THIN-FILM MEMBRANES WITH ZWITTERIONIC POLYMERS AND ALTERNATIVE SUPPORT STRUCTURES

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims priority to and the benefit of U.S. Provisional Patent Application No. 63/575,156, filed April 5, 2024; the disclosure of which is hereby incorporated by reference in its entirety.

FIELD OF THE DISCLOSURE

[0002] This disclosure relates generally to zwitterionic polymers and membranes made therefrom for filtration applications, such as, for example, ultrafiltration, superfiltration, nanofiltration, and reverse osmosis.

BACKGROUND

[0003] Membrane filtration is an important and promising method of water purification, reclamation, and reuse. Membranes of various pore sizes can be used for a wide range of objectives, from simply removing disease-causing microorganisms to desalination by reverse osmosis (RO). Membranes also serve as an efficient, simple, scalable separation method in various industries, such as food, beverage, dairy, and bio/pharmaceutical industries.

[0004] Membranes with improved selectivity, or ability to separate solutes with better precision, offer to improve the economic feasibility and energy efficiency of several other processes. For instance, membranes with improved selectivity between sulfate and chloride anions could alter the composition of seawater and wastewater for use as drilling fluid in offshore oil wells while operating at lower applied pressures. Membranes with extremely small pore sizes but low salt rejection can lead to highly improved effluent quality for challenging wastewater streams, particularly those with high organic content, such as those from the food industry.

[0005] Generally, typical composite membrane structures include a selective, anti-fouling, layer coated on a support material with a microporous polysulfone on a woven polyester. However, the microporous polysulfone has many disadvantages including, for example, production thereof requires the use of toxic, industrially and environmentally unfriendly solvents

(e.g., N-Methyl-2-pyrrolidone, Dimethylacetamide, Dimethylformamide) and generation of large amounts of waste from non-solvent induced phase separation (NIPS) processes to yield the appropriate microporous structure. Additionally, polysulfone is a highly engineered and relatively expensive polymer, with no intrinsic chemical compatibility for zwitterionic membranes. It would, therefore, be desirable to manufacture membranes in a more environmentally friendly and cost-effective manner.

SUMMARY

[0006] The current disclosure provides membranes, methods of manufacturing said membranes, and methods of using said membranes where the porous support layer is replaced by relatively inexpensive and common ceramic materials. Further provided herein are polymeric materials designed to create membranes in combination with the replacement materials that have improved operational properties.

[0007] In various implementations, the present disclosure relates to membranes made polymers comprising zwitterionic monomers and ceramic substrates. The production of zwitterionic membranes on ceramic supports allows for the covalent grafting of the polymeric selective layer on to the support layer, which can improve membrane stability under a variety of operating conditions. The present disclosure includes, without limitation, the following example implementations.

[0008] Embodiment 1: A filtration membrane comprising a porous support layer comprising a ceramic material and a polymeric layer coated onto the porous support layer to form a thin film composite membrane, wherein the polymeric layer comprises a zwitterionic copolymer.

[0009] Embodiment 2: The filtration membrane of the preceding Embodiment, wherein the ceramic material comprises a ceramic oxide, such as alumina.

[0010] Embodiment 3: The filtration membrane of Embodiment 1 or 2, or any combination thereof, wherein the alumina is selected from the group consisting of corundum, bayerite, boehmite, diaspore, or gibbsite.

[0011] Embodiment 4: The filtration membrane of Embodiment 1 to 3, or any combination thereof, wherein the porous support layer comprises a porosity of about 20% to about 80%, preferably about 30% to about 60%, and more preferably about 40% to about 50%.

[0012] Embodiment 5: The filtration membrane of Embodiment 1 to 4, or any combination thereof, wherein the porous support layer comprises a porosity of about at least 48% porosity.

[0013] Embodiment 6: The filtration membrane of Embodiment 1 to 5, or any combination thereof, wherein the porous support layer comprises a thickness of about 0.6 mm to about 3 mm, preferably about 0.8 mm to about 2 mm, and more preferably about 1.5 mm.

