



US 20110236764A1

(19) **United States**(12) **Patent Application Publication**
Takita et al.(10) **Pub. No.: US 2011/0236764 A1**(43) **Pub. Date: Sep. 29, 2011**(54) **MICROPOROUS MEMBRANES AND
METHODS FOR PRODUCING AND USING
SUCH MEMBRANES**(75) Inventors: **Kotaro Takita**, Nasushiobara (JP);
Junko Takita, legal representative,
Nasushiobara (JP); **Yoichi**
Matsuda, Nasushiobara (JP);
Sadakatsu Suzuki, Nasushiobara
(JP)(73) Assignee: **TORAY TONEN SPECIALTY
SEPARATOR GODO KAISHA**,
Nasushiobara-shi, Tochigi (JP)(21) Appl. No.: **13/129,670**(22) PCT Filed: **Oct. 30, 2009**(86) PCT No.: **PCT/JP2009/069016**§ 371 (c)(1),
(2), (4) Date:**May 17, 2011****Related U.S. Application Data**(60) Provisional application No. 61/115,410, filed on Nov.
17, 2008, provisional application No. 61/115,405,
filed on Nov. 17, 2008.(30) **Foreign Application Priority Data**Jan. 26, 2009 (EP) 09151318.4
Jan. 26, 2009 (EP) 09151320.0**Publication Classification**(51) **Int. Cl.**
H01M 2/16 (2006.01)
C08J 9/00 (2006.01)
C08F 10/02 (2006.01)(52) **U.S. Cl.** **429/249; 521/134**(57) **ABSTRACT**

The invention relates to microporous polymeric membranes suitable for use as battery separator film. The invention also relates to a method for producing such membranes, batteries containing such membranes as battery separators, methods for making such batteries, and methods for using such batteries.

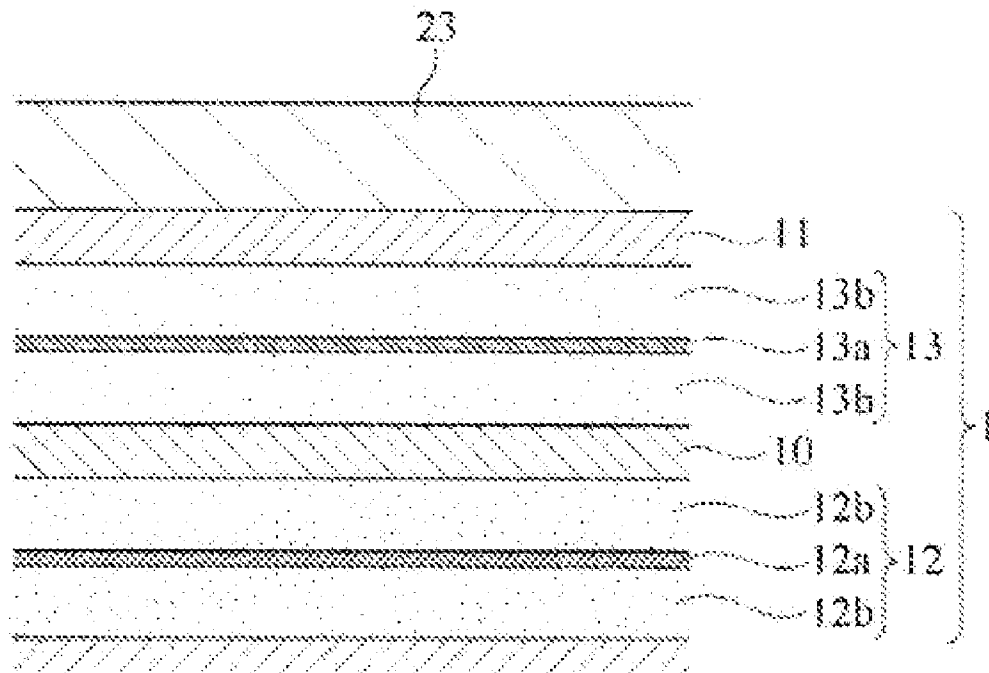


Fig. 1

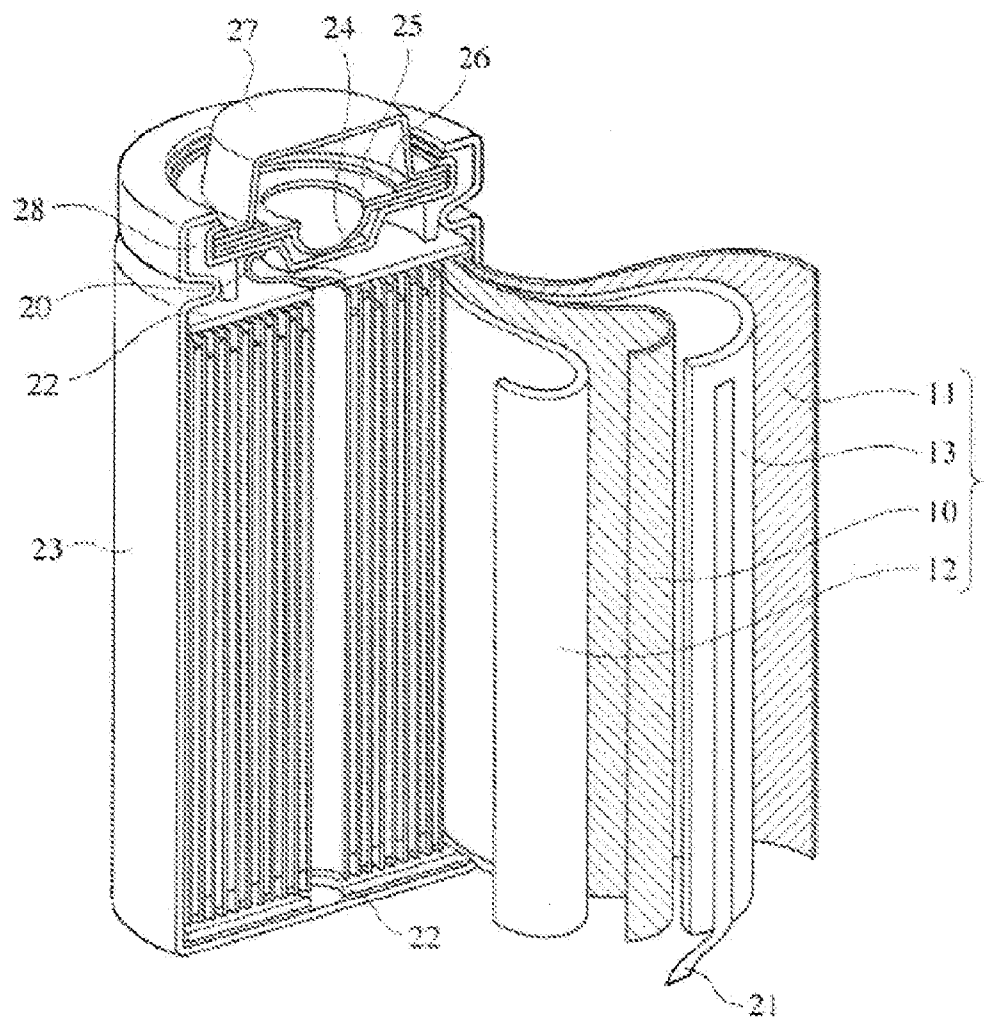
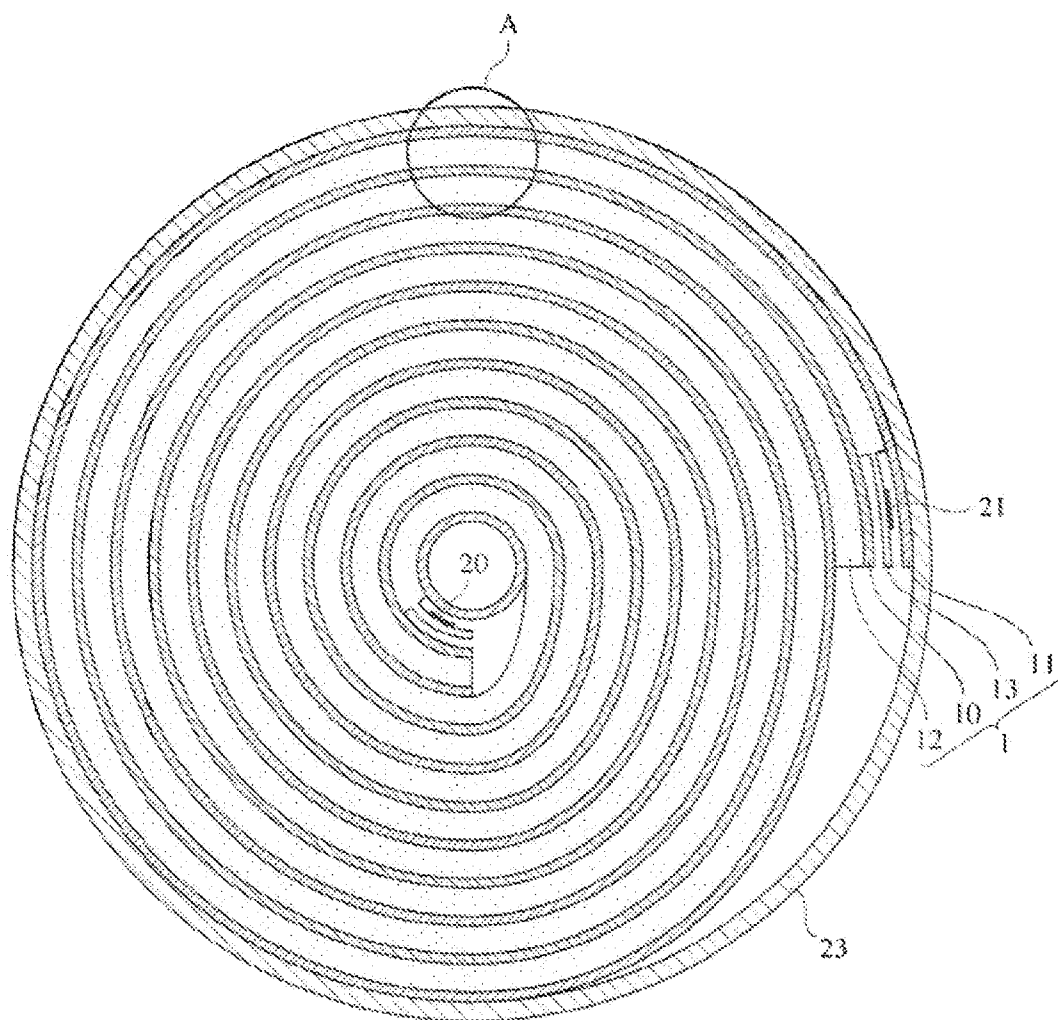


Fig. 2



MICROPOROUS MEMBRANES AND METHODS FOR PRODUCING AND USING SUCH MEMBRANES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority from U.S. Prov. App. Ser. No. 61/115,405, filed 17 Nov. 2008, U.S. Prov. App. Ser. No. 61/115,410, filed 17 Nov. 2008, EP09151320.0 filed 26 Jan. 2009, and EP09151318.4 filed 26 Jan. 2009, the contents of each of which are incorporated by reference in their entirety.

FIELD OF THE INVENTION

[0002] The invention relates to microporous polymeric membranes suitable for use as battery separator film. The invention also relates to a method for producing such membranes, batteries containing such membranes as battery separators, methods for making such batteries, and methods for using such batteries.

