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(54) **MULTILAYER CATION EXCHANGE CHLORALKALI MEMBRANE**

- (57) A multilayer cation exchange membrane for use in a chloralkali process comprising an carboxylate layer comprising a fluorinated ionomer containing carboxylate groups on one side of the membrane, an exterior sulfonate layer comprising a fluorinated ionomer containing sulfonate groups on the side of the membrane opposite the carboxylate layer, and an interior sulfonate layer comprising a fluorinated ionomer containing sulfonate groups between the carboxylate layer and the exterior sulfonate layer, the exterior sulfonate layer having an ion exchange ratio greater than about 11.3, and the interior sulfonate layer having an ion exchange ratio less than about 11.

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Description**FIELD OF THE INVENTION**

[0001] The invention relates to a multilayer cation exchange membrane for chloralkali electrolysis.

BACKGROUND OF THE INVENTION

[0002] Chlorine and alkali metal hydroxide, typically sodium or potassium hydroxide, are produced commercially in an electrolytic process from aqueous sodium or potassium chloride solutions, i.e., the chloralkali process. The most advanced technology for the chloralkali process employs membranes for separating the anode and cathode compartments that are made from fluorinated ionomers containing cation exchange ionic groups, i.e., cation exchange membranes.

[0003] Cation exchange membranes for the chloralkali process frequently employ a layer of a fluorinated ionomer containing carboxylate groups facing the cathode compartment. The carboxylate layer typically has a coating of inorganic particles such as zirconium dioxide, optionally in a polymer binder to provide for bubble release. The other side of the chloralkali membrane facing the anode compartment is layer of fluorinated ionomer containing sulfonate groups which typically has an inorganic particle coating like the coating facing the cathode compartment. The membranes often include a woven fabric reinforcement made of a fluoropolymer such as polytetrafluoroethylene (PTFE) or a combination of fluoropolymer fiber and "sacrificial" polymer fiber that dissolves in alkali metal hydroxide solutions, such as polyethylene terephthalate or polyvinyl alcohol. The reinforcing woven fabric is typically at least partially embedded in the membrane.

[0004] In a chloralkali cell, the membrane provides a physical barrier between the alkali metal hydroxide solution and hydrogen present in the cathode compartment and the chlorine and alkali metal chloride solution present in the anode compartments. In addition, another primary function of the ionomers in a chloralkali membrane is the transport of alkali metal ions through the membrane from anode to cathode. The carboxylate ionomer additionally provides selectivity by decreasing the migration of hydroxide ions from the cathode to the anode and improves current efficiency of the cell over using sulfonate ionomer alone. The sulfonate ionomer provides more effective ion transport than the carboxylate layer, i.e., lower resistance, and thus can decrease cell voltage.

[0005] The capacity of the carboxylate and sulfonate ionomers to transport alkali metal ions are often expressed in terms of equivalent weight or ion exchange ratio (IXR). Equivalent weight (EW) is defined to be the weight of the ionomer in acid form required to neutralize one equivalent of NaOH. Ion exchange ratio (IXR) is defined as the number of carbon atoms in the polymer backbone in relation to the cation exchange groups. Resistivity is another useful measurement to describe the capability to transport alkali metal ions, especially for sulfonate ionomers. Resistivity is measured using a specified set of conditions such as those described in the Test Methods of this application and is a measure of the intrinsic property of fluoroionomers with respect to the capability to transport alkali metal ions.

[0006] To attempt to optimize efficiency for operation of the chloralkali cell, the EW or IXR of the of the carboxylate and sulfonate ionomers are selected to achieve a balance of current efficiency and cell voltage properties. Two-layer membranes having a carboxylate ionomer with an EW of 1050 and IXR of 14.8 and a sulfonate ionomer with an EW of 920 and IXR of 11.5 provide a good balance of properties. However, if it is attempted to further reduce cell voltage by further reducing the EW, or IXR of the sulfonate polymer, current efficiency decreases.

[0007] Chloralkali membranes are known that have a layer of carboxylate ionomer and two layers of sulfonate ionomer of different ion exchange capacities. For example, Patent Publication No. US2017/0218526 discloses a membrane comprising a layer of carboxylate ionomer and at least two sulfonate ionomer layers. One of the sulfonate ionomer layers is adjacent to the carboxylate layer and one is not adjacent to the carboxylate layer. The membrane also includes a reinforcing material. The EW of the sulfonate layer adjacent to the carboxylate layer is higher than the EW of the sulfonate layer not adjacent to the carboxylate layer. (US2017/0218526 does not report EW but instead uses the term "ion exchange capacity" in meq/g units from which EW can be calculated by dividing 1000 by the ion exchange capacity. US2017/0218526 uses a transmission IR technique calibrated against known standards for determining ion exchange capacity.) US2017/0218526 describes that the three-layer structures are employed for the purpose of preventing peeling between the carboxylate layer and the sulfonate layer adjacent to the carboxylate layer that occurs if the EW of the sulfonate layer is low. However, the three-layer structure of US 2017/0218526 does not provide a significant decrease in voltage over two-layer membranes with optimized EW.

SUMMARY OF THE INVENTION

[0008] The invention provides a multilayer cation exchange membrane for use in a chloralkali process comprising a carboxylate layer comprising a fluorinated ionomer containing carboxylate groups on one side of the membrane, an exterior sulfonate layer comprising a fluorinated ionomer containing sulfonate groups on the side of the membrane

opposite the carboxylate layer, and an interior sulfonate layer comprising a fluorinated ionomer containing sulfonate groups between the carboxylate layer and the exterior sulfonate layer, the exterior sulfonate layer having an ion exchange ratio greater than about 11.3, and the interior sulfonate layer having an ion exchange ratio less than about 11.

[0009] The multilayer cation exchange membrane in accordance with the invention advantageously provides decreased cell voltage without loss in current efficiency when used in a chloralkali process.

[0010] Preferably, the interior sulfonate layer has an ion exchange ratio less than the ion exchange ratio of the exterior sulfonate layer by at least about 0.6.

[0011] Preferably, the carboxylate layer has an IXR of about 13.8 to about 16.

[0012] Preferably, the exterior sulfonate layer has an ion exchange ratio greater than about 11.5, more preferably about 11.3 to about 17.5, still more preferably about 11.3 to about 15.5, still more preferably about 11.3 to about 13.5, and most preferably about 11.3 to about 12.4.

[0013] Preferably, the interior sulfonate layer has an ion exchange ratio less than about 10.9, more preferably about 9.3 to about 11, more preferably, about 10 to about 11, still more preferably about 10 to about 10.9.

[0014] Preferably the membrane in accordance with the invention further comprises a woven fabric reinforcement, preferably embedded at least partially in the membrane. In a preferred embodiment, the woven fabric comprises fluoropolymer yarns having a denier less than about 100.

[0015] Preferably, the interior sulfonate layer has a thickness of at least about 40 micrometers, more preferably about 50 micrometers to about 200 micrometers, most preferably about 60 micrometers to about 100 micrometers. A membrane in accordance with the invention preferably has an exterior sulfonate layer having a thickness less than about 30 micrometers, more preferably, about 5 micrometers to about 30 micrometers, and most preferably, about 7 micrometers to about 25 micrometers.

[0016] In accordance with another embodiment of the invention, a multilayer cation exchange membrane is provided for use in a chloralkali process comprising a carboxylate layer comprising a fluorinated ionomer containing carboxylate groups on one side of the membrane, an exterior sulfonate layer comprising a fluorinated ionomer containing sulfonate groups on the side of the membrane opposite the carboxylate layer, and an interior sulfonate layer comprising a fluorinated ionomer containing sulfonate groups between the carboxylate layer and the exterior sulfonate layer, the exterior sulfonate layer having a resistivity greater than about 68.1 ohm-cm, and the interior sulfonate layer having a resistivity less than about 60.3 ohm-cm.

[0017] Preferably, interior sulfonate layer of the membrane has a resistivity less than the resistivity of the exterior sulfonate layer by at least about 15.5 ohm-cm.

[0018] Preferably, the carboxylate layer has an IXR of about 13.8 to about 16.

[0019] Preferably, the exterior sulfonate layer has a resistivity greater than about 73.2 ohm-cm, more preferably, about 68.1 ohm-cm to about 186.3 ohm-cm, still more preferably, about 68.1 ohm-cm to about 155.4 ohm-cm, still more preferably, about 68.1 ohm-cm to about 118.3 ohm-cm, and most preferably, about 68.1 ohm-cm to about 78.1 ohm-cm.

