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BILAYER POLYELECTROLYTE MEMBRANES

RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Applications Nos. 63/331007 filed April 14, 2022, 63/433574 filed December 19, 2022, 63/453499 filed March 21, 2023, and 63/454771 filed March 27, 2023. The entire teachings of each the above applications are incorporated herein by reference.

GOVERNMENT SUPPORT

[0002] This invention was made with government support under Grant No. DE-SC0021832 awarded by the Department of Energy and under Grant No. DE-AR0001242 awarded by ARPA-E. The government has certain rights in the invention.

BACKGROUND OF THE INVENTION

[0003] Proton exchange membrane-based fuel cells (PEMFCs) are eco-friendly energy conversion devices that operate at low temperatures and are more efficient than existing internal combustion engines. With these advantages, PEMFCs have emerged as a popular alternative to fossil fuels in the transportation industry and have the potential for use in a wide range of applications, such as portable devices and stationary power supply systems.

[0004] The proton exchange membrane (PEM) which conducts protons and serves to separate the cathode and the anode is one of the most important elements of a PEMFC. PEMs significantly affect the overall performance of fuel cells; thus, improving the efficiency of a fuel cell requires a PEM that has a high ionic conductivity, has a low fuel crossover, and provides high physicochemical and mechanical stability. Because a PEMFC uses a thin membrane as its electrolyte, these devices are more portable and compact than other types of fuel cells. However, the thin membrane can also allow the crossover of the fuel gas (hydrogen, H₂), which negatively affects the cell efficiency. Accordingly, PEMs with high ionic conductivity and reduced hydrogen crossover are needed.

SUMMARY OF THE INVENTION

[0005] In a first embodiment the invention is a bilayer polyelectrolyte membrane, comprising a first layer and a second layer, wherein: the first layer comprises a perfluorosulfonic acid (PFSA), and the second layer comprises a crosslinked polysulfonated polymer comprising sulfonated polyphenyl sulfone (sPPS), sulfonated polyether ether ketone (sPEEK), sulfonated polyphosphazene (sPOP), sulfonated polybenzimidazole (sPBI), sulfonated polyether sulfone (sPES), sulfonated polyphenylene oxide (sPPO), sulfonated polyarylene ether ketone (sPAEK), sulfonated poly(sulfone), sulfonated poly(sulfide sulfone), sulfonated polyimide (sPI), sulfonated poly(etherimide) (sPEI), sulfonated poly(amine), or a combination thereof, and wherein the first layer is disposed on the second layer.

[0006] In a second embodiment, the invention is a method of making a bilayer polyelectrolyte membrane described herein with respect to the first embodiment and various aspects thereof, comprising:

- a) providing a first layer having a first side, and a solution or suspension comprising a polysulfonated polymer and a crosslinking reagent,
- b) coating the first side of the first layer with the solution or suspension, thereby producing a coated first layer;
- c) exposing the coated first layer to conditions sufficient for the polysulfonated polymer and the crosslinking reagent to undergo a crosslinking reaction, thereby producing the bilayer polyelectrolyte membrane.

[0007] In a third embodiment the invention is a membrane electrode assembly (MEA), comprising: the bilayer polyelectrolyte membrane described herein with respect to the first embodiment and various aspects thereof; a cathode; and an anode, wherein the bilayer electrolyte membrane is disposed between the anode and the cathode.

[0008] In a fourth embodiment the invention is a fuel cell, comprising one or more of the MEAs described herein with respect to the third embodiment and various aspects thereof and one or more gas flow bipolar plates.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] The foregoing will be apparent from the following more particular description of example embodiments of the invention.

[0010] Figure 1 is a schematic representation of degradation of Nafion® membrane as a result of hydrogen crossover.

[0011] Figure 2 is a schematic representation of reduction in hydrogen crossover due to the presence of a crosslinked polymer layer on top of the PFSA layer, resulting in decreased degradation of the PFSA layer.

[0012] Figure 3 shows a plot demonstrating theoretical calculations of hydrogen crossover and resistance of coated PFSA membrane as a function of coating thicknesses.

[0013] Figure 4 shows a cyclic voltammogram of a Nafion® 211 membrane and a membrane comprising a layer of Nafion® 211 coated with crosslinked sulfonated polyphenyl sulfone (sPPS).

[0014] Figure 5 shows a plot demonstrating fuel cell polarization and power curves of a Nafion® 211 membrane (squares) and a membrane comprising a layer of Nafion® 211 coated with a layer of sPPS (diamonds).

[0015] Figure 6 shows a plot demonstrating the results of a faster accelerated stress test (FAST) of a Nafion® 211 membrane and a membrane comprising a layer of Nafion® 211 coated with a layer of crosslinked sPPS.

[0016] Figure 7 shows a schematic representation of a PEM-containing fuel cell.

[0017] Figure 8 shows a plot demonstrating water stability of sPPS before and after crosslinking.

[0018] Figure 9 shows a plot demonstrating a relationship between the degree of crosslinking and conductivity of crosslinked sPPS.

[0019] Figure 10 shows a plot demonstrating H₂ crossover through membranes comprising only Nafion® 211 or a layer of Nafion® 211 coated with a layer of crosslinked sPPS of varying thicknesses.

[0020] Figure 11 shows a plot demonstrating the relationship between the thickness of the crosslinked sPPS coating and durability of the resulting bilayer membrane.

[0021] Figure 12 shows a plot demonstrating H₂ crossover as a function of time in an accelerated stress test (AST) for membranes comprising only Nafion® 211 or a layer of Nafion® 211 coated with a layer of crosslinked sPPS of varying thicknesses.

[0022] Figure 13 shows a plot containing fuel cell polarization curves, with the dash lines corresponding to voltage-current curves (left axis) and the solid lines corresponding to current density curves (right axis). The squares indicate supported Aquivion® base layer and the triangles indicate Nafion® 211 base layer.

[0023] Figure 14 shows a plot demonstrating H₂ crossover through membranes comprising only a base layer (dark lines), or a base layer coated with 1.5 µm coatings of 40% crosslinked sPPS (light line).

[0024] Figure 15 shows the values of area specific resistance as measured by electrochemical impedance spectroscopy for a 25 µm Nafion® 211 membrane, a 1.5 µm 40% crosslinked sPPS membrane, and a bilayer membrane comprising a 25 µm Nafion® 211 layer with a 1.5 µm 40% crosslinked sPPS coating.

[0025] Figure 16 shows a ¹H NMR spectrum of sPPS.

[0026] Figures 17 shows a plot containing fuel cell polarization curves for 1.5 µm sPPS coated Nafion® 211 with various crosslinkers, with the dash lines corresponding to voltage-current curves (left axis) and the solid lines corresponding to current density curves (right axis). **1.3sHQ** is Nafion® 211 coated with ca. 1.5 µm sPPS crosslinked with 1.3 molecules of 2,5-dihydroxybenzenesulfonic acid per repeat unit of sPPS (30% crosslinked); **1.3HQ** is Nafion® 211 coated with ca. 1.5 µm sPPS crosslinked with 1.3 molecules of hydroquinone per repeat unit of sPPS (29% crosslinked); **1BP** is Nafion® 211 coated with ca. 1.5 µm sPPS crosslinked with 1 molecules of biphenyl per repeat unit of sPPS (32% crosslinked); **6EG** is Nafion® 211 coated with ca. 1.5 µm sPPS crosslinked with 6 molecules of ethylene glycol per repeat unit of sPPS (40% crosslinked).

[0027] Figure 18 shows a plot demonstrating H₂ crossover through membranes comprising Nafion® 211 coated with 1.5 µm coatings of sPPS crosslinked with various crosslinkers; 3sHQ: 0.513 mA/cm², 1.3HQ: 0.651 mA/cm², 1BP: 0.737 mA/cm², 6EG: 0.736 mA/cm², Nafion® 211: 1.39 mA/cm².

[0028] Figure 19 shows a plot containing fuel cell polarization curves for bilayer membranes comprising Nafion® 211 coated with sPPS, sPPO, or sPSU crosslinked with hydroquinone, with the dash lines corresponding to voltage-current curves (left axis) and the solid lines corresponding to current density curves (right axis). **sPPS** is Nafion® 211 coated with ca. 1.5 µm sPPS crosslinked with 1.3 molecules of hydroquinone per repeat unit of sPPS (29% crosslinked); **sPSU** is Nafion® 211 coated with ca. 1.5 µm sPSU crosslinked with 1.3

molecules of hydroquinone per repeat unit of sPSU (90% crosslinked); **sPPO** is Nafion® 211 coated with ca. 1.5 μm sPPO crosslinked with 0.5 molecules of hydroquinone per repeat unit (90% crosslinked).

[0029] Figure 20 shows a plot demonstrating H_2 crossover through bilayer membranes comprising Nafion® 211 coated with sPPS, sPPO, or sPSU crosslinked with hydroquinone; sPPS: 0.651 mA/cm^2 , sPSU: 1.216 mA/cm^2 , sPPO: 1.903 mA/cm^2 , Nafion 211: 1.39 mA/cm^2 (labels for the curves are the same as in Figure 19).

[0030] The foregoing will be apparent from the following more particular description of example embodiments of the invention, as illustrated in the accompanying drawings in which like reference characters refer to the same parts throughout the different views. The drawings are not necessarily to scale, emphasis instead being placed upon illustrating embodiments of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0031] A description of example embodiments of the invention follows.

[0032] Hydrogen crossover is an undesirable diffusion of hydrogen from the anode to the cathode through the membrane in a fuel cell. Hydrogen crossover can have at least three effects, including fuel efficiency reduction, cathode potential depression, and aggressive peroxide radical formation. The hydrogen which crosses over can directly react with oxygen at the cathode surface, resulting in a lower cathode potential than that of a lower fuel cell. More severely, this direct reaction between H_2 and O_2 at the cathode can produce peroxide radicals, which not only attack the catalyst layer but also the membrane, causing significant catalyst-layer and membrane degradation. In addition, it has been confirmed that the formation of hot-points or hydrogen peroxide by the highly exothermal chemical reaction between H_2 and O_2 can also lead to pin-holes in membranes, destroying the MEA and causing safety problems. An accelerated sintering of catalysts could be also caused by this hydrogen crossover.

[0033] In some embodiments, the present disclosure relates to a bilayer polyelectrolyte membrane which demonstrates reduced hydrogen crossover. The membrane comprises a layer of perfluorosulfonic acid (PFSA), such as Nafion®, and a coating comprising a crosslinked polysulfonated polyelectrolyte. Sulfonated polyelectrolytes such as polyphenyl

sulfone (sPPS), sulfonated polyether ether ketone (sPEEK), sulfonated polyphosphazene (sPOP), sulfonated polybenzimidazole (sPBI), sulfonated polyether sulfone (sPES), sulfonated polyphenylene oxide (sPPO), and sulfonated polyarylene ether ketone (sPAEK), sulfonated poly(sulfone), sulfonated poly(sulfide sulfone), sulfonated polyimide (sPI), sulfonated poly(etherimide) (sPEI), and sulfonated poly(amine) can be used in the coating layer. The coating layer has lower hydrogen penetration compared to the PFSA, thus reducing hydrogen crossover through the membrane (Figures 1 and 2).

[0034] The plot in Figure 3 demonstrates the design criteria for a coated membrane. The plot shows theoretical calculations of H₂ crossover and resistance of coated PFSA as a function of coating thicknesses. The cyclic voltammogram in Figure 4 shows hydrogen crossover measurement of Nafion® 211 and Nafion® 211 coated with 1 µm crosslinked sPPS. The plot in Figure 5 shows fuel cell polarization and power curves of Nafion® 211 and Nafion® 211 with a 1 µm crosslinked sPPS coating. These data show that the polymer coating reduces H₂ crossover by 44% compared to uncoated Nafion® 211. Furthermore, the results of Faster Accelerated Stress Test (FAST) in Figure 6 show that the presence of the crosslinked sPPS coating nearly doubles durability of the membrane. The membrane failure time for Nafion® 211 is about 5000 equivalent hours, while for Nafion® 211 with a 1 µm crosslinked sPPS coating the failure time is about 9500 equivalent hours.

Definitions

[0035] Numeric ranges are inclusive of the numbers defining the range. For example, “x is an integer between 5 and 14” means that x can be 5, 6, 7, 8, 9, 10, 11, 12, 13, or 14. Measured and measureable values are understood to be approximate, taking into account significant digits and the error associated with the measurement. As used in this application, the terms “about” and “approximately” have their art-understood meanings; use of one vs the other does not necessarily imply different scope. Unless otherwise indicated, numerals used in this application, with or without a modifying term such as “about” or “approximately”, should be understood to encompass normal divergence and/or fluctuations as would be appreciated by one of ordinary skill in the relevant art. In certain embodiments, the term “approximately” or “about” refers to a range of values that fall within 10%, 9%, 8%, 7%, 6%, 5%, 4%, 3%, 2%, 1%, or less in either direction (greater than or less than) of a stated

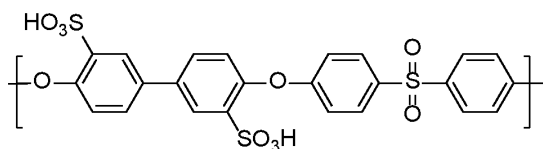
reference value unless otherwise stated or otherwise evident from the context (except where such number would exceed 100% of a possible value).

[0036] The term “bilayer polyelectrolyte membrane”, as used herein, refers to a membrane containing two layers disposed on top of each other, each layer comprising a polyelectrolyte. The two layers can adhere to each other through formation of chemical bonds or through Van der Waals interactions.

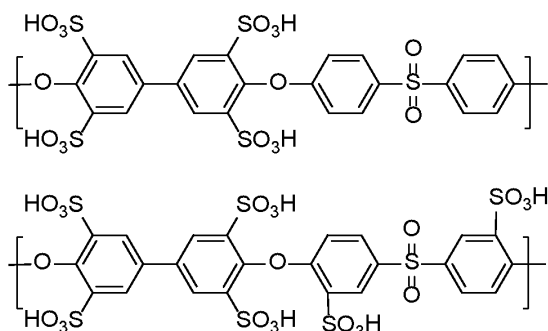
[0037] As used herein, the term “polysulfonated polymer” or “sulfonated polymer” refers to a polymer comprising a plurality of sulfonic acid or sulfonate salt groups: $\text{S(O)}_2\text{OH}$ or $\text{S(O)}_2\text{O}^-\text{M}^+$, where M^+ is a counterion.

[0038] As used herein, the term “degree of sulfonation” refers to the number of repeat units that have at least one sulfonic acid/sulfonate salt group. For example, 20% degree of sulfonation indicates a polymer that has 20 percent of its repeat units sulfonated, while 100% degree of sulfonation indicates every repeat unit in the polymer contains one sulfonic acid/sulfonate salt group. This may include polymers that contain multiple sulfonic acid/sulfonate salt groups per repeat unit (e.g., disulfonation, trisulfonation, tetrasulfonation, etc). In some embodiments, the sulfonated polymer can comprise on average 2 sulfonic acid groups per repeat unit, which corresponds to 200% degree of sulfonation. In some embodiments, the sulfonated polymer can comprise on average 2, 3, 4, or 5 sulfonic acid groups per repeat unit, which corresponds to 200%, 300%, 400%, or 500% degree of sulfonation, respectively. In some embodiments, the sulfonated polymer can comprise on average from 1.5 to 2.5 sulfonic acid groups per repeat unit, which corresponds to 150% to 200% degree of sulfonation.

[0039] The sulfonated polymers of the disclosure can also be characterized by the average number of sulfonic acid groups per repeat unit. For example, a sulfonated polyphenyl sulfone (sPPS) can comprise 1, 2, 3, 4, 5, 6, 7, or 8 sulfonic acid groups per repeat unit. For example, a repeat unit of sPPS can comprise 2 sulfonic acid groups:

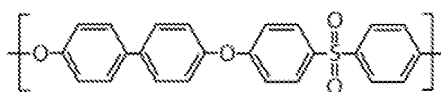


[0040] . Alternatively, a repeat unit of sPPS can comprise 4 or 6 sulfonic acid groups:



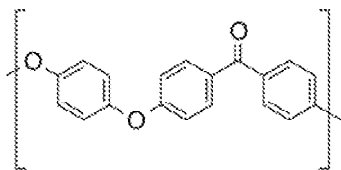
[0041] In a given polymer, some repeat units can have, for example, 1 sulfonic acid group, some repeat units can have 2 sulfonic acid groups, and some repeat units can have 3 or more sulfonic acid groups. Accordingly, the number of sulfonic acid groups per repeat unit that is measured in a bulk polymer by analyzing, for example, its ^1H NMR spectrum or ion exchange capacity, corresponds to the average number of sulfonic groups across all the repeat units of the polymer.

[0042] As used herein, the term “polyphenyl sulfone” refers to a polymer comprising the following repeat unit:



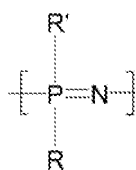
[0043] Sulfonated polyphenyl sulfone can comprise 1, 2, 3, 4, 5, 6, 7, or 8 sulfonic acid groups per repeat unit.

[0044] As used herein, the term “polyether ether ketone” refers to a polymer comprising the following repeat unit:

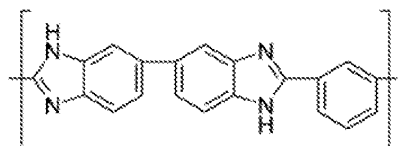


[0045] Sulfonated polyether ether ketone can comprise 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, or 12 sulfonic acid groups per repeat unit.

[0046] As used herein, the term “polyphosphazine” refers to a polymer comprising the following repeat unit:

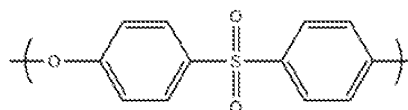


[0047] As used herein, the term “polybenzimidazole” refers to a polymer comprising the following repeat unit:



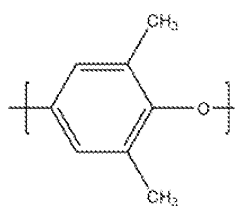
[0048] Sulfonated polybenzimidazole can comprise 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 sulfonic acid groups per repeat unit.

