

HIGH PERFORMANCE COMPOSITE MEMBRANES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application is based on and claims priority from U.S. Provisional Patent Application No. 63/516,805 filed July 31, 2023, the contents of which are incorporated herein by reference in their entirety.

STATEMENT OF GOVERNMENT SPONSORED RESEARCH

[0002] This invention was made with government support under DE-FOA-0001905 awarded by the U.S. Department of Energy. The government has certain rights in the invention.

TECHNICAL FIELD

[0003] The present embodiments relate generally to reverse osmosis, ultra-high pressure, compaction, flux and rejection, and more particularly to high performance composite membranes in connection with same.

BACKGROUND

[0004] By 2025, half of the world's population will live in water-stressed areas. The need to ensure sufficient and safe drinking water with potable quality is driving the search for technological solutions to address water shortages, given the broad societal and ecological benefits that stem from adequate water resources, including economic vitality, public health, national security, and ecosystem health. (WHO, World Health Organization, Drinking Water, in, 2021; M. Elimelech, W.A.J.s. Phillip, The future of seawater desalination: energy, technology, and the environment, Science 333 (2011) 712-717; J. Wu, M. Cao, D. Tong, Z. Finkelstein, E.M.J.N.C.W. Hoek, A critical review of point-of-use drinking water treatment in the United States, npj Clean Water 4 (2021) 40).

[0005] Reverse osmosis (RO) has become the most cost-effective and versatile water treatment technology available over the past fifty years, thanks to its potential for generating ultra-pure, potable, and reusable water from nearly any starting water source when properly combined with various pre-treatments. The total cost, including both the amortized capital expense (CapEx) and operating expense (OpEx), is heavily dependent on several factors, including the influent water quality, total dissolved solids (TDS), product water recovery, membrane selection, and system hydraulic design, especially for cases where brine disposal is

expensive. Feed waters with higher TDS are typically limited to lower recovery and higher energy/OpEx, and highly impaired water quality leads to higher CapEx, OpEx, and energy due to fouling, scaling, and the need for additional pre-treatment. Extensive research has been conducted to improve brackish water RO (BWRO), seawater RO (SWRO), and high-pressure RO (HPRO) membranes, providing a solid foundation for the development of ultra-high-pressure RO (UHPRO). However, there is still a significant need for improvements, for example in connection with the fundamental nature of membrane compaction.

[0006] It is against this technological backdrop that the present Applicant sought a technological solution to these and other problems rooted in this technology.

SUMMARY

[0007] The present disclosure relates to novel fully-thermoset composite (FTC) membranes, which may function as reverse osmosis (RO) or nanofiltration (NF) membranes in a range of applications.

[0008] In some aspects, a fully thermoset composite (FTC) membrane is disclosed. In some aspects, the FTC membrane comprises, consists of, or consists essentially of a dense cross-linked thermoset coating film formed over a porous cross-linked thermoset support membrane.

[0009] In yet another aspect, a method of obtaining the fully thermoset composite membrane is provided. In some aspects, the method comprises, consists of, or consists essentially of providing a porous support membrane, cross-linking the porous support membrane to form a porous thermoset support membrane, and coating a dense thermoset coating film on top of the porous thermoset support membrane.

[0010] In some aspects, the porous thermoset support membrane comprises, consists of, or consists essentially of a thermosetting polymer selected from the group of: allyl resins (Allyl), melamine formaldehyde (MF), phenol-formaldehyde (PF), silicone (SI), and an epoxy. In yet another aspect, the porous thermoset support membrane comprises, consists of, or consists essentially of an inherently cross-linkable thermoplastic polymer selected from the group of: polyimide (PI), polyamideimide (PAI), polyetherimide (PEI), polyurethane (PU), polyester (PET) and their associated derivatives. In yet another aspect, the porous thermoset porous support membrane comprises, consists of, or consists essentially of a thermoplastic polymer comprising, consisting of, or consisting essentially of: acrylonitrile-butadiene-styrene (ABS),

cellulose, regenerated cellulose, cellulose acetate, cellulose di-acetate, cellulose tri-acetate, ethylene vinyl alcohol, fluoroplastics such as PTFE, FEP, PFA, CTFE, ECTFE, ETFE and PVDF, polyacetals, polyacrylates, polyacrylonitrile (PAN) polyamides (PA) (e.g., NylonTM, KevlarTM, NomexTM and AramidTM materials), polyaryletherketone (PAEK), polybutadiene (PBD), polybutylene (PB), polycarbonate (PC), polydicyclopentadiene (PDCP), polyketone (PK), polyetheretherketone (PEEK), polyetherimide (PEI), polyethersulfone (PES), polyethylene (PE), polyethylenechlorinates (PEC), polymethylpentene (PMP), polyphenylene oxide (PPO), polyphenylene sulfide (PPS), polyethersulfone (PES), polyphenylsulfone (PPU), polyphthalamide (PTA), polypropylene (PP), polystyrene (PS), polysulfone (PSU), polyvinylchloride (PVC), chlorinated PVC (CPVC), and polyvinylidene chloride (PVDC).

[0011] In yet another aspect, the thermoplastic polymer has been chemically modified such that the backbone of the polymer becomes derivatized to comprise, consist of, or consist essentially of pendant functional groups that will readily react with a separate di-, tri-, tetra- or otherwise multi-functional molecules that crosslink neighboring polymer backbones to each other, thereby creating a thermoset matrix. In some aspects, the thermoplastic polymer is chloromethylated or bromomethylated. In some aspects, the thermoplastic polymer or derivatized version thereof is further derivatized to comprise, consist of, or consist essentially of pendant sulfonic acid, carboxylic acid, amine, amic acid, imine, alcohol, aldehyde, azide or other reactive groups.

[0012] In some aspects, the porous support membrane is crosslinked with a multifunctional crosslinking molecule with pendant reactive functional groups comprising, consisting of, or consisting essentially of, acids, amines, amic acids, imines, aldehydes, epoxides, azides or any combination thereof.

[0013] In some aspects, the FTC membrane further comprises, consists of, or consists essentially of covalent bonds embedded in the backbone of the porous thermoset support membrane.

[0014] In some aspects, the porous support membrane is made via an ex situ crosslinking process. In yet another aspect, the porous thermoset support membrane is made via an in situ crosslinking process.

[0015] In some aspects, the coating film is formed by dip coating, spray coating, spin coating, gravier coating or other solution-casting technique. In yet another aspect, the coating film is formed by interfacial polymerization. In yet another aspect, the coating film is formed by interfacial polymerization of a polyfunctional amine monomer and a polyfunctional acyl halide monomer. In some aspects, wherein the polyfunctional amine monomer used in the interfacial polymerization reaction to form the coating film comprises, consists of, or consists essentially of: triaminobenzene, polyetherimine, meta-phenylene diamine, para-phenylene diamine, 1,3,5-triaminobenzene, 3,5-diaminobenzoic acid, 2,4-diaminotoluene, 2,4-diaminoanisole, xylylene-diamine, ethylenediamine, propylenediamine, 1,4-diaminopropanol, resorcinol, phloroglucinol, quinone, piperazine, tris(2-diaminoethyl)amine as well as various imidazolidines, purines, pyridines, and pyrimidines. In some aspects, the polyfunctional acyl halide monomer used in the interfacial polymerization reaction to form the coating film comprises, consists of, or consists essentially of a di-, tri-, and tetra-functional acid chloride comprising trimesoyl chloride (TMC), isophthaloyl chloride or tetraacid chloride.

[0016] In some aspects, the porous support membrane comprises, consists of, or consists essentially of an inherently crosslinkable polymer and hexanediamine (HDA) is the cross-linking molecule used to form the porous support membrane. In yet another aspect, the porous support membrane comprises, consists of, or consists essentially of an inherently crosslinkable polymer and γ -aminopropyltrimethoxysilane (APTS) is the cross-linking molecule used to form the porous support membrane.

[0017] In some aspects, the FTC membrane is for use as an ultra-high pressure reverse osmosis (RO) membrane for the filtration of brine concentration. In some aspects, the filtration of brine concentration comprises, consists of, or consists essentially of the filtration seawater RO brine concentration, oil and gas produced water brine concentration, continental brine concentration, geothermal brine concentration or for the concentration of any other naturally or industrially occurring brine having an initial total dissolved solids concentration in excess of about 50 g/L.

[0018] In yet another aspect, the FTC membrane is for use as a high pressure reverse osmosis (RO) membrane for the filtration of seawater desalination or for desalination of any

other water source having an initial total dissolved solids concentration in the range of about 25 to 45 g/L or more preferably about 30 to 40 g/L.

[0019] In yet another aspect, the FTC membrane is use as a low pressure reverse osmosis (RO) membrane for the filtration of brackish water desalination, optionally, wherein the brackish water desalination comprises brackish groundwater, or for desalination of any other water source having an initial total dissolved solids concentration in the range of about 1 to 20 g/L and more preferably about 1 to 3 g/L.

[0020] In yet another aspect, the FTC membrane is for use as an ultra-low pressure reverse osmosis (RO) membrane for the filtration of advanced water treatment of municipal or industrial wastewater or for advanced water treatment of any other water source having an initial total dissolved solids concentration in the range of about 0.5 to 2 g/L, or more preferably about 0.8 to 1.5 g/L.

[0021] In yet another aspect, the FTC membrane is for use as a nanofiltration (RO) membrane in the application of water softening, wherein the membrane offers very high rejection of either divalent cations or anions, greater than 90% and more typically greater than 95%, including but not limited to calcium, magnesium or sulfate ions which may exist in brine, seawater, brackish groundwater, municipal or industrial wastewater or any other waters having a divalent cation content higher than is desired to utilize the softened water for another purpose.

[0022] In some aspects, ultra-high pressure RO (UHPRO) membranes used in membrane “brine concentration” including, but not limited to feedwaters comprising seawater RO brines, oil and gas produced water brines, continental brines, geothermal brines or for the concentration of any other naturally or industrially occurring brines having an initial total dissolved solids (TDS) concentrations in excess of about 50 g/L and often with initial TDS concentrations of 100 or 200 g/L.

[0023] In some aspects, high pressure RO membranes are used for the application of “seawater desalination” or for desalination of any other water source having an initial total dissolved solids concentration in the range of about 25 to 45 g/L or more typically about 30 to 40 g/L.

