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(54) **ELECTROCHEMICAL PRODUCTION OF WATER USING MIXED IONICALLY AND ELECTRONICALLY CONDUCTIVE MEMBRANES**

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(52) **U.S. Cl.**

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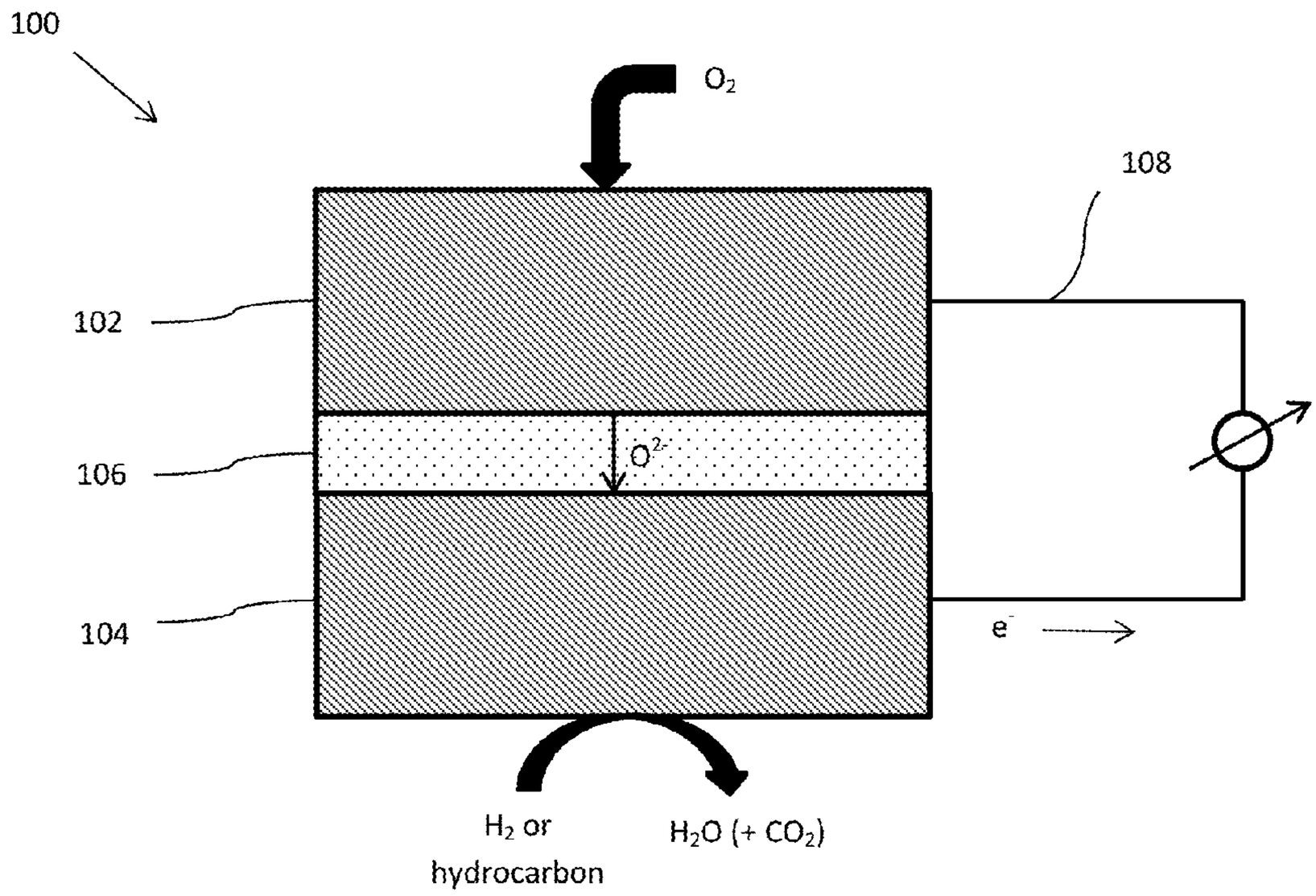
(57) **ABSTRACT**

Mixed ionically and electronically conductive membranes may be employed in electrochemical systems that are capable of producing water from air or molecular oxygen with high energy efficiency. The systems may comprise at least one electrochemical cell comprising: a first electrode and a second electrode, optionally in electrical communication via an external circuit; a mixed ionically and electronically conductive membrane interposed between and in contact with the first electrode and the second electrode; a hydrogen-containing gas supply in fluid communication with one of the first electrode and the second electrode; a molecular oxygen-containing gas supply in fluid communication with the other of the first electrode and the second electrode; and a first gas outlet extending from the first electrode and a second gas outlet extending from the second electrode.