[0020] Preferably, the interior sulfonate layer has a resistivity less than about 57.7 ohm-cm, more preferably, about 10.7 ohm-cm to about 60.3 ohm-cm, still more preferably, about 32.3 ohm-cm to about 60.3 ohm-cm, and most preferably, about 32.3 ohm-cm to about 57.7 ohm-cm.

[0021] Preferably, the membranes in accordance with the invention comprises a woven fabric reinforcement, more preferably, a woven fabric reinforcement embedded at least partially in the membrane. Preferably, the woven fabric comprises fluoropolymer yarns having a denier less than about 100.

[0022] In a preferred membrane in accordance with the invention, the interior sulfonate layer has a thickness of at least about 40 micrometers, more preferably, about 50 micrometers to about 200 micrometers, and most preferably, about 60 micrometers to about 100 micrometers.

[0023] Preferably, the exterior sulfonate layer has a thickness less than about 30 micrometers, more preferably about 5 micrometers to about 30 micrometers, and most preferably about 7 micrometers to about 25 micrometers.

[0024] In accordance with another embodiment of the invention, a multilayer cation exchange membrane is provided for use in a chloralkali process comprising a carboxylate layer comprising a fluorinated ionomer containing carboxylate groups on one side of the membrane, an exterior sulfonate layer comprising a fluorinated ionomer containing sulfonate groups on the side of the membrane opposite the carboxylate layer, and first and second interior sulfonate layers comprising fluorinated ionomer containing sulfonate groups between the carboxylate layer and the exterior sulfonate layer, the first interior sulfonate layer being between the carboxylate layer and the second interior sulfonate layer and the second interior sulfonate layer being between the first interior sulfonate layer and the exterior sulfonate layer, the exterior sulfonate layer having an ion exchange ratio greater than about 11.3, the first interior sulfonate layer having an ion exchange ratio greater than about 11.3, and the second interior sulfonate layer having an ion exchange ratio less than about 11.

[0025] Preferably, the second interior sulfonate layer has an ion exchange ratio less than the ion exchange ratio of the exterior sulfonate layer by at least about 0.6.

[0026] Preferably, the first interior sulfonate layer has an ion exchange ratio greater than the ion exchange ratio of the

second interior sulfonate layer by at least about 0.6.

[0027] Preferably, the carboxylate layer has an ion exchange ratio of about 13.8 to about 16.

[0028] Preferably the first interior sulfonate layer has an ion exchange ratio that differs from the ion exchange ratio of the carboxylate layer by no more than about 3.3.

[0029] In accordance with another embodiment of the invention, a multilayer cation exchange membrane is provided for use in a chloralkali process comprising a carboxylate layer comprising a fluorinated ionomer containing carboxylate groups on one side of the membrane, an exterior sulfonate layer comprising a fluorinated ionomer containing sulfonate groups on the side of the membrane opposite the carboxylate layer, and first and second interior sulfonate layers comprising fluorinated ionomer containing sulfonate groups between the carboxylate layer and the exterior sulfonate layer, the first interior sulfonate layer being between the carboxylate layer and the second interior sulfonate layer and the second interior sulfonate layer being between the first interior sulfonate layer and the exterior sulfonate layer, the exterior sulfonate layer having a resistivity greater than about 68.1 ohm-cm, the first interior sulfonate layer having a resistivity greater than about 68.1 ohm-cm, and the second interior sulfonate layer having a resistivity less than 60.3 ohm-cm.

[0030] Preferably, the second interior sulfonate layer has a resistivity less than the resistivity of the exterior sulfonate layer by at least about 15.5 ohm-cm.

[0031] Preferably, the first interior sulfonate layer has resistivity greater than the resistivity of the second interior sulfonate layer by at least about 15.5 ohm-cm.

[0032] Preferably, the carboxylate layer has an IXR of about 13.8 to about 16.

[0033] Preferably, the first interior sulfonate layer has an ion exchange ratio that differs from the ion exchange ratio of the carboxylate layer by no more than about 3.3.

[0034] A multilayer cation exchange membrane in accordance with the invention advantageously provides decreased cell voltage without loss in current efficiency when used in a chloralkali process.

DESCRIPTION OF THE FIGURES

[0035]

Figure 1 is a diagrammatical, partial cross-sectional view of one embodiment of a multilayer cation exchange membrane in accordance with the present invention.

Figure 2 is a diagrammatical, partial cross-sectional view of another embodiment of a multilayer cation exchange membrane in accordance with the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Fluorinated Ionomers

[0036] The membranes of the present invention employ fluorinated ionomers. The term "fluorinated ionomer" means polymer that is at least partially fluorinated and that contains ionic groups capable of ion exchange, i.e., cation exchange for the chloralkali process. Preferably, the ionomer is "highly fluorinated" which means that at least 90% of the total number of univalent atoms in the polymer are fluorine atoms. Most preferably, the ionomer is perfluorinated.

[0037] Preferably, the fluorinated ionomer comprises a polymer backbone with recurring side chains attached to the backbone with the side chains carrying the cation exchange groups. Possible fluorinated ionomers include homopolymers or copolymers of two or more monomers. Copolymers are typically formed from one monomer which is a nonfunctional monomer and which provides carbon atoms for the polymer backbone. A second monomer provides both carbon atoms for the polymer backbone and also contributes the side chain carrying the cation exchange group or a cation exchange group precursor which can be subsequently hydrolyzed to form the functional group. For example, copolymers of a first fluorinated olefin monomer together with a second fluorinated vinyl monomer with a side chain containing the cation exchange group or precursor. The first monomer may also have a side chain that does not interfere with the ion exchange function of the functional groups. Possible first monomers include tetrafluoroethylene (TFE), hexafluoropropylene, vinyl fluoride, vinylidene fluoride, trifluoroethylene, chlorotrifluoroethylene, perfluoro (alkyl vinyl ether), and mixtures thereof. Possible second monomers include a variety of fluorinated vinyl ethers with a desired side chain containing functional groups or precursor groups. Additional monomers can also be incorporated into these polymers if desired. For example, more than one type of first fluorinated olefin monomer can be used and, similarly, more than one type of second monomer can be used.

[0038] The term "carboxylate groups" is intended to refer to either carboxylic acid groups or salts of carboxylic acid, preferably alkali metal or ammonium salts. Fluorinated ionomer containing carboxylate groups is referred to in this

application as "carboxylate ionomer". Preferred functional groups are represented by the formula $-\text{CO}_2\text{X}$ wherein X is H, Li, Na, K or $\text{N}(\text{R}^1)(\text{R}^2)(\text{R}^3)(\text{R}^4)$ and R^1 , R^2 , R^3 , and R^4 are the same or different and are H, CH_3 or C_2H_5 . When used in a chloralkali process, the carboxylate groups will be in the alkali metal form, e.g., sodium or potassium, corresponding to the salt being electrolyzed. A class of preferred polymers for use in the present invention include a highly fluorinated, most preferably perfluorinated, carbon backbone with recurring side chains attached to the backbone with the side chains carrying the carboxylate functional groups. Ionomers of this type are disclosed in U.S. Patent 4,552,631 and preferably have the side chain $-\text{O}-\text{CF}_2\text{CF}(\text{CF}_3)-\text{O}-\text{CF}_2\text{CF}_2\text{CO}_2\text{X}$. This ionomer can be made by copolymerization of tetrafluoroethylene (TFE) and the perfluorinated vinyl ether $\text{CF}_2=\text{CF}-\text{O}-\text{CF}_2\text{CF}(\text{CF}_3)-\text{O}-\text{CF}_2\text{CF}_2\text{CO}_2\text{CH}_3$, the methyl ester of perfluoro(4,7-dioxa-5-methyl-8-nonenecarboxylic acid) (PDMNM), followed by conversion to carboxylate groups by hydrolysis of the methyl carboxylate groups. Another preferred carboxylate ionomer has the side chain $-\text{O}-\text{CF}_2\text{CF}_2\text{CF}_2\text{CO}_2\text{X}$ and can be made by copolymerization of tetrafluoroethylene (TFE) and the perfluorinated vinyl ether $\text{CF}_2=\text{CF}-\text{O}-\text{CF}_2\text{CF}_2\text{CF}_2\text{CO}_2\text{CH}_3$. While other esters can be used for film or bifilm fabrication, the methyl ester is the preferred since it is sufficiently stable during normal extrusion conditions.