[0014] Embodiment 7: The filtration membrane of Embodiment 1 to 6, or any combination thereof, wherein the polymeric layer is adhered to the porous support layer via covalent bonding.

[0015] Embodiment 8: The filtration membrane of Embodiment 1 to 7, or any combination thereof, wherein the polymeric layer is deposited on the porous support layer by at least one of drop-casting, wire rod coating, doctor blades, or other scaled techniques that produce thin flat sheet membranes.

[0016] Embodiment 9: The filtration membrane of Embodiment 1 to 8, or any combination thereof, wherein the wherein the polymeric layer comprises a thickness of about 5 μm to about 10 μm.

[0017] Embodiment 10: The filtration membrane of Embodiment 1 to 9, or any combination thereof, wherein the polymeric layer comprises a thickness of about 10 nm to about 10 um, alternatively a thickness of about 100 nm to about 2 um.

[0018] Embodiment 11: The filtration membrane of Embodiment 1 to 10, or any combination thereof, wherein the polymeric layer is disposed on top of the porous substrate.

[0019] Embodiment 12: The filtration membrane of Embodiment 1 to 11, or any combination thereof, wherein the polymeric layer comprises an average effective pore size of about 0.1 nm to about 2.0 nm, alternatively an average effective pore size of about 0.1 nm to about 1.2 nm, or alternatively an average effective pore size of about 0.5 nm to about 1.0 nm.

[0020] Embodiment 13: The filtration membrane of Embodiment 1 to 12, or any combination thereof, wherein the filtration membrane rejects charged solutes and salts.

[0021] Embodiment 14: The filtration membrane of Embodiment 1 to 13, or any combination thereof, wherein the filtration membrane has a molecular weight cut-off of at least 500 Daltons.

[0022] Embodiment 15: The filtration membrane of Embodiment 1 to 14, or any combination thereof, wherein the polymeric layer exhibits sulfate (SO42-) rejection of greater than 99%.

[0023] Embodiment 16: The filtration membrane of Embodiment 1 to 15, or any combination thereof, wherein the polymeric layer exhibits sulfate (SO42-) / chloride (Cl-) separation factor of greater than 50.

[0024] Embodiment 17: The filtration membrane of Embodiment 1 to 16, or any combination thereof, wherein the polymeric layer exhibits sulfate (SO42-) / chloride (Cl-) separation factor of greater than 75.

[0025] Embodiment 18: The filtration membrane of Embodiment 1 to 17, or any combination thereof, wherein the polymeric layer exhibits different anion rejections for salts with the same cation.

[0026] Embodiment 19: The filtration membrane of Embodiment 1 to 18, or any combination thereof, wherein the polymeric layer exhibits different anion rejections for salts selected among NaF, NaCl, NaBr, NaI, and NaClO4.

[0027] Embodiment 20: The filtration membrane of Embodiment 1 to 19, or any combination thereof, wherein the polymeric layer exhibits a fluoride (F-) / chloride (Cl-) separation factor of greater than 5.

[0028] Embodiment 21: The filtration membrane of Embodiment 1 to 20, or any combination thereof, wherein the polymeric layer exhibits a fluoride (F-) / chloride (Cl-) separation factor of about 8.

[0029] Embodiment 22: A process of filtering a liquid, the process comprising providing a filtration membrane in accordance with any one of the preceding Embodiments or combinations thereof; directing a liquid through the filtration membrane, first through the polymeric layer and then through the porous support layer; and collecting the liquid that permeates through the filtration membrane.

[0030] Embodiment 23: A method of making a filtration membrane comprising providing a porous support comprising a ceramic material; providing a polymer comprising a plurality of monomers, wherein at least some of the monomers are zwitterions; and depositing the polymer on to the porous substrate.

[0031] Generally, additional treatment steps are contemplated and considered within the scope of the invention, such as, for example, quenching, surface modification, cleaning,

deactivating, etc., and may be carried out with different solvents, radiation ranges, and processing times.

