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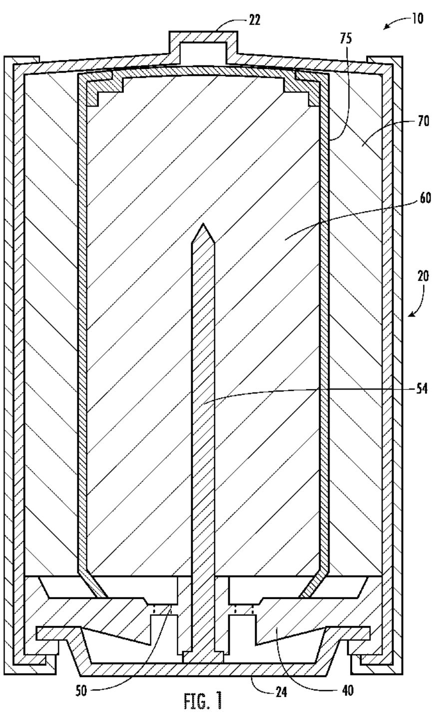

FIG. 1

(57) **Abstract:** Batteries, battery separators and methods of making such separators are provided. The separators can be used in various primary and secondary batteries. A battery separator includes a base layer comprising about 20% to about 50% by weight polyvinyl alcohol (PVA) and about 50% to about 80% by weight cellulose or a cellulose and a second layer in contact with the first layer and comprising PVA and a polysaccharide. The separator has a maximum pore size of less than about 2 μm and a mean pore size of less than about 1 μm. The difference between the maximum and mean pore sizes is less than about 2 μm, which decreases the overall distribution of pore sizes within the separator, thereby improving its performance.

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BATTERY SEPARATORS WITH REDUCED PORE SIZES

CROSS-REFERENCE TO RELATED APPLICATION

[0001] The present application is related and has right of priority to U.S. Provisional Patent Application No. 63/598,615 filed on November 14, 2023, which is incorporated by reference in its entireties for all purposes.

TECHNICAL FIELD

[0002] This description generally relates to primary and secondary batteries, battery separators and methods of making such separators and more particularly to a battery separator having a reduced pore size.

BACKGROUND

[0003] Separator papers for primary and secondary batteries serve as a mechanical barrier between the electrodes to prevent shorting while allowing for ionic transport through the electrolyte in the pores. Separators should have good mechanical integrity, chemical inertness, well-defined and consistent porosity and tortuosity in order to uniformly transport the ions between the electrodes. Separator papers used in such batteries often comprise blends of polyvinyl alcohol (PVA) fibers and cellulose, such as dissolving pulp, rayon or lyocell.

[0004] Using fibers in the manufacturing of battery separators provides numerous benefits. In addition to allowing for various fiber compositions, separators made from fibers may be designed at various levels of basis weight. The availability of low count PVA, as well as rayon fibers, has enabled a trend toward lighter material, targeting space savings in the cells to permit higher amounts of active material and enhance discharge performance. The use of fibers in the manufacturing of battery separators also contributes significantly to reduced costs as compared to more traditional polyolefin materials.

[0005] Furthermore, battery separators made from fibers allow for reduced pore sizes to help control the generation of dendrites which may hinder performance, or in some cases, cause short circuits. Reduced pore size also allows for battery separators to better block the penetration of active components of the electrode materials and any conductive additives.

SUMMARY

[0006] Batteries and battery separators are provided for use in a variety of different batteries, including, but not limited to, primary, secondary and/or stationary batteries, such as zinc-manganese dioxide (Zn/MnO_2), nickel-cadmium (Ni-Cd,), lithium-ion (Li-ion), nickel-hydrogen ($Ni-H_2$) batteries and the like.

[0007] In one aspect, a two-layer alkaline battery separator comprises a first base layer of about 20% to about 50% by weight polyvinyl alcohol (PVA) and about 50% to about 80% by weight cellulose based on the total dry weight of the first base layer, and a second layer in contact with a surface of the first base layer. The second layer comprises PVA and a polysaccharide. The separator has a maximum pore size of less than about 2.0 μm.

[0008] In various embodiments, the second layer comprises a coating adhered to a surface of the base layer. Applying the coating to the base layer further tightens the pore size, while keeping the wet ionic resistance or electrical resistance (also referred to as ionic resistivity and measured according to ASTM Test E7148-19 (2019)) from increasing to undesirable ranges. The base layer essentially functions as a ground layer that provides liquid absorption properties and a relatively tight pore structure, while the coating functions as a finishing layer that further tightens the porous structure and provides improved short circuit shielding. In addition, providing only two layers for the battery separator facilitates manufacturing and reduces the overall cost of the separator.

[0009] In embodiments, the separator consists of only the base layer and the coating. The coating has a relatively low basis weight compared to the base layer to mitigate the increase in ionic resistance across the separator. The ratio of the basis weight of the base layer to the coating layer may be about 2 to about 12, such as from about 2 to about 5 or from about 5 to about 8.

[0010] In embodiments, the maximum pore size of the separator is less than about 1.8 μm or about 1.6 μm or less.

[0011] In embodiments, the mean pore size of the separator is less than about 1.0 µm or about 0.7 µm or less.

[0012] In embodiments, the difference between the maximum pore size and the mean pore size of the separator is less than about 2.0 µm, or less than about 1.0 µm. Minimizing the difference between the maximum and mean pores sizes (i.e., the pore size distribution) of the separator improves the overall performance of the battery.

[0013] In embodiments, the base layer comprises a blend of polyvinyl alcohol and one of lyocell fibers, viscose fibers, dissolving pulp, mercerized pulp or a combination thereof. The base layer may include PVA in a percentage by dry weight of about 20% to about 50%, or about 35% to about 45%. In an exemplary embodiment, the PVA is present in the first layer in about 40% by dry weight. The cellulose may be present in a percentage by dry weight of about 50% to about 80% of the first layer, or about 55% to about 65%. In an exemplary embodiment, the cellulose comprises lyocell fibers and can be present in an amount of about 60% of the base layer based on the total dry weight of base layer.

[0014] In embodiments, the PVA in the first layer comprises non-soluble PVA fibers and a water soluble PVA binder. The PVA binder is generated by water soluble PVA fibers that change shape as water evaporates from the separator. In embodiments, the first layer comprises about 20% to about 30% by dry weight non-soluble PVA fibers, or about 25% by dry weight non-soluble PVA fibers, and about 10% to about 20% by dry weight water soluble PVA binder, or about 15% by dry weight water soluble PVA binder.

[0015] In embodiments, the non-soluble PVA fibers have a linear density greater than about 0.3 denier, or about 0.4 to about 0.6 denier, or about 0.5 denier. In other embodiments, the linear density is about 1.0 denier.

[0016] In embodiments, the polysaccharide in the second coating layer comprises a material selected from cellulose fibers, cellulose nanofilaments, microcrystalline cellulose, microcrystalline cellulose gel, starch, carboxymethyl cellulose (CMC), hydroxypropyl methylcellulose (HPMC), alginate, micro fibrillated cellulosic fibers, or combinations thereof. In one such embodiment, the coating comprises microcrystalline cellulose or microcrystalline cellulose gel in a percentage by dry weight of at least about 20%, or at least about 40% of the coating layer. In an exemplary embodiment, the gel is present in a percentage by weight of about 50% of the coating layer based on the total dry weight of coating.

[0017] The coating layer further comprises PVA, such as a high molecular weight PVA resin, or a water soluble PVA resin. In one embodiment, the second layer comprises PVA in a percentage by dry weight of at least about 20%, or at least about 40% of the coating layer. In an exemplary embodiment, the PVA is present in a percentage by dry weight of about 50% of the coating layer.

[0018] The ionic resistance of the separator is less than about 100 mOhm·cm^2, or less than about 95 mOhm·cm^2, or less than about 90 mOhm·cm^2, or less than about 80 mOhm·cm^2, or less than about 60 mOhm·cm^2. The KOH absorption of the separator may be at least about 80 g/m^2, or from about 80 g/m^2 to about 200 g/m^2 or about 100 g/m^2 to about 130 g/m^2.

[0019] The Gurley Air Resistance of the separator is at least about 500 sec/100ml, or at least about 750 sec/100ml, or at least about 1,000 sec/100ml, or at least about 1,450 sec/100ml. This relatively high air resistance reduces the amount of air that passes through the separator, which improves the overall performance of the battery.

[0020] In another aspect, a battery is provided comprising the separator described above. The battery may comprise a primary or a secondary battery, which may comprise a stationary battery. In various embodiments, the battery comprises a zinc-manganese dioxide (Zn/MnO_2), a nickel-cadmium (Ni-Cd,), a lithium-ion (Li-ion) or a nickel-hydrogen ($Ni-H_2$) battery.

[0021] In another aspect, a battery separator consists of a first layer of about 20% to about 50% by dry weight of polyvinyl alcohol (PVA) and about 50% to about 80% by dry weight cellulose and a coating in contact with a surface of the first layer. The coating comprises PVA and a polysaccharide. The ratio of basis weight of the first layer to the coating is about 2 to about 12.

[0022] In various embodiments, the ratio of basis weight of the first layer to the coating is about 2 to about 5, or about 5 to about 8.

