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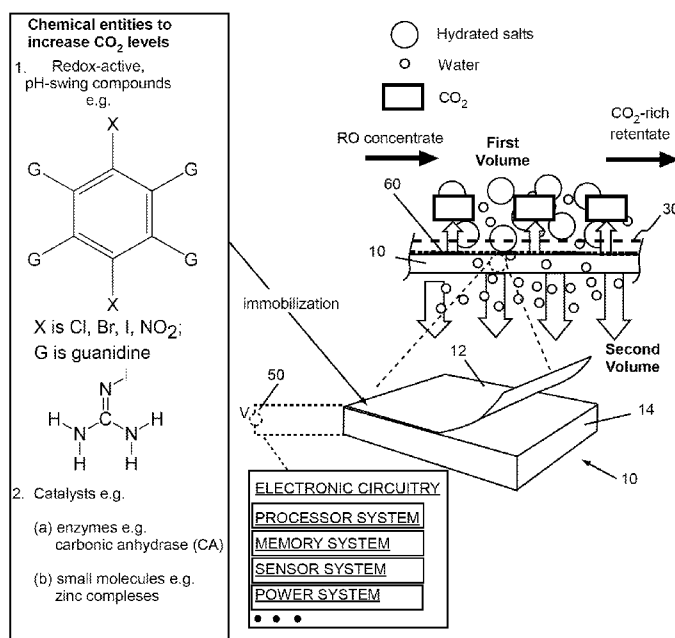


FIG. 1

(57) **Abstract:** A separation system for removing carbon dioxide from a liquid (or solution) includes a separation unit including a membrane separating a first volume from a second volume within the separation unit. The membrane is configured to allow water from the liquid flowing through the first volume to pass through the membrane to the second volume and to prevent at least a portion of one or more salt solutes in the liquid from passing through the membrane. Chemical entities are immobilized upon at least one of the membrane or upon a support, spaced from the membrane and positioned within the separation unit. The chemical entities are selected to increase the concentration of carbon dioxide in the liquid in the vicinity of chemical entities.





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SEPARATION DEVICES, SYSTEMS AND METHODS FOR REMOVAL OF CARBON DIOXIDE IN DESALINATION PROCESSES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims benefit of U.S. Provisional Patent Application Serial No. 63/452,882, filed March 17, 2023, the disclosure of which is incorporated herein by reference.

BACKGROUND

[0002] The following information is provided to assist the reader in understanding technologies disclosed below and the environment in which such technologies may typically be used. The terms used herein are not intended to be limited to any particular narrow interpretation unless clearly stated otherwise in this document. References set forth herein may facilitate understanding of the technologies or the background thereof. The disclosure of all references cited herein are incorporated by reference.

[0003] Direct ocean capture (DOC) methodologies provide a promising option for carbon removal to mitigate legacy carbon dioxide emissions exacerbating anthropogenic climate change. Such methodologies further provide a methodology for reversal of ocean acidification caused by anthropogenic CO₂ emissions.

[0004] A number of studies have been reported on electrochemical marine carbon dioxide removal (mCDR) in which electrochemical cells were used to separate seawater into basic and acidic streams to make more gaseous CO₂ available in the acidic stream before capturing the CO₂. Although such methods are effective at removing CO₂, they are impractical for large-scale direct ocean capture because the electrochemical processes are prohibitively expensive and energy-intensive. In that regard, such methodologies involve processing all of the seawater through an electrochemical cell.

[0005] The enzyme carbonic anhydrase, a natural and fast biocatalyst, has been used in a number of systems to promote carbon dioxide removal and capture. However, progress in the implementation and economics of carbon removal and capture from aqueous liquids remains limited.

[0006] It is thus desirable to develop improved technologies to achieve removal of CO₂ from seawater and other waters including dissolved CO₂.

SUMMARY

[0007] In one aspect, a separation system for removing carbon dioxide from a liquid (or solution) includes a separation unit including a membrane separating a first volume from a second volume within the separation unit. The membrane is configured to allow water from the liquid flowing through the first volume to pass through the membrane to the second volume and to prevent at least a portion of one or more salt solutes in the liquid from passing through the membrane. Chemical entities are immobilized upon (including on a surface thereof and, in a number of embodiments, within the body or matrix thereof) at least one of the membrane or upon a support, separated or spaced from the membrane surface and positioned within the separation unit. The chemical entities are selected to increase the concentration of carbon dioxide in the liquid in the vicinity of chemical entities. In a number of embodiments, the chemical entities are immobilized upon at least a surface of the membrane. The membrane may, for example, be a reverse osmosis membrane or a nanofiltration membrane. In a number of embodiments, the membrane includes, consists essentially of, or consists of one or more polymeric materials. In a number of embodiments, the chemical entities are chemically bonded (for example, covalently bonded) to the membrane.

[0008] The chemical entities may, for example, include at least one of catalyst compounds which catalyze conversion of bicarbonate ion into dissolved carbon dioxide or organic active redox compounds, wherein a pK_a of the organic active redox compounds is variable upon application of electrical energy thereto. The catalyst compounds may, for example, include carbonic anhydrase compounds or small-molecule compounds that mimic a carbonic anhydrase compound. In embodiments in which the chemical entities include organic redox active compounds, wherein a pK_a of the organic active redox compounds is variable upon application of electrical energy thereto, the separation system may further include a power source in electrical connection with the organic redox active compounds to provide electrical energy to the organic redox active compounds. The separation system may further include a control

system in operative connection with the power source to cycle electrical energy provided to the organic redox active compounds to cycle pH.

[0009] Organic active redox compounds may, for example, be selected from the group consisting of guanidine-functionalized aromatic compounds, phenazine compounds (for example, 2,3-dihydroxyphenazine) and active redox derivatives of such compounds. In embodiments wherein the chemical entities include small-molecule catalyst compounds that mimic a carbonic anhydrase, the small-molecule catalyst compounds may, for example, be zinc-containing compounds.

[0010] In a number of embodiments, the liquid is seawater or brackish water. In a number of embodiments, the liquids have sufficient alkalinity to dissolve significant CO₂ and form bicarbonate. The liquid may, for example, be a concentrate brine formed from treated seawater. The concentrate brine may, for example, be a concentrate effluent from another separation unit (for example, a reverse osmosis separation unit).

[0011] The separation system may further include at least one degasser unit in operative connection with the separation unit to remove carbon dioxide from at least one of a retentate which exits the second volume or a permeate which exits the second volume. The at least one degasser unit may, for example, be in operative connection with the separation unit to remove carbon dioxide from the retentate which exits the second volume.

[0012] In another aspect, a method of separating carbon dioxide from a liquid (or solution) including one or more salt solutes includes flowing the liquid through a first volume of a separation unit of a separation system. The separation unit includes a membrane separating the first volume from a second volume within the separation unit. The membrane is configured to allow water to pass through the membrane to the second volume and to prevent at least a portion of the salt solute from passing through the membrane, wherein chemical entities are immobilized upon at least one of the membrane or upon a support, separated or spaced from the membrane and positioned within the separation unit, the chemical entities being selected to increase the concentration of carbon dioxide in the liquid in the vicinity of the chemical entities. The separation system and liquid may, for example, be further characterized as described above and elsewhere herein.

[0013] In that regard, as described above, the chemical entities may be immobilized upon at least a surface of the membrane. The membrane may, for example, be a reverse osmosis membrane or a nanofiltration membrane. In a number of embodiments, the membrane includes, consists essentially of, or consists of one or more polymeric materials. In a number of embodiments, the chemical entities are chemically bonded (for example, covalently bonded) to the membrane.

[0014] The chemical entities may, for example, include at least one of catalyst compounds which catalyze conversion of bicarbonate ion into dissolved carbon dioxide or organic active redox compounds, wherein a pK_a of the organic active redox compounds is variable upon application of electrical energy thereto. The catalyst compounds may, for example, include carbonic anhydrase compounds or small-molecule compounds that mimic a carbonic anhydrase compound. In embodiments in which the chemical entities include organic redox active compounds, wherein a pK_a of the organic active redox compounds is variable upon application of electrical energy thereto, the separation system may further include a power source in electrical connection with the organic redox active compounds to provide electrical energy to the organic redox active compounds. The separation system may further include a control system in operative connection with the power source to cycle electrical energy provided to the organic redox active compounds to cycle pH.

[0015] Organic active redox compounds may, for example, be selected from the group consisting of guanidine-functionalized aromatic compounds, phenazine compounds (for example, 2,3-dihydroxyphenazine) and active redox derivatives of such compounds. In embodiments wherein the chemical entities include small-molecule catalyst compounds that mimic a carbonic anhydrase, the small-molecule catalyst compounds may, for example, be zinc-containing compounds.

[0016] In a number of embodiments, the liquid is seawater or brackish water. In a number of embodiments, the liquids have sufficient alkalinity to dissolve significant CO_2 and form bicarbonate. The liquid may, for example, be a concentrate brine formed from treated seawater. The concentrate brine may, for example, be a concentrate effluent from another separation unit (for example, a reverse osmosis separation unit).

[0017] The separation system may further include at least one degasser unit in operative connection with the separation unit to remove carbon dioxide from at least one of a retentate which exits the second volume or a permeate which exits the second volume. The at least one degasser unit may, for example, be in operative connection with the separation unit to remove carbon dioxide from the retentate which exits the second volume.

[0018] In another aspect, a membrane is configured to allow water from a liquid to pass through the membrane and to prevent at least a portion of a salt solute in the liquid (or solution) from passing through the membrane. The membrane includes chemical entities immobilized thereon. The chemical entities are selected to increase the concentration of carbon dioxide in the liquid in the vicinity of chemical entities. The membrane may be further characterized as described above and elsewhere herein.

[0019] In another aspect, a separation unit for removing carbon dioxide from a liquid includes a support positioned within a volume of the separation unit to contact the liquid, wherein chemical entities are immobilized upon the support. The chemical entities are selected to increase the concentration of carbon dioxide in the liquid in the vicinity of chemical entities. The chemical entities may be immobilized at least upon a surface of the support. As described above, the chemical entities may, for example, include at least one of catalyst compounds which catalyze conversion of bicarbonate ions into dissolved carbon dioxide or organic active redox compounds, wherein a pK_a of the organic active redox compounds is variable upon application of electrical energy thereto.

[0020] The chemical entities may, for example, include at least one of catalyst compounds which catalyze conversion of bicarbonate ion into dissolved carbon dioxide or organic active redox compounds, wherein a pK_a of the organic active redox compounds is variable upon application of electrical energy thereto. The catalyst compounds may, for example, include carbonic anhydrase compounds or small-molecule compounds that mimic a carbonic anhydrase compound.

