

(19) World Intellectual Property
Organization

International Office



(43) International Publication Date
November 26, 2015 (26.11.2015)

(10) International Publication Number
WO 2015/178351 A1

(51) International Patent Classification:

H01M 2/16 (2006.01) H01M 2/18 (2006.01)

(21) International Application No.:

PCT/JP2015/064224

(22) International Filing Date:

May 18, 2015 (18.05.2015)

(25) Filing Language:

Japanese

(26) Publication Language:

Japanese

(30) Priority Data:

JP 2014-104352 May 20, 2014 (20.05.2014) JP

JP 2014-168462 Aug. 21, 2014 (21.08.2014) JP

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(81) Designated Countries (All types of domestic protections possible unless expressly noted): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated Countries (All types of domestic protections possible unless expressly noted): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

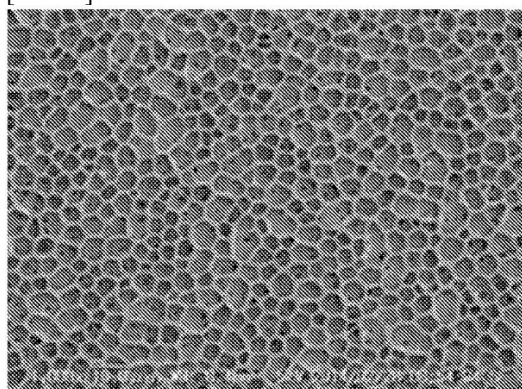
Attached Publications:

- International Search Report (Article 21(3) of the Paris Convention)

(54) Title: SEPARATOR FOR NONAQUEOUS SECONDARY BATTERIES, METHOD FOR PRODUCING SAME AND NON-AQUEOUS SECONDARY BATTERY

(54) Title: NON-AQUEOUS RECHARGEABLE BATTERY SEPARATOR, MANUFACTURING METHOD THEREOF, AND NON-AQUEOUS RECHARGEABLE BATTERY

[FIG. 1]



(57) Abstract: A separator for nonaqueous secondary batteries, which is provided with: a porous base that contains a thermoplastic resin; and a porous layer that is provided on one surface or both surfaces of the porous base and contains a polyvinylidene fluoride resin. The porous layer has a structure wherein a plurality of cells, each of which opened in the direction perpendicular to the surface of the porous layer, are aligned adjacent to each other in the plane direction of the porous layer, and has a contact angle with water of from 115° to 140°.

(57) Abstract: A non-aqueous rechargeable battery separator, provided with a porous base material containing a thermoplastic resin, and a porous layer provided on one surface or both surfaces of the porous base material, the porous layer having a structure in which a large number of cells that are open in a direction perpendicular to the surface of the porous layer are aligned adjacent to each other in the direction perpendicular to the surface of the porous layer and having a contact angle with water of 115° to 140°.

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SPECIFICATION

Title of Invention:

NON-AQUEOUS RECHARGEABLE BATTERY SEPARATOR, MANUFACTURING METHOD THEREOF, AND NON-AQUEOUS RECHARGEABLE BATTERY

Technical Field

[0001] The present invention relates to a non-aqueous rechargeable battery separator, a manufacturing method thereof, and a non-aqueous rechargeable battery.

Background Art

[0002] Non-aqueous rechargeable batteries, such as lithium ion rechargeable batteries, are widespread as power sources for portable electronic devices such as laptop computers, mobile phones, digital cameras, and camcorders.

[0003] In recent years, in conjunction with the size reduction and weight reduction of portable electronic devices, the outer covering of non-aqueous rechargeable batteries has been simplified and weight reduction has been achieved, and aluminum cannisters have been developed as an outer covering material in place of stainless steel cannisters, and furthermore, packs made of aluminum laminated films have been developed as an outer covering material in place of metal cannisters. However, because packs made of an aluminum laminated film are soft, in a battery that uses such pack as an outer covering material (a so-called soft pack battery), gaps are easily formed between the electrodes and the separator by external impact or expansion and contraction of the electrodes due to charging and discharging, and cycle life may decrease.

[0004] In order to solve the problems described above, technologies that increase adhesion between the electrodes and the separator have been proposed. Separators provided with a porous layer containing a polyvinylidene fluoride resin on a base material made of a polyolefin microporous film or the like are known as one of these technologies (for example, see patent documents 1 to 4). When the separator is superposed on the electrode and crimped by pressing or hot pressing, the separator adheres well to the electrode through the porous layer, and thus the cycle lifespan of the battery can be improved.

Prior Art Literature

Patent Documents

[0005] Patent Document 1: JP 2004-356102 A

Patent Document 2: WO 2005/049318

Patent Document 3: JP 4988972

Patent Document 4: JP 2013-54972 A

Summary of Invention

Problem to Be Solved by Invention

[0006] However, polyvinylidene fluoride resin is a resin that is easily charged, so a porous layer containing polyvinylidene fluoride resin easily takes on static electricity, and a separator provided with this porous layer may be inferior in handling properties. As a result, when a battery element is manufactured by winding a separator provided with a porous layer containing a polyvinylidene fluoride resin, and an electrode, one over the other, a problem occurs in that the electrode and the separator cause winding deviation and the manufacturing efficiency of the battery decreases.

[0007] Conversely, a separator having high electrolyte solution wettability is preferable in order to impregnate the separator with the electrolyte solution in a short period of time and with high uniformity when injecting the electrolyte solution after inserting the battery element into the exterior material.

[0008] Embodiment of the present invention were configured due to the above circumstances.

An object of the present invention is to provide a non-aqueous rechargeable battery separator that achieves excellent handling properties and high affinity with an electrolyte solution in a well-balanced manner.

Furthermore, an object of the present invention is to provide a non-aqueous rechargeable battery at high manufacturing efficiency.

Means for Solving Problem

[0009] Specific means for solving the problem include the following aspects.

[1] A non-aqueous rechargeable battery separator, provided with a porous base material containing a thermoplastic resin, and a porous layer provided on one surface or both surfaces of the porous base material and containing a polyvinylidene fluoride resin, the porous layer having a structure in which a

large number of cells open in a direction perpendicular to the surface of the porous layer are aligned adjacent to each other in the surface direction of the porous layer and having a contact angle with water of 115° to 140° .

[2] The non-aqueous rechargeable battery separator according to [1], wherein an average diameter of the opening portion of the cell is $0.1\ \mu\text{m}$ to $10\ \mu\text{m}$.

[3] The non-aqueous rechargeable battery separator according to [1] or [2], wherein a porosity of the porous layer is 40% to 80%.

[4] The non-aqueous rechargeable battery separator according to any of [1] to [3], wherein a charge damping half-life is 300 seconds or less, as measured on the porous layer.

[5] The non-aqueous rechargeable battery separator according to any of [1] to [4], wherein a time until dynamic wetting tension reaches 1.5 mN when immersed in an electrolyte solution is 10 seconds or less.

[6] The non-aqueous rechargeable battery separator according to any of [1] to [5], wherein the porous layer further contains a surfactant having an HLB value of 5.0 to 8.0, and the polyvinylidene fluoride resin and the surfactant are mixed inside the porous layer.

[7] The non-aqueous rechargeable battery separator according to [6], wherein a mass ratio of the polyvinylidene fluoride resin to the surfactant in the porous layer is 99.9:0.1 to 95.0:5.0.

[8] The non-aqueous rechargeable battery separator according to any of [1] to [7], wherein a peel strength between the porous base material and the porous layer is $0.1\ \text{N/cm}$ to $2.0\ \text{N/cm}$.

[9] The non-aqueous rechargeable battery separator according to any of [1] to [8], wherein the porous layer further contains a filler.

[10] The non-aqueous rechargeable battery separator according to any of [1] to [9], having the porous layer on both surfaces of the porous base material.

[11] The non-aqueous rechargeable battery separator according to any of [1] to [10], wherein the porous base material is a polyolefin microporous film containing polyethylene.

[12] The non-aqueous rechargeable battery separator according to any of [1] to [11], wherein the porous base material is a polyolefin microporous film containing polyethylene and polypropylene.

[13] A method for manufacturing the non-aqueous rechargeable battery separator according to any of [6] to [12], including a step for forming a coating layer by coating one surface or both surfaces of a porous base with a solution obtained by dissolving a polyvinylidene fluoride resin and a surfactant having an HLB value of 5.0 to 8.0 in a solvent and a step for forming a porous layer by removing the solvent from the coating layer.

[14] A non-aqueous rechargeable battery provided with a positive electrode, a negative electrode, and the non-aqueous rechargeable battery separator according to any of [1] to [12] disposed between the positive electrode and the negative electrode, wherein an electromotive force can be obtained by doping and dedoping lithium.

Effect of Invention

[0010] According to an embodiment of the present invention, a non-aqueous rechargeable battery separator is provided that achieves excellent handling properties and high affinity with an electrolyte solution in a well-balanced manner.

Furthermore, according to an embodiment of the present invention, a non-aqueous rechargeable battery can be provided at high manufacturing efficiency.

Brief Description of Drawings

[0011] [FIG. 1] An image obtained by observing the separator of example A1 using a scanning electron microscope from a direction perpendicular to the surface.

[FIG. 2] An image obtained by observing the separator of comparative example A2 using a scanning electron microscope from a direction perpendicular to the surface.

Embodiments of Invention

[0012] Embodiments of the present invention will be described below. These descriptions and examples exemplify the present invention and do not limit the scope of the present invention.

[0013] The numerical range indicated using "to" in the present Specification indicates a range that includes numerical values stated before and after "to" as a minimum value and a maximum value, respectively.

[0014] In the present Specification, "machine direction" means a length direction in a long porous base material and separator, and "width direction" means a direction orthogonal to the "machine direction."

In the present Specification, the "machine direction" is also referred to as "MD direction" and the "width direction" is also referred to as "TD direction."

[0015] <Non-Aqueous Rechargeable Battery Separator>

The non-aqueous rechargeable battery separator of the present disclosure (also referred to simply as "separator") is provided with a porous base material containing a thermoplastic resin, and a porous layer provided on one surface or both surfaces of the porous base material and containing a polyvinylidene fluoride resin, the porous layer having a structure in which a large number of cells open in a direction perpendicular to the surface of the porous layer are aligned adjacent to each other in the surface direction of the porous layer and having a contact angle with water of 115° to 140°. In the separator of the present disclosure, the porous layer is present as the outermost layer of the separator and is a layer in contact with the electrode.

