230 rue de Lorette, F-45160 Olivet (FR). GAUTHY, Fernand; Rue P. De Waet, 38, B-1780 Wemmel (BE). RAYMUNDO-PIÑERO, Encarnación; 109 Rue Guy de Maupassant, F-45100 Orléans (FR).

(74) Agents: VANDE GUCHT, Anne et al.; Solvay SA, Intellectual Property Department, Rue de Ransbeek, 310, B-1120 Bruxelles (BE).

(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, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, 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, 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, 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, ML, MR, NE, SN, TD, TG).

Published:

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

(54) Title: FLUOROPOLYMERS AS BINDER FOR THE ELECTRODES IN SUPERCAPACITORS

(57) Abstract: A supercapacitor device comprising at least one positive electrode, at least one negative electrode, a separator and an electrolyte, wherein at least one fluoropolymer including at least one functional group (f1) capable of conferring adhesion properties on said polymer is used as binder material for the electrodes.



Fluoropolymers as binder for the electrodes in supercapacitors

- [0001] This application claims priority to European application No. 12305094.0 filed on January 25, 2012, the whole content of this application being incorporated herein by reference for all purposes.
- [0002] The present invention relates to supercapacitors comprising fluoropolymers and to the use of fluoropolymers as binder materials for electrodes in supercapacitors.
- [0003] Supercapacitors comprise at least two electrodes which may be identical (symmetrical supercapacitors) or different (asymmetrical or hybrid supercapacitors).
- [0004] Active carbon electrodes are frequently used in supercapacitors of any type. The respective electrodes are thin electrodes generally obtained by depositing a paste on a current collector. The paste is usually a mixture of active material, diluent(s), percolator and binder(s). A well known binder for this purpose is polytetrafluoroethylene (PTFE).
- [0005] The binder serves to provide cohesion for the particles of active carbon which is usually in powder form, but without masking a large fraction of active surface area. The binder must furthermore enable the active material adhere to the current collector.
- [0006] Finally, the binder should confer a certain amount of flexibility, particularly while it is being assembled and while it is in operation.
- [0007] As the binder during operation may be in contact with the electrolyte of the capacitor, the binder should be preferably inert relative to the components of the electrolyte.
- [0008] As the energy density and the power density of the capacitor depends on the percolation of current between the grains of active carbon as well as the percolation of ions, the insulating binder should support such double percolations. In this regard, it is important that the binder does not interact excessively with the grains of the active carbon material in order to avoid reducing the active surface area which is important for the energy density of the capacitor. The compromise needs to be found so that the binder on

one hand ensures the cohesion between the grains of the active material and on the other side does not detrimentally influence active surface area.

- [0009] US 6,356,432 describes a supercapacitor comprising a non-aqueous electrolyte and two carbon electrodes with a binder comprising a mixture of carboxy methyl cellulose and a copolymer of styrene and butadiene.
- [0010] From the foregoing it becomes apparent that the nature and composition of the binder material has to be carefully designed to achieve optimum properties of the supercapacitor.
- [0011] It was thus an object of the present invention to provide new supercapacitors with improved binders and new binder materials for supercapacitors providing an improvement over binder materials known from the prior art.
- [0012] This objective has been achieved with the supercapacitors comprising fluoropolymers including at least one functional group (F1) capable of conferring adhesion properties on said polymer as binder materials for the electrodes. Preferred fluoropolymers are defined in the dependent claims and described in the detailed specification hereinafter.
- [0013] The fluoropolymers which can be used in accordance with the present invention may either be grafted fluoropolymers grafted by at least one compound containing at least one functional group capable of configuring adhesion properties of the fluoropolymer or may be copolymers comprising repeating units polymerized from at least one fluoromonomer and repeat units polymerized from at least one compound bearing at least one functional group capable of conferring adhesion properties on the polymer.
- [0014] Fluoropolymers used in accordance with the present invention comprise at least one fluoropolymer (A). The term "fluoropolymer" is understood to mean a polymer for which more than 50 % by weight of the monomer units are derived from at least one fluoromonomer. The fluoropolymer may be a homopolymer; it may also be a copolymer formed by several fluoromonomers with one another, or else a copolymer formed by one or more fluoromonomers with one or more non-fluorinated monomers. These

copolymers may, in particular, be random copolymers, block copolymers or grafted copolymers

[0015] The term "fluoromonomer" is understood to mean any monomer that comprises at least one fluorine atom; it customarily comprises at least one ethylenic unsaturation. As examples of fluoromonomers, mention may be made of fluorinated vinyl monomers, fluorinated styrene monomers such as 4-fluorostyrene, fluorinated (meth)acrylic monomers such as trifluoroethyl acrylate and fluorinated conjugated dienes such as 2-fluorobutadiene. The fluoromonomer is preferably a fluorinated vinyl monomer. The expression "fluorinated vinyl monomer" is understood to denote the monoethylenically-unsaturated fluorinated monomers that are aliphatic and that have one or more fluorine atoms and optionally, in addition, one or more chlorine atoms, as the only heteroatom(s). As examples of fluorinated vinyl monomers, mention may be made of vinyl monomers that are free of hydrogen atoms such as tetrafluoroethylene, hexafluoropropylene and chlorotrifluoroethylene, and partially hydrogenated fluorinated vinyl monomers such as vinyl fluoride, trifluoroethylene, 3,3,3-trifluoropropene and, with most particular mention, vinylidene fluoride.