[0049] As used herein, the term “polyether sulfone” refers to a polymer comprising the following repeat unit:



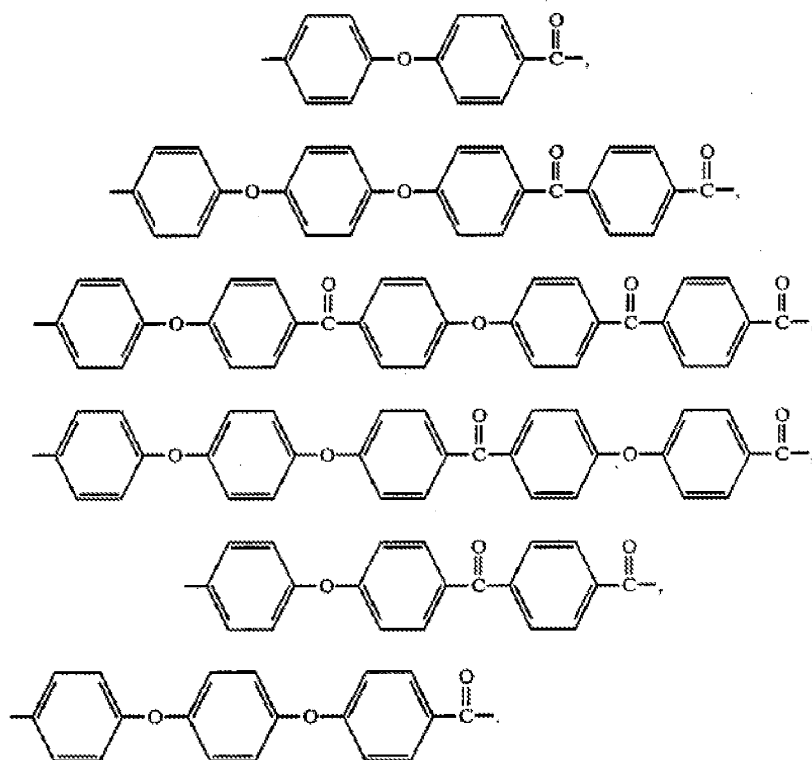
[0050] Sulfonated polyether sulfone can comprise 1, 2, 3, 4, 5, 6, 7, or 8 sulfonic acid groups per repeat unit.

[0051] As used herein, the term “polyphenylene oxide” refers to a polymer comprising the following repeat unit:



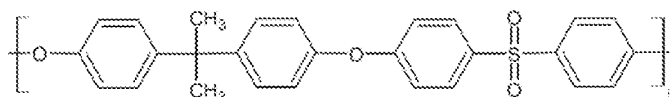
[0052] Sulfonated polyphenylene oxide can comprise 1 or 2 sulfonic acid groups per repeat unit.

[0053] As used herein, the term “polyarylene ether ketone” refers to a polymer comprising one or more of the following repeat units:



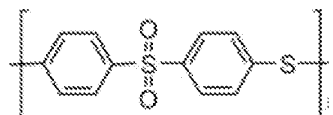
[0054] Sulfonated polyarylene ether ketone can comprise 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, or 20 sulfonic acid groups per repeat unit.

[0055] As used herein, the term “poly(sulfone)” refers to a polymer comprising the following repeat unit:



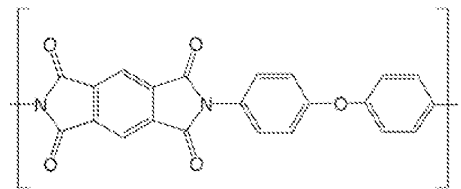
[0056] Sulfonated poly(sulfone) (sPSU) can comprise 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, or 16 sulfonic acid groups per repeat unit.

[0057] As used herein, the term “poly(sulfide sulfone)” refers to a polymer comprising the following repeat unit:



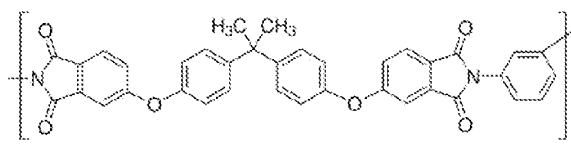
[0058] Sulfonated poly(sulfide sulfone) can comprise 1, 2, 3, 4, 5, 6, 7, or 8 sulfonic acid groups per repeat unit.

[0059] As used herein, the term “polyimide” refers to a polymer comprising the following repeat unit:



[0060] Sulfonated polyimide can comprise 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 sulfonic acid groups per repeat unit.

[0061] As used herein, the term “poly(etherimide)” refers to a polymer comprising the following repeat unit:



[0062] Sulfonated poly(etherimide) can comprise 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, or 18 sulfonic acid groups per repeat unit.

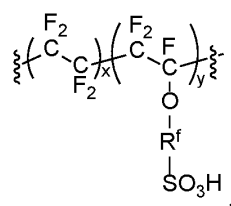
[0063] Any of the polymer repeat units described above can have one or more hydrogen atoms substituted with a -CN, -NO₂, -N₃, -OH, F, Cl, Br, I, oxo, -SO₂H, -SO₃H, -OR^{aa}, -NH(R^{aa})₂, -N(R^{aa})₂, -N(R^{aa})₃⁺X⁻, -SH, -SR^{aa}, -C(=O)R^{aa}, -CO₂H, -CHO, -CO₂R^{aa}, -OC(=O)R^{aa}, -OCO₂R^{aa}, -C(=O)N(R^{aa})₂, -OC(=O)N(R^{aa})₂, -NR^{aa}C(=O)R^{aa}, -NR^{aa}CO₂R^{aa}, -NR^{aa}C(=O)N(R^{aa})₂, -C(=NR^{aa})R^{aa}, -C(=O)NR^{aa}SO₂R^{aa}, -NR^{aa}SO₂R^{aa}, -SO₂N(R^{aa})₂, -SO₂R^{aa}, -SO₂OR^{aa}, -OSO₂R^{aa}, -S(=O)R^{aa}, -OS(=O)R^{aa}, -Si(R^{aa})₃, -OSi(R^{aa})₃, C₁₋₁₂ alkyl, C₁₋₁₂ alkoxy, C₁₋₁₂ haloalkyl, C₃₋₁₂ cycloalkyl, 3-16 membered heterocyclyl, and C₆₋₁₂ aryl, wherein X⁻ is a counterion and each instance of R^{aa} is, independently, selected from H, -OH, C₁₋₁₀ alkyl, C₁₋₁₀ haloalkyl, C₃₋₁₂ cycloalkyl, 5-16 membered heterocyclyl, and C₆₋₁₂ aryl, or two R^{aa} groups are joined to form a 3-16 membered heterocyclyl.

[0064] As used herein, the term “polyalcohol” refers to an alcohol comprising more than one hydroxyl group. Examples of polyalcohols include, but are not limited to, ethylene glycol, propylene glycol, 1,3-propanediol, 1,4-butanediol, glycerol, erythriol, xylitol, hydroquinone, catechol, resorcinol, and phloroglucinol.

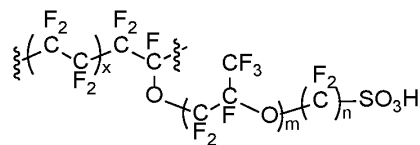
[0065] As used herein, the term “polyelectrolyte” refers to a polymer comprising repeat units bearing a charged or an ionizable group. Under a particular set of conditions a polyelectrolyte has a net negative or net positive charge. In some embodiments, a

polyelectrolyte is or comprises a polycation; in some embodiments, a polyelectrolyte is or comprises a polyanion. Polycations have a net positive charge and polyanions have a net negative charge. The net charge of a given polyelectrolyte may depend on the surrounding chemical conditions, e.g., on the pH.

[0066] As used herein, the term “perfluorosulfonic acid” refers to a polymer represented by the following structural formula:



where R^f represents a perfluoroalkylene or perfluorooxyalkylene group, and x and y the relative proportion of perfluoro monomer and sulfonated monomer respectively. As used herein, the terms “perfluoroalkylene” or “perfluorooxyalkylene” refer to an alkylene or an oxyalkylene groups in which all hydrogen atoms have been substituted with fluorines. A class of PFSA is represented by the structural formula (I):



Such PFSA are usually categorized according to their side-chain length. For example, Aquivion® (formerly Dow SSC) PFSA are commonly classified as short-side-chain (SSC) PFSA, while Nafion® is considered as a long-side-chain (LSC) PFSA. Examples of commercial PFSA include the following:

PFSA	m	n
Nafion®	1	2
Aciplex®	0-3	2-5
Flemion®	0 or 1	1-5
3M™	0	4
SSC	0	2

[0067] As used herein, the term “crosslinking” refers to formation of a covalent or ionic bond between a sulfonic acid group of the sulfonated polymer and the crosslinking reagent. For example, crosslinking refers to the formation of sulfonate esters as a result of the reaction between the sulfonic acid group of the sulfonated polymer and a polyol. In some embodiments, crosslinking refers to the formation of sulfonamides as a result of the reaction between the sulfonic acid group of the sulfonated polymer and a polyamine. As used herein, the term “crosslinking” does not refer to formation of a covalent or ionic bond between the crosslinking reagent and any functional group in the polymer repeat unit other than a sulfonic acid group.

[0068] As used herein, the term “crosslinked polymer” refers to a polymer in which two or more non-adjacent repeat units of the same main chain are connected via a crosslinking moiety. The term “crosslinked polymer” also refers to two or more different main chains connected via a plurality of crosslinking moieties.

[0069] As used herein, the term “crosslinking moiety” refers a polyvalent, for example, divalent or trivalent, moiety which forms a covalent bond with one or more non-adjacent repeat units of the same polymer main chain or with one or more repeat units of different main chains. A crosslinking moiety can comprise charged groups, for example, an ammonium group or a metal ion, which form an electrostatic/ionic bond with a sulfonic acid group attached to the repeat unit of the sulfonated polymer.

[0070] As used herein, the term “crosslinking reaction” refers to a chemical reaction between a sulfonic acid group attached to the repeat units of the sulfonated polymer and a crosslinking reagent, resulting in formation of a covalent or electrostatic/ionic bonds between the polymer chains and the crosslinking reagent.

[0071] As used herein, the term “conditions sufficient for the polymer and the crosslinking reagent to undergo a crosslinking reaction” refers to the external stimuli (e.g.

heat, UV light, microwave irradiation, presence of a chemical initiator, such as a radical initiator) as well as time necessary in order to form the crosslinked polymer.

[0072] As used herein, the term “gel fraction (%)” is calculated based on the following equation: $[[M(f)/M(i)]]*100$, where M(f) is the dry mass of the membrane exposed to a solvent that dissolves the original polymer and crosslinker, and M(i) is the dry mass of the membrane before exposure to a dissolving solvent. The gel fraction indicates the percent of polymer and linker that remains in the network after exposure to a solvent that dissolves each individual component.

[0073] As used herein, the term “repeat unit” (also known as a monomer unit) refers to a chemical moiety which periodically repeats itself to produce the complete polymer chain (except for the end-groups) by linking the repeat units together successively. A polymer can contain one or more different repeat units.

[0074] As used herein, the “main chain” of a polymer, or the “backbone” of the polymer, is the series of bonded atoms that together create the continuous chain of the molecule. As used herein, a “side chain” of a polymer is the series of bonded atoms which are pendent from the main chain of a polymer.

[0075] As used herein, “PFSA and the matrix polymer form an interpenetrating network” refers to a porous matrix that contains PFSA within its pores. A porous matrix can be impregnated with the PFSA, for example, by soaking the matrix in a solution of the PFSA or by spraying a solution of the PFSA on the porous matrix. Alternatively, the porous matrix can be impregnated with a solution of the PFSA monomer, followed by a polymerization reaction within the pores of the matrix.

[0076] As used herein, “unsupported membrane” refers to a membrane that contains only the PFSA layer and the crosslinked polysulfonated polymer layer and does not contain any other layers, supports, or reinforcements.

[0077] As used herein, the term “continuous layer” refers to layer that does not contain gaps or openings, such that any point on the layer can be connected to any other point on the layer by a straight line, and each point of that straight line belongs to the layer.

[0078] As used herein, the term “alkyl” refers to a radical of a straight-chain or branched saturated hydrocarbon group having from 1 to 10 carbon atoms (“C₁₋₁₀ alkyl”). In some embodiments, an alkyl group has 1 to 9 carbon atoms (“C₁₋₉ alkyl”). In some embodiments, an alkyl group has 1 to 8 carbon atoms (“C₁₋₈ alkyl”). In some embodiments, an alkyl group

has 1 to 7 carbon atoms ("C₁₋₇ alkyl"). In some embodiments, an alkyl group has 1 to 6 carbon atoms ("C₁₋₆ alkyl"). In some embodiments, an alkyl group has 1 to 5 carbon atoms ("C₁₋₅ alkyl"). In some embodiments, an alkyl group has 1 to 4 carbon atoms ("C₁₋₄ alkyl"). In some embodiments, an alkyl group has 1 to 3 carbon atoms ("C₁₋₃ alkyl"). In some embodiments, an alkyl group has 1 to 2 carbon atoms ("C₁₋₂ alkyl"). In some embodiments, an alkyl group has 1 carbon atom ("C₁ alkyl"). In some embodiments, an alkyl group has 2 to 6 carbon atoms ("C₂₋₆ alkyl"). Examples of C₁₋₆ alkyl groups include methyl (C₁), ethyl (C₂), propyl (C₃) (*e.g.*, n-propyl, isopropyl), butyl (C₄) (*e.g.*, n-butyl, tert-butyl, sec-butyl, isobutyl), pentyl (C₅) (*e.g.*, n-pentyl, 3-pentanyl, amyl, neopentyl, 3-methyl-2-butanyl, tertiary amyl), and hexyl (C₆) (*e.g.*, n-hexyl). Additional examples of alkyl groups include n-heptyl (C₇), n-octyl (C₈), and the like. Unless otherwise specified, each instance of an alkyl group is independently unsubstituted (an "unsubstituted alkyl") or substituted (a "substituted alkyl") with one or more substituents (*e.g.*, halogen, such as F). In certain embodiments, the alkyl group is an unsubstituted C₁₋₁₀ alkyl (such as unsubstituted C₁₋₆ alkyl, *e.g.*, -CH₃ (Me), unsubstituted ethyl (Et), unsubstituted propyl (Pr, *e.g.*, unsubstituted n-propyl (n-Pr), unsubstituted isopropyl (i-Pr)), unsubstituted butyl (Bu, *e.g.*, unsubstituted n-butyl (n-Bu), unsubstituted tert-butyl (tert-Bu or t-Bu), unsubstituted sec-butyl (sec-Bu), unsubstituted isobutyl (i-Bu)). In certain embodiments, the alkyl group is a substituted C₁₋₁₀ alkyl (such as substituted C₁₋₆ alkyl, *e.g.*, -CF₃, Bn).

[0079] As used herein, the term "alkenyl" refers to a radical of a straight-chain or branched hydrocarbon group having from 2 to 10 carbon atoms and one or more carbon-carbon double bonds (*e.g.*, 1, 2, 3, or 4 double bonds) ("C₂₋₁₀ alkenyl"). In some embodiments, an alkenyl group has 2 to 9 carbon atoms ("C₂₋₉ alkenyl"). In some embodiments, an alkenyl group has 2 to 8 carbon atoms ("C₂₋₈ alkenyl"). In some embodiments, an alkenyl group has 2 to 7 carbon atoms ("C₂₋₇ alkenyl"). In some embodiments, an alkenyl group has 2 to 6 carbon atoms ("C₂₋₆ alkenyl"). In some embodiments, an alkenyl group has 2 to 5 carbon atoms ("C₂₋₅ alkenyl"). In some embodiments, an alkenyl group has 2 to 4 carbon atoms ("C₂₋₄ alkenyl"). In some embodiments, an alkenyl group has 2 to 3 carbon atoms ("C₂₋₃ alkenyl"). In some embodiments, an alkenyl group has 2 carbon atoms ("C₂ alkenyl"). The one or more carbon-carbon double bonds can be internal (such as in 2-butenyl) or terminal (such as in 1-butenyl). Examples of C₂₋₄ alkenyl groups include, without limitation, vinyl (C₂), 1-propenyl (C₃), 2-

propenyl (C₃), 1-butenyl (C₄), 2-butenyl (C₄), and the like. Examples of C₂₋₆ alkenyl groups include the aforementioned C₂₋₄ alkenyl groups as well as pentenyl (C₅), hexenyl (C₆), and the like. Additional examples of alkenyl include heptenyl (C₇), octenyl (C₈), and the like. Unless otherwise specified, each instance of an alkenyl group is independently unsubstituted (an "unsubstituted alkenyl") or substituted (a "substituted alkenyl") with one or more substituents. In certain embodiments, the alkenyl group is an unsubstituted C₂₋₁₀ alkenyl. In certain embodiments, the alkenyl group is a substituted C₂₋₁₀ alkenyl.

[0080] As used herein, the term "alkynyl" refers to a radical of a straight-chain or branched hydrocarbon group having from 2 to 10 carbon atoms and one or more carbon-carbon triple bonds (*e.g.*, 1, 2, 3, or 4 triple bonds) ("C₂₋₁₀ alkynyl"). In some embodiments, an alkynyl group has 2 to 9 carbon atoms ("C₂₋₉ alkynyl"). In some embodiments, an alkynyl group has 2 to 8 carbon atoms ("C₂₋₈ alkynyl"). In some embodiments, an alkynyl group has 2 to 7 carbon atoms ("C₂₋₇ alkynyl"). In some embodiments, an alkynyl group has 2 to 6 carbon atoms ("C₂₋₆ alkynyl"). In some embodiments, an alkynyl group has 2 to 5 carbon atoms ("C₂₋₅ alkynyl"). In some embodiments, an alkynyl group has 2 to 4 carbon atoms ("C₂₋₄ alkynyl"). In some embodiments, an alkynyl group has 2 to 3 carbon atoms ("C₂₋₃ alkynyl"). In some embodiments, an alkynyl group has 2 carbon atoms ("C₂ alkynyl"). The one or more carbon-carbon triple bonds can be internal (such as in 2-butyne) or terminal (such as in 1-butyne). Examples of C₂₋₄ alkynyl groups include, without limitation, ethynyl (C₂), 1-propynyl (C₃), 2-propynyl (C₃), 1-butyne (C₄), 2-butyne (C₄), and the like. Examples of C₂₋₆ alkynyl groups include the aforementioned C₂₋₄ alkynyl groups as well as pentynyl (C₅), hexynyl (C₆), and the like. Additional examples of alkynyl include heptyne (C₇), octyne (C₈), and the like. Unless otherwise specified, each instance of an alkynyl group is independently unsubstituted (an "unsubstituted alkynyl") or substituted (a "substituted alkynyl") with one or more substituents. In certain embodiments, the alkynyl group is an unsubstituted C₂₋₁₀ alkynyl. In certain embodiments, the alkynyl group is a substituted C₂₋₁₀ alkynyl.

