COMPOSITE SEPARATOR, PREPARATION METHOD THEREOF AND USE THEREOF

TECHNICAL FIELD

[0001] The present application relates to the technical field of lithium-ion batteries, for example, to a composite separator, a preparation method thereof and use thereof.

BACKGROUND

[0002] In recent years, spontaneous combustion and explosion incidents of new energy electric vehicles have occurred frequently, which has aroused widespread attention and doubts about the safety of power lithium-ion batteries. One of the core reasons is that the performance of existing lithium-ion battery separators cannot meet the application requirements of high-specific-energy batteries. Power lithium-ion batteries require higher safety performance, larger capacity, uniform performance for long-term stable output, and high-rate charge and discharge performance.

[0003] To improve the safety of lithium-ion batteries and meet market demands, a new generation of nanofiber composite separators has emerged at present, which features ultra-thinness and ultra-heat resistance and can satisfy battery safety requirements. However, a major disadvantage of nanofiber composite separators is their high moisture content, which fails to meet the low moisture content requirements of many customers and limits their application scope. As is well known, high moisture content in battery cells will impair cell performance such as capacity and cycle life. As one of the core components of battery cells, the control of moisture content of the separator is naturally a top priority.

[0004] Therefore, it is desired in the art to develop a composite separator with low moisture content.

SUMMARY

[0005] The following is an overview of the subject matter described in detail herein. This summary is not intended to limit the protection scope of the claims.

[0006] The present application provides a composite separator, a preparation method thereof and use thereof. The composite separator provided in the present application exhibits excellent adhesion performance, and also can reduce a moisture content of the nanofiber membrane by more than 20%, meeting customers' requirements for moisture control of separators.

[0007] In a first aspect, the present application provides a composite separator. The composite separator includes a nanofiber membrane and a hydrophobic polymer resin layer, where the nanofiber membrane includes a nanofiber layer, and the hydrophobic polymer resin layer is modified on at least one surface of the nanofiber layer;

a ratio of an average volume pore diameter of the hydrophobic polymer resin layer to an average volume pore diameter of the nanofiber membrane is 1.3-1.75.

[0008] In a second aspect, the present application provides a preparation method of the composite separator as described in the first aspect, including the following steps:

(1) mixing raw materials for preparing the hydrophobic polymer resin layer to obtain a slurry;

(2) coating the slurry obtained in step (1) onto a surface of the nanofiber layer, and performing curing, solvent elution and drying, to obtain the composite separator.

[0009] In a third aspect, the present application provides use of the composite separator as described in the first aspect in a battery.

[0010] Compared with the related art, the present application achieves at least the following beneficial effects.

[0011] (1) In the present application, by controlling the average volume pore diameter of the hydrophobic polymer resin layer to be greater than the average volume pore diameter of the nanofiber membrane and controlling a pore diameter ratio of the

two within a specific range, the hydrophobic polymer resin layer can not only facilitate moisture discharge from the nanofiber membrane during a drying stage of the preparation process, but also effectively prevent the nanofiber membrane from absorbing moisture in air, thus ensuring the composite separator with low moisture content; in addition, the pore diameter ratio within the specific range also helps avoid pore blockage of the nanofiber membrane that would affect lithium ion conduction.

[0012] (2) The composite separator provided by the present application has excellent adhesion performance, low moisture content and outstanding heat resistance, which greatly improves safety performance, high-temperature cycle stability and nail penetration resistance of lithium-ion batteries, and is applicable to fields such as 3C (Computer, Communication and Consumer electronics), electric vehicles (EV) and energy storage.

[0013] Other aspects can be understood upon reading and comprehension of the accompanying drawings and detailed description.

DESCRIPTION OF THE DRAWINGS

[0014] The accompanying drawings are provided to facilitate further understanding of the technical solutions herein and constitute a part of the specification. Together with the embodiments of the present application, they serve to explain the technical solutions herein, and do not constitute a limitation to the technical solutions herein.

[0015] FIG. 1 is an SEM image of a composite separator provided in Example 5 (magnification: 50K).

DESCRIPTION OF EMBODIMENTS

[0016] To enable those skilled in the art to better understand the solutions of the present application, the present application will be described in further detail below.

[0017] As mentioned above, to improve the safety of lithium-ion batteries and meet market demands, a new generation of nanofiber composite separators has emerged at

present. These separators feature ultra-thin and ultra-heat resistance characteristics, and improve the pass rate of cell nail penetration tests at a battery level and meet battery safety requirements. Nevertheless, a major drawback of nanofiber composite separators lies in their high moisture content. As is well known, moisture content in battery cells affects their performances such as cell capacity and cycle life, so they cannot satisfy the low moisture requirements of many customers. Even after drying treatment, it is difficult to significantly reduce their moisture content, which is mainly related to the structure and material properties of nanofibers, thereby restricting their application scope.

[0018] Therefore, as one of the core components of battery cells, separators require an urgent control of their moisture content.

[0019] An embodiment of the present application provides a composite separator. The composite separator includes a nanofiber membrane and a hydrophobic polymer resin layer, where the nanofiber membrane includes a nanofiber layer, and the hydrophobic polymer resin layer is modified on at least one surface of the nanofiber layer;

a ratio of an average volume pore diameter of the hydrophobic polymer resin layer to an average volume pore diameter of the nanofiber membrane is 1.3-1.75.

