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(54) Title: BINDER COMPOSITION

(57) Abstract: Problems: to provide an electrode structure possessing improved flexibility and adhesion between electrodes and collectors with reduced amount of binder, in an electrode for a battery comprising electrode active material and binder. Solution: a binder composition comprising a fluorine resin (A) dissolvable in a predetermined organic solvent and a resin (B) which is not dissolvable or partly dissolvable in said predetermined organic solvent, said fluorine resin (A) comprising at least one polymer selected from the group comprising a fluorine polymer (A1) whose solution dissolved in N-methylpyrrolidone at a concentration of 8 % by weight possess a viscosity of 0.3 Pa.s to 20 Pa.s and a fluorine polymer (A2) having polar group, a weight ratio of A/B being 99/1 to 1/99.



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BINDER COMPOSITION

Technical field of Invention

This invention relates to a binder composition used for electrodes of
5 lithium ion battery.

Prior Arts

In lithium secondary batteries which are used recently in portable
device such as portable telephone, video camera and note type personal
10 computer, carbonous material such as coke and graphite that can dope and
de-dope lithium ions is used as negative pole active material (JP-A1- 62-
90863). Its positive electrode active material is made of oxide of transition
metal such as manganese oxide and vanadium pentaoxide, sulfide of
transition metal such as iron sulfide and titanium sulfide and their
15 composite compounds with lithium such as lithium cobalt compound oxide,
lithium cobalt nickel compound oxide, lithium manganese oxide.

These electrodes are produced generally by mixing fine particles of
electrode active materials with suitable amount of binder to prepare a paste,
coating the resulting paste onto a surface of a current collector, drying the
20 paste and then compressing the dried paste.

Binder used to produce such electrodes for secondary battery must
have enough resistance to organic solvent used in electrolyte and resistance
to active species which are produced during reaction on electrodes and
must have enough solubility to solvent which is used in its manufacturing
25 stage. PVDF resin satisfies these requirements and hence is used as binder
in many cases.

PVDF resin, however, have such problems that an active material
peels easily off the current collector because of its inherent property of poor

adhesion to metals so that the cycle characteristic of the resulting battery becomes very poor. In fact, adhesion between the current collector and the active material is not sufficient after the active material is compacted onto the current collector, in both cases of negative pole and
5 positive electrode.

JP-A1-5-6766 proposes to roughen a surface of the current collector to improve adhesion between the current collector and the electrode active materials. However, satisfactory adhesion cannot be obtained by this technique and improvement is required.

10 JP-A1-6-172452 proposes a copolymer of vinylidene fluoride and a monomer having carboxylic acid group. However, copolymerization of fluorine type monomer with other monomer having carboxylic acid group is not easy and hence this solution is not applicable to industrial mass-production plant.

15 JP-A1-9-82311 and JP-A1-9-82314 propose to add sulfur-containing organic compound having mercapto group into an electrode binder paste.

JP-A1-9-199132, JP-A1-9-199134 and JP-A1-9-199130 propose to add acryl resin having functional group or PVDF copolymer or both of
20 them to PVDF resin to prepare the binder. Addition of acryl resin, however, is not desirable from the viewpoint of electrochemical stability.

Problems to be solved by the invention

An object of this invention is to provide a binder composition
25 possessing satisfactory adhesion, bonding property and flexibility with a reduced proportion.

Means to solved the Problem

Inventors found such a fact that an electrochemically stable and enough flexible electrode can be produced by using a mixture of a fluorine resin (A) dissolvable in a predetermined organic solvent and a resin (B) which can be swollen but is not dissolve in the predetermined organic solvent as a binder for electrodes, provided that a solution of the fluorine resin (A) possesses enough high viscosity or the fluorine resin (A) have polar group, so that improve adhesion is realized between collectors and electrodes with reduced amount of the binder.

A weight ratio (A/B) of the fluorine resin (A) to the resin (B) is 99/1 to 1/99, preferably 80/20 to 5/95.

The fluorine resin (A) used in the present invention is homopolymer and copolymer of vinylfluoride. The homopolymer of vinylidene fluoride can be obtained by suspension polymerization or emulsion polymerization of vinylidene fluoride monomer and possess preferably a melt flow rate (MFR) at 230 °C under a load of 5 kg is 0.01 to 20 g/10 minutes, more preferably 0.05 to 2 g/10 minutes.

