The disclosure provides conductive membranes for water splitting and solar fuel generation. The membranes comprise an embedded semiconductive/photoactive material and an oxygen or hydrogen evolution catalyst. Also provided are chassis and cassettes containing the membranes for use in fuel generation.

10 Claims, 4 Drawing Sheets
References Cited

U.S. PATENT DOCUMENTS

5,834,069 A 11/1998 Berman .......... B01J 19/122 422/186.3
2009/0050204 A1 2/2009 Habib
2011/0278176 A1 11/2011 He

FOREIGN PATENT DOCUMENTS

JP 11-214720 8/1999
JP 2005-194609 7/2005
WO 03/050450 A2 1/2003
WO 2010/37014 A2 12/2010

OTHER PUBLICATIONS

Mohan et al., "Controlled growth of highly uniform, axial/radial direction-defined, individually addressable InP nanowire arrays", Nanotechnology 16 (2005) 2903-2907.
Shchetina et al., "Photoconverters Based on Silicon-Crystal Whiskers", Translated from Izmeritarnaya Teknika, No. 4, pp. 35-36, 1978.
Shimizu et al., "Synthesis of Vertical High-Density Epitaxial Si(100) Nanowire Arrays on a Si(100) Substrate Using an Anodic Aluminum Oxide Template", Advanced Materials, 19, 917-920 (2007).
References Cited

OTHER PUBLICATIONS


References Cited

OTHER PUBLICATIONS


* cited by examiner
SOLAR FUEL GENERATOR

CROSS REFERENCE TO RELATED APPLICATIONS

The present application claims priority to U.S. Provisional Application No. 61/586,621, filed Jan. 13, 2012, the disclosure of which is incorporated herein by reference in its entirety.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

This invention was made with government support under DE-SC0004993 (T-105569) awarded by U.S. Department of Energy. The government has certain rights in the invention. The invention described herein was made in the performance of work under a NASA contract, and is subject to the provisions of Public Law 96-517 (35 USC 202) in which the Contractor has elected to retain title.

FIELD OF THE INVENTION

The disclosure relates to fuel cells and compositions useful for solar fuel cells. More specifically the disclosure provides conductive membranes useful for solar fuel generation and water splitting.

BACKGROUND

Sources and methods to generate alternatives to fossil fuels are becoming of more importance as demands for fossil fuels increase.

SUMMARY

This disclosure provides fabrication methodologies and materials to construct two distinct liquid water or water vapor-fed solar fuel generators. The disclosure describes components that can be added to existing technology and therefore do not describe specific features required to store solar-generated fuels or to connect the individual assemblies into large-area modular arrays as these technology are well known in the art, though it should be understood that these would be the preferred embodiments in a practical end-user application.

Aspects of an overall device of the disclosure comprise light absorbers, optical windows, catalysts, membranes and chassis.

The disclosure provides a membrane having a first surface and a second surface, comprising: (i) a polymer mesh coated with a conducting polymer (anionic or cationic conducting polymer), comprising a plurality of photoactive structures or (ii) a conducting polymer (anionic or cationic conducting polymer), comprising a plurality of photoactive structures, wherein the conducting polymer is adhered to the polymer mesh substrate to form the membrane, wherein the plurality of semiconductive/photoactive structures are embedded in the membrane, and wherein all or a subset of the structures embedded in the membrane extend entirely through the membrane. In one embodiment, a portion of the membrane is sufficiently free of embedded photoactive structures wherein this sufficiently free portion of the membrane allows for anion or cation conduction. In another embodiment, the polymer mesh is comprised of polyethylene, polypropylene, and/or nylon based materials. In yet another embodiment, the conducting polymer is an anionomer. In a further embodiment, the anionomer is a sulfonated tetrafluoroethylene based fluoropolymer-copolymer. In another embodiment, the photoactive/semiconductive structures are comprised of a photoanodic based material. In a further embodiment, the photoanodic based material is selected from TiO₂, SrTiO₃, and/or chemically reduced SrTiO₃. In yet another embodiment, the first surface of the membrane comprising photoactive structures is exposed with one or more hydrogen or oxygen evolution catalysts. In yet another embodiment, the hydrochloric evolution catalyst includes catalytically active materials comprising one or more transition metals.