[0020] Exemplarily, the ratio of the average volume pore diameter of the hydrophobic polymer resin layer to the average volume pore diameter of the nanofiber membrane may be 1.3, 1.32, 1.34, 1.36, 1.38, 1.4, 1.42, 1.44, 1.46, 1.48, 1.5, 1.52, 1.54, 1.56, 1.58, 1.6, 1.62, 1.64, 1.66, 1.68, 1.7, 1.72, 1.74, 1.75, or a range defined by any two of the above values.

[0021] According to the research and analysis of the applicant, by controlling the average volume pore diameter of the hydrophobic polymer resin layer to be greater than the average volume pore diameter of the nanofiber membrane and controlling the ratio of the volume pore diameters of the two within a specific range, the hydrophobic polymer resin layer can not only facilitate moisture discharge from the nanofiber membrane during a drying stage of the preparation process, but also effectively prevent

the nanofiber membrane from absorbing moisture in air, thus ensuring low moisture content of the composite separator; in addition, the pore diameter ratio within the specific range also helps avoid pore blockage of the nanofiber layer that would affect lithium ion conduction.

[0022] It should be noted that the term "surface" refers to two surfaces of a membrane or layer that have the largest area and are disposed opposite to each other, and "at least one surface" refers to at least one of the two surfaces. The term "volume pore diameter" refers to a diameter of a pore of a layer or membrane in terms of volume, while the "surface pore diameter" mentioned later refers to a diameter of a pore on an outer surface (i.e., a surface on a side away from the nanofiber membrane in a thickness direction) of a layer or membrane.

[0023] In some embodiments, the hydrophobic polymer resin layer has a three-dimensional network structure. The three-dimensional network structure increases the tortuosity of pore channels in the hydrophobic polymer resin layer, further raising the difficulty of moisture ingress, and preventing the nanofiber membrane from absorbing moisture in air.

[0024] In some embodiments, the hydrophobic polymer resin layer has a minimum surface pore diameter (D_{min}) of 20-30 nm, an average surface pore diameter (D_{avg}) of 40-50 nm, and a maximum surface pore diameter (D_{max}) of 60-70 nm.

[0025] The minimum surface pore diameter (D_{min}) may be 20 nm, 21 nm, 22 nm, 23 nm, 24 nm, 25 nm, 26 nm, 27 nm, 28 nm, 29 nm, 30 nm, or a range defined by any two of the above values. The average surface pore diameter (D_{avg}) may be 40 nm, 41 nm, 42 nm, 43 nm, 44 nm, 45 nm, 46 nm, 47 nm, 48 nm, 49 nm, 50 nm, or a range defined by any two of the above values. The maximum surface pore diameter (D_{max}) may be 60 nm, 61 nm, 62 nm, 63 nm, 64 nm, 65 nm, 66 nm, 67 nm, 68 nm, 69 nm, 70 nm, or a range defined by any two of the above values.

[0026] When the surface pore diameter of the hydrophobic polymer resin layer falls within the above ranges, the pore diameter of the hydrophobic polymer resin layer presents a non-uniform structural feature, which may balance improvement of the

moisture discharge efficiency of the nanofiber membrane and inhibition of ambient moisture absorption by the nanofiber membrane, thus reducing an overall moisture of the composite separator while effectively enhancing lithium ion transmission efficiency.

[0027] In some embodiments, the hydrophobic polymer resin layer has a thickness of 0.1-0.4 μm, for example, 0.1 μm, 0.12 μm, 0.14 μm, 0.16 μm, 0.18 μm, 0.2 μm, 0.22 μm, 0.24 μm, 0.26 μm, 0.28 μm, 0.3 μm, 0.32 μm, 0.34 μm, 0.36 μm, 0.38 μm, 0.4 μm, or a range defined by any two of the above values.

[0028] By controlling the thickness of the hydrophobic polymer resin layer, an ultra-thin thickness is sufficient to block moisture absorption from air while effectively improving battery cycle performance. It can be understood that an air permeability increment of the composite separator modified with the hydrophobic polymer resin layer relative to the nanofiber membrane is below 30 sec/100ml.

[0029] The present application does not specifically limit the type of the hydrophobic polymer resin in the hydrophobic polymer resin layer, and polymer resins containing a hydrophobic group (group with no affinity for water, insoluble in water or with extremely low water solubility) in the related art may be selected as required.

[0030] In some embodiments, a molecular chain of the hydrophobic polymer resin in the hydrophobic polymer resin layer contains any one selected from a group consisting of fluoro group (-F), siloxane group, phenyl group, long-chain alkyl group (alkyl group with 6 or more main-chain carbon atoms) and cyano group, or a combination of at least two thereof.

[0031] In some embodiments, the hydrophobic polymer resin includes any one selected from a group consisting of polyvinylidene fluoride homopolymer, vinylidene fluoride-hexafluoropropylene copolymer, siloxane-modified polyimide, long-chain alkyl-modified polyimide (the alkyl has 6 or more main-chain carbon atoms), fluoromethyl-modified polyimide and cyano-modified polyimide, or a combination of at least two thereof.