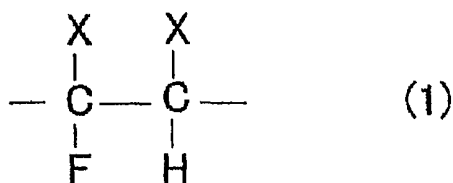
The copolymer of vinylidenefluoride is a copolymer of vinylidenefluoride and copolymerizable comonomer, provided that a proportion of vinylidenefluoride is 10 to 99 % by weight, preferably 50 to 99 % by weight. The copolymerizable comonomer may be fluorine monomer such as tetrafluoroethylene, hexafluoropropylene, trifluoroethylene, trifluorochloroethylene, vinylfluoride and perfluoroalkyl vinyl ether and unsaturated olefin monomer such as ethylene and propylene. More than one monomers can be used in combination. These copolymers can be prepared by suspension polymerization or emulsion polymerization of the monomer and possess preferably a melt flow rate (MFR) at 230 °C under a load of 5 kg is 0.01 to 20 g/10 minutes, more preferably 0.05 to 2 g/10 minutes.

The above-mentioned polyvinylidene fluoride and copolymer of vinylidene fluoride has preferably enough high viscosity when they are dissolved in organic solvent. A preferable range of viscosity is 0.3 Pa.s to 20 Pa.s in N-methylpyrrolidone at a density of 8 % by weight. In fact, if the
5 viscosity become lower than this range, the viscosity of a slurry obtained from the binder, electrode active material and solvent becomes too low to prepare homogeneous electrodes. On the contrary, if the viscosity becomes higher than this range, it is difficult to dissolve the rein uniformly in solvent.

10 In the present invention, it is preferable to use the denatured fluorine resin in which polar group is introduced for the total of the binder composition or for at lest a part thereof. Such denatured fluorine resin can be produced by copolymering fluorine monomer with monomer(s) possessing polar group (such as a process disclosed in JP-A1-6-172452), by
15 grafting a fluorine resin with a compound having polar group (such as a process disclosed in JA-A1-08-258464) or by partial dehydrogenfluorination of a fluorine resin followed by oxidation. The denatured fluorine resin is compatible with elastomer type resins so that homogeneous electrodes can be produced. A solution of this resin has
20 preferably enough high viscosity when it is dissolved in organic solvent and a preferable range of viscosity is 0.3 Pa.s to 20 Pa.s in N-methylpyrrolidone at a density of 8 % by weight.

The fluorine resin used in the partial dehydrogenfluorination followed by oxidation have following chemical structure:

25 formula 1



in which, X and X' is an atom selected from hydrogen and halogen atom (in particular, fluorine or chlorine), or perhaloalkyl (in particular, perfluoroalkyl).

5 The above-mentioned functional group having adhesive property by chemical reaction can be introduced in these fluorine resins.

The fluorine resin from which the chemically denatured fluorine type resin is prepared can be obtained by a polymerization of unsaturated olefin monomer. In practice, the fluorine type polymer represented by the
10 formula (1) can be obtained by polymerizing such monomer as having a fluorine atom bonded to a carbon atom and hydrogen atom bonded to a carbon atom, such as homopolymer of hydro fluorocarbon monomer and copolymer of unsaturated perfluoro monomer and one or more than one monomer containing hydrogen atom.

15 Unsaturated olefin monomer used to prepare the fluorine resin may be tetrafluoroethylene, hexafluoropropylene, vinylidene fluoride, trifluorochloroethylene, 2-chloropentafluoropropene, trifluoroethylene, perfluoroalkylvinyl ether, 1-hydropentafluoropropene, 2-hydropentafluoro propene, dichlorodifluoroethylene, 1,1-dichlorofluoroethylene and
20 perfluoro- 1,3-dioxsol (USP 4,558,142). Other unsaturated olefin monomer having no fluorine atom such as ethylene, propylene and butylene also can be used.

The fluorine resin can be prepared by known technique. For example, homopolymer of vinylidene fluoride can be obtained by
25 suspension polymerization of vinylidene fluoride (USP 3,553,185 and EP

0,120,524) or emulsion polymerization (USP 4,025,709, USP 4,569,978, USP 4,360,652, USP 4,626,396 and EP 0,655,468).

Unsaturated fluorinate olefin monomer is usually polymerized in a form of aqueous emulsion and can be copolymerized with olefin monomer
5 having no fluorine atom. In this case, water-soluble initiator such as ammonium or alkali metal persulfate and alkali metal permanganate or organic peroxide is used as an initiator. As emulsifier, ammonium salt or alkali metal salt of perfluorooctanoic acid or the like is used. Initiator used in case of aqueous colloid suspension may be those soluble in organic
10 phase such as dialkylperoxide, alkylhydroperoxide, dialkylperoxydicarbonate and dialkylazoperoxide. Dispersant may be methyl cellulose, methylhydroxy propyl cellulose, methylpropyl cellulose, methylhydroxyethyl cellulose or the like.

The fluorine resins are available on market and can be "KYNAR"
15 which is a product of ATOFINA SA.

The fluorine resin is preferably in a form of aqueous dispersion such as suspension or emulsion before it is denatured to the chemically denatured fluorine resin. Such dispersion is obtained by the above-mentioned polymerization technique. In fact, such fluorine resin is
20 subjected to partial dehydrogenfluoride reaction with base and then is oxidized with oxidizing agent to obtain the chemically denatured fluorine resin.