The disclosure also provides a chassis comprising the membrane described above in fluid contact with water on the first surface of the membrane, and the second surface of the membrane in light communication with a light source.

The disclosure also provides a method for producing a membrane of the disclosure, comprising suspending photoactive/semiconductive structures in a solution comprising a dissolved conducting polymer material; adhering the suspension to a polymer mesh; removing any surface coating on at least one or more surfaces of photoactive structures so that one or more surfaces of the structures are exposed on at least the first surface of the membrane. In a further embodiment, the method includes coating one or more of the surfaces of photoactive/semiconductive structures with one or more hydrogen or oxygen evolution catalysts. In yet another embodiment, the suspension is adhered to the polymer mesh by drying and/or heating. In one embodiment, the polymer mesh is comprised of polyethylene, polypropylene, and/or nylon based materials. In a further embodiment, the polymer mesh has a pore size of about 10 to 100 µm or more. In another embodiment, the conducting polymer is an anionomer. In a further embodiment, the anionomer is a sulfonated tetrafluoroethylene based fluoropolymer-copolymer. In another embodiment, the photoactive/semiconductive structures are comprised of a photoanodic based material. In a further embodiment, the photoanodic based material is selected from TiO₂, SrTiO₃, and/or chemically reduced SrTiO₃. In yet another embodiment, the first surface of the membrane comprising photoactive structures is exposed with one or more hydrogen or oxygen evolution catalysts. In yet another embodiment, the hydrogen evolution catalyst includes catalytically active materials comprising one or more transition metals.

No limitation is intended by the description of exemplary embodiments briefly described above or those described in additional detail below.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1A-B shows general structures of a membrane of the disclosure.

FIG. 2A-D shows an additional structure of the membrane and a general method of manufacture.

FIG. 3A-B shows a flow cassette comprising a membrane of the disclosure compartmentalizing two flow chambers.

FIG. 4 shows another embodiment of a flow cassette wherein the membranes are depicted vertically, while still providing two flow chambers.

DETAILED DESCRIPTION

As used herein and in the appended claims, the singular forms "a," "an," and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "a pillar" includes a plurality of such pillars and reference to "the particle" includes reference to one or more particles known to those skilled in the art, and so forth.
Also, the use of "or" means "and/or" unless stated otherwise. Similarly, "comprise," "comprised," "comprising" include," "includes," and "including" are interchangeable and not intended to be limiting.

It is to be further understood that where descriptions of various embodiments use the term "comprising," those skilled in the art would understand that in some specific instances, an embodiment can be alternatively described using language "consisting essentially of" or "consisting of."

By "about" is meant a quantity, level, value, number, frequency, percentage, dimension, size, amount, weight or length that varies by as much as 30, 25, 20, 25, 10, 9, 8, 7, 6, 5, 4, 3, 2 or 1% to a reference quantity, level, value, number, frequency, percentage, dimension, size, amount, weight or length.

With respect to ranges of values, the invention encompasses each intervening value between the upper and lower limits of the range to at least a tenth of the lower limit’s unit, unless the context clearly indicates otherwise. Further, the invention encompasses any other stated intervening values. Moreover, the invention also encompasses ranges excluding either or both of the upper and lower limits of the range, unless specifically excluded from the stated range.

Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood in the art to which this disclosure belongs. Although methods and materials similar or equivalent to those described herein can be used in the practice of the disclosed methods and compositions, the exemplary methods, devices and materials are described herein.

The publications discussed above and throughout the text are provided solely for their disclosure prior to the filing date of the present application. Nothing herein is to be construed as an admission that the inventors are not entitled to anate such disclosure by virtue of prior disclosure.