BACKGROUND OF THE INVENTION

[0003] Microporous membranes can be used as battery separators in, e.g., primary and secondary lithium batteries, lithium polymer batteries, nickel-hydrogen batteries, nickel-cadmium batteries, nickel-zinc batteries, silver-zinc secondary batteries; etc. When microporous polyolefin membranes are used for battery separators, particularly lithium ion battery separators, the membranes' characteristics significantly affect the properties, productivity and performance of the batteries. Accordingly, it is desirable for the microporous membrane to have resistance to thermal shrinkage, particularly at elevated temperature. Resistance to heat shrinkage can improve the battery's protection against internal short circuiting that might otherwise occur as the separator shrinks away from the edges of the battery's electrodes at elevated temperature.

[0004] European Patent Application Publication No. EP 1 905 586 (published Feb. 2, 2008) discloses multi-layer polymeric membranes useful as battery separator film. One of the membranes exemplified has a transverse direction heat shrinkage of 2% at 105° C.

[0005] Japanese patent document JP2000198866 (published Jul. 18, 2000) discloses multi-layer battery separator films having heat shrinkage values of 10%. The membrane comprises layers containing alpha-olefin/carbon monoxide copolymers and an inorganic species (cross-linked silicone powders).

[0006] PCT publication WO2007-049568 (published May 3, 2007) also discloses multi-layer battery separator films having a machine direction heat-shrinkage value of 4% and a transverse direction heat shrinkage value of 3%. The films of this reference comprise a core layer containing heat-resistant polymers or an inorganic filler.

[0007] U.S. Patent Publication 2007/0218271 discloses monolayer microporous films having machine and transverse direction heat shrinkage values of 4% or less. The films of this reference are produced from high density polyethylene having a weight-average molecular weight of 2×10^5 to 4×10^5 , containing not more than 5 wt. % of molecules with a molecular weight of 1×10^4 or less and not more than 5 wt. % of molecules having a molecular weight of 1×10^6 or more.

[0008] Japanese Patent Application Laid Open. No. JP2001-192467 discloses monolayer microporous membranes having transverse direction heat shrinkage values as low as 1.8%, but at a relatively low permeability (Gurley value of 684 seconds). Similarly, Japanese Patent Application Laid Open No. JP2001-172420 discloses monolayer microporous membranes having transverse direction heat shrinkage values as low as 1.1%, but at a Gurley value above 800.

[0009] While improvements have been made, there is still a need for battery separator film having increased resistance to heat shrinkage.

SUMMARY OF THE INVENTION

[0010] In an embodiment, the invention relates to a method for manufacturing a microporous membrane, comprising:

(a) stretching an extrudate in at least one of MD or TD, the extrudate comprising diluent and polyolefin having an $M_w > 1.0 \times 10^6$, and then removing at least a portion of the diluent from stretched extrudate to form a membrane having a first length along MD and a first width along TD;

(b) stretching the membrane in MD from the first length to a second length larger than the first length by a magnification factor in the range of from about 1.1 to about 1.5 and stretching the membrane in TD from the first width to a second width that is larger than the first width by a magnification factor in the range of from about 1.1 to about 1.3; and then

(c) reducing the second width to a third width, the third width being in the range of from the first width to about 1.1 times larger than the first width.

[0011] In another embodiment, the invention relates to monolayer microporous membrane comprising a polyolefin having an $M_w > 1.0 \times 10^6$, the membrane having a normalized air permeability $\leq 4.0 \times 10^2$ seconds/100 cm³/20 μm, and a heat shrinkage at 130° C. of $\leq 15\%$ in at least one planar direction.

[0012] In yet another embodiment, the invention relates to a battery comprising an anode, a cathode, an electrolyte, and monolayer microporous membrane comprising a polyolefin having an $M_w > 1.0 \times 10^6$, the membrane having a normalized air permeability $\leq 4.0 \times 10^2$ seconds/100 cm³/20 μm, and a heat shrinkage at 130° C. of $\leq 15\%$ in at least one planar direction, wherein the microporous membrane separates at least the anode from the cathode. The battery can be, e.g., a lithium ion primary or secondary battery. The battery can be used as a source or sink of electric charge, e.g., as a power source for an electric vehicle or hybrid electric vehicle.

[0013] In another embodiment, the invention relates to monolayer microporous membrane comprising a polyolefin, the polyolefin having an $M_w > 1.0 \times 10^6$, wherein the membrane has been subjected to orientation (a) in a first planar direction from a first size to a second size, the second size being in the range of from about (1.1·the first size) to about (1.5·the first size), (b) in a second planar direction from a third size to a fourth size, the first and second planar directions defining a planar angle the range of 60° to 120° and the fourth size being in the range of (1.1·the third size) to (1.3·the third size); and (c) in the second direction from the fourth size to a fifth size, the fifth size being (i) <the fourth size and (ii) in the range of from the third size to (1.1·the third size). Optionally, the membrane is an extruded membrane, wherein the first direction is the machine direction and the second direction is the transverse direction. Optionally, the oriented membrane has a normalized air permeability $\leq 4.0 \times 10^2$ seconds/100

cm³/20 μm, and a heat shrinkage at 130° C. of ≤15% in at least one planar direction. Optionally, the orientation is conducted while the membrane is exposed to a temperature ≤ the polyolefin's lowest melting peak, e.g., in the range of from (a) 30° C. less than the polyolefin's lowest crystal dispersion temperature to (b) the polyolefin's lowest melting peak; such as in the range of 70.0° C. to about 135° C., for example from about 80.0° C. to about 132° C. when the membrane comprises polyethylene or a mixture of polyethylene and polypropylene.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] FIG. 1 is a cross-sectioned, perspective view showing one example of cylindrical type lithium ion secondary battery comprising an electrode assembly of the present invention.

[0015] FIG. 2 is a cross-sectioned view showing the battery in FIG. 1.

[0016] FIG. 3 is an enlarged cross-sectioned view showing a portion A in FIG. 2.

DETAILED DESCRIPTION OF THE INVENTION

[0017] In an embodiment, the invention relates to a microporous film having improved resistance to heat shrinkage at elevated temperature. In another embodiment, the invention relates to a microporous membrane having a good balance of important properties including resistance to heat shrinkage at elevated temperature, high porosity, with suitable mechanical strength, permeability, and compression resistance. The membrane is permeable to liquids (e.g., water or polar electrolyte) at atmospheric pressure, and, consequently, the membrane can be used as battery separator film.

[0018] One battery failure mode involves the high temperature softening of membranes used as battery separator film, resulting in a loss of dimensional stability especially near the membrane's edges. Should the membrane's width decrease at a temperature above the membrane's shutdown temperature (generally much higher than 105° C.), the close spacing between anode, cathode, and separator can lead to an internal short circuit in the battery. This is particularly the case in prismatic and cylindrical batteries, where even a small change in membrane width can result in anode-cathode contact at or near the battery's edges.

[0019] The invention relates to the discovery of microporous membranes having better dimensional stability at elevated temperature, e.g., improved heat shrinkage properties. The improvement in heat shrinkage properties is observed not only at relatively low temperatures (e.g., below about 110° C., which is within the operating temperature range of conventional lithium ion batteries), but also at relatively high temperatures (e.g., above 125° C., or above 135° C., e.g., above the shutdown temperature of conventional battery separator film for lithium ion batteries).

[0020] Since the battery separator film might not be softened sufficiently at 105° C. to exhibit poor heat shrinkage, the film's heat shrinkage performance at 105° C. is not always a reliable indicator of the potential for internal battery short circuiting. In contrast, the film's maximum TD heat shrinkage in the molten state is measured at a temperature that is above the membrane's shutdown temperature, and thus can be a better indicator for this type of internal short circuiting. TD

heat shrinkage in the molten state is generally not predictable solely from the membrane's heat shrinkage performance at 105° C.

[1] Composition and Structure of the Microporous Membrane

[0021] In an embodiment, the microporous membrane comprises a polyolefin having a weight average molecular weight ("Mw") > 1.0 × 10⁶. The polyolefin can comprise, e.g., (a) a first polyethylene having a weight average molecular weight ("Mw") ≤ 1.0 × 10⁶ (referred to as the "first polyethylene") and at least one of (b) a polypropylene having an Mw > 1.0 × 10⁶ or (c) a second polyethylene having an Mw > 1.0 × 10⁶. In an embodiment, the microporous membrane is a monolayer membrane, i.e., it is not laminated or coextruded with additional layers. The membrane produced from the extrudate can consist essentially of or even consist of a single layer comprising polyethylene or polyethylene and polypropylene.

[0022] For the purpose of this description and the appended claims, the term "polymer" means a composition including a plurality of macromolecules, the macromolecules containing recurring units derived from one or more monomers. The macromolecules can have different size, molecular architecture, atomic content, etc. The term "polymer" includes macromolecules such as copolymer, terpolymer, etc., and encompasses individual polymer components and/or reactor blends. "Polypropylene" means polyolefin containing recurring propylene-derived units, e.g., polypropylene homopolymer and/or polypropylene copolymer wherein at least 85% (by number) of the recurring units are propylene units. "Polyethylene" means polyolefin containing recurring ethylene-derived units, e.g., polyethylene homopolymer and/or polyethylene copolymer wherein at least 85% (by number) of the recurring units are ethylene units.

[0023] Selected embodiments will now be described in more detail, but this description is not meant to foreclose other embodiments within the broader scope of the invention.

[0024] In an embodiment, the microporous membrane comprises the polypropylene in an amount ≤ 50.0 wt. %, the first polyethylene in an amount ≤ 99.0 wt. %, and the second polyethylene in an amount ≤ 50.0 wt. %, the weight percents being based on the weight of the microporous membrane, provided the microporous membrane contains at least one of the polypropylene or the second polyethylene. For example, in one embodiment the microporous membrane comprises (a) from about 1.0 wt. % to about 50.0 wt. %, e.g., from about 2.0 wt. % to about 40.0 wt. %, such as from about 5.0 wt. % to about 30.0 wt. %, of the polypropylene; (b) from about 25.0 wt. % to about 99.0 wt. %, e.g., from about 50.0 wt. % to about 90.0 wt. %, such as from about 60.0 wt. % to about 80.0 wt. % of the first polyethylene; and (c) from about 0.0 wt. % to about 50.0 wt. %, e.g., from about 5.0 wt. % to about 30.0 wt. %, such as from about 10.0 wt. % to about 20.0 wt. % of the second polyethylene.

[0025] In another embodiment, the microporous membrane comprises the first and second polyethylenes, the first polyethylene being present in an amount ≥ 60.0 wt. %, and the second polyethylene being present in an amount ≤ 40.0 wt. %, the weight percents being based on the weight of the microporous membrane. The membrane can be a polyethylene membrane that does not contain a significant amount of polypropylene, e.g., < about 1.0 wt. %, such as 0.0 wt. % to about 0.1 wt. % polypropylene based on the weight of the

membrane. For example, in one embodiment the microporous membrane is a polyethylene membrane which comprises from about 1.0 wt. % to about 40.0 wt. %, e.g., from about 10.0 wt. % to about 30.0 wt. %, of the second polyethylene and from about 60.0 wt. % to about 99.0 wt. %, e.g., from about 70.0 wt. % to about 90.0 wt. %, of the first polyethylene.

[0026] In an embodiment, the invention relates to a method for producing a mono-layer microporous membrane. In the production method, an initial method step involves combining polymer resins, such as polyethylene resins, with diluent and then extruding the diluent to make an extrudate. The process conditions in this initial step can be the same as those described in PCT Publication No. WO 2008/016174, for example, which is incorporated by reference herein in its entirety.

[0027] The polypropylene, the first and second polyethylenes, and the diluent used to produce the extrudate and the microporous membrane will now be described in more detail.