[0021] Organic active redox compounds may, for example, be selected from the group consisting of guanidine-functionalized aromatic compounds, phenazine compounds (for example, 2,3-dihydroxyphenazine) and active redox derivatives of such compounds. In

embodiments wherein the chemical entities include small-molecule catalyst compounds that mimic a carbonic anhydrase, the small-molecule catalyst compounds may, for example, be zinc-containing compounds.

[0022] In a further aspect, a method for removing carbon dioxide from a liquid includes positioning a support within a volume of a separation unit to contact the liquid, wherein chemical entities are immobilized upon the support as described herein, the chemical entities being selected to increase the concentration of carbon dioxide in the liquid in the vicinity of chemical entities. In general, any support providing a surface for immobilization of the chemical entities may be used. The chemical entities may be immobilized upon at least a surface of the support. As described above the chemical entities may, for example, include at least one of catalyst compounds which catalyze conversion of bicarbonate ions into dissolved carbon dioxide or organic redox active compounds, wherein a pKa of the organic active redox compounds is variable upon application of electrical energy thereto.

[0023] In still a further aspect, a support includes chemical entities immobilized thereon. The chemical entities includes at least one of small-molecule catalyst compounds which catalyze conversion of bicarbonate ions into dissolved carbon dioxide or organic active redox compounds, wherein a pKa of the organic active redox compounds is variable upon application of electrical energy thereto. In a number of embodiments, the chemical entities include organic active redox compounds, wherein a pKa of the organic active redox compounds is variable upon application of electrical energy thereto. The support may, for example, include, consist essentially of, or consist of one or more polymeric materials. In a number of embodiments, the chemical entities are chemically bonded to the support. The chemical entities may, for example, be covalently bonded to the support.

[0024] The present devices, systems, methods, and compositions along with the attributes and attendant advantages thereof, will best be appreciated and understood in view of the following detailed description taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0025] **Fig. 1** illustrates schematically a section of an embodiment of a separation device or unit including a desalination membrane hereof which incorporates chemical entities functional to increase carbon dioxide (CO₂) concentration levels.

[0026] **FIG. 2** illustrates a proposed catalytic mechanism for zinc-containing carbonic-anhydrase-functional mimics.

[0027] **FIG. 3** illustrates schematically an embodiment of a commercially available separation device (for example, available from DuPont of Wilmington, Delaware) modified with chemical entities hereof functional to provide CO₂ enrichment functionality in a desalination membrane of the separation device, wherein a portion of the housing is cut away and a number of layers of a spiral membrane assembly of the device are cut away and unrolled.

[0028] **FIG. 4** illustrates a system in which salt-concentrated retentate is fed to a separation device hereof for further removal of water and CO₂ enrichment, and wherein CO₂-rich retentate from the separation device hereof is fed to a degasser for CO₂ removal and storage.

[0029] **FIG. 5** illustrates a representative embodiment of synthesis of a terpolymer-based membrane for functionalization with a chemical entity selected to achieve an increase in CO₂ gas concentration levels.

[0030] **Fig. 6** illustrates a representative embodiment of synthesis of polysulfone-based copolymers suitable for covalent attachment of chemical entities selected to achieve an increase in CO₂ gas concentration levels.

[0031] **FIG. 7** illustrates a representative embodiment of synthesis of further polysulfone-based materials which may be prepared to include covalent attachment sites for chemical entities hereof or other interacting functionalities.

[0032] **FIG. 8** illustrates a synthetic route for synthesis of DHPZ.

[0033] **FIG. 9A** illustrates a representative embodiment of a 1D flat sheet membrane model for use in studies hereof.

[0034] **FIG. 9B** illustrates a reaction mechanism for a catalyzed/promoted reaction of HCO_3^- , wherein k_f and k_b are forward and backward/reverse kinetic rate constants, respectively.

DETAILED DESCRIPTION

[0035] It will be readily understood that the components of the embodiments, as generally described and illustrated in the figures herein, may be arranged and designed in a wide variety of different configurations in addition to the described representative embodiments. Thus, the following more detailed description of the representative embodiments, as illustrated in the figures, is not intended to limit the scope of the embodiments, as claimed, but is merely illustrative of representative embodiments.

[0036] Reference throughout this specification to “one embodiment” or “an embodiment” (or the like) means that a particular feature, structure, or characteristic described in connection with the embodiment is included in at least one embodiment. Thus, the appearance of the phrases “in one embodiment” or “in an embodiment” or the like in various places throughout this specification are not necessarily all referring to the same embodiment.

[0037] Furthermore, described features, structures, or characteristics may be combined in any suitable manner in one or more embodiments. In the following description, numerous specific details are provided to give a thorough understanding of embodiments. One skilled in the relevant art will recognize, however, that the various embodiments can be practiced without one or more of the specific details, or with other methods, components, materials, et cetera. In other instances, well known structures, materials, or operations are not shown or described in detail to avoid obfuscation.

[0038] As used herein and in the appended claims, the singular forms “a,” “an,” and “the” include plural references unless the context clearly dictates otherwise. Thus, for example, reference to “a membrane” includes a plurality of such membranes and equivalents thereof known to those skilled in the art, and so forth, and reference to “the membrane” is a reference to one or more such membranes and equivalents thereof known to those skilled in the art, and so forth. Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range. Unless otherwise indicated herein, each separate value, as well as intermediate ranges, are incorporated

into the specification as if individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contraindicated by the text.

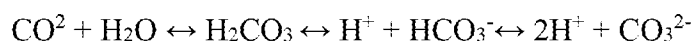
[0039] The terms “electronic circuitry”, “circuitry” or “circuit,” as used herein include, but are not limited to, hardware, firmware, software, or combinations of each to perform a function(s) or an action(s). For example, based on a desired feature or need, a circuit may include a software controlled microprocessor, discrete logic such as an application specific integrated circuit (ASIC), or other programmed logic device. A circuit may also be fully embodied as software. As used herein, “circuit” is considered synonymous with “logic.” The term “logic”, as used herein includes, but is not limited to, hardware, firmware, software, or combinations of each to perform a function(s) or an action(s), or to cause a function or action from another component. For example, based on a desired application or need, logic may include a software controlled microprocessor, discrete logic such as an application specific integrated circuit (ASIC), or other programmed logic device. Logic may also be fully embodied as software.

[0040] The term “processor,” as used herein includes, but is not limited to, one or more of virtually any number of processor systems or stand-alone processors, such as microprocessors, microcontrollers, central processing units (CPUs), and digital signal processors (DSPs), in any combination. The processor may be associated with various other circuits that support operation of the processor, such as random access memory (RAM), read-only memory (ROM), programmable read-only memory (PROM), erasable programmable read only memory (EPROM), clocks, decoders, memory controllers, or interrupt controllers, etc. These support circuits may be internal or external to the processor or its associated electronic packaging. The support circuits are in operative communication with the processor. The support circuits are not necessarily shown separate from the processor in block diagrams or other drawings.

[0041] The term “controller,” as used herein includes, but is not limited to, any circuit or device that coordinates and controls the operation of one or more input and/or output devices. A controller may, for example, include a device having one or more processors, microprocessors, or central processing units capable of being programmed to perform functions.

[0042] The term “software,” as used herein includes, but is not limited to, one or more computer readable or executable instructions that cause a computer or other electronic device to perform functions, actions, or behave in a desired manner. The instructions may be embodied in various forms such as routines, algorithms, modules, or programs including separate applications or code from dynamically linked libraries. Software may also be implemented in various forms such as a stand-alone program, a function call, a servlet, an applet, instructions stored in a memory, part of an operating system or other type of executable instructions. It will be appreciated by one of ordinary skill in the art that the form of software is dependent on, for example, requirements of a desired application, the environment it runs on, or the desires of a designer/programmer or the like.

[0043] In a number of embodiments of devices, systems, methods, and compositions hereof, immobilized chemical entities are used to increase the level of gaseous CO₂ in a liquid (for example, water such as seawater), to facilitate CO₂ removal from the liquid. Such liquids include dissolved CO₂, bicarbonate (HCO₃⁻), and carbonate (CO₃²⁻). In that regard, CO₂ dissolves in aqueous liquids in which it can react to form carbonic acid. Most of such acid typically dissociates to bicarbonate ions. Some further dissociates to carbonate ion according to the following equilibrium equation:



[0044] The chemical entities hereof increase the level of gaseous CO₂ in the vicinity of the immobilized chemical entities. In a number of embodiments, bicarbonate is catalytically converted to CO₂ using, for example, a catalyst such as a carbonic anhydrase (CA) or a CA mimic. In a number of embodiments, pH of water including dissolved CO₂ (for example, seawater) is locally lowered at, for example, a membrane surface to passively bubble off CO₂ gas using organic redox-active compounds. In representative embodiments discussed herein, the devices, systems, methods, and compositions hereof may, for example, leverage existing desalination infrastructure to minimize the costs of moving water and transporting species across a membrane. One skilled in the art appreciates, however, that the devices, systems, methods, and compositions hereof may be used in CO₂ removal from any aqueous liquid including dissolved CO₂.

[0045] **FIG. 1** illustrates schematically an embodiment of a section of a separation device hereof including a desalination membrane hereof which includes immobilized chemical entities. The chemical entities may, for example, be immobilized on a surface of the desalination membrane 10 (for example, on a first surface thereof), as well as on the surface of pores in membrane 10 as represented by active layer 12 in the lower portion of **FIG. 1**. The chemical entities may also be immobilized within the body or matrix of membrane 10 (as, for example, represented by microporous support 14 in **FIG. 1**). As described above, the chemical entities are functional to increase carbon dioxide (CO₂) levels. A first surface of membrane 10 is in contact with a first volume of the separation device. As known in the desalination membrane arts, membrane 10 is configured to allow water from a liquid solution flowing through the first volume to pass through membrane 10 to a second volume and to prevent at least a portion of one or more salt solutes in the solution from passing through membrane 10. In a number of embodiments, the chemical entities may, for example, be immobilized on a first surface or active surface 12 of the first side of membrane 10 and/or may be immobilized upon a support 30 (represented as a broken line in **FIG. 1**) separated from or spaced from membrane 10. Membrane 10 may, for example, be a reverse osmosis membrane or a nanofiltration membrane. Support 30 may, for example, be positioned adjacent to and at a suitable distance from the surface of the first side of membrane 10 to increase the concentration of CO₂ in the vicinity of the support and thereby in the vicinity of the surface of the first side of membrane 10.

