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(54) Title: LITHIUM ION BATTERY TIE LAYER

(57) Abstract: The invention relates to a polyvinylidene fluoride modified polymer tie layer, such as KYNAR® resins from Arkema, for adhering a separator to an electrode in a lithium ion battery. The polyvinylidene fluoride is either a copolymer having a low level (from 0.2 to 20 weight percent) of an adhesion-promoting comonomer, or a polyvinylidene homopolymer or copolymer modified by a low molecular weight, functional, polymer chain transfer agent. The copolymer promotes adhesion of the separator to an electrode, yet is able to withstand the harsh and oxidative environment in a lithium ion battery.



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LITHIUM ION BATTERY TIE LAYER

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FIELD OF THE INVENTION

The invention relates to a polyvinylidene fluoride modified polymer tie layer for adhering a separator to an electrode in a lithium ion battery. The polyvinylidene fluoride is either a copolymer having a low level (from 0.2 to 20 weight percent) of an adhesion-promoting comonomer, or a polyvinylidene homopolymer or copolymer modified by a low molecular weight, functional, polymer chain transfer agent. The copolymer promotes adhesion of the separator to an electrode, yet is able to withstand the harsh and oxidative environment in a lithium ion battery.

BACKGROUND OF THE INVENTION

Lithium batteries, including lithium metal batteries, lithium ion batteries, lithium polymer batteries, and lithium ion polymer batteries are finding increased usage due to the desire to increase voltages and energy densities compared to conventional batteries using aqueous electrolytes (such as Ni-MH batteries).

The lithium ion battery consists of stacks of anodes and cathodes, each set of anode and cathode separated by a separator to prevent short circuiting. During manufacture, the anode, cathode and separators must be aligned, and they must remain aligned in use. The process of initial alignment, and maintaining that alignment during battery use, is a problem that creates a bottleneck in manufacturing, and can be a problem in use, especially in the flexible pouch cell batteries.

Pouch cell lithium ion batteries were introduced in 1995 as a flexible, lightweight alternative to metallic cylinder batteries. These highly efficient batteries are used in consumer, military, and automotive applications, and are preferred due to their low packaging weight and high rate of heat dissipation. Because they are thin and flexible, pouch cell lithium ion batteries the preferred choice in high-end consumer electronics. The problem of alignment of the anode,

separator and cathode during manufacture of these pouch-type batteries is especially crucial - and there is a high rejection rate.

Current lithium ion batteries and lithium ion polymer batteries typically use polyolefin-based separators, either alone or coated with aluminum oxide or ceramic particles, to improve
5 heat stability, and to prevent a short circuit between a cathode and an anode. These polyolefin-based separators do not adhere well to the electrodes. Further, because such polyolefin-based separators have a melting point of 140°C or less, they may shrink melt when the temperature of a battery is increased by internal and/or external factors, and can short-circuit. The short circuit
10 can lead to accidents, such as explosion or fire in a battery, caused by the emission of electric energy. As a result, it is necessary to provide a separator that does not undergo heat shrinking at high temperature.

Adhesives, such as epoxies, provide good adhesion between electrodes and separators, but they are prone to oxidation at the cathode, and most adhesives dissolve in the harsh electrolyte environment of a battery.

15 To improve heat and chemical resistance, fluoropolymers have been used as the separator itself, or have been coated onto the separator as a binder. Such a coated separator is described in US 2015-0030906. These fluoropolymer binders and adhesives solve the problem found in non-fluoropolymer adhesives, which tend to oxidize at the cathode producing off-gassing and swelling of the battery. Anodes are non-oxidizing, and more friendly to non-fluoropolymers, but
20 the use of two different separators or coatings on either side of the same separator substrate requires extra materials and an extra processing step. An issue with fluoropolymer binders is that adhesion between fluoropolymers, such as polyvinylidene fluoride (PVDF) and electrodes is not ideal. Thick layers of greater than 5 microns of binder/adhesive are generally required for adequate adhesion.

25 There is a need for excellent initial and long-term adhesion between electrodes and separators in a battery stack. This is especially true in flexible (pouch-type) batteries in which differential pressure will work to move the stack out of alignment.

Soft (lower T_m) fluoropolymers, such as KYNAR SUPERFLEX[®] resin adhere well, but are too soft and can often swell extensively in the severe battery environment. There is a need

for a “sticky” fluoropolymer tie layer that can survive the severe oxidative environment of a lithium ion battery. The desired fluoropolymer tie layer must have a limited swelling in an electrolyte at elevated temperatures (no more than 100 volume percent, preferably less than 75 volume percent and more preferably less than 50 volume percent), must be easy to process (ease
5 of dissolution at 20 percent solids), be easy to laminate to the separator, and the tie layer formed must be porous.

There is an unmet need for a fluoropolymer binder that provides excellent adhesion between electrodes and separators, durability in the battery environment, and long term adhesion and alignment within Li ion battery stacks.