[0016] The separator according to the present disclosure is a separator provided with a porous layer containing a polyvinylidene fluoride resin on at least one surface of a porous base material containing a thermoplastic resin, and achieves excellent handling properties and high affinity with an electrolyte solution in a well-balanced manner. The separator according to the present disclosure can reduce the occurrence of defects when manufacturing a battery element by winding the separator and the electrode one over the other, and can improve the manufacturing efficiency of batteries.

[0017] In the separator according to the present disclosure, a porous layer containing a polyvinylidene fluoride resin has a honeycomb structure and has a contact angle with water of 115° to 140°, and as a result, the porous layer is less likely to suffer static electricity and the surface of the porous layer has high wettability with respect to an electrolyte solution. Therefore, it would follow that displacement of the separator is reduced when manufacturing a battery element by winding the separator and the electrode one over the other. Furthermore, it would follow that the winding core slips easily when the winding core is pulled out from the battery element, and that the deformation of the battery element is reduced. Furthermore, when impregnating the battery element manufactured by winding the separator and the electrode one over the other with the electrolyte solution, the battery element can be impregnated highly uniformly in a short time. Therefore, the separator of the present disclosure can improve the manufacturing efficiency of the battery.

[0018] The charging properties of the surface of the porous layer of the separator can be compared by measuring the charge damping half-life on the porous layer. The smaller the charge damping half-life, the lower the charging properties.

[0019] The separator of the present disclosure has a porous layer containing a polyvinylidene fluoride resin as the outermost layer on at least one surface thereof, and therefore has excellent adhesion to electrodes. Accordingly, non-aqueous rechargeable batteries to which the separator of the present disclosure is applied have improved battery cycle life.

[0020] Details of the porous base material and porous layer of the separator of the present disclosure will be described below.

[0021] [Porous Base Material]

In the present disclosure, a porous base material means a base material having pores or voids therein. Examples of such a base include a microporous film, a porous sheet made of fibrous material such as a nonwoven fabric or paper, and the like. In the present disclosure, a microporous film is preferred from the perspective of making the separator thinner and from the perspective of strength. The microporous film is a film having a structure in which a large number of micropores are provided and the micropores are connected, and in which gas or liquid can pass from one surface to the other surface.

[0022] The porous base material includes a thermoplastic resin. Examples of the thermoplastic resin include polyesters such as polyethylene terephthalate, polyolefins such as polyethylene and polypropylene, and the like. The thermoplastic resin is preferably a thermoplastic resin having a melting point of less than 200°C from the perspective of imparting a shutdown function to the porous base material. The shutdown function is a function that prevents thermal runaway of the battery by interrupting the movement of ions due to the material melting to close the pores of the porous base material when the battery temperature rises.

[0023] A microporous film containing a polyolefin (referred to as a "polyolefin microporous film") is preferable as the porous substrate. Examples of the polyolefin microporous film applied to a conventional battery separator a polyolefin microporous film, and it is preferable to select one having

sufficient mechanical properties and ionic permeability.

[0024] From the perspective of exhibiting the shutdown function, the polyolefin microporous film preferably contains polyethylene and the content of polyethylene is preferably 95 mass% or more.

[0025] From the perspective of imparting heat resistance to the polyolefin microporous film to the extent that the film does not easily break when exposed to high temperatures, a polyolefin microporous film containing polyethylene and polypropylene is preferable. Examples of such a polyolefin microporous film include a microporous film in which polyethylene and polypropylene are mixed in one layer. From the perspective of having both a shutdown function and heat resistance, the microporous film preferably contains 95 mass% or more of polyethylene and 5 mass% or less of polypropylene. Furthermore, from the perspective of compatibility between the shutdown function and heat resistance, a polyolefin microporous film having a layered structure of two or more layers, with at least one layer containing polyethylene and at least one layer containing polypropylene, is also preferable.

[0026] A polyolefin having a weight average molecular weight (Mw) of 100,000 to 5 million is preferable as the polyolefin contained in the polyolefin microporous film. When the weight average molecular weight is 100,000 or more, sufficient mechanical properties can be ensured. Conversely, when the weight average molecular weight is 5 million or less, shutdown characteristics are favorable, and the film is easily molded.

[0027] The polyolefin microporous film may be manufactured by, for example, the following method. Namely, this is a method of extruding a molten polyolefin resin from a T-die to form a sheet, crystallizing the sheet, stretching the crystallized sheet, and then heat-treating the sheet to form a microporous film. Alternatively, a polyolefin resin melted together with a plasticizer such as liquid paraffin is extruded from a T-die and cooled to form a sheet, which is stretched, and then the plasticizer is extracted and heat-treated to form a microporous film.

[0028] Examples of a porous sheet composed of a fibrous material include a porous sheet composed of a fibrous material made of a thermoplastic resin, such as a nonwoven fabric or paper.

[0029] The surface of the porous base material may be subjected to a corona treatment, a plasma treatment, a flame treatment, an ultraviolet irradiation treatment, or the like to improve wettability with a coating liquid for forming the porous layer.

[0030] From the perspective of obtaining good mechanical properties and internal resistance, the thickness of the porous base material is preferably 3 μm to 25 μm , and more preferably 5 μm to 20 μm .

[0031] From the perspective of preventing short circuit of the battery and obtaining sufficient ion permeability, a Gurley value (JISP8117 (2009)) of the porous base material is preferably 50 seconds/100 cc to 400 seconds/100 cc.

[0032] From the perspective of obtaining an appropriate film resistance and shutdown function, porosity of the porous base material is preferably 20% to 60%. A method for measuring the porosity of the porous base material in the present disclosure will be described below.

[0033] From the perspective of improving the manufacturing yield, a piercing strength of the porous base material is preferably 200 g or more. The piercing strength of the porous base material in the present disclosure indicates a maximum piercing load (g) measured by performing a piercing test under conditions of a curvature radius of 0.5 mm at the needle tip and a piercing speed of 2 mm/sec using a KES-G5 handy compression tester made by Kato Tech.

[0034] [Porous Layer]

In the present disclosure, the porous layer contains a polyvinylidene fluoride resin, is a layer provided as the outermost layer of the separator on one surface or both surfaces of a porous base material, and is a layer that adheres to an electrode when the separator and the electrode are pressed or hot pressed in an while superposed.

[0035] In the present disclosure, the porous layer is preferably present on both surfaces rather than on only one surface of the porous base material from the perspective of improving the cycle life of the battery. This is because when the porous layer is on both surfaces of the porous base material, both surfaces of the separator bond well to both electrodes with the porous layer therebetween.

[0036] In the present disclosure, the porous layer has a structure in which a large number of cells that are open in a direction perpendicular to the surface of the porous layer (that is, the direction perpendicular to the surface of the separator) are aligned adjacent to each other in the direction perpendicular to the surface of the porous layer (that is, the direction perpendicular to the surface of the separator). In other

words, the porous layer is partitioned into cells having a large number of openings by mesh-shaped partitions in the direction perpendicular to the surface of the porous layer (that is, the direction perpendicular to the surface of the separator) or in a direction close thereto.

- [0037] The lateral shape of the cells (the shape of the cross-section appearing when the cells are cut in the surface direction of the porous layer) is not limited. Examples of lateral shapes of the cells include circles, ellipses, triangles, rectangles, pentagons, hexagons, octagons, and the like, and a plurality of types of shapes may be mixed. The vertical shape of the cells (the shape of the cross-section appearing when the cells are cut in the direction perpendicular to the surface of the porous layer) is not limited. Examples of the vertical shape of the cells include a columnar shape, a conical shape, a tapered shape, an inversely tapered shape, and the like, and a plurality of types of shapes may be mixed.
- [0038] In the present Specification, a structure in which a large number of cells that are open in a direction perpendicular to a surface of a porous layer are aligned adjacent to each other in the direction perpendicular to the surface of a porous layer is also referred to as a "honeycomb structure." In the present Specification, when the structure is referred to as a "honeycomb structure," the shape in the horizontal direction and the shape in the vertical direction of the cells configuring the structure are not limited, and the shape in the horizontal direction includes a circle, an ellipse, a triangle, a square, a pentagon, a hexagon, an octagon, or the like, and the shape in the vertical direction includes a column, a cone, a taper, a reverse taper, or the like.
- [0039] In the present disclosure, the porous layer has a honeycomb structure, and therefore is believed to be resistant to static electricity and have improved wettability with respect to electrolyte solutions.
- [0040] The average diameter of the openings of the cells constituting the honeycomb structure is preferably 0.1 μm to 10 μm , more preferably 0.5 μm to 10 μm , and further preferably 1 μm to 10 μm . It is preferable that the average diameter of the cell openings is 0.1 μm or more because handling properties are more favorable. It is preferable that the average diameter of the opening of the cell is 10 μm or less because the wettability of the electrolyte solution is improved. The average diameter of the openings of the cells is obtained by observing the surface of the porous layer using a scanning electron microscope, selecting any 20 cells from the obtained image, finding the maximum diameter and the minimum diameter for each inner edge of the openings of the cells, calculating $\{(\text{maximum diameter} + \text{minimum diameter})/2\}$, and using the average value of the 20 cells as the average diameter of the openings of the cells.
- [0041] In the present disclosure, the cells that constitute the honeycomb structure may be holes that pass through the porous layer or may be recesses that do not pass through the porous layer. When the cells are recesses that do not pass through the porous layer, a thin layered region containing a polyvinylidene fluoride resin is present as part of the porous layer between voids of the cells and the surface of the porous base material. From the perspective of adhesion between the porous layer and the porous base material, the cells are preferably recesses that do not pass through the porous layer.
- [0042] In the separator of the present disclosure, the pores of cells that constitute the honeycomb structure in the porous layer and the micropores of the porous base material are connected, and gasses or liquids can pass from one surface to the other surface of the separator. When the cells are recesses that do not pass through the porous layer, it is preferable that a laminar region between the pores of the cell and the surface of the porous base material has a large number of micropores therein, and the pores of the cell and the micropores of the porous base material are connected by the micropores.
- [0043] One preferable example of the embodiment of the porous layer according to the present disclosure is a porous layer provided with a layered region that is in contact with a porous base material and has a large number of micropores therein, and a honeycomb structure that is present on the layered region.
- [0044] In the separator of the present disclosure, it can be confirmed that gasses or liquids can pass from one surface to the other surface by referring to the Gurley value. Specifically, it is preferable that a value obtained by subtracting the Gurley value of the porous substrate from the Gurley value of the separator is 1,800 seconds/100 cc or less, more preferably 1,500 seconds/100 cc or less, further preferably 1,000 seconds/100 cc or less, and further preferably 900 seconds/100 cc or less, and further preferably 800 seconds/100 cc or less.
- [0045] In the present disclosure, a thickness of a partition wall constituting a honeycomb structure (that is, a partition wall in which a porous layer is partitioned into a large number of cells) is, for example, 0.1 μm to 2 μm . It is preferable that a large number of micropores are present in the partition wall constituting the honeycomb structure, and it is preferable that the pores of adjacent cells are connected

by the micropores.