[0016] The expression "non-fluorinated monomer" is understood to mean any monomer that is free of fluorine atoms; it customarily comprises at least one ethylenic unsaturation. Examples of non-fluorinated monomers are: α -monoolefins such as, for example, ethylene and propylene; styrene and non-fluorinated styrene derivatives; non-fluorinated chloromonomers such as, for example, vinyl chloride and vinylidene chloride; non-fluorinated vinyl ethers; non-fluorinated vinyl esters such as, for example, vinyl acetate; (meth)acrylic esters, nitriles and amides such as acrylonitrile and acrylamide.

[0017] As examples of fluoropolymers, mention may especially be made of the homopolymers of vinylidene fluoride, vinyl fluoride, trifluoroethylene or chlorotrifluoroethylene, and the copolymers that these fluoromonomers form with one another or with at least one other fluoromonomer as defined above (including a fluoromonomer that does not contain hydrogen atoms,

such as tetrafluoroethylene or hexafluoropropylene). As examples of such copolymers and terpolymers, mention may be made of the copolymers and terpolymers of vinylidene fluoride and the copolymers and terpolymers of chlorotrifluoroethylene with at least one other fluoromonomer as defined above (including a fluoromonomer that does not contain hydrogen atoms, such as tetrafluoroethylene or hexafluoropropylene). Mention may also be made of the copolymers and terpolymers of at least one of the fluoromonomers mentioned above with at least one non-fluorinated monomer.

[0018] The fluoropolymer (A) according to the invention is preferably chosen from vinylidene fluoride polymers.

[0019] For the purposes of the present invention, a vinylidene fluoride polymer is a fluoropolymer (i.e. a polymer for which more than 50 % by weight of the monomer units are derived from at least one fluoromonomer), comprising monomer units derived from vinylidene fluoride.

[0020] As examples of vinylidene fluoride polymers, mention may especially be made of homopolymers of vinylidene fluoride, and copolymers thereof with other ethylenically unsaturated monomers, whether they are fluorinated (examples of other ethylenically unsaturated fluoromonomers are vinyl fluoride, trifluoroethylene, tetrafluoroethylene, chlorotrifluoroethylene and hexafluoropropylene) or non-fluorinated (examples of ethylenically unsaturated non-fluorinated monomers are α -monoolefins such as ethylene and propylene; styrene and non-fluorinated styrene derivatives; non-fluorinated chloromonomers such as vinyl chloride and vinylidene chloride; non-fluorinated vinyl ethers; non-fluorinated vinyl esters such as vinyl acetate; non-fluorinated (meth)acrylic esters, nitriles and amides such as acrylamide and acrylonitrile).

[0021] The vinylidene fluoride polymers preferably contain more than 50 % by weight of monomer units derived from vinylidene fluoride.

[0022] Particularly preferred vinylidene fluoride polymers are vinylidene fluoride homopolymers and random copolymers of vinylidene fluoride that contain 3 to 30, preferably 10 to 20 % by weight of a fluorinated comonomer chosen from hexafluoropropylene and chlorotrifluoroethylene.

- [0023] According to one embodiment of the invention, the fluoropolymer (A) is functionalized by grafting with at least one compound (a) - defined and described in detail hereinafter – which contains at least one functional group (f1) capable of conferring adhesion properties on said fluoropolymer.
- [0024] As an alternative possibility, the fluoropolymer (A) can be obtained by copolymerisation or by various coupling reactions during the (co)polymerization with the adequate compound (a) - defined and described in detail hereinafter – which contains at least one functional group (f1) capable of conferring adhesion properties on said fluoropolymer.
- [0025] The functional group (f1) may be any group having a reactivity or a polarity such that it enables the fluoropolymer to develop adhesion forces, even with respect to materials that it is not normally possible to adhere to this polymer. The group (f1) is generally chosen from the groups bearing at least one reactive function that does not take part in radical mechanisms. It is usually chosen from
- [0026] (f1.1) groups derived from carboxylic acids, also known more simply hereinbelow as "acid groups"; the carboxylic acids from which these groups originate may be monocarboxylic or dicarboxylic acids,
- [0027] (f1.2) groups derived from carboxylic anhydrides, resulting from the condensation of two carboxylic acid groups in the same molecule, also known more simply hereinbelow as "anhydride groups"; the carboxylic anhydrides that bear these groups may themselves derive from monocarboxylic or dicarboxylic acids,
- [0028] (f1.3) groups derived from carboxylic esters, also known more simply hereinbelow as "ester groups",
- [0029] (f1.4) groups derived from carboxylic amides, also known more simply hereinbelow as "amide groups",
- [0030] (f1.5) epoxy groups, derived from compounds containing a cyclic ether function,