[0024] In some aspects, low pressure RO membranes are used in the application of brackish water desalination, including brackish groundwater, or for desalination of any other

water source having an initial total dissolved solids concentration in the range of about 1 to 20 g/L and more typically about 1 to 3 g/L.

[0025] In some aspects, wherein providing the porous support membrane comprises dissolving a cross-linkable polymer of a desired weight percentage in a solvent. In some aspects, the desired weight percentage is about 5% to 50%, about 10 % to 30%, about 16% to 22%, or about 14% to 20%, or about 16% to 18%.

[0026] In some aspects, ultra-low pressure RO membranes are used in the application of “advanced water treatment” of municipal or industrial wastewater or for ultra-pure water production or for advanced water treatment of any other water source having an initial total dissolved solids concentration in the range of about 0.1 to 2 g/L, or more typically about 0.8 to 1.5 g/L.

[0027] In some aspects, nanofiltration (NF) membranes are used in the application of “water softening” wherein the membrane offers very high rejection of either divalent cations or anions, greater than 90% and more typically greater than 95%, including but not limited to calcium, magnesium or sulfate ions which may exist in brine, seawater, brackish groundwater, municipal or industrial wastewater, fresh but hard surface or ground waters, or any other waters having a divalent cation content higher than is desired to be used in an intended purpose.

[0028] While FTC NF and RO membranes may be made by a number of different approaches using a wide range of polymer and crosslinker chemistries, they are demonstrated herein via both *ex situ* and *in situ* crosslinked polyimide (PI) support membranes. These membranes exhibit superb compaction resistance, indicating the potential for achieving M/ZLD sustainably. Crosslinking PI with hexamethylenediamine converts it into a thermoset with strong mechanical strength and thermal resistance.

BRIEF DESCRIPTION OF THE DRAWINGS

[0029] These and other aspects and features of the present embodiments will become apparent to those ordinarily skilled in the art upon review of the following description of specific embodiments in conjunction with the accompanying figures, wherein:

[0030] Figs. 1(a) to 1(d) provide SEM images of example PI membranes according to embodiments and Figs. 1(e) to 1(h) provide corresponding threshold processed images of PI membranes according to embodiments.

[0031] Figs. 2(a) to 2(f) provide SEM images of example PI membranes according to embodiments.

[0032] Figs. 3(a) to 3(e) provide cross-sectional SEM images of example PI membranes according to embodiments and Fig. 3(f) provides images of conventional Dupont HPRO for comparison.

[0033] Fig. 4 illustrates example aspects of normalized water permeability of different example membranes including PI membranes according to embodiments.

[0034] Fig. 5 illustrates example aspects of water permeability and water flux of different example membranes at different pressures including PI membranes according to embodiments.

[0035] Fig. 6 illustrates example aspects of salt permeability and observed rejection of different example membranes including PI membranes according to embodiments.

[0036] Fig. 7 illustrates example aspects of water permeability and flux of example membranes at different temperatures at 60 bar including PI membranes according to embodiments.

[0037] Fig. 8 illustrates example aspects of salt permeability and rejection of example membranes at different temperatures at 60 bar including PI membranes according to embodiments.

[0038] Figs. 9(a) to 9(f) provide surface SEM images of different example membranes including PI membranes according to embodiments.

[0039] Figs. 10(a) to 10(f) provide cross-sectional SEM images of pristine and compacted membranes including PI membranes according to embodiments.

[0040] Fig. 11 illustrates example thickness loss of different example membranes after compaction at 207 bar including PI membranes according to embodiments.

[0041] Figs. 12A and 12B illustrate example aspects of reverse osmosis membranes according to embodiments.

DETAILED DESCRIPTION

[0042] The present embodiments will now be described in detail with reference to the drawings, which are provided as illustrative examples of the embodiments so as to enable those skilled in the art to practice the embodiments and alternatives apparent to those skilled in the art.

Notably, the figures and examples below are not meant to limit the scope of the present embodiments to a single embodiment, but other embodiments are possible by way of interchange of some or all of the described or illustrated elements. Moreover, where certain elements of the present embodiments can be partially or fully implemented using known components, only those portions of such known components that are necessary for an understanding of the present embodiments will be described, and detailed descriptions of other portions of such known components will be omitted so as not to obscure the present embodiments. Embodiments described as being implemented in software should not be limited thereto, but can include embodiments implemented in hardware, or combinations of software and hardware, and vice-versa, as will be apparent to those skilled in the art, unless otherwise specified herein. In the present specification, an embodiment showing a singular component should not be considered limiting; rather, the present disclosure is intended to encompass other embodiments including a plurality of the same component, and vice-versa, unless explicitly stated otherwise herein. Moreover, applicants do not intend for any term in the specification or claims to be ascribed an uncommon or special meaning unless explicitly set forth as such. Further, the present embodiments encompass present and future known equivalents to the known components referred to herein by way of illustration.

[0043] Provided herein are novel reverse osmosis (RO) membranes and methods of obtaining said membranes. The RO membranes may comprise, consist of, or consist essentially of cross-linked thermoset coating and support layers. In some aspects, the cross-linked coating layer is polymerized over a cross-linked porous support layer. By incorporating a cross-linked thin-film interfaced with a cross-linked porous support, the RO membranes disclosed herein provide superb compaction resistance, indicating the potential for achieving M/ZLD sustainably. Thus, the thin-film composite membrane may be interfacially polymerized and adjacent to the porous support membrane. Moreover, by cross-linking the porous support membrane into a thermoset, the membranes accomplish strong mechanical strength and thermal resistance.

[0044] Conventional RO membranes include porous supports having phase inverted thermoplastic polymers that are subject to deformation and creep under high pressure. These membranes are not suitable for high pressure reverse osmosis filtration systems, as they may be subject to undesirable compaction and embossing when utilized under high pressure conditions.

[0045] However, the RO membranes as described herein incorporating thin film active layer alongside cross-linked porous support membranes surprisingly demonstrate not only superior thermal and compaction resistance that resist collapse, but also minimal water permeance decline and low salt permeability.

[0046] As provided herein, the RO membranes may include fully thermoset composites, having both a thin film active layer and porous support layer that are cross-linked. The thermoset materials may include monomeric reactants that can be processed in liquid solutions to be phase inverted and simultaneously cross-linked.

[0047] A “thermoset” polymer, or thermosetting polymer, refers to a polymer that is obtained through irreversible hardening of a soft solid, viscous liquid, or powder. The polymer may be cured by heat, radiation, high pressure, or mixing with a catalyst. In some aspects, a thermoset polymer is irreversibly hardened.

[0048] Such materials include polycondensate materials such as Allyl Resins (Allyl), Melamine formaldehyde (MF), Phenol-formaldehyde Plastic (PF), (Phenolic), and Silicone, (SI) as well as Epoxy, which is a Thermoset polyadduct. Xue et al., “Nanostructured Graphene Oxide Composite Membranes with Ultra-permeability and Mechanical Robustness,” Nano Letters 20(4) (2020) 2209-2218

[0049] In some aspects, the thermoset composites for use as the thin film and/or cross-linked porous support membranes may include inherently cross-linkable thermoplastics. Inherently cross-linkable thermoplastics may include polymers that possess as part of their backbone chemistry functional groups that will react directly with certain other functional groups. An example is Polyimide (PI), which is a thermoplastic or thermoset polycondensate that reacts rapidly with amines. Cross-linked PI films are often made by immersing a PI film into a simple solvent like an alcohol containing multi-functional (di, tri or tetra) amines.

[0050] Other thermoset polymers include polyurethane (PU), which is a thermoplastic or thermoset polyadduct (typically reinforced) that result from the reaction of diisocyanates, dialcohols, dicarboxylic acids and other functional groups to create a range of hydrophilic to hydrophobic with varying mechanical properties. A final example is polyester, which is a thermoplastic or thermoset polycondensate that can be crosslinked with epoxides or other functionalities.

[0051] In some aspects, the thermoset polymers include a carboxylated polyimide. Exemplary carboxylated polyimides include BPDA-ODA (Biphenyl dianhydride - 4,4'-Oxydianiline), 6FDA-ODA (4,4'-Hexafluoroisopropylidene) diphthalic anhydride - 4,4'-Oxydianiline), BPDA-PDA (Biphenyl dianhydride – p-Phenylenediamine), BTDA-MPD (3,3',4,4'-Benzophenonetetracarboxylic dianhydride – m-Phenylenediamine), PMDA-ODA (Pyromellitic dianhydride - 4,4'-Oxydianiline)m s-BPDA (sulfone containing BPDA), s-ODA (sulfone containing ODA), or combinations thereof.

[0052] In some aspects, the thermoset polymers include a sulfonated polyimide. Exemplary sulfonated polyimides include 6FDA-ODA-SO₃H (4,4'-(Hexafluoroisopropylidene) diphthalic anhydride - 4,4'-Oxydianiline with sulfonic acid group), s-BPDA-PDA (sulfone containing Biphenyl dianhydride - p-Phenylenediamine), s-BTDA-MPD (sulfone containing 3,3',4,4'-Benzophenonetetracarboxylic dianhydride - m-Phenylenediamine), s-PMDA-ODA (sulfone containing Pyromellitic dianhydride - 4,4'-Oxydianiline), BPDA-ODA-SO₃H (Biphenyl dianhydride – 4,4'-Oxydianiline with sulfonic acid group), or combinations thereof.

[0053] In some aspects, the carboxylated or sulfonated polyimides are cross-linked with a diol. In some aspects, the carboxylated or sulfonated polyimides are cross-linked with Ethylene glycol, 1,3-Propanediol, 1,4-Butylene glycol, 1,4-Cyclohexanedimethanol, 1,4-Benzenedimethanol, 1,10-Decanediol, 2,2,3,3,4,4,5,5-Octafluorohexanediol, 1,5-Pentanediol, 1,6-Hexanediol, 1,7-Heptanediol, 1,8-Octanediol, 1,9-Nonanediol, 2,2-Dimethyl-1,3-propanediol (Neopentyl glycol), 2,3-Butanediol, 2,5-Hexanediol, Bisphenol A, Bisphenol S, or any combination thereof.