Within this description, the terms "wires," "rods," "whiskers," and "pillars" and other similar terms may be used synonymously, except as otherwise indicated. Generally, these terms refer to elongate structures which have lengths and widths, where the length is defined by the longest axis of the structure and the width is defined by the axis generally normal to the longest axis of the structure. The term "aspect ratio" refers to the ratio of a structure’s length to its width. Hence, the aspect ratios of the elongate structures will be greater than one. The terms "ball," "spheroid," "blob" and other similar terms may also be used synonymously, except as otherwise indicated. Generally, these terms refer to structures with the width defined by the longest axis of the structure and the length defined by the axis generally normal to the width. Hence, the aspect ratio of such structures will generally be unity or less than unity. Further the term "vertical" with reference to wires, rods, whiskers, pillars, etc., generally refers to structures that have a length direction that is elevated somewhat from horizontal. The term "vertical alignment" generally refers to an orientation or orientation of a structure or structures that is elevated from horizontal.

The structure or structures do not have to be spaced apart, unless otherwise indicated. Structures within an array all do not have to have the same orientation. The terms "vertically aligned array" or "vertically oriented array" generally refer to arrays of structures where the structures have orientations elevated from a horizontal orientation up to orientations completely normal to a horizontal orientation, but the structures within the array may or may not have all the same orientations with respect to horizontal.

The term "ordered" generally refers to the placement of elements in a specified or predetermined pattern where the elements have distinct spatial relationships to one another. Hence, the term "ordered array" generally refers to structures distributed within an area with distinct, specified or predetermined spatial relationships to one another. For example, the spatial relationships within an ordered array may be such that the structures are spaced apart from one another by generally equal distances. Other ordered arrays may vary using, but specified or predetermined, spacings. Within this description, the term "semiconductor" or "photoactive material" is generally used to refer to elements, structures, or devices, etc. comprising materials that have semiconductive properties, unless otherwise indicated. Such materials include, but are not limited to: elements from Group IV of the periodic table: materials including elements from Group II, Group III and Group IV of the periodic table: materials including elements from Group II and Group VI of the periodic table: materials including elements from Group I and Group VII of the periodic table: materials including elements from Group IV and Group VI of the periodic table: materials including elements from Group V and Group VI of the periodic table; and materials including elements from Group II and Group V of the periodic table. Other materials with semiconductive properties may include: layered semiconductors; miscellaneous oxides; some organic materials, and some magnetic materials. The term "semiconductor structure" or "photoactive structure" refers to a structure consisting of, at least in part, semiconductor material. A semiconductor structure may comprise either doped or undoped material. As used herein and throughout the disclosure a semiconductor material (sometimes referred to as photographic material) can be selected from the group consisting of TiO_2, CaTiO_3, SrTiO_3, SnO_2, Nb_2O_5, SrTaO_3, NbTaO_5, SnNbO_5, ZrO_2, V_2O_5, Al_2O_3, Nb_2O_5, Ta_2O_5, WO_3, B_2O_3, HfO_2, Y_2O_3, and SiO_2.