The dehydrogenfluorination of the fluorine resin is carried out in water or in organic solvent by means of base. The base which can be used
25 in the present invention is those disclosed in WO 98/08880 and may be hydroxide such as potassium hydroxide, sodium hydroxide, lithium hydroxide, ammonia water, carbonate such as potassium carbonate and sodium carbonate, tertiary amines, tetra ammonium hydroxide and metal

alkoxides. Amines having a hydrocarbon structure soluble in water or organic solvent partly or totally such as 1,8-diazobicyclo[5.4.0]undeca-7-en (DBU) and 1,4-diazobicyclo- 2.2.2-octane (DABCO) also can be used. The dehydrogenfluoride reaction of fluorine resin emulsified in aqueous medium is described in details in WO 98/08879 the contents of which forms a part of this specification.

The above-mentioned base is used together with catalyst. This catalyst may be tetrabutyl ammonium bromide (TBAB) and tetraalkyl phosphoric acid, alkylallyl phosphoric acid, alkyl ammonium halide and alkyl phosphate.

After the dehydrogenfluoride reaction, the resulting fluorine resin is subjected to oxidation reaction with oxidizing agent in aqueous medium. Hydrogen peroxide is advantageously used as the oxidizing agent because the reaction can be effected in water which is desirable comparing to organic solvent from the view point of environment and cost and because treatment of wastewater is easier than other oxidizing agents. Other oxidizing agent such as palladium halogenide such as PdCl_2 , chromium halogenide such as CrCl_4 , alkyl metal permanganate such as potassium permanganate, alkyl peroxide, a variety of peroxides and persulfuric acid also can be use alone or in combination with hydrogen peroxide.

The oxidation reaction of fluorine resin with hydrogen peroxide is carried out preferably at a pH of 6.5 to 8.0, more preferably between pH 6.7 and pH 7.6. If pH is lower than 6.7, the speed of oxidation reaction becomes too slow. On the other hand, if pH becomes higher than 8, hydrogen peroxide is decomposed so that the reaction can not be controlled. The oxidation reaction is effected at a temperature of 20°C to 100°C , preferably 50°C to 90°C .

Amount of hydrogen peroxide used in the oxidation reaction is 1 %

to 50 % by weight, preferably 2 % to 12 % with respect to the total amount of fluorine resin used.

The resulting denatured fluorine resin show remarkably higher adhesive property to organic and inorganic substrates in comparison with
5 fluorine resins which are not chemically denatured.

In the present invention, the fluorine resin (A) can be a mixture of 1 to 99 parts by weight of a resin selected from a group comprising denatured polyvinylidene fluoride resin having polar group and denatured vinylidene fluoride copolymer and 99 to 1 parts by weight of at least one
10 resin selected from a group comprising non-denatured poly vinylidene fluoride resin and denatured vinylidene fluoride copolymer.

The resin (B) used in the present invention is preferably a polymer selected from a group comprising diene type polymers, olefin type polymers, styrene type polymers, acrylate type polymers, polyamides or
15 polyimide type polymers, ester type polymers, cellulose type polymers and so on. Followings are examples of the resin (B):

Polybutadiene, polyisoprene, isoprene-isobutylene copolymer, natural rubber, diene type polymers such as styrene-1,3-butadiene copolymer, styrene-isoprene copolymer, 1,3-butadiene-isoprene-
20 acrylonitrile copolymer, styrene- 1,3-butadiene isoprene copolymer, 1,3-butadiene acrylonitrile copolymer, styrene-acrylonitrile-1,3-butadiene-methylmethacrylate copolymer, styrene-acrylonitrile- 1,3-butadiene-itaconic acid copolymer, styrene- acrylonitrile-1,3-butadiene-methylmethacrylate- fumaric acid copolymer, styrene- 1,3-butadiene-
25 itaconic acid-methylmethacrylate-acrylonitrile copolymer, acrylonitrile-1,3-butadiene- methacrylic acid -methylmethacrylate copolymer, styrene-1,3-butadiene-itaconic acid-methyl methacrylate- acrylonitrile copolymer and styrene-acrylonitrile-1,3-butadiene- methylmethacrylate- fumaric acid