- [0031] (f1.6)hydroxylated groups derived from alcohols, also known more simply hereinbelow as "alcohol groups"; the alcohols from which these groups originate may be monoalcohols or polyols,
- [0032] (f1.7)carbonyl groups, and
- [0033] (f1.8)hydrolysable groups containing a silyl group.
- [0034] Among all these groups, the epoxy groups (f1.5), the alcohol groups (f1.6) and the carbonyl groups (f1.7) are preferred. More particularly, the epoxy groups and the alcohol groups derived from diols are preferred. The alcohol groups derived from diols give the best results.
- [0035] As mentioned, the functionalization of the fluoropolymer (A) in this embodiment is carried out by grafting, to this polymer, at least one compound (a) that contains at least one functional group (f1). According to the invention, the functional group(s) (f1) borne by the compound(s) (a) may belong to the same family or to different families. Thus, it is in no way excluded to use both one compound (a) containing an epoxy group and another compound (a) containing one or more alcohol groups; similarly, it is in no way excluded to use a compound (a) containing both an ester group and another group, for example an epoxy or alcohol group.
- [0036] In order to be able to be grafted to the fluoropolymer (A), the compound (a) must also contain at least one group (g) that makes the grafting of said compound (a) to this polymer possible. This group (g) is generally chosen from:
- [0037] saturated or unsaturated hydrocarbon-based groups, capable of participating in radical mechanisms, such as additions or associations of radicals,
- [0038] amino or phenol groups capable of participating in reactions of nucleophilic character,
- [0039] groups capable of easily forming free radicals such as peroxy and azo groups.
- [0040] In case the fluoropolymer cannot be grafted directly, groups capable of easily reacting with free radicals such as iodine groups.
- [0041] bromine groups and chlorine groups (iodine groups being preferred) can be attached to the polymer backbone before grafting.

- [0042] Preferably, the group (g) is chosen from organic groups having at least one ethylenically unsaturated carbon-carbon bond, from amino groups and from peroxy groups. Organic groups having at least one terminal (α,β) ethylenically unsaturated carbon-carbon bond, such as vinyl, allyl, acryloyloxyalkyl and methacryloyloxyalkyl groups for example, are particularly preferred as the group (g). Allyl groups give the best results.
- [0043] Examples of compounds (a) that contain at least one organic group having at least one terminal (α,β) ethylenically unsaturated carbon-carbon bond as group (g) and at least one acid or anhydride group as group (f1) are unsaturated monocarboxylic or dicarboxylic acids such as acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, crotonic acid, citraconic acid, bicyclo[2.2.1]hept-2-ene-5,6-dicarboxylic acid, maleic anhydride, itaconic anhydride, crotonic anhydride and citraconic anhydride. Maleic anhydride is generally preferred, in particular for reasons of accessibility.
- [0044] Examples of compounds (a) that contain at least one organic group having at least one terminal (α,β) ethylenically unsaturated carbon-carbon bond as groups (g) and at least one ester group as group (f1) are vinyl acetate, vinyl propionate, monomethyl maleate, dimethyl maleate, methyl acrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, isobutyl acrylate, amyl acrylate, hexyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, n-butyl methacrylate, amyl methacrylate, hexyl methacrylate, 2-ethylhexyl methacrylate, diethyl fumarate, dimethyl itaconate and diethyl citraconate.
- [0045] Examples of compounds (a) that contain at least one organic group having at least one terminal (α,β) ethylenically unsaturated carbon-carbon bond as group (g) and at least one amide group as group (f1) are acrylamide and methacrylamide.
- [0046] An example of compound (a) that contains at least one organic group having at least one terminal (α,β) ethylenically unsaturated carbon-carbon bond as group (g) and at least one epoxy group as group (f1) is allyl glycidyl ether.

- [0047] Examples of compounds (a) that contain at least one organic group having at least one terminal (α,β) ethylenically unsaturated carbon-carbon bond as group (g) and at least one alcohol group as group (f1) are allyl alcohol and 3-allyloxy-1,2-propanediol.
- [0048] Examples of compounds (a) that contain at least one organic group having at least one terminal (α,β) ethylenically unsaturated carbon-carbon bond as group (g) and at least one carbonyl group as group (f1) are organic heterocyclic compounds containing a vinyl or allyl group attached to the heteroatom and the heterocycle of which bears the carbonyl bond, such as N-vinylpyrrolidone and N-vinylcaprolactam.
- [0049] Examples of compounds (a) that contain at least one organic group having at least one terminal (α,β) ethylenically unsaturated carbon-carbon bond as group (g) and at least one hydrolysable group containing a silyl group as group (f1) are vinyltrimethoxysilane, vinyltriethoxysilane, vinyltriacetoxysilane, vinyltris(β -methoxyethoxy)silane and γ -methacryloxypropyltrimethoxysilane.
- [0050] Examples of compounds (a) that contain at least one organic group having at least one terminal (α,β) ethylenically unsaturated carbon-carbon bond as group (g) and at least two functional groups (f1) of different nature, are: glycidyl acrylate and methacrylate (an ester group and an epoxy group as groups (f1)); hydroxyethyl acrylate and methacrylate and hydroxypropyl acrylate and methacrylate (an ester group and an alcohol group as groups (f1)), N-methylolmethacrylamide (an alcohol group and an amide group as groups(f1)).
- [0051] Among all the compounds (a), the compounds containing at least one functional group (f1) chosen from epoxy groups, alcohol groups and carbonyl groups, more particularly from alcohol groups derived from diols, are preferred. Allyl glycidyl ether, 3-allyloxy-1,2-propanediol, N-vinylpyrrolidone and N-vinylcaprolactam give good results. The best results were obtained with 3-allyloxy-1,2-propanediol.
- [0052] The grafting of the compound (a) to the fluoropolymer (A) may be carried out by any method known for this purpose. Depending on the chemical properties and the physical state of the compound (a), this grafting may be

carried out in the solid state, in solution, in suspension, in an aqueous medium or within an organic solvent. This grafting may also be carried out by irradiation, for example by means of an electron beam or by gamma radiation.