[0046] In the present disclosure, the surface of the porous layer has a contact angle with water of 115° to 140°. When the contact angle of the water on the surface of the porous layer is less than 115°, static electricity is more readily charged, and handling is difficult. From this perspective, the water contact angle is preferably 115° or more, and more preferably 120° or more. Conversely, when the contact angle of the water on the surface of the porous layer is greater than 140°, wettability with the electrolyte solution is insufficient. From this perspective, the water contact angle is preferably 140° or less, and more preferably 135° or less.

[0047] The water contact angle in the present disclosure is measured by using a contact angle meter (for example, Drop Master DM-301 made by Kyowa Interface Science), using distilled water as the water, and forming a 1 μ L water droplet on the surface of the porous layer using a syringe.

[0048] The presence or absence of the honeycomb structure in the porous layer, the size of the cells constituting the honeycomb structure, and the contact angle of the water on the surface of the porous layer can be controlled by various conditions when the porous layer is formed on the porous base material. Details will be given in the description of the separator manufacturing method described below.

[0049] In the present disclosure, the porous layer preferably has a porosity of 40% to 80% from the perspective of wettability with the electrolyte solution and ion permeability. A method for measuring the porosity of the porous layer in the present disclosure will be described below.

[0050] From the perspective of adhesion to the electrode and ion permeability, the thickness of the porous layer is preferably 0.5 μ m or more, more preferably 1 μ m or more, and further preferably 1.5 μ m or more, and preferably 5 μ m or less, more preferably 4 μ m or less, and further preferably 3 μ m or less on one side of the porous base material.

[0051] In the present disclosure, the porous layer is provided on one surface or both surfaces of the porous base material and is a porous layer containing at least a polyvinylidene fluoride resin. In the present disclosure, the porous layer may further contain other components such as other resins and fillers aside from polyvinylidene fluoride resins.

[0052] From the perspective of ionic permeability and adhesion to the electrode, the mass of the polyvinylidene fluoride resin contained in the porous layer is preferably 0.5 g/m² to 3.0 g/m² on one side of the porous base material, and more preferably 0.5 g/m² to 1.5 g/m². When the porous layer is formed on both surfaces of the porous base material, the mass of the polyvinylidene fluoride resin included in the porous layer is preferably 1.0 g/m² to 6.0 g/m², and more preferably 1.0 g/m² to 3.0 g/m².

[0053] [Polyvinylidene Fluoride Resin]

In the present disclosure, examples of polyvinylidene fluoride resins include a monopolymer of vinylidene fluoride (that is, polyvinylidene fluoride), a copolymer of vinylidene fluoride with another copolymerizable monomer (polyvinylidene fluoride copolymer), and a mixture thereof. Examples of monomers that can be copolymerized with vinylidene fluoride include tetrafluoroethylene, hexafluoropropylene, trifluoroethylene, trichloroethylene, vinyl fluoride, and the like, and one type or two or more types may be used. From the perspective of ensuring sufficient mechanical properties in a step of bonding the polyvinylidene fluoride resin to an electrode, the polyvinylidene fluoride resin preferably contains vinylidene fluoride in an amount of 70 mol% or more as a constituent unit, and preferably contains vinylidene fluoride in an amount of 94 mol% or more.

[0054] The polyvinylidene fluoride resin preferably has a weight average molecular weight (Mw) of 100,000 to 3 million. When the weight average molecular weight is 100,000 or more, there is a tendency for the adhesive strength of the porous layer to the electrode to be better. From this perspective, the weight average molecular weight is more preferably 400,000 or more. Conversely, when the weight average molecular weight is 3 million or less, the viscosity of the coating liquid is reduced, moldability is favorable, and the porous layer is more favorably porous. From this perspective, the weight average molecular weight is preferably 2 million or less, and further preferably 1.2 million or less. The weight average molecular weight of the polyvinylidene fluoride resin can be found by gel permeation chromatography (GPC method). The polyvinylidene fluoride resin having a relatively high molecular weight can be obtained by emulsion polymerization or suspension polymerization, and is preferably obtained by suspension polymerization.

[0055] [Other Resins]

In the present disclosure, the porous layer may contain other resins and fillers aside from

polyvinylidene fluoride resins. Examples of other resins include fluororubbers, acrylic resins, styrene-butadiene copolymers, homopolymers or copolymers of vinyl nitrile compounds (acrylonitrile, methacrylonitrile, and the like), carboxymethyl cellulose, hydroxyalkyl cellulose, polyvinyl alcohol, polyvinyl butyral, polyvinylpyrrolidone, polyethers (polyethylene oxide, polypropylene oxide, and the like), and the like.

[0056] The content of the other resins in the porous layer is preferably 5 mass% or less, more preferably 3 mass% or less, further preferably 1 mass% or less, and particularly preferably, other resins are not included.

[0057] [Other Additives]

In the present disclosure, the porous layer may contain a filler or other additive composed of an inorganic substance or an organic substance to improve slip properties and heat resistance of the separator. In such case, it is preferable that the content and particle size thereof be such that the effect of the present disclosure is not hindered.

[0058] The average particle size of the filler is preferably 0.01 μm to 10 μm . A lower limit of 0.1 μm or more is more preferable, and an upper limit of 5 μm or less is more preferable.

[0059] The particle size distribution of the filler is preferably $0.1 \mu\text{m} < d_{90} - d_{10} < 3 \mu\text{m}$. Here, d_{10} represents a 10% cumulative average particle size (μm) in a weight cumulative particle size distribution derived from a small particle side, and d_{90} represents a 90% cumulative average particle size (μm). Examples of measurement of particle size distribution include a method using a laser diffraction type particle size distribution measurement device (Master Sizer 2000 made by Sysmex), using water as the dispersion medium, and using a trace amount of the non-ionic surfactant Triton X-100 as the dispersant.

[0060] [Inorganic Fillers]

An inorganic filler in the present disclosure is preferably an electrochemically stable inorganic filler that is stable with respect to the electrolyte solution. Specific examples include: a metal hydroxide such as aluminum hydroxide, magnesium hydroxide, calcium hydroxide, chromium hydroxide, zirconium hydroxide, cerium hydroxide, nickel hydroxide, and boron hydroxide; metal oxides such as silica, alumina, zirconia, and magnesium oxide; carbonates such as calcium carbonate, and magnesium carbonate; sulfates such as barium sulfate and calcium sulfate; clay minerals such as calcium silicate and talc; and the like. The inorganic filler preferably contains at least one metal hydroxide and/or a metal oxide, and from the perspective of imparting flame retardancy and destaticizing effect, the inorganic filler preferably contains at least one metal hydroxide, more preferably magnesium hydroxide. One type of these inorganic fillers may be used alone, or two or more types may be used in combination. The inorganic filler may be surface-modified with a silane coupling agent or the like.

[0061] The particle shape of the inorganic filler is not limited and may be a shape that is close to a sphere or a plate shape, but from the perspective of suppressing short circuits in the battery, it is preferable to have plate-shaped particles or primary particles that are not agglomerated.

[0062] In the present disclosure, the content of the inorganic filler in the porous layer is preferably 1 mass% to 95 mass%, more preferably 5 mass% to 80 mass%, and further preferably 10 mass% to 50 mass%.

[0063] [Organic Fillers]

Examples of organic fillers in the present disclosure include crosslinked acrylic resins such as crosslinked polymethyl methacrylate and crosslinked polystyrene, and the like, with crosslinked polymethyl methacrylate being preferred.

[0064] [Surfactant Having HLB value of 5.0 to 8.0]

From the viewpoint of improving the ion permeability of the separator, the porous layer according to the present disclosure preferably contains a surfactant having an HLB value of 5.0 to 8.0, and the surfactant and the polyvinylidene fluoride resin are mixed inside the porous layer. It would follow that the ion permeability of the separator is improved by the surfactant existing and functioning at the interface between the porous layer and the porous base material.

[0065] In the present disclosure, the HLB value (hydrophile-lipophile balance value) is a value that indicates the degree of hydrophilicity and lipophilicity of the surfactant, and is a value calculated using the following formula.

[0066] $\text{HLB value} = 20 \times \text{total sum of the formula weight of the hydrophilic part/molecular weight}$

[0067] In the present disclosure, a surfactant having an HLB value of 5.0 to 8.0 may be a mixed surfactant in which a plurality of types of surfactants are mixed. The HLB value of the mixed surfactants is an

arithmetic mean obtained by weighting the HLB values of the component surfactants by mass percentage.

[0068] In the present disclosure, for example, it is preferable to select the surfactant having an HLB value of 5.0 to 8.0 from a polyoxyethylene fatty acid diester, a polyoxyethylene fatty acid monoester, a sorbitan fatty acid ester, a polyoxyethylene sorbitan fatty acid ester, a polyoxyethylene alkyl ether, a polyoxyalkylene alkyl ether, a polyoxyethylene polyoxypropylene block polymer, or the like, or to prepare a surfactant having an HLB value of 5.0 to 8.0 by combining a plurality of the above compounds and the like. In the present disclosure, it is more preferable to select a surfactant having an HLB value of 5.0 to 8.0 from sorbitan fatty acid esters, or to prepare a surfactant having an HLB value of 5.0 to 8.0 by combining a plurality of sorbitan fatty acid esters.

[0069] The mass ratio of the polyvinylidene fluoride resin to the surfactant having an HLB value of 5.0 to 8.0 in the porous layer is preferably 99.9:0.1 to 95.0:5.0. When the mass ratio of the surfactant is 0.1 or higher, the ion permeability of the porous layer improves. From this perspective, the mass ratio of the surfactant is preferably 0.2 or higher. Conversely, when the mass ratio of the surfactant is 5.0 or less, the peel strength between the porous base material and the porous layer is ensured. From this perspective, the mass ratio of the surfactant is more preferably 3.0 or less. Accordingly, the mass ratio is preferably 99.9:0.1 to 95.0:5.0, more preferably 99.9:0.1 to 97.0:3.0, and further preferably 99.8:0.2 to 97.0:3.0.