[2] Materials Used to Produce the Microporous Membrane

[0028] In an embodiment, the extrudate is produced from, at least one diluent and polyolefin having an $M_w > 1.0 \times 10^6$, e.g., the first polyethylene and at least one of the polypropylene or the second polyethylene. Optionally, inorganic species (such as species containing silicon and/or aluminum atoms, e.g., TiO_2), and/or heat-resistant polymers such as those described in PCT Publications WO 2007/132942 and WO 2008/016174 (both of which are incorporated by reference herein in their entirety) can be used to produce the extrudate. In an embodiment, these optional species are not used.

A. The First Polyethylene

[0029] The first polyethylene has an $M_w \leq 1.0 \times 10^6$, e.g., in the range of from about 1.0×10^5 to about 9.0×10^5 , for example from about 4.0×10^5 to about 8.0×10^5 . Optionally, the polyethylene has a molecular weight distribution ("MWD") ≤ 50.0 , e.g., in the range of from about 1.2 to about 25, such as from about 3.0 to about 15. For example, the first polyethylene can be one or more of a high density polyethylene ("HDPE"), a medium density polyethylene, a branched low density polyethylene, or a linear low density polyethylene.

[0030] In an embodiment, the first polyethylene has an amount of terminal unsaturation ≥ 0.2 per 1.0×10^5 carbon atoms, e.g., ≥ 5 per 1.0×10^5 carbon atoms, such as ≥ 10 per 1.0×10^5 carbon atoms. The amount of terminal unsaturation can be measured in accordance with the procedures described in PCT Publication WO97/23554, for example.

[0031] In an embodiment, the first polyethylene is at least one of (i) an ethylene homopolymer or (ii) a copolymer of ethylene and ≤ 10.0 mole % of a comonomer such as α -olefins, based on 100% by mole of the copolymer. Such a polymer or copolymer can be produced using a single-site catalyst. The comonomer can be, for example, one or more of propylene, butene-1, pentene-1, hexene-1, 4-methylpentene-1, octene-1, vinyl acetate, methyl methacrylate, or styrene.

[0032] The M_w and molecular weight distribution ("MWD", defined as M_w divided by the number average molecular weight, " M_n ") of the first polyethylene are determined using a High Temperature Size Exclusion Chromatograph, or "SEC", (GPC PL 220, available from Polymer

Laboratories), equipped with a differential refractive index detector (DRI). Three PLgel Mixed-B columns (available from Polymer Laboratories) are used. The nominal flow rate is $0.5 \text{ cm}^3/\text{min}$, and the nominal injection volume was $300 \mu\text{L}$. Transfer lines, columns, and the DRI detector are contained in an oven maintained at 145°C . The measurement is made in accordance with the procedure disclosed in "Macromolecules", Vol. 34, No. 19, pp. 6812-6820 (2001)".

[0033] The GPC solvent used is filtered Aldrich reagent grade 1,2,4-Trichlorobenzene (TCB) containing approximately 1000 ppm of butylated hydroxy toluene (BHT). The TCB is degassed with an online degasser prior to introduction into the SEC. Polymer solutions are prepared by placing dry polymer in a glass container, adding the desired amount of above TCB solvent, then heating the mixture at 160°C with continuous agitation for about 2 hours. The concentration of UHMWPE solution is 0.25 to 0.75 mg/ml. The sample solution is filtered offline before injecting into the GPC with $2 \mu\text{m}$ filter using a model SP260 Sample Prep Station (available from Polymer Laboratories).

[0034] The separation efficiency of the column set is calibrated with a calibration curve generated using seventeen individual polystyrene standards ranging in M_p (" M_p " being defined as the peak in M_w) from about 580 to about 10,000,000, which is used to generate the calibration curve. The polystyrene standards are obtained from Polymer Laboratories (Amherst, Mass.). A calibration curve (log M_p vs. retention volume) is generated by recording the retention volume at the peak in the DRI signal for each PS standard, and fitting this data set to a 2nd-order polynomial. Samples are analyzed using IGOR Pro, available from Wave Metrics, Inc.

B. The Second Polyethylene

[0035] The second polyethylene has an $M_w > 1.0 \times 10^6$, e.g., in the range of 1.1×10^6 to about 5.0×10^6 , for example from about 1.2×10^6 to about 3.0×10^6 , such as about 2.0×10^6 . Optionally, the second polyethylene has an $MWD \leq 50.0$, e.g., from about 1.5 to about 25, such as from about 4.0 to about 20.0 or about 4.5 to 10.0. For example, the second polyethylene can be an ultra-high molecular weight polyethylene ("UHMWPE"). In an embodiment, the second polyethylene is at least one of (i) an ethylene homopolymer or (ii) a copolymer of ethylene and ≤ 10.0 mole % of a comonomer, such as α -olefin, based on 100% by mole of the copolymer. The comonomer can be, for example, one or more of propylene, butene-1, pentene-1, hexene-1, 4-methylpentene-1, octene-1, vinyl acetate, methyl methacrylate, or styrene. Such a polymer or copolymer can be produced using a single-site catalyst.

C. The Polypropylene

[0036] The polypropylene has an $M_w > 1.0 \times 10^6$, for example from about 1.05×10^6 to about 2.0×10^6 , such as from about 1.1×10^6 to about 1.5×10^6 . Optionally, the polypropylene has an $MWD \leq 50.0$, e.g., from about 1.2 to about 25, or about 2.0 to about 6.0; and/or a heat of fusion (" ΔH_m ") $\geq 100.0 \text{ J/g}$, e.g., 110 J/g to 120 J/g , such as from about 113 J/g to 119 J/g or from 114 J/g to about 116 J/g . The polypropylene can be, for example, one or more of (i) a propylene homopolymer or (ii) a copolymer of propylene and ≤ 10.0 mole % of such a comonomer, such as α -olefin, based on 100% by mole of the entire copolymer. The copolymer can be a random or block copolymer. The comonomer can be, for

example, one or more of α -olefins such as ethylene, butene-1, pentene-1, hexene-1, 4-methylpentene-1, octene-1, vinyl acetate, methyl methacrylate, and styrene, etc.; and diolefins such as butadiene, 1,5-hexadiene, 1,7-octadiene, 1,9-decadiene, etc. Optionally, the polypropylene has one or more of the following properties: (i) the polypropylene is isotactic; (ii) the polypropylene has an elongational viscosity of at least about 50,000 Pa sec at a temperature of 230° C. and a strain rate of 25 sec⁻¹; (iii) the polypropylene has a melting peak (second melt) of at least about 160.0° C.; and/or (iv) the polypropylene has a Trouton's ratio of at least about 15 when measured at a temperature of about 230° C. and a strain rate of 25 sec⁻¹.

[0037] The polypropylene's ΔH_m , Mw, and MWD are determined by the methods disclosed in PCT Patent Publication No. WO2007/132942, which is incorporated by reference herein in its entirety.

[0038] The diluent is generally compatible with the polymers used to produce the extrudate. For example, the diluent can be any species capable of forming a single phase in conjunction with the resin at the extrusion temperature. Examples of the diluent include aliphatic or cyclic hydrocarbon such as nonane, decane, decalin and paraffin oil, and phthalic acid ester such as dibutyl phthalate and dioctyl phthalate. Among them, preferable is paraffin oil, which is harmless to human body, has high boiling point, and contains small amount of volatile components. Paraffin oil with kinetic viscosity of 20-200 cSt at 40° C. can be used. The diluent can be the same as those described in U.S. Patent Publication Nos. 2008/0057388 and 2008/0057389, both of which are incorporated by reference in their entirety.

[0039] In an embodiment, the polyolefin in the extrudate comprises polypropylene present in an amount of from about 1.0 wt. % to about 50.0 wt. %, e.g., from about 2.5 wt. % to about 40.0 wt. %, such as from about 5.0 wt. % to about 30.0 wt. %. The amount of first polyethylene used to produce the extrudate can be in the range of from about 25 wt. % to about 99.0 wt. %, e.g., from about 50.0 wt. % to about 90.0 wt. %, such as 60.0 wt. % to about 80.0 wt. %. The amount of second polyethylene used to produce the extrudate can be, e.g., in the range of from 0.0 wt. % to about 50.0 wt. %, e.g., from about 5.0 wt. % to about 30.0 wt. %, such as about 10.0 wt. % to about 20.0 wt. %. The weight percents of the polypropylene and first and second polyethylenes are based on the weight of the polymer used to produce the extrudate. When the membrane comprises polypropylene in amount >2.0 wt. %, and particularly greater than 2.5 wt. %, the membrane generally has a meltdown temperature that is higher than that of a membrane which does not contain a significant amount of polypropylene.

[0040] In another embodiment, the membrane does not contain a significant amount of polypropylene. In this embodiment, the polyolefin used to produce the extrudate comprises less than 0.1 wt. % polypropylene, such as when the polyolefin consists of or consists essentially of polyethylene. In this embodiment, the amount of second polyethylene used to produce the extrudate can be, e.g., in the range of from about 1.0 wt. % to about 40.0 wt. %, such as from about 10.0 wt. % to about 50.0 wt. %; and the amount of first polyethylene used to produce the extrudate can be, e.g., in the range of from about 60.0 wt. % to about 99.0 wt. %, such as from about 70.0 wt. % to about 90.0 wt. %. The weight percents of the first and second polyethylenes are based on the weight of the polymer used to produce the extrudate.

[0041] The extrudate is produced by combining polymer and at least one diluent. The amount of diluent used to produce the extrudate can be in the range, e.g., of from about 25.0 wt. % to about 99.0 wt. % based on the weight of the extrudate, with the balance of the weight of the extrudate being the polymer used to produce the extrudate, e.g., the combined first polyethylene and second polyethylene.

[0042] While the extrudate and the microporous membrane can contain copolymers, inorganic species (such as species containing silicon and/or aluminum atoms, e.g., SiO₂, TiO₂, Al₂O₃, etc.), and/or heat-resistant polymers such as those described in PCT Publication WO 2008/016174, these are not required. In an embodiment, the extrudate and membrane is substantially free of such materials. Substantially free in this context means the amount of such materials in the microporous membrane is less than 1.0 wt. %, or less than 0.1 wt. %, or less than 0.01 wt. %, based on the total weight of the polymer used to produce the extrudate.

[0043] The microporous membrane generally comprises the polyolefin used to produce the extrudate. A small amount of diluent or other species introduced during processing can also be present, generally in amounts less than 1.0 wt. % based on the weight of the microporous membrane. A small amount of polymer molecular weight degradation might occur during processing, but this is acceptable. In an embodiment, molecular weight degradation during processing, if any, causes the Mw of the polymers in the membrane to differ from the Mw of the polymers used to produce the membrane by no more than about 50.0%, or no more than about 1.0%, or no more than about 0.1%.