10 Through extensive research and development, a fluoropolymer tie layer has been developed to overcome the deficiencies of the prior art, and provide the excellent adhesion between electrodes and separators, along with durability in the battery environment. This tie layer provides the long term adhesion and alignment within Li ion battery stacks needed by the industry. The binder developed herein contains low levels of adhesion promoting monomer units,
15 resists excessive swelling in electrolyte at elevated temperature, can be easily dissolved at 20 percent solids, and is easily laminated. The copolymer provides an improvement in adhesion over PVDF homopolymer, and also exhibit longer life over non-fluorinated binder polymers – especially with cathodes.

SUMMARY OF THE INVENTION

20 The invention relates to a lithium ion battery comprising:

- a) an electrode;
- b) a cathode;
- c) a separator:

where the separator is adhered to said cathode, said anode, or adhered to and between both said
25 anode and said cathode by a functional polyvinylidene fluoride tie layer, said functional polyvinylidene fluoride being selected from: a) a copolymer comprising 0.2 to 20 weight percent, preferably 0.5 to 15 weight percent, and more preferably 1 to 10 weight percent of at least one adhesion-promoting comonomer, b) a modified fluoropolymer comprising from 0.1 to

25, preferably 1.0 to 15, more preferably from 2.2 to 10 weight percent of residual functional groups from one or more low molecular weight polymeric functional chain transfer agents, and c) a mixture of a) and b).

5 The invention further relates to a process for producing a lithium ion battery comprising the step of adhering a separator to at least one electrode using a polyvinylidene fluoride copolymer tie layer, wherein said polyvinylidene copolymer comprising 0.2 to 20 weight percent, preferably 0.5 to 15 weight percent, and more preferably 1 to 10 weight percent of at least one adhesion-promoting comonomer.

DETAILED DESCRIPTION OF THE INVENTION

10 The invention relates to a functional tie layer binder for use in adhering electrodes and separators together in a lithium ion battery, and especially in a flexible pouch-type battery. The binder is either a copolymer containing low levels of adhesion-promoting monomer units that are evenly distributed in the copolymer, or a polyvinylidene homopolymer or copolymer modified by a low molecular weight, functional, polymer chain transfer agent.

15 “Copolymer” is used to mean a polymer having two or more different monomer units. “Polymer” is used to mean both homopolymer and copolymers. Polymers may be straight chain, branched, star comb, block, or any other structure. The polymers may be homogeneous, heterogeneous, and may have a gradient distribution of co-monomer units. All references cited are incorporated herein by reference. As used herein, unless otherwise described, percent shall mean weight percent. Unless otherwise stated, molecular weight is a weight average molecular weight as measured by GPC, using a polymethyl methacrylate standard. In cases where the polymer contains some cross-linking, and GPC cannot be applied due to an insoluble polymer fraction, soluble fraction/ gel fraction or soluble fraction molecular weight after extraction from gel is used. Crystallinity and melting temperature are measured by DSC as described in ASTM
20 D3418 at heating rate of 10 C/min. Melt viscosity is measured in accordance with ASTM D3835 at 230°C expressed in k Poise @100 Sec⁻¹

Copolymer

The tie layer of the invention is primarily a fluoro-copolymer composed of 80 to 99 mole percent, and preferably 85 to 98.8 mole percent of one or more fluoromonomers that include, but

are not limited to, vinylidene fluoride (VDF), tetrafluoroethylene (TFE), ethylene-tetrafluoroethylene (ETFE) and/or chlorotrifluoroethylene (CTFE). The chemical inertness of the fluoropolymer provides long battery life compared to non-fluoropolymers. In a preferred embodiment, the copolymer contains 80 to 99 mole percent of VDF monomer units.

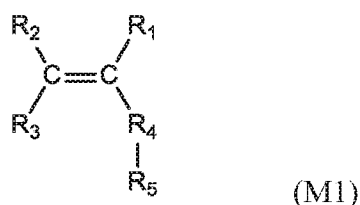
5 The copolymer also includes one or more “adhesive” comonomers at low levels of from 0.2 to 20 mole percent, preferably 0.5 to 15 mole percent, and most preferably 1 to 10 mole percent, based on the copolymer. Lower level result in no adhesive improvement over the homopolymer. Copolymers with higher levels of the comonomer could be too soft and tacky, making them more likely to dissolve in the battery environment. The presence of the adhesive
10 comonomer provides the copolymer with better adhesion than the fluoro-homopolymer.

Random copolymers are most useful, as this provides a better distribution of adhesive groups, leading to better adhesion, low swelling, and low extractability (little or no dissolution in the electrolyte). Graft copolymers are also contemplated by the invention.

Useful comonomers generally contain polar groups, or are high surface energy.
15 Examples of useful comonomers include, but are not limited to, one or more of the following: vinyl acetate, 2,3,3,3-tetrafluoropropene (HFO-1234yf), 2,3,3 trifluoropropene, hexafluoropropene (HFP), and 2-chloro-1,1-difluoroethylene (R-1122). HFP provides good adhesion, but may have reduced solvent resistance. Phosphate (meth)acrylates, (meth) acrylic acid, and hydroxyl-functional (meth)acrylic comonomers could also be used as the comonomer.