[0039] The term "sulfonate groups" is intended to refer to either sulfonic acid groups or salts of sulfonic acid, preferably alkali metal or ammonium salts. Fluorinated ionomer containing sulfonate groups is referred to in this application as "sulfonate ionomer". Preferred functional groups are represented by the formula $-\text{SO}_3\text{X}$ wherein X is H, Li, Na, K or $\text{N}(\text{R}^1)(\text{R}^2)(\text{R}^3)(\text{R}^4)$ and R^1 , R^2 , R^3 , and R^4 are the same or different and are H, CH_3 or C_2H_5 . When used in a chloralkali process, the sulfonate groups will be in the alkali metal form, e.g., sodium or potassium, corresponding to the salt being electrolyzed. A class of preferred polymers for use in the present invention include a highly fluorinated, most preferably perfluorinated, carbon backbone and the side chain is represented by the formula $-(\text{O}-\text{CF}_2\text{CFR}^f-\text{O}-\text{CF}_2\text{CFR}^f\text{SO}_3\text{X})_a$, wherein R^f and R^f are independently selected from F, Cl or a perfluorinated alkyl group having 1 to 10 carbon atoms, $a = 0, 1$ or 2 , and X is H, Li, Na, K or $\text{N}(\text{R}^1)(\text{R}^2)(\text{R}^3)(\text{R}^4)$ and R^1 , R^2 , R^3 , and R^4 are the same or different and are H, CH_3 or C_2H_5 . The preferred polymers include, for example, polymers disclosed in U.S. Patent 3,282,875 and in U.S. Patents 4,358,545 and 4,940,525. One preferred polymer comprises a perfluorocarbon backbone and the side chain is represented by the formula $-\text{O}-\text{CF}_2\text{CF}(\text{CF}_3)-\text{O}-\text{CF}_2\text{CF}_2\text{SO}_3\text{X}$, wherein X is as defined above. Polymers of this type are disclosed in U.S. Patent 3,282,875 and can be made by copolymerization of tetrafluoroethylene (TFE) and the perfluorinated vinyl ether $\text{CF}_2=\text{CF}-\text{O}-\text{CF}_2\text{CF}(\text{CF}_3)-\text{O}-\text{CF}_2\text{CF}_2\text{SO}_2\text{F}$, perfluoro(3,6-dioxa-4-methyl-7-octenesulfonyl fluoride) (PDMOF), followed by conversion to sulfonate groups by hydrolysis of the sulfonyl fluoride groups. One preferred polymer of the type disclosed in U.S. Patents 4,358,545 and 4,940,525 has the side chain $-\text{O}-\text{CF}_2\text{CF}_2\text{SO}_3\text{X}$, wherein X is as defined above. This polymer can be made by copolymerization of tetrafluoroethylene (TFE) and the perfluorinated vinyl ether $\text{CF}_2=\text{CF}-\text{O}-\text{CF}_2\text{CF}_2\text{SO}_2\text{F}$, perfluoro(3-oxa-4-pentenesulfonyl fluoride) (POPF), followed by hydrolysis.

[0040] For fluorinated ionomers of the type described above, the capacity for cation exchange capacity is often expressed in terms of equivalent weight (EW). Equivalent weight (EW) is defined to be the weight of the ionomer in acid form required to neutralize one equivalent of NaOH. However, because fluorinated ionomers have side chains with different chemical structures and chain lengths, equivalent weight values are ionomer specific and are not a desirable measure of chloralkali membrane performance for different fluorinated ionomers with different side chains, particularly when considering the selectivity of carboxylate ionomers, i.e., resistance to hydroxyl group crossover.

[0041] "Ion exchange ratio" or "IXR" is defined as number of carbon atoms in the polymer backbone in relation to the cation exchange groups and thus is a desirable value to describe or compare the capacity for ion exchange of different fluorinated ionomers, particularly for carboxylate ionomers. In the case of a sulfonate polymer where the polymer comprises a perfluorocarbon backbone and the side chain is $-\text{O}-\text{CF}_2-\text{CF}(\text{CF}_3)-\text{O}-\text{CF}_2-\text{CF}_2-\text{SO}_3\text{X}$ as disclosed in US 3,282,875, IXR for this polymer can be related to equivalent weight using the following formula: $50 \text{ IXR} + 344 = \text{EW}$. While generally the same IXR range is useful for sulfonate polymers disclosed in U.S. Patents 4,358,545 and 4,940,525, the equivalent weight corresponding to that IXR range is lower because of the lower molecular weight of the monomer unit containing the cation exchange group, i.e., it provides a shorter side chain. IXR for this polymer can be related to equivalent weight using the following formula: $50 \text{ IXR} + 178 = \text{EW}$. For carboxylate polymers having the side chain $-\text{O}-\text{CF}_2\text{CF}(\text{CF}_3)-\text{O}-\text{CF}_2\text{CF}_2\text{CO}_2\text{X}$, IXR for this polymer can be related to equivalent weight using the following formula: $50 \text{ IXR} + 308 = \text{EW}$. For carboxylate polymers having the side chain $-\text{O}-\text{CF}_2\text{CF}_2\text{CF}_2\text{CO}_2\text{X}$, IXR for this polymer can be related to equivalent weight using the following formula: $50 \text{ IXR} + 192 = \text{EW}$.

[0042] IXR is used in this application to describe either hydrolyzed ionomer which contains functional groups in acid or salt form or unhydrolyzed polymer which contains precursor groups which will subsequently be converted to the functional groups during the manufacture of the membranes, i.e., for sulfonate ionomers, typically the sulfonyl chloride or sulfonyl fluoride form, and for carboxylate ionomers, typically the methyl ester form.

Reinforcement

[0043] The membrane of the invention may be unreinforced or reinforced but for dimensional stability and greater tear resistance, it is preferable to incorporate reinforcement into the membrane. For this purpose, fluoropolymer reinforcement

is preferably used, most preferably a perfluoropolymer reinforcement. Perhalogenated polymers such as polychlorotri-fluoroethylene may also be used but perfluoropolymer reinforcements are preferable because they have better resistance to the chemicals in a chloralkali cell. Suitable perfluoropolymers include polytetrafluoroethylene or a melt-processable copolymers of tetrafluoroethylene with hexafluoropropylene and/or with perfluoro(propyl vinyl ether). While a porous fluoropolymer sheet or fluoropolymer fibrils or staple fiber may be used as reinforcement, preferred reinforcement is a woven fabric reinforcement. The fluoropolymer fiber may be woven into fabric using various weaves, such as the plain weave, basket weave, leno weave, or others. Relatively open weaves are preferred because the open fabrics provide less membrane resistance. Preferred center-to-center fiber spacing is in the range of about 200 to about 500 micrometers.

[0044] The fluoropolymer fibers used in the woven fabrics may be in the form of monofilaments or multifilament yarns. The monofilaments may be of round cross-section or may have specialized cross-sections. Oblong cross-sections, if suitably oriented to the membrane, can make it possible to get more reinforcing action with a thinner overall membrane. It is also desirable for some woven fabrics to include sacrificial yarns together with the fluoropolymer fibers such as polyethylene terephthalate or polyvinyl alcohol that dissolve in alkali metal hydroxide solutions. A range of fiber deniers and fabric weights may be used. Preferred fluoropolymer fiber has a denier of less than about 100, more preferably less than about 90, most preferably less than about 70. Deniers as low as about 5 can be used but preferably are at least about 20. The fabric employed may be calendared before lamination to reduce its thickness.

[0045] The most preferred fluoropolymer fiber for use in the woven fabric reinforcement are expanded polytetrafluoroethylene (ePTFE) monofilaments. Suitable monofilaments are available commercially from W. L. Gore & Associates, Inc., Newark, DE 19711.

Membrane Structures

[0046] Referring to Figure 1, a preferred multilayer cation exchange membrane 10 in accordance with the present invention is illustrated in a diagrammatical, partial cross-sectional view. Membrane 10 includes a carboxylate layer 12 of carboxylate ionomer on one side of the membrane for facing the cathode compartment of a chloralkali cell (not shown). Membrane 10 includes an exterior sulfonate layer 14 of sulfonate ionomer on the side of the membrane opposite the carboxylate layer for facing the anode compartment of a chloralkali cell (not shown). Between the carboxylate layer 12 and the exterior sulfonate layer, the membranes 10 includes an interior sulfonate layer 16.

[0047] The membrane 10 includes a woven fabric reinforcement which comprises expanded polytetrafluoroethylene (ePTFE) fiber monofilaments 18 and sacrificial multifilament yarns comprising polyethylene terephthalate (PET) filaments 20. ePTFE monofilaments 18 and PET filaments 20 are at least partially embedded in the membrane for the purpose of increasing membrane strength. It will be understood that the ePTFE monofilaments 18 and PET filaments 20 of the woven fabric reinforcement are shown primarily embedded in the interior sulfonate layer. However, woven fabric reinforcement can be embedded in any of the layers 12, 14 or 16 or the membrane or at the interface of adjacent layers so that it is partially embedded in more than one layer. Preferably, the woven fabric reinforcement is embedded at least partially in the membrane. For example, the woven fabric reinforcement can be suitably embedded in one or both of the exterior sulfonate layer 14 and the interior sulfonate layer 16.