- [0053] The grafting of the compound (a) to the fluoropolymer (A) is most generally carried out on a molten blend of the compound and polymer. It is possible to operate in batch mode, in kneaders, or continuously, in extruders.
- [0054] The reaction of grafting the compound (a) to the fluoropolymer (A) is usually promoted and initiated by a radical generator, at least when the group (g) of the compound (a) is not itself a group capable of easily forming free radicals, such as peroxy and azo groups. As a radical generator, use is generally made of compounds having a decomposition temperature between 120 and 350°C and a half life, in this temperature zone, of around one minute. The radical generator is preferably an organic peroxide, and more particularly an alkyl or aryl peroxide. Among these, mention may be made of benzoyl peroxide, dichlorobenzoyl peroxide, dicumyl peroxide, di(*t*-butyl) peroxide, *t*-butylcumyl peroxide, 1,3-di(2-*t*-butylperoxyisopropyl)benzene, 2,5-dimethyl-2,5-di(*t*-butylperoxy)hexane and 2,5-dimethyl-2,5-di(*t*-butylperoxy)-3-hexyne. 2,5-Dimethyl-2,5-di(*t*-butylperoxy)hexane and dicumyl peroxide are particularly preferred.
- [0055] When the grafting of the compound (a) to the fluoropolymer (A) is carried out continuously in an extruder, the radical generator and the compound (a) may be introduced in any manner so long as they are introduced continuously over time and they are well dispersed in the molten material. The radical generator and the compound (a) may be introduced by spraying, for example by means of a spray-type injector or an atomizer or by injection into the molten mass. The introduction of the radical generator and the compound (a) via a masterbatch with the powdered fluoropolymer (A) or via a masterbatch with a filler can also be envisaged.
- [0056] According to one particularly preferred embodiment, the compound (a) is introduced before the radical generator.

- [0057] The expression "reaction in molten mass" is understood to mean, for the purposes of the present invention, any reaction in the substantial absence of solvent or of diluent and at a temperature at least equal to the melting point of the fluoropolymer (A).
- [0058] The term "extruder" is understood to mean any continuous device comprising at least one feed zone and, at its outlet, a discharge zone preceded by a compression zone, the latter forcing the molten mass to pass through the discharge zone. The discharge zone may additionally be followed by a granulating device or by a device that gives the extruded material its final shape. Advantageously, use is made of known extruders based on the work of a single screw or of two screws which, in the latter case, may cooperate in a co-rotating or counter-rotating manner (same direction of rotation or opposite directions of rotation).
- [0059] Preferably, the extruder used according to the present invention is arranged so that it successively comprises one feed zone, one material melting zone, one homogenization zone, one reaction zone, optionally one zone for introducing additives, and one compression-discharge zone preceded by one degassing zone. Each of these zones has a very specific function and is at a very specific temperature.
- [0060] The feed zone has the role of carrying out the feeding of the fluoropolymer (A). It is customarily at a temperature less than or equal to 50°C.
- [0061] The material melting zone has the role of carrying out the melting of the material.
- [0062] The homogenization zone has the role of homogenizing the molten material.
- [0063] The reaction zone has the role of carrying out the reaction.
- [0064] The temperature in the melting zone and in the zone for homogenization of the material is customarily greater than or equal to the melting point of the fluoropolymer (A).
- [0065] The temperature in the reaction zone is customarily greater than or equal to the temperature at which the half life of the radical generator is less than the residence time of the material in this zone.

- [0066] The zone for introducing additives has the role of carrying out the introduction of additives when the latter are added into the extruder. The temperature of this zone is generally a function of the viscosity of the material and the nature of the additives added.
- [0067] The compression-discharge zone has the role of compressing the material and of carrying out the discharge of the latter. The temperature in the compression-discharge zone is generally a function of the viscosity of the material to be discharged.
- [0068] The compound (a) is preferably introduced into the extruder before the homogenization zone.
- [0069] The radical generator is preferably introduced into the reaction zone of the extruder.
- [0070] Whichever grafting method is used, the amount of compound (a) grafted to the polymer (A) expressed as amount of compound (a), is advantageously greater than 0.01% by weight, preferably 0.05 % by weight or, better still, 0.1% by weight, relative to the weight of polymer (A). Moreover, this amount is advantageously less than or equal to 5.0 % by weight, preferably 3.0 % and better still 2.0 % by weight. The metering is customarily carried out by a chemical route (titration).
- [0071] Quite remarkable adhesive properties and an exceptionally high thermal stability were observed when the polymer (A) being incorporated into the polymer compositions according to the invention was a fluoropolymer grafted by at least one compound (a) containing, as group (g), at least one organic group having at least one ethylenically unsaturated carbon-carbon bond and, as groups (f1), at least two alcohol groups. Therefore, such polymers are used in accordance with a preferred embodiment of the present invention.
- [0072] Such grafted fluoropolymers are preferably vinylidene fluoride polymers. Particularly preferably, they contain more than 50 % by weight of monomer units derived from vinylidene fluoride. Most particularly preferably, they are chosen from vinylidene fluoride homopolymers and random copolymers of vinylidene fluoride that contain 3 to 30, preferably 10 to 20 % by weight of

a fluorinated comonomer chosen from hexafluoropropylene and chlorotrifluoroethylene.