20 Other useful adhesive comonomers used in combination with the one or more fluoromonomers include, but are not limited to one or more of the following:

A) Vinyl alkyl acids, having as a comonomer (M1):

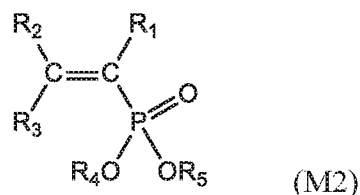


Wherein R1, R2, and R3 is a hydrogen or a halogen (F, Cl, Br, I).

Wherein R4 is a C1 to C16 linear, branched, aryl, or cycloalkyl group, a C1 to C16 fluorinated linear, branched, aryl or cycloalkyl group, an oligomer of hexfluoropropylene oxide or an oligomer of tetrafluoroethylene oxide.

- 5 Wherein R5 is carboxylic acid (C(O)OH), alkali metal carboxylate salt (COO⁻M⁺), ammonium carboxylate salt (COO⁻NH₄⁺), alkylammonium carboxylate salt (COO⁻N(Alk)₄⁺), alcohol (OH), amide (C(O)NH₂), dialkyl amide (C(O)NAlk₂), sulfonic acid (S(O)(O)OH), alkali metal sulfonate salt (S(O)(O)O⁻M⁺), ammonium sulfonate salt (S(O)(O)O⁻NH₄⁺), alkylammonium sulfonate salt (S(O)(O)O⁻N(Alk)₄⁺).

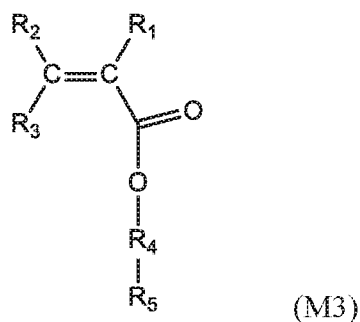
- 10 B) Vinyl alkyl acids, having the formula M2 below:



Wherein: R1, R2, and R3 is a hydrogen or a halogen (F, Cl, Br, I);

- Wherein: R4 and R5 are, separately, hydrogen, a C1 to C16 linear alkyl, branched alkyl, aryl, or cycloalkyl group, a C1 to C16 fluorinated linear alkyl, branched alkyl, aryl or cycloalkyl group,
 15 an oligomer of hexfluoropropylene oxide or an oligomer of tetrafluoroethylene oxide, alkali metal ion (Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺), ammonium ion (NH₄⁺), or alkylammonium (NAlk₄⁺)

C) Functional acrylates, having as a comonomer (M3):



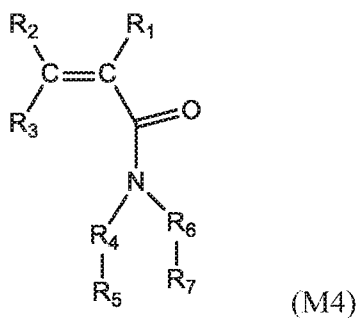
Wherein R1, R2, and R3 is a hydrogen or a halogen (F, Cl, Br, I);

Wherein R4 is a bond, C1 to C16 linear, branched, aryl, or cycloalkyl group, a C1 to C16 fluorinated linear, branched, aryl or cycloalkyl group, an oligomer of hexfluoropropylene oxide or an oligomer of tetrafluoroethylene oxide.

Wherein R5 is carboxylic acid (C(O)OH), alkali metal carboxylate salt (COO⁻M⁺), ammonium carboxylate salt (COO⁻NH₄⁺), alkylammonium carboxylate salt (COO⁻N(Alk)₄⁺), alcohol (OH),
 5 amide (C(O)NH₂), dialkyl amide (C(O)NAlk₂), sulfonic acid (S(O)(O)OH), alkali metal sulfonate salt (S(O)(O)O⁻M⁺), ammonium sulfonate salt (S(O)(O)O⁻NH₄⁺), alkylammonium sulfonate salt (S(O)(O)O⁻N(Alk)₄⁺), epoxide, C1 to C16 alkyl or cycloalkyl carbonate.

In one embodiment, two or more different functional acrylates was found to provide
 10 increased adhesion. While not being bound by any particular theory, it is believed that different functionalities, for example an alcohol and acid functionality, could react or crosslink to form ester groups. The two or more different functionalities preferably are present in the same terpolymer, but could also be a blend of two or more different copolymers.

D) Functional acrylamides, having as a comonomer (M4):



15

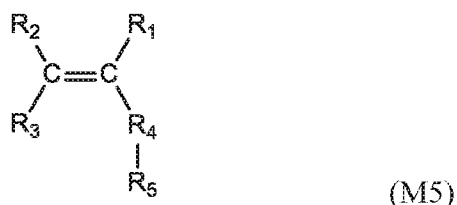
Wherein: R1, R2, and R3 is a hydrogen or a halogen (F, Cl, Br, I).