[0070] The porous layer according to the present disclosure may contain various types of dispersants, and the dispersant is added, for example, to a coating liquid for forming the porous layer to improve dispersibility, coatability, and storage stability. Furthermore, various additives such as humectants, antifoaming agents, and pH adjusting agents may be included in the porous layer according to the present disclosure, and these are added to the coating liquid, for example, to improve compatibility with the porous base material, to suppress air biting into the coating liquid, or as a pH adjusting agent.

[0071] [Characteristics of Non-Aqueous Rechargeable Battery Separator]

From the perspective of the energy density and output characteristics of the battery, the film thickness of the separator in the present disclosure is preferably 30 μm or less, more preferably 25 μm or less.

[0072] The puncture strength of the separator according to the present disclosure is preferably 250 g to 1000 g and more preferably 300 g to 600 g. The method for measuring the puncture strength of the separator is the same as the method for measuring the puncture strength of the porous base material.

[0073] From the perspective of adhesion to the electrode, handling properties, ion permeability, and mechanical properties, the porosity of the separator of the present disclosure is preferably 30% to 60%. The measuring method of the porosity of the separator in the present disclosure is similar to the measuring method of the porosity of the porous base material (described later).

[0074] From the perspective of balancing ion permeability and mechanical strength, the Gurley value (JISP8117 (2009)) of the separator of the present disclosure is preferably 50 seconds/100 cc to 1500 seconds/100 cc, more preferably 100 seconds/100 cc to 1500 seconds/100 cc, and further preferably 500 seconds/100 cc to 1500 seconds/100 cc.

[0075] It is preferable that the amount of water contained in the separator according to the present disclosure (based on mass) be 1000 ppm or less. As the amount of water in the separator decreases, the reaction between the electrolyte solution and water in the battery can be reduced, gas generation in the battery can be reduced, and the cycle characteristics of the battery are improved. From this perspective, the water content (by mass) contained in the separator is more preferably 800 ppm or less, and further preferably 500 ppm or less.

[0076] In the separator of the present disclosure, the peel strength between the porous layer and the porous base material is preferably 0.1 N/cm to 2.0 N/cm from the perspective of adhesion to the electrode and ion permeability. When the peel strength is at least 0.1 N/cm, the adhesion between the porous layer and the porous base material is excellent, and as a result, the adhesion between the electrode and the separator is favorable. From this perspective, the peel strength is preferably 0.1 N/cm or more, more preferably 0.2 N/cm or more, further preferably 0.3 N/cm or more, and further preferably 0.4 N/cm or more. When the peel strength is 2.0 N/cm or less, the separator has excellent ion permeability. From this perspective, the peel strength is preferably 2.0 N/cm or less, and more preferably 1.5 N/cm or less. A method for measuring peel strength in the present disclosure will be described below.

[0077] The separator of the present disclosure preferably has a charge damping half-life of 300 seconds or less as measured on the porous layer. The charge damping half-life measured on the porous layer is 300 seconds or less, whereby deterioration of handling properties caused by static electricity can be reduced. As a result, when the battery element is manufactured by winding the separator and the electrode one over the other, the occurrence of defective products can be reduced, and the manufacturing efficiency of the battery can be improved. From this perspective, the lower the value of the charge damping half-life measured on the porous layer, the more preferable.

[0078] In the present disclosure, the method for measuring the charge damping half-life of the separator is as follows.

Three separators are cut to a size of 45 mm in the MD direction $\times$ 45 mm in the TD direction, and this is used as a test piece. After allowing the test piece to stand in a dry room (dew point -60°C) for one hour, the test piece is destaticized for 10 seconds by a static eliminator, and then the charge damping half-life (seconds) is measured on the porous layer using a STATIC HONEST METER TYPE H-0110 made by Shishido Electrostatic, Ltd. The charge damping half-life is measured for each of the three test pieces, and the measured values are averaged.

[0079] For the separator of the present disclosure, from the perspective of achieving sufficient battery performance by impregnating an electrolyte solution with high uniformity in a short time, the time until the dynamic wetting tension reaches 1.5 mN when immersed in an electrolyte solution is preferably 10 seconds or less, and more preferably 5 seconds or less. From this perspective, the shorter the time, the more preferable.

[0080] In the present disclosure, the method for measuring the above time is as follows.

Three separators are cut to a size of 25 mm in the MD direction $\times$ 25 mm in the TD direction, and this is used as a test piece. Using a dynamic wettability tester (WET-6200 made by Rhesca Co., Ltd.) that uses the Wilhelmy method, a test piece is immersed in an electrolyte solution at room temperature, and the time (seconds) until the dynamic wetting tension reaches 1.5 mN is measured. 1 M LiBF₄-ethylene carbonate:methyl ethyl carbonate = 3:7 (mass ratio) is used as the electrolyte solution. The above time is measured for each of the three test pieces, and the measured values are averaged.

[0081] The charge damping half-life and wettability of the separator can be controlled by, for example, providing a honeycomb structure in the porous layer, the size of cells constituting the honeycomb structure, components contained in the porous layer, the thickness of the porous layer, and the like.

[0082] <Manufacturing Method of Non-Aqueous Rechargeable Battery Separator>

The separator can be manufactured by, for example, a method wherein the porous layer is formed on the porous base material by applying a coating liquid containing at least a polyvinylidene fluoride resin onto the porous base material to form a coating layer and then solidifying the polyvinylidene fluoride resin contained in the coating layer. Specific examples of the method for forming the porous layer having the honeycomb structure include the methods in (i) to (iii) below, and of these, the method in (i) below is preferable.

[0083] (i) A method including: producing a coating liquid by dissolving a polyvinylidene fluoride resin in a mixed solvent formed by mixing a good solvent and a poor solvent; forming a coating layer by coating the coating liquid on a porous base material; and removing the poor solvent from the coating layer after inducing a phase separation phenomenon by selectively removing the good solvent from the coating layer.

[0084] (ii) A method including: producing a coating liquid by dissolving a polyvinylidene fluoride resin in a good solvent containing a pore forming agent; forming a coating layer by coating the coating liquid on a porous base material; and solidifying the polyvinylidene fluoride resin and the pore forming agent by selectively removing the good solvent from the coating layer and then removing the pore forming agent via the good solvent of the pore forming agent.

[0085] (iii) A method including: producing a coating liquid by dissolving a polyvinylidene fluoride resin in a good solvent; coating the coating liquid on a porous base material to form a coating layer; and controlling the temperature and humidity around the coating layer to induce a phase separation phenomenon and then removing the good solvent from the coating layer.

[0086] In the case of the method in (i) above, examples of the good solvent used in the coating liquid include methyl ethyl ketone, acetone, tetrahydrofuran, a fluorine-based solvent, and mixtures thereof. Of these, methyl ethyl ketone, acetone, and tetrahydrofuran are preferable. The poor solvent used in the coating

liquid is not particularly limited as long as it does not dissolve polyvinylidene fluoride resins, and examples include water, methanol, ethanol, propyl alcohol, butyl alcohol, butanediol, ethylene glycol, propylene glycol, tripropylene glycol, toluene, ortho-xylene, meta-xylene, paraxylene, ethylbenzene, and mixtures thereof. It is preferable to add an appropriate amount of the poor solvent that can ensure a coating liquid that can be stably coated. From the perspective of selectively removing the good solvent first from the coating layer, the good solvent is preferably volatilized before the poor solvent in a dry atmosphere, and therefore, the boiling point of the good solvent is preferably lower than the boiling point of the poor solvent.

[0087] In the case of the method in (i) above, the content of the polyvinylidene fluoride resin in the coating liquid is preferably 1 mass% to 20 mass%. The mass ratio of the good solvent to the poor solvent in the coating liquid is preferably 80:20 to 99.5:0.5, more preferably 90:10 to 99:1. In the method in (i) above, the honeycomb structure and the fine porous structure may be controlled by appropriately selecting the type of solvent, the type of polyvinylidene fluoride resin, the composition of the coating liquid, the thickness of the porous layer, the coating amount of the porous layer, the drying atmosphere, the drying conditions (temperature, speed), and the like.

[0088] In the case of the method in (ii) above, the good solvent used in the coating liquid is not particularly limited as long as it is a solvent that dissolves the polyvinylidene fluoride resin, and examples include N-methylpyrrolidone, dimethylacetamide, dimethylformamide, dimethyl sulfoxide, γ -butyrolactone, ethylene carbonate, methyl ethyl ketone, acetone, ethyl acetate, tetrahydrofuran, fluorine-based solvent, and the like. Of these, N-methylpyrrolidone, dimethylacetamide, dimethylformamide, dimethyl sulfoxide, γ -butyrolactone, methyl ethyl ketone, acetone, and tetrahydrofuran are preferable. The pore forming agent used in the coating liquid is not particularly limited so long as it does not dissolve in a good solvent, and examples include inorganic salts that dissolve in water, such as NaCl, metal oxides that dissolve in strong acids, such as silica, mixtures thereof, and the like.

[0089] In the case of the method in (ii) above, the content of the polyvinylidene fluoride resin in the coating liquid is preferably 1 mass% to 20 mass%. The mass ratio of the polyvinylidene fluoride resin to the pore forming agent in the coating liquid is preferably 10:90 to 90:10, more preferably 20:80 to 80:20. In the method in (ii) above, the honeycomb structure and the fine porous structure may be controlled by appropriately selecting the type of solvent, the type of polyvinylidene fluoride resin, the type of pore forming agent, the composition of the coating liquid, the thickness of the porous layer, the coating amount of the porous layer, the drying atmosphere, the drying conditions (temperature, speed), and the like.

[0090] In the case of the method in (iii) above, examples of the good solvent used in the coating liquid include methyl ethyl ketone, acetone, tetrahydrofuran, a fluorine-based solvent, and mixtures thereof. Of these, a fluorine-based solvent is preferable. In the case of the method in (iii) above, condensation of water droplets, growth of water droplets, and packing of water droplets due to capillary phenomenon occur on the surface of the coating layer, and a template of a honeycomb structure is formed. Next, the honeycomb structure is formed by volatilizing the water droplets after the good solvent volatilizes. Therefore, a solvent having a lower boiling point than water and no compatibility with water is preferable as the good solvent used in the coating liquid.