The term "ordered array" generally refers to structures distributed within an area with distinct, specified or predetermined spatial relationships to one another. Hence, the term "ordered array" generally refers to structures distributed within an area with distinct, specified or predetermined spatial relationships to one another. For example, the spatial relationships within an ordered array may be such that the structures are spaced apart from one another by generally equal distances. Other ordered arrays may vary using, but specified or predetermined, spacings. Within this description, the term "semiconductor" or "photoactive material" is generally used to refer to elements, structures, or devices, etc. comprising materials that have semiconductive properties, unless otherwise indicated. Such materials include, but are not limited to: elements from Group IV of the periodic table: materials including elements from Group II, Group III and Group IV of the periodic table: materials including elements from Group II and Group VI of the periodic table: materials including elements from Group I and Group VII of the periodic table: materials including elements from Group IV and Group VI of the periodic table: materials including elements from Group V and Group VI of the periodic table; and materials including elements from Group II and Group V of the periodic table. Other materials with semiconductive properties may include: layered semiconductors; miscellaneous oxides; some organic materials, and some magnetic materials. The term "semiconductor structure" or "photoactive structure" refers to a structure consisting of, at least in part, semiconductor material. A semiconductor structure may comprise either doped or undoped material. As used herein and throughout the disclosure a semiconductor material (sometimes referred to as photographic material) can be selected from the group consisting of TiO_2, CaTiO_3, SrTiO_3, SnO_2, Nb_2O_5, SrTaO_3, NbTaO_5, SnNbO_5, ZrO_2, V_2O_5, Al_2O_3, Nb_2O_5, Ta_2O_5, WO_3, B_2O_3, HfO_2, Y_2O_3, and SiO_2.
formed in the absence of the mesh. The mesh 100 is coated
face 20 and the second surface 30. The semiconductive
prising a photoactive material/semiconductive material. As
omeric membrane 105.
ionomeric membrane has sufficient
roll-to-roll processes.
the disclosure along with one embodiment of manufacturing
method and can readily be adapted to commercial large scale
nitioned above, however, the mesh is not necessary where the
cluding single and double and triple junctions and other
structure is then coated upon the mesh substrate 100. As
strands of the conducting membrane and
cluding a conducting polymeric suspension. For example, the
embrane solution has sufficient viscosity to produce a
able to form an ionomer membrane. For example, the suspension can comprise a proton-conducting
material selected from the group consisting of tetrafluoroethylene-fluorovinyl ether copolymers having sulphonic acid groups or a fluorine-free ionomer
material selected from the group consisting of doped sulphonated polyether ketones, doped sulphonated or sulphanated aryl ketones, doped polybenzimidazoles and mixtures thereof.

The suspension comprising the suspended semiconductive
material is then coated upon the mesh substrate 100. As
shows in FIG. 2B, the mesh 100 is embedded within the
conducting polymer material along with the photoactive/
semiconductive structure 60; the mesh provides mechanical
strength to the embodiment depicted in FIG. 2. For example, a
suspension of photoanode particles (e.g., H₂-reduced
SrTiO₃) or other photoactive/semiconductive structure 60
including single and double and triple junctions and other
photoactive structures are prepared in a solution of dissolved
conducting membrane material (e.g., Nafion®) and the
suspension is aspirated, dip coated, or slurry coated onto the
polymer mesh substrate 100. Typically, the conducting
membrane solution has sufficient viscosity to produce a
stable non-settling suspension with the photoactive/semi-
conductive structure 60. After coating, this membrane can be
air dried following by a mild heating step at about 120°C for
2 hours to fully adhere the conducting membrane and
photoactive/semiconductive structures to the polymer mesh
substrate. In some embodiments, the conducting membrane
is anion conducting and in others cation conducting. In other
embodiments, wire arrays or other semiconductive/photo-
active structures can be mechanically inserted into an iono-
mer membrane. In this embodiment, a pristine ionomer
membrane is used (i.e., lacking semiconductive structures)
and the semiconductive structures are then mechanically
inserted into/through the membrane.

The relative mass of conducting membrane material and
photoactive/semiconductive structures should be balanced
to provide optimal free space for anion/cation conduction.
The mass fraction of photoactive/semiconductive structures
should be above the percolation threshold of about 25-50 wt
% or greater to assure electronic conduction across the
membrane, while leaving sufficient particle-free area to
allow for anion/cation conduction to minimize polarization
losses during operation.

The resulting conductive membrane 10 comprising photo-
tactive/semiconductive material comprises a first surface
20 and second surface 30. As prepared, the photoactive/
semiconductive structure 60 within the membrane will
typically have a thin surface coating of the conducting mem-
brane material, which can be, and should be, removed to
expose the particles for coating with a hydrogen reduction
catalyst or oxygen evolution catalyst. This selective removal
of the thin conducting film from the photoactive/semicon-
ductive structure 60 can be accomplished through a number
of methods including a solvent wipe, mechanical abrasion
with a fine abrasive, or a plasma etch.