[0046] As described above, the immobilized chemical entities may, for example, include a carbonic anhydrase, a carbonic anhydrase mimic (that is, small-molecule or low molecular weight catalyst compounds/complexes that mimic the catalytic activity of carbonic anhydrase), or redox active organic compounds. It has been shown that coating a hollow fiber membrane contactor with CA increased the rate of CO₂ absorption into carbonate solution by almost 200%. Without limitation to any mechanism, CA may, for example, enhance the rate of CO₂ removal on the seawater side of a membrane because it catalyzes both directions of the CO₂ absorption/desorption reaction ($CO_2 + OH^- \leftrightarrow HCO^-$). Using CA on the seawater side of a membrane allows one to go after HCO^- in addition to dissolved CO₂, which should dramatically improve CO₂ removal rate. In that regard, only approximately 0.5% of dissolved inorganic carbon in the ocean is in the form of CO₂ while approximately 89% is in the form of HCO^- .

[0047] Currently available synthetic mimics for carbonic anhydrase (CA) have yet to approach the high catalytic activity of CA. However, such mimics can approach the activity of the enzyme on a per-weight basis as a result of their significantly lower molecular weight. As an example, one of the most active CA functional mimics, Zn(cyclen)-, has only 5-fold lower activity by weight compared to CA. Additionally, small molecules can be used over a greater range of conditions and are more tolerant to heat than CA.

[0048] Improved small-molecule functional mimics of CA may be developed based upon mechanistic studies of CA-functional mimics. Such small-molecule catalyst compounds may, for example, be metal-containing compounds or complexes such as a zinc- or Zn-containing compounds. A proposed catalytic mechanism for CA-functional, Zn-containing mimics is illustrated in **FIG. 2**. Protonation/deprotonation and HCO_3^- binding/release have thus far been identified as the key steps for overall activity. The former is dependent on the pK_a of the bound H_2O and the latter on the lability and oxophilicity of the metal. Studies comparing CA activity on a Zn and Ni analogue indicates that Zn releases HCO_3^- much more easily, but deprotonation is limiting due to the higher pK_a of the ligated water. The optimal pK_a value for CA activity and other parameters governing HCO_3^- release are still not fully understood, which has impeded the development of more active CA mimics. In one approach to overcome such obstacles, Zn complexes with modified tri- and tetra- dentate N donor ligands may be synthesized. Modifications may, for example, include varying electron-donating or -withdrawing functionalities, secondary coordination sphere hydrogen-bonding interactions, and steric encumbrance around the active site. These complexes may be used to establish the optimal pK_a for deprotonation and subsequent CO_2 insertion into the metal hydroxide, and whether these steps can be facilitated with intramolecular hydrogen bonds. Furthermore, steric strain can also be optimized to facilitate HCO_3^- release.

[0049] In the case of redox active organic compounds, the pK_a of the compounds is variable upon application of electrical energy thereto. A power source 50 may be placed in electrical connection with the redox active organic compounds to provide electrical energy to the redox active organic compounds to control the pK_a thereof and cause pH swings in the vicinity of the redox active organic compounds. Redox active organic compounds may, for example, include one or more nitrogen (N) or sulfur (S) atom bound to a carbon π -system. Such carbon π -systems include aromatic compounds which include unsaturated cyclic hydrocarbons containing one or

more rings. Such rings may contain one or more heteroatoms (for example, N, or S) as known in the chemical arts. Representative examples of redox active organic compounds for use herein include redox-active guanidine-functionalized aromatics (GFAs; see, for example, a representative formula in **FIG. 1**), which include one or more guanidine groups bound to an aromatic ring structure (the guanidine groups may be unsubstituted, substituted and/or cyclic), and redox active phenazine compounds (that is, phenazine or an active redox derivative of phenazine such as DHPZ, 2,3-dihydroxyphenazine or phenazine-2,3-diol). Such redox active organic compounds (alternatively referred to as pH-swing compounds or pH mediators herein) can be used to convert $\text{HCO}_3^-/\text{CO}_3^{2-}$ to CO_2 through an electrochemically-driven pH-swings. In that regard, such compounds have reversible electrochemistry and significant changes in pK_a in different oxidation states. A control system may be placed in operative connection with the power source to cycle electrical energy provided to the redox active organic compounds to cycle pH. In their reduced form, the redox active organic compounds are Brønsted basic, increasing the pH of the solution. Upon oxidation, they become less basic than water, lowering the pH and favoring CO_2 dissolution. Thermodynamic modeling of systems using or including such compounds suggests that energetic efficiencies exceeding 35% can be achieved if a suitable compound is used. Because of potentially large, induced pH swings, the redox active organic compounds hereof should be stable under both acidic and alkaline conditions for extended periods of time. Furthermore, such compounds preferably exhibit mild reduction potentials to be stable in the presence of dissolved oxygen. Redox active organic compounds suitable for use herein are, for example, described in Himmel, H., Guanidines as Reagents in Proton-Coupled Electron Transfer Reactions and Redox Catalysts, *Synlett* (2018) 29, 1957-1977; Huang, C. et al., CO_2 Capture from Flue Gas Using Electrochemically Reversible Hydroquinone/Quinone Solution, *Energy Fuels* (2019), 33, 3380-3389; Xie, H. et al., Low-Energy Electrochemical Carbon Dioxide Capture Based on a Biological Redox Proton Carrier, *Cell Reports Physical Science* (May 20, 2020) 1, 100046; Jin, S., pH Swing Cycle for CO_2 Capture electrochemically driven through Proton-Coupled Electron Transfer, *Energy Environ. Sci.*, (2020) 13, 3706; Custelcean, R., et al., Direct Air Capture of CO_2 with Aqueous Peptides and Crystalline Guanidines, *Cell Reports Physical Science* (April 21, 2021), 2, 100385; and Hollas, A., et al., A Biometric High-Capacity Phenazine-Based Anolyte for Aqueous Organic Redox Flow Batteries, *Nature Energy*, (2018) 3, 508-514, the disclosures of which are incorporated herein by reference.

[0050] GFAs have a number of desirable properties for use as pH-mediators. In that regard, they have reversible redox properties at mild potentials which result in significant changes to their pK_a and are stable to O_2 and H_2O . The redox and pK_a properties are easily modified through synthetic modifications. A library of potential redox-active GFAs can be conveniently accessed in a one-pot synthesis through two steps. Covalent bonding to or absorption onto a membrane hereof of such compounds may be used to modify the local pH and adjust the equilibrium concentration of carbon dioxide and bicarbonate. Derivatives for absorption onto membranes may be readily tested and modified to, for example, generate stronger interactions (for example, charge-charge interactions, hydrogen-bonding interactions, pi-pi interactions, etc.).

[0051] Electrical energy may, for example, be transmitted to redox active organic compounds immobilized on the surface of membrane 10 hereof via a conductive mesh 60 (for example, a conductive carbon mesh; see **FIG. 1**) in electrical contact with the surface of membrane 10 and with power source 50. In a number of embodiments, electrical energy is transmitted via one or more current collectors as, for example, used in connection with fuel cells. See, for example, Braz, B., et al., Effect of the Current Collector Design on the Performance of a Passive Direct Methanol Fuel Cell, *Electrochimica Acta*, (2019), 200, 306-315 and Kuan, Y., et al., Development of a Current Collector with a Graphene Thin Film for a Proton Exchange Membrane Fuel Cell Module, *Molecules*, (2020), 25, 955, the disclosures of which are incorporated herein by reference. In a number of embodiments, the redox active organic compounds can be immobilized on mesh 60.

[0052] As illustrated in **FIG. 1**, power source 50 (and/or other system/device components) may be in electrical connection with or be a component of an electronic circuitry to provide control and/or analytics. Control of the potential applied to redox active organic compounds may be used to alter the oxidation state thereof as described herein. The electronic circuitry may, for example, include a processor system in communicative connection with a memory system. Software executable by the processor system may be stored on the memory system. A sensor system may be in communicative connection with the processor system to, for example, provide feedback control based on measured variables as known in the control arts. A power system may be provided to power the components of the electronic circuitry. The electronic circuitry may, for example, further include an input/output system, a user interface system, a communication system, etc. as known in the art and represented by an ellipsis in **FIG. 1**.

[0053] **FIG. 3** illustrates an embodiment of a commercially available separation device 100 including a semipermeable, reverse osmosis (RO) membrane for desalination such as a spiral wound FILMTEC™ RO composite membrane (available from DuPont) which has been modified to include chemical entities hereof. Such devices include a spiral wound membrane assembly 110 within a housing 104 having an end cap 108 (which is illustrated in a partially cut away state in **FIG. 3**). The edges of semipermeable membranes 120a and 120b in assembly 110 may for example, be sealed (for example, glued) together to form a permeate envelope/leaf encompassing a layer/spacer 130 of permeate carrier material. A plurality of such leaves may be present in device 100. There is a side glue line at the feed end and at the concentrate end of each leaf. A closing glue line is present at the outer diameter. An open side of a leaf is connected to and sealed against a perforated central part of the a product water tube 140, which collects the permeate from all leaves. The leaves are rolled and spaced by a feed spacer 150 therebetween. The feed spacers 150 provide a channel for the feed and concentrate flow. Feed solution enters the a face of device 100 and exits on the opposite end as concentrate. Chemical entities as described herein may be immobilized upon the RO membranes 120a and/or 120b. Under an applied pressure, higher than the solution osmotic pressure, only water can pass through the semi-permeable membrane, thereby removing other substances from water. In general, the pore size of a reverse osmosis membrane is quite small so that the membrane can effectively remove dissolved salts, colloids, microorganisms and organic matter from water.

[0054] In the embodiment illustrated in **FIG. 4**, a separation system 200 hereof includes first separation unit 210 (for example, a reverse osmosis (RO) desalination unit). The retentate/concentrate from first separation unit 210 (labeled RO concentrate in **FIG. 4**) is fed to a second separation unit 220 which may be an RO or a nanofiltration membrane (NF) device in which a membrane or membranes thereof is coated with chemical entities or groups as describe herein. An NF membrane may, for example, be used in pressure-driven liquid separation technologies such as desalination and shares a number of characteristics with an RO membrane. Unlike RO membranes, which have high rejection of virtually all dissolved solutes, however, NF membranes provide high rejection of multivalent ions, such as calcium, and low rejection of monovalent ions, such as chloride. Organic, thin-film composite NF membranes may, for example, have a pore size range of 0.1 to 10nm. NF membranes can operate at lower

pressures than RO membranes and offer selective solute rejection based on both size and charge.