[0081] The term "aryl" refers to a radical of a monocyclic or polycyclic (*e.g.*, bicyclic or tricyclic) 4n+2 aromatic ring system (*e.g.*, having 6, 10, or 14 π electrons shared in a cyclic array) having 6-14 ring carbon atoms and zero heteroatoms provided in the aromatic ring system ("C₆₋₁₄ aryl"). In some embodiments, an aryl group has 6 ring carbon atoms ("C₆ aryl"; *e.g.*, phenyl). In some embodiments, an aryl group has 10 ring carbon atoms ("C₁₀ aryl"; *e.g.*, naphthyl such as 1-naphthyl and 2-naphthyl). In some embodiments, an aryl group

has 14 ring carbon atoms ("C₁₄ aryl"; *e.g.*, anthracyl). "Aryl" also includes ring systems wherein the aryl ring, as defined above, is fused with one or more carbocyclyl or heterocyclyl groups wherein the radical or point of attachment is on the aryl ring, and in such instances, the number of carbon atoms continue to designate the number of carbon atoms in the aryl ring system. Unless otherwise specified, each instance of an aryl group is independently unsubstituted (an "unsubstituted aryl") or substituted (a "substituted aryl") with one or more substituents. In certain embodiments, the aryl group is an unsubstituted C₆₋₁₄ aryl. In certain embodiments, the aryl group is a substituted C₆₋₁₄ aryl.

[0082] The term "haloalkyl" refers to a substituted alkyl group, wherein one or more of the hydrogen atoms are independently replaced by a halogen, *e.g.*, fluoro, bromo, chloro, or iodo. In some embodiments, the haloalkyl moiety has 1 to 12 carbon atoms ("C₁₋₁₂ haloalkyl"). In some embodiments, the haloalkyl moiety has 1 to 6 carbon atoms ("C₁₋₆ haloalkyl"). In some embodiments, the haloalkyl moiety has 1 to 4 carbon atoms ("C₁₋₄ haloalkyl"). In some embodiments, the haloalkyl moiety has 1 to 3 carbon atoms ("C₁₋₃ haloalkyl"). In some embodiments, the haloalkyl moiety has 1 to 2 carbon atoms ("C₁₋₂ haloalkyl"). Examples of haloalkyl groups include -CHF₂, -CH₂F, -CF₃, -CH₂CF₃, -CF₂CF₃, -CF₂CF₂CF₃, -CCl₃, -CFCl₂, -CF₂Cl, and the like.

[0083] The term "sulfonic acid group" refers to the following group: -S(O)₂OH.

[0084] The term "sulfonate" refers to a salt or ester of sulfonic acid, -S(O)₂OR, where R represents a cation, such as a metal or ammonium cation, or an aliphatic or aromatic substituent. Examples of sulfonates include salts such as lithium sulfonate, sodium sulfonate, potassium sulfonate, or ammonium sulfonate. In some embodiments, the term "sulfonate" refers to an ester of sulfonic acid, for example, an optionally substituted C₁₋₁₂ alkyl sulfonate or an optionally substituted C₆₋₁₂ aryl sulfonate. In some embodiments, R is a multivalent (*e.g.*, bivalent or trivalent) radical forming a covalent or ionic bond with one or more sulfonic acid groups attached to the same or different sulfonated polymer chain, thus forming a crosslinking moiety together with the two or more -S(O)₂O- groups to which it is attached.

[0085] The term "sulfonamide" refers to an amide of sulfonic acid, -S(O)₂NRR', where R and R' is each a hydrogen or an optionally substituted aliphatic or aromatic substituent, such as optionally substituted C₁₋₁₂ alkyl or an optionally substituted C₆₋₁₂ aryl. In some embodiments, R and/or R' is each a multivalent (*e.g.*, bivalent or trivalent) radical forming a covalent or ionic bond with one or more sulfonic acid groups attached to the same or different

sulfonated polymer chain, thus forming a crosslinking moiety together with the two or more -S(O)₂O- groups to which it is attached.

[0086] Affixing the suffix "-ene" to a group indicates the group is a divalent moiety, e.g., alkylene is the divalent moiety of alkyl, alkenylene is the divalent moiety of alkenyl, alkynylene is the divalent moiety of alkynyl, and arylene is the divalent moiety of aryl.

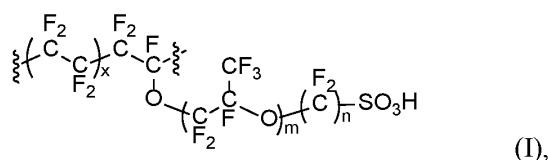
[0087] The term "substituted" refers to moieties having substituents replacing a hydrogen on one or more carbons of the backbone. It will be understood that "substitution" or "substituted with" includes the implicit proviso that such substitution is in accordance with permitted valence of the substituted atom and the substituent, and that the substitution results in a stable compound, e.g., which does not spontaneously undergo transformation such as by rearrangement, cyclization, elimination, etc. As used herein, the term "substituted" is contemplated to include all permissible substituents of organic compounds. In a broad aspect, the permissible substituents include acyclic and cyclic, branched and unbranched, carbocyclic and heterocyclic, aromatic and non-aromatic substituents of organic compounds. The permissible substituents can be one or more and the same or different for appropriate organic compounds. For purposes of this invention, the heteroatoms such as nitrogen may have hydrogen substituents and/or any permissible substituents of organic compounds described herein which satisfy the valences of the heteroatoms. Substituents can include any substituents described herein, for example, a halogen, a hydroxyl, a carbonyl (such as a carboxyl, an alkoxycarbonyl, a formyl, or an acyl), a thiocarbonyl (such as a thioester, a thioacetate, or a thioformate), an alkoxyl, a phosphoryl, a phosphate, a phosphonate, a phosphinate, an amino, an amido, an amidine, an imine, a cyano, a nitro, an azido, a sulfhydryl, an alkylthio, a sulfate, a sulfonate, a sulfamoyl, a sulfonamido, a sulfonyl, a heterocyclyl, an aralkyl, or an aromatic or heteroaromatic moiety. It will be understood by those skilled in the art that substituents can themselves be substituted, if appropriate. Unless specifically stated as "unsubstituted," references to chemical moieties herein are understood to include substituted variants. For example, reference to an "aryl" group or moiety implicitly includes both substituted and unsubstituted variants.

[0088] Exemplary carbon atom substituents include, but are not limited to, halogen, -CN, -NO₂, -N₃, -OH, F, Cl, Br, I, oxo, -SO₂H, -SO₃H, -OR^{aa}, -NH(R^{aa})₂, -N(R^{aa})₂, -N(R^{aa})₃⁺X⁻, -SH, -SR^{aa}, -C(=O)R^{aa}, -CO₂H, -CHO, -CO₂R^{aa}, -OC(=O)R^{aa}, -OCO₂R^{aa}, -C(=O)N(R^{aa})₂, -OC(=O)N(R^{aa})₂, -NR^{aa}C(=O)R^{aa}, -NR^{aa}CO₂R^{aa}, -NR^{aa}C(=O)N(R^{aa})₂, -C(=NR^{aa})R^{aa}, -

$C(=O)NR^{aa}SO_2R^{aa}$, $-NR^{aa}SO_2R^{aa}$, $-SO_2N(R^{aa})_2$, $-SO_2R^{aa}$, $-SO_2OR^{aa}$, $-OSO_2R^{aa}$, $-S(=O)R^{aa}$, $-OS(=O)R^{aa}$, $-Si(R^{aa})_3$, $-OSi(R^{aa})_3$, C_{1-12} alkyl, C_{1-12} haloalkyl, 3-16 membered heterocyclyl, and C_{6-12} aryl, wherein X^- is a counterion and each instance of R^{aa} is, independently, selected from H, $-OH$, C_{1-10} alkyl, C_{1-10} haloalkyl, C_{3-12} cycloalkyl, 5-16 membered heterocyclyl, and C_{6-12} aryl, or two R^{aa} groups are joined to form a 3-16 membered heterocyclyl.

[0089] In a first embodiment the invention is a bilayer polyelectrolyte membrane, comprising a first layer and a second layer, wherein: the first layer comprises a perfluorosulfonic acid (PFSA), and the second layer comprises a crosslinked polysulfonated polymer comprising sulfonated polyphenyl sulfone (sPPS), sulfonated polyether ether ketone (sPEEK), sulfonated polyphosphazene (sPOP), sulfonated polybenzimidazole (sPBI), sulfonated polyether sulfone (sPES), sulfonated polyphenylene oxide (sPPO), sulfonated polyarylene ether ketone (sPAEK), sulfonated poly(sulfone) (sPSU), sulfonated poly(sulfide sulfone), sulfonated polyimide (sPI), sulfonated poly(etherimide) (sPEI), sulfonated poly(amine), or a combination thereof, and wherein the first layer is disposed on the second layer.

[0090] In a first aspect of the first embodiment, the PFSA is a polymer comprising a repeat unit represented by structural formula (I):



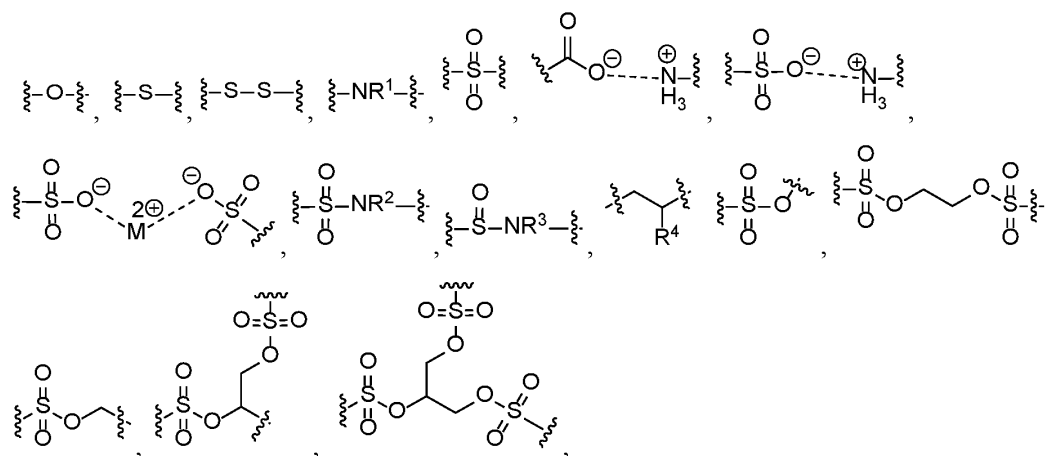
wherein x is an integer between 1 and 15, m is an integer between 0 and 2, n is an integer between 1 and 5, and Z represents a point of attachment to a neighboring repeat unit. For example, x is an integer between 5 and 14, m is 1 or 2, and n is 2 or 3. In certain cases, m is 1 and n is 2.

[0091] In a second aspect of the first embodiment, the PFSA is a polymer comprising from about 500 to about 1500 repeat units represented by structural formula (I). For example, the PFSA is a polymer comprising from about 600 to about 1400, from about 700 to about 1300, from about 800 to about 1200, or from about 900 to about 1100 repeat units represented by structural formula (I). For example, the PFSA is a polymer comprising about 1000 repeat units represented by structural formula (I). The remainder of features and

example features of the second aspect is as described above with respect to the first aspect of the first embodiment.

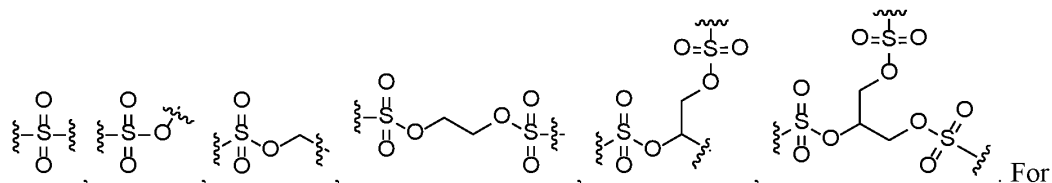
[0092] In a third aspect of the first embodiment, the crosslinked polysulfonated polymer comprises sulfonated polyphenyl sulfone (sPPS), sulfonated polyether ether ketone (sPEEK), sulfonated polyphosphazene (sPOP), sulfonated polybenzimidazole (sPBI), sulfonated polyether sulfone (sPES), sulfonated polyarylene ether ketone (sPAEK), sulfonated poly(sulfone) (sPSU), sulfonated poly(sulfide sulfone), sulfonated polyimide (sPI), sulfonated poly(etherimide) (sPEI), sulfonated poly(amine), or a combination thereof. For example, the crosslinked polysulfonated polymer comprises sPPS, sPES, sPSU, sulfonated poly(sulfide sulfone), or a combination thereof. For example, the crosslinked polysulfonated polymer comprises sPPS, sPES, sPSU, or a combination thereof. For example, the crosslinked polysulfonated polymer comprises sPPS, sPEEK, sPOP, or sPBI. For example, the crosslinked polysulfonated polymer comprises sPPS or sPSU. For example, the crosslinked polysulfonated polymer comprises sPPS. The remainder of features and example features of the third aspect is as described above with respect to the first and second aspects of the first embodiment.

[0093] In a fourth aspect of the first embodiment, the crosslinked polysulfonated polymer comprises a crosslinking moiety represented by one of the following structural formulas:

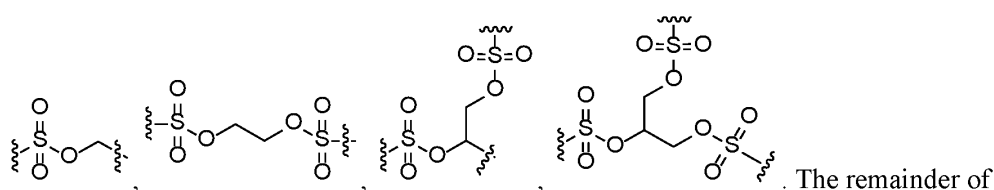


wherein each of R^1 , R^2 , R^3 , and R^4 is independently selected from H, C_{1-12} alkyl, C_{1-12} haloalkyl, C_{6-12} aryl, and C_{6-14} aryl(C_{1-12} alkylene); M^{2+} is selected from M^{2+} , Ca^{2+} , Ba^{2+} , and $Al(X)^{2+}$, wherein X is halide, acetate, or nitrate; and --- represents a point of attachment of

the crosslinking moiety to a repeat unit of the crosslinked polysulfonated polymer. For example, the crosslinking moiety is represented by one of the following structural formulas:



For example, the crosslinking moiety is represented by one of the following structural formulas:



The remainder of features and example features of the fourth aspect is as described above with respect to the first through the third aspects of the first embodiment.

[0094] In a fifth aspect of the first embodiment, the first layer further comprises a porous matrix comprising a matrix polymer, wherein the PFSA and the matrix polymer form an interpenetrating network. For example, the first layer comprises from about 50 wt.% to about 99 wt.% of PFSA, from about 55 wt.% to about 98 wt.% of PFSA, from about 60 wt.% to about 97 wt.% of PFSA, from about 70 wt.% to about 96 wt.% of PFSA, or from about 80 wt.% to about 96 wt.% of PFSA. For example, the first layer comprises from about 70 wt.% to about 99 wt.% of PFSA, such as from about 78 wt.% to about 95 wt.% of PFSA. The remainder of features and example features of the fifth aspect is as described above with respect to the first through the fourth aspects of the first embodiment.

[0095] In a sixth aspect of the first embodiment, the matrix polymer is polytetrafluoroethylene (PTFE). For example, the matrix polymer is expanded PTFE (ePTFE). The remainder of features and example features of the sixth aspect is as described above with respect to the first through the fifth aspects of the first embodiment.

[0096] In a seventh aspect of the first embodiment, the degree of sulfonation of the crosslinked polysulfonated polymer is from about 10% to about 400%. For example, the degree of sulfonation of the crosslinked polysulfonated polymer is from about 10% to about 100%, from about 20% to about 100%, from about 30% to about 100%, from about 40% to about 100%, from about 50% to about 100%, from about 60% to about 100%, from about

70% to about 100%, from about 80% to about 100%, from about 50% to about 200%, from about 80% to about 200%, from about 100% to about 200%, from about 100% to about 250%, from about 150% to about 200%, from about 100% to about 300%, from about 100% to about 350%, from about 100% to about 400%, from about 150% to about 250%, from about 150% to about 300%, from about 150% to about 350%, from about 150% to about 400%, from about 200% to about 300%, from about 200% to about 350%, from about 200% to about 400%, or from about 250% to about 350%. For example, the degree of sulfonation of the crosslinked polysulfonated polymer is about 20%, about 30%, about 40%, about 50%, about 60%, about 70%, about 80%, about 90%, about 100%, about 120%, about 140%, about 160%, about 180%, about 200%, about 220%, about 240%, about 260%, about 280%, about 300%, about 320%, about 340%, about 360%, about 380%, or about 400%. For example, the degree of sulfonation of the crosslinked polysulfonated polymer is from about 30% to about 90%, from about 40% to about 80%, or from about 50% to about 60%. The remainder of features and example features of the seventh aspect is as described above with respect to the first through the sixth aspects of the first embodiment.

[0097] In an eighth aspect of the first embodiment, the gel fraction of the crosslinked polysulfonated polymer is from about 50% to about 100%. For example, the gel fraction of the crosslinked polysulfonated polymer is about 50%, about 60%, about 70%, about 80%, about 90%, or about 100%. The remainder of features and example features of the eighth aspect is as described above with respect to the first through the seventh aspects of the first embodiment.

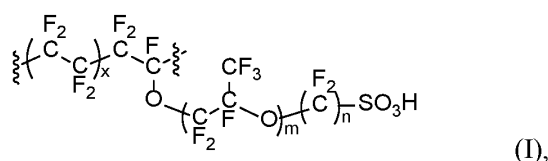
[0098] In a ninth aspect of the first embodiment, the thickness of the first layer is from about 5 μm to about 200 μm . For example, the thickness of the first layer is about 5 μm , about 10 μm , about 15 μm , about 20 μm , about 25 μm , about 30 μm , about 35 μm , about 40 μm , about 45 μm , about 50 μm , about 55 μm , about 60 μm , about 65 μm , about 70 μm , about 75 μm , about 80 μm , about 85 μm , about 90 μm , about 95 μm , about 100 μm , about 110 μm , about 120 μm , about 130 μm , about 140 μm , about 150 μm , about 160 μm , or about 170 μm , about 180 μm , about 190 μm , or about 200 μm . For example, the thickness of the first layer is from about 5 μm to about 175 μm . For example, the thickness of the first layer is about 25 μm . The remainder of features and example features of the ninth aspect is as described above with respect to the first through the eighth aspects of the first embodiment.