[0054] In yet further aspects, the thermoset polymers include a thermoplastic, which may include Acrylonitrile-Butadiene-Styrene, Cellulosic, Ethylene vinyl alcohol, a Fluoroplastics, (PTFE), (FEP, PFA, CTFE, ECTFE, ETFE) Ionomer, Liquid Crystal Polymer (LCP), Polyacetal, Polyacrylates, Polyacrylonitrile, (PAN) Polyamide, (PA) (Nylon), Polyamide-imide (PAI), Polyaryletherketone (PAEK), Polybutadiene (PBD), Polybutylene (PB), Polycarbonate (PC), Polydicyclopentadiene (PDCP), Polyektone (PK), Polyetheretherketone (PEEK), Polyetherimide (PEI), Polyethersulfone (PES), Polyethylene (PE), Polyethylenechlorinates (PEC), Polymethylpentene (PMP), Polyphenylene Oxide (PPO), Polyphenylene Sulfide (PPS), Polyphenylsulfone (PPU), Polyphthalamide (PTA), Polypropylene (PP), Polystyrene (PS),

Polysulfone (PSU), Polyvinylchloride (PVC), Polyvinylidene Chloride (PVDC), Polyvinylidene fluoride (PVDF), Thermoplastic elastomers (TPE), or any combination thereof.

[0055] While some thermoplastics are not inherently cross-linkable, the thermoplastics can be derivatized using various approaches to make then subsequently cross-linkable. Chloromethylation or bromomethylation followed by reaction acidic or basic groups like trimethylamine to produce a pendant quaternary ammonium ion may be used to derivative thermoplastics for use as cross-linkable thermoset polymers for incorporation as . For example, Vico et al. (2003) showed that membranes could be cast from a solution of bromomethylated polysulfone in chloroform (pro analysis, Merck) onto glass plates of known surface area. The solvent was removed by evaporation at room temperature. The film thickness was controlled by using constant mass of the bromomethylated polymer. The bromomethylation of polysulfone has been achieved by the procedure developed by Warshawsky et al. The polysulfone substrate (Udel structure) is shown in Figure 1 in its aminated form. The chemicals used for the bromomethylation reaction are polysulfone (Aldrich), bromomethyl octyl ether (90%, Aldrich), tin(IV) chloride (99%, Acros Organics), 1,2-dichloroethane (99+%, A.C.S. reagent, Aldrich), and methyl alcohol (pro analysis, Acros Organics). Further, for example, the amination reaction can be performed by immersing the bromo-methylated membrane in a solution containing 27% trimethylamine (solution of 45% in water, for synthesis, Merck), 20% methyl alcohol (pro analysis, Acros Organics), and 53% deionized water. The membrane remained in the amine solution for 24 h. The aminated membrane was rinsed with 0.5 M HCl (hydrochloric acid, pro analysis, min 37%, Acros Organics) and deionized water. During rinsing with 0.5 M HCl, the Br- ions originally present in the membrane are probably exchanged into Cl-.

[0056] The cross-linkable thermoplastics can be derivatized using click chemistry. Click chemistry reagents exist with a broad range of pendant functional groups (click reactive groups) and these include: Azide, Alkyne, Dibenzocyclooctyne (DBCO), trans-cyclooctene (TCO), Tetrazine or (bicyclo[6.1.0]nonyne) (BCN). These may exist where the reactive click reactive group exists in mono-, di-, tri- or tetra- functional states creating one or more points of reaction. The click reaction groups may be appended to aliphatic, aromatic, polyethylene glycol, zwitterionic or other functional groups, oligomers and polymers.

EXAMPLES

[0057] As set forth above, reverse osmosis (RO) has become the most cost-effective and versatile water treatment technology available over the past fifty years, thanks to its potential for generating ultra-pure, potable, and reusable water from nearly any starting water source when properly combined with various pre-treatments (E.M.V. Hoek, D. Jassby, R.B. Kaner, J. Wu, J. Wang, Y. Liu, U. Rao, Sustainable Desalination and Water Reuse, Morgan & Claypool Publishers, 2021; A. Edalat, E. Hoek, Techno-Economic Analysis of RO Desalination of Produced Water for Beneficial Reuse in California, *Water*, 12 (2020) 1850). The total cost, including both the amortized capital expense (CapEx) and operating expense (OpEx), is heavily dependent on several factors, including the influent water quality, total dissolved solids (TDS), product water recovery, membrane selection, and system hydraulic design, especially for cases where brine disposal is expensive. Feed waters with higher TDS are typically limited to lower recovery and higher energy/OpEx, and highly impaired water quality leads to higher CapEx, OpEx, and energy due to fouling, scaling, and the need for additional pre-treatment. The increasing demand for minimum and zero liquid discharge (MLD and ZLD) is driven by water scarcity, impaired surface and ground water quality, and sustainability imperatives (S.B. Grant, J.-D. Saphores, D.L. Feldman, A.J. Hamilton, T.D. Fletcher, P.L.M. Cook, M. Stewardson, B.F. Sanders, L.A. Levin, R.F. Ambrose, Taking the “waste” out of “wastewater” for human water security and ecosystem sustainability, *Sci.*, 337 (2012) 681-686; T. Tong, M. Elimelech, The global rise of zero liquid discharge for wastewater management: drivers, technologies, and future directions, *Environ. Sci. Technol.*, 50 (2016) 6846-6855; Z. Wang, A. Deshmukh, Y. Du, M. Elimelech, Minimal and zero liquid discharge with reverse osmosis using low-salt-rejection membranes, *Water Res.*, 170 (2020) 115317). MLD refers to a primary RO stage followed by a brine concentration process, while ZLD refers to a primary RO stage followed by brine concentration and salt crystallization processes. Thermal-driven desalination is currently the primary method for achieving MLD. Although mechanical vapor compression (MVC) is commonly used in MLD applications due to its superior energy efficiency compared to other phase-change-based desalination technologies (J. Wu, M. Cao, D. Tong, Z. Finkelstein, E.M.V. Hoek, A critical review of point-of-use drinking water treatment in the United States, *npj Clean Water*, (2021); D.M. Davenport, A. Deshmukh, J.R. Werber, M. Elimelech, High-pressure reverse osmosis for energy-efficient hypersaline brine desalination: current status, design

considerations, and research needs, *Environ. Sci. Technol. Lett.*, 5 (2018) 467-475), the specific energy consumption (SEC) for managing brine remains high, typically exceeding 20 kWh/m³. Ultra-high-pressure RO (UHPRO), which could theoretically reduce energy demand by ~50% compared to thermal brine concentration, is an attractive option for ZLD if integrated with high-efficiency hydraulic energy recovery devices (D.M. Davenport, C.L. Ritt, R. Verbeke, M. Dickmann, W. Egger, I.F.J. Vankelecom, M. Elimelech, Thin film composite membrane compaction in high-pressure reverse osmosis, *J. Membr. Sci.*, 610 (2020) 118268).

[0058] Figs. 12A and 12B illustrates example aspects of reverse osmosis according to embodiments. As shown in Fig. 12A, and as is well known, reverse osmosis is the process of osmosis in reverse. Osmosis occurs naturally without an external energy source, but reversing the osmosis process requires applying energy to the more saline solution to reverse the natural flow. A reverse osmosis membrane is a semi-permeable membrane that allows the passage of water molecules but not most of the dissolved salts, organics, bacteria, and pyrogens. However, the water must be “pushed” through the RO membrane by applying pressure greater than the naturally occurring osmotic pressure. As shown in Fig. 12A, reverse osmosis (RO) is a water purification process that uses a semi-permeable membrane to separate water molecules from other substances. When pressure is applied to the concentrated solution, the water molecules are forced through the semi-permeable membrane while the contaminants are not allowed through. RO typically works using a high-pressure pump to apply pressure on the salt side of the RO system and to force the water across the semi-permeable RO membrane, leaving almost all (95% to 99%) of dissolved salts behind in the reject stream.

[0059] Fig. 12B illustrates an example RO filter including an RO membrane, such as an RO membrane according to the present embodiments. As shown in Fig. 12B, feed water is pumped into an RO system and two types of water come out: good water (permeate) and bad water (concentrate). The “good” water has most contaminants removed and is called permeate. Another term for permeate is product water. Permeate is the water that was pushed through the RO membrane to remove nearly all contaminants. The “bad” water, called the concentrate, reject, or brine, is the leftover liquid with all the contaminants unable to pass through the RO membrane. All three terms are used interchangeably and mean the same thing. The simple schematic below shows how water flows through an RO system. As the feed water enters the

RO membrane under pressure (enough to overcome osmotic pressure) the water molecules pass through the semi-permeable membrane and the salts and other contaminants remain on the other side and are discharged from the system through the concentrate stream. The concentrate either goes to a drain or, in some circumstances, is fed back into the feed water supply and recycled through the RO system to save water.

[0060] Extensive research has been conducted to improve brackish water RO (BWRO), seawater RO (SWRO), and high-pressure RO (HPRO) membranes, providing a solid foundation for the development of ultra-high-pressure RO (UHPRO) membranes (M. Mulder, J. Mulder, Basic principles of membrane technology, Springer Science & Business Media, 1996). However, there is still a significant need for research to fill knowledge gaps, particularly regarding the fundamental nature of membrane compaction. Pendergast et al. described hand-cast thin film composite (TFC) RO membrane compaction at pressures up to 35 bar (500 psi) and observed a thickness reduction of about 20% to 30% and up to a 50% loss of water permeability (M.T.M. Pendergast, J.M. Nygaard, A.K. Ghosh, E.M.V. Hoek, Using nanocomposite materials technology to understand and control reverse osmosis membrane compaction, Desal. 261 (2010) 255-263). Davenport et al. (Id.) observed a 35% decrease in permeability and a 60% reduction in cross-sectional thickness after compacting seawater reverse osmosis at 150 bar. More recently, Wu et al. investigated commercial RO membrane compaction and embossing at pressures up to 207 bar, and they found that a 38% to 60% reduction in porous polysulfone layer thickness contributed to over 50% water permeability loss (J. Wu, B. Jung, A. Anvari, S. Im, M. Anderson, X. Zheng, D. Jassby, R.B. Kaner, D. Dlamini, A.J.D. Edalat, Reverse osmosis membrane compaction and embossing at ultra-high pressure operation, Desal. 537 (2022) 115875). A more robust and stable support membrane is therefore required for the UHPRO development.