[0055] In a number of embodiments as, for example, illustrated in **FIG. 4**, an NF separation unit is fed a high-salinity retentate from the first RO separation unit (first separation unit 210) to further concentrate salt and extract more water. In the case of a porous membrane such as an NP membrane, increased contact with immobilized chemical species can be achieved, making it easier and/or more efficient to convert bicarbonate to CO₂. The CO₂-rich retentate from second separation unit 220 may be sent to a degasser 230 to separate the CO₂ gas from the brine. The CO₂ gas can, for example, be compressed and stored or sequestered.

[0056] In a number of embodiments hereof, coatings including chemical entities hereof may be attached or immobilized on interfacially polymerized polyamide membranes. Such membranes are used for reverse osmosis applications. By incorporating the chemical entities hereof one may achieve both CO₂ removal and salt rejection (both monovalent and divalent) at the same time. The interfacial polymerization process may be leveraged for making water purification membranes. A number of such reactions schemes involve reaction between a di-functional amine and tri-functional acid chloride to form a crosslinked insoluble polyamide. Industrially, the polymerization is carried on a polymer porous support. The porous support containing the amine monomer (aqueous phase) is brought in contact with acid chloride monomer in a hydrocarbon phase. Amine monomer is believed to diffuse from water phase to organic phase and polyamide formation happens at the interface followed by precipitation of the polyamide thin film on the polysulfone support. An RO membrane may, for example, be functionalized with specific functional groups capable of reacting with the chemical coating. Further one may physically coat the chemical entity coating on commercial RO membranes.

[0057] In a representative scheme for functionalizing an RO membrane, a terpolymer chemistry route may be adopted where, in addition to the traditional amine (MPD) and acid chloride (TMC) monomers, a third monomer with varying functionality and structure is added in the polymerization process. As shown in **FIG. 5**, the X substituent in the third monomer may be chosen so that the resulting polyamide membrane will have functionality to chemically react with/attach to the chemical entities hereof.

[0058] One may also physically coat the chemical entities hereof on commercial RO membrane (for example, LE and XLE membranes available from DuPont) or covalently attached the chemical entities thereto if the membrane include (or are modifiable to include) suitable functionality for reaction with one or more groups of the chemical entities hereof . In a representative coating process, roll-to-roll coating may be used, which, for example, enables 12-inch wide roll-to-roll membrane production. Other coating techniques such as slot die and gravure coaters may be used.

[0059] As describe above, nanofiltration membranes have a unique property of rejecting divalent ions and allowing the passage of monovalent ions. This ensures high recovery at reasonable pressures, which can be even more critical for feed water with high salinity such as in embodiment hereof wherein an NF membrane is used to treat the RO concentrate brine. Using a NF membrane to treat the RO concentrate brine enables high membrane flux and helps to minimize fouling from sulfate scaling. Two representative approaches of using NF membranes for both CO₂ removal and further increased salt rejection from the RO concentrate brine are described below.

[0060] In one representative approach commercial NF membranes may be coated with chemical entity molecules hereof. One may, for example, select thin film composite, polyamide based commercial membranes, such as NF 270 and SR90 membranes (available from DuPont Water Solutions), based on their properties such as water permeability and salt rejection. For each membrane, the effect of chemical entity coating of the selected membrane on CO₂ removal may be studied while maintaining high water flux. Coating techniques as described above for RO membranes may be used.

[0061] In the second approach, NF membranes with a different chemistry and structure may be used. For example, polysulfone-based asymmetric NF membranes may be used. Disulfonated biphenol based polyarylene ether sulfones (BPS-X, where X is the degree of disulfonation) have been synthesized from condensation polymerization of biphenol, dichlorodiphenyl sulfone (DCDPS) and sulfonated dichlorodiphenyl sulfone (SDCDPS) (**FIG. 6**). By direct co-polymerization of a sulfonated monomer (SDCDPS), a precise control on degree of sulfonation can be achieved in contrast to the conventional post-sulfonation methods where sulfonation of a polysulfone with harsh reagents such as sulfuric acid can give

rise to unwanted side reactions and poor control on degree of sulfonation. One may synthesize BPS polymers with varying degree of disulfonation by changing the stoichiometry of the sulfonated (SDCDPS) and unsulfonated (DCDPS) monomers. See Paul, M., Park, H.B., Freeman, B.D., Roy, A., McGrath, J.E., Riffle, J.S. Synthesis and crosslinking of partially disulfonated poly(arylene ether sulfone) random copolymers as candidates for chlorine resistant reverse osmosis membranes, *Polymer*, Volume 49, Issue 9, 2243-2252 (2008). One may, for example, prepare asymmetric NF membranes from BPS polymers through phase inversion process where first a dense film of polymer will be cast from a homogeneous polymer solution by the automatic film applicator. The film may then be immersed in a bath of nonsolvent for coagulation and thus an asymmetric membrane will be prepared. The automated film applicator can, for example, provide a pathway to scale up by providing a means to study casting physics at a smaller scale. That knowledge can subsequently be leveraged for demonstrating the process in, for example, a roll-to-roll process.

[0062] The asymmetric sulfonated polysulfone based membranes may be coated with the chemical entities hereof for achieving CO₂ removal. Changes in the degree of sulfonation on membrane properties such as high permeability, good salt rejection may, for example, be used to maintain CO₂ removal. Furthermore, specific monomers with a functionality that can be attached to the coating, can be readily incorporated in the polymerization process.

[0063] Another, complementary series of polysulfone-based materials may be prepared that have covalent attachment sites for chemical entities hereof (for example, at least one of catalytically active or redox-active molecules). A synthetic scheme for representative examples of such polymers is illustrated in **FIG. 7**. Such polymers may be readily fabricated into membranes hereof which include a CA, a CA mimic, or organic redox-active molecules. The chemical bonding/attachment of proteins (such as the enzyme CA) to surfaces/functionalized polymers is known in the chemical arts.

[0064] A synthetic pathway related to that of **FIG. 7** has been developed for covalently modifying polysulfone-based copolymers. See, for example, Yang, Y., Ramos, T.L., Heo, J., Green, M.D., Zwitterionic poly(arylene ether sulfone) copolymer/poly(arylene ether sulfone) blends for fouling-resistant desalination membranes, *Journal of Membrane Science*, Volume 561, 69-78 (2018), and Yang, Y., Behbahani, H.S., Morgan, B.F., Beyer, F.L., Hocken, A., Green, M.D., Synthesis and

thermomechanical characteristics of zwitterionic poly(arylene ether sulfone) copolymers, *Polymer*, Volume 264, 125522 (2022). For example, a zwitterionic polymer with a tunable sulfobetaine concentration was prepared and then blended with a commercially available polysulfone (UDEL®). Adding up to 6 wt% of the zwitterionic functionality resulted in 25x increase in water permeation,. The membranes further exhibited resistance to fouling by bovine serum albumin, and the water perm- selectivity was stable in the presence of the hypochlorite ion (that is, a source of chlorine for water disinfection). The synthesis protocol has adapted to introduce a quaternary ammonium with an alkaline counterion, which enables the moisture-swing mediated CO₂ capture mechanism. Wang, T., Lackner, K.S., Wright, A.B., Moisture-swing sorption for carbon dioxide capture from ambient air: a thermodynamic analysis. *Physical Chemistry Chemical Physics*, 15, 504-514 (2013). Such studies highlight the adaptability of the synthesis protocol. For use in synthesis of polymers for forming the present membranes, the allyl groups are modified with the N,N-dimethylethanethiol (that is, in the first post-polymerization reaction in **FIG. 7**) followed by reactions with the redox-active molecules, with CA/modified CA, or with ligands for CA mimics. The concentration of the allyl group may be controlled by varying the ratio of BPA:DABA in the upper lefthand corner of **FIG. 7** through a simple step- growth co-polymerization. Concentrations of 5-35 mol% (DABA:BPA) may, for example, provide a sufficient concentration of the redox-active species.

[0065] As described above, the chemical entities may, for example, be physically immobilized or coated upon the membranes hereof. Representative examples of coating studies of DHPZ on a commercial desalination membranes are discussed in the Experimental section hereof. To improve stability of the DHPZ content of membranes in such studies, simultaneous casting of commercial Udel Polysulfone (P-1700) and DHPZ was carried out. Additionally, RO desalination membrane coupons have been successfully coated with guanidine-functionalized aromatic (GFA) groups that could be used to electrochemically lower the pH on the seawater-side of the membrane.

[0066] As described above, the chemical entities may be chemically bonded (for example, covalently bonded) to the membrane via, for example, reaction of a reactive group on the chemical entity with a reactive group on a polymer of the membrane. Covalent links of chemical entities hereof to membranes of mCDR will readily improve the system stability over time. Certain non-covalently or physically integrated groups may leach out over time.

However, selection of polymers with functionality that interact with such groups may improve stability. Moreover, trapping techniques may be used to improved stability of physically integrated groups. Comparison of chemical entities hereof on series of polymers (for example, synthesized via the synthetic techniques described herein, other synthetic techniques, or acquired commercially) may, for example, be used to determine how stability of the system performance depends on the functionality of the polymer and the functionality of the chemical entity integrated (either, via chemical bonding of physically) into the membrane.

[0067] In a number of embodiments hereof, the CO₂ is removed from the retentate. In other embodiments, the membrane may be configured to pass carbon dioxide therethrough (for example, under pressure) and the CO₂ may be removed from the permeate. The CO₂ may be present and removed from each of the retentate and the permeate.

[0068] An RO membrane will have a very high salt rejection (99.99+%). A very small amount of salt can thus transport through the membrane. Carbonate, because it is divalent, will have a more difficult time than bicarbonate passing through such membrane. A limited amount of carbonate, bicarbonate, and CO₂ (g) can pass through the membrane. In the case of a porous membrane, some salt may pass through the membrane. The salt rejection may, for example, be in the range of 60-70%. Likewise, some amount of carbonate, bicarbonate, and CO₂ (g) can pass through the membrane. The chemical entities hereof may, for example, be immobilized on either or both sides of the membrane (including within available pores and/or within the polymer matrix of the membrane or a support hereof) to facilitate CO₂ removal. In a number of embodiments hereof, the chemical entities are immobilized at least on the surface (including, for example, the surface of any pores available to the chemical entity during the immobilization process) of the membrane which contacts the retentate side of the membrane (that is, in contact with the first volume as set forth above).