[0044] In one embodiment, the invention relates to a microporous membrane comprising (a) from about 1.0 wt. % to about 50.0 wt. %, e.g., from about 2.0 wt. % to about 40.0 wt. %, such as from about 5.0 wt. % to about 30.0 wt. %, of the polypropylene; (b) from about 25.0 wt. % to about 99.0 wt. %, e.g., from about 50.0 wt. % to about 90.0 wt. %, such as 60.0 wt. % to about 80.0 wt. % of a first polyethylene; and (c) from about 0.0 wt. % to about 50.0 wt. %, e.g., from about 5.0 wt. % to about 30.0 wt. %, such as about 10.0 wt. % to about 20.0 wt. % of a second polyethylene; the membrane having a TD heat shrinkage at 105.0° C. $\leq$ about 2.5%, e.g., in the range of about 1.0% to about 2.3%, a TD heat shrinkage at 130.0° C. $\leq$ about 15.0%; e.g., in the range of about 5.0% to about 14.0%, and a maximum TD heat shrinkage in the molten state $\leq$ 10.0%, e.g., in the range of about 1.0% to about 9.0%; the first polyethylene having an Mw $\leq$ 1.0 $\times$ 10⁶, e.g., in the range of from about 1.0 $\times$ 10⁵ to about 9.0 $\times$ 10⁵, such as from about 4.0 $\times$ 10⁵ to about 8.0 $\times$ 10⁵, and an MWD $\leq$ 50.0, e.g., in the range of from about 1.2 to about 25, such as from about 3.0 to about 15; the second polyethylene having an Mw > 1.0 $\times$ 10⁶, e.g., in the range of about 1.1 $\times$ 10⁶ to about 5.0 $\times$ 10⁶, such as from about 1.2 $\times$ 10⁶ to about 3.0 $\times$ 10⁶, and an MWD $\leq$ 50.0, e.g., from about 1.5 to about 25, such as from about 4.0 to about 20.0; and the polypropylene having an Mw > 1.0 $\times$ 10⁶, e.g., from about 1.05 $\times$ 10⁶ to about 2.0 $\times$ 10⁶, such as about 1.1 $\times$ 10⁶ to about 1.5 $\times$ 10⁶, an MWD $\leq$ 50.0, e.g., from about 1.2 to about 25, such as about 2 to about 6, and a $\Delta H_m \geq$ 100.0 J/g, e.g., about 110 J/g to about 120 J/g, such as about 114 J/g to about 116 J/g.

[0045] In another embodiment, the microporous membrane contains polypropylene in an amount <0.1 wt. %, based on the weight of the microporous membrane. Such a membrane can comprise, for example, (a) from about 1.0 wt. % to about 40.0 wt. %, e.g., from about 10.0 wt. % to about 30.0 wt. %, of a

first polyethylene; and (b) from about 60.0 wt. % to about 99.0 wt. %, e.g., from about 70.0 wt. % to about 90.0 wt. %, of a second polyethylene; the membrane having a normalized air permeability $\leq 4.0 \times 10^2$ seconds/100 cm³/20 μ m, e.g., in the range of about 20.0 seconds/100 cm³/20 μ m to about 400.0 seconds/100 cm³/20 μ m, a TD heat shrinkage at 105° C. <1.9%, e.g., in the range of about 0.25% to about 1.5%, a TD heat shrinkage at 130° C. $\leq$ 15%, e.g., in the range of about 5.0% to 15%, and a maximum TD heat shrinkage in the molten state $\leq$ 10.0%, e.g., in the range of about 1.0% to about 7.0%; the first polyethylene having an Mw $\leq 1.0 \times 10^6$, e.g., in the range of from about 1.0×10^5 to about 9.0×10^5 , such as from about 4.0×10^5 to about 8.0×10^5 , and an MWD ≤ 50.0 , e.g., in the range of from about 1.2 to about 25, such as from about 3.0 to about 15; and the second polyethylene having an Mw $> 1.0 \times 10^6$, e.g., in the range of 1.1×10^6 to about 5.0×10^6 , such as from about 1.2×10^6 to about 3.0×10^6 , and an MWD ≤ 50.0 , e.g., from about 1.2 to about 25, such as from about 4.0 to about 20.0.

[0046] In an embodiment, the fraction of polyolefin in the membrane having a molecular weight $> 1.0 \times 10^6$ is at least 1.0 wt. %, based on the weight of the polyolefin in the membrane, e.g., at least 2.5 wt. %, such as in the range of about 2.5 wt. % to 50.0 wt. %.

[0047] Selected embodiments for producing the microporous membrane will now be described in more detail, but this description is not meant to foreclose other embodiments within the broader scope of the invention.

[3] Method of Producing the Microporous Membrane

[0048] In an embodiment, the microporous membrane is a monolayer (i.e., single-layer) membrane produced from polymer and diluent.

[0049] For example, the microporous membrane can be produced by a process comprising: producing a polymeric article, e.g., by combining polymer and diluent and extruding the combined polymer and diluent through a die to form an extrudate; optionally cooling the extrudate to form a cooled extrudate, e.g., a gel-like sheet; stretching the cooled extrudate in at least one planar direction; removing at least a portion of the diluent from the extrudate or cooled extrudate to form a membrane and optionally removing any remaining volatile species from the dried membrane. The dried membrane is subjected to orientation, e.g., stretching, (a) in a first planar direction from a first size to a second size, the second size being in the range of from about (1.1·the first size) to about (1.5·the first size), (b) in a second planar direction from a third size to a fourth size, the first and second planar directions defining a planar angle the range of 60° to 120° and the fourth size being in the range of (1.1·the third size) to (1.3·the third size); and (c) in the second direction from the fourth size to a fifth size, the fifth size being (i) <the fourth size and (ii) in the range of from the third size to (1.1·the third size).

[0050] An optional hot solvent treatment step, an optional heat setting step, an optional cross-linking step with ionizing radiation, and an optional hydrophilic treatment step, etc., as described in PCT Publication WO2008/016174 can be conducted if desired. Neither the number nor order of the optional steps is critical.

Combining Polymer and Diluent

[0051] The polymers as described above can be combined, e.g., by dry mixing or melt blending, and then the combined

polymers can be combined with at least one diluent (e.g., a membrane-forming solvent) to produce a mixture of polymer and diluent, e.g., a polymeric solution. Alternatively, the polymer(s) and diluent can be combined in a single step. The polymer-diluent mixture can contain additives such as one or more antioxidant. In an embodiment, the amount of such additives does not exceed 1 wt. % based on the weight of the polymeric solution.

[0052] The amount of diluent used to produce the extrudate is not critical, and can be in the range, e.g., of from about 25 wt. % to about 99 wt. % based on the weight of the combined diluent and polymer, with the balance being polymer, e.g., the combined first and second polyethylene.

Extruding

[0053] In an embodiment, the combined polymer and diluent are conducted from an extruder to a die.

[0054] The extrudate or cooled extrudate should have an appropriate thickness to produce, after the stretching steps, a final membrane having the desired thickness (generally 3 μ m or more). For example, the extrudate can have a thickness in the range of about 0.1 mm to about 10.0 mm, or about 0.5 mm to 5.0 mm. Extrusion is generally conducted with the mixture of polymer and diluent in the molten state. When a sheet-forming die is used, the die lip is generally heated to an elevated temperature, e.g., in the range of 140° C. to 250° C. Suitable process conditions for accomplishing the extrusion are disclosed in PCT Publications WO 2007/132942 and WO 2008/016174. The machine direction ("MD") is defined as the direction in which the extrudate is produced from the die. The transverse direction ("TD") is defined as the direction perpendicular to both MD and the thickness direction of the extrudate. The extrudate can be produced continuously from a die, or it can be produced from the die in portions (as is the case in batch processing) for example. The definitions of TD and MD are the same in both batch and continuous processing.

Formation of a Cooled Extrudate

[0055] The extrudate can be exposed to a temperature in the range of 15.0° C. to 25.0° C. to form a cooled extrudate. Cooling rate is not particularly critical. For example, the extrudate can be cooled at a cooling rate of at least about 30.0° C./minute until the temperature of the extrudate (the cooled temperature) is approximately equal to the extrudate's gelation temperature (or lower). Process conditions for cooling can be the same as those disclosed in PCT Publications No. WO 2008/016174 and WO 2007/132942, for example.

Stretching the Extrudate

[0056] The extrudate or cooled extrudate is stretched in at least one direction. The extrudate can be stretched by, for example, a tenter method, a roll method, an inflation method or a combination thereof, as described in PCT Publication No. WO 2008/016174, for example. The stretching may be conducted monoaxially or biaxially, though the biaxial stretching is preferable. In the case of biaxial stretching, any of simultaneous biaxial stretching, sequential stretching or multi-stage stretching (for instance, a combination of the simultaneous biaxial stretching and the sequential stretching) can be used, though simultaneous biaxial stretching is preferable. When biaxial stretching is used, the amount of magnification need not be the same in each stretching direction.

[0057] The stretching magnification can be, for example, 2 fold or more, preferably 3 to 30 fold in the case of monoaxial stretching. In the case of biaxial stretching, the stretching magnification can be, for example, 3 fold or more in any direction, namely 9 fold or more, such as 16 fold or more, e.g. 25 fold or more, in area magnification. An example for this stretching step would include stretching from about 9 fold to about 49 fold in area magnification. Again, the amount of stretch in either direction need not be the same. The magnification factor operates multiplicatively on film size. For example, a film having an initial width (TD) of 2.0 cm that is stretched in TD to a magnification of 4 fold will have a final width of 8.0 cm.

[0058] While not required, the stretching can be conducted while exposing the extrudate to a temperature in the range of from about the Tcd temperature Tm.

[0059] Tcd and Tm are defined as the crystal dispersion temperature and melting point of the polyethylene having the lowest melting point among the polyethylenes used to produce the extrudate (i.e., the first and second polyethylene). The crystal dispersion temperature is determined by measuring the temperature characteristics of dynamic viscoelasticity according to ASTM D 4065. In an embodiment where Tcd is in the range of about 90.0° C. to 100.0° C., the stretching temperature can be from about 90.0° C. to 125.0° C.; e.g., from about 100.0° C. to 125.0° C., such as from 105.0° C. to 125.0° C.

[0060] In an embodiment, the stretched extrudate undergoes an optional thermal treatment before diluent removal. In the thermal treatment, the stretched extrudate is exposed to a temperature that is higher (warmer) than the temperature to which the extrudate is exposed during stretching. The planar dimensions of the stretched extrudate (length in MD and width in TD) can be held constant while the stretched extrudate is exposed to the higher temperature. Since the extrudate contains polymer and diluent, its length and width are referred to as the “wet” length and “wet” width. In an embodiment, the stretched extrudate is exposed to a temperature in the range of 120.0° C. to 125° C. for a time sufficient to thermally treat the extrudate, e.g., a time in the range of 1.0 second to 1.0×10^2 seconds while the wet length and wet width are held constant, e.g., by using tenter clips to hold the stretched extrudate along its perimeter. In other words, during the thermal treatment, there is no magnification or demagnification (i.e., no dimensional change) of the stretched extrudate in MD or TD.

[0061] In this step and in other steps such as dry orientation and heat setting where the sample (e.g., the extrudate, dried extrudate, membrane, etc.) is exposed to an elevated temperature, this exposure can be accomplished by heating air and then conveying the heated air into proximity with the sample. The temperature of the heated air, which is generally controlled at a set point equal to the desired temperature, is then conducted toward the sample through a plenum for example. Other methods for exposing the sample to an elevated temperature, including conventional methods such as exposing the sample to a heated surface, infrared heating in an oven, etc. can be used with or instead heated air.

Removal of the Diluent

[0062] In an embodiment, at least a portion of the diluent is removed (or displaced) from the stretched extrudate to form a dried membrane. A displacing (or “washing”) solvent can be

used to remove (wash away, or displace) the diluent, as described in PCT Publication No. WO 2008/016174, for example.

[0063] In an embodiment, at least a portion of any remaining volatile species (e.g., washing solvent) is removed from the dried membrane after diluent removal. Any method capable of removing the washing solvent can be used, including conventional methods such as heat-drying, wind-drying (moving air), etc. Process conditions for removing volatile species such as washing solvent can be the same as those disclosed in PCT Publication No. WO 2008/016174, for example.

Stretching the Membrane (Dry Orientation)

[0064] The dried membrane is stretched (called “dry stretching” since at least a portion of the diluent has been removed or displaced) in at least MD. A dried membrane that has been dry stretched is called an “oriented” membrane. Before dry stretching, the dried membrane has an initial size in MD (a first dry length) and an initial size in TD (a first dry width). As used herein, the term “first dry width” refers to the size of the dried membrane in the transverse direction prior to the start of dry orientation. The term “first dry length” refers to the size of the dried membrane in the machine direction prior to the start of dry orientation. Tenter stretching equipment of the kind described in WO 2008/016174 can be used, for example.