[0023] In embodiments, the maximum pore size of the separator is less than about 2.0 µm, or less than about 1.8 µm or about 1.6 µm or less. In embodiments, the mean pore size of the separator is less than about 1.0 µm or about 0.7 µm or less. In embodiments, the difference between the maximum pore size and the mean pore size of the separator is less than about 2.0 µm, or less than about 1.0 µm.

[0024] In embodiments, the first layer comprises PVA in about 40% by weight and lyocell fibers in about 60% by weight based on the total dry weight of the first layer. The PVA may comprise both non-soluble PVA fibers and a water soluble PVA binder. The second layer comprises microcrystalline cellulose gel in a percentage by dry weight of about 50% and PVA, such as high molecular weight PVA resin, in a percentage by dry weight of about 50% of the coating layer.

[0025] In another aspect, a battery is provided comprising the separator described above. The battery may comprise a primary or a secondary battery, such as a stationary battery. In various embodiments, the battery comprises a zinc-manganese dioxide (Zn/MnO_2), nickel-cadmium (Ni-Cd,), lithium-ion (Li-ion) or nickel-hydrogen ($Ni\text{-}H_2$) battery.

[0026] In another aspect, an alkaline battery separator comprises a first layer of about 20% to about 50% by dry weight of polyvinyl alcohol (PVA) and about 50% to about 80% by dry weight cellulose, and a second layer of PVA and a polysaccharide in contact with a surface of the first layer. The difference between a maximum pore size and a mean pore size of the separator is less than about 2.0 µm, or less than about 1.0 µm.

[0027] In embodiments, a ratio of the maximum pore size to the mean pore size of the separator is about 1.0 to about 4.0 or about 1.5 to about 2.5. The maximum pore size may be less than about 300% of the mean pore size or less than about 250%.

[0028] In embodiments, the separator consists of only the first base layer and the second layer. In embodiments, the ratio of basis weight of the first layer to the second layer may be about 2 to about 12, or about 2 to about 5, or about 5 to about 8.

[0029] In another aspect, a battery is provided comprising the separator described above.

BRIEF DESCRIPTION OF THE DRAWINGS

[0030] The accompanying drawing, which is incorporated in and constitutes a part of this specification, illustrate an embodiment of the disclosure and, together with the description, serves to explain the principles of the disclosure.

[0031] FIG. 1 is a cross-sectional view of an alkaline battery;

[0032] FIG. 2A illustrates a cylindrical secondary battery;

[0033] FIG. 2B illustrates a flat jelly roll secondary battery;

[0034] FIG. 2C illustrates a stack of unit cells in a secondary battery;

[0035] FIG. 3A is a side view of a single sheet stacking arrangement for a secondary battery;

[0036] FIG. 3B is a side view of a Z-stacking arrangement for a secondary battery;

[0037] FIG. 3C is a side view of a cylindrical winding stacking arrangement for a secondary battery;

[0038] FIG. 3D is a side view of a prismatic winding stacking arrangement for a secondary battery; and

[0039] FIG. 4 is a cross-sectional view of a battery separator for an alkaline battery

DETAILED DESCRIPTION

[0040] This description and the accompanying drawings illustrate exemplary embodiments and should not be taken as limiting, with the claims defining the scope of the present disclosure, including equivalents. Various mechanical, compositional, structural, and operational changes may be made without departing from the scope of this description and the claims, including equivalents. In some instances, well-known structures and techniques have not been shown or described in detail so as not to obscure the disclosure. Like numbers in two or more figures represent the same or similar elements. Furthermore, elements and their associated aspects that are described in detail with reference to one embodiment may, whenever practical, be included in other embodiments in which they are not specifically shown or described. For example, if an element is described in detail with reference to one embodiment and is not described with reference to a second embodiment, the element may nevertheless be claimed as included in the second embodiment. Moreover, the depictions herein are for illustrative purposes only and do not necessarily reflect the actual shape, size, or dimensions of the system or illustrated components.

[0041] It is noted that, as used in this specification and the appended claims, the singular forms “a,” “an,” and “the,” and any singular use of any word, include plural references unless expressly and unequivocally limited to one reference. As used herein, the term “include” and its grammatical variants are intended to be non-limiting, such that recitation of items in a list is not to the exclusion of other like items that can be substituted or added to the listed items.

[0042] Batteries and battery separators and methods of making such separators are provided herein. The battery separators have reduced pore sizes to control the generation of dendrites and block the penetration of active components of the electrode materials and any conductive additives, while still maintaining desirable wet ionic resistance, thickness and absorption performance properties. The separators can be used in various batteries, including, but not limited to, primary and secondary batteries, such as stationary batteries, zinc-manganese dioxide (Zn/MnO_2), nickel-cadmium (Ni-Cd,), lithium-ion (Li-ion), nickel-hydrogen ($Ni\text{-}H_2$) batteries and the like.

[0043] In certain embodiments, as represented in FIG. 1, an alkaline battery 10 comprises a generally cylindrical casing 20 having positive and negative terminals 22, 24 extending from opposite sides of casing 20. Battery 10 may further include a protective cap 40, a pressure expansion seal 50 and a current collector 54, such as a brass pin. The battery 10 includes an anode 60 and a cathode 70. The cathode 70 may comprise, for example, a compressed paste of manganese dioxide with carbon powder added for increased conductivity. Anode 60 may comprise, for example, a dispersion of zinc powder in a gel containing a potassium hydroxide electrolyte. The hollow center of cathode 70 is lined with an ion conducting separator 75, which prevents contact of the electrode materials and short-circuiting of the cell. Battery 10 may comprise one or more layers of separator 75, with each layer comprising fibers as described below.

[0044] FIGS. 2A-2C illustrate various embodiments of secondary batteries that may incorporate the separators described herein, such as rechargeable batteries including nickel-cadmium (Ni-Cd), nickel-metal hydride (Ni-MH), and lithium-ion (Li-ion). In these batteries, an insulating sheet is laid down, then a thin layer of an anode material is laid down, a separator layer is applied, and a cathode material is layered on top. This sandwich is then rolled up and inserted into a hollow cylinder casing. The battery is sealed, metal contacts are attached, and an optional button top is applied if the battery is intended to replace an AAA/AA/C/D alkaline battery.

[0045] FIG. 2A illustrates a cylindrical secondary battery 100 that includes a cathode 110, an anode 120 and a separator 130. FIG. 2B illustrates a flat jelly roll secondary battery 200 that comprises a cathode 210, an anode 220 and a separator 230. FIG. 2C illustrates a representative stacking arrangement 250 of unit cells 260 that each include a cathode 262, a separator 264 and an anode 266.

[0046] FIGS. 3A-3D illustrate alternative stacking arrangements for secondary or rechargeable batteries incorporated the separators described herein. FIG. 3A illustrates a single sheet stacking arrangement 300 that comprises an anode 302, a cathode 304 and a separator 306. FIG. 3B illustrates a Z-stacking arrangement 310 that comprises an anode 312, a cathode 314 and a separator 316. The stacking process alternately stacks the cathode and anode and the separator through the sheet feeding mechanism to form stacked cores, which can produce regular-shaped or, for example, special-shaped lithium batteries with higher flexibility.

[0047] FIG. 3C illustrates a cylindrical winding stacking arrangement 320 that comprises an anode 322, a cathode 324 and a separator 326. FIG. 3D illustrates a prismatic winding stacking arrangement 330 that comprises an anode 332, a cathode 334 and a separator 336. The winding process generally comprises rolling the slitted cathode and anode and the separator together by controlling the speed, tension, relative position, etc. of the pole pieces. The characteristics of the process are particularly useful for lithium batteries with regular shapes.

[0048] In one embodiment, as represented by FIG. 4, a separator 80 for a battery comprises a first base layer 85 and a second coating layer 95. Base layer 85 comprises polyvinyl alcohol (PVA) and cellulose. The cellulose used in the base layer of the battery separator may include, but is not limited to, natural cellulose (wood fiber and pulp, cotton, hemp, etc.) and regenerated cellulose (e.g., rayon, viscose and/or Lyocell fibers). In embodiments, the second layer could include nanofilaments, micro fibrillated cellulosic fibers, microcrystalline cellulose or microcrystalline cellulose gel combinations thereof. In embodiments, the fibers of the second layer may be replaced or mixed with highly refined dissolving pulp or mercerized pulp, or a blend of these pulps with the cellulosic fibers. The base layer may include PVA in a percentage (by dry weight) of about 20% to about 50%, or about 35% to about 45%. In an exemplary embodiment, the PVA is present in about 40% by dry weight. The base layer may include cellulose in a percentage (by dry weight) of about 50% to about 80%, or about 55% to about 65%. In an exemplary embodiment, the cellulose comprises lyocell fibers present in about 60% by dry weight.

[0049] In embodiments, the PVA in the first layer initially comprises both water soluble PVA fibers and PVA fibers that are substantially insoluble at temperatures below about 40°C. This results in a first layer that comprises both PVA fibers and a water soluble PVA binder. The PVA binder is generated by the water soluble PVA fibers that change shape as water evaporates from the separator. The water insoluble PVA fibers maintain their shape during this evaporation process. In embodiments, the first layer comprises about 20% to about 30% by dry weight non-soluble PVA fibers, or about 25% by weight non-soluble PVA fibers, and about 10% to about 20% by weight soluble PVA binder, or about 15% by weight soluble PVA binder.