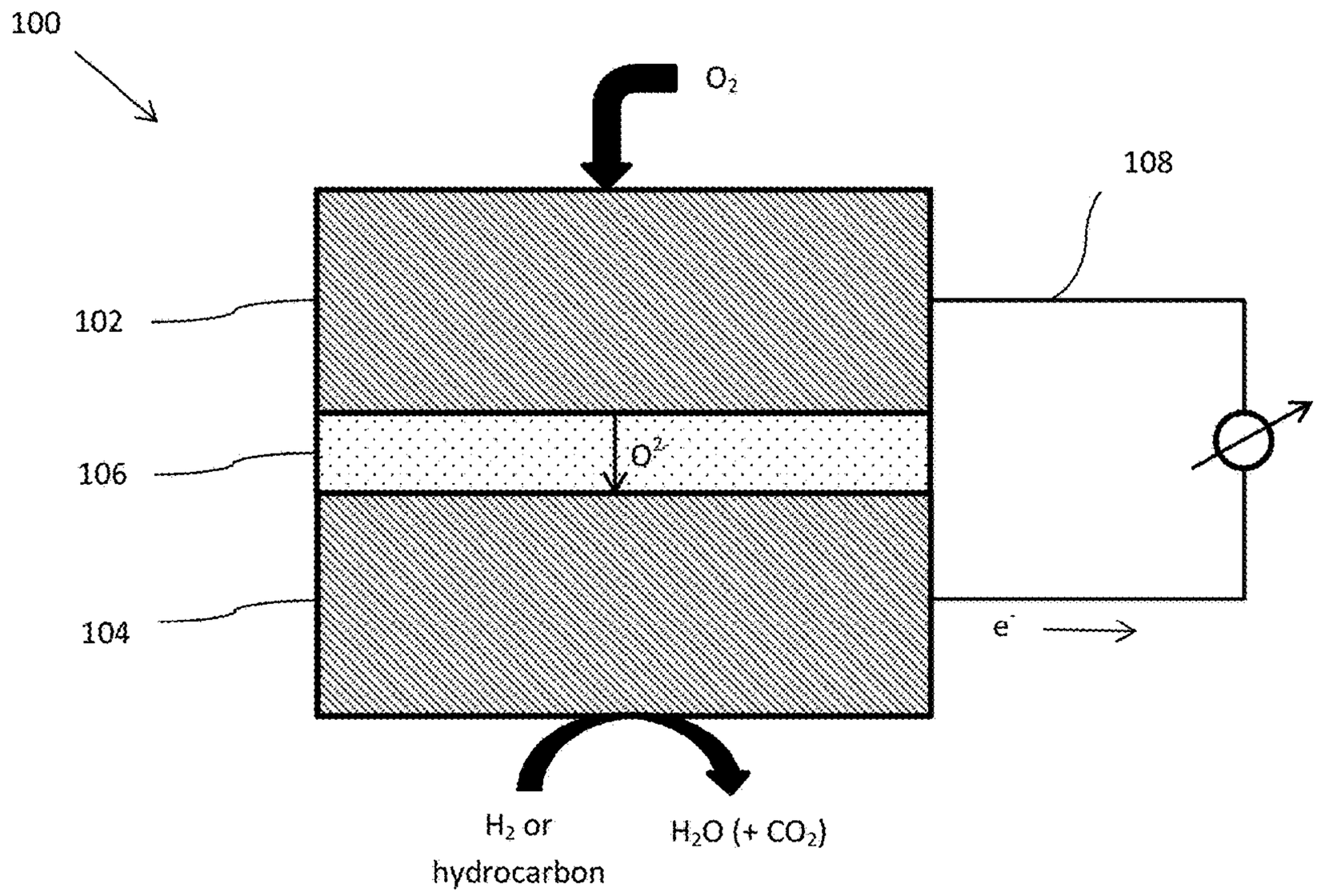

100
O_2
108
102
106
O^{2-}
104
e⁻
H_2 or
hydrocarbon
H_2O (+ CO_2)

FIG. 1A

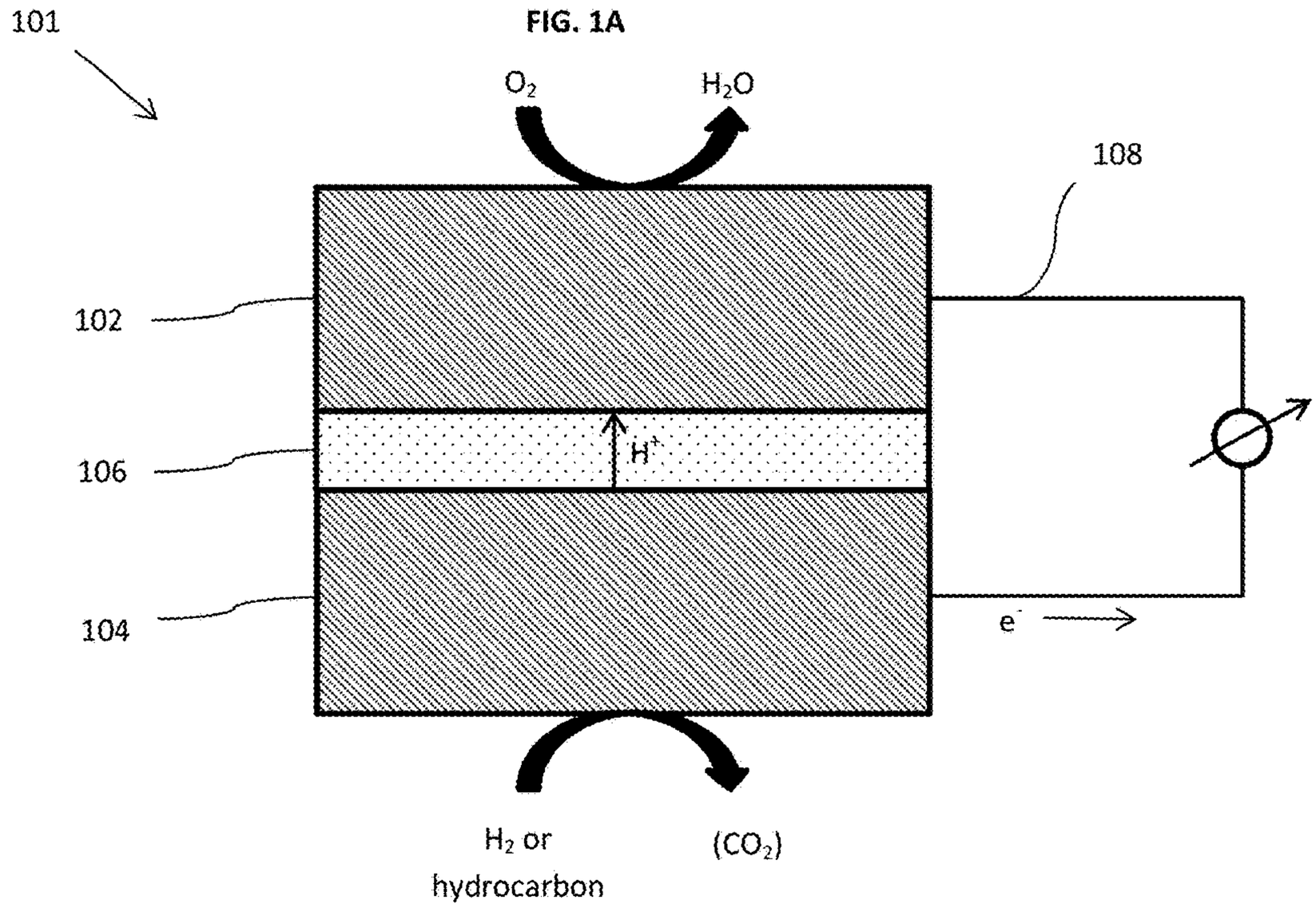

101
O_2
H_2O
108
102
106
H^+
104
e⁻
H_2 or
hydrocarbon
(CO_2)

FIG. 1B

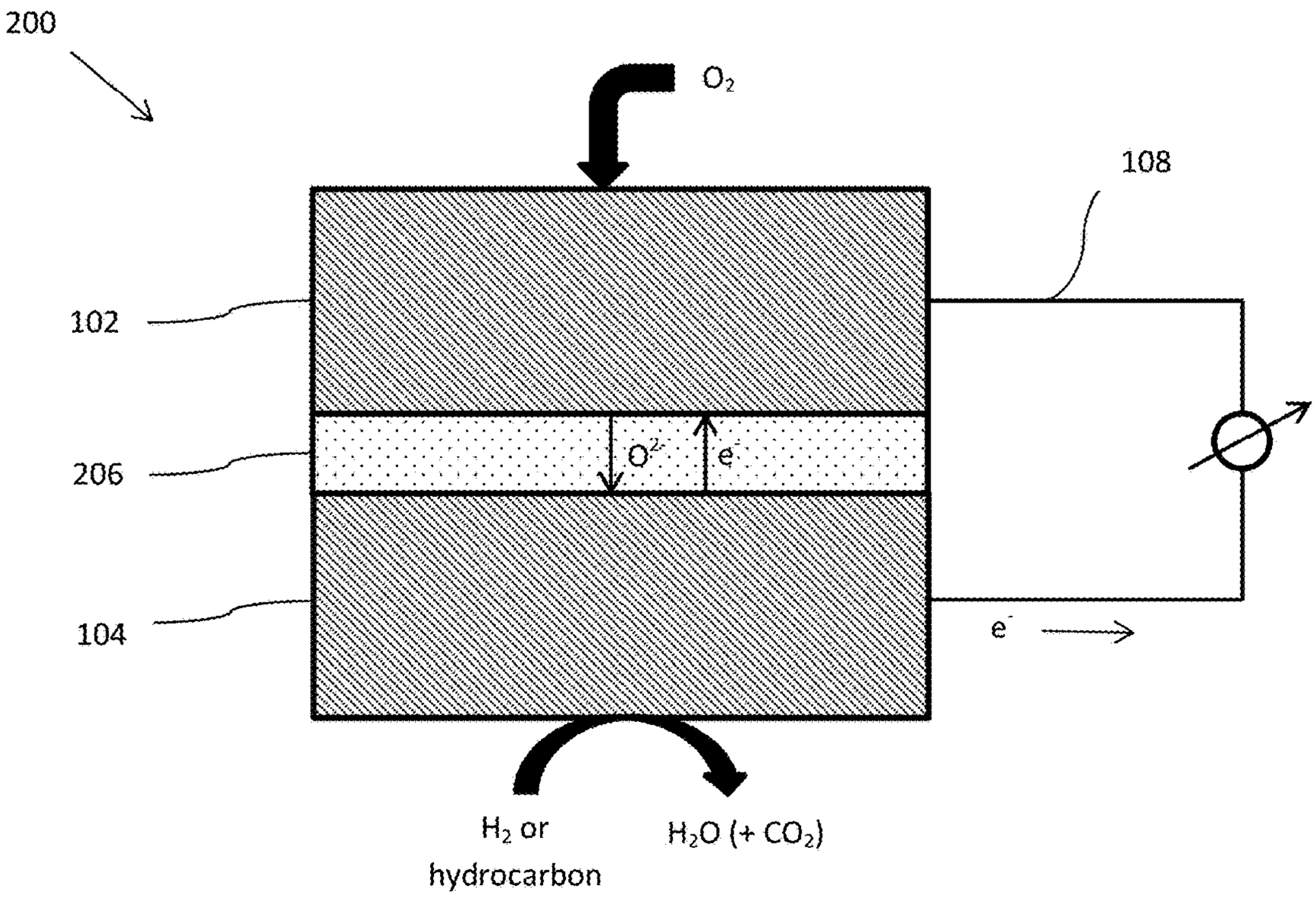

200
O_2
108
102
206
O^{2-}
e^-
104
e^-
H_2 or
hydrocarbon
H_2O (+ CO_2)

FIG. 2A

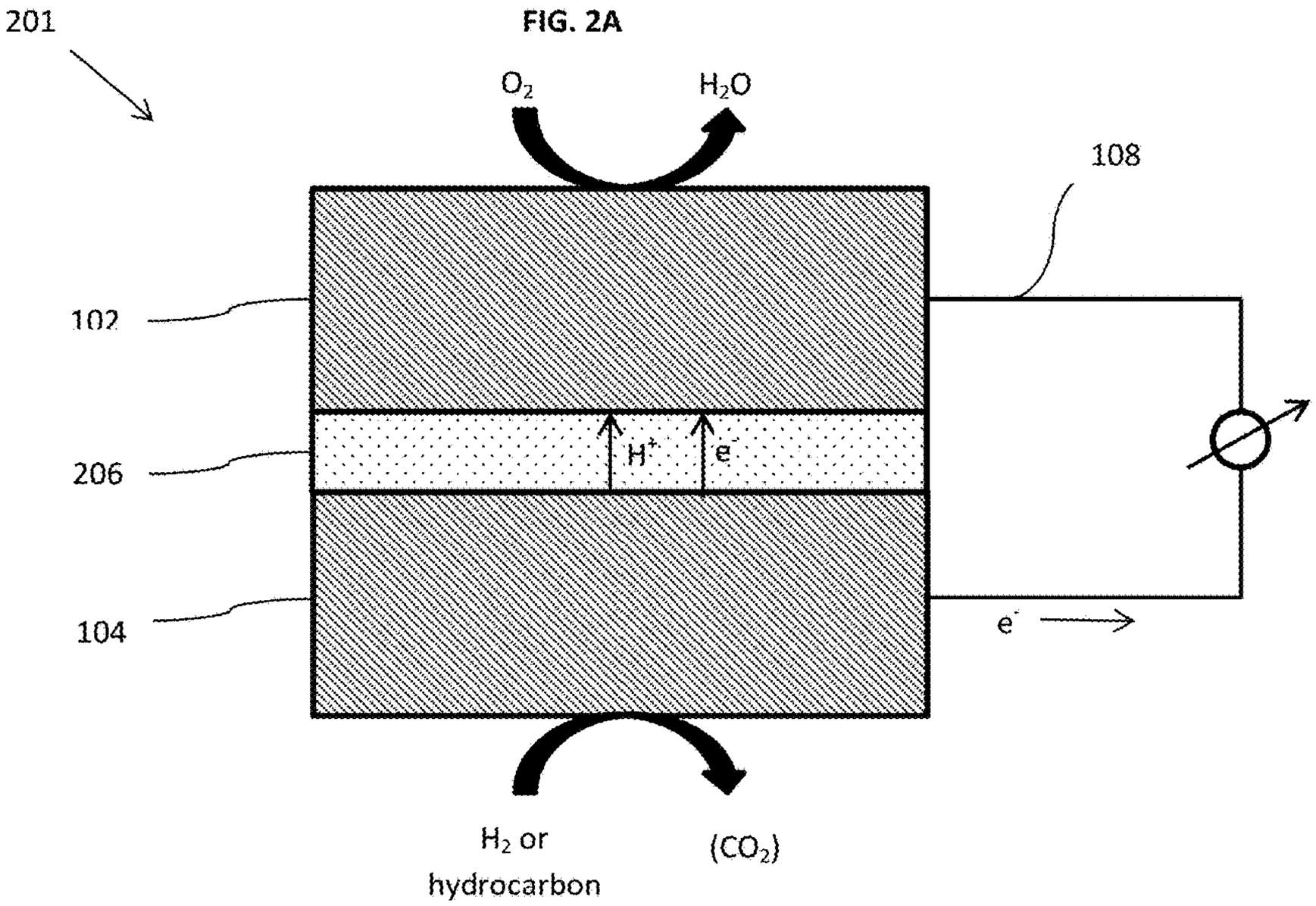

201
O_2
H_2O
108
102
206
H^+
e^-
104
e^-
H_2 or
hydrocarbon
(CO_2)

FIG. 2B

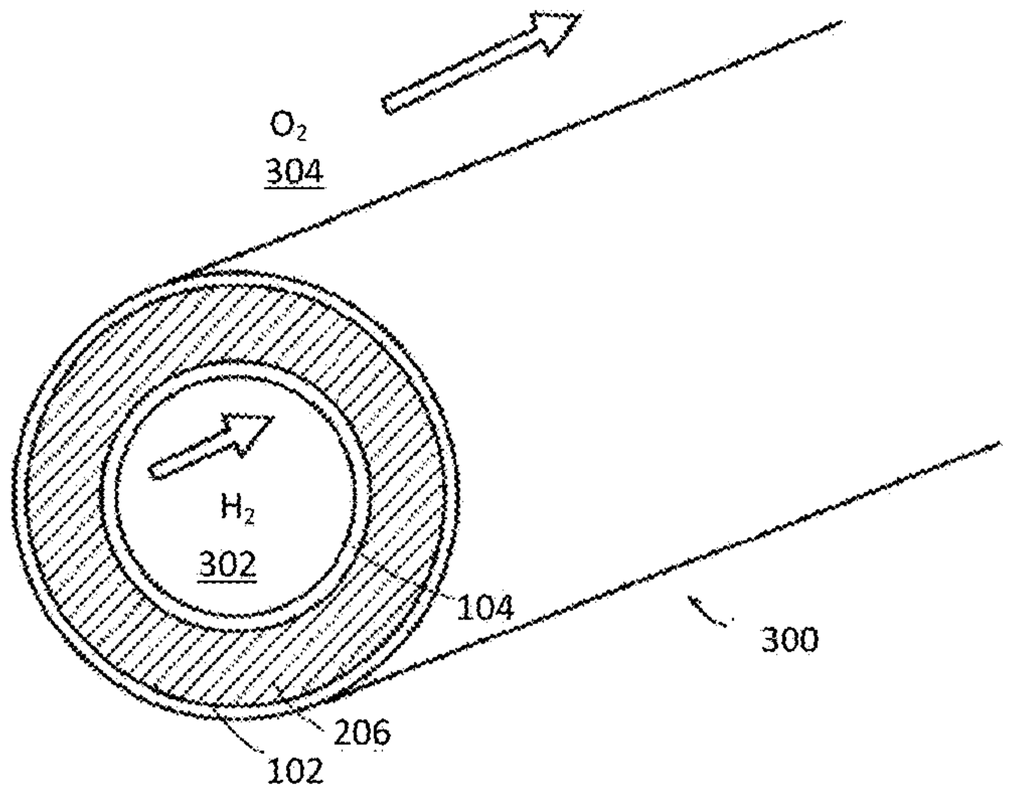

O_2
304
H_2
302
104
300
206
102

FIG. 3

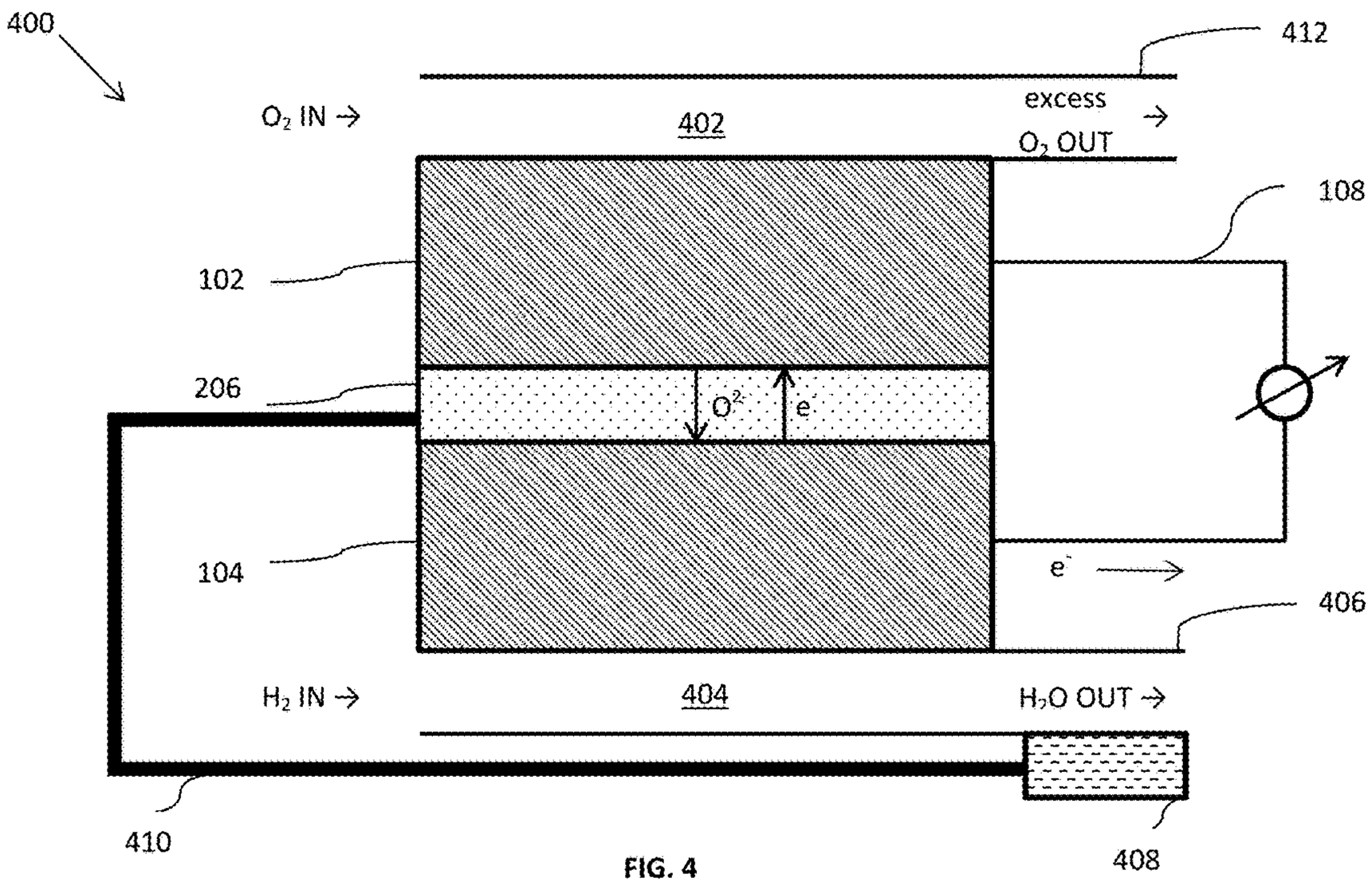

400
412
O_2 IN →
402
excess
O_2 OUT →
108
102
206
O^{2-}
e^-
104
e^- →
406
H_2 IN →
404
H_2O OUT →
410
408

FIG. 4

ELECTROCHEMICAL PRODUCTION OF WATER USING MIXED IONICALLY AND ELECTRONICALLY CONDUCTIVE MEMBRANES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims the benefit of priority under 35 U.S.C. § 119 from U.S. Provisional Patent Application 62/522,414, filed on Jun. 20, 2017 and incorporated herein by reference in its entirety.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] Not applicable.

BACKGROUND

[0003] Access to clean water is an ongoing issue in various geographic locations and certain working environments, such as upon a ship. When a source of clean water is not readily available, water production processes may be used to purify water from an existing water source or to produce the water de novo. Processes for water purification and/or de novo generation of water remain rather expensive at present, primarily due to their requirement for a high input of energy. Desalination plants, for example, may produce fresh water from seawater using a variety of processes, but costs associated with desalination remain high due to the significant energy input required. Other water production processes may face similar economic and/or energy efficiency challenges. Routine, low-cost access to clean water using more efficient production processes could have significant benefits, such as improved health and well being in underdeveloped countries where clean drinking water is not always readily available. Economic benefits may also be realized in processes and working environments where clean water is not otherwise readily available.