[0065] The dried membrane can be stretched in MD from the first dry length to a second dry length that is larger than the first dry length by a first magnification factor (the “MD dry stretching magnification factor”) in the range of from about 1.1 to about 1.5. When TD dry stretching is used, the dried membrane can be stretched in TD from the first dry width to a second dry width that is larger than the first dry width by a second magnification factor (the “TD dry stretching magnification factor”). Optionally, the TD dry stretching magnification factor is $\leq$ the MD dry stretching magnification factor, e.g., the first magnification factor is $>$ the second magnification factor. The TD dry stretching magnification factor can be in the range of from about 1.1 to about 1.3. The dry stretching (also called re-stretching since the diluent-containing extrudate has already been stretched) can be sequential or simultaneous in MD and TD. Since TD heat shrinkage generally has a greater effect on battery properties than does MD heat shrinkage, the amount of TD magnification generally does not exceed the amount of MD magnification. When TD dry stretching is used, the dry stretching can be simultaneous in MD and TD or sequential. When the dry stretching is sequential, generally MD stretching is conducted first followed by TD stretching.

[0066] The dry stretching can be conducted while exposing the dried membrane to a temperature $\leq T_m$, e.g., in the range of from about Tcd–30° C. to Tm. In an embodiment, the dry stretching is conducted with the membrane exposed to a temperature in the range of from about 70.0° C. to about 135.0° C., for example from about 80.0° C. to about 132.0° C. In an embodiment, the MD stretching is conducted before TD stretching, and

[0067] (i) the MD stretching is conducted while the membrane is exposed to a first temperature in the range of Tcd–30.0° C. to about Tm–10.0° C., for example 70.0° C. to about 125.0° C., or about 80.0° C. to about 120.0° C. and

[0068] (ii) the TD stretching is conducted while the membrane is exposed to a second temperature that is higher than the first temperature but lower than T_m , for example about 70.0° C. to about 135.0° C., or about 127.0° C. to about 132.0° C., or about 129.0° C. to about 131.0° C.

[0069] In an embodiment, the MD stretching magnification is in the range of from about 1.1 to about 1.5, such as 1.2 to 1.4; the TD dry stretching magnification is in the range of from about 1.1 to about 1.3, such as 1.15 to 1.25; the MD dry stretching is conducted before the TD dry stretching, the MD dry stretching is conducted while the membrane is exposed to a temperature in the range of 80.0° C. to about 120.0° C., and the TD dry stretching is conducted while the membrane is exposed to a temperature in the range of 129.0° C. to about 131.0° C.

[0070] The stretching rate is preferably 3%/second or more in the stretching direction (MD or TD), and the rate can be independently selected for MD and TD stretching. The stretching rate is preferably 5%/second or more, more preferably 10%/second or more, e.g., in the range of 5%/second to 25%/second. Though not particularly critical, the upper limit of the stretching rate is preferably 50%/second to prevent rupture of the membrane.

Controlled Reduction of the Membrane's Width

[0071] Following the dry stretching, the dried membrane is subjected to a controlled reduction in width from the second dry width to a third width, the third dry width being in the range of from the first dry width to about 1.1 times larger than the first dry width. The width reduction generally conducted while the membrane is exposed to a temperature $\geq T_{cd}$ -30.0° C., but no greater than T_m . For example, during width reduction the membrane can be exposed to a temperature in the range of from about 70.0° C. to about 135° C., such as from about 127° C. to about 132° C., e.g., from about 129° C. to about 131° C. In an embodiment, the decreasing of the membrane's width is conducted while the membrane is exposed to a temperature that is lower than T_m . In an embodiment, the third dry width is in the range of from 1.0 times larger than the first dry width to about 1.1 times larger than the first dry width.

[0072] It is believed that exposing the membrane to a temperature during the controlled width reduction that is $\geq$ the temperature to which the membrane was exposed during the TD stretching leads to greater resistance to heat shrinkage in the finished membrane.

Optional Heat Set

[0073] Optionally, the membrane is thermally treated (heat-set) at least once following diluent removal, e.g., after dry stretching, the controlled width reduction, or both. It is believed that heat-setting stabilizes crystals and makes uniform lamellas in the membrane. In an embodiment, the heat setting is conducted while exposing the membrane to a temperature in the range T_{cd} to T_m , e.g., a temperature e.g., in the range of from about 100° C. to about 135° C., such as from about 127° C. to about 132° C., or from about 129° C. to about 131° C. Generally, the heat setting is conducted for a time sufficient to form uniform lamellas in the membrane, e.g., a time in the range of 1 to 100 seconds. In an embodiment, the heat setting is operated under conventional heat-set "thermal fixation" conditions. The term "thermal fixation" refers to

heat-setting carried out while maintaining the length and width of the membrane substantially constant, e.g., by holding the membrane's perimeter with tenter clips during the heat setting.

[0074] Optionally, an annealing treatment can be conducted after the heat-set step. The annealing is a heat treatment with no load applied to the membrane, and can be conducted by using, e.g., a heating chamber with a belt conveyor or an air-floating-type heating chamber. The annealing may also be conducted continuously after the heat-setting with the tenter slackened. During annealing the membrane can be exposed to a temperature in the range of T_m or lower, e.g., in the range from about 60.0° C. to about T_m -5° C. Annealing is believed to provide the microporous membrane with improved permeability and strength.

[0075] Optional heated roller, hot solvent, cross linking, hydrophilizing, and coating treatments can be conducted if desired, e.g., as described in PCT Publication No. WO 2008/016174.

[4] Structure, Properties, and Composition of Microporous Membrane

[0076] In an embodiment, the membrane is a monolayer microporous membrane. The thickness of the monolayer membrane is generally in the range of from about 1.0 μm to about $1.0 \times 10^2 \mu\text{m}$, e.g., from about 5.0 μm to about 30.0 μm . The thickness of the microporous membrane can be measured by a contact thickness meter at 1.0 cm longitudinal intervals over the width of 20.0 cm, and then averaged to yield the membrane thickness. Thickness meters such as the Litematic available from Mitsutoyo Corporation are suitable. This method is also suitable for measuring thickness variation after heat compression, as described below. Non-contact thickness measurements are also suitable, e.g., optical thickness measurement methods.

[0077] Optionally, the microporous membrane has one or more of the following properties.

(a) Normalized Air Permeability $\leq 4.0 \times 10^2 \text{ sec}/100 \text{ cm}^3/20 \mu\text{m}$

[0078] In an embodiment, the membrane's normalized air permeability (Gurley value, normalized to an equivalent membrane thickness of 20 μm) is $\leq 400.0 \text{ seconds}/100 \text{ cm}^3/20 \mu\text{m}$, e.g., in the range of about 20.0 seconds/100 $\text{cm}^3/20 \mu\text{m}$ to about 400.0 seconds/100 $\text{cm}^3/20 \mu\text{m}$. Since the air permeability value is normalized to a film thickness of 20 μm , the air permeability value is expressed in units of "seconds/100 $\text{cm}^3/20 \mu\text{m}$ ". In an embodiment, the normalized air permeability is in the range of 100.0 seconds/100 $\text{cm}^3/20 \mu\text{m}$ to about 375 seconds/100 $\text{cm}^3/20 \mu\text{m}$. In an embodiment, the membrane comprises <0.1 wt. % polypropylene, based on the weight of the membrane, and the membrane's normalized air permeability is in the range of 100.0 seconds/100 $\text{cm}^3/20 \mu\text{m}$ to about 275 seconds/100 $\text{cm}^3/20 \mu\text{m}$. Normalized air permeability is measured according to JIS P8117, and the results are normalized to a value at a thickness of 20 μm using the equation $A = 20 \mu\text{m} \cdot (X)/T_1$, where X is the measured air permeability of a membrane having an actual thickness T_1 and A is the normalized air permeability at a thickness of 20 μm .

(b) Porosity in the Range of from about 25.0% to about 80.0% [0079] In an embodiment, the membrane has a porosity $\geq 25.0\%$, e.g., in the range of about 25.0% to about 80.0%, or 30.0% to 60.0%. The membrane's porosity is measured conventionally by comparing the membrane's actual weight to the weight of an equivalent non-porous membrane of the

same composition (equivalent in the sense of having the same length, width, and thickness). Porosity is then determined using the formula: Porosity % = $100 \times (w_2 - w_1) / w_2$, wherein “w1” is the actual weight of the microporous membrane and “w2” is the weight of the equivalent non-porous membrane having the same size and thickness.

(c) Normalized Pin Puncture Strength $\geq 3.0 \times 10^3$ mN/20 μ m

[0080] In an embodiment, the membrane has a normalized pin puncture strength $\geq 3.0 \times 10^3$ mN/20 μ m, e.g., in the range of 3.5×10^3 mN/20 μ m to 1.0×10^4 mN/20 μ m, such as 3,750 mN/20 μ m to 5,500 mN/20 μ m. In one embodiment, the membrane comprises polypropylene having an $M_w > 1.0 \times 10^6$, in an amount $\geq$ about 0.1 wt. % (e.g., ≥ 1.0 wt. %, such as $\geq$ about 2.5 wt. %) based on the weight of the membrane. In this embodiment, the membrane can have a normalized pin puncture strength of, e.g., ≥ 3500 mN/20 μ m. Pin puncture strength is defined as the maximum load measured when a microporous membrane having a thickness of T_1 is pricked with a needle of 1 mm in diameter with a spherical end surface (radius R of curvature: 0.5 mm) at a speed of 2 mm/second. The pin puncture strength (“S”) is normalized to a value at a membrane thickness of 20 μ m using the equation $S_2 = 20 \mu\text{m} \times (S_1) / T_1$, where S_1 is the measured pin puncture strength, S_2 is the normalized pin puncture strength, and T_1 is the average thickness of the membrane.

(d) Tensile Strength $\geq 4.0 \times 10^4$ kPa

[0081] In an embodiment, the membrane has an MD tensile strength $\geq 9.5 \times 10^4$ kPa, e.g., in the range of 95,000 to 110,000 kPa, and a TD tensile strength $\geq 9.0 \times 10^4$ kPa, e.g., in the range of 9.0×10^4 kPa to 1.1×10^5 kPa. Tensile strength is measured in MD and TD according to ASTM D-882A.

(e) Tensile Elongation of 100% or More

[0082] Tensile elongation is measured according to ASTM D-882A. In an embodiment, the membrane’s MD and TD tensile elongation are each $\geq 100.0\%$, e.g., in the range of 125.0% to 350.0%. In another embodiment, the membrane’s MD tensile elongation is in the range of, e.g., 125.0% to 250.0% and TD tensile elongation is in the range of, e.g., 140.0% to 300.0%.

(f) Thickness Variation Ratio after Heat Compression $\leq 20\%$

[0083] In an embodiment, the membrane’s thickness variation ratio after heat compression is $\leq 20\%$ of the thickness of the membrane before the heat compression, e.g., in the range of 5% to 10%. Thickness variation after heat compression is measured by subjecting the membrane to a compression of 2.2 MPa (22 kgf/cm²) in the thickness direction for five minutes while the membrane is exposed to a temperature of 90° C. The membrane’s thickness variation ratio is defined as the absolute value of (average thickness after compression – average thickness before compression) / (average thickness before compression) $\times 100$.