[0048] In accordance with the invention, the carboxylate layer 12 of the membrane 10 has an IXR of about 13.8 to about 16.0. This range has been found to desirable to achieve high current efficiencies a chloralkali cell, e.g., $\geq 96\%$. IXR ranges higher than about 16.0 generally results in an increased cell voltage which cannot be compensated for using more conductive, i.e., lower IXR sulfonate ionomer in the other layers 14 and 16. On the other hand, IXR ranges for the carboxylate layer lower than about 13.8 generally do not provide optimum selectivity and result in decreased current efficiencies.

[0049] In accordance with the invention, the exterior sulfonate layer 14 of the membrane 10 has an ion exchange ratio greater than about 11.3 (resistivity greater than about 68.1 ohm-cm) and the interior sulfonate layer 16 has an ion exchange ratio less than about 11 (resistivity less than about 60.3 ohm-cm). Preferably, the interior sulfonate layer 16 has an ion exchange ratio less than the ion exchange ratio of the exterior sulfonate layer 14 by at least about 0.6. Preferably, the interior sulfonate layer has a resistivity less than the resistivity of the exterior sulfonate layer by at least about 15.5 ohm-cm.

[0050] In a preferred form of the invention, the exterior sulfonate layer 14 has an ion exchange ratio greater than about 11.5 (resistivity greater than about 73.2 ohm-cm). Preferably, the exterior sulfonate layer 14 has an ion exchange ratio of about 11.3 to about 17.5 (resistivity of about 68.1 ohm-cm) to about 186.3 ohm-cm), more preferably, about 11.3 to about 15.5 (resistivity of about 68.1 ohm-cm to about 155.4 ohm-cm.), still more preferably about 11.3 to about 13.5 (resistivity of about 68.1 ohm-cm to about 118.3 ohm-cm), and most preferably, about 11.3 to about 12.4 (resistivity of about 68.1 ohm-cm to about 94.6 ohm-cm).

[0051] In a preferred form of the invention, the interior sulfonate layer 16 has an ion exchange ratio less than about 10.9 (resistivity less than about 57.7 ohm-cm). Preferably, the interior sulfonate layer 16 has an ion exchange ratio of about 9.3 to about 11 (resistivity of about 10.7 ohm-cm to about 60.3 ohm-cm), more preferably, about 10 to about 11

(resistivity of about 32.3 ohm-cm to about 60.3 ohm-cm), and most preferably, about 10 to about 10.9 (resistivity of about 32.3 ohm-cm to about 57.7 ohm-cm).

[0052] In a preferred form of the membrane 10 in accordance with the invention, the interior sulfonate layer 16 has a thickness of at least about 40 micrometers. Preferably, the interior sulfonate layer 16 has a thickness of about 50 micrometers to about 200 micrometers, more preferably about 60 micrometers to about 100 micrometers.

[0053] In another preferred form of the invention, the exterior sulfonate layer 16 has a thickness less than about 30 micrometers, preferably 5 micrometers to about 30 micrometers, and most preferably, about 7 micrometers to about 25 micrometers.

[0054] Although not intending to limit the invention to any theory or mode of operation, it has been discovered that that the exterior sulfonate layer 14, having a higher IXR than the interior layer 16, enables the invention to take advantage of the lower alkali metal ion resistance and decreased cell voltage provided by the lower IXR interior sulfonate layer 16 without a loss in current efficiency.

[0055] Referring to Figure 2, another preferred multilayer cation exchange membrane 110 in accordance with the present invention is illustrated in a diagrammatical, partial cross-sectional view. The membrane 110 includes a carboxylate layer 112 on one side of the membrane for facing the cathode compartment of a chloralkali cell (not shown). Multilayer membrane 110 includes an exterior sulfonate layer 114 on the side of the membrane opposite the carboxylate layer 112. Between the carboxylate layer 112 and the exterior sulfonate layer 114, the membrane 110 includes a first and second interior sulfonate layers comprising sulfonate ionomer, 117 and 116. The first interior sulfonate layer 117 is between the carboxylate layer 112 and the second interior sulfonate layer 116 and the second interior sulfonate layer 116 is between the first interior sulfonate layer 117 and the exterior sulfonate layer 114.

[0056] Like the membrane depicted in Figure 1, the multilayer membrane 110 preferably includes a woven fabric reinforcement which comprises expanded polytetrafluoroethylene (ePTFE) fiber monofilaments 118 and sacrificial multifilament yarns comprising polyethylene terephthalate (PET) filaments 120. ePTFE monofilaments 118 and PET filaments 120 are at least partially embedded in the membrane for the purpose of increasing membrane strength and embedded in the membrane 110 at locations similar to the multilayer membrane 10 shown in Figure 1 discussed above.

[0057] In the multilayer membrane 110 in accordance with the invention shown in Figure 2 the exterior sulfonate layer 114 has an ion exchange ratio greater than about 11.3 (resistivity greater than about 68.1 ohm-cm), the first interior sulfonate layer 117 has an ion exchange ratio greater than about 11.3 (resistivity greater than about 68.1), and the second interior sulfonate layer 116 has an ion exchange ratio less than about 11 (resistivity less than about 60.3 ohm-cm). Preferably, the second interior sulfonate layer 116 has an ion exchange ratio less than the ion exchange ratio of the exterior sulfonate layer 114 by at least about 0.6. Preferably, the second interior sulfonate layer has a resistivity less than the resistivity of the exterior sulfonate layer by at least about 15.5 ohm-cm.

[0058] In accordance with a preferred form of the invention, the first interior sulfonate layer 117 has an ion exchange ratio greater than the ion exchange ratio of the second interior sulfonate layer 116 by at least about 0.6. Preferably, the first interior sulfonate layer has resistivity greater than the resistivity of the second interior sulfonate layer by at least about 15.5 ohm-cm.

[0059] In the membrane 110 of Figure 2, it is preferred for the carboxylate layer to have an ion exchange ratio of about 13.8 to about 16.

[0060] It is also preferred for the first interior sulfonate layer 117 to have an ion exchange ratio that differs from the ion exchange ratio of the carboxylate layer 112 by no more than about 3.3.

[0061] Although not intending to limit the invention to any theory or mode of operation, it has been discovered that that the exterior sulfonate layer 114 having a higher ion exchange ratio than the second interior sulfonate layer 116 enables the invention to take advantage of the lower alkali metal ion resistance and decreased cell voltage provided by the lower ion exchange ratio of the second interior sulfonate layer 116 without a loss in current efficiency. It has further been discovered that the higher ion exchange ratio of the first interior layer 117 does not detract from the advantage of the lower alkali metal ion resistance and decreased cell voltage provided by the lower ion exchange ratio of the second interior sulfonate layer 116 without a loss in current efficiency. The higher ion exchange ratio of the first interior sulfonate layer 116, which preferably does not differ from the IXR of the carboxylate layer 112 by more than about 3.3, advantageously can provide resistance to delamination at the interface of the first interior sulfonate layer 116 and the carboxylate layer 112.

[0062] Although the membranes illustrated in Figures 1 and 2 have three and four layers, respectively, it will be understood that a membrane in accordance with the invention may have additional layers of the same or different fluorinated ionomers, of the same or different ion exchange ratio or resistivity values, and of the same or different thickness provided that the additional layers do not interfere with the decrease in voltage and maintenance of high current efficiencies provided by the invention. It is preferred for total layer thickness to be no greater than about 250 micrometers. Preferably, total layer thickness is about 75 micrometers to about 150 micrometers.

Manufacturing

[0063] Manufacturing methods that are known for chloralkali membranes can be adapted to manufacture the multilayer cation exchange membranes in accordance with the invention. Manufacturing can be performed with fluorinated ionomers in a melt processible precursor form, e.g., the carboxylate ionomer precursor contains methyl ester groups and the sulfonate ionomer contains sulfonyl fluoride groups. The multilayer membranes can be produced by lamination of separate extruded ionomer precursor films that can be assembled by lamination at elevated temperature. Alternatively, coextruded multilayer films can be used. For example, a bi-film of the carboxylate ionomer precursor and the sulfonate ionomer precursor can first be produced and then laminated to multiple single layer films of the extruded sulfonate ionomer precursor or to multilayer co-extruded sulfonate ionomer precursor films. The layers or multilayer film(s) are then laminated at elevated temperature to fuse the polymer layers with the woven fabric reinforcement between the desired layers or with the woven fabric reinforcement on the surface of the membrane to be embedded in an exterior layer. The membrane is then hydrolyzed in an aqueous alkali metal hydroxide solution, optionally containing an organic solvent such as dimethyl sulfoxide (DMSO), to convert the ionomer precursors to ionic form.