Wherein: R4 and R5, separately are a hydrogen, C1 to C16 linear, branched, aryl, or cycloalkyl group, a C1 to C16 fluorinated linear, branched, aryl or cycloalkyl group, an oligomer of
 20 hexfluoropropylene oxide or an oligomer of tetrafluoroethylene oxide.

Wherein: R5 and R6, separately are carboxylic acid (C(O)OH), alkali metal carboxylate salt (COO⁻M⁺), ammonium carboxylate salt (COO⁻NH₄⁺), alkylammonium carboxylate salt (COO⁻N(Alk)₄⁺), alcohol (OH), amide (C(O)NH₂), dialkyl amide (C(O)NAlk₂), sulfonic acid (S(O)(O)OH), alkali

metal sulfonate salt ($S(O)(O)O^{\cdot}M^{+}$), ammonium sulfonate salt ($S(O)(O)O^{\cdot}NH_4^{+}$), alkylammonium sulfonate salt ($S(O)(O)O^{\cdot}N(Alk)_4^{+}$), ketone ($C(O)$), or acetylacetonate ($C(O)-CH_2-C(O)$), or phosphonate ($P(O)(OH)_2$), alkali metal or ammonium phosphonate

E) Carbonates, containing the comonomer M5:

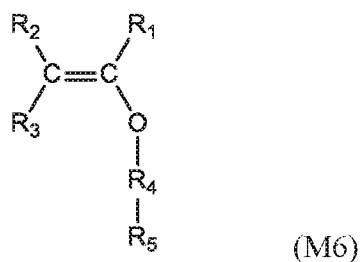


Wherein: R1, R2, and R3 is a hydrogen or a halogen (F, Cl, Br, I).

Wherein: R4 is a bond, a C1 to C16 linear alkyl, branched alkyl, aryl, or cycloalkyl group, a C1 to C16 fluorinated linear alkyl, branched alkyl, aryl or cycloalkyl group.

Wherein: R5 is C1 to C16 cycloalkyl group, a C1 to C16 fluorinated cycloalkyl group, containing a carbonate group as part of the cyclic structure.

F) Vinyl Ethers, having as a comonomer (M6):



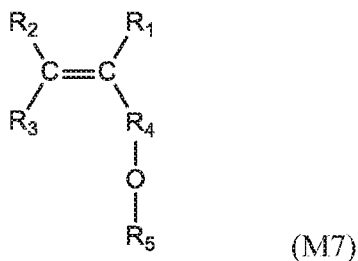
Wherein: R1, R2, and R3 is a hydrogen or a halogen (F, Cl, Br, I).

Wherein: R4 is a C1 to C16 linear, branched, aryl, or cycloalkyl group, a C1 to C16 fluorinated linear, branched, aryl or cycloalkyl group, an oligomer of hexfluoropropylene oxide or an oligomer of tetrafluoroethylene oxide.

Wherein: R5 is carboxylic acid ($C(O)OH$), alkali metal carboxylate salt ($COO^{\cdot}M^{+}$), ammonium carboxylate salt ($COO^{\cdot}NH_4^{+}$), alkylammonium carboxylate salt ($COO^{\cdot}N(Alk)_4^{+}$), alcohol (OH), amide ($C(O)NH_2$), dialkyl amide ($C(O)NAlk_2$), sulfonic acid ($S(O)(O)OH$), alkali metal sulfonate

salt (S(O)(O)O⁻M⁺), ammonium sulfonate salt (S(O)(O)O⁻NH₄⁺), alkylammonium sulfonate salt (S(O)(O)O⁻N(Alk)₄⁺), ketone (C(O)), acetylacetonate (C(O)-CH₂-C(O))

G) Allyloxy compounds having as a comonomer (M7):



5

Wherein: R1, R2, and R3 is a hydrogen or a halogen (F, Cl, Br, I).

Wherein: R4 is a C1 to C16 linear, branched, aryl, or cycloalkyl group, a C1 to C16 fluorinated linear, branched, aryl or cycloalkyl group, an oligomer of hexfluoropropylene oxide or an oligomer of tetrafluoroethylene oxide.

- 10 Wherein: R5 is carboxylic acid (C(O)OH), alkali metal carboxylate salt (COO⁻M⁺), ammonium carboxylate salt (COO⁻NH₄⁺), alkylammonium carboxylate salt (COO⁻N(Alk)₄⁺), alcohol (OH), amide (C(O)NH₂), dialkyl amide (C(O)NAlk₂), sulfonic acid (S(O)(O)OH), alkali metal sulfonate salt (S(O)(O)O⁻M⁺), ammonium sulfonate salt (S(O)(O)O⁻NH₄⁺), alkylammonium sulfonate salt (S(O)(O)O⁻N(Alk)₄⁺), ketone (C(O)), or acetylacetonate (C(O)-CH₂-C(O)), or phosphonate
- 15 (P(O)(OH)₂), alkali metal or ammonium phosphonate.