(g) Air Permeability after Heat Compression $\leq 7.0 \times 10^2$ sec/100 cm³

[0084] In an embodiment, the membrane’s air permeability after heat compression is $\leq 7.0 \times 10^2$ seconds/100 cm³, e.g., 100.0 seconds/100 cm³ to 675 seconds/100 cm³. Air permeability after heat compression is measured according to JIS P8117 after the membrane is subjected to a compression of 2.2 MPa (22 kgf/cm²) in the thickness direction for five minutes while the membrane is exposed to a temperature of 90° C. In an embodiment, the membrane comprises <0.1 wt. %

polypropylene, based on the weight of the membrane, and the membrane’s air permeability after heat compression is in the range of 1.0×10^2 seconds/100 cm³ to about 5.0×10^2 seconds/100 cm³/20 μ m.

(h) Shutdown Temperature $\leq 140.0^\circ$ C.

[0085] In an embodiment, the membrane has a shutdown temperature $\leq 140.0^\circ$ C., e.g., 132° C. to 138° C. The shutdown temperature of the microporous membrane is measured by a thermomechanical analyzer (TMA/SS6000 available from Seiko Instruments, Inc.) as follows: A rectangular sample of 3 mm $\times$ 50 mm is cut out of the microporous membrane such that the long axis of the sample is aligned with the transverse direction of the microporous membrane and the short axis is aligned with the machine direction. The sample is set in the thermomechanical analyzer at a chuck distance of 10.0 mm, i.e., the distance from the upper chuck to the lower chuck is 10.0 mm. The lower chuck is fixed and a load of 19.6 mN applied to the sample at the upper chuck. The chucks and sample are enclosed in a tube which can be heated. Starting at 30° C., the temperature inside the tube is elevated at a rate of 5° C./minute, and sample length change under the 19.6 mN load is measured at intervals of 0.5 second and recorded as temperature is increased. The temperature is increased to 200° C. “Shutdown temperature” is defined as the temperature of the inflection point observed at approximately the melting point of the polymer having the lowest melting point among the polymers used to produce the membrane.

(i) Electrolytic Solution Absorption Speed ≥ 2.5

[0086] In an embodiment, the membrane has an electrolytic solution absorption speed ≥ 2.5 , e.g., in the range of 3.0 to 5.0. Using a dynamic surface tension measuring apparatus (DCAT21 with high-precision electronic balance, available from Eko Instruments Co., Ltd.), a microporous membrane sample is immersed in an electrolytic solution for 6.0×10^2 seconds (electrolyte: 1 mol/L of LiPF₆, solvent: ethylene carbonate/dimethyl carbonate at a volume ratio of 3/7) kept at 18° C., to determine an electrolytic solution absorption speed by the formula of [weight (in grams) of microporous membrane after immersion/weight (in grams) of microporous membrane before immersion]. The electrolytic solution absorption speed is expressed by a relative value, assuming that the electrolytic solution absorption rate in the microporous membrane of Comparative Example 1 is 1.0. Battery separator film having a relatively high electrolytic solution absorption speed (e.g., ≥ 2.5) are desirable since less time is required for the separator to uptake the electrolyte during battery manufacturing, which in turn increases the rate at which the batteries can be produced.

(j) TD Heat Shrinkage at 105° C. $\leq 2.5\%$

[0087] In an embodiment, the membrane has a TD heat shrinkage at 105° C. $\leq 2.5\%$, for example from 1.0% to 2.3%. In another embodiment, the membrane comprises <0.1 wt. % polypropylene, based on the weight of the membrane, and the membrane has a TD heat shrinkage at 105° C. of, e.g., <1.9%, for example from 0.25% to 1.5%. The membrane’s heat shrinkage in orthogonal planar directions (e.g., MD or TD) at 105° C. is measured as follows:

(i) Measure the size of a test piece of microporous membrane at ambient temperature in both MD and TD, (ii) expose the test piece to a temperature of 105° C. for 8 hours with no

applied load, and then (iii) measure the size of the membrane in both MD and TD. The heat (or “thermal”) shrinkage in either the MD or TD can be obtained by dividing the result of measurement (i) by the result of measurement (ii) and expressing the resulting quotient as a percent.

[0088] In an embodiment, the membrane has an MD heat shrinkage at 105° C. $\leq 10\%$, for example from 1% to 8%.

(k) TD Heat Shrinkage at 130° C. $\leq 15\%$

[0089] The membrane can also be characterized by a heat shrinkage value measured at 130° C. The measurement is slightly different from the measurement of heat shrinkage at 105° C., reflecting the fact that the edges of the membrane parallel to the transverse direction are generally fixed within the battery, with a limited degree of freedom allowed for expansion or contraction (shrinkage) in the transverse direction, particularly near the center of the edges parallel to the machine direction. Accordingly, a square sample of microporous film measuring 50 mm along TD and 50 mm along MD is mounted in a frame, with the edges parallel to TD fixed to the frame (e.g., by tape) leaving a clear aperture of 35 mm in MD and 50 mm in TD. The frame with sample attached is then exposed to a temperature of 130° C. for thirty minutes, and then cooled. TD heat shrinkage generally causes the edges of the film parallel to MD to bow slightly inward (toward the center of the frame’s aperture). The shrinkage in TD (expressed as a percent) is equal to the length of the sample in TD before heating divided by the narrowest length (within the frame) of the sample in TD after heating times 100 percent.

[0090] In an embodiment, the membrane has a TD heat shrinkage at 130° C. $\leq 15\%$, for example from about 3.0% to about 15%. In another embodiment, the membrane has a TD heat shrinkage at 130° C. in the range of 5.0% to 13%.

(l) Maximum TD Shrinkage in Molten State $\leq 10.0\%$

[0091] Maximum shrinkage in the molten state in a planar direction of the membrane is measured by the following procedure:

[0092] Using the TMA procedure described for the measurement of meltdown temperature, the sample length measured in the temperature range of from 135° C. to 145° C. are recorded. The membrane shrinks, and the distance between the chucks decreases as the membrane shrinks. The maximum shrinkage in the molten state is defined as the sample length between the chucks measured at 23° C. (L1 equal to 10 mm) minus the minimum length measured generally in the range of about 135° C. to about 145° C. (equal to L2) divided by L1, i.e., $[L1 - L2]/L1 \times 100\%$. When TD maximum shrinkage is measured, the rectangular sample of 3 mm $\times$ 50 mm used is cut out of the microporous membrane such that the long axis of the sample is aligned with the transverse direction of the microporous membrane as it is produced in the process and the short axis is aligned with the machine direction. When MD maximum shrinkage is measured, the rectangular sample of 3 mm $\times$ 50 mm used is cut out of the microporous membrane such that the long axis of the sample is aligned with the machine direction of the microporous membrane as it is produced in the process and the short axis is aligned with the transverse direction.

[0093] In one embodiment, the membrane comprises polypropylene having an $M_w > 1.0 \times 10^6$, in an amount $\geq$ about 0.1 wt. % (e.g., ≥ 1.0 wt. %, such as $\geq$ about 2.5 wt. %) based

on the weight of the membrane. In this embodiment, the membrane’s maximum MD heat shrinkage in the molten state can be, e.g., $\leq 25\%$, or $\leq 20.0\%$, such as in the range of 1.0% to 25%, or 2.0% to 20.0%. In this embodiment, the membrane’s maximum TD shrinkage in the molten state can be, e.g., $\leq 10.0\%$, such as in the range of from about 1.0 to about 9.0%.

[0094] In another embodiment, the membrane comprises < 0.1 wt. % polypropylene, based on the weight of the membrane. In this embodiment, the membrane’s maximum MD heat shrinkage in the molten state can be, e.g., $\leq 35\%$, or $\leq 30.0\%$, such as in the range of 1.0% to 30.0%, or 2.0% to 25%. In this embodiment, the membrane’s maximum TD shrinkage in the molten state can be, e.g., $\leq 10.0\%$, such as in the range of from about 1.0% to about 7.0%.

(m) Meltdown Temperature $\geq 145^\circ$ C.

[0095] Meltdown temperature is measured by the following procedure: A rectangular sample of 3 mm $\times$ 50 mm is cut out of the microporous membrane such that the long axis of the sample is aligned with the transverse direction of the microporous membrane as it is produced in the process and the short axis is aligned with the machine direction. The sample is set in a thermomechanical analyzer (TMA/SS6000 available from Seiko Instruments, Inc.) at a chuck distance of 10.0 mm, i.e., the distance from the upper chuck to the lower chuck is 10.0 mm. The lower chuck is fixed and a load of 19.6 mN applied to the sample at the upper chuck. The chucks and sample are enclosed in a tube which can be heated. Starting at 30° C., the temperature inside the tube is elevated at a rate of 5° C./minute, and sample length change under the 19.6 mN load is measured at intervals of 0.5 second and recorded as temperature is increased. The temperature is increased to 200° C. The meltdown temperature of the sample is defined as the temperature at which the sample breaks, generally at a temperature in the range of about 170° C. to about 200° C.

[0096] In one embodiment, the membrane comprises polypropylene having an $M_w > 1.0 \times 10^6$, in an amount $\leq$ about 0.1 wt. % (e.g., ≤ 1.0 wt. %, such as $\leq$ about 2.5 wt. %) based on the weight of the membrane. In this embodiment, the membrane’s meltdown temperature can be, $\geq 170.0^\circ$ C., e.g., in the range of from 170.0° C. to 180.0° C.

[0097] In another embodiment, the membrane contains < 0.1 wt. % polypropylene, based on the weight of the membrane. In this embodiment, the meltdown temperature can be, e.g., in the range of from 145° C. to 155° C., such as 147° C. to 152° C.

Microporous Membrane Composition

Polymer

[0098] The microporous membrane generally comprises the same polymers used to produce the polymeric composition, in generally the same relative amounts. Washing solvent and/or process solvent (diluent) can also be present, generally in amounts less than 1 wt. % based on the weight of the microporous membrane. A small amount of polymer molecular weight degradation might occur during processing, but this is acceptable. In an embodiment where the polymer is polyolefin and the membrane is produced in a wet process, molecular weight degradation during processing, if any, causes the value of M_w of the polyolefin in the membrane to

differ from the Mw of the polymer used to produce the membrane by no more than about 50%, or no more than about 1%, or no more than about 0.1%.

[5] Battery

[0099] The microporous membranes of the invention are useful as battery separators in e.g., lithium ion primary and secondary batteries. Such batteries are described in PCT publication, WO 2008/016174 which is incorporated by reference herein in its entirety. The membrane generally has a thickness in the range of about 3.0 μm to about 200.0 μm , or about 5.0 μm to about 50.0 μm . Depending, e.g., on the choice of electrolyte, separator swelling might increase the final thickness to a value larger than 200 μm .

[0100] FIG. 1 shows an example of a cylindrical-type lithium ion secondary battery comprising two battery separators. The microporous membranes of the invention are suitable for use as battery separators in this type of battery. The battery has a toroidal-type electrode assembly 1 comprising a first separator 10, a second separator 11, a cathode sheet 13, and an anode sheet 12. The separators' thicknesses are not to scale, and are greatly magnified for the purpose of illustration. The toroidal-type electrode assembly 1 can be wound, e.g., such that the second separator 11 is arranged on an outer side of the cathode sheet 13, while the first separator 10 is arranged on the inner side of the cathode sheet. In this example, the second separator 11 is arranged on inside surface of the toroidal-type electrode assembly 1, as shown in FIG. 2.

[0101] In this example, an anodic active material layer 12b is formed on both sides of the current collector 12a, and a cathodic active material layer 13b is formed on both sides of the current collector 13a, as shown in FIG. 3. As shown in FIG. 2, an anode lead 20 is attached to an end portion of the anode sheet 12, and a cathode lead 21 is attached to an end portion of the cathode sheet 13. The anode lead 20 is connected with battery lid 27, and the cathode lead 21 is connected with the battery can 23.

[0102] While a battery of cylindrical form is illustrated, the invention is not limited thereto, and the separators of the invention are suitable for use in e.g., prismatic batteries such as those containing electrodes in the form of stacked plates of anode(s) 12 and a cathode (3) 13 alternately connected in parallel with the separators situated between the stacked anodes and cathodes.