[0050] The non-soluble PVA fibers have a linear density greater than about 0.3 denier, or about 0.4 to about 0.6 denier, or about 0.5 denier. In other embodiments, the linear density is about 1 denier.

[0051] The base layer has a maximum pore size of less than about 5 µm prior to applying the coating layer (discussed below). In certain embodiments, the maximum pore size is less than about 3 µm, or about 2.8 µm or less.

[0052] In embodiments, the base layer has a mean pore size of less than about 1 µm, or about 0.6 µm or less prior to applying the coating layer. The difference between the maximum pore size and a mean pore size of the base layer is less than about 3 µm, or equal to or less than about 2.2 µm.

[0053] As shown in FIG. 4, separator 80 comprises the base layer 85 as described above and a second coating layer 95 comprising PVA and a polysaccharide . The second layer is in contact with at least one major surface of the base layer, preferably a single side of the base layer.

The coating layer has a relatively low basis weight and thickness to mitigate the increase in ionic resistance across the separator. The ratio of basis weight of the first layer to the second layer may be about 2 to about 12, or about 2 to about 5, or about 5 to about 8.

[0054] The polysaccharide used in the coating layer of the battery separator may include, but is not limited to, natural cellulose (wood fiber and pulp, cotton, hemp, etc.) and regenerated cellulose (e.g., rayon and Lyocell fibers). In embodiments, the polysaccharide of the second layer may be nanofilaments, micro fibrillated cellulosic fibers or microcrystalline cellulose or cellulose gel. In embodiments, the polysaccharide may comprise starch, carboxymethyl cellulose (CMC), hydroxypropyl methylcellulose (HPMC), alginate or combinations thereof. In an exemplary embodiment, the cellulose comprises microcrystalline cellulose gel having a basis weight of about 0.5 g/m^2 to about 8 g/m^2, or about 1 g/m^2 to about 4 g/m^2 or about 3 g/m^2.

[0055] The coating layer may include PVA in a percentage (by dry weight) of about 40% to about 60%, or about 45% to about 55%. In an exemplary embodiment, the PVA comprises high molecular weight PVA resin in about 50% by dry weight. The coating layer may include cellulose in a percentage (by dry weight) of about 40% to about 60%, or about 45% to about 55%. In an exemplary embodiment, the cellulose comprises microcrystalline cellulose gel present in about 50% by dry weight.

[0056] Applying the coating to the first layer further tightens the pore size, while keeping the wet ionic resistance from increasing to undesirable ranges. The first layer essentially functions as a ground layer that provides liquid absorption properties and a relatively tight pore structure, while the coating functions as a finishing layer that further tightens the porous structure and provides improved short circuit shielding.

[0057] In embodiments, the separator (with the coating layer applied to a surface of the base layer) has a maximum pore size of less than about 2.0 µm, or less than about 1.8 µm or equal to or less than about 1.6 µm. In embodiments, the mean pore size of the separator is less than about 1.0 µm or less than about 0.7 µm. In embodiments, the difference between the maximum pore size and the mean pore size of the separator is less than about 2.0 µm, preferably less than about 1.0 µm.

[0058] The ionic resistance of the separator is less than about 100 mOhm·cm², or less than about 95 mOhm·cm², or less than about 90 mOhm·cm², or less than about 80 mOhm·cm², or less than about 60 mOhm·cm². The KOH absorption of the separator may be at least about 80 g/m², or from about 80 g/m² to about 140 g/m² or about 100 g/m² to about 200 g/m².

[0059] The Gurley Air Resistance of the separator is at least about 500 sec/100 ml, or at least about 750 sec/100 ml, or at least about 1,000 sec/100 ml, or at least about 1,450 sec/100 ml. This relatively high air resistance reduces the amount of air that passes through the separator, which improves the overall performance of the battery.

[0060] Generally, a method of making the separators described above includes a first step of forming a base layer by highly fibrillating a cellulose, for example, lyocell fibers, and optionally, cellulose. The lyocell manufacturing process mainly consists of five steps (Fink *et al.* 2001; Rosenau *et al.* 2001; Biganska and Navard 2005; Bredereck and Hermanutz 2005; Hauru *et al.* 2014):

[0061] 1) Dissolution: This step includes the disintegration of the pulp fibers and mixing with the solvent. Cellulose is dissolved in an aqueous system containing NMMO to form a dope of high viscosity. The pulp dissolution for the lyocell process is much simpler than that of the viscose process, where the dissolution of dissolving pulp consists of the mercerization stage (steeping with sodium hydroxide), aging, and xanthation using carbon disulfide.

[0062] 2) Filtration: The formed dope is filtered to remove coarse components. In comparison, the purification of the viscose process includes ripening, filtering, and degassing.

[0063] 3) Spinning regeneration: The dope is extruded through an orifice spinneret into an air gap, and then regenerated in a coagulation bath. In contrast to this, the production of viscose rayon requires a wet spinning process in an acid bath.

[0064] 4) Washing: The resulting lyocell fibers are washed and the residual NMMO is recovered and recycled; while the viscose fibers are also washed for removal of the residual CS2, the high volatility of CS2 may lead to its loss *via* evaporation, causing a negative environmental impact for the viscose process.

[0065] 5) Finishing: This step involves post-treatment of the fibers, including bleaching, finishing, and drying.

[0066] Cellulose fibrillation can be achieved using mechanical refiners such as a single disc refiner, a double disc refiner, a conical refiner, a rotating cylinder refiner, or other types of refiners used to mechanically grind or process cellulose or regenerated celluloses to fibrillate the fibers. The feed material for this process may be previously treated cellulosic material (such as wood chips, annual plants, etc.) formed into pulp. The previous treatment of the cellulosic material to produce pulp used as the feed material can be a result of chemical digestion, such as Kraft cooking, sulfite cooking, soda cooking, etc., mechanical refining, a combination of chemical digestion and refining, or other known processes.

[0067] A first layer is a wet laid paper layer. The first layer can be formed from an aqueous suspension of PVA fibers, PVA binder and refined cellulose fibers. In one embodiment, in forming the first layer, the aqueous suspension of fibers is deposited onto a porous forming surface (such as a flat wire, incline wire or cylinder formers) that allows water to drain thereby forming the web. During the drying process, water is evaporated from the base layer and at least some portion of the PVA fibers (i.e., the water-soluble fibers) changes shape as the water evaporates to form a PVA binder. A surfactant or wetting agent may subsequently be added after the drying of first layer by size-press, applicator roll, film-press, or spray to improve the wettability of the first layer, although in some embodiments, no wetting agent is used during this process. Suitable surfactants include, but are not limited to, ethoxylated fatty alcohols, alkyl polyglycoside, such as cocamidopropyl betaine and the like. The base layer material may be present in an amount between about 10 g/m^2 to 40g/m^2, in embodiments, in amounts between about 20 to 25 g/m^2.

[0068] In certain embodiments, a coating layer is created by blending water soluble polymers (e.g. polyvinyl alcohol resin) and microcrystalline cellulose gel, to create a blend of polyvinyl alcohol and microcrystalline cellulose gel. A surfactant or wetting agent may subsequently be added to the blend to improve the wettability of the second layer, or, in some embodiments, no wetting agent is used during this process. The second layer material may be present in an amount between 0.1 g/m^2 to 10 g/m^2, in embodiments, in amounts between 2.5 to 5.0 g/m^2, in yet another embodiment, in an amount that is about 3.0 to 3.5 g/m^2.

[0069] The second layer is used to coat a single side of the first layer, preferably the top of the second layer, to further tighten the pore size while keeping the wet ionic resistance from increasing to undesirable ranges. The coating technology used to apply the coating may be a bar coating, air knife coating, a curtain coating, a roll coater, slot die coater, spray coater, or a flexography printer with engraved anyloxed rolls.

EXAMPLES

[0070] The following non-limiting examples of illustrative battery separators were manufactured in accordance with the methods described above, with steps omitted where appropriate. Applicant manufactured and tested two different embodiments of battery separators: (1) a battery separator having a single layer of highly fibrillated lyocell fibers (i.e., cellulose) and polyvinyl alcohol (PVA) fibers and a PVA binder, wherein the lyocell fibers comprise about 60% by dry weight of the battery separator and the PVA fibers comprise about 40% by dry weight ("Single Layer"). The PVA fibers comprise about 25% by dry weight of the separator and the PVA binder comprises about 15% of the separator; and (2) a battery separator having a base layer of highly fibrillated lyocell fibers (i.e., cellulose) and polyvinyl alcohol (PVA) fibers and a PVA binder, wherein the lyocell fibers comprise about 60% by dry weight of the battery separator and the PVA fibers comprise about 40% by dry weight ("Single Layer"). The PVA fibers comprise about 25% by dry weight of the separator and the PVA binder comprises about 15% of the separator; and a second coating layer of high molecular weight PVA resin and a polysaccharide wherein the PVA resin and the polysaccharide each comprise about 50% by dry weight of the second layer ("Bi-Layer"). In Sample Nos. 1 through 3 and 6 through 8, the polysaccharide is a microcrystalline cellulose gel. In Sample No. 4, the polysaccharide is a starch. In Sample 5, the polysaccharide is an alginate.