[0032] The hydrophobic polymer resin layer may bind and coat the nanofiber layer, effectively preventing the nanofiber layer from absorbing moisture in air, and providing

a sufficient hydrophobic layer on the surface of the nanofiber layer to ensure low final moisture content of the nanofiber layer, without affecting the heat resistance, electrolyte wettability and other properties of the nanofiber layer. In addition, an interface layer for unidirectional moisture diffusion may be formed between the hydrophobic polymer resin layer and the nanofiber layer, to block moisture approach and synergistically reduces moisture content.

[0033] In the embodiments of the present application, unless otherwise specified, the nanofiber membrane may be purchased commercially or prepared with reference to the related art.

[0034] In some embodiments, the nanofiber membrane has an average volume pore diameter of 40-50 nm, for example, 40 nm, 41 nm, 42 nm, 43 nm, 44 nm, 45 nm, 46 nm, 47 nm, 48 nm, 49 nm, 50 nm, or a range defined by any two of the above values. This may improve the moisture discharge efficiency of the nanofiber membrane, thereby reducing the overall moisture of the composite separator while effectively enhancing lithium ion transmission efficiency.

[0035] Although the thickness of the nanofiber membrane is not particularly limited, it may optionally range from 1 μm to 50 μm, and more preferably from 3 μm to 20 μm. If this substrate has a thickness of less than 1 μm, then it is difficult to maintain mechanical properties, and if this substrate has a thickness of greater than 50 μm, then its electrochemical performance will be seriously affected.

[0036] In some embodiments, the nanofiber membrane includes a base membrane and a nanofiber layer disposed on at least one surface of the base membrane.

[0037] Specifically, the nanofiber layer includes one or more of organic nanofibers and inorganic nanofibers. The organic nanofibers may include at least one of cellulose nanofibers, aramid nanofibers, polypropylene nanofibers, etc. The inorganic nanofibers may include at least one of carbon nanotubes, silver nanowires, boron nitride nanowires, copper hydroxide nanowires, hydroxyapatite nanowires, attapulgite, etc. It is understood that nanofibers refer to linear materials with a diameter at a nanoscale (diameter of less than 1000 nm), a relatively large length, and a certain aspect ratio

(aspect ratio ≥10).

[0038] Specifically, the base membrane may be a porous membrane commonly used in the art. Exemplarily, the base membrane may be a polymer porous membrane, or a polymer porous membrane provided with a coating layer. The polymer porous membrane may be a polyethylene (PE) porous membrane, a polypropylene (PP) porous membrane, a polymethyl methacrylate (PMMA) porous membrane, polybutene (PB) porous membrane, or a multi-layer composite separator thereof. The multi-layer composite separator refers to a multi-layer composite porous membrane formed by laminating the above polymer porous membranes in any order, such as a PP-PE-PP three-layer composite separator, a PP-PE double-layer composite separator, a PP-PP-PE-PP four-layer composite separator, a PE-PP-PB three-layer composite membrane, a PP-PMMA-PP three-layer composite membrane, etc.

[0039] The polymer porous membrane provided with a coating layer refers to a polymer porous membrane with a coating layer provided on at least one surface thereof. The coating layer is not particularly limited and may be selected from commonly used ones in the art as required. For example, the coating layer may include inorganic particles such as alumina, boehmite, magnesium oxide, magnesium hydroxide, etc., or at least one of organic polymers such as polyimide, PMMA, PVDF, etc. For instance, the polyolefin porous membrane provided with the coating layer may be an alumina-coated polyolefin porous membrane, a boehmite-coated polyolefin porous membrane, a polyimide-coated polyolefin porous membrane, a PMMA-coated polyolefin porous membrane, or a PVDF-coated polyolefin porous membrane; the polyolefin porous membrane provided with the coating layer may also be a polyolefin porous membrane coated with a mixture of polyimide and alumina, a polyolefin porous membrane coated with a mixture of PVDF and alumina, or a polyolefin porous membrane coated with a mixture of PMMA and alumina, etc.

[0040] In the embodiments of the present application, the modification method of the hydrophobic polymer resin layer is not particularly limited, and may be realized by composite methods in the related art, such as slurry coating or hot-pressing lamination

of membrane layers. It is understood that the composite separator may be obtained by coating a slurry containing a hydrophobic polymer resin onto one side of the nanofiber layer of a commercially available nanofiber membrane; or may be obtained by modifying a nanofiber membrane with a hydrophobic polymer resin layer during preparation of the nanofiber membrane. For example, the composite separator is obtained by coating a nanofiber slurry on both surfaces of a base membrane and curing to obtain a nanofiber membrane, then coating a slurry containing a hydrophobic polymer resin on the nanofiber layer side. For example, a slurry containing a hydrophobic polymer resin is first coated on at least one surface of the base membrane to form a hydrophobic polymer resin modified layer, then a nanofiber slurry is coated on at least one surface of a composite of the hydrophobic polymer resin modified layer and the base membrane to obtain a nanofiber coating layer, and finally a hydrophobic polymer resin layer is thermally laminated on the surfaces of the nanofiber coating layer, thereby obtaining a composite separator with hydrophobic polymer resin layers modified on two surfaces of the nanofiber layers. The nanofiber slurry may be a slurry in the related art or a commercially available slurry.

[0041] In some embodiments, the hydrophobic polymer resin layer is modified on a surface of the nanofiber layer away from the base membrane.