copolymer; olefin polymers such as ethylene-propylene copolymer, ethylene-propylene-diene copolymer, polystyrene, polyethylene, polypropylene, ethylene-vinyl acetate copolymer, ethylene type ionomers, polyvinyl alcohol, polyvinylacetate, ethylene-vinyl alcohol copolymer, 5 chlorinated polyethylene, polyacrylic acid, polymethacrylic acid and chlorosulfonated polyethylene; styrene type polymers such as styrene-ethylene-butadiene copolymer, styrene-butadiene-propylene copolymer, styrene-isoprene copolymer, styrene-acrylic acid-butyl-itaconic acid-methylmethacrylate-acrylonitrile copolymer and styrene-acrylic acid-n- 10 butyl-itaconic acid-methyl methacrylate- acrylonitrile copolymer; acrylate type polymers such as polymethylmethacrylate, polymethylacrylate, polyethylacrylate, polybutylacrylate, acrylate-acrylonitrile copolymer and acrylic acid-ethylhexyl - methyl acrylate - acrylic acid - methoxy polyethyleneglycol mono methacrylate; polyamides and polyimide type 15 polymers such as polyamide 6, polyamide 66, polyamide 11, polyamide 12, aromatic polyamide and polyimide; ester condensation type polymers such as polyethyleneterephthalate, polybutyleneterephthalate; cellulose compounds such as carboxymethyl cellulose, carboxyethyl cellulose, hydroxymethyl cellulose, hydroxypropyl cellulose and carboxy ethylmethyl 20 cellulose (including their salts such as ammonium salts and alkali metal salts) ; block copolymers such as styrene-butadiene block copolymer, styrene-butadiene-styrene block copolymer, styrene-ethylene- butylene-styrene block copolymer, styrene-isoprene block copolymer and styrene-ethylene-propylene-styrene block copolymer ; and others 25 methylmethacrylate polymers. These polymers can be used alone or in combination.

These polymers used as resin (B) disperse totally or partly in the slurry in a form of particles and their particle size are in a range of 0.005 to

100 μ m, preferably 0.01 to 50 μ m, more preferably 0.05 to 30 μ m (after dispersed in a medium and dried, their longer and shorter diameters are measured by an electron microscope and an average of 100 particles is determined). If the particle size is too big, the particles used as binder can
5 not contact with active substance so that internal resistance of electrodes increases. On the contrary, if the particle size becomes smaller, an amount of binder increases so that a surface of active material is totally covered undesirably with the particles.

The resin (B) is not dissolvable or partly dissolvable in the
10 predetermined organic solvent used in preparation of the electrodes such as N- methylpyrrolidone (NMP). A proportion of none dissolved resin is more than 50 %, preferably more than 70 %, more preferably more than 80 %. In the present invention, the none dissolved proportion is calculated in a term of "NMP insoluble contents" as following. Namely, 1 g of the
15 polymer is dried at 100°C for 24 hours and the a weight of dried polymer is measured. Then, the polymer is immersed in 100 g of NMP at 25°C for 24 hours. After then, the polymer is screened by a 200 mesh sieve. Particles remained on the sieve is dried and weighted. "NMP insoluble contents" is determined from the following equation:

20 NMP insoluble contents =

$$(\text{weight of remained particles} / \text{weight of dried polymer}) \times 100$$

When the proportion of none dissolved resin is not higher than 50 %, satisfactory adhesion and flexibility can not be obtained with a reduced amount of binder.

25 Polymers whose proportion of none dissolved resin is not higher than 50 % can be cross-linked. Cross-linking can be done with self-cross-linking by irradiation of energy such as heat, light, radiation and electron beam or with cross-linking agent to introduce cross-link structure in the

polymer, or their combination.

The cross linking agent may be peroxide type cross-linking agent such as benzoyl peroxide, dichlorobenzoylperoxide, dicumylperoxide, di-tert-butyl peroxide, 2,5-dimethyl-2,5-di(peroxidebeozoate) hexyne- 3,1,4-
5 bis (tert-butylperoxidedipropyl)benzene, lauroylperoxide, tert-butyl peracetate, 2,5-dimethyl-2,5-di(tert-butylperoxy) hexyne-3,2,5-trimethyl-2,5-di(tert-butylperoxy) hexane, tert-butyl perbenzoate, tert-butyl perphenylacetate, tert-butylperisobuthylate, tert-butyl per-sec-octoate, tert-butylperpivarate, cumylpivarate and tert-butylperdiethylacetate ; azo
10 compounds such as dimethylazoisobutylate and azobisisobutyronitrile ; dimethacrylates such as ethyleneglycoldimethacrylate and diethylene glycoldimethacrylate; trimethacrylates such as trimethylolpropane trimethacrylat; diacrylates such aspolyethyleneglycol diacrylate and 1,3-butyleneglycoldiacrylate; triacrylates such as trimethylolpropane
15 triacrylate; and divinyl compounds such as divinylbenzene. Cross-linkable monomer such as dimethacrylates like ethyleneglycoldimethacrylate and diviynyl compounds like divinylbenzene are preferably used.

The polymer used in the present invention as the resin (B) may be other polymers than the above-mentioned polymers, possessing the gel
20 contents of more than 50 %, fluorine rubber, fluorine-containing polymer such as polytetrafluoroethylene, tetrafluoroethylene-hexafluoropropylene copolymer, tetrafluoroethylene-perfluoro alkyl vinyl ether copolymer, polychloro-trifluoroethylene, polyvinylfluoride, and ethylene-chlorotrifluoroethylene copolymer. To improve adhesion with collectors
25 and binding property with electrode active material, it is possible to copolymerized a small quantity of monomers having polar group at the polymerization stage or to introduce the polar group by chemical modification after polymerization.