[0004] A number of chemical reactions form water, oftentimes as a secondary product when producing a more highly valued material. The water formed during solution-phase and gas-phase chemical reactions sometimes may be contaminated with small amounts of various chemical byproducts, so it may not be suitable for direct use without additional purification. In addition, isolation of the water may be problematic in some instances. Electrochemical reactions, to the contrary, may have the capability to form higher purity water that may be readily isolated. Fuel cells, for example, form water as a byproduct of generating electricity via an electrochemical reaction between molecular oxygen and molecular hydrogen or other suitable fuel. Since the purpose of fuel cells is to produce electricity, not form water, the reaction efficiency for forming water is generally rather poor. Other electrochemical processes similarly are not presently optimized for producing and isolating clean water as a primary product.

BRIEF DESCRIPTION OF THE DRAWINGS

[0005] The following figures are included to illustrate certain aspects of the present disclosure, and should not be viewed as exclusive embodiments. The subject matter disclosed is capable of considerable modifications, alterations, combinations, and equivalents in form and function, without departing from the scope of this disclosure.

[0006] FIGS. **1**A and **1**B show illustrative cross-sectional diagrams of traditional fuel cells and their manner of operation.

[0007] FIGS. **2**A and **2**B show illustrative cross-sectional diagrams of electrochemical cells featuring a mixed ionically and electronically conductive membrane and their manner of operation.

[0008] FIG. **3** shows a diagram of an illustrative electrochemical cell formed in a tubular configuration.

[0009] FIG. **4** shows a diagram of an illustrative electrochemical water generation system configured to extract waste heat and to return at least a portion of the waste heat to the mixed ionically and electronically conductive membrane.

DETAILED DESCRIPTION

[0010] The present disclosure generally describes systems for generating water and, more specifically, electrochemical systems and methods for generating water at high-energy efficiencies.

[0011] As discussed above, production of water in an energy- and cost-efficient manner can oftentimes be problematic. Although electrochemical production of water may be advantageous over other water generation techniques, present electrochemical methods still fail to provide sufficiently high operating efficiencies.

[0012] The present disclosure describes how a traditional fuel cell can be modified to increase the chemical and energy efficiency with which water is produced. FIGS. **1**A and **1**B show illustrative cross-sectional diagrams of traditional fuel cells and their manner of operation. Each traditional fuel cell features an ion-conductive membrane separating a cathode and an anode. The ion-conductive membrane may be an oxygen ion-conductive membrane or a proton-conductive membrane. During operation, the ion-conductive membrane is held at an elevated temperature to maintain ionic mobility at or above a desired threshold value. Depending on which type of ion-conductive membrane is present, the operational principles of the fuel cell change slightly, as explained further in reference to FIGS. **1**A and **1**B.

[0013] As shown in FIG. **1**A, fuel cell **100** comprises cathode **102** and anode **104**, which are separated by ionically conductive membrane **106** interposed in between. In fuel cell **100**, ionically conductive membrane **106** is an oxygen ion-conductive membrane. A molecular oxygen-containing gas or air is supplied to cathode **102**, whereupon oxide ions are formed via reduction of molecular oxygen. The oxide ions migrate through ionically conductive membrane **106** (oxygen ion-conductive membrane) toward anode **104**. At anode **104**, the oxide ions react with molecular hydrogen or a hydrogen-containing gas to oxidize the molecular hydrogen or hydrogen-containing gas to form water and potentially other gaseous products. Water is the sole product formed when molecular hydrogen is supplied to anode **104**. If a hydrocarbon is instead supplied to anode **104**, carbon dioxide is produced concurrently with the water. Electrons released from the oxidation reaction travel through external circuit **108**, which establishes electrical communication between cathode **102** and anode **104**.

[0014] Fuel cell **101**, shown in FIG. **1**B, differs from fuel cell **100** in that ionically conductive membrane **106** is a proton-conductive membrane in fuel cell **101**. In fuel cell **101**, molecular hydrogen or a hydrogen-containing gas is again supplied to anode **104**. Oxidation of the molecular

hydrogen or hydrogen-containing gas takes place in anode **104** to generate protons. In the case of a hydrocarbon being supplied to anode **104**, carbon dioxide is also produced concurrently with the protons. The protons generated at anode **104** migrate through ionically conductive membrane **106** (proton-conductive membrane) toward cathode **102**, whereupon they react with molecular oxygen to form water. Electrons released from the oxidation reaction in anode **104** again travel through external circuit **108**.

[0015] As such, fuel cells **100** and **101** provide electrical power in the form of a current through external circuit **108**. Although water may be formed as a byproduct in either fuel cell configuration, the primary purpose of fuel cells **100** and **101** is to generate electrical power, not form water. The system components, including ionically conductive membrane **106**, are optimized for electricity production rather than water production. As a result, the water production may be rather inefficient with respect to the amounts of molecular oxygen and molecular hydrogen that are supplied.

[0016] The free electrons generated during an oxidation-reduction cycle in traditional fuel cells travel through external circuit **108**. Since all of the free electrons are devoted to current production in external circuit **108** of traditional fuel cells, the electron transfer processes to form water may be non-optimal.

[0017] In contrast to the ionically conductive membranes employed in traditional fuel cells, the present disclosure employs mixed ionically and electronically conductive membranes within an electrochemical cell architecture that may or may not employ an external circuit. As used herein, the term "mixed ionically and electronically conductive membrane" refers to a membrane material capable of transferring both ions and free electrons (or electron holes). All of the free electrons produced in an electrochemical reaction need not necessarily flow across a mixed ionically and electronically conductive membrane in the presence of an external circuit. Instead, a first portion of the free electrons may travel between the anode and the cathode in the external electrical circuit, and a second portion of the free electrons may travel across the mixed ionically and electronically conductive membrane. Up to 100% of the free electrons may travel across the mixed ionically and electronically conductive membrane when an external circuit is present. In the absence of an external electrical circuit, all of the free electrons or electron holes may travel between the anode and the cathode across the mixed ionically and electronically conductive membrane.

[0018] According to more specific embodiments, a mixed ionically and electronically conductive membrane may be fully dense (>95% of the theoretical density and/or <5% porosity) and not allow gaseous materials, such as molecular oxygen, air, hydrogen gas (molecular hydrogen), or gaseous hydrocarbons to pass through in un-ionized form. At least a majority of the pores that are present in the mixed ionically and electronically conductive membrane may be closed pores, so as to minimize the risk of gas mixing within the membrane. As such, substantially all of the mass transport taking place through a mixed ionically and electronically conductive membrane occurs in the form of ionic transport.

[0019] FIGS. **2**A and **2**B show illustrative cross-sectional diagrams of electrochemical cells **200** and **201**, corresponding to fuel cells **100** and **101** shown in FIGS. **1**A and **1**B, except for the substitution of mixed ionically and electronically conductive membrane therein **206**. Other than mixed ionically and electronically conductive membrane **206** and the optional nature of external circuit **108** in electrochemical cells **200** and **201**, the structural details in FIGS. **2**A and **2**B are similar to those of FIGS. **1**A and **1**B, and common reference characters are used to denote features having like functionality. The electrons (or electron holes) being conveyed across mixed ionically and electronically conductive membrane **206** are also shown in FIGS. **2**A and **2**B. The direction of electron flow through mixed ionically and electronically conductive membrane **206** is from anode **104** to cathode **102** in both cell configurations. Electron hole flow is in the opposite direction (not shown). Depending upon whether external circuit **108** is present, all or a portion of the electrons may flow through mixed ionically and electronically conductive membrane **206**.

[0020] Since electrochemical cells employing a mixed ionically and electronically conductive membrane carry fewer electrons through the external circuit, if present, than does a comparable electrochemical cell (traditional fuel cell) employing a membrane having only ionic conductivity, a lower current results. Given that the purpose of traditional fuel cells is for optimized electricity generation, there is no particular motivation to substitute a mixed ionically and electronically conductive membrane for the commonly used ionically conductive membranes, given the lower current resulting from mixed ionically and electronically conductive membranes in a similar cell architecture.

[0021] The present disclosure appreciates that while mixed ionically and electronically conductive membranes may lower the electrical current attainable from an electrochemical cell, if an external circuit is even present, such membranes may provide significant advantages from a water generation standpoint. Namely, the electrons travelling across the mixed ionically and electronically conductive membrane may make water generation more efficient by promoting a catalytic reaction at the interface between the mixed ionically and electronically conductive membrane and at least one of the cathode or the anode. That is, the electrons passing through the mixed ionically and electronically conductive membrane may be positioned in a location where they may more effectively promote a catalytic chemical reaction to generate water within the cathode or the anode. As a further advantage, the materials of at least some mixed ionically and electronically conductive membranes may be incorporated within the cathode or the anode to promote better matching of thermal expansion coefficients, thereby disfavoring structural delamination under operational heating.

[0022] Like the ionically conductive membranes of conventional fuel cells, high temperatures may facilitate ionic transport in the mixed ionically and electronically conductive membranes disclosed herein. Due to the high operating temperatures, the water produced from electrochemical cells featuring a mixed ionically and electronically conductive membrane may be produced in the form of steam. Condensation of the steam provides waste heat that must be addressed in some manner. Advantageously, in the electrochemical cells of the present disclosure, at least a portion of the waste heat withdrawn from the steam may be recycled to the mixed ionically and electronically conductive membrane to improve the overall energy efficiency of the electrochemical reactions for forming water. Alternately, the waste heat from the steam may be supplied to other waste heat conversion processes and/or waste heat from other sources may

be supplied to the mixed ionically and electronically conductive membrane. When an external circuit is connected to the electrochemical cells, an electrical current may be produced and used to power a load connected thereto. Alternately, the electrical power may be stored in a suitable energy storage device.