[0042] In some embodiments, the hydrophobic polymer resin layer may be prepared from the following raw materials.

[0043] The raw materials for preparing the hydrophobic polymer resin layer include the following components in percentage by weight:

hydrophobic polymer resin: 2%-10%;

pore-forming agent: 0.05%-3%; and

the remaining is solvent.

[0044] As an embodiment of the present application, by limiting the raw materials for preparing the hydrophobic polymer resin layer, a low concentration (2%-10%) of the hydrophobic polymer resin in the raw materials of the hydrophobic polymer resin layer can not only exert an effect of reducing moisture content, but also will not affect

the air permeability, heat resistance and electrolyte wettability of the nanofiber layer, and can also provide a certain adhesion performance.

[0045] In some embodiments, based on weight percentage of the raw materials of preparing the hydrophobic polymer resin layer, the content of the hydrophobic polymer resin may be 2%, 3%, 4%, 5%, 6%, 7%, 8%, 9%, 10%, or a range defined by any two of the above values.

[0046] In some embodiments, based on weight percentage of the raw materials of preparing the hydrophobic polymer resin layer, the content of the pore-forming agent may be 0.05%, 0.08%, 0.1%, 0.3%, 0.5%, 0.8%, 1%, 1.2%, 1.4%, 1.6%, 1.8%, 2%, 2.2%, 2.4%, 2.6%, 2.8%, 3%, or a range defined by any two of the above values.

[0047] Controlling the content of the pore-forming agent within this range can better control the pore diameter of the hydrophobic polymer resin layer and achieve more uniform pore structure distribution, thereby realizing moisture discharge from the nanofiber membrane and blocking moisture ingress, reducing the overall moisture of the composite separator while effectively improving lithium ion transmission efficiency.

[0048] In some embodiments, based on weight percentage of the raw materials of preparing the hydrophobic polymer resin layer, the content of the solvent may be 86%, 87%, 88%, 89%, 90%, 91%, 92%, 93%, 94%, 95%, 96%, 97%, or a range defined by any two of the above values.

[0049] In some embodiments, the molecular chain of the hydrophobic polymer resin contains any one of strong hydrophobic groups selected from a group consisting of fluoro group (-F), siloxane group, phenyl group, long-chain alkyl group (alkyl group with 6 or more main-chain carbon atoms) and cyano group, or a combination of at least two thereof.

[0050] In some embodiments, the hydrophobic polymer resin includes any one selected from a group consisting of polyvinylidene fluoride (PVDF) homopolymer, vinylidene fluoride-hexafluoropropylene copolymer [P(VDF-HFP)], siloxane-modified polyimide, long-chain alkyl-modified polyimide (the alkyl has 6 or more main-chain carbon atoms), fluoromethyl-modified polyimide and cyano-modified

polyimide, or a combination of at least two thereof.

[0051] In some embodiments, the raw materials for preparing the hydrophobic polymer resin layer further include a wetting agent in an amount of 0.3%-1% by weight, for example, 0.3%, 0.4%, 0.5%, 0.6%, 0.7%, 0.8%, 0.9%, 1%, or a range defined by any two of the above values. The wetting agent may improve the distribution uniformity of the hydrophobic polymer resin layer on the surface of the nanofiber membrane, achieve better coverage on the surface of the nanofiber membrane, and block moisture ingress into the nanofiber membrane.

[0052] In the embodiments of the present application, the types of the pore-forming agent and wetting agent are not particularly limited, and the pore-forming agent and wetting agent commonly used in the related art may be selected as required.

[0053] It is understood that the pore-forming agent is a liquid reagent that has poor compatibility with the hydrophobic polymer resin but good compatibility with the solvent.

[0054] In some embodiments, the pore-forming agent includes any one of water, polyethylene glycol (PEG), ethanol, etc, or a combination of at least two thereof.

[0055] In some embodiments, the wetting agent is an oil-based wetting agent. It should be understood that the oil-based wetting agent refers to a wetting agent compatible with organic solvents.

[0056] In some embodiments, the wetting agent includes any one of polyether siloxane copolymers, organosilicon dual-structured copolymers, polyacrylate copolymers, polyether-modified silicone oil copolymers or polyoxyethylene alkylamine copolymers, or a combination of at least two thereof.

[0057] In the embodiments of the present application, unless otherwise specified, the pore-forming agent and wetting agent are all commercially available.

[0058] The wetting agent of the present application provides excellent dynamic wetting effect during the preparation process of the composite separator. It may rapidly wet the nanofiber membrane substrate, enhance the effective coating of the hydrophobic polymer resin layer onto the nanofiber membrane surface, strengthen the adhesion

between the resin layer and the nanofiber membrane during drying, and promote the hydrophobic terminals of the hydrophobic polymer resin layer to face outward, to prevent moisture from entering the nanofiber membrane, thereby reducing the overall moisture of the composite separator.

[0059] In some embodiments, the solvent includes any one of acetone, N-methylpyrrolidone, N,N-dimethylacetamide (DMAC), etc., or a combination of at least two thereof.

[0060] In some embodiments, the present application provides a preparation method of the composite separator, including the following steps:

(1) mixing raw materials for preparing the hydrophobic polymer resin layer to obtain a slurry; and

(2) coating the slurry obtained in step (1) onto a surface of a nanofiber layer, and performing curing, solvent elution and drying, to obtain the composite separator.