Embodiment of Invention

The fluorine type adhesive resin composition according to the present invent is advantageously used in an electrode structure having a current collector to a surface of which at least one electrode active material is deposited with binder, to improve adhesion between the electrode active material and the current collector, to prevent active material from peel off the surface of the current collector in manufacturing stage, and to realize a battery improved in the cycle-characteristic.

In particular, the fluorine type adhesive resin composition according to the present invent is useful in non-aqueous type secondary battery, such as a binder for electrode of lithium ion secondary battery.

The current collector of electrode can be metal foil, metal mesh and three-dimensional porous body. Metal used for this current collector is such a metal that hardly forms an alloy with lithium and may be iron, nickel, cobalt, copper, aluminum, titanium, vanadium, chromium and manganese or alloys of these metals.

Negative pole active material as the electrode active material can be any material that can dope and de-dope lithium ions and may be mention cokes such as petroleum coke and carbon coke, carbon black such as acetylene black, nature or synthesis graphite, glass carbon, activated carbon, carbon fiber and carbonaceous materials such as sintered body obtained from organic polymer sintered in non-oxidation atmosphere.

Positive electrode active material as the electrode active material can be transition metal oxide such as manganese oxide and vanadium pentaoxide, iron sulfide, titanium sulfide and composite compound with lithium (such as lithium cobalt compound oxide, lithium cobalt nickel compound oxide, lithium manganese oxide).

The electrode can be produced by following manufacturing steps:

At first, a slurry of predetermined amounts of electrode active material and of the binder composition as binder is prepared by kneading them in the presence of solvent. The resulting slurry is applied onto an electrode current collector, dried and press-molded. If necessary, after the slurry is
5 applied, the coated layer is heated at 60 to 250 °C, preferably 80-200 °C for 1 minute to 10 hours. The electrode-constructing material may contain electro-conductive material and other additives (copper oxide etc), in if necessary.

Solvent used to prepare the slurry to be coated onto the electrode
10 current collector may be organic solvent such as N-methylpyrrolidone, N, N-dimethylholmeamide, tetrahydrofuran, dimethylacetoamide, dimethyl sulfoxide, hexamethylsulfonamide, tetramethyl urea, acetone and methyl ethyl ketone and water. The solvents can be used alone or in combination. Among them, N-methylpyrrolidone is preferably used. If necessary,
15 dispersant can be added and nonion type dispersant is preferably used.

An amount of binder to be added to the electrode active material is preferably 0.5 to 40 parts by weight, more preferably 1 to 20 parts by weight part with respect to 100 parts by weight of the electrode active material. This amount of binder varies or depends to nature and type of
20 battery and electrode and can be reduced when adhesion of the binder is improved.

The negative pole structure and anode structure are arranged at opposite sides of a liquid-permeable separator (a porous film made of, for example, polyethylene or polypropylene). Then, the separator is
25 impregnated with non-aqueous electrolyte to obtain a secondary battery.

This secondary battery consisting of a laminate of negative pole structure having active layers opposite sides / separator / positive pole structure having active layers opposite sides / separator is wound up into a

roll (spiral-roll) and is inserted into a bottomed metal casing. After the negative pole is connected to a negative terminal while positive pole is connected to a positive terminal, an assembly is impregnated with electrolyte, and then the metal casing is sealed to obtain a cylindrical
5 secondary battery.

The electrolyte used in the lithium ion secondary battery may be lithium salt dissolved in a non-aqueous organic solvent in a concentration of about 1 M. The lithium salt may be LiPF_6 , LiClO_4 , LiBF_4 , LiAsF_6 , LiSO_3CF_3 and $\text{Li}[(\text{SO}_2\text{CF}_3)_2\text{N}]$. The non-aqueous organic solvent may be
10 propylenecarbonate, ethylenecarbonate, 1,2-dimethoxyethane, 1,2-diethoxyethane, dimethylcarbonate, diethylcarbonate and methylethylcarbonate which can be used alone or in combination.

Examples

15 Now, the present invention will be explained with reference to Examples to which the present invention is not limited.

Synthesis example 1

Polyvinylidene fluoride (PVDF) latex (latex 1) was synthesized by
20 emulsion polymerization technique described in U.S. patent No. 4,025,709. This latex contains 42 % by weight of PVDF. A resin obtained by drying the latex has a melt index (MI) a 0.2 g/ 10 minutes at 230 °C under a load of 5 kg. The viscosity in NMP solution (resin concentration is 8 % by weight) determined by E type viscometer was 1.3 Pa·s.