[0023] Thus, electrochemical cells featuring a mixed ionically and electronically conductive membrane may provide a relatively simple system for generating water, particularly if the optional external circuit is not present. Moving parts of such water generation systems may be limited to auxiliary components, thereby providing long operational lifetimes. Moreover, efficiencies may be realized in the water generation systems by recycling waste heat withdrawn from the steam generated during their operation. Alternately, the waste heat can be redirected to other applications in need of a source of thermal energy. Efficiencies that are much greater than conventional methods of water production, such as desalination, may be realized.

[0024] Accordingly, the present disclosure describes electrochemical water generation systems, which differ from conventional fuel cells by employing a mixed ionically and electronically conductive membrane. The electrochemical water generation systems comprise at least one electrochemical cell, which comprises: a first electrode and a second electrode, optionally in electrical communication via an external circuit, a mixed ionically and electronically conductive membrane interposed between and in contact with the first electrode and the second electrode, a hydrogen-containing gas supply in fluid communication with one of the first electrode and the second electrode, a molecular oxygen-containing gas supply in fluid communication with the other of the first electrode and the second electrode, and a first gas outlet extending from the first electrode and a second gas outlet extending from the second electrode. In some embodiments, the external electrical circuit may be omitted, in which case the flow of electrons or electron holes occurs exclusively through the mixed ionically and electronically conductive membrane. In other embodiments, the external electrical circuit may be present, in which case a portion of the electrons may or may not flow through the external electrical circuit.

[0025] The molecular oxygen-containing gas supply may contain or be configured to supply substantially pure molecular oxygen (O_2 gas), in some embodiments. In other embodiments, the molecular oxygen-containing gas supply may contain or be configured to supply air, which comprises approximately 21% molecular oxygen in combination with approximately 78% nitrogen, 1% argon, and less than 1% carbon dioxide and other gases. Other gaseous mixtures comprising molecular oxygen, including air mixtures with other gases, may also be suitably present within the molecular oxygen-containing gas supply in alternative embodiments of the present disclosure. Thus, according to various embodiments of the present disclosure, the molecular oxygen-containing gas supply may contain or be configured to supply air or oxygen gas to the first electrode or the second electrode.

[0026] The hydrogen-containing gas supply may contain or be configured to supply any gas or gas mixture comprising molecular hydrogen (hydrogen gas) and/or one or more compounds comprising chemically bonded hydrogen. Thus, according to various embodiments of the present disclosure, the hydrogen-containing gas supply may contain or be configured to supply at least one of hydrogen gas, a hydrocarbon gas, or ammonia gas to the first electrode or the second electrode. Although hydrogen sulfide (H_2S) may also be reactive, it may be problematic due to its extreme toxicity and the toxicity of the sulfur dioxide (SO_2) formed therefrom. Hydrocarbon gases, for example, may be scrubbed to remove hydrogen sulfide and other sulfur-containing compounds before being introduced as a feed in the systems and methods of the present disclosure. As used herein, the term "hydrocarbon" refers to any compound containing hydrogen bound to carbon, including both saturated and/or unsaturated hydrocarbons, as well as those containing heteroatom substitution. Thus, the term "hydrocarbon," as used herein, is not limited to those compounds containing only carbon and hydrogen. In some embodiments, suitable hydrocarbon gases may include, for example, methane, ethane, propane, butane, ethylene, propylene, acetylene, or the like. In some embodiments, natural gas may be supplied as an electrochemical cell for purposes of generating water.

[0027] When hydrogen gas is supplied to the electrochemical water generation systems, pure water is produced along with electricity in the case of an exothermic reaction. In the case of hydrocarbons, oxides of carbon, nitrogen and sulfur may be produced in addition to water and electricity. Although the carbon, nitrogen, and sulfur oxides are greenhouse gases that may need to be addressed, emission values are typically lower than conventional combustion systems utilizing fossil fuels.

[0028] Depending upon whether oxygen ion conduction or proton conduction is desired, suitable mixed ionically and electronically conductive membranes may include materials such as, for example, defect ABO_{3-d} perovskites ($0<d<1$), doped δ-bismuth oxide (δ-Bi_2O_3), and doped cerium oxide (CeO_2), which may be in a mixed phase. Combinations of these materials may also be present in a mixed ionically and electronically conductive membrane. Dopants for δ-Bi_2O_3 and CeO_2 may be present in a non-zero amount up to about 35 atomic percent. Depending on composition, the defect ABO_{3-d} perovskites may be either an oxygen ion conductor or a proton conductor. Doped δ-bismuth oxide and doped cerium oxide are oxide ion conductors. Suitable defect ABO_{3-d} perovskites may include those in which A is selected from the group consisting of Ba, Fe, La, Ce and Sr, and B is selected from the group consisting of Zr, Cu, Fe and Co. Variables A and B need not necessarily represent a single atom, and mixtures of the choices of A and/or B may be selected that maintain charge neutrality and the desired type of ionic conduction. For example, in some embodiments, a barium cerate zironate perovskite-type species may be present in the mixed ionically and electronically conductive membrane. Additional materials or doped variants thereof that may suitably comprise a mixed ionically and electronically conductive membrane of the present disclosure include, for example, $SrTiO_3$, TiO_2, (La,Ba,Sr)(Mn,Fe,Co)O_{3-d} ($0<d<1$), La_2CuO_{4+d} ($0<d<0.5$), $LiFePO_4$ and $LiMnPO_4$.

[0029] According to some embodiments, the above mixed ionically and electronically conductive membrane may comprise a single-phase material. In other embodiments of the present disclosure, however, the mixed ionically and electronically conductive membrane may comprise a mixed-phase and/or multi- phase material comprising two or more distinct phases or materials. CeO_2 or doped CeO_2, for example, that has been exposed to high temperatures and a

reducing atmosphere may form CeO_{2-x} structures in a mixed phase that is a mixed ionic and electronic conductor.

[0030] According to other embodiments of the present disclosure, the mixed ionically and electronically conductive membrane may comprise a composite material having two or more distinct phases. In more specific embodiments, such composite materials may comprise an ionically conducting phase and an electronically conducting phase. In some embodiments, the electronically conducting phase may comprise a rare earth doped strontium titanate, other doped perovskite, or a metallic phase such as silver.

[0031] Without being bound by theory or mechanism, the mixed ionically and electronically conductive membranes are believed to transport oxygen ions or protons from a location of high chemical potential to a location of lower chemical potential, which is proportional to the partial pressures upon each side of the mixed ionically and electronically conductive membrane. Oxygen ion transport is believed to take place by a vacancy mechanism. Proton transport is believed to take place by association with water to form hydroxide ions, which are transportable across the mixed ionically and electronically conductive membrane.

[0032] In the case of the molecular oxygen-containing gas being O_2 and the hydrogen-containing gas being H_2, the cathodic and anodic reactions are specified by Formulas 1 and 2.

$$O_2+4e=2O^{2-} \tag{1}$$

$$H_2+\tfrac{1}{2}O_2=H_2O \tag{2}$$

[0033] The electromotive force (EMF) is therefore dependent upon the oxygen partial pressures at the anode and the cathode. The oxygen partial pressure at the anode is given by Formula 3

$$P_{O_2}=\left[\frac{P_{H_2O}}{P_{H_2}K_{(ox)}}\right]^2 \tag{3}$$

where $K_{(ox)}$ is the equilibrium constant for the oxidation reaction described above, P_{H_2} is the hydrogen gas partial pressure, and P_{H_2O} is the water partial pressure. Substitution in the Nernst equation leads to Formula 4

$$E=E^0+\frac{RT}{4F}\ln P_{O_2}+\frac{RT}{2F}\ln\frac{P_{H_2}}{P_{H_2O}} \tag{4}$$

where E° is the reversible voltage of the cell at standard state, R is the ideal gas constant, T is the temperature, and F is Faraday's constant. At standard state conditions, Formula 4 reduces to Formula 5.

$$E^0=\frac{RT}{2F}\ln K_{ox} \tag{5}$$

Further substitution of ΔG° in Formula 5 provides Formula 6, where ΔG° is the Gibbs free energy.

$$E^0=-\frac{\Delta G^0}{4F} \tag{6}$$

[0034] For the above reaction at 1250 K, ΔG° is −178.2 kJ/mol, which leads to an EMF value of 0.924 V. It is to be appreciated that the EMF value may differ when operating the cell at different temperatures or when a different hydrogen-containing gas is supplied as a reactant.

[0035] In some embodiments, multiple electrochemical cells may be connected in series and/or in parallel to form an electrochemical stack. Suitable electrochemical stack configurations are not considered to be particularly limited, either in the number of individual cells or in the specific stack design.

[0036] According to more specific embodiments of the present disclosure, the first electrode may be the cathode and the molecular oxygen-containing gas supply may be in fluid communication with the cathode, the second electrode may be an anode and the hydrogen-containing gas supply may be in fluid communication with the anode, and the mixed ionically and electronically conductive membrane may comprise an oxygen ion-conductive membrane. Such a cell configuration is shown in FIG. **2**A.

[0037] According to other more specific embodiments of the present disclosure, the first electrode may be the cathode and the molecular oxygen-containing gas supply may be in fluid communication with the cathode, the second electrode may be an anode and the hydrogen-containing gas supply may be in fluid communication with the anode, and the mixed ionically and electronically conductive membrane may comprise a proton-conductive membrane. Such a cell configuration is shown in FIG. **2**B.