[0061] In the embodiments of the present application, the coating may be performed by existing methods, such as dip coating, spray coating, roll printing, micro gravure coating, slot die coating, inclined plate coating, etc.

[0062] In some embodiments, the coating method in step (2) includes spray coating.

[0063] In some embodiments, the coating method in step (2) includes spray coating by an ultrasonic atomization process.

[0064] In some embodiments, the present application provides use of the composite separator in a battery.

[0065] In some embodiments, the battery includes a lithium-ion battery.

[0066] The technical solutions of the present application are further illustrated by the following specific embodiments. It should be appreciated by those skilled in the art that the embodiments are merely provided to facilitate understanding of the present application and shall not be construed as specific limitations thereto.

[0067] Unless otherwise specified, information on nanofiber membranes used in the examples and comparative examples of the present application are as follows.

[0068] Nanofiber membrane: Model No. SU810J99L, purchased from Shenzhen

Senior Technology Material Co., Ltd.

[0069] Nanofiber membrane: Model No. SU306J55C, purchased from Shenzhen Senior Technology Material Co., Ltd.

[0070] Example 1

[0071] The present example provides a composite separator, including a nanofiber membrane and a hydrophobic polymer resin layer. The nanofiber membrane includes a base membrane and nanofiber layers disposed on both surfaces of the base membrane. The surface of each nanofiber layer away from the base membrane is modified with the hydrophobic polymer resin layer.

[0072] The raw materials for preparing the hydrophobic polymer resin layer include the following components in percentage by weight:

hydrophobic polymer resin: 5%;

pore-forming agent: 0.5%;

wetting agent: 0.5%; and

solvent: balance;

where the hydrophobic polymer resin is PVDF-HFP (Arkema), the pore-forming agent is deionized water, the wetting agent is modified organosiloxane (BASF), and the solvent is N-methylpyrrolidone.

[0073] The preparation method of the composite separator includes the following steps:

(1) mixing the raw materials for preparing the hydrophobic polymer resin layer to obtain a slurry; and

(2) coating the slurry obtained in step (1) onto a surface of a nanofiber layer, performing curing at 25°C, solvent elution and drying processes, to obtain the composite separator.

[0074] Example 2

[0075] The present example provides a composite separator, including a nanofiber membrane and a hydrophobic polymer resin layer, where the nanofiber membrane includes a base membrane and nanofiber layers disposed on both surfaces of the base

membrane, and the hydrophobic polymer resin layer is modified on the surfaces of the nanofiber layers away from the base membrane.

[0076] The raw materials for preparing the hydrophobic polymer resin layer include the following components in percentage by weight:

hydrophobic polymer resin: 3%;

pore-forming agent: 0.05%;

wetting agent: 0.3%; and

solvent: balance;

where the hydrophobic polymer resin is polyvinylidene fluoride homopolymer (Arkema), the pore-forming agent is ethanol, the wetting agent is modified organosiloxane (BASF), and the solvent is N-methylpyrrolidone.

[0077] The preparation method of the composite separator includes the following steps:

(1) mixing the raw materials for preparing the hydrophobic polymer resin layer to obtain a slurry; and

(2) coating the slurry obtained in step (1) onto a surface of the nanofiber layer, performing curing at 25°C, solvent elution and drying processes, to obtain the composite separator.

[0078] Example 3

[0079] The present example provides a composite separator, including a nanofiber membrane and a hydrophobic polymer resin layer, where the nanofiber membrane includes a base membrane and nanofiber layers disposed on both surfaces of the base membrane, and the hydrophobic polymer resin layer is modified on the surfaces of the nanofiber layers away from the base membrane.

[0080] The raw materials for preparing the hydrophobic polymer resin layer include the following components in percentage by weight:

hydrophobic polymer resin: 10%;

pore-forming agent: 3%;

wetting agent: 1%; and

solvent: balance;

where the hydrophobic polymer resin is long-chain alkyl-modified polyimide (Shenzhen Yanyi), the pore-forming agent is PEG (polyethylene glycol, Mw = 1000 g/mol), the wetting agent is polyether-modified polysiloxane wetting agent (Hunan Guangxin), and the solvent is N-methylpyrrolidone.

[0081] The preparation method of the composite separator includes the following steps:

(1) mixing the raw materials for preparing the hydrophobic polymer resin layer to obtain a slurry; and

(2) coating the slurry obtained in step (1) onto the surface of the nanofiber layer, performing curing at 40°C, solvent elution and drying processes, to obtain the composite separator.

[0082] Example 4

[0083] The present example provides a composite separator, including a nanofiber membrane and a hydrophobic polymer resin layer, where the nanofiber membrane includes a base membrane and nanofiber layers disposed on both surfaces of the base membrane, and the hydrophobic polymer resin layer is modified on the surfaces of the nanofiber layers away from the base membrane.

[0084] The raw materials for preparing the hydrophobic polymer resin layer include the following components in percentage by weight:

hydrophobic polymer resin: 6%;

pore-forming agent: 2%;

wetting agent: 0.5%; and

solvent: balance;

where the hydrophobic polymer resin is long-chain alkyl-modified polyimide (Shenzhen Yanyi), the pore-forming agent is ethanol, the wetting agent is modified organosiloxane (BASF), and the solvent is acetone.