25

Synthesis example 2

Latex (latex 2) of copolymer of vinylidenefluoride and hexafluoro propylene (HFP) (a proportion of HFP is 11 % by weight) was synthesized

by the same emulsion polymerization technique as Synthesis example 1. This latex contains 11 % by weight of PVDF. A resin obtained by drying the latex has a melt index (MI) a 0.3 g/ 10 minutes at 230 °C under a load of 5 kg. The viscosity in NMP solution (resin concentration is 8 % by weight) determined by E type viscometer was 0.6 Pa· s.

Synthesis example 3

7.2kg of an aqueous solution containing 15 % by weight of sodium hydroxide was stored in a container of 20 liter and heated to a temperature of 70 °C . Into this solution, the above-mentioned latex 1 of 7.2 kg was added under stirring at 180 rpm at a rate of 0.72 kg/min. Dehydrogenfluorination reaction proceeds immediately to produce aggregates of PVDF of dark-brown. Color of the aggregates of PVDF became darker with time during the solution was left at the same temperature under stirring.

After the above-mentioned dehydrogenfluorination reaction with sodium hydroxide was effected for 30 minutes, the resulting reaction product was kept at 70 °C and 2.5 kg of 36 % of hydrochloric acid was added to adjust pH of 5. Then, 1.68 kg of 35 % hydrogen peroxide was added at a rate of 0.4 kg/mine and then aqueous solution of 15 % sodium hydroxide was added to adjust to pH of a range of 6.6 to 7.6.

Oxidation reaction was continued with adjusting the abovementioned pH range of the PVDF suspension by adding necessary amount of the same aqueous solution of sodium hydroxide. Aggregates of PVDF decolorized gradually with time and finally became light yellow. Oxidation treatment continued for 150 minutes. Then, aggregates was collected by filtering, washed with distilled water and dried at 105 °C to obtain fine particles.

The resulting resin powder was dissolved in NMP to obtain a solution of a concentration of 0.1 % by weight resin to which an absorbance was determined at 300 nm to find a value of 0.19. The viscosity in NMP solution (resin concentration is 8 % by weight) determined by E
5 type viscometer was 1.2 Pa.s.

Synthesis example 4

The latex 2 was treated by the same processing as Synthesis Example 3 but the time duration of the dehydrogenfluorination reaction
10 with aqueous solution of sodium hydroxide was changed to 230 minutes and the time duration of the oxidation reaction with hydrogen peroxide was changed to 75 minutes to obtain a resin.

The resulting resin was dissolved in NMP to obtain a solution of a concentration of 0.1 % by weight resin to which an absorbance was
15 determined at 300 nm to find a value of 0.154. The viscosity in NMP solution (resin concentration is 8 % by weight) determined by E type viscometer was 0.7 Pa.s.

Synthesis example 5

20 Latex (latex 5) of polyvinylidene fluoride (PVDF) was synthesized by the same emulsion polymerization technique as Synthesis example 1 but an amount of polymerization initiator is increased comparing to Synthesis example 1. This latex contains 45 % by weight of PVDF. A resin obtained by drying the latex has a melt index (MI) a 0.4 g/ 10 minutes at 230 °C
25 under a load of 5 kg. The viscosity in NMP solution (resin concentration is 8 % by weight) determined by E type viscometer was 0.2 Pa.s.

Reference examples 1 to 4

Each fluorine resin obtained in Synthesis Example 1 to 4 was dissolves in N-methyl pyrrolidone (NMP) to obtain a solution of 10 % by weight of resin. Each solution was applied on an aluminum plate and a copper plate each having a thickness of 1 mm and was left in 120 °C for 1
5 hour.

After the coated plates were dried under reduced pressure, films were cut into a plurality of square areas each having a side of 1 mm to effect Tessellate (cross cut) Adhesion Test (JIS K5400, 6.15). For all resins, the remaining % of the coated polymer film was 100 % in the
10 aluminum and copper plates.

Adhesion was tested also by Tape Peel Adhesion method. The result of remaining % of the coated polymer in this test also was 100 % in the aluminum and copper plates. From those results, it was confirmed that adhesion of the vinylidene fluoride resin composition to the metal plates
15 was good.

Example 1

10 g of the fluorine resin obtained in Synthesis example 1 was dissolved in 170 g of N-methyl pyrrolidone (NMP). Into the resulting
20 solution, 20 g of a powder of resin having an average particle size of 0.15 μ m and the NMP none dissolvable content is 95 % were added. This resin comprises styrene (40 parts by weight), butadiene (35 parts by weight), methylmethacrylate (20 parts by weight) and acrylonitrile (5 parts by weight). The resulting mixture was mixed uniformly in a homogenizer
25 to prepare a binder dispersion.

96 g of coal pitch coke pulverized in a ball mill as a carrier of negative pole active material was added to and dispersed into 33 g of the binder dispersion obtained above and a small amount of NMP was added to

adjust the viscosity of the slurry for negative electrodes.