[0061] Among other things, the present Applicant recognizes that replacing energy-intensive thermal desalination with an ultra-high pressure (up to 200 bar) reverse osmosis (UHPRO) process has the potential to reduce the energy consumption and cost of brine concentration by up to 50% (D.M. Davenport, A. Deshmukh, J.R. Werber, M. Elimelech “High-Pressure Reverse Osmosis for Energy-Efficient Hypersaline Brine Desalination: Current Status, Design Considerations, and Research Needs,” Environ. Sci. Technol. Lett. 5 (2018) 467–475); however, three major impediments to concentrating brines up to 250 g/L via RO membranes are:

(1) physical compaction and loss of permeability, (2) enhanced concentration polarization (CP) and trans-membrane osmotic pressure, and (3) mineral scaling, flux decline and membrane damage.

[0062] In accordance with these and other aspects, the present embodiments relate to novel thin-film composite (TFC) ultra-high pressure RO (UHPRO) membranes developed via ex-situ and in-situ crosslinked polyimide (PI) support membranes. These membranes exhibit superb compaction resistance, indicating the potential for achieving M/ZLD sustainably. Crosslinking PI with hexamethylenediamine converts it into a thermoset with strong mechanical strength and thermal resistance.

[0063] While commercial RO membranes experience over 50% membrane compaction at high pressures, TFC UHPRO membranes according to embodiments demonstrate less than 15% compaction at 200 bar, with insignificant water permeability decline. Cross-sectional SEM confirms less than 15% thickness reduction of the support layer, while commercial membranes exhibit 40% to 60% thickness loss, which causes the membrane compaction effect and performance loss. In addition to superior compaction resistance, the TFC UHPRO membranes according to embodiments produce low salt permeability with high rejections of up to 99.05% for NaCl solutions with concentrations up to 200,000 mg/L. Owing to the covalent bonds embedded in the backbone of the support membranes, TFCs are relatively inert to temperature change. And TFCs are therefore candidates for high temperature desalination applications.

[0064] **Example Materials**

[0065] Polyimide (PI) polymer (P84) was obtained from Ensinger Sintimid GmbH (Austria). All solvents used were HPLC grade. Isopropanol (IPA), hexane, 1,4-dioxane, N,N-dimethylformamide (DMF), methyl ethyl ketone (MEK) were obtained from Sigma Aldrich, US. Trimesoyl chloride (TMC) 98%, m-phenylenediamine (MPD) flakes > 99%, 1,6-hexanediamine (HDA) 99.5%, γ -aminopropyltrimethoxysilane (APTS), citric acid were obtained from Sigma Aldrich, US. MPD and TMC were used as monomers for the formation of the polyamide active layer via interfacial polymerization process, using distilled water and hexane as aqueous and organic phases, respectively. HDA and APTMS were used for the cross-linking of the polyimide support membranes. Nonwoven fabric for membrane casting was provided by AZTECH Corporation.

[0066] Ex-situ crosslinked PI support membranes preparation

[0067] Polymer dope solution was prepared by dissolving 16% to 22% (wt%) polyimide (P84) in DMF, or with 1,4-dioxane as co-solvent (solvent: cosolvent 1:3), and stirred overnight until complete dissolution was obtained. Once a viscous solution was formed, and the dope solution was placed in fume hood for 10 h to remove any entrapped air bubbles. The dope solution was then cast onto a polyester non-woven fabric taped to a glass plate using a casting knife (Elcometer, US.) set at a thickness of 100 μm at casting speed of 0.1m/s. Immediately after casting (evaporation time about 5 s), the membrane was immersed in a DI water bath or IPA bath for phase inversion. After 30 min, the membrane was placed in a new DI bath and left for 1 h to ensure sufficient removal of the solvents and stability of the membrane final structure. The wet membrane was then immersed in an IPA bath for 1 hour to displace water and solvents with IPA. For HDA crosslinking, the dewatered membrane was placed in the 20 g/L HDA-IPA bath for crosslinking, for 24 h. For APTMS crosslinking, membranes prepared via the phase inversion process were then immersed in a solution of 4 mol/L APTMS in MEK for 24 h. All crosslinked membranes were washed with IPA to remove excess crosslinker and stored in DI water before a polyamide coating was applied via interfacial polymerization.

[0068] In-situ crosslinked PI support membrane preparation

[0069] After the dope solution with a desired polymer concentration (16% to 20%) was prepared and degassed, solution was then cast onto a polyester non-woven fabric taped to a glass plate using a casting knife (Elcometer, US) set at a thickness of 100 μm at casting speed of 0.1 m/s. Immediately after casting (evaporation time about 5 s), the membrane was immersed in a 20 g/L HDA-IPA bath for phase inversion for 30 min. The in-situ crosslinked support membranes were then immersed into IPA for 1 h and then stored in DI water prior to interfacial polymerization process.

[0070] Interfacial polymerization for coating polyamide on the crosslinked support

[0071] A crosslinked support membrane (15 cm $\times$ 15 cm) taped to a glass plate (20 cm $\times$ 20 cm) was clamped under a customized polypropylene frame (10 cm $\times$ 10 cm $\times$ 3 cm). Then 250 mL aqueous solution of 6.0% (w/v) MPD was added to the frame where the support membrane sat underneath. After 2 min, the MPD solution was removed along with the frame. The support membrane was air-knifed (Exair, Cincinnati OH) with purified air remove excessive

solution on the membrane surface. And then a clean polypropylene frame (10 cm × 10 cm × 3 cm) was clamped atop the MPD-coated support. A solution of 0.18% (w/v) TMC in hexane was added to the frame. After 1 min coating time, the solution and the frame were removed. And the coated membrane was sitting on the glass plate for 1 min before curing. After 1 min, the coated membrane was hung vertically on a rack in the center of the oven (737F Isotemp Oven, Fisher Scientific) at 90°C for 3 min. Then the coated membrane was soaked in a 60°C citric acid bath at pH 3 for 15 min. Last, the membrane was soaked in a 60°C DI bath for 15 min. After the curing steps, the membrane was stored in DI water at room temperature prior to wet testing and characterization.

[0072] Membrane testing and characterization

[0073] Commercially-available, thin film composite HPRO membrane was obtained from Dupont (XUS1818, HPRO), tested and compared with UHPRO membranes in accordance with embodiments. Flux and rejection measurements were made using a rapidly-stirred, dead-end filtration cell (HP4750X Hastelloy Stirred Cell, Sterlitech Corp). The schematic of an example experimental filtration apparatus is shown in previous works (Id.). All membranes were tested at ultra high pressure, up to 207 bar (3,000 psi), supplied by high pressure N₂ gas (Airgas USA, Radnor, Pennsylvania, USA). Laboratory 18 MΩ de-ionized (DI) water was used in pure water permeability experiments; volumetric water flux was determined by collecting permeate in a plastic cup resting on a digital balance (OHAUS Pioneer® Precision, Ohaus Corp., Parsippany, New Jersey, USA) at different applied pressures. The filter cell accommodated 49 mm diameter membrane samples and 250 g of DI water per experiment. In salt rejection tests, different concentrations of NaCl (Sigma Aldrich, S7653) were prepared as feed solution to maintain ~14 bar (~200 psi) trans-membrane hydraulic pressure. For example, at 207 bar (3,000 psi), the osmotic pressure of the feed solution was set at 193 bar (2,800 psi), which is calculated via the following polynomial fit to data produced by a commercial geochemical modeling software (OLI Systems, Inc. Parsippany, NJ, USA):

$$\pi = 0.00111004c^2 + 0.741829c \quad (1)$$

where π is the osmotic pressure (bar), and c denotes salt concentration (g-NaCl/L-water). Water flux J_w and salt flux J_s are determined according to M. Mulder et al.:

$$J_w = A(\Delta p_m - \Delta \pi_m), \text{ and} \quad (2)$$

$$J_s = B \Delta c_m \quad (3)$$

[0074] Where A indicates the apparent water permeance of the membrane, Δp_m is the transmembrane hydraulic pressure, $\Delta \pi_m$ is the osmotic pressure difference across the membrane, B is the solute permeance of the membrane, and Δc_m is the trans-membrane concentration gradient. For experiments using de-ionized water as the feed, the trans-membrane osmotic pressure was negligible and ignored. The membrane's pure water permeance, A , can be determined from linear regression of flux versus applied pressure data.

[0075] The concentration polarization factor is calculated according to X. Jin, A. Jawor, S. Kim, E.M.V. Hoek, Effects of feed water temperature on separation performance and organic fouling of brackish water RO membranes, *Desal.*, 239 (2009) 346-359; J. Wang, D.S. Dlamini, A.K. Mishra, M.T.M. Pendergast, M.C.Y. Wong, B.B. Mamba, V. Freger, A.R.D. Verliefde, E.M.V. Hoek, A critical review of transport through osmotic membranes, *J. Membr. Sci.*, 454 (2014) 516-537; and E.M.V. Hoek, A.S. Kim, M. Elimelech, Influence of crossflow membrane filter geometry and shear rate on colloidal fouling in reverse osmosis and nanofiltration separations, *Environ. Eng. Sci.*, 19 (2002) 357-372:

$$CP = \frac{c_m}{c_f} = 1 - r_{ob} + r_{ob} \exp\left(\frac{J_w}{k_s c_f}\right), \quad (4)$$

where r_{ob} ($= 1 - c_p/c_f$) is the observed salt rejection, k_s the solute mass transfer coefficient, c_m the membrane surface salt concentration, and c_f the (bulk) feed salt concentration. For the turbulent flow in a stirred batch cell ($Re > 32,000$), the mass transfer coefficient is related to the Sherwood number (M. Mulder et al.), Sh , according to

$$k_s = Sh \frac{D}{d} \quad (5)$$

$$Sh = 0.04 Re^{0.75} \cdot Sc^{0.25}, \text{ and} \quad (6)$$

$$Re = \frac{d^2 \cdot n \cdot \rho}{\mu} \quad (7)$$

Here D is the diffusion coefficient, d the diameter of the stir cell, Re the Reynolds number, n the rotation speed revolutions per second, ρ the liquid mass density, μ the dynamic viscosity and Sc the Schmidt number ($= \nu/D$), where ν is the kinetic viscosity ($= \mu/\rho$). The intrinsic rejection r_s can be determined by:

$$r_s = 1 - \frac{c_p}{c_f \cdot CP} \quad (8)$$

$$B = \frac{J_w(1-r_s)}{r_s} \quad (9)$$

[0076] Also, since it is known that the A value of an RO membrane changes with the concentration of salt in the feedwater to which it is exposed (J. Wang, Y. Mo, S. Mahendra, E.M.V. Hoek, Effects of water chemistry on structure and performance of polyamide composite membranes, J. Membr. Sci., 452 (2014) 415-425), the A value in the presence of salt water can be determined from eq (2) where

$$\Delta\pi_m = (CP \cdot c_f - c_p) \quad (10)$$

[0077] Membrane samples were characterized via scanning electron microscope (SEM) (Zeiss Supra 40 VP, Carl Zeiss Microscopy, LLC, NY) analysis. Specifically, for cross-sectional SEM characterization of the membranes, both pristine and tested, the fabrics of all membranes were exfoliated from the thin film composite because it blocked the cross-sectional area of the

support and selective layers of the membranes. The SEM and images were also thresh-hold processed via NIH Image J software to calculate the porosity of the image. The extracted section was binarized using thresholding procedure. The porosity of the cross-section can be calculated thereby. X-Ray Photoelectron Spectrometer (XPS) (K-Alpha XPS) and contact angle goniometer (Model: 250, ramé-hart instrument co., Succasunna, New Jersey, USA). were employed to characterize the membranes. Differential scanning calorimetry (DSC) (PerkinElmer Inc. DSC-8500) were used to determine the glass transition temperature (T_g) of different polymers. These analyses were carried out at temperatures of between 30°C and 450°C at a heating and cooling rate of 10°C/min. The experiments were performed under nitrogen atmosphere at a flow rate of 20°C/min. The T_g of the polymers were taken from the second heating scan.

[0078] The degree of cross-linking of the PA active layers was calculated based on the O/N elemental ratio from the XPS spectra. The cross-linking degree indicates the proportion of fully cross-linked structure in the PA layer, where each acid chloride group (Cl – C = O) of TMC is bonded to the –NH₂ group of an amine monomer forming an amide structure.

[0079] The remaining proportion suggests a fully linear structure in which one chloride group of TMC remains unreacted and is eventually hydrolyzed to form a carboxylic acid. To calculate the cross-linking degree, we used the following equations:

$$\frac{O}{N} = \frac{2m+4n}{2m+2n}, \text{ and } m+n = 1 \quad (11)$$

where m and n are the cross-linked and linear portions, respectively. The cross-linking degree is then obtained by $m \times 100\%$.

[0080] **Results and Discussion**

[0081] **PI & crosslinked PI support membrane characteristics**

[0082] The surface scanning electron microscope (SEM) images and threshold-processed images are displayed in Figs. 1(a) to 1(h). More particularly, Figs. 1(a) to 1(d) provide SEM images of (a) 16%, (b) 18%, (c) 20% and (d) 22% polymer concentration PI membranes according to embodiments, while Figs. 1(e) to 1(h) provide corresponding threshold-processed images. The calculated porosity and contact angles are provided in Table 1. As the polymer concentration in the casting solution increases, the resulting support membrane becomes less

porous and less hydrophilic. Notably, polyimide (PI) support membranes are generally more hydrophilic than polysulfone-based support membranes. As a result, the amine monomer uptake of PI supports may differ from that of polysulfone supports. Furthermore, considering the high affinity of the amine monomer for the imide bond in the polymer backbone, a high amine monomer concentration of 6.0% (w/v) is used to ensure enough free amine monomer is available on the support membrane's surface for reaction during interfacial polymerization.

[0083] Figs. 2(a) to 2(f) provide surface SEM images of different support membranes according to embodiments, while Figs. 3(a) to 3(f) provides the corresponding cross-sectional SEM images. More particularly, Figs. 2(a) to 2(f) provide SEM images of (a) 20% PI (DMF) phase inverted in DI water; (b) 20% PI (DMF) phase inverted in IPA; (c) 20% PI (DMF:1,4-Dioxane = 1:3) phase inverted in IPA; (d) 20% PI (DMF) phase inverted in DI water and ex situ crosslinked with APTMS; (e) 20% PI (DMF:1,4-Dioxane = 1:3) phase inverted in IPA and ex situ crosslinked with HDA (f) 20% PI (DMF:1,4-Dioxane = 1:3) in situ crosslinked with HAD. Figs. 3(a) to 3(f) provide Cross-sectional SEM images of (a) 20% PI (DMF) phase inverted in DI water; (b) 20% PI (DMF:1,4-Dioxane = 1:3) phase inverted in IPA; (c) 20% PI (DMF) phase inverted in DI water and ex situ crosslinked with APTMS; (d) 20% PI (DMF:1,4-Dioxane = 1:3) in situ crosslinked with HDA; (e) 16% PI (DMF:1,4-Dioxane = 1:2) in situ crosslinked with HDA (f) Dupont HPRO.

[0084] As can be seen, utilizing alcohol as a coagulation bath instead of water slows down the phase inversion process, resulting in a less porous support membrane (Fig. 2(a) vs. Fig. 2(b)). To further enhance the mechanical stability of the support, the cosolvent 1,4-dioxane is combined with the solvent dimethylformamide (DMF) to further decelerate the phase inversion process (Fig. 2(b) vs. Fig. 2(c)). The cross-sectional SEM images confirm the transition from a finger-like morphology to a sponge-like morphology in the support when phase inversion is slowed down (Fig. 3(a) vs. Fig. 3(b)). The sponge-like structure favors the mechanical stability of the composite, whereas the fingerlike structure is prone to compaction and failure under high pressure. Consequently, a dense sponge-like support membrane is preferred in the ultra-high performance reverse osmosis (UHPRO) membrane design.

[0085] Both in-situ and ex-situ crosslinking of the support membranes tend to reduce surface porosity (Fig. 2(a) vs. Fig. 2(d), (e), (f)). The in-situ crosslinking procedure produces the

most dense support membranes both on the surface (Fig. 2(f)) and throughout the cross-section (Fig. 3(d)), contributing to their exceptional compaction resistance.

[0086] Table 1. Surface porosity and contact angle of PI membranes.

<i>Casting Solution Concentration (PI)</i>	<i>Surface Porosity (%)</i>	<i>Contact Angle (°)</i>	<i>Ref</i>
16%	16.3	62.4 ± 2	N/A
18%	14.6	63.7 ± 1	N/A
20%	13.2	61.5 ± 1	N/A
22%	10.1	59.3 ± 2	69 ± 2 [19]

[0087] UHPRO compaction resistance and performance evaluation

[0088] TFC RO membranes demonstrate superior compaction resistance compared to state-of-the-art HPRO membranes, as illustrated in Fig. 4. After losing approximately 10% (20% for APTS-20%) water permeability when pressure increases from 30 bar to 60 bar, the water permeability of the TFCs (in-situ and ex-situ 16%, 20%) remains stable and does not decrease significantly as pressure increases up to 200 bar. In contrast, the water permeability of commercial membranes declines dramatically with rising pressures. The exceptional compaction resistance of the TFCs can be attributed to their high mechanical stability.

[0089] The mechanical stability of the membrane is primarily determined by 1) material strength, and 2) composite structure. The polyimide, which forms the backbone of the TFCs and has a glass transition temperature (T_g) of 313°C, exhibits better mechanical stability than polysulfone—a polymer commonly used in preparing state-of-the-art reverse osmosis (RO) membranes ($T_g = 181^\circ\text{C}$)—under high pressure and high temperature conditions. The T_g values of the polymers are measured using differential scanning calorimetry (DSC), as presented in Table 4. By employing ex-situ or in-situ crosslinking of the PI, covalent bonds introduced to the polymer matrix are expected to further enhance the mechanical strength of the polyimide. An increase in T_g (from 313°C to 324°C) is observed after ex-situ crosslinking PI with hexanediamine (HDA), while a decrease in T_g (from 313°C to 297°C) occurs after ex-situ crosslinking PI with aminopropyltriethoxysilane (APTS). The increase in T_g indicates improved

mechanical strength and better thermal stability of the crosslinked PI. The decrease in T_g may result from the -O-Si-O- bond making the polymer more elastic instead of rigidifying the matrix (P. Gorgojo, M. Jimenez-Solomon, A.J.D. Livingston, Polyamide thin film composite membranes on cross-linked polyimide supports: Improvement of RO performance via activating solvent, *J. Membr. Sci.*, 344 (2014) 181-188; A. Ghosh, S.K. Sen, B. Dasgupta, S. Banerjee, B. Voit, Synthesis, characterization and gas transport properties of new poly (imide siloxane) copolymers from 4, 4'-(4, 4'-isopropylidenediphenoxy) bis (phthalic anhydride), *J. Membr. Sci.* 364 (2010) 211-218). No significant change in T_g is observed using the in-situ crosslinking method, likely due to the relatively shorter crosslinking duration (30 minutes) compared to the long-term ex-situ crosslinking (24 hours). However, during the in-situ crosslinking process, the polymer undergoes phase inversion while being crosslinked, where the kinetics of crosslinking are expected to be faster than the ex-situ method because more sites are available for crosslinking. As a result, the structures of the support membranes prepared via ex-situ versus in-situ crosslinking differ (Fig. 3(b) vs. Fig. 3(d)). In the in-situ TFC, a dense skin layer (near the surface) is formed, accompanied by a more porous support underneath, while the cross-section of the ex-situ TFC appears relatively homogenous. Compared to commercial RO support membranes with macro-pores that are prone to densification and compaction at high pressures, TFCs prepared via both ex-situ and in-situ crosslinking are dense and devoid of macro-pores in their support structures. The enhanced material strength, combined with the robust support membrane structures of TFCs, contributes to their outstanding compaction resistance.

[0090] The water permeability and water flux of TFCs and commercial RO membranes are displayed in Fig. 4 and Table 2. As discussed above, TFCs exhibit remarkable compaction resistance, where the water permeability of the membranes does not decrease significantly with increasing operating pressures. In contrast, the water permeability of commercial RO membranes declines dramatically as pressure rises. The water permeability of the membranes is highly dependent on the support membrane porosity. The trade-off of high compaction resistance, endowed by robust support, is the reduced water permeability due to limited porosity. However, it remains unclear whether high water permeability is necessary for ultra-high-pressure operating conditions.