[0099] In a tenth aspect of the first embodiment, the thickness of the second layer is from about 0.2 μm to about 175 μm . For example, the thickness of the second layer is about 0.2 μm , about 0.4 μm , about 0.6 μm , about 0.8 μm , about 1.0 μm , about 2.0 μm , about 3.0 μm , about 4.0 μm , about 5 μm , about 10 μm , about 15 μm , about 20 μm , about 25 μm , about 30 μm , about 35 μm , about 40 μm , about 45 μm , about 50 μm , about 55 μm , about 60 μm , about 65 μm , about 70 μm , about 75 μm , about 80 μm , about 85 μm , about 90 μm , about 95 μm , about 100 μm , about 110 μm , about 120 μm , about 130 μm , about 140 μm , about 150 μm , about 160 μm , or about 170 μm . For example, the thickness of the second layer is from about 0.2 μm to about 10 μm , from about 0.4 μm to about 5 μm , from about 0.6 μm to about 2 μm , from about 0.8 μm to about 1.5 μm . For example, the thickness of the second layer is about 0.75 μm . For example, the thickness of the second layer is about 1 μm . For example, the thickness of the second layer is about 1.5 μm . The remainder of features and example features of the tenth aspect is as described above with respect to the first through the ninth aspects of the first embodiment.

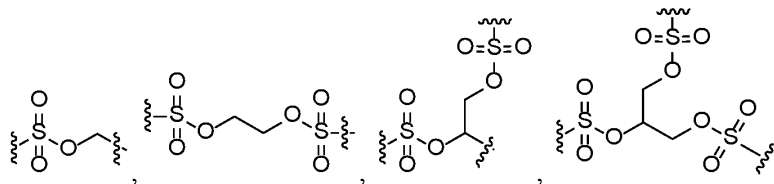
[00100] In an eleventh aspect of the first embodiment, the first layer is continuous. The remainder of features and example features of the eleventh aspect is as described above with respect to the first through the tenth aspects of the first embodiment.

[00101] In a twelfth aspect of the first embodiment, the membrane is unsupported. The remainder of features and example features of the twelfth aspect is as described above with respect to the first through the eleventh aspects of the first embodiment.

[00102] In a thirteenth aspect of the first embodiment, the PFSA is a polymer comprising a repeat unit represented by structural formula (I):

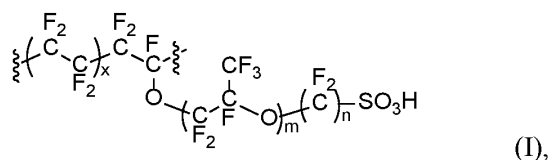


wherein x is an integer between 5 and 14, m is 1 or 2, and n is 2 or 3; and the crosslinked polysulfonated polymer comprises sPPS and a crosslinking moiety represented by one of the following structural formulas:

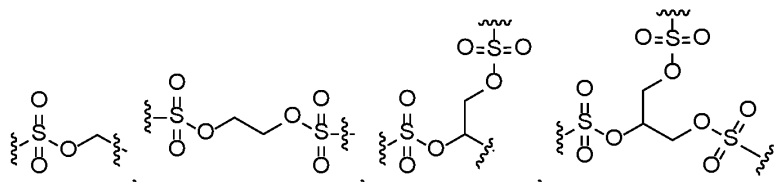


. The remainder of features and example features of the thirteenth aspect is as described above with respect to the first through the twelfth aspects of the first embodiment.

[00103] In a fourteenth aspect of the first embodiment, the first layer comprises a porous matrix comprising a matrix polymer, and wherein the PFSA and the matrix polymer form an interpenetrating network; the PFSA is a polymer comprising a repeat unit represented by structural formula (I):



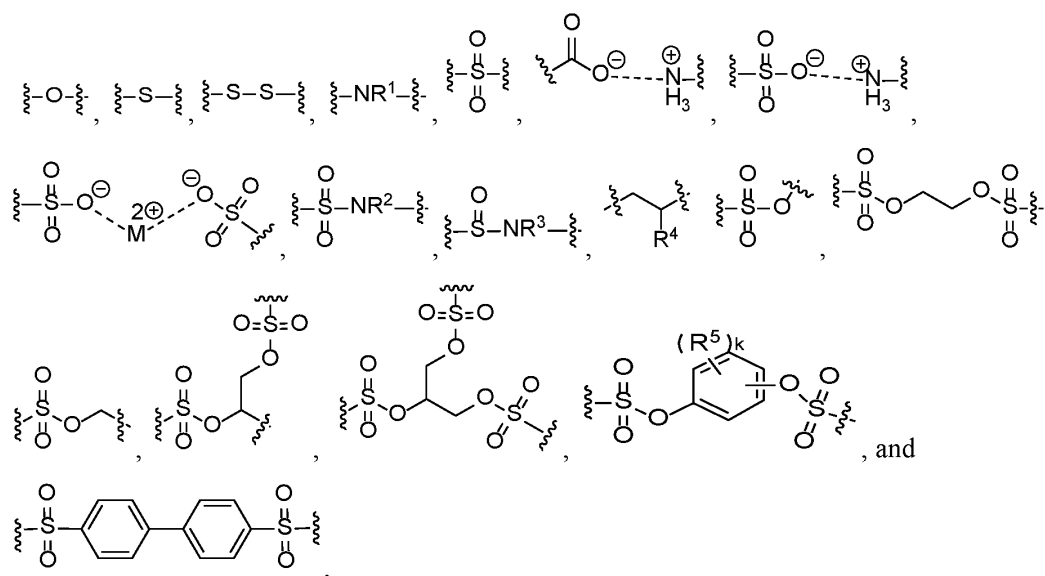
wherein x is an integer between 5 and 14, m is 1 or 2, and n is 2 or 3; the matrix polymer comprises ePTFE; and the crosslinked polysulfonated polymer comprises sPPS and a crosslinking moiety represented by one of the following structural formulas:



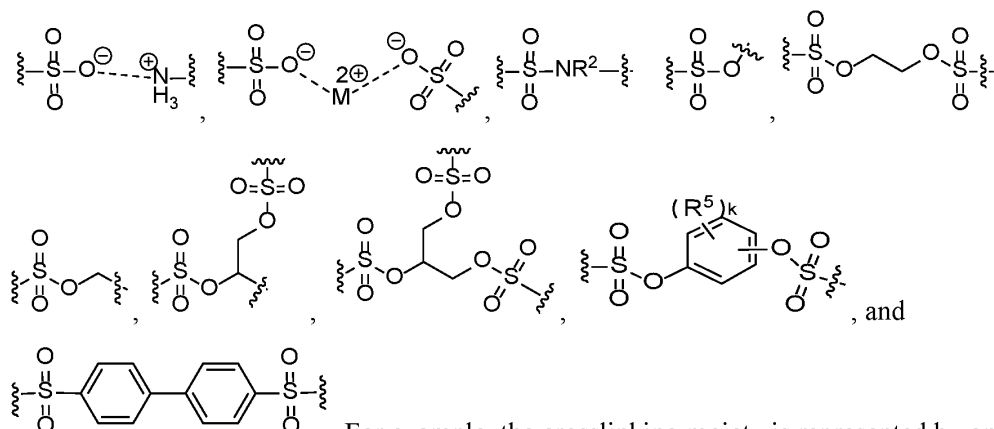
. The remainder of features and example features of the fourteenth aspect is as described above with respect to the first through the thirteenth aspects of the first embodiment

[00104] In a fifteenth aspect of the first embodiment, the crosslinked polysulfonated polymer is sulfonated polyphenyl sulfone (sPPS), sulfonated polyether ether ketone (sPEEK), sulfonated polyphosphazene (sPOP), sulfonated polybenzimidazole (sPBI), sulfonated polyether sulfone (sPES), sulfonated polyarylene ether ketone (sPAEK), sulfonated poly(sulfone) (sPSU), sulfonated poly(sulfide sulfone), sulfonated polyimide (sPI), sulfonated poly(etherimide) (sPEI), sulfonated poly(amine), or a combination thereof. For example, the crosslinked polysulfonated polymer is sPPS, sPES, sPSU, sulfonated poly(sulfide sulfone), or a combination thereof. For example, the crosslinked polysulfonated polymer is sPPS, sPES, sPSU, or a combination thereof. For example, the crosslinked

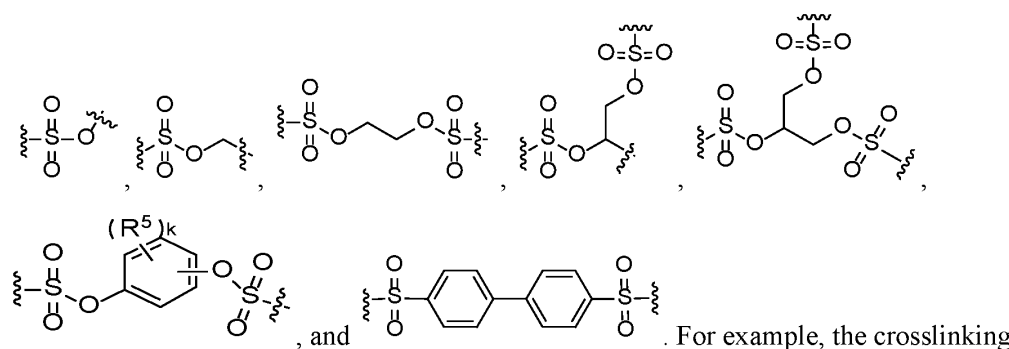
[00106] In a sixteenth aspect of the first embodiment, the crosslinked polysulfonated polymer comprises a crosslinking moiety represented by one of the following structural formulas:



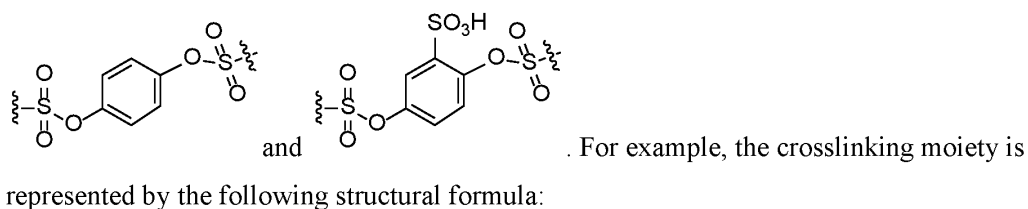
wherein each of R¹, R², R³, and R⁴ is independently selected from H, C₁₋₁₂ alkyl, C₁₋₁₂ haloalkyl, C₆₋₁₄ aryl, and C₆₋₁₄ aryl(C₁₋₁₂ alkylene); R⁵ is H or -SO₃H, M²⁺ is selected from Mr²⁺, Ca²⁺, Ba²⁺, and Al(X)²⁺, wherein X is halide, acetate, or nitrate; k is 1, 2, 3, or 4, and represents a point of attachment of the crosslinking moiety to a repeat unit of the crosslinked polysulfonated polymer. For example, the crosslinking moiety is represented by one of the following structural formulas:



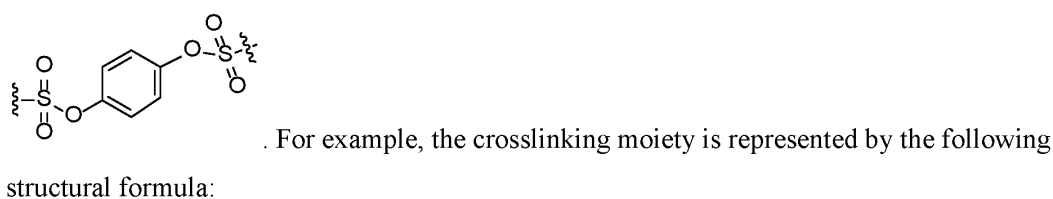
For example, the crosslinking moiety is represented by one of the following structural formulas:



moiety is represented by one of the following structural formulas:

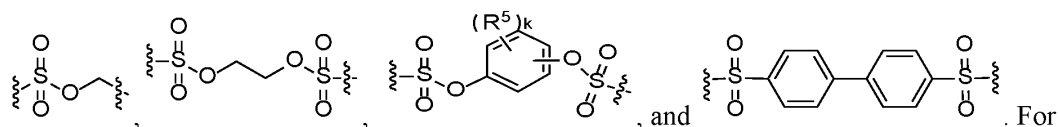


represented by the following structural formula:

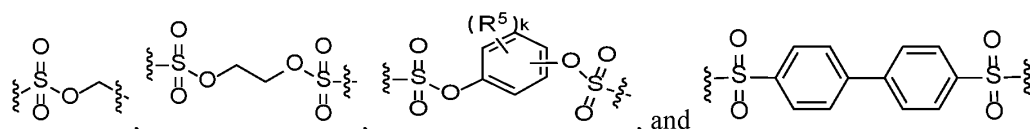


For example, R⁵ is H. For example, R⁵ is -SO₃H. The remainder of features and example features of the sixteenth aspect is as described above with respect to the first through the fifteenth aspects of the first embodiment.

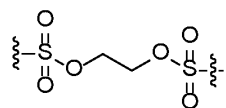
[00107] In a seventeenth aspect of the first embodiment, the crosslinked polysulfonated polymer comprises sPPS or sPSU, and the crosslinking moiety is represented by one of the following structural formulas:



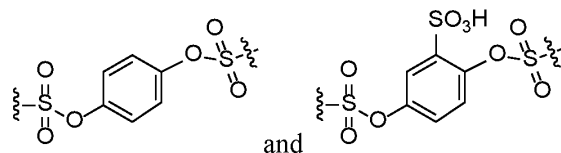
For example, the crosslinked polysulfonated polymer comprises sPPS and the crosslinking moiety is represented by one of the following structural formulas:



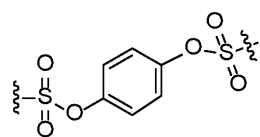
For example, the crosslinked polysulfonated polymer comprises sPPS and the crosslinking moiety is represented by the following structural formula:



For example, the crosslinked polysulfonated polymer comprises sPPS and the crosslinking moiety is represented by one of the following structural formulas:



For example, the crosslinked polysulfonated polymer comprises sPPS and the crosslinking moiety is represented by the following structural formula:



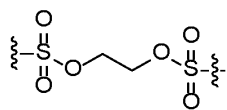
The remainder of features and example features of the seventeenth aspect is as described above with respect to the first through the sixteenth aspects of the first embodiment.

[00108] In an eighteenth aspect of the first embodiment, the crosslinked polysulfonated polymer comprises on average from about 0.5 to about 6 sulfonic acid, sulfonate, and sulfonamide groups, combined, per repeat unit. For example, the crosslinked polysulfonated polymer comprises on average from about 0.5 to about 2, from about 1 to about 3, from about 1.5 to about 2.5, from about 2 to about 4, from about 1.5 to about 3, or from about 2 to about

1.5 sulfonic acid, sulfonate, and sulfonamide groups, combined, per repeat unit. For example, the crosslinked polysulfonated polymer comprises on average about 0.5, about 1, about 1.5, about 2.0, about 2.5, or about 3 sulfonic acid, sulfonate, and sulfonamide groups, combined, per repeat unit. The remainder of features and example features of the eighteenth aspect is as described above with respect to the first through the seventeenth aspects of the first embodiment.

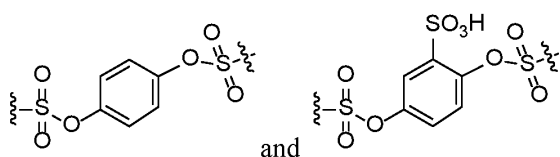
[00109] In a nineteenth aspect of the first embodiment, the degree of crosslinking of the crosslinked polysulfonated polymer is from about 10% to about 95%. For example, the degree of crosslinking of the crosslinked polysulfonated polymer is from about 15% to about 90%, from about 20% to about 80%, from about 20% to about 70%, from about 20% to about 60%, from about 20% to about 50%, from about 20% to about 45%, from about 20% to about 40%, from about 30% to about 50%, from about 25% to about 30%, or from about 30% to about 35%. For example, the degree of crosslinking of the crosslinked polysulfonated polymer is about 10%, about 15%, about 20%, about 25%, about 30%, about 35%, about 40%, about 45%, about 50%, about 55%, about 60%, about 65%, about 70%, about 75%, about 80%, about 85%, about 90%, or about 95%. The remainder of features and example features of the nineteenth aspect is as described above with respect to the first through the eighteenth aspects of the first embodiment.

[00110] In a twentieth aspect of the first embodiment, the membrane is unsupported, the crosslinked polysulfonated polymer is sPPS, and the crosslinking moiety is represented by the following structural formula:



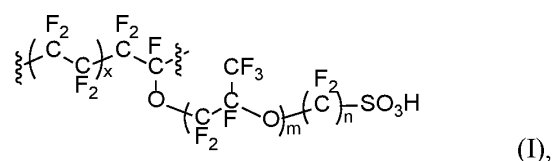
. The remainder of features and example features of the twentieth aspect is as described above with respect to the first through the nineteenth aspects of the first embodiment.

[00111] In a twenty-first aspect of the first embodiment, the membrane is unsupported, the crosslinked polysulfonated polymer is sPPS, and the crosslinking moiety is represented by one of the following structural formulas:

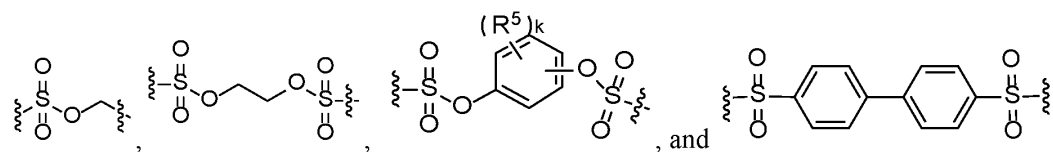


The remainder of features and example features of the twenty-first aspect is as described above with respect to the first through the twentieth aspects of the first embodiment.