[0085] The preparation method of the composite separator includes the following steps:

(1) mixing the raw materials for preparing the hydrophobic polymer resin layer to obtain a slurry; and

(2) coating the slurry obtained in step (1) onto a surface of the nanofiber layer, performing curing at 30°C, solvent elution and drying processes, to obtain the composite separator.

[0086] Example 5

[0087] The present example provides a composite separator, including a nanofiber membrane and a hydrophobic polymer resin layer, where the nanofiber membrane includes a base membrane and nanofiber layers disposed on both surfaces of the base membrane, and the hydrophobic polymer resin layer is modified on the surfaces of the nanofiber layers away from the base membrane.

[0088] The raw materials for preparing the hydrophobic polymer resin layer include the following components in percentage by weight:

hydrophobic polymer resin: 10%;

pore-forming agent: 1%;

wetting agent: 0.5%; and

solvent: balance;

where the hydrophobic polymer resin is long-chain alkyl-modified polyimide (Shenzhen Yanyi), the pore-forming agent is PEG (polyethylene glycol, Mw = 1000 g/mol), the wetting agent is modified organosiloxane (BASF), and the solvent is N,N-dimethylacetamide (DMAC).

[0089] The preparation method of the composite separator includes the following steps:

(1) mixing the raw materials for preparing the hydrophobic polymer resin layer to obtain a slurry; and

(2) coating the slurry obtained in step (1) onto a surface of the nanofiber layer, performing curing at 15°C, solvent elution and drying processes, to obtain the composite separator.

[0090] The composite separator provided in the present example was characterized

via SEM, as shown in FIG. 1. It can be observed that the hydrophobic polymer resin layer has a three-dimensional network structure with micropores distributed on its surface.

[0091] Comparative Example 1

[0092] The present comparative example provides a composite separator, including a nanofiber membrane and a hydrophobic polymer resin layer, where the nanofiber membrane includes a base membrane and nanofiber layers disposed on both surfaces of the base membrane, and the hydrophobic polymer resin layer is modified on the surfaces of the nanofiber layers away from the base membrane.

[0093] The raw materials for preparing the hydrophobic polymer resin layer include the following components in percentage by weight:

hydrophobic polymer resin: 15%;

pore-forming agent: 1%;

wetting agent: 1%; and

solvent: balance;

where the hydrophobic polymer resin is long-chain alkyl-modified polyimide (Shenzhen Yanyi), the pore-forming agent is ethanol, the wetting agent is modified organosiloxane (BASF), and the solvent is N-methylpyrrolidone.

[0094] The preparation method of the composite separator refers to Example 1.

[0095] Comparative Example 2

[0096] The present comparative example provides a composite separator, including a nanofiber membrane and a hydrophobic polymer resin layer, where the nanofiber membrane includes a base membrane and nanofiber layers disposed on both surfaces of the base membrane, and the hydrophobic polymer resin layer is modified on the surfaces of the nanofiber layers away from the base membrane.

[0097] The raw materials for preparing the hydrophobic polymer resin layer include the following components in percentage by weight:

hydrophobic polymer resin: 5%;

pore-forming agent: 5%;

wetting agent: 0.5%; and

solvent: balance;

where the hydrophobic polymer resin is PVDF-HFP (Arkema), the pore-forming agent is deionized water, the wetting agent is modified organosiloxane (BASF), and the solvent is N-methylpyrrolidone.

[0098] The preparation method of the composite separator refers to Example 1.

[0099] Comparative Example 3

[0100] The present comparative example provides a composite separator, including a nanofiber membrane and a hydrophobic polymer resin layer, where the nanofiber membrane includes a base membrane and nanofiber layers disposed on both surfaces of the base membrane, and the hydrophobic polymer resin layer is modified on the surfaces of the nanofiber layers away from the base membrane.

[0101] The raw materials for preparing the hydrophobic polymer resin layer include the following components in percentage by weight:

hydrophobic polymer resin: 5%;

pore-forming agent: 0.01%;

wetting agent: 0.5%; and

solvent: balance;

where the hydrophobic polymer resin is PVDF-HFP (Arkema), the pore-forming agent is deionized water, the wetting agent is modified organosiloxane (BASF), and the solvent is N-methylpyrrolidone.

[0102] The preparation method of the composite separator refers to Example 1.

[0103] Comparative Example 4

[0104] The present comparative example provides a composite separator, including a nanofiber membrane and a hydrophobic polymer resin layer, where the nanofiber membrane includes a base membrane and nanofiber layers disposed on both surfaces of the base membrane and the hydrophobic polymer resin layer is modified on the surfaces of the nanofiber layers away from the base membrane.

[0105] The raw materials for preparing the hydrophobic polymer resin layer include

the following components in percentage by weight:

hydrophobic polymer resin: 5%;

pore-forming agent: 0.5%;

wetting agent: 0.5%; and

solvent: balance;

where the hydrophobic polymer resin is PVDF-HFP (Arkema), the pore-forming agent is PVP, the wetting agent is modified organosiloxane (BASF), and the solvent is N-methylpyrrolidone.

[0106] The preparation method of the composite separator refers to Example 1.

[0107] Performance tests are performed on the composite separators provided in the examples and comparative examples, and the test methods are as follows.