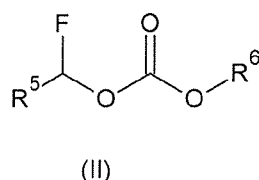
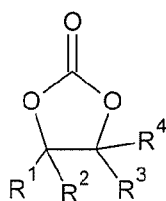
- [0073] The group (g) of the compound (a) of the grafted fluoropolymers is preferably an organic group containing at least one terminal (α,β) ethylenically unsaturated carbon-carbon bond. Particularly preferably, it is chosen from vinyl, allyl, acryloyloxyalkyl and methacryloyloxyalkyl groups. Most particularly preferably, it is an allyl group.
- [0074] The compound (a) of such grafted preferred fluoropolymers contains at most four alcohol groups. Particularly preferably, it contains at most three thereof. Most particularly preferably, it contains two such groups.
- [0075] The compound (a) of the preferred grafted fluoropolymers is preferably chosen from aliphatic and cycloaliphatic compounds. Particularly preferably, it is chosen from aliphatic compounds.
- [0076] Good results have been obtained when the compound (a) of the grafted fluoropolymers was an alkenediol, in particular when the grafted fluoropolymers in question were chosen from vinylidene fluoride homopolymers and random copolymers of vinylidene fluoride that contain 3 to 30, preferably 10 to 20 % by weight of a fluorinated comonomer chosen from hexafluoropropylene and chlorotrifluoroethylene.
- [0077] Excellent results have been obtained when the compound (a) of the fluoropolymers according to the present invention was 3-allyloxy-1,2-propanediol, in particular when the grafted fluoropolymers in question were chosen from vinylidene fluoride homopolymers and random copolymers of vinylidene fluoride that contain 3 to 30, preferably 10 to 20 % by weight of a fluorinated comonomer chosen from hexafluoropropylene and chlorotrifluoroethylene.
- [0078] According to another embodiment of the present invention the fluoropolymer including at least one functional group (f1) capable of conferring adhesion properties on said polymer is obtained by the copolymerization of a fluoromonomer as defined above and a compound bearing at least one functional group capable of conferring adhesion properties on the copolymer. The functional groups are as described above for the embodiment of grafting.

- [0079] The amount of repeat units derived from compound (a) copolymerized with the fluoromonomer(s), is advantageously greater than 0.1 % by weight, preferably 0.5 % by weight or, better still, 1 % by weight. Moreover, this amount is advantageously less than or equal to 20.0 % by weight, preferably 10 %, more preferably less than 5 % and better still 2.0 % by weight. The metering is customarily carried out by a chemical route (titration).
- [0080] The copolymerization and various coupling techniques can be achieved by any techniques known to the skilled person like e.g. suspension or emulsion or polymerization.
- [0081] Suitable copolymers usually comprise more than 50 % by weight of repeat units derived from the fluoromonomer and less than 50 wt% of repeat units derived from the compound bearing at least one functional group capable of conferring adhesion properties on the copolymer. Preferred are copolymers comprising at least 70, more preferably at least 80 and most preferably at least 90 wt% of repeat units derived from at least one fluoromonomer or a mixture of fluoromonomers as described in more detail above.
- [0082] A preferred group of copolymers which can be advantageously used in the supercapacitors of the present invention are copolymers comprising repeat units derived from vinylidene fluoride, 3-30 wt%, preferably 10 to 20 wt% of repeat units, based on the total weight of the repeat units, derived from at least one of hexafluoropropylene, chlorotrifluoroethylene and tetrafluoroethylene, and repeat units derived from at least one compound providing the functional group f1. The percentage of repeat units derived from compounds (a) is as given above for the embodiment of copolymerization.
- [0083] The copolymerization of fluoromonomers with such monomers is known per se to the skilled man and there is no need to give a detailed description of the reaction conditions here. Usual copolymerization processes have been described in the literature and reference is made thereto here.