[0091] The feed water in the example UHPRO process is hypersaline brine (above 34,000 mg/L), which is the concentrate from the conventional RO process where the feed water is either brackish water (1,000 to 15,000 mg/L TDS) or seawater (28,000 to 34,000 mg/L TDS). Consequently, the volume of the UHPRO process is up to 99 times lower than the volume of the conventional RO process, depending on the recovery of the initial low-pressure (below 60 bar) RO process. With a limited feed volume, high UHPRO water permeability may not be the most critical factor for overall process efficacy. However, membrane integrity and durability will undoubtedly be beneficial for lowering the overall operational expenditures (OPEX), thus reducing the total cost of the UHPRO process.

[0092] In addition to exceptional compaction resistance at high pressure, TFCs also exhibit considerably high salt rejection at various pressures, as displayed in Fig. 5 and Table 2. Among the TFCs, ex-situ-20% and in-situ-20% TFCs excel in salt rejection performance, achieving over 99% rejection at 60 bar and higher rejections than commercial RO membranes at 200 bar (96.88% and 98.40% respectively, versus 94.99% for Dupont HPRO). Solute permeability B (LMH) better represents the intrinsic property of the membrane compared to the observed rejection. It is noteworthy that the B value of both ex-situ-20% and in-situ-20% TFCs remains below 0.1 LMH at 200 bar. In contrast, the B value of Dupont HPRO increases from 0.12 LMH to 0.51 LMH after raising pressure from 30 bar to 200 bar.

[0093] The salt rejection and solute permeability of the membranes primarily reflect the crosslinking degree and film density of the active layer, typically polyamide, in the composite. Although the interfacial polymerization process for all TFCs presented herein follows identical procedures and monomer concentrations, the polyamide film formed atop the support membranes can be distinctively different due to factors such as varying surface porosity and pore distributions. As previously discussed, considering the high affinity of the amine monomer with the imide bond in the polymer backbone, a high amine monomer concentration of 6.0% (w/v) is used to ensure enough free amine monomer is present on the surface of the support membrane to react during interfacial polymerization. However, to either increase or decrease the active layer film density, the formula (monomer concentrations) needs to be customized for different support membranes according to their porosity, pore distribution, and affinity to the monomer, among other factors.

[0094] Ex-situ or in-situ crosslinking transforms the thermoplastic PI into a thermoset resin. Consequently, TFCs are potentially more temperature-tolerant than conventional TFCs. In general, both water permeability and solute permeability of RO membranes increase with rising temperature due to polymer swelling. As displayed in Fig. 6, the water permeability of all TFCs remains relatively stable after raising the temperature from 20°C to 60°C. Meanwhile, the water permeability of Dupont HPRO nearly doubles (from 1.15 LMH/BAR to 2.24 LMH/BAR) after increasing the temperature from 20°C to 60°C. The solute permeability of commercial RO membranes is even more adversely affected by temperature, with a roughly 10-fold increase in the B value observed (from 0.24 LMH to 2.33 LMH), as shown in Fig. 8 and Table 3. In contrast, the B value of TFCs is less affected by temperature; for ex-situ-20%, it increases from 0.07 to 0.25 LMH. With their resistance to temperature changes, TFCs are promising candidates for high-temperature desalination applications.

[0095] Table 2. Membrane performances at 20 degrees C and different feed pressures.

Membrane	Pressure (bar)	Jw (lmh)	Rob (%)	A (lmh/bar)	A/A ₂₀ (%)	B (lmh)	B/B ₂₀ (%)
20% APTMS <i>ex situ</i>	30	21.24	83.24%	0.77	100.00%	3.80	100.00%
	60	36.00	91.38%	0.58	75.32%	1.63	43.42%
	200	124.14	90.63%	0.60	77.92%	2.79	73.42%
20% HDA <i>ex situ</i>	30	7.30	98.60%	0.24	100.00%	0.07	100.00%
	60	14.40	99.05%	0.24	100.00%	0.07	100.00%
	200	42.00	96.88%	0.21	87.50%	0.10	141.86%
20% HDA <i>in situ</i>	30	10.50	96.93%	0.33	100.00%	0.18	100.00%
	60	18.60	99.02%	0.31	88.57%	0.08	44.44%
	200	60.00	98.40%	0.30	85.71%	0.06	33.33%
16% HDA <i>ex situ</i>	30	13.50	91.62%	0.43	100.00%	1.21	100.00%
	60	24.84	90.69%	0.41	91.11%	1.57	129.73%

16% HDA <i>in situ</i>	200	72.90	90.19%	0.36	80.00%	0.55	45.45%
	30	8.10	91.33%	0.27	100.00%	0.31	100.00%
	60	14.40	95.28%	0.24	88.89%	0.30	96.77%
Dupont HPRO	200	48.00	90.63%	0.24	88.89%	0.32	103.23%
	30	34.17	99.31%	1.25	100.00%	0.12	100.00%
	60	71.47	99.42%	1.15	92.00%	0.24	200.00%
	200	141.80	94.99%	0.69	55.20%	0.51	425.00%

[0096] Table 3. Membrane performances at different temperatures and 60 bar feed pressure.

Membrane	Temperature (°C)	Jw	Reb	A	A/A ₂₀	B	B/B ₂₀
		(lmh)	(%)	(lmh/bar)	(%)	(lmh)	(%)
20% APTMS <i>ex situ</i>	20	36.00	92.38%	0.58	100.00%	1.14	100.00%
	40	41.23	91.67%	0.69	118.97%	2.79	244.74%
	60	53.60	90.74%	0.89	153.45%	3.78	331.58%
20% HDA <i>ex situ</i>	20	14.40	99.05%	0.24	100.00%	0.07	100.00%
	40	15.23	98.70%	0.25	104.17%	0.17	242.86%
	60	18.53	98.13%	0.31	129.17%	0.23	337.14%
20% HDA <i>in situ</i>	20	18.60	99.02%	0.31	100.00%	0.08	100.00%
	40	21.44	98.64%	0.36	116.13%	0.25	312.50%
	60	28.04	97.11%	0.47	151.61%	0.67	837.50%
16% HDA <i>ex situ</i>	20	24.84	90.69%	0.41	100.00%	1.57	100.00%
	40	27.21	90.74%	0.45	109.76%	2.24	142.68%
	60	37.11	88.89%	0.62	151.22%	3.33	214.84%
16% HDA <i>in situ</i>	20	14.40	95.28%	0.24	100.00%	0.30	100.00%
	40	16.49	94.21%	0.27	112.50%	0.83	283.33%
	60	23.91	93.34%	0.40	166.67%	1.40	466.67%
Dupont HPRO	20	71.47	99.42%	1.15	100.00%	0.24	100.00%
	40	94.83	98.15%	1.58	137.39%	0.97	404.17%
	60	134.66	96.11%	2.24	194.78%	2.33	970.83%

[0097] The surface SEM (Figs. 9(a) to 9(f)) and the XPS surface elemental analysis (Table 4) characterize the active layer film density and crosslinking degree. The ex-situ-20% TFC (Fig. 9(a)) and commercial RO (Fig. 9(f)) display valley and ridge-like morphology, indicating a relatively well-crosslinked polyamide film. Correspondingly, the ex-situ-20% exhibits high rejection and low salt permeability at both low and high pressures. In contrast, some parts of the in-situ-20% surface (Fig. 9(b)) according to embodiments show lumps of polyamide, while other parts lack ridge and valley-like polyamide, indicating that some areas of the active layer are not fully crosslinked, contributing to the rejection decline at high pressure.

[0098] The surface morphologies of ex-situ-16% (Fig. 9(c)) and in-situ-16% (Fig. 9(d)) according to embodiments are similar. The polyamide active layers without notable ridge-valley structures indicate a poorly-formed film, which is why these two membranes exhibit lower salt rejection than the ex-situ-20% and in-situ-20%. Similarly, a poorly crosslinked polyamide active layer of the APTS-20% (Fig. 9(e)) results in relatively lower rejection and high salt permeability.

[0099] Although it is debatable whether it is better to use a high-rejection RO for UHP operation, the active layer crosslinking degree and film density can be tailored by altering various variables, such as monomer concentrations, additives in monomer solutions, curing steps, and post-treatments, among others.

[0100] To further confirm the superb compaction resistance of the TFC UHPRO, cross-sectional SEMs are taken to examine the membranes before and after compaction at 200 bar. As shown in Figs. 10(a) to 10(f), the TFCs membrane structure of embodiments (Figs. 10(a), 10(b), 10(c), 10(d)) remains identical to its pristine stage after 200 bar operation. In contrast, the macro pore structures of the commercial RO membrane are destroyed by high pressure, and the support matrix becomes densified compared to its pristine morphology (Figs. 10(e), 10(f)). Fig. 11 shows the thickness loss of the membranes before and after UHP operation. It is noteworthy that only about 13% thickness loss is observed for both ex-situ and in-situ TFCs, compared to a 42% thickness loss for the commercial RO. Moreover, the pristine TFCs are about 30% thinner than the commercial RO, indicating a high packing density of the TFCs when rolled into a spiral-wound module. In addition, the TFCs spiral-wound modules are less prone to causing operational problems due to a stable thickness across different pressures. The conventional TFC

spiral-wound module can become loose because of the significant change in membrane thickness and eventually lead to module failure in UHP operation.

[00101] Table 4. Membrane characteristics.

Sample	T _g (°C)	XPS surface elemental analysis				
		O (%)	N (%)	C (%)	O/N ratio	Crosslinking Degree (%)
PI	313					
PSU	181					
APTS 20%	177	12.58	7.76	79.66	1.62	29.01
Exsitu 16%	310	11.68	8.01	80.31	1.46	43.90
Insitu 16%	324	12.34	8.12	79.54	1.52	38.10
Exsitu 20%	311	10.88	8.81	80.31	1.23	69.06
Insitu 20%	323	11.42	79.50	9.08	1.26	65.49
Dupont HPRO	297	8.33	84.62	7.05	1.18	75.23

[00102] **Conclusions**

[00103] This work presents crosslinked thin-film composite (TFC) ultra-high pressure RO (UHPRO) membranes developed using ex-situ and in-situ crosslinked polyimide (PI) support membranes. These membranes exhibit superb compaction resistance, indicating the potential for achieving M/ZLD sustainably. Crosslinking PI porous supports with various diamines creates a thermoset support layer with improved mechanical strength and thermal resistance. While conventional PSU supported commercial RO membranes experience up to 50% membrane

compaction and similar permeance decline at 200 bar, TFC-RO membranes suffer less than 15% compaction with minimal water permeance decline. Moreover, the pristine TFCs are about 30% thinner than a commercial RO, suggesting one might achieve higher packing density when rolled into spiral-wound elements. Finally, the TFC UHPRO membranes according to embodiments produce low salt permeability with high rejections of up to 99% for feed solutions of 200,000 mg/L NaCl. The highly crosslinked support membranes are thermoset resins, relatively inert to temperature change, making them suitable candidates for high-temperature desalination applications.