[0091] In the case of the method in (iii) above, the content of the polyvinylidene fluoride resin in the coating liquid is preferably 1 mass% to 20 mass%. In the method in (iii) above, the honeycomb structure and the fine porous structure may be controlled by appropriately selecting the type of solvent, the type of polyvinylidene fluoride resin, the composition of the coating liquid, the thickness of the porous layer, the coating amount of the porous layer, the drying atmosphere, the drying conditions (temperature, speed), and the like.

[0092] In the methods in (i) to (iii) above, when a filler or other additive is added to the porous layer, it may be dissolved or dispersed in the coating liquid. The coating liquid may contain a dispersant such as a surfactant, a thickener, a wetting agent, an antifoaming agent, a pH adjusting agent, and the like. These additives may remain as long as they are electrochemically stable and do not interfere with the in-cell reaction within the range of use of the non-aqueous rechargeable battery.

[0093] When forming a porous layer in which a polyvinylidene fluoride resin and a surfactant having an HLB value of 5.0 to 8.0 are mixed as the porous layer, in the methods in (i) to (iii) above, the polyvinylidene fluoride resin and the surfactant having an HLB value of 5.0 to 8.0 may be dissolved in

a solvent to produce the coating liquid.

[0094] In the methods in (i) to (iii) above, examples of methods for applying the coating liquid to the porous base material include a knife coater method, a gravure coater method, a Meyer bar method, a die coater method, a reverse roll coater method, a roll coater method, a screen printing method, an inkjet method, a spray method, a dip method, and the like. When forming the porous layer on both surfaces of the porous base material, the coating liquid may be applied one surface at a time, but coating the coating liquid on both surfaces simultaneously is preferable from the perspective of productivity.

[0095] <Non-Aqueous Rechargeable Battery>

The non-aqueous rechargeable battery of the present disclosure is a non-aqueous rechargeable battery that obtains electromotive force by doping and dedoping lithium, and is provided with a positive electrode, a negative electrode, and the non-aqueous rechargeable battery separator of the present disclosure. Dope means storage, support, adsorption, or insertion, and means a phenomenon where lithium ions enter the active material of an electrode such as a positive electrode.

[0096] The non-aqueous rechargeable battery of the present disclosure is provided with a positive electrode, a negative electrode, and a separator disposed between the positive electrode and the negative electrode. The non-aqueous rechargeable battery of the present disclosure has, for example, a structure in which a battery element in which a negative electrode and a positive electrode face each other with a separator interposed therebetween is sealed in an outer covering material together with an electrolyte solution. The non-aqueous rechargeable battery of the present disclosure is suitable for non-aqueous electrolyte rechargeable batteries, particularly lithium ion rechargeable batteries.

[0097] The non-aqueous rechargeable battery of the present disclosure can be manufactured at high manufacturing efficiency by using the separator of the present disclosure as the separator.

[0098] Examples of aspects of the positive electrode, negative electrode, electrolyte solution, and exterior material provided in the non-aqueous rechargeable battery of the present disclosure will be described below.

[0099] The positive electrode has, for example, a structure in which an active material layer containing a positive electrode active material and a binder resin is molded on a collector. The active material layer may further contain a conduction adjuvant. Examples of the positive electrode active material include lithium-containing transition metal oxides and the like, and specific examples include LiCoO_2 , LiNiO_2 , $\text{LiMn}_{1/2}\text{Ni}_{1/2}\text{O}_2$, $\text{LiCo}_{1/3}\text{Mn}_{1/3}\text{Ni}_{1/3}\text{O}_2$, LiMn_2O_4 , LiFePO_4 , $\text{LiCo}_{1/2}\text{Ni}_{1/2}\text{O}_2$, $\text{LiAl}_{1/4}\text{Ni}_{3/4}\text{O}_2$, and the like. Examples of the binder resin include polyvinylidene fluoride-based resins and the like. Examples of the conduction adjuvant include carbon materials such as acetylene black, Ketjen black, and graphite powder. Examples of the current collector include aluminum foil, titanium foil, stainless steel foil, or the like having a thickness of 5 μm to 20 μm .

[0100] In the non-aqueous rechargeable battery of the present disclosure, when the porous layer of the separator is disposed on the positive electrode side, the layer has excellent oxidation resistance, and therefore, it is easy to apply a positive electrode active material such as $\text{LiMn}_{1/2}\text{Ni}_{1/2}\text{O}_2$ or $\text{LiCo}_{1/3}\text{Mn}_{1/3}\text{Ni}_{1/3}\text{O}_2$ that can operate at a high voltage of 4.2 V or higher, which is advantageous.

[0101] The negative electrode has, for example, a structure in which an active material layer containing a negative electrode active material and a binder resin is molded on a collector. The active material layer may further contain a conduction adjuvant. Examples of the negative electrode active material include materials that can electrochemically store lithium, specifically, examples include: carbon materials; alloys of lithium and silicon, tin, aluminum, and the like; and the like. Examples of the binder resin include polyvinylidene fluoride-based resins, styrene-butadiene rubber, and the like. Examples of the conduction adjuvant include carbon materials such as acetylene black, Ketjen black, and graphite powder. Examples of the current collector include copper foil, nickel foil, stainless steel foil, and the like having a thickness of 5 μm to 20 μm . Furthermore, a metal lithium foil may be used as the negative electrode in place of the negative electrode described above.

[0102] The electrolyte solution is, for example, a solution obtained by dissolving a lithium salt in a non-aqueous solvent. Examples of lithium salts include LiPF_6 , LiBF_4 , LiClO_4 , and the like. Examples of non-aqueous solvents include: cyclic carbonates such as ethylene carbonate, propylene carbonate, fluoroethylene carbonate, difluoroethylene carbonate, vinylene carbonate, and the like; chain carbonates such as dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, and fluorine substitution products thereof; cyclic esters such as γ -butyrolactone and γ -valerolactone; and these may

be used individually or used in combination. The electrolyte solution is preferably a mixture of a cyclic carbonate and a linear carbonate at a mass ratio (cyclic carbonate: linear carbonate) of 20:80 to 40:60, with a lithium salt dissolved therein at 0.5 M to 1.5 M.

[0103] Examples of the exterior material include a metal cannister, a pack made of an aluminum laminated film, and the like. Examples of battery shapes include rectangular, cylindrical, coin-shaped, and the like, and the separator of the present disclosure is suitable for any shape.

[0104] The non-aqueous rechargeable battery of the present disclosure may be manufactured, for example, by impregnating with an electrolyte solution a laminate in which a separator of the present disclosure is disposed between a positive electrode and a negative electrode, housing the laminate in an exterior material (for example, a pack manufactured of laminated aluminum film), and heat pressing the laminate over the exterior material.

[0105] When manufacturing a non-aqueous rechargeable battery, the method for arranging the separator between the positive electrode and the negative electrode may be a method for laminating at least one layer at a time in this order (a so-called stack method), or a method for stacking the positive electrode, separator, negative electrode, and separator, in that order, and winding them in the length direction.

Examples

[0106] The separator and the non-aqueous rechargeable battery according to the present disclosure will be described in further detail below using examples. However, the separator and the non-aqueous rechargeable battery of the present disclosure are not limited to the following examples.

[0107] <Measurement Method>

The measurement methods applied in the examples and comparative examples are as follows.

[0108] [Film Thickness]

The film thickness (μm) of the porous base material and the separator was found by measuring 20 points using a contact type thickness meter (LITEMATIC made by Mitutoyo) and averaging this. A cylindrical terminal having a diameter of 5 mm was used as the measuring terminal, and it was adjusted so that a load of 7 g was applied during measurement.

The coating thickness (μm) of the porous layer was found by subtracting the film thickness of the porous base material from the film thickness of the separator.

[0109] [Unit Weight]

The unit weight (mass per 1 m^2) was found by cutting the separator to $10\text{ cm} \times 30\text{ cm}$, measuring the mass thereof, and dividing the mass by the area.

[0110] [Coating Amount of Porous Layer]

The coating amount of the porous layer (g/m^2) was found by subtracting the basis weight of the porous base material from the basis weight of the separator.

[0111] [Gurley Value]

The Gurley value (seconds/100 cc) of the porous base material and separator was measured using a Gurley type densometer (G-B2C made by Toyo Seiki) in accordance with JISP8117 (2009).

[0112] [Porosity]

The porosity of the porous base material and the porous layer was found according to the following calculation method.

The constituent materials are a, b, c, ..., n, the mass of each constituent material is $W_a, W_b, W_c, \dots, W_n$ (g/cm^3), the true density of each constituent material is $d_a, d_b, d_c, \dots, d_n$ (g/cm^3), and when defining the thickness as t (cm), the porosity ε (%) is found by the following equation.

$$\varepsilon = \{1 - (W_a/d_a + W_b/d_b + W_c/d_c + \dots + W_n/d_n)/t\} \times 100$$

[0113] [Average Cell Opening Diameter]

The surface of the separator was observed using a scanning electron microscope (3D real surface view microscope VE-8800 made by Keyence). This was obtained by selecting any 20 cells from the obtained image, finding the maximum diameter and the minimum diameter for each inner edge of the openings of the cells, calculating $\{(\text{maximum diameter} + \text{minimum diameter})/2\}$, and using the average value of the 20 cells as the average diameter of the openings of the cells.

[0114] [Water Contact Angle]

The water contact angle on the porous layer surface was measured using a contact angle meter Drop Master DM-301 made by Kyowa Interface Science. Distilled water was used as the water, 1 μL of water droplets was formed on the surface of the separator using a syringe, and the contact angle was measured.

The contact angle was measured for 10 water droplets, and the average value was calculated.

[0115] [Charge Damping Half-Life]

Three separators were cut to a size of 45 mm in the MD direction × 45 mm in the TD direction, and this was used as a test piece. After allowing the test piece to stand in a dry room (dew point -60°C) for one hour, the test piece was destaticized for 10 seconds by a static eliminator, and then the charge damping half-life (seconds) was measured using a STATIC HONEST METER TYPE H-0110 made by Shishido Electrostatic, Ltd. The measured values of the three test pieces were averaged to determine the charge damping half-life (seconds) of the separator.

[0116] [Wettability with Electrolyte Solution]

Three separators were cut to a size of 25 mm in the MD direction × 25 mm in the TD direction, and this was used as a test piece. Using a dynamic wettability tester (WET-6200 made by Rhesca), a test piece was immersed in an electrolyte solution (1 M LiBF₄-ethylene carbonate: methyl ethyl carbonate = 3:7 (mass ratio)) at room temperature, and the time (seconds) until the dynamic wetting tension reached 1.5 mN was measured. The measured values of the three test pieces were averaged to determine an index of wettability of the separator.