TEST METHODS

Chloralkali Cell Performance:

[0064] A laboratory chloralkali electrolysis cell employing a zero gap, an activated cathode, and 100 cm² active area is used in the following examples to illustrate the operation and performance of membranes in accordance with the invention. A test is performed by installing a membrane sample in the laboratory cell and operating for 7 days under load at nominally 90°C, 32 wt% NaOH catholyte, 17.7 wt% (200 grams/liter) NaCl anolyte, and 6 kA/m² current density. The voltage results are the final day's cell voltage and the current efficiency results are the average of the last three day's current efficiency. Voltage Measurement (CV) for this cell is performed using a Moore Industries Model SPT Programmable Signal Converter that converts the voltage signal to digital and feeds into a distributed control system. The distributed control system averages the voltage during each 24-hr period to generate the average daily cell voltage. This voltage is corrected for caustic concentration, temperature, and excess cathode overvoltage to generate the Standard Voltage according to industry standard methods. The Standard Voltage is always given relative the cathode overvoltage at 90°C cell temperature, 32 wt% NaOH catholyte, 6 kA/cm² current density. Corrections are made for the small variations from these conditions. Current Efficiency Measurement (CE) using this cell is performed by measuring the total weight and caustic concentration of the liquid output from the cathode compartment over a 14-hr period. The caustic concentration is measured using a calibrated densitometer, which is checked daily with a 30% NaOH solution. The total NaOH production (weight times concentration) is divided by the theoretical production calculated from the collection time and the average current density, that is, the total current through the system. For each example reported below, two to eight identical membrane samples were tested. The reported values for voltage and current efficiency in Table 1 are averages of the two to eight tests.

Membrane Resistance in Sodium Ion Form

[0065] Membranes are preconditioned in water at 60°C for 6 hours. After preconditioning, the membranes are transferred into 24% NaCl/1%NaOH solution and soaked overnight. The solution is refreshed the following morning. The membranes are soaked in the solution until the time of measurement.

[0066] A 4-probe impedance technique in two-chamber cell fixture is used to measure the membrane resistance in liquid electrolyte of 24% NaCl/1%NaOH. The impedance spectroscopy is run using galvanostatic mode at 20 mA. Each compartment contains 50 mL solution. The tests are conducted at 21°C. A membrane is placed between the chambers with the active area of 0.785 cm². The sense probes are thin platinum wires that are placed 1 mm apart from the both surfaces of the membrane. The current electrodes are platinum mesh with approximate superficial area of 2 cm², placed 2 cm apart from the membranes.

[0067] The resistance is determined by high frequency intercept on Nyquist plot. The baseline resistance, R_B , is measured with the electrolyte solution without a membrane between the chambers. The membrane is then placed between two chambers with the electrolyte solution in both sides, leading to total resistance, R_T . The membrane resistance, R_M , is calculated from the difference between total resistance and the baseline resistance using the following formula.

$$R_M = R_T - R_B$$

[0068] The areal resistance (ohm-cm^2) is then R_M times the cell area, or 0.785 cm^2 . Further, the resistivity (in ohm-cm) is the areal resistance divided by the average thickness of the membrane sample in the active are. The areal resistance is a property of the membrane dimensions, whereas the resistivity at a specified set of conditions is an intrinsic property. Often, those skilled in the art use conductivity (Siemens/cm, also intrinsic) rather than resistance. The conductivity is simply the inverse of the resistivity.

EXAMPLES

[0069] Multilayer membranes illustrated in the Examples are made by the following procedure with the specified fluorinated ionomer precursor layers identified in Table 1 that are laminated and processed as described below. The carboxylate ionomer precursor used is a copolymer of tetrafluoroethylene (TFE) and the perfluorinated vinyl ether $\text{CF}_2=\text{CF}-\text{O}-\text{CF}_2\text{CF}(\text{CF}_3)-\text{O}-\text{CF}_2\text{CF}_2\text{CO}_2\text{CH}_3$. The sulfonate ionomer precursor is a copolymer of TFE and perfluorinated vinyl ether $\text{CF}_2=\text{CF}-\text{O}-\text{CF}_2\text{CF}(\text{CF}_3)-\text{O}-\text{CF}_2\text{CF}_2\text{SO}_2\text{F}$. In Table 1, there are examples of both three-layer membrane structures (examples 1-10) and four-layer membrane structures (examples 11-12). In all cases, the SR layers are numbered with SR1 being closest to the CR layer, SR2 being on the side of SR1 opposite the CR layer, and SR3 (if present) on the side of SR2 opposite the CR layer. For three-layer structures (examples 1-10) as are illustrated in Figure 1, CR designates the carboxylate ionomer layer 12 and SR1 and SR2 designate the interior and exterior sulfonate layers, respectively, i.e., sulfonate layer 16 and sulfonate layer 14 as shown in Figure 1. For membranes that have three sulfonate layers as depicted in Figure 2, CR designates the carboxylate ionomer layer 112 and SR3 designates the exterior sulfonate layer 114. With reference to Figure 2, SR1 and SR2 designate the two interior sulfonate layers 117 and 116, respectively, i.e., SR1 is an interior sulfonate layer 117 between the CR layer 112 and the second interior SR layer 116 and SR2 is a second interior sulfonate layer 116 between the first interior sulfonate layer 117 and the exterior sulfonate layer 114. The thickness, EW, and IXR of all layers and additionally the resistivity and areal resistance of the sulfonate ionomer layers are listed in Table 1.

[0070] A 4 foot (1.2 meter) wide bi-film of carboxylate ionomer and sulfonate ionomer precursors is first extruded first. Extrusion is performed at 270°C using two single-screw extruders, a die block, film die, chill roll, and take-up roll. Additional membrane layers are produced by extruding single layer sulfonate ionomer films of the same width using the same apparatus with a single extruder.

[0071] Reinforcing fabric is used that contains fibers of expanded tetrafluoroethylene (ePTFE) and polyethylene terephthalate in a plain weave with an alternating structure of 2 PET fibers and 1 ePTFE fiber in both directions. The reinforcing fabric has a center-to-center fiber spacing of about 350 micrometers. Fiber weights are varied as described in Table 1.

[0072] For lamination, the films are fed into a vacuum laminator on top of the fabric reinforcement, if used. The fabric is adjacent to a porous release paper that is then adjacent to the vacuum source. The carboxylate layer is positioned away from the vacuum source and the sulfonate layer towards the vacuum source. The conditions used for lamination are 200°C , -70 kPag vacuum, and a feed rate of 1-2 ft/min. (0.3 to 0.6 m/min.).

[0073] The laminated films are hydrolyzed for 25 min. at 75°C with 25% sodium hydroxide and 10% DMSO in water. The dry films are spray coated with a solution of sulfonate ionomer in acid form and zirconium dioxide (0.2-0.23 ratio polymer to zirconium dioxide) to a loading of about 0.3 mg/m^2 . Anode and cathode are coated similarly.

[0074] Cell voltage and current efficiency for the membranes listed in Table 2 are measured in the laboratory chloralkali cell using the test methods described above. The multilayer cation exchange membranes in accordance with the invention provide improved cell voltage over two-layer membranes while maintaining high current efficiencies.

Table 1

Ex	Total um	CR			SR1				
		CR μm	CR EW g	CR IXR	SR1 μm	SR1 EW g	SR1 IXR	SR1 Resistiv. Ohm-cm	SR1 Areal Resist. Ohm-cm ²
Comp. 1	127	11	1050	14.8	116	920	11.5	73.7	0.855
Comp. 2	102	9	1050	14.8	93	920	11.5	73.7	0.683
Comp. 3	127	13	1050	14.8	114	850	10.1	35.8	0.409
Comp.4	127	13	1050	14.8	114	890	10.9	58.2	0.665
5	127	9	1050	14.8	93	850	10.1	35.8	0.332
6	127	9	1050	14.8	93	885	10.8	55.5	0.515

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(continued)

		CR			SR1				
Ex	Total um	CR μm	CR EW g	CR IXR	SR1 μm	SR1 EW g	SR1 IXR	SR1 Resistiv. Ohm-cm	SR1 Areal Resist. Ohm-cm ²
7	102	9	1050	14.8	67	885	10.8	55.5	0.374
8	102	9	1050	14.8	67	885	10.8	55.5	0.374
Comp. 9	102	9	1050	14.8	25	920	11.5	73.7	0.184
10	102	9	1050	14.8	67	885	10.8	55.5	0.374
11	102	9	1050	14.8	67	885	10.8	55.5	0.374
12	102	9	1050	14.8	16	920	10.8	73.7	0.118
13	102	9	1050	14.8	16	920	10.8	73.7	0.118

Table 1 (cont.)