[0069] Experimental

[0070] 1. Incorporation of DHPZ in membranes. (a) Adhering DHPZ to commercially available membranes via physical bonds. The structure of 2,3-dihydroxyphenazin or DHPZ and a synthetic route for DHPZ is illustrated in **FIG. 8**. A number of studies were conducted on addition of the direct ocean capture or DOC active species DHPZ via physical mixing of

solution containing DHPZ power in deionized (DI) water with commercial membranes using the apparatus in which the membrane was suspended (via a steel wire suspension) within a container. In that regard, DHPZ in DI solutions were prepared and commercial membranes were submerged and held floated inside the stirring solution (for example, stirred via a magnetic stirrer within the solution). Commercial membranes such as the FILMTEC™ BW30 membrane (a reverse osmosis membrane for brackish water available from DuPont of Wilmington, Delaware), which is made from polyamide skin, polysulfone substrate and polyethylene non-woven support and DeltaMem AG membrane (Allschwil, Switzerland) which includes a polyvinyl alcohol selective layer on a polyacrylonitrile support were chosen as examples of commercial membranes.

[0071] After physical mixing, membranes changed color from white to the color of DHPZ powder (dark red/dark brown). SEM images showed changes on surfaces (top and bottom of membrane) and cross section of commercial membranes on a micrometer scale after physical mixing, which was a result of the DHPZ compound addition. The weight of membranes after physical mixing and subsequent washing of membranes to remove excess DHPZ was determined. An increase in weight was observed as a result of addition of DHPZ, and a continuous trend of decreasing weight was observed after multiple washes. Non-uniform DHPZ addition was observed for the commercial membranes after physical mixing in all studies. The non-uniformity and continuous trend of weight decrease after subsequent washing may, for example, be a result of stacking of DHPZ compounds on top of each other, from high concentration DHPZ and DI solutions.

[0072] Therefore, dropwise addition of a solution of DHPZ in DI water was studied. After dropwise addition, sufficient time was given for water to evaporate. The process was performed to add a thin and uniform layer of DHPZ on commercial membranes. The weight increase in membranes after drop-wise addition demonstrated adherence of DHPZ on the membranes. However, like the previous process, weight loss was observed after subsequent washing.

[0073] (b) Trapping DHPZ inside membrane structures via co-casting. To attain membranes with DHPZ content of increased stability, simultaneous casting of commercial UDEL® polysulfone (P-1700) microporous membrane (available from Solvay Specialty Polymers USA, LLC of Wilmington, Delaware) and DHPZ was investigated. In a representative process,

a 2.5 wt.% solution of DHPZ in dimethylformamide (DMF) was prepared. The solution was homogenized with sufficient stirring with using a vortexer. The homogenous solution was then poured inside a flat-bottom Druoplan petri dish). The dish was closed with a non-hermetically sealed pan and equilibrated with air overnight, to remove any bubbles that may have formed during vortexing. The petri dish containing the solution was then placed inside a vacuum oven operating at room temperature for 24 h. The vacuum oven temperature was increased to 40 C for 24 h, and then to 70 C for 24 h to slowly remove the DMF, to let the polymer chains time to relax and obtain a dense membrane structure. After subsequent washing, the dense membrane showed no weight loss indicating that the DHPZ is locked inside the polysulfone polymer chains.

[0074] A second form of membrane casting was carried out to fabricate porous membranes. In the second form of casting, 15 wt% solutions of UDEL polysulfone was prepared inside N-Methyl-2-pyrrolidone (NMP), and DHPZ was added to the solution with varying concentrations. The dense membranes were cast using a doctor blade with controlled thickness and precipitated using a non-solvent bath. As known in the art, doctor-blade coating may be used to form films with well-defined thicknesses and operate by placing a sharp blade at fixed distance from the surface to be covered. The coating solution is placed in in connection with the blade, and the blade is moved across in-line with the surface, thereby creating a wet film. Similar to what was observed for the dense membranes, the porous membranes cast with DHPZ showed no weight loss after subsequent washing with water, indicating the DHPZ is locked inside the polymer structure.

[0075] 2. Membrane testing/characterization. Membranes hereof may be tested and the data input into one or more models as described further below. Characteristic variables or parameters to be determined may, for example, include the water perm-selectivity and CO₂ removal performance of membranes prepared for mCDR in, for example, RO and/or NF stages of seawater treatment. Permeation data may, for example, be used to characterize the effects of polymer composition, membrane coating thickness, and transmembrane pressure drop on water permeation. Membrane microstructure may be characterized via photomicrographs.

[0076] In a number of representative studies, for example, a series of polymers (for example, prepared as described above) are fabricated into asymmetric membranes for RO purification of

synthetic seawater as well as NF membranes for treatment of high salinity RO retentate. The membranes may be tested using custom-built cross-flow permeation cells. Various permeation test equipment, including, for example (i) a dead-end permeation cell for pure water permeation experiments; (i) a positive pressure RO cross-flow cell for high salinity, seawater, brackish water, or pure water permeation and salt rejection studies; (iii) a negative pressure pervaporation cell for high salinity, seawater, brackish water, or pure water permeation and salt rejection studies; and (iv) a diffusion cell for measuring the diffusion coefficient of solutes within membranes may be used in characterizing membranes hereof. The water permeation and salt rejection performance of the RO and NF membranes hereof may be analyzed for pilot-scale deployment (for example, with a constraint of avoiding any reduction in water permselectivity). Additionally, the membrane cross-sectional microstructure may be analyzed with, for example, scanning electron microscopy or SEM, and the mechanical properties may be tested with a submersion tensile tester.

[0077] 3. Integrated membrane-based water treatment and mCDR. After testing the water permeation and salt rejection performance as describe above, integrated membrane-based water treatment and mCDR may be studied based on an apparatus as, for example, illustrated schematically in **FIG. 1**. In that regard, **FIG. 1** illustrates a simple schematic of a membrane hereof with a saline feed (either synthetic seawater or a high salinity feed to simulate RO retentate) and a pure water draw solution. The membrane could be a thin-film composite (TFC) membrane as shown for an RO stage, or an NF membrane (resembling the porous support in the TFC) that is coated or covalently-functionalized with at least one of CA, CA mimics, and organic active redox compounds.

[0078] In the case organic active redox compounds, electrodes along the base of the membrane support may be used to deliver an alternating potential to activate the redox-active species that will produce the localized reduction in pH. The evolved $\text{CO}_2(\text{g})$ will enter both the retentate and permeate streams and an HPLC degasser may be used to remove and concentrate the CO_2 . The concentration is determined using either an infrared gas analyzer (0-20%) or a gas chromatography instrument (0-100%).

[0079] The membranes may, for example, be evaluated to analyze the effects of coating versus covalent attachment of organic active redox compounds and CA mimics, the concentration

range of the redox-active species, salt concentration in the feed, transmembrane pressure drop, alternating potential frequency and magnitude, and temperature on the water perm-selectivity and CO₂ evolution performance. The data may be used as a feedback loop for experimental membrane fabrication studies and may be fed into one or more models as described below. Membranes may be selected on the basis of performance as characterized above for preparation at high surface areas using, for example, roll-to-roll coating etc.

[0080] 4. Membrane level and system-level modeling. Modelling may be used to supplement other studies hereof to, for example, assist in determining how such results would scale up to a larger system. Device-scale membrane modeling may be performed to determine how a full-scale membrane device would operate. Subsequently, a system-level techno-economic assessment may be performed to estimate the size and cost of a system based on the studied technology.

[0081] A 1D flat sheet model of the coated nanofiltration membrane has been adapted from existing 1D MATLAB® (mathematical computing software available from The MathWorks, Inc. of Natick, Massachusetts) models that were developed for similar carbon capture applications (see **FIG. 9A**). See Rivero, J.R., et al., Modeling Gas Separation in Flat Sheet Membrane Modules: Impact of Flow Channel Size, Carbon Capture Science & Technology, 6, 10093- (2023). One may, for example, adjust the properties of the membrane and two fluids to match the appropriate properties for the present application, and account for the CA, CA mimic, and organic active redox compound functionalized membrane surface chemistry by adding the catalyzed/promoted reaction illustrated in **FIG. 9B** using literature values for the kinetic rate constants k_f and k_b if they cannot readily be obtained experimentally. Changes made to the model to adapt it to the present technology include, for example, 1) modeling seawater instead of a gas mixture on the feed side, and 2) modeling a reverse osmosis or nanofiltration membrane rather than a gas-selective membrane. Further, a channel height variation feature in published version of the model need not be included in the present modeling studied. In general, the model of **FIG. 9A** is single retentate channel in a 1D flat sheet membrane model. The gas feed enters at the left-hand-side of the graphic, and the retentate gas exits at the right. The membrane model is discretized into n nodes along the length of the retentate channel. The model may, for example, be used to generate performance results, such as CO₂ profiles along the

length of the membrane. The results of experimental studies and modeling may, for example, be input into a techno-economic assessment.

[0082] 5. Techno-economic assessment. A techno-economic assessment may be performed to determine cost and size estimates for a system based various technologies hereof as described above to further determined if such technologies are competitive with other direct ocean capture options. The results of studies hereof and modeling may be used to estimate overall performance metrics (for example, rate of CO₂ gas production) for functionalized RO and/or NF membranes hereof. For example, various capital and operating costs associated with running a hybrid RO/direct ocean capture system such as, for example, the one shown in **FIG. 3** may be determined. The determined costs may be compared to benchmark data for a stand-alone RO desalination plant and to other direct ocean capture designs, to determine the cost-competitiveness of a technology. The capital expenditure (CAPEX) and operating expenses (OPEX) for each technology case along with its experimentally determined CO₂ production rates may be compared to determine technologies that are suitable, best suitable, optimizable, etc. for scale-up.

[0083] The foregoing description and accompanying drawings set forth a number of representative embodiments at the present time. Various modifications, additions and alternative designs will, of course, become apparent to those skilled in the art in light of the foregoing teachings without departing from the scope hereof, which is indicated by the following claims rather than by the foregoing description. All changes and variations that fall within the meaning and range of equivalency of the claims are to be embraced within their scope.