- [0084] The vinylidene fluoride polymers described above are suitable as binders for any type of electrode in supercapacitors where a binder is needed for the preparation. The skilled person will select the appropriate electrode materials depending on the intended final product and will thus also decide when a binder has to be used or not.
- [0085] As a general rule it is desirable to keep the binder content in the electrode as low as possible to obtain the desired cohesion of the binder and the active material and a good adhesion of the electrode to the metal collector. The less binder is used, the lower the viscosity can be adjusted and thus energy and power performance can be improved.
- [0086] Usually the electrodes are manufactured by first fabricating a paste from the electrode material, e.g. active carbon, a percolator and the binder and putting this into a solvent. Thereafter the paste is spread on a metal foil constituting the collector which may e.g. be a metal foil, in particular an aluminum foil, followed by drying at elevated temperatures and then calendaring the product to obtain the desired porosity.
- [0087] Electrodes with porosities of at least 50, preferably at least 70% usually yield the best performance properties for the supercapacitors.
- [0088] The supercapacitors in which the fluoropolymers in accordance with the present invention may be used as binder for the electrodes comprise the usual components of such supercapacitors besides the electrodes, namely also a separator and an electrolyte system. Respective products for these components have been described in the literature and are known to the skilled person. Accordingly, a detailed or exhaustive description of these components is not necessary here.
- [0089] Advantageously, the supercapacitors in which the fluoropolymers in accordance with the present invention may be used as binder for the electrodes further comprise at least one percolator. The percolator allows typically for electrical percolation phenomena, and can be defined as a chemical agent is capable of facilitating the move of electron and/or ions, preferably of both, through the electrodes, more precisely through their active masses. In accordance with the present invention, the chemical nature of the percolator is not particularly limited. Suitable percolators

include carbon black, especially highly porous carbon black, exfoliated graphite, graphene, carbon nanotubes, carbon nanohorns and mixtures thereof.

- [0090] Beneficial effects of the fluoropolymers as binder can be achieved regardless of the nature of the separator and of the electrolyte system, and thus the composition of the separator component and the composition of the electrolyte system component are not particularly critical.
- [0091] However, in certain cases it has proven to be advantageous if the separator also comprises a fluoropolymer of the type described above and thus supercapacitors of this type constitute another preferred embodiment of the present invention.
- [0092] Classical electrolytic capacitors consist of a series of combinations of electrodes, separated by an electrolyte, and between which dielectric oxide film is formed adjacent to the surface of one or both of the electrodes.
- [0093] In accordance with another preferred embodiment, the fluoropolymers are used as binder for electrodes in supercapacitors which comprise electrolyte system comprising organic solvents or mixtures of solvents which contain of from 0.1 to 30, preferably of from 0.2 to 20 and particularly preferably of from 0.5 to 10 wt%, based on the total weight of the electrolyte solvent, of a fluorinated carbonate of the general formulae I or II



[0094] (I)

[0095] wherein R¹ to R⁴, which may be the same or different, are independently selected from hydrogen, fluorine, C₁ to C₈ -alkyl and C₁ to C₈ haloalkyl which the proviso that at least one of R¹ to R⁴ is a fluorine atom or comprises a fluorine atom and R⁵ to R⁶, independently of one another are selected from hydrogen, C₁ to C₈ alkyl or C₁-C₈ haloalkyl.

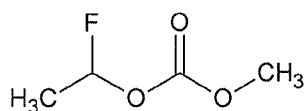
[0096] Such electrolyte systems may comprise one or more than one fluorinated carbonate. If mixtures of fluorinated carbonates are used, the weight percentages given above are applicable for the entire weight of the mixture of fluorinated carbonates in the electrolyte system.

[0097] Generally any fluorinated carbonate of formula I or II is suitable

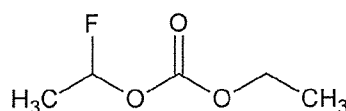
[0098] It may be noted here that fluorinated propylene carbonates (at least one of R^1 to R^4 is a methyl or a fluorinated methyl group) generally show a significantly higher viscosity than respective ethylene carbonates. The increased viscosity may lead to a decrease in ion conductivity of the electrolyte system, thus bearing the risk of deterioration of the performance properties of the supercapacitor. Accordingly, it might be advantageous to use as low as possible amounts of fluorinated carbonates in this case or to preferably use fluorinated ethylene carbonates instead of fluorinated propylene carbonates.

[0099] The viscosity also generally increases with increasing number of fluorine atoms in the fluorinated carbonate, which is also a factor the skilled person will take into account.

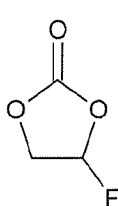
[00100] The following compounds represent preferred representatives of fluorinated carbonates for use in electrolyte systems.



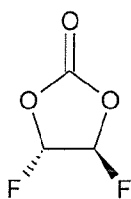
1-Fluoroethyl methyl carbonate



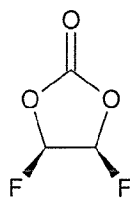
Ethyl-1-Fluoroethyl carbonate



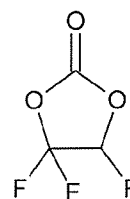
[00101] F1EC



trans-F2EC



cis-F2EC



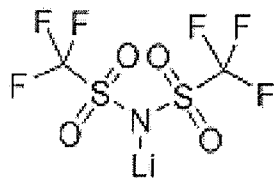
F3EC

[00102] As is apparent for the skilled person, F1EC represents monofluoro ethylene carbonate, F2EC represents difluoro ethylene carbonate and F3EC stands for trifluoro ethylene carbonate.

[00103] Based on the foregoing it is apparent that F1EC, ethyl 1-fluoroethyl carbonate and methyl 1-fluoroethyl carbonate, comprising one fluorine atom in the molecule are particularly preferred when a low viscosity is aimed at.