[0117] [Peel Strength]

Mending tape made by 3M was pasted on both surfaces of the separator so that the length direction matched the MD direction of the separator. Three separators, each having mending tape on both surfaces, were cut to a width of 10 mm, and this was used as a test piece. The mending tape was slightly peeled off together with the porous layer directly below from one end in the lengthwise direction of the test piece (that is, the MD direction of the separator), and a T-shaped peeling test was performed by gripping the two separated end portions using a Tensilon (RTC-1210A made by Orientec). The tensile rate in the T-shaped peeling test was set at 20 mm/min, the load (N) at the time the porous layer was peeled from the porous base material was measured, the loads from 10 mm to 40 mm after the start of measurement were collected at intervals of 0.4 mm, and the average thereof was calculated, and furthermore, the peel strength (N/cm) of the separator was determined by averaging the measured values of the three test pieces.

[0118] <Example A1>

A polyvinylidene fluoride-hexafluoropropylene copolymer (PVDF-HFP, KYNAR2800 made by Alkema) was dissolved in a mixed solvent of acetone and water mixed at a mass ratio of 95:5 to produce a coating liquid. The concentration of PVDF-HFP with respect to the coating liquid was 10 mass%.

This coating liquid was coated on both surfaces of a polyethylene microporous film (film thickness 9.1 μm, Gurley value 160 sec/100 cc, porosity 33%) which is a porous base material using a #6 bar coater, and coating layers were formed on both surfaces of the porous base material. This coating layer was dried at 60°C to obtain a separator having a porous layer on both surfaces of a polyethylene microporous film. The surface of the separator was observed using a scanning electron microscope (SEM), and it was confirmed that the porous layer had a honeycomb structure. SEM images obtained by observing the surface of the separator from the direction perpendicular to the surface are shown in FIG. 1.

[0119] <Example A2>

A separator having a porous layer on both surfaces of a polyethylene microporous film was obtained in the same way as in example A1, except that the mass ratio of acetone to water in the mixed solvent was changed to 97.5:2.5. The surface of the separator was observed using an SEM, and it was confirmed that the porous layer had a honeycomb structure.

[0120] <Comparative Example A1>

A separator was produced as shown below based on an example taught in JP 2004-356102 A.

A polyvinylidene fluoride-hexafluoropropylene copolymer (PVDF-HFP, KYNAR2800 made by Alkema) was dissolved in a mixed solvent of acetone, isopropanol, and water mixed at a mass ratio of 89.4:7.1:3.5 to produce a coating liquid. The concentration of PVDF-HFP with respect to the coating liquid was 2.6 mass%.

This coating liquid was coated on both surfaces of a polyethylene microporous film (film thickness 9.1 μm, Gurley value 160 sec/100 cc, porosity 33%) which is a porous base material using a #6 bar coater, and coating layers were formed on both surfaces of the porous base material. This coating layer was dried at 60°C to obtain a separator having a porous layer on both surfaces of a polyethylene

microporous film. The surface of the separator was observed using an SEM, and it was confirmed that the porous layer did not have a honeycomb structure. In this separator, the porous layer easily peels off, it is difficult to measure various physical properties of the porous layer and the separator, and moreover, it has not been possible to produce a battery using this separator.

[0121] <Comparative Example A2>

A separator having a porous layer on both surfaces of a polyethylene microporous film was obtained in the same way as in comparative example A1, except that the concentration of PVDF-HFP in the coating liquid was changed to 10 mass%. The surface of the separator was observed using an SEM, and it was confirmed that the porous layer did not have a honeycomb structure. SEM images obtained by observing the surface of the separator from the direction perpendicular to the surface are shown in FIG. 2.

[0122] <Comparative Example A3>

A polyvinylidene fluoride-hexafluoropropylene copolymer (PVDF-HFP, KYNAR2800 made by Alkema) was dissolved in a mixed solvent of dimethylacetamide and tripropylene glycol mixed at a mass ratio of 8:2 to produce a coating liquid. The concentration of PVDF-HFP with respect to the coating liquid was 8 mass%.

This coating liquid was applied to both surfaces of a polyethylene microporous film (film thickness 9.1 μm , Gurley value 160 sec/100 cc, porosity 33%) which is a porous base material, and a coating layer is formed on both surfaces of the porous base material. A composite film having coating layers on both surfaces of a porous base material was immersed in a coagulating liquid (water: dimethyl acetamide: tripropylene glycol = 57:30:13 [mass ratio], liquid temperature: 40°C), and a resin contained in the coating layers was solidified. Next, the composite film was washed with water and dried to obtain a separator having a porous layer on both surfaces of a polyethylene microporous film. The surface of the separator was observed using an SEM, and it was confirmed that the porous layer did not have a honeycomb structure.

[0123] <Comparative Example A4>

A separator having a porous layer on both surfaces of a polyethylene microporous film was obtained in the same way as in example A1, except that PVDF-HFP was changed from KYNAR2800 made by Arkema to Solef21216 made by Solvay. The surface of the separator was observed using an SEM, and it was confirmed that the porous layer had a honeycomb structure.

[0124] <Example B1>

A polyvinylidene fluoride-hexafluoropropylene copolymer (PVDF-HFP, made by Alkema Corporation KYNAR2800) and sorbitan monopalmitate (HLB value 6.7) as a surfactant were dissolved in a mixed solvent of acetone and water mixed at a mass ratio of 95:5 to produce a coating liquid. The mass ratio of PVDF-HFP and sorbitan monopalmitate contained in the coating liquid was set at 99.8:0.2, and the total concentration of both was set at 10 mass% with respect to the coating liquid.

This coating liquid was coated on both surfaces of a polyethylene microporous film (film thickness 9.1 μm , Gurley value 160 sec/100 cc, porosity 33%) which is a porous base material using a #6 bar coater, and coating layers were formed on both surfaces of the porous base material. This coating layer was dried at 60°C to obtain a separator having a porous layer on both surfaces of a polyethylene microporous film. The surface of the separator was observed by SEM, and it was confirmed that the porous layer had a honeycomb structure and a fine porous structure.

[0125] <Example B2>

A separator having a porous layer on both surfaces of a polyethylene microporous film was obtained in the same way as in example B1 except that the mass ratio of PVDF-HFP and sorbitan monopalmitate contained in the coating liquid was changed to 99.5:0.5. The surface of the separator was observed by SEM, and it was confirmed that the porous layer had a honeycomb structure and a fine porous structure.

[0126] <Example B3>

A separator having a porous layer on both surfaces of a polyethylene microporous film was obtained in the same way as in example B1 except that the mass ratio of PVDF-HFP and sorbitan monopalmitate contained in the coating liquid was changed to 99:1. The surface of the separator was observed by SEM, and it was confirmed that the porous layer had a honeycomb structure and a fine porous structure.

[0127] <Example B4>

A separator having a porous layer on both surfaces of a polyethylene microporous film was obtained

in the same way as in example B1 except that the mass ratio of PVDF-HFP and sorbitan monopalmitate contained in the coating liquid was changed to 98:2. The surface of the separator was observed by SEM, and it was confirmed that the porous layer had a honeycomb structure and a fine porous structure.

[0128] <Example B5>

A polyvinylidene fluoride-hexafluoropropylene copolymer (PVDF-HFP, KYNAR2800 made by Alkema) and sorbitan monopalmitate (HLB value 6.7) as a surfactant were dissolved in a mixed solvent of acetone and water mixed at a mass ratio of 95:5. The mass ratio of PVDF-HFP and sorbitan monopalmitate contained in this solution was set at 99:1, and the total concentration of both was set at 10 mass% with respect to this solution.

Furthermore, magnesium hydroxide (Kisuma 5P made by Kyowa Chemical) was dispersed as an inorganic filler in the solution described above to produce a coating liquid. The mass ratio of PVDF-HFP and magnesium hydroxide contained in the coating liquid was set at 80:20.

This coating liquid was coated on both surfaces of a polyethylene microporous film (film thickness 9.1 μm , Gurley value 160 sec/100 cc, porosity 33%) which is a porous base material using a #6 bar coater, and coating layers were formed on both surfaces of the porous base material. This coating layer was dried at 60°C to obtain a separator having a porous layer on both surfaces of a polyethylene microporous film. The surface of the separator was observed by SEM, and it was confirmed that the porous layer had a honeycomb structure and a fine porous structure.

[0129] <Example B6>

A separator having a porous layer on both surfaces of a polyethylene microporous film was obtained in the same way as in example B5, except that the mass ratio of PVDF-HFP and magnesium hydroxide contained in the coating liquid was changed to 60:40. The surface of the separator was observed by SEM, and it was confirmed that the porous layer had a honeycomb structure and a fine porous structure.

[0130] <Example B7>

A separator having a porous layer on both surfaces of a polyethylene microporous film was obtained in the same way as in example B1 except that sorbitan monopalmitate (HLB value 6.7) and sorbitan trioleate (HLB value 1.8) were used as surfactants at a mass ratio of 65.3:34.7, and the mass ratio of PVDF-HFP contained in the coating liquid to the surfactant was changed to 99:1. The surface of the separator was observed by SEM, and it was confirmed that the porous layer had a honeycomb structure and a fine porous structure.

[0131] <Example B8>

A separator having a porous layer on both surfaces of a polyethylene microporous film was obtained in the same way as in example B1, except that sorbitan monopalmitate (HLB value 6.7) and Tween 80 (PEG-20 sorbitan monooleate, HLB value 15.0) were used as surfactants at a mass ratio of 84.3:15.7, and the mass ratio of PVDF-HFP and the surfactants contained in the coating liquid was changed to 99:1. The surface of the separator was observed by SEM, and it was confirmed that the porous layer had a honeycomb structure and a fine porous structure.

[0132] <Example B9>

A separator having a porous layer on both surfaces of a polyethylene microporous film was obtained in the same way as in example B1, except that the surfactant was changed from sorbitan monopalmitate (HLB value 6.7) to sorbitan monostearate (HLB value 4.7), and the mass ratio of the surfactant to PVDF-HFP contained in the coating liquid was changed to 99:1. The surface of the separator was observed by SEM, and it was confirmed that the porous layer had a honeycomb structure and a fine porous structure.