WHAT IS CLAIMED IS:

1. A separation system for removing carbon dioxide from a liquid, comprising:

a separation unit comprising a membrane separating a first volume from a second volume within the separation unit, the membrane being configured to allow water from the liquid flowing through the first volume to pass through the membrane to the second volume and to prevent at least a portion of a salt solute in the liquid from passing through the membrane, wherein chemical entities are immobilized upon at least one of the membrane or upon a support, spaced from the membrane and positioned within the separation unit, the chemical entities being selected to increase the concentration of carbon dioxide in the liquid in the vicinity of chemical entities.
2. The separation system of claim 1 wherein the chemical entities are immobilized upon at least a surface of the membrane.
3. The separation system of claim 1 wherein the chemical entities comprise at least one of catalyst compounds which catalyze conversion of bicarbonate ion into dissolved carbon dioxide or organic active redox compounds, wherein a pKa of the organic active redox compounds is variable upon application of electrical energy thereto.
4. The separation system of claim 3 wherein the catalyst compounds comprise carbonic anhydrase compounds or small-molecule compounds that mimic a carbonic anhydrase compound.
5. The separation system of claim 1 wherein the membrane is a reverse osmosis membrane or a nanofiltration membrane.
6. The separation system of claim 1 wherein the chemical entities are chemically bonded to the membrane.
7. The separation system of claim 1 wherein the chemical entities comprise organic redox active compounds, wherein a pKa of the organic active redox compounds is variable upon application of electrical energy thereto, and the separation system further comprises a power source in electrical connection with the organic redox active compounds to provide electrical energy to the organic redox active compounds.

8. The separation system of claim 7 wherein the organic active redox compounds are selected from the group consisting of guanidine-functionalized aromatic compounds, phenazine, or redox active derivatives thereof, optionally wherein the redox active phenazine derivative is 2,3-dihydroxyphenazine.

9. The separation system of claim 7 further comprises a control system in operative connection with the power source to cycle electrical energy provided to the organic redox active compounds to cycle pH.

10. The separation system of claim 1 wherein the chemical entities comprise small-molecule catalyst compounds that mimic a carbonic anhydrase.

11. The separation system of claim 10 wherein the small-molecule catalyst compounds are zinc-containing compounds.

12. The separation system of any one of claims 1 through 11 wherein the liquid is seawater or brackish water.

13. The separation system of any one of claims 1 through 11 wherein the liquid is a concentrate brine formed from treated seawater.

14. The separation system of claim 13 wherein the concentrate brine is a concentrate effluent from another separation unit.

15. The separation system of claim 14 wherein the another separation unit is a reverse osmosis separation unit.

16. The separation system of claim 1 further comprising at least one degasser unit in operative connection with the separation unit to remove carbon dioxide from at least one of a retentate which exits the second volume or a permeate which exits the second volume.

17. The separation system of claim 16 wherein the at least one degasser unit is in operative connection with the separation unit to remove carbon dioxide from the retentate which exits the second volume.

18. A method of separating carbon dioxide from a liquid comprising a salt solute, comprising:

flowing the liquid through a first volume of a separation unit of a separation system, the separation unit comprising a membrane separating the first volume from a second volume within the separation unit, the membrane being configured to allow water to pass through the membrane to the second volume and to prevent at least a portion of the salt solute from passing through the membrane, wherein chemical entities are immobilized upon at least one of the membrane or upon a support, separate from the membrane and positioned within the separation unit, the chemical entities being selected to increase the concentration of carbon dioxide in the liquid in the vicinity of the chemical entities.

19. The method of claim 18 wherein the chemical entities are immobilized upon at least a surface of the membrane.

20. The method of claim 18 wherein the chemical entities comprise at least one of catalyst compounds which catalyze conversion of bicarbonate ion into dissolved carbon dioxide or organic active redox compounds, wherein a pKa of the organic active redox compounds is variable upon application of electrical energy thereto.

21. The separation system of claim 20 wherein the catalyst compounds comprise carbonic anhydrase compounds or small-molecule compounds that mimic a carbonic anhydrase compound.

22. The method of claim 18 wherein the membrane is a reverse osmosis membrane or a nanofiltration membrane.

23. The method of claim 18 wherein the chemical entities are chemically bonded to the membrane.

24. The method of claim 18 wherein the chemical entities comprise organic active redox compounds, wherein a pKa of the organic active redox compound is variable upon application of electrical energy thereto, and the separation system further comprises a power source in electrical connection with the organic active redox compounds, the method further

comprising providing electrical energy to the organic redox active compounds via the power source.

25. The method of claim 24 wherein the organic active redox compounds are selected from the group consisting of guanidine-functionalized aromatic compounds, phenazine, or redox active derivatives thereof, optionally wherein the redox active phenazine derivative is 2,3-dihydroxyphenazine.

26. The method of claim 24 further comprising controlling the power source to cycle electrical energy provided to the organic active redox compounds to increase and decrease the pH in the vicinity of a first side of the membrane.

27. The method of claim 18 wherein the chemical entities comprise small-molecule catalyst compounds that mimic carbonic anhydrase.

28. The method of claim 27 wherein the small-molecule catalyst compounds that mimic carbonic anhydrase are zinc-containing compound.

29. The method of any one of claims 18 through 28 wherein the liquid is seawater or brackish water.

30. The method of any one of claims 18 through 28 wherein the liquid is a concentrate brine formed from treated seawater.

31. The method of claim 30 wherein the concentrate brine is a concentrate effluent from another separation unit.

32. The method of claim 31 wherein the another separation unit is a reverse osmosis separation unit.

33. The method of any one of claims 18 through 28 further comprising removing carbon dioxide via at least one degasser unit in operative connection with the separation unit from at least one of (i) a retentate which exits the first volume or (ii) a permeate which exits the second volume.

34. The method of claim 33 wherein the at least one degasser unit is in operative connection with the retentate which exits the first volume.

35. A membrane configured to allow water from a liquid to pass through the membrane and to prevent at least a portion of a salt solute in the liquid from passing through the membrane, the membrane comprising chemical entities immobilized thereon, the chemical entities being selected to increase the concentration of carbon dioxide in the liquid in the vicinity of chemical entities.

36. The membrane of claim 35 wherein the chemical entities are immobilized upon at least a surface of the membrane.

37. The membrane of claim 35 wherein the chemical entities comprise at least one of catalyst compounds which catalyze conversion of bicarbonate ion into dissolved carbon dioxide or organic active redox compounds, wherein a pKa of the organic active redox compounds is variable upon application of electrical energy thereto.

38. The membrane of claim 37 wherein the catalyst compounds comprise carbonic anhydrase compounds or small-molecule compounds that mimic a carbonic anhydrase compound.

39. The membrane of claim 35 wherein the membrane is a reverse osmosis membrane or a nanofiltration membrane.

40. The membrane of claim 35 wherein the chemical entities are chemically bonded to the membrane.

41. The membrane of claim 35 wherein the chemical entities comprise organic active redox compounds, wherein a pKa of the organic active redox compounds is variable upon application of electrical energy thereto.

42. The membrane of claim 41 wherein the organic active redox compounds are selected from the group consisting of guanidine-functionalized aromatic compounds, phenazine, or redox active derivatives thereof, optionally wherein the redox active phenazine derivative is 2,3-dihydroxyphenazine.

43. The membrane of claim 35 wherein the chemical entities comprise small-molecule catalyst compounds that mimic a carbonic anhydrase.

44. The membrane of claim 43 wherein the small-molecule catalyst compounds are zinc-containing compounds.

45. A separation unit for removing carbon dioxide from a liquid, comprising:

a support positioned within a volume of the separation unit to contact the liquid, wherein chemical entities are immobilized upon the support, the chemical entities being selected to increase the concentration of carbon dioxide in the liquid in the vicinity of chemical entities.

46. The separation unit of claim 45 wherein the chemical entities are immobilized at least upon a surface of the support.

47. The separation unit of claim 45 wherein the chemical entities comprise at least one of catalyst compounds which catalyze conversion of bicarbonate ions into dissolved carbon dioxide or organic active redox compounds, wherein a pKa of the organic active redox compounds is variable upon application of electrical energy thereto.

48. The separation unit of claim 47 wherein the catalyst compounds comprise carbonic anhydrase compounds or small-molecule compounds that mimic a carbonic anhydrase compound.

49. The separation unit of claim 45 wherein the chemical entities are chemically bonded to the support.

50. The separation unit of claim 45 wherein the chemical entities comprise organic redox active compounds, wherein a pKa of the organic redox active compounds is variable upon application of electrical energy thereto.

51. The separation unit of claim 50 wherein the organic active redox compounds are selected from the group consisting of guanidine-functionalized aromatic compounds, phenazine, or redox active derivatives thereof, optionally wherein the redox active phenazine derivative is 2,3-dihydroxyphenazine.

52. The separation unit of claim 45 wherein the chemical entities comprise small-molecule catalyst compounds that mimic a carbonic anhydrase.

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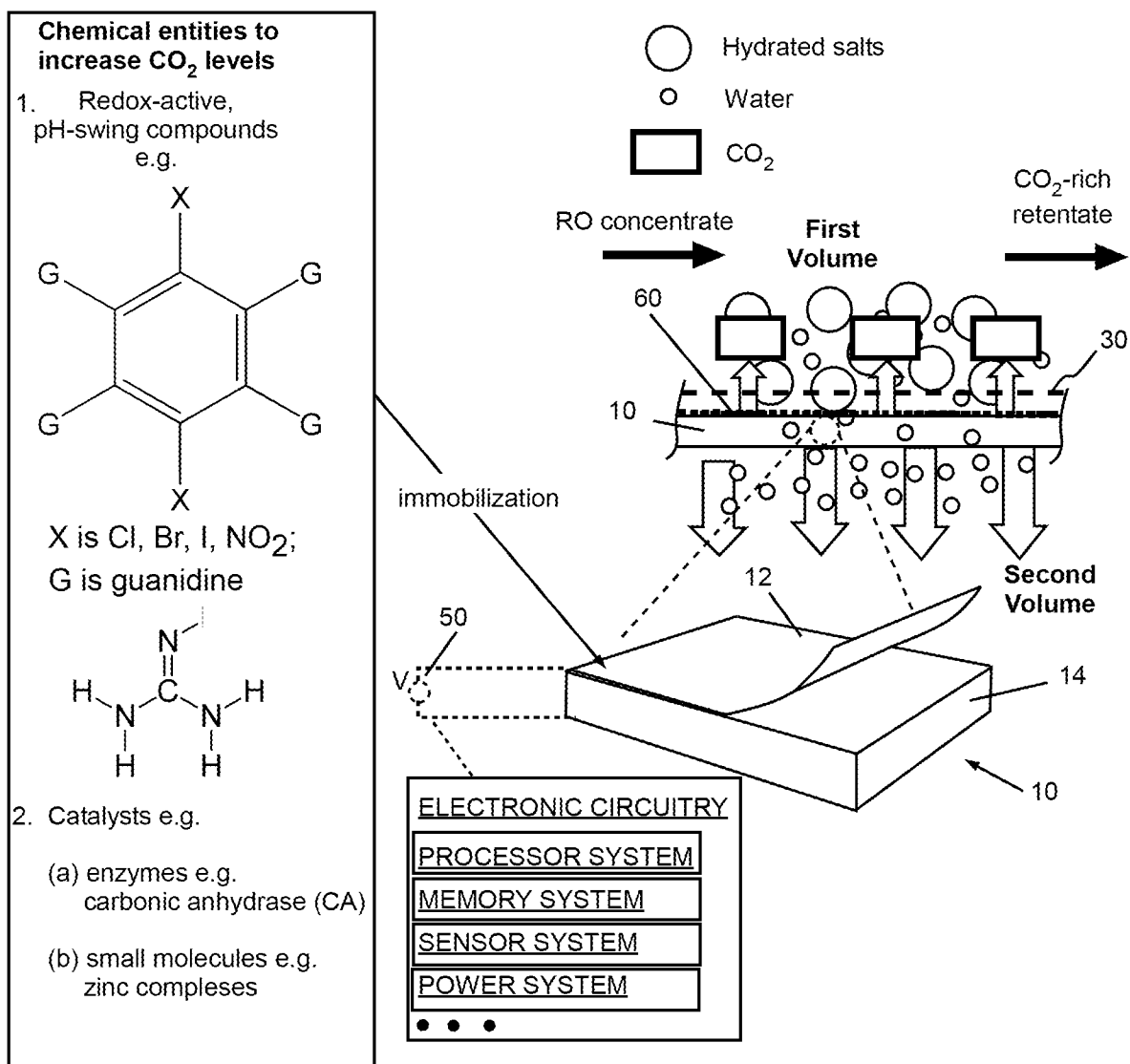


