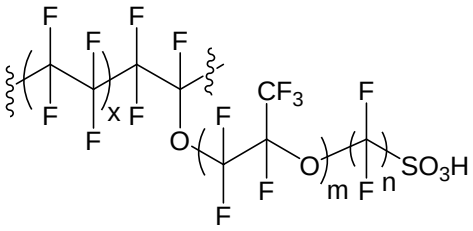
CLAIMS

1. A bilayer polyelectrolyte membrane, comprising:
a first layer disposed on a second layer, wherein:
the first layer comprises a perfluorosulfonic acid (PFSA) polymer, and
the second layer comprises crystalline metal oxide.

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



(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

the symbol ⌇ represents a point of attachment to a neighboring repeat unit.

3. The bilayer polyelectrolyte membrane of Claim 1 or 2, wherein the metal oxide comprises a reducible metal oxide.

4. The bilayer polyelectrolyte membrane of any one of Claims 1-3, wherein the metal oxide comprises titanium oxide, zirconium oxide, hafnium oxide, vanadium oxide, niobium, tantalum oxide, chromium oxide, molybdenum oxide, tungsten oxide, manganese oxide, iron oxide, cobalt oxide, nickel oxide, cerium oxide, gadolinium oxide, and samarium oxide, or a combination thereof.

5. The bilayer polyelectrolyte membrane of Claim 4, wherein the metal oxide comprises cerium oxide.

6. The bilayer polyelectrolyte membrane of any one of Claims 1-5, wherein the metal oxide is doped with one or more dopants.

7. The bilayer polyelectrolyte membrane of Claim 6, wherein the metal oxide doped with one or more dopants is selected from gadolinium doped cerium oxide, samarium doped cerium oxide, niobium doped titanium oxide, or cerium doped zirconium oxide.

8. The bilayer polyelectrolyte membrane of any one of Claims 1-7, wherein the second layer further comprises a polymer matrix, and the metal oxide is dispersed within the polymer matrix.

9. The bilayer polyelectrolyte membrane of Claim 8, wherein the polymer matrix comprises one or more first polymers selected from a polyether, a polysulfonate, a polysulfone, a poly(imidazole), a polysiloxane, a polyacrylate, a polysulfide, a polyolefin, a polyamide, a poly(triazole), a benzimidazole, a polyester, and a polycarbonate.

10. The bilayer polyelectrolyte membrane of Claim 8, wherein the one or more first polymers are selected from poly(ethylene glycol) (PEG), polyether ether ketone (PEEK), polytetrahydrofuran, polyvinyl butyral, poly(acrylonitrile-butadiene-styrene), polyetherpyridine, polyphenyl sulfone (PPS), polyphosphazene (POP), polybenzimidazole (PBI), polyether sulfone (PES), polyphenylene oxide (PPO), polyarylene ether ketone (PAEK), polysulfone, poly(sulfide sulfone), polyimide (PI), poly(etherimide) (PEI), polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), and poly(amine).

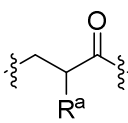
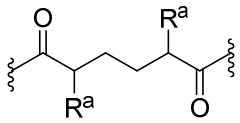
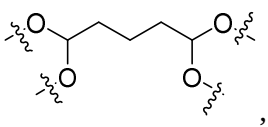
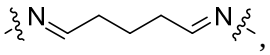
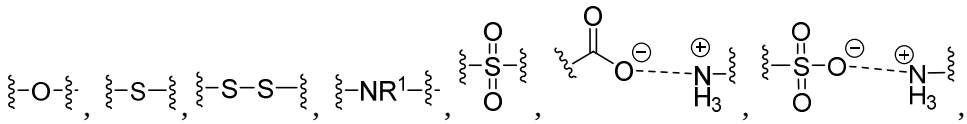
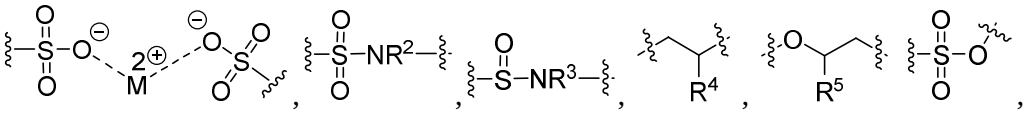
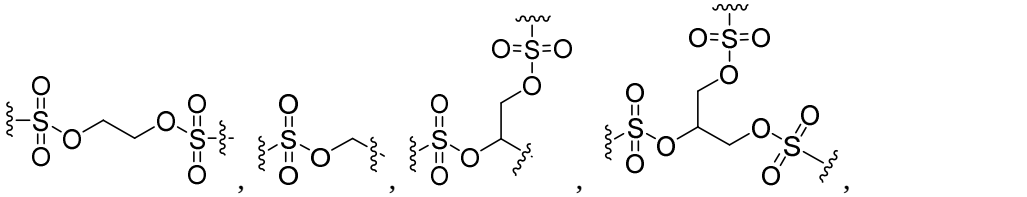
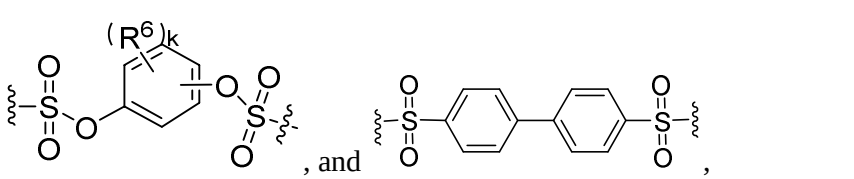
11. The bilayer polyelectrolyte membrane of Claim 8, wherein the first polymer is PEG-diacrylate (PEG(DA)).