[0071] Applicant measured various parameters of the Single Layer and Bi-Layer battery separators, including the basis weight in g/m^2 in compliance with ISO standard 536:2012, the thickness under 100 kPa (µm) in compliance with ISO standard 534:2011, the bulk index under 100 kPa [-] is calculated as a ratio of thickness to basis weight, the KOH Absorption in g/m^2 under a standard method of the industry which are further detailed below, the Gurley Air Resistance {s/100mL} in compliance with ISO standard 5636-5:2013, the mean pore size in µm, the largest or maximum pore size in µm, are measured according the description below. The ratio and deltas of the maximum pore size to the mean pore size are calculated with the measured pore sizes. The electrical resistance (mOhm·cm^2) is measured under standard methods of the industry which are further described below . All measurements were completed in an air-controlled room according to ISO 187:1993. The results of these measurements are shown below in Table 1 (Single Layer) and Table 2 (Bi-Layer).

[0072] The KOH Absorption in g/m^2 is measured as follows:

[0073] Separator material was cut into 100 mm x 100 mm square sheets. Specimen surface size was named A and its unit is m^2. Each 100 mm x 100 mm square specimen was individually weighed on a scale to determine the initial specimen weight. The initial specimen weight was named W_1. Then, each 100 mm x 100 mm specimen was individually soaked into a bath of caustic electrolyte. Such caustic electrolyte has a mass concentration of 34% Potassium Hydroxide and 2% Zinc Oxide. Electrolyte bath height was at least 1 cm. The whole 100 mm x 100 mm specimen was immerged flat and laid down flat at the bottom of the bath container for 10 minutes. After 10 minutes of immersion, the specimen 100 mm x 100 mm specimen was collected and maintained vertically, pinched by one of its 4 corners and let drained by gravity for 1 minute. The wet 100 mm x 100 mm specimen was then weighed on a scale to determine its wet weight named W_2. KOH Absorption in g/m^2 was calculated according to hereafter formula: KOH absorption (g/m^2) = $\frac{W_2 - W_1}{A}$.

[0074] The mean pore size in µm and the max pore size in µm was measured using a capillary flow porometers. In the literature, the mean pore size is also named Mean Flow Pore Size and the max pore size is also named Bubble Point Diameter or Largest Pore Size. In these embodiments, a capillary flow porometer from Porous Materials INC., model IPore-1100A with one holder setup was used to determine the mean pore size in µm and the max pore size in µm. The determination of the mean pore size and the max pore size was performed according to the manual of IPore-1100A porometer with use of the dry and wet curves method. The wetting liquid selected to determine the mean pore size and the max pore size was Galwick fluid having a surface tension of 15.9 dynes/cm. The used pressure range was between 0 and 100 psi and maximum flow rate was 160000 cc/min. In software “PMI Capwin software” it exists a default testing program.

To characterize this invention this program with following modifications was used:

Program parameters	Default values	Used values
Bubble flow	2 cc/min	10 cc/min
(Flow rate / Pressure change) * Time	50 F/PT	200 F/PT
Equilibrium iterations	5	3
Average iterations	20	15
Valve 2 incrementation	2 counts	7 counts
Pressure regulation incrementation	1.25 counts	0.25 counts

. Calculation of mean and max pore sizes is given by equipment. The delta (or difference) was calculated using the hereafter formula: Delta = Max Pore Size − Mean Pore Size and Delta was measured in µm.

[0075] The electrical resistance in mOhm·cm², noted ER, was determined according to ASTM D 7148A. In the literature, the electrical resistance in mOhm·cm² is also named ionic resistivity. The electrical resistivity was determined by using a jig with two bottom and top right cylindrical graphite electrodes having a diameter of 1 inch and 1.25 inches respectively. Each electrode included a current collector inserted in one of its circular base areas; the current collectors were connected to an impedance tester using electrical cables. The bottom electrode was immobile and mounted in a platform in such a way that one of its circular base areas was facing upwards, parallel to the ground and its opposite circular base area, having a current collector build in was facing downwards. The second top electrode was mobile. Each electrode's circular base areas non-connected to current collector was evenly polished using sandpaper. The two graphite electrodes were placed vertically in such a way that their respective polished base areas were facing one another. A caustic electrolyte was also used to determine the electrical resistance of a separator material. The caustic electrolyte had a mass concentration of 40% Potassium Hydroxide.

[0076] To determine the electrical resistance, the caustic electrolyte was applied on the bottom electrode polished base area in sufficient amount to cover the whole polished surface. To determine the overall electrical resistance of the wetted electrodes noted RC in Ohm, the second top electrode was set on top of the bottom electrode previously wetted using the caustic electrolyte in such a way that the caustic electrolyte formed a thin liquid interface in between the two electrodes. The RC value was read on the impedance tester. The total resistance of separator specimen, caustic electrolyte film and electrodes was noted RT in Ohm. RT was determined by placing a separator specimen previously soaked with the caustic electrolyte in between the two wetted electrodes. The RT value was read on the impedance tester. The separator specimen had a disk shape and 1 inch diameter. The separator specimen area was noted S and measured in cm^2. To guarantee that the porosity of separator specimen was fully soaked with the caustic electrolyte, the separator specimen remained at least 20 minutes fully immerged in a beaker containing the caustic electrolyte. To calculate the electrical resistance of separator ER in $Ohm{\cdot}cm^2$, the formula used was: $\mathrm{ER} = (RT - RC) \cdot \frac{S}{\text{Number of separator specimens}}$. Only one separator specimen was tested to determine its ER.

TABLE 1: Single Layer

Parameter	Sample 1	Sample 2	Sample 3
Basis Weight [g/m^2]	24	25.3	19.5
Thickness [μm]	69	68	54
Bulk Index (Basis weight/ thickness)	2.88	2.69	2.77
Basis Weight: 1st Layer [g/m^2]	24	25.3	19.5
Thickness: 1st Layer [μm]	69	68	54

Basis Weight: 2nd Layer [g/m²]	N/A	N/A	N/A
KOH Absorption [g/m²]	118	127	103
Mean Pore Size [µm]	0.5	0.5	0.6
Max Pore Size [µm]	2.2	2.6	2.8
Ratio between Max Pore Size and Mean Pore Size	4.4	5.1	4.8
Delta between Max Pore Size and Mean Pore Size [µm]	1.7	2.1	2.2
Ionic Resistivity [mOhm·cm²]	40	39	31
Gurley Air Resistance [second / 100mL]	15	13	9

[0077] As shown in Table 1, the single layer battery separator demonstrated reduced pore sizes, while maintaining the desirable wet ionic resistance and absorption performance. The mean pore sizes of the separators were all equal to or less than about 0.6 µm and the maximum pore sizes were all equal to or less than about 2.8 µm. The difference between the maximum and mean pore sizes ranged from about 1.7 µm to about 2.2 µm. In sample 1, a wetting agent or surfactant was not present in the separator and the maximum pore size was only about 2.2 µm.

[0078] At the same time, the electrical resistance of the separators were all less than 40 mOhm·cm$^{2.}$ The Gurley Air Resistance was in the range of 13 to 15 s/100mL and the KOH

Absorption was between about 103 g/m^2 and 127 g/m^2 or

TABLE 2: Bi-Layer

Parameter	Sample 1	Sample 2	Sample 3
Basis Weight [g/m^2]	27.3	28.6	22.9
Thickness [µm]	73	73	59
Bulk Index (Basis weight/ thickness)	2.67	2.55	2.58
Basis Weight: 1st Layer [g/m^2]	24	25.3	19.5
Thickness: 1st Layer [µm]	69	68	54
Basis Weight: 2nd Layer [g/m^2]	3.3	3.3	3.4
Thickness: 2nd Layer [µm]	5	5	5
KOH Absorption [g/m^2]	113	119	101
Mean Pore Size [µm]	Not Detected	0.7	0.7
Max Pore Size [µm]	0.1	1.3	1.6

Ratio between Max Pore Size and Mean Pore Size	_	1.95	2.2
Delta between Max Pore Size and Mean Pore Size[µm]	_	0.6	0.9
Ionic Resistivity [mOhm·cm²]	59	46	41
Gurley Air Resistance [second / 100mL]	45,200	2,765	1,455
Basis Weight Ratio	7.27	7.67	5.74

TABLE 2 (cont): Bi-Layer

Parameter	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8
Basis Weight [g/m^2]	29.0	29.3	29.7	30.8	33.0
Thickness [µm]	68	68	71	73	77
Bulk Index (Basis weight/ thickness)	2.34	2.32	2.39	2.37	2.33
Basis Weight: 1st Layer [g/m²]	26.0	26.0	25.0	25.0	25.0
Thickness: 1st Layer [µm]	66	66	68	68	68

Basis Weight: 2nd Layer [g/m²]	2.9	3.2	5.0	6.0	8.0
Thickness: 2nd Layer [µm]	2	2	3	5	9
KOH Absorption [g/m²]	86	107	NA	NA	NA
Mean Pore Size [µm]	0.2	0.5	Not Detected	Not Detected	Not Detected
Max Pore Size [µm]	0.8	1.2	0.1	0.1	0.1
Ratio between Max Pore Size and Mean Pore Size	3.90	2.33	-	-	-
Delta between Max Pore Size and Mean Pore Size[µm]	0.6	0.7	-	-	-
Electrical Resistance [mOhm·cm²]	90	64	60	70	76
Gurley Air Resistance [second / 100mL]	6972	569	45200	45200	45200
Basis Weight Ratio	8.97	8.13	5.00	4.17	3.13

[0079] As shown in Table 2 the Bi-Layer battery separator further reduced the mean and maximum pore sizes and the difference between the maximum and mean pore sizes (i.e., the pore size distribution) as compared to the Single Layer battery separator. In particular, the maximum pore sizes of the Bi-Layer separators ranged from about 1.6 µm to about 0.1 µm. In addition, the difference between maximum and mean pore sizes were less in the Bi-Layer samples than the difference between maximum and mean pore sizes in the Single Layer samples. Thus, the Bi-Layer samples had a tighter pore size distribution. For example, the delta between maximum pore sizes and mean pore sizes in samples 2 and 3 samples was about 0.6 µm and 0.9 µm, respectively.