[00104] Furthermore, non-cyclic carbonates generally are less viscous than cyclic carbonates which may be taken into account by the skilled person.

[00105] In accordance with another embodiment, the electrolyte may comprise 0.1 to 100, preferably 20-80 and more preferably 40-60 % by weight, based on the total weight of the electrolyte, of LiTFSI



[00106]

[00107] LiTFSI can be used alone or in combination with a fluorinated carbonate as described above.

[00108] The present invention can be particularly useful in hybrid supercapacitors, which comprise two different electrodes operating according to different electrochemical mechanisms (which is the reason for the term hybrid supercapacitor), one of which works in a similar albeit different way than the anode in lithium batteries. In principle such hybrid supercapacitors combine the energy storage principle of a lithium-ion secondary battery and an electric double-layer capacitor.

[00109] A capacitive material is characterized by a potential swing during the charge and discharge of the capacitor. The initial output potential difference of a symmetric cell with capacitive electrodes is 0V and the potentials diverge linearly during charging of cell. By contrast, the battery-like electrode is characterized by an almost constant potential during charging and discharging. Thus, in order to get the largest voltage in an asymmetric capacitor, where a capacitive electrode is replaced by a battery-like one, the potential of the selected battery-electrode must be close to the low or high limit of the potential window of the capacitive electrode.

[00110] Li-intercalation compounds ($\text{Li}_4\text{Ti}_5\text{O}_{12}$, WO_2 , LiCoO_2 , $\text{LiMn}_{1.2}\text{Ni}_{0.5}\text{O}_4$, etc.) have been proposed for electrodes of hybrid capacitors working in organic

electrolytes, the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /activated carbon system being one of the most intensively studied systems.

[00111] Hybrid supercapacitors may comprise a graphite negative electrode wherein lithium ions are previously intercalated; the later is combined with a porous carbon positive electrode and for both electrodes the fluoropolymers can be used as a binder. Respective systems may comprise a positive electrode based on activated carbon and a negative electrode based on graphite or hard carbon and have been described in the literature as Li-ion capacitors.

[00112] Hybrid supercapacitors comprising a positive electrode based on activated carbon and comprising at least 20, preferably at least 50 and most preferably at least 80 % activated carbon are preferred.

[00113] Furthermore, the negative electrode of hybrid supercapacitors in accordance with the present invention is preferably based on graphite and comprises at least 20, preferably at least 50 and more preferably at least 80% of graphite.

[00114] By a so-called pre-doping, i.e. the intercalation of lithium in a graphitic type material prior to the charge/discharge of the capacitor, the potential of the negative electrode can be lowered and the potential window of the positive electrode can be extended. To achieve this, an additional lithium ion source has to be provided and a Li foil has been used for this purpose.

[00115] Other systems which have been described comprise a positive electrode based on activated carbon and a negative electrode based on non-graphitizable carbon and again, the fluoropolymers defined hereinbefore may be used as a binder for these electrodes.

[00116] While the use of metallic lithium compounds has some benefits in improving energy density and cycle life, it also has some drawbacks, in particular from the view point of safety. In view of this it has been proposed to use suitable electrolyte systems where the intercalated lithium can be taken directly from the electrolyte (Beguin et al., J. Power Source 2008, 177, 643) and the electrode systems described therein for the electrodes of the supercapacitor can be preferably used in accordance with the present invention in another preferred embodiment.

[00117] Generally, the available surface at the electrodes limits the amount of energy which can be stored in a supercapacitor and thus it is advantageous to use electrode materials with high surface area. The skilled person knows such materials and will select the appropriate combination of electrodes based on his knowledge and the information provided in the prior art.

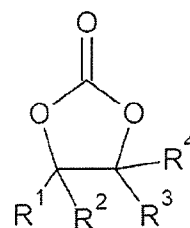
[00118] Graphene materials as supercapacitor electrode materials have also been described in the literature and may be used in accordance with another preferred embodiment of the present invention.

[00119] 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.

Claims

1. A supercapacitor device comprising at least one positive electrode, at least one negative electrode, a separator, an electrolyte and a binder, said binder comprising a fluoropolymer including at least one functional group (f1) capable of conferring adhesion properties on said polymer.
2. The supercapacitor in accordance with claim 1 wherein in the fluoropolymer more than 50 % by weight of the monomeric units are derived from a fluoromonomer.
3. The supercapacitor in accordance with claim 1 or 2 wherein the fluoropolymer is a homopolymer or a copolymer formed by several fluoromonomers or a copolymer of one or more fluoromonomers and one or more non-fluorinated monomers.
4. The supercapacitor in accordance with any of claims 1 to 3 wherein the functional group f1 is a group bearing at least one functional group which does not take part in radical mechanisms.
5. The supercapacitor in accordance with any of claims 1 to 4 wherein the functional group is selected from
 - (f1.1) groups derived from carboxylic acids,
 - (f1.2) groups derived from carboxylic anhydrides,
 - (f1.3) groups derived from carboxylic esters,
 - (f1.4) groups derived from carboxylic amides,
 - (f1.5) epoxy groups,
 - (f1.6) alcohol groups,
 - (f1.7) carbonyl groups, and
 - (f1.8) hydrolysable groups containing a silyl group.
6. The supercapacitor in accordance with claim 5 wherein the functional group is selected from epoxy groups, alcohol groups and carbonyl groups.
7. The supercapacitor in accordance with any of claims 1 to 6 wherein the fluoropolymer is a vinylidene fluoride polymer selected from homopolymers of vinylidene fluoride and copolymers thereof with other ethylenically unsaturated monomers, and the vinylidene fluoride polymer contains more than 50 % by weight of monomer units derived from vinylidene fluoride.