Ex	SR2					SR3					Fabric denier
	SR2 μm	SR2 EW g	SR2 IXR	SR2 Resistiv. Ohm-cm	SR2 Areal Resistance Ohm-cm ²	SR3 μm	SR3 EW	SR3 IXR	SR3 Resistiv. Ohm-cm	SR3 Areal Resist. Ohm-cm ²	
Comp. 1	-	-	-	-	-	-	-	-	-	-	90
Comp. 2	-	-	-	-	-	-	-	-	-	-	90
Comp. 3	-	-	-	-	-	-	-	-	-	-	90
Comp. 4	-	-	-	-	-	-	-	-	-	-	90
5	25	1000	13.1	110.4	0.28	-	-	-	-	-	90
6	25	1000	13.1	110.4	0.28	-	-	-	-	-	90
7	25	1000	13.1	110.4	0.28	-	-	-	-	-	90
8	25	920	11.5	73.7	0.187	-	-	-	-	-	90
Comp. 9	67	885	10.8	55.5	0.372	-	-	-	-	-	90
10	25	920	11.5	73.7	0.187	-	-	-	-	-	50
11	25	920	11.5	73.7	0.187	-	-	-	-	-	70
12	67	885	10.8	55.5	0.372	9	920	11.5	73.7	0.066	90
13	67	885	10.8	55.5	0.372	9	1000	13.1	110.4	0.099	90

Table 2

Ex	CV	CE (%)	Comp. Exmpl.	Delta V	Delta CE
Comp. 1	2.957	96.1			
Comp. 2	2.908	96			
Comp. 3	2.933	95.2	1	-0.023	-0.9
Comp. 4	2.934	94.9	1	-0.022	-1.3
5	2.925	95.9	1	-0.031	-0.2
6	2.937	96.1	1	-0.019	0
7	2.879	96	2	-0.029	0
8	2.852	96.3	2	-0.056	0.3
Comp. 9	2.834	95.3	2	-0.074	-0.7
10	2.846	96	2	-0.062	0.1
11	2.851	95.8	2	-0.057	-0.2
12	2.864	96.1	2	-0.044	0.1
13	2.865	96.6	2	-0.043	0.6

[0075] Comparative Examples 1 and 2 illustrate typical of commercial two-layer membranes and are baseline comparatives to illustrate improvement provided by the multilayer membranes in accordance with the invention. The polymers and reinforcements are similar, but the overall thickness is different. This thickness difference means that Example 1 at 127 μm (5 mils) has a cell voltage of about 50 mV higher than Example 2 at 102 μm (4 mils). Since some examples are 127 μm , and others are 102 μm , a comparison will be made to either Example 1 or Example 2 with the corresponding thickness as a baseline comparative. Examples 3-6 are 127 μm thick, and will be compared to Comparative Example 1.

[0076] Comparative Examples 3 and 4 illustrate the results that are obtained by using sulfonate ionomer with lower IXR and resistivity to attempt to reduce the voltage of the overall membrane. The effect on voltage is as expected, with a voltage improvement of slightly more than 20 mV from Comparative Example 1 with the same overall thickness. This is a desirable effect for voltage, but the current efficiency is also reduced about 1%, a significant loss that generally makes a membrane commercially unviable.

[0077] Examples 5 and 6 illustrate an embodiment of the invention as depicted in Figure 1 by reducing the thickness of the low IXR sulfonate ionomer layer used in Comparative Examples 3 and 4 by 25 μm , and adding 25 μm layer of sulfonate ionomer that is higher in IXR and resistivity, resulting in the same total thickness. These changes result in a comparable voltage improvement as found in Examples 3 and 4, but surprisingly, a current efficiency within measurement error of Example 1. These results show that the voltage can be reduced by lowering the IXR and resistivity of the bulk of the sulfonate ionomer, and the current efficiency retained, as long as the sulfonate ionomer against the anode compartment has an IXR or resistivity in a commercially typical range.

[0078] Example 7 and 8 also illustrate an embodiment of the invention as depicted in Figure 1 and shows that the same effect occurs on thinner membranes. Here the sulfonate ionomer in a structure similar to Example 2 is replaced by two layers: the interior layer having lower IXR and resistivity, and the outer layer having higher IXR and resistivity. As with Examples 5 and 6, we see a reduction in voltage by more than 20 mV, and a current efficiency which is essentially the same as Example 2.

[0079] Comparative Example 9 illustrates the results that are obtained by using sulfonate ionomer with lower IXR at the outer layer to attempt to reduce the voltage in multilayer membranes. Here the sulfonate ionomer in a structure similar to Example 2 is replaced by two layers: the outer layer having lower IXR and resistivity, and the inner layer having higher IXR and resistivity. The effect on voltage is as expected, with a voltage improvement over Comparative Example 2 with the same overall thickness. However, the current efficiency is reduced about 1%, which is not desirable.

[0080] Comparative Example 9 also illustrates the significant drop in the current efficiency when the low IXR sulfonate ionomer is used in the outer layer as opposed to Example 8. Both examples are made of the same sulfonate ionomers, one with high IXR and another with low IXR, but in the opposite order. They show comparable voltage improvement compared to Example 2. However, the current efficiency is retained in Example 8 with high IXR sulfonate ionomer in the outer layer whereas the current efficiency is reduced in Comparative Example 9.

[0081] Examples 10 and 11 illustrate the invention and are similar to Example 8 in structure, but the reinforcement

has been changed. The 90 denier ePTFE fibers have been replaced by 50 denier and 70 denier respectively, with no other changes to the fabric or membrane. In this case, the voltage is reduced further, but again the current efficiency is essentially unchanged. This shows that further voltage reductions to the structure, such as by reducing the resistance of the reinforcement, do not change the essential character of the invention.

[0082] Example 12 and 13 illustrate an embodiment of the invention as depicted in Figure 2 in which three sulfonate layers are employed but with a total thickness similar to Comparative Example 2. Both Examples 12 and 13 show the voltage improvement because of low IXR sulfonate replacing high IXR sulfonate ionomer in Example 2 with the similar thickness. Surprisingly, the current efficiency is again retained as the higher IXR sulfonate is used in the outer layer adjacent to the anode surface.

EMBODIMENTS

[0083]

1. A multilayer cation exchange membrane for use in a chloralkali process comprising a carboxylate layer comprising a fluorinated ionomer containing carboxylate groups on one side of the membrane, an exterior sulfonate layer comprising a fluorinated ionomer containing sulfonate groups on the side of the membrane opposite the carboxylate layer, and an interior sulfonate layer comprising a fluorinated ionomer containing sulfonate groups between the carboxylate layer and the exterior sulfonate layer, the exterior sulfonate layer having an ion exchange ratio greater than about 11.3, and the interior sulfonate layer having an ion exchange ratio less than about 11.

2. The membrane of embodiment 1 wherein the interior sulfonate layer has an ion exchange ratio less than the ion exchange ratio of the exterior sulfonate layer by at least about 0.6.

3. The membrane of embodiments 1 or 2 wherein the carboxylate layer has an IXR of about 13.8 to about 16.

4. The membrane of embodiments 1, 2, or 3 wherein the exterior sulfonate layer has an ion exchange ratio greater than about 11.5.

5. The membrane of embodiments 1, 2, or 3 wherein the exterior sulfonate layer has an ion exchange ratio of about 11.3 to about 17.5.

6. The membrane of embodiments 1, 2, or 3 wherein the exterior sulfonate layer has an ion exchange ratio of about 11.3 to about 15.5.

7. The membrane of embodiments 1, 2, or 3 wherein the exterior sulfonate layer has an ion exchange ratio of about 11.3 to about 13.5.

8. The membrane of embodiments 1, 2, or 3 wherein the exterior sulfonate layer has an ion exchange ratio or about 11.3 to about 12.4.

9. The membrane of any of the preceding embodiments wherein the interior sulfonate layer has an ion exchange ratio less than about 10.9.

10. The membrane of any of embodiments 1-8 wherein the interior sulfonate layer has an ion exchange ratio of about 9.3 to about 11.

11. The membrane of embodiments 1-8 wherein the interior sulfonate layer has an ion exchange ratio of about 10 to about 11.

12. The membrane of embodiments 1-8 wherein the interior sulfonate layers has an ion exchange ratio of about 10 to about 10.9.