[0108] (1) Moisture content of nanofiber membrane and composite separator

[0109] A sample to be tested is placed in an environment with humidity of ≤1% and dew point of ≤-30℃ for 2 h; 0.15 g of the sample is weighed and transferred into a sample vial and then is sealed; the test is conducted using a Karl Fischer moisture tester, where the baking conditions is set to 120℃ for 10 minutes was set, and the test data is recorded after the test is completed.

[0110] The moisture reduction amount is calculated by the following formula:

[0111] Moisture reduction amount = (Moisture content of nanofiber membrane − Moisture content of composite separator) / Moisture content of nanofiber membrane × 100%.

[0112] (2) Average volume pore diameter

[0113] The curves described in (a) and (b) below of the sample membrane are measured at 25℃ using a PMI instrument (Model No. CFP-1500AE, Jiayun Co., Ltd.) with Galwick as the wetting liquid (surface tension: 15.9 dyne/cm at 25℃);

where (a) is a pressure-flow curve measured with the sample immersed in the test fluid; and

(b) is the pressure-flow curve at half the flow rate measured under dry conditions;

based on a pressure value P at the intersection point of curves (a) and (b), an average volume pore diameter D of the porous substrate is calculated using the following formula (1):

$$D = 4\cos\theta \times r / P \times 1000 \ldots\ldots (1)$$

where D represents the average volume pore diameter (nm); r represents the surface tension of the test liquid (N/m); P represents the pressure at the above-mentioned intersection point (Pa); θ represents the contact angle between the sample membrane and the test liquid (°).

[0114] (3) Surface pore diameters of the hydrophobic polymer resin layer (D_{min}, D_{avg}, D_{max})

[0115] The surface of the composite separator is observed using a scanning electron microscope (SEM) (S-5500, manufactured by Hitachi High-Technologies Corporation) at a magnification of 20000×. The obtained image is imported into a computer, and the SEM image is binarized using the image processing software ImageJ to obtain an image with pore portions in black and structural portions in white. Each pore is fitted into a circle, and its diameter is measured. If the pore portions and structural portions cannot be clearly binarized due to contrast differences in the analyzed image, the pore portions are blackened first, followed by image processing, where the pores are fitted into circles, to calculate their minimum, average and maximum diameters. The value rounded to the first decimal place is taken as the pore diameter.

[0116] (4) Air permeability variation

[0117] The air permeability of the nanofiber membrane and the composite separator is tested respectively in accordance with the standard "GB/T 36363-2018 Polyolefin Separators for Lithium-ion Batteries", and the air permeability variation is calculated according to the following formula:

[0118] Air permeability variation = Air permeability of composite separator − Air permeability of nanofiber membrane.

[0119] (5) Ionic conductivity

[0120] Circular separator specimens with a diameter of 47 mm are cut from the

composite separator, and then placed between two electrodes (the area of the electrodes is not greater than the area of the separator specimens). The separator specimens are fully saturated with battery electrolyte; the resistance R (Ω) of the separator specimens is measured by the probe AC impedance technique. The ionic conductivity σ (unit: $S \cdot cm^{-1}$) of the electrolyte-saturated separator is then calculated according to the following formula, and the results are shown in Table 1:

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

where σ represents the ionic conductivity of the specimens in $S \cdot cm^{-1}$; R represents the slope of the separator specimen resistance (Ω) as a function of the number of the separator specimen layers; d represents the thickness of the separator specimens in μm; S represents the test area of the electrode in cm^2.

[0121] The performance test results are shown in Table 1.

[0122] Table 1

	Nanofiber membrane			Hydrophobic polymer resin layer				Air permeability variation /sec/100ml	Average volume pore diameter ratio	Composite separator		Moisture reduction /%
	Type	Moisture content /ppm	Average volume pore diameter /nm	Surface D_{min} /nm	Surface D_{avg} /nm	Surface D_{max} /nm	Thickness /μm			Moisture content /ppm	Ionic conductivity /$mS \cdot cm^{-1}$	
Example 1	SU810J99L	1842	41	21	45	68	0.15	10	1.46	1139	0.7	38
Example 2	SU810J99L	1827	38	25	48	69	0.3	20	1.53	1305	0.8	29
Example 3	SU810J99L	1842	41	27	54	73	0.25	16	1.37	1187	0.7	36
Example 4	SU810J99L	1827	41	29	46	65	0.28	18	1.46	1139	0.7	38
Example 5	SU306J55C	1909	45	24	49	67	0.4	25	1.44	1105	0.7	42
Comparative Example 1	SU810J99L	1890	41	17	40	103	0.15	10	1.95	1605	0.6	15
Comparative Example 2	SU810J99L	1890	41	30	50	93	0.15	11	1.90	1705	0.5	10
Comparative Example 3	SU810J99L	1890	41	21	37	59	0.15	10	1.85	1762	0.6	7

Comparative Example 4	SU306J55C	1909	44	18	38	54	0.15	10	1.25	1820	0.4	5

[0123] It can be seen from Table 1 that for the composite separator provided in the present application, by modifying the hydrophobic polymer resin on the surface of the nanofiber membrane, and controlling the ratio of the average volume pore diameter of the hydrophobic polymer resin layer to the average volume pore diameter of the nanofiber membrane within the range of 1.3-1.75, the moisture content of the nanofiber membrane may be reduced by more than 20% (29%-42%), with a final moisture content thereof being not more than 1305 ppm; while the composite separators provided in the comparative examples all have significantly higher moisture content.