[00112] In a twenty-second aspect of the first embodiment, the PFSA is a polymer comprising a repeat unit represented by structural formula (I):

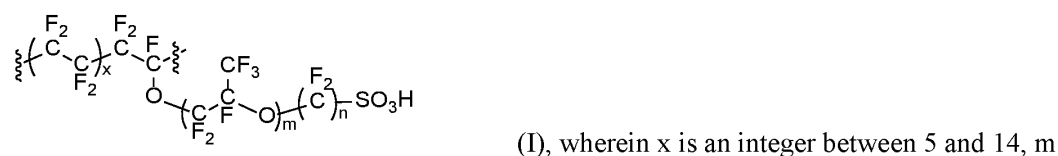


wherein x is an integer between 5 and 14, m is 1 or 2, and n is 2 or 3; and the crosslinked polysulfonated polymer comprises sPPS or sPSU, and the crosslinking moiety is represented by one of the following structural formulas:

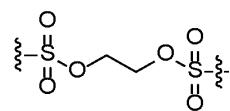


The remainder of features and example features of the twenty-second aspect is as described above with respect to the first through the twenty-first aspects of the first embodiment.

[00113] In a twenty-third aspect of the first embodiment, the membrane is unsupported, the PFSA is a polymer comprising a repeat unit represented by structural formula (I):



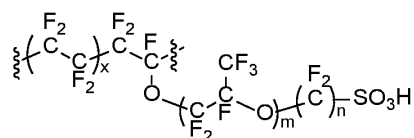
is 1 or 2, and n is 2 or 3; and further wherein the crosslinked polysulfonated polymer is sPPS, the crosslinking moiety is represented by the following structural formula:



, the degree of sulfonation of the sPPS is about 200%, the degree of crosslinking of the sPPS is about 40%, and the thickness of the second layer is from about 0.5 μm to about 2 μm . The remainder of features and example features of the twenty-third aspect

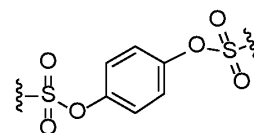
is as described above with respect to the first through the twenty-second aspects of the first embodiment.

[00114] In a twenty-fourth aspect of the first embodiment, the membrane is unsupported, the PFSA is a polymer comprising a repeat unit represented by structural formula (I):



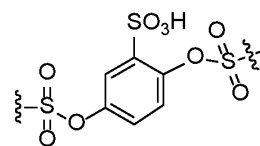
(I), wherein x is an integer between 5 and 14, m

is 1 or 2, and n is 2 or 3; and further wherein the crosslinked polysulfonated polymer is sPPS, the crosslinking moiety is represented by the following structural formula: the crosslinking



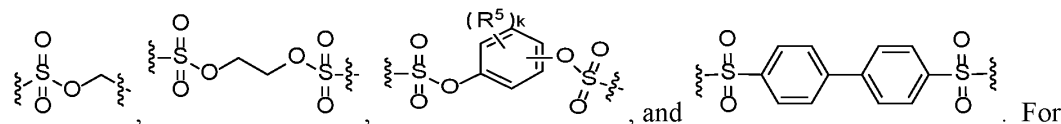
moiety is represented by one of the following structural formulas:

and

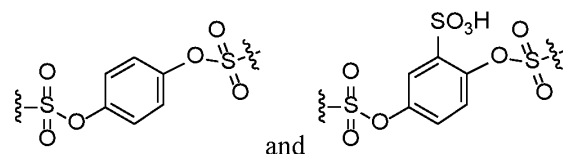


, the degree of sulfonation of the sPPS is about 200%, the degree of crosslinking of the sPPS is from about 25% to about 30%, and the thickness of the second layer is from about 1 μm to about 2 μm . The remainder of features and example features of the twenty-fourth aspect is as described above with respect to the first through the twenty-third aspects of the first embodiment.

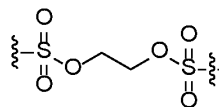
[00115] In a twenty-fifth aspect of the first embodiment, the first layer comprises a porous matrix comprising a matrix polymer, the PFSA and the matrix polymer form an interpenetrating network, and the crosslinked polysulfonated polymer comprises sPPS or sPSU. For example, the crosslinked polysulfonated polymer is sPPS. For example, the sPPS comprises a crosslinking moiety represented by one of the following structural formulas:



example, the crosslinking moiety is represented by one of the following structural formulas:



. For example, the crosslinking moiety is



represented by the following structural formula: . The remainder of features and example features of the twenty-fifth aspect is as described above with respect to the first through the twenty-fourth aspects of the first embodiment.

[00116] In a second embodiment, the invention is a method of making a bilayer polyelectrolyte membrane described herein with respect to the first embodiment and various aspects thereof, comprising:

- a) providing a first layer having a first side, and a solution or suspension comprising a polysulfonated polymer and a crosslinking reagent,
- b) coating the first side of the first layer with the solution or suspension, thereby producing a coated first layer;
- c) exposing the coated first layer to conditions sufficient for the polysulfonated polymer and the crosslinking reagent to undergo a crosslinking reaction, thereby producing the bilayer polyelectrolyte membrane.

[00117] In a first aspect of the second embodiment, the crosslinking reagent is selected from a polyalcohol, an amine, an epoxide, a thiol, or a compound comprising a terminal alkene or alkyne. For example, the crosslinking reagent is selected from glycerol, ethylene glycol, hydroquinone, 2,5-dihydroxybenzenesulfonic acid, 2,5-dihydroxybenzene-1,4-disulfonic acid, biphenyl, tetraglycidyl bis(p-aminophenyl)methane, phenylene diamine, 4,4'-thiobisbenzenethiol, and tetrafluoro styrene. For example, the crosslinking reagent is glycerol, ethylene glycol, hydroquinone, or 2,5-dihydroxybenzenesulfonic acid. For example, the crosslinking reagent is a polyalcohol, such as glycerol or ethylene glycol. For example, the crosslinking reagent is hydroquinone or 2,5-dihydroxybenzenesulfonic acid. The crosslinking reagent can be selected from glycerol, ethylene glycol, tetraglycidyl bis(p-aminophenyl)methane, phenylene diamine, 4,4'-thiobisbenzenethiol, and tetrafluoro styrene.

[00118] In a second aspect of the second embodiment, the conditions sufficient for the polysulfonated polymer and the crosslinking reagent to undergo a crosslinking reaction comprise heating the coated first layer to a crosslinking temperature from about 150 °C to about 200 °C for a crosslinking time from about 2 hours to about 96 hours. For example, the crosslinking temperature is about 150 °C, about 160 °C, about 170 °C, about 180 °C, about 190 °C, or about 200 °C. For example, the crosslinking temperature about is about 180 °C

and the crosslinking time is about 4 hours. For example, crosslinking time is about 2 hours, about 3 hours, about 4 hours, about 5 hours, about 6 hours, about 7 hours, about 8 hours, about 9 hours, about 10 hours, about 20 hours, about 30 hours, about 40 hours, about 50 hours, about 60 hours, about 70 hours, about 80 hours, or about 90 hours. For example, crosslinking time is about 4 hours. The remainder of features and example features of the second aspect is as described above with respect to the first aspect of the second embodiment.

[00119] In a second aspect of the second embodiment, coating the first side of the first layer with the first solution or suspension comprises spray-coating the first side of the first layer with the first solution or suspension. Alternatively, coating the first side of the first layer with the first solution or suspension comprises dip-coating, spin-coating, or flow-coating the first side of the first layer with the first solution or suspension. The remainder of features and example features of the third aspect is as described above with respect to the first and second aspects of the second embodiment.

[00120] In a third embodiment the invention is a membrane electrode assembly (MEA), comprising: the bilayer polyelectrolyte membrane described herein with respect to the first embodiment and various aspects thereof; a cathode; and an anode, wherein the bilayer electrolyte membrane is disposed between the anode and the cathode.

[00121] In a first aspect of the third embodiment, the cathode is disposed on the first layer of the bilayer electrolyte membrane and the anode is disposed on the second layer of the bilayer electrolyte membrane. Alternatively, wherein the anode is disposed on the first layer of the bilayer electrolyte membrane and the cathode is disposed on the second layer of the bilayer electrolyte membrane.

[00122] In a fourth embodiment the invention is a fuel cell, comprising one or more of the MEAs described herein with respect to the third embodiment and various aspects thereof and one or more gas flow bipolar plates.

[00123] In various embodiments the present invention is

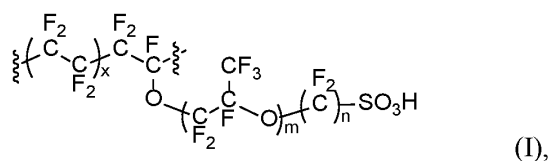
1. A bilayer polyelectrolyte membrane, comprising a first layer and a second layer, wherein:

the first layer comprises a perfluorosulfonic acid (PFSA), and

the second layer comprises a crosslinked polysulfonated polymer comprising sulfonated polyphenyl sulfone (sPPS), sulfonated polyether ether ketone (sPEEK), sulfonated polyphosphazene (sPOP), sulfonated polybenzimidazole (sPBI), sulfonated polyether sulfone

(sPES), sulfonated polyphenylene oxide (sPPO), sulfonated polyarylene ether ketone (sPAEK), sulfonated poly(sulfone), sulfonated poly(sulfide sulfone), sulfonated polyimide (sPI), sulfonated poly(etherimide) (sPEI), sulfonated poly(amine), or a combination thereof, and wherein the first layer is disposed on the second layer.

2. The bilayer polyelectrolyte membrane of Claim 1, wherein the PFSA is a polymer comprising a repeat unit represented by structural formula (I):



wherein

x is an integer between 1 and 15,

m is an integer between 0 and 2,

n is an integer between 1 and 5, and

ξ represents a point of attachment to a neighboring repeat unit.

3. The bilayer polyelectrolyte membrane of Claim 2, wherein

x is an integer between 5 and 14,

m is 1 or 2, and

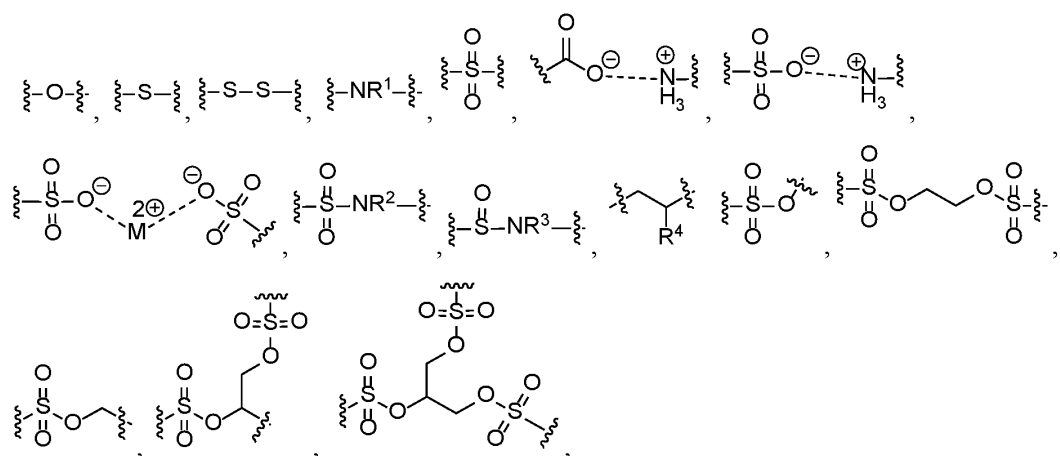
n is 2 or 3.

4. The bilayer polyelectrolyte membrane of Claim 2 or 3, wherein the PFSA is a polymer comprising from about 900 to about 1100 repeat units represented by structural formula (I).

5. The bilayer polyelectrolyte membrane of any one of Claims 1-4, wherein the crosslinked polysulfonated polymer comprises sPPS, sPEEK, sPOP, or sPBI.

6. The bilayer polyelectrolyte membrane of Claims 5, wherein the crosslinked polysulfonated polymer comprises sPPS.

7. The bilayer polyelectrolyte membrane of any one of Claims 1-6, wherein the crosslinked polysulfonated polymer comprises a crosslinking moiety represented by one of the following structural formulas:



wherein

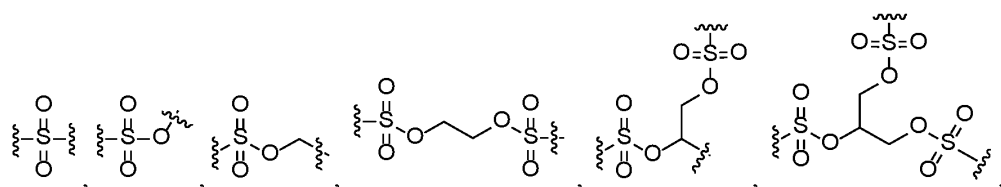
each of R^1 , R^2 , R^3 , and R^4 is independently selected from H, C_{1-12} alkyl, C_{1-12} haloalkyl, C_{6-14} aryl, and C_{6-14} aryl(C_{1-12} alkylene);

M^{2+} is selected from Mr^{2+} , Ca^{2+} , Ba^{2+} , and $Al(X)^{2+}$, wherein X is halide, acetate, or nitrate;

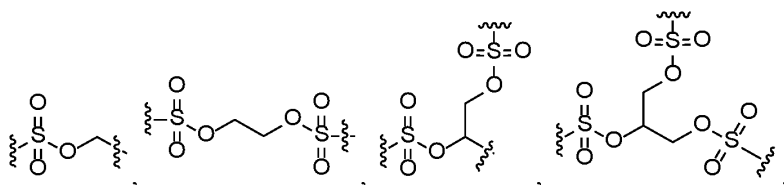
and

⋯ represents a point of attachment of the crosslinking moiety to a repeat unit of the crosslinked polysulfonated polymer.

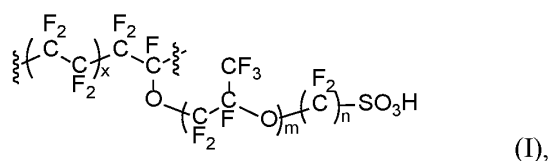
8. The bilayer polyelectrolyte membrane of Claim 7, wherein the crosslinking moiety is represented by one of the following structural formulas:



9. The bilayer polyelectrolyte membrane of Claim 7, wherein the crosslinking moiety is represented by one of the following structural formulas:



10. The bilayer polyelectrolyte membrane of any one of Claims 1-9, wherein the first layer further comprises a porous matrix comprising a matrix polymer, and wherein the PFSA and the matrix polymer form an interpenetrating network.
11. The bilayer polyelectrolyte membrane of Claim 10, wherein the first layer comprises from about 70 wt.% to about 99 wt.% of PFSA.
12. The bilayer polyelectrolyte membrane of Claim 10, wherein the first layer comprises from about 78 wt.% to about 95 wt.% of PFSA.
13. The bilayer polyelectrolyte membrane of any one of Claims 10-12, wherein the matrix polymer is polytetrafluoroethylene (PTFE).
14. The bilayer polyelectrolyte membrane of Claim 13, wherein the matrix polymer is expanded polytetrafluoroethylene (ePTFE).
15. The bilayer polyelectrolyte membrane of any one of Claims 1-14, wherein the degree of sulfonation of the crosslinked polysulfonated polymer is from about 20% to about 100%.
16. The bilayer polyelectrolyte membrane of Claim 15, wherein the degree of sulfonation of the crosslinked polysulfonated polymer is from about 40% to about 80%.
17. The bilayer polyelectrolyte membrane of Claim 15, wherein the degree of sulfonation of the crosslinked polysulfonated polymer is from about 50% to about 60%.
18. The bilayer polyelectrolyte membrane of any one of Claims 1-17, wherein the gel fraction of the crosslinked polysulfonated polymer is from about 50% to about 100%.
19. The bilayer polyelectrolyte membrane of any one of Claims 1-18, wherein the thickness of the first layer is from about 5 μm to about 175 μm .
20. The bilayer polyelectrolyte membrane of any one of Claims 1-19, wherein the thickness of the second layer is from about 0.2 μm to about 170 μm .
21. The bilayer polyelectrolyte membrane of Claim 20, wherein the thickness of the second layer is from about 0.2 μm to about 10 μm .
22. The bilayer polyelectrolyte membrane of any one of Claims 1-21, wherein the first layer is continuous.
23. The bilayer polyelectrolyte membrane of any one of Claims 1-22, wherein the membrane is unsupported.
24. The bilayer polyelectrolyte membrane of Claim 1, wherein:
the PFSA is a polymer comprising a repeat unit represented by structural formula (I):



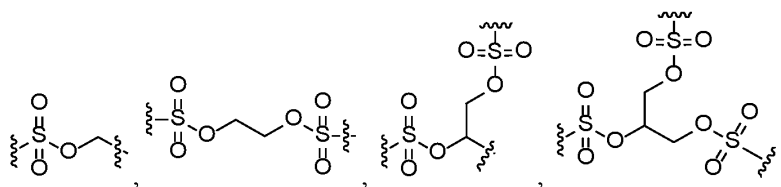
wherein

x is an integer between 5 and 14,

m is 1 or 2, and

n is 2 or 3; and

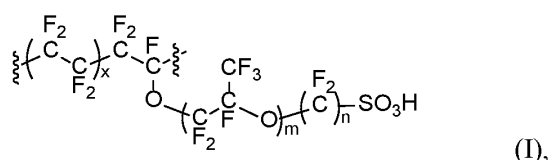
the crosslinked polysulfonated polymer comprises sPPS and a crosslinking moiety represented by one of the following structural formulas:



25. The bilayer polyelectrolyte membrane of Claim 1, wherein:

the first layer comprises a porous matrix comprising a matrix polymer, and wherein the PFSA and the matrix polymer form an interpenetrating network;

the PFSA is a polymer comprising a repeat unit represented by structural formula (I):



wherein

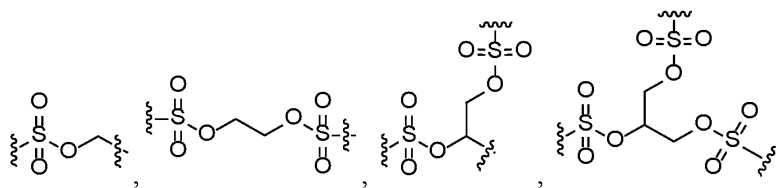
x is an integer between 5 and 14,

m is 1 or 2, and

n is 2 or 3;

the matrix polymer comprises ePTFE; and

the crosslinked polysulfonated polymer comprises sPPS and a crosslinking moiety represented by one of the following structural formulas:



26. A method of making a bilayer polyelectrolyte membrane of any one of Claims 1-25, comprising:
- providing a first layer having a first side, and a solution or suspension comprising a polysulfonated polymer and a crosslinking reagent,
 - coating the first side of the first layer with the solution or suspension, thereby producing a coated first layer;
 - exposing the coated first layer to conditions sufficient for the polysulfonated polymer and the crosslinking reagent to undergo a crosslinking reaction, thereby producing the bilayer polyelectrolyte membrane.
27. The method of Claim 26, wherein the crosslinking reagent is selected from a polyalcohol, an amine, an epoxide, a thiol, or a compound comprising a terminal alkene or alkyne.
28. The method of Claim 26, wherein the crosslinking reagent is selected from glycerol, ethylene glycol, tetraglycidyl bis(p-aminophenyl)methane, phenylene diamine, 4,4'-thiobisbenzenethiol, and tetrafluoro styrene.
29. The method of Claim 26, wherein the crosslinking reagent is polyalcohol.
30. The method of Claim 29, wherein the crosslinking reagent is ethylene glycol or glycerol.
31. The method of any one of Claims 26-30, wherein the conditions sufficient for the polysulfonated polymer and the crosslinking reagent to undergo a crosslinking reaction comprise heating the coated first layer to a crosslinking temperature from about 150 °C to about 200 °C for a crosslinking time from about 2 hours to about 96 hours.
32. The method of Claim 31, wherein the crosslinking temperature is about 180 °C.
33. The method of Claim 31, wherein the crosslinking time is about 4 hours.