13. The membrane of any of the preceding embodiments further comprising a woven fabric reinforcement.

14. The membrane of embodiment 13 wherein the woven fabric reinforcement is embedded at least partially in the membrane.

15. The membranes of embodiments 13 or 14 wherein the woven fabric comprises fluoropolymer yarns having a denier less than about 100.

16. The membrane of any of the preceding embodiments wherein the interior sulfonate layer has a thickness of at least about 40 micrometers.

17. The membrane of any of embodiments 1-15 wherein the interior sulfonate layer has a thickness of about 50 micrometers to about 200 micrometers.

18. The membrane of any of embodiments 1-15 wherein the interior sulfonate layer has a thickness of about 60 micrometers to about 100 micrometers.

19. The membrane of the preceding embodiments wherein the exterior sulfonate layer has a thickness less than about 30 micrometers.

20. The membrane of embodiments 1-18 wherein the exterior sulfonate layer has a thickness of about 5 micrometers to about 30 micrometers.

21. The membrane of embodiments 1-18 wherein the exterior sulfonate layer has a thickness of about 7 micrometers to about 25 micrometers.

22. A multilayer cation exchange membrane for use in a chloralkali process comprising an carboxylate layer comprising a fluorinated ionomer containing carboxylate groups on one side of the membrane, an exterior sulfonate layer comprising a fluorinated ionomer containing sulfonate groups on the side of the membrane opposite the carboxylate layer, and an interior sulfonate layer comprising a fluorinated ionomer containing sulfonate groups between the carboxylate layer and the exterior sulfonate layer, the exterior sulfonate layer having a resistivity greater than about 68.1 ohm-cm, and the interior sulfonate layer having a resistivity less than about 60.3 ohm-cm.

23. The membrane of embodiment 22 wherein the interior sulfonate layer has a resistivity less than the resistivity of the exterior sulfonate layer by at least about 15.5 ohm-cm.

24. The membrane of embodiments 22-23 wherein the carboxylate layer has an IXR of about 13.8 to about 16.

25. The membrane of embodiments 22, 23, or 24 wherein the exterior sulfonate layer has a resistivity greater than about 73.2 ohm-cm.

26. The membrane of embodiments 22, 23, or 24 wherein the exterior sulfonate layer has a resistivity of about 68.1 ohm-cm to about 186.3 ohm-cm.

27. The membrane of embodiments 22, 23, or 24 wherein the exterior sulfonate layer has a resistivity of about 68.1 ohm-cm to about 155.4 ohm-cm.

28. The membrane of embodiments 22, 23, or 24 wherein the exterior sulfonate layer has a resistivity of about 68.1 ohm-cm to about 118.3 ohm-cm.

29. The membrane of embodiments 22, 23, or 24 wherein the exterior sulfonate layer has a resistivity of about 68.1 ohm-cm to about 78.1 ohm-cm.

30. The membrane of any of embodiments 22-29 wherein the interior sulfonate layer has a resistivity less than about 57.7 ohm-cm.

31. The membrane of any of embodiments 22-29 wherein the interior sulfonate layer has a resistivity of about 10.7 ohm-cm to about 60.3 ohm-cm.

32. The membrane of embodiments 22-29 wherein the interior sulfonate layer has a resistivity of about 32.3 ohm-cm to about 60.3 ohm-cm.

33. The membrane of embodiments 22-29 wherein the interior sulfonate layers has a resistivity of about 32.3 ohm-

cm to about 57.7 ohm-cm.

34. The membrane of any of embodiments 22-33 further comprising a woven fabric reinforcement.

35. The membrane of embodiment 34 wherein the woven fabric reinforcement is embedded at least partially in the membrane.

36. The membranes of embodiments 34 of 35 wherein the woven fabric comprises fluoropolymer yarns having a denier less than about 100.

37. The membrane of any of embodiments 22-36 wherein the interior sulfonate layer has a thickness of at least about 40 micrometers.

38. The membrane of any of embodiments 22-36 wherein the interior sulfonate layer has a thickness of about 50 micrometers to about 200 micrometers.

39. The membrane of any of embodiments 22-36 wherein the interior sulfonate layer has a thickness of about 60 micrometers to about 100 micrometers.

40. The membrane of any of embodiments 22-39 wherein the exterior sulfonate layer has a thickness less than about 30 micrometers.

41. The membrane of embodiments 22-39 wherein the exterior sulfonate layer has a thickness of about 5 micrometers to about 30 micrometers.

42. The membrane of embodiments 22-39 wherein the exterior sulfonate layer has a thickness of about 7 micrometers to about 25 micrometers.

43. A multilayer cation exchange membrane for use in a chloralkali process comprising a carboxylate layer comprising a fluorinated ionomer containing carboxylate groups on one side of the membrane, an exterior sulfonate layer comprising a fluorinated ionomer containing sulfonate groups on the side of the membrane opposite the carboxylate layer, and first and second interior sulfonate layers comprising fluorinated ionomer containing sulfonate groups between the carboxylate layer and the exterior sulfonate layer, the first interior sulfonate layer being between the carboxylate layer and the second interior sulfonate layer and the second interior sulfonate layer being between the first interior sulfonate layer and the exterior sulfonate layer, the exterior sulfonate layer having an ion exchange ratio greater than about 11.3, the first interior sulfonate layer having an ion exchange ratio greater than about 11.3, and the second interior sulfonate layer having an ion exchange ratio less than about 11.

44. The membrane of embodiment 43 wherein the second interior sulfonate layer has an ion exchange ratio less than the ion exchange ratio of the exterior sulfonate layer by at least about 0.6.

45. The membrane of embodiments 43 or 44 wherein the first interior sulfonate layer has an ion exchange ratio greater than the ion exchange ratio of the second interior sulfonate layer by at least about 0.6.

46. The membrane of any of embodiments 43-45 wherein the carboxylate layer has an ion exchange ratio of about 13.8 to about 16.

47. The membrane of any of embodiments 43-46 wherein the first interior sulfonate layer has an ion exchange ratio that differs from the ion exchange ratio of the carboxylate layer by no more than about 3.3.

48. A multilayer cation exchange membrane for use in a chloralkali process comprising a carboxylate layer comprising a fluorinated ionomer containing carboxylate groups on one side of the membrane, an exterior sulfonate layer comprising a fluorinated ionomer containing sulfonate groups on the side of the membrane opposite the carboxylate layer, and first and second interior sulfonate layers comprising fluorinated ionomer containing sulfonate groups between the carboxylate layer and the exterior sulfonate layer, the first interior sulfonate layer being between the carboxylate layer and the second interior sulfonate layer and the second interior sulfonate layer being between the first interior sulfonate layer and the exterior sulfonate layer, the exterior sulfonate layer having a resistivity greater than about 68.1 ohm-cm, the first interior sulfonate layer having a resistivity greater than about 68.1 ohm-cm, and

the second interior sulfonate layer having a resistivity less than 60.3 ohm-cm.

49. The membrane of embodiment 48 wherein the second interior sulfonate layer has a resistivity less than the resistivity of the exterior sulfonate layer by at least about 15.5 ohm-cm.

50. The membrane of embodiments 48 or 49 wherein the first interior sulfonate layer has resistivity greater than the resistivity of the second interior sulfonate layer by at least about 15.5 ohm-cm.

51. The membrane of any of embodiments 48-50 wherein the carboxylate layer has an IXR of about 13.8 to about 16.

52. The membrane of any of embodiments 48-51 wherein the first interior sulfonate layer has an ion exchange ratio that differs from the ion exchange ratio of the carboxylate layer by no more than about 3.3.