Functional Chain Transfer Agents

The functional chain transfer agents of the invention are low molecular weight, functional polymers. By low molecular weight is meant a polymer with a degree of polymerization of less than or equal to 1,000, and preferably less than 800. In a preferred embodiment, the weight

20 average molecular weight of the polymeric chain transfer agent, as measured by GPC, is 20,000 g/mole or less, more preferably 15,000 g/mole, and more preferably less than 10,000 g/mole. In one embodiment the weight average molecular weight is less than 5,000 g/mole. The low molecular weight functional chain transfer agent is a polymer or an oligomer having two or more monomer units, and preferably at three or more monomer units.

By functional polymeric chain transfer agents, as used in the invention, is meant that the low molecular weight polymer chain transfer agent contains one or more different functional groups. The chain transfer agent has the formula $-(CH_2-CH_2)_y - X - R$,

where y is a integer of between 2 to 1000, X is a linking group including, but not limited to, a covalent or ionic bond, an alkyl, alkene, alkyne, substituted alkyl, substituted alkene, aryl, ester, ether, ketone, amine, amid, amide, organo-silane, and R is a functional group.

The functional group (R) provides functionality, and can be provided by the polymerization of functional monomers – either as the sole monomer, or as a comonomer. The functionality could also be added by a post-polymerization reaction or grafting. Useful functional groups include, but are not limited to, carboxylic, hydroxyl, siloxane, ether, ester, sulfonic, phosphoric, phosphonic, sulfuric, amide and epoxy groups, or a mixture thereof.

In addition to the low molecular weight, functional chain transfer agent of the invention, other chain transfer agents typically used in the polymerization of fluoropolymers may also be added at levels to provide the desired molecular weight.

In general, a portion of, or all of the chain transfer agent is added to the initial charge, to prevent the formation of extremely high molecular weight polymer that is non-soluble in polar solvents – and which exists as gels. The remainder of the chain transfer agent can then be added continuously, or in small portions through the remainder of the polymerization.

The functional fluoropolymers of the invention may optionally be blended with compatible fluoropolymers and non-fluoropolymers to form the final tie layer composition.

The manner of practicing the invention will now be generally described with respect to a specific preferred embodiment thereof, namely polyvinylidene fluoride based copolymers prepared in aqueous emulsion polymerization using non-fluorinated emulsifier as the principle emulsifier. Although the invention has been generally illustrated with respect to PVDF copolymers, one of skill in the art will recognize that analogous polymerization and application techniques can be applied to the preparation of other copolymers of fluorinated monomers. While non-fluorinated surfactants are preferred, the use of fluorosurfactants is also anticipated by this invention.

Polymerization Process

With respect to the preferred method of making the fluoropolymer of the present invention, initially, deionized water, at least one surfactant – typically at a level of from 0.01 to less than 2.0 weight percent based on the amount of monomer, preferably non-fluorinated
5 surfactant, and a portion of the chain transfer agent are introduced into a reactor followed by deoxygenation. After the reactor reaches the desired temperature, vinylidene fluoride (VDF) monomer and optional comonomer are added to the reactor. Depending on the reactivity of the comonomer, none, a portion of, or all of the comonomer is added to the initial charge. The remainder of the comonomer can then be added continuously, or in small portions through the
10 remainder of the polymerization to reach a predetermined ratio to VDF in the final polymer. The manner of adding the comonomer is done to provide a fairly homogeneous distribution of the comonomer units in the copolymer. Next a free radical initiator is introduced to the reactor with suitable flow rate to maintain proper polymerization rate. Once the reaction has started or simultaneously with the beginning of the reaction, the rest of low molecular weight functional
15 polymer chain transfer agent and fluoromonomer(s) are continuously fed at a desired ratio into the reactor. After reaching the desired polymer solids level, the feed of the monomers can be stopped, while the charge of the initiator is preferably maintained to consume any residual monomers in the reactor. The initiator charge can then be stopped, the reactor pressure dropped and the reactor cooled. The unreacted monomers can be vented and the fluoropolymer
20 dispersion collected through a drain port or other collection means. The fluoropolymer dispersion can then be isolated using standard isolation techniques such as oven drying, spray drying, shear or acid coagulation followed by drying and so on, or the functional fluoropolymer may be kept in the emulsion form for subsequent applications. The primary functional fluoropolymer particles formed have an average particle size of less than 500 nm, preferably in
25 the range of 20 to 400 nm, and most preferably in the range of from 50 to 300 nm.

Additives

The tie layer composition of the invention may optionally include 0 to 15 weight percent based on the copolymer, and preferably 0.1 to 10 weight percent of additives, including but not limited to thickeners, pH adjusting agents, anti-settling agents, surfactants, wetting agents, fillers,

anti-foaming agents, and fugitive adhesion promoters. Metal oxides, such as alumina, silica, zinc oxide, barium oxide, and titanium oxide are preferred additives. .

Process

5 A lithium ion battery tie layer of the invention can be added into the battery stack by several means. In one embodiment, a PVDF copolymer is produced by emulsion polymerization, as described above. Additives, if any, are then either added into the emulsion, or the emulsion is dried, and the additives are dry-blended into the PVDF copolymer to form a tie layer composition.