[0133] <Example B10>

A separator having a porous layer on both surfaces of a polyethylene microporous film was obtained in the same way as in example B1, except that sorbitan monopalmitate was not included in the coating liquid. The separator was immersed in a liquid containing sorbitan monopalmitate (HLB value 6.7) added to water as a surfactant to obtain a separator having a surfactant added to the porous layer. In the porous layer of the separator, the polyvinylidene fluoride resin and the surfactant are not in a mixed state, and the surfactant is not interposed between the polyethylene microporous film and the porous layer. The surface of the separator was observed by SEM, and it was confirmed that the porous layer had a honeycomb structure and a fine porous structure.

[0134] <Comparative Example B1>

A separator having a porous layer on both surfaces of a polyethylene microporous film was obtained in the same way as in example B1 except that the mass ratio of PVDF-HFP and sorbitan monopalmitate contained in the coating liquid was changed to 90:10. The surface of the separator was observed using SEM, and it was confirmed that the porous layer did not have a honeycomb structure and had a structure with only a few micropores formed therein.

[0135] <Comparative Example B2>

A polyvinylidene fluoride-hexafluoropropylene copolymer (PVDF-HFP, KYNAR2800 made by Alkema) and sorbitan monopalmitate (HLB value 6.7) as a surfactant were dissolved in a mixed solvent of acetone, isopropanol, and water mixed at a mass ratio of 89.4:7.1:3.5 to produce a coating liquid. The mass ratio of PVDF-HFP and sorbitan monopalmitate contained in the coating liquid was set at 99:1, and the total concentration of both was set at 10 mass% with respect to the coating liquid.

This coating liquid was coated on both surfaces of a polyethylene microporous film (film thickness 9.1 μm , Gurley value 160 sec/100 cc, porosity 33%) which is a porous base material using a #6 bar coater, and coating layers were formed on both surfaces of the porous base material. This coating layer was dried at 60°C to obtain a separator having a porous layer on both surfaces of a polyethylene microporous film. The surface of the separator was observed by SEM, and it was confirmed that the porous layer did not have a honeycomb structure and was a porous structure having micropores distributed highly uniformly.

[0136] <Comparative Example B3>

A separator having a porous layer on both surfaces of a polyethylene microporous film was obtained in the same way as in example B5, except that the mass ratio of PVDF-HFP and magnesium hydroxide contained in the coating liquid was changed to 40:60. The surface of the separator was observed by SEM, and it was confirmed that the porous layer did not have a honeycomb structure and was a porous structure having micropores distributed highly uniformly.

[0137] <Test of Battery Manufacturing Efficiency>

Two separators (108 mm wide) were prepared and stacked, and one end in the MD direction was wound around a stainless steel core. A positive electrode (106.5 mm wide) was sandwiched between two separators, a negative electrode (107 mm wide) was disposed on one separator, and this laminate was wound to produce 50 wound electrode bodies one after the other. When the separator from the positive electrode had a protrusion amount in a range of 1.5 mm $\pm$ 0.3 mm, the separator from the negative electrode had a protrusion amount in a range of 1.0 mm $\pm$ 0.3 mm, and that the laminated portion of the two separators had not been shifted, it was determined that the test was successful. Conversely, when the above was not the case, it was determined that the test was failed. Then, the number ratio (%) of the successful wound electrode bodies is calculated and classified as follows.

A: Success rate of 100%

B: Success rate of 90% or more but less than 100%

C: Success rate of less than 90%

[0138] <Battery Performance Test>

[Production of Negative Electrode]

A negative electrode slurry was produced by mixing 300 g of artificial graphite, which is a negative electrode active material, 7.5 g of a water-soluble dispersion containing 40 mass% of a modified styrene-butadiene copolymer, which is a binder, 3 g of carboxymethyl cellulose, which is a thickener, and an appropriate amount of water by stirring using a dual-arm mixer. This negative electrode slurry was applied to a copper foil, which is a negative electrode collector and has a thickness of 10 μm , and then the copper foil was dried and pressed to obtain a negative electrode having a negative electrode active material layer.

[0139] [Production of Positive Electrode]

89.5 g of lithium cobalt oxide powder, which is a positive electrode active material, 4.5 g of acetylene black, which is a conducting aid, and 6 g of polyvinylidene fluoride, which is a binder, were dissolved in N-methyl-pyrrolidone so that the concentration of polyvinylidene fluoride was 6 mass%, and stirred in a dual-arm mixer to produce a positive electrode slurry. This positive electrode slurry was applied to an aluminum foil, which is a positive electrode collector and has a thickness of 20 μm , and then the copper foil was dried and pressed to obtain a positive electrode having a positive electrode active material layer.

[0140] [Production of Battery]

A lead tab was welded to each of the positive electrode and the negative electrode, and the positive electrode and the negative electrode were joined via a separator to produce a battery element. This battery element was housed in an aluminum pack, the electrolyte solution was impregnated therein, and this was sealed using a vacuum sealer. 1 M LiPF₆-ethylene carbonate:ethyl methyl carbonate (mass ratio 3:7) was used as the electrolyte solution. Then, a test rechargeable battery was obtained by performing a hot press (load: 20 kg per cm² of electrode, temperature: 90°C, press time: 2 minutes) using a hot press machine on an aluminum pack containing the battery element and the electrolyte solution.

[0141] [Cycle Characteristic Test]

A test rechargeable battery was charged and discharged for 100 cycles, and a capacity retention rate (%) after 100 cycles was found and used as an index of cycle characteristics. In this test, the charge was 0.5 C or 1.0 C at a constant current constant voltage charge of 4.2 V, and the discharge was 0.5 C or 1.0 C at constant current discharge with a 2.75 V cutoff. In example A1 and the like, the charge and discharge current was 0.5 C, and in example B1 and the like, the charge and discharge current was 1.0 C.

[0142] [Confirmation of Adhesion Between Separator and Electrode]

The test rechargeable battery after the cycle characteristics test was disassembled, and adhesiveness between the separator and the electrode was confirmed from the viewpoints of adhesive force and uniformity.

[0143] - Adhesive Strength -

The battery element was removed from the aluminum pack and cut into two pieces to obtain two test pieces. A 180-degree peel test of the positive electrode was performed using one test piece, and a 180-degree peel test of the negative electrode was performed using another test piece. The 180-degree peel test was performed at a tensile rate of 20 mm/min using a Tensilon (RTC-1210A made by Orientec). The load (N) when the positive electrode or the negative electrode peels from the test piece was measured, the load from 10 mm to 40 mm after the start of measurement was collected at intervals of 0.4 mm, and the average value thereof was calculated. Then, relative values for the positive electrode and the negative electrode were calculated for the other examples and comparative examples, normalized to the average value of example A1 or example B1 as 100.

[0144] - Uniformity -

After finishing the 180-degree peel test, the surfaces of the positive electrode and the negative electrode that were in contact with the separator were visually observed and classified as follows.

G1: Substantially all of the porous layer of the separator was adhered to the electrode surface. Uniformity is favorable.

G2: Most of the porous layer of the separator is adhered to the electrode surface, but a portion thereof is damaged.

NG: Most of the porous layer of the separator was significantly damaged during a 180-degree peel test, and substantially none is adhered to the electrode surface. Uniformity is poor.

[0145] Table 1 and Table 3 show various physical properties of the separators for each example and for each comparative example. In comparative examples wherein the porous layer does not have a honeycomb structure, the average diameter of the micropores present on the surface of the porous layer is indicated instead of the average diameter of the openings of the cells.

Table 2 and Table 4 show the evaluation results for rechargeable batteries produced using the separators for each example and for each comparative example.

[0146]

[Table 1]

	Porous layer						Separator					
	Coating thickness (total of both surfaces)	Coating amount (total of both surfaces)	Porosity	Honeycomb structure	Cell opening average diameter	Water contact angle	Unit weight	Film thickness	Gurley value	Charge damping half-life	Electrolyte solution wettability	Peel strength
	μm	g/cm^2	%		μm	degrees	g/cm^2	μm	s/100cc	seconds	seconds	N/cm
Example A1	4.5	2.7	67.1	Yes	4.1	129	8.4	13.6	1257	276	4.0	0.84
Example A2	4.6	2.6	68.1	Yes	4.3	135	8.4	13.7	1210	265	3.8	0.81
Comparative Example A2	2.4	2.1	52.0	No	0.5	111	7.8	11.5	530	449	3.3	0.68
Comparative Example A3	2.4	2.1	51.8	No	0.2	95	7.6	11.5	210	954	3.3	0.22
Comparative Example A4	1.9	2.3	30.8	Yes	2.5	113	8.1	11.0	5000+	492	11.7	1.15

[0147]

[Table 2]

	Battery manufacturing efficiency	Cycle characteristics (capacity retention rate)	Adhesion to positive electrode		Adhesion to negative electrode	
			Adhesive force	Uniformity	Adhesive force	Uniformity
Example A1	A	89%	100	G1	100	G1
Example A2	A	90%	100	G1	100	G1
Comparative Example A2	C	86%	86	G1	85	G1
Comparative Example A3	C	90%	98	G1	99	G1
Comparative Example A4	C	85%	95	G1	96	G1

[0148]

[Table 3]

	Porous layer									Separator					
	PVDF resin: Mg(OH) ₂	HBL value of surfactant	PVDF resin: surfactant	Coating thickness (total of both surfaces)	Coating amount (total of both surfaces)	Porosity	Honey comb structure	Cell opening average diameter	Water contact angle	Unit weight	Film thickness	Gurley value	Charge damping half-life	Electrolyte solution wettability	Peel strength
	Mass ratio		Mass ratio	μm	g/cm^2	%		μm	Degrees	g/cm^2	μm	s/100cc	seconds	seconds	N/cm
Example B1	100:0	6.7	99.8:0.2	3.6	2.19	66	Yes	4.2	129	7.93	12.7	993	275	4.0	0.88
Example B2	100:0	6.7	99.5:0.5	3.7	2.21	66	Yes	4.1	129	7.95	12.8	825	274	3.9	1.02
Example B3	100:0	6.7	99:1	4.8	2.25	74	Yes	4.0	128	7.99	13.9	716	270	4.0	0.39
Example B4	100:0	6.7	98:2	4.4	2.75	65	Yes	4.3	126	8.54	13.5	774	263	3.8	0.30
Example B5	80:20	6.7	99:1	5.6	3.63	63	Yes	4.0	124	9.36	14.6	697	268	3.6	1.25
Example B6	60:40	6.7	99:1	5.1	3.75	59	Yes	4.0	124	9.48	14.2	795	267	3.7	1.26
Example B7	100:0	5.0	99:1	4.6	2.35	71	Yes	3.7	130	8.09	13.7	766	270	3.8	0.42
Example B8	100:0	8.0	99:1	4.7	2.40	71	Yes	4.4	125	8.14	13.8	742	267	3.8	0.38
Example B9	100:0	4.7	99:1	4.2	2.79	63	Yes	3.6	128	8.63	13.3	1804	293	4.0	1.87
Example B10	100:0	6.7	Applied to surface	4.6	2.70	67	Yes	4.1	128	8.44	13.6	1260	280	4.0	0.84
Comparative Example B1	100:0	6.7	90:10	2.0	2.26	36	No	0.2	97	8.00	11.1	5000+	74	Not measurable	Not measurable
Comparative Example B2	100:0	6.7	99:1	6.3	3.51	69	No	0.5	111	9.24	15.4	386	452	3.3	0.54
Comparative Example B3	40:60	6.7	99:1	5.2	3.75	60	No	0.6	114	9.49	14.3	585	310	3.7	0.23