[0080] In sample 1, a wetting agent or surfactant was not present in the separator and the maximum pore size was only about 0.1 µm.

[0081] Applicant notes that the mean pore size of Bi-Layer sample 1, sample 6, sample7, and sample 8 were undetected which means that it was less than about 0.1 µm.

[0082] The electrical resistance for the Bi-Layer samples ranged from about 41-90 mOhm·cm^2. The KOH absorption ranged from about 86 to about 119 g/m^2.

[0083] The Gurley Air Resistance ranged from about 500 to over 45,000 second /100 mL. Thus, the Bi-Layer samples had a significantly increased air resistance as compared to the single layer samples, which results in a substantial improvement to the performance of the battery.

[0084] While the invention has been described in detail herein in accordance with certain preferred embodiments thereof, many modifications and changes therein may be effected by those skilled in the art. Accordingly, the foregoing disclosure should not be construed to be limited thereby but should be construed to include such aforementioned obvious variations and be limited only by the spirit and scope of the following claims.

[0085] For example, in a first aspect, a first embodiment is a two-layer battery separator comprising a first layer comprising about 20% to about 50% by weight polyvinyl alcohol and about 50% to about 80% by weight cellulose based on the total dry weight of the first layer and a second layer in contact with a surface of the first layer and comprising polyvinyl alcohol and a polysaccharide. The separator has a maximum pore size of less than about 2.0 µm.

[0086] A second embodiment is the first embodiment, wherein the maximum pore size is less than or equal to about 1.6 µm.

[0087] A third embodiment is any combination of the first 2 embodiments, wherein a mean pore size of the separator is less than about 1.0 µm

[0088] A 4th embodiment is any combination of the first 3 embodiments, wherein the mean pore size is equal to or less than about 0.7 µm.

[0089] A 5th embodiment is any combination of the first 4 embodiments, wherein a difference between the maximum pore size and a mean pore size of the separator is less than about 2.0 µm.

[0090] A 6th embodiment is any combination of the first 5 embodiments, wherein a difference between the maximum pore size and a mean pore size of the separator is less than about 1.0 µm.

[0091] A 7th embodiment is any combination of the first 6 embodiments, wherein the second layer comprises a coating adhered to the surface of the first layer.

[0092] An 8th embodiment is any combination of the first 7 embodiments, wherein the first layer comprises about 35% to about 45% by weight polyvinyl alcohol and about 55% to about 65% by weight cellulose or a regenerated cellulose.

[0093] A 9th embodiment is any combination of the first 8 embodiments, wherein the first layer comprises about 40% by weight polyvinyl alcohol and about 60% by weight cellulose or a regenerated cellulose.

[0094] A 10th embodiment is any combination of the first 9 embodiments, wherein the PVA in the first layer comprises soluble and non-soluble PVA fibers.

[0095] An 11th embodiment is any combination of the first 10 embodiments, wherein the first layer comprises about 20% to about 30% by weight non-soluble PVA fibers and about 10% to about 20% by weight soluble PVA fibers.

[0096] A 12th embodiment is any combination of the first 11 embodiments, wherein the non-soluble PVA fibers are about 25% by weight of the first layer and the soluble PVA fibers are about 15% by weight of the first layer.

[0097] A 13th embodiment is any combination of the first 12 embodiments, wherein the non-soluble PVA fibers have a linear density greater than about 0.3 denier.

[0098] A 14th embodiment is any combination of the first 13 embodiments, wherein the linear density is about 0.4 denier to about 0.6 denier.

[0099] A 15th embodiment is any combination of the first 14 embodiments, wherein the linear density is about 0.5 denier.

[00100] A 16th embodiment is any combination of the first 15 embodiments, wherein the polysaccharide comprises a material selected from a group consisting of cellulose fibers, cellulose nanofilaments, microcrystalline cellulose, microcrystalline cellulose gel, starch, carboxymethyl cellulose (CMC), hydroxypropyl methylcellulose (HPMC), alginate, micro fibrillated cellulosic fibers or combinations thereof.

[00101] A 17th embodiment is any combination of the first 16 embodiments, wherein the second layer comprises about 45% to about 55% by dry weight polyvinyl alcohol and about 45% to about 55% by dry weight cellulose.

[00102] A 18th embodiment is any combination of the first 17 embodiments, wherein the second layer comprises about 50% by dry weight polyvinyl alcohol and about 50% by dry weight cellulose.

[00103] A 19th embodiment is any combination of the first 18 embodiments, wherein the PVA in the second layer comprises a water soluble PVA resin and the polysaccharide comprises a microcrystalline cellulose gel.

[00104] A 20th embodiment is any combination of the first 19 embodiments, wherein a ratio of a basis weight of the first layer to a basis weight of the second layer is about 2 to about 12.

[00105] A 21st embodiment is any combination of the first 20 embodiments, wherein the ratio is about 5 to about 8.

[00106] An 22nd embodiment is any combination of the first 21 embodiments, wherein the first layer does not contain a surfactant and the maximum pore size is less than about 0.2 µm.

[00107] A 23rd embodiment is any combination of the first 22 embodiments, wherein a maximum pore size of the separator is about 0.1 µm or less.

[00108] A 24th embodiment is any combination of the first 23 embodiments, wherein the ionic resistance of the separator is less than about 100 mOhm·cm^2.

[00109] A 25th embodiment is any combination of the first 24 embodiments, wherein a KOH absorption of the separator is at least about 80 g/m^2.

[00110] A 26th embodiment is any combination of the first 25 embodiments, wherein a Gurley Air Resistance of the separator is at least about 500 second / 100 mL, or at least about 1000 second / 100 mL.

[00111] A 27th embodiment is any combination of the first 26 embodiments, wherein the Gurley Air Resistance is at least about 1400 second / 100 mL.

[00112] In another aspect, a primary battery is provided comprising the battery separator of any of the above 27 embodiments.

[00113] In another aspect, a secondary battery is provided comprising the battery separator of any of the above 27 embodiments.

[00114] In another aspect, a stationary battery is provided comprising the battery separator of any of the above 27 embodiments.

[00115] In another aspect, an alkaline battery is provided comprising the battery separator of any of the above 27 embodiments.

[00116] In another aspect, a first embodiment is a two-layer battery separator comprising a first layer comprising about 20% to about 50% by weight polyvinyl alcohol and about 50% to about 80% by weight cellulose or a regenerated cellulose and a second layer in contact with a surface of the first layer and comprising polyvinyl alcohol fibers and a polysaccharide. The difference between a maximum pore size and a mean pore size of the separator is less than about 2.0 µm.

[00117] A second embodiment is the first embodiment, wherein the difference between the maximum pore size and the mean pore size of the separator is less than about 1.0 µm.

[00118] A 3rd embodiment is any combination of the first 2 embodiments, wherein a ratio of the maximum pore size to the mean pore size is about 1.0 to about 4.0.

[00119] A 4th embodiment is any combination of the first 3 embodiments, wherein the ratio is about 1.5 to about 2.5.

[00120] A 5th embodiment is any combination of the first 4 embodiments, wherein the first layer comprises about 35% to about 45% by weight polyvinyl alcohol and about 55% to about 65% by weight cellulose fibers or a regenerated cellulose.

[00121] A 6th embodiment is any combination of the first 5 embodiments, wherein the first layer comprises about 40% by weight polyvinyl alcohol and about 60% by weight cellulose fibers or a regenerated cellulose.

[00122] A 7th embodiment is any combination of the first 6 embodiments, wherein the polysaccharide comprises a material selected from a group consisting of cellulose fibers, cellulose nanofilaments, microcrystalline cellulose, microcrystalline cellulose gel, starch, carboxymethyl cellulose (CMC), hydroxypropyl methylcellulose (HPMC), alginate, micro fibrillated cellulosic fibers or combinations thereof.

[00123] An 8th embodiment is any combination of the first 7 embodiments, wherein the second layer comprises about 45% to about 55% by weight polyvinyl alcohol and about 45% to about 55% by weight cellulose.

[00124] A 9th embodiment is any combination of the first 8 embodiments, wherein the second layer comprises about 50% by weight polyvinyl alcohol resin and about 50% by weight microcrystalline cellulose gel.

[00125] A 10th embodiment is any combination of the first 9 embodiments, wherein the second layer comprises a coating adhered to the surface of the first layer.

[00126] In another aspect, a primary battery is provided comprising the battery separator of

any of the above 10 embodiments.

[00127] In another aspect, a secondary battery is provided comprising the battery separator of any of the above 10 embodiments.