This slurry was applied onto a surface of a copper foil having a thickness of 20 μm , as a current collector and dried at 130 °C for 15 minutes to obtain an electrode structure (as negative pole) having a
5 thickness 110 μm and a width of 20 mm.

An adhesive tape was glued to a electrode active layer on a surface of the electrode structure to determine the peel adhesion between the current collector and the electrode active layer by a tensile tester to find a peel strength of 20 g/cm. In another adhesion test, the electrode structure
10 was wound around a cylinder having a diameter 1 mm and the peel adhesion was measured to find no peel of the electrode active layer in this case also. These facts showed that adhesion between the electrode active material and the current collector was very strong and flexibility of electrodes is sufficient so that batteries can be produced in actual
15 manufacturing line without problem.

The electrode structure was immersed in ethylene carbonate and left for 3 days at 60 °C but no peel of the electrode active layer was observed.

91 g of LiCoO_2 (as a positive electrode active material), 3 g of acetylene black (as a conductor) and 20 g of the binder dispersion were
20 mixed uniformly and NMP was added to obtain a slurry (paste). This slurry was applied to a surface of aluminum foil having a thickness of 20 μm (as a current collector) and dried at 130 °C for 15 minutes to produce an electrode structure (used as a positive electrode) having a thickness 100 μm and a width of 20 mm. Peel adhesion between the current collector and
25 the electrode active layer was 25 g/cm. In another adhesion test, the electrode structure was wound around a cylinder having a diameter 1 mm and the peel adhesion was measured to find no peel of the electrode active layer in this case also.

The electrode structure was immersed in ethylene carbonate and left for 3 days at 60 °C but no peel of the electrode active layer was observed.

Example 2

5 Procedure of Example 1 was repeated but the fluorine resin was replaced by the denatured polyvinylidene fluoride resin obtained in Synthesis example 3 to obtain a binder dispersion. Negative pole and positive pole were prepared with this dispersion.

 Adhesion strength between the collectors and the electrode active
10 layer was determined by the same method as Example 1 to find values of 50 g/cm and 55 g/cm for negative electrode and positive electrode respectively. In the winding adhesion test in which the electrode structure was wound around a cylinder having a diameter 1 mm, no peel of the electrode active layer was observed. Adhesion was improved comparing to
15 Example 1. The electrode structure was immersed in ethylene carbonate and left for 3 days at 60 °C but no peel of the electrode active layer was observed.

Example 3

20 10 g of the fluorine resin obtained in Synthesis example 2 was dissolved in 270 g of N-methyl pyrrolidone (NMP). Into the resulting solution, 20 g of a powder of resin having an average particle size of 0.2µm and the NMP none dissolvable content is 97 % were added. This resin comprises styrene (30 parts by weight), 1,3-butadiene (40 parts by weight),
25 methylmethacrylate (30 parts by weight) and divinylbenzene (2 parts by weight). The resulting mixture was mixed uniformly in a homogenizer to prepare a binder dispersion.

Negative pole and positive pole were prepared with this dispersion

and adhesion strength between the collectors and the electrode active layer was determined by the same method as Example 1 to find values of 23 g/cm and 25 g/cm for negative electrode and positive electrode respectively. In the winding adhesion test in which the electrode structure
5 was wound around a cylinder having a diameter 1 mm, no peel of the electrode active layer was observed. These facts showed that adhesion between the electrode active material and the current collector was very strong and flexibility of electrodes is sufficient so that batteries can be produced in actual manufacturing line without problem.

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Example 4

5 g of the fluorine resin obtained in Synthesis example 1 and 5 g of the denatured vinylidene fluoride copolymer obtained in Synthesis example 4 were dissolved in 270 g of N-methyl pyrrolidone (NMP). Into the
15 resulting solution, 20 g of a powder of resin having an average particle size of 0.2 μ m and the NMP none dissolvable content is 97 % were added. This resin comprises styrene (30 parts by weight), 1,3-butadiene (40 parts by weight), methylmethacrylate (30 parts by weight) and divinylbenzene (2 parts by weight). The resulting mixture was mixed uniformly in a
20 homogenizer to prepare a binder dispersion.

Negative pole and positive pole were prepared with this dispersion and adhesion strength between the collectors and the electrode active layer was determined by the same method as Example 1 to find values of 53 g/cm and 55 g/cm for negative electrode and positive electrode
25 respectively. In the winding adhesion test in which the electrode structure was wound around a cylinder having a diameter 1 mm, no peel of the electrode active layer was observed. Thus, adhesion was improved comparing to Example 3.

Comparative example 1

10 g of polyvinylidene fluoride obtained in the Synthesis example 1 was dissolved in 90 g of NMP to prepare a binder solution.