[00104] Among various advantages, the present embodiments enable development of nano-composite compaction-resistant UHPRO flat-sheet membranes and 3D printed permeate spacers that resist collapse of UHPRO membranes into permeate flow channels at pressures up to 200 bar, and further enable the development of electrically-conducting fouling/scaling-resistant coatings. Additionally, embodiments enable development of a new optimized UHPRO spacer, and an optimized module design for electro-active UHPRO membranes.

[00105] It is possible that embodiments can obtain more than 50% reduction in energy and cost of brine concentration relative to conventional thermal methods – moving brine concentration significantly towards pipe parity, and this UHPRO represents an automated, resilient, intensified, modular and electrified process.

[00106] Compaction-resistant flat-sheet UHPRO membranes according to embodiments can be fabricated by embedding carbon, boron-nitride and silicon-carbide nanotubes within the support membrane layer. Previous results with zeolite, silica and metal nanoparticles were promising but it is hypothesized that the “rebar-like” high aspect-ratio of nanotubes will provide better compaction resistance. New penetration-resistant permeate carrier materials will be designed and 3D printed with a dual-asymmetric skinned structure to prevent the flat-sheet membrane from penetrating into the drainage channels. Flat-sheet UHPRO membranes can be tested over standard tricot mesh permeate spacers and novel 3D printed permeate spacers while concentrating brines up to 250,000 mg/L at feed pressures up to 206 bar (3,000 psi) including benchmarking against commercially available membranes (Hydronautics PRO-XP1 and Filmtec XUS).

[00107] Compaction-resistant supports according to embodiments can be coated with a percolating network of carbon nanotubes, and cross-linked with a salt-rejecting polyamide layer to form an electrically conducting UHPRO material (de Lannoy, C.F.O.; Jassby, D.; Gloe, K.; Gordon, A. D.; Wiesner, M. R., Aquatic biofouling prevention by electrically charged nanocomposite polymer thin film membranes. *Environ. Sci. Technol.* 47(6) (2013) 2760-2768.) The membrane can be paired with a Pt-coated Ti counter-electrode in a lab-scale cross-flow module, with both connected to an external waveform generator. A range of AC and DC conditions (frequency, magnitude) can be applied to the membrane surface while it is being used to concentrate brines to a concentration of 250,000 mg/L. Water flux, salt/solute rejections, and membrane autopsies can be used to evaluate the impacts of the applied electrical fields on separation performance, scaling and fouling.

[00108] The present embodiments have the potential to significantly advance RO membrane-based brine concentration up to 250 g/L, which could enable membrane brine concentration to displace thermal brine concentration. An achievable goal is energy savings and cost reduction up to 50%, which – combined with the modular and scalable nature of RO technology – would transform utilization of non-traditional water sources enabling cost-effective minimal liquid discharge at any scale.

[00109] The herein described subject matter sometimes illustrates different components contained within, or connected with, different other components. It is to be understood that such depicted architectures are illustrative, and that in fact many other architectures can be implemented which achieve the same functionality. In a conceptual sense, any arrangement of components to achieve the same functionality is effectively "associated" such that the desired functionality is achieved. Hence, any two components herein combined to achieve a particular functionality can be seen as "associated with" each other such that the desired functionality is achieved, irrespective of architectures or intermedial components. Likewise, any two components so associated can also be viewed as being "operably connected," or "operably coupled," to each other to achieve the desired functionality, and any two components capable of being so associated can also be viewed as being "operably coupleable," to each other to achieve the desired functionality. Specific examples of operably coupleable include but are not limited to physically mateable and/or physically interacting components and/or wirelessly interactable

and/or wirelessly interacting components and/or logically interacting and/or logically interactable components.

[00110] With respect to the use of plural and/or singular terms herein, those having skill in the art can translate from the plural to the singular and/or from the singular to the plural as is appropriate to the context and/or application. The various singular/plural permutations may be expressly set forth herein for sake of clarity.

[00111] It will be understood by those within the art that, in general, terms used herein, and especially in the appended claims (e.g., bodies of the appended claims) are generally intended as "open" terms (e.g., the term "including" should be interpreted as "including but not limited to," the term "having" should be interpreted as "having at least," the term "includes" should be interpreted as "includes but is not limited to," etc.).

[00112] Although the figures and description may illustrate a specific order of method steps, the order of such steps may differ from what is depicted and described, unless specified differently above. Also, two or more steps may be performed concurrently or with partial concurrence, unless specified differently above. Such variation may depend, for example, on the software and hardware systems chosen and on designer choice. All such variations are within the scope of the disclosure. Likewise, software implementations of the described methods could be accomplished with standard programming techniques with rule-based logic and other logic to accomplish the various connection steps, processing steps, comparison steps, and decision steps.

[00113] It will be further understood by those within the art that if a specific number of an introduced claim recitation is intended, such an intent will be explicitly recited in the claim, and in the absence of such recitation, no such intent is present. For example, as an aid to understanding, the following appended claims may contain usage of the introductory phrases "at least one" and "one or more" to introduce claim recitations. However, the use of such phrases should not be construed to imply that the introduction of a claim recitation by the indefinite articles "a" or "an" limits any particular claim containing such introduced claim recitation to inventions containing only one such recitation, even when the same claim includes the introductory phrases "one or more" or "at least one" and indefinite articles such as "a" or "an" (e.g., "a" and/or "an" should typically be interpreted to mean "at least one" or "one or more"); the same holds true for the use of definite articles used to introduce claim recitations. In addition,

even if a specific number of an introduced claim recitation is explicitly recited, those skilled in the art will recognize that such recitation should typically be interpreted to mean at least the recited number (e.g., the bare recitation of "two recitations," without other modifiers, typically means at least two recitations, or two or more recitations).

[00114] Furthermore, in those instances where a convention analogous to "at least one of A, B, and C, etc." is used, in general such a construction is intended in the sense one having skill in the art would understand the convention (e.g., "a system having at least one of A, B, and C" would include but not be limited to systems that have A alone, B alone, C alone, A and B together, A and C together, B and C together, and/or A, B, and C together, etc.). In those instances where a convention analogous to "at least one of A, B, or C, etc." is used, in general, such a construction is intended in the sense one having skill in the art would understand the convention (e.g., "a system having at least one of A, B, or C" would include but not be limited to systems that have A alone, B alone, C alone, A and B together, A and C together, B and C together, and/or A, B, and C together, etc.). It will be further understood by those within the art that virtually any disjunctive word and/or phrase presenting two or more alternative terms, whether in the description, claims, or drawings, should be understood to contemplate the possibilities of including one of the terms, either of the terms, or both terms. For example, the phrase "A or B" will be understood to include the possibilities of "A" or "B" or "A and B."

[00115] Further, unless otherwise noted, the use of the words "approximate," "about," "around," "substantially," etc., mean plus or minus ten percent.

[00116] Although the present embodiments have been particularly described with reference to preferred examples thereof, it should be readily apparent to those of ordinary skill in the art that changes and modifications in the form and details may be made without departing from the spirit and scope of the present disclosure. It is intended that the appended claims encompass such changes and modifications.

WHAT IS CLAIMED IS:

1. A fully-thermoset composite (FTC) membrane comprising a dense cross-linked thermoset coating film formed over a porous cross-linked thermoset support membrane.
2. The FTC membrane of claim 1, wherein the porous thermoset support membrane comprises a thermosetting polymer selected from the group of: allyl resins (Allyl), melamine formaldehyde (MF), phenol-formaldehyde (PF), silicone (SI), and an epoxy.
3. The FTC membrane of claim 1, wherein the porous thermoset support membrane comprises an inherently cross-linkable thermoplastic polymer selected from the group of: polyimide (PI), polyamideimide (PAI), polyetherimide (PEI), polyurethane (PU), polyester (PET) and their associated derivatives.
4. The FTC membrane of claim 1, wherein the porous thermoset porous support membrane comprises a thermoplastic polymer selected from the group of: acrylonitrile-butadiene-styrene (ABS), cellulose, regenerated cellulose, cellulose acetate, cellulose di-acetate, cellulose tri-acetate, ethylene vinyl alcohol, fluoroplastics such as PTFE, FEP, PFA, CTFE, ECTFE, ETFE and PVDF, polyacetals, polyacrylates, polyacrylonitrile (PAN) polyamides (PA) (e.g., NylonTM, KevlarTM, NomexTM and AramidTM materials), polyaryletherketone (PAEK), polybutadiene (PBD), polybutylene (PB), polycarbonate (PC), polydicyclopentadiene (PDCP), polyektone (PK), polyetheretherketone (PEEK), polyetherimide (PEI), polyethersulfone (PES), polyethylene (PE), polyethylenechlorinates (PEC), polymethylpentene (PMP), polyphenylene oxide (PPO), polyphenylene sulfide (PPS), polyethersulfone (PES), polyphenylsulfone (PPU), polyphthalamide (PTA), polypropylene (PP), polystyrene (PS), polysulfone (PSU), polyvinylchloride (PVC), chlorinated PVC (CPVC), and polyvinylidene chloride (PVDC).
5. The FTC membrane of claim 4, wherein the thermoplastic polymer has been chemically modified such that the backbone of the polymer becomes derivatized to comprise pendant functional groups that will readily react with a separate di-, tri-, tetra- or otherwise multi-

functional molecules that crosslink neighboring polymer backbones to each other, thereby creating a thermoset matrix.

6. The FTC membrane of claim 5, wherein the thermoplastic polymer is chloromethylated or bromomethylated.

7. The FTC membrane of claims 5 or 6, wherein the thermoplastic polymer or derivatized version thereof is further derivatized to comprise pendant sulfonic acid, carboxylic acid, amine, amic acid, imine, alcohol, aldehyde, azide or other reactive groups.