[00128] In another aspect, a stationary battery is provided comprising the battery separator of any of the above 10 embodiments.

[00129] In another aspect, an alkaline battery is provided comprising the battery separator of any of the above 10 embodiments.

[00130] In another aspect, a first embodiment is a battery separator comprising a first layer comprising about 20% to about 50% by weight polyvinyl alcohol and about 50% to about 80% by weight cellulose or a regenerated cellulose and a coating in contact with a surface of the first layer and comprising polyvinyl alcohol and a polysaccharide, wherein a ratio of a basis weight of the first layer to a basis weight of the coating is about 2 to about 12.

[00131] A second embodiment is the first embodiment, wherein the ratio of basis weight is about 5 to about 8.

[00132] A third embodiment is any combination of the first 2 embodiments, wherein the separator consists of the first layer and the coating.

[00133] A 4^{th} embodiment is any combination of the first 3 embodiments, wherein the separator has a maximum pore size of less than about 2.0 µm.

[00134] A 5^{th} embodiment is any combination of the first 4 embodiments, wherein the maximum pore size is less than about 1.6 µm.

[00135] A 6^{th} embodiment is any combination of the first 5 embodiments, wherein a mean pore size of the separator is less than about 1.0 µm.

[00136] A 7^{th} embodiment is any combination of the first 6 embodiments, wherein a difference between the maximum pore size and the mean pore size of the separator is less than about 1.0 µm.

[00137] An 8th embodiment is any combination of the first 7 embodiments, wherein the first layer comprises about 40% by weight polyvinyl alcohol and about 60% by weight cellulose fibers.

[00138] A 9th embodiment is any combination of the first 8 embodiments, wherein the coating comprises about 50% by weight polyvinyl alcohol and about 50% by weight microcrystalline cellulose gel.

[00139] In another aspect, an alkaline or stationary battery is provided comprising the battery separator of the first 9 embodiments.

[00140] In another aspect, a first embodiment is a battery separator comprising a first layer comprising about 20% to about 50% by weight polyvinyl alcohol (PVA) fibers and about 50% to about 80% by weight cellulose or a regenerated cellulose, wherein the PVA fibers have a linear density greater than about 0.3 denier and a second layer in contact with a surface of the first layer and comprising polyvinyl alcohol and a polysaccharide.

[00141] A second embodiment is the first embodiment, wherein the first layer comprises a PVA binder and the PVA fibers.

[00142] A 3rd embodiment is any combination of the first 2 embodiments, wherein the linear density of the PVA fibers in the first layer is about 0.4 denier to about 0.6 denier.

[00143] A 4th embodiment is any combination of the first 3 embodiments, wherein the linear density of the PVA fibers in the first layer is about 0.5 denier.

What is claimed is:

1. A two-layer battery separator comprising:

a first layer comprising about 20% to about 50% by weight polyvinyl alcohol (PVA) and about 50% to about 80% by weight cellulose based on a total dry weight of the first layer;

a second layer in contact with a surface of the first layer and comprising PVA and a polysaccharide; and

wherein the separator has a maximum pore size of less than about 2.0 µm.

2. The battery separator of claim 1, wherein the maximum pore size is less than or equal to about 1.6 µm.

3. The battery separator of claim 1, wherein a mean pore size of the separator is less than about 1.0 µm

4. The battery separator of claim 3, wherein the mean pore size is equal to or less than about 0.7 µm.

5. The battery separator of claim 1, wherein a difference between the maximum pore size and a mean pore size of the separator is less than about 2.0 µm.

6. The battery separator of claim 1, wherein a difference between the maximum pore size and a mean pore size of the separator is less than about 1.0 µm.

7. The battery separator of claim 1, wherein the second layer comprises a coating adhered to the surface of the first layer.

8. The battery separator of claim 1, wherein the first layer comprises about 35% to about 45% by weight PVA and about 55% to about 65% by weight cellulose or a regenerated cellulose based on the total dry weight of the first layer.

9. The battery separator of claim 1, wherein the first layer comprises about 40% by weight PVA and about 60% by weight cellulose or a regenerated cellulose based on the total dry weight of the first layer.

10. The battery separator of claim 1, wherein the PVA in the first layer comprises soluble and non-soluble PVA fibers.

11. The battery separator of claim 10, wherein the first layer comprises about 20% to about 30% by weight non-soluble PVA fibers and about 10% to about 20% by weight soluble PVA fibers based on the total dry weight of the first layer.

12. The battery separator of claim 10, wherein the non-soluble PVA fibers are about 25% by weight of the first layer and the soluble PVA fibers are about 15% by weight of the first layer based on the total dry weight of the first layer.

13. The battery separator of claim 10, wherein the non-soluble PVA fibers have a linear density greater than about 0.3 denier.

14. The battery separator of claim 13, wherein the linear density is about 0.4 denier to about 0.6 denier.

15. The battery separator of claim 13, wherein the linear density is about 0.5 denier.

16. The battery separator of claim 1, wherein the polysaccharide comprises a material selected from a group consisting of cellulose fibers, cellulose nanofilaments, microcrystalline cellulose, microcrystalline cellulose gel, starch, carboxymethyl cellulose (CMC), hydroxypropyl methylcellulose (HPMC), alginate, micro fibrillated cellulosic fibers or combinations thereof.

17. The battery separator of claim 1, wherein the second layer comprises about 45% to about 55% by weight PVA and about 45% to about 55% by weight cellulose based on a total dry weight of the second layer.

18. The battery separator of claim 1, wherein the second layer comprises about 50% by weight PVA and about 50% by weight cellulose based on a total dry weight of the second layer.

19. The battery separator of claim 1, wherein the PVA in the second layer comprises a water soluble PVA resin and the polysaccharide comprises a microcrystalline cellulose gel, a starch, or an alginate.

20. The battery separator of claim 1, wherein a ratio of a basis weight of the first layer to a basis weight of the second layer is about 2 to about 12.

21. The battery separator of claim 20, wherein the ratio is about 5 to about 8.

22. The battery separator of claim 20, wherein the ratio is about 2 to about 5.

23. The battery separator of claim 22, wherein a maximum pore size of the separator is about 0.2 μm or less.

24. The battery separator of claim 1, wherein the ionic resistance of the separator is less than about 100 mOhm·cm^2.

25. The battery separator of claim 1, wherein a KOH absorption of the separator is at least about 80 g/m^2.

26. The alkaline battery separator of claim 1, wherein a Gurley Air Resistance of the separator is at least about 500 second / 100 mL, or at least about 1000 second / 100 mL.

27. The alkaline battery separator of claim 26, wherein the Gurley Air Resistance is at least about 1400 second / 100 mL.

28. A primary battery comprising the battery separator of claim 1.

29. A secondary battery comprising the battery separator of claim 1.

30. A stationary battery comprising the battery separator of claim 1.

31. An alkaline battery comprising the battery separator of claim 1.

32. A two-layer battery separator comprising:

a first layer comprising about 20% to about 50% by weight polyvinyl alcohol (PVA) and about 50% to about 80% by weight cellulose or a regenerated cellulose based on a total dry weight of the first layer;

a second layer in contact with a surface of the first layer and comprising PVA fibers and a polysaccharide; and

wherein a delta between a maximum pore size and a mean pore size of the separator is less than about 2.0 μm.

33. The battery separator of claim 32, wherein the delta between the maximum pore size and the mean pore size of the separator is less than about 1.0 μm.

34. The battery separator of claim 32, wherein a ratio of the maximum pore size to the mean pore size is about 1.0 to about 4.0.

35. The battery separator of claim 34, wherein the ratio is about 1.5 to about 2.5.

36. The battery separator of claim 32, wherein the first layer comprises about 35% to about 45% by weight PVA and about 55% to about 65% by weight cellulose fibers or a regenerated cellulose based on the total dry weight of the first layer.

37. The battery separator of claim 36, wherein the first layer comprises about 40% by weight PVA and about 60% by weight cellulose fibers or a regenerated cellulose based on the total dry weight of the first layer.

38. The battery separator of claim 32, wherein the polysaccharide comprises a material selected from a group consisting of cellulose fibers, cellulose nanofilaments, microcrystalline cellulose, microcrystalline cellulose gel, starch, carboxymethyl cellulose (CMC), hydroxypropyl methylcellulose (HPMC), alginate, micro fibrillated cellulosic fibers or combinations thereof.

39. The alkaline battery separator of claim 32, wherein the second layer comprises about 45% to about 55% by weight PVA and about 45% to about 55% by weight polysaccharide based on a total dry weight of the second layer.

40. The alkaline battery separator of claim 32, wherein the second layer comprises about 50% by weight PVA resin and about 50% by weight microcrystalline cellulose gel based on a total dry weight of the second layer.

41. The alkaline battery separator of claim 32, wherein the second layer comprises a coating adhered to the surface of the first layer.

42. A primary battery comprising the battery separator of claim 32.

43. A secondary battery comprising the battery separator of claim 32.

44. A stationary battery comprising the battery separator of claim 32.

45. An alkaline battery comprising the battery separator of claim 32.

46. A battery separator comprising:

a first layer comprising about 20% to about 50% by weight polyvinyl alcohol (PVA) and about 50% to about 80% by weight cellulose or a regenerated cellulose based on a total dry weight of the first layer; and

a second layer in contact with a surface of the first layer and comprising PVA and a polysaccharide, wherein a ratio of a basis weight of the first layer to a basis weight of the coating is about 2 to about 12.