[0124] The applicant declares that the present application illustrates the composite separator, the preparation method thereof and the use thereof through the above examples, but the present application is not limited to the above examples, that is, it does not mean that the present application must rely on the above examples for implementation. Those skilled in the art should understand that any improvement to the present application, equivalent substitution of the raw materials selected for the present application, addition of auxiliary components, and selection of specific implementation modes all fall within the protection scope and disclosure scope of the present application.

CLAIMS

1. A composite separator, comprising a nanofiber membrane and a hydrophobic polymer resin layer, wherein the nanofiber membrane comprises a nanofiber layer, and the hydrophobic polymer resin layer is modified on at least one surface of the nanofiber layer;

a ratio of an average volume pore diameter of the hydrophobic polymer resin layer to an average volume pore diameter of the nanofiber membrane is 1.3-1.75.

2. The composite separator according to claim 1, wherein the hydrophobic polymer resin layer has a three-dimensional network structure.

3. The composite separator according to claim 1 or 2, wherein the hydrophobic polymer resin layer has a minimum surface pore diameter of 20-30 nm, an average surface pore diameter of 40-50 nm, and a maximum surface pore diameter of 60-70 nm.

4. The composite separator according to any one of claims 1-3, wherein the hydrophobic polymer resin layer has a thickness of 0.1-0.4 μm.

5. The composite separator according to any one of claims 1-4, wherein an air permeability increment of the composite separator relative to the nanofiber membrane is below 30 sec/100ml.

6. The composite separator according to any one of claims 1-5, wherein a molecular chain of a hydrophobic polymer resin in the hydrophobic polymer resin layer contains any one selected from a group consisting of fluoro group, siloxane group, phenyl group, long-chain alkyl group and cyano group, or a combination of at least two thereof.

7. The composite separator according to any one of claims 1-5, wherein the hydrophobic polymer resin comprises any one selected from a group consisting of polyvinylidene fluoride homopolymer, vinylidene fluoride-hexafluoropropylene copolymer, siloxane-modified polyimide, long-chain alkyl-modified polyimide, fluoromethyl-modified polyimide and cyano-modified polyimide, or a combination of at least two thereof.

8. The composite separator according to any one of claims 1-7, wherein the nanofiber membrane has an average volume pore diameter of 40-50 nm.

9. The composite separator according to any one of claims 1-7, wherein the nanofiber membrane comprises a base membrane, and the nanofiber layer is disposed

on at least one surface of the base membrane.

10. The composite separator according to any one of claims 1-7, wherein the hydrophobic polymer resin layer is modified on a surface of the nanofiber layer away from the base membrane.

11. The composite separator according to any one of claims 1-10, wherein raw materials for preparing the hydrophobic polymer resin layer comprise the following components in percentage by weight:

hydrophobic polymer resin: 2%-10%;

pore-forming agent: 0.05%-3%; and

solvent: balance.

12. The composite separator according to claim 11, wherein the molecular chain of the hydrophobic polymer resin contains any one selected from a group consisting of fluoro group, siloxane group, phenyl group, long-chain alkyl group and cyano group, or a combination of at least two thereof.

13. The composite separator according to claim 11, wherein the hydrophobic polymer resin comprises any one selected from a group consisting of polyvinylidene fluoride homopolymer, vinylidene fluoride-hexafluoropropylene copolymer, siloxane-modified polyimide, long-chain alkyl-modified polyimide, fluoromethyl-modified polyimide and cyano-modified polyimide, or a combination of at least two thereof.

14. The composite separator according to any one of claims 11-13, wherein the pore-forming agent comprises any one selected from a group consisting of water, polyethylene glycol and ethanol, or a combination of at least two thereof.

15. The composite separator according to any one of claims 11-13, wherein the raw materials for preparing the hydrophobic polymer resin layer further comprise a wetting agent in an amount of 0.3%-1% by weight.

16. The composite separator according to any one of claims 11-13, wherein the wetting agent is an oil-based wetting agent; and

the wetting agent comprises any one selected from a group consisting of polyether siloxane copolymers, organosilicon dual-structured copolymers, polyacrylate copolymers, polyether-modified silicone oil copolymers or polyoxyethylene alkylamine copolymers, or a combination of at least two thereof.

17. The composite separator according to any one of claims 11-13, wherein the solvent comprises any one selected from a group consisting of acetone, N-

methylpyrrolidone and N,N-dimethylacetamide, or a combination of at least two thereof.

18. A preparation method of the composite separator according to any one of claims 1-17, comprising the following steps:

(1) mixing raw materials for preparing the hydrophobic polymer resin layer to obtain a slurry; and

(2) coating the slurry obtained in step (1) onto a surface of the nanofiber layer, and performing curing, solvent elution and drying, to obtain the composite separator.

19. The preparation method of the composite separator according to claim 18, wherein a coating method in step (2) comprises spray coating;

the coating method in step (2) comprises spray coating by an ultrasonic atomization process.

20. Use of the composite separator according to any one of claims 1-17 in a battery;

the battery comprises a lithium-ion battery.