[0038] Although FIGS. **2**A and **2**B have shown cathode **102** and anode **104** disposed in a planar configuration, with mixed ionically and electronically conductive membrane **206** interposed in between, it is to be appreciated that other cell configurations also lie within the scope of the present disclosure. In some embodiments, cathode **102**, anode **104**, and mixed ionically and electronically conductive membrane **206** may be disposed in a tubular configuration, in which these elements collectively comprise the wall of the tube. FIG. **3** shows a diagram of an illustrative electrochemical cell configuration in which cathode **102**, anode **104** and mixed ionically and electronically conductive membrane **206** are arranged in a tubular configuration within electrochemical cell **300**. Passage **302** extends within the interior of electrochemical cell **302**. A hydrogen-containing gas (e.g., hydrogen gas or a hydrocarbon) may circulate through passage **302** to supply the hydrogen-containing gas to anode **104**. A molecular oxygen-containing gas may be located within exterior space **304** adjacent to cathode **102** and supply molecular oxygen thereto. In alternative embodiments, the positions of cathode **102** and anode **104** may be reversed, in which case molecular oxygen-containing gas may instead circulate through passage **302** and hydrogen-containing gas may be located in exterior space **304**. In the interest of clarity, no external circuit is shown in FIG. **3**.

[0039] Tubular electrochemical cells, such as that shown in FIG. **3**, may be fabricated using extrusion and coating techniques. As an example of suitable fabrication techniques, an anode slurry may be prepared comprising electrolyte powder and cellulose as the binder. The anode components may be mixed with water using an industrial

mixer for **1-2** hours and left to age overnight. A vacuum may be placed over the anode slurry to allow for removal of excess air. Anode tubes may be extruded from the anode slurry using a ram extruder and a custom made die. The anode tubes may be allowed to dry, cut to a desired length, dip-coated in an electrolyte slurry and allowed to dry. The electrolyte slurry may be mixed with organic ingredients such as binder (polyvinyl butyral), dispersant (fish oil) and solvents (toluene and ethanol). The desired electrolyte thickness may be achieved through multiple electrolyte coatings. After reaching a desired electrolyte thickness, the tubes may be sintered at 1200-1450° C. for 6-18 hours in air. Next, the electrolyte-coated anode tubes may be dip-coated in a cathode slurry containing organic ingredients similar with those of the electrolyte slurry. The cathode dip-coated tubes may be dried in air and sintered at 800-1000° C. for 1-6 hours in air to complete the tubular cell fabrication.

[0040] Suitable materials for forming the cathode and/or the anode may be catalytically active toward promoting water formation (specifically toward generating oxygen ions or protons), according to some embodiments. In particular embodiments in which the mixed ionically and electronically conductive membrane comprises an oxygen ion-conductive material, the anode may comprise a catalytically active material to promote water formation therein. Similarly, when the mixed ionically and electronically conductive membrane comprises a proton-conductive material, the cathode may comprise a catalytically active material to promote water formation. In more specific embodiments, both the cathode and the anode may comprise suitable catalytically active materials to more effectively promote water formation in one of the electrodes, depending upon whether an oxygen ion-conductive membrane or a proton-conductive membrane is present. Suitable materials that may be present, particularly in the electrode where water is being formed, may include, for example, Ni, Ce, Co, Fe, Cu, Zn, Sc, Ti, V, Cr, Mn, or any oxide thereof. In particular embodiments, the anode may comprise one or more of these materials. In some or other embodiments, the material(s) comprising the mixed ionically and electronically conductive membrane may also be present in at least a portion of the cathode and/or the anode.

[0041] The electrochemical reaction to generate water releases electrons, a portion of which may flow as a current through the external circuit and a portion of which may travel through the mixed ionically and electronically conductive membrane. No additional electrical current needs to be applied to promote the electrochemical reaction to generate water, unless the electrochemical reaction is endothermic, in which case an additional current may be applied. Application of additional electrical current may be advantageous, however, to promote more efficient formation of the ionic species in either electrode. In some embodiments, the current generated from the electrochemical reaction to form water may be supplied to a load in electrical communication with the external circuit.

[0042] According to further embodiments, the electrochemical water generation systems described herein may comprise a heat exchanger in thermal communication with at least one of the first gas outlet and the second gas outlet. In more specific embodiments, the heat exchanger may be configured to withdraw waste heat from steam produced in the first electrode or the second electrode.

[0043] Thus, depending on the particular electrode in which water is formed, the heat exchanger may be in thermal communication with the gas outlet extending from either the cathode or the anode.

[0044] Accordingly, in some specific embodiments, the heat exchanger may be in thermal communication with the second gas outlet, and the second gas outlet may be configured to withdraw steam from the second electrode (anode). In other specific embodiments, the heat exchanger may be in thermal communication with the first gas outlet, and the first gas outlet may be configured to withdraw steam from the first electrode (cathode).

[0045] Suitable heat exchangers for use in the present disclosure may be configured to withdraw excess heat from a fluid, particularly steam. The excess heat from the steam may be withdrawn by directly contacting the steam with a component of the heat exchanger, or the heat exchanger may be in thermal communication with a conduit through which the steam is travelling. In some embodiments, the heat exchanger may be configured to supply waste heat extracted from at least one of the first gas outlet and the second gas outlet to the mixed ionically and electronically conductive membrane. Returning the waste heat from the steam to the mixed ionically and electronically conductive membrane may lead to more efficient operation of the electrochemical water generation systems.

[0046] Direct conversion of the chemical energy to the products and electrical energy is not limited by the Carnot cycle efficiency. Hence, cell efficiencies are greater than those in desalination plants. Chemical efficiencies between 50-60% may be possible. If waste heat is returned to the mixed ionically and electronically conductive membrane, an overall system efficiency of up to 80-90% or even greater may be realizable.

[0047] Heat exchangers suitable for use in the embodiments herein are not considered to be particularly limited. Illustrative heat exchangers that may be suitable for use in the various embodiments of the present disclosure include, for example, shell and tube heat exchangers, plate heat exchangers, plate and shell heat exchangers, plate fin heat exchangers, microchannel heat exchangers, heat pipes, or direct contact heat exchangers. Choice of a suitable heat exchanger may be application-specific, particularly depending upon whether or not the waste heat is recycled to the mixed ionically and electronically conductive membrane. If the waste heat is not recycled to the mixed ionically and electronically conductive membrane, the waste heat may be utilized in other applications in need of excess thermal energy. In illustrative embodiments, the waste heat may be supplied to promote chemical reactions such as desalination, and heating or cooling applications.

[0048] FIG. **4** shows a diagram of an illustrative electrochemical water generation system **400** configured to extract waste heat from a gas outlet and to return at least a portion of the waste heat to the mixed ionically and electronically conductive membrane. Namely, as shown in FIG. **4**, molecular oxygen (or air) flows through conduit **402** adjacent to cathode **102**, such that the molecular oxygen can diffuse into and/or flow through porosity within cathode **102**. Similarly, hydrogen gas (or a hydrocarbon) flows through conduit **404** adjacent to anode **104**, such that the hydrogen gas (or hydrocarbon) can diffuse into porosity within anode **104**. Water produced in anode **104** exits from conduit **404** in the form of steam through gas outlet **406**. Upon exiting gas

outlet **406**, the steam may condense as liquid water and be collected (collection apparatus not shown). As discussed above, external circuit **108** is optional in electrochemical water generation system **400**.

[0049] Heat exchanger **408** is in thermal communication with gas outlet **406**. Heat exchanger **408** may collect waste heat from the steam within gas outlet **406** to facilitate its condensation into liquid water. According to some embodiments, the waste heat accumulated in heat exchanger **408** may then be returned to mixed ionically and electronically conductive membrane **206** via thermal conduit **410** to facilitate ionic conductivity therein. It is to be appreciated that other heat sources, including other sources of waste heat, may be in thermal communication with mixed ionically and electronically conductive membrane **206** in addition to or as an alternative to that provided from heat exchanger **408**. For example, in alternative embodiments, the waste heat output of a power plant, gas turbine or other heat source may be in thermal communication with mixed ionically and electronically conductive membrane **206** to improve the overall energy efficiency.

[0050] Although FIG. **4** has shown an electrochemical water generation system **400** utilizing an oxygen ion-conductive membrane, it is to be appreciated that a proton-conductive membrane may be utilized in alternative embodiments. In such embodiments, heat exchanger **408** may be in thermal communication with gas outlet **412** of conduit **402** in order to withdraw waste heat produced in cathode **102** in this cell configuration. In the interest of brevity, this alternative cell configuration is not shown in further detail in the drawings.

[0051] Accordingly, in more specific embodiments, electrochemical water generation systems disclosed herein may comprise at least one electrochemical cell comprising: a cathode and an anode, optionally in electrical communication via an external circuit; a mixed ionically and electronically conductive membrane interposed between and in contact with the cathode and the anode, the mixed ionically and electronically conductive membrane comprising an oxygen ion-conductive material; a hydrogen-containing gas supply in fluid communication with the anode; a molecular oxygen-containing gas supply in fluid communication with the cathode; a gas outlet extending from the anode; and a heat exchanger in thermal communication with the gas outlet. In more specific embodiments, the heat exchanger may be configured to supply waste heat extracted from the gas outlet to the mixed ionically and electronically conductive membrane.

[0052] In other more specific embodiments, electrochemical water generation systems disclosed herein may comprise at least one electrochemical cell comprising: a cathode and an anode, optionally in electrical communication via an external circuit; a mixed ionically and electronically conductive membrane interposed between and in contact with the cathode and the anode, the mixed ionically and electronically conductive membrane comprising a proton-conductive material; a hydrogen-containing gas supply in fluid communication with the anode; a molecular oxygen-containing gas supply in fluid communication with the cathode; a gas outlet extending from the cathode; and a heat exchanger in thermal communication with the gas outlet. In more specific embodiments, the heat exchanger may be configured to supply waste heat extracted from the gas outlet to the mixed ionically and electronically conductive membrane.