47. The battery separator of claim 46, wherein the ratio of basis weight is about 5 to about 8.

48. The battery separator of claim 46, wherein the separator consists of the first layer and the coating.

49. The battery separator of claim 46, wherein the separator has a maximum pore size of less than about 2.0 μm.

50. The battery separator of claim 49, wherein the maximum pore size is less than about 1.6 μm.

51. The battery separator of claim 46, wherein a mean pore size of the separator is less than about 1.0 μm.

52. The battery separator of claim 51, wherein a delta between the maximum pore size and the mean pore size of the separator is less than about 1.0 µm.

53. The battery separator of claim 46, wherein the first layer comprises about 40% by weight polyvinyl alcohol and about 60% by weight cellulose fibers based on the total dry weight of the first layer.

54. The battery separator of claim 46, wherein the coating comprises about 50% by weight polyvinyl alcohol and about 50% by weight microcrystalline cellulose gel, a starch or an alginate based on a total dry weight of the coating.

55. A primary or secondary battery comprising the battery separator of claim 46.

56. A battery separator comprising:

a first layer comprising about 20% to about 50% by weight polyvinyl alcohol (PVA) fibers and about 50% to about 80% by weight cellulose or a regenerated cellulose based on a total dry weight of the first layer, wherein at least some of the PVA fibers have a linear density greater than about 0.3 denier; and

a second layer in contact with a surface of the first layer and comprising PVA and a polysaccharide.

57. The alkaline battery separator of claim 56, wherein the first layer comprises a PVA binder and the PVA fibers.

58. The alkaline battery separator of claim 57, wherein the linear density of the PVA fibers in the first layer is about 0.4 denier to about 0.6 denier.

59. The alkaline battery separator of claim 56, wherein the linear density of the PVA fibers in the first layer is about 0.5 denier.

60. A method of making a battery separator comprising:

forming a first layer comprising about 20% to about 50% by weight polyvinyl alcohol (PVA) and about 50% to about 80% by weight cellulose based on a total dry weight of the first layer;

bonding a second layer to a surface of the first layer, the second layer comprising PVA and a polysaccharide such that the separator has a maximum pore size of less than about 2.0 µm.

61. The process of claim 60, further comprising fibrillating the cellulose in the first layer.

62. The process of claim 61, further comprising forming an aqueous suspension of PVA fibers, PVA binder and the cellulose.

63. The process of claim 61, further comprising drying water-soluble fibers to form the PVA binder.

64. The process of claim 60, further comprising blending water soluble polymers and microcrystalline cellulose gel to create a blend of polyvinyl alcohol and microcrystalline cellulose gel as the second layer.

65. The process of claim 60, further comprising blending water soluble polymers and a starch or an alginate to create a blend of polyvinyl alcohol and the starch or the alginate as the second layer.