34. The method of any one of Claims 26-33, wherein coating the first side of the first layer with the first solution or suspension comprises spray-coating the first side of the first layer with the first solution or suspension.
35. A membrane electrode assembly (MEA), comprising:
the bilayer polyelectrolyte membrane of any one of Claims 1-25;
a cathode; and
an anode,
wherein the bilayer electrolyte membrane is disposed between the anode and the cathode.
36. The MEA of Claim 35, wherein the cathode is disposed on the first layer of the bilayer electrolyte membrane and the anode is disposed on the second layer of the bilayer electrolyte membrane.
37. The MEA of Claim 35, wherein the anode is disposed on the first layer of the bilayer electrolyte membrane and the cathode is disposed on the second layer of the bilayer electrolyte membrane.
38. A fuel cell, comprising one or more of the MEAs of any one of Claims 35-37 and one or more gas flow bipolar plates.

Examples

Materials

[00124] PPS (Solvay Radel R-5000, MW=5000) was purchased from Solvay. Sulfuric acid (H_2SO_4) was purchased from Sigma-Aldrich (95-98%, CAS 7664-93-9). Ethylene glycol was purchased from Sigma-Aldrich ($\geq 99\%$, CAS 107-21-1). Nafion® 211 PFSA membrane (NR-211) was purchased from Fuel Cell Store.

Example 1. Sulfonation of PPS.

[00125] **General Procedure:** PPS was sulfonated by reacting the polymer with H_2SO_4 . PPS was dissolved in concentrated H_2SO_4 at a concentration 25 mg/mL and stirred at 60-70 °C for 10-48 hrs. The sulfonated polymer was precipitated by adding the reaction mixture dropwise to H_2O at 0 °C. The resulting precipitated polymer was centrifuged and isolated. The sulfonated PPS (sPPS) was redispersed in H_2O at room temperature and washed using dialysis until neutral pH was registered. The washed sPPS was dried on a hot plate to provide

the final product. The degree of sulfonation of sPPS can be tuned by adjusting the reaction time (1-72 hrs).

[00126] Example synthesis: PPS (Radel-5000 NT) was sulfonated by reacting the polymer with H₂SO₄. PPS resin was ground into a powder using an industrial grinder. PPS powder (20 g) was dissolved in concentrated H₂SO₄ at a concentration 25 mg/mL and stirred at 60 °C for 8 hrs. The resulting sulfonated polymer was precipitated by adding the reaction mixture dropwise to H₂O at 0 °C. The resulting precipitated polymer was centrifuged and isolated. The sulfonated PPS (sPPS) was redispersed in H₂O at room temperature and washed using dialysis until neutral pH was registered. The washed sPPS was dried on a hot plate to provide the final product. The yield of the reaction was determined by mass to be 91%. The resulting product had a titration determined IEC of 3.605 meq/g (corresponding to 2.0 sulfonic acids per repeat unit), as measured according to the procedure described in Example 3.

[00127] ¹H NMR of the sulfonated polymers was measured at a concentration of about 10 wt.% in DMSO-d₆ to confirm the polymer structure and degree of sulfonation. The ¹H NMR spectrum was acquired with a 500 MHz Bruker Ultrashield 500 Plus Spectrometer and processed using SpinWorks 4. The ¹H NMR experiments were performed using a pulse angle of 30° and a pulse delay of 5s with 32 scans. The ¹H NMR spectrum of the prepared sPPS is shown in Figure 16. Integration of the peaks as shown below in Table 1 was used to establish the number and positions of the sulfonic acid groups in the repeat unit as shown in Figure 16.

[00128] Table 1. ¹H NMR peak integrals for sPPS, ¹H NMR IEC values, and IEC value determined by titration.

Peak Identity	A	B	C	D	E
Peak Integrations (H/RU)	4.03	4	2.05	2	2.12
Ratio with peak C	0.51	0.51	-	1.02	0.97
Sulfonic acids per RU	2.03	2.05	-	2.05	1.93
IEC (meq/g)	3.59	3.61	-	3.61	3.46
Average NMR IEC	3.57				
Titration IEC	3.61				

[00129] Peaks were integrated and normalized by setting the peak integration of peak B to a value of 4, which is the number of B site protons per repeat unit (Table 1). The identity of peak B is assigned based on the steric and electronic protection of the B sites from

sulfonation by the presence of the sulfone linkage. The number of sulfonic acid moieties per repeat unit was calculated by the ratio of peak integrations with peak C. Further, IEC values were calculated based on the peak integration values as follows. The value of IEC is related to the weight of material per sulfonic acid moieties. This is known as the effective weight (EW). Since the prepared sPPS has a monopolymer backbone, a ratio of the C peak integral (which matched the number of the sulfonic acid groups in the structure) with any hydrogen peak was used to calculate sulfonic acids per repeat unit using the following equation:

$$\frac{SO_3H}{RU} = \frac{\int C \text{ peak}}{\int \text{Reference peak}} * [\text{Number of reference H per RU}]$$

[00130] The number of sulfonic acid moieties per repeat unit was converted to EW according following equation:

$$EW = \frac{MW_{RU}}{\left[\frac{SO_3H}{RU}\right]} + MW_{SO_3H},$$

where MW_{RU} is the molecular weight of the repeat unit (400 g/mol for PPS) and MW_{SO_3H} is the molecular weight of a sulfonic acid moiety (82 g/mol). EW was then converted to IEC as follows:

$$IEC = \frac{1000}{EW}$$

[00131] The obtained numbers for IEC based on each of the integrated peaks in the 1H NMR spectrum of sPPS, as well as the average number, are in excellent alignment with the experimental IEC value obtained by titration (see Table 1). This alignment demonstrates that there are no other significant sulfonation locations on the repeat unit, and that the sPPS contains two sulfonic acid moieties per repeat unit, which are located on the biphenyl portion of the backbone as shown in Figure 16.

Example 2. Casting freestanding sPPS membranes.

[00132] Solutions of 1–5 wt.% sPPS in an ethylene glycol:water mixture were added to a Kapton trough. The solution was allowed to dry overnight. The dried sPPS membranes were crosslinked by condensation reaction with the residual ethylene glycol by heating to 180 °C for 4 hours under flowing nitrogen to achieve a water stable sPPS polymer membrane.

Example 3. Determination of ion exchange capacity and degree of crosslinking.

The ion exchange capacity (IEC) of the sPPS polymer and crosslinked sPPS membranes was measured by titration. A piece of polymer or membrane was dried in an oven for 12 hours at 100 °C under flowing nitrogen before being weighed to determine the mass of material (W_{dry}). The dried material was soaked in 20 mL of 2M NaCl for 30 minutes before 10 μ L of phenolphthalein was added. A standardized solution of NaOH (C_{NaOH} , 0.01M) was added dropwise until the solution became tinted pink. The volume of NaOH solution added (V_{NaOH}) was recorded. IEC was then calculated as follows:

$$IEC \left(\frac{meq}{g} \right) = \frac{C_{NaOH} * V_{NaOH}}{W_{dry}}$$

[00133] The degree of crosslinking (%) is defined as the fraction of sulfonic acid moieties that are reacted with a crosslinker molecule. Degree of crosslinking was calculated as follows:

$$Degree\ of\ crosslinking\ (\%) = \frac{[IEC_{polymer} - IEC_{crosslinked}]}{IEC_{polymer}} * 100$$

Example 4. Conductivity measurements of freestanding membranes.

[00134] Membrane conductivity was measured in 4-point probe geometry in a Scribner Bekttech BT-112 HT conductivity cell with an Admiral Squidstat potentiostat. Conductivity was assessed by current measurements during linear sweep voltammetry from -0.5 V to 0.5 V. Conductivity was then calculated from the current-voltage slope with sample thickness.

[00135] Upon crosslinking of the sPPS materials loss of proton concentration results in a non-linear decrease in membrane conductivity. The relationship between conductivity and degree of crosslinking is shown in Figure 9.

Example 5. Spray-coating of Nafion® membrane with sPPS and ethylene glycol as crosslinker.

[00136] A Sono-tek Exactacoat coating system was used to deposit sPPS onto Nafion® membranes. The spraying solution consisted of 0.5 wt.% or 0.75 wt.% sPPS in H₂O and varying amounts of crosslinker (ethylene glycol or glycerol). In the case of ethylene glycol 6 molecules of ethylene glycol per repeat unit of the polymer were added. The solution was stirred for 30-60 min prior to use. The Nafion® membrane substrate was held under vacuum during deposition. The following parameters were used for the spray-coating: power 0.8-1.3

W, nozzle height 40 mm, temperature 60 °C, flow rate 0.25-0.5 mL/min. The number of polymer layers was adjusted for the desired coating thickness. 75 layers were deposited to achieve 1.5 µm thickness of the sPPS coating, and 38 layers were deposited to achieve 0.75 µm thickness. The following ranges can be used for the spray-coating parameters: sPPS solution concentration: 0.05-20 wt. %; substrate temperature: 5-200 °C; nozzle height: 10-70 mm; flow rate: 0.1-4 mL/min; power: 0.8-5W; crosslinker amount (specific to ethylene glycol and glycerol): 0.2–12 molecules/repeat unit of sPPS.

Example 6. Crosslinking the sPPS coating on Nafion® membrane.

[00137] The sPPS coating on a Nafion® membrane was crosslinked using ethylene glycol or glycerol. To perform the crosslinking, the sPPS coated Nafion® membrane was heated to 180 °C for either 4 hours under flowing nitrogen while held under tension with tape to an aluminum mask or as a series of temperature steps over 4 days to achieve a water stable sPPS polymer coating. The resulting coatings had 30–50% degree of crosslinking.

Example 7. Preparation of membrane electrode assembly.

[00138] The bilayer polyelectrolyte membrane was used in a membrane electrode assembly (MEA) and tested in a single fuel cell with 5 cm² active area. For MEA preparation, a 3 inch x 3 inch membrane was placed between two gas diffusion electrodes (GDEs) with 0.2 mg Pt/cm² (20% Pt on Vulcan carbon) on Sigracet 22 BB, each with an area of 5 cm². The GDEs had pre-deposited catalyst layer on the side of microporous layer and were implemented with the catalyst layer interfacing the membrane. 3 inch x 3 inch PTFE gaskets with 5 cm² windows were placed on each side of the membrane to encompass the gas diffusion electrodes to prevent the leak of reactant gases. The gasket thickness is adjusted to allow for 80% compression of the GDEs when the MEA is tightened between two fuel cell end plates.

Example 8. Testing of bilayer polyelectrolyte membrane in a fuel cell.

[00139] The membrane performance was evaluated in a fuel cell via H₂ crossover measurement, fuel cell polarization curve, and accelerated stress test.

[00140] *H₂ crossover measurements*

[00141] H₂ crossover was measured by performing cyclic voltammetry where cathode side electrode was scanned between 0.1 V and 0.8 V with a voltage scan rate of 2 mV/s at 80 °C and 100% RH with 0.4 lpm H₂ flow on the anode side and 0.4 lpm Ar flow on the cathode side with no backpressure. Fuel cell polarization curve was measured by conducting constant voltage measurements from open circuit potential to 0.3 V back to open circuit potential at a 0.5 V increment between open circuit potential to 0.7 V and a 1 V increment between 0.7 V to 0.3 V at 80 °C at various RH values with 0.2 lpm H₂ flow on the anode side and 0.2 lpm air or O₂ flow on the cathode side with a backpressure of 50 kPa_g. The obtained data are shown in Figures 4 and 10. The studied membranes were coated with sPPS with 40% degree of crosslinking. The data show that hydrogen crossover is modified from 1.33 mA/cm² (0 μm coating) to 1.05 mA/cm² (0.75 μm coating) to 0.84 mA/cm² (1.5 μm coating), thus demonstrating that low gas permeability coating decreases hydrogen crossover through PFSA-based membranes.

[00142] *Electrochemical impedance spectroscopy*

[00143] Electrochemical impedance spectroscopy was performed at 150 mA/cm² with 75 mA/cm² excitation amplitude under H₂ pump mode. Measurements were performed at 80 °C and 100% RH with 0.05 lpm H₂ flow on the anode side and 0.05 lpm Ar flow on the cathode side with no backpressure.

[00144] The data in Figure 15 unexpectedly demonstrate that in a bilayer membrane comprising Nafion® 211 and crosslinked sPPS the sPPS and Nafion® layers show no contact resistance between each other, which means that a proton experiences no extra resistance by moving between the layers. Contact resistance between hetero-materials is frequently observed in conductive systems and presents a significant barrier to layered geometries. Thus, a bilayer system comprising two materials layered on top of each other is expected to show a drop in ion conductivity due to interfacial/contact resistance. To evaluate contact resistance in the bilayer membrane, the area specific resistances (ASR) of 25 μm Nafion® 211 membrane, 1.5 μm 40% crosslinked sPPS membrane, and a bilayer membrane (25 μm Nafion® 211 with 1.5 μm 40% crosslinked sPPS coating) were measured in a single cell fuel cell. Unexpectedly, the ASR of the bilayer system was nearly equal to the sum of the ASR values of the individual layers.

[00145] *Accelerated stress tests (ASTs)*

[00146] ASTs were conducted under one of the following protocols:

[00147] Protocol A: AST included an aggressive strenuous phase and a periodic hydration phase, with the duration of each phase amounting to 4.5 h and 0.5 h, respectively. During the aggressive strenuous phase the cell was set to 110 °C with 0.1 lpm H₂ flow on the anode and 0.1 lpm O₂ flow on the cathode with no backpressure, and both gases at 30% RH. During the hydration phase the cell was set to 80 °C with 0.1 lpm H₂ flow on the anode and 0.1 lpm O₂ flow on the cathode with no backpressure, and both gases at 100% RH. The results of the tests are shown in Figure 6.

[00148] Protocol B: AST was conducted by applying an RH cycle where gases were switched between 0 and 100% RH at a 2 min interval while keeping the cell at open circuit. The cell was held at 90 °C, with 0.1 lpm H₂ flow on the anode and 0.1 lpm air flow on the cathode with no backpressure. H₂ crossover was measured and exhaust water was collected periodically during the accelerated stress test. The results of the tests are shown in Figures 11 and 12.

[00149] The data in Figure 11 show that Nafion® 211 membranes with increasing crosslinked sPPS coating thickness demonstrate improved durability. The durability increase with thicker coatings is found to be disproportionately large when compared to change in overall membrane thickness. Specifically, Nafion® 211 (25 µm) with a 1.5 µm of 40% crosslinked sPPS coating withstands the test conditions for a period of time that is 3 times longer than that for Nafion® 211 despite being only 6% thicker.

[00150] The data in Figure 12 confirm that Nafion® 211 membranes with thicker crosslinked sPPS coatings (40% degree of crosslinking) exhibit substantially higher durability. Additionally, the increase in H₂ crossover at the end of life in membranes with thicker coatings happens significantly more gradually compared to the rapid deterioration in hydrogen crossover in membranes with thinner or no coating. The observed gradual membrane deterioration near the end of life in membranes with thicker coatings is unexpected and enables improved safety features in hydrogen devices to prevent catastrophic degradation at the end of life.

[00151] The data in Figure 12 additionally show that bilayer membranes comprising Nafion® 211 and a crosslinked sPPS coating are more durable compared to a single layer Nafion® 211 membrane and a crosslinked sPPS membrane by themselves. Crosslinked sPPS membranes have fuel cell durability of less than 100 hours (see, e.g., Kim JD et al., “Chemically Crosslinked Sulfonated Polyphenylsulfone (CSPPSU) Membranes for PEM

Fuel Cells,” Membranes, 10(2):31 (2020)). Similarly, Nafion® 211 demonstrates AST durability of significantly less than 100 hours (Figure 12). Unexpectedly, a bilayer membrane comprising a Nafion® 211 base layer with a 1.5 μm 40% crosslinked sPPS coating demonstrates substantially longer durability than either component material by at least 3 times (Figure 12).

Example 9. Evaluation of water stability of crosslinked sPPS membranes.

[00152] Water stability of the coating material before and after crosslinking was evaluated by cyclically drying the membrane at 80 °C for 12 hours and collecting its mass before immersion in refluxing water for 20–25 hours. As synthesized, sPPS freestanding membranes were highly soluble in water. Non-crosslinked sPPS membranes immersed in boiling water quickly dissolve completely. Following the ethylene glycol crosslinking procedure, 40% crosslinked sPPS freestanding membranes demonstrated excellent stability to boiling water with less than 3% weight loss after 120 hours. The results of the tests are shown in Figure 8.

Example 10. Testing of coated PFSA membranes comprising various PFSA layers.

[00153] PFSA base membranes of various thickness from multiple vendors (supported Aquivion® (20 μm thickness) and Nafion® 211 (25 μm thickness) with crosslinked sPPS coatings (1.5 μm coatings of 40% degree of crosslinking) were examined. When operated in a single cell fuel cell, the coated membranes demonstrated full functionality as proton exchange membranes (see Figure 13). Additionally, the hydrogen crossover was substantially decreased for coated membranes compared to the uncoated baseline (Figure 14). The data demonstrated that the approach of coating a PFSA layer with a layer of crosslinked sulfonated polymer is applicable to all major PFSA-based commercial membranes and enables significant increases in fuel cell power density while simultaneously decreasing hydrogen crossover.