[0053] Similarly, according to some or other various embodiments, the present disclosure provides methods for electrochemically forming water. In some embodiments, the methods may comprise: supplying a molecular oxygen-containing gas to a first electrode of an electrochemical cell and a hydrogen-containing gas to a second electrode of an electrochemical cell having a mixed ionically and electronically conductive membrane interposed between and in contact with the first electrode and the second electrode, the first electrode and the second electrode optionally being in electrical communication via an external circuit; heating the mixed ionically and electronically conductive membrane to a temperature at or above that needed to maintain ionic mobility in the mixed ionically and electronically conductive membrane at or above a predetermined level; generating an ionic species from the molecular oxygen-containing gas or the hydrogen-containing gas in one of the first electrode or the second electrode; migrating the ionic species across the mixed ionically and electronically conductive membrane to the other of the first electrode or the second electrode; after migrating across the mixed ionically and electronically conductive membrane, reacting the ionic species in one of the first electrode or the second electrode to form water in the form of steam; and withdrawing the steam from one of the first electrode or the second electrode. The mixed ionically and electronically conductive membrane may comprise an oxygen ion-conductive membrane or a proton-conductive membrane, and the steam may be withdrawn from either the first electrode or the second electrode depending upon which type of ionically and electronically conductive membrane is present, as discussed in further detail herein.

[0054] According to further embodiments, the methods of the present disclosure may comprise interacting the steam with a heat exchanger in thermal communication with a gas outlet containing the steam to withdraw waste heat, and supplying the waste heat to the mixed ionically and electronically conductive membrane. Withdrawal of waste heat from the steam may affect condensation of the steam into liquid water, according to some embodiments. The methods of the present disclosure may still further comprise collecting the liquid water, such as in a suitable container. The collected water may be potable and used for drinking purposes, or it may be used for conducting one or more secondary reactions, according to some embodiments.

[0055] The temperature needed to maintain ionic mobility at a predetermined level in the mixed ionically and electronically conductive membrane may vary depending upon the chosen membrane material. Moreover, the chosen degree of ionic mobility may vary depending upon the desired rate of water generation. In more specific embodiments, the temperature needed to maintain ionic mobility may range between about 300° C. and about 1000° C., or between about 300° C. and about 800° C., or between about 300° C. and about 700° C., or between about 300° C. and about 400° C., or between about 400° C. and about 500° C., or between about 500° C. and about 500° C., or between about 600° C. and about 700° C. Temperatures within a suitable range to maintain ionic mobility at a desired level may also promote correspondingly high current density values within the electrochemical cell. Temperatures for proton-conductive mem-

branes may, in some embodiments, be kept below about 700° C. to maintain a partial pressure of water to promote proton transport, whereas oxygen ion-conductive membranes may be suitably operated at temperatures up to about 1000° C., according to other embodiments. Electrochemical reaction kinetics may also affect the observed current density values.

[0056] Embodiments disclosed herein include:

[0057] A. Electrochemical water generation systems. The systems comprise: at least one electrochemical cell comprising: a first electrode and a second electrode, optionally in electrical communication via an external circuit; a mixed ionically and electronically conductive membrane interposed between and in contact with the first electrode and the second electrode; a hydrogen-containing gas supply in fluid communication with one of the first electrode and the second electrode; a molecular oxygen-containing gas supply in fluid communication with the other of the first electrode and the second electrode; and a first gas outlet extending from the first electrode and a second gas outlet extending from the second electrode.

[0058] B. Electrochemical water generation systems for anodic production of water. The systems comprise: at least one electrochemical cell comprising: a cathode and an anode, optionally in electrical communication via an external circuit; a mixed ionically and electronically conductive membrane interposed between and in contact with the cathode and the anode, the mixed ionically and electronically conductive membrane comprising an oxygen ion-conductive material; a hydrogen-containing gas supply in fluid communication with the anode; a molecular oxygen-containing gas supply in fluid communication with the cathode; a gas outlet extending from the anode; and a heat exchanger in thermal communication with the gas outlet.

[0059] C. Methods for producing water using a mixed ionically and electronically conductive membrane. The methods comprise: supplying a molecular oxygen-containing gas to a first electrode of an electrochemical cell and a hydrogen-containing gas to a second electrode of an electrochemical cell; wherein a mixed ionically and electronically conductive membrane is interposed between and in contact with the first electrode and the second electrode; and wherein the first electrode and the second electrode are optionally in electrical communication via an external circuit; heating the mixed ionically and electronically conductive membrane to a temperature at or above that needed to maintain ionic mobility in the mixed ionically and electronically conductive membrane at or above a predetermined level; generating an ionic species from the molecular oxygen-containing gas or the hydrogen-containing gas in one of the first electrode or the second electrode; migrating the ionic species across the mixed ionically and electronically conductive membrane to the other of the first electrode or the second electrode; after migrating across the mixed ionically and electronically conductive membrane, reacting the ionic species in one of the first electrode or the second electrode to form water in the form of steam; and withdrawing the steam from one of the first electrode or the second electrode.

[0060] Each of embodiments A, B, and C may have one or more of the following additional elements in any combination.

[0061] Element 1: wherein the system further comprises: a heat exchanger in thermal communication with at least one of the first gas outlet and the second gas outlet.

[0062] Element 2: wherein the heat exchanger is configured to supply waste heat extracted from at least one of the first gas outlet and the second gas outlet to the mixed ionically and electronically conductive membrane.

[0063] Element 3: wherein the first electrode is a cathode and the molecular oxygen-containing gas supply is in fluid communication with the cathode, the second electrode is an anode and the hydrogen-containing gas supply is in fluid communication with the anode, and the mixed ionically and electronically conductive membrane comprises an oxygen ion-conductive membrane.

[0064] Element 4: wherein the oxygen ion-conductive membrane comprises at least one material selected from the group consisting of a defect ABO_{3-d} perovskite (0,d<1), doped δ-Bi_2O_3, and doped, mixed-phase cerium oxide; wherein A is selected from the group consisting of Ba, Fe, La, Ce, and Sr, and B is selected from the group consisting of Zr, Cu, Fe and Co.

[0065] Element 5: wherein the heat exchanger is in thermal communication with the second gas outlet, and the second gas outlet is configured to withdraw steam from the second electrode.

[0066] Element 6: wherein the first electrode is a cathode and the molecular oxygen-containing gas supply is in fluid communication with the cathode, the second electrode is an anode and the hydrogen-containing gas supply is in fluid communication with the anode, and the mixed ionically and electronically conductive membrane comprises a proton-conductive membrane.

[0067] Element 7: wherein the heat exchanger is in thermal communication with the first gas outlet, and the first gas outlet is configured to withdraw steam from the first electrode.

[0068] Element 8: wherein the molecular oxygen-containing gas supply is configured to supply air or oxygen gas to the first electrode or the second electrode.

[0069] Element 9: wherein the hydrogen-containing gas supply is configured to supply at least one of hydrogen gas, a hydrocarbon gas, or ammonia gas to the first electrode or the second electrode.

[0070] Element 10: wherein the mixed ionically and electronically conductive membrane comprises a single-phase material.

[0071] Element 11: wherein the heat exchanger is configured to supply waste heat extracted from the gas outlet to the mixed ionically and electronically conductive membrane.

[0072] Element 12: wherein the method further comprises: interacting the steam with a heat exchanger in thermal communication with a gas outlet containing the steam to withdraw waste heat; and supplying the waste heat to the mixed ionically and electronically conductive membrane.

[0073] Element 13: wherein the temperature needed to maintain ionic mobility at or above a predetermined level ranges between about 300° C. and about 1000° C.

[0074] Element 14: wherein at least one of the first electrode or the second electrode comprises a material that is catalytically active toward reacting the ionic species to form water.

[0075] By way of non-limiting example, exemplary combinations applicable to A, B, and C include: The system of A in combination with elements 1 and 2; 1-3; 1 and 3; 1, 3 and 4; 1-4; 1 and 5; 1 and 6; 1, 2 and 5; 1, 2 and 6; 1, 6 and 7; 1, 2, 6 and 7; 1 and 8; 1 and 9; 3 and 4; 3 and 5; 3-5; 3, 4, and 8; 3 and 8; 3 and 9; 3, 4 and 9; 6 and 7; 6 and 8; 6-8;

6, 7 and 9; 6 and 9; 8 and 9; 1 and 14; 1, 2 and 14; 1, 3 and 14; 1, 5 and 14; 3 and 14; 3, 4 and 14; 3, 5 and 14; 3, 8 and 14; 3, 9 and 14; 6 and 14; 6, 7 and 14; 6, 8 and 14; 8 and 14; and 9 and 14. The system of B in combination with elements 4 and 8; 4 and 11; 4, 8 and 9; 4 and 9; 8 and 11; 9 and 11; 4 and 14; 4, 8 and 14; 4, 11 and 14; 4, 8, 9 and 14; 4, 9 and 14; 8 and 14; 9 and 14; 8, 11 and 14; 9, 11 and 14; and 11 and 14. The method of C in combination with elements 3 and 12; 3, 4 and 12; 6 and 12; 6 and 13; 6 and 14; 3, 4 and 14; 3 and 14; 8 and 14; 9 and 14; 8, 9 and 14; 8 and 13; and 9 and 13.