Claims

1. A multilayer cation exchange membrane for use in a chloralkali process comprising an carboxylate layer comprising a fluorinated ionomer containing carboxylate groups on one side of the membrane, an exterior sulfonate layer comprising a fluorinated ionomer containing sulfonate groups on the side of the membrane opposite the carboxylate layer, and an interior sulfonate layer comprising a fluorinated ionomer containing sulfonate groups between the carboxylate layer and the exterior sulfonate layer, the exterior sulfonate layer having a resistivity greater than about 68.1 ohm-cm, and the interior sulfonate layer having a resistivity less than about 60.3 ohm-cm.
2. The membrane of claim 1 wherein the interior sulfonate layer has a resistivity less than the resistivity of the exterior sulfonate layer by at least about 15.5 ohm-cm.
3. The membrane of claims 1 or 2 wherein the carboxylate layer has an IXR of about 13.8 to about 16.
4. The membrane of claims 1, 2, or 3 wherein the exterior sulfonate layer has a resistivity greater than about 73.2 ohm-cm.
5. The membrane of claims 1, 2, or 3 wherein the exterior sulfonate layer has a resistivity of about 68.1 ohm-cm to about 186.3 ohm-cm, preferably a resistivity of about 68.1 ohm-cm to about 155.4 ohm-cm, more preferably a resistivity of about 68.1 ohm-cm to about 118.3 ohm-cm, and even more preferably a resistivity of about 68.1 ohm-cm to about 78.1 ohm-cm.
6. The membrane of any of claims 1-5 wherein the interior sulfonate layer has a resistivity less than about 57.7 ohm-cm.
7. The membrane of any of claims 1-5 wherein the interior sulfonate layer has a resistivity of about 10.7 ohm-cm to about 60.3 ohm-cm, preferably a resistivity of about 32.3 ohm-cm to about 60.3 ohm-cm, and more preferably a resistivity of about 32.3 ohm-cm to about 57.7 ohm-cm.
8. The membrane of any of claims 1-7 further comprising a woven fabric reinforcement.
9. The membrane of claim 8 wherein the woven fabric reinforcement is embedded at least partially in the membrane.
10. The membranes of claims 8 or 9 wherein the woven fabric comprises fluoropolymer yarns having a denier less than about 100.
11. The membrane of any of claims 1-10 wherein the interior sulfonate layer has a thickness of at least about 40 micrometers, preferably a thickness of about 50 micrometers to about 200 micrometers, and more preferably a thickness of about 60 micrometers to about 100 micrometers.
12. The membrane of any of claims 1-18 wherein the exterior sulfonate layer has a thickness less than about 30 micrometers, preferably a thickness of about 5 micrometers to about 30 micrometers, and more preferably a thickness of about 7 micrometers to about 25 micrometers.
13. A multilayer cation exchange membrane for use in a chloralkali process comprising a carboxylate layer comprising

a fluorinated ionomer containing carboxylate groups on one side of the membrane, an exterior sulfonate layer comprising a fluorinated ionomer containing sulfonate groups on the side of the membrane opposite the carboxylate layer, and first and second interior sulfonate layers comprising fluorinated ionomer containing sulfonate groups between the carboxylate layer and the exterior sulfonate layer, the first interior sulfonate layer being between the carboxylate layer and the second interior sulfonate layer and the second interior sulfonate layer being between the first interior sulfonate layer and the exterior sulfonate layer, the exterior sulfonate layer having a resistivity greater than about 68.1 ohm-cm, the first interior sulfonate layer having a resistivity greater than about 68.1 ohm-cm, and the second interior sulfonate layer having a resistivity less than 60.3 ohm-cm.

14. The membrane of claim 13 wherein the second interior sulfonate layer has a resistivity less than the resistivity of the exterior sulfonate layer by at least about 15.5 ohm-cm, and/or wherein the first interior sulfonate layer has resistivity greater than the resistivity of the second interior sulfonate layer by at least about 15.5 ohm-cm.

15. The membrane of any of claims 13 to 14 wherein the carboxylate layer has an IXR of about 13.8 to about 16, and/or wherein the first interior sulfonate layer has an ion exchange ratio that differs from the ion exchange ratio of the carboxylate layer by no more than about 3.3.

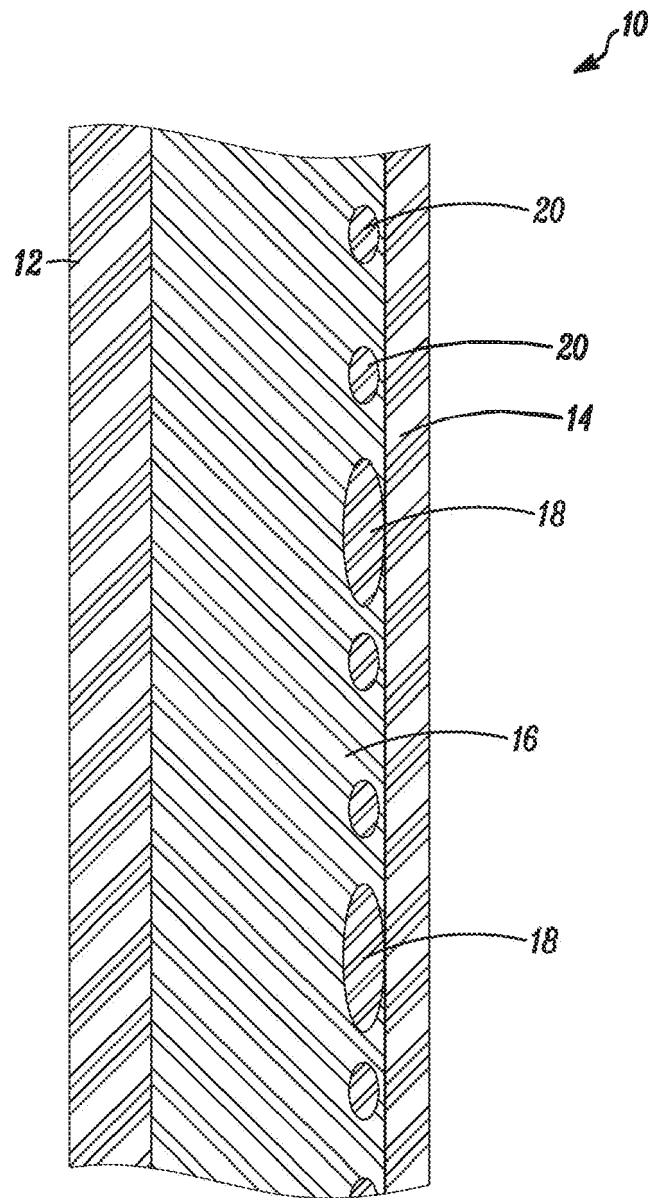


FIG. 1

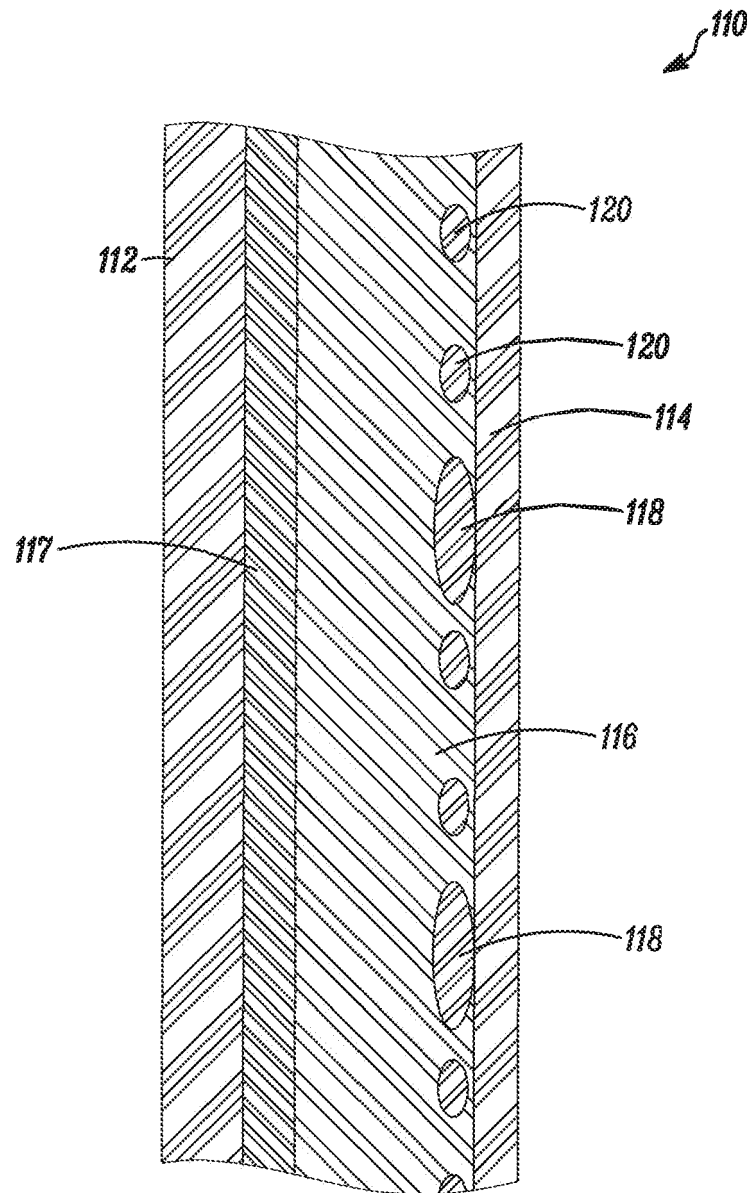


FIG. 2

REFERENCES CITED IN THE DESCRIPTION

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