Example 11. Evaluation of swelling and delamination in membranes.

[00154] Dimensional stability of the membranes was evaluated by measuring the size and thickness of a membrane using a ruler and micrometer, soaking it in 80 °C water for 1 hour, and re-measuring its size and thickness after the 80 °C water soak. Nafion® 211 exhibited substantially different degree of swelling in 80 °C water (28–33%) compared to free-standing

40% crosslinked sPPS (147–209%), free-standing 90% crosslinked sPSU (0%), and free-standing 90% crosslinked sPPO (8%). The large disparity in material swelling was expected to cause significant delamination of the layers in the coated bilayer systems. However, bilayer membranes comprising a 1.5 μm polysulfonated polymer layer and a 25 μm Nafion® 211 layer did not delaminate after exposure to water at 80 °C for 1 hour. Instead the swelling properties closely matched those the Nafion® 211 membrane for sPPS and sPSU (see Table 2). Furthermore, no evidence of bilayer delamination was found during AST evaluations which repeatedly hydrated and dehydrated the membranes cyclically.

[00155] Table 2. Swelling values for Nafion® 211, 40% crosslinked sPPS, and a bilayer membrane comprising 1.5 μm -thick coating of crosslinked sPPS on Nafion® 211.

Material	2-Dimensional swelling (80 °C, 1 hour)	3-Dimensional swelling (80° C, 1 hour)
Nafion® 211 (25 μm)	28%	33%
40% crosslinked sPPS	147%	209%
1.5 μm crosslinked sPPS on Nafion® 211	28%	36%
90% crosslinked sPSU	0%	0%
1.5 μm sPSU on Nafion 211	21%	31%
90% crosslinked sPPO	8%	8%
1.5 μm sPPO on Nafion 211	0%	11%

Without wishing to be bound by any particular theory, it is believed that the claimed polymers of the disclosure exhibit unexpected performance in a bilayer membrane as a result of a polymer backbone comprising moieties with a nucleophilic lone pair and moieties with an electrophilic aromatic ring. The nucleophilic lone pair exhibits electrostatic attraction to protons on the sulfonic acid moieties of the PFSA surface while the electrophilic aromatic ring exhibits electrostatic attraction to the deprotonated sulfonic acid moieties (sulfonate moieties) on the PFSA surface. In a representative number of the claimed polymers these electrostatic interactions were surprisingly demonstrated to be sufficient to overcome the mechanical force enacted by significantly mismatched swelling between the layers, preventing delamination of the layers.

Example 12. Preparation of bilayer membrane comprising a layer of Nafion® 211 coated with sPPS crosslinked with hydroquinone

[00156] Spray-coating of Nafion® membrane with sPPS and hydroquinone solution.

[00157] A Sono-tek ExactaCoat coating system was used to deposit sPPS onto Nafion® membranes. The spraying solution was prepared with 0.75 wt.% sPPS and 0.19 wt.% hydroquinone (1.3 hydroquinone molecules per sPPS repeat unit) in H₂O. The solution was stirred for 30-60 min prior to use. The Nafion® membrane substrate was held under vacuum during deposition. The following parameters were used for the spray-coating: power 0.8-1.3 W, nozzle height 40 mm, temperature 60 °C, flow rate 0.25-0.5 mL/min. The number of polymer layers was adjusted for the desired coating thickness. 75 layers were deposited to achieve 1.5 µm thickness of the sPPS coating. The following ranges can be used for the spray-coating parameters: sPPS solution concentration: 0.05-15 wt. %; substrate temperature: 20-200 °C; nozzle height: 10-70 mm; flow rate: 0.1-4 mL/min; power: 0.8-5W; crosslinker amount: 0.1-4 molecules/repeat unit of sPPS.

[00158] Crosslinking the sPPS coating on Nafion® membrane.

[00159] The sPPS coating on a Nafion® membrane was crosslinked using hydroquinone. To perform the crosslinking the sPPS coated Nafion® membrane was heated to 200 °C for 2 hours under flowing nitrogen while held under tension with tape to an aluminum mask to achieve a water stable sPPS polymer coating. The resulting coatings were 25-30% crosslinked.

Example 13. Preparation of bilayer membrane comprising a layer of Nafion® 211 coated with sPPS crosslinked with 2,5-dihydroxybenzenesulfonic acid

[00160] Spray-coating of Nafion® membrane with sPPS and 2,5-dihydroxybenzenesulfonic acid solution.

[00161] A Sono-tek ExactaCoat coating system was used to deposit sPPS onto Nafion® membranes. The spraying solution was prepared with 0.75 wt.% sPPS and 0.39 wt.% potassium salt of 2,5-dihydroxybenzenesulfonic acid (1.3 molecules of potassium salt of 2,5-dihydroxybenzenesulfonic acid per sPPS repeat unit) in H₂O. The solution was stirred for 30-60 min prior to use. The Nafion® membrane substrate was held under vacuum during deposition. The following parameters were used for the spray-coating: power 0.8-1.3 W, nozzle height 40 mm, temperature 60 °C, flow rate 0.25-0.5 mL/min. The number of polymer layers was adjusted for the desired coating thickness. 75 layers were deposited to achieve 1.5 µm thickness of the sPPS coating. The following ranges can be used for the spray-coating

parameters: sPPS solution concentration: 0.05-15 wt.%; substrate temperature: 20-200 °C; nozzle height: 10-70 mm; flow rate: 0.1-4 mL/min; power: 0.8-5W; crosslinker amount: 0.1–4 molecules/repeat unit of sPPS.

[00162] Crosslinking the sPPS coating on Nafion® membrane.

[00163] The sPPS coating on a Nafion® membrane was crosslinked potassium salt of 2,5-dihydroxybenzenesulfonic acid. To perform the crosslinking, the sPPS coated Nafion® membrane was heated to 200 °C for 2 hours under flowing nitrogen while held under tension with tape to an aluminum mask to achieve a water stable sPPS polymer coating. The resulting coatings were 25–30% crosslinked.

[00164] Acidification of 2,5-dihydroxybenzenesulfonic acid-crosslinked sPPS

[00165] Crosslinked membranes were treated with 1M HCl aqueous solution for 1 hour at 25 °C. The membranes were removed from the HCl solution and rinsed 3–4 times with DI water until the effluent water remained neutral. The membranes were then dried at 25 °C.

Example 14. Preparation of bilayer membrane comprising a layer of Nafion® 211 coated with sPPS crosslinked with biphenyl

[00166] Spray-coating of Nafion® membrane with sPPS and biphenyl solution.

[00167] A Sono-tek ExactaCoat coating system was used to deposit sPPS onto Nafion® membranes. The spraying solution was prepared with 0.75 wt.% sPPS and 0.2 wt.% biphenyl (1 biphenyl molecule per sPPS repeat unit) in ethanol. The solution was stirred for 30-60 min prior to use. The Nafion® membrane substrate was held under vacuum during deposition. The following parameters were used for the spray-coating: power 0.8-1.3 W, nozzle height 40 mm, temperature 60 °C, flow rate 0.25-0.5 mL/min. The number of polymer layers was adjusted for the desired coating thickness. 75 layers were deposited to achieve 1.5 µm thickness of the sPPS coating. The following ranges can be used for the spray-coating parameters: sPPS solution concentration: 0.05-15 wt.%; substrate temperature: 20-200 °C; nozzle height: 10-70 mm; flow rate: 0.1-4 mL/min; power: 0.8-5W; crosslinker amount: 0.1–4 molecules/repeat unit of sPPS.

[00168] Crosslinking the sPPS coating on Nafion® membrane.

[00169] The sPPS coating on a Nafion® membrane was crosslinked using biphenyl. To perform the crosslinking, the sPPS coated Nafion® membrane was heated to 200 °C for 2 hours under flowing nitrogen while held under tension with tape to an aluminum mask to

achieve a water stable sPPS polymer coating. The resulting coatings were 30–35% crosslinked.

[00170] Properties of sPPS-coated membranes prepared with different crosslinkers according to Examples 6 and 12-14 were examined. Fuel cell polarization and power curves of the bilayer membranes and uncoated Nafion® 211 demonstrate that all examined membranes are fully functional as proton exchange membranes (Figure 17).

[00171] H₂ crossover studies performed according to Example 8 show that bilayer membranes prepared with sPPS and biphenyl, hydroquinone, and 2,5-dihydroxybenzenesulfonic acid reduce H₂ crossover as efficiently as sPPS crosslinked with ethylene glycol or better (Figure 18). Comparison with H₂ crossover in Nafion® 211 as shown in Figure 10 demonstrates significant improvement in H₂ crossover for sPPS-based bilayer membranes crosslinked with all examined crosslinkers.

Example 15. Preparation of bilayer membrane comprising a layer of Nafion® 211 coated with sPSU crosslinked with hydroquinone

[00172] Sulfonation of PSU

[00173] PSU was sulfonated by reacting the polymer with H₂SO₄. PSU resin was ground into a powder using an industrial grinder. 20 mL of concentrated sulfuric acid was heated to 60 °C under mechanical stirring. Once the sulfuric acid reached 60 °C, 2g of ground sPSU was added. Once the sPSU was dissolved, the reaction was allowed to proceed for 8 hours at 60 °C while stirring. The sulfonated polymer was precipitated by adding the reaction mixture dropwise to H₂O at 0 °C. The resulting precipitated polymer was centrifuged and isolated. The sulfonated PSU (sPSU) was redispersed in H₂O at room temperature and washed using dialysis until neutral pH was registered. The washed sPPS was dried on a hot plate to provide the final product.

[00174] Spray-coating of Nafion® membrane with sPSU and hydroquinone solution.

[00175] A Sono-tek Exactacoat coating system was used to deposit sPSU onto Nafion® membranes. The spraying solution was prepared with 0.75 wt.% sPSU and 0.177 wt.% hydroquinone (1.3 hydroquinone molecules per sPSU repeat unit) in H₂O. The solution was stirred for 30-60 min prior to use. The Nafion® membrane substrate was held under vacuum during deposition. The following parameters were used for the spray-coating: power 0.8-1.3 W, nozzle height 40 mm, temperature 60 °C, flow rate 0.25-0.5 mL/min. The number of

polymer layers was adjusted for the desired coating thickness. 75 layers were deposited to achieve 1.5 μm thickness of the sPPS coating. The following ranges can be used for the spray-coating parameters: sPSU solution concentration: 0.05-15 wt. %; substrate temperature: 20-200 $^{\circ}\text{C}$; nozzle height: 10-70 mm; flow rate: 0.1-4 mL/min; power: 0.8-5W; crosslinker amount: 0-4 molecules/repeat unit of sPSU.

[00176] Crosslinking the sPSU coating on Nafion® membrane.

[00177] The sPSU coating on a Nafion® membrane was crosslinked using hydroquinone. To perform the crosslinking, the sPSU coated Nafion® membrane was heated to 200 $^{\circ}\text{C}$ for 2 hours under flowing nitrogen while held under tension with tape to an aluminum mask to achieve a water stable sPSU polymer coating. The resulting coatings were 90% crosslinked.

Example 16. Preparation of bilayer membrane comprising a layer of Nafion® 211 coated with sPPO crosslinked with hydroquinone

[00178] Sulfonation of PPO

[00179] PPO was dissolved in chloroform at a concentration of 100 mg/mL under nitrogen purging. The PPO in chloroform was allowed to stir in an ice bath (0 $^{\circ}\text{C}$) for 30 min prior to sulfonation. Chlorosulfonic acid at a 1:1 molar ratio with PPO was added dropwise to the PPO solution. The reaction was allowed to proceed for 30 min before being terminated by addition of DI water. The sulfonated PPO (sPPO) was redispersed in H_2O at room temperature and washed using dialysis until neutral pH was registered. The washed sPPO was dried on a hot plate to provide the final product.

[00180] Spray-coating of Nafion® membrane with sPPO and hydroquinone solution.

[00181] A Sono-tek Exactacoat coating system was used to deposit sPPO onto Nafion® membranes. The spraying solution was prepared with 0.75 wt.% sPPO and 0.385 wt.% or 0.077 wt.% hydroquinone (0.5 or 0.1 hydroquinone molecules per sPPO repeat unit) in 1:1 H_2O :ethanol solution. The solution was stirred for 30-60 min prior to use. The Nafion® membrane substrate was held under vacuum during deposition. The following parameters were used for the spray-coating: power 0.8-1.3 W, nozzle height 40 mm, temperature 60 $^{\circ}\text{C}$, flow rate 0.25-0.5 mL/min. The number of polymer layers was adjusted for the desired coating thickness. 75 layers were deposited to achieve 1.5 μm thickness of the sPPS coating. The following ranges can be used for the spray-coating parameters: sPPS solution concentration: 0.05-15 wt. %; substrate temperature: 20-200 $^{\circ}\text{C}$; nozzle height: 10-70 mm;

flow rate: 0.1-4 mL/min; power: 0.8-5W; crosslinker amount: 0.05–4 molecules/repeat unit of sPPO.

[00182] Crosslinking the sPPO coating on Nafion® membrane.

[00183] The sPPO coating on a Nafion® membrane was crosslinked using hydroquinone. To perform the crosslinking, the sPPO coated Nafion® membrane was heated to 200 °C for 2 hours under flowing nitrogen while held under tension with tape to an aluminum mask to achieve a water stable sPPO polymer coating. The resulting coatings were 20% and 90% crosslinked for 0.1 and 0.5 hydroquinone per repeat unit of sPPO, respectively.

[00184] Properties of bilayer membranes with coatings comprising sPPS, sPSU, and sPPO crosslinked with hydroquinone and prepared according to Examples 6, 15, and 16 were examined. Fuel cell polarization and power curves of the bilayer membranes and uncoated Nafion® 211 are shown in Figure 19.

[00185] Data obtained in H₂ crossover studies performed according to Example 8 on bilayer membranes with coatings comprising sPPS, sPSU, and sPPO crosslinked with hydroquinone is shown in Figure 20.

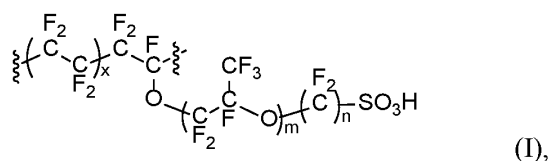
[00186] The teachings of all patents, published applications and references cited herein are incorporated by reference in their entirety.

[00187] While this invention has been particularly shown and described with references to example embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the scope of the invention encompassed by the appended claims.

CLAIMS

What is claimed is:

1. A bilayer polyelectrolyte membrane, comprising a first layer and a second layer, wherein:
 - the first layer comprises a perfluorosulfonic acid (PFSA), and
 - the second layer comprises a crosslinked polysulfonated polymer comprising sulfonated polyphenyl sulfone (sPPS), sulfonated polyether ether ketone (sPEEK), sulfonated polyphosphazene (sPOP), sulfonated polybenzimidazole (sPBI), sulfonated polyether sulfone (sPES), sulfonated polyphenylene oxide (sPPO), sulfonated polyarylene ether ketone (sPAEK), sulfonated poly(sulfone), sulfonated poly(sulfide sulfone), sulfonated polyimide (sPI), sulfonated poly(etherimide) (sPEI), sulfonated poly(amine), or a combination thereof, and wherein the first layer is disposed on the second layer.
2. The bilayer polyelectrolyte membrane of Claim 1, wherein the PFSA is a polymer comprising a repeat unit represented by structural formula (I):



wherein

x is an integer between 1 and 15,

m is an integer between 0 and 2,

n is an integer between 1 and 5, and

represents a point of attachment to a neighboring repeat unit.

3. The bilayer polyelectrolyte membrane of Claim 2, wherein

x is an integer between 5 and 14,

m is 1 or 2, and

n is 2 or 3.

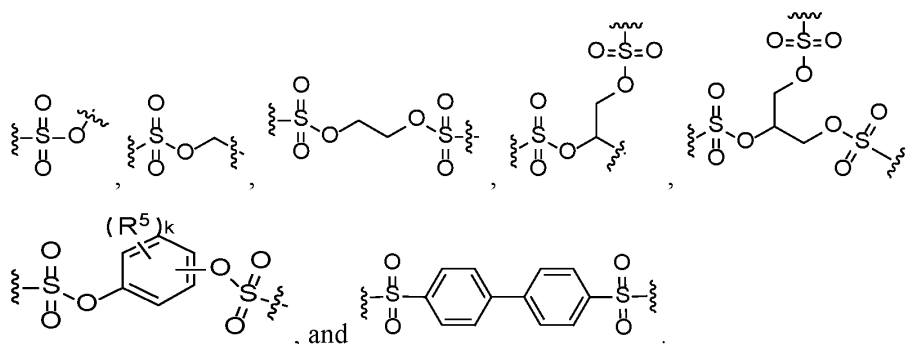
---O--- , ---S--- , ---S---S--- , $\text{---NR}^1\text{---}$, ---C(=O)--- , $\text{---C(=O)O}^-\text{---NH}_3^+\text{---}$, $\text{---C(=O)O}^-\text{---NH}_3^+\text{---}$,
 $\text{---S(=O)}_2\text{O}^-\text{---M}^{2+}\text{---O}^-\text{S(=O)}_2\text{---}$, $\text{---C(=O)NR}^2\text{---}$, $\text{---C(=O)NR}^3\text{---}$, $\text{---CH}_2\text{CH(R}^4\text{)---}$, ---C(=O)O--- , $\text{---C(=O)OCH}_2\text{CH}_2\text{OC(=O)---}$,
 $\text{---C(=O)OCH}_2\text{CH(C(=O)OCH}_2\text{CH}_2\text{OC(=O)---)CH}_2\text{CH}_2\text{OC(=O)---}$, $\text{---C(=O)OCH}_2\text{CH(C(=O)OCH}_2\text{CH}_2\text{OC(=O)---)CH}_2\text{CH}_2\text{OC(=O)---}$,
 $\text{---C(=O)OCH}_2\text{CH(C(=O)OCH}_2\text{CH}_2\text{OC(=O)---)CH}_2\text{CH}_2\text{OC(=O)---}$, $\text{---C(=O)OCH}_2\text{CH(C(=O)OCH}_2\text{CH}_2\text{OC(=O)---)CH}_2\text{CH}_2\text{OC(=O)---}$, and
 $\text{---C(=O)C}_6\text{H}_4\text{---C}_6\text{H}_4\text{---C(=O)---}$

represents a point of attachment of the crosslinking moiety to a repeat unit of the crosslinked polysulfonated polymer.