[0076] Unless otherwise indicated, all numbers expressing quantities and the like in the present specification and associated claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the embodiments of the present disclosure. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claim, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[0077] One or more illustrative embodiments incorporating various features are presented herein. Not all features of a physical implementation are described or shown in this application for the sake of clarity. It is understood that in the development of a physical embodiment incorporating the embodiments of the present disclosure, numerous implementation-specific decisions must be made to achieve the developer's goals, such as compliance with system-related, business-related, government-related and other constraints, which vary by implementation and from time to time. While a developer's efforts might be time-consuming, such efforts would be, nevertheless, a routine undertaking for those of ordinary skill in the art and having benefit of this disclosure.

[0078] While various systems, tools and methods are described herein in terms of "comprising" various components or steps, the systems, tools and methods can also "consist essentially of" or "consist of" the various components and steps.

[0079] As used herein, the phrase "at least one of" preceding a series of items, with the terms "and" or "or" to separate any of the items, modifies the list as a whole, rather than each member of the list (i.e., each item). The phrase "at least one of" allows a meaning that includes at least one of any one of the items, and/or at least one of any combination of the items, and/or at least one of each of the items. By way of example, the phrases "at least one of A, B, and C" or "at least one of A, B, or C" each refer to only A, only B, or only C; any combination of A, B, and C; and/or at least one of each of A, B, and C.

[0080] Therefore, the disclosed systems, tools and methods are well adapted to attain the ends and advantages mentioned as well as those that are inherent therein. The particular embodiments disclosed above are illustrative only, as the teachings of the present disclosure may be modified and practiced in different but equivalent manners apparent to those skilled in the art having the benefit of the teachings herein. Furthermore, no limitations are intended to the details of construction or design herein shown, other than as described in the claims below. It is therefore evident that the particular illustrative embodiments disclosed above may be altered, combined, or modified and all such variations are considered within the scope of the present disclosure. The systems, tools and methods illustratively disclosed herein may suitably be practiced in the absence of any element that is not specifically disclosed herein and/or any optional element disclosed herein. While systems, tools and methods are described in terms of "comprising," "containing," or "including" various components or steps, the systems, tools and methods can also "consist essentially of" or "consist of" the various components and steps. All numbers and ranges disclosed above may vary by some amount. Whenever a numerical range with a lower limit and an upper limit is disclosed, any number and any included range falling within the range is specifically disclosed. In particular, every range of values (of the form, "from about a to about b," or, equivalently, "from approximately a to b," or, equivalently, "from approximately a-b") disclosed herein is to be understood to set forth every number and range encompassed within the broader range of values. Also, the terms in the claims have their plain, ordinary meaning unless otherwise explicitly and clearly defined by the patentee. Moreover, the indefinite articles "a" or "an," as used in the claims, are defined herein to mean one or more than one of the elements that it introduces. If there is any conflict in the usages of a word or term in this specification and one or more patent or other documents that may be incorporated herein by reference, the definitions that are consistent with this specification should be adopted.

What is claimed is the following:

1. An electrochemical water generation system, comprising:

at least one electrochemical cell comprising:

a first electrode and a second electrode, optionally in electrical communication via an external circuit;

a mixed ionically and electronically conductive membrane interposed between and in contact with the first electrode and the second electrode;

a hydrogen-containing gas supply in fluid communication with one of the first electrode and the second electrode;

a molecular oxygen-containing gas supply in fluid communication with the other of the first electrode and the second electrode; and

a first gas outlet extending from the first electrode and a second gas outlet extending from the second electrode.

2. The electrochemical water generation system of claim **1**, further comprising:

a heat exchanger in thermal communication with at least one of the first gas outlet and the second gas outlet.

3. The electrochemical water generation system of claim **2**, wherein the heat exchanger is configured to supply waste heat extracted from at least one of the first gas outlet and the second gas outlet to the mixed ionically and electronically conductive membrane.

4. The electrochemical water generation system of claim **2**, wherein the first electrode is a cathode and the molecular oxygen-containing gas supply is in fluid communication with the cathode, the second electrode is an anode and the hydrogen-containing gas supply is in fluid communication with the anode, and the mixed ionically and electronically conductive membrane comprises an oxygen ion-conductive membrane.

5. The electrochemical water generation system of claim **4**, wherein the oxygen ion-conductive membrane comprises at least one material selected from the group consisting of a defect ABO_{3-d} perovskite (0,d<1), doped δ-Bi_2O_3, and doped, mixed-phase cerium oxide;

wherein A is selected from the group consisting of Ba, Fe, La, Ce, and Sr, and B is selected from the group consisting of Zr, Cu, Fe and Co.

6. The electrochemical water generation system of claim **4**, wherein the heat exchanger is in thermal communication with the second gas outlet, and the second gas outlet is configured to withdraw steam from the second electrode.

7. The electrochemical water generation system of claim **2**, wherein the first electrode is a cathode and the molecular oxygen-containing gas supply is in fluid communication with the cathode, the second electrode is an anode and the hydrogen-containing gas supply is in fluid communication with the anode, and the mixed ionically and electronically conductive membrane comprises a proton-conductive membrane.

8. The electrochemical water generation system of claim **7**, wherein the heat exchanger is in thermal communication with the first gas outlet, and the first gas outlet is configured to withdraw steam from the first electrode.

9. The electrochemical water generation system of claim **1**, wherein the molecular oxygen-containing gas supply is configured to supply air or oxygen gas to the first electrode or the second electrode.

10. The electrochemical water generation system of claim **1**, wherein the hydrogen-containing gas supply is configured to supply at least one of hydrogen gas, a hydrocarbon gas, or ammonia gas to the first electrode or the second electrode.

11. The electrochemical water generation system of claim **1**, wherein the mixed ionically and electronically conductive membrane comprises a single-phase material.

12. An electrochemical water generation system, comprising:

at least one electrochemical cell comprising:

a cathode and an anode, optionally in electrical communication via an external circuit;

a mixed ionically and electronically conductive membrane interposed between and in contact with the cathode and the anode, the mixed ionically and electronically conductive membrane comprising an oxygen ion-conductive material;

a hydrogen-containing gas supply in fluid communication with the anode;

a molecular oxygen-containing gas supply in fluid communication with the cathode;

a gas outlet extending from the anode; and

a heat exchanger in thermal communication with the gas outlet.

13. The electrochemical water generation system of claim **12**, wherein the heat exchanger is configured to supply waste heat extracted from the gas outlet to the mixed ionically and electronically conductive membrane.

14. The electrochemical water generation system of claim **12**, wherein the oxygen ion-conductive membrane comprises at least one material selected from the group consisting of a defect ABO_{3-d} perovskite (0,d<1), doped δ-Bi_2O_3, and doped, mixed-phase cerium oxide;

wherein A is selected from the group consisting of Ba, Fe, La, Ce, and Sr, and B is selected from the group consisting of Zr, Cu, Fe and Co.

15. A method for generating water, comprising:

supplying a molecular oxygen-containing gas to a first electrode of an electrochemical cell and a hydrogen-containing gas to a second electrode of an electrochemical cell;

wherein a mixed ionically and electronically conductive membrane is interposed between and in contact with the first electrode and the second electrode; and

wherein the first electrode and the second electrode are optionally in electrical communication via an external circuit;

heating the mixed ionically and electronically conductive membrane to a temperature at or above that needed to maintain ionic mobility in the mixed ionically and electronically conductive membrane at or above a predetermined level;

generating an ionic species from the molecular oxygen-containing gas or the hydrogen-containing gas in one of the first electrode or the second electrode;

migrating the ionic species across the mixed ionically and electronically conductive membrane to the other of the first electrode or the second electrode;

after migrating across the mixed ionically and electronically conductive membrane, reacting the ionic species in one of the first electrode or the second electrode to form water in the form of steam; and

withdrawing the steam from one of the first electrode or the second electrode.

16. The method of claim **15**, further comprising:

interacting the steam with a heat exchanger in thermal communication with a gas outlet containing the steam to withdraw waste heat; and

supplying the waste heat to the mixed ionically and electronically conductive membrane.

17. The method of claim **15**, wherein the first electrode is a cathode and the molecular oxygen-containing gas supply is in fluid communication with the cathode, the second electrode is an anode and the hydrogen-containing gas supply is in fluid communication with the anode, and the mixed ionically and electronically conductive membrane comprises an oxygen ion-conductive membrane.

18. The method of claim **17**, wherein the oxygen ion-conductive membrane comprises at least one material selected from the group consisting of a defect ABO_{3-d} perovskite (0,d<1), doped δ-Bi_2O_3, and doped, mixed-phase cerium oxide;

wherein A is selected from the group consisting of Ba, Fe, La, Ce, and Sr, and B is selected from the group consisting of Zr, Cu, Fe and Co.

19. The method of claim **15**, wherein the first electrode is a cathode and the molecular oxygen-containing gas supply is in fluid communication with the cathode, the second electrode is an anode and the hydrogen-containing gas supply is in fluid communication with the anode, and the mixed ionically and electronically conductive membrane comprises a proton-conductive membrane.

20. The method of claim **15**, wherein the hydrogen-containing gas comprises at least one gas selected from the group consisting of hydrogen gas, a hydrocarbon gas, ammonia gas, and any combination thereof.

21. The method of claim **15**, wherein the temperature needed to maintain ionic mobility at or above a predetermined level ranges between about 300° C. and about 1000° C.

22. The method of claim **15**, wherein at least one of the first electrode or the second electrode comprises a material that is catalytically active toward reacting the ionic species to form water.

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