FIG. 1

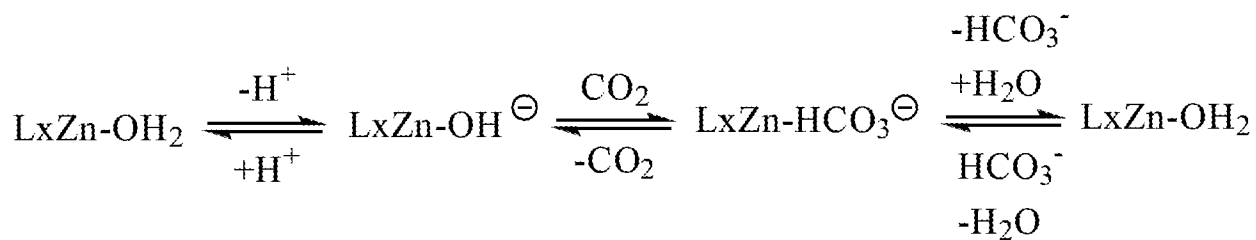
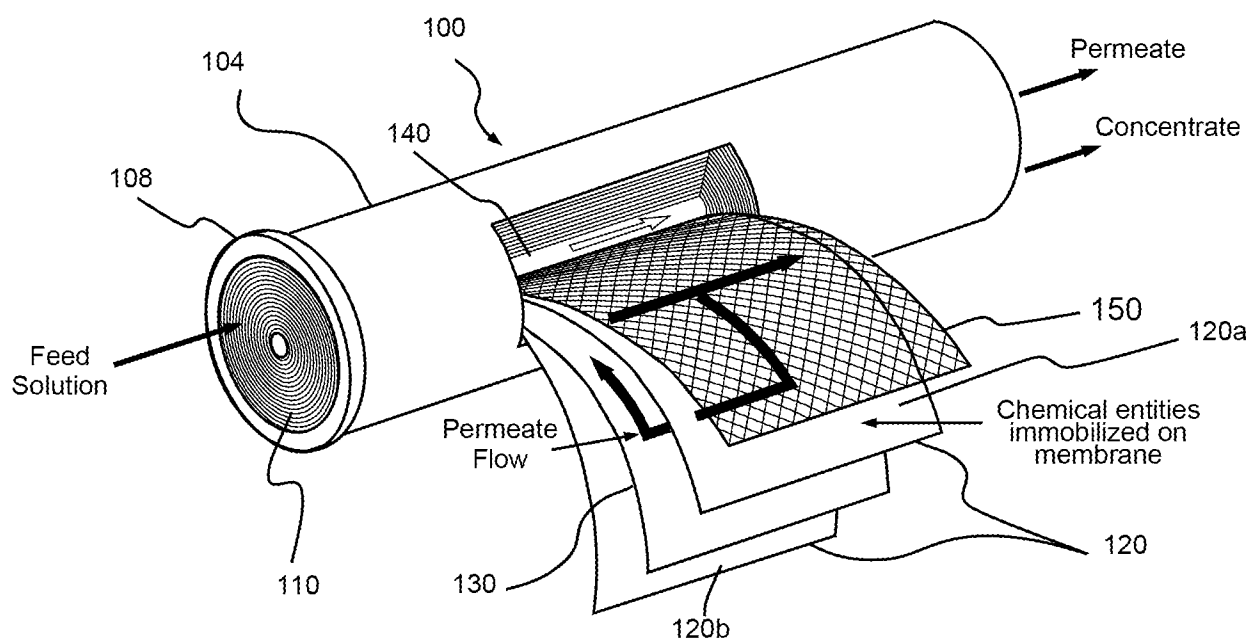