[0149]

[Table 4]

	Battery manufacturing efficiency	Cycle characteristics (capacity retention rate)	Adhesion to positive electrode		Adhesion to negative electrode	
			Adhesive force	Uniformity	Adhesive force	Uniformity
Example B1	A	91%	100	G1	100	G1
Example B2	A	92%	100	G1	100	G1
Example B3	A	94%	100	G1	100	G1
Example B4	A	94%	100	G1	100	G1
Example B5	A	95%	100	G1	100	G1
Example B6	A	94%	100	G1	100	G1
Example B7	A	93%	100	G1	100	G1
Example B8	A	94%	100	G1	100	G1
Example B9	A	86%	100	G1	100	G1
Example B10	A	87%	100	G1	100	G1
Comparative Example B1	A	72%	10	NG	15	NG
Comparative Example B2	C	96%	100	G1	100	G1
Comparative Example B3	B	95%	98	G1	98	G1

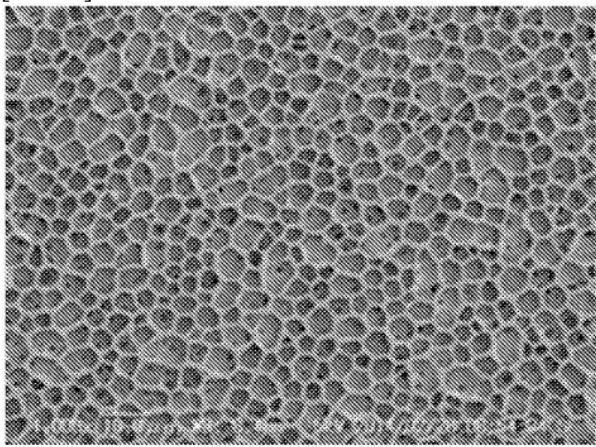
[0150] The disclosure of Japanese Patent Application No. 2014-104352, filed on May 20, 2014, and the disclosure of Japanese Patent Application No. 2014-168462, filed on August 21, 2014, are incorporated by reference into the present Specification in their entirety.

[0151] All documents, patent applications, and technical standards described in the present Specification are incorporated by reference into the present Specification in the same way if the incorporation of individual documents, patent applications, and technical standards by reference were described specifically and individually.

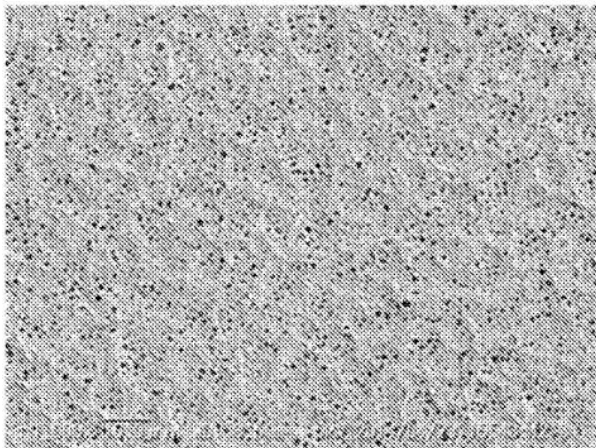
Scope of Claims

- [Claim 1] A non-aqueous rechargeable battery separator, comprising:
a porous base material containing a thermoplastic resin; and
a porous layer provided on one surface or both surfaces of the porous base material, the porous layer having a structure in which a large number of cells that are open in a direction perpendicular to the surface of the porous layer are aligned adjacent to each other in the direction perpendicular to the surface of the porous layer and having a contact angle with water of 115° to 140°.
- [Claim 2] The non-aqueous rechargeable battery separator according to claim 1, wherein the average diameter of the opening portion of the cell is 0.1 μm to 10 μm .
- [Claim 3] The non-aqueous rechargeable battery separator according to claim 1 or claim 2, wherein a porosity of the porous layer is 40% to 80%.
- [Claim 4] The non-aqueous rechargeable battery separator according to any one of claim 1 to claim 3, wherein a charge damping half-life is 300 seconds or less, as measured on the porous layer.
- [Claim 5] The non-aqueous rechargeable battery separator according to any one of claim 1 to claim 4, wherein a time until dynamic wetting tension reaches 1.5 mN when immersed in an electrolyte solution is 10 seconds or less.
- [Claim 6] The non-aqueous rechargeable battery separator according to any one of claim 1 to claim 5, wherein the porous layer further contains a surfactant having an HLB value of 5.0 to 8.0, and the polyvinylidene fluoride resin and the surfactant are mixed inside the porous layer.
- [Claim 7] The non-aqueous rechargeable battery separator according to claim 6, wherein a mass ratio of the polyvinylidene fluoride resin to the surfactant in the porous layer is 99.9:0.1 to 95.0:5.0.
- [Claim 8] The non-aqueous rechargeable battery separator according to any one of claim 1 to claim 7, wherein a peel strength between the porous base material and the porous layer is 0.1 N/cm to 2.0 N/cm.
- [Claim 9] The non-aqueous rechargeable battery separator according to any one of claim 1 to claim 8, wherein the porous layer further contains a filler.
- [Claim 10] The non-aqueous rechargeable battery separator according to any one of claim 1 to claim 9, having the porous layer on both surfaces of the porous base material.
- [Claim 11] The non-aqueous rechargeable battery separator according to any one of claim 1 to claim 10, wherein the porous base material is a polyolefin microporous film containing polyethylene.
- [Claim 12] The non-aqueous rechargeable battery separator according to any one of claim 1 to claim 11, wherein the porous base material is a polyolefin microporous film containing polyethylene and polypropylene.
- [Claim 13] A method for manufacturing the non-aqueous rechargeable battery separator according to any one of claim 6 to claim 12, comprising:
a step for forming a coating layer by coating one surface or both surfaces of a porous base with a solution obtained by dissolving a polyvinylidene fluoride resin and a surfactant having an HLB value of 5.0 to 8.0 in a solvent; and
a step for forming a porous layer by removing the solvent from the coating layer.
- [Claim 14] A non-aqueous rechargeable battery provided with a positive electrode, a negative electrode, and the non-aqueous rechargeable battery separator according to any one of claim 1 to claim 12 disposed between the positive electrode and the negative electrode, wherein an electromotive force can be obtained by doping and dedoping lithium.

[FIG. 1]



[FIG. 2]



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2015/064224

A. CLASSIFICATION OF SUBJECT MATTER

H01M2/16(2006.01) i, H01M2/18(2006.01) i

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)

H01M2/16, H01M2/18

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

Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2015
 Kokai Jitsuyo Shinan Koho 1971-2015 Toroku Jitsuyo Shinan Koho 1994-2015

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y A	JP 2012-104291 A (Sony Corp.), 31 May 2012 (31.05.2012), paragraphs [0021] to [0027], [0067], [0112] to [0123]; table 3; fig. 1 & US 2012/0115009 A1 & CN 102468465 A	1, 3, 8-12, 14 2 4-7, 13
Y	JP 2010-092881 A (Teijin Ltd.), 22 April 2010 (22.04.2010), claim 1; paragraph [0069]; table 6 & JP 2010-92882 A & JP 4575521 B2 & US 2011/0143185 A1 & WO 2010/021248 A1 & CN 102160211 A & KR 10-2011-0050517 A & TW 201027827 A	2

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Date of the actual completion of the international search
13 July 2015 (13.07.15)Date of mailing of the international search report
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Japan Patent Office
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Tokyo 100-8915, Japan

Authorized officer

Telephone No.

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International application No.

PCT/JP2015/064224

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	JP 2012-227066 A (Sony Corp.), 15 November 2012 (15.11.2012), paragraphs [0047] to [0054]; fig. 2, 4 & US 2012/0268072 A1	1-14
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A	JP 2013-054972 A (Sony Corp.), 21 March 2013 (21.03.2013), fig. 4 (Family: none)	1-14

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2015/064224

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Int.Cl. H01M2/16(2006.01)i, H01M2/18(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

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Date of the actual completion of the international search
13 July 2015 (13.07.15)Date of mailing of the international search report
21 July 2015 (21.07.15)Name and mailing address of the ISA/
Japan Patent Office (ISA/JP)
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Telephone No. 03-3581-1101 Ext. 3477

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INTERNATIONAL SEARCH REPORT

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Y	JP 2011-023162 A (Teijin Ltd.), 03 February 2011 (03.02.2011), table 1 (Family: none)	2
A	JP 2012-227066 A (Sony Corp.), 15 November 2012 (15.11.2012), paragraphs [0047] to [0054]; fig. 2, 4 & US 2012/0268072 A1	1-14
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DECLARATION OF TRANSLATOR

I, Eric Vance, hereby declare as follows:

1. I personally performed the attached translation from Japanese into English of the patent that is entitled “非水系二次電池用セパレータ、その製造方法及び非水系二次電池” in Japanese and “NON-AQUEOUS RECHARGEABLE BATTERY SEPARATOR, MANUFACTURING METHOD THEREOF, AND NON-AQUEOUS RECHARGEABLE BATTERY” in English (also attached).

2. The attached translation is, to the best of my knowledge, a true, full and accurate translation of the attached Japanese document.

3. I am competent to perform this translation, because I have JLPT N1 certification, baccalaureate degrees in Japanese and biology, and seven years of experience as a professional patent translator.

4. I declare under the penalty of perjury under the laws of the United States that the foregoing is true and correct; and further declare that I am aware that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 1001 of Title 18 of the United States Code.

Dated: 11/30/2024



Eric Vance