[0032] These and other features, aspects, and advantages of the disclosure will be apparent from a reading of the following detailed description together with the accompanying drawings, which are briefly described below. The invention includes any combination of two, three, four, or more of the above-noted embodiments as well as combinations of any two, three, four, or more features or elements set forth in this disclosure, regardless of whether such features or elements are expressly combined in a specific embodiment description herein. This disclosure is intended to be read holistically such that any separable features or elements of the disclosed invention, in any of its various aspects and embodiments, should be viewed as intended to be combinable unless the context clearly dictates otherwise.

BRIEF DESCRIPTION OF THE FIGURES

[0033] Having thus described aspects of the disclosure in the foregoing general terms, reference will now be made to the accompanying drawings, which are not necessarily drawn to scale, and wherein:

[0034] FIG. 1 depicts an enlarged cross-sectional side view of a portion of a filtration membrane made in accordance with one or more embodiments of the present disclosure;

[0035] FIG. 2 depicts a series of representative structures of zwitterionic polymers that may be used for making a filtration membrane in accordance with one or more embodiments of the disclosure;

[0036] FIGS. 3A and 3B are pictorial representations of sample membranes produced for testing purposes in accordance with one or more embodiments of the disclosure;

[0037] FIG. 4 is a graphical representation of Fourier Transform Infrared Spectroscopy analysis of a membrane made in accordance with one or more embodiments of the disclosure as compared to a membrane having a neat support;

[0038] FIGS. 5A-5C are pictorial representations of scanning electron microscope images of the membranes of FIGS. 3A and 3B; and

[0039] FIG. 6 is a graphical representation of the permeability over time of a membrane support in accordance with one or more embodiments of the disclosure.

DETAILED DESCRIPTION

[0040] Some implementations of the present disclosure will now be described more fully hereinafter with reference to the accompanying figures, in which some, but not all implementations of the disclosure are shown. Indeed, various implementations of the disclosure may be embodied in many different forms and should not be construed as limited to the implementations set forth herein; rather, these example implementations are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the disclosure to those skilled in the art. Like reference numerals refer to like elements throughout.

[0041] FIG. 1 depicts one example of a filtration membrane 100 manufactured in accordance with the present disclosure. As shown, the membrane 100 includes a porous support layer 104 with a polymeric layer 102 disposed on a top surface 106 of the porous support layer 104. Generally, the specific size, thickness, porosity, material, etc. of the support layer 104 will be selected to suit a particular application.

[0042] In the disclosed embodiments, the support layer 104 is a ceramic material, such as aluminum oxide, hereafter referred to generally as alumina. This alternative support layer does not rely on the NIPS processes or generate large amounts of waste. One of alumina's most common forms has the chemical formula of Al_2O_3 and is often referred to as corundum; however, other forms are contemplated and considered within the scope of the disclosure, such as, for example, bayerite [α-$Al(OH)_3$], boehmite [γ-AlOOH], diaspore [α-AlOOH], and gibbsite [γ -$Al(OH)_3$]. In addition to alumina's utility as a support layer for zwitterionic polymer membranes 100, certain forms of alumina (e.g., those containing aluminum hydroxide) facilitate formation of covalent bonds between the zwitterionic polymer 102 and the ceramic support layer 104.

[0043] Other ceramic materials are contemplated and considered within the scope of the disclosure, such as, for example, beryllia, ceria, titania, zirconia oxides, silicon carbide, and in certain embodiments, non-oxide materials. Additionally, the ceramic support layers 104 can be shaped using injection molding, die pressing, isostatic pressing, slip casting, diamond machining, or extrusion.