Negative pole and positive pole were prepared with this binder solution and adhesion strength between the collectors and the electrode active layer was determined by the same method as Example 1 to find values of 5 g/cm and 6 g/cm for negative electrode and positive electrode respectively. In the winding adhesion test in which the electrode structure was wound around a cylinder having a diameter 1 mm, peel of the electrode active layer was observed. Separation was observed in several parts in electrode active layers when the electrode structure was immersed in ethylene carbonate and left for 3 days at 60 °C.

Comparative example 2

Procedure of Example 1 was repeated but the fluorine resin was replaced by the polyvinylidene fluoride resin obtained in Synthesis example 5 to obtain a binder dispersion. Negative pole and positive pole were prepared with this dispersion but electrodes of uniform thickness could not be obtained. Adhesion strength between the collectors and the electrode active layer determined by the same method as Example 1 was 3 g/cm and 5 g/cm for negative electrode and positive electrode respectively. In the winding adhesion test in which the electrode structure was wound around a cylinder having a diameter 1 mm, peel of the electrode active layer was observed. Separation also was observed in several parts in electrode active layers when the electrode structure was immersed in ethylene carbonate and left for 3 days at 60 °C.

Advantages of the Invention

Sufficient adhesion strength between electrodes and collectors can be realized with a reduced amount of binder composition by using such a binder composition according to the present invention that comprises a fluorine resin dissolvable in a predetermined organic solvent and a resin
5 which is totally insoluble or partly insoluble in the organic solvent as binder for electrodes of lithium ion battery. The resulting electrode structure shows improved flexibility so that separation between the electrode active material and collectors in a manufacturing line can be prevented. The charge-discharge capacitance of a secondary battery
10 obtained doesn't shows no deteriorated even after repeated charge-discharge operations.

CLAIMS

Claim 1 A binder composition comprising a fluorine resin (A) dissolvable in a predetermined organic solvent and a resin (B) which is not
5 dissolvable or partly dissolvable in said predetermined organic solvent, said
fluorine resin (A) comprising at least one polymer selected from the group
comprising a fluorine polymer (A1) whose solution dissolved in N-
methylpyrrolidone at a concentration of 8 % by weight possess a viscosity
of 0.3 Pa.s to 20 Pa.s and a fluorine polymer (A2) having polar group, a
10 weight ratio of A/B being 99/1 to 1/99.

Claim 2 The binder composition set forth in claim 1, wherein
said fluorine polymer (A1) is polyvinylidene fluoride resin.

Claim 3 The binder composition set forth in claim 1, wherein
said fluorine polymer (A2) is a denatured polyvinylidenefluoride resin
15 having polar group.

Claim 4 The binder composition set forth in claim 1, wherein
said fluorine resin (A) is a mixture of polyvinylidene fluoride resin and a
denatured polyvinylidenefluoride resin having polar group.

Claim 5 The binder composition set forth in any one of
20 claims 1 to 3, wherein said fluorine polymer (A1) is a copolymer of
vinylidene fluoride and at least monomer selected from a group comprising
tetrafluoroethylene, hexafluoropropylene, trifluoroethylene and
trifluorochloroethylene, a proportion of said vinylidenefluoride being 50 to
98 % by weight.

25 Claim 6 The binder composition set forth in claim 1, 2 or 5,
wherein said fluorine polymer (A2) is a denatured vinylidenefluoride
copolymer of vinylidene fluoride and at least one monomer selected from a
group comprising tetrafluoroethylene, hexafluoropropylene, trifluoro

ethylene and trifluorochloroethylene which is denatured with polar group introduced.

Claim 7 The binder composition set forth in any one of claims 1 to 6, wherein said fluorine polymer (A2) having polar group is a
5 fluorine polymer whose solution dissolved in N-methylpyrrolidone at a concentration of 8 % by weight possess a viscosity of 0.2 Pa.s to 20 Pa.s.

Claim 8 The binder composition set forth in claim 1 and 7, wherein said fluorine resin (A) is a mixture of 1 to 99 parts by weight of a resin selected from a group comprising denatured polyvinylidene fluoride
10 resin having polar group and said denatured vinylidene fluoride copolymer set forth in claim 6 and 99 to 1 parts by weight of at least one resin selected from a group comprising non-denatured poly vinylidene fluoride resin and said denatured vinylidene fluoride copolymer set forth in claim 5.

Claim 9 The binder composition set forth in claims 3 to 5, 7
15 and 8, wherein said denatured polyvinylidene fluoride resin is obtained by subjecting polyvinylidene fluoride resin to partial dehydrogen fluoride reaction and oxidation reaction.

Claim 10 The binder composition set forth in any one of claims 6 to 8, wherein said denatured polyvinylidene fluoride copolymer is
20 obtained by subjecting said polyvinylidene fluoride copolymer set forth in claim 5 to partial dehydrogen fluoride reaction and oxidation reaction.

Claim 11 The binder composition set forth in any one of claims 1 to 10, wherein said resin B is an elastomer which is cross-linked chemically.