10 The resultant copolymer tie-layer composition can be converted into a free standing film, using any method known in the art, such as by blow molding, solution casting, or thin film extrusion process. Said film is less than 10 microns, preferably less than 7 microns, and most preferably about 5 microns or even less in thickness. The copolymer tie-layer composition can also be formed into a film onto a carrier film. The free standing thin film tie layer can be placed between the separator and an electrode, followed by heat lamination. The tie-layer film on the
15 carrier film can be transferred onto either the electrode or the separator, the carrier film removed, then either the separator or electrode placed on top of the tie-layer film then the stack heat laminated.

Alternately a multi-slot-die-casting can be used with the tie layer on the surface of the separator, the anode, or the cathode -- to reduce production costs.

20 In another embodiment, the tie layer composition is coated onto the separator, using any method known in the art including but not limited to gravure, dip or roll coating, and ink jet printing, or any of electrodes as a solvent or preferably aqueous coating, dried, and placed against an electrode. The coating formed should be a porous coating for best performance. Tie layer coatings formed from an aqueous dispersion result in a layer of discrete, functional
25 fluoropolymer particles having a particle size of less than 500 nm.

In a preferred embodiment, the tie layer is placed on the cathode.

Heat lamination is a preferred means to adhere the stack (anode/tie layer/separator/tie layer/ cathode together. The application of heat at 50 to 90°C and preferably 60-80°C can aid in

adhesion. Wetting of the coated separator with electrolyte during assembly can also aid in good adhesion.

Within this specification embodiments have been described in a way which enables a clear and concise specification to be written, but it is intended and will be appreciated that
5 embodiments may be variously combined or separated without parting from the invention. For example, it will be appreciated that all preferred features described herein are applicable to all aspects of the invention described herein.

Aspects of the invention include:

1. A lithium ion battery comprising:

- 10 a) an electrode;
 b) a cathode;
 c) a separator:

wherein said separator is adhered to said cathode, said anode, or both said anode and said cathode by a functional polyvinylidene fluoride tie layer, said functional polyvinylidene fluoride
15 being selected from: a) a copolymer comprising 0.2 to 20 weight percent, preferably 0.5 to 15 weight percent, and more preferably 1 to 10 weight percent of at least one adhesion-promoting comonomer, b) a modified fluoropolymer comprising from 0.1 to 25, preferably 1.0 to 15, more preferably from 2.2 to 10 weight percent of residual functional groups from one or more low molecular weight polymeric functional chain transfer agents, and c) a mixture of a) and b).

20 2. The lithium ion battery of aspect 1, wherein said tie layer has a thickness of from 0.5 to 10 microns, preferably from 0.7 to less than 5 microns, and most preferably from 1 to 4 microns.

3. The lithium ion battery of aspects 1 or 2, wherein said lithium ion battery is a pouch-type battery.

4. The lithium ion battery of any of aspects 1 to 3, wherein said comonomer comprises at least
25 one comonomer selected from the group consisting of vinyl acetate, HFO-1234yf, HFP, 2-chloro-1,1-difluoroethylene (R-1122), and phosphate (meth)acrylates.

5. The lithium ion battery of any of aspects 1 to 4, wherein said copolymer is a random copolymer or graft copolymer.
6. The lithium ion battery of any of aspects 1 to 5, wherein said separator is coated with an aqueous polyvinylidene fluoride binder composition.
- 5 7. The lithium ion battery of any of aspects 1 to 6, wherein said anode and/or said cathode is coated with an aqueous polyvinylidene fluoride binder.
8. The modified fluoropolymer of any of aspects 1 to 7, wherein said modified fluoropolymer comprises from 2.2 to 10 weight percent of said residual functional groups.
9. The modified fluoropolymer of any of aspects 1 to 8, wherein said modified fluoropolymer
10 comprises one or more fluoropolymer blocks and one or more blocks of said residual functional groups from one or more low molecular weight polymeric functional chain transfer agents
10. The modified fluoropolymer of any of aspects 1 to 9, wherein said residual functional groups are selected from the group consisting of carboxylic, hydroxyl, siloxane, ester, ether, sulfonic, phosphoric, phosphonic, sulfuric, amide, epoxy groups, and mixtures thereof.
- 15 11. A process for producing a lithium ion battery comprising the step of adhering a separator to an electrode using a polyvinylidene fluoride copolymer tie layer, wherein said polyvinylidene copolymer comprising 0.2 to 20 weight percent, preferably 0.5 to 15 weight percent, and more preferably 1 to 10 weight percent of at least one adhesion-promoting comonomer.
12. The process of aspect 11, wherein said tie layer is applied as a coating to either said
20 separator, said electrode, or both, and said electrode and separator are placed in direct contact, wherein said polyvinylidene fluoride copolymer tie layer is cured.
13. The process of aspects 11 or 12, wherein said polyvinylidene fluoride copolymer is in the form of a thin tie-layer sheet, said sheet placed directly between said separator and said electrode, followed by heat lamination.
- 25 14. The process of any of aspects 11 to 13, wherein said heat lamination occurs at a temperature of from 50 to 100°C, preferably from 60 to 80°C.