Subsequent to polymerization and exposure of the photo-
tactive/semiconductive structure 60, a layer of catalysts 70
is then coated on at least one surface (e.g., a second surface
30). The catalyst can be any number of catalysts useful as
hydrogen or oxygen evolution. For example, suitable hydro-
gen evolution catalyst can be selected from the group
consisting of Pt, Co, Cu, Fe, MoSₓ where x is nominally—2,
but may be sub or super-stoichiometric, Ni, CoMo, CoW,
FeMo, NiCo, NiFe, NiFeC, NiFeS, NiMnS, NiMo, NiMo₆,
suitable oxygen evolution catalysts that can be used in the methods and composition of the disclosure can be selected from the group consisting of IrOx where x is nominally =2, but may be sub or super-stoichiometric; Pt, Co, Co/(PO₄)₃⁻, CoOP, Cu, Fe, Mn, Ni, Ni/(BO₃)₃⁻, NiP, Pb, CoFe, Co₃O₅, FeMn, NiCo, NiCr, NiCu, NiFe, NiLa, NiLa, NiPSe₂O₅, NiSn, NiZn and NiMoFe. For example, the exposed photovoltaic/semiconductive structure 60 are then coated with a hydrogen reduction catalyst 70 such as Pt, or other catalysts that are needed to produce the desired fuels, on one or both sides of the photovoltaic/semiconductive structure 60 embedded in the membrane. This may be accomplished by a number of methods including sputter deposition, evaporation, screen printing, electroless deposition, electrophoresis, or photo-electrophoresis by way of immersing the hydrogen reduction side of the membrane in an aqueous Pt(II) or Pt(IV) solution and illuminating the opposite side to drive the photoelectrochemical deposition. The latter two approaches are useful since these techniques will selectively deposit the catalyst only at the exposed photovoltaic/semiconductive structure 60 sites, in contrast to sputter deposition, for example, which will deposit the catalyst unselectively across the photoanode particles as well as the conducting membrane.