66. The process of claim 64, further comprising coating the second layer to a surface of the first layer.

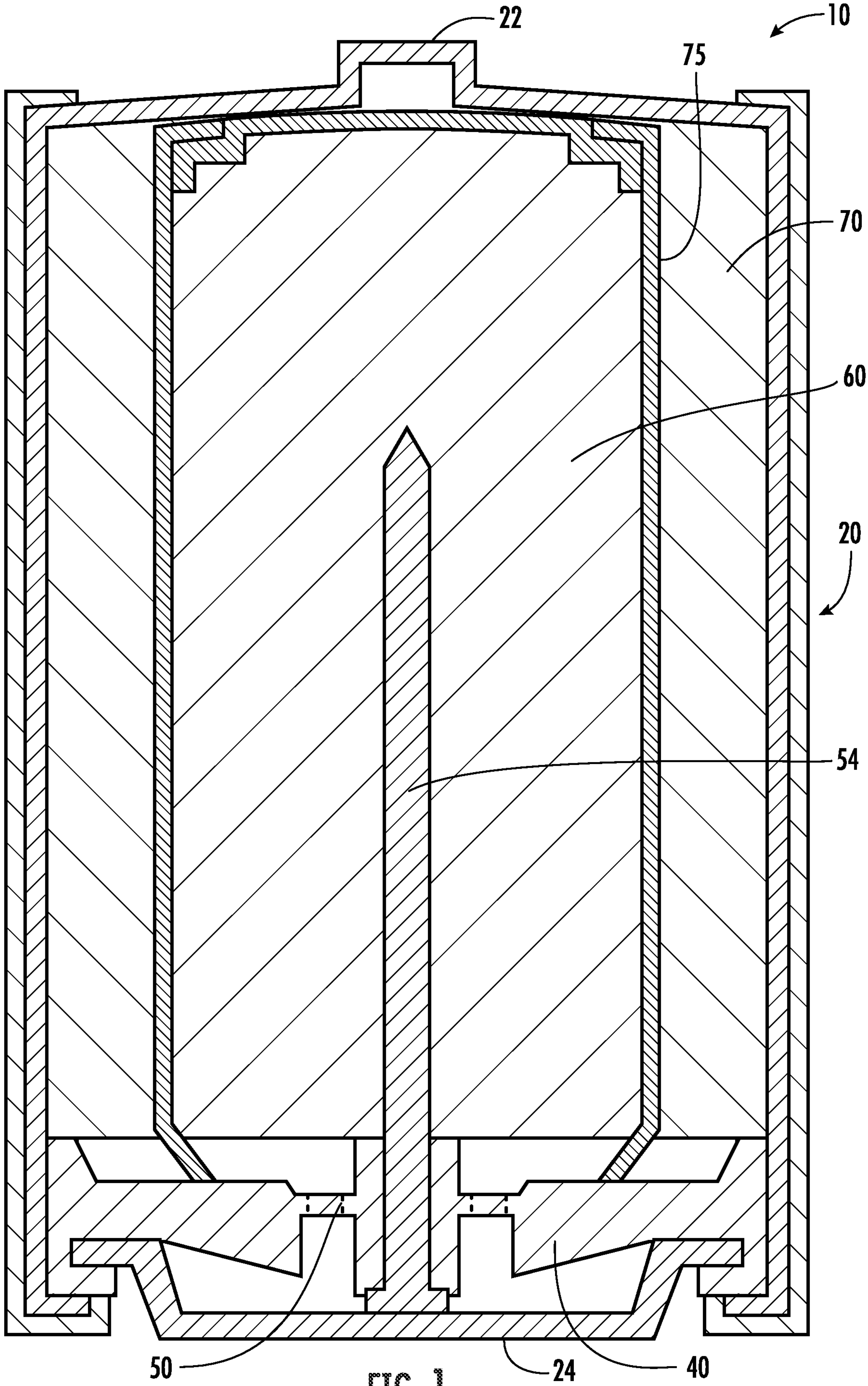

FIG. 1

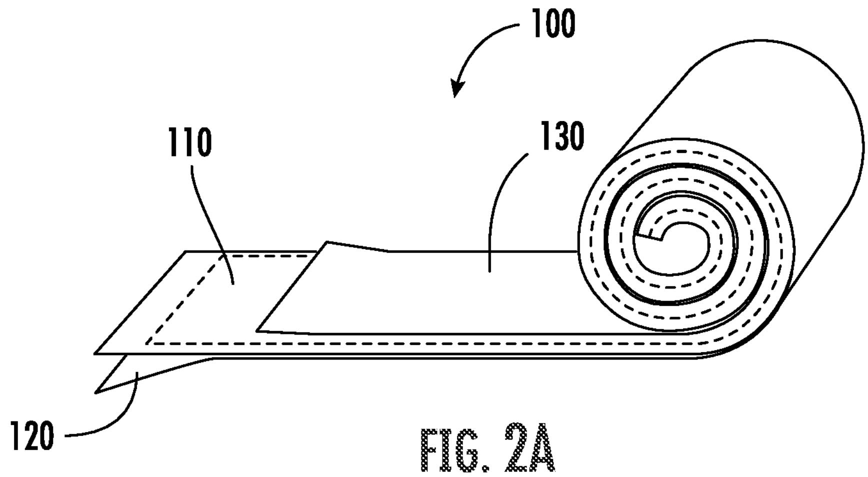

FIG. 2A

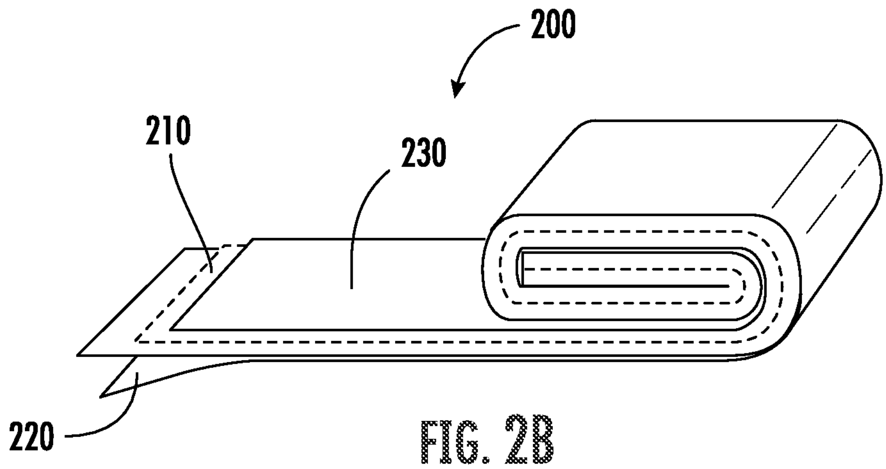

FIG. 2B

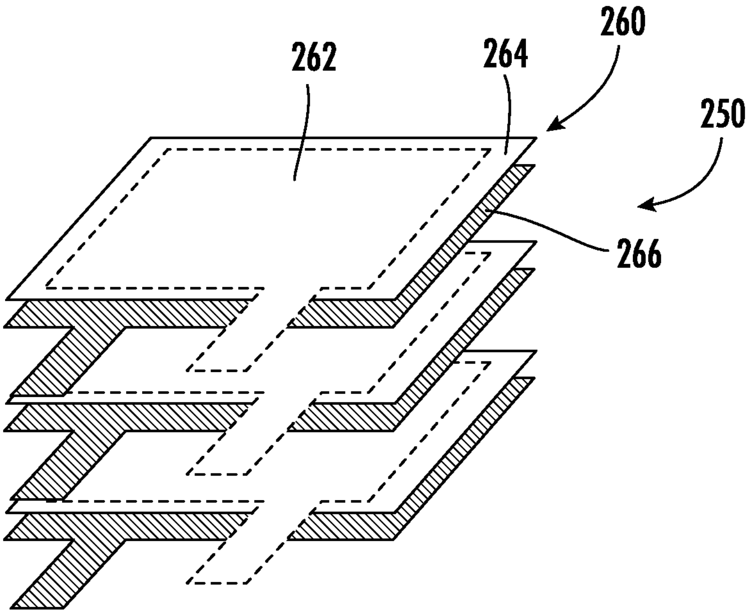

FIG. 2C

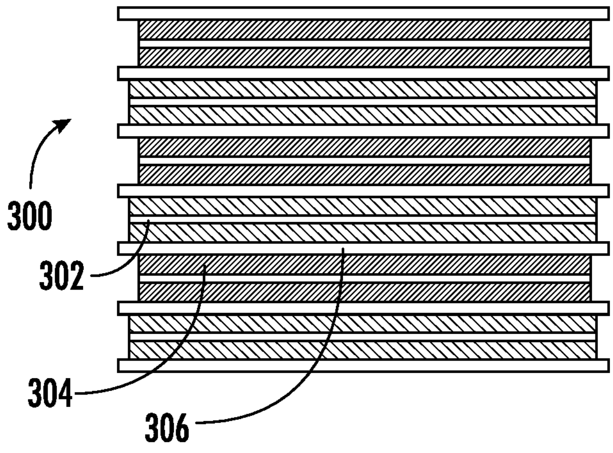

FIG. 3A

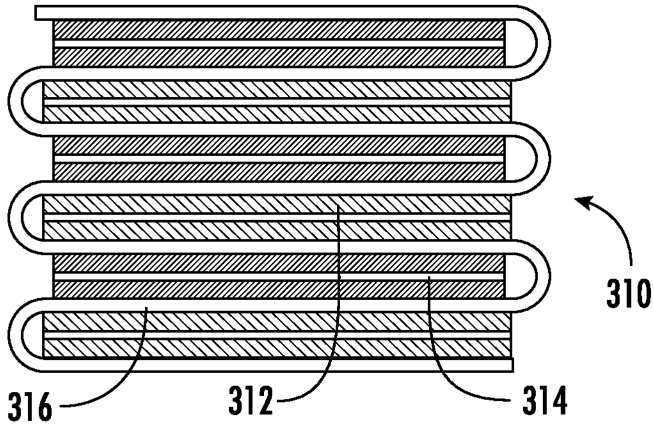

FIG. 3B

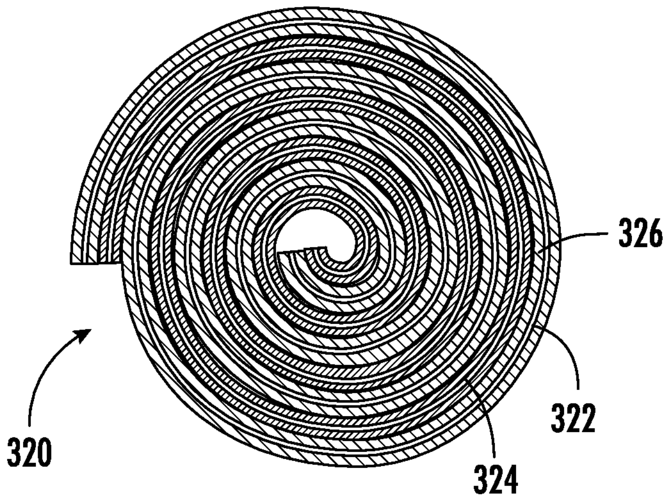

FIG. 3C

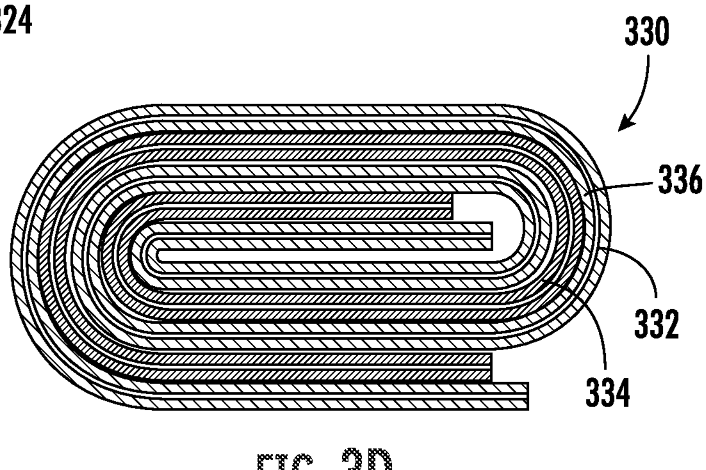

FIG. 3D

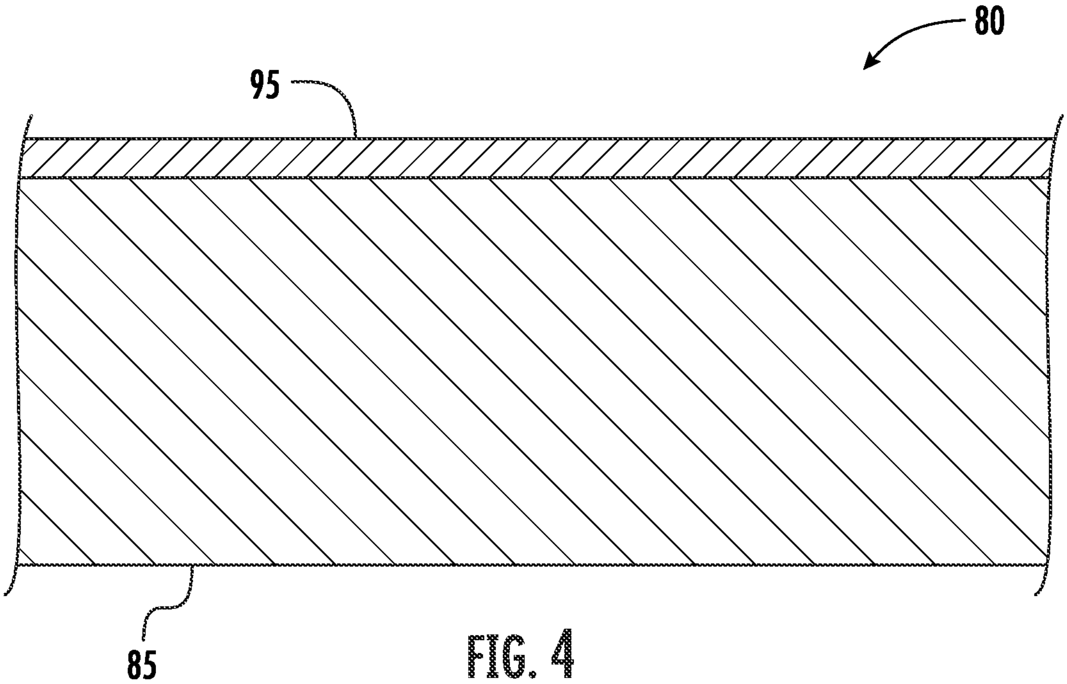

FIG. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2024/055626

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01M50/414 H01M50/429 H01M50/449 H01M50/489 H01M50/491
ADD.

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)
H01M

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2018/331340 A1 (LINTZ TIMOTHY SCOTT [US] ET AL) 15 November 2018 (2018-11-15) figures 1-2; example 1 paragraphs [0052] - [0053] -----	1-66
X	US 2023/086918 A1 (MOTIN VINCENT [FR] ET AL) 23 March 2023 (2023-03-23) examples 1, 3-5; table 1 paragraphs [0051] - [0056] -----	1-55, 60-66
X	US 2013/183569 A1 (HAYAKAWA TOMOHIRO [JP] ET AL) 18 July 2013 (2013-07-18) example 1; table 1 paragraphs [0083] - [0102] -----	56-59

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
21 January 2025	30/01/2025

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Agra-Gutierrez, C

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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