[0103] When the battery is assembled, the anode sheet 12, the cathode sheet 13, and the first and second separators 10, 11 are impregnated with the electrolytic solution, so that the separator 10, 11 (microporous membranes) are provided with ion permeability. The impregnation treatment can be conducted, e.g., by immersing electrode assembly 1 in the electrolytic solution at room temperature. A cylindrical type lithium ion secondary battery can be produced by inserting the toroidal-type electrode assembly 1 (see FIG. 1) into a battery can 23 having an insulation plate 22 at the bottom, injecting the electrolytic solution into the battery can 23, covering the electrode assembly 1 with a insulation plate 22, caulking a battery lid (24, 25, 26, and 27) to the battery can 23 via a gasket 28. The battery lid functions as an anode terminal.

[0104] FIG. 3 (oriented so that the battery lid, i.e., the anode terminal of FIG. 1, is toward the right) illustrates the advantage of using a separator having diminished tendency to TD heat shrinkage as the battery temperature increases. One role of the separator is to prevent contact of the anodic active

material layer and the cathodic active material layer. In the event of a significant amount of TD heat shrinkage, the thin edges of the separators 10 and 11 move away from the battery lid (move leftward in FIG. 3), thereby allowing contact between the anodic active material layer and the cathodic active material layer, resulting in a short circuit. Since the separators can be quite thin, usually less than 200 μm , the anodic active material layer and the cathodic active material layer can be quite close. Consequently, even a small decrease in the amount of separator TD shrinkage at elevated battery temperature can make a significant improvement in the battery's resistance to internal short circuiting.

[0105] The battery is useful as a power source for one or more electrical or electronic components. Such components include passive components such as resistors, capacitors, inductors, including, e.g., transformers; electromotive devices such as electric motors and electric generators, and electronic devices such as diodes, transistors, and integrated circuits. The components can be connected to the battery in series and/or parallel electrical circuits to form a battery system. The circuits can be connected to the battery directly or indirectly. For example, electricity flowing from the battery can be converted electrochemically (e.g., by a second battery or fuel cell) and/or electromechanically (e.g., by an electric motor operating an electric generator) before the electricity is dissipated or stored in a one or more of the components. The battery system can be used as a power source for moving an electric vehicle or hybrid electric vehicle, for example. In one embodiment, the battery is electrically connected to an electric motor and/or an electric generator for powering an electric vehicle or hybrid electric vehicle.

[0106] The present invention will be explained in more detail referring to Examples below without intention of restricting the scope of the present invention.

Example 1

[0107] A polyolefin composition is made by dry mixing (a) 70 wt. % of a first polyethylene resin having an Mw of 5.6×10^5 and an MWD of 4.05, (b) 30 wt. % polypropylene resin having an Mw of 1.1×10^6 , an MWD of 5, and a heat of fusion of 114 J/g. The first polyethylene has a Tm of 135° C. and a Tcd of 100° C.

[0108] A polyolefin solution is produced as follows: 30 wt. % of the combined polyethylene and polypropylene (the polyolefin composition) is charged into a strong-blending double-screw extruder having an inner diameter of 58 mm and L/D of 42, and 70 wt. % of liquid paraffin diluent (50 cst at 40° C.) is supplied to the double-screw extruder via a side feeder, the weight percents being based on the weight of the polyolefin solution. Melt-blending is conducted at 210° C. and 200 rpm. The polyolefin solution is extruded from a T-die mounted to the double-screw extruder. The extrudate is cooled while passing through cooling rolls having a surface temperature of 40° C., to form a cooled extrudate, i.e. gel-like sheet.

[0109] Using a tenter-stretching machine, the extrudate (gel-like sheet) is biaxially stretched (simultaneously in MD and TD) to a magnification of 5 fold in each of MD and TD while exposing the extrudate to a temperature of 117° C. The stretched gel-like sheet is fixed to an aluminum frame of 20 cm $\times$ 20 cm, immersed in a bath of methylene chloride controlled at 25° C. to remove the liquid paraffin with vibration of 100 rpm for 3 minutes, and dried by an air flow at room temperature. At the start of dry orientation, the membrane has

an initial size in TD (the first dry width) and an initial size in MD (the first dry length). The dried membrane is first stretched by a batch-stretching machine to an MD magnification of 1.4 fold (to a second dry length) while exposing the membrane to a temperature of 110° C. and holding its width constant. The dried membrane is then stretched by a batch-stretching machine to a TD magnification of 1.2 fold (to a second dry width) while exposing the membrane to a temperature of 130° C. and holding the membrane's length constant at the second dry length. The membrane is then subjected to a controlled reduction in width from the second dry width to a third dry width that is equal to the first dry width, i.e., to a final magnification of 1.0 fold, while exposing the membrane to a temperature of 130° C. and maintaining the membrane's length constant at the second dry length. In other words, the membrane's width is reduced to the membrane's initial size in TD at the start of dry orientation while holding the membrane's length in MD constant at the second dry length. After the membrane's width is reduced to the initial width, it is then heat-set by exposing the membrane to a temperature of 129° C. for 10 minutes.

Example 2

[0110] Example 1 is repeated except that the polyolefin composition is produced from 70 wt. % of the first polyethylene, 10 wt. % of a second polyethylene having an Mw of 1.9×10^6 and an MWD of 5.09, and 20 wt. % of the polypropylene; the membrane is exposed to a temperature of 90° C. during the MD dry orientation; the MD dry orientation magnification is 1.3 fold; and the heat setting temperature is 130° C.

Example 3

[0111] Example 2 is repeated except that the polyolefin composition is produced from 60 wt. % of the first polyethylene, 20 wt. % of the second polyethylene, and 20 wt. % of the polypropylene; the membrane is exposed to a temperature of 115° C. during the MD dry orientation; and the MD dry orientation magnification is 1.2 fold.

Example 4

[0112] Example 2 is repeated except that the polyolefin composition is produced from 60 wt. % of the first polyethylene, 30 wt. % of the second polyethylene, and 10 wt. % of the polypropylene; and the membrane is exposed to a temperature of 115° C. during the MD dry orientation.

Example 5

[0113] Example 1 is repeated except the polyolefin composition comprises 70 wt. % of the first polyethylene resin and 30% of the second polyethylene resin, the extrudate is exposed to a temperature of 120° C. during biaxial orientation; and the membrane is exposed to a temperature of 130° C. during heat setting.

Example 6

[0114] Example 5 is repeated except the polyolefin composition comprises 80% of the first polyethylene resin and 20% of the second polyethylene resin; 25 wt. % of the polyolefin composition is charged into the double-screw extruder; the simultaneous biaxial stretching is conducted while exposing the extrudate to a temperature of 116° C.; the magnification in

the MD dry stretching is 1.3; the membrane is exposed to a temperature of 129° C. during TD dry stretching and the width reduction; and the membrane is exposed to a temperature of 129° C. during heat setting.

Example 7

[0115] Example 6 is repeated except 28.5 wt. % of the polyolefin composition is charged into the double-screw extruder; the extrudate is exposed to a temperature of 117° C. during simultaneous biaxial stretching; the magnification factor in the MD dry stretching is 1.2; the MD dry stretching is conducted while the membrane is exposed to a temperature of 120° C.; the membrane is exposed to a temperature of 128° C. during the TD stretching and the width reduction; and the membrane is exposed to a temperature of 128° C. during the heat setting.

Example 8

[0116] Example 6 is repeated except; the membrane is exposed to a temperature of 90° C. during the MD dry stretching; the membrane is exposed to a temperature of 130° C. during the TD dry stretching and width reduction; the membrane's width is reduced to a magnification of 1.1 fold; and the membrane is exposed to a temperature of 130° C. during the heat setting.

Comparative Example 1

[0117] Example 2 is repeated that the polyolefin composition is produced from 70 wt. % of the first polyethylene and 30 wt. % of the second polyethylene (no polypropylene); the extrudate is exposed to a temperature of 117° C. during the simultaneous biaxial orientation; the membrane was not subjected to dry orientation; and the heat setting temperature is 127° C.

Comparative Example 2

[0118] Example 2 is repeated that the polyolefin composition is produced from 60 wt. % of the first polyethylene, 10 wt. % of the second polyethylene, and 30 wt. % of the polypropylene; the extrudate is exposed to a temperature of 118° C. during the simultaneous biaxial orientation; the membrane was not subjected to MD dry orientation; TD dry orientation was conducted to a magnification of 1.3 while exposing the membrane to a temperature of 125° C., with no reduction in width after TD dry orientation, and (v) and the heat setting temperature is 125° C.

Comparative Example 3

[0119] Comparative Example 2 is repeated that the membrane is subjected to MD dry orientation, with the membrane exposed to a temperature of 115° C. during the MD dry orientation; the MD dry orientation magnification is 1.2 fold; the membrane is exposed to a temperature of 130° C. during the TD dry orientation; and the heat setting temperature is 130° C.

Comparative Example 4

[0120] Comparative Example 3 is repeated except that the polypropylene's Mw is 1.5×10^6 , MWD is 3.2, and heat of fusion is 78 J/g; (ii) the membrane is subjected to TD dry orientation at a magnification of 1.2 fold and then a controlled

reduction in width to a final magnification of 1.0 fold while exposing the membrane to a temperature of 130° C.

Comparative Example 5

[0121] Example 3 is repeated except that the polypropylene has an Mw of 7×10^5 , an MWD of 11, and a heat of fusion of 103 J/g; the extrudate was exposed to a temperature of 113.5° C. during biaxial extrudate stretching, the membrane is exposed to a temperature of 115° C. during the MD dry orientation; the MD dry orientation magnification is 1.3 fold; and the membrane is exposed to a temperature of 127° C. during the TD dry stretching, the controlled reduction in width, and the heat setting.

Comparative Example 6

[0122] Comparative Example 1 is repeated except the polyolefin composition comprises 95 wt. % of the first polyethylene resin, and 5 wt. % of the second polyethylene resin; 40 wt. % of the polyolefin composition is charged into the double-screw extruder; the extrudate is exposed to a temperature of 119° C. during the simultaneous biaxial stretching; there is no

MD dry stretching; the membrane is exposed to a temperature of 119° C. during the TD dry stretching; the TD dry stretching is conducted to a magnification of 1.4 fold; and the membrane is exposed to a temperature of 130° C. during the heat-setting. There is no width reduction step.

Comparative Example 7

[0123] Comparative Example 1 is repeated except the polyolefin composition comprises 80 wt. % of the first polyethylene resin and 20 wt. % of the second polyethylene resin; there is no MD dry stretching; the membrane is exposed to a temperature of 115° C. during TD dry stretching; the TD dry stretching is conducted to a magnification of 1.4 fold; width reduction is conducted to a magnification of 1.0 fold at 126° C.; and the membrane is exposed to a temperature of 126° C. during the heat-setting.

Properties

[0124] The properties of the microporous membranes obtained in the Examples and Comparative Examples are measured by the methods described above. The results are shown in the following tables.