As briefly described above the semiconductive/photovoltaic structures can be generated as particles, rods, whiskers, blobs, wires and various other structures, the dimensions of which can be controlled for various applications. For example, micro- and nano-particles of the foregoing can be generated using known methods (see, e.g., U.S. Pat. Publ. Nos.: 20130012636, 20130012630, 20120529888, 20120329209, 20120318168, 20120308650, 20120327639, the disclosure of which are incorporated herein by reference). Furthermore, methods of generating micro- and nanowires comprising the foregoing are also known. For example, fabrication of vertically-aligned Si wire arrays from a Si wafer substrate is described. In one embodiment (as described more fully below), the wires can be embedded in a conducting polymer membrane. Various methods of growing wires are known. For example, to grow wires, an Si <111> wafer may be used as the material from which the semiconductor structures are grown. All or portions of the wafer may be doped. For example, a degenerately doped N-type Si wafer may be used. A surface oxide layer is thermally grown on the wafer. The surface oxide layer may be grown to a thickness of 285 µm, 300 µm, or other thicknesses. The oxide layer may also be deposited via chemical vapor deposition (CVD) or other methods known in the art. A photoresist layer is applied. The photoresist layer may comprise Si183 photoreist from MicroChem Corp. (Newton, Mass., USA) or other photoreisist material. The photoreisist layer is then exposed to a desired array pattern and developed with a developer to form a desired pattern of holes in the resist layer. The developer may comprise MF-319 or other developers known in the art. The patterned resist layer is then used to etch the oxide layer on the Si wafer. Etching of the oxide layer may be achieved by using hydrofluoric acid compositions such as buffered HF (9% HF, 32% NH₄F) from Transene Company, Inc. (Danvers, Mass., USA). Other etching techniques known in the art may also be used to etch the oxide layer. The result of the etching will be a pattern of holes in the oxide layer. A growth catalyst is then thermally evaporated onto the resist layer and into the holes in the oxide layer. For example, 500 nm of gold may be thermally evaporated onto the resist layer and into the holes. Other catalysts, such as, but not limited to, Cu, Pt or Ni, may also be used. Lift-off of the photoresist layer is then performed, leaving catalyst islands separated by the oxide in the oxide layer. The wafer with the patterned oxide layer and the deposited catalyst may then be annealed. Typically, the annealing is performed at a temperature between 900 to 1000° C. or at a temperature of about 1050° C. for 20 minutes with the application of 1 atm of H₂ at a flow rate of 1000 sccm (where SCCM denotes cubic centimeters per minute at STP). Growth of wires on the wafer is then performed. The growth of wires in a wire array is accomplished through the application of a growth gas. Typically, the wires are grown in a mixture of H₂ (1000 sccm) and SiCl₄ (20 sccm) at about 1 atm. The wires may be grown for between 20 to 30 minutes at temperatures between 850° C. to 1100° C. or with different growth times, pressures, and or flow rates. After the fabrication of the semiconductor structures, a polymer mesh comprising pore sizes of about 10-100 µm or more is applied and/or a conductive polymer slurry is applied to encapsulate the semiconductor structures grown on the substrate. The polymer material is polymerized and then the removal of the encapsulated structures embedded in the polymer layer can be accomplished. Using this technique micro- or nano-wires can be obtained that extend through a proton conducting membrane from one surface of the membrane to the opposite surface of the membrane (see, e.g., FIG. 1B). Alternatively, the semiconductor structures are mechanically inserted into a pristine membrane.

Once the water splitting membrane 10 is prepared, it can then be mounted inside a suitable chassis (see, e.g., FIG. 3A-B). Referring to FIG 3A-B, a top frame 120 and bottom frame 130 will enclose and seal a UV transparent window 130 and membrane 10. Fill ports comprising threaded members 150 are present in both the top frame 120 and bottom frame 130. This may be initially fabricated using a three dimensional inkjet-style rapid prototyping Object printer though in the typical embodiments it would be fabricated in more conventional low-cost polymer extrusion, casting, and/or stamping operations. The system will include a water feed port for continuous operation. A design feature is a simple and robust water-tight gas vent which consists of a hydrophobic membrane inserted as a gasket within the vent port. This membrane in its present design is a commercially available amorphous carbon/polyytetrafluoroethylene (PTFE) binder membrane (Goretx) that allows the gases to be transported from the assembly while keeping the liquid water out of the gas vent. To deliver the product gas (H₂) or liquid (such as methanol) at practically high pressures for storage, a simple in-line check valve with a selectable release pressure is incorporated into the both product lines. Both check valves on the O₂ generation and H₂ generation sides must have the same release pressure to avoid pressure differentials across the two compartments which may damage the membrane. The assembly can be sealed by a number of means including snap-tight connections between the top and bottom components, or by filling tongue-groove interfaces with commercially available fluoropolymer caulks such as Fluoroxy Viton-based caulks. The assembly can be fabricated with a slight tilt either in the membrane or the entire assembly to facilitate movement of the photogenerated gas bubbles away from the catalyst and light absorbing sites toward the gas vents. In another embodiment, the assembly can be fabricated with textured window to provide light focusing on the membrane. The membrane can also be modified to accept a water vapor rather than liquid water.
feed. This may be accomplished by re-depositing a thin conducting membrane onto the light absorber and catalyst particles to provide appropriate triple phase water molarity and pH and incorporating a passive water delivery system to maintain optimal membrane hydration such as a deliquescent salt (e.g. ZnCl₂) frit feed.