8. The supercapacitor in accordance with any of claims 1 to 7 wherein the functional group is introduced into the fluoropolymer by grafting and/or by copolymerization.
9. The supercapacitor in accordance with claim 8 wherein the fluoropolymer is functionalized by grafting with at least one compound (a) which contains at least one functional group (f1) capable of conferring adhesion properties on said fluoropolymer.
10. The supercapacitor in accordance with claim 8 wherein the fluoropolymer is obtained by copolymerisation with a compound (a) which contains at least one functional group (f1) capable of conferring adhesion properties on said fluoropolymer.
11. The supercapacitor in accordance with claim 9 or 10 wherein the compound (a) contains at least one organic group (g) having at least one terminal (α,β) ethylenically unsaturated carbon-carbon bond and at least two functional groups (f1) of different nature.
12. The supercapacitor in accordance with claim 11, wherein the two functional groups (f1) of different nature are an ester group and an epoxy group, or an ester group and an alcohol group, or an alcohol group and an amide group.
13. The supercapacitor in accordance with claim 12, wherein the compound (a) is chosen from glycidyl acrylate, glycidyl methacrylate, hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate and N-methylolmethacrylamide.
14. The supercapacitor in accordance with any of previous claims comprising an electrolyte based on organic solvents wherein the electrolyte comprises of from 0.1 to 30 percent by weight, based on the entire weight of the solvents in the

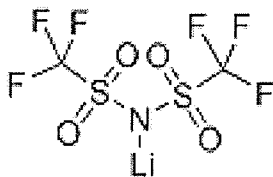


(I)

electrolyte, of at least one fluorinated carbonate of formula
 wherein R^1 to R^4 , which may be the same or different, are independently
 selected from hydrogen, fluorine, C_1 to C_8 -alkyl and C_1 to C_8 haloalkyl which

the proviso that at least one of R¹ to R⁴ is a fluorine atom or comprises a fluorine atom.

15. The supercapacitor in accordance with any of previous claims comprising organic electrolytes which contain from 0.1 to 100 percent by weight of LITFSI



16. The supercapacitor according to anyone of the preceding claims which further comprises a percolator.
17. The supercapacitor according to anyone of the preceding claims which is a hybrid supercapacitor.
18. Use of fluoropolymers including at least one functional group (f1) capable of conferring adhesion properties on said polymer as binder material for the electrodes of supercapacitors.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/051397

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01G9/042 H01G9/20 H01G9/155 H01M4/62 H01M10/0569
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)
H01G 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, COMPENDEX, FSTA, INSPEC, PAJ, IBM-TDB, 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 2008/149887 A1 (WANG JIAN [JP] ET AL) 26 June 2008 (2008-06-26)	1-13, 16-18
Y	paragraphs [0001], [0016], [0017] claims 1-12	14,15

X	EP 0 791 973 A2 (KUREHA CHEMICAL IND CO LTD [JP]) 27 August 1997 (1997-08-27) page 1, line 5 - line 8 page 3, lines 13-19 page 5, line 52 - line 55 claims 2-4	1-13, 16-18

Y	US 2008/145763 A1 (KOH MEITEN [JP] ET AL) 19 June 2008 (2008-06-19) paragraphs [0066], [0067] claims 1-9	14,15

	-/--	



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

6 March 2013

Date of mailing of the international search report

19/03/2013

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

Götz, Heide

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/051397

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2010/062344 A1 (KOH MEITEN [JP] ET AL) 11 March 2010 (2010-03-11) paragraph [0054] claims 1-5 -----	14,15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2013/051397

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2008149887	A1	26-06-2008	CN 101558092 A 14-10-2009
			CN 101563375 A 21-10-2009
			JP 2010514140 A 30-04-2010
			US 2008149887 A1 26-06-2008
			US 2010068622 A1 18-03-2010
			WO 2008079393 A1 03-07-2008
EP 0791973	A2	27-08-1997	CA 2198074 A1 22-08-1997
			DE 69710104 D1 14-03-2002
			DE 69710104 T2 31-10-2002
			EP 0791973 A2 27-08-1997
			JP 3703582 B2 05-10-2005
			JP 9289023 A 04-11-1997
			SG 70585 A1 22-02-2000
			US 5776637 A 07-07-1998
US 2008145763	A1	19-06-2008	CN 101120474 A 06-02-2008
			JP 4645648 B2 09-03-2011
			KR 20070107768 A 07-11-2007
			US 2008145763 A1 19-06-2008
			WO 2006088009 A1 24-08-2006
US 2010062344	A1	11-03-2010	CN 101606266 A 16-12-2009
			KR 20090117783 A 12-11-2009
			US 2010062344 A1 11-03-2010
			WO 2008096729 A1 14-08-2008