TABLE 1

PROPERTIES	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8
Thickness μm	21.0	19.5	20.4	20.9	20.2	16.3	16.0	16.0
Normalized Air Perm. ($\text{sec}/100 \text{ cm}^3/2 \mu\text{m}$)	320	275	315	250	251	185	150	145
Porosity %	42	37	36	37	37	37	42	43
Normalized Punct. Strength (mN)	4067	3802	3822	4018	4410	3724	4214	3920
Tensile Strength	107800	102900	98000	107800	156800	133770	132300	132300
MD/TD (kPa)	99960	95060	97020	102900	137200	99960	107800	99960
Tensile Elongation	135	150	160	155	125	140	140	140
MD/TD (%)	155	300	290	260	180	160	180	180
Heat Shrinkage 105° C.	7.5	6.0	6.0	6.5	6.5	4.5	2.0	2.7
MD/TD (%)	2.3	1.5	1.6	2.0	1.0	0.8	0.5	1.0
Heat Shrinkage 130° C. TD (%)	13.1	9.4	11.2	10.3	15.0	9.5	5.2	10.0
Elec. Soln. Sorpt. Speed	3.1	3.2	3.1	3.0	3.5	3.9	3.7	3.8
Thick. Var. Aft. Heat Comp. (%)	8.0	9.0	9.0	8.0	7.0	9.0	9.0	9.0
Air Perm. Aft. Heat Comp. (seconds/100 cm^3)	650	600	640	590	480	430	268	258
Shutdown Temp. ° C.	134	134	134	134	132	132	132	133
Meltdown Temp. ° C.	174	173	173	171	149	147	149	148
Max. MD Shrinkage in Molten State (%)	24	22	19	22	20.0	30.5	12.5	12.5
Max. TD Shrinkage in molten state (%)	8.0	2.0	4.0	3.0	5.9	4.4	2.0	5.1

TABLE 2

PROPERTIES	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6	Comparative Example 7
Thickness μm	20.1	21.2	19.6	19.9	21.8	19.5	20.1
Normalized Air Perm. ($\text{sec}/100 \text{ cm}^3/2 \mu\text{m}$)	550	215	197	420	248	250	255
Porosity %	39	46	38	41	40	40	40
Normalized Punct. Strength (mN)	5390	4459	4018	3234	3528	4704	3577
Tensile Strength	181300	102900	106820	82320	90160	117600	107800
MD/TD (kPa)	147000	139160	112700	73500	81340	151900	93100
Tensile Elongation	140	150	160	110	140	150	180
MD/TD (%)	240	145	190	180	200	110	270
Heat Shrinkage 105° C.	6.5	6.5	5.0	5.5	5.0	2.0	6.0
MD/TD (%)	6.0	9.9	6.0	2.7	2.4	3.0	0.0
Heat Shrinkage 130° C. TD (%)	35	38	29	19	17.2	15.7	20.4

TABLE 2-continued

PROPERTIES	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6	Comparative Example 7
Elec. Soln. Sorpt. Speed	1.0	3.3	3.6	2.3	3.4	4.0	1.0
Thick. Var. Aft. Heat Comp. (%)	7.0	12	10.0	14	13	7.0	11
Air Perm. Aft. Heat Comp. (seconds/100 cm ³)	1049	610	490	980	580	550	1445
Shutdown Temp. ° C.	134	134	134	134	134	133	132
Meltdown Temp. ° C.	153	174	174	162	170	144	150
Max. MD Shrinkage In Molten State (%)	38	25	18	25	19	17.5	30.2
Max. TD Shrinkage In Molten State (%)	35	39	34	10.0	10.0	38.0	10.0

[0125] It is noted from Table 1 that the microporous membrane of the present invention exhibits a good balance of important properties such as a TD heat shrinkage at 105° C. of 2.5% or less, a TD heat shrinkage at 130° C. of 15% or less, and a maximum TD shrinkage in the molten state of 10.0% or less, with good mechanical strength and compression resistance. The microporous membranes of the invention also have suitable air permeability, pin puncture strength, tensile rupture strength and tensile rupture elongation, with little variation of thickness and air permeability after heat compression. On the other hand, the microporous membrane products of the Comparative Examples exhibit generally higher air permeability Gurley values, higher air permeability after heat compression Gurley values, and higher maximum TD shrinkage in the molten state.

[0126] Battery separators formed by the microporous polyolefin membranes of the present invention provide batteries with suitable safety, heat resistance, storage properties and productivity.

[0127] All patents, test procedures, and other documents cited herein, including priority documents, are fully incorporated by reference to the extent such disclosure is not inconsistent and for all jurisdictions in which such incorporation is permitted.

[0128] While the illustrative forms disclosed herein have been described with particularity, it will be understood that various other modifications will be apparent to and can be readily made by those skilled in the art without departing from the spirit and scope of the disclosure. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the examples and descriptions set forth herein but rather that the claims be construed as encompassing all the features of patentable novelty which reside herein, including all features which would be treated as equivalents thereof by those skilled in the art to which this disclosure pertains.

[0129] When numerical lower limits and numerical upper limits are listed herein, ranges from any lower limit to any upper limit are contemplated.

1. A monolayer microporous membrane comprising a polyolefin having an $M_w > 1.0 \times 10^6$, the membrane having a normalized air permeability $\leq 4.0 \times 10^2$ seconds/100 cm³/20 μ m, and a heat shrinkage at 130° C. of $\leq 15\%$ in at least one planar direction.

2. The microporous membrane of claim 1, wherein the planar direction is TD and the membrane has heat shrinkage at 105° C. in at least one planar direction of $\leq 2.5\%$.

3. The membrane of claim 1, wherein the membrane has a maximum shrinkage in the molten state in at least one planar direction of $\leq 10.0\%$.

4. The microporous membrane of claim 1, wherein the polyolefin comprises (a) a first polyethylene, and further comprises at least one of (b) polypropylene having an $M_w > 1.0 \times 10^6$ or (c) a second polyethylene having an $M_w > 1.0 \times 10^6$.

5. The microporous membrane of claim 4, wherein the first polyethylene has an M_w in the range of 1.0×10^5 to 9.0×10^5 and an MWD in the range of from 3.0 to 15, the second polyethylene has an M_w in the range of 1.1×10^6 to 5.0×10^6 and an MWD in the range of 4.0 to 20.0, and the polypropylene has an M_w in the range of from 1.05×10^6 to about 2.0×10^6 , an MWD in the range of 2.0 to 6.0, and a $\Delta H_m \geq 100.0$ J/g.

6. The microporous membrane of claim 5, wherein the polyolefin comprises from 60.0 wt. % to 99.0 wt. % of the first polyethylene and from 1.0 wt. % to 40.0 wt. % of the second polyethylene.

7. The microporous membrane of claim 6, wherein the membrane has one or more of (1) a thickness in the range of 1.0 μ m to 50.0 μ m, (2) a porosity in the range of from 25.0% to 80.0%, (3) a normalized pin puncture strength $\geq 3.0 \times 10^3$ mN/20 μ m, (4) a tensile strength $\geq 4.0 \times 10^4$ kPa, (5) a TD tensile elongation $\geq 100\%$, (6) a meltdown temperature $\geq 145^\circ$ C., (7) a shutdown temperature $\leq 140.0^\circ$ C., (8) a thickness variation after heat compression $\leq 20\%$, (9) an air permeability after heat compression $\leq 7.0 \times 10^2$ sec/100 cm³, or (10) TD heat shrinkage at 105° C. in the range of 0.25% to 1.5%.

8. The microporous membrane of claim 4, wherein the polyolefin comprises (a) from 1.0 wt. % to 50.0 wt. % of the polypropylene, (b) from 25.0 wt. % to 99.0 wt. % of the first polyethylene, and (c) from 0.0 wt. % to 50.0 wt. % of the second polyethylene.

9. The microporous membrane of claim 8, wherein the polypropylene is an isotactic polypropylene having an M_w in the range of 1.1×10^6 to 1.5×10^6 , and a ΔH_m in the range of 110 J/g to 120 J/g.

10. The microporous membrane of claim 9, wherein the membrane has one or more of (1) a thickness in the range of 1.0 μ m to 50.0 μ m, (2) a porosity in the range of from 25% to 80.0%, (3) a normalized pin puncture strength $\geq 3.5 \times 10^3$ mN/20 μ m, (4) a tensile strength $\geq 4.0 \times 10^4$ kPa, (5) a tensile elongation $\geq 100\%$, (6) a meltdown temperature $\geq 170.0^\circ$ C., (7) a shutdown temperature $\leq 140.0^\circ$ C., (8) a thickness variation after heat compression $\leq 20\%$, (9) an air permeability after heat compression $\leq 7.0 \times 10^2$ sec/100 cm³, or (10) a TD heat shrinkage at 105° C. in the range of 1.0% to 2.3%.

11. A method for manufacturing a microporous membrane, comprising:

- (a) stretching an extrudate in at least one of MD or TD, the extrudate comprising diluent and a polyolefin having an $M_w > 1.0 \times 10^6$, and then removing at least a portion of the diluent from stretched extrudate to form a membrane having a first length along MD and a first width along TD;
- (b) stretching the membrane in MD from the first length to a second length larger than the first length by a first magnification factor in the range of from about 1.1 to about 1.5 and stretching the membrane in TD from the first width to a second width that is larger than the first width by a second magnification factor in the range of from about 1.1 to about 1.3; and then
- (c) reducing the second width to a third width, the third width being in the range of from the first width to about 1.1 times larger than the first width.

12. The method of claim **11**, wherein the MD and TD stretching of step (a) are each conducted to a magnification factor in the range of 3 fold to 9 fold while the extrudate is exposed to a temperature during stretching in the range of T_{cd} to T_m .

13. The method of claim **11**, further comprising heat setting the membrane following steps (b) and/or (c).

14. The method of claim **11**, wherein during step (b) the MD stretching is conducted before the TD stretching, wherein the first magnification factor is $>$ the second magnification factor, and wherein

- (i) the MD stretching is conducted while the membrane is exposed to a first temperature in the range of $T_{cd} - 30^\circ \text{C}$. to about $T_m - 10^\circ \text{C}$. and
- (ii) the TD stretching is conducted while the membrane is exposed to a second temperature that is higher than the first temperature but lower than T_m ; and

wherein the reducing of step (c) is conducted while the membrane is exposed to a temperature $\geq$ the second temperature.

15. The method of claim **11**, wherein the polyolefin comprises (a) a first polyethylene, and further comprises at least one of (b) polypropylene having an $M_w > 1.0 \times 10^6$ or (c) a second polyethylene having an $M_w > 1.0 \times 10^6$.

16. The method of claim **15**, wherein the second polyethylene has an M_w in the range of 1.1×10^6 to about 5.0×10^6 and an MWD in the range of 4.0 to 20.0, the first polyethylene has an M_w in the range of 1.0×10^5 to 9.0×10^5 and an MWD in the range of from 3.0 to 15.0, and the polypropylene has an M_w in the range of from 1.05×10^6 to about 2.0×10^6 , an MWD in the range of 2.0 to 6.0, and a $\Delta H_m \geq 100.0 \text{ J/g}$

17. The method of claim **16**, wherein the polyolefin comprises from 60.0 wt. % to 99.0 wt. % of the first polyethylene and from 1.0 wt. % to 40.0 wt. % of the second polyethylene.

18. The method of claim **15**, wherein the polyolefin comprises (a) from 1.0 wt. % to 50.0 wt. % of the polypropylene, (b) from 25.0 wt. % to 99.0 wt. % of the first polyethylene, and (c) from 0.0 wt. % to 50.0 wt. % of the second polyethylene.

19. The method of claim **18**, wherein the polypropylene is an isotactic polypropylene having an M_w in the range of 1.1×10^6 to 1.5×10^6 , and a ΔH_m in the range of 110 J/g to 120 J/g.

20. (canceled)

21. A battery comprising an anode, a cathode, an electrolyte, and a monolayer microporous membrane comprising polypropylene having an $M_w > 1.0 \times 10^6$, the membrane having a normalized air permeability $\leq 4.0 \times 10^2$ seconds/100 $\text{cm}^3/20 \mu\text{m}$, and a heat shrinkage at 105°C . in at least one planar direction $\leq 2.5\%$; wherein the microporous membrane separates at least the anode from the cathode.

22-23. (canceled)

* * * * *