[0044] The polymeric layer 102 may include a wide variety of zwitterionic polymers as disclosed herein. FIG. 2 depicts several representative structures of zwitterionic polymers of the class that contain repeat units with silyl ether content that upon hydrolysis and subsequent condensation, may crosslink into a sol-gel network. Sol-gel routes are also well-known among alumina/aluminum hydroxide materials, and the formation of covalent Si-O-Al bonds that may chemically adhere the ceramic support to the polymer membrane, which is advantageous in many applications. As shown in FIG. 2, representative 150 is typically a MPC-styrene-silane copolymer, representative 152 is MPC (2-Methacryloyloxyethyl phosphorylcholine), and representative 154 is silane (3-[Diethoxy(methyl)silyl]propyl Methacrylate). The various % monomer content may vary to suit a particular application.

[0045] Examples of polymeric layers that include zwitterionic monomers/polymers (e.g., PMMA-r-SBMA, styrene-r-MPC, or TFEMA-r-SB2VP) are described in U.S. Pat. No. 10,150,088, U.S. Pat. Pub. Nos. 2022/0220241A1, 2018/0133650A1, and PCT Appl. Nos. PCT/US2021/032793, PCT/US2022/025981, PCT/US2017/057517, and PCT/US2022/041055; *Constructing zwitterionic surface of nanofiltration membrane for high flux and antifouling performance*, by Mi et al., Journal of Membrane Science, 2017, and *Preparation of novel positively charged copolymer membranes for nanofiltration*, by Ji et al., Journal of Membrane Science, 2011, the entire disclosures of which are hereby incorporated herein by reference.

[0046] In order to carry out various experiments on membranes made in accordance with one or more embodiments of the invention, Applicant cast zwitterionic polymers 202 on intermediate scale flat sheet alumina supports 204. See FIG. 3A, which depicts membrane samples of about 6 inches x 6 inches that have been wire rod coated with a zwitterionic solution and sample discs 200 were removed therefrom for membrane testing. As shown in FIG. 3B, the presence of the zwitterionic polymer visually changed the surface of the supports. Specifically, the presence of the polymeric membrane is visibly apparent from the newly glossy surface, compared to the non-reflective surface of the starting support material. During production, different methods for depositing/forming the zwitterionic polymeric layer on the ceramic support may be used, such as, for example, drop-casting, wire rod coating, doctor blades, and other scaled techniques that produce thin flat sheet membranes, and techniques that make application on different support geometries possible.

[0047] In some embodiments, the ceramic supports 104, 204 may be subjected to different pre- or post-treatment processes to enhance casting. For example, in some embodiments, the pre-treatment consists of performing a cleaning protocol on the support surface, such as, air dusting off loose ceramic material, adhesive rolling to remove addition debris, a plasma surface treatment, and/or a corona surface treatment. See Table 2 below. Post-treatment may include different drying protocols, for example, exposing the membrane after casting to an 80 °C environment (e.g., via an oven) for 24 hours; however, the temperatures and times will vary to suit a particular application.

[0048] FIG. 4 graphically represents the results of the spectroscopic analysis of the sample membranes 200 and a membrane with a conventional Neat selective layer on an alumina support. The analysis was carried out via Fourier Transform Infrared Spectroscopy (FTIR). As shown, the membrane sample 200 exhibits a polymeric signal with several peaks in the 1000-1700 cm^{-1} region as compared to the Neat membrane support.

[0049] Zwitterionic membranes may be prepared in accordance with one or more embodiments of the disclosure with selective polymeric layers 302 having varying thicknesses deposited on a ceramic (e.g., alumina) support. The support layer 304 and the polymeric layer 302 are easily identified via microscopic techniques such as the SEM images shown in FIGS. 5A-5C. FIGS. 5A and 5B show a continuous polymeric layer 302 on the alumina support 304 that is between about 5-10 μm thick, although layers of about 1 μm and below have been demonstrated. FIG. 5C shows that the polymeric layer 302 is continuous, smooth and non-defective at up to 800X magnification.