15. The process of any of aspects 11 to 14, wherein said tie layer is adhered to either the electrode, the separator, or both individually, followed by placing the tie-layer/electrode, and/or tie-layer/separator, directly in contact with the corresponding electrode or separator, followed by the step of heat lamination.

- 5 16. The process of any of aspects 11 to 15, wherein said separator is wetted with electrolyte prior to assembly.

EXAMPLES

10 Example-A

Into a 2-gallon stainless steel reactor was charged: 4000 grams of deionized water and 4.0 grams of PLURONIC 31R1 (non- fluorinated non-ionic surfactant from BASF). Agitation was begun at 72 rpm and the reactor was heated. After the reactor temperature reached the desired set point of 100 °C, VDF and HFP monomer were introduced to the reactor with a VDF/HFP
15 ratio of 36. Reactor pressure was then raised to 650 psi by charging approximately 400 grams of total monomers into the reactor. After the reactor pressure was stabilized, 75.0 grams of initiator solution made of 2.0 wt% potassium persulfate and 6.0 wt % SOKALAN cp-10 (low molecular weight polyacrylic acid from BASF) were added to the reactor to initiate polymerization. Upon initiation, the ratio of HFP to VDF was so adjusted to arrive at 10% HFP to total monomers in
20 the feed. The rate of further addition of the initiator solution was also adjusted to obtain and maintain a final combined VDF and HFP polymerization rate of roughly 600 grams per hour. The VDF and HPF copolymerization was continued until approximately 1800 grams of VDF was introduced in the reaction mass. The HFP feed was stopped but VDF feed continued till approximately 2000 grams of VDF was fed to the reactor. The VDF feed was stopped and the
25 batch was allowed to react-out at the reaction temperature to consume residual monomer at decreasing pressure. After 20 minutes, the initiator feed and agitation were stopped and the reactor was cooled, vented and the latex recovered. Solids in the recovered latex were determined by gravimetric technique and were about 34 weight% and melt viscosity of about 72 kp according to ASTM method D-3835 measured at 450 °F and 100 sec⁻¹. The melting
30 temperature of resin was measured in accordance with ASTMD3418 and was found to be about

135 °C. The weight average particle size was measured by NICOMP laser light scattering instrument and was found to be about 160 nm.

Example-B

5 Into a 2-gallon stainless steel reactor was charged: 4000 grams of deionized water and 4.0 grams of PLURONIC 31R1 (non- fluorinated non-ionic surfactant from BASF). Agitation was begun at 72 rpm and the reactor was heated. After the reactor temperature reached the desired set point of 100 °C, VDF monomer was introduced to reactor until the reactor pressure was reached 650 psi by charging approximately 400 grams of monomer into the reactor. After the
10 reactor pressure was stabilized, 75.0 grams of initiator solution made of 2.0 wt% potassium persulfate and 6.0 wt % SOKALAN cp-10 (low molecular weight polyacrylic acid from BASF) were added to the reactor to initiate polymerization. Upon initiation, the ratio of HFO-1234yf to VDF was so adjusted to arrive at 2% HFO-1234yf to total monomers in the feed. The rate of further addition of the initiator solution was also adjusted to obtain and maintain a final VDF
15 polymerization rate of roughly 600 grams per hour. The VDF and HFO-1234yf copolymerization was continued until approximately 2000 grams of VDF was introduced in the reaction mass. The HFO-1234yf feed was stopped but VDF feed continued till approximately 2200 grams of VDF was fed to the reactor. The VDF feed was stopped and the batch was allowed to react-out at the reaction temperature to consume residual monomer at decreasing pressure. After 20 minutes, the
20 initiator feed and agitation were stopped and the reactor was cooled, vented and the latex recovered. Solids in the recovered latex were determined by gravimetric technique and were about 33 weight% and melt viscosity of about 66 kp according to ASTM method D-3835 measured at 450 °F and 100 sec⁻¹. The melting temperature of resin was measured in accordance with ASTMD3418 and was found to be about 160 °C. The weight average particle size was
25 measured by NICOMP laser light scattering instrument and was found to be about 160 nm.

Applicant Examples:

The functional fluoropolymer formed in Examples A and B are applied to an anode or cathode as the tie layer by the following means:

The functional fluoropolymer of Examples A or B can be blow molded into a free-standing film of 2-6 microns thickness. The film is then heat laminated between a cathode and a separator.

5 In an alternative embodiment, the functional fluoropolymer of Examples A or B can be coated onto an electrode (cathode or anode) to form a tie layer of from 0.1 to 5 microns, preferably 1 to 3 microns in thickness. The coated electrode is then placed in a stack beside a separator membrane, and laminated in place.