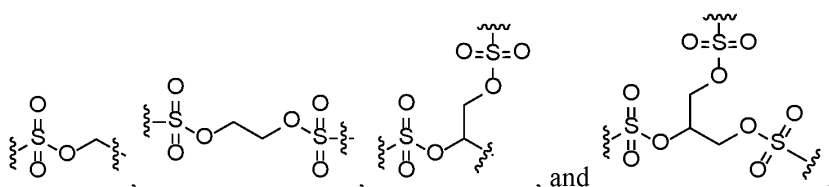
6. The bilayer polyelectrolyte membrane of Claim 5, wherein the crosslinking moiety is represented by one of the following structural formulas:

[illegible]

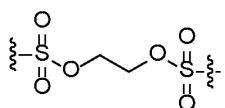
8. The bilayer polyelectrolyte membrane of Claim 5, wherein the crosslinking moiety is represented by one of the following structural formulas:



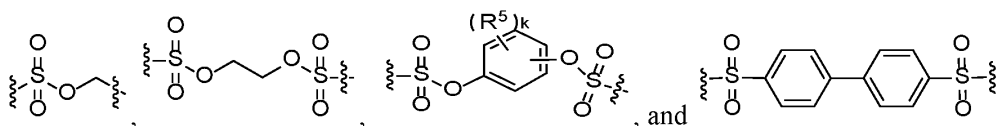
9. The bilayer polyelectrolyte membrane of Claim 5, wherein the crosslinking moiety is represented by one of the following structural formulas:



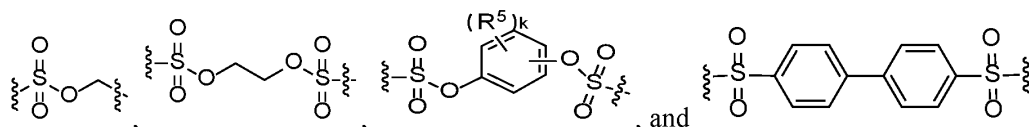
10. The bilayer polyelectrolyte membrane of Claim 5, wherein the crosslinking moiety is represented by the following structural formula:



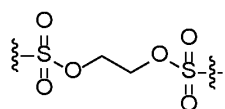
11. The bilayer polyelectrolyte membrane of Claim 5, wherein the crosslinked polysulfonated polymer comprises sPPS or sPSU, and the crosslinking moiety is represented by one of the following structural formulas:



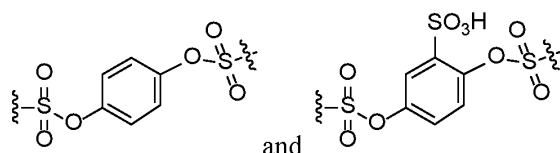
12. The bilayer polyelectrolyte membrane of Claim 5, wherein the crosslinked polysulfonated polymer comprises sPPS and the crosslinking moiety is represented by one of the following structural formulas:



13. The bilayer polyelectrolyte membrane of Claim 5, wherein the crosslinked polysulfonated polymer comprises sPPS and the crosslinking moiety is represented by the following structural formula:



14. The bilayer polyelectrolyte membrane of Claim 5, wherein the crosslinked polysulfonated polymer comprises sPPS and the crosslinking moiety is represented by one of the following structural formulas:



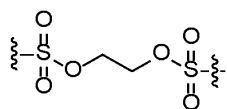
15. The bilayer polyelectrolyte membrane of any one of Claims 1-10, wherein comprises a crosslinked polysulfonated polymer comprising sulfonated polyphenyl sulfone (sPPS), sulfonated polyether ether ketone (sPEEK), sulfonated polyphosphazene (sPOP), sulfonated polybenzimidazole (sPBI), sulfonated polyether sulfone (sPES), sulfonated polyarylene ether ketone (sPAEK), sulfonated poly(sulfone), sulfonated poly(sulfide sulfone), sulfonated polyimide (sPI), sulfonated poly(etherimide) (sPEI), sulfonated poly(amine), or a combination thereof.

16. The bilayer polyelectrolyte membrane of Claim 15, wherein the crosslinked polysulfonated polymer comprises sPPS, sPEEK, sPOP, or sPBI.

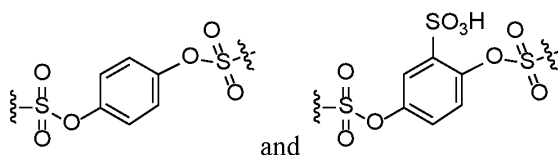
17. The bilayer polyelectrolyte membrane of Claim 15, wherein the crosslinked polysulfonated polymer comprises sPPS.
18. The bilayer polyelectrolyte membrane of any one of Claims 1-17, wherein the first layer further comprises a porous matrix comprising a matrix polymer, and wherein the PFSA and the matrix polymer form an interpenetrating network.
19. The bilayer polyelectrolyte membrane of Claim 18, wherein the first layer comprises from about 70 wt.% to about 99 wt.% of PFSA.
20. The bilayer polyelectrolyte membrane of Claim 18, wherein the first layer comprises from about 78 wt.% to about 95 wt.% of PFSA.
21. The bilayer polyelectrolyte membrane of any one of Claims 18-20, wherein the matrix polymer is polytetrafluoroethylene (PTFE).
22. The bilayer polyelectrolyte membrane of Claim 21, wherein the matrix polymer is expanded polytetrafluoroethylene (ePTFE).
23. The bilayer polyelectrolyte membrane of any one of Claims 1-22, wherein the degree of sulfonation of the crosslinked polysulfonated polymer is from about 20% to about 100%.
24. The bilayer polyelectrolyte membrane of Claim 23, wherein the degree of sulfonation of the crosslinked polysulfonated polymer is from about 40% to about 80%.
25. The bilayer polyelectrolyte membrane of Claim 23, wherein the degree of sulfonation of the crosslinked polysulfonated polymer is from about 50% to about 60%.
26. The bilayer polyelectrolyte membrane of any one of Claims 1-22, wherein the degree of sulfonation of the crosslinked polysulfonated polymer is from about 100% to about 300%.

27. The bilayer polyelectrolyte membrane of Claim 26, wherein the degree of sulfonation of the crosslinked polysulfonated polymer is about 200%.
28. The bilayer polyelectrolyte membrane of any one of Claims 1-22, wherein the crosslinked polysulfonated polymer comprises on average from about 1 to about 3 sulfonic acid, sulfonate, and sulfonamide groups, combined, per repeat unit.
29. The bilayer polyelectrolyte membrane of Claim 28, wherein the crosslinked polysulfonated polymer comprises on average about 2 sulfonic acid, sulfonate, and sulfonamide groups, combined, per repeat unit.
30. The bilayer polyelectrolyte membrane of any one of Claims 1-29, wherein the gel fraction of the crosslinked polysulfonated polymer is from about 50% to about 100%.
31. The bilayer polyelectrolyte membrane of any one of Claims 1-29, wherein the degree of crosslinking of the crosslinked polysulfonated polymer is from about 10% to about 95%.
32. The bilayer polyelectrolyte membrane of any one of Claims 1-29, wherein the degree of crosslinking of the crosslinked polysulfonated polymer is about 40%.
33. The bilayer polyelectrolyte membrane of any one of Claims 1-32, wherein the thickness of the first layer is from about 5 μm to about 175 μm .
34. The bilayer polyelectrolyte membrane of Claim 33, wherein the thickness of the first layer is about 25 μm .
35. The bilayer polyelectrolyte membrane of any one of Claims 1-34, wherein the thickness of the second layer is from about 0.2 μm to about 170 μm .
36. The bilayer polyelectrolyte membrane of Claim 35, wherein the thickness of the second layer is from about 0.2 μm to about 10 μm .

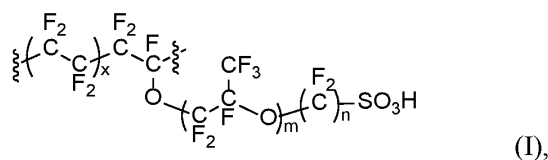
37. The bilayer polyelectrolyte membrane of Claim 36, wherein the thickness of the second layer is from about 0.5 μm to about 2 μm .
38. The bilayer polyelectrolyte membrane of any one of Claims 1-37, wherein the first layer is continuous.
39. The bilayer polyelectrolyte membrane of any one of Claims 1-38, wherein the membrane is unsupported.
40. The bilayer polyelectrolyte membrane of any one of Claims 1-16 and 18-39, wherein:
the membrane is unsupported,
the crosslinked polysulfonated polymer is sPPS, and
the crosslinking moiety is represented by the following structural formula:



41. The bilayer polyelectrolyte membrane of Claim 8, wherein:
the membrane is unsupported,
the crosslinked polysulfonated polymer is sPPS, and
the crosslinking moiety is represented by one of the following structural formulas:



42. The bilayer polyelectrolyte membrane of Claim 5, wherein:
the PFSA is a polymer comprising a repeat unit represented by structural formula (I):



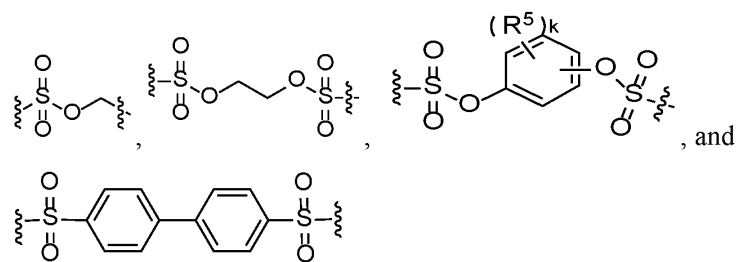
wherein

x is an integer between 5 and 14,

m is 1 or 2, and

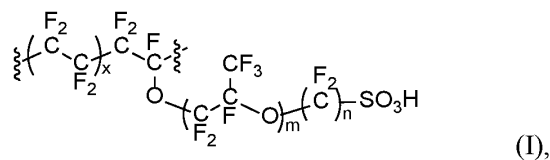
n is 2 or 3; and

the crosslinked polysulfonated polymer comprises sPPS or sPSU, and the crosslinking moiety is represented by one of the following structural formulas:



43. The bilayer polyelectrolyte membrane of Claim 5, wherein:

the PFSA is a polymer comprising a repeat unit represented by structural formula (I):



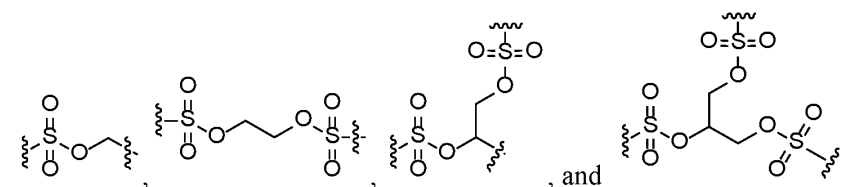
wherein

x is an integer between 5 and 14,

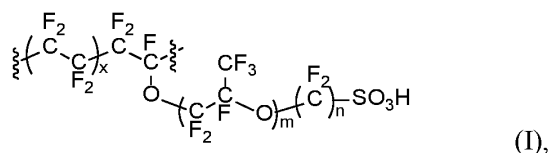
m is 1 or 2, and

n is 2 or 3; and

the crosslinked polysulfonated polymer comprises sPPS and a crosslinking moiety represented by one of the following structural formulas:



44. The bilayer polyelectrolyte membrane of Claim 5, wherein:
the membrane is unsupported,
the PFSA is a polymer comprising a repeat unit represented by structural formula (I):



wherein

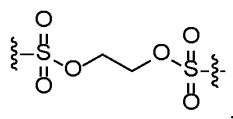
x is an integer between 5 and 14,

m is 1 or 2, and

n is 2 or 3; and further wherein

the crosslinked polysulfonated polymer is sPPS,

the crosslinking moiety is represented by the following structural formula:

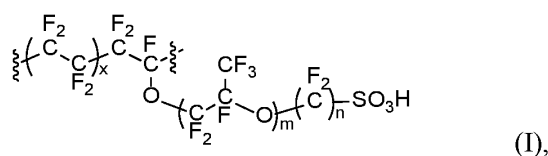


the degree of sulfonation of the sPPS is about 200%,

the degree of crosslinking of the sPPS is about 40%, and

the thickness of the second layer is from about 0.5 μm to about 2 μm .

45. The bilayer polyelectrolyte membrane of Claim 5, wherein:
the membrane is unsupported,
the PFSA is a polymer comprising a repeat unit represented by structural formula (I):



wherein

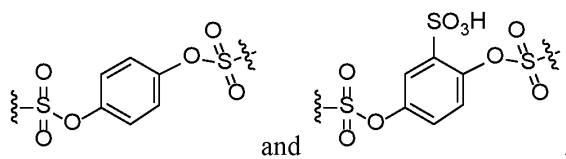
x is an integer between 5 and 14,

m is 1 or 2, and

n is 2 or 3; and further wherein

the crosslinked polysulfonated polymer is sPPS,

the crosslinking moiety is represented by one of the the following structural formulas:



the degree of sulfonation of the sPPS is about 200%,

the degree of crosslinking of the sPPS is from about 25% to about 30%, and

the thickness of the second layer is from about 1 μm to about 2 μm .

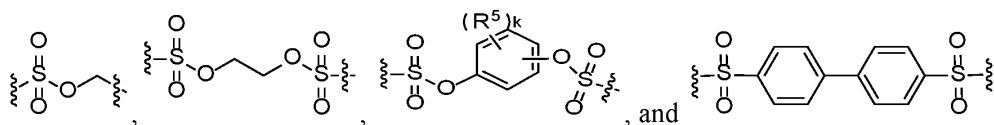
46. The bilayer polyelectrolyte membrane of any one of Claims 5-42, wherein:

the first layer comprises a porous matrix comprising a matrix polymer,

the PFSA and the matrix polymer form an interpenetrating network, and

the crosslinked polysulfonated polymer is sPPS.

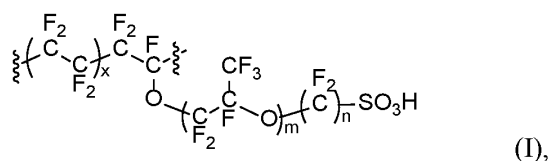
47. The bilayer polyelectrolyte membrane of Claim 46, wherein the crosslinking moiety is represented by one of the following structural formulas:



48. The bilayer polyelectrolyte membrane of Claim 5, wherein:

the first layer comprises a porous matrix comprising a matrix polymer, and wherein the PFSA and the matrix polymer form an interpenetrating network;

the PFSA is a polymer comprising a repeat unit represented by structural formula (I):



wherein

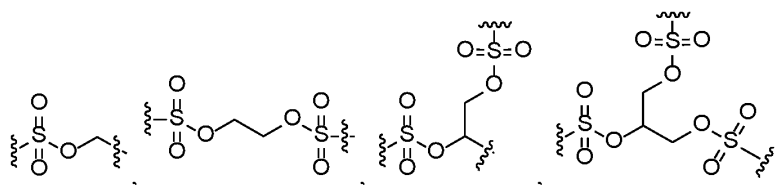
x is an integer between 5 and 14,

m is 1 or 2, and

n is 2 or 3;

the matrix polymer comprises ePTFE; and

the crosslinked polysulfonated polymer comprises sPPS and a crosslinking moiety represented by one of the following structural formulas:



49. A method of making a bilayer polyelectrolyte membrane of any one of Claims 1-48, comprising:
- a) providing a first layer having a first side, and a solution or suspension comprising a polysulfonated polymer and a crosslinking reagent,
 - b) coating the first side of the first layer with the solution or suspension, thereby producing a coated first layer;
 - c) exposing the coated first layer to conditions sufficient for the polysulfonated polymer and the crosslinking reagent to undergo a crosslinking reaction, thereby producing the bilayer polyelectrolyte membrane.
50. The method of Claim 49, wherein the crosslinking reagent is selected from a polyalcohol, an amine, an epoxide, a thiol, or a compound comprising a terminal alkene or alkyne.
51. The method of Claim 49, wherein the crosslinking reagent is selected from glycerol, ethylene glycol, hydroquinone, 2,5-dihydroxybenzenesulfonic acid, 2,5-dihydroxybenzene-1,4-disulfonic acid, biphenyl, tetraglycidyl bis(p-aminophenyl)methane, phenylene diamine, 4,4'-thiobisbenzenethiol, and tetrafluoro styrene.
52. The method of Claim 49, wherein the crosslinking reagent is selected from glycerol, ethylene glycol, tetraglycidyl bis(p-aminophenyl)methane, phenylene diamine, 4,4'-thiobisbenzenethiol, and tetrafluoro styrene.

53. The method of Claim 49, wherein the crosslinking reagent is polyalcohol.
54. The method of Claim 49, wherein the crosslinking reagent is ethylene glycol or glycerol.
55. The method of Claim 49, wherein the crosslinking reagent is hydroquinone or 2,5-dihydroxybenzenesulfonic acid.
56. The method of any one of Claims 49-55, wherein the conditions sufficient for the polysulfonated polymer and the crosslinking reagent to undergo a crosslinking reaction comprise heating the coated first layer to a crosslinking temperature from about 150 °C to about 200 °C for a crosslinking time from about 2 hours to about 96 hours.
57. The method of Claim 56, wherein the crosslinking temperature is about 180 °C.
58. The method of Claim 56, wherein the crosslinking time is about 4 hours.
59. The method of any one of Claims 49-58, wherein coating the first side of the first layer with the first solution or suspension comprises spray-coating the first side of the first layer with the first solution or suspension.
60. A membrane electrode assembly (MEA), comprising:
the bilayer polyelectrolyte membrane of any one of Claims 1-48;
a cathode; and
an anode,
wherein the bilayer electrolyte membrane is disposed between the anode and the cathode.
61. The MEA of Claim 60, wherein the cathode is disposed on the first layer of the bilayer electrolyte membrane and the anode is disposed on the second layer of the bilayer electrolyte membrane.

62. The MEA of Claim 60, wherein the anode is disposed on the first layer of the bilayer electrolyte membrane and the cathode is disposed on the second layer of the bilayer electrolyte membrane.

63. A fuel cell, comprising one or more of the MEAs of any one of Claims 60-62 and one or more gas flow bipolar plates.