FIG. 2

**FIG. 3**

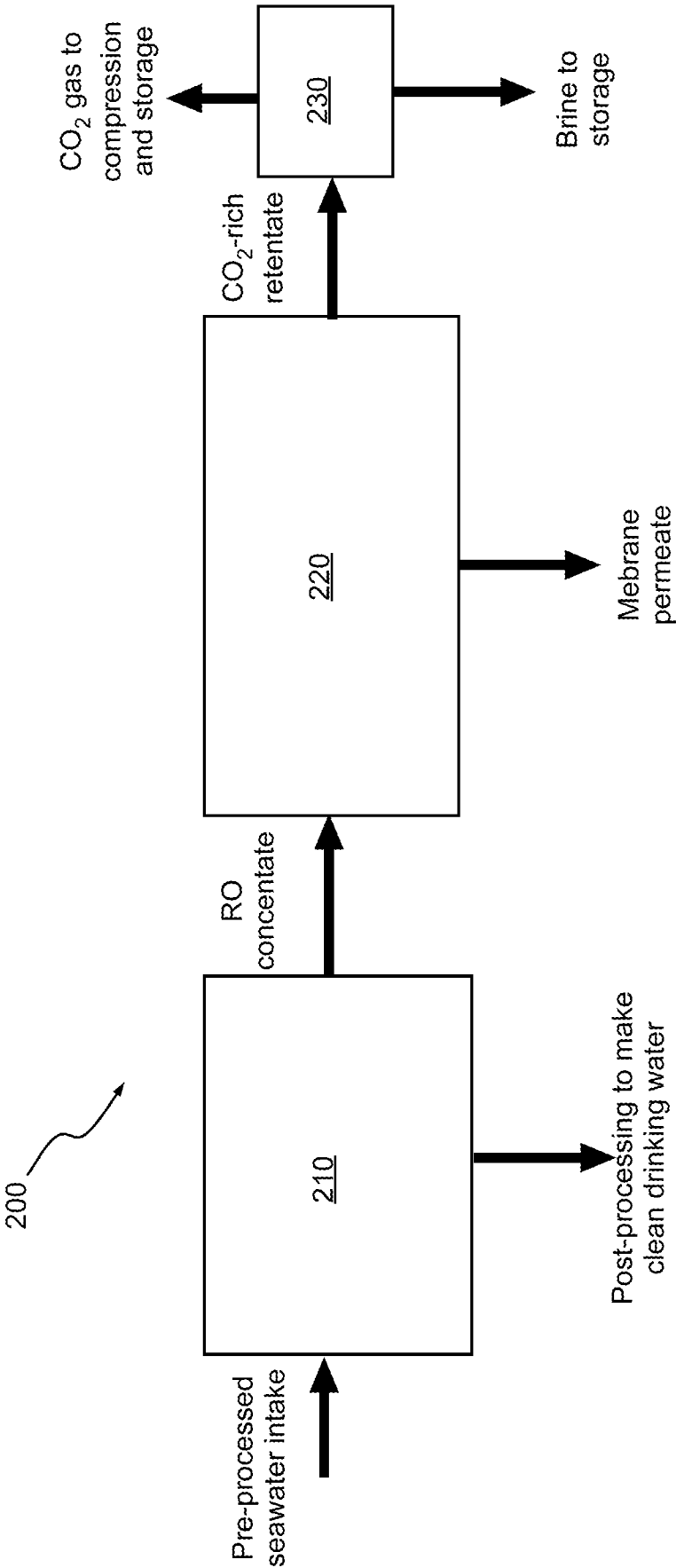


FIG. 4

FIG. 5

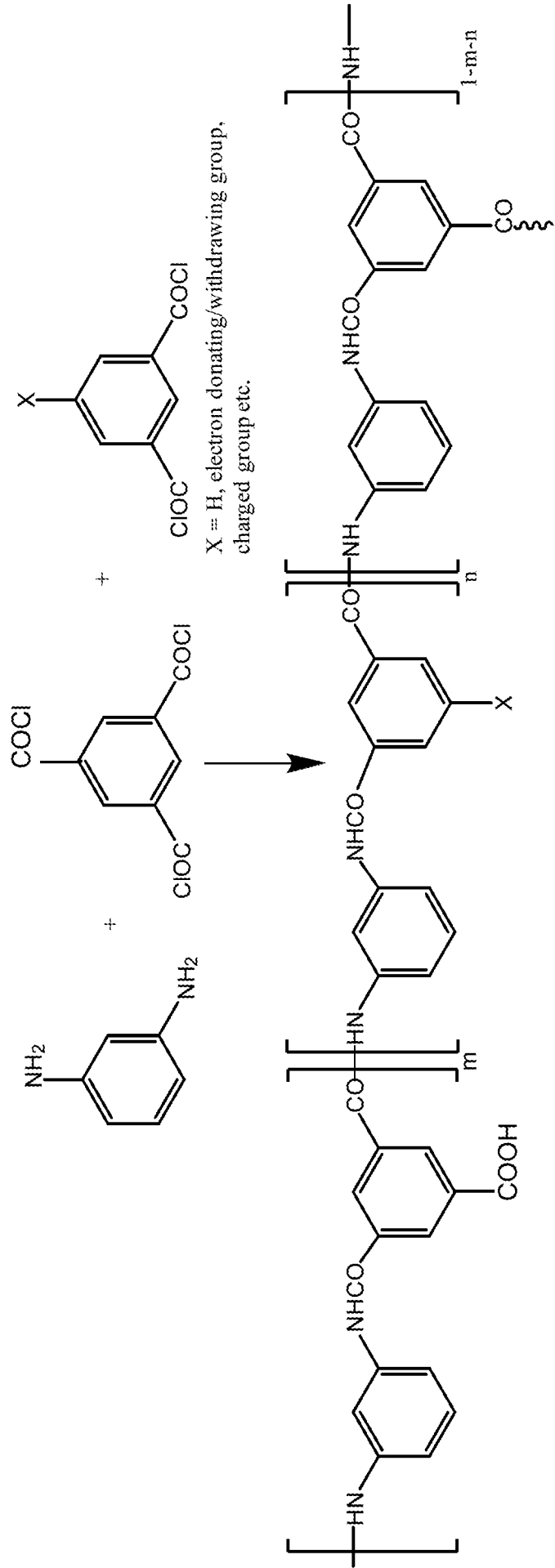
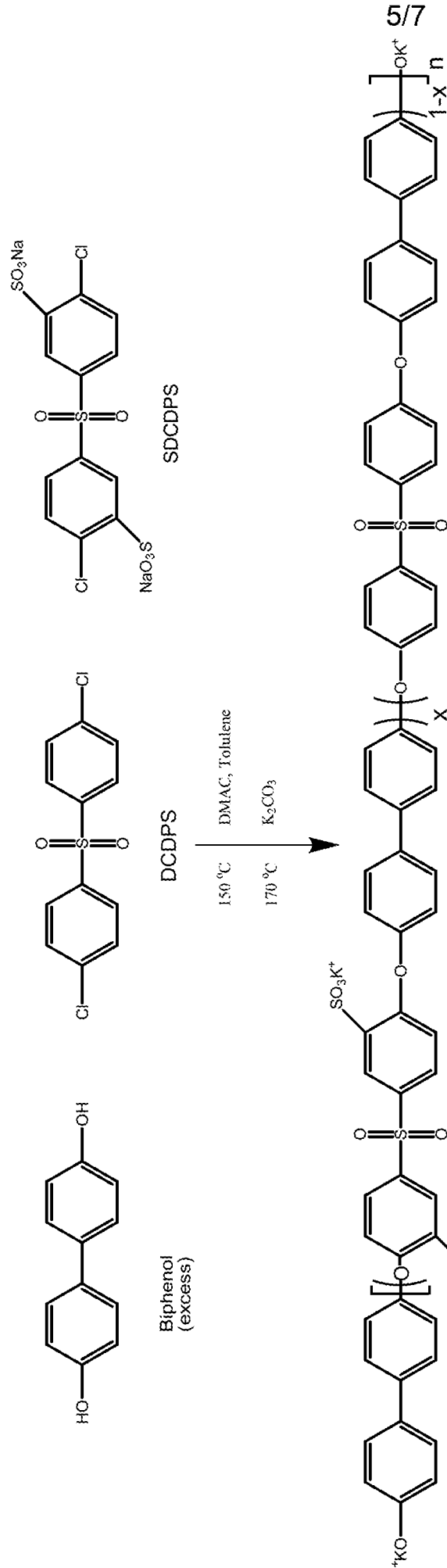


FIG. 6



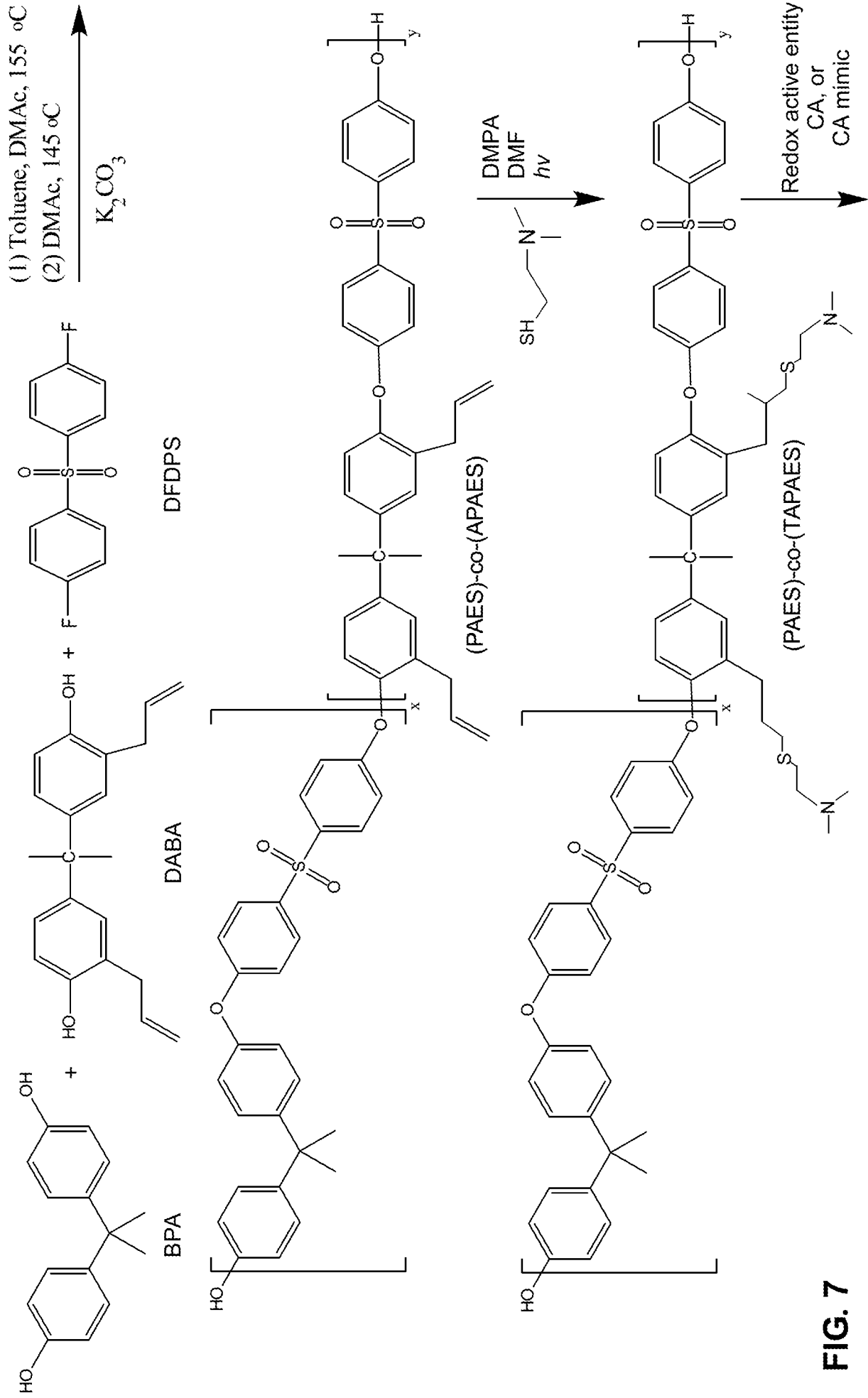
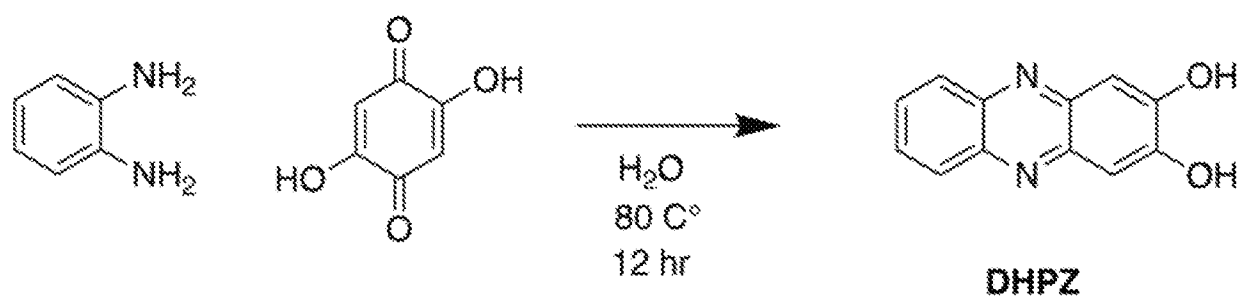
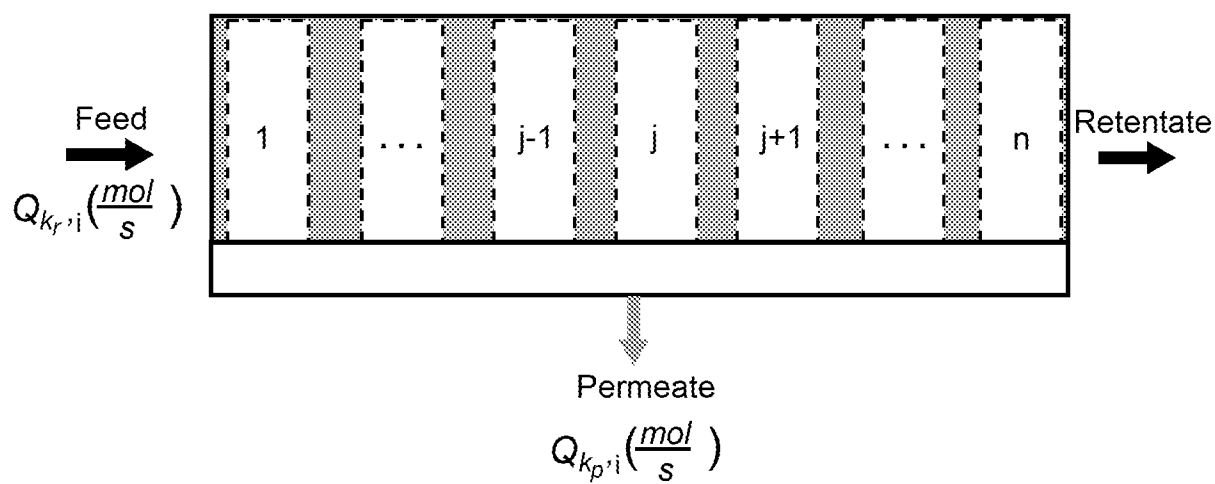
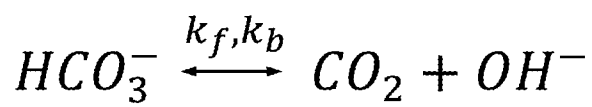


FIG. 7

**FIG. 8****FIG. 9A****FIG. 9B**