12. The bilayer polyelectrolyte membrane of Claim 9 or 10, wherein the one or more first polymers are sulfonated.

13. The bilayer polyelectrolyte membrane of Claim 10 or 12, wherein the first polymer is sulfonated PPS (sPPS).

14. The bilayer polyelectrolyte membrane of any one of Claims 9-13, wherein at least one of the one or more first polymers is crosslinked.

15. The bilayer polyelectrolyte membrane of Claim 14, wherein the at least one of the one or more first polymers comprise a crosslinking moiety represented by one of the following structural formulas:

C_{2-6} alkylene, , , , , , , , , and ,

wherein:

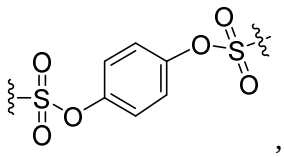
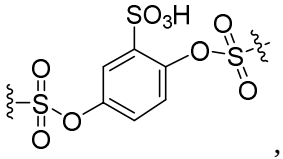
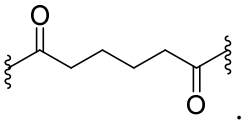
each of R^1, R^2, R^3, R^4, and R^5 is independently selected from H, C_{1-12} alkyl, C_{1-12} haloalkyl, C_{6-14} aryl, and C_{6-14} aryl(C_{1-12} alkylene);

R^6 is H or -SO_3H,

R^a is H or C_{1-12} alkyl;

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

the symbol "" represents a point of attachment of the crosslinking moiety to a repeat unit of the one or more first polymer.

16. The bilayer polyelectrolyte membrane of Claim 15, wherein the crosslinking moiety is represented by one of the following structural formulas: , , and .

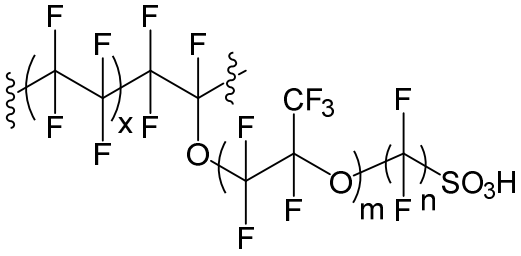
17. The bilayer polyelectrolyte membrane of any one of Claims 1-16, wherein the first layer further comprises a porous matrix comprising a second polymer, and wherein the PFSA polymer and the second polymer form an interpenetrating network.

18. The bilayer polyelectrolyte membrane of any one of Claims 1-17, wherein the first layer is continuous and/or the second layer is continuous.

19. The bilayer polyelectrolyte membrane of any one of Claims 1-18, wherein the membrane is unsupported.

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

the first layer consists of PFSA, wherein the PFSA is a polymer comprising a repeat unit represented by structural formula (I):

 (I),

wherein:

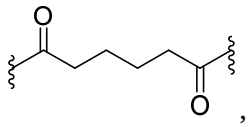
x is an integer between 5 and 14,

m is 1 or 2, and

n is 2 or 3;

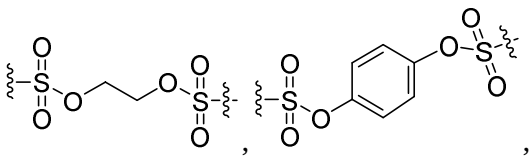
the metal oxide is CeO_2, and

(i) the second layer further comprises crosslinked PEG(DA) comprising a crosslinking moiety represented by the following structural formula:

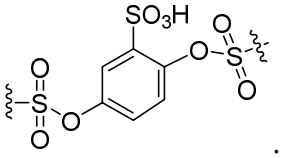


, or

(ii) the second layer further comprises crosslinked sPPS comprising a crosslinking moiety represented by one of the following structural formulas:



, and



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21. The bilayer polyelectrolyte membrane of Claim 20, wherein:

the membrane is unsupported,

the crystalline particles of CeO_2 have a characteristic dimension of about 4 nm,

the second layer further comprises crosslinked PEG(DA), and

the degree of crosslinking of crosslinked PEG(DA) is about 70%.

22. The bilayer polyelectrolyte membrane of any one of Claims 1-7, wherein:

the second layer further comprises a glass, and

the metal oxide is dispersed within the glass.

23. A method of making a bilayer polyelectrolyte membrane of any one of Claims 1-21, comprising:

providing a first layer having a first side, and a suspension comprising a metal oxide and a solvent; and

coating the first side of the first layer with the suspension, thereby producing a coated first layer.

24. A membrane electrode assembly (MEA), comprising:

the bilayer polyelectrolyte membrane of any one of Claims 1-23;

a cathode; and

an anode,

wherein the bilayer electrolyte membrane is disposed between the anode and the cathode.

25. A fuel cell, comprising one or more of the MEAs of Claim 24 and one or more gas flow bipolar plates.