8. The FTC membrane of any one of claims 1-7, wherein the porous support membrane is crosslinked with a multifunctional crosslinking molecule with pendant reactive functional groups selected from the group of: acids, amines, amic acids, imines, aldehydes, epoxides, azides, or any combination thereof.

9. The FTC membrane of any one of claims 1-8, further comprising covalent bonds embedded in the backbone of the porous thermoset support membrane.

10. The FTC membrane of any one of claims 1-9, wherein the porous support membrane is made via an ex situ crosslinking process.

11. The FTC membrane of any one of claims 1-9, wherein the porous thermoset support membrane is made via an in situ crosslinking process.

12. The FTC membrane of any one of claims 1-11, wherein the coating film is formed by dip coating, spray coating, spin coating, gravier coating or other solution-casting technique.

13. The FTC membrane of any one of claims 1-11, wherein the coating film is formed by interfacial polymerization.

14. The FTC membrane of any one of claims 1-11, wherein the coating film is formed by interfacial polymerization of a polyfunctional amine monomer and a polyfunctional acyl halide monomer.
15. The FTC membrane of any one of claim 14, wherein the polyfunctional amine monomer used in the interfacial polymerization reaction to form the coating film is selected from the group of: triaminobenzene, polyetherimine, meta-phenylene diamine, para-phenylene diamine, 1,3,5-triaminobenzene, 3,5-diaminobenzoic acid, 2,4-diaminotoluene, 2,4-diaminoanisole, xylylene-diamine, ethylenediamine, propylenediamine, 1,4-diaminopropanol, resorcinol, phloroglucinol, quinone, piperazine, tris(2-diaminoethyl)amine as well as various imidazolidines, purines, pyridines and pyrimidines.
16. The FTC membrane of any one of claim 14, the polyfunctional acyl halide monomer used in the interfacial polymerization reaction to form the coating film is selected from the group of: a di-, tri-, and tetra-functional acid chloride comprising trimesoyl chloride (TMC), isophthaloyl chloride or tetraacid chloride.
17. The FTC membrane of any one of claims 1-16, wherein porous support membrane comprises an inherently crosslinkable polymer and hexanediamine (HDA) is the cross-linking molecule used to form the porous support membrane.
18. The FTC membrane of any one of claims 1-16, wherein the porous support membrane comprises an inherently crosslinkable polymer and γ -aminopropyltrimethoxysilane (APTS) is the cross-linking molecule used to form the porous support membrane.
19. The FTC membrane of claims 1-18, for use as an ultra-high pressure reverse osmosis (RO) membrane for the filtration of brine concentration, optionally, wherein the filtration of brine concentration comprises the filtration seawater RO brine concentration, oil and gas produced water brine concentration, continental brine concentration, geothermal brine

concentration or for the concentration of any other naturally or industrially occurring brine having an initial total dissolved solids concentration in excess of about 50 g/L.

20. The FTC membrane of claims 1-18 for use as a high pressure reverse osmosis (RO) membrane for the filtration of seawater desalination or for desalination of any other water source having an initial total dissolved solids concentration in the range of about 25 to 45 g/L or more preferably about 30 to 40 g/L.

21. The FTC membrane of claims 1-18 for use as a low pressure reverse osmosis (RO) membrane for the filtration of brackish water desalination, optionally, wherein the brackish water desalination comprises brackish groundwater, or for desalination of any other water source having an initial total dissolved solids concentration in the range of about 1 to 20 g/L and more preferably about 1 to 3 g/L.

22. The FTC membrane of claims 1-18 for use as an ultra-low pressure reverse osmosis (RO) membrane for the filtration of advanced water treatment of municipal or industrial wastewater or for advanced water treatment of any other water source having an initial total dissolved solids concentration in the range of about 0.5 to 2 g/L, or more preferably about 0.8 to 1.5 g/L.

23. The FTC membrane of claims 1-18 for use as a nanofiltration (RO) membrane in the application of water softening, wherein the membrane offers very high rejection of either divalent cations or anions, greater than 90% and more typically greater than 95%, including but not limited to calcium, magnesium or sulfate ions which may exist in brine, seawater, brackish groundwater, municipal or industrial wastewater or any other waters having a divalent cation content higher than is desired to utilize the softened water for another purpose.

24. A method of obtaining a fully thermoset composite reverse osmosis (FTCRO) membrane, comprising:

a. providing a porous support membrane;

- b. cross-linking the porous support membrane to form a porous thermoset support membrane; and
- c. coating a dense thermoset coating film on top of the porous thermoset support membrane.

25. The method of claim 24, wherein the porous thermoset support membrane comprises a thermoset polymer, including but not limited to allyl resins (Allyl), melamine formaldehyde (MF), phenol-formaldehyde (PF), silicone (SI) or epoxy.

26. The method of claim 24, wherein the porous thermoset support membrane comprises an inherently cross-linkable thermoplastic polymer, including but not limited to polyimide (PI), polyamideimide (PAI), polyetherimide (PEI), polyurethane (PU), or polyester (PET) and their associated derivatives.

27. The method of claim 24, wherein the porous thermoset porous support membrane comprises a thermoplastic polymer including but not limited to acrylonitrile-butadiene-styrene (ABS), cellulose, regenerated cellulose, cellulose acetate, cellulose di-acetate, cellulose tri-acetate, ethylene vinyl alcohol, fluoroplastics such as PTFE, FEP, PFA, CTFE, ECTFE, ETFE and PVDF, polyacetals, polyacrylates, polyacrylonitrile (PAN) polyamides (PA) (e.g., NylonTM, KevlarTM, NomexTM and AramidTM materials), polyaryletherketone (PAEK), polybutadiene (PBD), polybutylene (PB), polycarbonate (PC), polydicyclopentadiene (PDCP), polyektone (PK), polyetheretherketone (PEEK), polyetherimide (PEI), polyethersulfone (PES), polyethylene (PE), polyethylenechlorinates (PEC), polymethylpentene (PMP), polyphenylene oxide (PPO), polyphenylene sulfide (PPS), polyethersulfone (PES), polyphenylsulfone (PPU), polyphthalamide (PTA), polypropylene (PP), polystyrene (PS), polysulfone (PSU), polyvinylchloride (PVC), chlorinated PVC (CPVC), or polyvinylidene chloride (PVDC).

28. The method of claim 27, wherein the thermoplastic polymer has been chemically modified by any route – either before or after forming into a porous membrane – such that the backbone of the polymer becomes derivatized to varying extents to include pendant functional groups that will readily react with a separate di-, tri-, tetra- or otherwise multi-functional

molecules that crosslink neighboring polymer backbones to each other, thereby creating a thermoset matrix.

29. The method of claim 28, wherein the thermoplastic polymer is chloromethylated or bromomethylated, which allows the thermoplastic polymer to be further derivatized.

30. The method of claims 27 or 28, wherein the thermoplastic polymer or derivatized version is further derivatized to comprise pendant sulfonic acid, carboxylic acid, amine, amic acid, imine, alcohol, aldehyde, azide or other reactive groups.

31. The method of any one of claims 24 to 30, wherein the cross-linked porous support membrane is crosslinked with a multifunctional crosslinking molecule with pendant reactive functional groups including, but not limited to alcohols, acids, amines, amic acids, imines, aldehydes, epoxides, azides or any combination thereof.

32. The method of any one of claims 24 to 30, further comprising covalent bonds embedded in the backbone of the porous thermoset support membrane.

33. The method of any one of claims 24 to 32, wherein the porous thermoset support membrane is made via an ex situ crosslinking process.

34. The method of any one of claims 24 to 33, wherein the porous thermoset support membrane is made via an in situ crosslinking process.

35. The method of any one of claims 24 to 34, wherein the coating film is formed by dip coating, spray coating, spin coating, gravier coating or other solution-casting technique.

36. The method of any one of claims 24 to 34, wherein the coating film is formed by interfacial polymerization.

37. The method of any one of claims 24 to 34, wherein the coating film is formed by interfacial polymerization of a polyfunctional amine monomer and a polyfunctional acyl halide monomer.

38. The method of any one of claim 37, wherein the polyfunctional amine monomer used in the interfacial polymerization reaction to form the coating film includes, but is not limited to diaminobenzene, triaminobenzene, polyetherimine, meta-phenylene diamine, para-phenylene diamine, 1,3,5-triaminobenzene, 3,5-diaminobenzoic acid, 2,4-diaminotoluene, 2,4-diaminoanisole, xylylene-diamine, ethylenediamine, propylenediamine, 1,4-diaminopropanol, resorcinol, phloroglucinol, quinone, piperazine, tris(2-diaminoethyl)amine as well as various imidazolines, purines, pyridines and pyrimidines.

39. The method of any one of claim 37, the polyfunctional acyl halide monomer used in the interfacial polymerization reaction to form the coating film is selected from the group consisting of di-, tri-, and tetra-functional acid chlorides including but not limited to trimesoyl chloride (TMC), isophthaloyl chloride or tetraacid chloride.

40. The method of any one of claims 24 to 39, wherein polyimide is the inherently crosslinkable polymer and hexanediamine (HDA) is the cross-linking molecule used to form the porous thermoset support membrane.

41. The method of any one of claims 24 to 39, wherein polyimide is the inherently crosslinkable polymer and γ -aminopropyltrimethoxysilane (APTS) is the cross-linking molecule used to form the porous thermoset support membrane.

42. The method of any one of claims 24 to 41, wherein the cross-linked porous support membrane comprises a polyimide, a polyetherimide, a sulfonated, carboxylated, aminated or iminated polysulfone, polyethersulfone or polyphenylsulfone thermoplastic.

43. The method of any one of claims 24 to 42, wherein providing the porous support membrane comprises dissolving a cross-linkable polymer of a desired weight percentage in a solvent.
44. The method of claims 24 to 43, wherein the desired weight percentage is about 5% to 50%, about 10 % to 30%, about 16% to 22%, or about 14% to 20%, or about 16% to 18%.
45. The method of any of claims 24 to 44, wherein cross-linking the porous support membrane comprises an ex-situ cross-linking.
46. The method of any of claims 24 to 45, wherein cross-linking the porous support membrane comprises an in-situ cross-linking.