Experiments:

[0050] Certain ceramics, even alumina, may be acquired in forms impermeable to water, which would not be suitable as a support material for a water purification membrane, or in forms that are highly permeable to water. In one example an alumina support with a nominal 13% porosity was tested and was found to be impermeable to water at up to 50 psi, in another example an alumina support with a nominal 48% porosity had a permeability of > 100 (Liter/m^2/h)/bar (LMHb) when tested for water permeance. This latter example, illustrated graphically in FIG. 6, varies between about 200-425 LMHb, which is of a desired high

permeability to not further restrict permeation relative to the selective zwitterionic membrane layer. This is data is representative of an uncoated support without the selective membrane, and is meant for comparative purposes with the permeation data, which helps show that the support has been coated. After successful coating of the zwitterionic polymer, water permeability is controlled to <50 LMHb, and the composite of zwitterionic membrane and alumina support becomes selective to the permeation of small molecules.

[0051] In one experiment, vitamin B12, a molecule with a molar mass of 1,355 g/mol, was used to determine rejection efficiency of a filtration membrane in accordance with one or more embodiments of the disclosure. Alumina support layer (104, 204, 304) is non-selective towards vitamin B12, allowing full permeation of both water and vitamin B12, whereas the zwitterionic polymeric layer (102, 202, 302) allows for the permeation of water and near complete retention of vitamin B12. As shown in Table 1, the zwitterionic membranes (e.g., 200) having the polymeric layer deposited on to the alumina support layer demonstrate near full rejection of the vitamin B12, and furthermore, continue to demonstrate rejection of the vitamin B12 after applying a 5 psi backflushing pressure.

Sample	Concentrate B12 Abs (UV-Vis)	Permeate B12 Abs (UV-Vis)	B12 Rejection (%)
a-1	0.982	0.018	98.2
a-2	0.897	0.016	98.2
b-1	1.328	0.007	99.5
b-2	1.145	0.009	99.2
a-1 (after 5 psi backflush)	1.03	0.011	98.9
b-2 (after 5 psi backflush)	1.289	0.007	99.5

Table 1: Water permeance and B12 rejection measurements of the zwitterionic coated alumina membranes, with backflushing indicated.

[0052] In some embodiments and depending on the specific materials used, it may be beneficial to treat the surface of the support substrate to functionalize the surface. For example, treatments that increase the surface energy of the support substrate may be used to improve covalent bonding between the polymeric layer and the porous support layer. Table 2 depicts the surface energies of treated vs untreated alumina (rough and smooth sides). Measurements were taken with three different dyne pens (in dyne(cm) = (mJ/m^2) for a variety of surface materials and treatments. Dyne levels were 32, 46, and 58.

SURFACE	32	46	58
Alumina smooth	O	O	O
Alumina rough	O	√	X
* Alumina rough (CW)	√	√	√
X = no wetting, no flow; O = wetting & flow; √ = wetting, but no or relatively slow flow through actual; and CW = corona wand treated.			

Table 2: Support Substrate Materials and Surface Energies Thereof with Different Surface Treatments.

[0053] After the polymeric layer is applied, dried, and processed as necessary, the membrane can be used to assemble a variety of module forms, such as spiral wound, tubular, or plate and frame. Additional details regarding the manufacture of the membranes disclosed herein may be found in PCT Publication Nos. WO2021/232018 and WO2020/231797, and the following articles: Lounder, S. J., Asatekin, A. *Zwitterionic Ion-Selective Membranes with Tunable Subnanometer Pores and Excellent Fouling Resistance*. Chem. Mater. 2021, 33, 12, 4408–4416 and Lounder, S. J., Asatekin, A. *Interaction-Based Ion Selectivity Exhibited by Self-Assembled, Cross-Linked Zwitterionic Copolymer Membranes*. Proc Natl Acad Sci USA (In Proof, 2021); the entire disclosures of which are hereby incorporated by reference herein.

[0054] Many modifications and other implementations of the disclosure will come to mind to one skilled in the art to which this disclosure pertains having the benefit of the teachings presented in the foregoing descriptions and the associated figures. Therefore, it is to be understood that the disclosure is not to be limited to the specific implementations disclosed herein and that modifications and other implementations are intended to be included within the scope of the appended claims. Although specific terms are employed herein, they are used in a generic and descriptive sense only and not for purposes of limitation.