What is claimed is

1. A lithium ion battery comprising:

a) an electrode;

5 b) a cathode;

c) a separator;

wherein said separator is adhered to said cathode, said anode, or both said anode and said cathode by a functional polyvinylidene fluoride tie layer, said functional polyvinylidene fluoride being selected from: a) a copolymer comprising 0.2 to 20 weight percent, preferably 0.5 to 15
10 weight percent, and more preferably 1 to 10 weight percent of at least one adhesion-promoting comonomer, b) a modified fluoropolymer comprising from 0.1 to 25, preferably 1.0 to 15, more preferably from 2.2 to 10 weight percent of residual functional groups from one or more low molecular weight polymeric functional chain transfer agents, and c) a mixture of a) and b).

2. The lithium ion battery of claim 1, wherein said tie layer has a thickness of from 0.5 to 10
15 microns, preferably from 0.7 to less than 5 microns, and most preferably from 1 to 4 microns.

3. The lithium ion battery of claim 1, wherein said lithium ion battery is a pouch-type battery.

4. The lithium ion battery of claim 1, wherein said comonomer comprises at least one comonomer selected from the group consisting of vinyl acetate, HFO-1234yf, HFP, 2-chloro-1-1-difluoroethyleme (R-1122), and phosphate (meth)acrylates.

20 5. The lithium ion battery of claim 1, wherein said comonomer comprises at least one comonomer selected from the group consisting of: vinyl alkyl acids, vinyl phosphonates, functional acrylates and blends thereof, functional acrylamides, carbonates, vinyl ethers, and alkoxy compounds.

6. The lithium ion battery of claim 1, wherein said copolymer is a random copolymer or graft
25 copolymer.

7. The lithium ion battery of claim 1, wherein said separator is coated with an aqueous polyvinylidene fluoride binder composition.

8. The lithium ion battery of claim 1, wherein said anode and/or said cathode is coated with an aqueous polyvinylidene fluoride binder.
9. The modified fluoropolymer of claim 1, wherein said modified fluoropolymer comprises from 2.2 to 10 weight percent of said residual functional groups.
- 5 10. The modified fluoropolymer of claim 1, wherein said modified fluoropolymer comprises one or more fluoropolymer blocks and one or more blocks of said residual functional groups from one or more low molecular weight polymeric functional chain transfer agents.
11. The modified fluoropolymer of claim 10, wherein said blocks of residual functional chain transfer groups comprise low molecular weight poly(meth)acrylic blocks.
- 10 12. The modified fluoropolymer of claim 1, wherein said residual functional groups are selected from the group consisting of carboxylic, hydroxyl, siloxane, ester, ether, sulfonic, phosphoric, phosphonic, sulfuric, amide, epoxy groups, and mixtures thereof.
13. A process for producing a lithium ion battery comprising the step of adhering a separator to an electrode using a polyvinylidene fluoride copolymer tie layer, wherein said polyvinylidene
15 copolymer comprising 0.2 to 20 weight percent, preferably 0.5 to 15 weight percent, and more preferably 1 to 10 weight percent of at least one adhesion-promoting comonomer.
14. The process of claim 13, wherein said tie layer is applied as a coating to either said separator, said electrode, or both, and said electrode and separator are placed in direct contact, wherein said polyvinylidene fluoride copolymer tie layer is cured.
- 20 15. The process of claim 13, wherein said polyvinylidene fluoride copolymer is in the form of a thin tie-layer sheet, said sheet placed directly between said separator and said electrode, followed by heat lamination.
16. The process of claim 13, wherein said heat lamination occurs at a temperature of from 50 to 100°C, preferably from 60 to 80°C.
- 25 17. The process of claim 13, wherein said tie layer is adhered to either the electrode, the separator, or both individually, followed by placing the tie-layer/electrode, and/or tie-layer/separator, directly in contact with the corresponding electrode or separator, followed by the step of heat lamination.

18. The process of claim 13, wherein said separator is wetted with electrolyte prior to assembly.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US18/26842

A. CLASSIFICATION OF SUBJECT MATTER

IPC - B32B 7/12, 27/30, 27/08; H01G 11/48, 11/52; H01M 8/1004, 2/16, 4/62, 8/12 (2018.01)
 CPC - B32B 27/304, 7/12; H01M 4/0404, 2/1673, 10/0525, 4/623, 4/1399, 4/8668, 10/052, 2/1666, 8/1004, 2/1686, 2/168, 2/145

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)

See Search History document

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

See Search History document

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

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2016/149238A1 (ARKEMA, INC.) September 22, 2016; pages 2-9; abstract	1, 4-10, 12-15, 17 & 18
Y		2-3, 11 & 16
Y	US 2006/0110549 A1 (WANG, Y et al.) May 25, 2006; paragraph [0106]; claim 9	2
Y	US 2014/0205882 A1 (FARASIS ENERGY INC.) July 24, 2014; paragraph [0006]	3
Y	US 2012/0094183 A1 (DEITERS, J et al.) April 19 2012; paragraphs [0023] & [0053]	11
Y	US 2015/0311490 A1 (ZEON CORP.) October 29, 2015; paragraphs [0067]-[0069]	16

☐ 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

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"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

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Date of mailing of the international search report

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