FIG. 4 shows yet another embodiment of a chassis for fuel generation. In this design, strips of photovoltaic cells of sufficiently high open circuit voltage necessary to support water electrolysis and associated overpotentials (for example, a triple junction amorphous Si or a dual junction GaAs/Al₆₇₆₃-GaAs) are mounted on a support structure at a slight angle 200. In order to limit corrosion of the photovoltaic cells in the electrolyte, the photovoltaic cell may incorporate protective films such that the photovoltaic cell is not in direct contact with the electrolyte. These films may be electronically conductive and transparent or semi-transparent to minimize light absorption on the illuminated side of the photovoltaic. The conductive transparent or semi-transparent film is typically fluorine doped tin oxide (SnO:F), but also may be selected from the group consisting of In₂O₃:Sn, SnO₂:Sb, CdSnO₄, TiN, ZnO:Al, Zn₂SnO₄, ZnSnO₃ and Cd₂SnO₄. On the photovoltaic side, the side that is not illuminated during operation, a transparent, semi-transparent, or fully opaque electronically conductive protective film may be incorporated. This film is typically tantalum, but may be any other metal, highly doped semiconductor, or conductive polymer recognized by those skilled in the art as resistant to corrosion. The light absorbing side of the photovoltaic strips can be coated with an oxygen evolution catalyst (e.g. IrO₂). The non-illuminated side of the photovoltaic is coated with a hydrogen reduction catalyst (e.g., Pt). The vertical portions of the assembly between the strips of photovoltaics 200 are conducting membranes 210. In this embodiment, the illuminated side of the assembly presents a 100% photovoltaic surface. That is, no orthogonally illuminated surface of the photovoltaic strips 200 is coated with an oxygen evolution catalyst (e.g. IrO₂). The photovoltaic—membrane or the entire assembly to facilitate movement of the photogenerated gas bubbles away from the catalyst and light absorbing sites toward the gas vents. The assembly can be fabricated with a slight tilt either in the photovoltaic-membrane or the entire assembly to facilitate light focusing on the membrane. The assembly can also be modified to accept a water vapor rather than liquid water feed. This may be accomplished by depositing a thin conducting membrane onto both sides of the photovoltaic and catalyst particles to provide appropriate triple phase water molarity and pH and incorporating a passive water delivery system to maintain membrane hydration such as a deliquescent salt (e.g. ZnCl₂) frit feed.

What is claimed is:

1. A membrane comprising a first surface and a second surface, the membrane comprising:
   - a polymer mesh coated with a conducting ionomeric polymer material, having a plurality of photoactive structures;
   - wherein the conducting ionomeric polymer material is adhered to the polymer mesh substrate to form the membrane,
   - wherein the plurality of photoactive structures are embedded in the membrane,

2. The membrane of claim 1, wherein a portion of the membrane is sufficiently free of embedded photoactive structures; wherein this sufficiently free portion of the membrane allows for cation or anion conduction.

3. The membrane of claim 1, wherein the polymer mesh is comprised of polyethylene, polypropylene, and/or nylon based materials.

4. The membrane of claim 1, wherein the polymer mesh has a pore size of at least 100 μm.

5. The membrane of claim 1, where the ionomeric polymer material is a sulfonated tetrafluoroethylene based fluoro-polymer-copolymer.
6. The membrane of claim 1, wherein the photoactive structures are comprised of a photoanodic based material.

7. The membrane of claim 6, wherein the photoanodic based material is selected from TiO$_2$, SrTiO$_3$, and/or chemically reduced SrTiO$_3$.

8. The membrane of claim 1, wherein a first surface of the membrane comprising photoactive structures is coated with one or more hydrogen reduction catalysts.

9. The membrane of claim 8, wherein the hydrogen reduction catalyst includes catalytically active materials comprising one or more transition metals.

10. A chassis comprising the membrane of claim 1 in fluid contact with water on the first surface of the membrane, and the second surface of the membrane with a hydrophobic liquid-tight gas permeable film.