WHAT IS CLAIMED IS:

1. A filtration membrane comprising:

a porous support layer comprising a ceramic material; and

a polymeric layer coated onto the porous support layer to form a thin film composite membrane, wherein the polymeric layer comprises a zwitterionic copolymer.

2. The filtration membrane of claim 1, wherein the ceramic material comprises a ceramic oxide, such as alumina.

3. The filtration membrane of claim 1, wherein the alumina is selected from the group consisting of corundum, bayerite, boehmite, diaspore, or gibbsite.

4. The filtration membrane of anyone of the preceding claims, wherein the porous support layer comprises a porosity of about 20% to about 80%, preferably about 30% to about 60%, and more preferably about 40% to about 50%.

5. The filtration membrane of anyone of the preceding claims, wherein the porous support layer comprises a porosity of about at least 48% porosity.

6. The filtration membrane of anyone of the preceding claims, wherein the porous support layer comprises a thickness of about 0.6 mm to about 3 mm.

7. The filtration membrane of any one of the preceding claims, wherein the polymeric layer is adhered to the porous support layer via covalent bonding.

8. The filtration membrane of any one of the preceding claims, wherein the polymeric layer is deposited on the porous support layer by at least one of drop-casting, wire rod coating, doctor blades, or other scaled techniques that produce thin flat sheet membranes.

9. The filtration membrane of any one of the preceding claims, wherein the polymeric layer comprises a thickness of about 5 μm to about 10 μm.

10. The filtration membrane of anyone of the preceding claims, wherein the polymeric layer comprises a thickness of about 10 nm to about 10 um, alternatively a thickness of about 100 nm to about 2 um.

11. The filtration membrane of anyone of the preceding claims, wherein the polymeric layer is disposed on top of the porous substrate.

12. The filtration membrane of anyone of the preceding claims, wherein the polymeric layer comprises an average effective pore size of about 0.1 nm to about 2.0 nm, alternatively an average effective pore size of about 0.1 nm to about 1.2 nm, or alternatively an average effective pore size of about 0.5 nm to about 1.0 nm.

13. The filtration membrane of anyone of the preceding claims, wherein the filtration membrane rejects charged solutes and salts.

14. The filtration membrane of anyone of the preceding claims, wherein the filtration membrane has a molecular weight cut-off of at least 500 Daltons.

15. The filtration membrane of anyone of the preceding claims, wherein the polymeric layer exhibits sulfate (SO_4^{2-}) rejection of greater than 99%.

16. The filtration membrane of anyone of the preceding claims, wherein the polymeric layer exhibits sulfate (SO_4^{2-}) / chloride (Cl-) separation factor of greater than 50.

17. The filtration membrane of anyone of the preceding claims, wherein the polymeric layer exhibits sulfate (SO_4^{2-}) / chloride (Cl-) separation factor of greater than 75.

18. The filtration membrane of anyone of the preceding claims, wherein the polymeric layer exhibits different anion rejections for salts with the same cation.

19. The filtration membrane of anyone of the preceding claims, wherein the polymeric layer exhibits different anion rejections for salts selected among NaF, NaCl, NaBr, NaI, and $NaClO_4$.

20. The filtration membrane of anyone of the preceding claims, wherein the polymeric layer exhibits a fluoride (F-) / chloride (Cl-) separation factor of greater than 5.

21. The filtration membrane of anyone of the preceding claims, wherein the polymeric layer exhibits a fluoride (F-) / chloride (Cl-) separation factor of about 8.

22. A process of filtering a liquid, the process comprising:

providing a filtration membrane of any one of the preceding claims;

directing a liquid through the filtration membrane, first through the polymeric layer and then through the porous support layer; and

collecting the liquid that permeates through the filtration membrane.

23. A method of making a filtration membrane comprising:

providing a porous support comprising a ceramic material;

providing a polymer comprising a plurality of monomers, wherein at least some of the monomers are zwitterions; and

depositing the polymer on to the porous substrate.